DYNAMIC BEHAVIOR OF RECYCLE SYSTEM: REACTOR – DISTILLATION COLUMN

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ABSTRACT

A recycle system consisting of a reactor and distillation column is considered. Two order reaction A+B $\rightarrow$ C takes place in liquid phase continuous stirred tank reactor (CSTR). Distillate is used as recycle, but final product C is taken from a bottom of the column.

Analyses of possible operating modes of system Reactor- Distillation Column are examined. It has been shown that an existence of continuum of steady states is possible in the reactor for the operating mode with a full use of feed reactants A and B. An algorithm of a transfer of the system for the operating mode with full utilization of feed and intermediate reactants is given.

INTRODUCTION

A construction of the technological schemes with a recycle of non-reacting feed and intermediate reactants of a reaction is an effective way of solving a problem of their complete utilization. A block scheme of the system is presented on a figure 1.
However a feedback causes multiple appearance of the steady states in a reactor and instability of the system.

Therefore, it is beneficial to consider dynamic behavior of the system Reactor - Distillation Column. The dynamic behavior of such systems and their control has been examined in the articles [1-5]. In article [2] authors proposed a new approach for the analyses of the recycle system Reactor – Distillation Column. It is supposed that a separating capacity of distillation column is infinite. Then a mathematical model of the recycle system is formed as a system of differential equations with a variable structure. The right-hand sides of differential equations have a different expression as a dependence on a value of a distillate of the column.

The qualitative properties of this system also exist when the distillation column is characterized by a finite (but high enough) separating capacity.

MATHEMATICAL MODEL OF THE SYSTEM: REACTOR – DISTILLATION COLUMN

Second order reaction A + B $\rightarrow$ C takes place in liquid continuous stirred tank reactor. Separation of final product C of the reaction, from the feed reactants A and B takes place in distillation column.

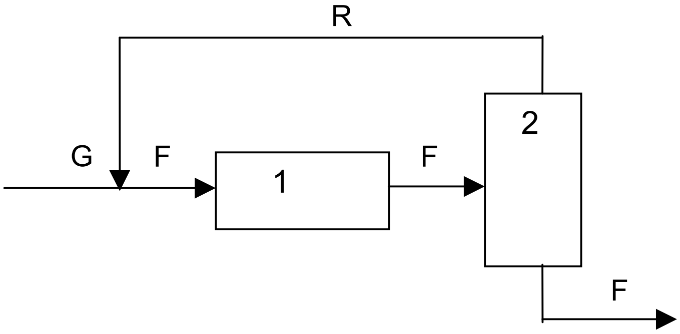

Fig.1. A Block scheme of system Reactor – Distillation Column,
1 – Reactor, 2 – Distillation Column

Suppose that a separating capacity of a distillation column is infinite.
Let the relative fugacities of the components to be in the following relation:

$$\alpha_A > \alpha_B > \alpha_C. \tag{1}$$

Distillate of the column is used as a recycle, but final product C, having the least fugacity, is taken from the bottom of the column.

To simplify analysis, suppose, that inert components are absent in the reactor and reaction rate is defined by an expression

$$r = kx_1x_2. \tag{2}$$

Then the mathematical model of the recycle system Continuous Stirred Tank Reactor - Distillation Column (CSTR-DC) may by written as follows:
CSTR:

$$V\frac{dx_1}{dt} = Gx_1^{(0)} - Vkx_1x_2 - Fx_1 + Rx_1^*, \tag{3}$$

$$V\frac{dx_2}{dt} = Gx_2^{(0)} - Vkx_1x_2 - Fx_2 + Rx_2^*, \tag{4}$$

$$Vc_p\rho\frac{dT}{dt} = Gc_p\rho T^{(0)} - Fc_p\rho T + Rc_p\rho T^* + (-\Delta H)\,kx_1x_2 + U(T_x - T)\,; \tag{5}$$

Distillation Column:

$$x_i^* = \frac{F}{R}x_i \quad i = 1{,}2, \text{ if}, \bar{x} \in D_1 : x_1 + x_2 \le \frac{R}{F}, \tag{6}$$

$$\begin{cases} x_1^* = \dfrac{F}{R}x_1 \\ x_2^* = 1 - \dfrac{F}{R}x_1 \end{cases} , \text{if}, \bar{x} \in D_2 : x_1 < \frac{R}{F} < x_1 + x_2, \tag{7}$$

$$\begin{matrix} x_1^* = 1 \\ x_2^* = 0 \end{matrix} \quad ,\text{if } \bar{x} \in D_3 : x_1 > \frac{R}{F}. \qquad (8)$$

Taking into account, that a dimension of the concentration is mole fractions, the concentration of final product C is found as follows:

$$x_3 = 1 - x_1 - x_2. \qquad (9)$$

Since the separating capacity of Distillation Column is infinite then there are only three operating modes of Distillation Column and only one component may be distributed. The operating modes of Distillation Column are presented on the figure 2.

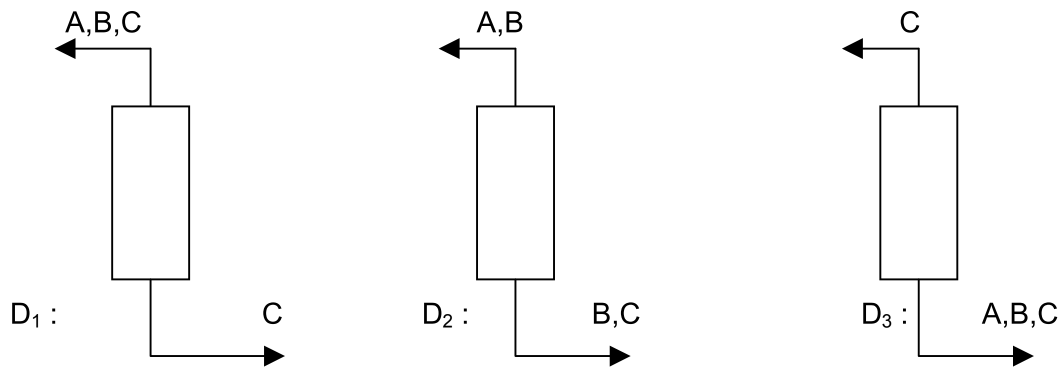

Fig.2. Three operating modes of distillation column

The phase space of the system is divided into three regions D_1, D_2, D_3, which correspond to three operating modes of Distillation Column. Portrait of these regions is presented on the figure 3.

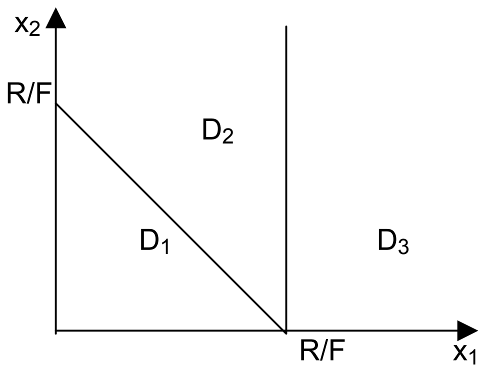

Fig.3. Division of phase space into three regions: D_1, D_2, D_3

The right-hand sides of a system differential equations (3), (4) have different structure in each region D_i, i=1,2,3.

In the region D_1 a component C is distributed: all components are in overhead distillate of the column and only heaviest component C is in the bottom of the column.

In the region D_2 a component B is distributed: the components A and B are in the overhead distillate of the column and the components B and C are in the bottom of the column.

In the region D_3 a component A is distributed: only the lightest component A is in the overhead distillate of column and all components are in the bottom of the column.

SYSTEM MATHEMATICAL MODEL INVESTIGATION

Operating mode with a full use of feed reactants A and B exists in a region D_1. Mathematical model of the Reactor in recycle system in steady state in accordance with formulas (3-6) is written as follows:

$$Gx_{1f} - Vkx_1x_2 = 0, \tag{10}$$
$$Gx_{2f} - Vkx_1x_2 = 0, \tag{11}$$
$$c_p \rho (GT_f - FT + RT^*) + V(- \Delta H)kx_1x_2 + U(T_c - T) = 0. \tag{12}$$

In this operating mode the concentrations of the reactants A and B in the feed must be in stochiometric ratio: $x_{1f} = x_{2f}$ [6].
Then equations (10), (11) are written as:

$$Gx_{1f} - Vkx_1x_2 = 0, \tag{13}$$
$$Gx_{1f} - Vkx_1x_2 = 0. \tag{14}$$

The equations (13) and (14) are identical, then there is only one equation (13) to find the concentrations x_1 and x_2. So, there is continuum (an infinite set) of the solutions of equation system (12) - (14).

The steady value of a temperature is defined by the following formula:

$$T = \frac{1}{Fc_p\rho + U}\left(c_p\rho\left(GT_f + RT^*\right) + UT_C + Gx_{1f}\left(-\Delta H\right)\right). \tag{15}$$

Let $x_{1f} = x_{2f} = 0.5$mol/mol. Then equation (13) is rewritten as follows:

$$x_1 = \frac{G}{2VA_0}\exp\left(\frac{E}{R_gT}\right)\frac{1}{x_2}. \tag{16}$$

The steady value of temperature is defined by formula (15).
In the equation (16) the concentration x_2 may be any value, from the interval $x_{2min}<x_2<x_{2max}$. The limits of this interval are defined from equation (16) and the condition (4):

$$x_{2\,min} = \frac{R}{2F} - \sqrt{\left(\frac{R}{2F}\right)^2 - D}\,, \tag{17}$$

$$x_{2\,max} = \frac{R}{2F} + \sqrt{\left(\frac{R}{2F}\right)^2 - D}\,, \tag{18}$$

where parameter D is defined as

$$D = \frac{G}{2VA}\exp\left(\frac{E}{R_g T}\right). \qquad (19)$$

The same interval of the steady values exists for the concentration x_1:$x_{1min}<x_1<x_{1max}$, where $x_{1max}=x_{2max}$, $x_{1min}=x_{2min}$.

The operating mode with a full use of feed and intermediate reactants exists, if the value of the recycle is greater than minimum value R_{min}. The value of R_{min} is defined if x_1 is equal to x_2 from (4):

$$R_{min} = \frac{2G\sqrt{D}}{1-2\sqrt{D}}. \qquad (20)$$

The length of the interval of the steady values of the concentrations x_1 and x_2 - $\Delta x_i = x_{i\,max} - x_{i\,min}$, i=1,2 is defined as follows:

$$\Delta x_i = 2\sqrt{\left(\frac{R}{2F}\right)^2 - D}\text{, i=1,2.} \qquad (21)$$

It decreases, if the value of the recycle is reduced, and it is zero, if R becomes equal to R_{min}. The steady state is singular in this case.

The concentration of the final product C-x_3 also may be any value from the interval [x_{3min}, x_{3max}]. The concentration x_3 is maximum, if x_1 is equal to x_2:

$$x_{3\,max} = 1 - 2\sqrt{D} \qquad (22)$$

and the concentration x_3 is minimum, if $x_1=x_{1min}$, $x_2=x_{2max}$ and $x_1=x_{1max}$, $x_2=x_{2min}$:

$$x_{3\,min} = 1 - \frac{R}{F} \qquad (23)$$

Since equations (13) and (14) are identical for the operating mode with a full use of feed reactants A and B then the polynomial characteristic for stability analysis will have one root, which is equal to zero. Consequently, the steady states can be at best on the boundary of the region of stability at the state of neutral balance.

In a region D_2 a system exists for operating mode with a full use of a reactant A.

A material balance of the CSTR in this regime in steady state is written as follows:

$$Gx_{1f} - Vkx_1x_2 = 0, \qquad (24)$$
$$Gx_{2f} - Vkx_1x_2 - Fx_2 + R - Fx_1 = 0. \qquad (25)$$

From equations (24), (25) one can obtain following relation:

$$G(x_{1f} - x_{2f}) = R - F(x_1 + x_2). \qquad (26)$$

It is obvious that the steady state does not exist in the region D_2, if the feed reactants A and B are introduced into the system in the stoichiometric ratio. In accordance with condition of the regime existence (7) and equality (26) this regime is only possible to reach, if $x_{2f} > x_{1f}$.

The value of temperature at this regime is defined by formula (15).

In the region D_3 system exists for the operating mode, when only lightest component A is presented in a recycle.

Material balance of the reactor in steady state for the operating mode is written as follows:

$$Gx_{1f} - Vkx_1 x_2 - Fx_1 + R = 0, \quad (27)$$

$$Gx_{2f} - Vkx_1x_2 - Fx_2 = 0. \quad (28)$$

The steady state exists under following condition $x_{1f} > x_{2f}$.
Let's examine dynamic behavior of the system.
The phase trajectories of the system are presented on the figures 4,5.

1. Let an initial point of a calculation to be in the region D_1, ($x_0 \in D_1$). If the feed reactants A and B are introduced into the system in the stoichiometric ratio ($x_{1f} = x_{2f}$) and value of recycle is greater than a minimum value of recycle ($R>R_{min}$), then a representative point of a system goes to one of continuum of steady states. The portrait of phase trajectories is presented on a figure 4a.

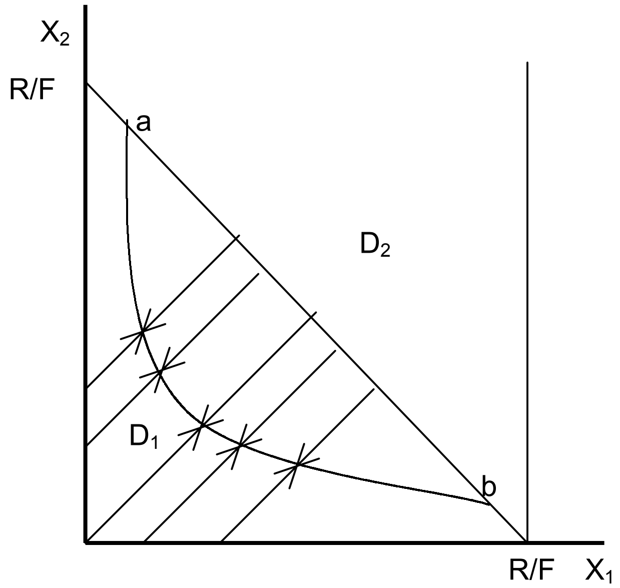

Fig.4a. Portrait of phase trajectories of the system if $x \in D_1$, $x_{1f}=x_{2f}$, $R>R_{min}$ (curve ab is continuum of the steady state)

2. The phase trajectories of the system go to singular asymptotic stability steady state in a region D_3 (d), if a value of a recycle R is less than R_{min}. Portrait of the phase trajectories of the system is presented on a figure 4b.

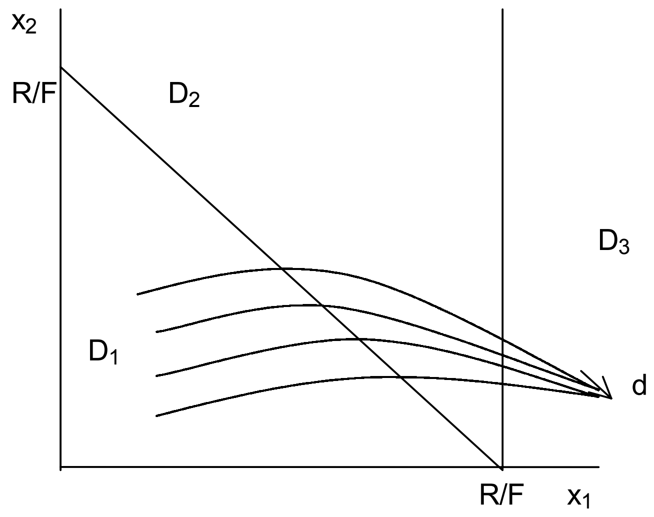

Fig.4b. A portrait of the phase trajectories of the system
if $x \in D_1$ $x_{1f}=x_{2f}$, $R<R_{min}$

3. It is necessary to carry out following algorithm in order to transfer the system from a region D_3 to a region D_1 for the operating mode with full use of feed and intermediate reactants A and B:

a) to fix a value of the recycle R greater than minimum value of the recycle R_{min} and to fix the concentrations of the components A and B in the feed: in the ratio $x_{2f}>x_{1f}$. Then the phase trajectories go to the region D_2 through the region D_1;

b) when the concentrations x_2 and x_1 will be equal, then it is necessary to restore the introduction of the feed reactants A and B in the system in the stoichiometric ratio: $x_{1f} = x_{2f}$ (see a point c on a fig.5). Then the representative point goes to one of continuum of steady states to point e.

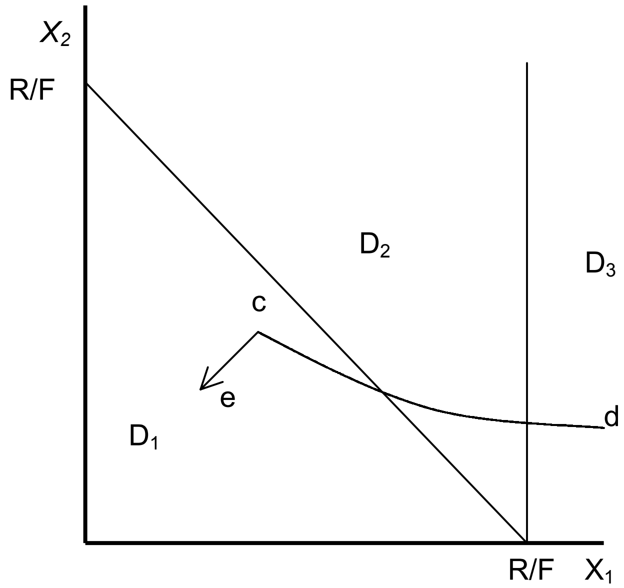

Fig.5 A transfer of the system in the region D_1: from point d to point c, if $R>R_{min}$, $x_{2f}>x_{1f}$ and from point c to point e if $x_{1f}=x_{2f}$

CONCLUSION

The qualitative properties of the system Reactor – Distillation Column also exist if the distillation column is characterized by a finite (but high enough) separating capacity. Continuum steady states are shown as a dependence of the calculated values of the concentrations A and B of initial approximation of the iterative procedure of the calculation of the system Reactor – Distillation Column. If there are the fluctuations of the concentrations of feed reactants A and B in the input of the system, then the concentrations of these reactants in the reactor can change continuously for the operating mode with full utilization of feed reactants A and B into the limits of the possible interval (17), (18). When the concentrations overstep the limits of the interval then the operating mode with a full utilization of feed reactants is failed and non-reacting feed reactants A and B will be present in the bottom of the column.

Therefore it is necessary to carry out an automatic control of the system in order to keep the operating mode with a full utilization of feed reactants A and B. If the operating mode with a full utilization of feed reactants A and B is failed then in order to restore this operating mode it is necessary to carry out a special given algorithm.

NOMENCLATURE

A_0 – pre-exponential factor;
C_p-specific heat capacity, cal/(g K);
D_i – the i-th region of phase space of the system;
E – energy of activation, cal/mol;
F - flow rate of a mixture feed into the reactor, m^3/h;
G - flow rate of a mixture feed into the system, m^3/h;

ΔH -heat effect of the reaction, cal/mol;
k - rate constant of the reaction;
R-flow rate of the recycled mixture, m^3/h;
R_g – gas constant;
r - rate of a reaction ;
T- mixture temperature, K;
T_c-coolant temperature, K;
U - heat transfer coefficient, $W/(m^2 K)$;
V - reactor volume, m^3;
x - concentration vector;
x_i - concentration of the i-th component, mol fraction;
α – relative fugacity of component;
p - density of a mixture.

Subscripts and superscripts.
i -reactant number;
min - minimum value;
* - recycle.

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- distillation column;
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