

CONTROL OF CASCADE OF CSTR WITH AN AUTOCATALYTIC REACTION. ISOTHERMAL REGIME

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Dedicated to late Academician Eduard Hála.

Regime stability of a cascade of continuous stirred reactors operated isothermally is analyzed for a reaction with autocatalytic type of kinetic law. Consequences of the regime unstabilities are discussed and control algorithms suggested to operate the cascade in both stable and unstable operating points. Numerical simulations are used to test the algorithms. Reaction calorimetry serves as the source of information on the reactor state in conversion control in unstable states if no on-line analytical method is available to measure conversion.

The continuous stirred tank reactor (CSTR) with an autocatalytic reaction can have multiple steady states at constant reaction temperature¹. To operate the reactor or a cascade of reactors in unstable operating points, a feedback control algorithm must be applied. When developing the algorithm, practical constraints have to be respected. As storage of the reaction mixture between the reactors is impossible, the feed rates into all cascade members are equal and cannot be manipulated as independent variables. For many reactions heat exchangers cannot be inserted between the reactors and the inlet temperature of each reactor is determined by the exit temperature of the stream-up member of the cascade. Due to these limitations the number of manipulable variables which could be used for the regime control is limited. These limitations cause no serious problems in control of reactions with positive reaction order. For these reactions the only problem is the temperature control. If an effective temperature control is achieved, all operating points are stable and stabilization of the feed rate results in a stable cascade regime. For chemical reactions with an autocatalytic type of kinetics even if isothermal operation is ensured, multiple stationary regimes with some unstable operating points may appear. The autocatalytic kinetics is typical for some polymerizations with chain mechanism² and for reactions catalyzed by microorganisms. In the paper the conversion control problems of a cascade with effective independent temperature control are analyzed.

THEORETICAL

The reactors are supposed to be ideally mixed and equipped with a cooling system with intensive coolant recycling (Fig. 1). The cooling system is described as an ideally mixed cell. The temperature of the cooling system is supposed to be efficiently controlled by a "master-slave" controller that means that the cooling system temperature can be stabilized as an independent input variable. The reactors have favourable heat transfer area to volume ratio to remove the reaction heat at small temperature difference between the reaction mixture and the coolant. Consequently, the stationary states are stable from the point of view of the thermal regime.

The key component balance of the reactor number I

$$\dot{V}_{cA}(0) [X(I-1) - X(I)] + r(I) V_r(I) = V_r(I) dX(I)/d\tau. \quad (1)$$

Heat balance of the reactor number I

$$\begin{aligned} \dot{V} \rho c_p [T(I-1) - T(I)] + r(I) V_r(I) \cdot (-\Delta H) + \dot{Q}_{s,i}(I) = \\ = K(I) A(I) [T(I) - T_c(I)] + V_r(I) \rho c_p dT(I)/d\tau. \end{aligned} \quad (2)$$

Heat balance of the cooling system

$$\begin{aligned} \dot{V}_{cs}(I) \rho_c c_{pc} [T_{ci}(I) - T_c(I)] + K(I) A(I) [T(I) - T_c(I)] = \\ = V_{cs}(I) \rho_c c_{pc} dT_c(I)/d\tau. \end{aligned} \quad (3)$$

To simulate the temperature control the "master-slave" control mode was used (the cascade control system). The first controller reads the reaction temperature and gives the set value of the cooling system temperature. The second controller uses this set

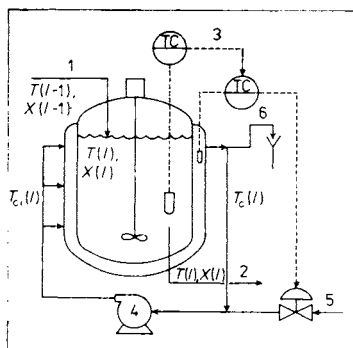


FIG. 1

Scheme of cascade member I . 1 Feed; 2 outlet; 3 temperature "master-slave" control; 4 recycling pump; 5 fresh coolant feed; 6 exit of coolant

value to control the temperature of the cooling system. For both controllers the algorithm of a proportional controller with bias was used

$$T_c^s(I) = T_{c0}^s(I) + G_1[T^s(I) - T(I)] \quad (4)$$

$$\dot{V}_{fc}(I) = \dot{V}_{fc0}(I) + G_2[T_c(I) - T_c^s(I)]. \quad (5)$$

To describe the autocatalytic behaviour of the reaction the following rate equation was used

$$r(I) = kc_A(I) [1 + k_a c_B(I)]^n \quad (6)$$

with $n = 3$, where c_A is the concentration of the reactant, c_B concentration of the product.

The dependence of the constants k and k_a on temperature was expressed by equations

$$k = k_0 \exp[-E/RT(I)] \quad (7)$$

$$k_a = k_{a0} \exp[-E_a/RT(I)]. \quad (8)$$

The effect of temperature on viscosity of the reaction mixture was described by equation³

$$\eta = \eta_0 \exp[E_\eta/RT(I)]. \quad (9)$$

The viscosity of the reaction mixture in dependence on conversion was determined from Arrhenius–Kendall equation⁴

$$\ln \eta = x_A \ln \eta_A + x_B \ln \eta_B, \quad (10)$$

where x_A and x_B are the molar fractions of the reactant and the product respectively.

For calculation of the heat dissipated by the snack stirrer and of the heat transfer coefficient usual criterial equations were used⁴.

The list of parameter values is given in Table I.

RESULTS AND DISCUSSION

Degrees of Freedom

The number of degrees of freedom depends on the control goal formulation. In many industrial processes (for example in polymerizations) the reaction temperature is fixed to keep the product quality at a standard value. The reaction volumes of the

reactors are fixed from practical reasons and cannot be varied, too. Then the following situations can be met:

Case 1. The reaction temperature, the reactors volumes and the cascade load are fixed. The system has no degree of freedom, the exit degree of conversion cannot be controlled, its value results from the properties of the system.

Case 2. The reaction temperature is fixed and the cascade load can be manipulated. Then the degree of conversion in one selected cascade member can be controlled using a feedback controller. The control is limited to one reactor due to the fact that the feed rate is equal for all cascade members.

In case 1, only stable operating points can be utilized because there is no manipulable inlet variable available for the feedback stabilization of unstable states. In case 2, both stable and unstable operating points can be utilized using the feed rate as the manipulated variable.

TABLE I
Parameter values

Parameter	Dimension	Value
$c_A(0)$	mol m^{-3}	6 800
c_p	$\text{J kg}^{-1} \text{K}^{-1}$	2 100
c_{pc}	$\text{J kg}^{-1} \text{K}^{-1}$	4 200
E	J mol^{-1}	60 000
E_a	J mol^{-1}	40 000
E_η	J mol^{-1}	48 000
ΔH	J mol^{-1}	-40 000
G_1	—	5
G_2	$\text{m}^3 \text{s}^{-1} \text{K}^{-1}$	$5 \cdot 10^{-5}$
k_0	s^{-1}	$1 \cdot 17 \cdot 10^2$
k_{a0}	$\text{m}^3 \text{mol}^{-1}$	$1 \cdot 33 \cdot 10^2$
n	—	3
R	$\text{J mol}^{-1} \text{K}^{-1}$	8 314
T^s	K	411
\dot{V}	$\text{m}^3 \text{s}^{-1}$	$5 \cdot 5 \cdot 10^{-4}$
\dot{V}_c	$\text{m}^3 \text{s}^{-1}$	$2 \cdot 5 \cdot 10^{-3}$
V_{cs}	m^3	0.5
V_r	m^3	2.1
η_0	Pa s	$1 \cdot 10^{-3}$
ϱ	kg m^{-3}	900
ϱ_c	kg m^{-3}	1 000

Stability Analysis

If an independent isothermal temperature control is ensured, the only source of instability of an operating point may be the concentration instability (isothermal instability). The instability is caused by unstable orientation of the driving force of dynamic concentration changes (conversion changes) in the vicinity of the operating point.

If the reaction rate can be expressed as a function of a single concentration variable (for example conversion) the dynamic equation for cascade member can be expressed by Eq. (1). At constant temperature the operating point is stable if the condition is fulfilled

$$\frac{dr(I)}{dX(I)} < \frac{\dot{V}}{V_r(I)}. \quad (11)$$

For one state variable (conversion) the state space reduces to a "state straight line" and the driving forces can be represented in a simple graphical form. Examples are given in Figs 2 and 3. Fig. 2 illustrates a regime with one stable state, Fig. 3 a regime with three stationary states, two being stable and one unstable.

Consequences of Steady States Multiplicity

If in any reactor of the cascade three steady states can exist at the given load, more than one set of stationary states of the cascade must be expected. Unless the member

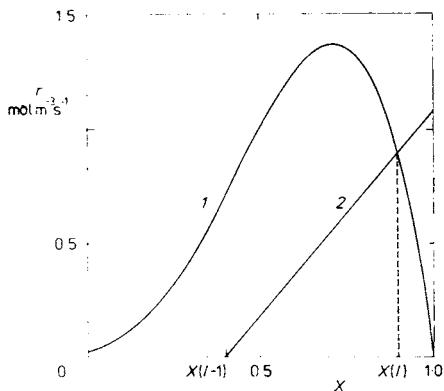


FIG. 2

Graphical representation of the key component balance for the cascade member *I*, one stable state existing. 1 Rate of consumption; 2 net rate of input by the feed

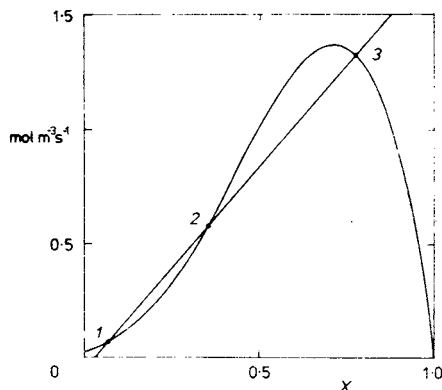


FIG. 3

Graphical representation of the key component balance for the cascade member *I*, three states existing. 1, 3 Stable states; 2 unstable state

with multiple steady states is the last one, its multiplicity affects steady states of all stream-down reactors. An example of all combinations of steady states for four member cascade is given in Fig. 4. From the practical point of view of the conversion control it is essential that existence of multiple steady states in more than one reactor is improbable. Taking the second reactor as an example, multiple steady states can exist only for the steady state with the lowest reaction rate of the first reactor. If the first reactor is operated in the unstable state or in the high reaction rate state, multiplicity is impossible in the second cascade member.

Fig. 5 indicates that the steady state multiplicity can exist only in certain range of load. In Fig. 6 and 7 an example of the effect of load on stationary conversions in cascade member 1 and 2 is described. The stable states 2A in the second member correspond to the states 1A (stable high reaction rate states of the first cascade member). The stable states 2B of the second member correspond to the unstable states 1B in the first member. If the first member is operated in the stable low reaction rate state 1C the second member can be operated in three states, two of them (2CI and 2CIII) being stable and one (2CII) unstable.

In the stable states the reactor can be operated without feedback concentration control that means that the regime of the cascade can be stabilized through stabilizing the feed rate, inlet composition and reaction temperature. If the open-loop unstable operating point should be employed, a feedback controller must be applied to keep

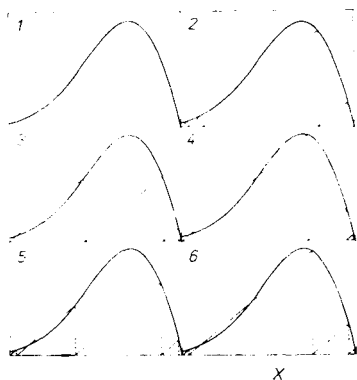


FIG. 4

All combinations of steady states in a four member cascade. 1 Reaction rate as a function of conversion; 2–6 graphical representation of the key component balance for individual cases

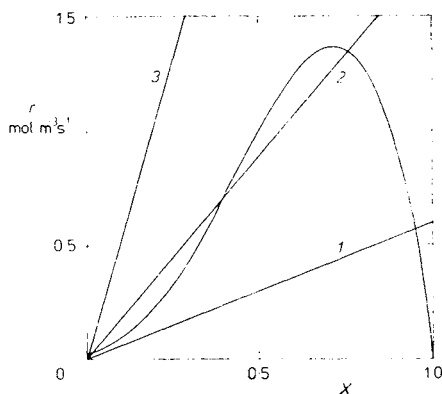


FIG. 5

The effect of load changes on the key component balance 1 $\dot{V}/V_r(I) = 0.88 \cdot 10^{-4} \text{ s}^{-1}$; 2 $\dot{V}/V_r(I) = 2.65 \cdot 10^{-4} \text{ s}^{-1}$; 3 $\dot{V}/V_r(I) = 5.13 \cdot 10^{-4} \text{ s}^{-1}$

the conversion in the unstable operating point. Furthermore, if multiplicity exists, special start-up procedure must be developed to reach the desired set of the operating states.

When designing the control system, it is advantageous to reach a cascade regime without great differences in heat production between the cascade members. From this point of view utilization of unstable states could be useful. If three states exist, they differ in the stationary reaction rates. The reaction rates corresponding to the stable states may be either too high or too low. In this case utilization of the unstable states could be useful to achieve equalized heat production in the reactors.

Stabilization of Conversion by Feedback Control

An on-line analytical method must be available for the conversion stabilization. As the feed rate is common to all cascade members, the feedback control can be applied to one reactor only. The other must be operated as dependent units without feedback control. If the regime of one reactor is unstable, the feedback control must be applied to the unstable cascade member. Stabilization of more than one cascade member in unstable operating points is impossible.

In control simulations the reactant feed rate was used as the manipulated variable. In the ideally mixed reactor the feed rate represents a very efficient manipulated variable having rapid response⁵. Consequently, a very simple algorithm can be used to control conversion in unstable states. A bang-bang algorithm (relay with switching

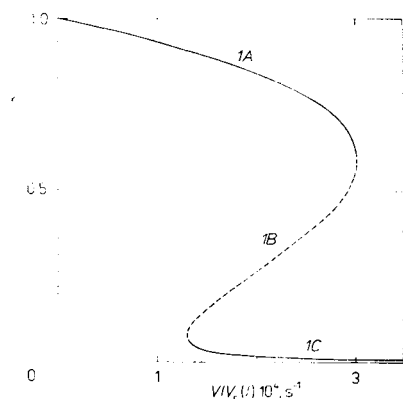


FIG. 6

Stationary conversion as a function of load for the cascade member No. 1. *1A* High reaction rate stable states; *1C* low reaction rate stable states; *1B* unstable states

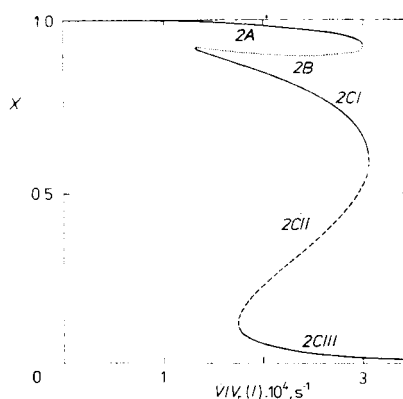


FIG. 7

Stationary conversion as a function of load for the cascade member No. 2. *2A*, *2B*, *2CI*, *2CIII* Stable states, *2CII* unstable states

difference) was tested. It is supposed that the conversion of the key component can be continuously measured by a rapid response on-line method. The algorithm is defined in the following way: Two limits of the switching difference are defined: X_{\min} and X_{\max} , where $X_{\min} < X_{\max}$. The feed rate is manipulated according to the following conditions:

$$\text{IF } X < X_{\min} \text{ THEN } \dot{V} = 0 \quad (12)$$

$$\text{IF } X > X_{\max} \text{ THEN } \dot{V} = \dot{V}_1 \quad (13)$$

$$\text{IF } X_{\min} < X < X_{\max} \text{ AND } dX/d\tau < 0 \text{ THEN } \dot{V} = \dot{V}_1 \quad (14)$$

$$\text{IF } X_{\min} < X < X_{\max} \text{ AND } dX/d\tau > 0 \text{ THEN } \dot{V} = 0 \quad (15)$$

An example of control simulation is given in Fig. 8. In a cascade of three reactors the first one is operated in an unstable state. The feed is preheated to the reaction temperature. The amplitude of conversion oscillations in the first reactor is determined by the control algorithm, and thus by the switching difference ($X_{\max} - X_{\min}$). The amplitudes of oscillations in other two reactors are proportional to the ratio of the mean reaction rates

$$(X_{\max} - X_{\min})_I = (X_{\max} - X_{\min})_1 r(I)/r(1), \quad (16)$$

where $r(I)$ is the mean reaction rate in the I -th reactor, $r(1)$ the mean reaction rate in the first reactor. Oscillations are not dangerous for the control safety.

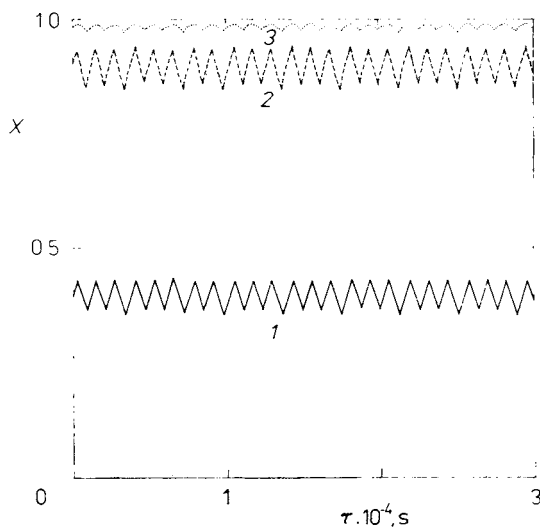


FIG. 8

Feedback control of cascade using on-line analytical method. 1 First reactor operated in unstable operating point; 2 second reactor in stable operating point; 3 third reactor in stable operating point

Control of Reactor with Cold Feed

In the first reactor significant amount of heat can be consumed to heat the cold feed to the reaction temperature. The cold feed acts as additional cooling. In this case the bang-bang algorithm, which is effective for safe stabilization of conversion, complicates the temperature control. The change of the feed rate represents a jump change of the cooling rate. This results in subcooling of the reactor content after the cold feed is switched on. Comparison of the first reactor control with preheated and cold feed is given in Fig. 9.

Utilization of Reaction Calorimetry for Conversion Control

The method of feedback control described above cannot be applied if no analytical method for rapid on-line conversion measurement is available. Then a suitable substituting measurable quantity must be found for the feedback control. Reaction calorimetry represents one possibility to solve the problem. The reaction calorimetry consists in evaluating the rate of heat production.

Stabilization of the rate of heat production can result in stabilization of conversion if the following conditions are fulfilled:

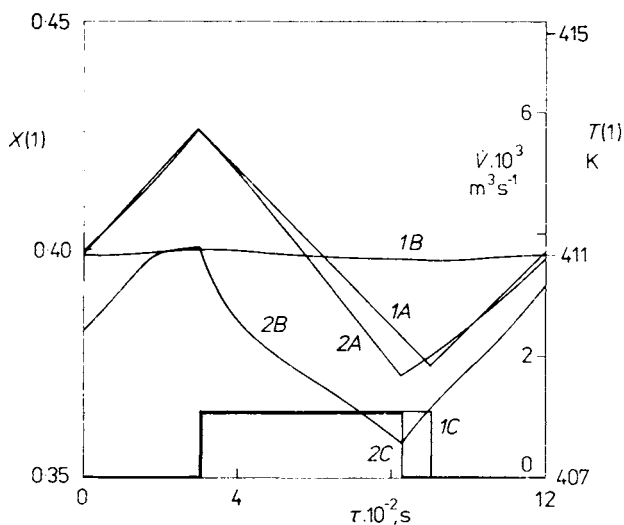


FIG. 9

Comparison of the first reactor control with preheated and cold feed using on-line analytical method. One switching cycle is presented. 1 $T(0) = 411$ K; 2 $T(0) = 370$ K; A conversion; B temperature; C feed rate as functions of time

The reaction temperature is stabilized at a constant value. The reactivity of the reaction mixture (the rate constant) is fully reproducible (no changes of the catalyst or initiator activity affect the reaction rate). The rate of heat production is a monotonous function of conversion within certain interval including the set value of conversion. The rate of heat production must be sensitive to conversion changes (the reaction must not be zero order to conversion). The sign of the first derivative $d\dot{Q}/dX$ must be known (positive order or autocatalytic region of the kinetic law). The reaction calorimetry was tested in two modifications:

Modification 1: The rate of heat production is evaluated from the heat balance of the cooling system.

Neglecting dynamic accumulation of heat in the cooling system and heat loss into the surroundings the heat balance of the cooling system can be written in the following simplified form

$$\dot{Q} = \dot{V}_c \rho_c c_{pc} (T_c - T_{ci}), \quad (17)$$

where \dot{Q} is the heat flux from the reaction mixture into the cooling system. To evaluate the heat flux the flowrate of the coolant, its inlet and exit temperatures must be measured.

For exothermic reactions the main item of heat production is the reaction heat. For reactions in viscous media (e.g. polymerizations) additional heat is added by the stirrer. The amount of dissipated heat depends on the mixture viscosity, consequently it changes with conversion if the mixture viscosity changes with conversion. The additional heat affects the sensitivity of the heat production rate to conversion changes. For a positive order region, the sensitivity of the heat production rate can be diminished by compensation of the reaction heat decrease by the dissipated heat increase. In highly viscous media dissipated heat increase may outweigh the reaction heat decrease and the total heat production increases ($d\dot{Q}/dX > 0$) in this region (Fig. 10). For an autocatalytic region, a synergetic effect can be expected. The effects of conversion increase on heat production and parameters connected with cooling of polymerization reactors are given in Table II and in Fig. 10.

Modification 2: The pseudostationary driving force of cooling was used as the substituting controlled variable. The relation of this variable to the rate of heat production is given by equation

$$(T - T_c) \approx \dot{Q}/KA. \quad (18)$$

That means that the dependence of the driving force on conversion is affected by the changes of the heat transfer coefficient. In the positive order region this effect diminishes while in autocatalytic region augments the sensitivity of the driving force to conversion changes (Table II).

In simulations the algorithm of the relay with switching difference was used. The algorithm must be applied in two logic variants according to the sign of derivative $d\dot{Q}/dX$.

TABLE II

Effects of conversion increase on heat production and parameters connected with cooling of polymerization reactors

Variable	Positive order region ^a	Autocatalytic region ^a
Reaction heat	--	+
Viscosity	+	+
Dissipated heat	+	+
Heat transfer coefficient	-	--
Cooling driving force	+	+

^a + Increase; - decrease.

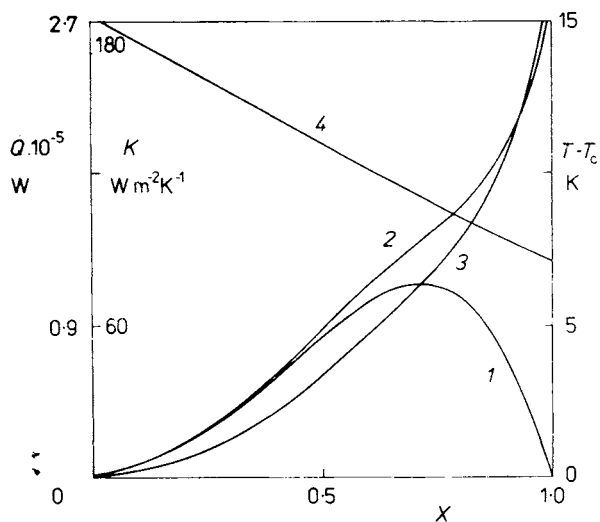


FIG. 10

Effect of conversion on heat production and other parameters connected with reactor cooling. 1 Reaction heat production; 2 total heat production; 3 driving force of cooling ($T - T_c$); 4 heat transfer coefficient K

1. $d\dot{Q}/dX < 0$ (positive order region with low heat production by the stirrer)

$$\text{IF } \dot{Q} < \dot{Q}_{\min} \text{ THEN } \dot{V} = \dot{V}_1 \quad (19)$$

$$\text{IF } \dot{Q} > \dot{Q}_{\max} \text{ THEN } \dot{V} = 0 \quad (20)$$

$$\text{IF } \dot{Q}_{\min} < \dot{Q} < \dot{Q}_{\max} \text{ AND } d\dot{Q}/d\tau < 0 \text{ THEN } \dot{V} = 0 \quad (21)$$

$$\text{IF } \dot{Q}_{\min} < \dot{Q} < \dot{Q}_{\max} \text{ AND } d\dot{Q}/d\tau > 0 \text{ THEN } \dot{V} = \dot{V}_1. \quad (22)$$

2. $d\dot{Q}/dX > 0$ (autocatalytic region or positive order reaction with high heat production by the stirrer)

$$\text{IF } \dot{Q} < \dot{Q}_{\min} \text{ THEN } \dot{V} = 0 \quad (23)$$

$$\text{IF } \dot{Q} > \dot{Q}_{\max} \text{ THEN } \dot{V} = \dot{V}_1 \quad (24)$$

$$\text{IF } \dot{Q}_{\min} < \dot{Q} < \dot{Q}_{\max} \text{ AND } d\dot{Q}/d\tau < 0 \text{ THEN } \dot{V} = \dot{V}_1 \quad (25)$$

$$\text{IF } \dot{Q}_{\min} < \dot{Q} < \dot{Q}_{\max} \text{ AND } d\dot{Q}/d\tau > 0 \text{ THEN } \dot{V} = 0. \quad (26)$$

Both substituting controlled variables proved to be suitable for control. Example of simulated control for modification 2 is given in Fig. 11. This modification is simpler because the flow rate of the coolant need not be measured, of course, the method is difficult to apply if the driving force is too small.

Reaction calorimetry in combination with the bang-bang control algorithm cannot be used for the first reactor with cold feed. The reaction temperature is not stabilized (Fig. 9) and therefore the heat production rate is not a monotonous function of conversion.

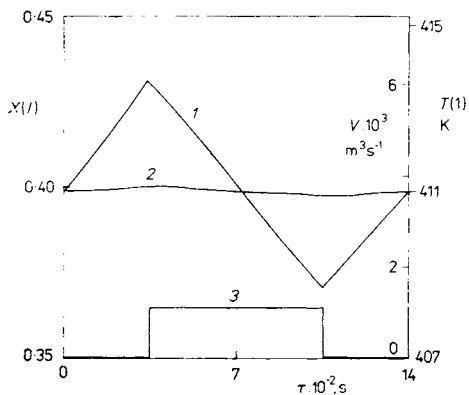


FIG. 11

Feedback control of the first reactor using reaction calorimetry (modification 2). One switching cycle is presented. 1 Conversion; 2 temperature; 3 feed rate as functions of time

SYMBOLS

A	heat transfer area, m^2
c	concentration, $mol\ m^{-3}$
c_p	specific heat capacity of reaction mixture, $J\ kg^{-1}\ K^{-1}$
c_{pc}	specific heat capacity of coolant, $J\ kg^{-1}\ K^{-1}$
E	activation energy, $J\ mol^{-1}$
E_a	constant in Eq. (8), $J\ mol^{-1}$
E_η	constant in Eq. (9), $J\ mol^{-1}$
G_1	controller gain
G_2	controller gain, $m^3\ s^{-1}\ K^{-1}$
ΔH	reaction enthalpy, $J\ mol^{-1}$
I	number of the cascade member
K	heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
k	rate constant, s^{-1}
k_a	constant in rate equation, $m^3\ mol^{-1}$
k_0	constant in Eq. (7), s^{-1}
k_{a0}	constant in Eq. (8), $m^3\ mol^{-1}$
n	constant in rate equation
\dot{Q}	heat flux, W
$\dot{Q}_{min}, \dot{Q}_{max}$	limits of the switching difference of the controller, W
\dot{Q}_{st}	input of heat introduced by the stirrer, W
r	reaction rate, $mol\ m^{-3}\ s^{-1}$
R	versatile gas constant, $J\ mol^{-1}\ K^{-1}$
T	temperature of the reaction mixture, K
T_c	exit temperature of coolant, K
T_{ci}	inlet temperature of coolant, K
\dot{V}	volume flow rate of the reaction mixture, $m^3\ s^{-1}$
\dot{V}_c	volume flow rate of coolant, $m^3\ s^{-1}$
V_{cs}	volume of the cooling system, m^3
\dot{V}_{fc}	volume flow rate of fresh coolant, $m^3\ s^{-1}$
V_r	volume of reaction mixture, m^3
x	molar fraction
X	degree of conversion
X_{max}, X_{min}	limits of the switching difference of the controller
η	viscosity, $Pa\ s$
η_0	constant in Eq. (9), $Pa\ s$
ρ	density of reaction mixture, $kg\ m^{-3}$
ρ_c	density of coolant, $kg\ m^{-3}$
τ	time, s

Subscripts

A	reactant (key component)
B	product
0	basic value

Superscript

s	setpoint value
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