Organic Nanoaerosol in Coal Mines: Formation Mechanism and Explosibility

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ABSTRACT

The mechanism of aerosol formation in coal mines during the operation of a longwall shearer was studied using a diffusion battery, optical counter, and by means of Transmission Electron Microscopy (TEM). The aerosol number concentration was measured to be (2–5) × 10⁵ cm⁻³. The aerosol size spectrum contained three modes, at about 10, 100, and 1000 nm. The first mode relates to single (primary) particles formed by the homogeneous nucleation of supersaturated organic vapor. This vapor is formed by the evaporation of organic matter from coal due to the release of frictional heat at the interface between the cutting pick and coal. The second mode relates to the particles that are aggregates formed by coagulation of primary particles. The third mode relates to the particles formed by direct grinding of coal by the cutting picks.

The laboratory studies of organic aerosol formation in a flow coal grinding machine showed that the size spectrum and morphology of aerosol from the grinding machine were close to those in the coal mine. This fact confirms the thesis that the release of frictional heat is the driving force for the formation of organic aerosol. The analysis of gas-phase products in the outflow of the grinding machine showed that along with aerosol formation, gas products such as CO, CO₂, CH₄, C₂H₆, H₂O are released from coal due to the frictional heat. Methane and ethane concentrations in the flow reached 10 and 5 vol. %, respectively.

To demonstrate the explosibility of organic aerosol, the combustion of organic aerosol in the air was studied. It was shown that the lower explosive limit for organic aerosol is less than 50 g m⁻³. A conclusion is made that the formation of organic aerosol is to be taken into account when estimating the safety limits in coal mines.

Keywords: Aerosol generation; Agglomeration; Carbonaceous aerosols; Nucleation; Homogeneous; Air pollution.

INTRODUCTION

Coal mining is an industry employing over 7 million people worldwide. Underground fires and explosions in coal mines represent a serious and constant threat to the safety of mine workers. More than 5 hundred disasters resulting in thousands of mine worker deaths have occurred in mines all over the world during the XX century. Just during the years 1985–2009, eight serious fires and explosions occurred in the USA resulting in 58 deaths of miners (NFPA report, 2010). In Russia, more than a dozen major coal mine disasters occurred during the 21-st century (Oparin and Skritskiy, 2010; ICE report, 2014). The reasons for these accidents are still not understood well enough, and the fundamental studies of the formation of explosive mixtures in coal mines are necessary.

Methane is explosive within the concentration range of 5–15 vol. % in air, and most often it has been the cause of devastating mine explosions. During the last decades, methane emissions in coal faces increased significantly because of higher mining productivity (EPA report, 2009). The fine coal dust can significantly contribute into the explosion hazard as it can be dispersed and ignited by methane gas ignition (Lebecki and Romanchenko, 2012).

Explosions in coal mines start with the ignition of flammable atmosphere. Most often ignition occurs due to frictional, flame and electrical ignition sources (Phillips, 1996). The frictional ignition by the mining machine cutter picks is to a higher extent responsible for the majority of fires (Pomroy and Carigiet, 1995; Phillips, 1996). The source of heat in frictional ignition is the hot material (hot streak)
left behind by the pick. The temperature of the hot streak is often governed by the phase transition in the impact point between metallic and rock materials. In this case, the hot spot is composed of a surface layer of either molten rock or metal (Trueman, 1985).

The major flammable component of the atmosphere in coal mines is methane released during coal mining. However, other flammable additives not only affect the lower explosive limit of methane but also take part in ignition. A considerable contribution into explosibility of gas mixture is made by higher hydrocarbons that can generate flammable vapor (Cashdollar, 2008). In some coal mines, significant inflows of liquid hydrocarbons occur, so they are to be pumped out continuously (Cashdollar, 2008; Wang et al., 2014). On the other hand, the frictional heating of coal results in coal pyrolysis and finally leads to the release of volatile products from the organic components of coal (Badzioch and Hawksley, 1970; Ladner, 1988; Wanzl, 1988; Butuzova, 2009). The nucleation of these products results in the formation of organic aerosol composed of polycyclic aromatic hydrocarbons, alkanes and organic acids (Chen et al., 2008; Wang et al., 2013). The effect of these organic aerosol additives on methane/air combustion is to be investigated.

In our previous papers (Baklanov et al., 2015; Valiulin et al., 2016) some preliminary results were obtained, demonstrating high concentration of nanoaerosol generated by a longwall shearer in a coal mine of the Kuznetsk Basin (Russia). However, the size distribution function for the coal mine aerosol was measured in these papers for the limited range of diameters 3–200 nm, and, therefore, the relationship between the nano-size and micron-size particles was not accurately determined. Besides, high water concentration in the mine atmosphere strongly affected the thermophoretical sampling for TEM which complicated the morphology analysis of nanosized particles. In the present work the size spectra of coal mine aerosol were measured in the range 3–10000 nm and the three modes typical for atmospheric aerosol (the nucleation, accumulation, and coarse particle modes) were observed for the first time in the coal mine atmosphere. In addition, more sophisticated sampling equipment was used to obtain better quality TEM images of coal mine nanoaerosol. As a result, the analysis of particle morphology clarified the mechanism of organic aerosol formation.

Laboratory coal grinding experiments were also carried out in our previous works to simulate the operation of a longwall shearer. It was found that the coal grinding machine generates both nano-sized and micron-sized modes of aerosol with the concentration comparable to that in mine. The addition of grinding products (aerosol and gaseous species) to a lean methane-air mixture affects the combustion characteristics in a spherical 10 L bomb. A conclusion was made that the main reason of an increase in inflammability was the organic species emitted from coal due to heat release during grinding. However, the relative contributions from organic aerosol and gaseous hydrocarbons to inflammability were not determined in that investigation. In the present paper the emission of gaseous products during coal grinding is measured in comparison with nanoaerosol, and the combustion of pure organic aerosol (without the addition of gaseous hydrocarbons) is investigated to clarify the possible contribution of organic aerosol into the explosibility of ambient atmosphere in coal mines.

MATERIALS AND METHODS

To measure the nanoaerosol size spectrum and number concentration both in the coal mine and in laboratory, the aerosol spectrometer (Dubtsov et al., 2017) and photoelectric counter are used. Both devices were designed and built at the Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia. The aerosol spectrometer and photoelectric counter cover together the particle diameter range 0.003–10 μm. The aerosol concentration range is $10^3$–$5 \times 10^5$ cm$^{-3}$ for both devices (without diluter). Using the diluter, the highest limit of concentration can be augmented by three orders of magnitude.

The size and shape of aerosol particles formed in the coal mine and in the laboratory grinding machine are studied using a JEM 100SX transmission electron microscope (TEM). Sampling for TEM in the coal mine is carried out thermophoretically. A special sampler consisting of a quartz tube with the inner diameter 1.0 cm is used (Fig. 1). An electron microscopy grid covered with polyvinyl formal film is fixed to the inner wall of the tube. The tube is cooled from outside using a Dewar vessel with liquid nitrogen and a metallic cooling rod. The atmospheric air is sucked into the tube through a silica air dryer with the flow rate of 7 cm$^3$ s$^{-1}$ using a micro-pump. Thus, due to the radial

![Fig. 1. Schematic of aerosol sampling for TEM in the longwall area.](image-url)
temperature gradient, aerosol particles are deposited onto the grid. In laboratory experiments, sampling for TEM measurements is carried out using the thermoprecipitator as described by Gonzalez et al. (2005).

For the laboratory study of nanoaerosol formation during coal crushing, a grinding machine was constructed (Fig. 2). The main unit of this set-up is a grinding mill. The grinding mill consists of the electric motor chamber and the grinding chamber 200 cm³ in volume. In the latter chamber, coal is crushed by the rotating picks. The rotation frequency is 6000 revolutions per minute. The rotating radius is 7.0 cm. The mass of loaded coal is 25 g. An inert gas (Ar or He) comes to the inlet of the motor chamber and then to the grinding chamber with the flow rate of 3–10 cm³ s⁻¹. During coal crushing, the temperature in the grinding chamber is controlled by the K-type thermocouple. After the motor is switched on, the temperature reaches the stationary level of 80°C very quickly (within five minutes).

To understand the mechanism of organic aerosol formation, coal evaporation/pyrolysis in a flow heating chamber is carried out. The heating chamber consists of a horizontal quartz tube (with the inner diameter of 1.4 cm) and an outer three-sectional oven 12 cm long. (Fig. 3) A flow of air (or inert gas) is supplied to the inlet of the tube with the flow rate of 3–10 cm³ s⁻¹ (at room temperature and atmospheric pressure) through a high-efficiency Petrianov aerosol filter (Kirsch et al., 1975). The axial temperature profiles in the heating zone are measured with a K-type thermocouple with a bare junction diameter of 100 µm. A zone of constant temperature is formed in the middle of the heated part of the tube. Before the experiment, a crucible with coal is charged into the constant-temperature zone. Then the temperature is increased to 600–750 K. Due to heating, hydrocarbons are released from coal, which results in aerosol formation.

The gaseous products from coal heating or mechanical treatment in the grinding machine are analyzed using a Bruker Vector 22 FTIR spectrometer and a SRS (Stanford Research Systems) mass spectrometer, Model RGA 300. For this purpose, the flux from the flow heating chamber or the grinding machine passed through the Petrianov aerosol filter, and then to the IR optical cell or mass spectrometer.

The combustion of organic aerosol in the air (as well as methane/air mixtures) is studied in a spherical bomb with the volume of 10 L, built at the Institute of Chemical Kinetics and Combustion (Novosibirsk), equipped with the inlet and outlet ports with valves. The combustible mixture passes through the bomb during some time, then the inlet and outlet valves are closed. The centrally located Ni/Cr heater is used to ignite the mixture. The pressure is recorded with an inductive pressure transducer with the pressure range of 0–30 atm.

The coal samples for the laboratory studies were taken from the Kuzbass “November 7th” Mine (Leninsk-Kuznetsky, Russia).

RESULTS AND DISCUSSION

Concentration, Size, and Morphology of Aerosol Particles in the Coal Mine “November 7th”.

The aerosol number concentration and size spectrum at the longwall face were measured with the aerosol spectrometer and optical counter running in parallel. These devises were placed 30 m downstream of the operating shearer (using the chilled water sprays). The aerosol number concentration was measured to be 5 × 10⁵ cm⁻³. A typical size spectrum obtained in these measurements is shown in Fig. 4. One can see that the size spectrum consists of three modes at about 10, 100 and 1000 nm. The modes at 10 and 100 nm give the dominant contribution to the total number concentration and, therefore, it is natural to assume that these two modes are due to aerosol formation from gaseous precursors. Indeed, normally it is impossible to obtain such a high concentration by grinding (Maynard and Zimmer, 2002; Zimmer and Maynard, 2002), and taking into account strong dilution with the air blown at the longwall face, we suppose that the 10 nm mode (primary particles) is formed by the homogeneous nucleation from the organic vapor due

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**Fig. 2.** Schematic of experiments with the grinding machine.
to the local heating of coal by shearer cutting picks, and the 100 nm mode originates from the coagulation of primary particles. The coarse mode at about 1000 nm is formed directly due to coal grinding. The number concentration of the coarse particles was measured to be in the range (0.5–2.0) × 10^4 cm⁻³, i.e., more than 90% of total number concentration comes from the nanosized particles.

Sampling for TEM analysis was made at the same place as the concentration/size spectrum measurements. Typical TEM images obtained from these samples are shown in Figs. 5(a)–5(f).

Fig. 5(a) demonstrates the particles of irregular shape, about 1 µm in size. It is natural to assume that these particles are formed due to direct coal grinding. However, there are particles of another type (Fig. 5(b)), which were probably formed from the organic vapour. These particles are aggregates composed of small primary particles. These aggregates can reach the size of a few microns (Figs. 5(c), 5(d)). In some cases a lot of single primary particles can be observed (Figs. 5(e), 5(f)). Thus, the morphology of aerosol particles supports our starting assumption that modes 1 and 2 in the size spectrum are formed due to the homogeneous nucleation from supersaturated vapor, followed by coagulation.

Some aggregates contain more than a thousand primary particles (Fig. 5(d)), which means that the initial concentration of single primary particles in the nucleation zone is very high. Let us estimate the initial concentration of supersaturated vapor giving rise to such a large aggregate. The initial stage of aerosol formation is the release of hydrocarbon vapor due to frictional heat generated from shearer cutting picks. The hydrocarbon vapor gets mixed with the blown air within the characteristic time of about 0.01 s. This time can be estimated as the ratio of the characteristic size of the hot streak generated by the pick (a few centimeters) to the blowing air velocity (a few meters per second). After being formed, the vapor gets cooled rapidly from the temperature of 700–1000 K (Phillips, 1996; McDonald, 1992) to the room temperature. Due to temperature decrease, the vapor becomes supersaturated, and homogeneous nucleation starts.

As a result, single primary particles are formed with the initial number concentration \( C_0 \). Then coagulation of
primary particles occurs. For simple estimations, one can suppose that the typical coagulation time is equal to the vapor-air mixing time $t \approx 0.01$ s. Coagulation is governed by the second order kinetics:

$$\frac{C}{C_0} \approx 1 + ktC_0 \approx ktC_0$$  \hspace{1cm} (1)

where $C$ is the current concentration of primary particles, $k \approx 10^{-9}$ cm$^3$ s$^{-1}$ (Fuchs, 1964) is the coagulation rate constant. The ratio $C_0/C \approx 1000$ is equal to the mean number of primary particles per aggregate. Then the initial concentration of primary particles just at the hot streak is obtained from Eq. (1)

$$C_0 \approx \frac{C_0}{kt} \approx \frac{1000}{10^{-9} \cdot 0.01} = 10^{14} \text{ cm}^{-3}$$  \hspace{1cm} (2)

Now we can estimate the concentration $C_V$ of vapor which gave rise to these primary particles. One can see from Figs. 5(c) and 5(d) that the typical diameter of primary particles is $d \approx 50$ nm. The density of organic particles is about $\rho \approx 1$ g cm$^{-3}$, and the characteristic molar mass of hydrocarbons released from coal is $M \approx 300$ g mol$^{-1}$, then we get the mean number $N$ of molecules per primary particle

$$N \approx \frac{\pi d^3}{6} \rho \frac{N_A}{M}$$

$$= \frac{\pi \cdot 1.25 \cdot 10^{-16}(\text{cm}^3)}{6} \cdot 1 \text{ (g/cm}^3) \cdot \frac{6.02 \cdot 10^{23}(\text{mol}^{-1})}{300(\text{g/mol})}$$

$$= 1.3 \cdot 10^7$$  \hspace{1cm} (3)

where $N_A$ is Avogadro constant. Then, from Eqs. (2) and (3) we obtain

$$C_V = C_0N \approx 10^{19} \text{ cm}^{-3}$$  \hspace{1cm} (4)

For simple estimates, the vapor temperature at the hot streak can be set about 700 K. For this temperature, the vapor concentration $C_a$ corresponding to the atmospheric pressure is

$$C_a = \frac{P_a}{k_B T} \approx \frac{1.01 \cdot 10^5(\text{dyne/cm}^2)}{1.38 \cdot 10^{-16}(\text{erg/K}) \cdot 700(\text{K})} \approx 1.0 \cdot 10^{19} \text{ cm}^{-3}$$  \hspace{1cm} (5)

where $P_a$ is the atmospheric pressure, $k_B$ is Boltzmann constant. Thus, one can see from the comparison between Eqs. (4) and (5) that the vapour concentration $C_V$ is approximately equal to that at atmospheric pressure. Therefore, one may conclude that the release of hydrocarbons
from coal occurs due to the boiling of organic components. Indeed, the hot streak temperature is governed by the phase transition at the interface between the pick and coal. It is believed that the maximum temperature of a hot spot is the melting point of either the tool material or the rock (Trueman, 1985). However, the coal of the mine “November 7th” contains about 35% of volatile matter (alkanes, polycyclic aromatic hydrocarbons etc.). It is natural to assume that the temperature of coal around the hot streak is stabilized at the boiling point of these hydrocarbons which is 600–800 K for alkanes C$_{20}$–C$_{40}$ (Grigoriev and Meylikhov, 1991). This means that the vapour temperature of 700 K was chosen correctly.

To prove our assumption that the nanoaerosol in the coal mine is formed due to the local boiling of hydrocarbons at the interface between cutting picks and coal, the laboratory studies of hydrocarbon release during the mechanical treatment and direct heating of coal were carried out.

**Formation of Aerosol and Gaseous Products during the Mechanical Treatment of Coal**

Fig. 6 shows the TEM image of aerosol particles sampled thermophoretically at the outlet of grinding machine in accordance with the schematic described in Sec. 2. One can see coarse micron-sized particles formed by direct crushing of coal, and aggregates consisting of small spherical primary particles. These spherical particles can be formed only from gaseous precursors. This agrees with our assumption that the nano-sized particles are formed by the homogeneous nucleation from supersaturated vapor due to the release of frictional heat.

The chemical composition of organic nanoparticles formed by mechanical treatment of coal was studied in our previous paper (Valiulin et al., 2016). Analysis by means of gas chromatography – mass spectrometry show that the chromatograms from coal extract were identical to those from organic nanoparticles except for light alkanes C$_{10}$–C$_{13}$ which were absent from the chromatograms of particles (the vapor of these species was probably undersaturated in the nucleation zone). These results also support our assumption of the evaporation-nucleation mechanism of nanoparticle formation.

The size spectrum of aerosol particles as measured at the outlet of the grinding machine is shown in Fig. 7. One can see a good agreement between this spectrum and that measured in the coal mine (Fig. 4). Both spectra reveal the same modes at about 10–20, 100–200 and 1000–4000 nm, which are from single nanoparticles, aggregates and coarse particles formed by crushing, respectively. Thus, both the TEM images and particle size spectra bring us to the conclusion that the work of grinding machine (as well as the operation of a longwall shearer) results in local heating of coal, followed by the organic vapor release and homogeneous nucleation. The size distributions from mine and grinding machine aerosol are typical for atmospheric aerosol which is normally categorized by size into three modes: the nucleation, accumulation, and coarse particle modes. The nucleation mode consists of small particles (most often 5–50 nm in diameter) formed by gas-to- particle conversion. The accumulation mode (100 < particle diameter < 1000 nm) includes coagulated nucleation-mode particles. These particles coagulate too slowly to reach the coarse-particle mode, and, therefore, they have a long lifetime in the atmosphere. The coarse-particle mode (with a size larger than 1000 nm) consists of windblown dust, pollen, mechanically generated anthropogenic particles and has a short lifetime in the atmosphere.

A good agreement between the particle morphology and size spectra for particles formed in mine and laboratory allows concluding that the grinding machine simulates the shearer well enough. Therefore, it seems to be important to study the kinetics of the release of gaseous products from coal in the grinding machine as this may add to the understanding of the formation of combustible atmosphere in coal mines.

The analysis of gaseous products in the outflow of the grinding machine was carried out by means of mass spectrometry and IR spectroscopy. During the operation of the grinding machine, a flow of He was supplied to the inlet with the flow rate of 3.5 cm$^3$ s$^{-1}$. The mass spectrometric analysis has shown that the main components of gaseous...
products are CO, CO$_2$, H$_2$O, methane and higher alkanes (see Fig. 8). The molar fraction of C$_2$H$_6$ in higher alkanes is about 0.85.

The IR spectra were recorded using a flow optical cell, which made it possible to monitor gas composition during the operation of the grinding machine. A typical example is shown in Fig. 9. One can see the characteristic vibrational absorbance bands from CO, CO$_2$, H$_2$O, as well as the rotational-vibrational structure of CH$_4$. As ethane is dominant among the higher alkanes, we attribute the broad band at 3000 cm$^{-1}$ (C-H stretching vibrations) to C$_2$H$_6$ molecules.

The mass concentration of the organic aerosol in the outflow of the grinding machine was also determined. For this purpose, the mass of volatile components in coal was determined before and after the treatment in the grinding machine. To this end, a sample of coal was heated in the flow heating chamber (under the flow of Ar) up to 870 K with the heating rate of 3.0 K s$^{-1}$. Then the temperature was kept constant for 30 min. The mass of volatile compounds was determined as the total mass loss due to heating. The difference of the masses of volatiles before and after the treatment in the grinding machine (per unit mass of coal) gives the total mass concentration of volatiles which were released into the gas phase due to the mechanical action on coal. Subtracting the mass concentration of CO, CO$_2$, CH$_4$, C$_2$H$_6$, H$_2$O (as determined from IR measurements) we obtained the mass concentration of organic aerosol in the grinding machine outflow. This organic aerosol is present in the form of nanoaerosol and as an organic deposit on the surface of coarse coal particles (due to particle and vapor deposition).

The concentration of gaseous products and organic aerosol in the outflow of grinding machine as a function of time is shown in Fig. 10. One can see that the concentrations of methane, ethane, CO$_2$, CO reached their maxima after about 3.5 min; the aerosol concentration came to a constant value after about 8 min, and the concentration of water increased monotonically with the operation time. The maximum concentration of methane is about 10 molar % (65 g m$^{-3}$), which means that the frictional release of

**Fig. 7.** A typical size spectrum measured at the outlet of the grinding machine.

**Fig. 8.** A mass spectrum of gaseous products sampled at the outlet of the grinding machine.
methane from the coal face can contribute essentially to the inflammability of the atmosphere near the cutting picks. The steady mass concentration of organic aerosol is about 100 g m\(^{-3}\), which is even more than the mass concentration of methane in the maximum. Thus, organic aerosol can probably contribute even more into inflammability than methane. One should note that the organic nanoaerosol number concentration is \(4 \times 10^7\) cm\(^{-3}\) when at the stationary level after eight minutes of grinding, which is 100 times higher than the mean aerosol number concentration at the longwall face during the shearer operation. Relatively low aerosol concentration in the mine with respect to the grinding machine is due to strong dilution by the mine blowing ventilation. One can assume that the mass concentration of organic matter in the longwall atmosphere is also 100 times less than in the grinder outflow, i.e., about 1 g m\(^{-3}\).

**Aerosol and Gaseous Product Formation in Direct Heating of Coal and Coal-Tar Pitch**

As follows from the experimental data, the reason of the formation of organic aerosol in the mine is heat release due to the mechanical treatment of coal. The reason of gaseous product formation during grinding (Figs. 8–10) is also local coal heating. To demonstrate the effect of thermal treatment, we have measured the concentration of gaseous and aerosol products formed due to the direct heating of coal in the flow heating chamber. The flux of He with the flow rate of 8.3 cm\(^3\) s\(^{-1}\) was supplied to the inlet of the chamber. A coal sample (2.0 g) was placed into the chamber, and the chamber was heated with the rate of 2.5 K s\(^{-1}\) up to the temperature of 670 K. Then the temperature was kept fixed during half an hour. The outlet concentration of products is shown in Fig. 11 as a function of heating time. As can be seen, the concentrations of CH\(_4\), C\(_2\)H\(_6\), CO, CO\(_2\), H\(_2\)O, as well as organic aerosol have reached their maxima at a time interval between 5 and 10 min. The values of maximum concentrations are comparable with those in the outflow of grinding machine, which supports our assumption of the thermal nature of gaseous products and aerosol formation. To achieve better understanding of the effect of heating, we studied the changes of coal morphology due to heating. Fig. 12 shows the images of a piece of coal before (a) and after heating under air to 670 K with the rate of 1.5 K s\(^{-1}\). One can see that the sample swelled out considerably. The reason of an increase in volume is probably boiling of hydrocarbons in the carbon matrix.
As the mass of organic aerosol formed at the longwall face can be large enough, the knowledge of the aerosol explosibility is necessary. Since both grinding and direct heating result in the formation of organic aerosol together with combustible gases, one should find the way to synthesize organic aerosol without gaseous products. For this purpose, we extracted the coal-tar pitch by heating coal at a temperature of 620 K in the atmosphere of Ar for five hours. Then the collected coal-tar pitch was placed into a bubbler flask, and a flow of Ar was blown through for eight hours at 373 K to remove volatile hydrocarbons. The coal-tar pitch sample prepared in such a way was then used to generate the organic aerosol without admixture of gaseous hydrocarbons. To this end, the pitch was placed into the flow heating chamber in the same manner as it was done before with coal. The number concentration and mean diameter vs. heating temperature are shown in Fig. 13 for the aerosol generated from the pitch by evaporation - nucleation. In that case, 1 g of pitch was charged in the chamber, and Ar was used as a carrier with the flow rate of 10 cm$^3$ s$^{-1}$.

To demonstrate the explosibility of organic aerosol, the bomb was connected in series with the flow heating chamber (charged by the coal-tar pitch) as described in Sec. 2. The filtered pure air was supplied to the inlet of the chamber as a carrier. The temperature of heating chamber was increased with the flow rate of 4 K s$^{-1}$ up to the temperature of 740 K, then the temperature was kept constant for 4 min. The aerosol generation rate was varied by the amount of pitch charged to the heating chamber (in the range of 4–10 g). The aerosol mass concentration in the bomb was measured by passing the outflow through the aerosol filter and weighting. The IR analysis of the outlet mixture showed that the contribution from the gaseous hydrocarbons in the aerosol mixture is less than 2.0 weight % of the total amount of organic particles. Fig. 14(a) shows the pressure $P$ in the

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**Fig. 11.** Concentrations of gaseous products and organic aerosol in the outlet of heating chamber charged with coal as a feedstock vs. time.

**Fig. 12.** A piece of coal before (a) and after (b) heating.

**Fig. 13.** Aerosol number concentration and mean diameter at the outlet of the flow heating chamber charged with the coal-tar pitch as a feedstock vs. heating temperature.
bomb after ignition as a function of time for the organic aerosol in the air (for two concentrations) and for methane-air mixture. The curves demonstrate maxima corresponding to the time when the flame has reached the walls. The maximum times are about 0.4, 0.5 and 0.9 s for the aerosol with mass concentration 100 g m\(^{-3}\) (dense aerosol), methane-air mixture (42 g m\(^{-3}\)) and aerosol with mass concentration 50 g m\(^{-3}\) (lean aerosol), respectively. This means that the flame velocity is maximal for the dense aerosol and minimal for the lean one. The lean aerosol demonstrates the time of maximum almost twice as long as that for the methane-air mixture. However, hydrocarbon mass concentrations for these two mixtures are close to each other. This seeming discrepancy is due to aerosol evaporation in the flame front, which is time and energy consuming. Fig. 14(b) demonstrates the derivatives \(dP/dt\) as functions of time. One can see that the highest derivative (140 atm s\(^{-1}\)) is for the dense aerosol, which is 2.3 times larger than that for the methane-air mixture (60 atm s\(^{-1}\)), and the lowest derivative is for the lean aerosol (17 atm s\(^{-1}\)) being 3.5 times less than that for methane-air mixture. Thus, the lean aerosol demonstrates a very low derivative, especially at the initial combustion time (< 0.6 s) in contrast to the methane-air mixture. However, both mixtures are close to their lower explosive limits (LEL).

Fig. 14. Pressure (a) and time derivative (b) vs. time dependences for the combustion of aerosol in air and methane/air mixtures. Mass concentrations are shown in the graph.

For methane, the LEL is 33 g m\(^{-3}\). The LEL for the organic aerosol is probably close to that of higher alkanes. Thus, for example, the LEL for heptane is 45 g m\(^{-3}\) (Flasinska et al., 2012).

CONCLUSIONS

Direct measurements with the aerosol spectrometer and optical counter at the longwall face of coal mine show that aerosol is formed in high concentration: \((2–5) \times 10^5\) cm\(^{-3}\). The aerosol size spectrum revealed three modes, at about 10, 100 and 1000 nm. The TEM analyses showed that the first mode is due to the single (primary) particles formed by the homogeneous nucleation of supersaturated vapor, which was formed by the evaporation of the organic matter from coal due to the frictional heat release. The second-mode particles are aggregates formed by coagulation of primary particles. The particles of the third mode are formed by direct grinding of coal by the cutting picks. Simple estimations show that the vapor pressure in the region of homogeneous nucleation is equal to 1 atm, which means that the organic vapor is released due to the boiling of organic matter in coal.

To clarify the mechanism of organic aerosol formation, laboratory experiments were carried out. We studied the formation of organic aerosol in the grinding machine. The size spectrum and morphology of aerosol from the grinding machine were close to those in the coal mine, which supported our assumption that the frictional heat release is the driving force for the formation of organic aerosol. The analysis of gas-phase products in the outflow of the grinding machine showed that along with aerosol formation, CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_6\), H\(_2\)O are released from coal due to the frictional heat. Direct heating of coal shows that the same gaseous and aerosol products are formed in quantities comparable with those in the grinding machine, giving another support to our assumption of the thermal nature of the aerosol formation process. To demonstrate the explosibility of organic aerosol, we generated it by heating coal-tar pitch to remove the effect from other explosive gaseous products of coal treatment. It was shown that even the organic aerosol mass concentration of 50 g m\(^{-3}\) is explosive. In view of the fact that the mass of organic aerosol formed from coal treatment is even higher than that of combustible gaseous products, the formation of organic aerosol is to be taken into account when estimating the safety limits in coal mines.

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