Methods for Controlling the Properties of Nanoporous Layers in Granules of Porous Ammonium Nitrate: Stage of Drying

N. O. Artyukhova, J. Krmela, V. Krmelova, and A. E. Artyukhov

1 Introduction

Porous ammonium nitrate (PAN) granules are obtained by the following methods [1–3]:

1. Granulation of melt in granulation towers with addition of pore-forming and modifying additives.
2. Heat treatment of granules.
3. Humidification and drying of the granules.

The main quality index of PAN is the absorptivity and retentivity to diesel fuel. Each of the noted methods provides the necessary value of these indices; at the same time, the environmental production indicators decrease (method 1), the strength of the granules is lost (method 2), the production scheme becomes more complicated (method 3).

N. O. Artyukhova (✉) · A. E. Artyukhov
Department of Marketing, Sumy State University, 2, Rymskogo-Korsakova Str., Sumy 40007, Ukraine
e-mail: n.artyukhova@pohnp.sumdu.edu.ua

A. E. Artyukhov
e-mail: a.artyukhov@pohnp.sumdu.edu.ua

J. Krmela
Department of Numerical Methods and Computational Modeling, Alexander Dubcek University of Trencin, 491/30, I. Krasku, 02001 Puchov, Slovak Republic
e-mail: jan.krmela@fpt.tnuni.sk

V. Krmelova
Department of Materials Technologies and Environment, Alexander Dubcek University of Trencin, 491/30, I. Krasku, 02001 Puchov, Slovak Republic
e-mail: vladimira.krmelova@fpt.tnuni.sk

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O. Fesenko and L. Yatsenko (eds.), *Nanomaterials and Nanocomposites, Nanostructure Surfaces, and Their Applications*, Springer Proceedings in Physics 263, https://doi.org/10.1007/978-3-030-74741-1_13

A promising technique for obtaining PAN is to combine the heat treatment and humidification of granules in small-sized vortex granulators.

The main advantages of the PAN granules production in a vortex flow are:

- reduction of the residence time for granules in the workspace of the device and maintaining their strength properties;
- quantity reduction of heat treatment cycles for granules;
- combination of the humidification and drying stages in one device;
- classification of granules by size;
- decrease in the overall dimensions of the granulation equipment.

It is necessary to predict theoretically how the granule will be warmed up and moisture will be removed to obtain a high-quality porous structure. This mathematical model enables determining the conditions for uniform heat treatment and drying of granules in the hot heat transfer agent's flow.

Although there are many studies devoted to PAN production (e.g. [1–6]), they do not observe the nanoporous structure of the surface and deep layers of the granule. The granule absorptivity depends on the pore size on the surface of the granule. The retentivity of the granule depends on the size of the internal pores. The correct selection of the technology for obtaining PAN allows providing a given pore size on the surface and inside the granule.

One should note that the destruction of a granule can also occur at the stage of nanoporous structure formation during humidification and heat treatment, for example, in vortex granulators [7–11]. Despite the satisfactory results after introducing vortex granulators into the PAN production technology, the object of research includes the mechanisms for controlling the residence time of a granule in the workspace of this device. In this work, the authors continue the research on introducing the drying stage to eliminate the possible overheating of the granule and its collision with other granules and the wall of the device in the swirling heat transfer agent's intense flow. The necessity to introduce the final drying stage using multistage shelf units [8, 12, 13] is substantiated in works [14, 15]. The choice of this type of dryer is based on a comparative analysis of modern methods of effective dewatering of dispersed materials and effective two-phase systems such as fluidized bed [16–20].

The additional drying stage in the decreasing velocity regime in the active (but less turbulized) hydrodynamic mode will make it possible to achieve the following changes in the nanoporous structure of granules (in comparison with an undried sample):

- an increase in the number of micropores and mesopores of curvilinear configuration;
- an increase in the share of curvilinear macropores in the total number of nanopores;
- an increase in the surface nanopores depth.

These changes increase the retentivity rate of the granule and the reliable retention time of the diesel distillate in the granule.

The thermodynamic conditions to produce the PAN granules have a decisive effect on the nanoporous structure, features of pores, their number, relative porous surface area, etc. Based on the importance of this index, the authors modeled the thermodynamic operating conditions of a gravitational shelf dryer at the final drying stage.

Principal scheme of the PAN obtaining unit with the use of equipment with highly turbulized flows is shown in Fig. 1.

The target technological processes in PAN production are heat treatment of the ordinary ammonium nitrate after humidification and the PAN final drying, significant secondary process—cleaning of the waste drying agent before its release into the atmosphere or utilization. Given this, basic algorithm of the granulation unit's calculation (technological scheme of the unit is shown in Fig. 2) will be based on the defining of technological operation conditions and constructive characteristics of the vortex granulator (VG), gravitational shelf dryer (GSD), and absorber (A) with vortex mass transfer–separation contact elements.

In general, the algorithm to calculate the main technological equipment of the granulation unit to obtain PAN, can be presented as a scheme, as shown in Fig. 3. One or several software products, which together constitute automated complex of the granulation unit calculation, correspond each block of the scheme.

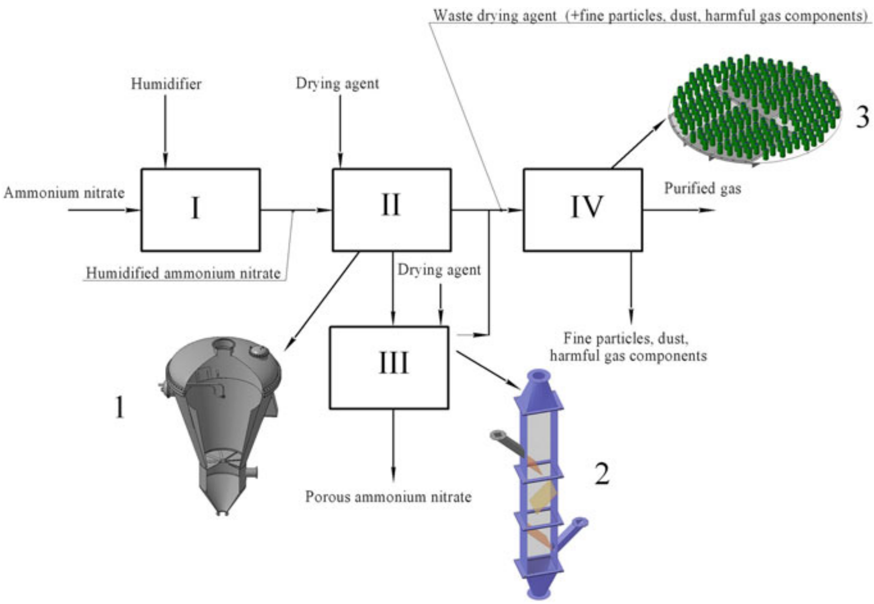


Fig. 1 Diagram of porous ammonium nitrate production according to the method [8, 11–15]: I—humidification of ordinary ammonium nitrate; II—heat treatment and drying of ordinary ammonium nitrate after humidification;—III—final drying PAN; IV—cleaning of exhaust gases; 1—vortex granulator; 2—multistage gravitational shelf dryer; 3—contact tray with heat and mass transfer–separation elements

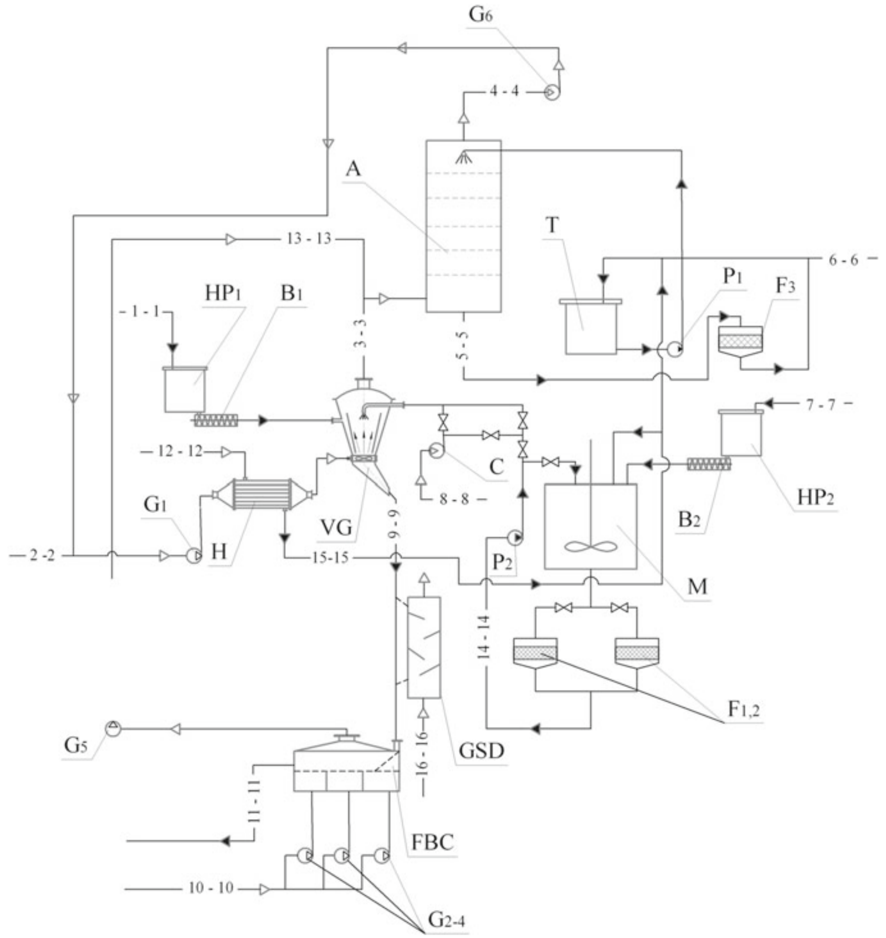


Fig. 2 Technological scheme of the porous ammonium nitrate production. *Elements of the installation: VG—vortex granulator; H—heater; GHD—gravitational shelf dryer; FBC – fluidized bed cooler; A—absorber; F—filter; M—mixer; B—batcher; HP—hopper; G—gas blower; P—pump; T—tank; C—compressor. The main flows*: 1–1—seeding agent; 2–2—manufacturing air; 3–3—polluted air; 4–4—purified air; 5–5—polluted water; 6–6—water; 7–7—substandard granules; 8–8—air for spraying of liquid material (solution, melt); 9–9—product; 10–10—air for cooling of granules; 11–11—granules for packaging; 12–12—steam; 13–13—dusty gas; 14–14—liquid material (solution, melt); 15–15—water condensate; 16–16—drying agent

2 Calculation of Technological Parameters

In order to study the influence made by the hydrodynamic regime of the gravitational shelf dryer's operation on the nanoporous structure of the granule after final drying, the experimental stand was created (Fig. 4).

Other devices and equipment include:

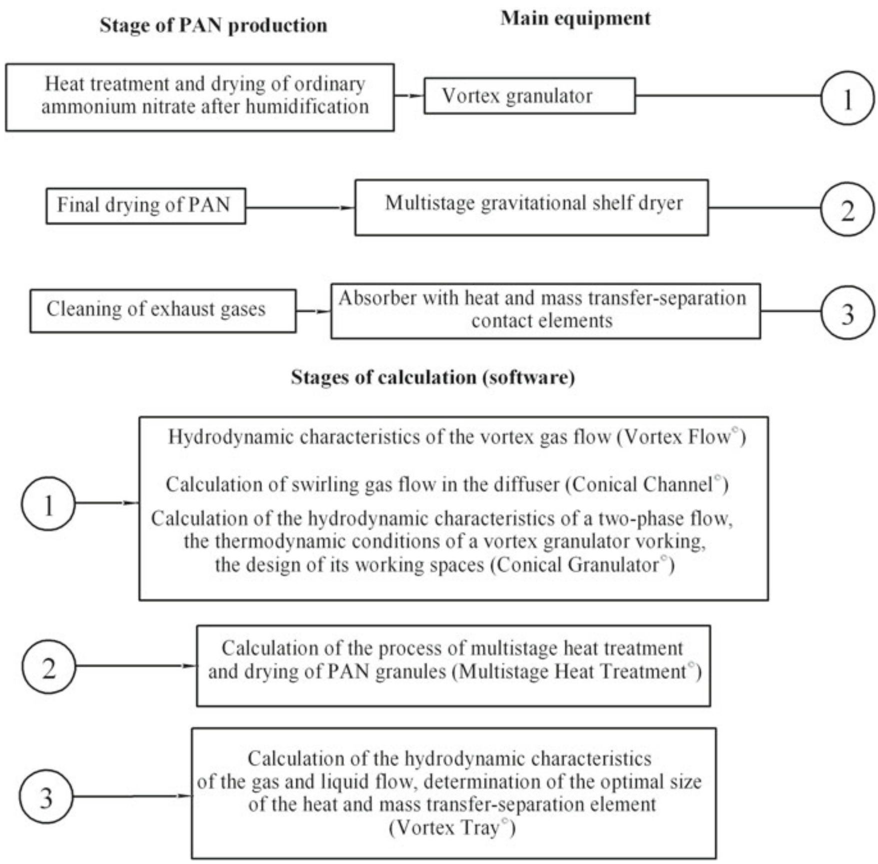


Fig. 3 Algorithm of the main technological calculation of the PAN obtaining granulation unit

- temperature in the calorifier is measured by TC10-C thermocouple; self-recording potentiometer КСП-3;
- temperature in the workspace of granulator is measured by thermal imager Fluke Ti25, pyrometer Victor 305B;
- humidity of granules and air is measured by the multimeter DT-838.

The theoretical calculation of the kinetics for the granule heating process and its mass changing are presented in Figs. 5 and 6.

Heating of the granule surface and removing moisture from it is carried out at a constant drying velocity. In this case, the heating and drying front are mixed in parallel. It enables obtaining a porous structure of the granule at low thermal stresses in the core. As the heating and drying front moves deeper into the granule, the drying velocity decreases. The heat treatment time must be increased to remove the required amount of moisture from the granule. Besides, it is essential to prevent overheating of the granule core. It will lead to the formation of pores in the form of cracks, not

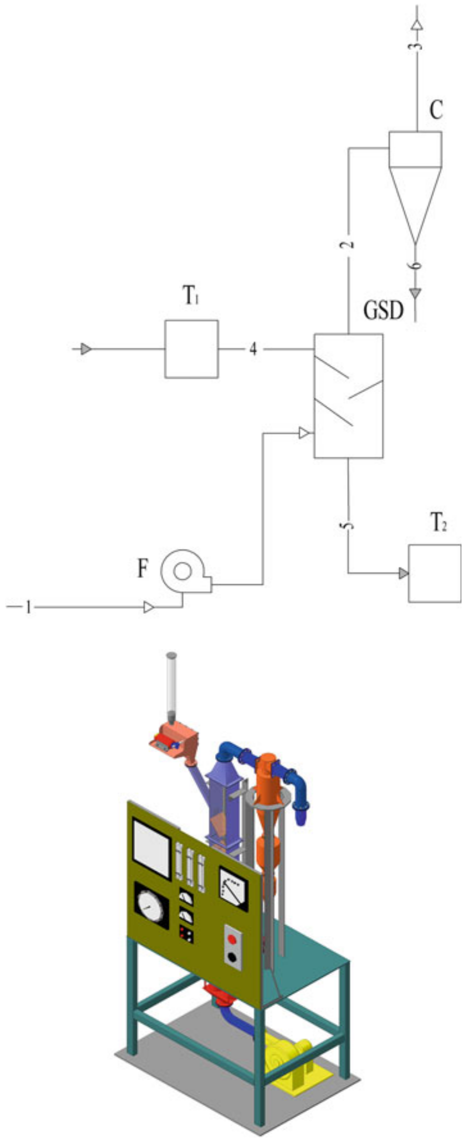


Fig. 4 Schematic diagram of the experimental setup for the study of shelf devices: F—fan; GSD—gravitational shelf unit; C—cyclone; T1, T2—containers (tanks); 1—drying agent; 2—waste drying agent; 3—purified gas; 4—PAN; 5—PAN after final drying; 6—fine particles

due to evaporation but due to the mechanical destruction. In this case, the strength of the granule is significantly reduced.

Multistage Heat Treatment© *the mathematical model, underlying the software product, is demonstrated in* [8, 11–13].

The Multistage Heat Treatment© program is necessary to calculate heat treatment and dehydration processes (if required) in the multistage drying, granulation and cooling devices of the weighted layer. The calculation results are the value of the

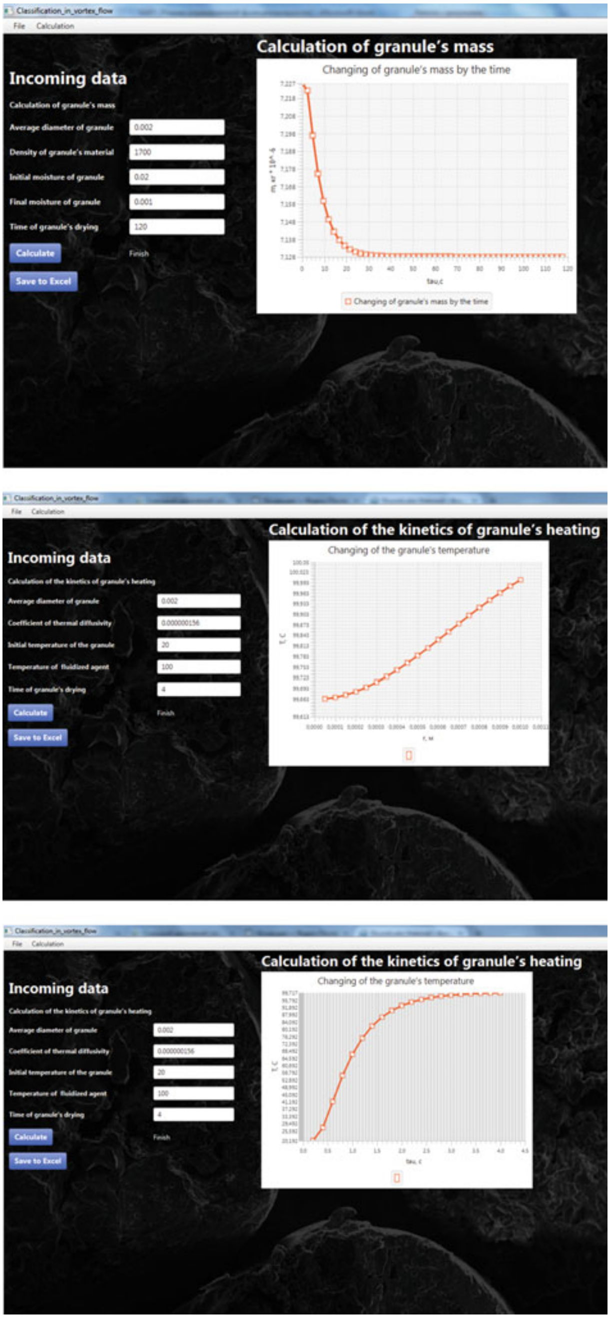
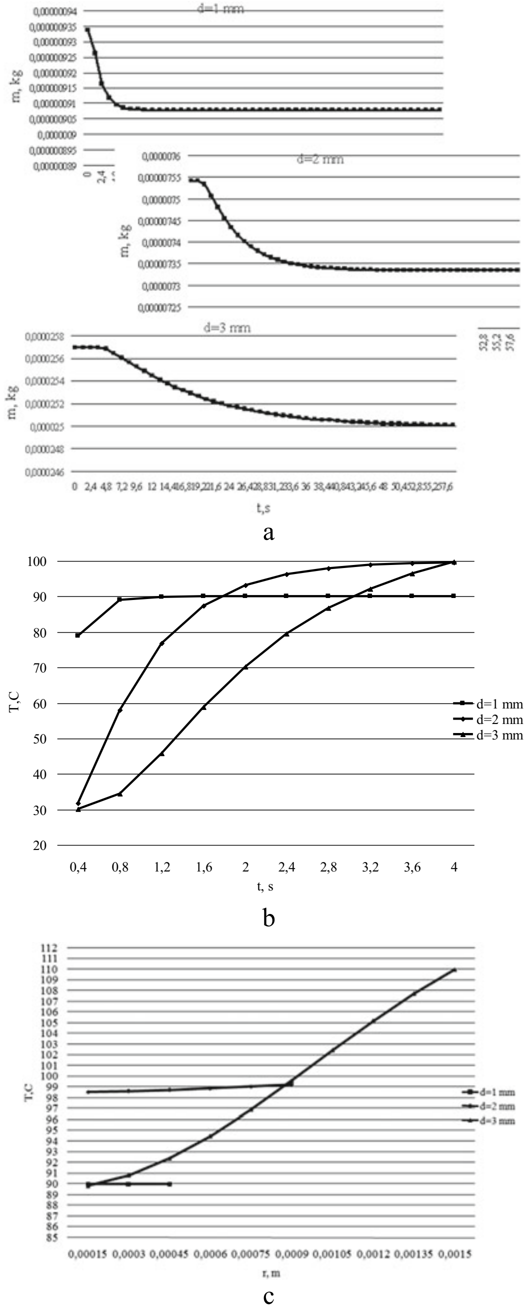


Fig. 5 Program interface for calculating the mass of a granule **a**, windows for calculating the heating kinetics of a granule **b**, **c**

Fig. 6 Results of calculating the mass of the granule **a**, the heating kinetics of the granule **b**, **c**



temperature and humidity of the dispersed material and the gas flow (drying or heat transfer agent) before and after each stage of the multistage device. The heat treatment process is calculated in the gas flow direction (from the lower to upper sections of the device). The heat treatment process is calculated in the direction of the gas flow (from the lower to the upper sections of the device).

When starting work with the program, the equation system of the mathematical model appears on the screen (Fig. 7).

The user enters the initial data in the corresponding cells (Fig. 8).

The working field of the program after entering the initial data will have the form as shown in Fig. 9.

The next step is to carry out the calculation (Fig. 10). The corresponding command makes it possible to calculate the required values.

The calculation results are displayed in a separate window (Fig. 11).

```
k1:=(t1k1-t2k1)/(t1н1-t2н1)=E11;
k2:=(x2k1-x1k1)/(x2н1-x1н1)=E21;
k3:=G2*Cм*(t2k1-t2н1)+Gм*Cв*(x2k1*t2k1-x2н1*t2н1)=G1*Cc*(t1н1-t1k1)+Gc*Cв*
(x1н1*t1н1-x1k1*t1k1);
k4:=Gм*(x2н1-x2k1)=Gc*(x1k1-x1н1);
```

Fig. 7 Mathematical model for calculation

```
t1н1:=___;t2k1:=___;x1н1:=___;x2k1:=___;
G2:=___;G1:=___;Cм:=___;Cв:=___;Cc:=___;E11:=___;E21:=___;
```

Fig. 8 Input of initial data

$$k1 := \frac{t1k1 - t2k1}{t1\text{н}1 - t2\text{н}1} = E11$$

$$k2 := \frac{x2k1 - x1k1}{x2\text{н}1 - x1\text{н}1} = E21$$

$$k3 := G2\ C\text{м}\ (t2k1 - t2\text{н}1) + G\text{м}\ C\text{в}\ (x2k1\ t2k1 - x2\text{н}1\ t2\text{н}1) = G1\ Cc\ (t1\text{н}1 - t1k1) + Gc\ C\text{в}\ (x1\text{н}1\ t1\text{н}1 - x1k1\ t1k1)$$

$$k4 := G\text{м}\ (x2\text{н}1 - x2k1) = Gc\ (x1k1 - x1\text{н}1)$$

t1н1 := ___

t2k1 := ___

x1н1 := ___

x2k1 := ___

G2 := ___

G1 := ___

Cм := ___

Cв := ___

Cc := ___

E11 := ___

E21 := ___

Fig. 9 Working area of the program

```
rez:=solve({k1,k2,k3,k4},{t1k1,t2н1,x2н1,x1k1});
```

Fig. 10 Calculation

```
rez := {t1k2 =          , t2н2=        , x1k2 =          , x2н2 =          }
```

Fig. 11 Calculation results

```
t1н2:=t1k1;t2k2:=t2н1;x1н2:=x1k1;x2k2:=x2н1;
```

Fig. 12 Initial data to calculate the subsequent heat treatment stages

After the calculation of the first stage, the user proceeds to further calculations. The mathematical model equations at the next step are similar to the previous ones. The peculiarity of the calculation at each subsequent stage is to use the calculation results of the flow features in the previous stage, which are the initial data for the calculation (Fig. 12).

3 Properties of Nanoporous Layers in Granules of PAN

Figure 13 shows the electron microscopy results of the surface of PAN granules with various diameters after the final drying stage.

Analysis of these figures shows the following features of the nanoporous structure morphology:

- with an increase in the diameter of the granule, the nanoporous surface becomes more uniform thanks to the regular heating of the granule;
- an increase in the time for heat treatment with a slight decrease in temperature enables to avoid the formation of several "mechanical" pores arising from the thermal stress actions;
- the formation of a developed network of twisted nanopores occurs when the granule is not overheated;
- with an increase in the granule polydispersity degree, the small fraction is characterized by an uneven network of predominantly rectilinear nanopores;
- it is necessary to adjust the ratio between the drying agent's flows and granules (dispersed material) to reduce the temperature stress effect on the granule. Such an optimization calculation is a task for further research.

The values of the relative porous surface of the PAN granule for different diameters are presented in Fig. 14.

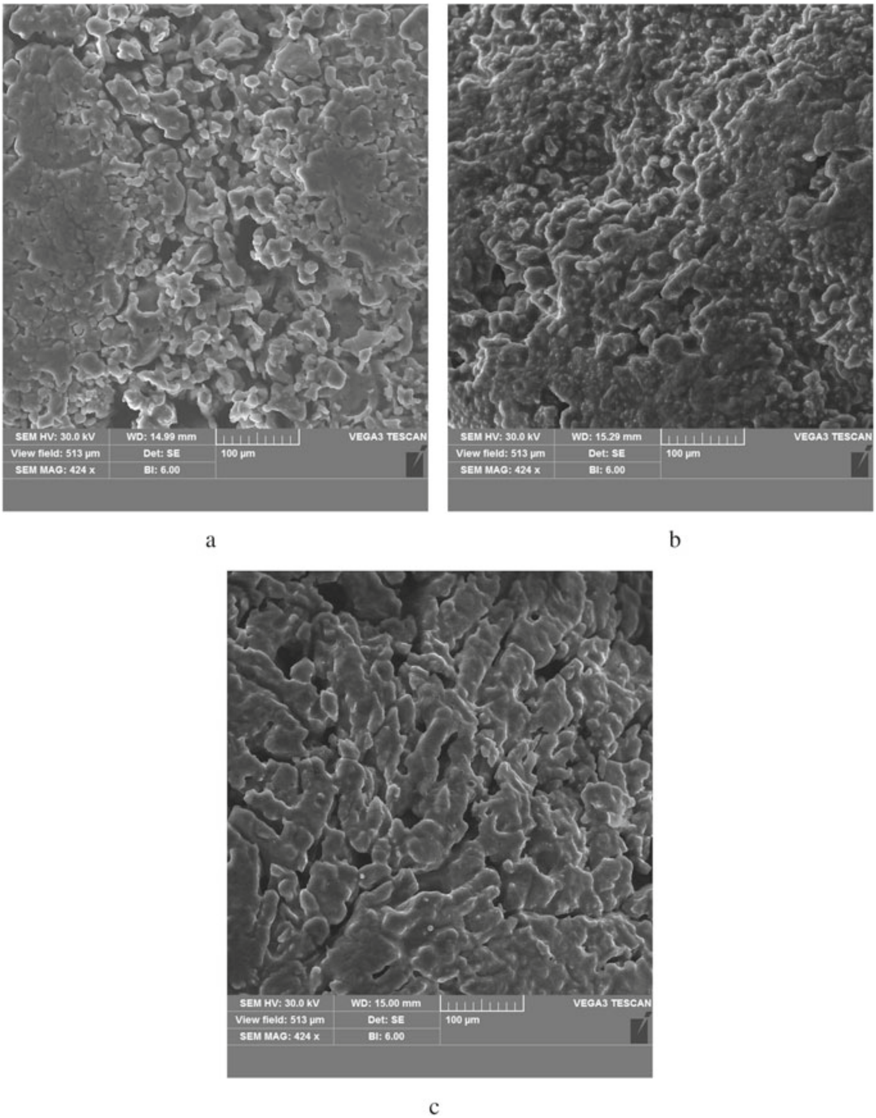


Fig. 13 Electron microscopy results of the surface of PAN granules with various diameters after the final drying stage: **a**–**d** = 1 mm; **b**–**d** = 2 mm; **c**–**d** = 3 mm

4 Conclusions

The obtained results indicate that the final drying stage of PAN granules provides an increase in their quality and shelf life without loss of retentivity toward diesel distillate.

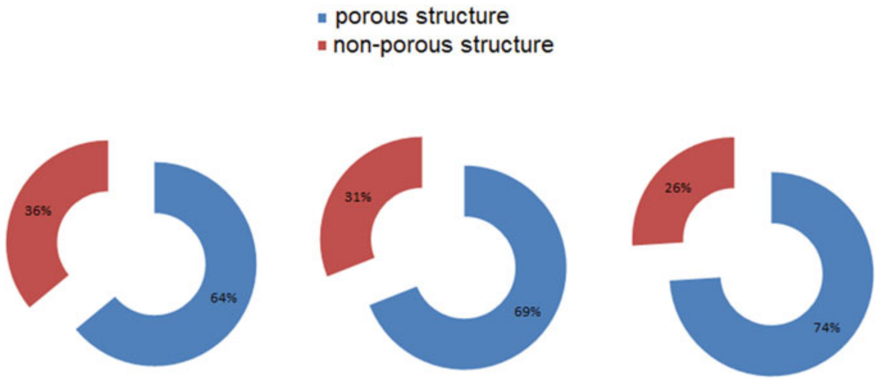


Fig. 14 Values of the relative porous surface of the PAN granule for different diameters: **a–d** = 1 mm; **b–d** = 2 mm; **c–d** = 3 mm

The introduction of this stage increases the total energy capacity of the production; however, the use of multistage shelf dryers enables:

- to section the internal space of the device with the formation of the heat–mass exchange steps;
- to differentiate the distribution of flows between stages;
- to provide gradual regulation for the driving force of heat–mass transfer;
- to achieve optimization of the cost ratio of interacting flows;
- to create an active hydrodynamic mode of flow interaction;
- to reduce the specific energy consumption for the intensification of the process.

Acknowledgements This research work had been supported by the Ministry of Science and Education of Ukraine under the project «Technological bases of multistage convective drying in small-sized devices with utilization and heat recovery units», project No. 0120U100476 and by the Cultural and Educational Grant Agency of the Slovak Republic (KEGA), project No. KEGA 002TnUAD-4/2019.

References

1. Zygmunt B, Buczkowski D (2007) Influence of ammonium nitrate prills' properties on detonation velocity of ANFO. Propellants Explos Pyrotech 32(5):41–414
2. Kubota N (2015) Propellants and explosives: thermochemical aspects of combustion, 3rd edn. Wiley-VCH Verlag & Co, Weinheim
3. Lipinska K (2005) Demilitarized propellants as ingredients in commercial explosives. In: European federation of explosives engineers: Brighton conference proceedings, Brighton, pp 493–498
4. Erode GM (2013) Ammonium nitrate explosives for civil applications: slurries, emulsions and ammonium nitrate fuel oils. Wiley-VCH Verlag & Co, Weinheim

5. Martin G, Barbour W (2003) Industrial nitrogen compounds and explosives. Watchmaker Publishing, Chemical Manufacture and Analysis
6. Janssen TJ (2011) Explosive materials: classification. Nova Science Publishers, Inc., Composition and Properties
7. Artyukhov AE, Artyukhova NO, Ivaniia AV (2018) Creation of software for constructive calculation of devices with active hydrodynamics. In: Proceedings of the 14th international conference on advanced trends in radioelectronics, telecommunications and computer engineering (TCSET 2018), 2018-April, pp 139–142
8. Obodiak V, Artyukhova N, Artyukhov A (2020) Calculation of the residence time of dispersed phase in sectioned devices: theoretical basics and software implementation. Lecture Notes Mech Eng 813–820
9. Artyukhov AE, Obodiak VK, Boiko PG, Rossi PC (2017) Computer modeling of hydrodynamic and heat-mass transfer processes in the vortex type granulation devices. CEUR Workshop Proc 1844:33–47
10. Artyukhov AE, Sklabinskyi VI (2017) Investigation of the temperature field of coolant in the installations for obtaining 3D nanostructured porous surface layer on the granules of ammonium nitrate. J Nano Electron Phys 9(1):01015-1–01015-4
11. Artyukhov AE, Sklabinskyi VI (2013) Experimental and industrial implementation of porous ammonium nitrate producing process in vortex granulators. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu 6:42–48
12. Artyukhova N, Krmela J (2019) Nanoporous structure of the ammonium nitrate granules at the final drying: the effect of the dryer operation mode. J Nano Electron Phys 11(4):04006-1–04006-4
13. Artyukhova NA (2018) Multistage finish drying of the N_4HNO_3 porous granules as a factor for nanoporous structure quality improvement. J Nano Electron Phys 10(3):03030-1–03030-5
14. Artyukhov A, Artyukhova N (2018) Utilization of dust and ammonia from exhaust gases: new solutions for dryers with different types of fluidized bed. J Environ Health Sci Eng 16(2):193–204
15. Artyukhova N (2020) Morphological features of the nanoporous structure in the ammonium nitrate granules at the final drying stage in multistage devices. J Nano Electro Phys 12(4):04036-1–04036-6
16. Wan Daud WR (2008) Fluidized bed dryers—recent advances. Adv Powder Technol 19(5):403–418
17. Mujumdar AS (2006) Handbook of industrial drying. Taylor & Francis Group, Boca Raton
18. Sinaiski EG (2010) Hydromechanics: theory and fundamentals. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
19. Crowe C (2006) Multiphase flow handbook. Taylor & Francis Group, Boca Raton
20. Kudra T, Mujumdar AS (2002) Advanced drying technologies. Marcel Dekker, New York