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Selective Dimerization of Ethylene to But-1-ene under the Conditions of Industrial Process. I. Influence of Temperature and Pressure on the Rate of the Process in a Bubbling Type Reactor

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Abstract—Analysis of mass and heat balance in the reaction node of the process of ethylene dimerization into but-1-ene under the industrial conditions is performed. It is found that ethylene concentration in the reactor liquid phase by a complex way depends on the reactor temperature, pressure and but-1-ene concentration in the liquid phase. Optimal process temperature is 80−90°C, operating pressure in the reactor is 0.6−0.8 MPa. Increase in pressure above 1 MPa practically excludes heat withdraw via but-1-ene evaporation and makes the system of heat withdrawing ineffective.

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But-1-ene is the most widespread, after ethylene and propylene, monomer of olefin series and it is more and more used in the plastics industry for the synthesis of linear medium and low density polyethylene, isotactic polybutene, polybutylene oils and copolymers with propylene. For the solving a problem of obtaining but-1-ene of polymerization purity grade, a new technology of high-selective catalytic dimerization of ethylene into but-1-ene has been developed.

Now in the world industrial practice two variants of technology for manufacturing but-1-ene of polymerization purity are in application:

—The variant "Alfa-okhtol" [1–3] developed in the Institute of Probems of Chemical Physics, Russian Academy of Sciences in cooperation with industrial branch institutions and applied in the beginning of 80th of 20th century in the biggest plants in Kazan and Budenovsk for manufacturing polyethylene; its principal scheme is shown in Fig. 1.

—The variant "Alfa-butol" of the French Oil Institute, applied in 80th of 20th century [4], based on the investigations of the Institute of Probems of Chemical Physics, Russian Academy of Science.

In both these variants the process of ethylene dimerization is perrgformed in liqid phase with the homogenous catalytic system tetrabutoxytitan–tralkylaluminum–modificator. As a solvent basically is applied a mixture of isohexenes (hereinafter in the text hexenes) formed as by-products in the process of ethylene dimerization, or a mixture of but-1-ene and hexenes. In the process of dimerization a mixture of but-1-ene and hexenes of the following composition is formed: hex-1-ene 10 wt %, 2-ethylbut-1-ene 60 wt %, 3-methylpent-1-ene 30 wt %. Besides hexenes, as a side product in a small amount are formed octenes and a polymer, which in the further consideration are not accounted for.

Mathematic model of the reaction of ethylene dimerization into but-1-ene on the $Ti(OR)_4$–AlR'_3 catalytic system has been considered in [5].

The technology of dimerization in the "Alfa-okhtol" variant (Fig. 1) assumes *heat withdrawing* by circulation of evaporating liquid phase from the reactor I as a vapor-gas mixture (g_3 flow) through condenser II with further returning of the gas phase (g_6 flow) and a part of liquid phase (g_9 flow) from the condenser II into reactor I. The material flows by this scheme are shown in Fig. 2.

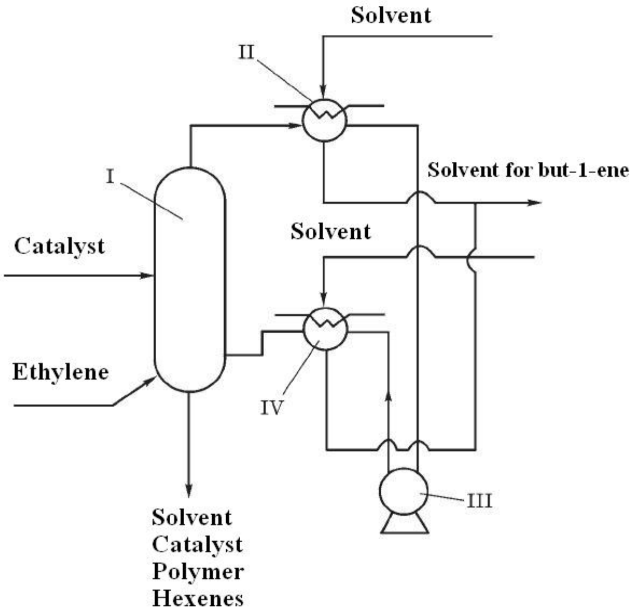

Fig. 1. Principal technological scheme of reaction node for ethlene to but-1-ene dimerizationaccording in “Alfa-okhtol” process. (I) reactor, (II, IV) condensers, (III) circulation compressor.

Such a technology is used in the processes of polymerization of low molecular weight olefins [6] and in suspension ethylene and propylene copolymerization [7].

When liquid phase presents in the reactor and condenser, all abovementioned hydrocarbons are in equilibrium. The ethylene, but-1-ene and hexenes concentrations in gas and liquid phases depend on several factors:

The process temperature,

Pressure in the reactor I,

The process selectivity,

Values of the flows g_2, g_5 and g_6, (Fig. 2),

Ratio of the flows g_3/g_4 and g_9/g_7.

Taking into account a large number of variables defining composition of liquid and gas phases, it was attempted to develop algorithms of mass and heat balances proceeding from the suggestion that gas and liquid phase are in equilibrium and the relations below are fulfilled.

For the reactor I:

$$Y^p_{c2} + Y^p_{c4} + Y^p_{c6} = 1, \tag{1}$$

$$X^p_{c2} + X^p_{c4} + X^p_{c6} = 1, \tag{2}$$

$$K^p_i = Y^p_i / X^p_i\ . \tag{3}$$

$$g_4 = g_3\,(I - E^p) / E^p, \tag{4}$$

where g_3, g_4 denote amount of gas and liquid, respectively, leaving reactor I, kgmol/h; Y^p_{c2}, Y^p_{c4}, Y^p_{c6}, X^p_{c2}, X^p_{c4}, X^p_{c6} are molar fractions of ethylene, but-1-ene and hexenes in gas (Y) and liquid (X) phases of the reactor, K^p_i are the constants of phase equilibrium for ethylene, but-1-ene and hexenes at the temperature and pressure that occurred in the reactor (elucidated by

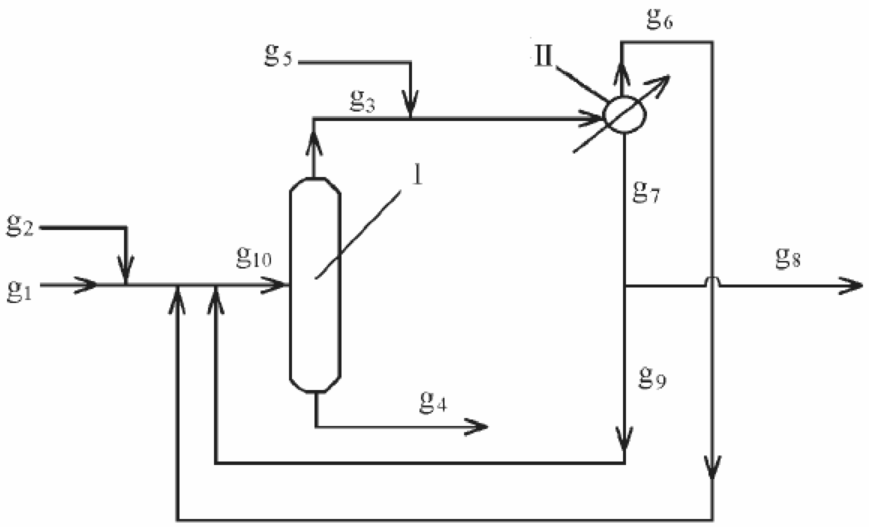

Fig. 2. Scheme of material flows in the reaction node for ethylene to but-1-ene dimerization by “Alfa-okhtol” process.
(I) reactor, (II) condenser. Flows: (g_1) ethylene, (g_2, g_5) hexenes, (g_3) vapor-gas mixture from the reactor to condenser, (g_4) liquid phase from the reactor bottom, (g_6) gas phase from condenser to the reactor, (g_7) liquid phase from condenser, (g_8) liquid phase from condenser to rectification, (g_9) liquid phase from condenser to reactor, (g_{10}) the sum of flows g_1, g_2, g_6, and g_7.

calculation or from published data); E^p is mole fraction of distillate of the g_{10} flow feeding into the reactor

$$g_{10} = g_3 / E^p. \quad (5)$$

For the determination of olefins (ethylene, but-1-ene and hexenes) concentrations in the reactor liquid or gas phase it should be defined concentration of one of them and operating conditions in the reactor, e.g.:

$X^p_{c4} = 0.1; 0.25; 0.5; 0.75$

Temperature 50, 60, 70, 80, 90°C

Pressure 0.6, 0.8, 1.0 MPa

For condenser II:

$$Y^x_{c2} + Y^x_{c4} + Y^x_{c6} = 1, \quad (6)$$
$$X^x_{c2} + X^x_{c4} + X^x_{c6} = 1, \quad (7)$$
$$K^x_i = Y^x_i / X^x_i, \quad (8)$$
$$g_7 = g_6 (I - E^x) / E^x, \quad (9)$$

where g_6, g_7 denote amount of gas and liquid, respectively, leaving condenser II, kgmol/h; Y^x_{c2}, Y^x_{c4}, Y^x_{c6}, X^x_{c2}, X^x_{c4}, X^x_{c6} are molar fractions of ethylene, but-1-ene and hexenes in gas (Y) and liquid (X) phases of the condenser, K^x_i are the constants of phase equilibrium for ethylene, but-1-ene and hexenes at the given temperature and pressure 0.6, 0.8, 1.0 MPa; E^x is mole fraction of distillate of the g_{11} flow (under the conditions occurred in the condenser), hence

$$g_{11} = g_6 / E^x, \quad (10)$$
$$g_{11} = g_3 + g_5, \quad (11)$$
$$g_5 = g_3 \cdot A. \quad (12)$$

The A value can vary in the range 0–1.0, optimally 0–0.1.

The liquid phase from the condenser (g_7 flow) is devided into two flows:

1. The flow g_8 is directed to rectification.

2. The flow g_9 is returned to the reactor for heat withdrawing

$$g_9 = B \cdot g_7. \quad (13)$$

The B value can vary from 0 to 1, and further we take it equal to 0.1; 0.5; 0.9.

Relations between the concentrations of components in the reactor gas phase and condenser liquid phase are expressed as follows:

$$X^x_{C2} = Y^p_{C2}/(I+A)[E^x(K^x_{C2} - 1) + 1], \quad (14)$$
$$X^x_{C4} = Y^p_{C4}/(I+A)[E^x(K^x_{C4} - 1) + 1], \quad (15)$$
$$X^x_{C6} = Y^p_{C6} + A/(I+A)[E^x(K^x_{C6} - 1) + 1]. \quad (16)$$

The reactor mass balance of dimerization on the but-1-ene is expressed as:

$$g_3 \cdot Y^p_{C4} + g_4 \cdot X^p_{C4} = g_6 \cdot Y^x_{C4} + g_9 \cdot X^x_{C4} + G_{C4} \quad (17)$$

where G_{C4} is amount of the formed but-1-ene in kgmol/h, other flows are shown in Fig. 2 and by relations (1, 2, 6, 7).

Using above relations (1)–(16) we transform relation (17) to otain the following dependence:

$$G_{C4} = g_3 X^p_{C4} \cdot [E_p(K^p_{C4} - 1) + 1/E_p$$
$$- K^p_{C4} \cdot E_x(K^x_{C4} - B) + B/E_x(K^x_{C4} - 1) + 1] \quad (18)$$

The amount of ethylene g^{C4}_{C2} consumed for the formation of but-1-ene in kgmol/h equals:

$$g^{C4}_{C2} = 2G_{C4} \quad (19)$$

The total amount of ethylene used for the formation of but-1-ene and hexenes g^{C4+C6}_{C2} is expressed by the relation:

$$g^{C4+C6}_{C2} = 2G_{C4} \quad (20)$$

where S is the process selectivity of dimerization on but-1-ene.

The mass balance on ethylene is expressed as:

$$g_1 = g_{эт}^{C4+C6} + g_4 X^p_{C2} + g_8 X^x_{C2} \quad (21)$$

The mass balance on hexenes is expressed by the relations below:

Amount of the formed hexenes

$$G_{C6} = 2G_{C4}(1 - S)/3S. \quad (22)$$

$$g_1 = g_3 \left(\frac{2X^P_{C_4}}{S} \left[\frac{E^P \left(K^P_{C_4} - 1\right) + 1}{E^P} - \frac{K^P_{C_4} E^X \left(K^X_{C_4} - B\right) + B}{E^X \left(K^X_{C_4} - 1\right) + 1} \right] + X^P_{C_2} \left[\frac{1 - E^P}{E^P} + \frac{K^P_{C_2} (1 - B)(1 - E^X)}{E^X \left(K^X_{C_2} - 1\right) + 1} \right] \right),$$

$$g_2 = g_3\left(X^P_{C_6}\left[K^P_{C_6} + \frac{1 - E^P}{E^P}\right] - \left(K^P_{C_6}X^P_{C_6} + A\right)\left[B\left(1 - E^X\right)\left(1 + A\right) + \frac{E^X}{E^X\left(K^X_{C_6} - 1\right) + 1}\right]\right) -$$

$$- g_3\frac{2X^P_{C_4}\left(1 - S\right)}{3S}\left[\frac{E^P\left(K^P_{C_4} - 1\right) + 1}{E^P} - K^P_{C_4}\frac{E^X\left(K^X_{C_4} - B\right) + B}{E^X\left(K^X_{C_4} - 1\right) + 1}\right].$$

Amount of hexenes G_{C6}^{g3+g4} leaving reactor with the flows g_3 and g_4:

$$g_{C6}^{g3+g4} = g_3 \cdot Y^p_{C6} + g_4 X^p_{C6}. \tag{23}$$

Amount of hexenes formed in the dimerization process and incoming with the flows g_6 and g_9

$$g_{C6}^{g6+g9+Gc6} = g_9 X^x_{C6} + g_6 Y^x_{C6} + G_{C6}. \tag{24}$$

and

$$g_2 = g_{C6}^{g3+g4} - g_{C6}^{g6+g9+Gc6}. \tag{25}$$

Transforming relations 21 and 25 and using (1) to (20) we obtain expressions for g_1 and g_2 showing (see Fig. 2) that they are functions of the flow g_3, but-1-ene concentration in the liquid phase of the reactor X^p_{c4}, phase equilibrium constants K_i at the temperatures in the reactor and in condenser, and of B value:

The flow value g_1 will be shown to depend also on ethylene concentration in the reactor liquid phse X^p_{c2} and flow g_2 on the hexenes concentration X^p_{c6}, A value and the process selectivity.

Such a system has many solutions, and for obtaining certain relations it is necessary:

define flow g_3 = 1 kgmol/h
define molar concentration X^p_{c4} = 0.1, 0.25, 0.5
define A = 0, 0.1
define B = 0.1, 0.5, 0.9

At the given dimerization conditions on temperature and pressure, the values of all flow can be calculated. These values will be true when the reactor heat balance is fulfilled.

Income of heat into the reactor is expressed by the relation

$$Q_{income} = Q_1 + Q_6 + Q_9 + Q_2 + Q_{reaction}, \tag{26}$$

where Q_{income}, Q_1, Q_6, Q_9, Q_2 and $Q_{reaction}$, are the amount of heat incoming to the reactor totally, of the flows g_1, g_2, g_6, g_9, and of the reaction heat, respectively.

The heat outcome from the reactor is expressed by the relation:

$$Q_{outcome} = Q_3 + Q_4 + Q_{loss}, \tag{27}$$

where $Q_{outcome}$, Q_3, Q_4, and Q_{loss} are respectively total outcoming heat, the heat of flows g_3, and g_4 and the

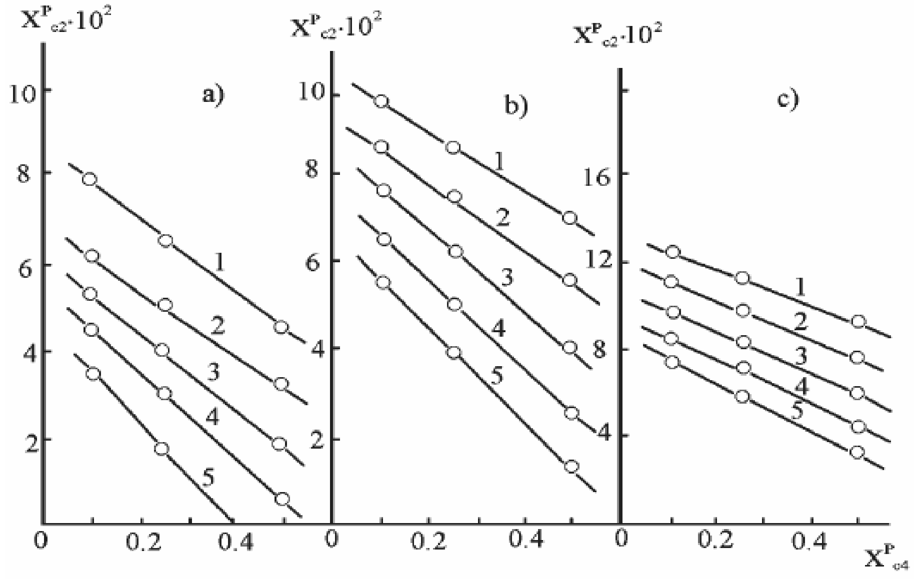

Fig. 3. Plots of ethylene concentration in the reactor liquid phase on but-1-ene concentration in the reactor liquid phase at different temperature and pressure. Pressure, MPa: (a) 0.6, (b) 0.8, (c) 1.0. Temperature, ºC: (1) 50, (2) 60, (3) 70, (4) 80, (5) 90.

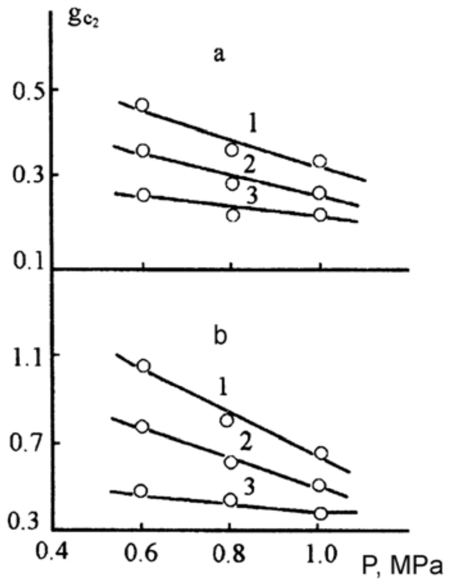

Fig. 4. Plots of ethylene amount g_{C2} consumed for the formation of but-1-ene and hexenes, on the process pressure, at $X^P_{C4} = 0.1$; B= 0.1, 0.5, 0.9; (a) at the temperature 80ºC, (b) at the temperature 90ºC.

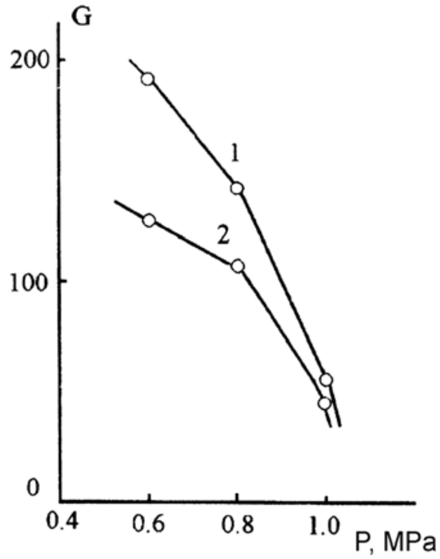

Fig. 5. Dependence of maximum productivity of reaction node G on the pressure; (1) A = 0; (2) A = 0.1.

losses of heat to environment.

$$Q_{income} = Q_3 + Q_4 + Q_{outcome} . \qquad (28)$$

Join solution of the above relations allows to analyze influence of temperature and pressure on the process rete in the bubble type reactor.

The rate and selectivity of the dimerization process an hence the values of g_1, g_2 flows are affected by the concentration of ethylene in the recator liquid phase which in turn, as seen from Fig. 3, depends on the following factors: pressure, temperature and but-1-ene concentration in the reactor liquid phase.

Analysis of the data obtained shows that increase in pressure from 0.6 to 1.0 MPa increases ethylene concentration by the factor 1.5 to 2; increase in the process temperature from 50°C to 90°C decreases ethylene concentration in the reactor liquid phase by the factor 1.5 to 3, increase in but-1-ene concentration in the reactor liquid phase leads to decrease in ethylene concentration by the factor 1.5 to 2. Hence, maximum ethylene concentration occurs at the pressure 1.0 MPa, Δt = 50°C, and at mimimum concentration of but-1-ene in the reactor liquid phase.

Further analysis shows that temperature and pressure affect oppositely the ethylene concentration in the reactor liquid phase and on the amount of consumed ethylene.

Despite the increase of ethylene concentration in the reactor liquid phase, the amount of ethylene consumed for the formation of but-1-ene and hexenes falls down. The plots obtained are shown in Fig. 4.

The reaction node productivity as a dependence on the pressure is defined by the expression:

$$G = \frac{g_6 \cdot g_{c2} \cdot P_{work}}{E_x \left(1 + A\right)} \text{kgmol/h},$$

where g_6 is is circulation compressor discharge (flow g_6), Ex is the distillate fraction in condenser, g_2 is amount of ethylene consumed in the process of ethylene dimerization at the value of flow g_3 = 1 kgmol/h, P_{work} is working pressure.

The calculations show that maximum output of the reaction node falls by factor more than 3 in the pressure range 0.6 to 1.0 MPa (Fig. 5). Hence, it can be said that increase in pressure over 1.0 MPa practically excludes heat withdraw in account of evaporation of but-1-ene and makes this system of heat withdraw ineffective.

The dependence of ethylene amount on the temperature in the reactor or on the temperature difference between reactor and condenser Δt ($t_{condenser}$ = 40ºC), which can be consumed for the dimerization reaction

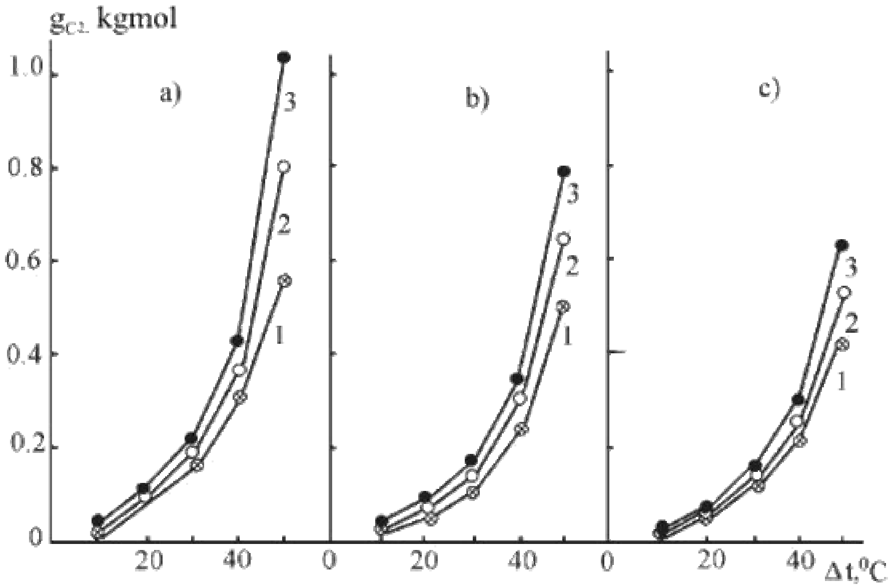

Fig. 6. Plots of ethylene amount g_{C2} consumed for the formation of but-1-ene and hexenes, on the difference in the reactor and condenser temperatures Δt. Pressure, MPa: (a) 0.6, (b) 0.8, (c) 1.0; parameters: $X^{P}_{C4} = 0.1$; A = 0; B: (1) 0.1, (2) 0.5, (3) 0.9.

without disturbance of heat and mass balances, is shown in Fig. 6. As seen, at Δt = 10ºC the reaction node maximum output is minimal, while at Δt = 40 to 50ºC it increases sharply. Depending on the pressure and B value the output at Δt = 40ºC grows by the factor 10 to 20, at Δt = 50ºC by factor 20 to 70. It should be noted that B value does not affect output at the Δt = 10ºC, while at Δt = 50ºC increase in B from 0.1 to 0.9 leads to increase in output by factor 1.5 to 2.

Thus, considering two characteristics of the industrial process of ethylene to but-1-ene dimerization in the bubble type reactor, the reactor productivity (amount of ethylene consumed g_1) and ethylene concentration in the reactor liquid phase it possible to conclude:

–Increase in the process temperature to 90ºC leads to grow in amount of consumed ethylene.

–Increase in pressure is not reasonable because grow in the reaction node productivity is much lower than increase in ethylene concentration in the reactor liquid phase and besides is restricted by the conditions of heat withdraw.

–Ethylene concentration in the reactor liquid phase by complicate way depends on the reactor temperature, pressure and but-1-ene concentration in liquid phase.

Hence, for the considered scheme of technological process the optimum temperature in the reactor is 80 to 90ºC, the optimum pressure is 0.6 to 0.8 MPa.

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