

CONTROL OF THE ADIABATIC FLOW REACTOR BY FEEDING THE CATALYST SOLUTION

Josef HORÁK, Zina SOJKOVÁ and František JIRÁČEK

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

Received March 1st, 1978

Control algorithm of the operating temperature is described in the reactor, which is operated at constant temperature and composition of the inlet mixture. The temperature is controlled by dosing a constant volume of the catalyst solution. The dosing frequency is determined according to the reaction temperature (deviation of the temperature from the desired value and the sign of the derivative of temperature). The control algorithm has been verified experimentally for the laboratory reactor in unstable steady state.

This study is related to our recent publications^{1,2} (the literature survey is given there). Dosing of the catalyst can be used for control of reactors in which takes place a reaction catalysed by the dissolved catalyst which passes with the mixture through the reactor. In the same manner it is possible to make use of dosing the initiator in chain reactions of microorganism in biochemical reactions. The aim of this study is to propose a simple mode of control which does not require application of action elements varying continuously the rate of dosing of the catalyst. For control is applied the two-position controller by which it is possible to feed (dose) into the reactor a certain constant volume of the catalyst solution. The aim of control is stabilisation of the operating temperature of the reactor on the given value. It is assumed that the temperature and composition of the inlet mixture is constant. Then stabilisation of the reaction temperature leads in adiabatic reactor also to stabilisation of the outlet degree of conversion.

As the disturbance quantities are considered the activity of solution of the catalyst and the rate of feeding of the initial reaction components into the reactor.

THEORETICAL

Description of the Control Algorithm

The reactor is controlled according to changes in the reaction temperature. If the temperature of the reaction mixture is lower or equal to the set value T_s and simultaneously it decreases with time, into the reactor is added a volume of the catalyst

solution V_c with the concentration c_{cr} . If the addition of the catalyst does not lead to the increase in temperature of the mixture the addition of the catalyst is repeated. The volume V_c is thus added as long as there holds

$$T \leq T_s \quad \text{and} \quad dT/dt < 0.$$

Mathematical Model

It is assumed that at constant inlet composition and inlet temperature of the mixture is the reaction rate a function of the degree of conversion of the reactant and is proportional to the concentration of the catalyst

$$r = c_c f(x). \quad (1)$$

Dynamic behaviour of the adiabatic stirred flow reactor can be then described by relations

$$dx/dt = r/c_{Ai} - F_i x/V, \quad (2)$$

$$dc_c/dt = F_i(c_{ci} - c_c)/V. \quad (2a)$$

As the steady state of the reactor is denoted the operating point for which there holds

$$dx/dt = 0, \quad dc_c/dt = 0,$$

$$x = x_s, \quad c_c = c_{cs}.$$

For studies of the reactor behaviour in close vicinity of steady state the linearized model is used in which the values of quantities x and c_c are expressed as linear functions of deviations from values corresponding to the steady state

$$X = (x - x_s)/x_s, \quad Z = (c_c - c_{cs})/c_{cs} \quad (3, 3a)$$

and the reaction rate is described by the relation

$$r = r_s(1 + \alpha x_s X)(1 + Z).$$

The significance of the constant α is obvious from Fig. 1. Behaviour of the reactor can be then described by the system of dimensionless differential equations

$$dX/d\tau = AX + Z, \quad (4)$$

$$dZ/d\tau = 1/D, \quad (4a)$$

where the dimensionless time τ and parameters A and D are defined by relations

$$\tau = tF_i/V_s, \quad A = \alpha x_s - 1, \quad D = c_{cs}/(c_{ci} - c_{cs}). \quad (5, 5a, 5b)$$

The parameter A is characterizing properties of the reaction and reactor, parameter D properties of the controller. For the studied control algorithm (concentration of catalyst in the feed is $c_{ci} = 0$) the parameter D has the value $D = -1$.

The catalyst is charged at the instant when the quantity X becomes equal to non-zero (the given degree of conversion x_s is reached). Course of reaction at the instant when the catalyst is charged up to the instant when the quantity X again becomes equal to zero and the catalyst should be charged again is denoted as the operating control cycle. Behaviour of the reactor during this operating cycle is described by the equation

$$dX/dZ = D(AX + Z), \quad (6)$$

which is derived from Eqs (4) and (4a). At the beginning of the operating cycle the condition holds

$$Z = Z_i, \quad X = 0$$

Solution of Eq. (6) can be then written in the form

$$X = -Z/A - 1/(A^2D) + [Z_i/A + 1/(A^2D)] \exp [AD(Z - Z_i)]. \quad (7)$$

At the end of the operating cycle the quantity X becomes also equal to zero and the

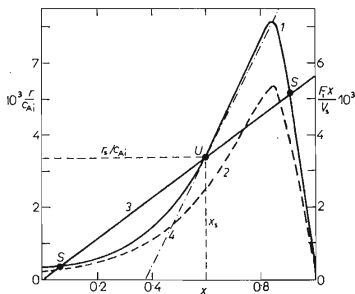


FIG. 1
Steady States of the Adiabatic Stirred Flow Reactor

1 Dependence of reaction rate on degree of conversion for the reactant for $c_{cs} = 1.33 \cdot 10^{-2}$ kmol/m³; 2 $c_{cs} = 1.0 \cdot 10^{-2}$ kmol/m³; 3 dependence $F_i x / V_s$ on degree of conversion; 4 linearised dependence of reaction rate on degree of conversion ($\text{tg } \varphi = r_s \alpha x_s / c_{Ai}$); S stable steady states of the reactor; U unstable state ($x_s = 0.6$).

quantity Z equal to Z_e . It can be determined from the relation

$$-Z_e/A - 1/(A^2D) + [Z_i/A + 1/(A^2D)] \exp [AD(Z_e - Z_i)] = 0. \quad (7a)$$

Eq. (7a) was solved numerically by the method of interval halving.

Method of Analysis of Stability

The method of point transformation (the method of the representing point) was used³ for determination of stability of the system. The catalyst is dosed when some given temperature T_s (given degree of conversion x_s) is reached. Such amount of catalyst must be added, that the temperature of the reaction mixture after addition of the catalyst increases. This is satisfied when after dosing of the catalyst is its concentration in the mixture greater than the concentration c_{es} corresponding to the steady state (to the given operating point, Fig. 1 and 3).

The temperature dependence of the mixture after addition of the catalyst up to the instant when the temperature of the mixture again decreases to the temperature T_s and the catalyst should be fed (during the operating cycle) is determined by the concentration of the catalyst just after dosing. This concentration at the beginning of the operating cycle n is denoted as c_c^n . At the end of the operating cycle the catalyst concentration has the value c_{ce}^n . After addition of catalyst its concentration increases to the value c_c^{n+1} , which is simultaneously the inlet concentration into the cycle $n + 1$. If the plot of concentration dependence c_{ce}^n or c_c^{n+1} on c_c^n is constructed then each point on the curve "represents" the operating cycle with the catalyst's inlet concentration c_c^n and final concentration c_{ce}^n . The plot enables to read off the succeeding changes of the catalyst concentration c_c^n from one cycle to another cycle and so to determine also the position of limiting cycles and their stability.

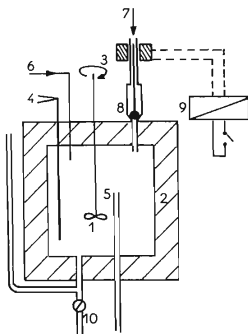


FIG. 2

Schematic View of the Apparatus

1 Reactor; 2 polystyrene insulation of reactor; 3 stirrer; 4 thermocouple; 5 overflow; 6 feed of reactants; 7 feed of catalyst; 8 spherical valve; 9 electromagnetic relays with timer; 10 safety outlet with level gauge.

The dependence of quantities c_{ce}^n and c_c^n was computed from the linearised model according to Eq. (7a) (Fig. 3). For the concentration c_c^{n+1} then results the relation

$$c_c^{n+1} = c_{ce}^n + N \Delta c_c, \quad N = 1, 2, 3, \dots \quad (8)$$

where N is the smallest integer for which there holds

$$c_c^{n+1} > c_{cs}.$$

It thus denotes the number of catalyst volumes V_c with the concentration c_{cf} which were charged into the $n + 1$ st cycle at the beginning of the operating cycle.

EXPERIMENTAL

The used model reaction and the apparatus are identical with those used in the previous paper². The model reaction was oxidation of ethanol by hydrogen peroxide catalysed homogeneously by ferric ions. The reaction rate can be described by the equation

$$r = k_{st} c_{Ai}(1 - x) c_c \exp(-E/RT),$$

where the constants have the values $k_{st} = 7 \cdot 10^{13} \text{ m}^3/(\text{kmol s})$, $E = 90 \text{ kJ/mol H}_2\text{O}_2$. The reaction is strongly exothermic ($\Delta H = -275 \text{ kJ/mol H}_2\text{O}_2$).

The used apparatus is schematically drawn in Fig. 2. Into the laboratory adiabatic stirred flow reactor were separately dosed the reactants which were the hydrogen peroxide and ethyl alcohol. The catalyst solution (ferric nitrate) was dosed by use of the two-position spherical valve, controlled through the electromagnetic relay with the time switch (type TP 11) by which the length of time of dosing was fixed. The relay was controlled by hand.

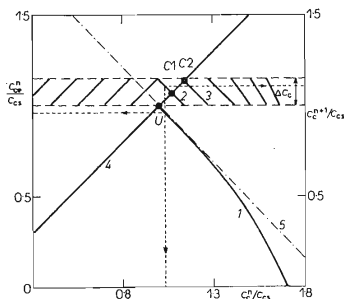


FIG. 3

Determination of Position of the Limiting Cycle for Control of the Reactor in Unstable State

$A = 1.4534$; U unstable state of reactor; $C1$ unstable limiting cycle for $N = 1$; $C2$ unstable cycle for $N = 2$; 1 dependence of quantities c_{ce}^n and c_c^n ; 2 dependence of quantities c_c^{n+1} and c_c^n for $N = 1$; 3 dependence of quantities c_c^{n+1} and c_c^n for $N = 2$; 4 dependence $c_c^{n+1} = c_{ce}^n$; 5 graphical plot of derivation dc_{ce}^n/dc_c^n .

The constant volume of the mixture in the reactor during the experiment was $V_s = 2.15 \cdot 10^{-4} \text{ m}^3$ and was fixed by the overflow.

During the experiment the temperature of the mixture was measured by use of the thermocouple with the value of the time constant 6s. In samples of the mixture withdrawn from the reactor was manganometrically determined the content of hydrogen peroxide and by titration by sodium hydroxide with phenolphthaleine the content of acetic acid. The result of measurement were the dependences of temperature of the mixture in the reactor on time.

The reactor was brought into the given steady state in the discontinuous regime. When the temperature of the mixture has reached the given value $T_s = 333 \text{ K}$ (or the value of degree of conversion of hydrogen peroxide $x_s = 0.6$) the feed was started and the control of the reactor was switched on. The feed rate was $F_i = 1.2 \cdot 10^{-6} \text{ m}^3/\text{s}$ with the temperature $T_i = 294 \text{ K}$. In all experiments the concentration of reactants in the feed was $c_{Ai} = 1.2 \text{ kmol/m}^3$ of hydrogen peroxide and $c_{Bi} = 0.62 \text{ kmol/m}^3$ of ethyl alcohol. Concentration of the catalyst in the mixture corresponding to the given steady state was $c_{cs} = 1.22 \cdot 10^{-2} \text{ kmol/m}^3$. Concentration of the dosed catalyst was $c_{cf} = 0.5 \text{ kmol/m}^3$.

RESULTS AND DISCUSSION

Number and Stability of Limiting Cycles

As the catalyst is dosed discontinuously into the reaction mixture in the reactor it is not possible by the control to arrange for the reactor to rest in the operating point. Temperature of the mixture during the operating cycle always deviates from the given value T_s (to higher values). The aim of control is to reach the stationary limiting cycle in which are the deviations insignificant.

In the plots of dependence of quantities c_c^{n+1} on c_c^n are the limiting cycles represented by intersections of this dependence with the diagonal (line of dependence of $c_c^{n+1} = c_c^n$). The example of graphical determination of the position of limiting cycles is given in Fig. 3.

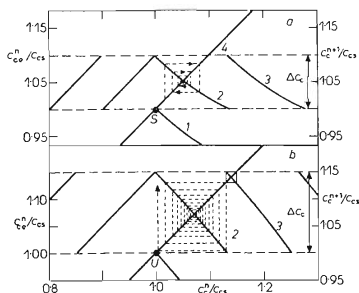


FIG. 4

Changes in Catalyst Concentration at the Beginning of the Operating Cycle from Cycle to Cycle

a Control in stable state of the reactor ($A = -0.6$); *b* control in unsteady state ($A = 1.4534$); *S* stable state of the reactor; other symbols used are the same as those in Fig. 3.

The steady state of the reactor is stable² when there holds the inequality

$$|dc_c^{n+1}/dc_c^n| < 1. \quad (9)$$

From the analysis of results obtained from the linearised model also resulted that in all cases when the control in stable state is concerned there holds

$$0 > dc_{ce}^n/dc_c^n > -1. \quad (9a)$$

Thus there exists only one limiting cycle which is stable. The example of concentration changes of the catalyst from one cycle to the other is given in Fig. 4a.

On the contrary, if the control in the unstable state of the reactor is concerned (point *U* in Fig. 3) the condition holds

$$dc_{ce}^n/dc_c^n < -1. \quad (9b)$$

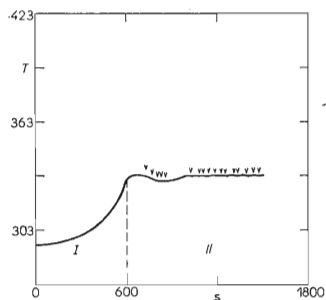


FIG. 5

Example of Experimental Temperature Dependence at Introduction of the Reactor into the Given Unstable State

I Discontinuous reactor regime; *II* continuous reactor regime; \downarrow instant of dosing of the catalyst solution having the volume $V_c = 1.2 \cdot 10^{-6} \text{ m}^3$.

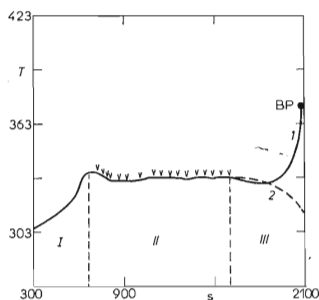


FIG. 6

Experimental Verification of Instability of Steady State of Reactor

I Introduction of the reactor into the given state; *II* control of reactor according to the described algorithm. $V_c = 2 \cdot 10^{-6} \text{ m}^3$; *III* catalyst is fed in regular time intervals; *1* volume $V_c = 2 \cdot 10^{-6} \text{ m}^3$ fed after 60 s; *2* volume $V_c = 1 \cdot 10^{-6} \text{ m}^3$ fed after 30 s, BP boiling point.

In such a case there must necessarily exist more than one limiting cycles which are all unstable. The results of control are then periodical changes in concentration of the catalyst within the interval $\langle c_{cs}; c_{cs} + N \cdot \Delta c_c \rangle$. In some cases there might happen, due to the agreement of random properties of the system, a periodical repetition of some system of concentrations of the catalyst.

In the control of the reactor in unstable state there interchange individual additions of the catalyst ($N = 1$) with two-fold or even multifold ($N = 2, 3 \dots$). But the analysis has demonstrated that in the relatively large surrounding of the operating point is the slope of the curve of dependence of quantities c_{ce}^n and c_c^n close to the value -1 . Thus as long as the changes in the concentration of the catalyst are small at dosing, there dominate simple additions of the catalyst. Examples of the calculated and experimental results are for this case given in Figs 4b, 5 to 8.

Selection of the Value V_c

The volume of the fed catalyst solution V_c is the only fixable constant of the controller. The change in the catalyst concentration in the reactor is related with the added volume V_c having the concentration of the catalyst c_{cf} by the relation

$$\Delta c_c = c_{cf} V_c / V_s. \quad (10)$$

In the case of the ideal controller the control is the better the smaller is the value Δc_c . With its increasing value temperature deviations from the required value also

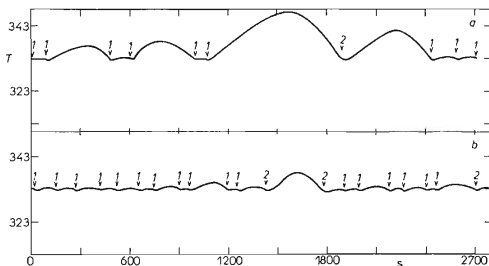


FIG. 7

Experimental Temperature Dependence of the Mixture on Time at Control of Reactor in Unstable State

a $V_c = 2.4 \cdot 10^{-6} \text{ m}^3$; b $V_c = 1.9 \cdot 10^{-6} \text{ m}^3$, $\Delta t = 9 \text{ s}$; \downarrow simple addition of catalyst; $\downarrow\downarrow$ double addition.

increase (Fig. 8). This is profound especially in the control in the unstable state of the reactor, when it is possible from some certain value Δc_c to observe such worsening of quality of control that the result must be qualified as run-away (Fig. 8, curves 6 and 7). From simulation computations performed with the nonlinearized model of the reactor there results that the process proceeds so that the temperature in the reactor increases during the operating cycle with the mixture practically completely converted. The temperature returns to the required temperature when the concentration of the catalyst in the reactor is very small and it is necessary to add multiple doses of the catalyst. The calculated and experimental examples are given in Figs 9 and 10.

In practical realisation of the control algorithm it is necessary, after each addition of the fixed amount of catalyst to evaluate the sign of the derivative only after elapse of some guard time Δt so that an erroneous addition of multiple dosis of the catalyst is not taking place ($N > 1$) due to noise and transport lag of the instruments.

The reliability of control is then dependent both on the choice of V_c (Fig. 8) and selection of quantities which eliminate the effect of noise and small sensitivity of instruments *e.g.* of the value Δt . If a too "weak" protection is selected which means also a small value Δt , the repeated dosing of the catalyst takes place even when this is not requirable with stochastic elements introduced into the equipment. Overdosing

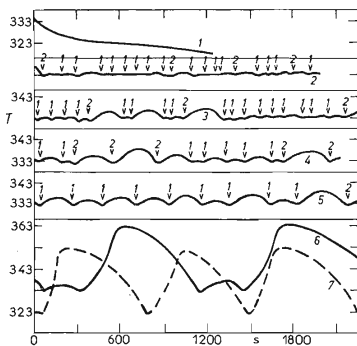


FIG. 8

Effect of Volume of the Fed Catalyst Solution on Quality of Control

1 $V_c = 0.9 \cdot 10^{-6} \text{ m}^3$ (volume is fed each 9 s); 2 $1.4 \cdot 10^{-6}$; 3 $1.9 \cdot 10^{-6}$; 4 $2.3 \cdot 10^{-6}$; 5 $2.8 \cdot 10^{-6}$; 6 $3 \cdot 10^{-6}$; 7 $5.2 \cdot 10^{-6}$; other symbols used are the same as those in Fig. 7.

of the catalyst deteriorates the quality of control. If a large value Δt is chosen the repeated dosing of the catalyst is related with departure from the required temperature. This can lead in extreme cases in combination with a small value Δc_c to the case where the addition of the catalyst cannot even compensate the decrease in the reaction rate due to the decrease in temperature during this time interval Δt . The reaction rate then steadily decreases and the reactor "extincts". Experimental examples are given in Fig. 8 (curve 1) and in Fig. 11.

The frequency of dosing can be estimated from the fact that the mean catalyst concentration in the reactor must at least approximately correspond to the concentration c_{cs} . The frequency is then equal to the value of ratio $F_1 c_{cs} / (V_c c_{cf})$.

One operating cycle should be longer than is the transport lag of the input signal and the time constant of the controller.

Disturbances

If we assume that the temperature and composition of the mixture at the inlet into the reactor is stabilized then two types of disturbances can occur. Firstly the feed rate, secondly the concentration of active compounds in the solution of the catalyst

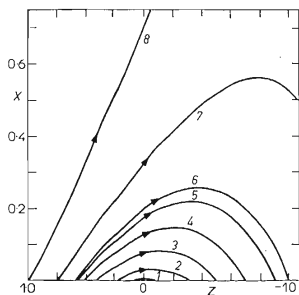


FIG. 9

Calculated Example on the Effect of Fed Volume of Catalyst Solution on the Form of Operating Cycle at Control of Reactor in Unstable State

$A = 1.4534$; $1 V_c = 0.6 \cdot 10^{-6} \text{ m}^3$; $2 1.1 \cdot 10^{-6}$; $3 1.3 \cdot 10^{-6}$; $4 2.4 \cdot 10^{-6}$; $5 2.5 \cdot 10^{-6}$; $6 2.6 \cdot 10^{-6}$; $7 3 \cdot 10^{-6}$; $8 4.5 \cdot 10^{-6}$.

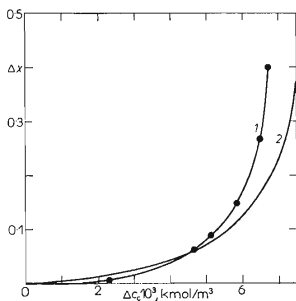


FIG. 10

Example of Dependence of Maximum Degree of Conversion of Reactant During the Operating Cycle on the Amount of Added Catalyst

$\Delta x = x - x_s$; 1 experimental dependence; 2 calculated dependence.

can change. The same consequences has the change in the concentration of catalytic poisons in the fed reaction mixture or the change in concentration of the catalytically acting compounds in the feed.

The change in the feed rate must be compensated by the change in the catalyst concentration in the reactor *i.e.* by the change in c_{cs} . From the point of view of control the step change in the feed rate results in two consequences. First of all a step change in c_{cs} takes place *i.e.* in the reactor there is suddenly an excess of catalyst (at the decrease of the feed rate) or insufficiency of the catalyst (at increase of the feed rate). The used algorithm of control can balance the insufficiency of the catalyst so that the catalyst is repeatedly added until the temperature starts to increase. But against the surplus of catalyst neither the algorithm nor any other algorithm gives any protection as the inlet of the catalyst must be left closed till the content of the catalyst in the reactor is decreased by the outlet stream. If such situations occur during the operation of the reactor other means must be used *e.g.* addition of the catalyst poison.

Even the step change in the concentration of the active component in the solution of the catalyst is not causing a step change inside the reactor. Its consequences are thus not so "hard" as in the case of changes in the feed rate. There takes place a successive change in the value c_{cf} (at constant value V_c) which leads to the consequences discussed in the paragraph on selection of the value c_c . From our results

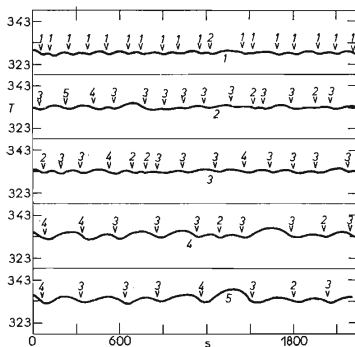


FIG. 11

Effect of Time Interval Δt on Quality of Control

1, 2, 3, 4 ... single, two-, three-, four-fold, ... *etc.* addition of catalyst solution with the volume $V_c = 1.9 \cdot 10^{-6} \text{ m}^3$; 1 $\Delta t = 9 \text{ s}$; 2 7 s; 3 5 s; 4 3 s; 5 0.5 s.

it is possible to conclude that it is possible at the control in unstable state to assume that this simple model of control is capable to compensate changes in concentration of the active component in a relatively small range accounting approximately to 30 to 40% (Figs 12 and 13). In the case the activity of the catalyst would change more it is necessary to use the adaptable model of control when the value V_c would be changed according to the activity of the catalyst. Informations on the activity of the catalyst can be obtained *e.g.* from the frequency of addition of the catalyst. One of the possibilities is to choose the volume V_c so that the rate of addition would be approximately constant which of course considerably complicates the control algorithm.

CONCLUSIONS

The results and experimental verifications prove that it is possible to control the reactor also in the unstable state with relatively simple means. The proposed mode of control is not requiring the use of the dosing equipment which is continuously changing the feed rate of the catalyst. When the adaptive equipment is not used the structure of the controller is also very simple. On the contrary it is not possible to expect

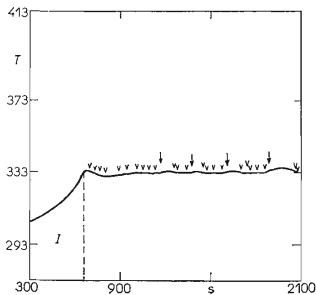


FIG. 12

Effect of Disturbance in Dosing of the Catalyst on Quality of Control

I Introduction of the reactor into the given state; \vee addition of catalyst solution having the volume $V_c = 1.2 \cdot 10^{-6} \text{ m}^3$; \downarrow disturbance (trace of catalyst in the mixture of reactants fed into the reactor).

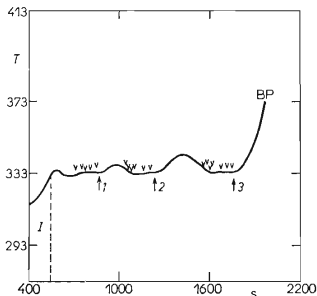


FIG. 13

Effect of Size of Disturbance in Concentration of the Fed Catalyst on Quality Control

\downarrow Disturbance simulated by addition of the catalyst solution having the concentration 0.5 kmol/m^3 ; 1 volume of solution $2 \cdot 10^{-6} \text{ m}^3$; 2 $2.5 \cdot 10^{-6}$; 3 $3 \cdot 10^{-6}$; BP boiling point; other symbols used are the same as those used in Fig. 12.

that the proposed mode of control will be capable to operate at conditions when the catalyst activity is varying by one or more orders of magnitude. Then it is necessary to introduce the adaptive elements. In this case is also necessary that the start of the operation is performed by manual adjustment.

LIST OF SYMBOLS

- A dimensionless parameter defined by Eq. (5a)
 c_{Ai} concentration of compound A in feed (kmol/m^3)
 c_{Bi} concentration of compound B in feed (kmol/m^3)
 c_c concentration of catalyst in the reactor (kmol/m^3)
 c_{cf} concentration of catalyst in the feed solution (kmol/m^3)
 c_{ci} concentration of catalyst in the feed into reactor (kmol/m^3)
 c_{ce} concentration of catalyst in the reactor at the end of the operating cycle (kmol/m^3)
 c_{cs} concentration of catalyst in the reactor corresponding to the given steady state (kmol/m^3)
 D dimensionless parameter defined by Eq. (5b)
 E activation energy of reaction (kJ/molA)
 F_i volume flow rate of feed of reactants into the reactor (m^3/s)
 k_{st} constant in the rate equation of reaction ($\text{m}^3/\text{kmol s}$)
 n operating cycle
 N number of volumes of the catalyst solution dosed at the beginning of the operating cycle into the reactor
 r reactor rate ($\text{kmol A/m}^3 \text{ s}$)
 r_s reaction rate in the given steady state of the reactor ($\text{kmol/m}^3 \text{ s}$)
 R gas constant
 t time (s)
 T temperature of the reaction mixture in the reactor (K)
 T_i temperature of feed (K)
 T_s temperature of the mixture corresponding to the given steady state of reactor (K)
 V volume of the mixture in the reactor (m^3)
 V_c volume of the catalyst solution dosed into the reactor (m^3)
 V_s volume of the reaction mixture in the reactor corresponding to the given steady state (m^3)
 x degree of conversion of compound A in the reactor
 x_s degree of conversion in steady state of reactor
 X dimensionless degree of conversion defined by Eq. (3)
 Z dimensionless catalyst concentration defined by Eq. (3a)
 Z_i quantity Z at the beginning of the operating cycle ($X = 0$)
 Z_e quantity Z at the end of the operating cycle ($X = 0$)
 $\alpha = \frac{E \Delta T_{ad}}{RT_s^2} - \frac{1}{1 - x_s}$ dimensionless parameter
 ΔH heat of reaction (kJ/mol A)
 Δc_c change in catalyst concentration in reactor after dosing (Eq. (10)) (kmol/m^3)
 Δt time interval (s)
 ΔT temperature difference (K)
 ΔT_{ad} adiabatic temperature rise due to the reaction (K)
 τ dimensionless time defined by Eq. (5)

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