EFFECT OF EXTERNAL HEAT AND MASS TRANSFER ON STEADY STATES OF NON-ISOTHERMAL NON-ADIABATIC CONTINUOUS STIRRED TANK REACTOR

F.Jiráček and J.Horák

Department of Organic Technology,
Institute of Chemical Technology, 166 28 Prague 6

The effect of heat and mass transfer at the external surface of catalyst particles on steady states of non-isothermal, non-adiabatic continuous stirred, tank reactor is studied on a mathematical model for the exothermic first order reaction. Examples are given on behaviour of the reactor when there exist three steady states of the reactor. The results of calculations are verified experimentally in a laboratory reactor for the reaction of oxygen with hydrogen. The possibility of existence of isolated branches of steady reactor states (so-called isol) has been proved experimentally.

The behaviour of a reactor can be affected for an exothermic catalytic reaction by heat transfer between the reaction mixture and the heat carrier as well as by the imperfect mass and heat transfer at the external surface of the catalyst particle (further on referred to as: the external mass and heat transfer). In chemical literature is described in detail the behaviour of an isothermal and adiabatic reactor for the exothermic non catalyzed or homogeneously catalyzed reactions[1-8,14-16]. These reactors represent the limiting cases of behaviour. Only in some papers also the effect of heat transfer between the reaction mixture in a reactor and the surrounding bath[9-10,18] was studied. Simultaneous effect of external mass and heat transfer on behaviour of the reactor has not yet been studied.

THEORETICAL

In the reactor an exothermic first order reaction takes place. It is assumed that the reaction rate is a function of partial pressure of a single reactant A and of temperature at the external surface of the catalyst particle

$$r_R = k_{00} p_{As} \exp\left(E(T_s - T_{00})/(RT_{00}T_s)\right) . \tag{1}$$

The effect of external heat and mass transfer on the reaction rate is described by a method identical to that applied in the last study[11]. The result is the dimensionless

relation for the reaction rate on composition and temperature in the reactor

$$R\beta = (P_A - R\beta\Phi)\exp\left(\Theta\,\frac{R\beta\Phi\Omega + \Delta T}{1 + R\beta\Phi\Omega + \Delta T}\right). \tag{2}$$

The individual parameters Θ, Φ and Ω were discussed in the papers published earlier[11-12]. It is also assumed that the reactor is operated as an ideally stirred reactor in steady state and that the physico-chemical properties of the reaction mixture at the reactor inlet and outlet are identical. After transformation into a dimensionless form, the balances of component A and of heat in the reactor are given by the relations

$$R\beta\mathrm{Da} = 1 - P_A, \tag{3}$$

$$R\beta\Theta\Omega = \Delta T(B + 1/A) - \Delta T_0/A, \tag{3a}$$

where Da is the modified Damkoehler's number

$$\mathrm{Da} = WRT_{00}r_{00}/(F p_{A0}). \tag{4}$$

In these equations A is the parameter characterizing the ratio of the heat transferred from the external surface of catalyst particles into the reaction mixture and the heat transferred from the reactor into the bath

$$A = Wk_h a_m/(Ph), \tag{4a}$$

and B is the parameter characterizing the ratio between the heat carried away by the reaction mixture at the reactor outlet and the heat transferred from the external surface of catalyst particles into the bulk of mixture

$$B = Fc_p\gamma/(Wk_h a_m) \tag{4b}$$

and ϑ is the dimensionless adiabatic input of thermal energy

$$\vartheta = \Delta T_{ad}/T_{00} = \Phi\Omega/(\mathrm{Da}B). \tag{4c}$$

For numerical solution of the system of Eqs (2), (3) and (3a) is advantageous to combine these equations into a single one which is then valid for behaviour of the whole reactor

$$(1 - R\beta\,\mathrm{Da} - R\beta\Phi)\exp\left[\Theta\,\frac{R\beta\Phi\Omega + (AR\beta\Phi\Omega + \Delta T_0)/(1 + AB)}{1 + R\beta\Phi\Omega + (AR\beta\Phi\Omega + \Delta T_0)/(1 + AB)}\right] - R\beta = 0 \tag{5}$$

This equation has been solved numerically on the Computer Tesla 200 by the regula falsi method.

EXPERIMENTAL

The reaction between hydrogen and oxygen (with air) was used as the model reaction. The catalyst was platinum on alumina (0·3 weight percentage of Pt) in the form of pellets 4·5 . 4·5 mm. The reactor volume was 11·3 cm³ and was insulated by polystyrene (the reactor bath was thus surrounding the reactor). In the reactor was situated the propeller mixer 10 mm in diamater rotating at 400 r.p.m. The measurement has been performed at atmospheric presure and laboratory temperature (temperature of the reactor's environment) in the range of hydrogen concentrations with air from 0 to 5 volume %. During the experiment were measured in steady state the temperature of the reaction mixture in the reactor, temperature in the centre of catalyst particles and hydrogen concentration in the mixture at the reactor outlet. The analytical method and measurement of temperature of particles is described in detail in the last publication[17].

In each measurement, the hydrogen concentration at the inlet was fixed and then the temperature of the reaction mixture in the reactor, temperature of the catalyst particles and hydrogen concentration in the mixture at the reactor outlet were measured at constant rate, temperature and feed concentration. As soon as the measured quantities were constant, the values corresponding to steady states were measured. Temperature of the feed and of the environment laboratory were identical. The measurements were performed at various feed rates, the obtained results were the dependence of reaction rate and of temperature difference between the particle and the bulk of reaction mixture on the degree of conversion of hydrogen.

For the given geometrical arrangement of the reactor its behaviour could have been affected by changes of hydrogen concentration in the feed, heat and mass transfer itensity at the external surface of catalyst particle and by changes of hydrodynamic conditions in the reactor (by changing the position of the catalyst particle in respect to the mixer).

RESULTS AND DISCUSSION

In nonisothermal nonadiabatic reactor where the effect of imperfect external heat and mass transfer is of prime importance, the course of exothermic reaction is affected by the twofold autothermic effect. It is manifested both by superheating of the bulk of reaction mixture in respect to the surrounding bath as well as by superheating of the catalyst particles in comparison to the bulk of reaction mixture. The ratio of heat transfer intensity between the reactor and the bath and the heat removed by the reaction mixture is decisive for the role of superheating of the bulk of reaction

mixture (in the considered mathematical model characterized by the product of parameters A and B). The state of the reactor as concerns this heat transfer can vary between two limiting states. The first is the isothermal reactor (the product of parameters AB is very small) while the second state is the adiabatic reactor (the value of product is large). In both limiting states the behaviour of the reactor (dependence of the reaction rate on composition of the reaction mixture in the reactor) is independent on the feed rate of the reaction mixture. This is because from the mathematical model all quantities in which the feed rate appeared were eliminated. Thus for determination of steady states of the reactor graphical solution can be used[12].

In nonisothermal nonadiabatic reactor which operates between two limiting states both cooling mechanism of the reaction mixture are made use of while the ratio of both components of heat removed from the reactor depends on the feed rate. At large feed rate the controlling mechanism is the adiabatic cooling (removal of heat by the outlet reaction mixture) while at low feed rate the removal of heat through the reactor wall into the media is prevailing. Thus behaviour of the reactor at high feed rates (small degree of conversion of the reactant) is close to the adiabatic reactor and at small feed rates (large degree of conversion) close to the isothermal reactor. The effects which can appear in the nonisothermal, nonadiabatic reactor can be therefore estimated if the behaviour of the isothermal and adiabatic reactors are known.

The behaviour of the isothermal reactor with the effect of external mass and heat transfer was studied in the preceding paper[12]. It was found that the reaction rate increased (in reactions with the positive reaction order) with the increasing concentration of the reactant. Due to the autothermal effects on the catalyst particles
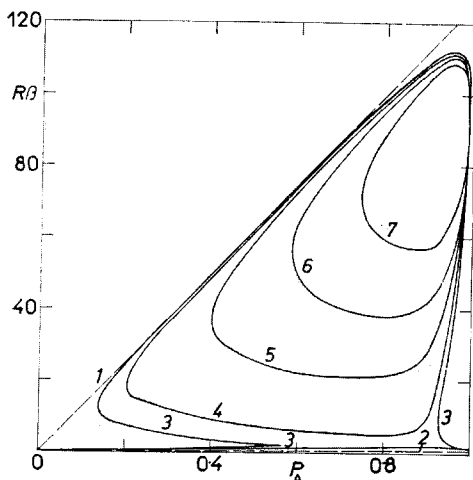

Fig. 1

Effect of Heat Transfer Intensity Between the the Reactor and Bath on Steady States of Nonisothermal Nonadiabatic Continuous Stirred Tank Reactor

$\Theta = 25$, $\Phi = 0.008$, $\Omega = 0.4$, $\Delta T_0 = 0$, $B = 20$ (Da $= 0.0001$); 1 diffusion region, 2 kinetic region, 3 $A = 8$, 4 5, 5 2, 6 1, 7 0.5.

a considerable increase in the reaction rate can take place in a narrow interval of concentrations. Sometimes as many as three states of particles exist at one concentration. The existence of three steady states of particles is the necessary though not sufficient condition for the existence of multiplicity of reactor states (as long as the multiplicity of states of particles is not shifted into the region of large conversions). There can exist at one feed rate as many as three steady states of the reactor. The phenomenon appears which is known as the "ignition" and "extinction". The extinction takes place by an increase in the conversion, ignition by its decrease. Multiplicity of steady states of the reactor of this type are further-on called the isothermal multiplicity.
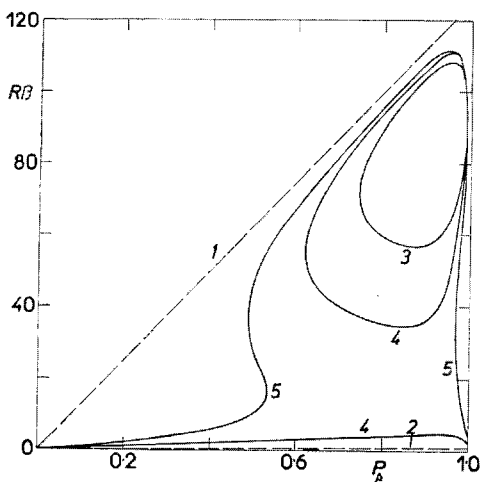

FIG. 2

Effect of Heat Transfer Intensity Between the Reactor and Bath on Steady States of Nonisothermal Nonadiabatic Continuous Stirred Tank Reactor

$\Theta = 30$, $\Phi = 0.01$, $\Omega = 0.5165$, $\Delta T_0 = 0$, $B = 20/Da = 0.001$); *1* diffusion region, *2* kinetic region, *3* $A = 50$, *4* 5, *5* 1, *6* 0.1, *7* 0.001.

FIG. 3

Effect of Feed Temperature on Steady States of the Reactor for Examples Given in Fig. 1

$A = 0.5$; *1* diffusion region, *2* kinetic region, *3* $\Delta T_0 = 0.4$, *4* 0.05, *5* 0.10.
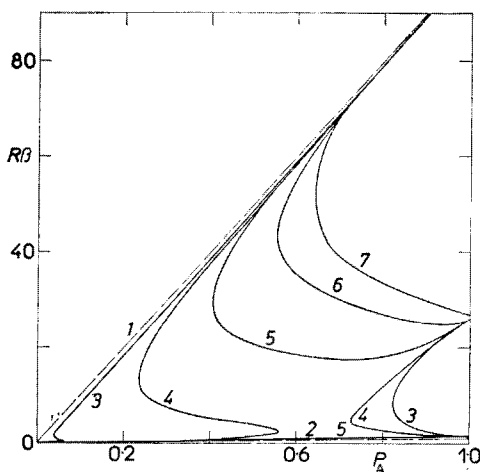
In the adiabatic reactor for an exothermic reaction the reaction rate might increased conversion of the reactant[13]. This phenomenon can be observed at low conversions and is the result of the effect of increase in temperature of the mixture on the reaction rate. Under certain conditions there can exist at one feed rate as many as three steady states of the reactor. When the effect of external mass and heat transfer in an adiabatic reactor is significant there can exist the region of conversions in which at one conversion the particle has three steady states. The multiplicity of states of particle is at the same time the sufficient condition for multiplicity of states of the reactor. Extinction takes place due to decreasing degree of conversion, ignition by its increase. The multiplicity of steady states of the reactor of this type is called

Fig. 4

Effect of Feed Temperature on Steady States of the Reactor for the Example Given in Fig. 2

$A = 0.001$; *1* diffusion region, *2* kinetic region, *3* $\Delta T_0 = -0.1$, *4* 0, *5* 0.02, *6* 0.05, *7* 0.10.
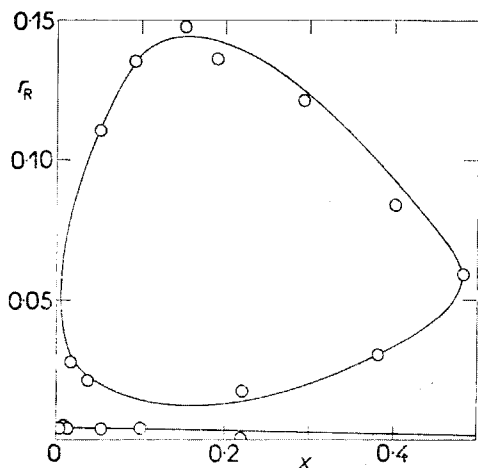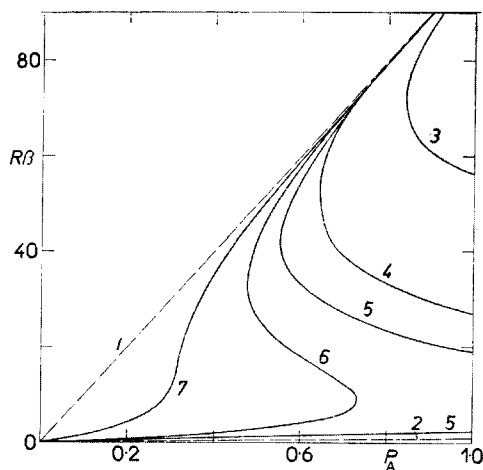

Fig. 5

Example of Experimental Dependence of Reaction Rate on Conversion of Hydrogen at Concentration in Feed $c_{H_0} = 7.539 . 10^{-4}$ mol/l

$T_0 = 291.1$ K, $W = 0.0728$ g.

the adiabatic multiplicity. Superheating of catalyst particles is introducing a new situation into the behaviour of the reactor in the region of adiabatic multiplicity. It is the existence of multiple states at one conversion. Without considering the superheating of the particles multiple states can exist at one feed rate but not at one conversion.

From the given survey is obvious that the simultaneous effect of superheating of the bulk of reaction mixture in the reactor and the catalyst particle enables formation of a very wide spectrum of behaviour of the nonisothermal non-adiabatic reactor. At increasing the feed rate (decreasing the value of the Damkoehler number) the states of the reactor are transferred into isothermal states at the temperature of the bath
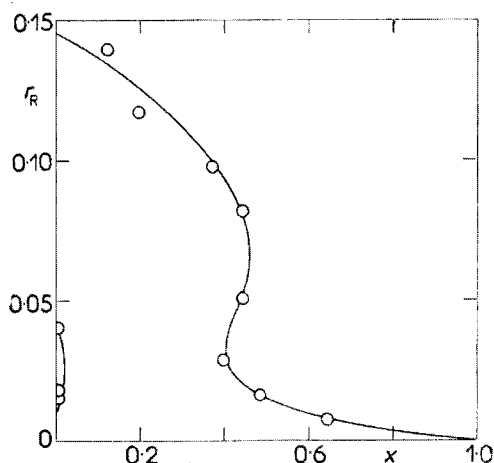

Fig. 6

Example of Experimental Dependence of Temperature Difference Between the Catalyst Particles and the Bulk of Reaction Mixture on Conversion of Hydrogen for Feed Concentration $c_{H_0} = 8 \cdot 357 \, . \, 10^{-4}$ mol/l

Other conditions are identical with those in Fig. 5.

Fig. 7

Example of Experimental Dependence of Reaction Rate on Conversion of Hydrogen for Feed Concentration $c_{H_0} = 7 \cdot 93 \, . \, 10^{-4}$ mol/l

Other conditions are identical with those in Fig. 5.
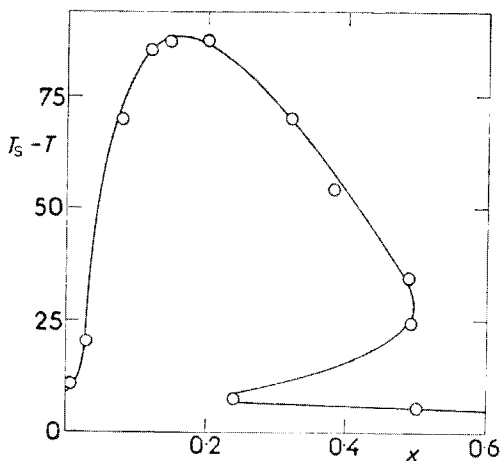
to the adiabatic reactor at the temperature of the feed. There can exist both the multiplicity of states of the reactor of isothermal type and of the adiabatic type or of both simultaneously.

The calculated examples of steady states of reactors are given in Figs 1 and 2. Both these examples differ in the significance of the effect of external mass and heat transfer and the shape of the rate equation of the reaction (temperature dependence of the rate constant). At a small cooling intensity through the wall of the reactor (large value of the parameter A) there exists a multiplicity of the calculated dependence both of the isothermal and the adiabatic type. In the case of smaller significance of the effect of external mass and heat transfer (Fig. 1), both types of multiplicities are inside the interval of conversions of the reactant in the range from zero to one. In the case of more profound effect of external mass and heat transfer (Fig. 2) the part of the region of multiplicity of adiabatic type is already beyond this interval and one of the points is missing. The possibility of simultaneous existence of both types of multiplicity has been predicted by Van Heerden[1] and was confirmed theoretically on a mathematical model of nonisothermal nonadiabatic continuous stirred tank reactor for an exothermic reaction in the homogeneous phase by Furusawa and Nishimura[10].

With increasing cooling intensity of the reactor through the wall both multiplicities merge and form separate steady states of the reactor (forming an isola) where the ignition point does not exist but where exist two points of extinction. Extinction takes place both by increased and decreased 'conversion. It is possible to bring the reactor into steady states with large reaction rates on the isola only by deeply affecting its regime. Finally, at a very high cooling intensity through the reactor wall these isolas disappear and the reactor behaves as isothermal.
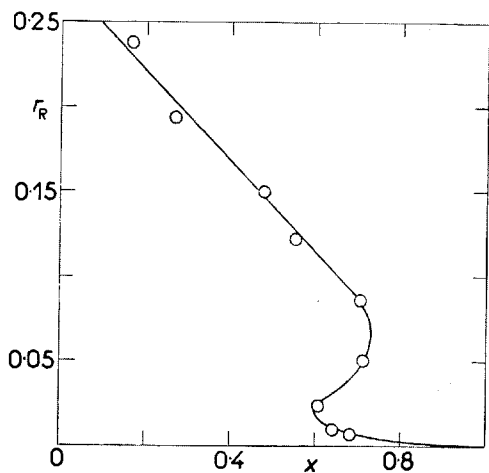

Fig. 8

Example of Experimental Dependence of Reaction Rate on Conversion of Hydrogen for Feed Concentration $c_{H_0} = 1 \cdot 047 \cdot 10^{-3}$ mol/l

Other conditions are identical with those in Fig. 5.

The behaviour of the reactor is also dependent on the relation between the temperature of the bath and the temperature of the feed. Increasing temperature of the feed in comparison to the temperature of the bath the multiplicity of the adiabatic type slowly disappears and the transfer of the regime of catalyst particles into the diffusion region takes place (Figs 3 and 4). On the contrary with decreasing feed temperature the behaviour of the reactor is closer to the behaviour of the isothermal reactor.

It can be expected that the discussed phenomena can be encountered in practice *e.g.* in the rocket technique or in the catalytic purification of the exhaust gases.

The made experiments have proved the possible existence of most of the discussed cases. The examples of the measured results are given in Figs 5 to 8. Under the given design conditions it was possible to affect the behaviour of the reactor by selection of the inlet concentration of hydrogen. The dependences which prove the possibility of existance of both types of multiplicities of steady states of the reactor, are measured in a relatively narrow range of the inlet concentration. As the catalyst is always changing its activity in dependence on time, it is possible to expect that at one inlet concentration the one type of dependence will be transferred into the second. In agreement with this conclusion is also explained the fact that the sequence of individual types is not kept up with regard to the values of the inlet concentration.

The analysis of stability of steady states of the reactor is not discussed in this paper. But from the results given in the last paper[12] results that in case when the most important capacity of the system is the thermal capacity of catalyst particles, all steady states are stable with the exception of saddle points *i.e.* with the exception of steady states of the reactor, which are the middle ones from three possible at one feed rate. Position of these unstable steady states of the reactor were estimated from the experimental temperature of catalyst particles below which the regime of the reactor transfers into the kinetic region and above it into the diffusion region.

LIST OF SYMBOLS

A	parameter defined by Eq. (*4a*)
a_m	external surface of catalyst particles in a unit of mass
B	parameter defined by Eq. (*4b*)
$^cH_0$	hydrogen concentration in the feed into the reactor (mol/l)
c_p	specific heat of the mixture
Da	Damkoehler number (Eq. (*4*))
E	activation energy of reaction
F	volumetric feed rate of mixture into the reactor
ΔH	heat of reaction
h	heat transfer coefficient from the reactor into the bath
k_{GA}	mass transfer coefficient at the external surface of catalyst particles
k_h	heat transfer coefficient at the external surface of particles
k_{00}	rate constant at temperature T_{00}

P area of heat transfer in the reactor

p_A, p_{A0}, p_{As} partial pressures of the reactant in the bulk of reaction mixture, in the feed and on the external surface of particles

$p_A = p_A/p_{A0}$ dimensionless partial pressure in the bulk of the reaction mixture

r_{00} reaction rate at temperature T_{00} and pressure p_{A0} under conditions when the effect of external heat and mass transfer is eliminated

r_R reaction rate $(mol/g_{rat}\ h)$

R gas constant

$R\beta = r_R/r_{00}$ dimensionless reaction rate

T temperature of the bulk of reaction mixture (K)

T_0 temperature of bath   (K)

T_{00} temperature of feed   (K)

T_S temperature of the external surface of particles   (K)

$\Delta T = (T - T_{00})/T_{00}$ dimensionless temperature of the bulk of reaction mixture

$\Delta T_0 = (T_0 - T_{00})/T_{00}$ dimensionless temperature of the bath

$\Delta T_s = (T_s - T_{00})/T_{00}$ dimensionless temperature of the external surface of particles

ΔT_{ad} adiabatic increase in temperature

W mass of catalyst   (g)

x degree of conversion

γ density of mixture

$\Theta = E/RT_{00}$ dimensionless activation energy

$\Phi = r_{00}/k_{GA}a_m p_{A0}$ dimensionless parameter

$\Omega = (-\Delta H) k_{GA} p_{A0}/k_h T_{00}$ dimensionless parameter

ϑ dimensionless adiabatic rise in temperature   (Eq. (4c))

REFERENCES

1. Van Heerden C.: Ind. Eng. Chem. *45*, 1245 (1953); Chem. Eng. Sci. *8*, 133 (1958).
2. Bilous O., Amundson N. R.: AIChE J. *1*, 513 (1955).
3. Aris R., Amundson N. R.: Chem. Eng. Sci. *7*, 131 (1958).
4. Douglas J. M., Rippin D. W.: Chem. Eng. Sci. *21*, 305 (1966).
5. Schmitz R. A., Amundson N. R.: Chem. Eng. Sci. *18*, 265 (1963).
6. Liu S. L., Amundson N. R.: Z. Elektrochem. *65*, 276 (1961).
7. Goldstein P. R., Amundson N. R.: Chem. Eng. Sci. *20*, 449, 447, 501 (1965).
8. Hlaváček V., Kubíček M., Jelínek J.: Chem. Eng. Sci. *25*, 1441 (1970).
9. Kylstra F. J.: III. European Symp. on Chem. Reaction Eng., Amsterdam 1964.
10. Furusawa T., Nashimura H.: Chem. Eng. Sci. *1*, 180 (1967).
11. Horák J., Jiráček F.: This Journal *35*, 1760 (1970).
12. Horák J., Jiráček F.: This Journal *36*, 1720 (1971).
13. Mamula P.: *Thesis*. Institute of Chemical Technology, Prague 1973.
14. Longwell J. P., Weiss M. A.: Ind. Eng. Chem. *47*, 1634 (1955).
15. Furusawa Z., Nashimura H., Miyauchi T.: J. Chem. Eng. Jap. *2*, 95 (1969).
16. Vetasa S. A., Schmitz R. A.: AIChE J. *16*, 410 (1970).
17. Jiráček F., Havlíček M., Horák J.: This Journal *36*, 64 (1971).
18. Uppal A., Ray W. H.: Chem. Eng. Sci. *29*, 967 (1974).

Translated by M. Rylek.