Intensification of mixing and heat exchange in polymerizes

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Abstract. In this article, polymerization processes are carried out under various physicochemical conditions. The reaction medium can be a solution of the polymer in a monomer or solvent with a viscosity from 10^{-3} to 10^{2} -10^{3} Pa, a suspension of solid polymer particles in a hydrocarbon diluent or water with a polymer concentration from 10 to 60%, aqueous dispersions, gas systems solid. Thermodynamic conditions and kinetic characteristics can also vary within wide limits: temperature from 70 to 300 °C, and contact time from tens of seconds to several hours. Polymerization processes typically involve significant heat release (60-100 kJ/mol). In a number of cases, directly or indirectly, temperature and hydrodynamic (shear) conditions affect the molecular weight distribution or dispersed composition of polymer particles and, thus, determine the physical and mechanical properties of the polymer. Naturally, the implementation of the necessary temperature, concentration, and hydrodynamic conditions depends on the design and type of reactor.

1 Introduction

While traditional type reactors are applicable for low-intensity processes, the creation of high-performance polymerization processes requires the development of special reactors.
This necessitates the assessment and selection of meaningful models of mixing (hydrodynamics) and heat transfer, allowing, in particular, a targeted search for ways to intensify processes for a diverse class of structures. Models of mixing and heat transfer. Stirring in the polymerize should ensure distributions of concentrations and temperatures in the reactor volume corresponding to the kinetic scheme of the process, as well as the ability to control these distributions." However, it is not always necessary to implement the conditions of "ideal mixing" (uniformity of local characteristics of the process) throughout

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the entire volume of the reactor. In some cases, in cases, it is preferable to have inhomogeneous (specified) fields of concentrations and temperatures in the longitudinal direction. At the same time, as a rule, to obtain a homogeneous product it is necessary to ensure homogeneity in the transverse direction. It is not always possible to combine longitudinal heterogeneity and transverse homogeneity (especially when the longitudinal and transverse ones are comparable). Transverse dimensions of the reactor. This requires special techniques, for example, sectioning with mechanical or bubbling mixing inside each section.

A detailed review of models and methods for calculating mixing processes in standard apparatus is given in monographs [1-3]. When the viscosity of the mixed medium is low (developed turbulent flow regime), various diffusion or diffusion-circulation models are used. The methodology for creating such models includes the following stages: based on direct observations, selection of a simplified flow diagram of the medium in the apparatus, recording of balance relationships (balances of power, torque, kinetic energy in integral or differential forms) to determine the averaged hydrodynamic characteristics of the circulation flow rate, velocity profile, local energy dissipation; finding coefficients of turbulent diffusion based on certain semi-empirical hypotheses of turbulence. Naturally, such models contain certain empirical constants determined from a comparison of calculated and experimental data.

Similar models can be used for viscous media, when the hydrodynamic situation cannot be interpreted as turbulent, but when, due to the continuous supply of energy in the apparatus due to the movement of blades and other elements, intense large-scale transport takes place. Effective diffusion coefficients in this case can be determined from energy dissipation [4]. However, with very high viscosity of the media, a continuous creeping flow (without special measures for organizing hydrodynamics) can no longer provide intense large-scale transport. Then the conditions for sufficiently satisfactory mixing are: the presence of a circulation movement, a change in the direction of the current lines, and their movement in space. In particular, the simplest solution may be, for example, the use of belt and screw mixers, the mixing models for which are given in [2].

2 Methods

Polymerization processes in dispersed media have certain features, since solid polymer particles in some cases are sources of heat generation (the catalyst is enclosed in a growing polymer particle). To describe the distribution of solid particles over the height and radius of the apparatus, the equations of the corresponding transport models must be supplemented with terms that take into account the convective flow of particles under the influence of gravity and centrifugal forces [2]:

$$\gamma i = \bar{\upsilon} i \phi i \quad (1)$$

Where γi is the flux density ῡi is the sedimentation rate of the particle ϕi is the concentration of particles of the i-th fraction. In most cases, the particle size distribution can be ignored. Then it is advisable to use the relation:

$$\gamma = \bar{\upsilon}\phi \; \bar{\upsilon} = \bar{\upsilon}_0 \; [\![(1-\phi)]\!] \; ^a \quad (2)$$

where $\bar{\upsilon}$ and $\bar{\upsilon}_0$ are the speed of constrained and free deposition, respectively; and exponent ($a \geq 4.5$).

For example, at $\phi = 0.5$ and $a = 4.5$, the sedimentation rate decreases by approximately 20 times, which in the inertial mode of sedimentation corresponds to a decrease in the hydraulic diameter of particles by ~400 times. When mixing concentrated suspensions, the intensity of heat transfer can also significantly decrease [5].

Thus, for simple devices there are models that make it possible to describe large-scale transfer processes already at the development stage. It should be noted, however, that these models, as a rule, do not take into account transfer processes in special zones (stagnation zones, places where flows close, etc.), where insufficient mixing intensity can lead to the formation of lumps, sticking of the polymer to the walls, and other undesirable consequences. Heat transfer problems in polymerization equipment are distinguished by a variety of hydrodynamic conditions and technical solutions for the design of polymerizes. Apparatuses with stirrers and bubbling apparatuses are often used as polymerizes, and to increase their specific heat transfer surface, heat exchange elements are installed inside the apparatus. Along with various empirical dependencies for calculating heat transfer under these complex hydrodynamic conditions, some generalizations of heat transfer problems are proposed. Thus, in works [2, 3, 6] it is assumed that the intensity of heat transfer is determined by small-scale turbulent pulsations (on the order of the thickness of the viscous sublayer) with some hypotheses of their attenuation near the wall. Using the principles of the boundary layer theory [7] and local isochron turbulence [8, 9], in works 12, 61 the dependence of the heat transfer coefficient (a) on energy dissipation (specific power consumption) was obtained in the form:

$$\alpha = 0.267\lambda\,(\varepsilon/\nu)\,\mathrm{pr} \tag{3}$$

where is the kinematic viscosity of the medium; Prandtl criterion; And the thermal conductivity coefficient. Note that a relationship of the form (3) can be found directly by citing empirical data on

$$\mathrm{Nu}=c\mathrm{Re}\ 2/3\mathrm{Pr}\ 1/3 \tag{4}$$

to the dependence on energy dissipation, where c is a constant coefficient; Re Reynolds criterion: Nu- Nusselt criterion. In most cases, according to experimental data, Nu~Pga, which corresponds to the dependence of the attenuation of the speed of turbulent pulsations ochu (distance from the wall), the justification of which is convincingly confirmed by statistical processing of numerous experimental data on heat transfer in pipes [10]. Since for polymerization processes the Pr criterion can vary from 1 to 10%, the calculation error associated with the degree at Pr (1/3 or 1/4) will be quite noticeable. Relationship (3), like other similar dependencies, satisfactorily describes heat transfer in apparatus with stirrers and bubbling reactors at Re-10-10 values and is unsuitable when the viscosity of the stirred medium increases. In addition, dependence of the form (3) gives underestimated results for values of $\mathrm{Re} \geq 10$, since, as shown in [10], most experimental and semi-empirical correlations, in particular for pipes, correspond to Nu~(C/2)RePr a relation (3)-Nu~(C/2)Rep. (where C is the resistance coefficient). In fact, this is a consequence of the fact that for near-wall regions the application of the provisions of local isochron turbulence is a rough approximation.

However, the most significant thing is that this model does not take into account the influence of the size and geometry of the heat exchange elements. In addition, the average energy dissipation value is used. This is illegal for suspensions, especially in cases where

built-in elements are installed in the apparatus. In practice, it follows from relation (3) that the only way to intensify heat transfer is to increase the mixing power. Taking into account the weak dependence of a on ε (a ~ ε1/4), it is obvious that this intensification path is suitable only for low-intensity processes and is limited by the optimal ratio of mixing power and removed polymerization heat [4].

3 Results and discussion

An alternative heat transfer model was proposed in [11]. In this model, the tangential stress on the wall t and the size of large-scale longitudinal pulsations (flows) near wall 1 are taken as the initial quantities that determine the intensity of heat transfer. In this case, it is possible to obtain an analytical solution [12], suitable for any mode and not requiring special hypotheses about the damping of pulsations near the wall. In [11], the following relationship was established for calculating the heat transfer coefficient:

$$\alpha l/\lambda = 0.77(\tau l2/\mu v)\ 1/3\ (\mu/(\mu\ ct)\ )1/6\ Pr1/3 \qquad (5)$$

Where and on the dynamic viscosity of the medium, respectively, in the apparatus and at its walls. From equation (5) it follows that a~1-1/3, i.e., it is possible to intensify heat transfer by reducing the characteristic size.

In many cases, shear stresses on the wall of the apparatus, built-in elements, and rotating heat exchange elements can be easily determined based on the moment of resistance (pressure drop). This, firstly, removes the problem of identifying the unevenness of energy dissipation in the volume of the reactor, and, secondly, it makes it possible to outline ways to increase energy costs in the heat exchange zone by organizing the flow (in standard devices, the proportion of power effectively used to intensify heat exchange is extremely small (1-5%). Naturally, dependence (5) a=/(t) can be transformed to the form a=(r) and written in the traditional form Nu=/(Re,Pr) [13] with the corresponding determining dimensions (4). For laminar mode a ~ ε1/6, for turbulent mode a ~ ε2/9, to model [2].

For the practical use of equation (5), the following notes should be made on determining the characteristic size of longitudinal pulsations 1. For laminar and moderately developed turbulent modes ι is determined by the geometry of the apparatus: laminar flow inside pipes 1-11, transverse flow around pipes -1 4tr, apparatus with a stirrer - 1~Dan mode at large Re (Re> 101-105) scale pro- (Dan is the diameter of the apparatus). In the case of turbulent (Dan is the diameter of the apparatus). In the case of a turbulent regime at large Re (Re> 104-105), the scale of longitudinal pulsations is determined from the balance of tangential stresses for the average flow in the apparatus and for the model of longitudinal pulsations in the form of a laminar boundary layer flowing around a plate of length 1 with the corresponding velocity value at the outer boundary [4]. In particular, this model implies that 1~(C/Re) 1/2 and, therefore, Nu~(C1/2)/2RePr1/3.

Thus, the considered model is a good basis for the analysis and synthesis of various designs of reactors for polymerization under any flow regimes.

Intensification of heat exchange with moderate heat release. The distinction between moderate and large heat release during the process is conditional. Moderate heat release refers to the conditions under which the required thermal regime, productivity, and thermal stability are achieved by fairly simple, well-known methods of intensifying heat transfer, i.e., no special solutions are required for the organization of hydrodynamics and heat transfer.

The simplest design (type) of a reactor that provides these conditions is an apparatus with a stirrer and a jacket, without internal heat exchange devices, with or without

reflective partitions. The choice of the type of mixer in it is determined mainly by the viscosity of the medium, and the mixing mode (rotation speed of the mixer, power, technological requirements for homogenization, uniformity of the temperature field, etc.) based on the corresponding models [2]. In some cases (even with a moderate thermal load), the surface of the jacket is not enough to remove the heat of polymerization when the viscosity of the reaction medium is low. In such cases, to intensify heat transfer, built-in heat exchange devices are used in the form of a central or several peripheral coils, radial partitions made of pipes, etc. From the point of view of the heat transfer model, the use of surfaces made of pipes is rational due to the low value of 1. However, the hydrodynamics of an apparatus with a central coil lead to the fact that the value of in near the tubes is significantly less than in the volume of the apparatus, which causes a decrease in the heat transfer coefficient [14, 15].

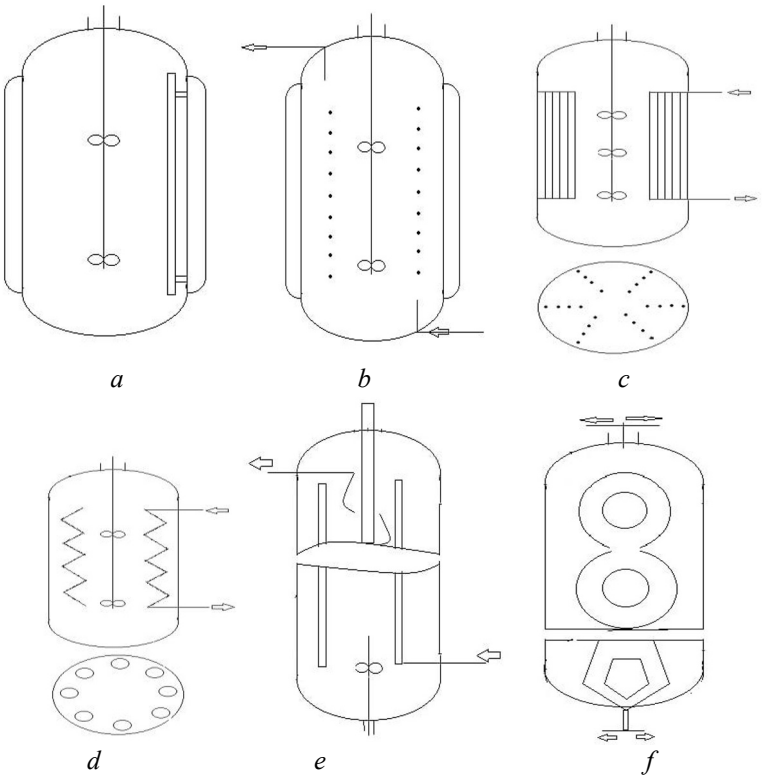

Fig. 1. Reactor designs for low-intensity processes under various conditions.

From this point of view, devices with radial tubular partitions have an advantage. At the same time, when the volume of the apparatus is significantly saturated with such elements (conventionally F>2Fo, where and o is the surface of the internal devices and jacket, respectively), shielding part of the volume of the apparatus causes a decrease in aft in an and a decrease in r in it, which leads not only to a decrease in a, but also to overgrowing, uneven distribution of the polymer in volume and other undesirable consequences. Elements in the form of peripheral coils are more preferable, and the heat exchange surface can be increased by 2-4 times without compromising the intensity of mixing, since the axial circulation that occurs in such devices eliminates the possibility of the occurrence of stagnant zones to have a better function of the molecules [12, 16, 17]. When carrying out

processes in viscous media, devices with a central circulation pipe are sometimes used, which can be cooled. However, the intensification of heat transfer in this case is insignificant.

In some cases, it is advisable to use scraper mixers or special tubular belt or frame mixers with coolant supplied into the pipes [18]. In the first case, intensification of heat transfer is achieved mainly by clearing the more viscous polymer layer formed near the wall due to a decrease in temperature and an increase in residence time; in the second, by increasing the shear stress on the rotating elements and reducing the characteristic scale 1. In this case, a increases in 1.5-3 times. When carrying out processes with low heat release, screw-type reactors are sometimes used. They are characterized by a high value of b and, therefore, a significant a. However, due to the small volume, and therefore small surface, heat transfer through the surface makes only a small contribution to the overall thermal balance of such reactors, which are used mainly for fast or low-performance polymerization processes in adiabatic mode.

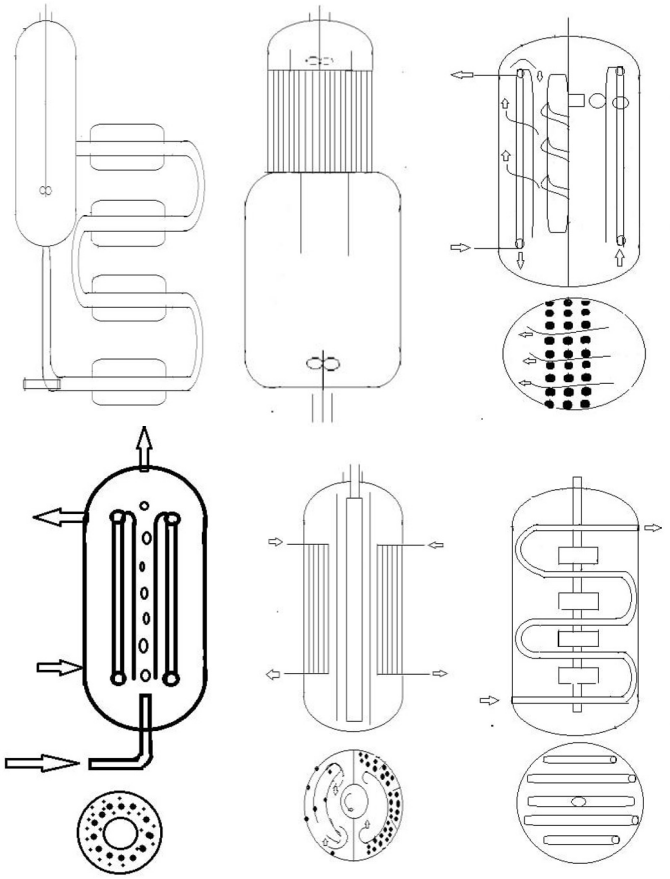

Fig. 2. Schemes of reactors with an organized hydrodynamic structure for carrying out high-intensity processes under various conditions.

A comparative assessment of the technical solutions discussed above is illustrated in Figure 1. When comparing them, the product a in an apparatus with a stirrer and a jacket without internal heat exchange devices is conventionally taken as a unit. The listed methods for intensifying heat transfer make it possible to increase a by 3-6 times. This is due to the

fact that in these devices the fraction of the supplied power dissipated in the heat exchange area is only 1-10%, and also because a significant increase in the specific heat transfer surface without compromising mixing is impossible without a special organization of the hydrodynamic structure.

Intensification of mixing and heat transfer in devices with organized hydrodynamics. The formulated principles (increasing energy dissipation directly in the heat exchange zone without increasing total energy consumption, reducing the characteristic size of the elements of heat exchange devices, eliminating the formation of micro and macro stagnant zones) can be implemented by creating compact heat exchange zones in the reaction volume and organizing intensive circulation through these zones and the rest part of the reactor. The heat exchange surface can be built-in or remote, however, in the latter case, energy costs for circulation increase and more complex equipment is required.

In Figure 2 shows a number of reactor schemes with organized hydrodynamics, designed for carrying out high-intensity polymerization processes in dispersed media and solutions of moderate viscosity (p = 10-2-10 Pas). The exception is apparatus 2, d, suitable for media with a viscosity of 102-103 Pas. All structures (except Figure 2, e) are characterized by the presence of intense internal circulation.

The device shown in Figure 2a is a combination of capacitive and tubular circulation (loop) reactors. This makes it possible to combine the requirements of a large heat exchange surface and short homogenization time, i.e., quickly smoothing out unevenness of concentrations and temperatures that arise, for example, when the catalyst supply fluctuates. The mixing model in such a reactor is presented in [19]. The reactor under consideration is applicable only in cases of developed turbulent regime (Re≥10 10-Pas*) or μ.

The reactor shown in Figure 2, b, combines a capacitive apparatus with a stirrer and a two-pass shell-and-tube heat exchanger, through which the reaction medium is circulated using a low-speed (due to low circuit resistance) device. The advantages of this reactor are that when sedimenting a suspension, the upper circulation device operates in a clean environment, eroding the sediment, as well as the simplicity of the corresponding models of hydrodynamics and heat transfer**. The reactor under consideration is effective only for low-viscosity media (p ~ 10-3 Pa.s), i.e., under turbulent flow conditions in tubes.

The most interesting is a reactor with radial-axial circulation (Figure 2, c), in which an annular bundle of tubes flows around the reaction medium in the radial direction. This reactor is suitable for media with a viscosity of up to 10 Pas, since its circulation circuit has low hydraulic resistance. It is characterized by high heat transfer coefficients, since 50-70% of the power dissipates in the heat exchange zone (and not 1-10%, as in standard reactors). The mixing model in reactors of this type also the technology [20] is based on taking into account the dependence of the axial velocity on the longitudinal coordinate. In addition, it uses the usual [2] approximations and assumptions: in a turbulent flow regime in the flow core, ideal mixing in the transverse direction is assumed within the central and peripheral zones; in a laminar regime, a parabolic axial velocity profile and ideal mixing at turns are assumed. It is noteworthy that this reactor also provides intensified mixing. From a comparison of the concentration equalization curves (Figure 3) in the considered and standard pipe-in-pipe apparatus (power and circulation flow are assumed to be equal), it is clear that the homogenization time in a reactor with radial-axial circulation is significantly longer.

A similar apparatus is the bubble reactor shown in Figure 2, d. Its advantages are especially significant compared to a shell-and-tube gas-lift reactor, since already at p ~ 10-2 Pa-s a laminar regime begins in the tubes. Therefore, in a bubble reactor the heat transfer coefficient and circulation flow rate are 4-6 times higher than in a shell-and-tube gas-lift apparatus.

For highly viscous media, screw mixers are usually used. However, a reactor with a smooth rotor (Figure 2e) and two or more circulation zones in the transverse direction is more efficient. This apparatus differs from a reactor with a screw mixer in that it has a significantly higher circulation rate at equal energy costs. In addition, transverse circulation is insensitive to the possible entry of a low-viscosity medium into the gap, which leads to disruption of the performance of screw mixers. At the same time, the reactor under consideration does not provide intensive mixing in the direction normal to the streamlines, which is consistent with the model [21] of macromixings of highly viscous media. Model [21] assumes that the homogenization of highly viscous media is carried out by fractal transformation of the interface through a series of successive shear deformations of the flow. In this case, the scale of heterogeneity is determined by the relation:

where λo is the initial scale of inhomogeneity - $\gamma \approx \sqrt{\varepsilon/\mu}$ –t total deformation; t mixing time a(Δγ) shift function at Δγ one deformation step, having a maximum at Δγ = 3-6.

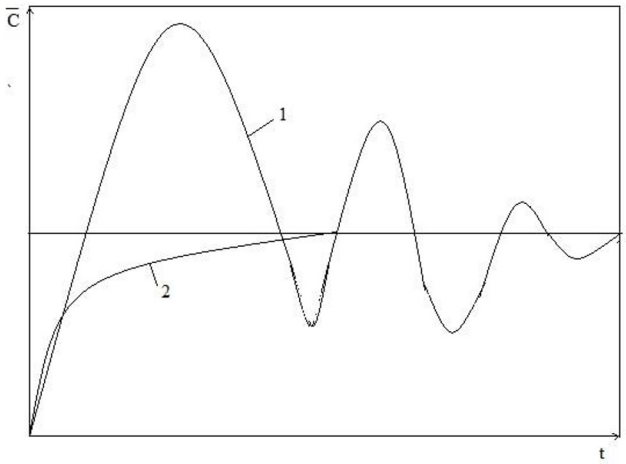

Fig. 3. Concentration equalization curves in a reactor with radial-axial circulation (curve 1) and a standard pipe-in-pipe apparatus (curve 2).

From expression (8) it follows that effective mixing requires reducing the initial scale and ensuring a random change in the direction of deformation after a certain time. Special techniques that ensure these conditions are discussed in [21-26]. Finally, an example of a technical solution that made it possible to combine the requirements of ideal displacement in the longitudinal and satisfactory mixing in the transverse directions is the reactor shown in Figure 2, e.

Organized hydrodynamics and fouling of solid surfaces. The mechanisms of fouling of solid surfaces under polymerization conditions are complex and diverse. In this regard, the influence of mixing conditions on this process is ambiguous and often unpredictable, but at least one case is available for theoretical analysis. This is a flow along the surface of a polymerizing liquid, the viscosity of which increases sharply with time. At the same time, due to the tendency to zero speed (and, consequently, an increase in the residence time) on the wall, a stationary layer of solid material grows on it. As applied to the flow of polymerizing media through pipes and channels, a model of such a process was developed in [22, 23]. Their authors do not take into account diffusion effects, which is explained by the small coefficient of molecular diffusion in liquids. However, our theoretical analysis shows that taking into account molecular diffusion in the transverse direction allows us to draw a number of important conclusions. Thus, it turns out that, in accordance with this model, surface overgrowing begins at (10)

$$x>x^*\cong 0.6\gamma\ D1/2m\ T\ 3/2 \quad (10)$$

where 7 is the characteristic reaction time; D - molecular diffusion coefficient; y shear rate; length of the entrance area that is not overgrown**; x is the distance from the leading edge of the streamlined surface.

At the same time, the rate of overgrowth, even without taking into account diffusion, is determined by the relation

$$u= (\pi 2\ x)/4\gamma T2>0 \text{ at } x>0 \quad (11)$$

In pipes, the value x has the meaning of the length of the pipe section, and in relation to apparatus with a stirrer, the length of the corresponding helical flow line.

4 Conclusion

From expressions (10) and (11) it follows that intensifying mixing by increasing power (increasing y) can only reduce the rate of overgrowth and increase the length of the inlet section x*. At the same time, the organization of the flow structure, which ensures a decrease in the hydrodynamic scale ι, can eliminate surface fouling at moderate energy costs. and increase flow structures.

The presented does not exhaust the variety of technical solutions for creating polymerizes, including those for high-intensity processes. However, they show how, using the proposed techniques, it is possible at an early stage of development to formulate the basic principles of the organization of the hydrodynamic structure, select effective types of reactors taking into account the specific kinetic, physicochemical and technological features of the process, and carry out their modeling and scaling. In this case, the requirements of technological reliability (for example, in terms of preventing fouling), mechanical performance, ease of use and environmental friendliness must be taken into account.

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