Control of an Autothermal Network of Nonstationary Catalytic Reactors

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Forced nonstationary reactors allow us to carry out low exothermic catalytic reactions autothermally. The use of internal regenerative heat recovery is much more efficient than the use of external heat exchangers (Matros, 1985); in fact, large amounts of energy may be required to maintain the reaction temperature, and the heat-exchange section can become very large, especially if the concentration of the reactants or the exothermicity of the reaction is very low. Applications have been proposed, for example, for SO_2 oxidation, ammonia synthesis, methanol production, and especially in the field of catalytic destruction of volatile organic compounds (VOC) containing emissions.

The tubular reactor with periodical flow reversal has been widely investigated in recent years (Boreskov and Matros, 1983; Matros and Bunimovich, 1996) but little attention has been given to the performance of a network of reactors in series, in which a set of valves allows us to vary the feed position, periodically changing the sequence of reactors, but maintaining the flow direction, with the heat front propagating in a closed circle.

Matros suggested a network of two catalytic reactors in series, but little is known about the performance and behavior of this design (Haynes and Caram, 1994). Preliminary work carried out by the authors (Barresi et al., 1997; Brinkmann et al., 1999) showed that a three-reactor network can, in some cases, be competitive with the reverse-flow reactor, as it reduces emissions due to washout of the untreated gases, but requires a more sophisticated control.

The aim of this work is to investigate by simulation the influence of the control policy on the performance and stability of a network of three reactors; the autothermal behavior with low exothermal reactions will be considered. The catalytic combustion of waste gases containing a low concentration of VOCs in adiabatic reactors will be investigated in detail; this is a simplified approach to the problem, and for this reason the heat losses at the wall have been neglected, but this is reasonable for commercial-size reactors.

Because a large part of the bed acts as a heat exchanger, it can be replaced by inert material: in the case studied, only a small end section of the bed is catalytically active.

It will be shown that the use of a fixed switching time is generally not appropriate for the reactor network; a more robust periodic strategy using a two-point temperature control must be implemented in order to assure safe startup and stability in case the load varies.

The Model

Figure 1 shows a network of three reactors in series, operating at atmospheric pressure. Each packed-bed reactor is 3 m long and filled with spherical pellets (6 mm diameter). It consists of a large inert section for heat exchange and a relatively small catalytically active part (20%) near the outlet. A set of valves enables the feed position to vary.

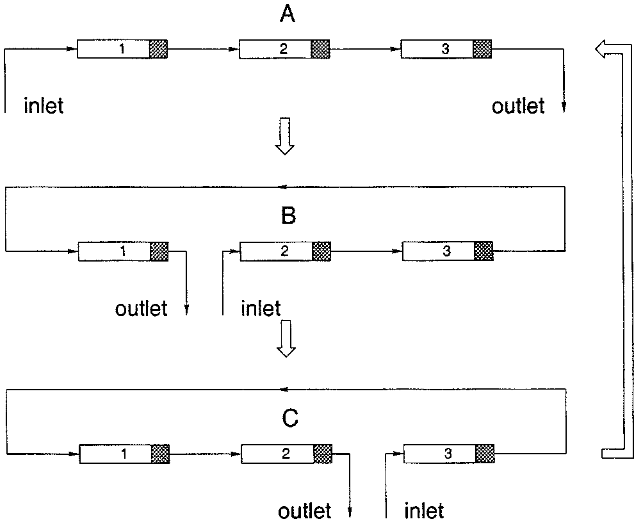

Figure 1. Three-reactor network with variable feed position.

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A heterogeneous one-dimensional mathematical model has been developed to investigate the performance and influence of the control policy. The adiabatic model considers the dispersive transport of energy and mass in the gas phase; solid-bed conductivity ($\lambda_S = 0.18$ J m^{-2} s^{-1} K^{-1}) has not been taken into account in the solid-phase energy balance, but the effect has been included in the axial heat-dispersion coefficient, considering an effective gas conductivity, k_{eff}. It is assumed that no accumulation of mass occurs near the solid surface, where the combustible reacts according to a first-order law; pressure loss inside the reactor is neglected, and heat capacity is assumed to be constant.

The balance equations for the catalytically active sections are given below (the inert section is described by Eqs. 1 and 2 only, as there is no mass transfer to the solid):

$$\rho_G \frac{\partial T_G}{\partial t} = -\upsilon \rho_G \frac{\partial T_G}{\partial x} + \frac{k_{\text{eff}}}{c_{p,G}} \frac{\partial^2 T_G}{\partial x^2} + \frac{ha}{c_{p,G}\epsilon}(T_S - T_G) \quad (1)$$

$$\frac{\partial T_S}{\partial t} = \frac{k_G a(-\Delta H)}{\rho_S c_{p,S}(1-\epsilon)} \frac{\rho_G}{\overline{M}}(y_G - y_S) - \frac{ha}{\rho_S c_{p,S}(1-\epsilon)}(T_S - T_G) \quad (2)$$

$$\frac{\partial(\rho_G y_G)}{\partial t} = -\frac{\partial(\upsilon \rho_G y_G)}{\partial x} + D_{\text{eff}} \frac{\partial^2(\rho_G y_G)}{\partial x^2} - \frac{k_G a}{\epsilon}\rho_G(y_G - y_S) \quad (3)$$

$$0 = k\,a(y_G - y_S) - k_\infty \exp(E_A/RT_S)\, y_S. \quad (4)$$

The interstitial velocity υ has been used; subscripts G and S refer to gas and solid, respectively. For the gas phase Danckwerts boundary conditions are assumed. A list of the parameters used in the simulation for the reference condition is given in Table 1; the corresponding adiabatic temperature rise, ΔT_{ad}, is 10 K. The kinetic constants are those determined by Van de Beld (1995) for ethene combustion. Heat- and mass-transfer and dispersion coefficients have been evaluated using the correlations proposed by Van de Beld (1995).

The PDE system is solved using spatial discretization and an ODE-solver based on Gear's method. Further details on the model and its solution are given in an earlier article (Brinkmann et al., 1999).

Table 1. Parameter Values Used in Simulations

$c_{p,G}$ (J·kg^{-1}·K^{-1})	1,373
$c_{p,S}$ (J·kg^{-1}·K^{-1})	1,000
E_A (J·mol^{-1})	57,800
$-\Delta H$ (J·mol^{-1})	1,323,000
k_∞ (s^{-1})	0.18
$\overline{M}$ (kg·mol^{-1})	0.029
$T_{G,\text{feed}}$ (K)	293
u_0 (m·s^{-1})	0.4
$y_{G,\text{feed}}$	0.0003
ϵ	0.4
ρ_S (kg·m^{-3})	2,220

Results

Dimensionless variables will be employed to show the results: gas temperature, $\tau_G = T_G/T_{\text{G,feed}}$, gas concentration, $Y_G = y_G/y_{\text{G,feed}}$, and time, $s = t\,\upsilon_0/L$. Concentration and temperature profiles are shown along the dimensionless coordinate z ($= x/L$), with the three beds connected in the proper sequence: $z = 0$ will always indicate the inlet point while $z = 3$ is the outlet.

To start up the device it is necessary to preheat it, using an electric system or a gas burner, prior to beginning to feed the cold waste gases; in the simulations a uniform initial temperature (T_{pr}) is considered. On feeding the waste gases, the reactor packing cools at the inlet, the gases being heated up themselves, while in the catalytically active parts of the reactors, and mainly in the first (hot) active section where combustible concentration is still relatively large, the temperature increases due to the exothermic reaction.

A temperature front moving in the gas flow direction is created; its velocity is very small in comparison to the gas velocity; the active portion of the first reactor ($z = 0.8$) is reached by the heat front after 1500 residence times for a preheating temperature of 530 K; in the conditions considered, the gas and solid temperature differ by a few degrees only (Brinkmann et al., 1999). After a sufficiently long time, the next reactor is partially heated by the reaction energy. If no control action is taken, the temperature front passes through the first active zone, cooling the catalyst to below ignition temperature. The reaction is stopped and any unburned combustible enters the second, still hot reactor; this is an undesirable, since part of the catalyst is not in use.

To avoid the lightoff of the whole system it is necessary to introduce a proper automatic control system.

Choice of the best control policy

The easiest possible control strategy is to define a fixed cycle period and to act at the end of the period. The performance of this type of open-loop periodic control is shown in Figure 2 for different switching periods (made dimensionless by dividing the period by the gas residence time at inlet conditions). It must be pointed out that the exit gas concentration and temperature change during each period, and the cycles averages are shown.

It can be noted that for cycle periods in the range 2050–2075 residence times, a very good conversion is obtained after startup, but shorter or longer switching times do not result in a periodically stable operational state: after a transient, the reactant molar fraction at the exit approaches unity (that means no conversion) and the farther the switching period is from the narrow stability region, the faster the extinction rate. The mechanism for sensitivity and instability is simple: the proper switching period is closely related to the velocity of the heat front; if it is too long, the first section is cooled too much, and the gases do not reach the catalysts at the required temperature, while if it is too short, there is no time to accumulate enough heat in the second reactor before switching. The increased average heat loss at unfavorable periods cannot be compensated for by reactive heat development, and the system gradually "lights off."

The heat-front velocity, on the other hand, depends only on the ratio of the solid and gas heat capacity and, most im-

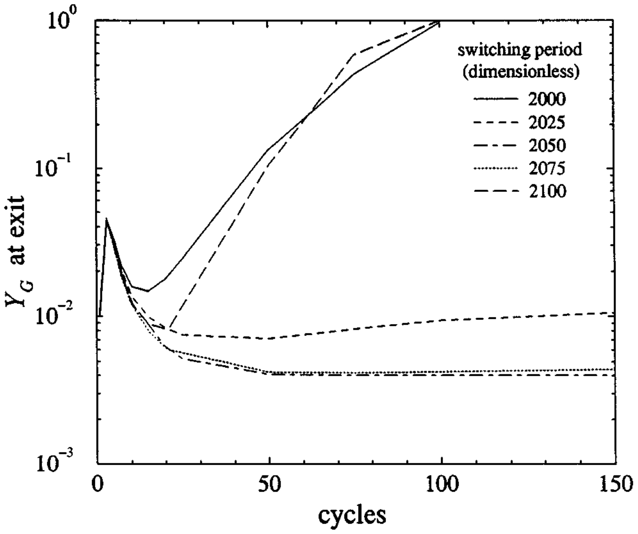

Figure 2. Performance of three reactors in series with fixed switching period ($T_{pr} = 530$ K); the time-averaged exit concentration is shown.

portantly, on the mass flow of gas, if heat transfer is sufficiently fast. Thus, as a consequence of the narrow stability range, it would be possible to use this strategy only if the period can be fixed in advance with an error smaller than 2 percent. But, if the gas velocity is subject to fluctuations, this strategy is obviously inadequate for any kind of reactor configuration. In addition, it is not certain that an effective pseudo-steady-state can be reached, since the convergence to such a state is very slow. For instance, in all simulations using this control strategy, the maximum temperature is still far from its asymptotic value even after 200 switches. Finally, there is no way to control $T_{\max}$, so that overheating and consequent catalyst destruction can occur.

For these reasons, feedback control has been investigated as well.

Since the combustible load is higher in the first section and a minimum temperature should be achieved in the catalyst in order to maintain the reaction, a single-point control strategy has been tried first, to avoid the aforementioned problems. If the gas temperature at the beginning of the first catalytic bed drops below a certain value, the feed position is switched in order to regenerate the inactive part of the first reactor.

Different values of the temperature setpoint have been considered, but without satisfactory results. The behavior of the system is shown in Figure 3, where the gas temperature profiles are shown for two different choices of the switch temperature T_{sw}.

If the controller setpoint is chosen sufficiently high to maintain the reaction (Figure 3, upper graph), during startup the cycle period diminishes progressively and the switch condition is fulfilled immediately after the sixth switch (compare the temperature profile at the end of cycle six with the previous ones, remembering that gas and solid profiles are very close); as a consequence, no stable operation can be obtained. If, on the other hand, the setpoint is chosen closer to room temperature (lower graph), the time–space-average catalyst temperature becomes so low that the reaction lights off even at a higher combustible load; it can be seen that the heat stored increases up to the 25th cycle, but then decreases. It may be difficult to find an intermediate value of possibly stable operation, and is unlikely to be safe with respect to fluctuations of inlet conditions.

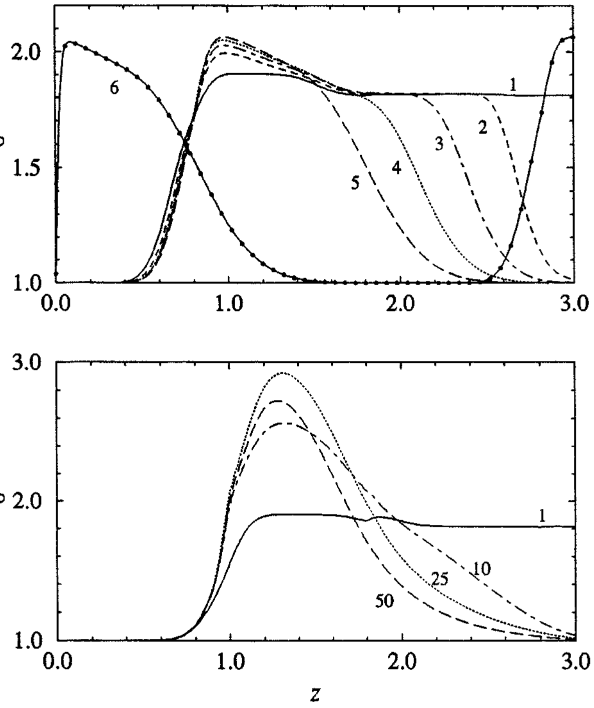

Figure 3. Temperature profile at the end of the *i*th cycle (indicated on the plot) during startup ($T_{pr} =$ 530 K) using a feedback control with single-point temperature measurement.

Two different setpoints are considered: $T_{sw} = 500$ K (upper graph), and $T_{sw} = 330$ K (lower graph).

To improve the robustness of the system, an additional temperature measurement located at the beginning of the second catalyst bed has been implemented, and the switch condition has been given as follows: the feed position is changed only if the local temperature in the first reactor drops below setpoint 1 and in the second reactor is above setpoint 2. During the first five or six cycles, it is the first controller that determines the period. The temperature profile becomes steeper and gradually takes the form of an asymmetric bell-shaped curve (see Figure 4), which is similar to what happened in the previous case with the lower temperature setpoint. By the seventh cycle (more generally, before the tenth), however, the switch condition in the second section takes control, and the period duration remains constant. Note that the temperature profiles are still changing, but unlike the previous case, the heat storage is not significantly reduced. While the final time period is soon reached, conversion and maximum temperature take much longer to reach their final values, namely 50–100 cycles (Figure 5). Finally, a periodic state of operation is attained, typically after 100 to 200 switches; this periodic state, which is also referred to as the pseudo-steady-state, is characterized by identical temperature profiles at the beginning of each cycle, and by constant time-averaged conversion.

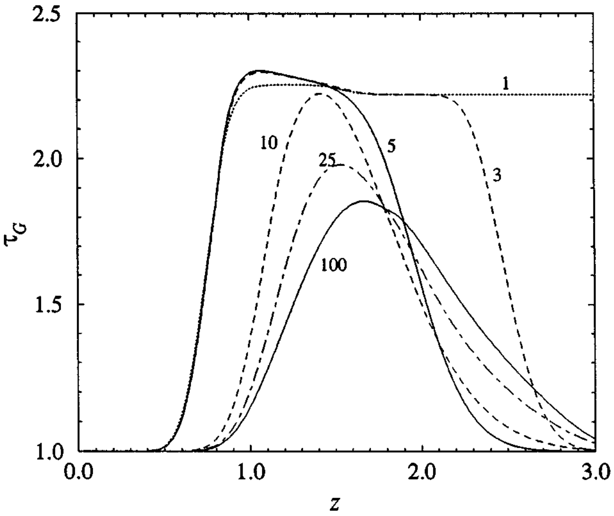

Figure 4. Temperature profile at the end of the *i*th cycle (indicated on the plot) during startup (T_{pr} = 530 K) using a feedback control with two-point temperature measurement.

$T_{sw,1} = 530$ K; $T_{sw,2} = 535$ K.

This strategy, which will be referred to as two-point control, enables stable autothermal operation even at a low combustible load, with a reasonable choice of setpoints.

As the controller in the first section only determines the period length during the first few cycles, its setpoint has no effect on the final conversion. The effect of the second controller setpoint on conversion is demonstrated in Table 2; however, the choice of setpoints has no significant effect on the cycle time, as only the steepness of the profiles increases with the setpoints. If the setpoint $T_{sw,2}$ is chosen below 530 K, the average catalyst temperature is too low, and thus heat development by reaction is not sufficiently large to maintain autothermal operation. Increasing the setpoint to 640 K leads to a conversion as high as 98%. However, a higher setpoint also requires a higher preheat temperature and thus more energy before startup. The overall operation time will determine whether or not the higher setpoint is economically favorable.

With the control strategy just described and the chosen set of parameters, autothermal operation is possible with a VOC concentration corresponding to an adiabatic temperature rise as low as 10 K, with conversion higher than 60%.

Response to disturbances

The system reaction to disturbances in mass flow rate and combustible load is of the utmost importance. The two-point control strategy works reliably with respect to a sudden change in combustible load. In Figure 6 a negative step of the inlet concentration ($\Delta T_{ad} = 30$ K $\rightarrow 10$ K) occurs after cy-

Table 2. Effect of Setpoints on Conversion and Maximum Temperature for Two-Point Control

$T_{sw,1}$ K	$T_{sw,2}$ K	T_{pr} K	η	T_{max} K
530	350	530	—	—
530	450	530	—	—
530	500	530	—	—
530	535	530	0.61	550
530	560	570	0.81	593
530	590	600	0.91	625
530	640	650	0.98	665

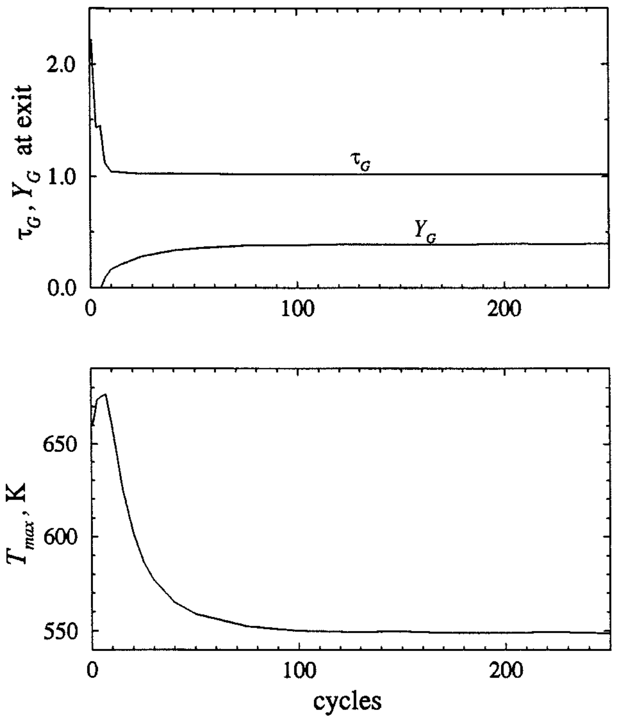

Figure 5. Time-averaged outlet temperature and concentration (upper graph) and maximum solid temperature (lower graph), during startup; two-point controller, conditions as in Figure 4.

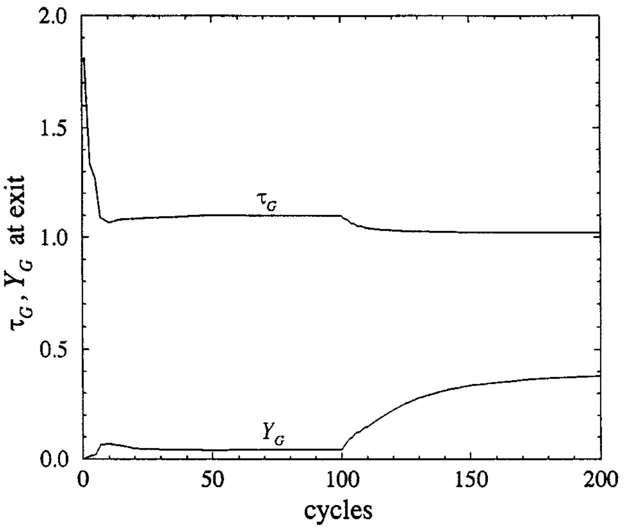

Figure 6. Response to a negative step in combustible load ($\Delta T_{ad} = 30$ K $\rightarrow 10$ K); two-point control, settings as in Figure 4.

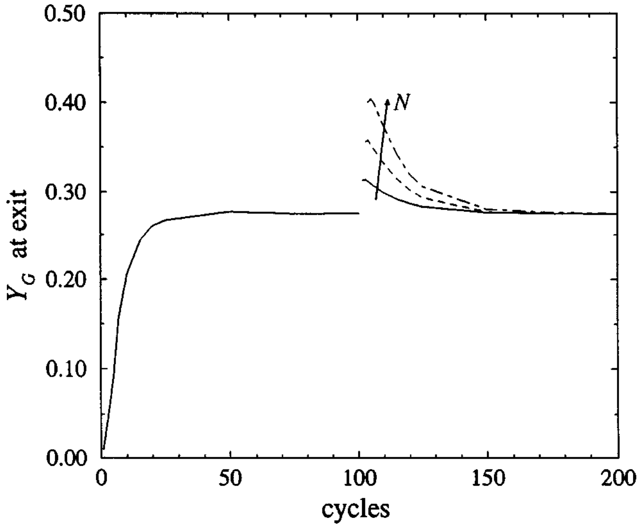

Figure 7. Response of the network after *N* cycles with zero load ($N = 1, 2, 3$); settings as in Figure 4.

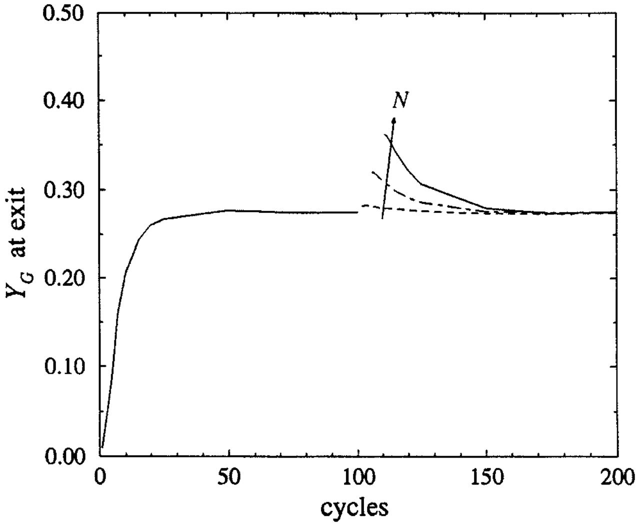

Figure 8. Response of the network after *N* cycles with 25% increased flow rate ($N = 1, 5, 10$); settings as in Figure 4.

cle number 100 (that is, after the pseudo-steady-state has been reached). The average outlet concentration, related to the respective inlet concentration, slowly converges into the same value obtained directly from startup at $\Delta T_{ad} = 10$ K.

Another point is how the system reacts when the combustible load drops to zero for a certain time. This situation is depicted in Figure 7. Starting from the pseudo-steady-state at $\Delta T_{ad} = 10$ K, the system sustains three cycles with zero load, that is, even after the third cycle of zero load (that is, about 100 min without lighting) the system is able to return automatically to the original point of operation, even if it takes about 50 cycles to do so, and during the transition the average conversion is lower. However, at a higher load the network will react even more stably and probably faster, as temperature and energy recovery are higher than in the limit conditions of stable operation. Similarly, a 25% increase in gas flow rate is tolerated for more than ten cycles. If flow velocity is reduced to its original value before lightoff, the system returns to its original point of operation after at most 50 cycles, as shown in Figure 8. The simulations shown in Figures 7 and 8 have been carried out assuming constant values of the heat and mass transport parameters throughout the reactor (see Brinkmann et al., 1999).

Conclusions

Numerical simulation reveals that the network of three catalytic reactors in series with large inert sections, operated in forced nonstationary conditions, is a suitable design for VOC oxidation at low concentration.

It is an interesting example of a sequence of reactors that cannot operate in the steady state, but for which there exists a successful periodic control policy that switches feed among the reactors. Open-loop periodic control with fixed switching periods gives excellent conversion, but as it is very sensitive to model parameter, it is confined to a narrow range and is not stable at variable inlet conditions. A more robust periodic strategy can be implemented through feedback control, measuring temperature at two points and using simple decision logic.

This strategy serves for startup and is stable with respect to fluctuations of inlet concentration and also of gas flow rate, but conversion depends on setpoints, and thus on preheat temperature. This preliminary work showed that the choice of the second temperature setpoint is the critical one, as it determines the required preheating temperature and affects conversion. Future work is scheduled to find a simpler system model that allows us to address the problem of finding an optimal set of switching thresholds.

This example could also serve as a test case for exploring the question of simultaneous reactor and control design.

Acknowledgments

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Notation

a = specific interfacial area, m^{-1}
c_p = heat capacity, $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
D_{eff} = mass-dispersion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
E_A = activation energy, $\text{J}\cdot\text{mol}^{-1}$
h = heat-transfer coefficient, $\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
$-\Delta H$ = heat of reaction, $\text{J}\cdot\text{mol}^{-1}$
k_∞ = kinetic preexponential factor, s^{-1}
k_G = mass-transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
L = reactor length, m
$\overline{M}$ = mean molar weight, $\text{kg}\cdot\text{mol}^{-1}$
R = universal gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
u = surface-gas velocity, $\text{m}\cdot\text{s}^{-1}$
x = axial space coordinate, m
y = reactant molar fraction
ϵ = void fraction
η = conversion
ρ = density, $\text{kg}\cdot\text{m}^{-3}$

Subscripts

0 = inlet conditions
feed = in feed stream

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