ANALYSIS OF THE OSCILLATORY BEHAVIOUR OF AN INDUSTRIAL REACTOR FOR OXONATION OF PROPENE; COMBINED MODELS

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Models have been used of the flow of the liquid phase in the reactor (cascade of two ideally mixed cells of different size, two equal-size cells with recycle, two equal-size cells with inlets to both cells and a model of two equal-size cells preceded with a back flow element with plug flow) to analyse the oscillatory states of an industrial reactor. Stable and instable steady states have been classified using analysis of pseudosteady states of conversion and temperature supplemented with a simulation of the dynamic behaviour. It has been found that the deviations of the flow from an ideally mixed system may expand the region of the oscillatory behaviour. The detailed information about the character of the flow in the reactor and the way of feeding the reactor has been also found important for the analysis of stability.

The oscillatory behaviour has been analysed of an industrial reactor for hydroformylation of propylene. Cool propylene, synthesis gas and a solution of cobalt catalyst enter the examined cylindrical reactor without impeller. The reaction that takes place here, together with the side reactions, at the temperature of about 410 K and the pressure of 30 MPa is first-order with respect to propylene. The cooling of the system is ensured by a set of cooling coils and the cold fed stream of propylene. Permanent temperature oscillations existed in the reaction mixture at increased loads on the industrial reactor. In the first communication[1] the cause for the appearance of the oscillations of the industrial reactor was studied on a model of a perfectly mixed cell. The analysis showed that the model explained the oscillatory behaviour only when an improbably high value of the activation energy, 109 kJ/mole, was used. The second communication[2] analysed the response of the reactor to an inlet impulse of a radioactive tracer and more complex models of the flow were sought, capable of describing the experimentally found response. The aim of this work is to analyse the cause for the instabilities of the reactor using more sophisticated models of the flow of liquid phase.

THEORETICAL

Mathematical models. A review of the studied models is furnished in Fig. 1. The behaviour of the first cell of the cascade is described by the following mass and enthalpy balances

$$\mathrm{d}c_F/\mathrm{d}\tau = (\dot{V} - \dot{V}_S)/V_F \cdot c_I + \dot{V}_R/V_F \cdot c_E - (\dot{V} - \dot{V}_S + \dot{V}_R)/V_F \cdot c_F - r_F \qquad (1)$$

$$\mathrm{d}T_F/\mathrm{d}\tau = (\dot{V} - \dot{V}_S)/V_F \cdot (T_I - T_0) + \dot{V}_R/V_F \cdot (T_E - T_0) - (\dot{V} - \dot{V}_S + \dot{V}_R)/V_F \cdot$$
$$\cdot (T_F - T_0) + r_F(-\Delta H)/(\varrho \cdot c_p) - \dot{Q}_F/(V_F \cdot \varrho \cdot c_p) \qquad (2)$$

with the initial conditions $\tau = 0$, $c_F = c_{F0}$, $T_F = T_0$.
The second cell was described by the following equations

$$\mathrm{d}c_E/\mathrm{d}\tau = (\dot{V} - \dot{V}_S + \dot{V}_R)/V_S \cdot c_F + \dot{V}_S/V_S \cdot c_I - \dot{V}/V_S \cdot c_E - \dot{V}_R/V_S \cdot c_E - r_S \qquad (3)$$

$$\mathrm{d}T_E/\mathrm{d}\tau = (\dot{V} - \dot{V}_S + \dot{V}_R)/V_S \cdot (T_F - T_0) + \dot{V}_S/V_S \cdot (T_I - T_0) -$$
$$- \dot{V}/V_S(T_E - T_0) - \dot{V}_R/V_S(T_E - T_0) + r_S(-\Delta H)/(\varrho \cdot c_p) - \dot{Q}_S/(V_S \cdot \varrho \cdot c_p) \qquad (4)$$

with the initial conditions $\tau = 0$, $c_E = c_{E0}$, $T_E = T_0$.
The element with the plug flow was described by

$$u \cdot \partial c/\partial l + \partial c/\partial \tau = -r \qquad (5)$$

$$u \cdot \partial T/\partial l + \partial T/\partial \tau = r \cdot (-\Delta H)/(\varrho \cdot c_p) - 4A/(\varrho \cdot c_p \cdot D) \cdot (T - T_c) \qquad (6)$$

FIG. 1
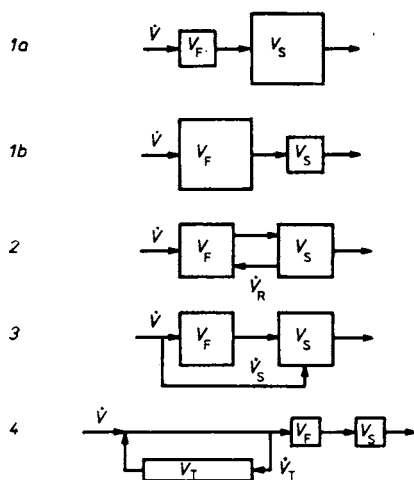
Review of used models. *1a*, *1b* cascade of two different-size cells; *2* cascade of two equal-size cells with back flow; *3* cascade of two equal-size cells with inlet to both cells; *4* combined model of two equal-size cells and a recycle with plug flow

with the boundary conditions

$$\dot{V}_T . c(L) + \dot{V} . c_1 = (\dot{V} + \dot{V}_T) . c(0) \tag{7}$$

$$\dot{V}_T . T(L) + \dot{V} . T_1 = (\dot{V} + \dot{V}_T) . T(0) . \tag{8}$$

The initial conditions for Eqs (5) and (6) were determined by the solution of the balance equations in the steady state. In view of the considerable uncertainty of the literature data[3-7] regarding the activation energy of the reaction, the stability of the regime was investigated for two limiting values, namely 66 and 109 kJ/mole. The equations describing the ideally mixed cells were solved by the standard Runge––Kutta method, the partial differential equations for the tubular reactor were solved by a simplified Gauss elimination method after transformation into the dimensionless and difference form.

Stability analysis. The character of the steady states for the ideally mixed cells was studied by the method described in refs[1-7] based on the observation of the curves of pseudosteady states of the temperature and conversion in the reaction rate *versus* degree-of-conversion phase plane. The stability of the models was also assessed by the dynamic simulation with the initial conditions close to the steady state values. The departure of the reactor from the steady state was simulated by an increase of the reaction temperature by 2 K.

RESULTS AND DISCUSSION

The literature gives for the activation energy values 66 and 109 kJ/mole. The value 66 kJ/mole was taken as more reliable as it was obtained recently by direct experimental measurement in the same factory where we studied the reactor. Higher values, on the contrary, come from older papers.

The adequacy of the description of the reactor was judged on the basis ofcomparison of the results of analysis with the observed facts. The analysis determined the stability of the system for the limiting values of the activation energy 66 and 109 kJ/mole for the principal operating regime as well as the regime at increased load. In the industrial reactor the principal regime was stable while the experimental regime displayed oscillatory behaviour.

Further we determined the minimum activation energy for which the given model predicted the oscillatory behaviour under the principal operating regime. This value of the activation energy was taken to be a measure of the "degree of instability of the regime".

During the analysis of stability considerable attention was paid to the stability of regime of the first members of the cascade. The behaviour of the first member is decisive for the overall stability, and, at the same time, the existence of instabilities

here is much more likely than in the second member. The first member of the cascade is fed by a cold stream of propene which increases the aptitude of the regime to instabilities. In addition, the concentration of the reactants, as well as the reaction rate in the first cell, is higher than in the second cell.

The results of stability analysis of the models are summarized in Tables I and II.

TABLE I

Review of the number and character of the steady states for the principal reactor load (data in parentheses) and the increased load NS — unconditionally stable; NI — unconditionally instable; CS — conditionally stable

Model number	Number of states		Character of states	
	$E = 66$ kJ/mole	$E = 109$ kJ/mole	$E = 66$ kJ/mole	$E = 109$ kJ/mole
1a	3	3	NS, NI[a], CS	NS, NI[a], CS
	(3)	(3)	(NS, NI[a], CS)	(NS, NI[a], CS)
1b	1	1	CS	CS
	(1)	(1)	(CS)	(CS)
2	1	3	CS	CS, NI, CS[a]
	(1)	(1)	(CS)	(CS)
3	1	1	CS	CS
	(1)	(1)	(CS)	(CS)
4	1	3	CS	CS, NI, CS[a]
	(1)	(1)	(CS)	(CS)

[a] States corresponding to operating regime of the reactor.

TABLE II

Review of stability of the regime for two limiting values of the activation energy and maximum values of the activation energy for the stable regime

Model number	$E = 66$ kJ/mole	$E = 109$ kJ/mole	Maximum value of E kJ/mole
1a	instable	instable	43—44
1b	stable	instable	71—72
2	instable	instable	65—66
3	stable	instable	71—72
4	stable	instable	67—68

Cascade of two different-size ideally mixed cells (models 1a and 1b). Analysis of the distribution of the residence times in this system led to the conclusion that the response of the system is approximately described by a cascade of two cells with the ratio of volumes $V_F/V_S = 0.25$ or $V_F/V_S = 4$. These two alternatives cannot be distinguished as they give identical responses to an inlet signal of the traces. The trajectory of the pseudosteady states of the temperature and conversion are presented for the ratio of volumes of the cells $V_F/V_S = 0.25$ (model *1a*) in Figs 2 and 3. Three steady states exist for the given model with the two limiting values of the activation energy for the principal and the elevated load. To the operating temperature corresponds the intermediate state exhibiting unconditional stability. This conclusion, however, is at odds with the experience as the principal operating regime of the industrial reactor was found stable. The analysis of the dynamic behaviour showed that a transition from the stable to instable behaviour takes place at increased loads already at an improbably low value of the activation energy of 43 to 44 kJ/mole.

With the opposite ratio of the size of the cells, $V_F/V_S = 4$, only one steady state exists, namely one with conditional stability (Figs 4 and 5). The stability of the model is therefore dependent on the ratio of the thermal and mass capacities of the system.

Dynamic simulation was used to analyse stability in more detail. It was found that at increased loads and the value of the activation energy 71 to 72 kJ/mole the regime was instable. The behaviour of the cascade of two cells with a larger first member approaches the perfectly mixed reactor. Since we consider the value of the activation energy 66 kJ/mole probable it may be concluded that this model leads to too stable systems.

Cascade of two equal-size mixed cells with the back flow of the reaction mixture. The pattern of the trajectories of the pseudosteady states in the phase plane is shown in Figs 6 and 7. For the activation energy 66 kJ/mole, the principal as well as the increased load, the results of the analysis were the states with conditional stability. At increased load and the activation energy 109 kJ/mole we could always prove the existence of three steady states. The state with the lowest reaction rate was conditionally stable, the intermediate state was unconditionally instable. The state with the highest reaction rate was conditionally stable and corresponded to the operating regime of the industrial reactor. The analysis of the dynamic behaviour showed that at increased feed rate of propylene the model passes into the instable region at the activation energy 65 to 66 kJ/mole. The behaviour of the model therefore corresponds to the observed stability of the industrial reactor.

Cascade of two equal-size ideally mixed cells with an inlet to both cells (model 3). From Figs 8 and 9 it may be seen that the state of the first member of the cascade of the cells at the principal and increased load is conditionally stable. The value of
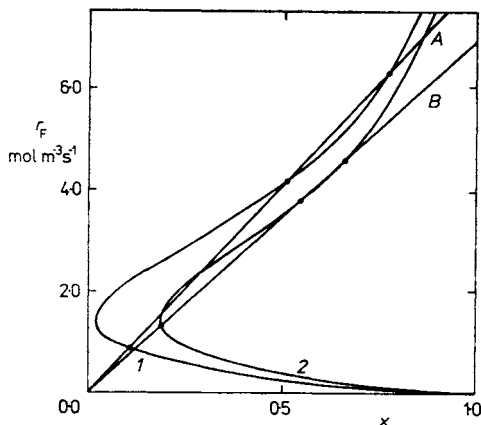
FIG. 2

Determination of the position and characteristic of the steady state for the first member of the model *1a* and activation energy $E = 66$ kJ/mole. *1A* increased load; *2B* principal load
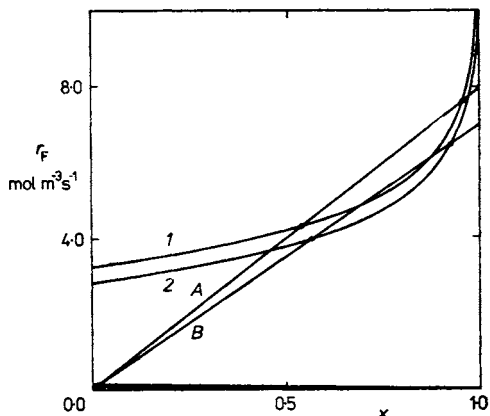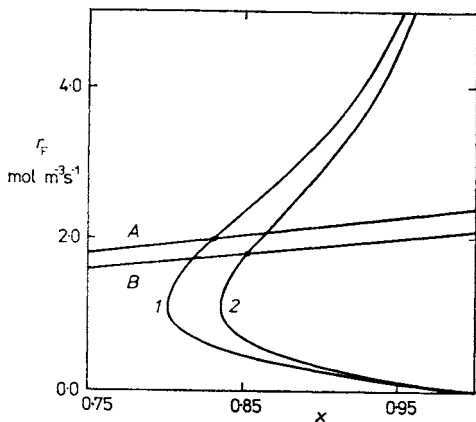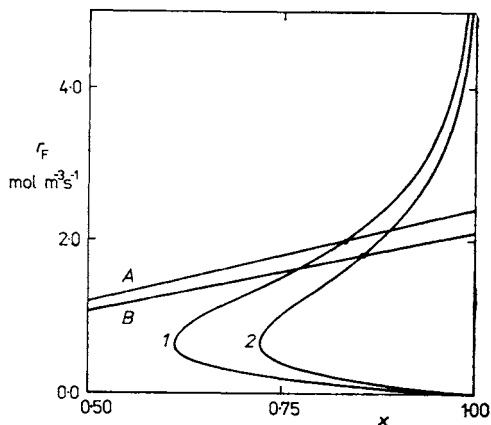

FIG. 3

Determination of the position and characteristic of the steady state for the first member of the model *1a* and activation energy $E = 109$ kJ/mole. *1A* increased load; *2B* principal load
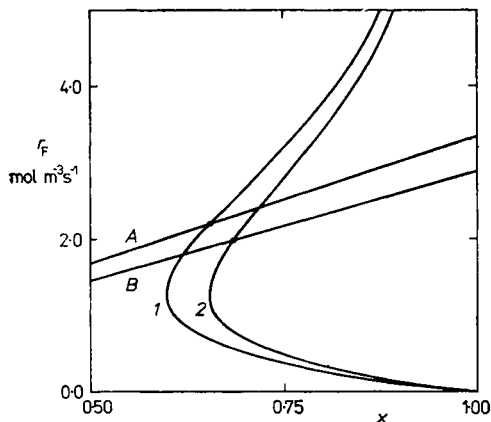

FIG. 4

Determination of the position and characteristic of the steady state for the first member of the model *1b* and activation energy $E = 66$ kJ/mole. *1A* increased load; *2B* principal load

FIG. 5

Determination of the position and characteristic of the steady state for the first member of the model *1b* and activation energy $E = 109$ kJ/mole. *1A* increased load; *2B* principal load
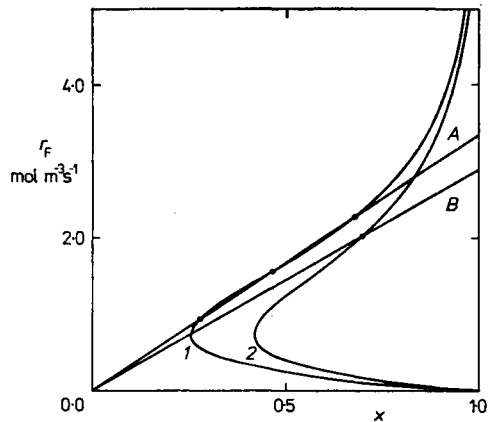
FIG. 6

Determination of the position and characteristic of the steady state for the first member of the model 2 and activation energy $E = 66$ kJ/mole. *1A* increased load; *2B* principal load

FIG. 7

Determination of the position and characteristic of the steady state for the first member of the model 2 and activation energy $E = 109$ kJ/mole. *1A* increased load; *2B* principal load
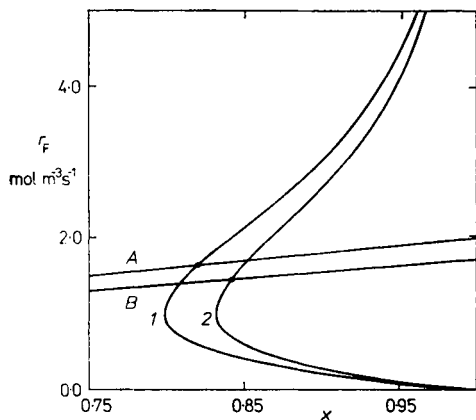

FIG. 8

Determination of the position and characteristic of the steady state for the first member of the model 3 and activation energy $E = 66$ kJ/mole. *1A* increased load; *2B* principal load
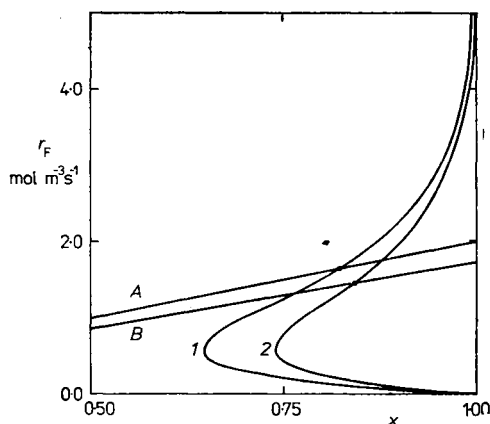

FIG. 9

Determination of the position and characteristic of the steady state for the first member of the model 3 and activation energy $E = 109$ kJ/mole. *1A* increased load; *2B* principal load

the activation energy is without effect on the character of the steady state. Analysis of the dynamic behaviour indicated appearance of instability at increased loads with the value of the activation energy 71 to 72 kJ/mole. This model thus behaved similarly as model *1b*.

Combined model of two equal-size ideally mixed cells and a recycle with plug flow (*model 4*). From the analysis of the pseudosteady states of the first member of the cascade it follows that the steady states display conditional stability (Figs 10 and 11). An exception is the value of the activation energy 109 kJ/mole for which, at an increased feed of propylene, we could prove the existence of three steady states. From these the intermediate state may be characterized as an unconditionally instable state. The simulation of the dynamic behaviour at the increased load showed that an approximate limit between the stable and the instable behaviour is represented by the value of the activation energy 67 to 68 kJ/mole. Further increase of the activation energy caused instable behaviour of the element with the plug flow preceeding the cascade. As the model explains most faithfully the observed facts, as well as the response of the reactor to an impulse of the tracer[2], it may be regarded as the most reliable. From this finding it may be concluded that the flow of the liquid phase in the reactor, induced by feed gases and thermal effects is relatively complicated. A possible pattern of the flow of the liquid phase is shown in Fig. 12.
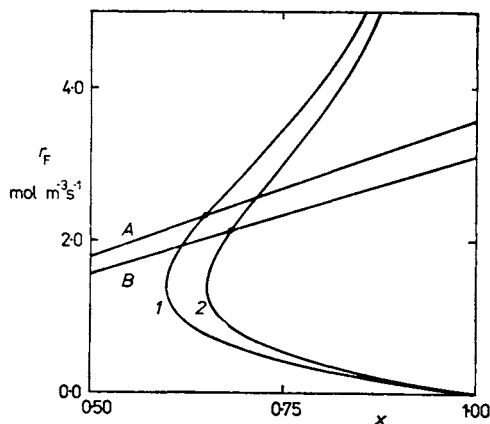

Fig. 10

Determination of the position and characteristic of the steady state for the first member of the model *4* and activation energy $E = 66$ kJ/mole. *1A* increased load; *2B* principal load
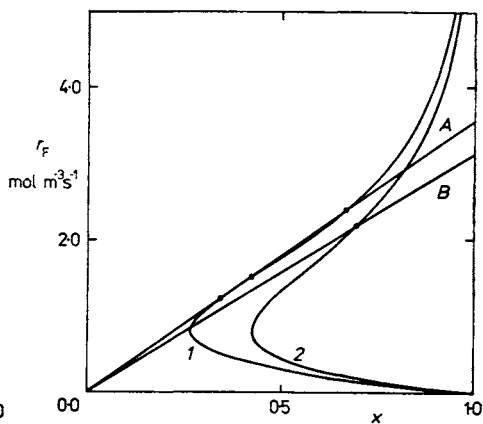
Fig. 11

Determination of the position and characteristic of the steady state for the first member of the model *4* and activation energy $E = 109$ kJ/mole. *1A* increased load; *2B* principal load

The analysis of the psuedosteady states of individual models indicated that the operating point of the oxonation reactor has a corresponding steady state with conditional stability. An exception represented the model $1a$ with the volume ratio of the cells $V_F/V_S = 0·25$. For this model the steady state may be characterized by un-
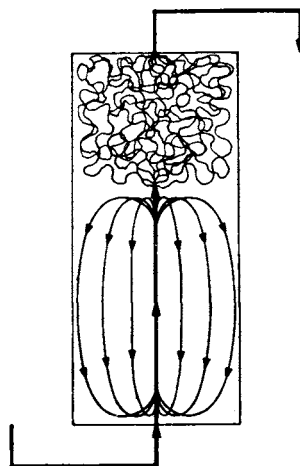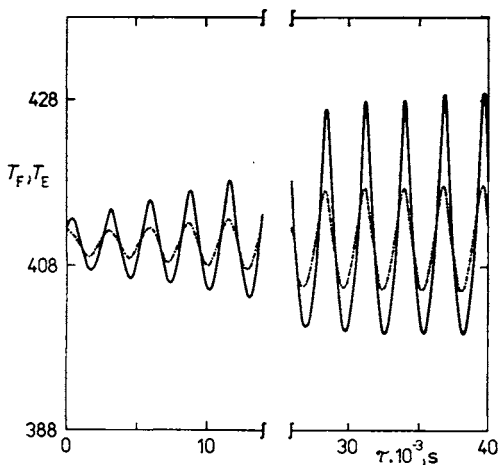

FIG. 12

Probable flow pattern of the liquid phase

FIG. 13

Simulated course of temperature in the first (solid line) and the second (dot-and-dash line) cell of the model $1b$ at increased load for activation energy $E = 75$ kJ/mole
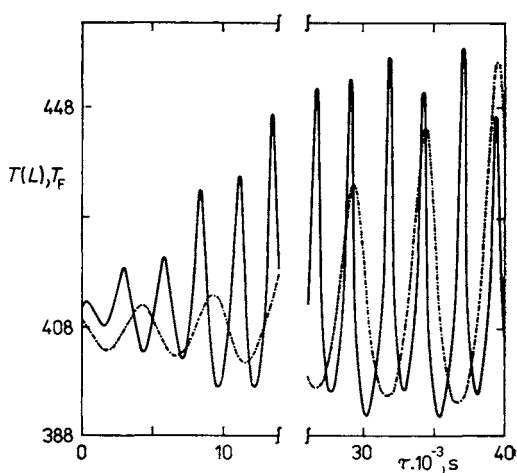

FIG. 14

Simulated course of temperature in the first cell (solid line) and in plug flow (dot-and-dash line) of the model 4 at increased load for activation energy $E = 70$ kJ/mole

conditional stability. The oscillatory behaviour of the industrial reactor at increased load can therefore be explained by a charge of the steady states as their stability depended on the ratio of the thermal and mass capacity of the system.

Simulation of the dynamic behaviour has shown that the limiting value of the activation energy, which brings about permanent oscillations, ranges between 65 and 72 kJ/mole. This result roughly corresponds to the experimentally found value of the activation energy 66 kJ/mole. The results of the mathematical modeling of the ideally mixed cell, which passed into the instable region with the activation energy exceeding 109 kJ/mole, as well as the results of the simulation using combined models showed that even relatively minor changes in the character of the flow of the liquid phase are significant for the assessment of stability.

The analysis of the dynamic behaviour of cellular models confirmed decisive role of the first member of the cascade on the stability of the system as a whole. Fig. 13 shows the time dependence of temperature in the first and the second cell of the cascade of ideally mixed cells with the volume ratio $V_F/V_S = 4$. The figure shows that the temperature maxima in the first member of the cascade are markedly more conspicuous than those for individual models and these maxima ranged between 20 and 30 K which is in good agreement with the operational data.

The decisive element for the stability of the model with plug flow was also the first cell of the cascade which displayed instable behaviour at lower values of the activation energy than the element with plug flow. The frequency of the oscillations in the cells was higher than those in the tubular reactor (see Fig. 14).

The analyses revealed that the oscillatory behaviour of the industrial reactor cannot be accounted for by the change of the character of the steady state. The dynamic behaviour of the models of the flow of the liquid phase exhibits at increased loads temperature oscillations at the values of the activation energy close to the experimental value of 66 kJ/mole. Since for the ideally mixed system the region of instable behaviour shifts toward values of the activation energy above 109 kJ/mole, one can put forth as a possible cause of the oscillations of the hydroformylation reactor the imperfect mixing of the reaction mixture.

LIST OF SYMBOLS

c	concentration of propylene in plug flow element, mole/m^3
c_E	concentration of propylene at the outlet from the 2nd cell, mole/m^3
c_{E0}	steady state concentration in reactor, mole/m^3
c_F	concentration of propylene in the 1st cell, mole/m^3
c_{F0}	steady state concentration in reactor, mole/m^3
c_I	inlet concentration of propylene, mole/m^3
$c(L)$	outlet concentration of propylene from plug flow element, mole/m^3
c_p	specific heat of reaction mixture, J/kg K
$c(0)$	inlet concentration of propylene into the plug flow element, mole/m^3
D	diameter of plug flow element, m

E	activation energy, J/mole
ΔH	heat of reaction, J/mole
K	heat transfer coefficient, W/m^2
L	distance within plug flow element, m
$\dot{Q}_F$	heat removed by cooling in the 1st cell, W
$\dot{Q}_S$	heat removed by cooling in the 2nd cell, W
r	reaction rate in plug flow element, $mole/m^3$ s
r_F	reaction rate in the 1st cell, $mole/m^3$ s
r_S	reaction rate in the 2nd cell, $mole/m^3$ s
T	temperature in plug flow element, K
T_C	temperature of coolant, K
T_E	outlet temperature from the 2nd cell, K
T_I	inlet temperature, K
T_F	temperature in the 1st cell, K
$T(L)$	outlet temperature from plug flow element, K
$T(0)$	inlet temperature into plug flow element, K
T_0	reference temperature, K
u	linear velocity of reaction mixture in plug flow element, m/s
$\dot{V}$	volume flow rate of liquid phase, m^3/s
V_F	volume of the 1st cell of cascade, m^3
$\dot{V}_S$	inlet volume flow rate into the 2nd cell of cascade, m^3/s
V_S	volume of the 2nd cell of cascade, m^3
$\dot{V}_R$	volume flow rate of back flow, m^3/s
$\dot{V}_T$	volume flow rate in plug flow element, m^3/s
x	conversion
ϱ	density of reaction mixture, kg/m^3
τ	time, s

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