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REPORT
ON RESEARCH WORK

Small-scale energy-saving modules with the use of multifunctional devices with intensive hydrodynamics for the production, modification and encapsulation of granules

DEVELOPMENT AND CREATION OF RESEARCH EQUIPMENT FOR MODULATION AND / OR ENCAPSULATION UNITS OF GRANULES WITH DIFFERENT FLUIDIZED BED CONFIGURATION, CARRYING OUT OF TESTING

(intermediate)

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ABSTRACT

Report on research work: 42 p., 18 figures, 1 table, 3 references.

NANOPOROUS STRUCTURE, AMMONIUM NITRATE, HUMIDIFICATION, VORTEX GRANULATOR, TWO-COMPONENT FERTILIZERS, POROUS STRUCTURE, MICROPORES AND MACROPORES, POROSITY, EFFECTIVE COEFFICIENT OF THERMAL CONDUCTIVITY, TEMPERATURE PROFILE, HEATING TIME, TEMPERATURE REGIME.

Research object – hydrodynamic and heat-mass transfer characteristics of the target and supporting processes in the granulation modules with intensive hydrodynamics.

The aim of the research is a theoretical description and experimental study of the equipment for the production of monodisperse droplets from solutions and melts with vibrating influence on the melt stream and the granulation and drying of mineral fertilizers in the devices with active hydrodynamics.

The following new scientific results were obtained during the research:

1. A theoretical model of the conditions for the formation of the porous structure of ammonium nitrate granules and the application of an organic shell in a vortex granulator has been created. The influence of the porosity of the granules on the intensity of heat transfer in them is shown.

2. Experimental data of research conditions of formation of the porous structure of granules of ammonium nitrate in the vortex granulator are received. The influence of hydrodynamic and thermodynamic conditions of the process implementation on the peculiarities of the formation of the porous structure in the granule of porous ammonium nitrate (size, depth, the shape of pores, relative porous surface, etc.) is established.

3. The experimental data of research of the drying of granules of porous ammonium nitrate in multistage shelf devices is received. The influence of the

construction of perforated shelf contacts on the residence time of the granules in the apparatus and the morphology of the granule's porous surface is shown.

4. Data on the effect of wetting intensity of ordinary ammonium nitrate granules on the nanoporous structure of granules are obtained. The compositions of solutions for the stage of wetting the granules are proposed.

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INTRODUCTION

Report section "Introduction" is prepared in according to data [1] and references in this work.

The granulated ammonium nitrate has been widely used in agriculture as an effective nitrogen fertilizer. The native industry produces an ordinary ammonium nitrate by the proven technologies, which have been improved for more than fifty years. At the same time, the ammonium nitrate is used as a component of the industrial explosive substance ANFO (ammonium nitrate / fuel oil) in the industry. Such ammonium nitrate, called porous ammonium nitrate (PAN), differs significantly by its properties from the ordinary ammonium nitrate. The ordinary ammonium nitrate can also be a component of ANFO, however, it has several disadvantages:

1. The ordinary ammonium nitrate is covered with a special shell, which prevents the premature dissolution of the granules after its addition into the soil. The protective shell prevents access to the inner pores of the granules.

2. The ordinary ammonium nitrate can be chalked, causing a significant reduction (and, in fact, loss) of the ability to explode in a mixture with diesel fuel.

3. The ordinary ammonium nitrate does not have sufficient porosity for successful retention of the diesel fuel distillate inside the granule.

4. The ordinary ammonium nitrate has a certain number of pores, but their nature is mechanical, not modifying. These are the pores that are obtained as a result of the destruction of the granules (cracks, chips, caverns). Such pores are large enough (10^{-6}-10-4 m) and it is difficult to hold the diesel fuel distillate (when transporting ANFO to the blasting places, the diesel fuel distillate flows out of the granule and ideally stays on the surface, at worst - leaves the surface of the granule).

The production of PAN from the ordinary ammonium nitrate by the method of humidification and heat treatment (the method is one of the most energy-efficient and environmentally safe) requires special hydrodynamic and thermodynamic conditions, as well as rational selection of the type and construction of the main technological equipment in granulation. The main task of the technology to produce PAN from the ordinary ammonium nitrate is to form a network of nanopores on the granule surface and in the surface layers, keeping the strength of the core. Vortex granulators have the following advantages:

- the possibility significantly to reduce the overall dimensions (in particular, the height) of the workspace due to the variable height of the cross-sectional area and the possibility of internal circulation of the seeding agent;
- control of the granules' residence time in the workspace;
- the ability to control the motion of granules in the workspace;
- the possibility to create intensive turbulence in the workspace;
- universality (the ability to carry out granulation and drying processes in one device);
- processability and ease of production;
- possibility of fast adjustment and change of constructive and technological parameters if necessary.

1 THERMODYNAMIC CALCULATION OF VORTEX GRANULATOR OPERATION FOR PRODUCING OF AMMONIUM NITRATE WITH NANOPOROUS STRUCTURE

This report section is prepared in according to data [2] and references in this work.

According to the previous studies in the field of PAN granules production, thermodynamic and hydrodynamic conditions (temperature, gas velocity, time of contact of the granules with hot gas (air) environment) are the main factors which form the porous structure. In addition, having removed the bulk of the moisture and having formed the pores, the granules need to undergo some drying process to ensure the required strength. Otherwise, the granules can significantly lose their strength.

Thus, in the calculations, it is necessary to predict the kinetics description of granule heating and to determine the minimum drying time, the value of which exceeds the required time to warm the granules to the desired temperature.

The granule is a spherical body with pores, the peculiar size of which is the radius R and in terms of the physicochemical properties in the calculations - the structure of the granule’s substance (including, moisture content as the main index).

In order to describe the influence of the thermodynamic parameters of the gas flow on the humidified granule, a physical model was investigated. It is based on the following principles:

- the selected diameter of the granules is determinant for the entire set of granules in the workspace, i.e. the formation of the porous structure in the granules with the selected diameter preferably defines the porous structure of the entire granules flow;

- the granule is washed by a stream of gas (air) which has a constant temperature.

Thus, one may accurately assume that the surface temperature of the granules during the whole residence time in the workspace will be constant;

- due to the fact that the granules are small in size from 1 mm to 4 mm, and the vast majority of granules obtained at nitrogen plants, are granules in size from 2 mm to

3 mm, we can suppose that due to the hygroscopicity of the granules, the humidification process should be minimized. So, one may presuppose that moisture saturation occurs along the radius according to a linear law;

- the pore-formation starts consecutively from the top layer. The pore-formation front moves along the radius of the granule to its centre, representing a spherical surface;

- evaporating moisture is freely removed from the granule through the formed pores in the previous layers of the substance with a larger diameter, “external” layers (these layers are located closer to the surface of the granule) which form the granule;

- the proportionality of the formed pores in the granules with the steam extracted from moisture is the reason for the fact that the retention capacity of the granules is greater than the moisture content.

Based on the above assumptions, it is possible to create a mathematical model to determine the basic hydro- and thermodynamic parameters, the effect of which enables it to create a porous structure in the granules.

The temperature distribution in the PAN granule is described by the differential equation:

$$\frac{d}{d\tau}(rT(r,\tau)) = a\left(\frac{d^2}{dr^2}(rT(r,\tau))\right) \tag{1}$$

where r – current radius, a – thermal diffusivity coefficient.

The solution of this equation will be the following:

$$T(r,\tau) = T_C - (T_C - T_0)\times \\ \times\left(\sum_{n=1}^{\infty}\left(\frac{2(\sin(n\pi) - n\pi\cos(n\pi))R\sin\left(\frac{n\pi r}{R}\right)e^{\left(\frac{n^2\pi^2 a\tau}{R^2}\right)}}{(n\pi - \sin(n\pi)\cos(n\pi))rn\pi}\right)\right). \tag{2}$$

As a result of the drying process, the diameter of the granules increases due to the modification transitions and the porous structure formation.

Thus, the granule together with the heat transfer agent will be heated to a predetermined temperature, and only then the moisture will be removed. This factor increases the total required residence time of the granules in the device. The calculations of the above mathematical model showed that 8 seconds are required to complete the heating process of the granules with d = 2 mm at a temperature of 20 ° C - 120 ° C in a stream of heat transfer agent with a temperature up to 120°. If we perform a gradual calculation taking into account that with the introduction of granules or moistening the heat transfer agent is cooled, then gradual heating of the granules to a temperature of 120 ° will take a time interval 3-3.5 times longer than in the previous case. The results of experimental studies of the workspace heating kinetics in the vortex granulator under different conditions, which are given below, make the basis to determine the heat transfer agent's temperature with the gradual heating of the granules simultaneously with the heat transfer agent's flow.

Based on the value dm of dry substance, the weight of the elemental volume dV of granules, taking into account the presence of moisture, is

$$dm = \rho_{gr}(1 + U(r,\tau))r^2 \sin\theta d\theta d\phi dr\ , \tag{3}$$

where $dV = r^2 \sin\theta d\theta d\phi dr$ - elementary volume value.

On the other hand, the mass of "dry" granule with radius R in general is

$$Msr = 2\int_0^R \int_0^\pi \int_0^\pi \rho_{gr} r^2 \sin(\Theta) d\Theta d\phi dr\ , \tag{4}$$

or after integrating

$$Ms = \frac{4}{3} \cdot \rho_{gr} \cdot \pi \cdot R^3 . \tag{5}$$

Given the fact that *U* is a function from *r* and drying time τ

$$Mg_{n=\infty}(\tau) = \frac{4}{3}\rho_{\text{г}} \times \\ \times \left(1 + \frac{\int_0^R U_p + \left(U_0 - U_p\right)\left(\sum_{n=1}^{\infty} \left(\frac{2(\sin(n\pi) - n\pi\cos(n\pi)) R \sin\left(\frac{n\pi r}{R}\right) e^{\left(-\frac{n\pi m\tau}{R}\right)}}{(n\pi - \sin(n\pi)\cos(n\pi)) r n\pi} \right)\right) dr}{R} \right) \pi R^3 \tag{6}$$

where *m* – diffusion coefficient.

Besides, the above equation takes into account the fact that the moisture content of the granule takes some average value, which is calculated based on the integral properties.

The calculations show that the sum of the first two components is significant in solving the differential equation describing the mass transfer during the drying process. Further calculation of the sum leads to a change in the result obtained in the seventh digit of the fractional part. Based on this conclusion, it is possible to calculate the first two coefficients of the sum. Thus, the equation to determine the change in humidity over time takes the following form

$$Us(\tau) = \frac{\int_0^R U_p + (U_0 - U_p \left(\frac{2R\sin\left(\frac{\pi r}{R}\right) e^{\left(-\frac{\pi^2 m\tau}{R^2}\right)}}{\pi r} - \frac{R\sin\left(\frac{2\pi r}{R}\right) e^{\left(-\frac{4\pi^2 m\tau}{R^2}\right)}}{\pi r} \right) dr}{R} \tag{7}$$

Integrating the obtained formula, it is possible to receive a dependency to find the mass of the granules at any time during the drying process

$$Mg(\tau)=\frac{4}{3}\rho_c\pi R^3\times$$

$$\times\left(1+\frac{\int\limits_0^R U_p+\left(U_0-U_p\right)\left(\frac{2R\sin\left(\frac{\pi r}{R}\right)e^{\left(-\frac{\pi^2 m\tau}{R^2}\right)}}{\pi r}-\frac{R\sin\left(\frac{2\pi r}{R}\right)e^{\left(-\frac{4\pi^2 m\tau}{R^2}\right)}}{\pi r}\right)dr}{R}\right)+$$

$$+2R\left(\sum_{n=1}^{\infty}\left(\frac{\sin\left(\frac{n\pi r}{R}\right)(-\sin(n\pi)+n\pi\cos(n\pi))e^{\left(-\frac{n^2\pi^2 m\tau}{R^2}\right)}}{(n\pi-\sin(n\pi)\cos(n\pi))n}\right)U_p)dr. \quad (8)$$

Within the framework of the scientific work vortex granulator stand to obtain PAN granules (fig. 1) is used.

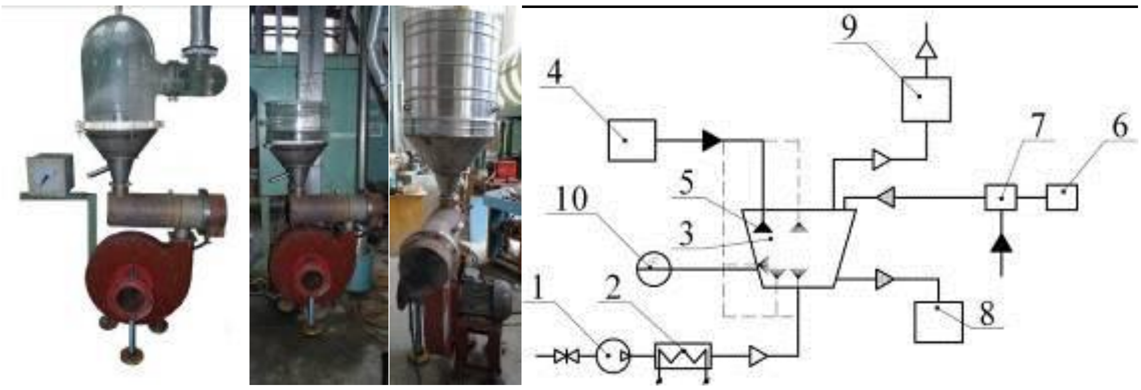


Fig. 1. The unit of the study on hydrodynamics of the vortex granulator workspace, thermodynamic conditions to obtain granules (with different configuration of the workspace): 1 - gas blower; 2 - heater; 3 - vortex granulator; 4 - container for preparation of the humidifier; 5 - nozzle; 6 - container of granules; 7 - container of pre-humidification (used when moistening); 8 – container for finished granules; 9 - the degree of purification of outgoing gases (bubbler); 10 - recording potentiometer. The dashed line shows the variants of the nozzle installation.

Devices and equipment:

– determine the hydrodynamic features of the flows motion – TES 1340 Hot-Wire Anemometer;

– temperature measurement in air heater – self-recording-register potentiometer;

– measurement of granulator workspace temperature – thermal imager Fluke Ti25;

– measurement of moisture granules – Multimeter DT-838;

– study of the microstructure of granules – microscope KONUSPIX-450X KONUS, scanning electron microscope VEGA3 XM and X-ray spectrometer with an energy dispersion.

The results of the experimental study of the drying agent's temperature field in the vortex granulator workspace are presented in Fig. 2,3. It should be noted that with the increase of the flow twisting degree one can observe the alignment of the temperature field in the granulator workspace. Intensification of the flow motion (turbulization due to the directed vortex movement) lets to distinguish an "active" zone, where the heat treatment process occurs with maximum intensity in the device.

Based on literature data, the heat-mass transfer processes occur with the highest intensity in the so-called "active" zone (heat-mass transfer zone, directly above the gas distribution device of the granulator or dryer with a fluidized bed. The height of this zone with the same features of the heat transfer agent depends on the type of gas-distributing device. Varying the design of the gas-distributing device (degree of the drying agent's flow twisting), it is possible to achieve an increase in the height of the "active" zone to that height of the zone of the predominant vortex motion of the granules.

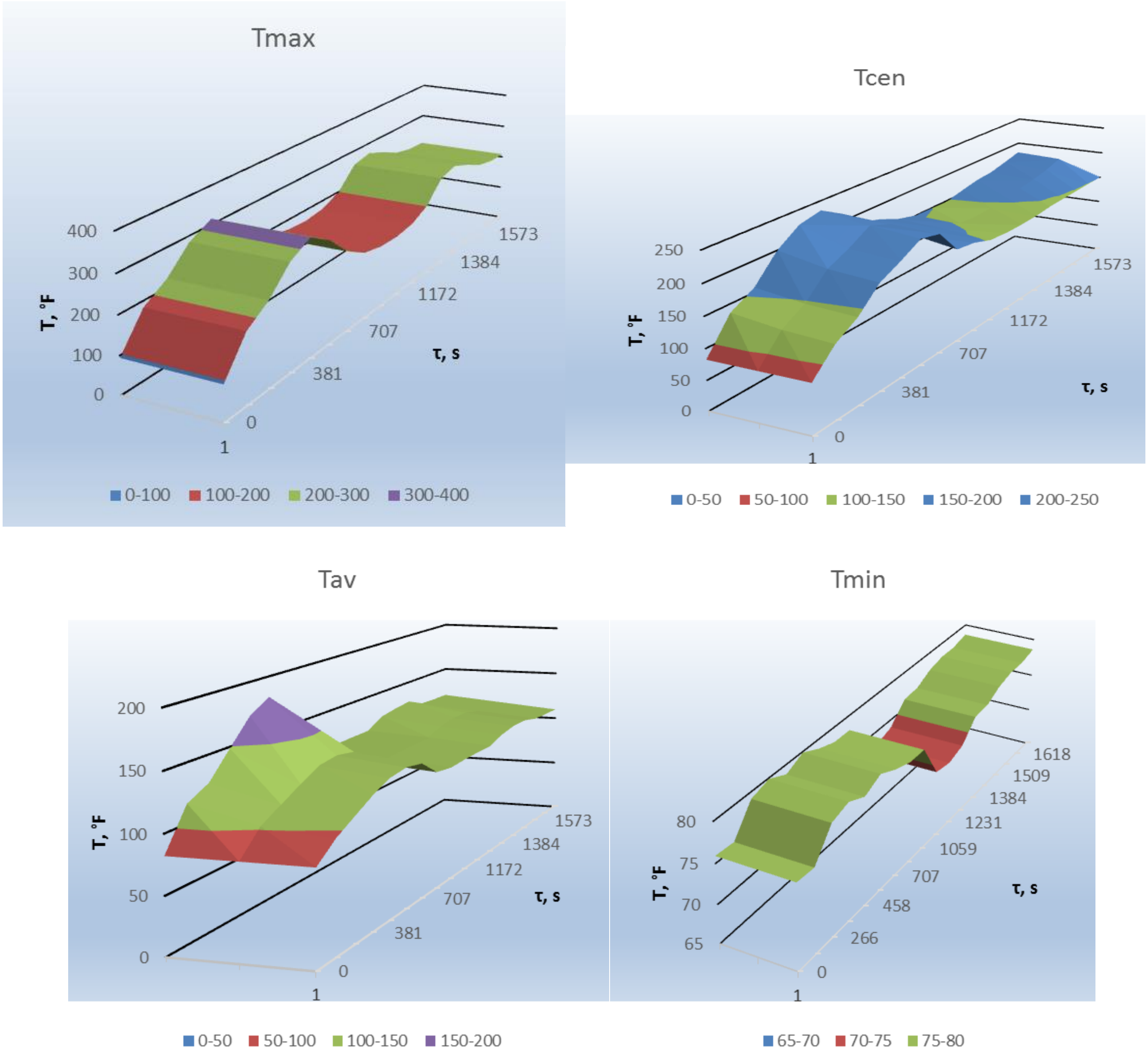
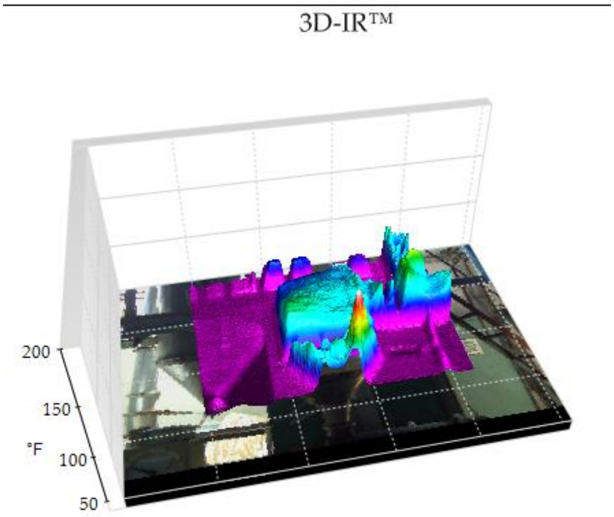


Fig. 2. Dynamics of the temperature change in the vortex granulator workspace depending on the intensity of solubilizer (drying agent) twisting (circular velocity of the drying agent 5.2-8.1 m/s) Temperature of the liquid agent: T_{min} - minimum temperature; T_{max} - maximum temperature; T_{av} - average temperature; T_{cen} - temperature in the center. Granule injection time is 650 s.



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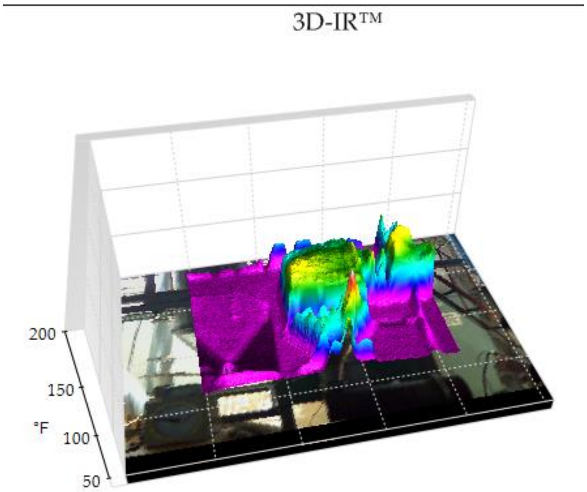


b

Fig. 3. Data of thermal imaging studies of the vortex granulator workspace: a - access to the operating mode; b - operating mode

In order to confirm the experimental law regarding the temperature distribution in the vortex granulator workspace, in this work, a computer modelling of the temperature field of the twisted flow of a drying agent was carried out. The modelling results are presented in fig. 4. Satisfactory convergence between the experiment and modelling results in the operating (steady) mode of the vortex granulator operation is pointed out.

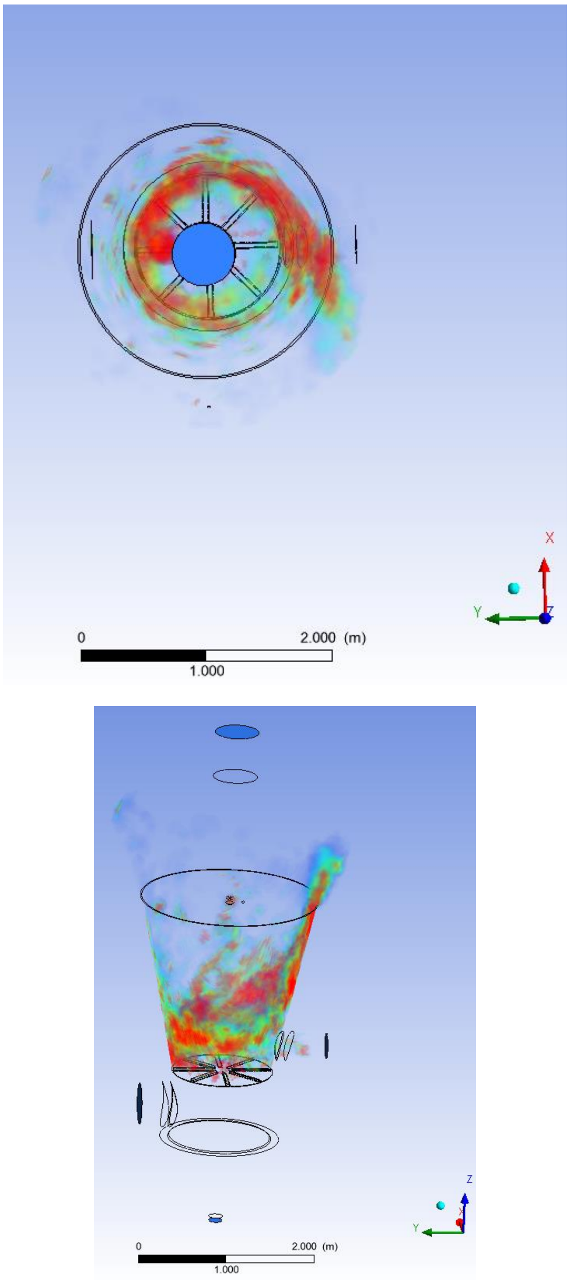
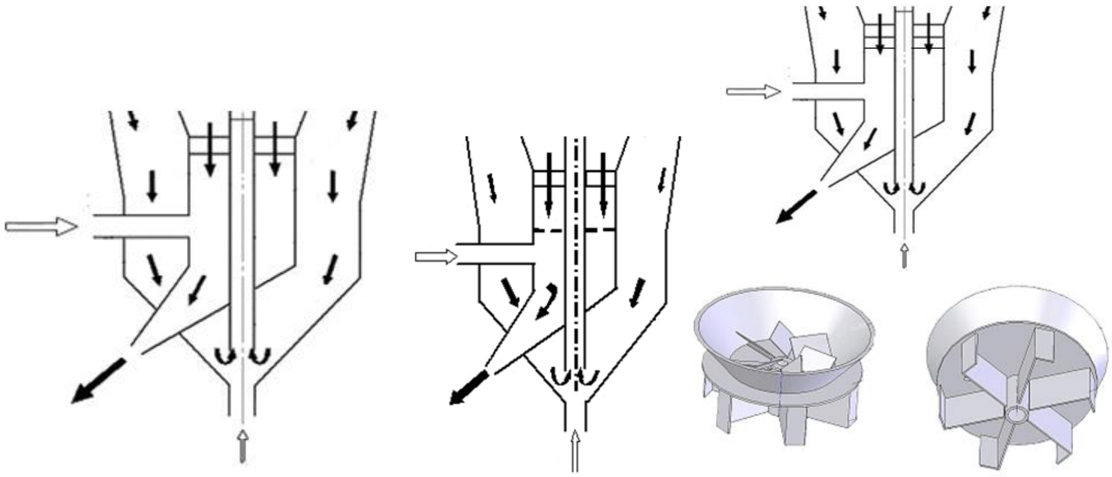


Fig. 4. The computer modelling results regarding the drying agent temperature field in the vortex granulator workspace

The model for calculation of the granule heating and drying kinetics proposed in the first section of the chapter, and the results to determine the drying agent's temperature field in a vortex granulator, let to carry out the thermodynamic calculation of the nanoporous structure obtaining process in the PAN granule. The received data of the temperature field are introduced to the calculation formulas in order to define the required time of the heat treatment process of PAN granules. Further, this paper presents constructive solutions regarding the methods to stabilize the drying agent's vortex flow, as well as the research findings of the nanoporous granule structure (nanoporous structure obtained at different twisting velocities of the drying agent).

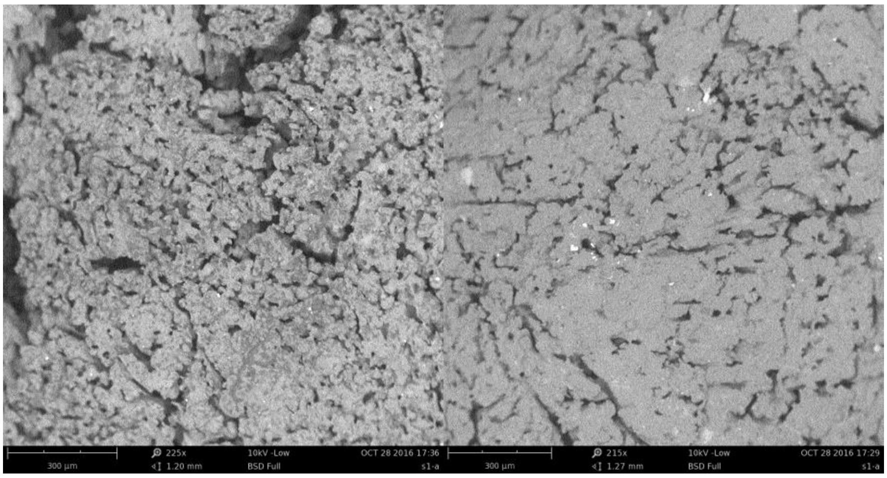
Fig. 5 demonstrates the construction of the gas-distributing unit in the vortex granulator without stabilization and with the stabilization of the drying agent's flow. The introduction of additional knots in the vortex granulator's construction practically does not complicate the production of the device and does not increase its price. However, as you can see below, such constructive solutions have a significant effect on the quality of the nanoporous surface in the PAN granules.



a b c

Fig. 5. The construction of the gas-distributing units in the vortex granulator: a - without stabilization of the drying agent 's flow motion; b - with stabilization grid under the vortex gas-distributing unit; c - with a two-stage swirler.

The nanoporous surface microscopy is performed in two steps. At the first stage, the effect of the temperature field (at different degrees of the drying agent's twisted flow in the same range as in fig. 2) on the nanoporous structure is investigated. The results of this microscopy are shown in fig. 6. The granules are obtained in a vortex granulator without stabilizing the drying agent's vortex flow.



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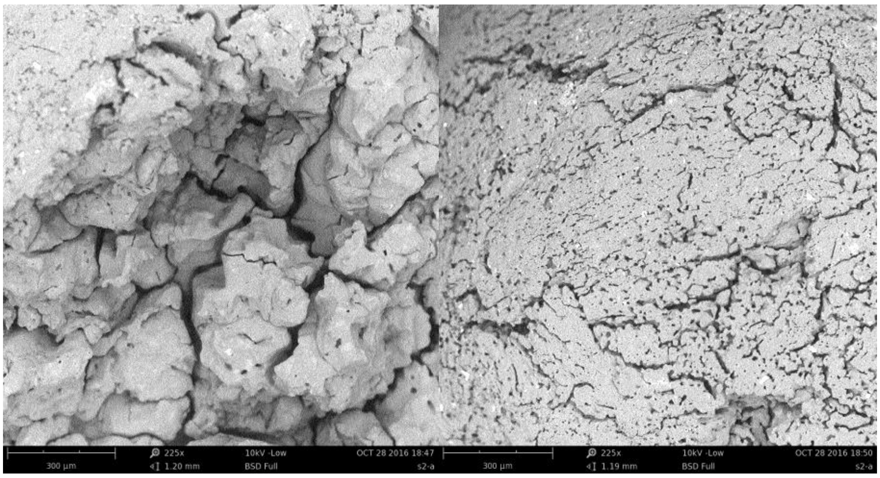

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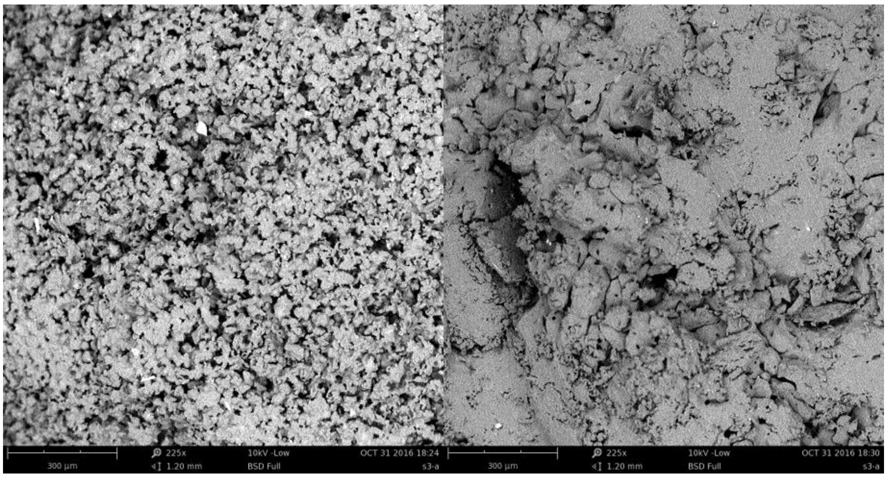
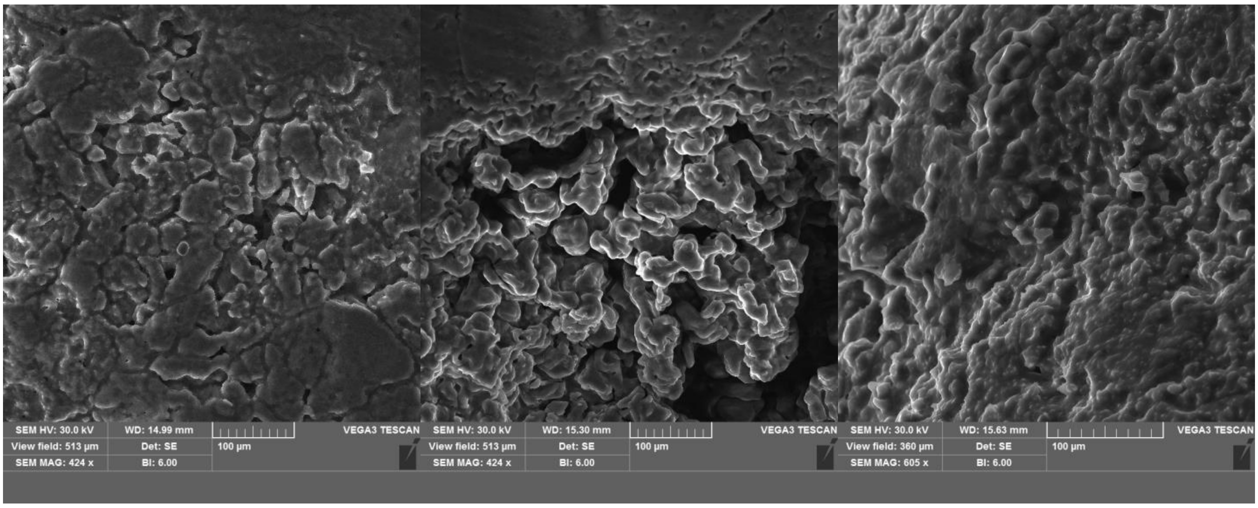


c

Fig. 6. Microscopy of the nanoporous surface in the granules obtained at different temperature distributions in the vortex granulator (according to fig. 2): a - circumferential velocity of 5.2 m/s; b - circumferential velocity of 6.5 m/s; c - the circumferential velocity 8.1 m/s. Left photo - PAN granule obtained in the "active" zone of the granulator, right photo - PAN granule obtained over the "active" granulator zone

Data analysis fig. 6 confirms the assumption that the best quality of the nanoporous layer is obtained in the vortex granulator's "active" zone. You can also clearly see an increase in the relative area of the nanoporous surface of the PAN granule with an increase in the degree of the drying agent flow twisting. A further increase in the drying agent's twisting causes damages in the granule caused by the intensive collision of the granules with each other and with the walls in the granulator. Besides, an increase of the drying agent twisting degree over 8.1 m/s leads to an increase in heat loss in the granulator's "active" zone through the wall of the device. Data from fig. 6 shows that the relative area of the nanoporous surface can be increased. Therefore, at the second stage of the research is devoted to the microscopy of granule samples obtained in granulators with stabilization of the drying agent's vortex flow. The results of these studies are presented in fig. 7.

Fig. 7 confirms the assumption about improving the nanoporous surface quality in the PAN granule due to the rational selection of a method to stabilize the vortex flow of a drying agent.



a b c

Fig. 7. Microscopy of the nanoporous surface of the granules obtained by using various methods of stabilizing the drying agent's vortex flow: a - granulator with a stabilization grid under the vortex gas-distributing unit; b - granulator with a two-stage swirler.

The data of experimental studies to define the relative area of the nanoporous surface in the PAN granule are summarized in Table 1.

Table 1 Identification of the relative area in the nanoporous surface of the PAN granule

Stabilization type	The relative area of the porous surface, m^2/m^2, at					
	V=5,2 m/s		V=6,5 m/s		V=8,1 m/s	
	in the "active" zone of the granulator	above the "active" zone of the granulator	in the "active" zone of the granulator	above the "active" zone of the granulator	in the "active" zone of the granulator	above the "active" zone of the granulator
Without stabilization	0.36	0.25	0.39	0.28	0.41	0.3
Granulator with stabilization grid under the vortex gas-distributing unit	-	-	-	-	0.45	-
Granulator with two-stage swirler	-	-	-	-	0.48	-

Note: the “-” sign indicates the fields for which the studies were not carried out in view of determining the optimal conditions for the process to obtain the nanoporous layer on the PAN granule at the previous stages in the research

2 EFFECT OF TEMPERATURE ON FORMATION OF NANOPOROUS STRUCTURE OF GRANULE SHELL

Report section "Introduction" is prepared in according to data [3] and references in this work.

The two-layer granule with an organic shell is a solid core, that is, the primary granule of nitrogen fertilizers namely ammonium nitrate or urea. In the process of granulation in a fluidized bed, a layer of organic suspension, such as chicken manure, is applied on the core. By thermal drying of the granule outer shell, one obtains a porous shell of a certain structure. Size of pores, shape of their surface and nature of the curves, porosity of the shell depends on the temperature of the gas flow and duration of granules heating.

The process of heat transfer inside the granule, assuming its spherical shape, is described by the Fourier differential heat equation:

$$\frac{\partial t(r,\tau)}{\partial \tau} = a_T \left(\frac{\partial^2 t(r,\tau)}{\partial r^2} + \frac{2}{r} \frac{\partial t(r,\tau)}{\partial r} \right), \tag{9}$$

where $t\,(r,\tau)$ is granule temperature at a point with the current radius r during the time τ, °C; r – current radius of the granule, m; a_T – coefficient of thermal conductivity of the granule material, m^2/s; τ – granule heating time, s.

The well-known solution of equation (9) at:

initial conditions (the initial temperature distribution over volume of the granule is considered to be uniform)

$$\tau > \tau_0, 0 < r < R, t(r,\tau_0) = f(r); \tag{10}$$

symmetry conditions

$$t(0,\tau) \neq \infty, \frac{\partial t(0,\tau)}{\partial r} = 0; \tag{11}$$

boundary conditions of the third kind, providing for the equality of heat flows from the gas to the surface of the granule and from it into the middle of the core

$$\lambda_T \frac{\partial t(r,\tau)}{\partial r} = \alpha\left[t(r,\tau) - t_{med}\right], \tag{12}$$

look like:

$$\frac{t_{med} - t(r,\tau)}{t_{med} - t_i} = \sum_{n=1}^{\infty} A_n \frac{\sin\left(\mu_n \frac{r}{R}\right)}{\mu_n \frac{r}{R}} \exp\left(-\mu_n^2 \cdot Fo\right), \tag{13}$$

where t_i is the initial temperature of the granule, °C; t_{med} – temperature of the gas medium, °C; R – granule outer radius, m; Fo – Fourier criterion; A_n, μ_n – constant and root of the equation, $A_1=f(Bi)$, $\mu_1=f(Bi)$; Bi – Biot criterion; λ_T – thermal conductivity coefficient of the particle material, W/(m·K).

Since the process of granule heating during granulation is quite long ($Fo \geq 0.3$), the infinite series in equation (5) quickly converges and we can restrict ourselves to only the first member of the series (n=1) in this equation.

Then equation (13) takes the form:

$$\frac{t_{med} - t(r,\tau)}{t_{med} - t_i} = A_1 \frac{\sin\left(\mu_1 \frac{r}{R}\right)}{\mu_1 \frac{r}{R}} \exp\left(-\mu_1^2 \cdot Fo\right). \tag{14}$$

Equation (14) makes it possible to determine the temperature profile by the granule radius when it is heated with gas from the surface to the center of the granule. Then from equation (6), temperature of the granule along its current radius is:

$$t(r,\tau) = t_{med} - (t_{med} - t_i) A_1 \frac{\sin\left(\mu_1 \frac{r}{R}\right)}{\mu_1 \frac{r}{R}} \exp\left(-\mu_1^2 Fo\right). \tag{15}$$

Since the granules are small in size, within 1–4 mm, to determine the temperature profile it is enough to determine the temperature on the surface of the granule, in the center of the granule and the average integral in the volume of the granule.

In the first case, assuming $r=R$ (granule surface) from equation (15) we obtain the expression for determining the temperature on the granule surface

$$t_P(r,\tau) = t_{med} - (t_{med} - t_i) A_1 \frac{\sin \mu_1}{\mu_1} \exp\left(-\mu_1^2 Fo\right). \tag{16}$$

In the second case, assuming $r \to 0$ (center of the granule) from equation (15) we obtain the expression for determining the temperature in the center of the granule

$$t_C(r,\tau) = t_{med} - (t_{med} - t_i) A_1 \exp\left(-\mu_1^2 Fo\right). \tag{17}$$

Using the formula for the integral average temperature in the volume of the granule

$$t_{ia}(\tau) = \frac{3}{R^3} \int_0^R r^2 \cdot t(r,\tau)\, dr. \tag{18}$$

in the third case, one obtains the expression for determining the volume-averaged temperature of the granule:

$$t_{ai}(r,\tau) = t_{med} - (t_{med} - t_i) \frac{6A_2}{\mu_1^2} \exp\left(-\mu_1^2 Fo\right). \tag{19}$$

The rate of granules heating and, accordingly, the rate of temperature profile change according to formula (15), is also determined by the thermal conductivity value of the granule material. This parameter is included in the Biot criterion and in the Fourier criterion through the thermal conductivity coefficient.

It is important to present a significant picture of the thermal conductivity of the granule material dependence on the structural characteristics of the porous shell. Structure diagram of the two-layer granule “solid core – porous shell” (fig. 8) provides that the solid core occupies 70 % of the granule’s volume, and the porous layer – 30 % of the volume.

Based on the presented structure of the two-layer granule, it follows that the thermal conductivity of the granule material is not the same: the thermal conductivity is lower in the porous shell than that in the solid core, since in the porous layer the heat transfer by thermal conductivity decreases due to pores filled with gas. That is, in a porous shell, the resulting coefficient of thermal conductivity is always less than the corresponding coefficient in a solid body. This is explained by the following reasons:

1) part of the outer layer is covered with gas pores, wherin thermal conductivity of gas is considerably lower than the coefficient of thermal conductivity of a continuous body. Therefore, the heat flow taken relative to cross-sectional area of the porous shell forms a certain fraction of the flow that would be transported in the absence of pores in the shell. This fraction is equal to the fraction of the free section of the total number of pores, that is, the porosity of the layer;

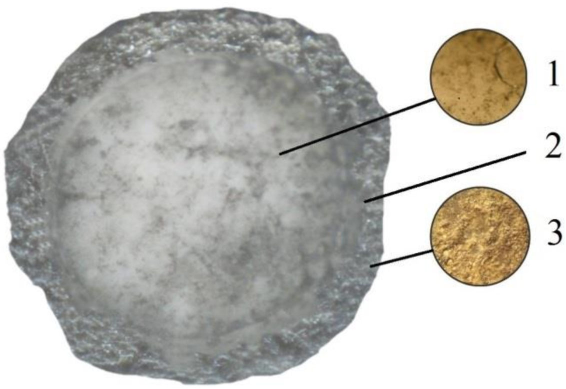


Fig. 8. Structure of organo-mineral granules: 1 – mineral core (urea); 2 – transition section; 3 – dry organic shell (chicken manure).

2) since pores are of irregular geometric shape, namely in the form of channels, alternating narrowing and expansion zones of the pore cross sections, additional resistance to heat transfer by thermal conductivity arises;

3) wavy porous channels lengthen the path of heat transfer by thermal conductivity through the gas layer;

4) the smaller the pore size, the greater the number of pores per unit volume of the granule with the same total porosity. It reduces value of the thermal conductivity coefficient.

Considering the above, the modified coefficient of “limited” thermal conductivity through the porous layer is

$$\lambda_{CT} = \frac{\lambda_E}{k_{sh} \cdot k_w \cdot k_p}, \tag{20}$$

where λ_E is the effective coefficient of thermal conductivity, depending on the porosity of the layer ε, $\lambda_E = f(\varepsilon)$, $0<\varepsilon<1$; k_{sh} – pore shape coefficient; k_w – coefficient of pore weaving; k_p – pore size coefficient.

Thermal conductivity of the porous layer is an effective value that is intermediate between the thermal conductivity of the granule solid core and the thermal conductivity of the gas contained in the pores.

One proceeds from the simplified model of Kriescher, according to which the porous body in the section is alternating layers of a solid body and gas layers. In this case, the heat flow moves both parallel to the layers and perpendicular to them.

In the first case, one obtains:

$$\lambda_E = (1-\varepsilon)\,\lambda_T + \varepsilon\lambda_G. \tag{21}$$

In the second case:

$$\lambda_E = \frac{\lambda_T \cdot \lambda_G}{(1-\varepsilon)\lambda_G + \varepsilon\lambda_T}, \tag{22}$$

where λ_T, λ_G – thermal conductivity of the granule material and gas in the pores, respectively, W/(m·K).

Then the average value of the effective thermal conductivity is

$$\lambda_E = \frac{0,5\left[(1-\varepsilon)\lambda_T + \varepsilon\lambda_G)\right]\left[(1-\varepsilon)\lambda_G + \varepsilon\lambda_T\right] + \lambda_T\lambda_G}{(1-\varepsilon)\lambda_G + \varepsilon\lambda_T}. \tag{23}$$

Analyzing equations (21)–(23), it can be seen that with increasing porosity of the layer, the thermal conductivity value decreases. Clarification of the nature and rate of this decrease is of a great interest, since thermal conductivity of the solid granule skeleton is tens of times higher than thermal conductivity of the gas inside pores. For example, mineral solid component parts of granules have thermal conductivity in the range of 0.15–0.45 W/(m·K), and thermal conductivity of air at 0°C is equal to 0.024 W/(m·K). Thermal conductivity of air is theoretically the lowest limit of the porous layer thermal conductivity. Values of the thermal conductivity coefficient can approach this limit when the heat transfer in the granule is minimized due to the presence of only touch contacts between the adjacent sections of the solid skeleton, i.e., in a layer with high porosity. These touch contacts have significant thermal resistance to heat transfer. Influence of the main solid skeleton is insignificant. Only at low porosity influence of continuous contact can be decisive, since a significant part of the heat flow is transferred inside the granule by its solid constituent parts.

Thus, taking into account these features, it should be noted that values of the coefficients k_{sh}, k_w, k_p included in formula (20) should be greater than 1.

Formulas (20) and (23) are used to determine the surface temperature of a two-layer granule according to equation (16) and the temperature profile within $0.7R<r<R$ according to equation (15). When determining temperature in the center of the granule with equation (17) of the temperature profile for $r<0.7R$ using equation (15), the thermal conductivity λ_T of the granule solid component is taken into account. When determining the volume-averaged temperature of a two-layer granule according to equation (19), the reduced thermal conductivity coefficient according to the equation is:

$$\lambda_R = 0,7\lambda_T + 0,3\lambda_E. \tag{24}$$

The results of mathematical modeling are obtained in comparison for a continuous granule with porosity ε=0 and a porous granule with values of $0.1 \le \varepsilon \le 0.7$.

The graph (fig. 9) shows the dependence $S_S=f(d_p)$, according to the equation

$$S_S = \frac{2\varepsilon}{d_p \cdot \rho_g}, \tag{25}$$

where S_S is the total specific pore surface, m^2/kg; ε – granule porosity, $0<\varepsilon<1$; d_p – equivalent pore size, m; ρ_g – density of the granule material, kg/m^3.

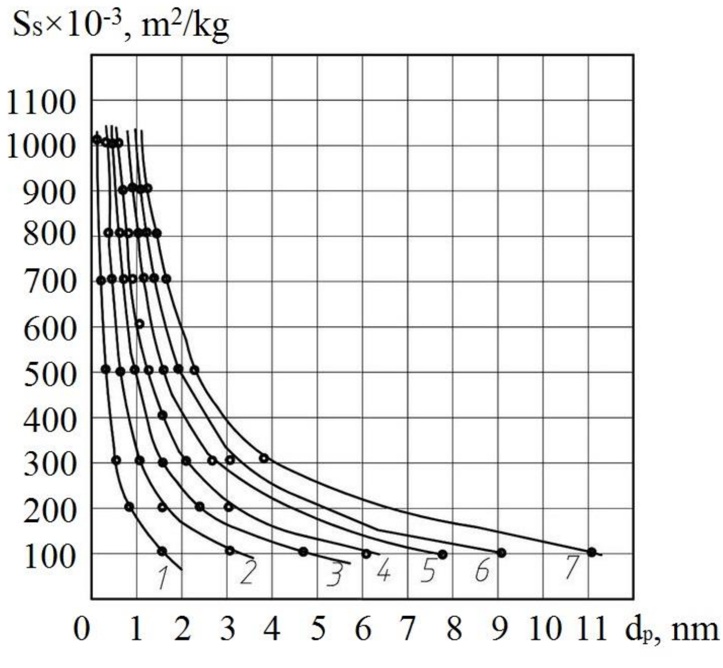


Fig. 9. Dependence of the specific pore surface on pore size: *1* – ε = 0.1; *2* – ε = 0.2; *3* – ε = 0.3; *4* – ε = 0.4; *5* – ε = 0.5; *6* – ε = 0.6; *7* – ε = 0.7.

Graphs of the dependence $S_S=f(d_p)$ show definite relationship between the specific surface of pores with their size and granule porosity. With the specific pore surface in the range (100–1000)·10^{-3} m^2/kg and with ε=0.1–0.7, we have micropores with a size d_p=0.2–10 nm. With the decrease of the specific surface of pores to less than 10·10^{-3} m^2/kg and at ε>0.5–0.7, there appear intermediate pores (mesopores) of size d_p=50–100 nm and we approach the initial boundary of appearing macropores of size d_p>100 nm.

Dependence of the effective coefficient of the granule thermal conductivity on its porosity, according to equation (23), first shows a rapid decrease of the thermal conductivity coefficient value during transition from the continuous structure of the granule (ε=0) to the beginning of the porous structure formation (ε=0.1), and then a proportional decrease in thermal conductivity within the change in the porosity of the granule $0.1<\varepsilon<0.7$.

The volume-averaged temperature of granule heating to a certain temperature is defined as

$$t = t_{med} - \left(t_{med} - t_i\right)\frac{6A_2}{\mu_1^2}\exp\left(-\mu_1^2\frac{\lambda_E\cdot\tau}{c\cdot\rho\cdot R^2}\right), \tag{26}$$

and granule heating time

$$\tau_h = \frac{R^2\cdot c\cdot\rho}{\lambda_E\cdot\mu_1^2}\ln\left[\frac{6A_2}{\mu_1^2\left(\dfrac{t_{med}-t}{t_{med}-t_i}\right)}\right]. \tag{27}$$

where in addition to the above designations, c – the specific heat of the granule, J/kg·K; ρ – granule density, kg/m^3.

The numerical values of the constants A_1, A_2 and the root μ_1 are found from the tables or graphically using the nomograms. This determination method makes it difficult to use a computer in an engineering calculation algorithm. Therefore, the authors using the least squares method processed the data of the monograph tables and obtained regression equations to determine the constants A_1, A_2 in the range $0.1<Bi<4.0$, which is typical for suspended and fluidized beds:

$$A_1 = 0.274(Bi) + 1.0, \text{ at } 0 < Bi \le 0.1; \quad (28)$$

$$A_1 = 0.29(Bi) + 1.0, \text{ at } 0.1 < Bi \le 1.0; \quad (29)$$

$$A_1 = 0.183(Bi) + 1.1, \text{ at } 1.0 < Bi \le 2.0; \quad (30)$$

$$A_1 = 0.13(Bi) + 1.22, \text{ at } 2.0 < Bi \le 4.0; \quad (31)$$

$$A_2 = 0.47(Bi) + 0.01, \text{ at } 0.1 \le Bi < 0.5; \quad (32)$$

$$A_2 = 0.325(Bi) + 0.06, \text{ at } 0.5 \le Bi < 1.0; \quad (33)$$

$$A_2 = 0.30(Bi) + 0.1, \text{ at } 1.0 \le Bi \le 2.0; \quad (34)$$

$$A_2 = 0.25(Bi) + 0.05, \text{ at } 2.0 < Bi \le 4.0. \quad (35)$$

Root μ_1 is determined:

$$\mu_1 = \frac{в + \sqrt{в^2 - 4c}}{2}, \quad (36)$$

or

$$\mu_1 = \sqrt{\frac{Bi^2}{A_2} - Bi^2 + Bi}, \quad (37)$$

where

$$в = \frac{2Bi}{A_1}; \qquad (38)$$

$$c = \frac{\left(Bi^2 - Bi\right)\left(2 - A_1\right)}{A_1}. \qquad (39)$$

Dependence of the granule heating time on its porosity, according to equation (27), shows a sharp increase in the heating time of the granule (approximately 2 times) during the transition from a continuous granule (ε=0) to a granule with initial porosity (ε=0.1). Then heating time gradually increases and granule porosity reaches the level 0.1 <ε<0.3; further rapid increase of granule heating time causes porosity in range 0.3<ε<0.6. The latter is caused by a significant decrease of areas of the granule solid skeleton, that have less resistance to the heat conductivity process. This is proved by the nature of curves in the dependence $t=f(\tau)$ (fig. 10) during heating of granules in the gas medium with an initial temperature of 65°C.

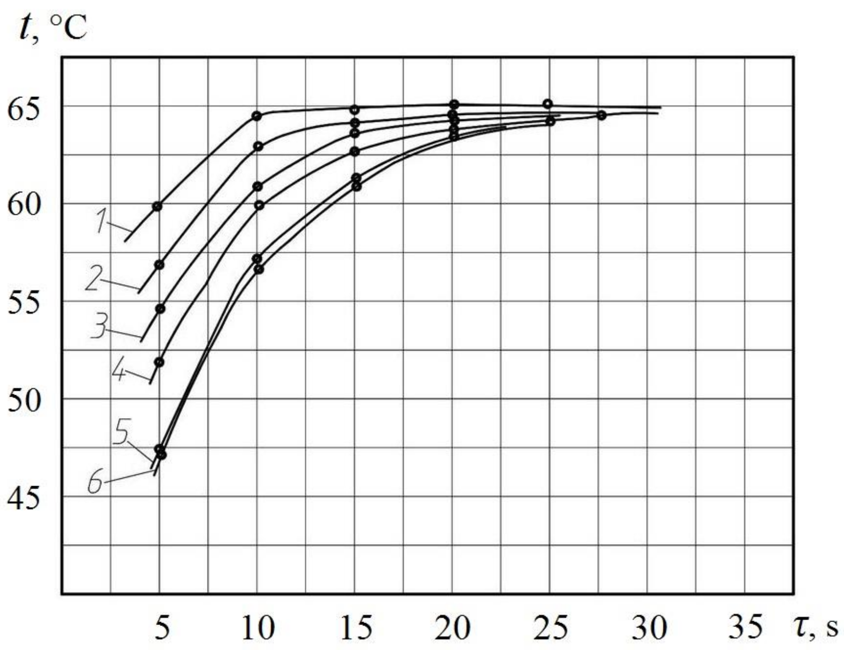


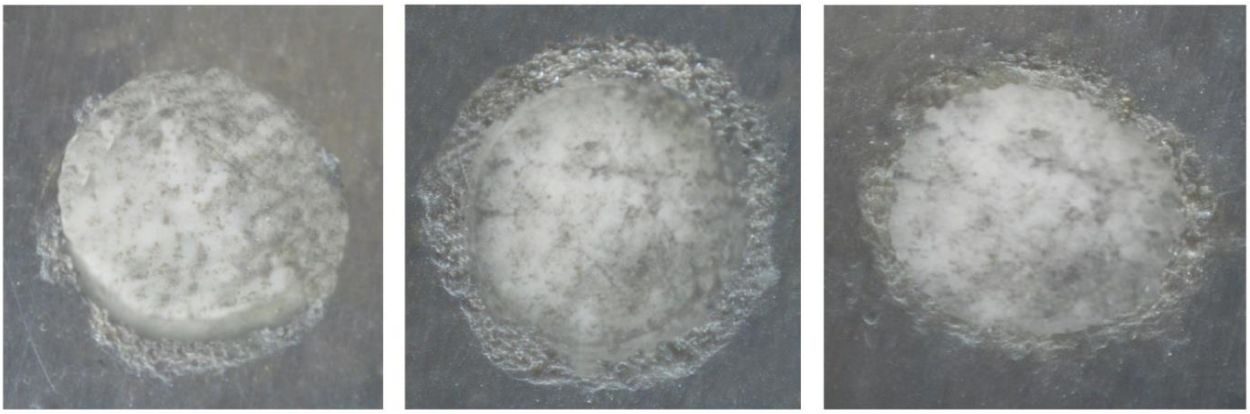
Fig. 10. Dependence of the granule heating temperature on time: *1* – ε = 0.1; *2* – ε = 0.2; *3* – ε = 0.3; *4* – ε = 0.4; *5* – ε = 0.5; *6* – ε = 0.6.

During laboratory studies film coating of an organic suspension was applied on mineral granules and temperature of gas medium in the fluidized bed of granules was maintained in the range of 40–80°C. The following temperature conditions of the granulation process were established experimentally:

1. At the temperature within 40–50°C, droplets of the suspension do not spread over the surface of the granule, but attach to one side of the granule, and form a big growth which is as big as a drop itself (fig 11,a).

2. When temperature of the fluidized bed is 60–65°C, droplets of the suspension spread over the surface of the mineral granules and liquid starts to evaporate intensively, forming a thin solid layer of dry organics (fig 11,b). As it can be seen from the graphs in Fig. 3, at 20–25 seconds of heating the granules, their temperature reaches 65°C and then remains constant, that is, the indicated value is the limiting temperature of granule heating. Moreover, the granule outer shell is of sufficiently dense structure with micro- and mesopores on its surface.

3. Increase of the fluidized bed temperature above the limiting value, namely, up to 70–80°C, causes the formation of irregular surface with deep cracks which is accompanied with chipping of organic substance in separate places of the granules and thus new organic cores appear (fig 11,c). The porosity of such granules increase, macropores are formed.



a b c

Fig. 11 Cut of the carbamide granule, encapsulated with chicken manure at the appropriate temperature: a – 40–50°C; b – 60–65°C; c – 70–80°C.

3 EFFECT OF THE INTENSITY OF AMMONIUM NITRATE GRANULES HUMIDIFICATION ON THE QUANTITATIVE AND QUALITATIVE COMPOSITION OF THE FINAL GRANULES NANOPOROUS STRUCTURE

This report section is prepared in according to data [2] and references in this work.

The pore structure of the finished PAN granules is effected by such indices as the type of humidifier, the degree of granules humidification and the heat treatment mode. In literature data, the dependence of the qualitative and quantitative features of the PAN granules porous structure on the type of humidifier is investigated. For laboratory tests, a laboratory a vortex granulator unit is used (fig. 12). The batch of the initial ammonium nitrate granules is heated to a predetermined temperature, then the granules are moistened (humidifier - water) and subsequent heat treatment is carried out (8 minutes at a temperature of a layer - 108 ° C, thermodynamic parameters are taken according to the results of previous studies). Samples of finished PAN granules are studied by microscope (scanning electron microscope eTescan Vega 3, formation of the carbon film on the granule surface - Carbon evaporation head CA7625 and SC7620 high resolution, manual Sputter Coater).

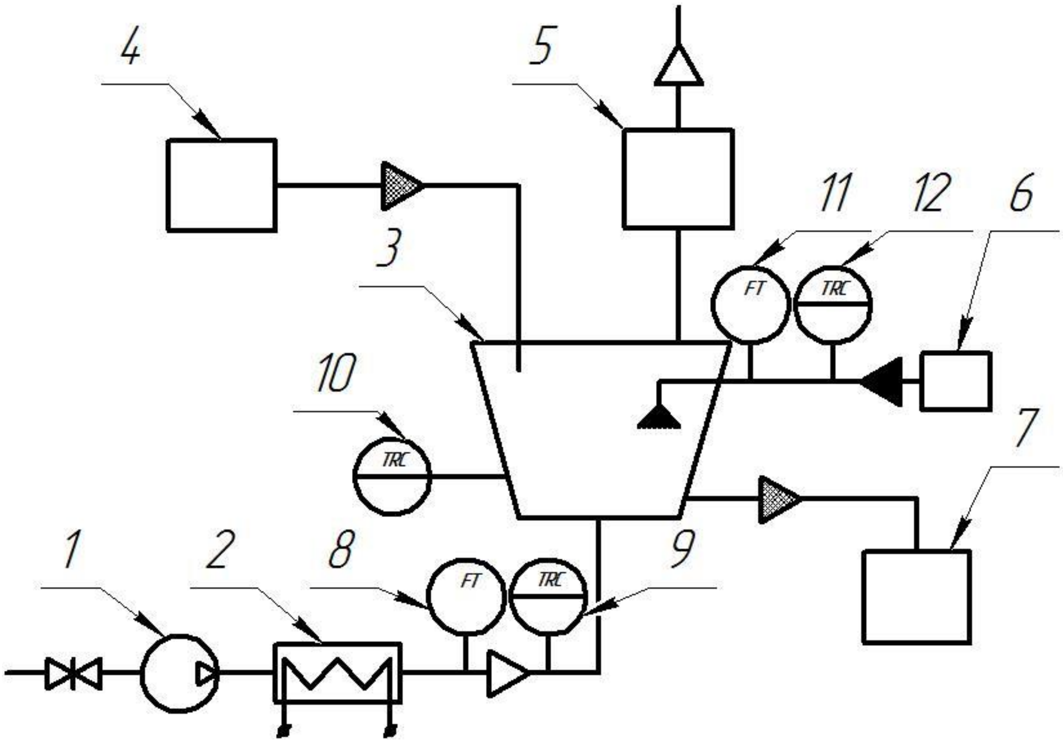


Fig. 11. The scheme of the laboratory vortex granulator unit: 1 – gas blower; 2 – heater; 3 – vortex granulator; 4 – container for granules; 5 – waste gas cleaning stage; 6 – container for preparation of humidifier; 7 – container of finished granules; 8 – automation device for measure the air flow; 9 – automation device for measure the temperature of air; 10 – automation device for measure the temperature of layer; 11 – automation device for measure the humidifier flow; 12 – automation device for measure the temperature of humidifier

It is important to determine the first and second critical velocities (the rate of fluidization beginning and the rate of the granules ablation) for the fluidized bed. The first critical velocity is calculated by the formula:

$$\omega_1 = \frac{\mathrm{Re} \cdot \mu_{fa}}{\rho_{fa} \cdot d} \tag{40}$$

where *Re* - the Reynolds criterion, μ_{fa} - the viscosity of the fluidizing agent, ρ_{fa} - the density of the fluidizing agent, and *d* - the diameter of the fluidized bed particles (PAN granules).

The Reynolds criterion is calculated by the formula:

$$\mathrm{Re} = \frac{Ar}{1400 + 5,22 \cdot \sqrt{Ar}} \tag{41}$$

where Ar – Archimedes criterion.

Archimedes criterion is calculated by the formula:

$$Ar = \frac{d^3 \cdot \rho_{fa} \cdot g \cdot \rho_{fbp}}{\mu_{fa}^2} \tag{42}$$

where ρ_{fbp} – density of the fluidized bed particles (PAN granules)

The second critical velocity is calculated by the formula:

$$\omega_2 = \frac{\mu_{fa}}{d \cdot \rho_{fa}} \cdot \left(\frac{Ar}{18 + 0,575 \cdot \sqrt{Ar}} \right) \tag{43}$$

At the stage of the granules humidification, their diameter remains the same, but the mass increases. It leads to an increase in the density of the granules ρ_{fbp}, to an increase in the value of the Archimedes criterion Ar, an increase in the values of the first and second critical velocities. Thus, humidifying the granules, it is necessary gradually to increase the solubilizer’s motion velocity.

The range of the granulator stable operation (critical velocities of fluidization) for a vortex fluidized bed of dry granules and granules humidified to a predetermined humidity, is calculated using the author's software product (fig. 12). The literature data also show the main hydrodynamic indices of a vortex granulator operation, used in the experimental and industrial production line of PAN.

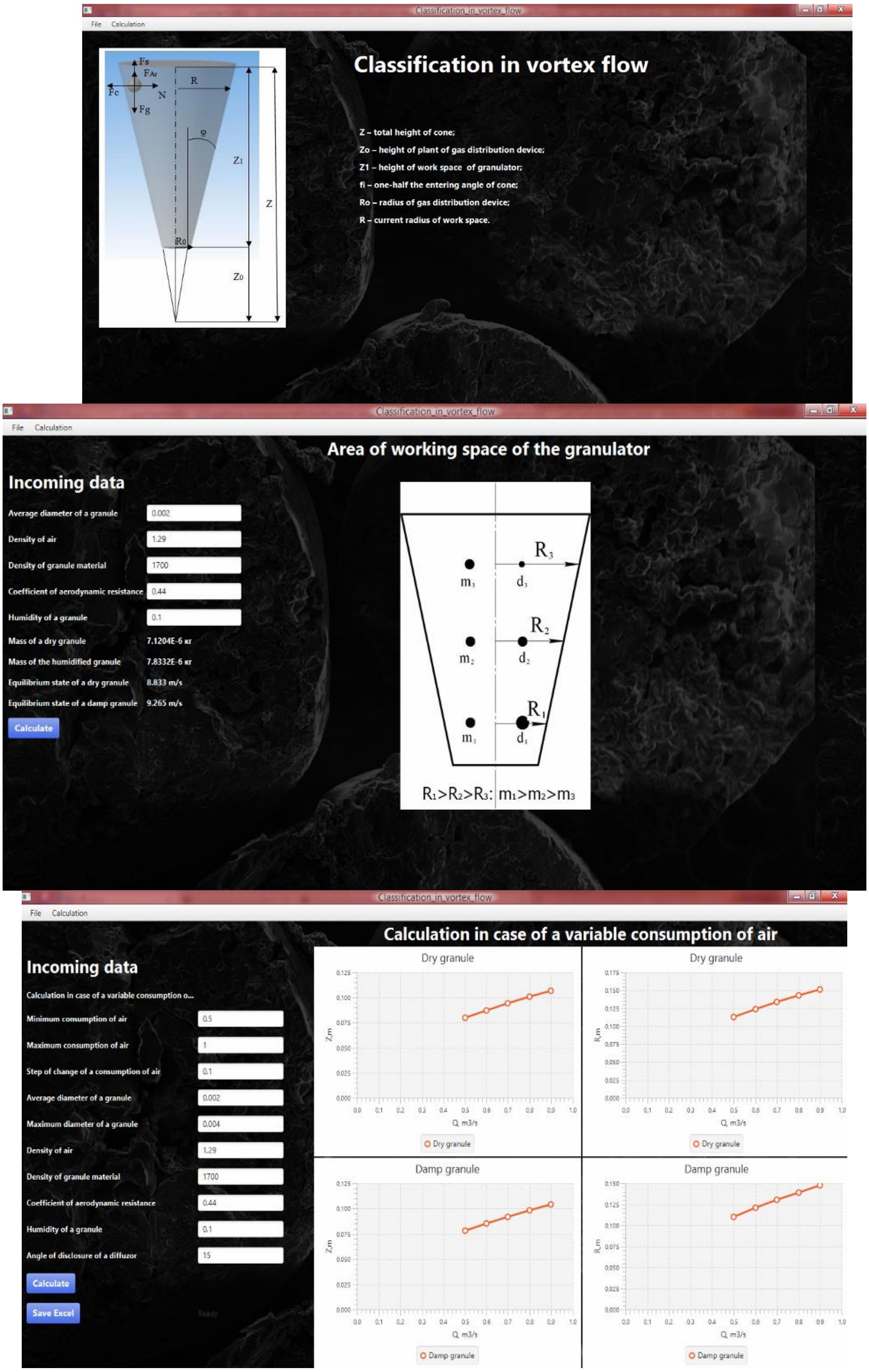


Fig. 12. The software product Classification in vortex flow© : calculation block for the vortex granulator stable operation range

Depending on the granules humidification mode during the modification of the PAN granules in the vortex granulator, the qualitative and quantitative features of the porous structure in the finished granules are changed.

During the tests and analysis of their results, the following humidification modes are distinguished (fig. 13):

- The uneven humidification mode (less than 50 g of water per 1 kg of ammonium nitrate granules);
- Optimal humidification mode (50 – 150 g of water per 1 kg of ammonium nitrate granules);
- High humidification mode (150 – 300 g of water per 1 kg of ammonium nitrate granules);
- Excessive humidification mode (more than 300 g of water per 1 kg of ammonium nitrate granules).

When using the uneven humidification mode, the finished PAN granules have an undeveloped porous structure (fig. 14). The number and size of pores of the finished granules do not almost differ from the initial granules. Under conditions of low humidity of the granules and their subsequent heat treatment, there are local areas with the melted surface.

Under conditions of the optimal humidification mode, the finished PAN granules have a developed porous structure with a large number of macropores (more than 50 nm) and mesopores (2 – 50 nm) (fig. 15). There are no areas with melted surface or local sections with undeveloped porous structure.

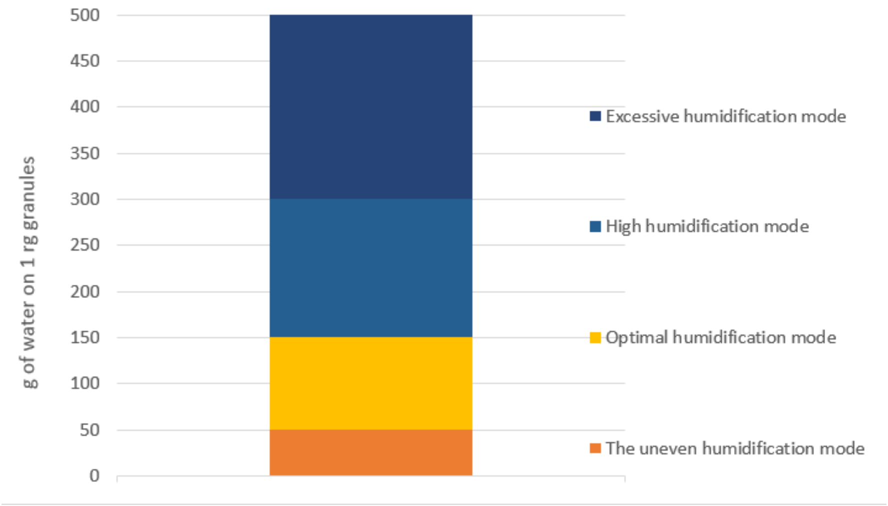
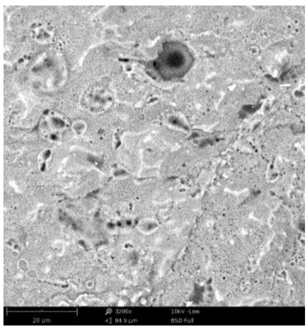


Fig. 13. Diagram of humidification modes (depending on the amount of humidifier)



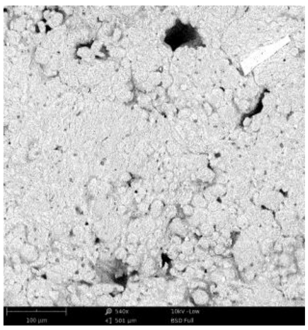
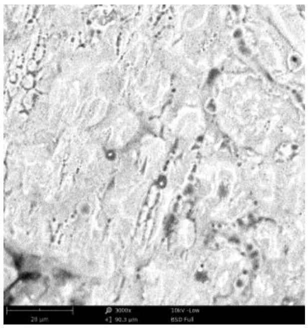


Fig. 14. The surface of the PAN granules (uneven humidification mode) with undeveloped porosity and local areas with a melted surface



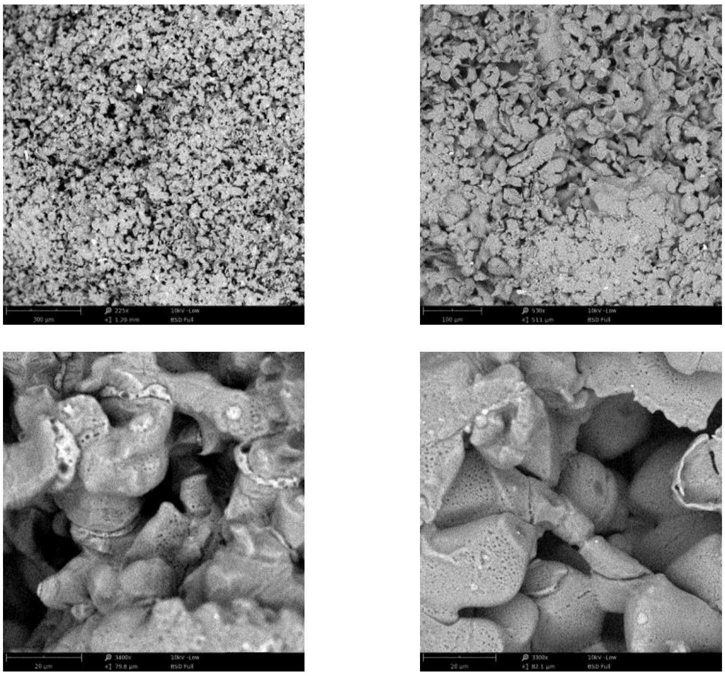


Fig. 15. The surface of the PAN granules (optimal humidification mode) with developed porous structure with macropores and mesopores

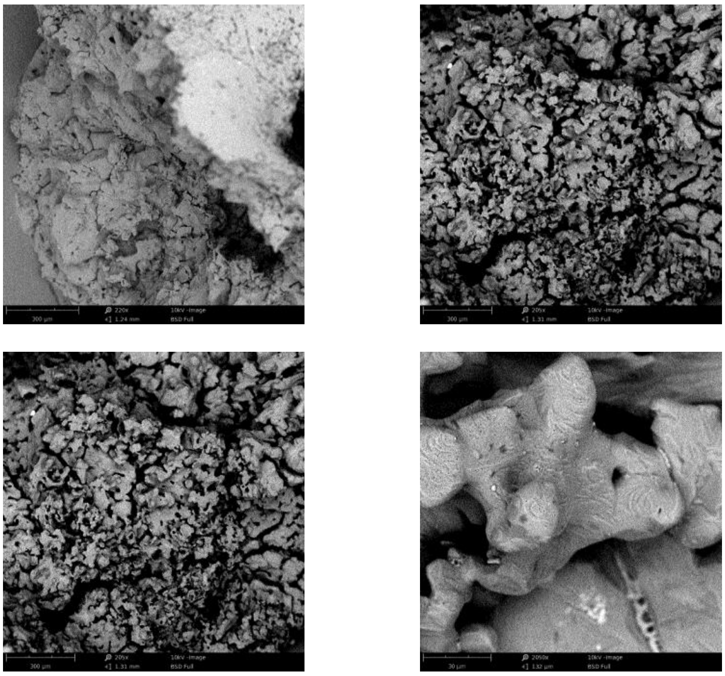


Fig. 16. The surface of the PAN granules (high humidification mode) with a lot of chips and cracks, granule agglomeration tendency

Further increase in the intensity of humidification (the high humidification mode) leads to the over-humidification of PAN granules. During subsequent heat treatment, significant destructive phenomena (cracks and chips) occur due to considerable pore-formation (fig. 16). Besides, increasing the moisture intensity, the tendency of granules to agglomeration increases, which impairs the qualitative features of the finished product.

When the intensity of the granules humidification increases, their destruction and partial dissolution occur. The fluidized bed of granules in the vortex granulator loses its stability and "falls", causing the necessity to stop the unit and clean it.

The graphical dependence of the qualitative and quantitative porosity features of the PAN granules on the moisture intensity is shown in fig. 17 (surface layers) and fig. 18 (inner layers).

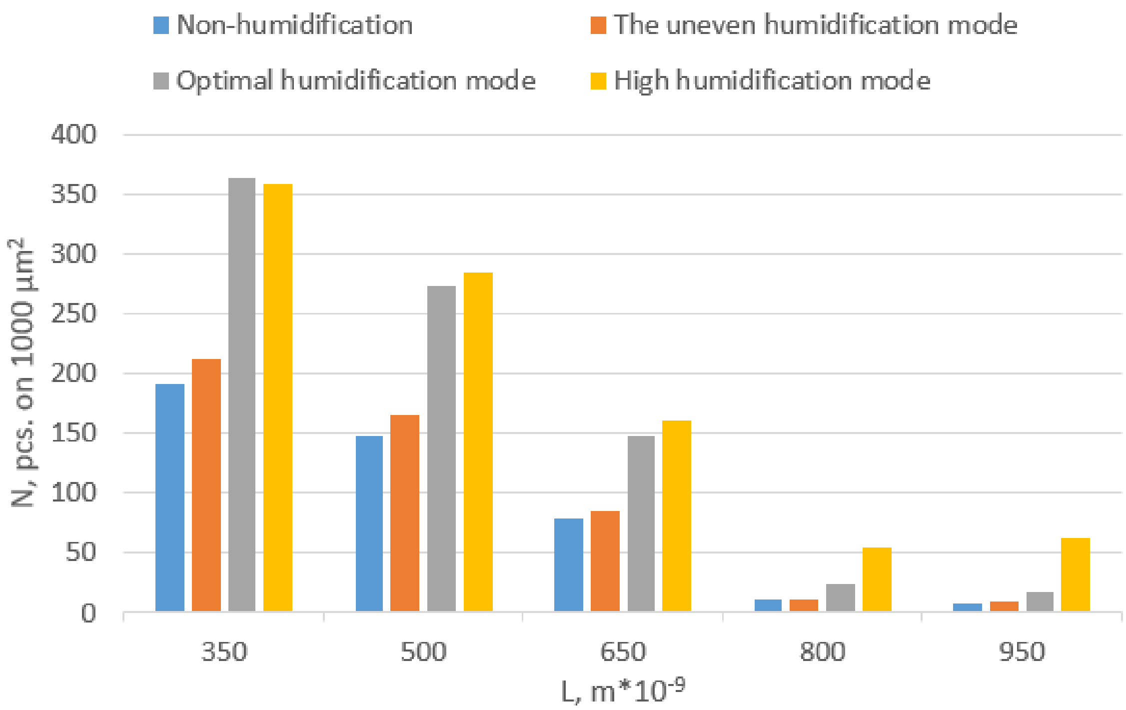


Fig. 17. Dependence of qualitative and quantitative features of PAN granules porosity on moisture intensity (surface layers)

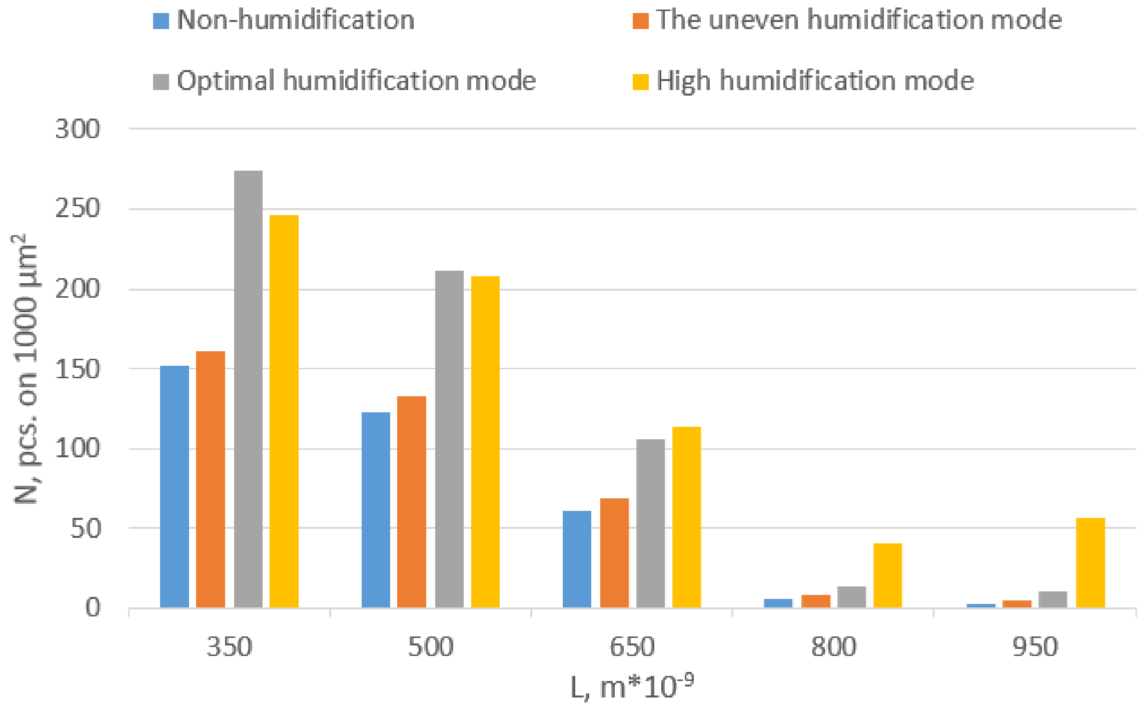


Fig. 18. Dependence of qualitative and quantitative features of PAN granules porosity on moisture intensity (inner layers)

CONCLUSIONS

This section is prepared in according to data [1-3].

The nanoporous structure quality of the PAN granules largely depends on the thermodynamic operation mode of the vortex granulator. Rational selection of the drying agent's flow twisting degree and the twisting stabilization method lets us achieve an extended network of nanopores on the surface in the granules, which provide access to the internal pores (where the diesel distillate will be retained). During the creation of an optimization calculation algorithm, the change in the nanoporous structure of the ammonium nitrate granule in the specified temperature ranges and the intensity of the fluidizing agent motion was taken into account. An optimal thermodynamic range (main modes) of the vortex granulator work which enables to obtain NH_4NO_3 granules with branchy net of pores with required size on the surface of the sample and inside it is proposed.

Nanoporous structure of organic fertilizer granules is described and the presence of micropores with a size of 0.2–10 nm and mesopores with a size of 50–100 nm in the solid skeleton of the granules are grounded. Influence of granule solid skeleton porosity on the process of its thermal conductivity during heating of the granule in a gas medium is shown. One proposed formulas for determining the effective coefficient of thermal conductivity depending on the porosity of the granule and true thermal conductivity coefficients of the solid skeleton and gas in the hollow sections of the granule. Decrease of heat conductivity with increasing of granule porosity is shown. Analytical expressions for determining of the temperature profile and granule heating time, taking into account its porosity are obtained. It is explained that high granule porosity cause increase of the heating time and decrease of the granule temperature.

In order to obtain PAN granules with a developed porous structure, it is necessary to use the optimal humidification mode, technological parameters of which are demonstrated in this research. If this mode is not kept, the humidification and heat treatment stages will be ineffective (the uneven humidification mode), or the commodity qualities of the finished product will be deteriorated (high humidification mode).

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