

EFFECT OF VOLATILES ON IGNITION DELAY IN COAL DUST GAS SUSPENSIONS WITHIN SHOCK WAVES

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We present the results from an experimental study into the dynamics involved in the formation and the unique features of ignition in shock gas suspensions of coal dust with a dispersion of $<40 \mu\text{m}$ and a volatile content of 9, 26, and 55%. We have determined the ignition delays τ_{ig} for coal dusts in air and in pure oxygen for a range of Mach numbers from 2.6 to 4.0 in an incident shock wave. We have established that the quantity τ_{ig} as well as the nature of the function $\tau_{ig}(1/T)$ are significantly affected by the kinetics of the volatile yield, in addition to the kinetics of volatile ignition. We have derived an approximation expression for τ_{ig} as a function of the content of volatiles, the temperature of the medium, and the partial pressure of the oxygen.

Because of the increasing attention devoted to the problem of explosion safety in work with powder and dust combustible materials, great interest has been evidenced in research into the processes of ignition, combustion, and detonation of gas suspensions of organic dust in shock waves (SW) [1-8]. We know that the characteristics of ignition and the explosive properties of organic dust depend to a considerable extent on the quantity and composition of the volatile materials which are formed in the thermal decomposition of the fuel. This applies particularly to coal dust, in which the content of volatile materials varies over a broad range. At the present time we have fewer studies of the mechanism of ignition applicable to organic dust in SW than for gas mixtures, and numerous questions have not been adequately clarified. In particular, no studies have been conducted into the influence exerted by volatile substances on the delay of ignition in coal-dust gas suspensions in SW.

APPARATUS AND METHOD OF DIAGNOSTICS

The experiments were conducted with a shock tube [8]. The high- and low-pressure sections were 1.5 and 5 m in length, respectively, with the cross section of the channel having dimensions of 52 mm^2 . Helium at a pressure of $p_4 = 2.5\text{-}5.0 \text{ MPa}$ was used as the propulsion gas, and either oxygen or air with $p_1 = 0.01\text{-}0.6 \text{ MPa}$ served as the working gas, the range of Mach numbers $M = 2.5\text{-}4.0$ for the incident SW. The parameters of the gas behind the incident and reflected SW were determined from the tables given in [9, 10], calculated for a real gas, with consideration given to the temperature dependence of the adiabatic exponent. The pressure of the propulsion and working gases were chosen so that the pressure behind the front of the reflected SW be constant ($p_5 = 2.3 \text{ MPa}$), independent of M . The studies were carried out with dust from black coking coal in which the content of the volatile materials was $V_0 = 9$ and 26% of the combustible mass, and tests were also carried out on lignite with $V_0 = 55\%$, which produced fractions with a particle size of $d < 40 \mu\text{m}$ through a mesh.

One of the most frequently used methods of producing gas suspensions in shock-tube experiments was employed here, namely the pulverization of the powder by the gas flow which moved behind the front of the passing SW. A coal-dust specimen of mass $m = 1\text{-}20 \text{ mg}$ in the form of a compact charge was pulverized against a flat substrate with a diameter of 10 mm, mounted at the level of the channel axis at a distance of $l_0 = 70\text{-}150 \text{ mm}$ from the closed end of the tube.

The dynamics of two-phase mixture formation was tracked by means of a high-speed multiframe laser shadow visualization procedure. The duration of the exposure ($\sim 30 \text{ nsec}$), the number of frames, and the time intervals Δt between the frames were established in this case by means of a laser stroboscopic light source [11], and the frames were separated spatially by means of a ZhFR-3 high-speed reflecting self-activated photorecorder. The synchronization system provided the required time sequence for the actuation of individual shock-tube elements and of the diagnostic apparatus, thus precisely coordinating light pulse generation to the instant of SW passage through a particular area. Each experiment yielded a series of 15-20 frames, reflecting the dynamics of the process over 300-400 μsec , including the stage of gas-suspension formation in the passing SW and the interaction of the reflected SW with the coal-dust gas-suspension cloud being formed.

We also used a method of scanning photographically the luminescence of burning particles in the investigation of ignition and combustion of coal-dust gas suspensions in a complex with multiframe shadow laser visualization, accomplished with the aid of a second high-speed ZhFR-1 photorecorder. Synchronization of this process with the instant of SW reflection, as well as the

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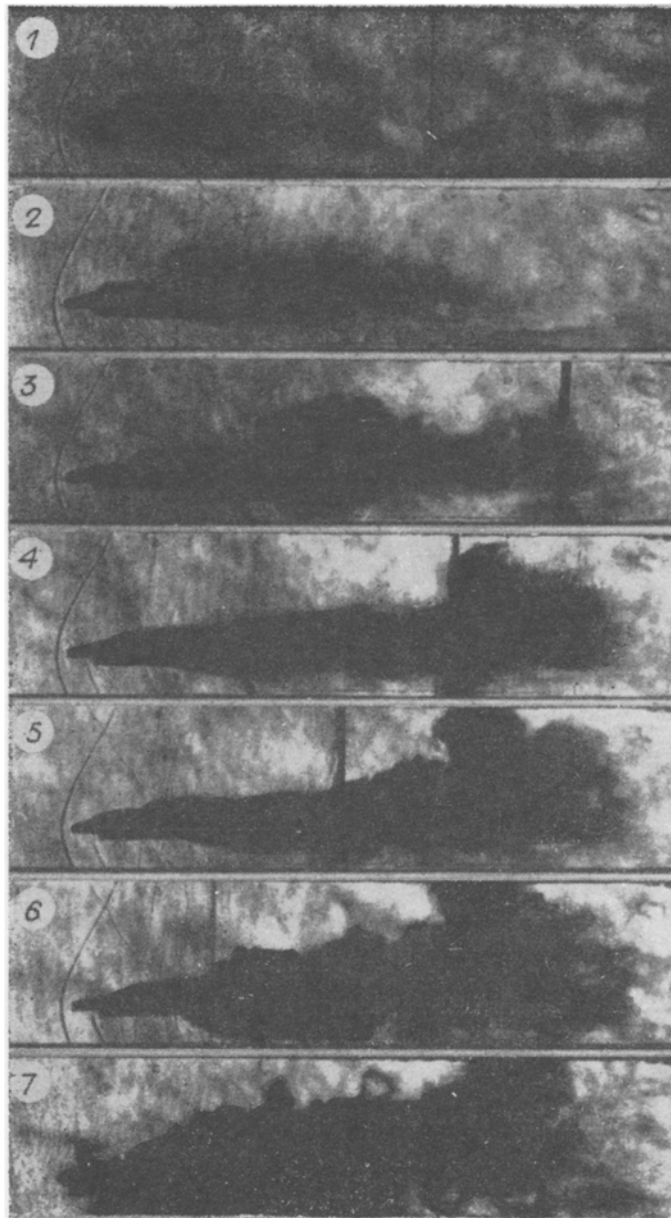


Fig. 1. Dynamics of the formation of a cloud of coal dust gas suspension in a shock wave; $M = 2.6$, $d \leq 40$ μm , $\Delta t = 40$ μsec .

the introduction of a time scale, were accomplished with a series of light pulses generated by a laser stroboscope, which was actuated by a signal from a piezosensor, mounted on the reflecting wall.

EXPERIMENTAL RESULTS

Figures 1 and 2 show a series of shadow photographs, illustrating the dynamics of the interaction between a suspension of coal dust and the passing and reflected SW at $M = 2.6$ and 4.0 , respectively. The passing wave moves from the left (the front is visible in frame 1) and is reflected from the wall located at the right-hand edge of the frame (the subsequent positions of the reflected SW front can be seen in frames 2-6). The intervals between the frames are $\Delta t = 40$ μsec . Photographs similar to these enable us to trace the dynamics of disperse-phase pulverization, and to establish the instant in time when the entire dust charge enters the suspended state, as well as to estimate the dimensions of the forming gas-suspension cloud and the dust concentration average through the cloud. Thus, according to Fig. 1, total pulverization of a charge of mass $m \approx 20$ mg corresponds to frame 7, and here the gas-suspension cloud occupies a volume of ~ 20 cm^3 , which corresponds to a volume-averaged dust concentration of ~ 1 kg/m^3 . A more detailed analysis of these photographs shows that as the SW interacts with the coal-dust charge, a gas-suspension cloud

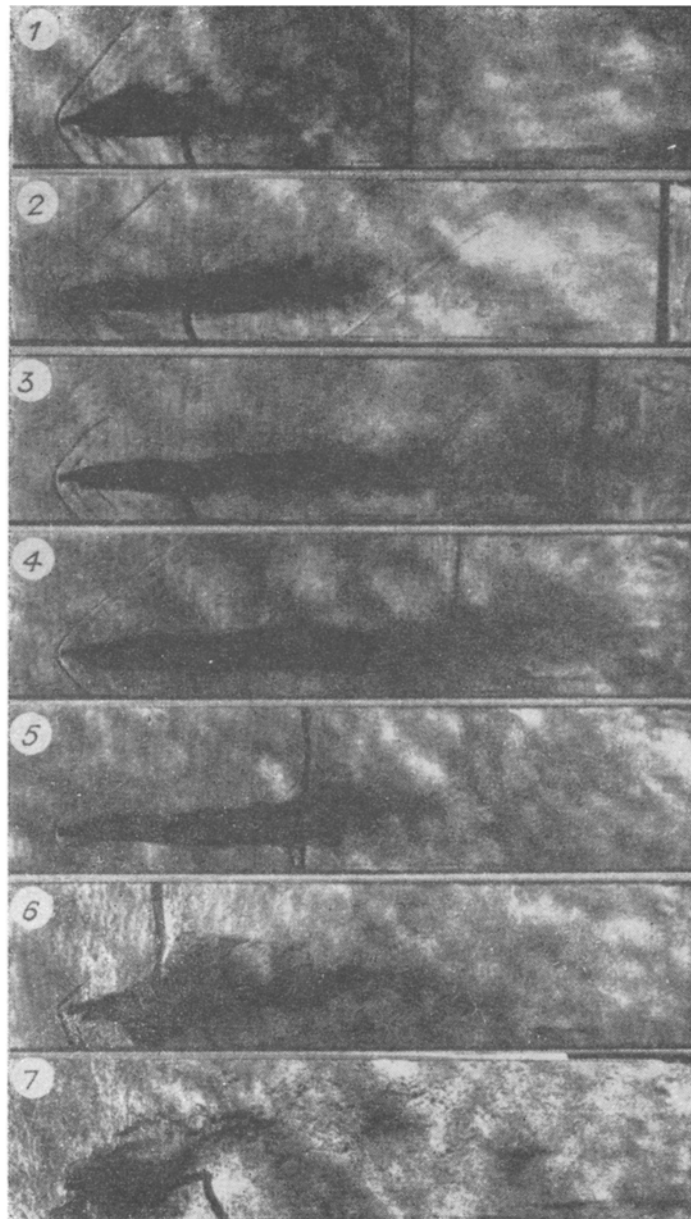


Fig. 2. Mixture formation and ignition of a coal dust gas suspension in shock wave compressed oxygen near a reflecting wall; $M = 4$, $V_0 = 55\%$, $\Delta t = 40 \mu\text{sec}$.

is formed, with a substantially nonuniform dust concentration distribution in space, and changing with time. This follows from the qualitative difference in the transparency of the gas-suspension cloud, both in terms of length and time.

These photographs also make it possible to achieve a quantitative estimate of the dust concentration at the boundary separating the optically transparent and nontransparent regions of the gas suspension. Indeed, the minimum calculated concentration of particles with diameter d , capable completely of covering a parallel beam of light at an optical thickness D corresponding to the transverse dimension of the cloud at this boundary is equal to $k_0 = 4/(\pi d^2 D)$, and the mass dust concentration $g_0 = k_0 \pi d^3 \rho / 6 = 2\rho d / 3D$. According to Fig. 2 (frames 2 and 3), $D \approx 8 \text{ mm}$, $\rho \approx 1.2 \text{ g/cm}^3$, $g_0 \approx 1$ and 4 kg/m^3 for particles with $d = 10$ and $40 \mu\text{m}$. Changing the shape of the charge and the distance from the substrate to the reflecting wall, we can alter the coal-dust concentration averaged through the gas-suspension cloud. However, in all cases within this process of gas-suspension formation we produce an elongated cloud of the dust-gas mixture with a significantly nonuniform distribution of dispersed-phase concentration.

The visualization method enables us to study the processes of ignition and combustion in gas suspensions, as well as to find the position in space for the focus of ignition and to determine the flame propagation speed through the cloud of the combustible mixture. Thus, it is seen in frame 4 of Fig. 1 that ignition occurs here, and its focus is found immediately behind the front of the reflected SW at $\sim 30 \text{ mm}$ from the reflecting wall. The process of gas-suspension burning is accompanied, first of all, by the exposure

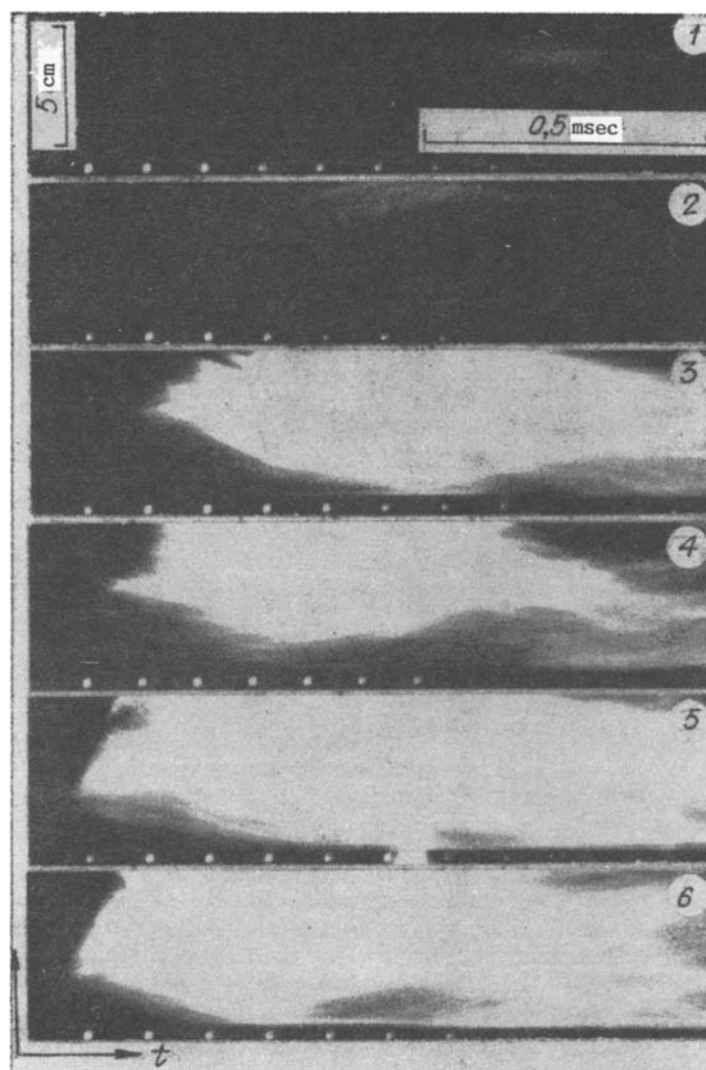


Fig. 3. Photographic scan of the ignition of coal dust gas suspension behind a shock wave in air; $V_0 = 9\%$, $d \leq 40 \mu\text{m}$. M: 1) 3.53; 2) 3.65; 3) 3.75; 4) 3.82; 5) 3.91; 6) 4.0.

of the shadow image of the disperse phase, governed primarily by the rapid burning up of the finest particles and, secondly, by a change in the shadow pattern outside of the gas-suspension cloud, associated with the propagation of thermal disturbances through the gas. It follows from Fig. 4, frame 5 that the front of the thermal disturbance follows behind the front of the reflected SW at a distance of $\sim 2 \text{ mm}$.

Results from our study into the process of ignition and combustion of gas mixtures by the photoscanning method of particle luminescence are shown in Fig. 3. The substrate carrying the coal dust ($V_0 = 9\%$) with a mass $m = 10 \text{ mg}$ was positioned 75 mm from the reflecting end. In the lower portion of the photoscanner we see images of the light pulses used for purposes of synchronization to the instant of SW reflection and to set the time scale. The duration of the intervals between pulses is given by $\Delta t = 100 \pm 0.2 \mu\text{sec}$. The light line in the left-hand portion of the photographs corresponds to the trajectory of the motion of the reflected SW front as determined from the shadow photographs. Figure 3 clearly shows the instant and location of ignition for the gas suspension, the nature and time of its burning, as well as individual tracks corresponding to large particles of this fraction.

In the present study the period of ignition delay τ_{ig} was defined as the minimum interval of time between the instants at which the front of the reflected SW passed the area where the ignition focus was located and where luminescence of the solid particles began. The total cloud burning time for the gas suspension was determined from the duration of disperse-phase luminescence.

The resulting data indicate that ignition begins in the fine particles, since at the initial stage of burning the tracks exhibit no clearly defined boundaries, such as is the case in the final stage. The focus of ignition, as a rule, is situated at some distance L from the reflecting wall (in the given series of experiments $L \geq 10\text{-}20 \text{ mm}$) and with a reduction in the intensity of the SW it shifts away from the wall to the position of the original charge location, i.e., to a region with a higher concentration of particles.

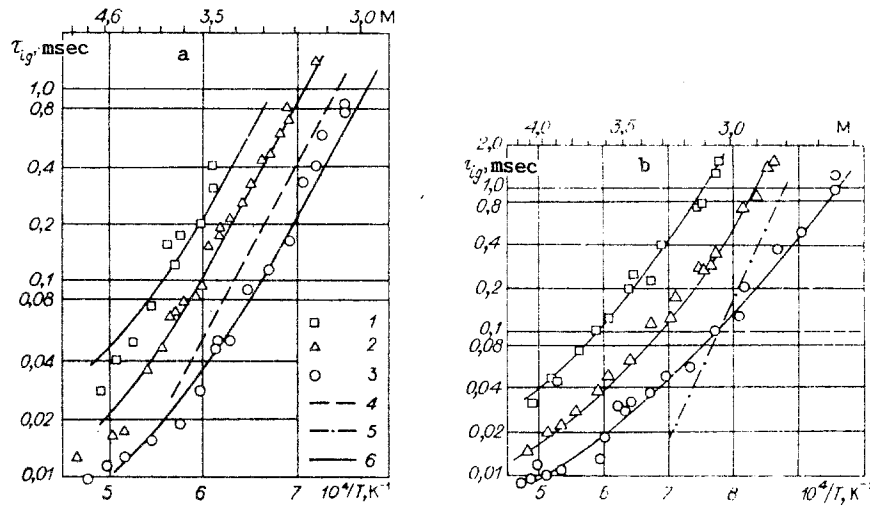


Fig. 4. Ignition delays in coal dust gas suspensions in air (a) and in oxygen (b). V_0 , %: 1) 9; 2) 26; 3) 55; 4) 2% CH_4 in air; 5) CH_4 in oxygen; 6) calculation based on formula (5).

With a reduction in M and a corresponding drop in the temperature of the gas behind the reflected SW, the value of τ_{ig} increases and the overall quantity of ignited particles and their burning time are reduced. Numerous experiments have shown that a change in the duration of the time that the gas suspension remains in the passing SW has virtually no effect on the nature and delay of coal-dust ignition in the reflected SW. (In this series of experiments l_0 was varied from 30 to 600 mm.)

We should take note of the fact that the majority of the ignition delay results encountered in the literature have been derived by methods based on photoelectric recording of flame luminescence (see, for example, [2, 5-7]). Here we measure the time interval τ_* between the instants of SW reflection and the appearance of luminescence, which was taken as the period of ignition induction. In connection with the fact that the focus of ignition is situated at some distance L from the reflecting wall, with such a definition of τ_{ig} there arises a systematic error $\Delta\tau_{ig} = \tau_* - \tau_{ig} = L/v_R$, where v_R represents the velocity of the reflected SW front. We can see from Fig. 3, frames 5 and 6, that for small τ_{ig} the value of $\Delta\tau_{ig}$ may exceed the value of τ_{ig} by factors of 10 and more. Therefore, in the determination of the ignition induction periods of heterogeneous mixtures with nonuniform distribution of disperse-phase concentration it is essential that we employ methods which make it possible to record both the time and space coordinate of the ignition focus.

Thus, the cited results show that the simultaneous use of a complex of two highly informative and mutually enhancing methods of multiframe shadow laser visualization and photographic scanning of the luminescence of burning particles allows us with greater conviction to interpret the results of our research into the processes of ignition, and thus to elevate the reliability of the results obtained.

Figure 4a shows the ignition delay in coal-dust gas mixtures with various contents of volatile substances as functions of the temperature of the air behind the reflected SW. However, here we have the data from [12], derived in the ignition of a methane-air mixture behind the reflected SW for the case in which $p_5 = 0.33$ MPa. The results for these same coal-dust specimens in an atmosphere of pure oxygen behind the reflected SW can be seen in Fig. 4b. Here we also show the function $\tau_{ig}(1/T)$ from [13] for a methane-oxygen mixture recalculated on the basis of the relationship $\tau_{ig} = 1.19 \cdot 10^{-12} [CH_4]^{0.48} \times [O_2]^{-1.94} \times \exp(194,000/RT)$ presented in this study with respect to the partial oxygen pressure behind the front of the reflected SW for $p_5 = 2.3$ MPa.

These results show the presence of a clearly defined effect on the part of the volatile substances on ignition delay in coal-dust gas suspensions. Particular attention should be devoted to the nonlinear nature of the relationship $\ln \tau_{ig} = f(1/T)$ for each of these mixtures. The latter indicates that this particular process is governed by the simultaneous effect of several different mechanisms, which to varying degrees affect the ignition mechanism, depending on the composition and temperature of the medium. We can see from Fig. 4 that when $T < 1700$ K ($1/T > 6 \cdot 10^{-4} K^{-1}$) the slopes of the curves $\ln \tau_{ig} = f(1/T)$ in the case of dust- and methane-air mixtures coincide. This provides a basis for our assumption that in the case under consideration ($T = 1300-1700$ K) the values of τ_{ig} are primarily determined by the kinetics of the ignition of the volatile substances (CH_4). For a dust-oxygen mixture the slope of the curve $\ln \tau_{ig} = f(1/T)$ does not coincide with the slope of a methane-oxygen mixture, and this is true virtually over the entire range of studied temperatures, although at low T there is a trend for these to approach one another (see Fig. 4b). Consequently, there is a decisive role here in the formation of the induction period that is ascribed not so much to the mechanism of ignition for the volatile materials, but rather, and this will be demonstrated below, to the volatile yield mechanism.

DISCUSSION OF RESULTS

Studies of the ignition mechanisms for solid organic fuels, conducted under steady-state conditions (see, for example [14, 15]), have demonstrated that thermal decomposition of the organic mass occurs during the process in which a particle of the fuel is heated, and this is associated with a release of volatile substances which saturate the boundary layer about the particle and counteract the diffusion of the oxidants toward the surface of the coke. The composition of the volatile substances includes a significant quantity of combustible components (CH_4 , as well as H_2 , C_nH_m , etc.), and these govern the process. The burning of the volatile substances about a particle promotes a rapid rise in particle temperature and the ignition of the coke residue.

The igniting of a solid organic fuel particle can be divided into relatively independent stages: the heating of the particle to the release of volatiles, the release of the volatiles, their ignition and combustion, and the ignition of the coke residue. These stages proceed at various speeds, duration, and degree of influence on the process, in dependence on such specific conditions as temperature, pressure, oxidant composition, fuel form, fuel dispersion, etc. It is obvious that in order to estimate the period of delay it is essential that we take into consideration the effect of these factors on the time characteristics of each of the above-enumerated stages preceding ignition.

Assuming that the preignition stages proceed sequentially, the delay period can be regarded as the sum of the following characteristic times: τ_1 is the time of inert particle heating to a temperature at which intensive decomposition of the organic mass sets in ($T_s \geq 1000 \text{ K}$ [7]); τ_2 is the time of volatile release, defined by the rate of the pyrolysis reaction; τ_3 is the induction time for the ignition of the volatiles. Since it is assumed [14] that the time required for the burning of the volatiles and for the ignition of the coke residue is small in comparison with the previous stages, we have $\tau_{\text{ig}} = \tau_1 + \tau_2 + \tau_3$.

We can isolate three characteristic segments [16] in the heating stage of a spherical solid fuel particle entering the high-temperature zone behind the front of a reflected SW: the heating due to convective heat exchange during the time of particle acceleration in the passing SW, the heating due to convective heat exchange in deceleration of the particle behind the front of the reflected SW, and the heating that is ascribed to heat conduction in the quiescent gas behind the reflected SW. The time required to heat the particles to T_s behind the front of the reflected SW is determined from the expression

$$\tau_1 = \frac{c\rho d^2}{6\lambda_g \langle \text{Nu} \rangle} \ln \left[\frac{T_5 - T_{s0}}{T_5 - T_s} \right], \quad (1)$$

where T and λ are the temperature and coefficient of thermal conductivity for the gas; c , ρ , and d represent the heat capacity, density, and particle diameter. The value of T_{s0} to which the particle is heated during stay time within the passing SW can be estimated from the expression

$$T_{s0} = T_2 - (T_2 - T_0) \exp \left[- \frac{6\lambda_2 \langle \text{Nu}_2 \rangle t_b}{\rho d^2 c \langle v \rangle} \right].$$

Here $\langle \text{Nu}_2 \rangle = \frac{1}{t_i} \int_0^{t_i} \text{Nu}_i(t) dt$ is the time-averaged Nusselt number which is determined from the formula $\text{Nu}_i = 2 + 0.46\text{Re}_i^{0.55}\text{Pr}_i^{0.33}$, Pr is Prandtl number; $\text{Re}_i = \rho_i[u_i - v(t)]d/\mu_i$ is the Reynolds number; $u_i - v(t) = u_i \exp(-t/t_i)$; $t_i = 4\rho d/3C_d\rho_i u_i$ is the characteristic time of velocity relaxation in the particle; C_d is the coefficient of aerodynamic drag; v denotes the particle velocity; ρ_i , μ_i , and u_i are the density, coefficient of viscosity, and gas velocity; the subscripts $i = 2$ and 5 correspond to the parameters of the gas behind the passing and reflected SW.

In order to evaluate the heating time we have to specify the dimensions of the particles with which ignition of the gas suspension begins. It was noted earlier that ignition of a polydisperse coal-dust fraction with $d < 40 \mu\text{m}$ begins at the smallest particles. Microscopic analysis of this fraction demonstrated that it contains a substantial quantity of particles with $d \approx 1 \mu\text{m}$. Thus, if we assume that the most probable particle dimension for the onset of gas-suspension ignition is $\sim 1 \mu\text{m}$, the time required for their heating even up to $T_s \approx 0.9T_5$ does not exceed $5 \mu\text{sec}$. A comparison of this estimate with the data shown in Fig. 4 shows that the time of inert heating plays a noticeable role only when $T_5 \geq 2000 \text{ K}$.

With rapid particle heating we must take into consideration the kinetics involved in the volatile yield. The quantity of released volatile substances depends on the extent to which they are contained in the original material and the speed with which specific groups of bonds are broken. The total quantity of volatile substances released at the instant of time t is defined by the relationship [14]

$$V = V_0 \sum_{j=1}^n c_{0j} \left\{ 1 - \exp \left[- \int_0^t k_{0j} \exp(-E_{vj}/RT_s(t)) dt \right] \right\}, \quad (2)$$

where V_0 represents the content of volatile substances, i.e., the total quantity of volatile substances which can be released with completion of the pyrolysis process; n is the number of reaction groups taken into consideration in description of pyrolysis; c_{0j} is a quantitative characteristic defined by the reaction group; k_{0j} and E_{vj} are the kinetic constants characterizing the breaking of bonds in this group; $T_s(t)$ represents the change in particle temperature over time. To evaluate the time required for the release of volatile substances from coal particles with $d \approx 1 \mu\text{m}$ we can use the single-component pyrolysis scheme ($n = 1, C_{01} = 1$), which proceeds under isothermal conditions [$T_s(t) = 0.9T_5$]. In this case

$$V = V_0 \{1 - \exp[-tk_0 \exp(-E/RT_s)]\}.$$

We will assume that the ignition of coal particles under conditions in which the kinetics of volatile yield is a limiting factor proceeds without absorption of the energy released in the combustion of a specific quantity $V = a$ of volatiles. The time for the release of such a quantity of volatile substances will then be expressed as

$$\tau_2 = A \ln \left(\frac{V_0}{V_0 - a} \right) \exp(E_v/RT_s). \quad (3)$$

The single-component scheme is extremely approximate in its description of the process of volatile yield, and the kinetic characteristics therefore assume various values for markedly diverse rates of particle heating [14]. The authors know of no studies which contain the kinetic characteristics of pyrolysis at particle heating rates of $\sim 10^6$ - 10^8 K/sec. With consideration of the above the values of A , a , and E_v were therefore chosen on the basis of the nature of the experimental relationship $\ln \tau_{ig} = f(1/T)$ in the region of high temperatures attained in the ignition of coal dust in an atmosphere of pure oxygen.

With a reduction in the temperature of the medium, the volatile ignition kinetics begin to play a limiting role. It should be noted that to the present time there exists no complete physical model which makes it possible through calculation to determine the ignition delays for organic fuels. Therefore, researchers proceed, as a rule, by deriving empirical relationships and for purposes of approximating experimental data they make use of the familiar equation [17]:

$$\tau_3 = kP^n \exp(E_a/RT),$$

where p and T are the pressure and temperature of the medium; n is a number which determines the effective sequence of reactions; k is a constant which is dependent on the composition of the mixture; E_a is the effective activation energy.

It is assumed [2, 7, 14, 15] that the primary component of the volatiles formed in high-temperature pyrolysis of coal dust is methane. The processes of methane ignition have been studied by numerous authors under a variety of conditions. The most reliable data on methane ignition delay both in oxygen [13, 18-20] and in air [12] were derived with the aid of a shock-tube method. These studies were conducted for a temperature range from 800 to 2600 K with $p_2 \leq 0.2$ MPa [13] with, and this is significant, mixtures strongly diluted with argon or nitrogen (70-95% Ar, N_2) and methane concentrations generally not exceeding 3-5% [12, 13, 18-20]. For purposes of describing the methane ignition delay data we use, as a rule, an expression of the form

$$\tau_3 = kc_f^m c_O^n \exp(E_a/RT),$$

where c_f and c_O represent the concentration of the fuel and oxygen; m and n denote the sequence of reactions for methane and oxygen.

We should note that despite the large number of experimental studies of the kinetics and mechanisms of methane oxidation, the region of high temperatures (>1500 K) remains little studied, and the data found in the literature are contradictory in nature. Such is the case with the values of $E_a = 86$ - 230 kJ/mole, $m = 0.3$ - 0.48 , $n = -1.0$ to 1.94 found in various studies (see, for example, the review in [18], as well as [13, 19, 20]).

Research into the processes of ignition for a series of more complex hydrocarbons (from propane to kerosene) with a concentration of fuel or the products of its pyrolysis exceeding 3-5%, showed that a change in c_f either has virtually no effect on the ignition delay ($m = 0$) [21], or it is contradictory in nature in comparison to methane ($m < 0$) [22], while the influence of c_O remains rather strong ($n = -0.6$ to -2.9), with the values of E_a , however, falling within the same limits as in the case of methane.

Analysis of the results shown in Fig. 4 shows that with an increase in the volatile content (and correspondingly in the methane concentration $c_f \sim V_0$) there is a reduction in the ignition delay of the coal-air mixture, and the nature of the relationship $\ln \tau_{ig} = f(1/T)$ undergoes virtually no change. When we take the above into consideration, we might assume that the local methane concentrations in the ignition foci exceed 3-5% and the effect of the volatile content on ignition delay makes its effect evident through a change in the sequence of oxygen reactions, i.e., $n \sim \varphi(V_0)$. The expression for the period of induction in the ignition of the volatiles can then be written as follows:

$$\tau_3 = BV_0^{0.3} p^{-(1+bV_0)} \exp(E_a/RT). \quad (4)$$

The final expression for the induction period of coal particle ignition where $d \approx 1 \mu\text{m}$, derived with consideration of the analysis undertaken here and comparison to the experimental data exhibits the following form:

$$\begin{aligned} \tau_{ig} = & 3 \cdot 10^{-6} + 5,5 \cdot 10^{-6} \ln \left(\frac{V_0}{V_0 - 0,04} \right) \exp(10\,000/T_5) + \\ & + 2 \cdot 10^{-9} V_0^{0,3} (p/p_0)^{-(1+3,7V_0)} \exp(23\,000/T_5), \text{ sec,} \end{aligned} \quad (5)$$

where p is the partial oxygen pressure; $p_0 = 0.1 \text{ MPa}$.

The quantity $E_a = 190 \text{ kJ/mole}$ obtained in comparison with experimental data is found to be in good agreement with the data for methane—oxygen ($E_a = 194$ [13] and 195 kJ/mole [19]) and methane—air mixtures ($E_a = 187 \text{ kJ/mole}$ [12]). The value of $E_v = 83 \text{ kJ/mole}$ corresponds to a particle heating rate of $10^6 \cdot 10^8 \text{ K/sec}$. For purposes of comparison let us note that with a coal-particle heating rate of $1\text{--}100 \text{ K/sec}$, $E_v = 30 \text{ kJ/mole}$ [14]. We can see from Fig. 4 that expression (5), derived in the assumption of a preignition process involving numerous stages, satisfactorily describes the ignition delay data for various coal-dust specimens, both in air and in an atmosphere of pure oxygen.

In conclusion, let us note that despite the fact that relationship (5) has been derived for particles with $d \approx 1 \mu\text{m}$, it can be recommended for purposes of estimating τ_{ig} and for polydisperse fractions, since in the majority of real situations these fractions contain rather fine particles. And as demonstrated by experiments, it is precisely with these fine particles that the process of ignition in the polydisperse coal-dust fractions begins. In our analysis of the ignition of larger particles we cannot neglect the time required for the heating of the particle [expression (1)] and it is essential that we take into consideration the effect of a change in particle temperature on the kinetics of volatile yield (2).

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FRactal Structure Formation in Explosion

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In the explosion of condensed explosive materials the release of free carbon is typical. The chemical reaction can proceed under conditions of diamond stability. Some results relative to the diamond phase have been described in [1, 2]; experiments performed in 1963-1965 are recalled in [3]. Note has been taken in [1-5] of the ultradispersion in diamond powders. The powder grains are conglomerates consisting of particles with characteristic dimensions of about 40 Å.

A two-stage model of particle growth in the condensed phase during an explosion [6, 7] has been introduced in the present study. By means of coagulation small compact particles are formed in the first stage, while in the second stage the particles are combined into aggregates (clusters) exhibiting a fractal structure, which is confirmed by data from small-angle x-ray scattering. The possibility of a fractal nature for aggregates in stored powders is cited in [2, 8].

In our opinion, the formation of fractal clusters must take place directly behind the detonation front, i.e., within microseconds. This leads to consequences which may be important in understanding the physics of detonation.

In an explosion free carbon is released within $\sim 0.1 \mu\text{sec}$, i.e., the time of the chemical reaction within the front of the detonation wave. The characteristic time t_H of hydrodynamic disintegration is expressed in units of microseconds. The quantity of carbon may be $>10\%$ of the charge mass, which corresponds to an atom concentration of $n_C \sim 10^{22} \text{ cm}^{-3}$. With such strong nonequilibrium, virtually every particle collision must lead to their merging into one another, i.e., the initial stage of particle growth must be rapid coagulation.

The Smolukhovskii theory of rapid coagulation [9] brings us to the following results. The mean particle mass (in the units of mass of the carbon atom) increases linearly over time [10]:

$$\langle m \rangle \sim K n_C t,$$

where the coagulation constant $K = 4kT/3\eta$; η is the viscosity of the detonation product. Let us note that because of the great density of the medium, particle motion, even of the smallest particles, proceeds in the diffusion Stokes regime. This serves to validate the Smolukhovskii theory for all particle sizes. In a rarefied medium such as, for example, atmospheric air, for particles small in comparison to the intrinsic Brownian mean-free path, coagulation is slightly accelerated (the free-molecular regime) [11].

We will take the temperature $T \approx 3000 \text{ K}$ of the detonation product (DP) and the viscosity $\eta = 10^{-2}$ poise [10^4 dynes/cm^2] on the basis of computations presented in [12] (the elementary gas-kinetic estimate from [13] yields $3 \cdot 10^{-3}$ poise). Then the product $K n_C \approx 10^{12} \text{ 1/sec}$. Within the time $t_H \sim 1 \mu\text{sec}$ particles consisting, on the average, of 10^6 atoms with dimensions of $\sim 200 \text{ Å}$ must be formed. Indeed, characteristic is a particle dimension of 40 Å, i.e., the mass is smaller by 2 orders of magnitude. At the same time, the experiment from [5] shows no relationship between particle size and t_H (proportional to the dimensions of the charge). Consequently, the growth of compact particles must be limited.

Furthermore, we will assume that two particles will combine with one another when they meet, provided that at least one of these contain atoms smaller than $m_0 = 10^3$, i.e., in terms of size $< 20 \text{ Å}$. There are a number of arguments in favor of such a condition [2], in particular, a reduction in the effective melting temperature for small particles [14]. As a result, small particles may react in the manner of liquid droplets, whereas large particles will not enter into combination. An analogous effect is achieved by the rise in fluctuations for small particles and the increase in the relative role of the surface. Of course, a realistic transition from unitary to zero probability of particle combination will not be pronounced, and the characteristic value of m_0 should be understood as a quantity chosen on the basis of its order of magnitude. The model being discussed here will therefore serve as a first approximation, and its use is justified by the imprecision with which the characteristics of the medium and of the coagulation process are known.

Let us introduce the concentration n_m for particles containing m atoms. The Smolukhovskii system of equations has the form

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