INTENSIFICATION OF COOLING IN A BATCH REACTOR WITH AN EXOTHERMIC REACTION BY NONISOTHERMAL CONTROL IN STABLE PSEUDOSTATIONARY STATES

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An algorithm is set up and tested for the temperature control of a batch reactor consisting in jump changes in the inlet temperature of entering coolant. This temperature is so chosen that its difference from the temperature of the reaction mixture is near the highest difference at which the stable pseudostationary state of the system still exists. For the prediction of the new coolant inlet temperature, a zero-order reaction model is used with an adaptive parameter estimated from the experimentally established value of the maximum of the reaction mixture overheating at the previous coolant temperature.

The conventional temperature control of chemical reactors is based on the stabilization of the coolant flow and temperature. This approach which can be referred to as pseudoisothermal control, is commonly applied in laboratories as the simplest possible way of control. In laboratory reactors, which possess a favourable cooling area-to-volume ratio, pseudoisothermal control often ensures a constant temperature of the reaction mixture. In industrial reactors, however, where the cooling area-to-volume ratio is much less favourable, the pseudoisothermal control approach may lead to difficulties. In some productions, *e.g.*, of medicaments, special chemicals, or pure chemicals, the reactions have to be performed in standardized equipment whose heat exchange area cannot be varied. Pseudoisothermal control then is either impracticable, if the reaction temperature is predetermined, or inconvenient because a low temperature of the heat carrier has to be used and the efficiency of the reactor is consequently low.

Reactions for which the reactor efficiency can be increased by nonisothermal control can be classed in three groups: *1*) Reversible exothermic reactions or reaction systems with different activation energies. For these it is frequently possible to determine the optimum temperature profile to which the maximum reactor efficiency corresponds. *2*) Reactions associated with deactivation of catalyst, starter, or enzyme, the rate of which increases with increasing temperature. In this case, too, the optimum temperature profile corresponding to the highest reactor efficiency can be established.

3) Processes where the reactor efficiency is limited by the cooling rate, *i.e.*, by the rate of the reaction heat removal from the reaction mixture.

Papers dealing with processes of groups *1* and *2* have been reviewed[1,2]. The aim of the present work was to propose a procedure for optimization of reactor performance in group *3*. In our previous papers a method has been suggested for non-isothermal control by which the efficiency could be raised considerably. The method is based on the use of working states that are unstable[3-5]. This approach, which necessitates feedback temperature control, is simple only in case that the cooling system possesses a low inertia[5,6]; in reactors with a high cooling system inertia the utilization of unstable states is rather hazardous. It is safer to make use of open-loop stable states only. Still, even for them it is possible to attain an enhanced efficiency by means of nonisothermal control.

The objective of this work was to design and test a nonisothermal way of control in stable states.

EXPERIMENTAL

Laboratory reactor. A batch reactor[7,8] (Dewar flask), volume 560 ml, was used. The reaction heat was removed by a cooler with an exchange area of 39 cm^2, submerged in the reaction mixture. Water served as coolant and its temperature was controlled by a conventional thermostat. The jump changes in the temperature of entering coolant were achieved by switching over the temperature setting of the thermostat, the time constant of which was 20 s.

The model reaction was the highly exothermic oxidation of ethanol by hydrogen peroxide homogeneously catalyzed with iron(III) ions[7]. The reaction enthalpy is -275 kJ mol^{-1} with respect to hydrogen peroxide. The initial concentrations of hydrogen peroxide, ethanol, and iron(III) ions were 2·04, 0·84, and 1·77 mol l^{-1}, respectively. The adiabatic temperature increase of the reaction was 130 K, the activation energy was 90 kJ mol^{-1}.

Simulation apparatus. The effect of inertia of the cooling system on the control quality was studied in an apparatus where the evolution of heat by chemical reaction was simulated by computer-controlled electric heating, similar to that reported by Mukesh and Cooper[9]. Our apparatus was modified so that the dynamic properties of the cooling system could be varied while keeping the heat exchange area constant. The apparatus consisted of two rectangular metal vessels with a common wall constituting the heat exchange surface. Water both simulated the reaction mixture and served as coolant. Of the two vessels, the larger one with a volume of 23 l, served as the reactor; the volume of water in it was 13·3 l. The reactor was equipped with a mechanical stirrer and two heating coils whose instantaneous power was controlled by a computer according to the rate equation chosen; the maximum power was 1·6 kW. The other vessel, of a volume of 10 l, constituted the cooler. The inlet temperature of the passing water was thermostat-controlled. The heat exchange surface area of the cooler was 540 cm^2. The dynamic properties of the cooler could be varied either by changing its volume by inserting polystyrene boards, or by dividing it into flowed-through and unflowed-through parts. The latter made up the thermal capacity of the reactor wall and at the same-time hindered the heat transfer from the reactor to the cooler. (Fig. 1). In this manner a higher order of dynamic response of the cooler could be achieved. The temperatures in all components of the apparatus were measured with thermocouples, the time constant of which was 4—5 s.

Digital measuring system. An on-line 3052 A Automatic Data Acquisition System of Hewlett–
–Packard was employed for the temperature recording, chemical reaction simulation, and reactor
control. The system consisted of an HP 9835 A desk-top control unit together with an HP 3455 A
digital voltmeter, an HP 3495 A channel switch, and an HP 98035 A time unit.

CONTROL ALGORITHMS

Pseudoisothermal process. The control is based on the stabilization of the coolant
flow rate and inlet temperature. The major problem of the control is in the choice
of the temperature of entering coolant. This temperature must be chosen so that the
system is in a stable pseudostationary state in which the rate of heat generation
by the reaction equals the rate of cooling by the wall. The occurrence of such a stable
pseudostationary state is manifested by a flat maximum in the plot of reaction tempe-
rature *vs* time at low or medium degrees of conversion. In the maximum we have

$$dT/dt = 0 \,. \tag{1}$$

The highest reaction mixture overheating with respect to the heat carrier at which the
stable pseudostationary state still exists was estimated from a zero-order model.
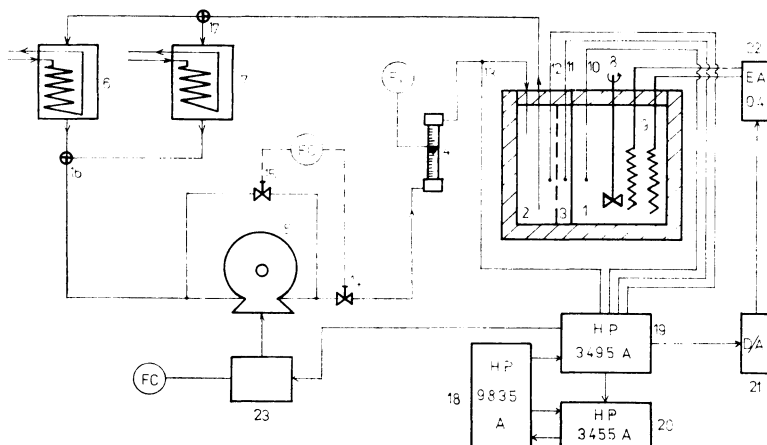This model was set up assuming that the reaction rate depends on temperature

Fig. 1

Simulation apparatus. **1** Reactor, **2** cooler (flowed-through part), **3** unflowed-through part,
4 rotameter, **5** pump, **6, 7** thermostats, **8** stirrer, **9** electric heating, **10**—**13** thermocouples, **14**—**15**
throttle valves, **16, 17** three-way valves, **18** control computer, **19** channel switch, **20** digital volt-
meter, **21** D/A converter, **22** thyristor unit, **23** relay

only and that the cooling rate is a linear function of the temperature difference between the reaction mixture and the entering coolant. In the pseudostationary state then,

$$r_{h,i} \exp\left[E(T_{ps} - T_{ci})/RT_{ps}T_{ci}\right] = k_c(T_{ps} - T_{ci}). \qquad (2)$$

For the highest temperature difference $(T_{ps} - T_{ci})_{max}$, the condition

$$(d/dT_{ps})\left\{r_{h,i} \exp\left[E(T_{ps} - T_{ci})/RT_{ps}T_{ci}\right]\right\} = (d/dT_{ps})\left[k_c(T_{ps} - T_{ci})\right] \qquad (3)$$

must also be satisfied. A graphical illustration of the determination of the highest permissible overheating from the zero-order model is shown in Fig. 2. In the application of this control, safety precautions must be taken and the temperature of entering heat carrier must be chosen so that the observed overheating should be lower than the highest permissible value. A safety coefficient for the control in the stable pseudo-steady state can be defined as the ratio

$$S = (T_{ps} - T_{ci})_{max}/(T_{ps} - T_{ci})_{obs}, \qquad (4)$$

where subscript obs refers to the observed overheating.

Nonisothermal control in stable pseudostationary states. For reactions that are other than zero-order, the inlet temperature of heat carrier for the pseudoisothermal control must be chosen so that the pseudostationary state would exist even at the highest reactivity of the reaction mixture (which is at the beginning for reactions of a positive order). This highest reactivity region constrains the use of heat exchange
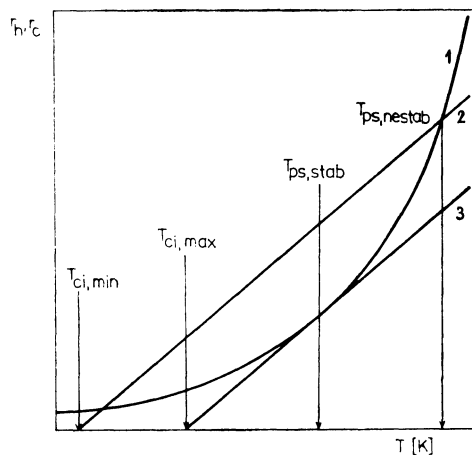

FIG. 2

Graphical method for the determination of the highest permissible overheating. *1* Heat generation curve, *2, 3* heat removal straight lines

surfaces because beyond this region the $(T_{ps} - T_{ci})$ temperature difference is smaller than as conforms to the control safety precautions.

The purpose of the nonisothermal control is, by jump changes in the temperature of entering coolant, to keep the pseudostationary temperature difference at a pre-selected value determined by the relation

$$(T_{ps} - T_{ci}) = (T_{ps} - T_{ci})_{max}/S , \tag{5}$$

where S is a given safety coefficient value.

Control principle: The inlet temperature is set to a followed level $T_{ci,n}$ and stabilized on it until the pseudostationary state is reached, *i.e.*, until the temperature maximum is observed. At this moment the pseudostationary difference $(T_{ps,n} - T_{ci,n})$ is determined. In the pseudostationary state $(dT/dt = 0)$,

$$k_c(T_{ps,n} - T_{ci,n})_{obs} = r_{h,n} . \tag{6}$$

The adaptive parameter $r_{h,n}/k_c$ is then determined from the observed temperature difference, and the new temperature at which the safety coefficient equals the desired value S is estimated. The prediction is made employing a zero-order model derived assuming that the effect of the degree of conversion on the reaction rate and the cooling coefficient can be neglected. The new temperatures $T_{ps,n+1}$ and $T_{ci,n+1}$ are obtained by solving the system of equations

$$(T_{ps} - T_{ci})_{max}/S_{n+1}(T_{ps,n} - T_{ci,n}) =$$

$$= \exp\left[E(T_{ps,n+1} - T_{ps,n})/RT_{ps,n}T_{ps,n+1}\right] \tag{7}$$

$$T_{ci,n+1} = T_{ps,n+1} - (T_{ps} - T_{ci})_{max}/S_{n+1} . \tag{8}$$

The inlet temperature of heat carrier then is changed to the new value, $T_{ci,n+1}$, and the procedure is repeated.

Protection against noise. In the experiments, the reaction temperature data contained a noise component. To eliminate its effect, a tolerance for the maximum temperature control ΔT_{reg} was chosen so that the value was higher than the noise bandwidth in the temperature data. A value of 1 K was actually taken for ΔT_{reg}.

Indication of the temperature maximum: Indication of the temperature maximum is the starting point in the identification of the system. Erroneous determination of the maximum can bring about control failure (uncontrolled temperature rise), particularly if the assessed value is lower than the true value. Denote the instantane-

ous samples temperature T_{obs} and the highest temperature reading after the change in the temperature of entering coolant T_{max}. The occurrence of the maximum is indicated by the fulfilling of the condition

$$(T_{max} - T_{obs}) > \Delta T_{reg} .$$
(9)

Prediction and indication of the moment of the inlet temperature switching: In order to avoid the need to vary the inlet temperature of heat carrier by less than the thermostat precision, the prediction is carried out for the temperature difference obeying the relation

$$(T_{ps} - T_{ci})_{pred} = (T_{ps} - T_{ci})_{max}/S + \Delta T_{reg} .$$
(10)

The switching to the new temperature of entering coolant then is accomplished after the condition

$$(T_{obs} - T_{ci}) < (T_{ps} - T_{ci})_{max}/S - \Delta T_{reg}$$
(11)

is met. The procedure is illustrated by Fig. 3.

Modification of the procedure for reactors with a low inertia of the cooling system. In such reactors, the jump changes in the temperature of entering coolant can be combined with shutting and opening of coolant flow.

Control principle: During the transition of the thermostat temperature from one temperature to another, the flow of coolant through the cooler is stopped. The reaction mixture temperature increases in the adiabatic regime up to the value $T_{ps,n+1}$.
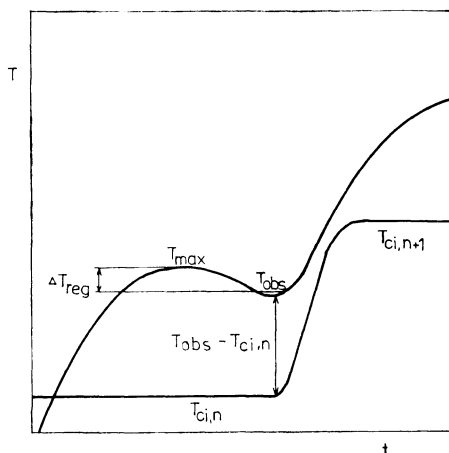

FIG. 3

Illustration of the procedure for the maximum temperature indication, prediction and indication of the moment of the inlet temperature switching

The coolant flow is then restored and the pseudostationary state is indicated according to Eq. (9). When the conditions (9) and (11) are simulatenously satisfied, the coolant flow is stopped, the new inlet temperature T_{ci} is set, and the procedure is repeated. An example of the application of this algorithm is shown in Fig. 4. For systems with a high inertia of the cooling system this procedure is hazardous, the system entering the cooling stage with the cooler heated up.

RESULTS AND DISCUSSION

Classification of Reactions from the Control Safety Aspect

For batch reactors in which hazard of uncontrolled increase in the reaction temperature exists, the processes are conveniently divided into two groups: processes where the hazard grows with increasing degree of conversion, and processes where the hazard diminishes with increasing degree of conversion.

The first group encompasses reactions with autocatalytic kinetics, reactions leading to an increased viscosity of the reaction mixture, reactions where the activation energy increases with the degree of conversion, and reactions where the cooling surface soon becomes choked. For this group the nonisothermal control is hazardous for the following reasons:

The pseudostationary temperature of the reaction mixture with the stabilized temperature of entering coolant increases with time. The pseudostationary state thus cannot be indicated *via* condition (1), and a more sophisticated procedure has to be applied.
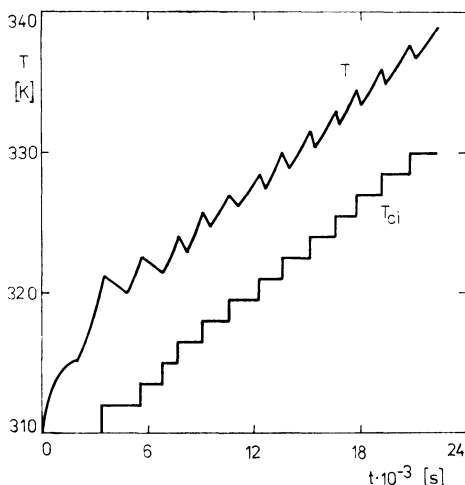

FIG. 4

Example of the application of the modified nonisothermal control to reactors with a low inertia of the cooling system

The pseudostationary temperature of the reaction mixture corresponding to a constant safety coefficient decreases with time. With the adaptive control it is therefore necessary to lower the temperature of entering coolant, which places high demands on the dynamic response of the reactor cooling system and the control loop to changes in the coolant temperature. Any delay may be deleterious.

By using the zero-order model for the prediction of the new inlet temperature of coolant, the changes in the properties of the system associated with the transition from the existing level to the new level are disregarded. In the group of reactions in question, the error arising from this is oriented in a hazardous direction and can bring about an uncontrolled temperature rise, similarly as the control loop lag. For reactions in the second group, on the other hand, the error in the prediction contributes to safety.

Demands Placed on the Accuracy of the Coolant Inlet
Temperature Control

One of the problems of the method under discussion consists in the high sensitivity of the pseudostationary temperature to changes in the inlet temperature of coolant in the region where the safety coefficient approaches unity. A compromise has to be made for the control. The reactor efficiency is approximately proportional to the $(T_{ps} - T_{ci})$ temperature difference. As this difference approaches the $(T_{ps} - T_{ci})_{max}$ value, however, the tolerable error in the new inlet temperature setting decreases. The demands put on the temperature control accuracy are clear from Fig. 5. The
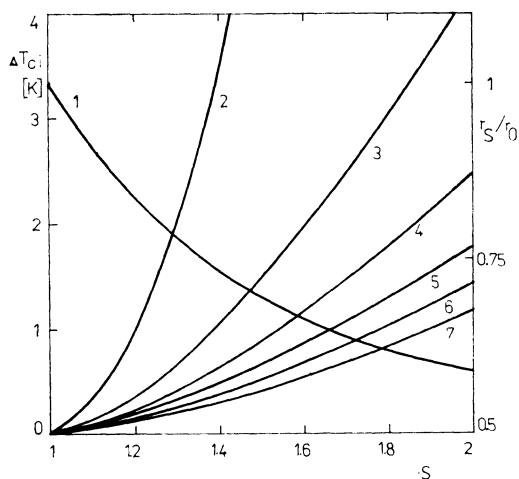

FIG. 5

Relative decrease in the reactor efficiency r_S/r_O (curve *1*) and permitted error in the inlet temperature estimate in dependence on the safety coefficient for the values of the E/RT_{ci}^2 parameter of 0·014 *2*, 0·047 *3*, 0·078 *4*, 0·108 *5*, 0·139 *6*, 0·168 *7*

adverse consequences of the high parametric sensitivity of the temperature maximum to the temperature of entering coolant are illustrated by the experimental results shown in Fig. 6. Clearly, the overheating of the reaction mixture with respect to coolant varies considerably during the experiment, and its accurate control is difficult.

Demands Placed on the Dynamic Properties of the Cooling System

Two components must be included in the cooling system, *viz.* the cooling jacket or coil, the accumulation in which introduces a temperature control lag, and the entire equipment for the implementation of the jump changes in the inlet temperature of coolant, including the control loop. For reactions with dimininishing hazard the cooling system lag is not dangerous, it lowers, however, the reactor efficiency because the time of transition from a temperature to another is thus extended. An example of the effect of inertia of the cooler on the course of the process is shown in Fig. 7.

The heat exchanger control loop for controlling the entering coolant temperature must be adjusted to prevent overcontrol during the transfer from one temperature to another. A transient temperature increase can be hazardous. In case that the
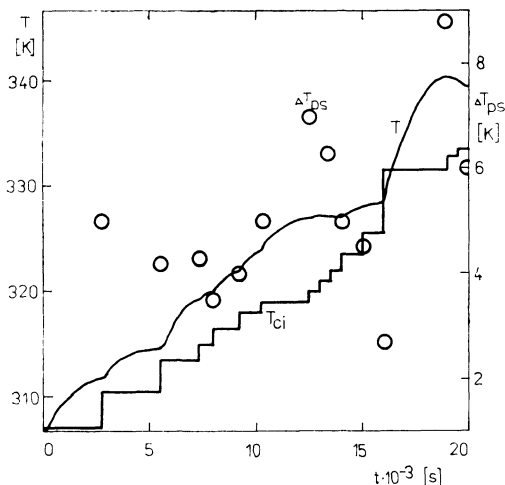

FIG. 6

Illustration of the inaccuracy in the reaction mixture overheating control. Dependence of the entering coolant temperature T_{ci}, reaction mixture temperature T and overheating in pseudostationary states T_{ps} on time
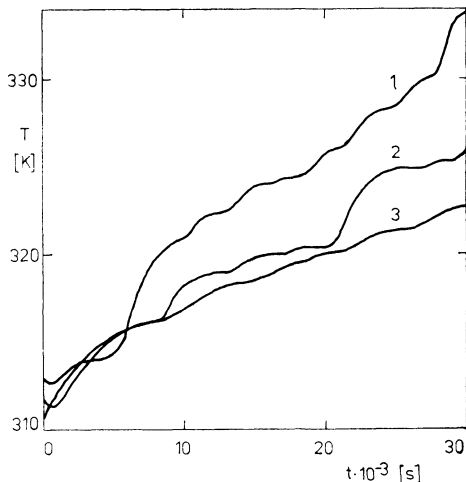
FIG. 7

Effect of cooling system inertia on the non-isothermal temperature control. Time constant of cooler (s): *1* 40, *2* 80, *3* 160

changes in the inlet temperature of coolant are accomplished by mixing the entering flow with the coolant leaving the system, any feedback between the inlet temperature of coolant and the temperature inside the reactor must be prevented. Hence, a perfect stabilization of the inlet temperature of coolant is imperative.

Reactor Efficiency

The reactor efficiency depends on the chosen safety coefficient value. Ideally, a proportionality relation should apply, in reality, however, the efficiency is lower than as corresponds to the safety coefficient value. Since a zero-order model was employed for the prediction of the new inlet temperature of heat carrier, the actual pseudo-stationary temperature differences $(T_{ps} - T_{ci})$ are lower than the preselected values. This is due to the fact that the degree of conversion increases during the transition from the $T_{ci,n}$ level to the $T_{ci,n+1}$ level. This change lowers the reaction rate and is disregarded in the prediction. Thus the zero-order model makes for a safety reserve, and so safety coefficient values as high as unity can be chosen without failure. Examples of the course of temperatures and true safety coefficients are given in Fig. 8.
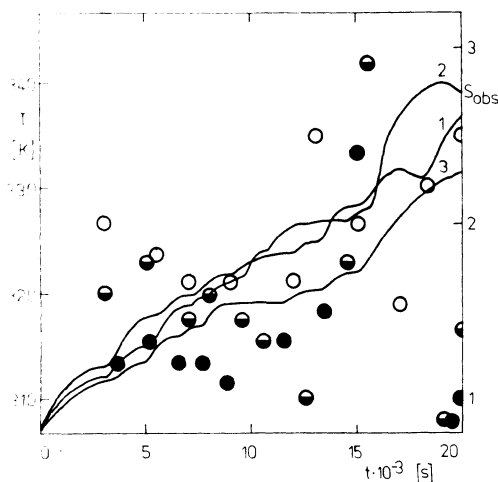

FIG. 8

Course of the reaction mixture temperature and the true safety coefficient value in the nonisothermal control, for the values of the safety coefficient S: 1 1 (O), 2 1·25 (◉), 3 (1·67 (●)
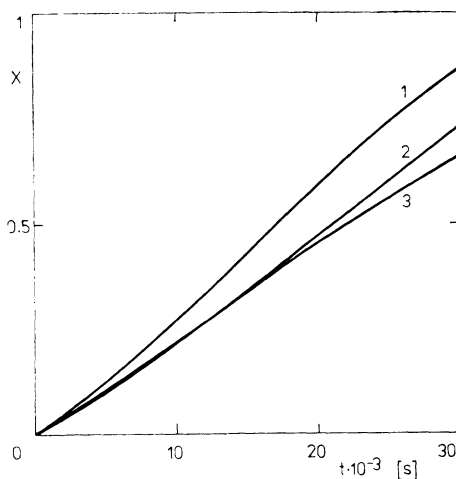
FIG. 9

Effect of the cooling system inertia on the reactor efficiency. Time constant of cooler (s): 1 40, 2 80, 3 160

The changes in the degree of conversion during the transition from a level $T_{ci,n}$ to a level $T_{ci,n+1}$ are also affected by the inertia of the cooling system; with a higher inertia the transition takes a longer time, and consequently, the reactor efficiency is lower. An example of the effect of the cooling system inertia on the reactor efficiency is given in Fig. 9. The high sensitivity of the reaction mixture temperature to the temperature of entering coolant has a considerable effect on the course of the process. This sensitivity makes the effect of noise more marked and so a precise control of the safety coefficient is difficult and differences in the efficiency for different required values of this coefficient are not substantial.

Comparison of Efficiency for the Various Methods of Control

The efficiency of the reactor was compared for the control in stable states, for the pseudoisothermal control, and for the control in unstable pseudostationary states. The way of control in unstable states has been described previously[3-5]; it is only applicable to reactors with a low inertia of the cooling system. In unstable states the temperature is controlled by feedback employing the coolant flow rate as the action parameter; the temperature of entering coolant is constant.
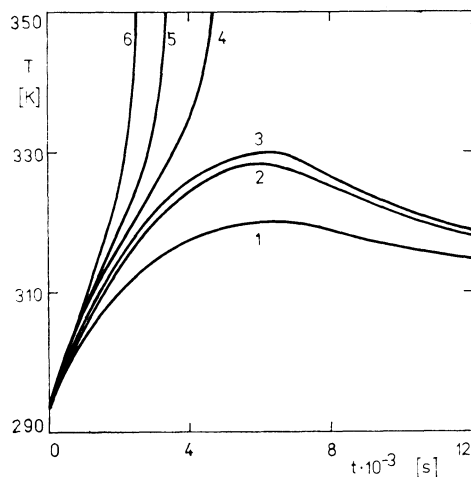

FIG. 10

Examples of the reaction mixture temperature course for the pseudoisothermal control. Temperature of entering coolant (K): *1* 313, *2* 315, *3* 316, *4* 317, *5* 318, *6* 323
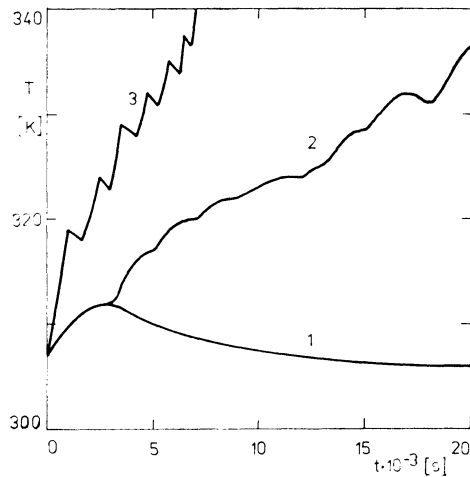
FIG. 11

Comparison of the reaction mixture temperature course for the three control methods treated. *1* Pseudoisothermal control, *2* control in stable states, *3* control in unstable states

The comparison of the efficiency has no absolute validity, the differences being dependent on the reaction order and on the lowest attainable temperature of coolant. With the isothermal control the efficiency depends on the coolant temperature chosen. The temperature course, for various temperatures of coolant, is shown in Fig. 10. The results bear out the well-known fact that in the critical overheating range the temperature course is very sensitive to changes in the coolant temperature. The temperature course for the three ways of control is depicted in Fig. 11 demonstrating that the efficiency ratio, at a degree of conversion of 0·9, can be characterized as follows:

pseudoisothermal control 1
control in stable states 2
control in unstable states 5

The differences in efficiency increase with increasing degree of conversion.

CONCLUSIONS

The results indicate that by applying the nonisothermal method of control of performance of batch reactors, the cooling capacity of the reactor can be exploited to a greater extent whereupon its efficiency is increased. A substantial efficiency increase can be achieved by making use of the control in unstable pseudostationary states. This increase only depends on the lowest attainable temperature of coolant and on the ultimate degree of conversion. The control in unstable states is thus to be preferred if the dynamic properties of the cooling system permit it. The nonisothermal control in stable states is considerably less efficient and its use is justified only in cases where the cooling system possesses a high inertia. With this way of control, the increase in efficiency also depends on the order of the reaction.

LIST OF SYMBOLS

E activation energy $(J\ mol^{-1})$
k_c coefficient of cooling (s^{-1})
R universal gas constant $(J\ mol^{-1}\ K^{-1})$
r_h heat generation rate $(K\ s^{-1})$
S safety coefficient
T temperature (K)
t time (s)

Subscripts

ci coolant inlet
n temperature level number
ps pseudostationary state

REFERENCES

1. Rippin D. W. T.: Proc.-CHEMCOMP 1982; Chem. Process Anal. Des. Using Comput. 1982 43—66 (Eng.).
2. Rippin D. W. T.: Comput. Chem. Eng. *1983*, 7(3), 137—156 (Eng.).
3. Horák J., Jiráček F., Ježová L.: This Journal *47*, 251 (1982).
4. Jiráček F., Horák J.: This Journal *48*, 449 (1983).
5. Jiráček F., Horák J.: This Journal *47*, 454 (1982).
6. Jiráček F., Horák J.: This Journal *48*, 2473 (1983).
7. Horák J., Jiráček F., Ježová L.: This Journal *48*, 2627 (1983).
8. Horák J., Jiráček F., Ježová L.: This Journal *47*, 446 (1982).
9. Mukesh D., Cooper A. R.: Ind. Eng. Chem. Fundam. *22*, 145 (1983).

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