THE DYNAMICS
OF THE POLYMERIZATION PROCESSES*

By

E. SIMONYI

Department of Applied Chemistry, Polytechnical University, Budapest

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Presented by Dr. I. PORUBSZKY

A number of problems arose when the principles of chemical reactor control were examined. For solving them it was necessary to form a mathematical model and to carry out its theoretical study. In this paper those kinds of problems are treated that we met within our practical work on the automation of the chemical reactors for some polymerization processes.

In the presence of the initiator, when the quasistationary proceeding of a reaction is assumed, the kinetics of the free-radical polymerization is described by two equations [1]:

$$\frac{dM}{dt} = - a_1 \exp\left(- E_1/RT\right) M^\alpha I^\beta \tag{1}$$

$$\frac{dI}{dt} = - a_2 \exp\left(-E_2/RT\right) I \tag{2}$$

where M is the concentration of the monomer,
I is the concentration of the initiator,
α, β are the orders of polymerization reaction carried out by the monomer and the initiator,
a_1, a_2 are the pre-exponential multiples,
E_1 is the total energy of activation,
E_2 is the activation energy of the initiator decomposition,
R is the universal gas constant,
T is the absolute temperature, and
t is the time.

The rate of consumption of the monomer is determined by Equ. (1), the decomposition rate of the initiator by Equ. (2).

If the polymerization is carried out in a continuous stirred tank reactor, its behaviour is described by a set of differential equations of the material and heat balance in the following form.

The balance of the materials for the monomer:

$$\frac{dM}{dt} = - a_1 \exp\left(- E/RT\right) M^z I^\beta + \frac{q}{V}(M_i - M), \tag{3}$$

the balance of the materials for the initiator:

$$\frac{dI}{dt} = - a_2 \exp\left(- E_2/RT\right) I + \frac{q}{V}(I_i - I), \tag{4}$$

the heat balance for the reactor:

$$\frac{dT}{dt} = \frac{H \cdot a_1}{c\varrho} \exp\left(- E_1/RT\right) M^z I^\beta +$$
$$+ \frac{Sh}{\varrho cV}(T_\omega - T) + \frac{q}{V}(T_i - T). \tag{5}$$

Here q is the volumetric rate of the reacting mixture motion through the reactor. M_i the inlet concentration of the monomer, I_i the inlet concentration of the initiator, H the heat effect of polymerization, ϱ and c are the density and the specific heat of a reacting mixture correspondingly, assumed to be constant, S is the surface, through which the heat exchange occurs between the reactor and the environment, V is the volume of the reactor, h is the heat-transfer coefficient, T_ω is the temperature of the wall of the reactor, T_i is the temperature of the reacting mixture at the reactor inlet.

The study of the mathematical model of the polymerization reactor aimed to determine the number of the possible steady-state positions and their topological types, to ascertain the possible conditions of the reactor operation, to determine the values of the parameters, at which the transition from one kind of conditions to another occurs and thereby to study the stability of the reactor "at large".

The experiment was carried out with the aid of a new stability-test method.

First the mathematical model of the reactor of ethylene polymerization with $\beta=1/2$ was studied by P. J. HOFTYZER and T. N. ZWIETERING [1]. They proved, that the system may possess one to five steady-state positions. B. V. VOLJTER and his assistants continued this study [2] and obtained by dividing the plane of parameters y_0, x_0 into regions which correspond to one, three, or five steady-state positions. The phase pictures of the system were also plotted and it was proved that the existence of limit cycles is impossible by the autothermal process ($\omega = 0$). There is one stable position in case of one steady-state position, 2 stable and 1 non-stable in case of three and 3 stable and 2 non-stable with five.

Let us consider the case when the reaction rate does not depend on the monomer concentration and therefore it is possible to assume M^α from Equ. (1) to be constant and equal to M_i^2. The model of the studied system is reduced to the two equations (4) and (5).

If dimensionless variables are used, the dimensionless concentration of the initiator:

$$x = \left[\frac{R H a_1 M_i^\alpha}{(E_2 - E_1) a_2 c\varrho} \right]^{1/\beta} I \tag{6}$$

the dimensionless temperature of the mixture

$$y = \frac{RT}{E_2 - E_1} \tag{7}$$

and the dimensionless time:

$$\tau = a_2 t \tag{8}$$

are introduced, then the equations (4) and (5) will bear the following form:

$$\frac{dx}{d\tau} = - x \exp\left(- \frac{1 + u}{y} \right) + v(x_0 - x) \equiv P \tag{9}$$

$$\frac{dy}{d\tau} = x^\beta \exp(- u\,y) + v(1 + \omega)(y_0 - y) \equiv Q \tag{10}$$

where

$$u = \frac{E_1}{E_2 - E_1}\,; \quad v = \frac{q}{a_2 V}\,; \quad \omega = \frac{S \cdot h}{q \cdot \varrho \cdot c}\,.$$

Let us consider now the first quarter of phase plane x, y of equations (9) and (10), as the negative values of the variable have no physical sense.

Substituting the values

$$\beta = 0.5 \quad u = 1.25$$

into equations (9) and (10), the polymerization of ethylene can be examined.

According to the method developed by us, the experiment consists of the following steps:

1. determination of the steady-state positions.

2. determination of the directivity-curves, which was introduced by us (it will be defined later),

3. determination of the directivity-vectors (they are also introduced by us) on the phase-plane.

4. utilization of a satisfactory condition of the absolute stability.

1. The system is in steady-state position, if

$$P = Q = 0$$

that is, where

$$0 = -x_s \exp\left[-2.25/y_s\right] + v(x_0 - x_s) \tag{11}$$

and

$$0 = x_s^{0.5} \exp\left[-1.25/y_s\right] + v(1 + \omega)(y_0 - y_s). \tag{12}$$

The equations for x_s and y_s can be solved only by approximating methods.

2. The directivity-curves are those that satisfy the conditions:
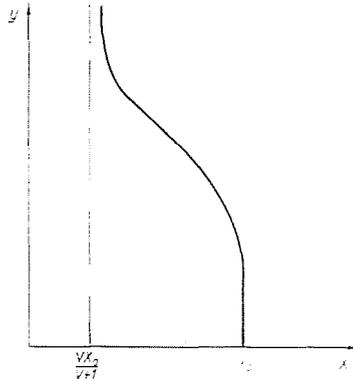
$$P = 0$$

or

$$Q = 0$$

Fig. 1

on the phase plane. Along these lines

$$\frac{dx}{d\tau} = 0$$

(this means that the x coordinate does not change with time), or

$$\frac{dy}{d\tau} = 0$$

(this means that the y coordinate does not change with time). In our case the P-directivity sign $(P = 0)$, by arranging the equation (9)

$$x = \frac{vx_0}{v + \exp\left[2.25/y\right]} \ .$$

The Q-directivity sign can be derived by arranging Equ. (10). If

$$A \equiv v(1 + \omega)$$

then

$$x = \{A(y - y_0)\exp\left[1.25/y\right]\}^2 .$$

By differentiating according to y:

$$\frac{dx}{dy} = 2 A^2(y - y_0) \exp\ [2.5/y] \cdot \left\{1 - \frac{1.25(y - y_0)}{y^2}\right\}.$$

If

$$0 < y < + \infty$$

then the differential quotient is finite. Extreme value can occur, where

$$y = y_0 = y_1$$
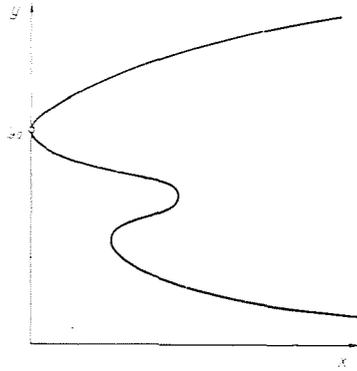
or

$$y_{2.3} = \frac{1.25 \pm \sqrt{1.4375 - 5\,y_0}}{2}\ .$$

Fig. 2

The radix is real, if

$$y_0 \leq 5/16$$

that is

$$\frac{E_1}{RT_0} > 4$$

and this is fulfilled. As x is only at the points

$$y = y_0$$

has zero value, at other points it is positive, and

$$\lim_{y=0} x \rightarrow + \infty$$

$$\lim_{y \rightarrow \infty} x \rightarrow + \infty$$

and, at the second and third extreme values

$$y_{2.3} < y_0 = y_1$$

and thus the curve shown by *Fig. 2* resulted.

3. The directivity-vector can be defined by the following **equation**:

$$\bar{w} = \text{sign}(P)\,\bar{i} + \text{sign}(Q)\,\bar{j}$$

(the function "sign" means the sign of the independent variable). The directivity-vector is characteristic of the direction of motion on the phase-plane. In course of the experiments first the signs of certain components of the directivity-vector on the phase-plane, then the resulting vector are determined.
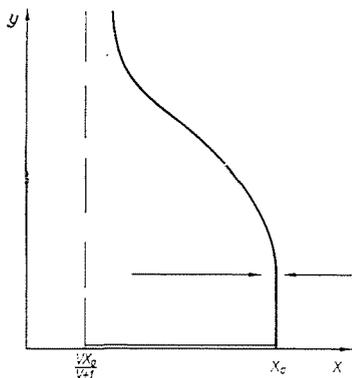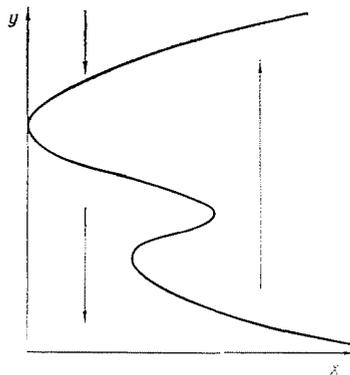

Fig. 3   Fig. 4

a) The directivity-vector has no component in the *x*-direction at the directivity sign *P*, as

$$P = 0 .$$

b) The directivity-vector has no component in *y*-direction at the directivity sign *Q*, as

$$Q = 0 .$$

c) The component being in the *x*-direction is positive, if

$$P > 0$$

that is

$$x < \frac{vx_0}{v + \exp[-2.25/y]} = x_{P=0}$$

and negative, if

$$x > x_{P=0} .$$

d) The component being in *y*-direction is positive, if

$$Q > 0$$

that is

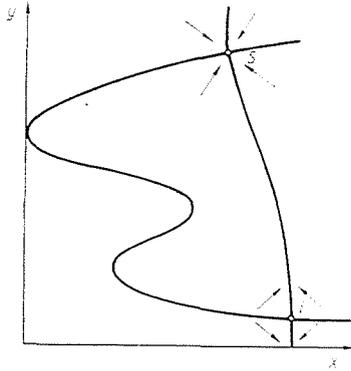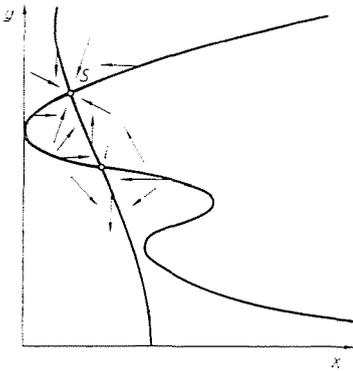$$x^{0.5} > A(y - y_0) \exp [1.25/y] \geq 0$$

and from this

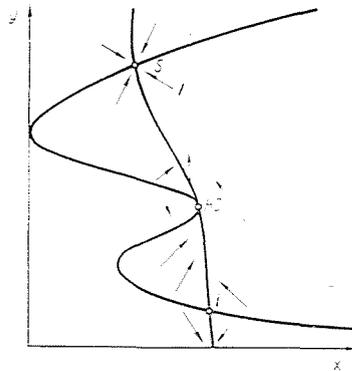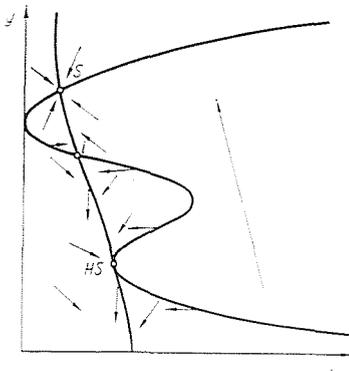$$x > \{A(y - y_0) \exp [1.25/y]\}^2 = x_{Q=0}$$

and negative, if

$$x < x_{Q=0}$$

and thus the resultant is as shown by *Figs. 5—9.*

Figs 5—6

Figs 7—8

4. In the cases shown by *Figs* 5 and 6 the system has two steady-state positions (a stable and a non-stable). A smaller conversion and a higher temperature, thus worse operation belong to the stable point of operation shown by *Fig. 6*, compared to that of *Fig. 5*.

In the cases shown in *Figs* 7 and 8 the system has three steady-state positions (a stable, a non-stable and a semi-stable). The semi-stable position

is stable against certain disturbing signals and non-stable against other ones. Here the stable operating point shown by *Fig.* 7 is more favourable.

A system, having four steady-state positions (two stable and two non-stable) is shown in *Fig.* 9. More favourable of them is that one, which has higher rate of conversion although at higher temperature, this point being stable also at even high overheating.
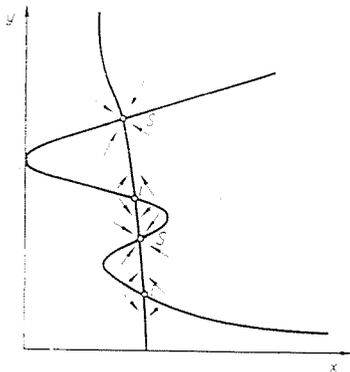

Fig. 9

By proper determination of the parameters (input concentration, input temperature, flow velocity) the equipment could be operated to the most advantageous operating point.

Summary

The dynamics of the free-radical polymerization was studied in a continuous stirred tank reactor. The study of the mathematical model of the reactor aimed to determine the number of the possible steady-state positions and their stability. The experiment was carried out with the aid of a new stability-test method. By proper determination of the parameters (input concentration, temperature, flow velocity) the equipment could be operated at the most advantageous operating point.

References

1. HOFTYZER, P. I., ZWIETERING, TH. N.: Chem. Engng. Sci. 14, 261 (1961).
2. VOLJTER, B. V., SALNIKOV, I. E., SOFIEV, A. E., SHATKHAN, F. A.: IFAC 1966, 48D.

Endre SIMONYI, Budapest XI., Egry J. u. 20—22, Hungary