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Influence of reactor temperature conditions on the recycle flow rate

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Objectives. *The problem of optimizing chemical flow sheets according to energy costs associated with recycling flows is at present quite relevant. The current article investigates the influence of temperature conditions on the recycle flow rate, securing the specified conversion of the recycled flow sheet "reactor – separation unit."*

Methods. *The study's main method is the mathematical simulation of a recycled flow sheet based on material balance and chemical kinetics equations. This model assumes that the separation unit can form the recycle and outlet flows of any specified compositions.*

Results. *The mathematical model recycle flows provides the full reagent conversion of recycled flow sheet depends on the reactor type and the temperature conditions in it. It was established that the dependence of the recycle flow rate on the reactor temperature for endothermic reactions has monotonously decreasing shape. The most interesting are exothermic reactions for which the dependence of the recycle flow rate on the reactor temperature curve has a minimum. It is proved that the "reactor – separation unit" system with the plug flow reactor has lower optimal recycle flow rate than the recycled system with the continuous stirred tank reactor. For the adiabatic reactor the dependence of total conversion recycle flow rate on the inlet reactor temperature was investigated. It has been proven that the optimal recycle flow rate is equal to the minimum recycle flow rate for total conversion in the "reactor – separation unit" system.*

Conclusions. *It has been established that isothermal operation conditions are the best in terms of the recycle flow rate, securing the specified conversion for the system.*

Keywords: *recycled systems, reactor temperature conditions, recycle flows, conversion on system.*

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Влияние температурного режима реактора на величину рециркулирующего потока

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Цели. *Исследование влияние температурного режима в реакторе на величину рецикла, обеспечивающего заданную конверсию в рециркуляционной системе «реактор – блок разделения».*
Методы. *Математическое моделирование на основе уравнений материального баланса и химической кинетики. Предполагается, что блок разделения может создавать рецикл и выходной поток любого заданного состава.*
Результаты. *В вычислительном эксперименте определены величины рециклов, обеспечивающие 100%-ную конверсию в системе в зависимости от типа реактора и температурного режима в нем. Было установлено, что для эндотермических реакций зависимость величины рецикла от температуры имеет монотонно убывающий характер. Наибольший интерес представляет случай экзотермических реакций, для которых зависимость рецикла от температуры имеет вид кривой с минимумом. Показано, что для случая реактора идеального вытеснения оптимальный рециркулирующий поток меньше, чем для случая реактора идеального смешения. Для случая адиабатического реактора исследована зависимость рецикла, обеспечивающего 100%-ную конверсию в системе от температуры на входе в реактор. Установлено, что оптимальной является некоторая минимальная температура, ниже которой 100%-ная конверсия не может быть достигнута.*
Заключение. *Изотермический режим в реакторе идеального вытеснения является наилучшим с точки зрения величины рецикла, обеспечивающей заданную конверсию в системе «реактор – блок разделения».*

Ключевые слова: *рециркуляционные системы, температурный режим реактора, рецикловые потоки, конверсия в системе.*

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Introduction

In the vast majority of industrial chemical flow sheets (CFS) there are recirculating flows, the presence of which in some cases allows one to achieve high values of conversion and selectivity in the system [1–3]. On the other hand, the values of recirculating flows directly affect the energy costs of CFS associated with pumping flows and with a change in the flow aggregation state [4, 5]. The task of optimizing the CFS according to energy costs is relevant. At the pre-design development stage, it can be reduced to the problem of optimizing the CFS according to the recirculating flow value, which is necessary to achieve a given conversion rate in the system.

The present work is devoted to the nature of the recycle value relationship in the "reactor – separation unit" system with temperature conditions in various types of reactors for the simplest reversible reaction A⇔B. The system works in a stationary mode.

Mathematical model of a recycled system

The structure of the "reactor – separation unit" recycled system is shown in Fig. 1.

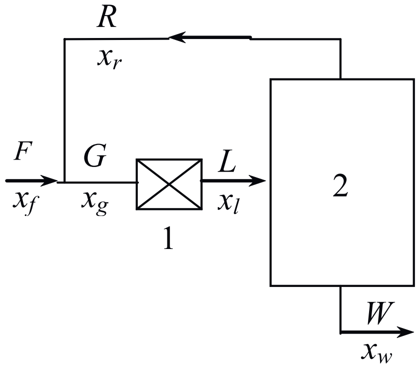

Fig. 1. "Reactor – separation unit" recycled system: 1 – chemical reactor; 2 – reaction separation unit (*See further down in the text for a list of symbols*).

To form a mathematical model of the system, we write material balances according to their elements (flow designations are shown in Fig. 1). We will use molar quantities, so flows will be measured in kmol/h, and concentrations in molar fractions.

Material balance for the mixer:

$$G = F + R \tag{1}$$

$$Gx_g = Fx_f + Rx_r \tag{2}$$

for the separation unit:

$$L = W + R \tag{3}$$

$$Lx_l = Wx_W + Rx_r \tag{4}$$

for the reactor:

$$G = L \tag{5}$$

$$Lx_l = Gx_g - P \tag{6}$$

and for the system:

$$Fx_f - Wx_w = P \tag{8}$$

$$F = W \tag{9}$$

In equations (6) and (8), *P* is the reactor productivity characterizing the amount of reagent converted into a product per unit time, kmol/h.

For further analysis of the system, the assumption is made that the separation unit is capable of creating recycle *R* and product *W* flows of any given composition, even up to pure components. Pure reagent A ($x_f = 1$) in the amount of *F* (kmol/h) is supplied to the system input. The recycle also consists of a pure reagent A ($x_r = 1$). The chemical reaction rate *w* obeys the power law in the form:

$$w = k^+ x - k^-(1 - x)\,, \tag{10}$$

where *x* is the mole fraction of reagent A; $w = k^+,\ k^-$ are the rate constants of the forward and reverse reactions, respectively, kmol/(m^3·h).

Under the condition of 100% conversion in the system, reagent A is absent in the product flow of the system, then $x_w = 0$. In this case, from (8) it follows

$$P = F\,, \tag{11}$$

that is, the reactor productivity corresponds to the amount of reagent supplied to the system input.

Recirculation system with a continuous ideally stirred-tank reactor

For a continuous ideally stirred-tank reactor (CISTR), in which the temperature and composition are identical throughout the entire volume, the expression for productivity is the multiplication of the volume by the reactor and the reaction rate, and with (10) in mind has the form:

$$P = Vw = V(k^+ + k^-)x_l - Vk^-\,. \tag{12}$$

Applying condition (11) to (12), we obtain the expression for the continuous ideally stirred-tank reactor’s composition, which is realized at 100% conversion in the system:

$$x_l = x_{100} = \frac{F + Vk^-}{V(k^+ + k^-)}\,. \tag{13}$$

The material balance of the separation unit, taking into account (9), is written as:

$$L = F + R \tag{14}$$

$$Lx_l = Fx_W + Rx_r \tag{15}$$

Substituting expressions (14) and (13) in (15), and also assuming the assumption $x_r = 1$, we obtain:

$$(F + R_{100})\frac{F + Vk^-}{V(k^+ + k^-)} = R_{100}\,. \tag{16}$$

Let us express from (16) the value of the recycle corresponding to 100% conversion:

$$R_{100} = \frac{F(F + Vk^-)}{Vk^+ - F}\,. \tag{17}$$

As can be seen, the recycle value corresponding to 100% conversion in the system is determined by the amount of reagent *F* in the system inlet, the reactor volume, and the rate constants of the forward and reverse reactions, which, in turn, depend on the temperature in accordance with the Arrhenius equation:

$$k^+ = k_0^+ e^{-\frac{E^+}{R_g T}}, k^- = k_0^- e^{-\frac{E^-}{R_g T}}\,, \tag{18}$$

where k_0^+, k_0^- are pre-exponential factors for the rate constants of the forward and reverse reactions, respectively, h^{-1}; E^+, E^- are activation energies for forward and reverse reactions, respectively, J/mol; R_g = 8.314 J/(mol·K) is the universal gas constant.

Substituting (18) into (17), we obtain an expression showing the temperature dependence of R_{100}:

$$R_{100} = \frac{F^2 + FVk_0^- e^{-\frac{E^-}{R_g T}}}{Vk_0^+ e^{-\frac{E^+}{R_g T}} - F}. \tag{19}$$

From (19) it follows that the positive recycle values R_{100} will be obtained with non-negative values of the denominator. So, for fixed values of the reactor volume, power flow, and the parameters of the Arrhenius equation, there is a minimum temperature in the reactor at which the desired reactor productivity and conversion in the system can be achieved:

$$T \ge T_{\min} = \frac{E^+}{R_g}\left[Ln\left(\frac{Vk_0^+}{F}\right)\right]^{-1}. \tag{20}$$

It is also seen from (19) that $R_{100} \to \infty$ at $T \to T_{\min}$. Therefore, the minimum temperature determined by (20) is the vertical asymptote of dependence (19).

During an unlimited increase in temperature, the recycle value R_{100} tends to the limit value:

$$R_{100}^{\infty} = \lim_{T\to\infty} R_{100} = \frac{F^2 + FVk_0^-}{Vk_0^+ - F}. \tag{21}$$

To identify the nature of the dependence $R_{100}(T)$ (19), we write the expressions for the derivative taking into account (18):

$$\frac{dR_{100}}{dT} = -\frac{(E^+ + E^-)F^2V(k^+ + k^-) + (E^+ - E^-)F^2V^2k^+k^-}{R_gT^2(Vk^+ - F)^2}. \tag{22}$$

It can be seen from (22), that for $E^+ \ge E^-$ the derivative is negative at any temperature; consequently, the dependence $R_{100}(T)$ has a monotonously decreasing character, shown in Fig. 2, curve a. In the case $E^+ < E^-$ the derivative can be both positive and negative, and then extrema can be on the dependence $R_{100}(T)$.

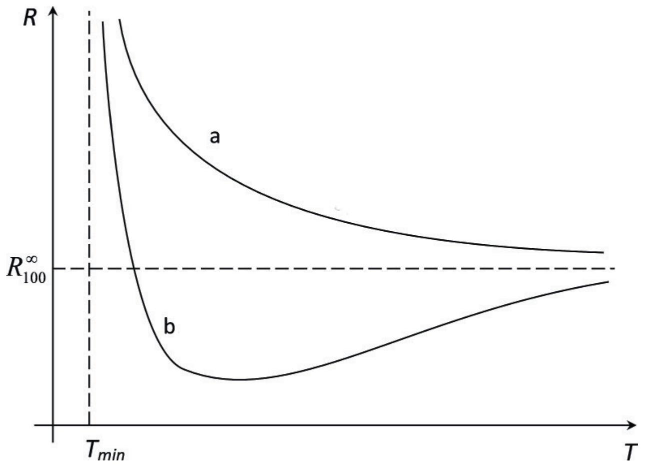

Fig. 2. Qualitative view of the temperature dependence of recycle value R_{100} in the continuous ideally stirred-tank reactor. Ratio of activation energies of forward and reverse reactions:
a) $E^+ \ge E^-$; b) $E^+ < E^-$.

From published data [6] it is known that in the case of exothermic reactions (and this is just the case $E^+ < E^-$) the dependence of the reactor productivity on temperature, at fixed values of the reactor load and the reactor volume, has the form of a curve with a maximum, in other words, there is some optimal temperature corresponding to maximum performance. The presence of a maximum is explained by the fact that, in the case of $E^+ < E^-$ as the temperature increases, the rate constant k^- increases faster than the rate constant k^+. This leads to a greater increase in the rate of reverse reaction and, as a consequence, to a decrease in reactor productivity. On the other hand, at a fixed temperature, the productivity of the reactor is directly related to the reactor load G, which in our case, in accordance with (1), consists of power and recycle flows. So, it can be expected that at temperatures other than optimal, a higher recycle value will be required to achieve a given productivity value than at an optimum temperature. It follows that for the case of $E^+ < E^-$ the dependence curve $R_{100}(T)$ will have a minimum, as shown in Fig. 2, curve b.

Recirculation system in an ideal plug-flow reactor

Since the composition of the reaction mixture and, consequently, the reaction rate in an ideal plug-flow reactor (IPFR) are continuously changing along the length of the reactor, the expression for the productivity value has the form of:

$$P = \int_0^V w(u)du\,, \qquad (23)$$

wher u is the current volume of the reactor, V is the total reactor volume.

At this stage, we are taking into consider the case of an isothermal reactor, in which the temperature is the same throughout the volume. We obtain the form of the speed dependence on the current reactor volume, which is a part of (23). From the material balance for an infinitely small element of volume it follows that:

$$-(F+R)dx - wdu = 0\,. \qquad (24)$$

We express from (10) the mole fraction x:

$$x = \frac{w+k^-}{k^+ + k^-}\,. \qquad (25)$$

Differentiating the left and right sides of (25), we obtain:

$$dx = \frac{1}{k^+ + k^-}dw\,. \qquad (26)$$

Substituting (26) into (24), we obtain the differential equation with separable variables:

$$\frac{dw}{du} + \frac{k^+ + k^-}{F+R}w = 0\,,$$

whose solution with the initial condition of $w\ (u = 0) = w_0$ will have the form:

$$w = w_0 e^{-u\frac{k^+ + k^-}{F+R}}\,. \qquad (27)$$

From (10) it follows that under the assumptions made on the feed and recycling, consisting of a pure reagent, the initial velocity will be equal to the rate constant of the forward reaction:

$$w_0 = k^+\,. \qquad (28)$$

We substitute (27) and (28) into (23), after integration we obtain:

$$P = \frac{k^+(R+F)}{k^+ + k^-}\left[1 - e^{-\frac{V(k^+ + k^-)}{R+F}}\right]. \qquad (29)$$

Combining (29) with the condition of 100% conversion (11), we obtain the equation for the recycle value R_{100}:

$$\frac{k^+(R_{100}+F)}{k^+ + k^-}\left[1 - e^{-\frac{V(k^+ + k^-)}{R_{100}+F}}\right] - F = 0\,. \qquad (30)$$

From the form of equation (30) it follows that its solution with respect to the recycle value R_{100} is possible only via numerical methods.

Figure 3 shows the results of solution (19) and (30) with the following initial data: the system power flow is F = 100 kmol/h; the reactor volume is V = 1 m^3; the Arrhenius equation parameters for the forward reaction rate constant are $k_0^+ = 4.75 \cdot 10^{14}$ kmol/(m^3·h), E^+ = 78 000 J/mol, for the reverse reaction k_0^- = $2.37 \cdot 10^{18}$ kmol/(m^3·h), and E^- = 107 000 J/mol.

Figure 3 shows that in the temperature range under consideration, the dependences of the recycle value on temperature for both types of reactors have a characteristic minimum. It should also be noted that the minimum R_{100} recycle value for the case of an ideal plug flow reactor is less (curve a) than for the case of a continuous ideally stirred-tank reactor (curve b). This is due to the fact that for the same volume and load values, an ideal plug flow reactor is characterized by higher productivity; therefore, to achieve a given productivity, it requires a lower load, and, therefore, a recycle.

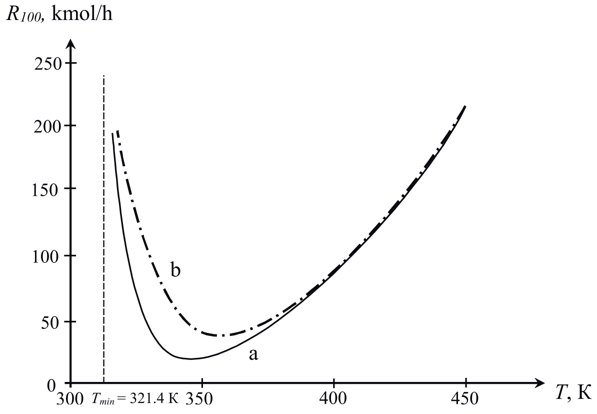

Fig. 3. Temperature dependence of the recycle value R_{100} on the recirculation system with isothermal reactors of various types:
a) an ideal plug-flow reactor;
b) a continuous ideally stirred-tank reactor.

Recirculation system in an adiabatic plug-flow reactor (under ideal conditions)

In the case of an adiabatic plug-flow reactor, the temperature along the length of the reactor changes in accordance with the thermal effect of the reaction, and therefore, the equation (30) cannot be used to find the recycle value. For this case, the mathematical model includes non-linear differential equations for material and heat balance with respect to composition and temperature, which cannot be solved analytically. Therefore, the adiabatic reactor with recycle was simulated in the Aspen Plus software package in accordance with the scheme shown in Fig. 4.

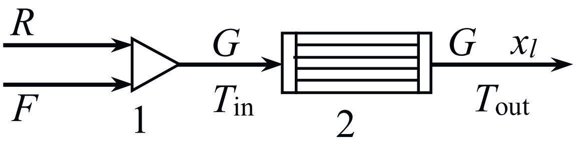

Fig. 4. The scheme of an adiabatic plug-flow reactor: 1 – mixer; 2 – reactor.

The reactor was modeled as a tubular one with a tube diameter of 0.05 m and a tube length of 3 m. The power value *F*, kinetic parameters, and the reactor volume were set to be the same as in the previous calculation for an isothermal reactor. The change in the reaction's enthalpy is $\Delta H = -30\ 000$ J/mol. In the course of calculations, at various values of the temperature of the incoming flow T_{in}, the value of the recycle *R* was determined in which the condition (31) was satisfied:

$$G(1-x_l)=F\ , \tag{31}$$

which, in turn, corresponds to the condition of 100% conversion in the system (11). The calculation results are presented in Fig. 5.

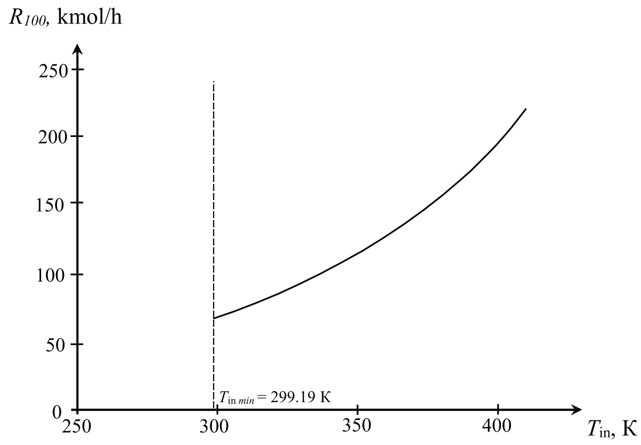

Fig. 5. Temperature dependence of the recycle value R_{100} for a recirculation system with an adiabatic plug-flow reactor.

Figure 5 shows that the optimal recycle value R_{100} for the temperature at the reactor's inlet corresponds to a minimum temperature $T_{in\ min}$, below which the reactor's productivity corresponding to the condition in (31) is not achieved. Therefore, at $T < T_{in}$ min the achieving of 100% conversion is impossible in a system with an adiabatic plug-flow reactor of a given volume. Figure 6 shows the temperature and reagent concentration profiles along the length of the reactor with optimal recycling.

Figure 6 shows that a change in temperature and composition occurs along the entire length of the reactor, and the rate of change of temperature is consistent with the rate of change in the composition. The result obtained indicates the effective work of the entire reactor volume. For comparison, Figure 7 shows the temperature and composition profiles at T_{in} = 310 K and R_{100} = 76.6 kmol/h.

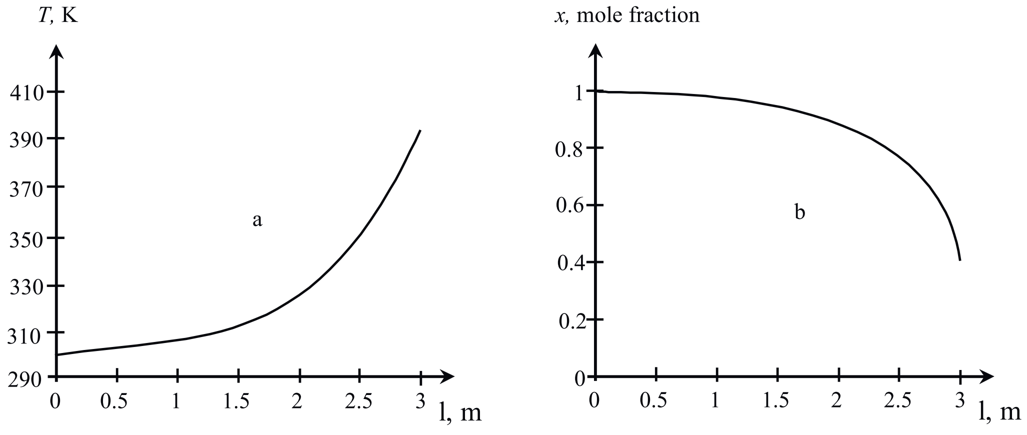

Fig. 6. Temperature (a) and composition (b) profiles along the length of the reactor at an optimal recycle value R_{100} = 68.4 kmol/h and $T_{in} = T_{in\ min}$ = 299.19 K.

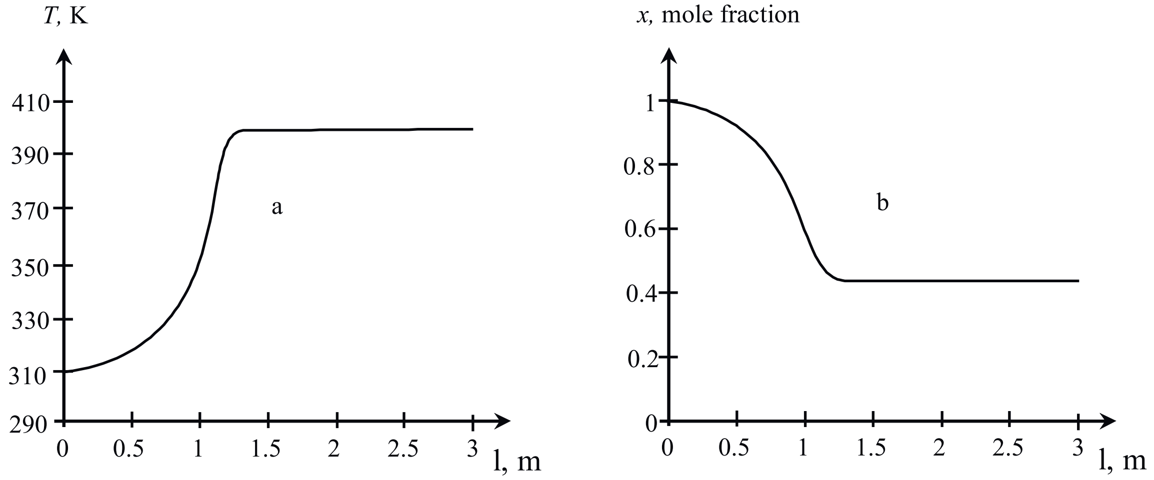

Fig. 7. Temperature (a) and composition (b) profiles along the length of the reactor with a recycle value R_{100} = 76.6 kmol/h and T_{in} = 310 K.

It can be seen from Fig. 7 that, at a reactor length of $l > 1.3$ m, the temperature and composition cease to change. This is due to the fact that the composition in the reactor becomes almost equilibrium and the rate of chemical conversion is close to zero. Therefore, this part of the length of the reactor does not consume the reagent and does not produce the product, in other words, it does not operate. Thus, with an increase in the temperature of the inlet flow, the desired reactor productivity can be achieved with a smaller reactor volume, but this requires a large recycle value. From the result obtained, it can be concluded that the optimal value of the recycle necessary to achieve a given conversion corresponds to the most efficient reactor work. It should be noted that this conclusion is valid under the assumption made on an idealized separation unit forming the recycle of a certain composition.

A comparison of the results presented in Figs. 3 and 5 shows that for the isothermal plug-flow reactor (under ideal conditions), the optimal value of R_{100} is less than for the adiabatic reactor (under ideal conditions). Therefore, in order to achieve the optimal recycle value corresponding to the given conversion in the system, it is necessary to maintain the isothermal mode in the reactor. It should be noted that for reactions with a significant thermal effect, it is much more difficult to achieve an isothermal mode in the reactor than an adiabatic one. In addition, with a lower recycle value for an isothermal reactor, there will be additional costs for the refrigerant supplied to the annulus of the reactor to remove the heat of the reaction.

Conclusions

So, according to a reversible reaction A⇔B with a fixed recycle composition, a correlation between the recycle value securing the given conversion in the "reactor – separation unit" system and the temperature in the reactor has been revealed. For an exothermic reaction, the possibility of the existence of an optimum temperature corresponding to the minimum value of the recycle is shown.

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List of symbols used in this report: A, B – reaction mixture components; E^+, E^- – activation energy of forward and reverse reactions, respectively, J/mol; F – power flow of the "reactor – separation unit" system, kmol/h; G – flow entering the reactor, kmol/h; k^+, k^- – rate constant of forward and reverse reactions, respectively, kmol/(m^3·h); k_0^+, k_0^- – pre-exponential factor in the Arrhenius equation for the forward and reverse reactions, respectively, kmol/(m^3·h); l – reactor length, m; L – flow, leaving the reactor, kmol/h; P – reactor productivity, kmol/h; R – recycle flow, kmol/h; R_{100} – recycle flow value corresponding to 100% conversion, kmol/h; R_{100}^{∞} – recycle limit corresponding to infinite temperature, kmol/h; R_g – universal gas constant, 8.314 J/(mol·K); T – temperature, K; T_{min} – the minimum temperature in the reactor at which it is possible to achieve 100% conversion in the "reactor – separation unit" system, K; T_{in} – adiabatic reactor inlet temperature, K; T_{out} – adiabatic reactor outlet temperature , K; $T_{in\ min}$ – minimum adiabatic reactor inlet temperature, at which 100% conversion in the "reactor – separation unit" system is possible, K; u – current reactor volume, integration variable (23), m^3; V – total reactor volume, m^3; W – the flow leaving the "reactor – separation unit" system, kmol/h; x – molar fraction of reagent A in the reaction mass; x_f – molar fraction of reagent A in the feed flow of the "reactor – separation unit" system; x_g – molar fraction of reagent A in the flow entering the reactor; x_l – molar fraction of reagent A in the flow leaving the reactor; x_r – molar fraction of reagent A in the recycle flow; x_w – molar fraction of reagent A in the flow leaving the "reactor – separation unit" system.

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