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Performance of selective catalytic exothermic reactions in the "reversed heat wave" mode: a way to improve selectivity

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Abstract

The paper considers the model system of exothermic catalytic selective and complete conversion reactions, occurring according to the scheme $A + m[B] \Rightarrow C + [\cdot]$, $C + [B] \Rightarrow D + [\cdot]$, $B + [\cdot] \Rightarrow [B]$, where A and B initial reagents, C desired product (of selective conversion), D undesirable by-product (of complete conversion), [B] reagent B, chemisorbed at the catalyst surface, $[\cdot]$ vacant catalyst active site. Numerical simulation of the system behavior in fixed adiabatic catalyst bed showed that being compared to steady-state regimes it is possible to significantly improve the desired product yield and catalyst unit productivity by application of nonstationary regimes, based on periodical, separated in time, feeding of reagents A and B. The most interesting results were obtained for process performance in "reversed heat wave" mode, when temperature front of reaction is moving upstream the flow of the reaction mixture. Such operation regime is characterized with significant decrease of maximum catalyst temperature, therefore, expanded possibility to increase inlet concentration of reagents and with increased selectivity of conversion into target products.

Keywords: Direct heat wave; Reversed heat wave; Forced feed composition cycling

1. Introduction

Improvement of selectivity and desired product yield in complex reaction systems is one of the major problems in catalytic reaction engineering and also one of the main challenges in the catalytic reaction engineering area. Such objectives may be met in various industrially important application areas, such as selective oxidation, oxidative dehydrogenation, selective hydrogenation, halogenation processes, etc.

Usually such problems are solved by development of new highly selective catalysts and by optimization of process operation parameters, though it cannot guarantee the desired results in all cases.

One of the most prospective approaches for solution of the problem is application of transient nonstationary regimes [1] and, in particular, forced feed composition cycling (FFCC) in the packed catalyst bed, meaning periodical alteration of reactor feed between oxidation and reduction mixtures up to the limit case of periodical separate feeding of oxidant and reductant. Such approach may provide enhancement of selectivity as it was shown for numerous reaction systems (detailed overview is given in [2]). Particularly, studies [3,4] dedicated to propane oxidative dehydrogenation at vanadia catalysts demonstrated that FFCC provided by periodical oscillations of propane/oxygen concentration ratio in feed leads to increase of propylene yield compared to steady-state conditions, with maximum C_3H_6 production at separate feeding of reagents. Similar results were obtained for many other catalytic reactions. Some efforts are also made in development of industrial technologies based on described principle [5].

It may be stated that application of FFCC attains significant interest of researchers. At the same time, in most cases the observed experimental results relate to isothermal laboratory reactors and do not take into account the possible heat effects of reactions and related unsteady-state phenomena in the adiabatic catalyst bed, therefore, these results cannot give direct answer on possible efficiency of FFCC in process conditions. Moreover, account of interaction between all these effects may give additional possibilities for development of new catalytic processes.

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Nomenclature

a	chemisorption capacity of the catalyst in relation of reagent B
c, c^{cat}	reagents concentrations in the gas phase and near the catalyst surface, respectively (molar fractions)
C_p	gas heat capacity (kJ/st m^3 K)
E_j	activation energies of reactions (kJ/mol)
k, k_0	kinetic constants and pre-exponential (s^{-1})
l	axial coordinate in the catalyst bed (m)
L	total catalyst bed length (m)
m	reaction (1) rate order in relation to θ
n	reaction (2) rate order in relation to θ
q	intensity of heat flow during catalyst bed heating (kW/m^2)
Q_j	heat effects of reactions (kJ/mol)
R	universal gas constant (kJ/mol K)
S	selectivity
S_{sp}	specific geometrical external surface area of catalyst pellets in the bed (m^{-1})
t	time (s)
T, T_{cat}	temperatures of gas and catalyst, respectively (K)
u	superficial gas velocity (m/s)
W_j	rates of reaction stages (s^{-1})
X	conversion of reagent A
Y	desired product yield
Greek letters	
α	heat exchange coefficient (kW/m^2 K)
β_i	mass exchange coefficients (s^{-1})
γ	volume heat capacity of the catalyst (kJ/st m^3 K)
ε	void volume fraction of the catalyst bed
θ	surface concentration of chemisorbed reagent B
λ_{eff}	effective heat conductivity of the catalyst bed (kW/m K)
ν_i	stoichiometric coefficients for reagent B in reactions (1) and (2), respectively
Subscripts and superscripts	
i, j	indexes of reagent and reaction numbers
in	value at the catalyst bed inlet
init	initial value

2. Problem formulation

Let us consider the simplest model scheme of selective reaction, composed from consecutive steps of partial and complete conversion:

$$\mathrm{A} + \nu_1\mathrm{B} \Rightarrow \mathrm{C}$$

$$\mathrm{C} + \nu_2\mathrm{B} \Rightarrow \mathrm{D}$$

where A and B are the initial reagents, C the desired product, D the undesirable byproduct. Let us propose that catalytic reaction occurs according to Eley–Rideal mechanism via the intermediate chemisorption of reagent B. In this case the reaction scheme may be represented as follows:

$$\mathrm{A} + \nu_1[\mathrm{B}] \Rightarrow \mathrm{C} + [\cdot] \qquad (1)$$

$$\mathrm{C} + \nu_2[\mathrm{B}] \Rightarrow \mathrm{D} + [\cdot] \qquad (2)$$

$$\mathrm{B} + [\cdot] \Rightarrow [\mathrm{B}] \qquad (3)$$

where [B] is the reagent B, chemisorbed at the catalyst surface, [·] vacant active site.

Let us also propose that all stages (1)–(3) are exothermic with their activation energies rising in a sequence $E_1 < E_2 < E_3$. The latter means that temperature increase will lead to simultaneous rise of reagents conversion and decrease of reaction selectivity. As it also may be seen from scheme (1)–(3), desired product selectivity will decrease with rise of reagent B concentration, due to acceleration of undesired product D formation according to reaction (2).

Such regularities, though they are arbitrary, nevertheless are quite typical for such important reaction systems as selective oxidation of hydrocarbons [4]. In this case reagent A corresponds to hydrocarbon, B corresponds to oxygen.

The aim of the current study is simulation of reactions (1)–(3) with account of reaction heat effects and heat/mass transfer processes in the adiabatic catalyst bed both in steady-state and transient (FFCC) regimes.

3. Mathematical model and simulation technique

For description of processes in the catalyst bed one-dimensional two-temperature model of adiabatic catalyst bed, given below, was used. Model was constructed on the assumptions of plug flow regime, absence of intraparticle diffusion limitations and quasi-stationarity of gaseous reaction mixture parameters in relation to inertial catalyst state properties. Besides, to simplify the study on this stage it was proposed that reaction does not lead to significant changing of reaction mixture volume and heat capacity

$$\beta_i S_{\mathrm{sp}}(c_i^{\mathrm{cat}} - c_i) = \sum_j \nu_{ij} W_j \qquad (4)$$

$$u\frac{\partial c_i}{\partial l} + \beta_i S_{\mathrm{sp}}(c_i - c_i^{\mathrm{cat}}) = 0 \qquad (5)$$

$$a\frac{\partial \theta}{\partial t} = -\nu_1 W_1 - \nu_2 W_2 + W_3 \qquad (6)$$

$$uC_p\frac{\partial T}{\partial l}+\alpha S_{\mathrm{sp}}(T-T_{\mathrm{cat}})=0 \tag{7}$$

$$(1-\varepsilon)\gamma\frac{\partial T_{\mathrm{cat}}}{\partial t}=\lambda_{\mathrm{eff}}\frac{\partial^2 T_{\mathrm{cat}}}{\partial l^2}+\alpha S_{\mathrm{sp}}(T-T_{\mathrm{cat}})+\sum_j Q_jW_j \tag{8}$$

with boundary conditions:

$$l=0\Rightarrow\begin{cases}T=T_{\mathrm{in}}\\ \lambda_{\mathrm{eff}}\dfrac{\partial T_{\mathrm{cat}}}{\partial l}=0\\ A_i=A_i^{\mathrm{in}}\end{cases} \tag{9}$$

$$l=L\Rightarrow\lambda_{\mathrm{eff}}\frac{\partial T_{\mathrm{cat}}}{\partial l}=0 \tag{10}$$

$$t=0\Rightarrow\begin{cases}\theta(l)=\theta_{\mathrm{init}}\\ T_{\mathrm{cat}}(l)=T_{\mathrm{cat}}^{\mathrm{init}}\end{cases} \tag{11}$$

Kinetic equations for rates of reactions W_j were preliminary formulated on the basis of mass-action law:

$$W_1=k_1c_{\mathrm{A}}^{\mathrm{cat}}\theta^m \tag{12}$$

$$W_2=k_2c_{\mathrm{C}}^{\mathrm{cat}}\theta^n \tag{13}$$

$$W_3=k_3c_{\mathrm{B}}^{\mathrm{cat}}(1-\theta) \tag{14}$$

with temperature dependence of rate constants values given by Arrhenius law:

$$k_j=k_{0j}\exp\left(-\frac{E_j}{RT_{\mathrm{cat}}}\right) \tag{15}$$

As soon as reactions with participation of chemisorbed reagents (1) and (2) are, as a rule, consecutive, the values of reaction rate order in relation to θ (m and n) in Eqs. (12) and (13) may be quite reasonably may be taken equal to 1.

Solution of the set of Eqs. (4)–(15) was performed numerically with application of balanced finite approximations algorithm [6]. Solution method contained two levels of iterations, the first one providing direct solution of mass balance Eqs. (4)–(6) and (12)–(15), the second one providing solution of heat balance equations (7) and (8).

For model study the following basic parameters values were taken: $Q_1 = 850$ kJ/mol, $Q_2 = 1250$ kJ/mol, $Q_3 = 2100$ kJ/mol, $k_{01} = 1\times10^3\,\mathrm{s}^{-1}$, $k_{02} = 5\times10^3\,\mathrm{s}^{-1}$, $k_{03} = 5\times10^6\,\mathrm{s}^{-1}$, $\varepsilon = 0.4$, $u = 0.1$ m/s, $L = 0.1$ m, $\nu_1 = 1$, $\nu_2 = 9$, $m = 1$, $n = 1$, $E_1 = 75$ kJ/mol, $E_2 = 100$ kJ/mol, $E_3 = 200$ kJ/mol, $a = 50$, $\gamma = 1900\,\mathrm{kJ/m^3\,K}$, $C_p = 1.3\,\mathrm{kJ/st\,m^3\,K}$.

Heat and mass transfer parameters (α, β_i, λ_{eff}) and specific surface S_{sp} were defined from standard equations for fixed bed of granular catalyst [7], assuming equivalent diameter of catalysts pellets equal to 1.5 mm. It is necessary to note, that kinetic parameters were chosen rather arbitrary, but this circumstance is not playing a key role here, because the aim of the model study was just detection of qualitative regularities.

The following parameters were used as characteristics of process performance:

- conversion of initial reagent A $X=(c_{\mathrm{A}}^{\mathrm{in}}-c_{\mathrm{A}}^{\mathrm{in}})/c_{\mathrm{A}}^{\mathrm{in}}$;
- selectivity of A conversion into desired product C $S=c_{\mathrm{C}}^{\mathrm{out}}/(c_{\mathrm{A}}^{\mathrm{in}}-c_{\mathrm{A}}^{\mathrm{out}})$;
- desired product yield $Y = XS$;
- maximum temperature in the catalyst bed T_{max}.

4. Simulation results

4.1. Steady-state regimes

At the first stage the modeling of steady-state regimes was performed. Fig. 1 demonstrates typical temperature and concentration profiles along the catalyst bed length. It is seen that both gas and catalyst temperatures are rising to the bed outlet due to heat of reactions (1)–(3). The conversion of initial reagent A (X) and yield of desired product C (Y) are rising to the outlet of the bed simultaneously with decrease of selectivity (S) caused by interaction of product C according to reaction (2) into products of deep conversion, which is accelerated at higher temperatures.

Obviously, maximum yield of desired product in the adiabatic bed is limited by objective factors. First of all, the

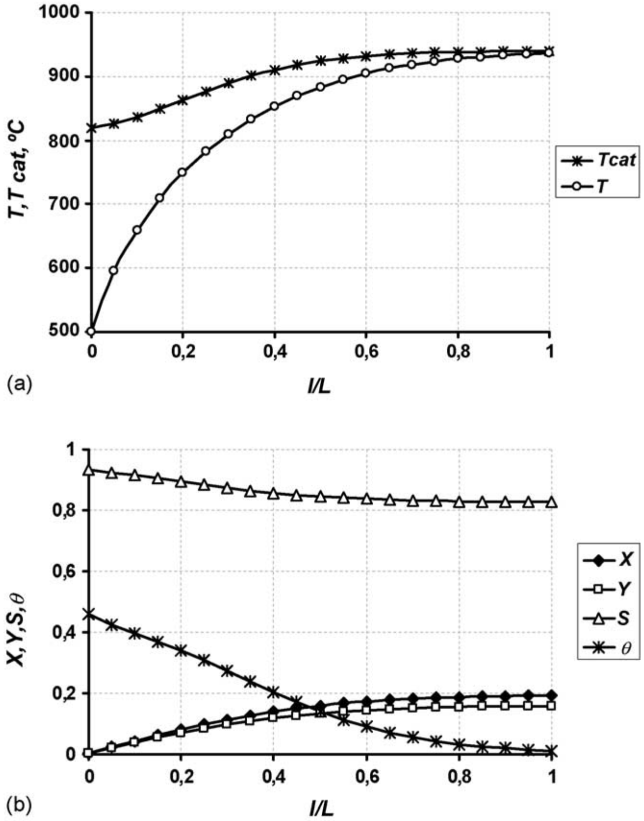

Fig. 1. Profiles of gas and catalyst temperatures (a), conversion, selectivity, yield and θ (b) along the bed length in the steady-state regime at $c_{\mathrm{A}}^{\mathrm{in}}=0.01$, $c_{\mathrm{B}}^{\mathrm{in}}=0.005$, $T_{\mathrm{in}}=500\,^{\circ}\mathrm{C}$, $T_{\mathrm{in}}=500\,^{\circ}\mathrm{C}$.

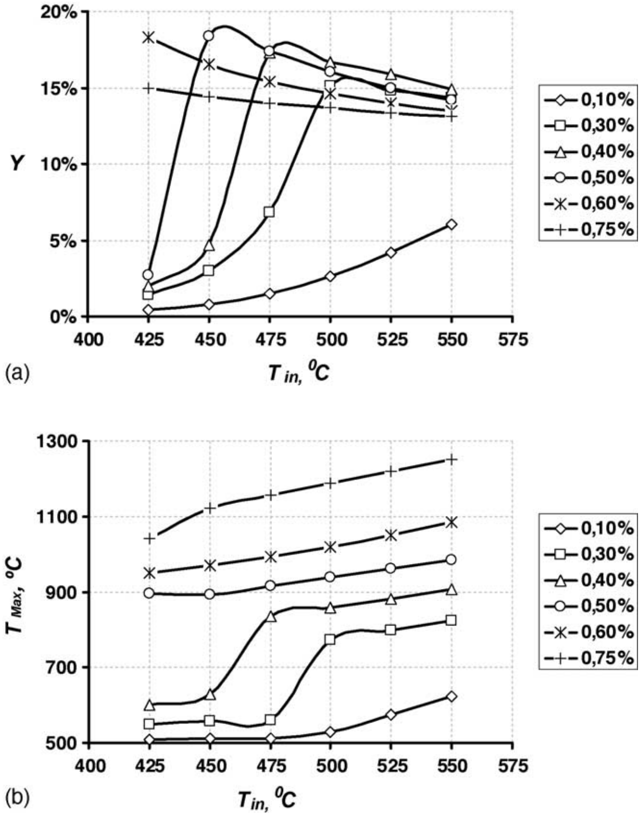

Fig. 2. Dependence of desired product C yield (a) and maximum catalyst temperature (b) in the steady-state regime upon T_{in} and c_{B}^{in} (values are given in the right part of figures) for $c_{\text{A}}^{\text{in}} = 0.01$ (1%).

limitations relate to initial concentrations of reagents, because their high values lead to overheating of the bed, which, in turn, stimulates occurrence of deep conversion reaction and decrease of selectivity, while their low values lead to low unit productivity of the catalyst. Then, such limitations relate to gas inlet temperature (T_{in}): from one hand, T_{in} must be high enough to provide acceptable conversion of reagents and, from the other hand, its rise leads to increase of $T_{\max}$, causing selectivity decrease.

Fig. 2 demonstrates the simulation results under variation of inlet gas temperature and initial concentration of reagent B. It is seen, that maximum yield of desired product is achieved at concentration ratio A/B twice higher than required by stoichiometry of target reaction with absolute values being quite low (not higher than 1 vol.%). Increase of reagent A concentration (up to 99%) causes some increase of selectivity, though overall product yield stays practically unchanged, because it is limited by a deficit of reagent B. At the same time increase of c_{B}^{in} is unreasonable, because it will lead to significant temperature rise and selectivity decrease.

4.2. *Nonstationary regime—"direct heat wave"*

Let us consider FFCC nonstationary regime when reagents A and B are fed separately in different phases of process cycle. In this case transient phenomena related both to temperature and concentrations may appear in the catalyst bed. Generally, such transient processes are well known. In particular, the theory of temperature fronts in adiabatic catalyst bed was described in [8], and, moreover, there are some publications directly related to such phenomena in the processes with dynamically changing state of the catalyst surface [9,10].

The most interesting for us is the cycle, when reagent A is fed into the adiabatic bed of catalyst, which surface is preliminary saturated with reagent B.

Feeding of the heated reaction gas into preheated catalyst bed leads to intensive interaction of reagent A with chemisorbed B, resulting in fast and significant overheating of the catalyst and, therefore, in extremely low selectivity. Similar phenomena are observed at feeding of cold gas into heated bed, when the gas is quickly heated due to heat exchange with hot catalyst.

More "soft" regime of reactions (1) and (2) performance is possible at feeding of heated gas into cold bed. In this case catalyst at the inlet part of the bed starts heating because of heat exchange with gas flow. Gradual increase of catalyst temperature leads to beginning of interaction between reagent A and chemisorbed reagent B, causing the reaction heat emission and further heating of the catalyst. When catalyst temperature exceeds the temperature of the gas flow interfacial heat exchange provides gas heating and transfer of the heat into areas of the bed, situated more far from the gas inlet, where similar processes are occurring. As a result, the heat and concentration waves, moving in direction co-current with the gas flow, are formed in the bed ("downstream" front).

Fig. 3 shows profiles of temperature and surface concentration of chemisorbed reagent B (θ) along the catalyst bed length in different time moments after start of the feeding of the heated gas flow, containing reagent A, into cold catalyst bed. It is seen (Fig. 3a) that in the initial phase of the process cycle the formation of the front is observed, and afterwards such front is characterized with established character, with its main parameters (propagation velocity, temperature and concentration gradients along the bed length, maximum temperature, reagents conversion, reaction selectivity and product yield) remaining constant until the end of the cycle (Fig. 4).

4.3. *Nonstationary regime—"reversed heat wave" [11]*

Let us consider nonstationary regime which is formed during feeding of cold reaction gas, containing reagent A, into cold bed of catalyst saturated with chemisorbed reagent B under increase of catalyst temperature in the outlet part of the bed by application of external heat flow q to this part of the bed during fixed heating time t_{heat}. Such heating may be described in the model by changing of boundary condition (10) for the following one:

$$0 < t < t_{\text{heat}}; \quad l = L \Rightarrow \lambda_{\text{eff}} \frac{\partial T_{\text{cat}}}{\partial l} = q \tag{16}$$

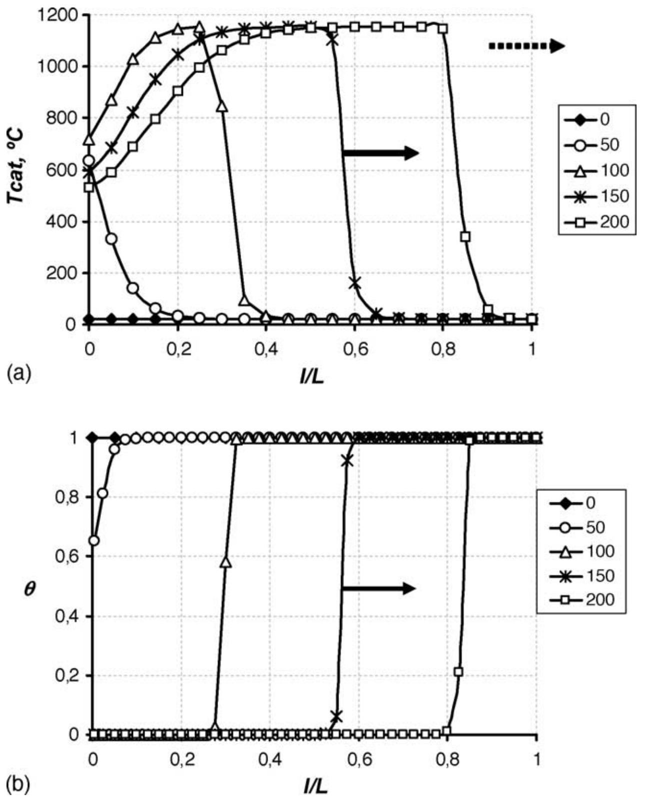

Fig. 3. Profiles of catalyst temperature (a) and surface concentration of reagent B (b) along the bed length in the different time moments (values shown in the right part of figures) under feeding of preheated reagent A flow to the cold catalyst bed, preliminary saturated with reagent B (“direct heat wave”). Conditions: $c_{\mathrm{A}}^{\mathrm{in}} = 1$, $c_{\mathrm{B}}^{\mathrm{in}} = 0$, $T_{\mathrm{in}} = 500\,^{\circ}\mathrm{C}$, $T_{\mathrm{cat}}^{\mathrm{init}} = 20\,^{\circ}\mathrm{C}$, $\theta_{\mathrm{init}} = 1$. Front propagation direction is shown by solid arrow, gas flow direction is shown by dashed arrow.

In that case the reactions (1) and (2) start to occur with emission of reaction heat in this part of the bed during catalyst temperature increase. Heat conductivity of the bed will cause heating of the catalyst and reaction initiation in the bed areas more closed to the inlet part. If the conductive heat flow will exceed heat transfer from catalyst to more cold reaction gas, then it will lead to formation of the heat and concentration fronts moving counter-current to the gas flow direction (upstream front or “reversed heat wave”).

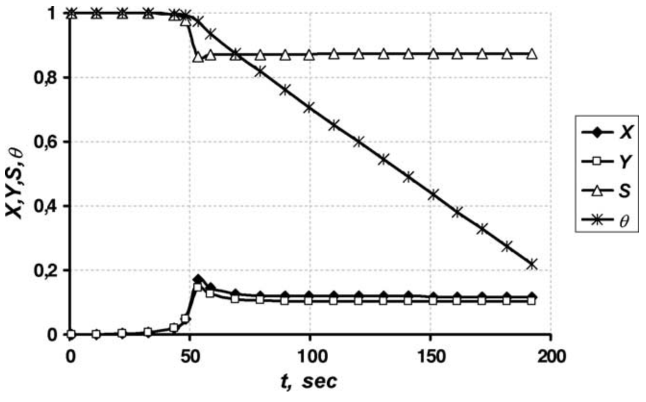

Fig. 4. Time changing of conversion, selectivity, yield and average (per bed length) surface concentration of reagent B in “direct heat wave”. Conditions: see Fig. 3.

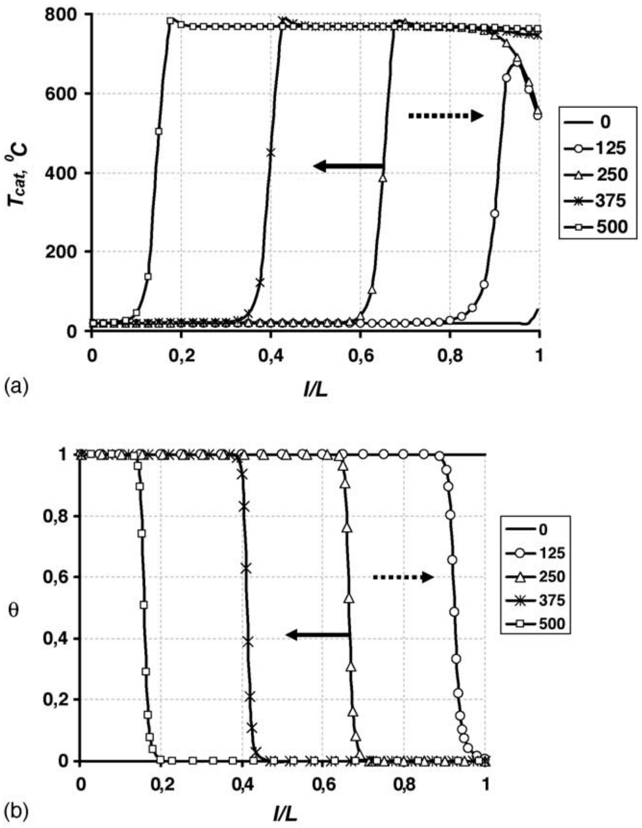

Fig. 5. Profiles of catalyst temperature (a) and surface concentration of reagent B (b) along the bed length in the different time moments (values shown in the right part of figures) under feeding of preheated reagent A flow to the cold catalyst bed, preliminary saturated with reagent B, in a “reversed heat wave” operation mode. Conditions: $c_{\mathrm{A}}^{\mathrm{in}} = 1$, $C_{\mathrm{B}}^{\mathrm{in}} = 0$, $T_{\mathrm{in}} = 20\,^{\circ}\mathrm{C}$, $T_{\mathrm{cat}}^{\mathrm{init}} = 20\,^{\circ}\mathrm{C}$, $\theta_{\mathrm{init}} = 1$, $t_{\mathrm{heat}} = 250\,\mathrm{s}$, $u = 0.1\,\mathrm{m/s}$, $a = 50$. Front propagation direction is shown by solid arrow, gas flow direction is shown by dashed arrow.

Theoretically the possibility of existence of such front was described in [8], furthermore, there are experimental confirmations of its formation and propagation in processes with changing state of the catalyst [12].

Typical structure of the upstream front and changing of its parameters in time is given in Figs. 5 and 6. It is seen that front has a clearly established character. The area of reactions occurrence is limited by a rather thin moving zone: in the part of the bed more closed to the gas inlet the reaction do not occur because of insufficient catalyst temperature, while in the bed part more close to outlet they do not proceed due to absence of reagent B at the catalyst surface.

Dislike the “downstream” front in this case action of interfacial heat exchange is counter-current to action of conductive heat transfer and reaction heat emission. Correspondingly, maximum catalyst temperature in “reversed heat wave” is lower than in “direct” one, resulting in increased reaction selectivity. Furthermore, inside the reaction zone itself the

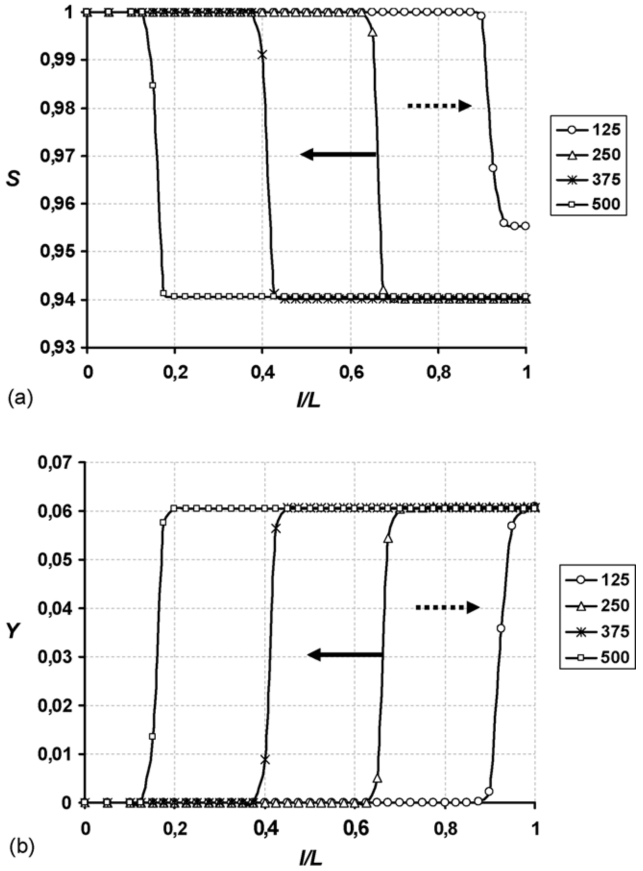

Fig. 6. Profiles of selectivity (a) and desired product yield (b) along the bed length in different time moments in a “reversed heat wave” operation mode. Conditions: see Fig. 5.

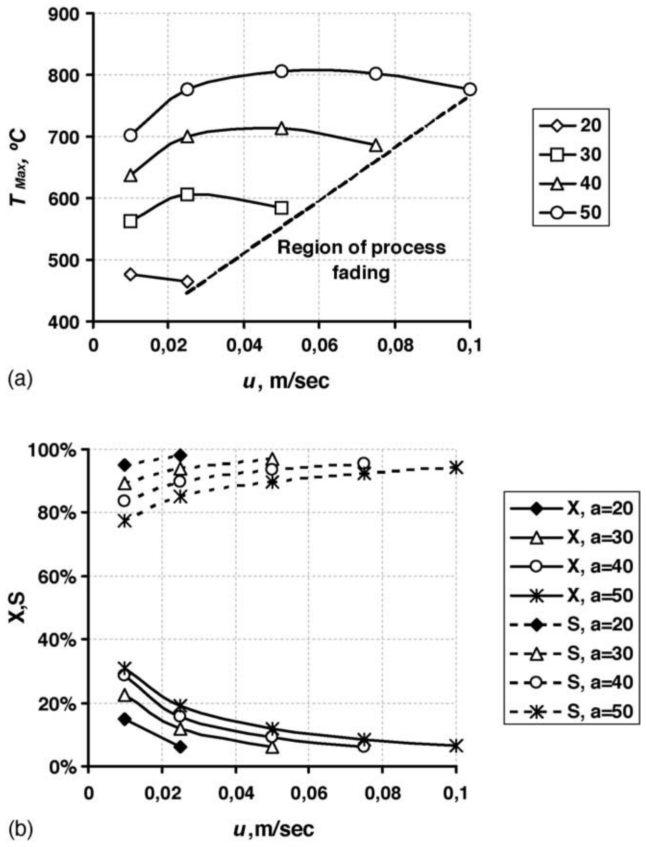

Fig. 7. Dependence of process parameters in a “reversed heat wave” operation mode upon gas linear velocity and chemisorption capacity of the catalyst (values of *a* shown in the right part of figures).

surface concentration of reagent B decrease is combined with the rise of the catalyst temperature, thus decreasing the rate of deep conversion reaction (2) and providing additional gain in selectivity. From the other hand, relative thickness of the reaction zone and lower temperatures lead to some decrease of total conversion of reagent A in comparison with “downstream” front.

Obviously, the reaction characteristics in “upstream” front and possibility of its existence in general significantly depend upon process performance conditions. First of all, the most valuable factors are the processes of heat exchange and heat conduction, which intensity is defined by geometrical parameters of catalyst pellets and reaction gas flow velocity u. The second factor is reaction heat emission, which is defined by both heat effects of reactions and value of catalyst chemisorption capacity a, the later also influencing such valuable technological process parameter as maximum duration of the cycle between switching of feed composition. Fig. 7 shows changing of “reversed heat wave” parameters under variation of a and u. It is seen, that at high gas velocities and low catalyst chemisorption capacity the heat exchange is dominating over heat emission and heat conduction, resulting in fading of reaction processes in the beginning of the process cycle and preventing “upstream” front formation. Increase of gas velocity leads to decrease of gas residence time in the reaction zone with following decrease of conversion with simultaneous selectivity rise (Fig. 7b). This situation, in turn, produces complicated dependence $T_{\max}$ from u, having a maximum in the area of middle values of u (Fig. 7a). Increase of catalyst capacity a always leads to the rise of maximum temperature, conversion and desired product yield, though with some decrease of selectivity.

Unlike the “downstream” case, influence of intensity of heat conduction on “upstream” front parameters is quite pronounced. Variation of heat conductivity coefficient showed that with rise of λ_{eff} the reaction zone is getting wider, what leads to conversion and desired product rise with simultaneous selectivity decrease. As a result, in the area of low λ_{eff} values the maximum temperature in the “upstream” front is rising with the increase of conductivity coefficient. At higher values of λ_{eff}, when the conversion is changing less significantly, intensification of heat conduction leads decrease of $T_{\max}$ due to more intensive dissipation of reaction heat. Besides mentioned parameters, increase of λ_{eff} also expands the area of process parameters which provide possibility of “upstream” front formation.

Table 1
Comparative parameters of process operation modes

No.	Parameter	Steady-state	Direct heat wave	Reversed heat wave
1	Maximum temperature in the catalyst bed (°C)	958	1153	780
2	Maximum conversion of feed reagent (%)	0.5	9.9	6.4
3	Selectivity (%)	99.4	89.5	94.2
4	Maximum desired product yield (%)	0.5	8.7	6.0

Therefore, variation of process performance conditions in "upstream" front regime (such as gas velocity, chemisorption capacity of the catalyst, effective heat conductivity of the catalyst bed) it is possible to optimize conversion/selectivity ratio in rather wide area in respect to process feasibility requirements.

5. Comparison of simulation results

Characteristics of all simulated regimes in comparable conditions ($c_{\mathrm{A}}^{\mathrm{in}} = 1$, $u = 0.1$ m/s, $L = 0.1$ m) are given in Table 1.

It is seen that maximum temperature for comparable conversions and product yield in both nonstationary FFCC regimes is significantly lower than in steady-state case. This is explained by the fact that in FFCC regime total heat emission in stages (1)–(3) is distributed among two process cycles, i.e. heat of reaction (3) during reagent A feeding is excluded from the system, because this reaction is performed in the separate process cycle. Moreover, significant part of reaction heat is utilized for heating of the catalyst, having low temperature in the beginning of each cycle. In the "reversed heat wave" the additional decrease of maximum temperature is also produced by counter-current action of heat-exchange and heat conductivity.

The possibility to decrease maximum temperature, in turn, defines the possibility to achieve in FFCC mode of operation higher reagents conversion with appropriate selectivity and, therefore, much higher desired product yield, than in steady-state regime. This circumstance is very important, because it gives the possibility to proportionally increase unit productivity of the catalyst and, thus, to significantly improve process feasibility.

Additional positive factor is higher concentration of desired product in outlet reaction gas, giving the way to simplify the product separation stage of the process.

References

[1] Yu.Sh. Matros, Catalytic Processes Under Unsteady-State Conditions, Elsevier Science Publishers, Amsterdam, 1988.

[2] P.L. Silveston, Composition Modulation of Catalytic Reactors, Gordon and Breach Science Publishers, 1998.

[3] D. Creaser, et al., Appl. Catal. A: Gen. 187 (1999) 147–160.

[4] R. Grabowski, et al., Appl. Catal. A: Gen. 232 (2002) 277–288.

[5] S.D. Jackson, F. King, G. Shipley, E.H. Stitt, US Patent 6,291,686 (2001).

[6] V.I. Drobyshevitch, V.P. Il'in, Computing Center SD RAS, Preprint No. 307, 1981.

[7] M.E. Aerov, O.M. Todes, D.A. Narinskii, Apparatus with Stationary Granular Bed, Khimia, Leningrad, 1979.

[8] O.V. Kiselev, Theoretical Investigation of Propagation of Heat Waves in the Catalyst Bed, Boreskov Institute of Catalysis, Novosibirsk, 1993.

[9] A.N. Zagoruiko, et al., Chem. Eng. Sci. 51 (1996) 2989–2994.

[10] A. Salden, G. Eigenberger, Chem. Eng. Sci. 56 (2001) 1605–1611.

[11] A.N. Zagoruiko, V.N. Tomilov, Russian Patent 2,002,134,060 (2002).

[12] L.I. Kalinkina, et al., Proceedings of the International Conference on Unsteady-State Processes in Catalysis, Novosibirsk, USSR, June 5–8, VSP, Utrecht, 1990, p. 525.