
STATIONARY STATES OF CHEMICAL REACTOR CONNECTED TO A SEPARATION UNIT

Josef HORÁK, Petr ROSOL and Lubomír PIÁLEK

Department of Organic Technology,

Prague Institute of Chemical Technology, 166 28 Prague 6

Received February 8, 1990

Accepted April 18, 1990

Stationary states are analyzed of an isothermal chemical reactor connected by direct recycle with a separation unit from which a part of mixture enriched by the initial substances is returned into the reactor. It was found out that recycling can be the cause of the existence of multiple stationary states of system. The effect is discussed of kinetic law of chemical reaction and separation function of separation unit on the number of stationary states and their stability. The method based on the determination of trajectories of pseudostationary states of the initial substance concentrations in phase plane was used for analysis.

From the point of view of the effect of recycling the substances on the regime of chemical reactor, it is advantageous to distinguish indirect and direct recycling. In case of indirect recycling, the mixture taken away from the reactor is separated into single pure substances which are then stored and reused as feedstock. The reactor inlet is so stabilized by independence of the inlet stream composition on the regime of reactor and separation unit. When using the direct recycle, the separation equipment, in which the initial substances are not isolated as pure, is inserted behind the reactor. The stream enriched by the initial substances is returned into the reactor, the stream depleted is carried away to further treatment. So, the direct recycle brings into the system new feedbacks which complicate the reactor behaviour, e.g., they may be the cause of existence of multiplicity of stationary states. An example of the system with direct recycle may be a bioreactor followed by a separation equipment in which a part of stream is enriched with microorganisms and returned back into the reactor whereas the stream deprived of microorganisms is taken for further treatment.

The behaviour of system with direct recycle is studied in this work on using a mathematical model for the case when the rate of chemical reaction depends only on the concentrations of initial substances. The effect of the reaction kinetic law, function of separation unit and the ratio of feeding the initial substances on the system stationary states is studied.

THEORETICAL

The balance scheme of the equipment studied is given in Fig. 1. Stream 1 and recycled stream 3 enter the reactor. The reaction mixture is led by stream 2 from the reactor into the separation equipment where it is separated into stream 3 enriched with initial substances and stream 4 enriched with products. Stream 3 is returned back into the reactor and stream 4 leaves the system.

It is assumed that the mixture retention in the system is invariable, therefore holds

$$F_1 = F_4, \quad (1)$$

where F_j is the volume flow rate in the j -th stream ($\text{m}^3 \text{s}^{-1}$).

Chemical Reaction

It is assumed that the chemical reaction

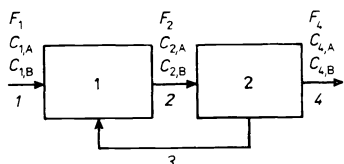


FIG. 1

The balance scheme of system and designation of quantities. 1 Reactor, 2 separation unit

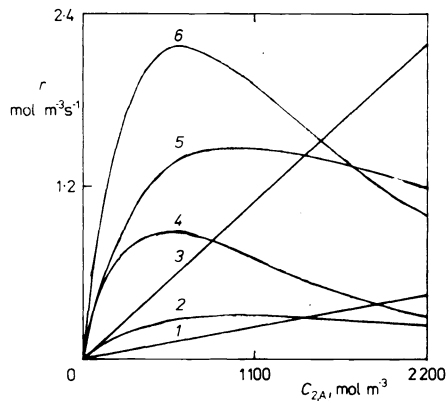


FIG. 2

The examples of dependences of reaction rate on the concentration of substance A in reactor. 1 Rate equation 2 (Table I), $C_{2,B} = 100 \text{ mol m}^{-3}$; 2 rate equation 5, $C_{2,B} = 100 \text{ mol m}^{-3}$; 3 rate equation 2, $C_{2,B} = 500 \text{ mol m}^{-3}$; 4 rate equation 11, $C_{2,B} = 100 \text{ mol m}^{-3}$; 5 rate equation 5, $C_{2,B} = 500 \text{ mol m}^{-3}$; 6 rate equation 11, $C_{2,B} = 500 \text{ mol m}^{-3}$

takes place in the reactor. To describe the reaction kinetics, the rate equation was used making it possible to express the inhibition effect of initial substances on the reaction rate

$$r = \frac{kC_{2,A}C_{2,B}}{(1 + k_A C_{2,A} + k_B C_{2,B})^N}, \quad (3)$$

where k is the reaction rate constant ($\text{mol}^{-1} \text{m}^3 \text{s}^{-1}$), k_A and k_B are the constants expressing the inhibition effect of initial substances ($\text{mol}^{-1} \text{m}^3$), and N is an integer. The survey of values of rate equation constants used in simulations is given in Table I.

For the value of $N = 0$, the rate equation turns to the second-order reaction equation. For $N \neq 0$ it simulates the reaction behaviour whose rate at low concentrations grows with increasing concentration of component, at higher concentrations it is diminished. This type of behaviour is to be observed with some catalytic or biochemical reactions. The chosen examples of dependences of reaction rate on the component concentration are illustrated in Fig. 2. Curves 1 and 3 correspond to the second-order reaction, curves 2 and 5 to the reaction inhibited by substance A and curves 4 and 6 to the reaction inhibited by both initial substances.

Chemical Reactor

As to the reactor, it is assumed that it is a thoroughly stirred CSTR and works in stationary state at invariable volume and constant temperature. To describe the

TABLE I

The survey of values of constants of the rate equations used in simulations in terms of Eq. (3)

Rate equation	$k \cdot 10^6$ $\text{mol}^{-1} \text{m}^3 \text{s}^{-1}$	$k_A \cdot 10^4$ $\text{mol}^{-1} \text{m}^3$	$k_B \cdot 10^4$ $\text{mol}^{-1} \text{m}^3$	N
1	1.0	0	0	0
2	2.0	0	0	0
3	3.0	0	0	0
4	8.0	5.0	0	3
5	1.0	5.0	0	3
5	10	5.0	0	3
6	12	10	0	3
7	15	10	0	3
8	15	6.0	0	5
9	30	5.3	4.7	4
10	33	5.0	5.0	4
11	65	5.0	5.0	5

reactor function, the mass balance of initial substances corresponding to stationary state was used:

$$C_{1,i}F_1 - C_{4,i}F_4 = -v_i r V_r, \quad (4)$$

where $C_{1,i}$ and $C_{4,i}$ are the molar concentrations of the i -th initial substance in streams 1 and 4 (mol m^{-3}), v_i is the stoichiometric coefficient, r is the reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$), V_r the reactor volume (m^3). The left-hand side of the equation represents the rate of the substance inlet into the system and the right-hand side the rate of the substance decrease by chemical reaction.

Separation Unit

To describe the function of separation equipment, a simple model was used describing the relation between the inlet and outlet concentrations of component. For each component the separation efficiency was defined by the relation

$$E_i = 1 - C_{4,i}/C_{2,i}. \quad (5)$$

The maximum value of efficiency $E_i = 1$ corresponds to the case when the concentration of the i -th initial substance in stream 4 is zero; consequently, the substance passes fully into stream 3. If separation of a substance from the reaction mixture stream does not occur, and the values of its concentration in streams 2 and 4 are identical, the efficiency acquires value $E_i = 0$.

It is assumed that the efficiency of separation equipment for each component depends only on its concentration in the stream entering the separation unit. This dependence is described by the function which will be designated as the separation function of component

$$E_i = E_i(C_{2,i}). \quad (6)$$

An initial substance may accumulate in the system by recycling. When analyzing it is assumed that a certain highest permitted concentration of initial substance $C_{\max,i}$ is set, after its reaching it is necessary to change the unit regime and to prevent further concentration increase, e.g., by discharging a part of stream 3 rich in initial substance. To include this fact into the model, two unit regimes were defined.

In the unlimited recycling regime, i.e. with the component concentration in reactor lower than the highest permitted value $C_{\max,i}$, the degree of separation is determined by the course of separation function. After exceeding the value of $C_{\max,i}$, a part of mixture must leave without separating. This fact is simulated by decreasing the separation efficiency. This regime will be designated as that of limited recycling. Examples of separation functions were chosen so as to cover the main types of

behaviour of separation unit (Fig. 3). Curve 4 corresponds to the case of perfect separation of initial substance, curve 2 to the case when the separation is imperfect and the efficiency of separation does not depend on the component concentration. Curves 1 and 3 describe the case when the efficiency of separation increases with increasing component concentration. The survey of separation functions used in simulations is given in Table II.

RESULTS AND DISCUSSION

In a reactor without recycling, the concentrations of initial substances and products are mutually dependent; at the given inlet composition, it is possible to describe the composition of reaction mixture in terms of the conversion of an only key component and stoichiometric equation (2). In reactor with direct recycle, the concentrations of substances become mutually independent, which substantially complicates the description of system and, in principle, increases the demands on investigating the reaction kinetics; then it is necessary to investigate the individual effect of single substances on the reaction rate. The number of state variables in the system with recycle is determined by the number of components whose concentrations influence directly the reaction rate.

In case of a reaction of two initial substances, the system has two state variables, $C_{2,A}$ and $C_{2,B}$. The balance described by Eq. (4) must be fulfilled simultaneously for both the substances in stationary state. To analyze the behaviour of system, it is advantageous to employ the graphical solution based on the construction of trajectories of pseudostationary states of system in phase plane $C_{2,A} - C_{2,B}$. The trajectory of pseudostationary states of concentration $C_{2,A}$ represents loci at which the driving force of changes of concentration $C_{2,A}$ is zero. The position of the point designating the instantaneous state of system with respect to this trajectory determines the direction of the concentration movement of this initial substance in phase plane. Analogously, the pseudostationary trajectory of substance B determines the direction of movement of concentration $C_{2,B}$.

The trajectories of pseudostationary states of concentration of substance A were obtained by numerical solution of balance (4) for various values of concentration $C_{2,B}$ and for substance B, the other way round. The solutions obtained were then plotted in the phase plane. An example of the trajectory course with the designation of direction of concentration movements is illustrated in Fig. 4.

The stationary states of system are determined by intersections of curves of pseudostationary solutions. The stability of stationary states can be estimated on the basis of the direction of movement in its vicinity. The movement in the state space is determined by a vector whose components are driving forces of changes in concentration of both initial substances (Fig. 4).

TABLE II
The survey of separation functions used in simulations

Separation function	Unlimited recycling	Limited recycling
1	$E_i = 0.50$	$E_i = -1.67 \cdot 10^{-3} \cdot C_{2,i} + 3.67$
2	$E_i = 0.90$	$E_i = -3.00 \cdot 10^{-3} \cdot C_{2,i} + 6.60$
3	$E_i = 1.00$	$E_i = -1.67 \cdot 10^{-3} \cdot C_{2,i} + 4.17$
4	$E_i = 1.00$	$E_i = -3.33 \cdot 10^{-3} \cdot C_{2,i} + 7.33$
5	$E_i = 3.68 \cdot 10^{-4} \cdot C_{2,i}$	$E_i = -2.33 \cdot 10^{-3} \cdot C_{2,i} + 5.13$
6	$E_i = 3.68 \cdot 10^{-4} \cdot C_{2,i} + 0.30$	$E_i = -2.33 \cdot 10^{-3} \cdot C_{2,i} + 5.43$
7	$E_i = 5.26 \cdot 10^{-4} \cdot C_{2,i}$	$E_i = -1.05 \cdot 10^{-3} \cdot C_{2,i} + 3.00$
8	$E_i = 5.26 \cdot 10^{-4} \cdot C_{2,i}$	$E_i = -3.33 \cdot 10^{-3} \cdot C_{2,i} + 7.33$
9	$E_i = 1.19 \cdot 10^{-1} \cdot \ln(C_{2,i} + 1)$	$E_i = -3.00 \cdot 10^{-3} \cdot C_{2,i} + 6.60$
10	$E_i = 1.32 \cdot 10^{-1} \cdot \ln(C_{2,i} + 1)$	$E_i = -3.33 \cdot 10^{-3} \cdot C_{2,i} + 7.33$

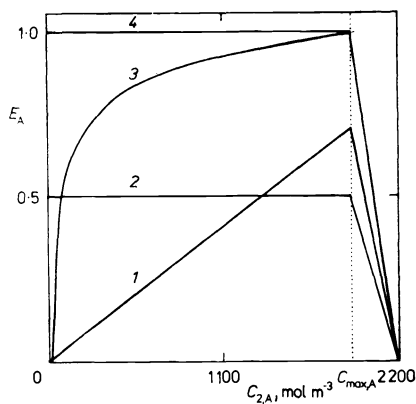


FIG. 3

The examples of course of separation functions. 1 Separation function 5 (Table II); 2 separation function 1; 3 separation function 10; 4 separation function 4

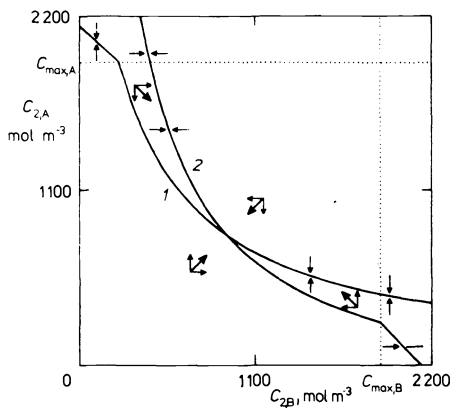


FIG. 4

The orientation of driving forces of changes of concentrations of initial substances and movement of system in the vicinity of stationary state. Rate equation 2 (Table I), substance A, B: separation function 1 (Table II), 1 trajectory of pseudostationary concentrations $C_{2,A}$, 2 trajectory of pseudostationary concentrations $C_{2,B}$

Second-Order Reaction

The number of stationary states and their position in phase plane depend on the separation functions of both components and on the stoichiometric ratio of their feeding into system. From the technological point of view, the most advantageous case is the existence of the only stationary state lying in the region of unlimited recycle ($C_{2,A} < C_{\max,A}$, $C_{2,B} < C_{\max,B}$). This state is stable (Fig. 4).

If the substances are fed into the reactor in nonstoichiometric ratio and separated according to a similar separation function, the accumulation of the substance supplied to excess takes place in the reactor, and the conditions of stationary state are fulfilled only in the region of limited recycle. The stationary state is stable but disadvantageous from the technological point of view. Analogous as to the type of solution is the case when the substances are fed into the reactor in a stoichiometric ratio but the separation functions differ considerably (Fig. 5a).

With certain combinations of separation functions and stoichiometry of feeding, the system shows three stationary states from which one lies in the region of total recycle and remaining two behind its boundaries (Fig. 5b). The technologically required middle stationary state is unstable and forms a dividing line of domains of

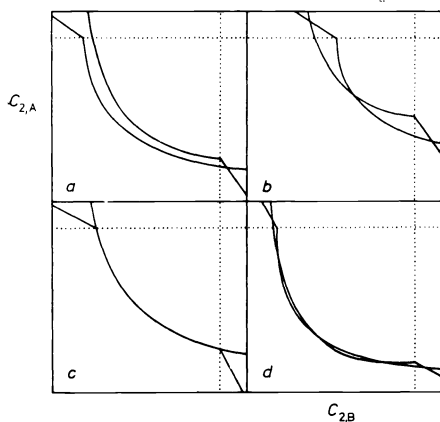


FIG. 5

The trajectory course of pseudostationary states of concentrations of initial substances, second order reaction. *a* Rate equation 2 (Table I), substance A: separation function 5 (Table II), substance B: separation function 6; *b* rate equation 1, substance A, B: separation function 7; *c* rate equation 2, substance A, B: separation function 4; *d* rate equation 3, substance A, B: separation function 7

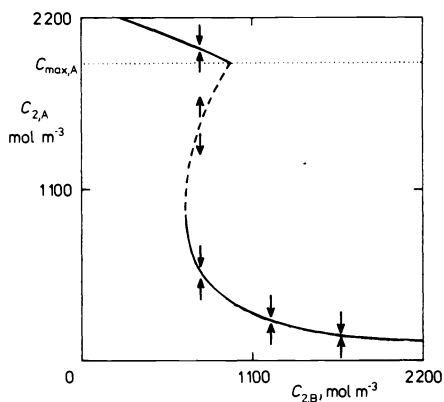


FIG. 6

The orientation of driving forces of changes of concentration of substance A with respect to the trajectory of pseudostationary states. Rate equation 4 (Table I), separation function 6 (Table II), solid line: stable states, dashed line: unstable states

both side stable states. In a real case, the regime would therefore be stabilized in one of these states lying outside the region of unlimited recycle and consequently disadvantageous from the technological point of view.

A special theoretical case is the situation when the initial substances are fed in the accurate stoichiometric ratio and are thoroughly separated ($E_A = 1, E_B = 1$). Then both the trajectories of pseudostationary states in the region of total recycle will merge together, and the condition of stationary state is fulfilled for the infinite number of combinations of substance A and B (Fig. 5c). This limiting case was studied by Boyarinov and Duev¹⁻⁷. In a real process, the system would show a large number of stationary states (5, 7, 9, ...), every odd being stable and every even unstable (Fig. 5d). With respect to the fact that the course of both curves of pseudo-stationary solutions is very close in the whole region of unlimited recycle, even a small change of some system parameters would lead not only to the shift of position of stationary states in phase space but also to the qualitative changes of solution, e.g., to the solution given in Fig. 5a, b.

Reaction Inhibited by One Initial Substance

If a reaction is inhibited by substance A, as many as three pseudostationary states of concentration of substance A may exist in phase plane. The state with highest and lowest stationary concentration of substance A is stable, the middle state is unstable. The driving force of changes of concentration of initial substance A is oriented in the direction of the trajectory representing the stable states and from the part of trajectory representing the unstable states (Fig. 6). The stability of stationary states can be estimated from the direction of resultant vector of movement in the vicinity of the stationary state. The accurate information on the regime stability in stationary state would be yielded by the analysis of dynamic behaviour comprising the dynamic properties of reactor and separation equipment.

TABLE III
Data on the reactor regime

Parameter	Value	Dimension
$C_{1,A}$	$1.9 \cdot 10^3$	mol m^{-3}
$C_{1,B}$	$1.9 \cdot 10^3$	mol m^{-3}
F_1	$1.0 \cdot 10^{-3}$	$\text{m}^3 \text{s}^{-1}$
F_2	$1.5 \cdot 10^{-3}$	$\text{m}^3 \text{s}^{-1}$
V_r	1	m^3
ν_A	-1	-
ν_B	-1	-

For the reaction with inhibiting effect of initial substance there exist more types of the system behaviour. The selected types of behaviour are illustrated in Fig. 7. The system may have only one stationary state lying outside the region of unlimited recycle (Fig. 7a). This state is stable. In Fig. 7b, the situation is illustrated in which there exists the only stationary state in the region of unlimited recycle. This state is conditionally stable, it means that its stability depends on the dynamic properties of system. Its stability would be decided on the basis of dynamic analysis. The system may have greater number of stationary states (3, 5, 7, ...) as well of which every odd is stable or conditionally stable and every even unstable (Fig. 7c). In case of the accurately stoichiometric feed of initial substances and their thorough separation, the system has infinite number of stable, conditionally stable and unstable stationary states (Fig. 7d). More detailed information on the properties of such a system could be obtained only by studying its dynamic behaviour.

Reaction Inhibited by Both Initial Substances

For this type of kinetic law, three pseudostationary states of concentration of sub-

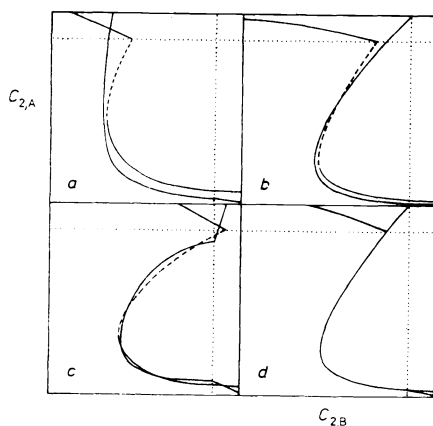


FIG. 7

The trajectory course of pseudostationary states of concentrations of initial substances, reaction inhibited by substance A. *a* Rate equation 4 (Table I), substance A: separation function 6 (Table II), substance B: separation function 5; *b* rate equation 8, substance A, B: separation function 1; *c* rate equation 6, substance A, B: separation function 7; *d* rate equation 7, substance A, B: separation function 3

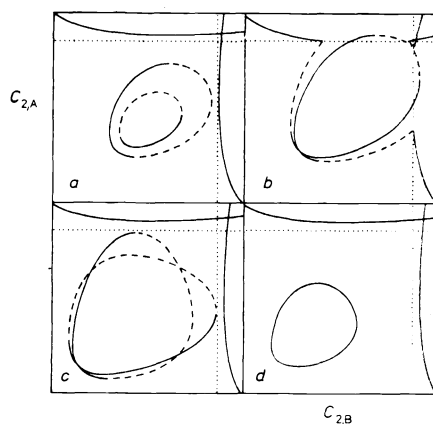


FIG. 8

The trajectory course of pseudostationary states of concentrations of initial substances, reaction inhibited by both initial substances. *a* Rate equation 9 (Table I), substance A: separation function 10 (Table II), substance B: separation function 9; *b* rate equation 10, substance A, B: separation function 2; *c* rate equation 11, substance A, B: separation function 8; *d* rate equation 11, substance A, B: separation function 4

stance A in a certain interval of concentrations $C_{2,B}$ and three pseudostationary states of concentration of substance B in a certain interval of concentrations $C_{2,A}$ may exist. Both side states are stable and the middle one is unstable. If there exist three pseudostationary states of concentrations for both initial substances, then parts of both pseudostationary trajectories have the shape of closed or semiclosed curves. Examples of the system behaviour are given in Fig. 8. Fig. 8a illustrates the case when the system has only one solution outside the region of unlimited recycle. In Fig. 8b and 8c, the system has 3 and 5 solutions, respectively. From the practical point of view, the most advantageous is the state lying most deeply in the region of unlimited recycle which is stable. If the substances are fed in the stoichiometric ratio and thoroughly separated then both the curves of pseudostationary solutions in the region of unlimited recycle merge again (Fig. 8d).

The analysis of behaviour of the system consisting of reactor with separation unit proves that the system behaviour can be in principle different from the behaviour of reactor alone. The behaviour complexity may be one of difficulties which it is necessary to solve when developing so-called closed technologies, i.e. technologies with high degree of recycling all substances. In a great many cases the limitations set to recycling predetermine the properties of stationary state because the stationary state lies in the region of limited recycle. Its position is therefore influenced by the algorithm of recycle control.

SYMBOLS

$C_{j,i}$	molar concentration of i -th component in j -th stream, mol m^{-3}
$C_{\text{max},i}$	maximum admissible concentration of i -th component in reactor, mol m^{-3}
E_i	efficiency of separating i -th component
F_j	volume flow rate of j -th stream, $\text{m}^3 \text{s}^{-1}$
k	rate constant, $\text{mol}^{-1} \text{m}^3 \text{s}^{-1}$
k_A, k_B	constants of rate equation expressing inhibiting effect of initial substances, $\text{mol}^{-1} \text{m}^3$
N	constant of rate equation
r	reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
V_r	reactor volume, m^3
v_i	stoichiometric coefficient

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Translated by J. Linek.