PHENOMENON OF THE EXISTENCE OF CONTINUUM OF STEADY STATES IN THE RECYCLE SYSTEM: REACTOR - SEPARATING UNIT.

Anatolij I. Boyarinov*
Mendelleev Chemical University of Russia, Moscow, Russia

Stanislav I. Duev+
+*Kazan State Technological University, Kazan, Russia*

Abstract

A reactor-separator recycle system is studied. The unreacted feed and intermediate reactants leaving the reactor are separated from the end products of the reaction and are recycled. A generalized condition that can be used to judge the existence of a family of steady states for the operational mode which complete utilization of feed and intermediate reactants is proposed. A plug-flow reactor in which the second-order reaction A+B—2C proceed with complete utilization of the feed reactants A and B is shown to be characterized by a family of steady states in which the concentrations of reactants in the reactor can take an infinite of steady-state values lying within a bounded region (interval).

Keywords

Recycle system: Reactor – Separating unit, Multiplicity of steady states, Stability.

Introduction.

An efficient way to solve the problem of minimizing chemical industrial wastes is recycling unreacted feed materials. For this purpose the reactor-separator recycle system can be used (Fig. 1) However a feedback causes an appearance of multiplicity of the steady states in the reactor. A problem of the steady states multiplicity in chemical reactor has been examined for a long time by van Herden (1953), Frank-Kamenetski (1955) and other. Also there are numerous articles in which the problem of the steady states multiplicity and stability of the reactor with recycle has been analysed (Lass and Amundsen(1967), Reily and Schmitz (1966), Perlmutter (1972), Gawdzic, Berezowski (1987) and other). The existence of the finite set of steady states (odd number) in the reactor was indicated in all these works. But an appearance of qualitatively new properties in the reactor taking place in the recycle system: reactor – separating unit is possible. It is shown as an existence of continuum (infinite set) steady states in the reactor (Boyarinov, Duev (1980, 1985, 1988)). Continuum of the steady states is possible to be only in recycle system for the operational mode with a complete use of feed and intermediate reactants.

Conditions for the existence for the operational mode with a complete utilization of feed and intermediate reactants.

For the reactor-separator recycle system, of interest is the operatoral mode in which the complete utilization of feed and intermediate reactants is achieved. This operational mode is possible only when the unreacted feed and intormediate components are separated from the final products and are entirely returned to the reactor.

We will consider a reactor with l feed and intermediate reactants. Assuming that the separator efficiency is sufficient for the whole mass of unreacted feed and intermediate components to be returned to the reactor, we can write the expression

$$Fx_i = Rx_i,\ i=\overline{1,l}. \qquad (1)$$

Equality (1) means that the mass velocity of reactant i leaving the reactor is equal to the mass velocity of this reactant in the recycle. Equality (1) immediately follows from the material-balance for the fluxes in the recycle system:

$$F\text{x}=R\text{x}^{*}+G\text{x}^{\text{out}}, \qquad (2)$$

Because l feed and intermediate reactants will not be present in the flux leaving the system.

Equality (1) is one of the necessary conditions for the operational mode with complete utilization of feed and intermediate reactants. Another necessary condition for the feasibility of this mode is the introduction of feed and intermediate reactants in the stoichiometric ratio. Otherwise, it would be necessary to remove an excess part of unreacted feed components from the system, which would be in components from the system, which would be in conflict with the requirement of their complete utilization.

We assume that a complex chemical reaction described by the matrix of stoichiometric coefficients **A** proceeds in the reactor. The first *l* rows of the matrix **A** correspond to the feed and intermediate reactants and form a submatrix **A*** in the matrix **A.** In this case, the condition that the feed and intermediate reactants are introduced into the system in the stoichiometric ratio can be written as Boyarinov, Duev (1980):

$$x^{in} = -\frac{1}{M} A^{*} J, \qquad (3)$$

Where **J** is the column vector of dimension *p* (equal to the number of elementary reaction steps) with elements equal to unity for forward reaction steps and to zero for reverse ones. The scalar quantity *M is* determined from the equation

$$M = -1 A^{*} J, \qquad (4)$$

Where 1 is the row vector of dimension *l* with elements equal to 1.

Thus, for the operational mode with complete utilization of feed and intermediate reactants to be feasible, conditions (1) and Eq. (3) should be satisfied. As the final reaction products and inert materials may be present in the recycle, the following condition should

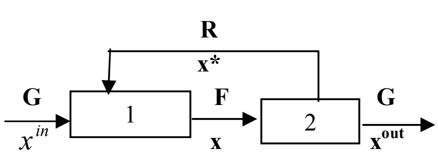

Figure 1. Reactor-separator recycle system: (1)-reactor, (2)- separator.

also be satisfied:

$$F \sum_{i=1}^{1} x_i \le R \; . \qquad (5)$$

Condition for the existence of a continuum (infinite set) of steady states.

The overall steady state material balance for the recycle system (Fig.1) can be written in vector form as

$$G x^{in} + V A r_{av} - G x^{out} = 0, \qquad (6)$$

where $\mathbf{r_{av}}$ is the column vector of dimension *p* consisting of the rates of elementary steps in the complex reaction which are averaged over the reactor volume.

Generally, the column vector of the rates of elementary steps averaged over the reactor volume can be written using the mean-value theorem as

$$r_{av}(x(\Omega), T(\Omega)) = \frac{1}{V} \iiint_{\Omega} r(x,T) dv, \quad (7)$$

where **r(x,T)** is the vector of elementary-step rates which depends on spatial coordinates *v* is the volume element, and Q is the region of integration, which depends on the reactor configuration.

For the operational mode with complete utilization of feed and intermediate reactants and where conditions (1) and Eq. (3) are fulfilled, equation (6) for *l* feed and intermediate reactants is written as

$$A^{*}(V r_{av} - GJ/M) = 0 \qquad (8)$$

If the rank *s* of the matrix **A*** is less than the number of feed and intermediate reactants *l* **(**that is, the matrix **A*** includes linearly dependent rows), then an *(l-s)*-parameter family (continuum) of steady states exists for the operational mode with complete utilization of feed and intermediate reactants. Indeed, if *s<l,* then *s* equations in system Eq. (8) can be basic and the remaining *(l-s)* educations can be expressed as a linear combination of *l* basic equations Consequently, only *s* equations are linearly independent in system Eq. (8). The remaining (*l-s)* dependent equations can be excluded from consideration, because they do not include new functional relations. In this case, only *s* material-balance equations are available to find *l* unknown concentrations of components leaving the reactor. As a result, the concentrations of (*l-s)* reaction components $x_{s+1}, \ldots, x_l$ are indeterminate and can take any values from the set of steady-state values defined by mode-existence condition (5).

Reaction A + B → C proceeds in a plug-flow reactor.

Let the second-order reaction A+B ⟶ 2C proceeds in the adiabatic plug-flow reactor. The matrix A* for this case is given by

$$A^{*} = \begin{pmatrix} -1 \\ -1 \end{pmatrix} \qquad (9)$$

Its rank *s* equal to unity and is less than the number of feed reactants *l*=2. Therefore, a one-parameter family of steady states exists for the operational mode with complete utilization of reactants A and B. The mathematical model for the reactor under steady-state operating conditions is given by

$$\frac{F dx_1}{S dz} = -r,$$
$$\frac{F dx_2}{S dz} = -r, \qquad (10)$$
$$c_P \rho \frac{F dT}{S dz} = (-\Delta H) r$$

For the simplicity of analysis, we assume that no inert components are present in the reactor. In this case, the concentration of the final product C in the reactor is given by

$$x_3 = 1 - x_1 - x_2 \qquad (11)$$

The boundary conditions to systems Eq. (10) for the operational mode with complete utilization of feed reactants A and B can be written as

$$x_1\big|_{Z=0} = \frac{G}{F} x_1^{in} + x_1\big|_{Z=L},$$
$$x_2\big|_{Z=0} = \frac{G}{F} x_2^{in} + x_2\big|_{Z=L}, \qquad (12)$$
$$T\big|_{Z=0} = \frac{G}{F} T^{in} + \frac{R}{F} T^{*}.$$

Since this operational mode can be achieved only when the feed reactants A and B are introduced into the feed flux in the stoichiometric ratio, the equality $x^{in}_1 = x^{in}_2$ is fulfilled.

Since the first two equations in system (10) and corresponding boundary conditions (12) coincide, the boundary-value problem given by Eq. (10) and Eq. (12) will have an infinite set of solutions. As the number of unknowns is one greater than the number of equations, the infinite set of solutions can be interpreted as a one-parameter family of solutions. Thus, a one-parameter family of steady states in which the concentrations of reactants A and B can take an infinite number of steady-state values will exist for the operational mode under consideration. The steady value of temperature at the outlet of he reactor is singular and may be found from the equations (10),(12):

$$T_{z=L} = \left(\frac{G x_1^{in}(-\Delta H)}{c_p \rho} + RT^{*} + GT^{in}\right)/F \qquad (13)$$

When calculating the boundary-value problem numerically, the reaction rate was written as $r = kx_1x_2$, where the specific reaction rate *k* was determined from the Arrhenius formula.

Figures 2,3 qualitatively illustrate the calculated results for the boundary-value problem given by Eq. (10) and Eq. (12).

Figure 2 illustrates the family of steady states at the reactor outlet projected on the x_1 x_2 plane. The steady-state concentrations of the feed reactants A and B at the reactor outlet can take values within the interval $[x_i^{min} x_i^{max}]$, i=1,2; where x_i^{min} and x_i^{max} are the minimum and maximum steady-state values of the concentration x_i, respectively. Figure 3 illustrates the family of steady-state profiles of the concentration x_1 along the reactor.

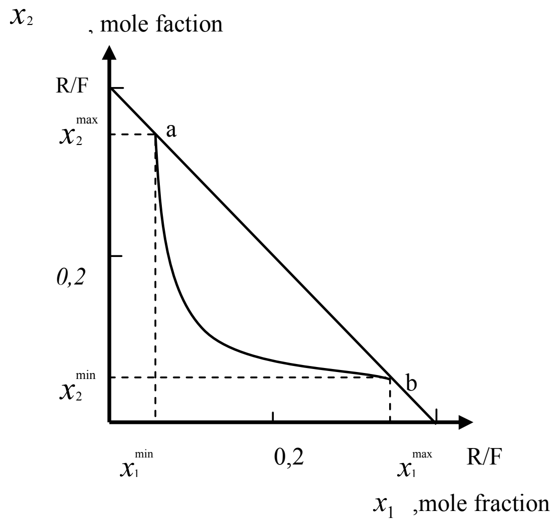

Figure 2**.** Continuum of steady states at the reactor outlet (curve *ab*) projected on the x_1 x_2 plane.

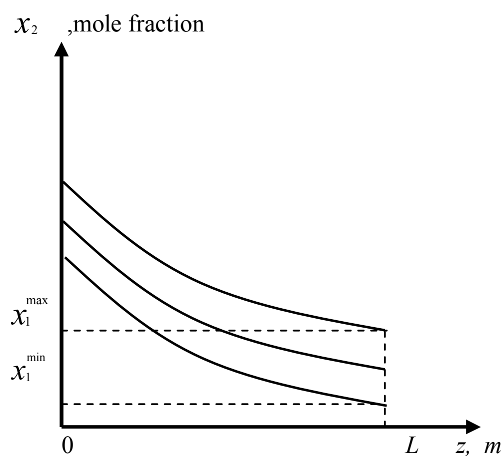

Figure 3**.** Family of steady-states profiles of concentration x_1 along the reactor.

Conclusions

The infinite set of steady states in the operational mode with complete utilization of feed reactants A and B also exists when the separator is characterized by a finite (but high enough) separation efficiency Boyarinov, Duev, Kalinkin (1984).

Numerical calculations of a recycle system consisting of a plug-flow reactor and a rectifying column supported the qualitative results obtained by solving the boundary-value problem given by Eq. (10) and Eq. (12). The column distillate in which all components were present was used as recycle and the end product C, whose volatility is the least, was drawn off via the column recoiled. Because the separation process is not perfect, the feed reactants A and B were present in insignificant amounts in the recoiled of the rectifying column.

Thus, continuum of steady states in which the concentrations of feed reactants can take an infinite number of steady-state values confined in interval $(x_i^{\min} \; x_i^{max}\}$ (i= 1,2) exists in the plug-flow reactor functioning in reactor-separator recycle system in which the reaction A+B $\rightarrow$2C proceeds with complete utilization of the feed reactants A and B. Ttese steady states can not be of asymptotic stability. They can at best be on the boundary of the stability region at the state of neutral balance (Boyarinov, Duev, 1988,1985). Therefore it is necessary to carry out an automatic control to keep this operational mode.

Nomenclature

c_p- specific heat capacity, cal/(g K);
F- flux of the mixture entering the reactor, m^3/h;
G- flux of the mixture entering the system, m^3/h;
-ΔH- heat effect of the reaction, cal/mol;
k- specific reaction rate;
L- reaction length, m;
l- number of feed and intermediate reactants;
p- number of elementary reaction steps;
R- flux of recalculating mixture, m^3/h;
r- reaction rate;
S- cross-sectional area, m^2;
T- mixture temperature, K;
V- reactor volume, m^3;
x_1- mole fraction of reactant i;
x- vector of the mole fractions of components in the reactor;
z- current reactor length, m.

Subscripts and superscripts

in- inlet;
out- outlet;
i= $\overline{1,l}$- number of a reaction;
j= $\overline{1,p}$- number of a reaction step;
max- maximum value;
min- minimum value;
*- recycle.

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