Modeling of colloidal systems in technological processes

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Abstract. The article describes the main methods of mathematical modeling of industrial free-dispersed systems. The method of constructing the regression equation by the method of linear and nonlinear installation of coefficients is proposed. The fundamentals of tensor and harmonic approaches to the analysis of disperse systems are considered, which allow optimizing the equations of material and energy balance in the conditions of industrial operation of dispersions.

When solving practical problems of optimizing the composition and properties of industrial dispersed systems (suspensions, emulsions and foams), it becomes necessary to create elementary mathematical models that allow, based on a small number of laboratory experiments, to predict the behavior of dispersion at certain stages of the technological cycle.

It is convenient to use certain technological parameters of the dispersed system as response functions in such models, and as variable factors, physical parameters of the technological process (pressure, temperature, pH, etc.), the concentration of the dispersed phase, the average dispersion of colloidal particles, the concentration of emulsifiers for salt-resistant emulsions [1] and the content of demulsifiers for the destruction of water-oil emulsions [2], the concentration of water-soluble polymer stabilizers for aluminosilicate suspensions [3, 4], foaming agents and foam stabilizers (for foams). The general challenge of modeling is to answer the following questions:
- how will the technological parameter of dispersion change when the variable factors (physical conditions of the process and the composition of the system) change?
- how will a change in one or more variable factors affect the greatness of the response function of the system?
- what combination of variable factors will provide the optimal value of the technological parameter of dispersion, corresponding to the maximum technical and economic efficiency of the process?

The problem of technical and economic optimization of the composition and properties of dispersed systems used in various industries is very relevant, since its successful solution can significantly reduce the material consumption of technological cycles, as well as minimize the risk of emergencies or the production of low-quality products. Conducting express tests when choosing the dosage of chemical reagents and the method of processing industrial dispersions is insufficient to achieve a directed transformation of technological characteristics, since the available laboratory
equipment in many cases does not allow accurately reproducing the thermobaric and dynamic conditions characteristic of a real technological process. Mathematical modeling of technological parameters (response functions) of dispersed systems allows for a short period of time to determine the optimal composition of a dispersed system, choosing for optimization the most significant efficiency factor, which can be used as one or another technological parameter requiring correction. There are several approaches to calculating the efficiency factor of industrial dispersion. Let us assume, for example, that the technological parameter of the system ($\xi_i$) depends on the temperature (T), pressure (P) and the concentrations of the dispersed phase and other chemical components ($C_i$).

$$\xi_i = f(P, T, C_i)$$ \hspace{1cm} (1)

To determine the required number of equations of type (1), we can use the Gibbs phase rule [5], which allows us to determine the number of degrees of freedom F according to the following equation:

$$F = C - P + 2 + n,$$

where: C - the number of components of the solution;

P - the number of phases;

n - the number of dispersed phases.

It should be noted that, as applied to dispersed systems, the independent degrees of freedom are temperature, pressure, and dispersion. With a given component composition, the system tends to the maximum number of degrees of freedom. There is no doubt that water in most technological processes has 2 degrees of freedom associated with pressure and temperature. When colloidal particles enter the water, the system acquires a new third degree of freedom associated with dispersion. Thus, the minimum number of degrees of freedom of an industrial dispersion is 3. The requirement to further increase the efficiency of the dispersed system forces the introduction of various water-soluble polymers into it. From the point of view of thermodynamics, polymer treatment of the dispersion increases the number of degrees of freedom to 4, since by increasing the number of components of the system, it does not change the number of phases present.

Consider first a variational method for calculating the technological parameters of dispersion. Each of these parameters ($\xi_i$) can be characterized by a system of equations, the number of which is determined by the number of degrees of freedom of the system [6]. When carrying out basic experiments, the variation of the values of each degree of freedom should be the maximum possible for the conditions in which the operation of this dispersion is planned. For example, if the system is characterized by the number $F = 3$, then three degrees of freedom are used in the calculations: pressure (P), temperature (T), and concentration of the dispersed phase ($C_d$). The temperature variation is carried out in the interval $\Delta T = T_{\text{max}} - T_{\text{min}}$, and the concentration variation - in the interval $\Delta C = C_{\text{max}} - C_{\text{min}}$. An approximate solution to the problem of finding the technological parameter $\xi_i$ for various values of the degrees of freedom is carried out using the following system of equations:

$$aP_1 + bT_{\text{min}} + nC_{\text{min}} = \xi_1$$

$$aP_1 + bT_{\text{max}} + nC_{\text{min}} = \xi_2$$

$$aP_1 + bT_{\text{min}} + nC_{\text{max}} = \xi_3$$ \hspace{1cm} (2)

where: a, b, n - the required characteristic coefficients in the final regression equation.

In this case, the determinant of system (1) D, composed of the boundary values of the intervals of variation of the degrees of freedom, is a constant value and has the form:

$$D = \begin{vmatrix} P_1 T_{\text{min}} & C_{\text{min}} \\ P_1 T_{\text{max}} & C_{\text{min}} \\ P_1 T_{\text{min}} & C_{\text{max}} \end{vmatrix}$$

The order of the determinant depends primarily on the number of degrees of freedom of the dispersion. Real dispersed systems are described, as a rule, by determinants of the fourth and higher orders.
Solving the system of equations (2), we obtain a regression equation that makes it possible to approximately calculate the value of the dispersed technological parameter for any intermediate values of the degrees of freedom:

\[ aP + bT + nC = \xi \]  

Equation (3) also allows you to calculate the required concentration of the dispersed phase (C) to ensure the specified values of the technological parameters of the system.

However, in reality, the variational method gives a large amount of calculation error, since it implies a direct relationship between the technological parameter (ξ) and the corresponding degree of freedom of the system (P, T or C). In addition, when constructing the system of equations (1), one of the variable characteristics (in this case, the pressure P) remains unchanged, so the number of equations required to take into account all variable factors obviously exceeds the number of degrees of freedom of the system.

To take into account the nonlinearity of expression (1), the characteristic coefficients in the regression equation can be represented as partial derivatives of the response function with respect to the corresponding variable factor, which makes it possible to differentiate equation (3) by presenting the increment of the parameter ξ as a total differential [7]:

\[ d\xi = \left( \frac{\partial \xi}{\partial T} \right)_{P,C} dT + \left( \frac{\partial \xi}{\partial P} \right)_{T,C} dP + \left( \frac{\partial \xi}{\partial C} \right)_{P,T} dC \]  

To find the integral form of equation (4), the method of "installation" of the characteristic coefficients is used. Let the selected response function of the system ξ depend on one of the varied parameters according to the hyperbolic law. This is most often true for the concentration of the colloidal phase or chemical reagent (emulsifier, polymer stabilizer, etc.).

\[ \xi = \frac{\alpha}{C_i} \]  

where: \( \alpha \) - coefficient depending on concentration \( C_i \).

To determine the form of function (5), experimental values of \( \xi \) are required for the maximum \( C_{\text{max}} \) and minimum \( C_{\text{min}} \) concentrations. Measurements are made at the point corresponding to the minimum technologically significant values of \( P_{\text{min}} \) and \( T_{\text{min}} \). As a result, we get two new dependencies:

\[ \xi^* = \frac{\alpha_{\text{min}}}{C_i} \]
\[ \xi^* = \frac{\alpha_{\text{max}}}{C_i} \]  

where: \( \alpha_{\text{min}} \) - coefficient corresponding to the experimental point (\( C_{\text{min}}, P_{\text{min}}, T_{\text{min}} \)),

\( \alpha_{\text{max}} \) - coefficient corresponding to the experimental point (\( C_{\text{max}}, P_{\text{min}}, T_{\text{min}} \))

Thus, the coefficient \( \alpha \) is a function that varies linearly from \( \alpha_{\text{min}} \) to \( \alpha_{\text{max}} \) in the concentration range [\( C_{\text{min}}; C_{\text{max}} \)]:

\[ \alpha = \alpha_1 + \alpha_2 C_i \]  

where: \( \alpha_1, \alpha_2 \) - calculated coefficients of linear approximation of the dependence \( \alpha (C_i) \).

Therefore, equation (5) can be represented as follows:

\[ \xi = \frac{(\alpha_1 + \alpha_2 C_i)}{C_i} \]  

In turn, the coefficients \( \alpha_1, \alpha_2 \) are functions of the remaining variable factors (P, T). To introduce pressure into equation (5), a pair hyperbolic function is constructed in the same way at the extreme points of the variable range [Pmin; Pmax]. To construct it, 4 experimental points are needed: \( (C_{\text{min}}, P_{\text{min}}, T_{\text{min}}), (C_{\text{max}}, P_{\text{min}}, T_{\text{min}}), (C_{\text{min}}, P_{\text{max}}, T_{\text{min}}), (C_{\text{max}}, P_{\text{max}}, T_{\text{min}}) \).

\[ \xi^* = \frac{(\alpha_{1\text{min}} + \alpha_{2\text{min}} C_i)}{C_i} \]
\[ \xi^* = \frac{(\alpha_{1\text{max}} + \alpha_{2\text{max}} C_i)}{C_i} \]  

where: \( \alpha_{1\text{min}}, \alpha_{2\text{min}} \) - calculated coefficients of linear approximation of the dependence...
\[ \alpha (C_i) \text{ at } P_{\min}; \]
\[ \alpha_{1\text{max}}, \alpha_{2\text{max}} \text{ - calculated coefficients of linear approximation of the dependence} \]
\[ \alpha (C_i) \text{ at } P_{\max}. \]

As a rule, in a certain technologically significant range of variation, the thermobaric dependence of the response function is approximately linear. Therefore, the coefficients \( \alpha_1 \) and \( \alpha_2 \) in the pair equation (9) can be represented as linear functions of pressure:
\[
\begin{align*}
\alpha_1 &= \alpha_3 + \alpha_4 P \\
\alpha_2 &= \alpha_5 + \alpha_6 P
\end{align*}
\]
(10)

where: \( \alpha_3, \alpha_4, \alpha_5, \alpha_6 \) - calculated coefficients of linear approximation of the dependences \( \alpha_1(P) \) and \( \alpha_2(P) \).

Combining (9) and (10), we obtain the dependence of the response function on pressure and concentration at \( T_{\min} \):
\[
\xi = \left[ (\alpha_3 + \alpha_4 P) + (\alpha_5 + \alpha_6 P) C_i \right] C_i ÷ C_i
\]
(11)

Accordingly, to introduce temperature into equation (11), 8 experimental points are required: \( (C_{\min}, P_{\min}, T_{\min}), (C_{\max}, P_{\min}, T_{\min}), (C_{\min}, P_{\max}, T_{\min}), (C_{\max}, P_{\min}, T_{\max}), (C_{\min}, P_{\max}, T_{\max}), (C_{\max}, P_{\min}, T_{\max}), (C_{\min}, P_{\max}, T_{\max}), (C_{\max}, P_{\max}, T_{\max}) \).

As a result, we obtain the equation of the response function in integral form from three variable variables, which contains 8 coefficients:
\[
\xi = \left[ (\alpha_7 + \alpha_8 T) + (\alpha_9 + \alpha_{10} T) P \right] + \left[ (\alpha_{11} + \alpha_{12} T) + (\alpha_{13} + \alpha_{14} T) P \right] C_i ÷ C_i,
\]
(12)

where: \( \alpha_7, \alpha_8, \alpha_9, \alpha_{10}, \alpha_{11}, \alpha_{12}, \alpha_{13}, \alpha_{14} \) - calculated coefficients of linear approximation of the dependences \( \alpha_3(T), \alpha_4(T), \alpha_5(T), \alpha_6(T) \).

Thus, the number of experimental points \( N \) increases with an increase in the number of variable factors \( n \) according to the power rule: \( N = 2^n \). Equations (11) and (12) make it possible to solve the direct problem of modeling the technological process: to calculate the possible change in the response function while simultaneously changing, respectively, two or three variable factors. The adequacy of the method for installing the coefficients is checked by the degree of correspondence of the calculation results to the actual data: the calculated and actual values of the technological parameter should not differ by more than 10 - 15%. To improve the accuracy of the model, the simplest linear approximations of the coefficients \( \alpha(C_i) \), \( \alpha_1(P) \), \( \alpha_2(P) \), \( \alpha_3(T) \), \( \alpha_4(T) \), \( \alpha_5(T) \), \( \alpha_6(T) \) can be transformed into power, hyperbolic, or logarithmic. At the same time, an increase in the number of varied factors \( n \) (degrees of freedom of the system) taken into account leads to a proportional increase in the number of "embedded" coefficients \( N' \) of the final integral regression equation, the number of which depends on the selected approximations. In the case of the linear dependences used above, the number of coefficients is equal to the number of experimental points: \( N' = N = 2^n \).

To solve the inverse problem associated with finding the values of variable factors for a known value of the response function, it is necessary to differentiate equation (12) for each of the varied parameters. For simplicity, we will choose for differentiation a two-parameter equation (11), assuming that the temperature during the technological process is unchanged \( (T = \text{const}) \). Then the partial derivatives in equation (4) will have the form:
\[
\begin{align*}
\left( \frac{\partial \xi}{\partial P} \right)_{T,C_i} &= \alpha_4/C_i + \alpha_6; \\
\left( \frac{\partial \xi}{\partial C_i} \right)_{P,T} &= - \left( \alpha_3 + \alpha_4 P \right) C_i^{-2}
\end{align*}
\]
(13)

When solving the inverse problem associated with determining the increment of the response function \( \xi \) with a simultaneous change in variable factors \( (T, P, C_i) \), one can use vector analysis [8], which is based on the construction of the gradient of function (1):
\[
\text{grad } \xi = \left( \frac{\partial \xi}{\partial C_k} \right)_{T,P,C_i} e_1 + \left( \frac{\partial \xi}{\partial C_i} \right)_{P,T,C_k} e_2
\]
(14)

During the operation of the dispersed system, the change in the components of the vector (14) is caused by a gradual decrease in the concentration of the colloidal phase \( C_{k_i} \), as well as the...
concentrations of the chemical components $C_i$ (emulsifiers, foaming agents, etc.); therefore, the value of grad $\xi$ can only change in modulus. In an unchanged coordinate system, it is most probable that the direction of the vector grad $\xi$ remains unchanged with an inevitable decrease in the concentrations of the system components. Denoting the partial derivatives in equation (14) through the partial technological functions $\xi_k^*$ and $\xi_i^*$, we get:

$$\frac{\xi_k^*}{\xi_i^*} = \text{const},$$

where: $\xi_k^* = \left(\frac{\partial \xi}{\partial C_k}\right)$, $\xi_i^* = \left(\frac{\partial \xi}{\partial C_i}\right)$

Let rewrite expressions (11) and (13) for the conditions of the vector equation (14) with respect to the concentrations of the colloidal phase ($C_k$) and chemical components of the dispersed system ($C_i$), assuming the pressure and temperature are unchanged under the conditions of the technological process:

$$\xi = \left[(\alpha_3 + \alpha_4 \cdot C_k) + (\alpha_5 + \alpha_6 \cdot C_k) \cdot C_i\right]/C_i$$

(16)

$$\left(\frac{\partial \xi}{\partial C_k}\right)_{P,T,C_i} = \alpha_4/C_i + \alpha_6;$$

$$\left(\frac{\partial \xi}{\partial C_i}\right)_{P,T,C_k} = - (\alpha_3 + \alpha_4 \cdot C_k) \cdot C_i^{-2}$$

(17)

Solving the system of equations (15) and (16), the instantaneous values of the concentrations of the colloidal phase $C_k$ and the chemical components of the dispersed system $C_i$ are calculated, corresponding to the current value of the response function $\xi$.

During the operation of a dispersed system, the measured values of technological parameters undergo oscillations, for the description of which it is convenient to use the harmonic Fourier analysis [9] of the corresponding time diagrams. For this, it is necessary to use not the values of the response function themselves, but their increments between two adjacent measurements during the transition of the system from the state characterized by the moment of time $\tau_1$ to the next state corresponding to the moment of time $\tau_2$: $\Delta \xi = \xi_{\tau_2} - \xi_{\tau_1}$. At the same time, it is advisable to present the response function in energy units (J), defining it as a useful work of a dispersed system, the implementation of which becomes possible as a result of the periodic introduction of certain chemical reagents (emulsifiers, polymer stabilizers, etc.) into the system. In the course of the technological process, due to various reasons (adsorption, thermal destruction, etc.), the concentrations of the components of the system decrease, and periodic additional treatment of the dispersion with chemical reagents is carried out to ensure the optimal value of the response function.

We assume that the entire considered observation period $\Theta$ for the increments of the technological parameter is $2\pi$, and 2 necessary conditions of the Fourier transforms are fulfilled: the function $\Delta \xi (\tau)$ with a period of $2\pi$ is absolutely integrable in the interval $[-\pi; \pi]$; the function $\Delta \xi (\tau)$ is single-valued piecewise continuous and piecewise monotone.

$$\Delta \xi(\tau) = A_0/2 + \sum_{n=1}^{\infty} (A_n \sin(\omega \cdot \tau + \Delta \varphi_n)), \text{ where: } \omega = 2\pi n/\Theta$$

(18)

The number of harmonic components (n) in the function $\Delta \xi (\tau)$ is determined by the number of measurements of a given technological parameter $\xi$ in the time interval $\Theta$.

Let, for example, in a technological process, the increments in the concentrations of a non-ionic surfactant ($\Delta C_p$), a polymer stabilizer ($\Delta C_l$), a colloidal phase ($\Delta C_p$), and an alkalinity regulator ($\Delta C_{oh}$) affect the magnitude of the response function of a dispersed system.
Expansion of the functions $\Delta \xi (\tau)$ and $\Delta C_i (\tau)$ in a Fourier series allows you to isolate the main low-frequency harmonic oscillation, determine the amplitude ($A_1$) and phase shift ($\Delta \varphi_1$) (Figure 3, Table 1).
Figure 3. Basic harmonic oscillations (frequency $2\pi/\Theta$) allocated by the decomposition of the periodic functions in a number of Fourier.

Table 1. Parameters of the main oscillation of periodic functions $\Delta\xi(\tau)$ and $\Delta C_i(\tau)$.

| Periodic function | Basic vibration parameters $[A_0/2 + A_1 \cdot \sin(\omega x + \Delta \varphi)]$ | Phase shift $\Delta \varphi$, rad. | Phase shift $\alpha_i$ relative to the vector $\Delta \xi$, rad. |
|-------------------|-------------------------------------------------|----------------------------------|-----------------------------------|
| $\Delta F(\tau)$  | 0.192                                            | 0.127                            | 0                                 |
| $\Delta C_p(\tau)$| 0.034                                            | 0.830                            | 0.703                             |
| $\Delta C_L(\tau)$| 0.205                                            | -1.141                           | -1.268                            |
| $\Delta C_b(\tau)$| 0.883                                            | 0.752                            | 0.625                             |
| $\Delta C_{oh}(\tau)$ | 0.007                                           | 0.427                            | 0.300                             |

According to the results of the Fourier analysis presented in Table 1, the changes in the value of the response function are ahead of the fluctuations in the concentration of the polymer stabilizer ($\Delta C_i(\tau)$) in phase, but lag behind the fluctuations in the rest of the components of the dispersed system. The maximum technological effect from the use of chemical reagents is achieved only if the phase of the main fluctuations of their concentrations $\Delta C_i(\tau)$ and the main fluctuation of the selected response function $\Delta \xi(\tau)$ coincide.

If the abscissa axis coincides in direction with the vector $\Delta \xi$, then the relationship between the main oscillations of periodic functions can be represented in the form of vector diagrams, in which each function $\Delta C_i(\tau)$ corresponds to a vector, which is plotted from the origin and is equal in magnitude to the amplitude of the main oscillation $A_1$. The angle between the vector and the abscissa axis $\alpha_i$ is equal to the difference between the phase shifts of the main oscillations of the given concentration function $\Delta C_i(\tau)$ and the response function: $\alpha_i = \Delta \varphi_{1c} - \Delta \varphi_{1f}$ (Table 1).

The resulting vector $A_c$ of concentration fluctuations is determined as the vector sum of the amplitudes of each chemical component of the dispersed system:

$$A_c = A_{1p} + A_{1L} + A_{1b} + A_{1oh} \quad (19)$$

Vector addition (19) makes it possible to determine the coordinates ($A_c; A_y$) and the value of the resulting concentration vector $A_c$:
Ах = А1п cos(αп)+ А1Л cos(αЛ)+ А1об cos(αоб) = 0,811
Ау = А1п sin(αп)+ А1Л sin(αЛ)+ А1об sin(αоб) = 0,346
Ас = (Ах² + Ау²)¹/² = 0,881

The ratio between the coordinates Аx and Аy shows how many times the part of the chemical energy of the components of the system, potentially converted into useful work, exceeds the share of chemical energy that is spent on overcoming the inertia of the system and is dissipated. In this case, the ratio between the coordinate Аx of the vector Аc and the modulus of the vector Δζ (amplitude А1F) characterizes the degree of conversion of the chemical energy of the components of the system into an increment of the response function (useful work).

The cosine of the angle between the vector Аc and the abscissa axis (cos (β)), with which the direction of the vector Δζ coincides, characterizes the resulting phase shift between the main fluctuations in the concentrations of chemical components and the response function of the system:

cos(β) = Ах / Ас = 0,811 / 0,881 = 0,92                                       (20)

During the operation of dispersed systems in various technological processes, it is necessary to strive to ensure that the dissipation of chemical energy to overcome the inertia of the system is minimal, and the value of cos (β) is as close to 1 as possible.

Thus, the basics of elementary modeling of colloidal systems in technological processes are considered. With a nonlinear dependence of the technological parameter (response function) of the system on variable factors (degrees of freedom), the method of installation of coefficients is used, which makes it possible to construct an adequate regression equation based on a minimum number of laboratory experiments.

Using the concept of the total differential of the response function and assuming that the ratios of partial derivatives remain unchanged, it is possible to approximately estimate the increment of the technological parameter of the system with varying variable factors (temperature, pressure, dispersion and concentrations of chemical components). During the operation of a dispersed system, its technological parameters change within certain limits and are optimized due to the periodic introduction of chemical components. The use of Fourier analysis of oscillations of the response function and the concentrations of system components makes it possible to assess the degree of efficiency of technological process control.

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