ANALYSIS OF THE HEAT TRANSFER IN A TUBULAR
HIGH-DENSITY POLYETHYLENE POLYMERIZER

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A semiempirical method is used for determining the heat-transfer coefficients in a polymerizer. The phase constitution of the ethylene—polyethylene system is analyzed for the purpose of evaluating the experimental data.

A tubular reactor for polymerizing ethylene under high pressure ($p \geq 100$ MN/m^2) comprises a long (several hundred meters) thick-walled tube with a jacket containing the coolant liquid. While such a reactor has features which make it superior to an autoclave, its design requires a rather precise calculation of the temperature field determined by the simultaneous processes of heat generation (the reaction is highly exothermal) and heat transfer through the tube walls. Calculation of the heat transfer is difficult because of the lack of test data on the heat transfer from the reacting medium.

The purpose of this study is an experimental analysis of the heat transfer in a tubular polymerizer and a derivation of numerical formulas for designing industrial reactors. Such a device operating under normal conditions is analyzed here by the semiempirical method resting on the following premises:

1) the polymerizer is treated as an ideal extruder [1] (speed, temperature, and concentration of components in the reacting mixture assumed uniform across a transverse tube section);

2) the temperature distribution in the reacting medium along the tube can be described by a functional relation (a polynomial, for instance), which approximates the result of temperature measurements performed over a sufficiently long stabilizing period under given conditions:

$$T = f(z); \tag{1}$$

3) the reaction rate, the ethylene transformation (conversion) level, and the rate of heat generation are determined by a simultaneous solution of Eq. (1) and the equations of material balance for the components of the reacting mixture:

$$\frac{dg_i}{dz} = -\frac{\rho f}{G} r_i; \quad i = 1, 2, \ldots, j. \tag{2}$$

The kinetic equations

$$r_i = \frac{dg_i}{d\tau} = r_i(g_i, p, T)$$

are considered first in the quasisteady approximation [2]; the necessary constants are determined from experimental data [3].

The procedure for calculating the heat-transfer coefficients is as follows:

1. The reactor is subdivided into several segments of equal lengths and the heat balance is established for each segment:

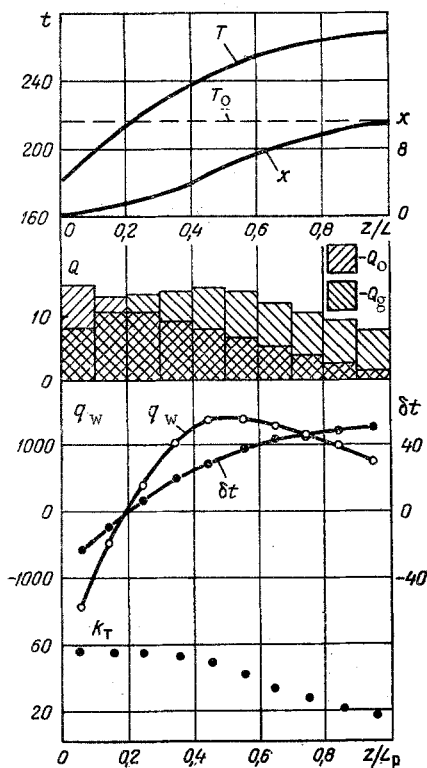a) the heat generated by the reaction is

$$Q_g = G \Delta H_p \Delta x,$$

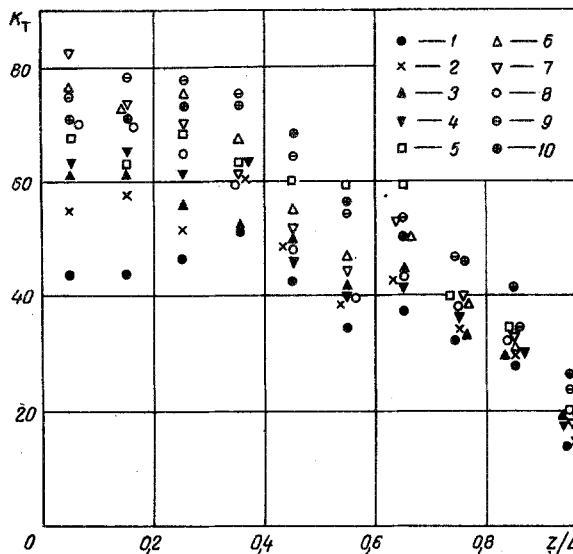Fig. 1. Typical calculation of heat balances and heat-transfer coefficients for tube segments: q_W, W/m; δt, °C.

Fig. 2. Experimental values of heat-transfer coefficients for an industrial reactor [1-10) experiment numbers].

where $\Delta x_n = x_{n+1} - x_n$ is the increment of conversion level across the n-th segment, as calculated;

b) the heat expended on raising the gas temperature is

$$Q_o = Gc_p \Delta T,$$

where $\Delta T_n = T_{n+1} - T_n$ is the temperature drop across the n-th segment, as read off the curve (1);

c) the heat dissipated through the tube wall is

$$Q_w = Q_g - Q_o,$$

or per unit segment length

$$q_w = \frac{Q_g - Q_h}{l_n}.$$

2. A curve is plotted representing the q_d-distribution along the tube. The temperature of the coolant liquid T_o is assumed constant (in the test reactor it did not vary by more than 1-2°C) and equal to the gas temperature at the point where $q_W = 0$ (determined graphically).

3. The mean temperature difference along a segment

$$\delta \overline{T} = \overline{T} - \overline{T}_o$$

is calculated next, where

$$\overline{T} = \frac{T_{n+1} + T_n}{2}.$$

4. The heat-transfer coefficient for a segment is defined as

$$k_{\text{т}} = \frac{q_w}{\delta T}.$$

TABLE 1. Essential Parameters of Tested Operating Modes in an Industrial Reactor

Test No. (Figs.2,4)	Pressure, MN/m^2	Gas flow rate, kg/sec	Concentration of initiator, ppm	Conversion level, %	
				measured	calculated
1	125	1,33	42	9,5	10,4
2	128	1,33	35	9,7	10,0
3	132	1,33	23	9,7	9,8
4	135	1,33	29	11,5	11,0
5	137	1,33	32	9,8	10,4
6	140	1,33	26	9,6	10,1
7	141	1,33	25	9,85	9,8
8	143	1,33	23	10,1	10,1
9	144	1,33	20	9,0	8,7
10	144	1,33	23	10,3	9,5

A typical calculation is shown in Fig. 1.

Calculations were performed for the reactor operating modes which met the following requirements: a) the discrepancy between calculated and measured conversion values did not exceed ±10%; b) the graphically determined temperature of the coolant liquid did not differ by more than ±5°C from its actual temperature.

The essential average parameter values for the various tested operating modes of an industrial reactor are given in Table 1; the experimental data obtained by the procedure given here are shown in Fig. 2. It is evident from the diagram that the heat-transfer coefficient decreases rapidly along the tube. The wide spread of test points can be explained not only by the measurement errors and by the inaccuracy of the calculation procedure but also by a stratification in terms of pressure: higher heat-transfer coefficients correspond to higher pressures.

We will now consider the phase constitution of the reacting medium under conditions prevailing in an industrial polymerizer (p ≥ 100 MN/m^2, T = 440-550°K). According to the experimental studies in [4, 5], at relatively low pressures and temperatures the polyethylene–ethylene system is heterogeneous: one phase (the "gas") consists of almost pure ethylene, while the other (the "liquid") is a solution of ethylene in melted polyethylene. As the pressure and the temperature are raised, the solubility of ethylene in polyethylene increases; at a certain definite level the entire gas has been dissolved and the system becomes homogeneous. The equation which describes this transition to a homogeneous system has been derived in [6]:

$$(1 - \tilde{T}^{-1})(\tilde{p} - 1) = -\frac{T^*}{p^*} B(x), \qquad (3)$$

where

$$\tilde{T} = T/T^*; \quad \tilde{p} = p/p^*;$$

$$T^* = 293.23°K; \quad p^* = 61 \text{ MN/m}^2.$$

In Fig. 3 the phase diagram of the polyethylene–ethylene system is shown; the boundary between the heterogeneous and the homogeneous state corresponds to Eq. (3). On the same diagram are plotted trajectories of the reactor process (change of state of the medium during its flow through the tube) for three modes of operation each corresponding to a different pressure. The solid lines here refer to a pressure drop $\Delta p = 0$ along the tube (i.e., the pressure drop in the flowing medium is small relative to the absolute reactor pressure) and the dashed lines refer to a linear overall pressure drop $\Delta p = 20$ MN/m^2 (measurements on an industrial reactor yielded $\Delta p = 15$-20 MN/m^2). A comparison of trajectories has shown that considerable pressure drops observed in the reactor result in significant shifts of the phase constitution of the reacting medium toward heterogeneity. It can be seen in Fig. 3 that at reactor exit pressures up to ~150 MN/m^2 the reacting medium is heterogeneous along the entire tube, which is favorable for the formation of a moving film of the "liquid" phase at the tube wall. The polymer, which is continuously produced by the reaction, reaches the tube walls by way of turbulent pulsations and the film grows in thickness (while remaining quite thin as compared to the tube diameter), causing an increase in its thermal resistance and a decrease in the heat-transfer coefficient all along the reactor.

From the phase diagram one can also evaluate the "liquid" content of a phase. For this, from the point on the trajectory which corresponds to a specific state of the reacting mixture one must draw a horizontal line till it intersects the phase boundary, whereupon one determines the polymer concentration in the film. By making such an evaluation with two different trajectories for two different pressures, one can verify that a higher pressure corresponds to a lower polymer concentration in the film and, consequently, to a lower-viscosity "liquid" and a thinner film. This accounts for the stratification of test values of k_T with respect to pressure.

In order to evaluate the test data in Fig. 2 in terms of the total thermal resistance, which defines the heat-transfer coefficient, we set up an expression for the thermal resistance of the film:
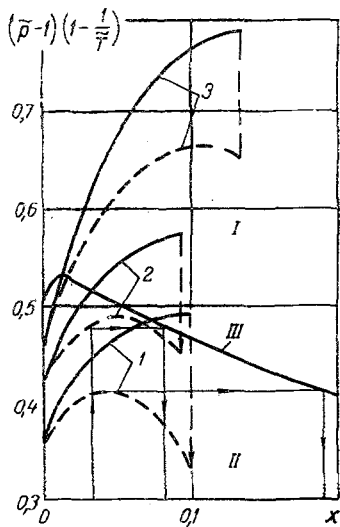
Fig. 3

Fig. 4

Fig. 3. Phase diagram of the polyethylene–ethylene system and reactor process trajectories: 1) p = 125 MN/m^2; 2) 145 MN/m^2; 3) 180 MN/m^2; I) homogeneous region; II) heterogeneous region; III) transition boundary.
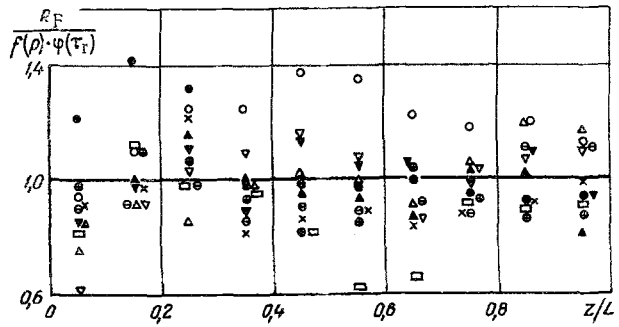
Fig. 4. Approximation of test data by Eq. (5); notation as in Fig. 2.

$$R_F = \frac{\pi}{k_r} - \left[\frac{1}{\alpha d} + \frac{1}{2\lambda_w} \ln\frac{d_0}{d} + \frac{1}{\alpha_0 d_0} \right]. \tag{4}$$

The thermal resistance terms inside the brackets of (4) can be calculated without difficulties. R_F depends on the pressure and on the space coordinate (or, more precisely, on the residence time of the reaction medium in the apparatus):

$$R_F = f(p, \tau_r), $$

where

$$\tau_r = \frac{z}{v}. $$

The data were evaluated by the Brandon multiple-correlations method [7], assuming that the various parameters affect the value of R_F sufficiently independently of one another, i.e., that

$$R_F = f(p)\,\varphi(\tau_r). \tag{5}$$

As a result, we have obtained the following regression equation:

$$R_F = (0.0358 - 0.00122\tau_r + 0.0000392\tau_r^2)(5 - 0.029p). \tag{5a}$$

The degree of approximation can be estimated with the aid of Fig. 4. The test data correspond to Eq. (5a) with a mean-squared error of 15%.

A basic drawback of Eq. (5) is that it does not account for the effects of hydrodynamic flow parameters on the thermal resistance of the film. According to a theoretical analysis of the laminar film flow in a tube [8], the film thickness (and, therefore, its thermal resistance) depends on the Reynolds number for the inner core of gas, namely:

$$R_F \sim \frac{\delta}{d} \sim \mathrm{Re}^{-0.5}. \tag{6}$$

Since the gas rate was constant in all tests (Re = 6·10^5), we may now transform Eq. (5) with the aid of Eq. (6) into

$$R_F = \frac{140}{\mathrm{Re}^{0.5}}(1 - 0.034\tau_r + 0.00109\tau_r^2)(1 - 0.0058p). \tag{7}$$

Equation (7) accounts for the effect of essential parameters on the thermal resistance of the film and may be used for calculating the temperatures in reactors at pressures p ≤ 150 MN/m^2.

As indicated by Fig. 3 at higher pressures the reacting system can exist in a heterogeneous state only near the tube entrance section. Only a homogeneous solution passes through the main reactor section and, at low conversion levels, its viscosity may become sufficiently low to sustain a turbulent flow. Thus, one may assume that raising the pressure improves the heat transfer in a reactor.

NOTATION

c_p	is the specific heat, J/kg·deg;
d	is the diameter, m;
f	is the cross-sectional area of the tube, m²;
G	is the gas flow rate, kg/sec;
g	is the mass content of a component in the mixture;
ΔH_p	is the heat effect of the reaction, J/kg;
k_T	is the heat-transmission coefficient, W/m·deg;
l	is the tube length, m;
p	is the pressure, MN/m²;
Q	is the rate of heat generation (absorption), W;
R	is the thermal resistance, m·deg/W;
r	is the rate of reaction, sec⁻¹;
T	is the temperature, °K;
v	is the velocity of the reacting mixture, m/sec;
x	is the conversion level in the reactor, %;
z	is the axial coordinate in the reactor, m;
α	is the heat-transfer coefficient, W/m²·deg;
ρ	is the density, kg/m³;
λ	is the thermal conductivity, W/m·deg;
τ	is the time, sec.

Subscripts

i	denotes the i-th component of mixture;
n	denotes the n-th segment of tube;
o	denotes external diameter of tube;
w	denotes wall of tube.

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