
CONTROL OF THE STIRRED FLOW REACTOR IN UNSTABLE STATE CONTROL THROUGH STEP CHANGES IN THE VOLUME OF THE REACTION MIXTURE

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Possibilities of the control of an adiabatic stirred flow reactor with an exothermic first order reaction in unstable state are studied. The control is studied both on the linearized mathematical model and on the model reaction of oxidation by hydrogen peroxide catalyzed by ferric ions. The control is based on step changes in the volume of the reaction mixture at constant conditions at the reactor inlet. The aim is stabilization of the outlet degree of conversion of the reactant. From the theoretical study on the mathematical model resulted that control of the reactor by step changes of the volume can be a very simple and effective method of control in the unstable steady state. The results of theoretical studies have been verified experimentally.

The control of chemical reactors in unstable state is an interesting problem which was recently studied by a number of authors. For example Root and Schmitz¹ have studied the tubular reactor with recycle. They concluded that it was not possible to control the reactor in the unstable state. Auskaitis and Engel² have studied the behaviour of the adiabatic batch reactor in which part of the content was left as the recycle after termination of the reaction. They determined that the reactor cannot be operated in the unstable state if the time of operating cycle is kept constant. But experimentally they have proved that the reactor can be controlled in the unstable state so that the cycle is terminated when the temperature corresponding to the unstable state is reached. The model of operation of the reactor represents thus one of possible ways of control of the reactor by use of periodic operation. The control of the isothermal stirred flow reactor in unstable state at autocatalytic reaction was studied on the mathematical model by Jutila and Uronen³. Step changes were used for control of the inlet concentration of the reactant at constant volume of the reaction mixture in the reactor. The aim was to stabilize the conversion. It resulted that it is possible to reach the state when the conversion slightly oscillates around the required value. The authors have also made an analysis of the stability of limiting cycles on which the state of the reactor moves at the use of relais with hysteresis. This method of control represents also one of modes of control of the adiabatic reactor. The adiabatic reactor with exothermic reaction and the isothermal reactor with an autocatalytic reaction are quite identical as long as is the inlet temperature and composition in the adiabatic reactor constant and thermal capacity of the reactor wall is negligible. Other studies are devoted to control of the stirred flow reactor with heat transfer *e.g.* theoretical studies by Aris and Amundson^{4,5} and experimental studies by Chang and Schmitz⁶.

The adiabatic stirred flow reactor is first of all subjected to dynamic studies of properties and stability^{7,8} especially as there can exist multiple steady states. The majority of authors are

studying the case when there are given the volume of the reactor and values of inlet parameters of the reactor *i.e.* the composition, temperature and volumetric flow rate of the feed. The reactor then does not have a degree of freedom and the outlet conversion of the reaction mixture is a dependent quantity. At the existence of multiple states there can exist three values of conversion at one set of inlet parameters. The survey of literature on the problematics of dynamic behaviour, stability of steady states and control of chemical reactors is given in studies by Uppala, Ray and Poor⁹ and Schmitz¹⁰.

In practical application of the adiabatic stirred flow reactor is usually given the conversion in the reactor and the aim of control is stabilization of conversion at the given value. Solution of this problem is the aim of this study. For control of the reactor in the unstable steady state are used step changes in the volume of the reaction mixture in the reactor. The results obtained from studies on the mathematical model are verified experimentally in the laboratory reactor on the model reaction.

THEORETICAL

In all studied cases is the aim the control of stabilization of the outlet conversion of the reactant. The reaction mixture can leave the reactor only with this conversion. It is assumed that the rate of outlet of the reaction mixture from the reactor is so high that it is possible to neglect the changes in conversion during the outlet.

The solved cases are divided into two groups: I. Noncatalytic reactions and catalyzed reactions by dissolved or suspended catalyst which is part of the inlet and outlet stream, *i.e.* it is passing through the reactor with the reaction mixture. II. Heterogeneous catalyzed reaction, in which the catalyst remains in the reactor.

The complexity of the reactor control depends on quantities and parameters given. The survey of solved problems is given in Table I.

Mathematical Model

The operating cycle in the adiabatic stirred flow reactor (ACSTR) is described by equations

$$dx/dt = r/c_{Ai} - F_1x/V, \quad (1)$$

$$dV/dt = F_i - F_e, \quad (2)$$

with the boundary conditions:

$$\text{for } t = 0 \text{ is } x = x_s, V = V_1,$$

$$\text{for } t = t \text{ is } x = x_s, V = V_e. \quad (3)$$

The degree of conversion of the reactant A and temperature of the mixture in the reactor are bound by the relation

$$T = T_i + \Delta T_{ad}x. \quad (4)$$

The reaction rate is expressed by use of the first order reaction rate equation

$$r = k_i c_{Ai} c_K (1 - x) \exp \left[\frac{E \Delta T_{ad}x}{RT_i(T_i + \Delta T_{ad}x)} \right]. \quad (5)$$

All computations were performed with the values of parameters evaluated on basis of measurements with the model reaction in the laboratory reactor: $k_i = 7 \cdot 10^{13} \text{ m}^3/\text{kmol}$; $c_{Ai} = 1.2 \text{ kmol/m}^3$; $c_K = 0.013 \text{ kmol/m}^3$; $x_s = 0.6$; $T_s = 333 \text{ K}$; $V_s = 2.15 \cdot 10^{-4} \text{ m}^3$; $T_i = 293.1 \text{ K}$; $E = 90 \text{ kJ/mol}_A$; $\Delta H = -275 \text{ kJ/mol}_A$; $\Delta T_{ad} = 67.5 \text{ K}$; $V_{\max} = 9.2 \cdot 10^{-4} \text{ m}^3$; $F_i = 1.2 \cdot 10^{-6} \text{ m}^3/\text{s}$; $r_s/c_{Ai} = 3.3 \cdot 10^{-3} \text{ s}^{-1}$.

An example of the dependence of the reaction rate on degree of conversion of the reactant in ACSTR is given in Fig. 1. It is obvious, from this dependence that the reactor can be at certain conditions operated in three steady states two of which are stable and one (the middle one) unstable.

TABLE I

Summarized Solved Examples

The outlet degree of conversion is always the quantity controlled, composition and temperature of the feed are given.

Symbol	Given Quantities		Dependent quantities	Note
IA	volume of reactor	F_i, F_e	reactor output	ref. ²
IB	F_i	F_e	reactor volume	
IIA	volume of reactor catalyst amount	F_i, F_e	reactor output	analogy with IA
IIB	F_i catalyst amount	F_e	reactor output	not possible to control

In close environment of the steady state, characterized by quantities x_s , T_s , V_s and r_s it is possible to use the linear approximation

$$r = r_s(1 + \alpha \Delta x), \quad (6)$$

where the parameter is defined by the relation

$$\alpha = \frac{E \Delta T_{ad}}{RT_s^2} - \frac{1}{1 - x_s}. \quad (7)$$

The system of differential equations (1) and (2) can be then transformed into the equivalent system of linear equations and by their analytical solution the relation can be obtained for calculation of the dependence of the degree of conversion on the change in volume of the mixture in the reactor

$$\Delta x = -B/A + C/A^2 + C \Delta V/A + W \exp(A \Delta V). \quad (8)$$

The integration constant W has the form

$$W = (B/A - C/A^2 - C \Delta V_i/A) \exp(-A \Delta V_i). \quad (9)$$

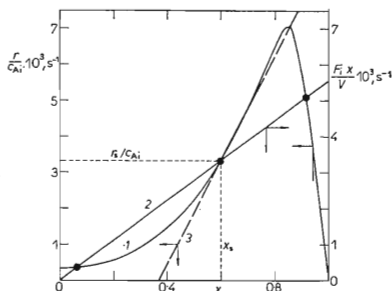
The operating cycle of the reactor is then given by the boundary conditions

$$\text{for } \Delta V = \Delta V_i \text{ is } \Delta x = 0, \quad (10)$$

$$\text{for } \Delta V = \Delta V_e \text{ is } \Delta x = 0.$$

FIG. 1
Steady States of the Adiabatic Stirred Flow Reactor with Exothermic First Order Reaction

1 Dependence r/c_{A1} on degree of conversion of reactant A , 2 dependence $F_1 x/V$ on degree of conversion, 3 linearized dependence r/c_{A1} in degree of conversion, full points denote steady states of the reactor for conditions given below Eq. (5) in this paper.



The quantities Δx , ΔV and parameters A , B , and C are defined by the relations

$$\Delta x = x - x_s, \quad \Delta V = (V_{\max} - V)/V_{\max}, \quad (11a)$$

$$A = - \left(\frac{r_s}{c_{A1}} \alpha - \frac{F_i}{V_s} \right) \frac{V_{\max}}{F_i}, \quad (11b)$$

$$B = -(x_s \Delta V_s)/(1 - \Delta V_s)^2, \quad (11c)$$

$$C = -x_s/(1 - \Delta V_s)^2, \quad (11d)$$

where V_s is the volume of the reactor mixture in the stirred flow reactor which operates in steady state at the degree of conversion x_s . Its value results from Eq. (1) for $dx/dt = 0$. The parameters A , B , C are in the case of an unstable steady state of the reactor smaller than zero, for stable steady states is then A greater than zero and B and C become negative. In the solved example the given parameters have the values $A = -6.067$, $B = -8.418$, $C = -10.986$.

After arrangement it is possible to obtain from the given relations also the equation for calculation of the dependence of the final volume of the mixture in the reactor on the initial volume if the condition on reaching the degree of conversion corresponding to the steady state of the reactor ($\Delta x = 0$) is met

$$-\Delta V_s + 1/A + \Delta V_e + (\Delta V_s - 1/A - \Delta V_i) \exp [A(\Delta V_e - \Delta V_i)] = 0. \quad (12)$$

The given equation has an implicate character and was solved numerically by the half-interval method on the computer Tesla 200.

ALGORITHM OF CONTROL IA

This mode of control of the reactor in unstable state is equivalent to the procedure described in literature² for control of the adiabatic batch reactor. The operating cycle of the reactor can be described in the following way: In the reactor at the given initial conditions characterized by the volume of the mixture in the reactor V_i , reaction in the discontinuous regime takes place. After reaching the given degree of conversion x_s the volume V_N is quickly discharged from the reactor and the volume decreases from the value V_i to the value V_e . By a quick feeding of the original mixture is the volume of the reactor again brought to the volume V_i . The reaction takes place in the batch regime, till the value is reached with the degree of conversion x_s . The steady operating cycle of the reactor is always stable independently of the stability or instability of the state of the stirred flow reactor.

The steady operating cycle is defined as the operating cycle (or system of several operating cycles) with the volume of the mixture constant at the beginning and at the end and the degree of conversion being x_s .

The given example represents a very simple and reliable mode of control of the reactor in the state which is for the given feed rate instable. But the stability is reached at the account of the reactor output becoming a dependent quantity. This mode of control cannot be used where the reactor output is prescribed *e.g.* for control of the cascade of reactors.

ALGORITHM OF CONTROL IB

The operating cycle of the reactor can be described: The feed with the given volume flow rate F_i , inlet composition c_{Ai} , c_K and inlet temperature T_i is continuously fed into the reactor. The rate with which the mixture leaves the reactor F_e is equal to zero. At the beginning of the operating cycle is the volume of the reaction mixture V_i , the degree of conversion x_s . The volume of the mixture in the reactor increases, the degree of conversion at the beginning decreases and then increases. The volume V_N is quickly discharged in the moment in which the degree of conversion again reaches the value x_s and the volume of the mixture has the value V_e . The volume of the mixture in the reactor has the value

$$V_{iN} = V_e - V_N. \quad (13)$$

The new operating cycle is repeated with the initial volume $V_i = V_{iN}$.

Limiting of Operating Region of the Initial Volume of the Mixture V_i

To avoid the failure of the control of the reactor the volume V_i must be inside the operating region

$$V_i \in (V_{i \min}, V_{i \max}).$$

$V_{i \max}$ is the upper critical volume. For $V_i > V_{i \max}$ the degree of conversion increases and is not returning back to the given value x_s . $V_{i \max}$ equals to the volume of the stirred flow reactor in steady state at constant flow rate of feed F_i and degree of conversion x_s . It is determined by the relation

$$V_{i \max} = F_i c_{Ai} x_s / r_s = V_s.$$

$V_{i \min}$ is the lower critical volume. Its existence results from the limitation of the size of the reactor V_{\max} . For the initial volume of the mixture $V_i < V_{i \min}$ during the operating cycle the volume of the mixture increases to the value V_{\max} before the degree of conversion x_s is reached. The value $V_{i \min}$ results from the relation (12).

This relation will have the solution, when the condition is met

$$\Delta V_i < (\Delta V_s - 1/A) = \Delta V_{i \min}.$$

At the control of the reactor it is necessary to take into account variation of the inlet quantities. Due to its effect both $V_{i \min}$ and $V_{i \max}$ are changing in the same direction, they increase with increasing inlet temperature of the feed, activity of the catalyst and with decreasing feed rate. For control of the reactor it is necessary to limit the operating region by the least favourable values, i.e. the largest value $V_{i \min}$ and smallest value $V_{i \max}$.

Choice of Function of Dependence of Quantities V_e and V_i

The dependence of quantity V_e on the initial volume of the mixture V_i can be determined by solution of the Eq. (12). The example of the calculated dependence is given in Fig. 2. From it according to relation (13) thus results also dependence of the quantity V_{iN} on initial volume V_i . The point of intersection of this dependence (further on denoted as the dependence V_{iN}) with the diagonal $V_i = V_e$ is then giving the position of the steady cycle ACSTR (point B in Fig. 2). The location of the steady cycle is characterized by the corresponding value of initial volume of the mixture V_i (according to definition of steady cycle this initial volume equals also to the final volume).

From the analysis of stability resulted that this steady cycle is stable as long as the condition is satisfied

$$|dV_{iN}/dV_i| < 1. \quad (14)$$

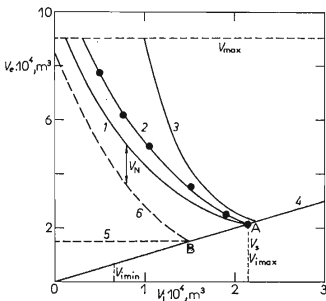


FIG. 2

Dependence of Final Volume of the Mixture in Operating Cycle on Initial Volume

A 6.067, B 8.418, C 10.986; 1 dependence of quantity V_e calculated from the linearized model (Eq. (12)), 2 experimental dependence of quantity V_e , 3 dependence of quantity V_e calculated from Eqs (1) and (2), 4 dependence $V_i = V_e$, 5 dependence of quantity V_{iN} for the mode of control IB 1 ($V_{iN} = 1.5 \cdot 10^{-4} \text{ m}^3$), 6 dependence of quantity V_{iN} for the mode of control IB 2a ($V_{iN} = 1.5 \cdot 10^{-4} \text{ m}^3$), A unstable state ACSTR, B steady cycle of the reactor.

The value of quantity V_i is the parameter by which it is possible to affect the control of the reactor. At the choice of this initial volume in the operating cycle of the reactor there exists a number of possibilities.

1. Initial volume V_i is chosen constant, independent of the process (without regard to the volume of the mixture in the reactor at the end of the preceding operating cycle). The volume V_N is thus during the individual operating cycles chosen so as the quantity V_{iN} should have a constant value (straight line 5 in Fig. 2). This method is advantageous as it secures stability of the operating cycle as the values V_i and x_s are always fixed at the beginning of the cycle. The steady cycle is always stable as the condition of stability (14) is met (derivation is equal to zero). Examples of such steady cycles formed by one operating cycle and a corresponding unsteady state ACSTR which is characterized by quantities x_s , V_s (point A in Fig. 2) are given in Figs 3 and 4. But the given mode of control is not able to adapt itself to changes *e.g.* to changes in activity of the catalyst. The value V_i must be chosen inside the operating

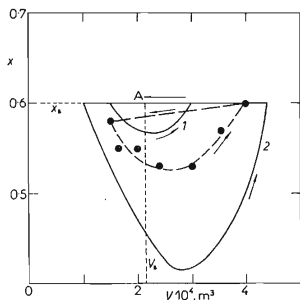


FIG. 3

Algorithm of Control IB 1. Examples of Steady Composed of a Single Operating Cycle

A unstable state ACSTR, dashed line with full points denotes the experimental dependence of the degree of conversion on volume of mixture in reactor for $V_{iN} = 1.5 \cdot 10^{-4} \text{ m}^3$, solid line denotes the dependence calculated from the linearized model (Eq. (8)); 1 $V_{iN} = 1 \cdot 10^{-4} \text{ m}^3$, 2 $V_{iN} = 1.5 \cdot 10^{-4} \text{ m}^3$.

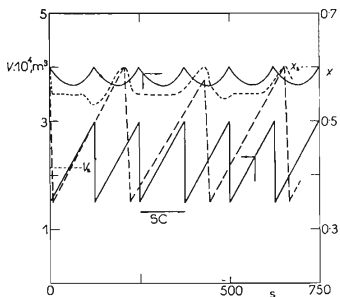


FIG. 4

Algorithm of Control of the Reactor IB 1. Examples of Degree of Conversion and Volume of the Mixture in Steady Cycle on Time for $V_{iN} = 1.5 \cdot 10^{-4} \text{ m}^3$.

Solid line denotes the calculated dependences, dashed line the experimental dependences, SC denotes one steady cycle.

region. This leads usually to operation of the reactor at the large difference of volumes V_N . The exit from the reactor is then variable which can render the control of the succeeding equipment and deteriorate the utilization of the volume of the reactor.

2. Initial volume V_i is chosen variable in dependence on the value V_c . This mode of control has already the adaptable elements. Selection of the constant value V_i is necessary, where the change in parameters of the system are quite random which is very improbable. Due to mixing of the inlet mixture with the volume of the reactor the step changes in the inlet streams are also manifested inside the reactor as a number of succeeding changes of the state from a cycle to a cycle.

2a. At the end of the operating cycle is in the moment of reaching the degree of conversion x_s suddenly discharged a constant volume of the mixture $V_i = V_{iN}$. If $V_{iN} < V_s$ the operating cycle is repeated. If $V_{iN} > V_s$ the control fails as the degree of conversion monotonously increases and it does not return to the value x_s .

Analysis of Stability of the Steady Cycle

Similarly, as in the last example is the steady cycle determined by the intersection of the curve of dependence V_{iN} with the diagonal $V_i = V_c$. The calculated example is given in Fig. 2 (point B). The analysis of steady cycles is in this case more complicated. From relation (12), for values of derivations of quantity V_c or V_{iN} according to V_i , result the relations

$$dV_c/dV_i = dV_{iN}/dV_i = \frac{(V_i - V_s)\beta}{V_{\max}/A + (V_i - V_s - V_{\max}/A)\beta}, \quad (15)$$

$$d^2V_c/dV_i^2 = d^2V_{iN}/dV_i^2 = \frac{(1 - \beta)\beta}{(V_{\max}/A + (V_i - V_{\max}/A)\beta)^3} (V_{\max}/A) \cdot \\ \cdot (V_i - V_s + V_{\max}/A + (V_i - V_s - V_{\max}/A)\beta), \quad (15a)$$

where β represents

$$\beta = \exp \left[\frac{A(V_i - V_{iN} - V_N)}{V_{\max}} \right].$$

The steady cycle is stable when the condition (14) is satisfied *i.e.* when

$$d^2V_{iN}/dV_i^2 < 0, \quad d^2V_c/dV_i^2 < 0.$$

The given conditions of stability can be satisfied only when the parameter A becomes positive *i.e.* in the case of stable steady states of the reactor. In the given way thus the

reactor cannot be controlled in the unstable state ($A < 0$) as the steady cycle is unstable. The example of calculated operating cycles is plotted in Fig. 5.

Modification of this mode of control is the control with the constant time of exit of the mixture from the reactor. At the end of the operating cycle is, in the moment when the degree of conversion x_s is reached, for the time t_N open the outlet from the reactor and the volume of the mixture is decreased for the value V_N which depends on the height of the reaction mixture in the reactor. Also in this case is the steady cycle unstable.

2b. At the end of the operating cycle, in the moment when the degree of conversion x_s is again reached, is suddenly discharged the volume V_N . If the new initial volume of the reaction mixture $V_i = V_{iN}$ is smaller than V_s the operating cycle repeats. But if it is greater than V_s the volume V_N is again discharged so that the new initial volume $V_i = V_{iN1}$ is obtained. This procedure of discharge of the mixture from the reactor for the value V_N can be repeated so that V_{iNM} is smaller than V_s ($M = 1, 2, 3 \dots$ denotes the number of repeated discharges of the mixture). The new initial volume of the next operating cycle is then given by the value $V_i = V_{iNM}$.

The computations of the operating cycles give the results according to which in some time a regular repeating of the series of volumes V_{iNM} and to them corresponding final volumes V_e takes place, while the volumes of the mixture at the beginning and at the end of this series are the same. This repeated serie represents a steady cycle

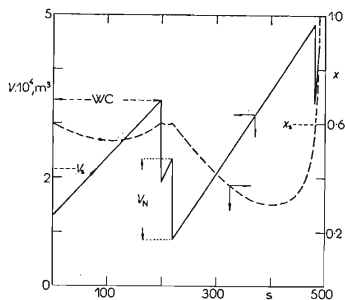


FIG. 5

Algorithm of Control of the Reactor 1B 2a. Examples of Calculated Degrees of Conversion and Volume of the Mixture in Operating Cycles on Time for $V_N = 1.5 \cdot 10^{-4} \text{ m}^3$. WC denotes one operating cycle.

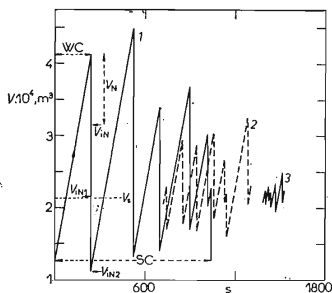


FIG. 6

Algorithm of Control of the Reactor 1B 2b. Examples of Calculated Dependences of Volume of the Mixture in Steady Cycles on Time for Different Values of Quantity V_N 1 $V_N = 1 \cdot 10^{-4} \text{ m}^3$, 2 $6 \cdot 10^{-5}$, 3 $2 \cdot 10^{-5}$. WC denotes one operating cycle, SC denotes the steady cycle.

of the reactor which is composed of several operating cycles. Examples of such steady cycles for various volumes V_N are given in Figs 6 and 7. It is obvious that these steady cycles are stable. From the examples also results that with increasing volume V_N the range increases in which the volume of the mixture oscillates between the values V_i and V_e i.e. to the deterioration of the utilization of the reactor volume and quality of control.

Similar results can be also obtained when the reactor is controlled by use of changes in the volume of the mixture which are determined by the time of discharge of the reactor t_N .

ALGORITHM OF CONTROL IIA

In the case of heterogeneously catalyzed reactions is the behaviour ACSTR described by the relations

$$dx/dt = rW/(Vc_{Ai}) - F_i x/V, \quad (16)$$

$$dV/dt = F_i - F_e. \quad (17)$$

If the amount of catalyst W in the volume of the reactor V is constant the system of differential equations (16) and (17) is identical with the system of Eqs (1) and (2). This method of control of the reactor is thus identical with the method IA.

ALGORITHM OF CONTROL IIB

It is obvious from Eq. (16) that the sign with the derivation dx/dt is independent of the volume of the mixture in the reactor. By the change in the volume it is not possible to affect the direction of changes in the degree of conversion. The degree of

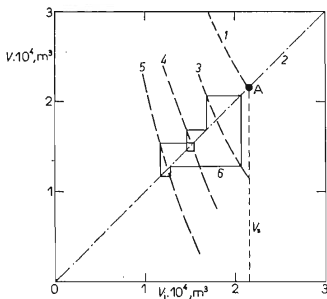


FIG. 7

Algorithm of Control of the Reactor IB 2b. Example of Calculated Steady Cycle for the Quantity $V_N = 1 \cdot 10^{-4} \text{ m}^3$ (example 1 in Fig. 6)

A unstable state ACSTR, 1 dependence of final volume V_e in operating cycles on initial volume V_i , 2 dependence $V_i = V_e$, 3-5 dependences of quantity V_{iN_M} for $M = 1-3$ on initial volume of the mixture, 6 steady cycle composed of six operating cycles

conversion is spontaneously, independently of changes in the volume steadied on the value corresponding to the condition $dx/dt = 0$ in Eq. (16). In the case there exist multiple states of the reactor it is steadied on the value corresponding to one of stable states. By changes in the volume it is not possible to control the degree of conversion.

It results from the given theoretical analysis that the control ACSTR by step changes in the volume can be a very simple and effective method of control also at conditions when the corresponding state of the reactor operating with constant inlet flow rates is unstable. The complexity of the problem depends on quantities which are given. If it is not required that the reactor should operate with the given output the control in the unstable state is very simple. If the output is given the control is more complex. With catalytic reactors in which the catalyst persists in the reactor is the control sometimes impossible. Then it is necessary to use the control through changes in the amount of catalyst or to introduce another impulse quantity.

EXPERIMENTAL

Model reaction. Oxidation of ethanole by hydrogen peroxide, homogeneously catalyzed by ferric ions was used as the model reaction. On basis of data measured in the adiabatic discontinuous reactor it was determined that the given reaction is of the first order to hydrogen peroxide and the catalyst and zero order to ethanole. The data were also used for limitation of reaction conditions suitable for the control of ACSTR in the unstable state.

Apparatus. The measurement was carried out in the adiabatic stirred flow reactor with the volume 920 cm^3 . The reactor is in diameter 8 cm and 20 cm high and is made of perspex equipped with the polystyrene insulation. By comparison of the amount of heat originated by the chemical reaction and the heat removed into the surrounding it was determined that the thermal losses account to about 1%. The reaction mixture in the reactor was stirred by the polyethylene stirrer with the diameter 2 cm. The reactants, hydrogen peroxide and ethanol with ferric nitrate were fed with the accuracy 5% by peristaltic pumps. The fed compounds were brought to the temperature 20°C . The outlet of the mixture from the reactor was realised by use of two outlets.

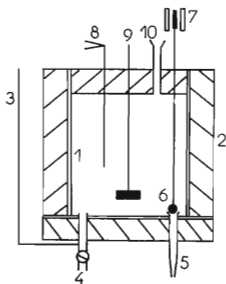


FIG. 8

Laboratory Adiabatic Stirred Flow Reactor
1 Reactor, 2 insulation, 3 level gauge, 4 emergency outlet of mixture from the reactor, 5 outlet of mixture controlled by the spherical valve 6, 7 relays, 8 thermocouple, 9 stirrer, 10 feed inlet.

One was used for quick discharge of the mixture the second was formed by a glass spherical two-position valve operated by electromagnetic relays. This one was used for realisation of step changes in the volume of the mixture at the control of the reactor. Schematically is the arrangement of the reactor drawn in Fig. 8.

Measurement of volume and temperature of the mixture. In the experiments the temperature and volume of the mixture in the reactor were continuously measured. The volume was measured by use of the level gauge, temperature by use of the copper-constantan thermocouple (diameter of the wire 0.1 mm) situated in the glass capillary. The time constant of the thermocouple was 10 s. As it was not possible to make the continuous analysis of the mixture the temperature measurement was used for determination of the degree of conversion of hydrogen peroxide (Eq. (4)).

Measuring method. The reactor was brought into the given steady state in the discontinuous regime. After filling the reactor to the operating volume with the composition of the initial mixture corresponding to the feed the temperature started to be measured in the reactor. When the temperature reached the values close but lower than is the given value (corresponding to the degree of conversion x_3) the feed started to be introduced. The outlet from the reactor was operated by hand by use of a valve and the relays. The result of measurement were dependences of the volume and temperature of the mixture in the reactor (degree of conversion of hydrogen peroxide) on time.

RESULTS

Experimental studies on the ACSTR control by step changes in the volume of the mixture were performed at the conditions which exist when the multiple steady states of the reactor exist. The corresponding dependence of the reaction rate on the degree

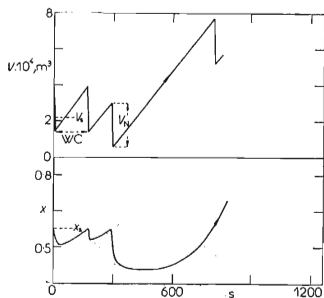


FIG. 9

Mode of Control of the Reactor IB 2a. Examples of Experimental Dependences of Degree of Conversion and Volume of the Mixture in Operating Cycles on Time for Value of the Quantity $V_N = 2.5 \cdot 10^{-4} \text{ m}^3$

WC denotes one operating cycle.

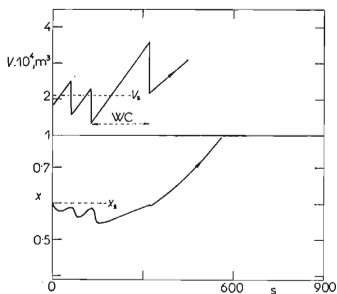


FIG. 10

Mode of Control of the Reactor IB 2a Modified. Examples of Experimental Dependences of Degree of Conversion and Volume of the Mixture in Operating Cycles on Time for Value of the Quantity $t_N = 6 \text{ s}$

WC denotes one operating cycle.

of conversion of hydrogen peroxide is given in Fig. 1. The parameters at the inlet into the reactor were constant during the experiment, temperature of the feed 20°C, volumetric feed rate F_i was 1.2 cm³/s, concentration of ethyl alcohol 0.62 kmol/m³, hydrogen peroxide 1.2 kmol/m³ and catalyst 0.013 kmol/m³. To these conditions corresponds the unstable steady state of the reactor, characterized by the degree of conversion $x_s = 0.6$ i.e. by the temperature 60°C and the volume of the mixture in the reactor $V_s = 215$ cm³.

At the control of the reactor by step changes in the volume the reactor was operated in the semicontinuous regime. The feed was continuously fed into the reactor and the mixture was discharged from the reactor in steps always after reaching the given degree of conversion (temperature of the mixture). The measured dependence of the final volume of the mixture V_e in the operating cycle in dependence on the initial volume V_i is given in Fig. 2 (curve 2).

ALGORITHM OF CONTROL IB 1

The volume of the mixture at the beginning of the operating cycle was always constant, independent of the volume at the end of the cycle. The examples of the measured dependences are given in Figs 3 and 4. The results of experiments have confirmed the conclusions reached in the study on the control on the mathematical model. The control of the reactor in unstable state is stable.

ALGORITHM OF CONTROL IB 2a

At the end of the operating cycle, in the moment the given degree of conversion is again reached, is suddenly discharged the constant volume V_N . Examples of the measured dependences are given in Fig. 9. In Fig. 10 are plotted the measured dependences at the modified mode of control with the constant time of discharge of the mixture from the reactor t_N . In agreement with the results of the study of control on the mathematical model it was proved that this mode of control is unstable.

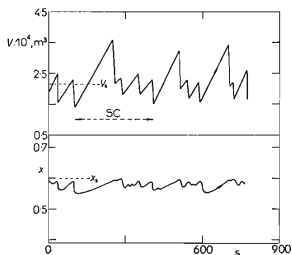


FIG. 11

Mode of Control of the Reactor IB 2b modified. Examples of Experimental Dependences of Degree of Conversion and Volume of the Mixture in Operating Cycles on Time for the Value of Quantity $t_N = 6$ s
SC denotes the steady cycle.

ALGORITHM OF CONTROL IB 2b

At the end of the operating cycle, in the moment the given degree of conversion is again reached, is suddenly discharged the volume of the mixture V_N or in the modified mode of control is the outlet from the reactor open for the time t_N . If the new initial volume of the mixture is smaller than the volume corresponding to the steady state of the reactor V_s the operating cycle is repeated. If the new initial volume is greater than V_s , the volume V_N is again discharged, or the mixture is discharged for the time t_N . This procedure could be repeated. Experimentally was verified only the modified method of control *i.e.* the control by the use of the time of discharge of the mixture from the reactor t_N . Examples of measured dependences are plotted in Fig. 11. It was proved, in agreement with the results of studies on the mathematical model, that this mode of control is stable.

LIST OF SYMBOLS

A	parameter defined by Eq. (11b)
B	parameter defined by Eq. (11c)
C	parameter defined by Eq. (11d)
c_{A1}, c_k	concentration of the inlet compound and catalyst in the feed, kmol/m^3
E	activation energy of the reaction, kJ/mol_A
F_i, F_c	volumetric flow rate of the feed and discharge of the mixture from the reactor, m^3/s
k_i	reaction rate constant at temperature T_i , $\text{m}^3 \text{s}^{-1} \text{kmol}_K^{-1}$
r, r_s	reaction rate or rate in steady state, $\text{kmol}_A/\text{m}^3 \text{s}$
T, T_i	temperature of the reaction mixture or temperature of feed (K)
t	time, s
V	volume of the mixture, m^3
V_{\max}	maximum volume of the reactor, m^3
V_s	volume of the mixture corresponding to the steady state, m^3
V_i, V_c	initial and final volume of the mixture in the operating cycle, m^3
V_N	step change in the volume of the mixture, m^3
V_{iN}	initial volume of the mixture defined by Eq. (13), m^3
$V_{i\min}, V_{i\max}$	critical values of initial volumes of the mixture V_i , m^3
W	integration constant defined by Eq. (9) or amount of catalyst, m^3
x, x_s	degree of conversion of the reactant or degree of conversion in steady state
α	parameter defined by Eq. (7)
β	dimensionless parameter
ΔH	heat of reaction, kJ/mol_A
ΔT_{ad}	adiabatic temperature rise, K
$\Delta V = (V_{\max} - V)/V_{\max}$	dimensionless volume of the mixture
$\Delta V_s = (V_{\max} - V_s)/V_{\max}$	dimensionless volume of the mixture in steady state
$\Delta V_i = (V_{\max} - V_i)/V_{\max}$	dimensionless initial volume V_i
$\Delta V_c = (V_{\max} - V_c)/V_{\max}$	dimensionless final volume V_c
$\Delta V_{i\min} = (V_{\max} - V_{i\min})/V_{\max}$	dimensionless volume $V_{i\min}$
Δx	deviation of the degree of conversion from the value in steady state.

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