BATCH REACTOR WITH CLOSED SYSTEM OF THE COOLANT. GENERAL ANALYSIS

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Received October 25th, 1976

The methods are proposed for studies on behaviour of periodically operated batch and semibatch reactors with the coupling between individual operating cycles and continuous reactors controlled by step changes of inlet quantities. The methods are based on numerical and graphical procedures. Examples are given on application of these methods to studies on the character and stability of steady cycles of the batch reactor with the closed bath of the coolant (heat carrier) at exothermic first order reaction. The reactor together with the bath of the coolant is operated autothermally.

Behaviour of the batch reactor with the exothermic reaction is studied where the heat transfer takes place only with the closed bath of the coolant (heat carrier). The reactor together with the bath forms the adiabatic system which is operated in the autothermal regime (Fig. 1).

At the beginning of each operating cycle is the original reaction mixture suddenly fed into the reactor. During the operating cycle the heat is transferred at first from the coolant into the reaction mixture (the coolant is thus heating the mixture) at the end of the cycle on the contrary the heat is transferred from the reaction mixture to the

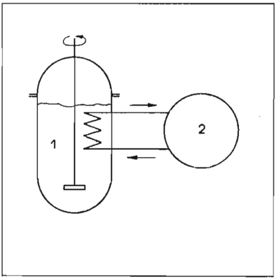

FIG. 1
Batch Reactor with Closed System of the Coolant
1 Reactor, *2* coolant.

coolant (is accumulated in the coolant). At the instant when the required composition of the reaction mixture is reached, the mixture is suddenly discharged from the reactor and the cycle is terminated. The new cycle begins with the temperature of the coolant equal to the final temperature of the coolant from the preceding cycle and so forms the coupling between the operating cycles. In this paper the steady cycles and their stability are studied.

The studied system can be considered to be the flow reactor operated periodically. Thus the studied reactor has elements of behaviour similar to other types of reactors operated periodically.

An example is the adiabatic reactor which has been studied by Ausikaitis and Engel[1]. These authors are describing the operation of the reactor so that after termination of the operating cycle part of the reaction mixture is suddently discharged and a part is left in the reactor as the recycle. New cycle is started by feeding the inlet mixture to the mixture left in the reactor. It was proved that at constant time of the operating cycle, constant inlet conditions and constant ratio of flow rates of cycle to the inlet mixture the reactor could have three steady states, one of which was unstable. The effort to control the reactor in the unstable state (at constant time of the cycle) was not successful. But the authors succeeded in controlling the reactor so that the cycle was terminated when the selected temperature was reached which corresponded to the unstable state. The authors have proved that the reactor behaves identically as the tube flow reactor with the adiabatic recycle which was studied by Root and Schmitz[2]. Several studies have been devoted to behaviour of the reactor in the case when some of the inlet quantities are changing periodically. The aim of these studies has been the increase of the reactor output or the increase of the yield of the product[3-12]. These studies have been summarized in the paper by Baylei[13].

MATHEMATICAL MODEL

In derivation of the model of the batch reactor the following simplifying assumptions were made: The reactor is filled and discharged immediatelly *i.e.* the course of the reaction during the feeding and discharge can be neglected. For a simple exothermic first order reaction of the type A=R, under assumption of constant physico-chemical properties of the reaction mixture and the coolant, the operating cycle is described by the system of equations

$$\mathrm{d}x/\mathrm{d}t = r/c_{\mathrm{A0}}\,, \tag{1}$$

$$\mathrm{d}T/\mathrm{d}t = (r/c_{\mathrm{A0}})\,(-\Delta H)\,c_{\mathrm{A0}}/(Vc_{\mathrm{p}}\varrho) - (k_{\mathrm{h}}P/(Vc_{\mathrm{p}}\varrho))\,(T - T_{\mathrm{c}})\,, \tag{2}$$

$$\mathrm{d}T_{\mathrm{c}}/\mathrm{d}t = (k_{\mathrm{h}}P/(V_{\mathrm{c}}c_{\mathrm{pc}}\varrho_{\mathrm{c}}))\,(T - T_{\mathrm{c}})\,, \tag{3}$$

with the initial conditions

$$t = 0\,, \quad x = 0\,, \quad T = T_0\,, \quad T_{\mathrm{c}} = T_{\mathrm{cN}}\,. \tag{4}$$

By introduction of the first order reaction rate equation

$$r/c_{A0} = k_{st}(1 - x) \exp \left(E(T - T_{st})/(R_g T T_{st})\right), \tag{5}$$

the given system of equations can be transformed into the dimensionless form

$$\mathrm{d}x/\mathrm{dDa} = (1 - x) \exp \left(\Theta \, \Delta T/(1 + \Delta T)\right), \tag{6}$$

$$\mathrm{d}\,\Delta T/\mathrm{dDa} = \Delta T_{ad}(1 - x) \exp \left(\Theta \, \Delta T/(1 + \Delta T)\right) - K(\Delta T - \Delta T_c), \tag{7}$$

$$\mathrm{d}\,\Delta T_c/\mathrm{dDa} = K\, B(\Delta T - \Delta T_c), \tag{8}$$

with the initial conditions

$$\mathrm{Da} = 0\,, \quad x = 0\,, \quad \Delta T = \Delta T_0\,, \quad \Delta T_c = \Delta T_{cN}\,. \tag{9}$$

In Eqs (5) to (8) the parameters K and B are defined by relations

$$K = k_h P/(V c_p \varrho k_{st}), \tag{10}$$

$$B = V c_p \varrho/(V_c c_{pc} \varrho_c). \tag{11}$$

The parameter K is characterizing the intensity of heat transfer between the reaction mixture in the reactor and the bath of the coolant, parameter B the ratio of thermal capacities of the mixture and the coolant.

The system of equations has been solved numerically on the digital computer by the Hamming method.

Method of Determination of Steady States and Their Stability

To avoid misuse of introduced terms the term cycle is reserved for the operating cycle of the reactor. The cycle to which the regime of the reactor in the limit is approaching, when the reactor is operated at constant conditions, is denoted as steady state.

For studies of behaviour of the reactor, methods have been developed which have a more general application in the analysis of behaviours of batch reactors and semi-continuous reactors with the coupling between individual operating cycles and analysis of continous reactors controlled by use of step changes of some quantities (control by use of relais).

Let us denote the part of the system which is transferred after termination of the operating cycle into the next cycle as the recycled stream. Part of the system which is participating in the process only in the given cycle, is denoted as the flow stream. For example, in case of the batch reactor with closed system of the coolant, the recycled stream is the coolant and the flow stream is the reaction mixture in the reactor.

The method can be applied to cases in which the state of the recycled stream can be characterized by a single state variable R and where to each value of the state variable at the inlet into the N-th cycle R_N corresponds a unique form of the operating cycle. The given requirements are satisfied when there holds: *1*) The amount, composition and temperature and other properties of the recycled stream are mutually dependent. The dependence results either from properties of the system itself or is given by the control algorithm. *2*) The amount and properties of the flow stream which enters the operating cycle are either constant or dependent on the state of the recycled stream at the inlet into the N-th operating cycle R_N. The dependence must be determined by the prescribed control algorithm. *3*) The reactor control during the operating cycle must be determined by the prescribed control altgorihm so that to each inlet quantity R_N is adjoined the unique mode of control. *4*) Moment of termination of the operating cycle is defined so that to each inlet value of the state quantity of the recycled stream R_N corresponds a single one, uniquely defined state of the system in which the operating cycle is terminated.

When the above given limitations are met, each operating cycle is represented by the inlet value R_N and it is possible to determine the dependence of the state variable at the outlet from the N-th cycle R_{N+1} on this inlet value

$$R_{N+1} = F(R_N)\,, \tag{12}$$

where $F(R_N)$ is a function the shape of which is dependent on properties of the system alone and on the algorithm of control. It is not possible to make general conclusions concerning the shape of this functional dependence. Its shape results either from measurement on the given object or from the numerical solution of the mathematical model of the reactor (represented *e.g.* by Eqs (*6*) to (*9*)). Thus it is suitable to base the determination of steady states and their stability on studies of properties of the dependence defined by relation (*12*) which is given graphically.

Under the term "steady state" (of periodically operated reactor) is understood in this study such smallest system K of succeeding operating cycles for which there holds that the output state variable from the cycle $N + K - 1$ is identical with the inlet value into the cycle N:

$$R_{N+K} = R_N\,, \quad K = 1, 2, 3, \ldots \tag{13}$$

GRAPHICAL METHOD OF DETERMINATION OF STEADY STATES

Graphical plot of the function R_{N+1} enables determination of state variable R at repeating of the operating cycles. For the selected value R_N it is possible to read off the corresponding outlet value R_{N+1} on the curve of its functional dependence. By plotting the horizontal straight line ($R_{N+1} = R_{N+1}$) through this point it is possible to determine the inlet value of the state variable R into the following cycle. This inlet value is situated at the intersection of this horizontal straight line with the diagonal $R_{N+1} = R_N$ (the axis of the first and third quadrante). By repeating the procedure it is possible to study the changes of the state variable of the recycled stream at repeated operating cycles.

Steady States Composed of one Operating Cycle

These steady states are defined by condition (*13*) for $K = 1$. Thus they are situated at the intercept of the curve representing the functional dependence $R_{N+1} = F(R_N)$ (further on denoted as the function R_{N+1}) with the diagonal $R_{N+1} = R_N$.

There can be four types of steady states according to the value of the slope of the curve representing function R_{N+1} in steady state $(dR_{N+1}/dR_N)_u$ (the subscript u denotes the steady state). Individual cases are given in Table I and are schematically plotted in Fig. 2.

Table I

Steady States Composed of a Single Operating Cycle and Their Asymptotic Stability
The Symbols *a*, *b*, *c*, *d* are identical with those in Fig. 2.

Character of the state	Stability	$(dR_{N+1}/dR_N)_u$
Node (*a*)	stable	$\langle 0, 1)$
Node (*b*)	unstable	$(1, \infty)$
Focus (*c*)	stable	$(-1, 0)$
Focus (*d*)	unstable	$(-\infty, -1\rangle$

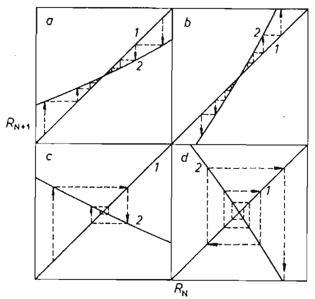

Fig. 2

Steady State Composed of a Single Operating Cycle

1 Dependence $R_{N+1} = R_N$, *2* dependence $R_{N+1} = F(R_N)$; *a* stable node, *b* unstable node, *c* stable focus, *d* unstable focus.

Steady States Composed of Two Operating Cycles

Steady states composed of two operating cycles are defined by condition (*13*) for $K = 2$. Determination of such steady state by the graphical procedure means to find the square with vertices parallel with the coordinate axis and with their opposing vertices on the diagonal $R_{N+1} = R_N$ and the other two on the curve of function R_{N+1}. For determination of steady state it is advantageous to use symmetric diagram of the curve function R_{N+1} according to the straight line $R_{N+1} = R_N$ (the symmetric dependence of this function will be further on denoted as the function $R_{N+1,s}$).

The steady states composed of two operating cycles are then given as intercepts of the curves of functions R_{N+1} and $R_{N+1,s}$. It is possible to determine from values of slopes of these curves in steady state the character and assymptotic stability of steady states. The method of sampling of the state changes by use of the symmetric diagram obvious from Fig. 3.

At the existence of steady state composed of two operating cycles there can originate eight possibilities. Their summary is given in Figs 4 and 5. In Figs 6 and 7 are given examples of state changes which correspond to individual types of steady states. The conditions of stability and characteristics of steady states are given in Table II.

For stability and character of steady state is decisive the value of quantity A determined by the ratio of slopes of curves of functions R_{N+1} and $R_{N+1,s}$ in steady state

$$A = (dR_{N+1}/dR_N)_u/(dR_{N+1,s}/dR_N)_u = (dR_{N+1}/dR_{N+1,s})_u\,. \qquad (15)$$

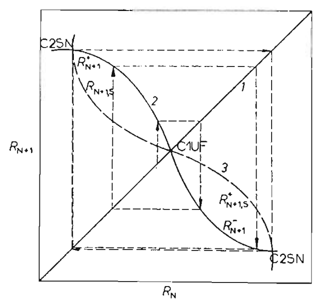

FIG. 3

Example of Use of Symmetric Diagram for Determination of Changes of System States

1 Dependence $R_{N+1} = R_N$, *2* dependence $R_{N+1} = F(R_N)$, *3* symmetric dependence $R_{N+1,s} = F(R_N)$; C1UF steady state of the type unstable focus composed of a single operating cycle, C2SN steady state of the type stable node composed of two operating cycles; R^+_{N+1} function R_{N+1} in semiplane $R_{N+1} > R_N$, $R^+_{N+1,s}$ symmetric diagram of this function, R^-_{N+1} function R_{N+1} in the semiplane $R_{N+1} < R_N$, $R^-_{N+1,s}$ symmetric diagram of this function.

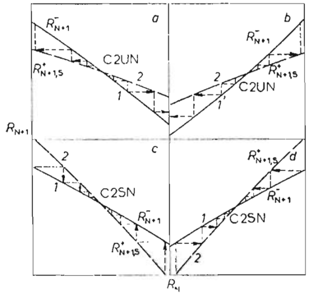

Fig. 4

Steady States Composed of Two Operating Cycles

1 Dependence $R_{N+1} = F(R_N)$, *2* symmetric dependence; *a*, *b* unstable node *c*, *d* stable node; other symbols are identical with those in Fig. 3.

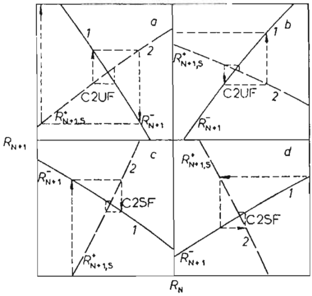

FIG. 5

Steady States Composed of Two Operating Cycles

a,*b* Unstable focus, *c*,*d* stable focus; other symbols are identical with those in Fig. 4.

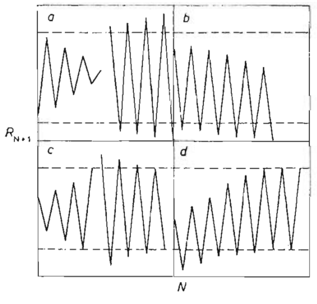

FIG. 6

Example of Variation of State Variable *R* for Different Types of Steady State Composed of Two Operating Cycles

Symbols used are identical with those in Fig. 4.

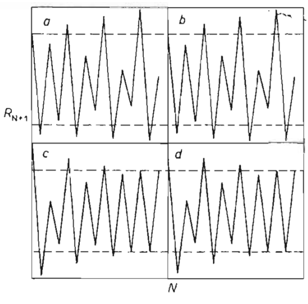

FIG. 7

Example of Variation of State Variable *R* for Various Types of Steady States Composed of Two Operating Cycles

Symbols used are identical with those in Fig. 5

As for slopes of curves the relation holds

$$(\mathrm{d}R_{N+1}/\mathrm{d}R_N)_u \cdot (\mathrm{d}R_{N+1,s}/\mathrm{d}R_N)_u = 1\,, \tag{15a}$$

it is equal if the relation (*15*) is evaluated for the intercept of curves in the semiplane $R_{N+1} = R_N$ or for the intercept symmetrical to it in the semiplane $R_{N+1} = R_N$.

TABLE II

Steady States Composed of Two operating Cycles and Their Asymptotic Stability

Symbols used are identical with those in Fig. 3.

+1 Denotes the value of state variable greater than the upper steady state, −1 the value smaller than the upper state, +2 value greater than the lower steady state, −2 smaller than the lower state

Character and stability	$\left(\frac{\mathrm{d}R_{N+1}}{\mathrm{d}R_N}\right)_u$	$\left(\frac{\mathrm{d}R_{N+1,s}}{\mathrm{d}R_N}\right)_u$	$\left(\frac{\mathrm{d}R_{N+1}}{\mathrm{d}R_{N+1,s}}\right)_u$	Order of changes of quantity R_{N+1}
Stable node	>0	>0	>1	$-1-2-1-2,\ +1+2+1+2$
Stable node	<0	<0	>1	$-1+2-1+2,\ +1-2+1-2$
Unstable node	>0	>0	<1	$-1-2-1-2,\ +1+2+1+2$
Unstable node	<0	<0	<1	$-1+2-1+2,\ +1-2+1-2$
Stable focus	>0	<0	0 to -1	$+1+2-1-2$
Stable focus	<0	>0	0 to -1	$+1-2-1+2$
Unstable focus	>0	<0	<1	$-1-2+1+2$
Unstable focus	<0	>0	<-1	$-1+2+1-2$

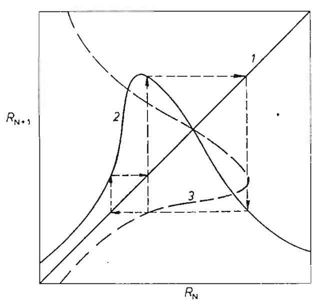

FIG. 8

Steady States Composed of Three Operating Cycles

Symbols used are identical with those in Fig. 3.

For the value $A < 1$ it is the stable node, for $A \in (0, 1)$ it is the unstable node. If $A \in (-1, 0)$, the steady state is stable focus, and for $A < (-1)$ the steady state is an unstable focus.

Steady States Composed of Three Operating Cycles

We can transform the problem of finding the steady state for the use of the symmetric curve into the problem of finding a rectangle whose sides are parrallel with the coordinate axis, with one vertex situated on the diagonal $R_{N+1} = R_N$ and the remaining three on the curves of functions R_{N+1} and $R_{N+1,s}$ in the semiplane $R_{N+1} = R_N$. The examples are given in Fig. 8.

While the steady states composed of two operating cycles are necessarily symmetric, the steady states composed of three operating cycles must be asymmetric. The number of combinations which can so originate is large and it is thus not possible to investigate all of them. But if the function R_{N+1} has a small number of extremes and inflex points it is possible to assume that the most probable will be steady states in which the slopes of curves at all points are positive or negative only at a single point.

The criteria of stability of steady states can be obtained by the next procedure. We denote by numbers vertices of the square in the direction of motion so that the point one is the vertex from which the motion starts horizontally to the right. Then on stability decides the values of the quantity A defined by the relation

$$A = (\mathrm{d}R_{N+1}/\mathrm{d}R_N)_1 \cdot (\mathrm{d}R_{N+1}/\mathrm{d}R_N)_3/(\mathrm{d}R_{N+1,s}/\mathrm{d}R_N)_2 \cdot (\mathrm{d}R_{N+1,s}/\mathrm{d}R_N)_4 \,. \quad (16)$$

If the value of quantity A is positive the steady state is the node, if it is negative it is the focus. If the value of quantity A in absolute value is smaller than one the state is stable. The same table holds here as for the states composed of a single operating cycle, *i.e.* the Table I.

Steady States Composed of Four Operating Cycles

These steady states can be of three types according to the way the values of the state variable vary in the steady state in the semiplane $R_{N+1} > R_N$. If we denote by symbol + values of the state variable in the semiplane $R_{N+1} > R_N$ and by symbol − values in the semiplane $R_{N+1} < R_N$, the variation of the state variable in steady state can be expressed schematically

$$R^+_{N+1,u},\ R^+_{N+1,u},\ R^+_{N+1,u},\ R^-_{N+1,u}\,,$$

or on the contrary

$$R^-_{N+1,u},\ R^-_{N+1,u},\ R^-_{N+1,u},\ R^+_{N+1,u}$$

and for asymmetric states

$$R^{+}_{N+1,u},\ R^{+}_{N+1,u},\ R^{-}_{N+1,u},\ R^{-}_{N+1,u}\,,$$

and vice versa

$$R^{+}_{N+1,u},\ R^{-}_{N+1,u},\ R^{+}_{N+1,u},\ R^{-}_{N+1,u}$$

for symmetrical steady states.

Determination of these steady states can be transferred to the problem of finding the square whose sides are parallel with the coordinate axis and whose vertices are situated on curves of function R_{N+1} and $R_{N+1,s}$. The examples are given in Fig. 9. The value of quantity A (Eq. (*16*)) is decisive for stability of the state, for the characteristics of state then hold the same conclusions as for steady states composed of three operating cycles.

Numerical Method of Evaluation of Steady States

For numerical evaluation, the functional dependence $R_{N+1} = F(R_N)$ must be either described by empirical formula or given by the table of values in which it is possible to interpolate.

So given function then enables to generate the dependences of values of state variable after one, two, three to M cycles on the inlet value into the N-th cycle

$$R_{N+M} = F(F(F(\ldots F(R_N)\ldots))) = F^M(R_N)\,. \qquad (14)$$

(F^M denotes the functional).

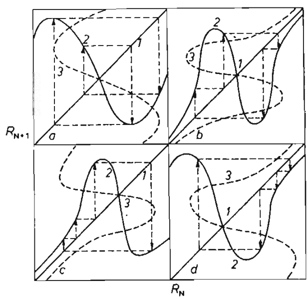

FIG. 9

Steady States Composed of Four Operating Cycles

a, *b* Asymmetric state, *c*, *d* symmetric state; other symbols used are identical with those in Fig. 3.

From these it is possible to determine the steady state composed of K operating cycles by the next procedure: *1*) All values of the state variable R_N are determined, the functional dependence of which described by Eq. (*14*) satisfies the condition

$$R_{N+M} = R_N \tag{14a}$$

for $M \in \langle 1, K \rangle$. These values are denoted as R_{Nu}. *2*) All values of the state variable R_N which satisfy the condition defined by Eq. (*14a*) for $M < K$ are eliminated. *3*) If there are K remaining values, the steady state is formed of K operating cycles. If their number is $L \times K$, where L is an integer it means that there exist L steady states composed of K operating cycles.

Individual steady states can be differentiated by comparison of derivatives of function R_{N+K} in the points R_{Nu}

$$\left(\frac{dR_{N+K}}{dR_N}\right)_{R_{Nu}}.$$

The value of derivative must be identical for all values R_{Nu} which correspond to one state (Eq. (*14b*)).

For the analysis of the asymptotic stability we define the quantity A

$$A = \frac{dR_{N+K}}{dR_N} = \left(\frac{dR_{N+K}}{dR_{N+K-1}}\right) \ldots \left(\frac{dR_{N+2}}{dR_{N+1}}\right) \cdot \left(\frac{dR_{N+1}}{dR_N}\right) =$$
$$= \left(\frac{dR_{N+1}}{dR_N}\right)_{R_{Nu1}} \cdot \left(\frac{dR_{N+1}}{dR_N}\right)_{R_{Nu2}} \ldots \left(\frac{dR_{N+1}}{dR_N}\right)_{R_{NuK}}, \tag{14b}$$

where R_{Nu1} to R_{NuK} are values of R_{Nu} corresponding to one steady state.

According to the value of quantity A the steady states can be of four types. Their summary is given in Table I (the term node denotes steady states which the state variable R_{N+K} approaches monotonously if they are stable or from which it monotonously departs if they are unstable. The term focus denotes steady states at which the oscillations can be observed *i.e.* interchange of values smaller and larger than the value corresponding to the steady state).

Application to the Batch Reactor with the Closed System of the Coolant

In the reactor with the closed system of the coolant the state of the recycled stream (coolant) is characterized as its inlet temperature. For determination of the number and properties of steady states it is thus necessary to study the dependence of temperature of the coolant at the end of the operating cycle $\Delta T_{c,N+1}$ on temperature of the coolant at the inlet into the cycle $\Delta T_{c,N}$.

The given dependences were obtained by numerical solution of the system of Eqs (*6*) to (*8*). As the shape of the functional dependence depends on definition of the instant in which the cycle is terminated, it is necessary to discuss individual method of termination of the cycle.

Termination at Constant Degree of Conversion

This termination seems to be the most logical. In comparison to other terminations of cycles it has the advantage that the product has the prescribed composition also during the reaching of the steady state. This has a considerable importance when during the operation a change of some parameter takes place. *e.g.* of the catalyst activity, activity of the iniciator, clodging of heat transfer areas etc. An example of the calculated dependence of quantities $\Delta T_{c,N+1}$ and $\Delta T_{c,N}$ for this method of termination of the cycle is given in Fig. 10. This demonstrates that in this method the steady state composed of one operating cycle can be unstable, while there exists a steady state composed of two operating cycles (Figs 11 and 12). An example of the temperature dependence of the reaction mixture, coolant and degree of conversion in steady state composed of two operating cycles is given in Fig. 13.

The existence of a simple unstable steady state is conditioned by the extreme temperature dependence of the reaction mixture at the inlet and temperature dependence of the coolant (high parametric sensitivity). This results from the condition for unstability of steady state of the type focus (Table I) and the total heat

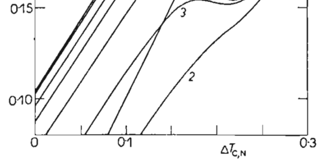

FIG. 10

Batch Reactor with Closed System of the Coolant

The cycle is terminated at constant degree of conversion

$\Theta = 30$, $K = 500$, $B = 0{\cdot}3$, $\Delta T_{ad} = 0{\cdot}7$, $\Delta T_0 = -0{\cdot}25$; *1* $x_{N+1} = 0$, *2* 0·3, *3* 0·6, *4* 0·8, *5* 0·9, *6* 0·95, *7* 0·995, *8* 1·0.

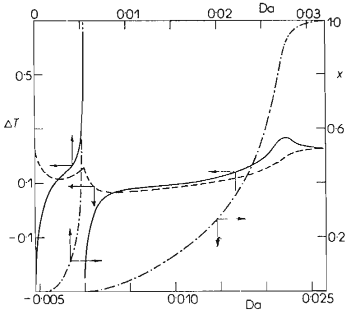

FIG. 11

Batch Reactor with Closed System of the Coolant; The Case I for $x_{N+1} = 0.995$

1 Dependence $\Delta T_{c,N+1} = \Delta T_{c,N}$, *2* dependence $\Delta T_{c,N+1} = F(\Delta T_{c,N})$, *3* symmetric dependence; other symbols used are identical with those in Fig. 3.

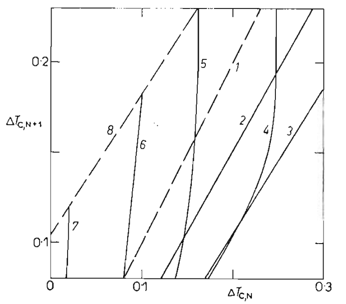

FIG. 12

Variation of Temperature of Coolant at the Outlet from the Operating Cycle for the Case Given in Fig. 11

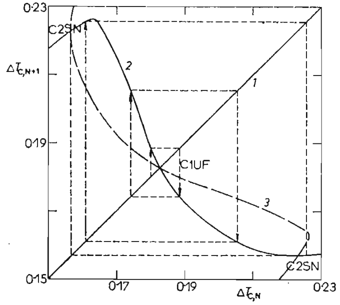

FIG. 13

Example of Variation of Temperature of the Reaction Mixture, Coolant and Degree of Conversion in Steady State Composed of Two Operating Cycles

Solid line denotes temperature of the mixture, dashed line temperature of the coolant, dashed and dotted line degree of conversion.

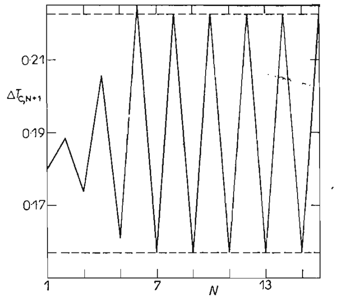

FIG. 14

Batch Reactor with Closed System of Coolant II

The cycle is terminated at constant length of the cycle.

1 $x_{N+1} = 0$, *2* Da = 0·0005, *3* 0·002, *4* 0·004, *5* 0·02, *6* 0·1, *7* 0·5, *8* $x_{N+1} = 1{\cdot}0$.

balance in the system which is given by relation

$$(\mathrm{d}\,\Delta T_{N+1}/\mathrm{d}\,\Delta T_{c,N})_u = B^{-1}(1 - (\mathrm{d}\,\Delta T_{c,N+1}/\mathrm{d}\,\Delta T_{c,N})_u)\,. \qquad (17)$$

(the index u denotes, similarly as in the preceeding examples, the steady state). As the value of derivative $(\mathrm{d}\,\Delta T_{c,N+1}/\mathrm{d}\,\Delta T_{c,N})_u$ in Eq. *17* is within the limits $-\infty$ up to -1 and $B < 1$, the derivative $\mathrm{d}T_{N+1}/\mathrm{d}T_{c,Nu}$ has a big positive value. The reason of simultaneous existence of a steady state composed of two operating cycles is then the next phenomena: In the first cycle the chemical reaction takes place slowly, the cycle takes a long time and thus large amount of heat is transferred from the reaction mixture into the coolant. As the result, the inlet temperature of the coolant entering the next cycle is higher. This causes the speeding up of the chemical reaction and shortening of the cycle. This results in the less perfect heat transfer between the reaction mixture and the coolant. The coolant enters the next cycle with a lower temperature.

It is possible to expect that the dependence of quantities $\Delta T_{c,N+1}$ and $\Delta T_{c,N}$ keeps approximatelly the form given in Fig. 10. But due to changes in viscosity with temperature *etc.* it can become deformed. The steady state composed of two operating cycles can be stable but also unstable. Also the possibility of existence of steady states composed of several operating cycles cannot be eliminated. The asymmetric states would come into consideration with reactors using either heat losses into the surrounding or with simultaneous cooling and accumulation.

Termination at Constant Length of the Cycle

This method is the simplest as it is not necessary to obtain information on the way the process takes place. The moment of termination of the cycle is given by the length of the cycle. Examples of the calculated dependence of quantities $\Delta T_{c,N+1}$ and $\Delta T_{c,N}$ at constant length of the cycle are given in Fig. 14. It is obvious that this form of termination can lead to the existence of multiple steady states composed of a single operating cycle of the type stable or unstable node. Two of these states are stable nodes, one is the unstable node. The behaviour of the reactor is analogous to the behaviour of other reactors with multiple steady states. In this method of termination of cycles it is not possible to expect steady state composed of several operating cycles. As the dependence of quantities $\Delta T_{c,N+1}$ and $\Delta T_{c,N}$ is increasing monotonously it is not possible to expect steady states of the type stable and unstable focus.

Termination at Constant Outlet Temperature of the Reaction Mixture

As the studied system is the autothermal system, the temperature of the reaction mixture in steady state is related to the final degree of conversion. By fixing the constant outlet temperature of the mixture it would be thus possible to fix simultaneously the degree of conversion in steady state. This mode of control of the reactor would be suitable as it substitutes the analysis of the mixture by temperature measurements. But a detailed analysis proves that it could cause problems.

1) The reaction mixture is reaching in a certain region twice the selected temperature as the temperature of the reaction mixture passes through the maximum. Then it is necessary, at the control of the reactor, to define if the cycle should be terminated when the required temperature of the mixture is reached for the first or second time. *2*) The reaction mixture cannot reach the required temperature at all inlet temperatures of the coolant. Below a certain limiting temperature of the coolant the mixture cannot reach the required temperature because even at total conversion of the mixture there does not form sufficient amount of heat which could heat the mixture to the required temperature. Here, it is necessary to use some other definition of termination of the cycle.

An example of the calculated dependence of quantities $\Delta T_{c,N+1}$ and $\Delta T_{c,N}$ is given in Fig. 15. From the calculations result that the steady state can be an unstable focus beside which there exists a stable state composed of two operating cycles.

Termination at Constant Outlet Temperature of the Coolant

This method of termination of the cycle secures stability of the steady state as the inlet temperature of the coolant is stabilized. But if it would be desirable to reach the prescribed degree of conversion, it is necessary to change successively the inlet temperature of the coolant so that the required degree of conversion would be simultaneously reached. This could cause difficulties when some of parameters are variable *e.g.* activity of the catalyst, of the initiator *etc.*

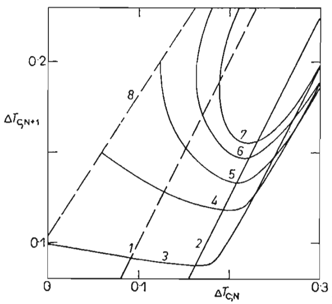

FIG. 15

Batch Reactor with Closed System of Coolant III

The cycle is terminated at constant outlet temperature of the mixture *1* $x_{N+1} = 0$, *2* $\Delta T_{N+1} = 0$, *3* 0·1, *4* 0·15, *5* 0·20, *6* 0·3, *7* 0·6, *8* $x_{N+1} = 1·0$.

LIST OF SYMBOLS

A	criterion of stability of steady cycle
B	parameter defined by relation (*11*)
c_{A0}	initial concentration of the reactant A in the reaction mixture
c_p, c_{pc}	specific heat of mixture or coolant
$Da = t \cdot k_{st}$	Damköhler number
E	activation energy of reaction
k_h	heat transfer coefficient between the reaction mixture and the coolant
k_{st}	reaction rate constant at standard conditions
K	parameter defined by Eq. (*10*)
P	area for heat transfer between the reaction mixture and the coolant
R	state quantity
R_g	gas constant
R_N, R_{N+1}	values of state variable at the inlet and outlet of the Nth operating cycle
t	time
T	temperature of the reaction mixture
T_c	temperature of the outlet
$T_{c,N}$, $T_{c,N+1}$, T_N	temperature of the coolant at the inlet and outlet of the Nth operating cycle or temperature of the mixture at the inlet into the Nth cycle
T_{st}	standard temperature
V, V_c	volume of the reaction mixture and coolant
x, x_{N+1}	degree of conversion of the reactant or degree of conversion at the outlet from the N-th operating cycle
ΔH	heat of reaction
$\Delta T = (T - T_{st})/T_{st}$	dimensionless temperature of the mixture
$\Delta T_{ad} = (-\Delta H)\, c_{A0}/(c_p \varrho T_{st})$	dimensionless adiabatic temperature rise
$\Delta T_c = (T_c - T_{st})/T_{st}$	dimensionless temperature of the coolant
ΔT_0, $\Delta T_{c,N}$	input values of quantities ΔT and ΔT_c in the Nth cycle
ΔT_{N+1}, $\Delta T_{c,N+1}$	outlet values of quantities ΔT and ΔT_c in the Nth cycle
$\Theta = E/R_g T_{st}$	constant
ϱ, ϱ_c	density of the mixture and coolant

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Translated by M. Rylek.