Ensuring a Temperature Conditions in a Reactor for Functionalization of Carbon Nanotubes

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Abstract

The problem of providing a temperature conditions in a stirrer-equipped capacitive device is considered for the functionalization of carbon nanotubes using titanium stearate in a nanodispersed liquid medium, with a supply of carbon dioxide. The analysis of mixing methods and set-up of the temperature conditions in the reactor was carried out. Based on the differential equations of heat conductivity, a mathematical model of the temperature field of a flow moving in the mode of ideal displacement through a channel of constant cross section formed by the surfaces of the half-tube and the body was developed. The calculation of the temperature field over the current time interval includes multiple solutions of heat conductivity problems with subsequent consideration of all the components of the local heat balance. Based on the results of the calculations, the dependences of changes in the temperature of the nanodispersed medium in the capacitive reactor on the beginning time and the relative half-tube length were plotted.

Introduction

Any complex technology passes through a series of stages constituting a kind of life cycle – from the origin of the idea to the immediate application. Forming the reactor shape makes it possible to determine the ways of solving problems, for which the technology of functionalization is developed [1].

The reactor is understood herein as a combination of indicative basic properties and relationships between its elements, which determine its capabilities and mechanisms of its implementation. The reactor is a set of elements and means adapted and technically suitable for protection against negative environmental influences, which are in relationships with each other and form a certain integrity and unity.

In the present work, we will characterize a batch functionalization reactor, the components of which are as follows:

– components reflecting the arrangement of the reactor elements and the nanodispersed (working) medium in space;

– components reflecting the state of the nanodispersed medium, zones of environmental impact, reactor loading/unloading, etc.

Features of functionalization of carbon nanotubes with titanium stearate

The initial (stock) solution of triethanolamine stearate and triethanolamine titanate has a slightly alkaline reaction and is stable at this pH value [2, 3]. This system also acts as a surfactant for dispersion of carbon nanotubes (**CNTs**). When the pH is lowered, which is achieved by saturation of the nanodispersed medium (solution mixture) with carbon dioxide, the system loses stability, and titanium stearate precipitates on the surface of hydrophilic CNTs. The loss of stability of the system is probably due to protonation of the amine group bound to the chelate complex together with the titanium atom. In this case, the stability of the complex decreases, and the titanium ion binds to the stearate anion and carboxyl groups on the CNT surface.

The triethanolamine is transferred to its carbonate and bicarbonate. Theoretically, all the titanium from the initial solution should be deposited over the CNT surface.

In the reactor considered herein, the nanodispersed mixture containing CNTs was saturated with carbon dioxide at the interface of the contacting phases, without gas bubbling. The amount of the liquid (fluid) adsorbed by the gas depends, first of all, on the properties and size of the contact surface [4, 7].

The paper [5] showed the emergence of destructive changes during the CNT covalent functionalization, which can negatively affect the quality of CNTs and the mechanical and electrophysical properties of composites modified with them. In this case, it is possible to ensure conditions for chemical treatment, under which CNTs with a given value of the degree of functionalization retain the structure of graphene layers.

According to the given scheme, CNTs functionalized with titanium stearate with the required parameters can be obtained by strictly observing the temperature conditions, including the heating of the reaction mass and maintenance of its temperature during the process being implemented [6].

Maintenance of the required temperature conditions of the working medium in the reactor depends on the way it is stirred, namely:

– hydrodynamic mixing by means of a pump and bypass contour providing the feeding of the nanodispersed medium from the bottom of the reactor to its upper zone and subsequent film flow of the medium with adsorption of carbon dioxide;

– stirring the nanodispersed medium by means of a stirrer located inside the reactor.

In the first case, the temperature conditions of the nanodispersed medium in the functionalization reactor are maintained by means of a typical external heat exchanger placed in the bypass loop. From outside, the reactor shell is covered with a thermal insulation layer.

In the second case, the temperature conditions of the nanodispersed medium are maintained by heating the vessel through the heat exchange casing. The latter is also covered externally by the above-mentioned layer. Here, using a capacitive cylindrical device of a vertical design with an elliptical bottom, a mixing device and outer casing seems the most rational option.

Construction of a mathematical model of the reactor temperature conditions

The purpose of mathematical modeling of heat transfer in the reactor casing is to determine the operating modes of the device that ensure the implementation of the liquid-phase functionalization of CNTs under industrial conditions.

The problem of optimization of thermal processes in capacitive reactors can be formulated as follows. It is necessary to find the surface of the casing (Fc), the form (vt) and the initial temperature (t_{0cool}) of the coolant in the casing, and the duration of reactor operation cycles requiring supply or removal of a large amount of heat (τ), under which the coolant operating costs are minimal when using the capacitive reactor.

When compiling a mathematical model, differential equations of heat conductivity are used. The choice of this approach is based on the following assumptions [8–10]:

– the most reliable data on thermal processes taking place in capacitive reactors can be obtained based on the mathematical modeling of temperature fields of a d medium, a coolant and structural elements that affect the course of thermal processes;

– the calculation of local heat fluxes (flows) through the structural elements of the capacitive reactor makes it possible to recalculate the temperatures of the product and the coolant on the basis of local thermal balances under different conditions of their motion (these calculations are feasible if the temperature fields inside the above-mentioned reactor elements are known);

– the spatial non-stationary temperature field is described by the differential Fourier–Kirchhoff equation, which describes the field based on the fundamental laws of heat transfer in space, taking into account all the thermal effects that occur in the operation of the capacitive reactor;

– the partition of the thermal process into spatially-temporal discrete regions eliminates the need for setting up a non-linear heat conduction problem. Hereafter the isolated discrete region will be called local.

Let us consider the derivation of an equation describing the temperature situation in the casing, which provides the operating temperature in the nanodispersed medium when supplying carbon dioxide from above. The coolant moves along the channel formed by the outer wall of the reactor vessel and the inner wall of the casing half-tubes. In deriving the equation, the following assumptions are used:

– the temperature of the coolant along the half-tube channel section is constant;

– the coolant represents an incompressible fluid;

– the thermophysical characteristics of the coolant do not depend on the temperature;

– the cross-sectional area of the annular channel is constant.

The assumption of the independence of the coolant thermophysical characteristics on the temperature is due to the insignificant size of the half-tube channel. Let us consider the non-stationary temperature conditions. The coolant flushes the channel walls at two different temperatures varying in time and along the length of the elementary region. The temperature field of the capacitive reactor coated with the half-tube casing presents a combination of the following temperature fields:

– temperature field of the working medium in the reactor;

– temperature field of the coolant flow in the half-tube casing channels;

– the temperature field of the thermally insulated sections of the reactor vessel not covered with the half-tube casing channels;

– the temperature field of the reactor vessel sections in contact with the coolant flow in the half-tube casing;

– the temperature field of the heat-insulated half-tube wall.

When developing a mathematical model, the following assumptions are made:

– the working medium in the device is considered in the ideal mixing mode, its temperature varies only in time;

– the coolant in the half-tube casing channel is considered in the turbulent conditions of ideal displacement, its temperature varies along the channel length and in time;

– the above-mentioned temperature fields are considered as sets of local temperature fields for discretized space-time regions, within each of which the thermal physical characteristics of substances and structural materials, as well as the kinetic characteristics of thermal processes, are considered constant, corresponding to the average temperatures of the components in the considered regions.

For each local region, the following assumptions can be made:

– the temperature field of the working medium in the reactor is determined from the heat balance conditions taking into account all operating heat sources;

– the temperature field of the coolant flow in the half-tube casing channels is simulated by the solution of the corresponding Cauchy problem;

– the temperature field of the heat-insulated sections of the device vessel not covered by the half-tube casing channels is simulated by the problem of stationary thermal conductivity for a hollow two-layered cylinder;

– the temperature field of the device vessel sections in contact with the coolant flow in the half-tube casing is simulated by the problem of stationary thermal conductivity for a hollow single-layered cylinder;

– the temperature field of the heat-insulated half-tube wall is simulated by the problem of stationary thermal conductivity for a hollow two-layer cylinder;

– the longitudinal heat flow in the device vessel wall is simulated by the solution of the corresponding boundary value problem.

The temperature field of a flow moving in the conditions of ideal displacement through a channel of constant cross section formed by two surfaces with different temperatures is described by the following equation

$$\frac{d\,t(x)}{d\,x}+K\,t(x)=S,\qquad(1)$$

$$K=\frac{\alpha_1 P_1+\alpha_2 P_2}{Gc}\,,\quad S=\frac{\alpha_1 P_1 t_{F1}+\alpha_2 P_2 t_{F2}}{Gc},\qquad(2)$$

where x is the spatial coordinate in the flow direction, $t(x)$ is the current fluid temperature, G is the mass flow rate of the liquid, c is the heat capacity of the liquid, P_i is the perimeter of the i-th channel wall, α_i is the convective heat transfer coefficient from the i-th wall channel to the liquid, t_{Fi} is the temperature of the i-th channel wall, $i = 1, 2$ is the channel surface index.

Under the initial condition of $t(0)=t_0$, the solution of equation (1) has the following form:

$$t(x)=V+(t_0-V)\exp(-K\,x),\qquad(3)$$

$$V=\frac{\alpha_1 P_1 t_{F1}+\alpha_2 P_2 t_{F2}}{\alpha_1 P_1+\alpha_2 P_2}.\qquad(4)$$

The average temperature of the liquid in the section of length Δx is

$$\bar{t}=\frac{1}{\Delta x}\int_0^{\Delta x} t(x)dx=V+\frac{(t_0-V)}{K\,\Delta x}(1-\exp(-K\,x)).\qquad(5)$$

The problem of stationary thermal conductivity for a hollow two-layered unbounded cylinder is as follows:

$$\frac{d^2 t_i(r_i)}{d\,r_i^2}+\frac{1}{r_i}\frac{dt_i(r_i)}{d\,r_i},\qquad i=1,2,\ R_{i-1}\le r_i \le R_i;\qquad(6)$$

$$\lambda_1\frac{d\,t_1(R_0)}{d\,r_1}-\alpha_1\,(t_1(R_0)-t_{c1})=0;\qquad(7)$$

$$\lambda_2 \frac{d\,t_2(R_2)}{d\,r_2} + \alpha_2\,(t_2(R_2) - t_{c2}) = 0; \qquad (8)$$

$$t_1(R_1) = t_2(R_1); \qquad \lambda_1 \frac{d\,t_1(R_1)}{d\,r_1} = \lambda_2 \frac{d\,t_2(R_1)}{d\,r_2}. \qquad (9)$$

Here, $t_i(r_i)$ is the temperature field of the i-th layer of the cylinder, ${}^\circ$C, as a function of the radial coordinate r_i, m; R_i is the outer radius of the i-th layer of the cylinder, m; λ_i is the thermal conductivity of the material of the i-th layer of the cylinder, W/(m·K); α_1, α_2 are the coefficients of heat transfer from the cylinder surfaces to the internal and external media, res pectively, W/(m²·K); t_{c1}, t_{c2} are the medium temperatures from the inner and outer sides, respectively, ${}^\circ$C.

The solution of the problem (6) – (9) has the form:

$$t_i(r_i) = A_i + B_i \ln(r_i) - \frac{q_i\,r_i^2}{4\lambda_i}, \qquad (10)$$

where

$$B_1 = \frac{t_{c2} - t_{c1} + V}{\ln\left(\frac{R_1}{R_0}\right) + \frac{\lambda_1}{\lambda_2}\ln\left(\frac{R_2}{R_1}\right) + \lambda_1\left(\frac{1}{R_2\,\alpha_2} + \frac{1}{R_0\,\alpha_1}\right)}; \qquad (11)$$

$$A_1 = t_{c1} + \frac{q_1 R_0}{2}\left(\frac{R_0}{2\lambda_1} - \frac{1}{\alpha_1}\right) - B_1\left(\ln(R_0) - \frac{\lambda_1}{\alpha_1 R_0}\right); \qquad (12)$$

$$B_2 = \frac{\lambda_1}{\lambda_2}\,B_1 + \frac{R_1^2\,(q_2 - q_1)}{2\lambda_2}; \qquad (13)$$

$$A_2 = t_{c2} + \frac{q_2 R_2}{2}\left(\frac{R_2}{2\lambda_2} + \frac{1}{\alpha_2}\right) - B_2\left(\ln(R_2) + \frac{\lambda_2}{\alpha_2 R_2}\right); \qquad (14)$$

$$V = \frac{q_2}{4\lambda_2}\left(R_2^2 - R_1^2\right) - \frac{R_1^2}{2\lambda_2}(q_2 - q_1)\ln\left(\frac{R_2}{R_1}\right) + \frac{q_2 R_2}{2\alpha_2} - $$

$$- \frac{R_1^2}{2\alpha_2 R_2}(q_2 - q_1) + \frac{q_1}{4\lambda_1}\left(R_1^2 - R_0^2\right) + \frac{q_1 R_0}{2\alpha_1}. \qquad (15)$$

The problem of stationary thermal conductivity for a hollow single-layered unbounded cylinder is as follows:

$$\frac{d^2 t(r)}{d r^2} + \frac{1}{r}\frac{d\,t(r)}{d\,r} = 0, \qquad R_1 \le r \le R_2; \qquad (16)$$

$$\lambda \frac{d\,t(R_1)}{dR} - \alpha_1\,(t(R_1) - t_{c1}) = 0; \qquad (17)$$

$$\lambda \frac{d\,t(R_2)}{dR} + \alpha_2\,(t(R_2) - t_{c2}) = 0. \qquad (18)$$

Here $t(r)$ is the temperature field of the cylinder, ${}^\circ$C, as a function of the radial coordinate r, m; R_1, R_2 are the inner and outer radii of the cylinder, respectively, m; λ is the thermal conductivity of the cylinder material, W/(m·K); α_1, α_2 are the coefficients of heat transfer from the cylinder surfaces to the internal and external media, respectively, W/(m²·K); t_{c1}, t_{c2} are the medium temperatures from the inner and outer sides, respectively, ${}^\circ$C.

The solution of the problem (16) – (18) has the form:

$$t(r) = A\ln(r) + B; \qquad (19)$$

$$B = t_{c1} + A\left(\frac{\lambda}{\alpha_1 R_1} - \ln(R_1)\right); \qquad (20)$$

$$A = \frac{t_{c2} - t_{c1}}{\dfrac{\lambda}{\alpha_2 R_2} + \dfrac{\lambda}{\alpha_1 R_1} + \ln\left(\dfrac{R_2}{R_1}\right)}. \qquad (21)$$

The longitudinal heat flow in the vessel wall is determined on the basis of mathematical modeling of the longitudinal temperature distribution in the corresponding structural element.

$$\frac{d^2 T(x)}{d x^2} - k^2\,T(x) = 0; \qquad (22)$$

$$T(0) = t(0) - \frac{m}{k^2}; \qquad (23)$$

$$\frac{d\,T(L_x)}{d x} = 0; \qquad (24)$$

$$k^2 = \alpha_1 + \alpha_2; \quad m = \frac{(\alpha_1 t_1 + \alpha_2 t_2)}{\lambda\,h}; \quad T(x) = t(x) - \frac{m}{k^2}. \qquad (25)$$

Here, x is the spatial longitudinal coordinate, m; $T(x)$ is the temperature field, ${}^\circ$C; t_1, t_2 are the ambient temperatures, ${}^\circ$C; λ is the coefficient of thermal conductivity of the structural material W/(m·K); α_1, α_2 are the coefficients of convective heat transfer from the external surfaces of the structural element to the environment, W/(m2·K); L_x is the length of the section considered in the heat flow direction, m; h is the thickness of the structural element, m.

The solution of problem (22) – (24) has the form:

$$T(x) = C_1\,\text{ch}(k\,x) + C_2\,\text{sh}(k\,x), \qquad (26)$$

where

$$C_1 = t(0) - \frac{m}{k^2}; \qquad (27)$$
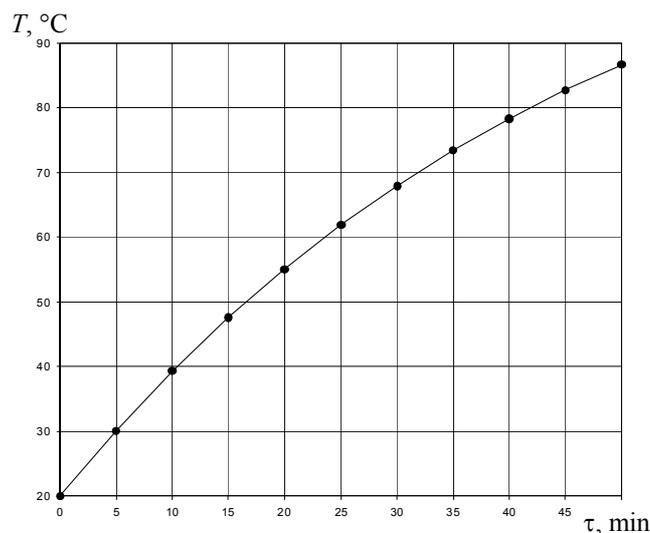
$$C_2 = -C_1\,\text{th}(k\,L_x). \qquad (28)$$

Fig. 1. Temperature changes in the reactor

Fig. 2. Change in temperature by the relative length
of the half-tube (0–1) as a function of time (0–50 min)

Thus, the calculation of the temperature field of the device for the current time interval includes a multiple solution of the above-mentioned heat conduction problems with subsequent consideration of all the components of the local heat balance. An iterative algorithm involving multiple uses of the solutions of the problems considered is due to the necessity of matching the temperature fields of the interacting components of the system through the appropriate boundary conditions.

In the modeling and design of the capacitive reactor, two main tasks can be distinguished, which include the calculation of the non-stationary temperature field:

– determination of the non-stationary temperature field in the working area according to the geometric dimensions of the reactor, the coolant flow and the initial temperature distribution in all the reactor elements;

– determination of the conditions and design parameters ensuring the functioning of the capacitive reactor. This task is solved most often.

The adequacy of the mathematical model of the capacitive reactor was verified by comparing the calculated data with the results of experiments carried out under laboratory conditions. The deviation of the experimental values from the calculated values does not exceed 10 %. Taking into account the results of the calculation of the non-stationary temperature field in the half-tube casing (number of approaches-4, number of turns in the approach-2), a rector for preparing a nanodispersed suspension was designed to functionalize CNTs having a weight of 300 kg, with the AMT-300 oil used as coolant.
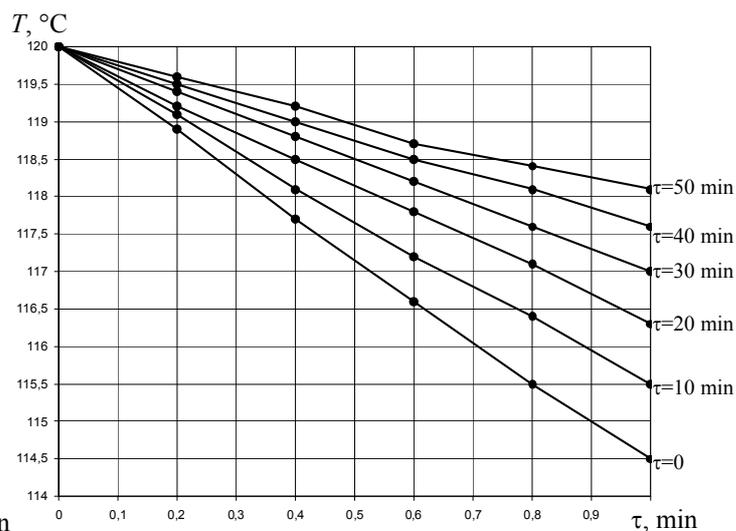
Fig. 1 demonstrates the calculated temperature changes in the reactor resulting from the calculation (abscissa axis – time, min, ordinate axis – temperature, °C).

The graph shown in Fig. 2 indicates a high uniformity in the heating of the nanodispersed medium and a relatively fast beginning of the conditions (the abscissa axis is the relative length of the half-tube approach, and the ordinate axis is the temperature, °C).

At the initial moment of time, the temperature difference was 5.5 °C for the entire half-tube length, whereat after 50 min, at the time of the beginning of the conditions, it was only 1.8 °C due to the heating of the structure.

Conclusions

When using a capacitive device, a large number of operations are carried out for processing liquid products: heating, cooling, aging of liquids; distillation of volatile fractions; chemical transformations; dissolution of granular and bulk materials; mixing of liquids; and partial loading of components. In real production processes, various combinations of these operations take place. As a rule, all of them occur in non-stationary temperature conditions. The design of the half-tube casing makes it possible to control the temperature conditions in the reactor by disconnecting the section (approach) both at full and partial loading of the reactor volume.

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