

Influence of the Nanoaerosol Fraction of Industrial Coal Dust on the Combustion of Methane–Air Mixtures

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Abstract: The mechanism of formation of nanosized aerosol particles during mechanical grinding of coal from Kuzbass mines is studied. The concentration and size spectrum of aerosol particles in a mine tunnel during cutter operation were measured using an aerosol spectrometer. It is found that 90% of the particles are less than 200 nm in size. In the nanometer range, there are two peaks corresponding to average diameters of 20 and 150 nm, the first of which is due to single particles, and the second to aggregates consisting of single particles. The formation of aerosol during mechanical coal grinding in a continuous flow mill was studied. The spectrum and morphology of the particles produced in the laboratory mill are in qualitative agreement with those for the nanoaerosol formed in the mine. The influence of the coal aerosol on the combustion of gas mixtures was studied. Laboratory experiments showed that the presence of the nanoaerosol in a lean methane–air mixture significantly increased its explosibility. This was manifested in an increase in the maximum pressure and a significant increase in the pressure rise rate during explosion. The study leads to the conclusion that the nanoaerosol is formed from the organic coal components released into the gas phase during local heating of coal on the cutter teeth.

Keywords: coal nanoaerosol, combustion of a methane–air mixture, aerosol formation in coal mines, explosions in coal mines.

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INTRODUCTION

The explosion of coal dust in mines often lead to disasters involving many human casualties and severe economic losses. Coal dust explosion is a dynamic phenomenon of great destructive power which occurs in a very a short time. The greatest danger in this process is suspended (airborne) dust, i.e., solid particles in an aerosol state. An important feature is that, in addition to coal dust, the mine atmosphere may also contain methane, a source of increased danger. Even at concentrations below the lean flammability limit, methane can increase the risk of dust explosion by forming with it a so-called hybrid mixture [1, 2].

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Despite the measures taken in the second half of the 20th century, the dust explosion hazard in coal mines has not been eliminated at the beginning of the 21st century. The advent of modern coal mining technology has led to a significant increase in the proportion of dust fractions in coal and hence an increase in the danger of dust explosion at mining, processing, and transport facilities. The most serious accidents of recent years, with the possible participation of coal dust were the explosions at the Barakov (2000), Taizhina (2004), Esaul'skaya (2005), Tomskaya (2006), Zasyad'ko (2007), Yubileinaya (2007), Ul'yanovskaya (2007), Komsomol'skaya (2007), Raspadskaya (2010), Sukhodol'skaya-Vostochnaya (2011), and Vorkutinskaya (2013) mines. These accidents indicate that the physicochemical processes involved in mining have been insufficiently studied. Correct evaluation of the explosion hazard in mining requires additional studies of the formation mechanism of coal aerosol and its effect on the combustion of air mixtures [3].

The ignition of dust-air mixtures has been studied since the end of the 19th century. Such studies are usually conducted in a spherical bomb [4–6], a tube [7, 8] or premixed flame [9] with a high content ($10\text{--}100\text{ g/m}^3$) of dust particles with a size of several tens of micrometers. Our preliminary studies [10] suggest that the experiments mentioned above do not adequately model the coal mine environment. In recent decades, high-performance heading-and-winning machines of a new generation have been developed, whose operation produces nanosized coal dust. In this connection, it is very important to study the influence of nanosized coal aerosol particles on the combustion of dust-gas mixtures.

This study is a continuation of [10]. Its aim is to investigate the formation mechanism of nanosized organic aerosol particles by mechanical crushing of coal grinding and the possible influence of this aerosol on the mine explosion safety. Direct measurements of the concentration, size spectrum, and morphology of the aerosol formed during cutter operation in the 7 Noyabrya and Erunakovskaya VIII mines (Kuznetsk coal basin) were performed. In addition, the formation of coal aerosol by mechanical grinding of coal taken from the aforementioned mines and the ignition of a lean dust-methane-air mixture in a reaction vessel were studied under laboratory conditions.

EXPERIMENTAL

The nanosized component of the coal aerosol was studied using a portable diffusion aerosol spectrometer (No. 60907-15, The State Register of Measuring Instruments) developed at the Institute of Chemical Kinetics

and Combustion, Siberian Branch, Russian Academy of Sciences (ICKC SB RAS). The spectrometer consists of a diffusion battery, a condensation enlarger of aerosol particles, and an optical particle counter [11–13]. The operating principle of the device is based on determining the nanoparticle size distribution from the known dependence of the diffusion coefficient of particles on their size [14, 15]. For this, the proportion of aerosol particles (slip ratio) that passed through the sections of the diffusion battery consisting of sets of wire screens is measured. The particles that passed through one section enter the condensation chamber, where they are enlarged to an optically measurable size. Then the concentration of these particles is measured by an optical counter from the light-scattering signal from each individual particle. A similar procedure is performed for each section. A mathematical model and a computer code for solving the inverse problem has been developed [13], making it possible to determine the nanoparticle size distribution from their slip ratios. Thus, the aerosol spectrometer measures the total aerosol concentration in the range of $10\text{--}2 \cdot 10^5\text{ cm}^{-3}$ (without dilution) and the nanoparticle size distribution in the range of 3–250 nm.

The morphology of the coal aerosol was studied using a JEM 100 SX transmission electron microscope. Samples for electron microscopy were thermophoretically collected. Sampling directly in the mine was performed using a quartz tube (inner diameter of 1.0 cm) through which an air flow containing nanosized aerosol particles was forced. The volumetric flow rate through the tube was 1 liter/min. The flow passed over a special electron-microscopic copper grid coated with polyvinyl formal film (transparent to the electron beam in the microscope). The grid was pressed against the inner surface of the tube, with the outer surface of the tube being cooled by liquid nitrogen. Thus, a radial temperature gradient was produced in the region of the grid. The deposition of aerosol particles on the grid was caused by thermophoresis—directed motion of particles under a temperature gradient [16]. Under the laboratory conditions, particles were deposited on the grid using the thermoprecipitator described in [17].

A dust generator (mill) with a working volume of 500 cm^3 was developed and manufactured to perform laboratory experiments on the dispersion of coal and to study the role of the nanosized aerosol component during combustion of methane-air mixtures. The principle of its operation is based on mechanical coal grinding by rotating blades in a chamber purged with filtered air or a methane-air mixture at a flow rate of 1 liter/min. The radius of rotation of the grinding blade edge is 90 mm, and the speed of rotation is 3000 rpm.

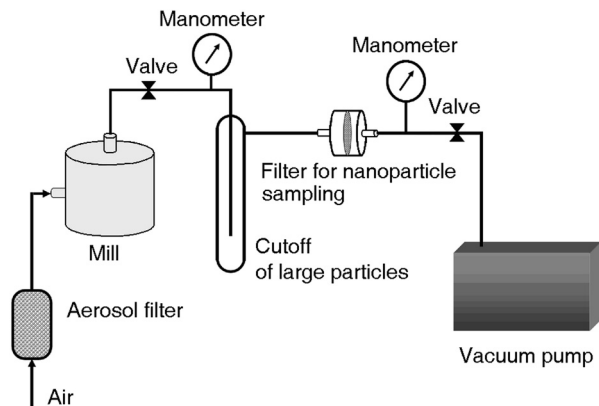


Fig. 1. Diagram of the sampling setup for gas chromatography-mass spectrometry.

Gas chromatography-mass spectrometry was used to compare the chemical composition of the original coal and the nanoaerosol resulting from mechanical coal grinding. The setup for sampling nanoparticles for gas chromatography-mass spectrometry is shown schematically in Fig. 1. A pressure of 100 torr is set in the cutoff of large particles by means of pumping and regulating the valves. The essence of this method is that the direction of the aerosol flow leaving the central tube is abruptly changed. The characteristic turning radius of the flow is $r = 0.2$ cm. At an initial volumetric flow rate through the mill (at a pressure of 1 atm) of 1 liter/min, the linear flow velocity through the central tube with an inner diameter of 0.2 cm at a pressure of 100 torr is $v \approx 4000$ cm/s. The characteristic boundary diameter of particle deposition on the cutoff walls (cutoff diameter) can be estimated from the relation [18, 19]

$$\sqrt{\text{Stk}} \approx 0.48. \quad (1)$$

Here

$$\text{Stk} = \tau v / r \quad (2)$$

is the Stokes number and τ is the particle relaxation time (the time required for a particle to take the flow velocity under changed conditions) evaluated by the formula [18]

$$\tau = \rho d^2 C / 18 \eta, \quad (3)$$

where ρ is the density of the particle material (i.e., the actual density of coal equal to ≈ 1.5 g/cm³ [20]), d is the particle diameter, η is the dynamic viscosity of the carrier gas, which for air at room temperature is equal to $1.8 \cdot 10^{-4}$ P, C is the Cunningham constant:

$$C = 1 + \frac{2\lambda}{d} \left[A + Q \exp\left(-\frac{bd}{2\lambda}\right) \right], \quad (4)$$

λ is the mean free path of air molecules, equal to $5.1 \cdot 10^{-5}$ cm at a temperature of 298 K and a pressure of 100 torr, $A = 1.257$, $Q = 0.400$, $b = 1.100$ [19]. Thus, using relations (1)–(4), we obtain a cutoff diameter of 1 μm . In other words, after the cutoff, the typical particle size in the flow is less than 1 μm . These particles were then deposited on a Whatman GF/A glass filter. Sampling was carried out for 15 min, after which the filter with the precipitate was washed with a 1 : 1 mixture of alcohol and benzene or with ultra-high-purity hexane. Extraction from the original coal was performed using ultra-high-purity hexane. Coal was wetted in it for 12 h, after which. Hexane was filtered off using a paper filter. The resulting solutions were analyzed on a Saturn 2000 (Varian) gas chromatograph-mass spectrometer.

The influence of the coal aerosol on the combustion of gas mixtures was investigated using a 10 liter spherical reaction vessel equipped with optical windows (bomb) designed in the ICKC SB RAS. This volume of the bomb is optimal because it is large enough to neglect the influence of the walls and is easy to handle, in contrast to larger vessels.

The experiment setup was performed as follows. A lean methane–air mixture [6.5% (vol.) CH₄] was passed through a coal dust generator and the flow enriched with the aerosol was then passed through the bomb with a volumetric rate of 1 liter/min at atmospheric pressure and room temperature. The nanoaerosol concentration was measured at the outlet of the bomb with the diffusion aerosol spectrometer. In 10 min, the flow was shut off, and the bomb was cut off from the aerosol line by valves. Spark ignition was used. After the ignition of the mixture, the bomb pressure was measured with a pressure gauge in the real-time mode.

The volume concentration of CH₄ in the mixture of 6.5% was chosen from the following considerations. This mixture is close to the very lean (5.3%), but at the same time, it is fairly energetic. Its flame has a spherical shape, and the center of mass does not rise significantly during combustion, which provides combustion conditions close to adiabatic during the entire process. At the same time, this mixture contains a sufficient amount of excess oxygen (stoichiometry 9.5%) to provide combustion of the aerosol.

The position of the flame front in time was recorded using the schlieren method. A parallel laser beam with a wavelength of 520 nm was passed through the bomb and was collected by a lens on a fiber 0.2 mm in diameter. When a refractive index gradient occurred, the light deviated and did not fall on the fiber. Scattered light was recorded by a high-speed AOS Technologies AG X-PRI camera at a shooting rate of 1000 frames/s.

To study aerosol formation during nucleation of the supersaturated vapor of organic coal components, a flow-type evaporation-nucleation system was designed. The main element of the system is a flow nucleation chamber (aerosol generator), which is a quartz tube with an inner diameter of 0.9 cm with external heating. The temperature in the tube ranged within 300–1000°C. A quartz spoon with coal (Erunakovskoe field) was placed in the hot zone inside the tube. Filtered air is fed at a volumetric flow rate of 1 liter/min at the entrance of the tube (at atmospheric pressure and room temperature). When passing along the hot zone, the flow is saturated with the vapor of organic components released from the coal. As the flow exits the hot zone, its temperature reduces, the vapor becomes supersaturated, and homogeneous nucleation begins. In the initial stages of nucleation, the particles grow due to vapor condensation. As the carrier gas flow with the vapor moves further, its temperature continues to fall, the supersaturation increases, and, as a consequence, the nucleation rate increases progressively. As a result, at high heating temperature, the particle concentration reaches a certain limit, which is controlled by coagulation. At the exit, the concentration and size of the aerosol particles are measured with the aerosol spectrometer.

The rate of accumulation of the aerosol mass at the aerosol filter mounted at the generator exit was measured to determine the mass concentration of the nanoaerosol formed in the nucleation chamber. The procedure was as follows. The heater temperature was rapidly (within 2 min) increased to 400°C, after which the temperature was maintained constant for a predetermined time. The flow was then stopped and the filter was weighed on an analytical balance. The mass of the aerosol deposited on the filter was determined from the difference between the mass of the filter before and after the experiment.

The chemical composition of the aerosol formed by heating coal in the nucleation chamber was determined by gas chromatography-mass spectrometry. For this, a Drexel bottle was placed at the generator outlet, and the aerosol was thermophoretically deposited into it with external cooling by liquid nitrogen. After the completion of the deposition, the Drexel bottle was filled with ultra-high-purity hexane, and the resulting solution was analyzed on the gas chromatograph-mass spectrometer.

The influence of the evaporation-nucleation aerosol on the combustion of methane-air mixtures in a 10-liter bomb was investigated in the same manner as the aerosol formed in the mill. A lean methane-air mixture was fed to the inlet of the heated nucleation chamber. The mixture with the organic aerosol

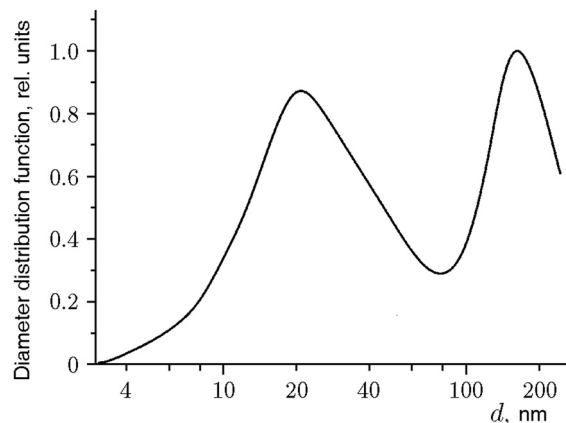


Fig. 2. Nanoaerosol particle size spectrum measured in a gallery of the 7 Noyabrya mine: total concentration $1.1 \cdot 10^5 \text{ cm}^{-3}$, 90% (number fraction) particles with a diameter less than 200 nm.

particles formed in the generator was forced at a flow rate of 1 liter/min through the bomb at atmospheric pressure and room temperature. The temperature of the generator heater rose to 370°C within 2 min, and the bomb was then purged with the flow for 3 min at a constant temperature of the generator. The flow then stopped and the bomb was cut off from the external environment by valves, after which ignition of the mixture in the bomb occurred.

MEASUREMENTS IN MINES

Figure 2 shows a typical particle size spectrum of the nanoaerosol in a conveyor gallery of the 7 Noyabrya mine measured using the diffusion aerosol spectrometer (gas-flame coal, volatile content of 33.5% [20]). The total particle number concentration was $1.1 \cdot 10^5 \text{ cm}^{-3}$, with about 90% of the particles having a size less than 200 nm. Note that the typical aerosol formed by grinding of solids usually has particle sizes of one to several tens of micrometers with the distribution maximum at about 10 μm [21]. As can be seen in Fig. 2, the distribution peaks correspond to particle diameters of 20 and 150 nm. Such aerosol can be formed only during nucleation from the gas phase [22].

Note that the measured concentration far exceeds (by, at least, one order of magnitude) the typical concentration of the aerosol formed by grinding solids. Such a high concentration is only possible when the aerosol is formed from the gas phase (for example, during nucleation from supersaturated vapor) [21, 22]. Note that the peak at 20 nm may be assigned to primary aerosol particles (resulting from nucleation and reaching the final size due to vapor condensation), and the peak

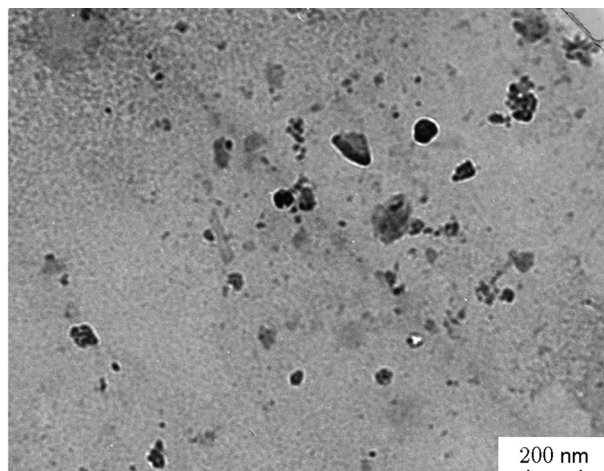


Fig. 3. Electron micrographs of nanoparticles formed during cutter operation.

around 150 nm is due to the coagulation of primary particles. The presence of the coagulation aerosol indicates that the local concentration of the original aerosol was high—not less than 10^8 particles/cm³ (maximum possible concentration in the coagulation) because at lower concentrations, coagulation cannot occur during the real time of aerosol formation (<1 s) at a coagulation constant of about 10^{-9} – 10^{-8} cm³/s at room temperature for polydisperse aerosol [19].

To examine the morphology of the nanoparticles formed in mining, samples were collected on electron microscopic grids for transmission electron microscopic analysis. The sampling was performed at the Erunakovskaya VIII mine (gas-flame coal, volatile content of 37%) during cutter operation. The sampler was located 30 m downstream from the cutter in the mine tunnel. Electron micrographs of the nanoparticles are shown in Fig. 3. It is evident that the nanoaerosol is formed in the form of individual particles with a diameter of 10–50 nm and in the form of aggregates consisting of primary particles, on the average, of 10 primary particles. The formation of aggregates indicates a high rate of coagulation in the aerosol formation zone; in other words, the local concentration of the aerosol in the region of cutter operating area was not less than 10^8 particles/cm³.

Thus, the electron microscopic analysis of the aerosol particles sampled in the mine tunnel confirmed the assumption made on the basis of measurements of the aerosol by the diffusion spectrometer that the nanoaerosol resulting from the mechanical crushing of coal consists of two types of particles—primary single particles and aggregates formed by coagulation of single particles.

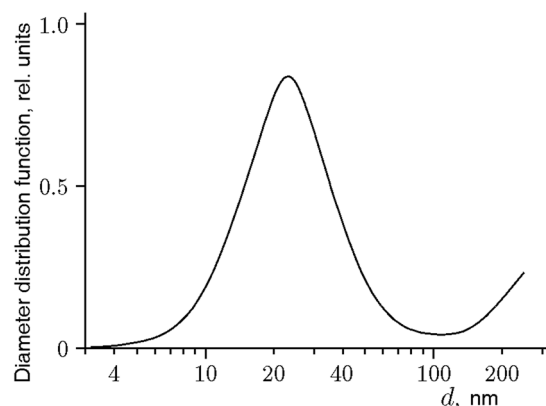


Fig. 4. Typical particle size spectrum of the nano-sized fraction of the aerosol obtained by mill-grinding of the Erunakovo field coal: total concentration 10^6 cm⁻³, coal feeding mass 10 g.

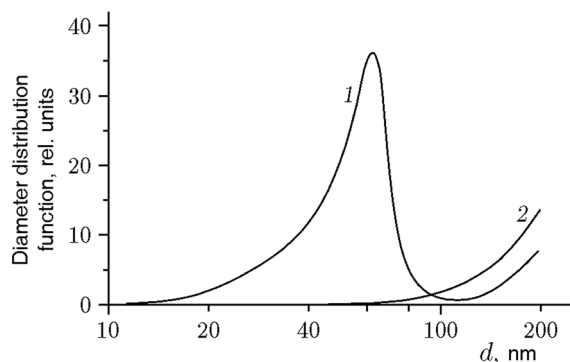


Fig. 5. Particle size spectra of the coal aerosol produced at different times of operation of the coal dust generator: Erunakovo field coal, coal feeding mass 10 g; (1) generator operation time 10 min and concentration of particles larger than 200 nm $2 \cdot 10^5$ cm⁻³; (2) generator operation time 50 min and concentration of particles larger than 200 nm $1.7 \cdot 10^5$ cm⁻³.

To verify our assumption that the nanosized aerosol fraction produced by mechanical coal crushing, we performed laboratory studies of the formation of the coal aerosol in the mill.

LABORATORY STUDY OF THE AEROSOL FORMED DURING MECHANICAL DISPERSION OF COAL

The typical particle sizes obtained by mill grinding of the Erunakovo field coal is shown in Fig. 4. The typical size of the nanosized mode is 20 nm, and the number concentration of the nanoaerosol (with a size less

than 200 nm) is $\approx 80\%$. It is important to note that the resulting spectrum is qualitatively consistent with the spectrum measured in the 7 Noyabrya mine. In both cases, the main contribution to the total number of particles is due to the nanosized fraction (80–90%), for which the typical diameter of the nanosized mode is 20 nm. In the normal mill operation, the temperature of the chamber wall increases to 150°C . On the cutter edge, it is obviously even higher. The wall temperature is dependent on the amount of the original coal fed into the chamber. If the coal amount is reduced in a steady-state regime, the chamber temperature is 60°C . Note that in the latter case, the nanosized component of the aerosol is absent. Thus, it can be assumed that the formation of the nanoaerosol is due to the evaporation of the organic components of coal with the formation of supersaturated vapor and its subsequent nucleation. This assumption is also supported by the fact that the concentration of the nanoaerosol depends on the dust generator operation time. Typically, at a chamber wall temperature of 150°C the maximum concentration of the nanoaerosol component was achieved in 15–20 min of operation. Then it gradually decreased and was practically absent in the particle spectrum after 1 h of operation (see spectrum 2 in Fig. 5). Moreover, the concentration of particles larger than 200 nm did not significantly change with time. This decrease in the nanoaerosol concentration with time can be explained by the depletion of the organic component of the coal.

Typical electron micrographs of the aerosol particles obtained by mechanical mill grinding of coal are shown in Fig. 6. It can be seen that the bulk of the aerosol is present in the form of particles of characteristic irregular shape, ranging in size from one to several micrometers. Along with the coarse fraction of aerosol particles, a nanosized fraction is observed in the images. The nanosized particles are aggregates of single primary particles.

The primary particle size distribution obtained by processing electron micrographs is presented in Fig. 7. The characteristic particle size is about 15–20 nm. The geometric diameter d_g for each aggregate in the electron micrographs was determined by the formula [23]

$$d_g = \sqrt{LW}, \quad (5)$$

where L and W are the length and width of the aggregate.

Figure 8 shows the aggregate size distribution. Their typical diameter is about 50 nm. The morphology of the aggregates is usually described using the so-called fractal-like dimension D_f , which is the exponent in the equation relating the mass M of an aggregate to its size [21, 23, 24]:

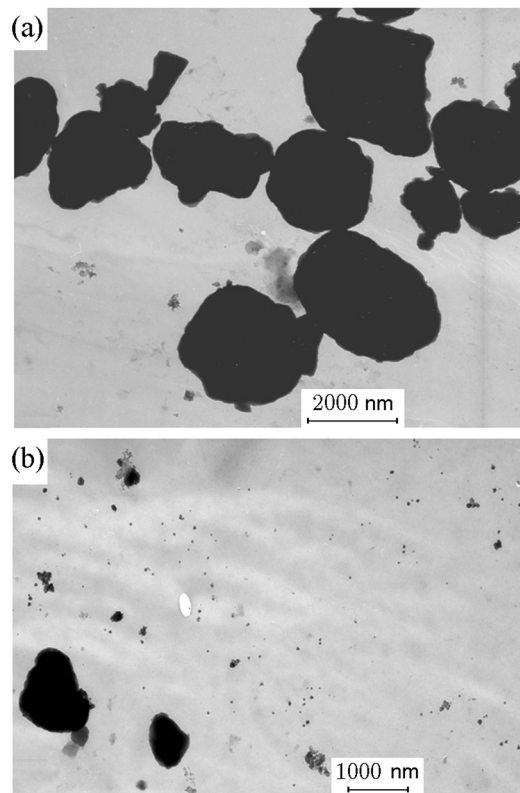


Fig. 6. Electron micrographs of aerosol particles obtained by mechanical coal grinding: (a) large 1–2 μm particles formed by mechanical coal grinding; (b) 10–300 nm aggregates consisting of primary 15–20 nm particles formed by evaporation of the organic components of coal followed by nucleation.

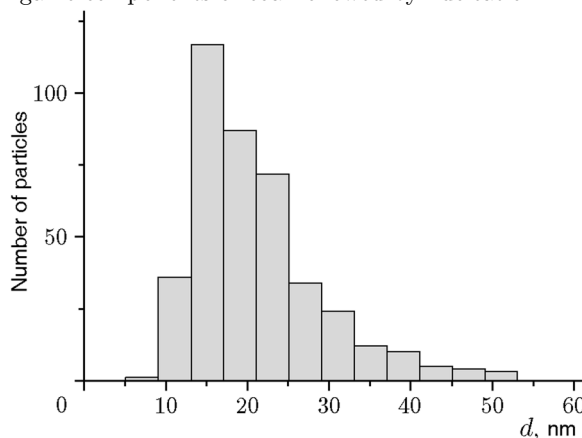


Fig. 7. Size distribution of primary particles.

$$M = Ad_g^{D_f}, \quad (6)$$

where A is the coefficient of proportionality. To determine the mass (in relative units), we measured the integral density of the image of each aggregate. This procedure included the following steps. TIF images were an-

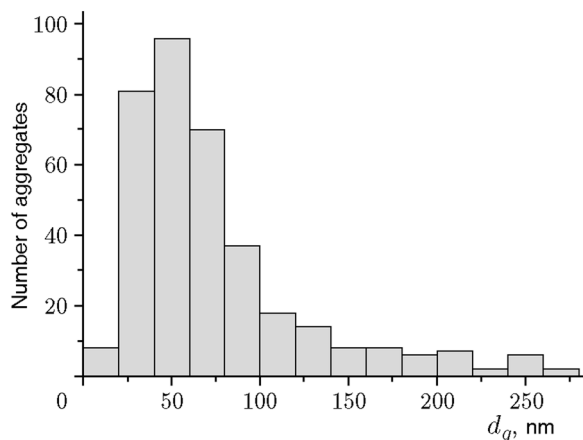


Fig. 8. Geometric equivalent diameter distribution of aggregates.

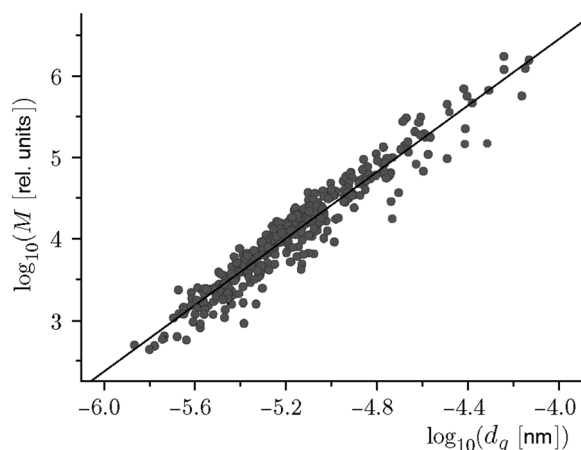


Fig. 9. Mass of aggregates versus equivalent geometric diameter: the curve corresponds to a fractal dimension $D_f = 2.0 \pm 0.1$.

alyzed. The integral density was determined as the sum of the relative grayness of all pixels that constituted the image of the aggregate (the background grayness value were subtracted). It was assumed that the local density in the image of the aggregate is proportional to the local thickness of the original aggregate. Thus, the mass of the original aggregate is proportional to the corresponding integral density of its image. This approximation is acceptable as it is known that the fractal dimension of a two-dimensional projection approximately corresponds to the value of D_f of the original three-dimensional object for $D_f \leq 2$ [23, 24].

Figure 9 shows the dependence of the mass of the aggregates on the geometric diameter in logarithmic coordinates. The aggregates are described by the fractal dimension $D_f = 2.0 \pm 0.1$. The fractal dimen-

sion depends on the mechanism of formation of aggregates from primary particles. If aggregation is limited by the Brownian diffusion of primary particles, then $D_f \approx 1.7$ – 1.9 [25–27]. If aggregates are restructured during formation and/or condensation of vapor on the surface of the aggregate or if aggregation is controlled by adhesion, then $D_f = 2$ – 3 [21, 23, 24, 28, 29]. Obviously, in our case, diffusion aggregation occurs. The fact that the measured fractal dimension is slightly larger than the typical values for diffusion aggregation may be due to both the restructuring of aggregates and vapor condensation during the growth of aggregates. Comparison of the characteristic size of primary particles and the size of aggregates based on fractal dimension allows us to estimate the average number of primary particles in an aggregate, which was 10 ± 1 . This estimate is consistent with the number of primary particles in the aggregates sampled in the mine.

To compare the chemical composition of the original coal and the nanoaerosol formed by mechanical mill grinding of the coal, the coal extract and the aerosol particles collected on the filter were analyzed by gas chromatography-mass spectrometry (Fig. 10). It can be seen that the spectra of the aerosol particles and coal are similar. The most intense lines are due to alkanes. Besides alkanes, the coal and aerosol particles include polyaromatic compounds containing three or four condensed aromatic rings—alkyl derivatives of phenanthrene, anthracene, and pyrene. In the nanoaerosol spectrum (Fig. 10b), unlike in the spectrum of the original coal, C_{10} – C_{13} light alkanes are absent, which may be due to the fact that during heating in the mill, they are rapidly released before the start of formation of the aerosol in large quantities. The compositions of aromatic compounds in the aerosol and the original coal are approximately equal. The weight ratio of alkanes and aromatics in both spectra is 1 : 1. Therefore, it can be suggested that the source of the aerosol whose spectrum is shown in Fig. 4 are the organic components of the coal which released into the gas phase during local coal heating. Since the mass of the vapor of the organic components released from the coal can be quite high, it is interesting to find out how this aerosol can influence the combustion of methane–air mixtures.

INFLUENCE OF THE COAL NANOAEROSOL ON METHANE–AIR COMBUSTION

Figure 11a shows curves of the bomb pressure versus time after ignition for a pure methane–air mixture and the mixture with aerosol. It is seen that the aerosol

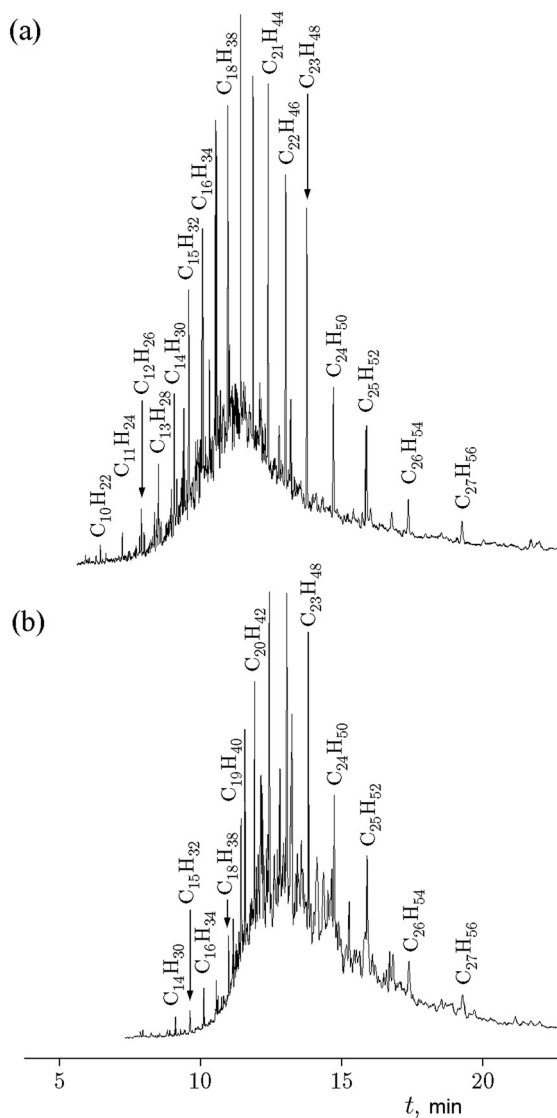


Fig. 10. Chromatography-mass spectrum of the coal extract (Erunakovo field) in hexane [(a); extraction time 60 h] and the nanoaerosol formed by mechanical coal grinding [(b); the solvent is a 1 : 1 mixture of ethanol and benzene].

produced by mill grinding of coal affects the combustion process. In particular, its presence leads to a substantial (severalfold) increase in the bomb pressure growth rate compared to the pure mixture (Fig. 11b). In addition, special experiments were carried out to compare two pressure rise curves for explosions of aerosol-methane-air mixtures. In the first case, the spectrum of the aerosol produced by coal grinding contained the nanosized component, along with the coarse fraction (see spectrum 1 in Fig. 5). In the second case, only the coarse component (see spectrum 2 in Fig. 5) was

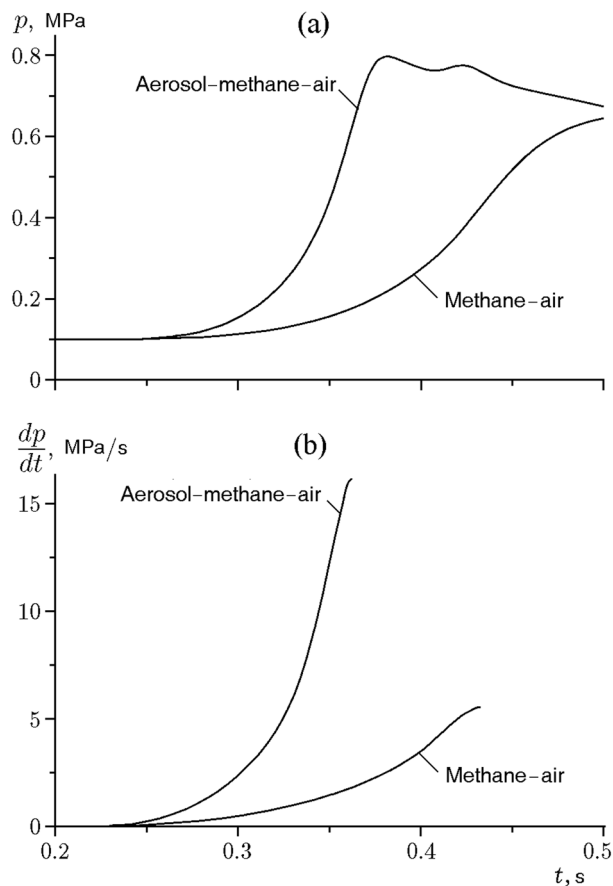


Fig. 11. Bomb pressure (a) and the rate of its increase (b) versus time during ignition of a mixture of aerosol-methane (6.5%)-air and a mixture of methane (6.5%)-air: coal from the 7 Noyabrya mine, mass of coal in the mill 10 g; the bomb was purged with the dust-methane-air mixture for 5 min.

present in the spectrum. Comparison of these two pressure rise curves with the pressure curve for the explosion of the methane-air mixture shows that the addition of the large-sized coal aerosol to the methane-air mixture does not change the nature of the explosion, i.e., the pressure rise curve for the aerosol-methane-air mixture is very similar to that for methane-air mixture. At the same time, in the presence of the nanosized fraction in the coal aerosol, the pressure rise curve for the methane-air mixture with the aerosol differs from that of the methane-air mixture (see Fig. 11b). Therefore, it can be argued that it is the nanosized fraction that influences the combustion of the methane-air mixture.

Flame images obtained by the schlieren method are shown in Fig. 12. It is seen that the presence of the nanoaerosol leads to a change in the flame structure, making it more cellular (Fig. 12b).

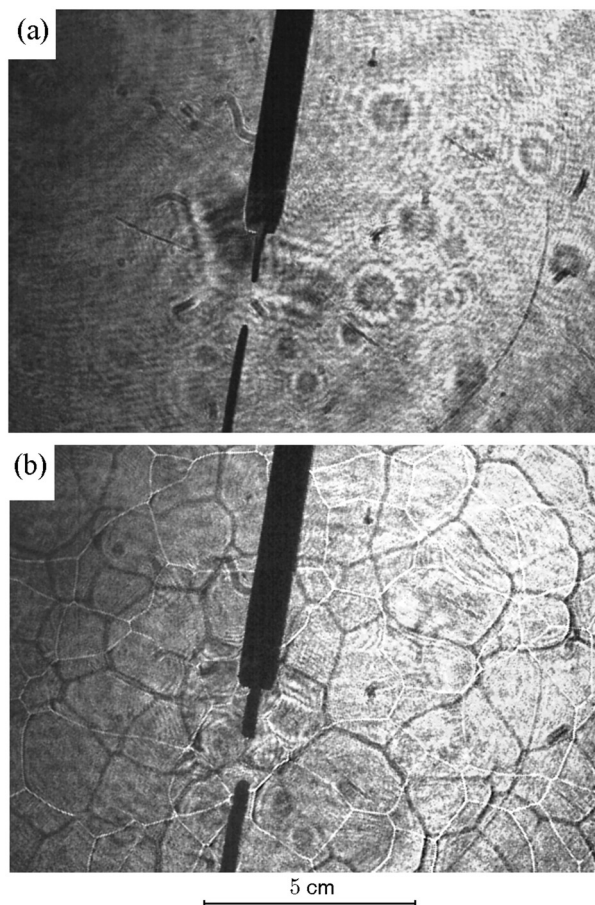


Fig. 12. Schlieren images of methane-air flame (a) and methane-dust-air flame (b) obtained with a laser light source.

The experiments suggest that during mechanical coal grinding, a local temperature rise results in the release of gaseous organic components, followed by nucleation and aggregation. This organic nanoaerosol has a significant influence on the combustion of the methane-air mixture. It is important that in order for this effect to be significant, the mass concentration of the organic nanoaerosol should be comparable to the mass concentration of methane in the mixture. Measurements of the spectrum and concentration of the nanoaerosol in the mine and in laboratory experiments showed that the typical concentration of the nanoparticles obtained by coal grinding was in the range of 10^5 – 10^6 cm^{-3} , with an average size of 20–100 nm. We estimate the upper limit of the mass concentration of these particles for a concentration of 10^6 cm^{-3} , a particle diameter of 100 nm, and a density of the particle material (organic components) of 1 g/cm^3 . Then the mass concentration of particles will be $5 \cdot 10^{-4}$ g/m^3 . In this case, the mass concentration of methane in the mixture of 6.5% CH_4 + air

is 42 g/m^3 . Obviously, at such a low mass concentration of nanoparticles, it is impossible to speak of the influence of aerosol on the combustion process. An explanation of the observed effect of the nanoaerosol on combustion is that coal grinding produces not only the nanoaerosol but also a large-sized fraction, which is inactive during combustion but on whose surface a large amount of organic vapor is condensed and nanoparticles are deposited. Importantly, the coagulation constant of micron particles with nanometer particles is five orders of magnitude higher than the coagulation constant of nanoparticles of the same size [14]. This implies that in the zone of aerosol formation, most of the nanoparticles formed by nucleation of supersaturated vapor are not in the gas phase but on the surface of large micron particles formed by coal grinding. The presence of nanoaerosol is a qualitative factor indicating that the mixture contains a large number of organic components released from coal. During combustion of aerosol-methane-air mixtures, organic components evaporate from the surface of micron and submicron particles into the gas phase, and the mass concentration of organic components in the mixture becomes comparable to that for methane, which causes an increase in the pressure rise rate and the maximum pressure.

Thus, summing up the results of the experimental study of the nanoaerosol produced by mechanical coal grinding in mines and under laboratory, we can conclude that the main contribution to the formation of the nanoaerosol is due to the homogeneous nucleation of the supersaturated vapor of organic compounds released during mechanical coal grinding as a result of local temperature rise. Evidence in favor of the homogeneous nucleation mechanism are the following facts. The concentration of the nanoaerosol fraction in the mine atmosphere measured by the diffusion aerosol spectrometer is 10^5 $\text{cm}^{-3} \cdot \text{s}^{-1}$. Since the air flow forced through the mine tunnel dilutes the resulting aerosol by at least three orders of magnitude, it can be argued that in the zone of aerosol formation, the particle concentration should be not less than 10^8 $\text{cm}^{-3} \cdot \text{s}^{-1}$. Electron-microscopic analysis of aerosol samples collected in the mine showed the presence of aggregates consisting on average of 10 primary particles, which also implies that in the zone of aerosol formation, the initial particle concentration is not less than 10^8 $\text{cm}^{-3} \cdot \text{s}^{-1}$. Such high aerosol concentration cannot be caused by the formation of particles due to grinding of solids. Its high value indicates that the aerosol formed from gaseous precursors [14, 21, 22]. Gas chromatography-mass spectrometry data suggest that the nanoaerosol formed from the supersaturated vapor of organic components present in the original coal. Investigation of the explosion of

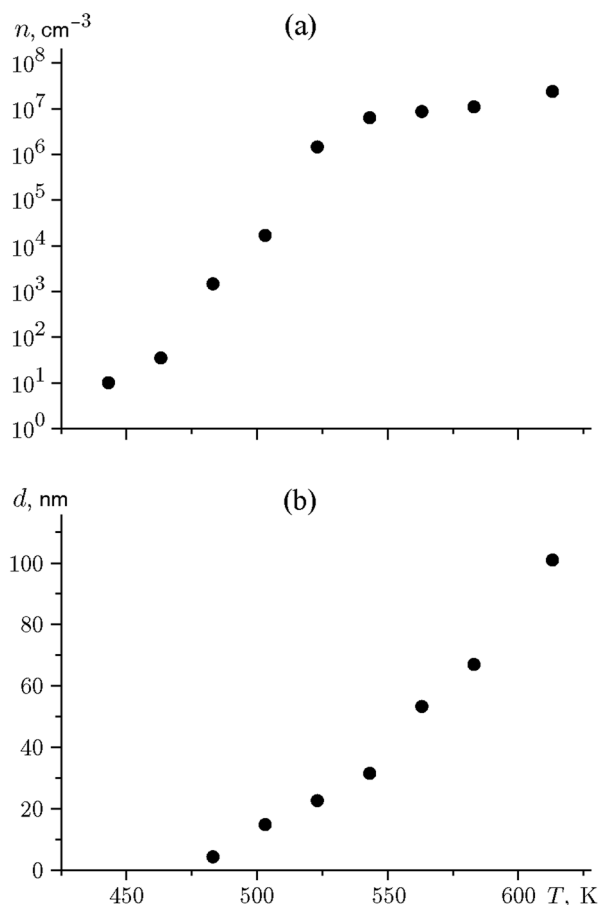


Fig. 13. Concentration (a), and average diameter (b) of the aerosol obtained by evaporation-nucleation versus generator heating temperature.

the aerosol-methane mixture showed that this organic aerosol can have a significant influence on the combustion of gas mixtures. The next section is devoted to the properties of this nanoaerosol formed by heating coal.

FORMATION OF NANOAEROSOL FROM COAL DURING EVAPORATION-NUCLEATION

Figure 13 shows concentration curves of the aerosol produced in the nucleation chamber and the average diameter of the aerosol at the chamber outlet versus heating temperature. It is seen that at a temperature of 540 K, the concentration reaches 10^7 cm^{-3} and then practically does not increase with increasing temperature. The concentration reaches a constant value because the concentration at high temperature is controlled by coagulation. The fact is that the coagulation rate is quadratically related to the concentration, which

is expressed by the kinetic equation [14]

$$\frac{dn}{dt} = -kn^2, \quad (7)$$

where n is the concentration of aerosol particles, k is the coagulation constant (here to simplify the evaluation, we assume that it does not depend on the size of coagulating particles). Equation (7) is called the basic equation of coagulation. It is written in integral form as

$$n = \frac{n_0}{1 + n_0kt}, \quad (8)$$

where n_0 is the initial concentration of the aerosol. For sufficiently high initial concentrations, Eq. (8) has the form

$$n \approx \frac{1}{kt}, \quad (9)$$

i.e., the aerosol concentration does not depend on the initial value and is only determined by the constant k and the coagulation time. It is this feature that is responsible for the aerosol concentration reaching a constant value at $T = 540 \text{ K}$. Indeed, for a typical coagulation time of 10 s and a coagulation constant of $\approx 3 \cdot 10^{-9} \text{ cm}^3/\text{s}$ for polydisperse aerosol [19], Eq. (9) implies that the concentration cannot be significantly higher than 10^7 cm^{-3} . Slight increase in the concentration with increasing temperature in excess of 540 K is due to the fact that with increasing temperature, the size of coagulating particles increases and, consequently, the coagulation constant decreases.

Note that Fig. 13 shows the results of stationary measurements. In these measurements, the temperature was increased stepwise by 20 K. At the initial time, during the next rise in temperature, the aerosol concentration sharply increases due to a sharp increase in the gas release rate, after which the gas release rate decreases and the process enters a steady-state regime. A completely different picture is observed with a sharp temperature rise immediately to high values. In this case, the size and concentration of aerosol particles will be considerably higher than those shown in Fig. 13. An electron micrograph of evaporation-nucleation nanoparticles is shown in Fig. 14 for the case of steady-state generator operation.

Figure 15 shows the dependence of the mass of the aerosol deposit collected on the filter at the outlet of the nucleation chamber during its operation. By the time of 10 min, the aerosol content was 13.7% of the mass of the original coal sample.

The gas chromatography mass spectrum of the aerosol obtained by evaporation-nucleation is identical to that of the nanoaerosol formed by mechanical coal grinding. This coincidence of chemical compositions

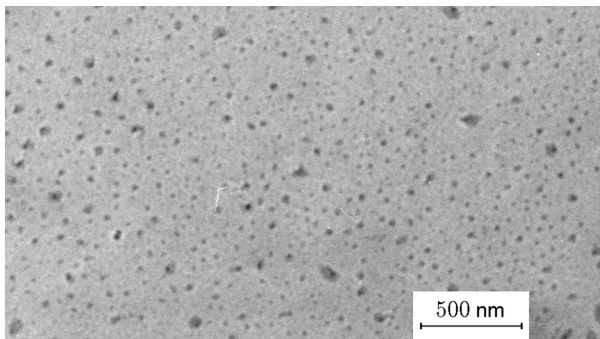


Fig. 14. An electron micrograph of the evaporation-nucleation aerosol (sublimation temperature 310°C).

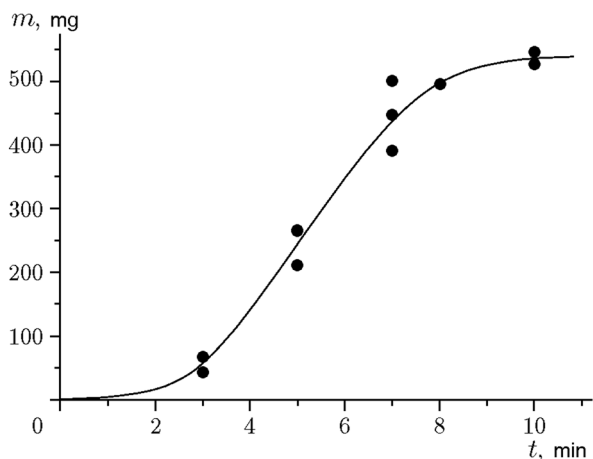


Fig. 15. Mass of the aerosol deposit versus time of collection on a Petryanov filter: initial mass of coal placed in the generator 4 g; generator temperature 400°C.

suggests that the formation of the nanoaerosol during the mechanical coal grinding is due to the release of organic components into the gas phase resulting from local heating of coal under mechanical treatment.

Figure 16 shows the dependence of the bomb pressure on time during explosion of a pure methane-air mixture containing the evaporation-nucleation aerosol. It can be seen that in the mixture with the aerosol, the pressure rise rate and the maximum pressure are higher. Thus, in the case of the pure mixture, the maximum pressure is 0.65 MPa, and in the aerosol mixture, it is 0.8 MPa. This increase in the maximum pressure is due to the higher content of fuel in the mixture with the aerosol. The addition of the aerosol increases the pressure rise rate by almost an order of magnitude.

Figure 17 shows pressure rise-versus-time curves for explosions of methane-air and aerosol-air mixtures. It is evident that the evaporation-nucleation aerosol formed from the coal can be ignited without methane

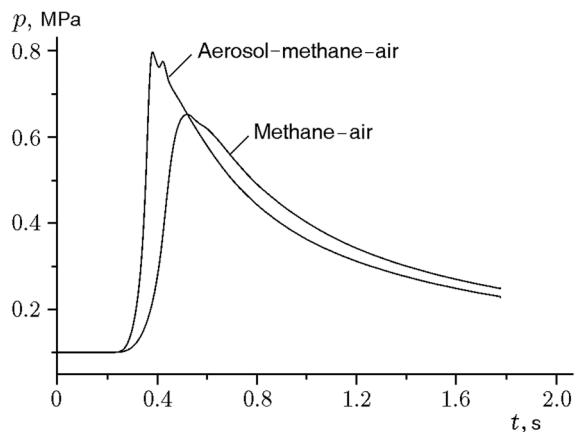


Fig. 16. Bomb pressure versus time during ignition of following mixtures: methane (42 g/m³, 6.5%) + air; evaporation-nucleation aerosol (20 g/m³) + methane (42 g/m³) + air.

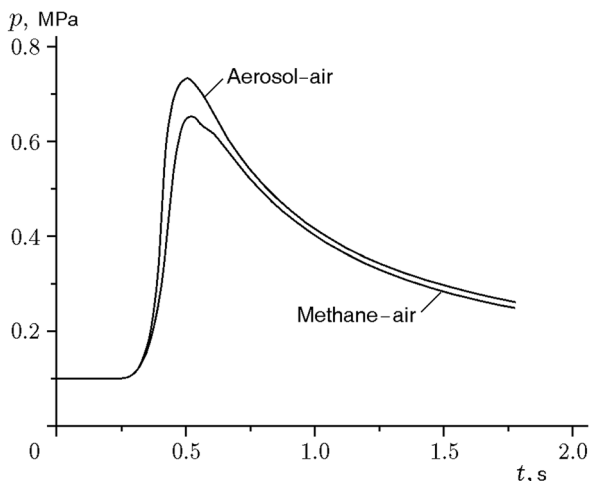


Fig. 17. Bomb pressure versus time during ignition of the evaporation-nucleation aerosol (145 g/m³, sublimation temperature of 350°C) in comparison with a mixture of methane (42 g/m³, 6.5%) + air.

additives. It is worth mentioning that heating of the evaporation-nucleation aerosol also leads to the release of combustible gases, such as CH₄, C₂H₆, and CO. The degree of influence of these gases on the combustion of the aerosol-air mixture will be investigated in our further study.

To illustrate the evaporation-nucleation aerosols formed during rapid heating of the generator, Fig. 18 shows successive images of the vessel filled with the aerosol from the nucleation chamber for 1 min. The aerosol concentration is so high that it is visible to the naked eye. Note that the aerosol becomes visible to the naked eye during rapid heating starting at a heater

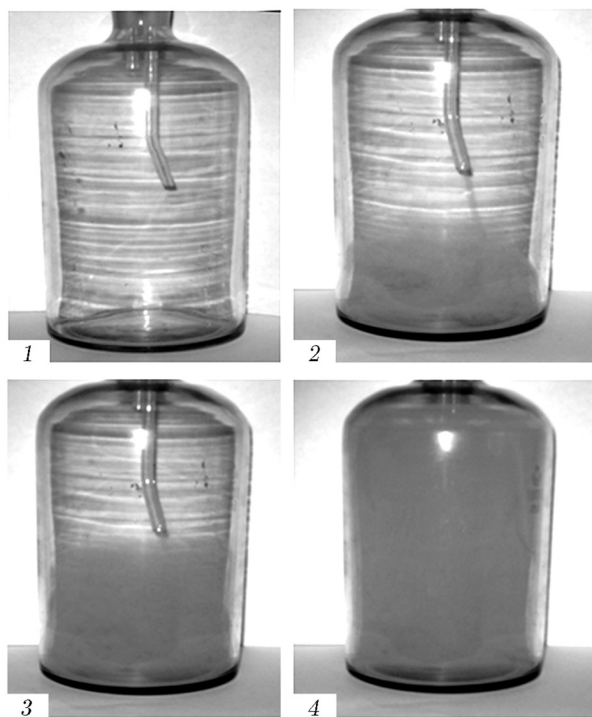


Fig. 18. Successive stages in the filling of the 1-liter vessel for 1 min: generator temperature 370°C, mass of the original coal fed into the generator 4 g.

temperature of 610 K. This behavior is understandable. During heating of the nucleation chamber, the organic components in coal are a liquid solution. The temperature of 610 K is approximately equal to the boiling point of C₂₀ alkane [30], one of the major organic components of coal. It can therefore be suggested that a large amount of organic aerosol is formed upon reaching the boiling point of the solution of organic components in the coal. Once the boiling point is reached, a phase transition occurs, accompanied by macroscopic transfer of vapor, which, in turn, leads to a drastic increase in the rate of aerosol formation.

CONCLUSIONS

The study of the concentration, particle size, and morphology of the aerosol generated at Kuzbass coal mines, as well as the laboratory studies of aerosol formation from coal exposed to mechanical action and heating allow the following assumptions to be made. Mechanical coal grinding by the cutter or a laboratory mill causes local coal heating, during which a large amount of organic compounds is released from coal into the gas phase. After reaching the ambient temperature, the vapor becomes supersaturated. High supersatura-

tion of the vapor leads to the formation of an organic nanoaerosol due to homogeneous nucleation. In addition, vapor condensation and deposition of nanoparticles on the surface of large micron and submicron particles formed by direct coal grinding occur. The high concentration of nanoaerosol particles in the aerosol formation zone (not less than $10^8 \text{ cm}^{-3} \cdot \text{s}^{-1}$) indicates that organic components are released from the coal into the gas phase in large amounts comparable with the methane content in explosive methane–air mixtures. The study of the explosion of dust–methane–air mixtures has shown that the addition of the coal aerosol to a methane–air mixture significantly increases the pressure rise rate during explosion and the maximum pressure. The presence of this aerosol in methane–air mixtures can significantly shift the flammability limit. It is important to note that the mass concentration of the organic nanoaerosol present in air during mechanical coal grinding is relatively small. However, the presence of the nanoaerosol at a concentration of 10^5 cm^{-3} may indicate the presence of organic components deposited on the surface of the coarse aerosol in an amount sufficient to appreciably affect the ignition of methane–air mixtures. In other words, the nanoaerosol can serve as an indicator of a potentially explosive situation. However, this aerosol is not detected by modern methods of explosion control in mines. The only method of organic aerosol monitoring are nanoaerosol means for measuring concentration and size.

To make recommendations for minimizing the effect of the nanosized aerosol fraction on the explosion of the coal dust mixture, it is necessary to continue the studies described in this paper and implement these studies on a large scale.

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REFERENCES

1. K. A. Lebetzki and S. B. Romanchenko, *Dust Explosion Hazard of Mining* (Promtshlennaya Bezopasnost, Moscow, 2012), Vol. 6 [in Russian].
2. V. C. Marshall, *Major Chemical Hazards* (John Wiley, New York, 1987).
3. *Analysis of Explosion Containment Systems in Coal Mines and Evaluation of Their Performance: Research Report of the Interdepartmental Commission on Explosives* (Academy of Mining Sciences, Moscow, 2014) [in Russian].
4. G.-D. Gong, C.-H. Bai, and Q.-M. Liu, “Study on Explosion Process of Methane-Coal Dust Mixture,” *J. Coal Sci. Eng.* **19** (3), 332–336 (2013).

5. A. D. Gillies and S. Jackson, "Some Investigations into the Explosibility of Mine Dust Laden Atmospheres," Coal Operators Conf. Wollongong, 626–640 (1998).
6. C. Bai, G. Gong, Q. Liu, Y. Chen, and G. Niu, "The Explosion Overpressure Field and Flame Propagation of Methane–Air and Methane–Coal Dust/Air Mixtures," Saf. Sci. **49**, 1349–1354 (2011).
7. Q. Liu, C. Bai, X. Li, L. Jiang, and W. Dai, "Coal Dust/Air Explosions in a Large-Scale tube," Fuel **89**, 329–335 (2010).
8. Q. Liu, Y. Hu, C. Bai, and M. Chen, "Methane/Coal Dust/Air Explosions and Their Suppression by Solid Particle Suppressing Agents in a Large-Scale Experimental Tube," J. Loss Prevent. Process Ind. **26**, 310–316 (2013).
9. S. R. Rockwell and A. S. Rangwala, "Influence of Coal Dust on Premixed Turbulent Methane–Air Flames," Combust. Flame **160**, 635–640 (2013).
10. A. M. Baklanov, S. V. Valiulin, S. N. Dubtsov, V. V. Zama-shchikov, V. I. Klishin, A. E. Kontorovich, A. A. Korzhavin, A. A. Onischuk, D. Yu. Paleev, and P. A. Pur-tov, "Nanoaerosol Fraction in Industrial Coal Dust and Its Effect on the Explosibility of Coal Dust–Methane–Air Mixtures," Dokl. Akad. Nauk **461** (3), 295–299 (2015).
11. A. Ankilov, A. Baklanov, R. Mavliev, S. Eremenko, G. P. Reichel, and A. Majerowicz, "Comparison of the Novosibirsk Automated Diffusion Battery with the Vi-enna Electron Mobility Spectrometer," J. Aerosol Sci. **22** (Suppl. 1), S325–S328 (1991).
12. P. A. Mavliev, A. N. Ankilov, A. M. Baklanov, A. M. Gorbunov, N. A. Kakutkina, K. P. Kutsenogii, S. E. Pashchenko, and V. I. Makarov, "Using a Screen-Type Diffusion Battery to Determine the Aerosol Dis-persion," Kolloid. Zh. **46** (6), 1136–1141 (1984).
13. R. A. Mavliev and A. N. Ankilov, "Methods of Process-ing Data for a Screen-Type Diffusion Battery," Colloid. Zh. **47** (3), 523–530 (1985).
14. N. A. Fuks, *Mechanics of Aerosols* (Izd. Akad. Nauk SSSR, Moscow, 1955) [in Russian].
15. Y. S. Cheng, H. C. Yeh, and K. J. Brinsko, "Use of Wire Screens as a Fan Model Filter," Aerosol Sci. Technol. **4** (2), 165–174 (1985).
16. *Aerosol Measurement: Principles, Techniques, and Ap-plications*, Ed. by P. A. Baron and K. Willeke (Wiley Interscience, New York, 2001).
17. D. Gonzalez, A. G. Nasibulin, A. M. Baklanov, S. D. Shandakov, D. P. Brown, P. Queipo, and E. I. Kauppinen, "A New Thermophoretic Precipitator for Collection of Nanometer-Sized Aerosol Particles," Aerosol Sci. Technol. **39**, 1064–1071 (2005).
18. W. C. Hinds, *Aerosol Technology. Properties, Behav-ior, and Measurement of Airborne Particles* (Wiley In-terscience, New York, 1999).
19. P. C. Reist, *Aerosol Science and Technology* (McGraw-Hill, New York, 1993).
20. V. V. Rashevskii, V. B. Artem'ev, and S. A. Silyutin, *Quality of SUEK Coals* (Kuchkovo Pole, Moscow, 2010).
21. S. K. Friedlander, *Smoke, Dust, and Haze* (Oxford Univ. Press, New York–Oxford, 2000).
22. N. A. Fuks and A. G. Sutugin, *Highly Dispersed Aerosols* (VINITI, Moscow, 1969) [in Russian].
23. R. J. Samson, G. W. Mulholland, and J. W. Gentry, "Structural Analysis of Soot Agglomerates," Langmuir. **3**, 272–281 (1987).
24. S. N. Rogak, U. Baltensperger, and R. C. Flagan, "Mea-surement of Mass Transfer to Agglomerate Aerosols," Aerosol Sci. Technol. **14**, 447–458 (1991).
25. V. V. Karasev, A. A. Onischuk, O. G. Glotov, A. M. Baklanov, A. G. Maryasov, V. E. Zarko, V. N. Panfilov, A. I. Levykin, and K. K. Sabelfeld, "For-mation of Charged Aggregates of Al₂O₃ Nanoparticles by Combustion of Aluminum Droplets in Air," Combust. Flame **138**, 40–54 (2004).
26. A. A. Onischuk, S. di Stasio, V. V. Karasev, et al., "Evolution of Structure and Charge of Soot Aggregates During and After Formation in a Propane/Air Diffusion Flame," Aerosol Sci. **34**, 383–403 (2003).
27. A. A. Onischuk, V. P. Strumin, V. V. Karasev, and V. N. Panfilov, "Formation of Electrical Dipoles During Agglomeration of Uncharged Particles of Hydrogenated Silicon," Aerosol Sci. **32**, 87–105 (2001).
28. M. Katzer, A. P. Weber, and G. Kasper, "Collision Ki-netics and Electrostatic Dispersion of Airborne Submi-crometer Fractal Agglomerates," J. Colloid and Inter-face Sci. **240**, 67–77 (2001).
29. H. D. Jang and S. K. Friedlander, "Restructuring of Chain Aggregates of Titania Nanoparticles in the Gas Phase," Aerosol Sci. Technol. **29** 81–91 (1998).
30. *Physical Quantities*, Ed. by I. S. Grigor'ev and E. Z. Mei-likhov (Energoizdat, Moscow, 1991) [in Russian].