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NANOCLUSTER INITIATION OF COMBUSTION OF OFF-GRADE HYDROCARBON FUELS

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We have performed large-scale experiments on burning, in the regime of nanocluster pulsating combustion, such off-grade fuels as straw oil, hydrocarbon fuel, exhaust crankcase waste, crude oil, and others on the laboratory prototype of the self-contained burner of the Institute of Thermal Physics, Siberian Branch of the Russian Academy of Sciences. The application of modern diagnostics has made it possible to obtain a large body of information on the features of the physicochemical processes of such combustion in the presence of superheated steam. The experimental and theoretical studies have shown that as a result of the heterogeneous-catalytic decomposition of water molecules on soot nanoclusters in the mixing zone, high concentrations of the OH radical are formed and that this decomposition can be effective on carbon particles of size 1–5 nm at temperatures characteristic of traditional flares. The generation of an active OH radical leads to a significant increase in the rates of chemical reactions and a stable high-temperature combustion of "heavy" fuels with the observance of ecological norms.

Keywords: *nanoparticle, cluster, combustion, off-grade fuel, burner.*

Introduction. Present-day trends in the world fuel market show the steady increase in prices for high-quality kinds of energy carriers such as gas, oil, coking coal, etc. This leads to an unjustifiably large increase in the rates for thermal and electric energy, rolled metal, building materials, and other products. The price of the fuel component in a GDP unit can be decreased by involving huge stocks of various off-grade fuels in the turnover. Among them are waste crankcase oils and lubricants, pitches and polluted boiler oils, and many other combustible compositions.

In connection with the strategy of large-scale development of coal power engineering in Russia by the year 2030 [1], the amount of small carbon fractions having no sufficient demand in thermal power engineering will also increase. For the energetic use of such low-grade wastes, the application of oil sintering combining the processes of cleaning and partial dehydration is possible. The thus obtained carbon-oil product can be used as the basis for preparing carbon suspensions.

Water-coal fuels [2] are promising because of their undoubted advantages: the possibility of conveyance by pipes, fire and explosion safety, environmental safety, possibility of improving the quality by means of physicochemical activation with the aid of disintegrators, vibratory mills, cavitators, etc. With such a method of coal processing, dispersion of its particles in water to the micron level, homogenization of the product being processed, and intensification of the chemical reactions by a factor of tens, hundreds, and sometimes thousands take place.

It is known that oil processing of solid impurities leads to the formation of a large quantity of oil slimes representing combustible wastes (their yield is 7 kg per ton of processed oil [3]). Coal slimes are in great demand for increasing the thermal value of water-coal fuels, since due to them high-calorific hydrocarbons are included in the composition of the latter.

At the current stage, the application of various composite fuels is also urgent [4, 5]. These are coal-peat-boiler oil, organo-water-coal, water-boiler oil, oil-carbon, and other fuels.

The necessity for wide use of essentially "worthless" and "practically free" fuels is also dictated by other important circumstances. First, the most convenient energy carriers such as oil and gas are exhausted quickly (by histori-

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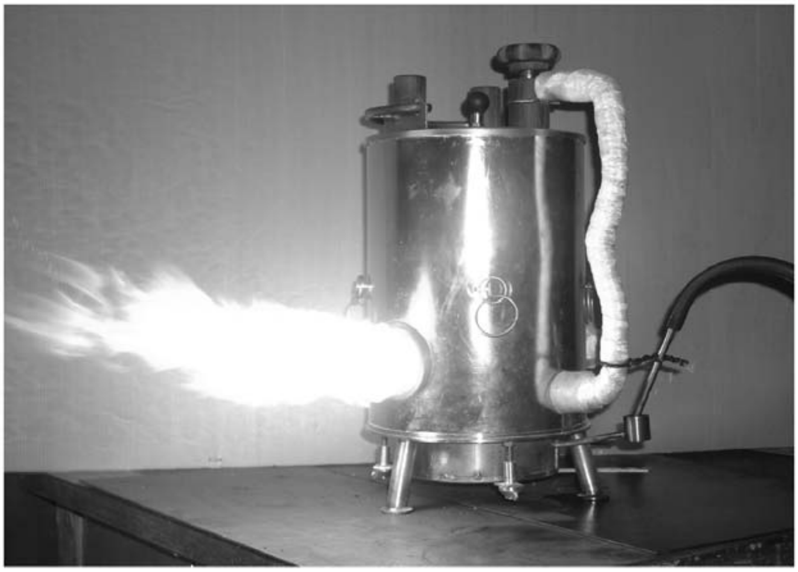

Fig. 1. Burner-demonstrator of power 20 kW.

cal measures). According to the data of the World Energy Council, with the existing rates of consumption, oil deposits will last for 40 years, and gas deposits — 60 years. Second is the low level of useful utilization of the already extracted primary power resources, which in Russia is no more than one third. Third, the economies of the majority of countries are power-intensive and power-consuming. For instance, Russia expends, on average, two to three times more equivalent fuel than other technically developed countries.

The chief reason for the insufficient demand for off-grade fuels as an additional fuel resource is the absence in the world of circulated burners that burn energy efficiently and ecologically safely the above-mentioned series of "heavy" fuels. The urgency here consists of the necessity of creating compact self-contained heat generators on a new scientific basis.

New Principle and Design of a Burner for Burning Off-Grade Fuel. The proposed self-contained burner is based on an original method for burning hydrocarbon-containing liquid fuels whose distinguishing feature, according to the patent of [6], is separate feeding into the combustion chamber of two flows: 1) fuel+air; 2) superheated steam. The first "hardware" version of the burner-demonstrator of power of the order of 5 kW with burning straw oil was realized by the engineer M. S. Vigriyanov. The first series of investigations of combustion processes was carried out on this burner. The following principle of ignition and burn-out of the off-grade combustible composition was postulated. The primary flame arises from the combustion of a "poor" hydrocarbon-containing fuel under the conditions of partial or complete cut-off of the air (oxidizer) supply. At the initial stage, in the combustion chamber an aerosol sooty flame with given parameters of particles is formed. Then, due to the impulse of the superheated steam piercing the primary flame, a secondary flame arises, where on clusters of sooty nanoparticles catalytic decomposition of water vapor molecules occurs. This leads to the creation of the necessary conditions for effective burning of "heavy" fuels and sustaining their stable combustion. On the basis of the given principle and the experiments performed, at the Siberian integrated chemical plant of Seversk an improved variant of the burner-demonstrator of power 20 kW burning mainly straw oil was created and investigated (Fig. 1).

Preliminary tests of the burner-demonstrator led to the following results. The level of CO emission compared to the data for a burner of equal power of the leading (in this sphere) company Weishaupt (Germany) is 200 times lower, and of NO 18 times lower; soot at the exit from the burner is practically absent. Full independence of the burner was achieved (no additional kinds of energy, such as electric, pneumatic energy, etc. are required). Moving and galling parts are absent. There is no need for auxiliary equipment (pump, compressor, automatics, etc.). Compared to the widely sold (in Russia) burning device of the German company "Volko Ekkel" (kerogas stove type), the proposed burner-demonstrator operates reliably under foul-weather conditions (snow, rain, strong wind, etc.). Additional advan-

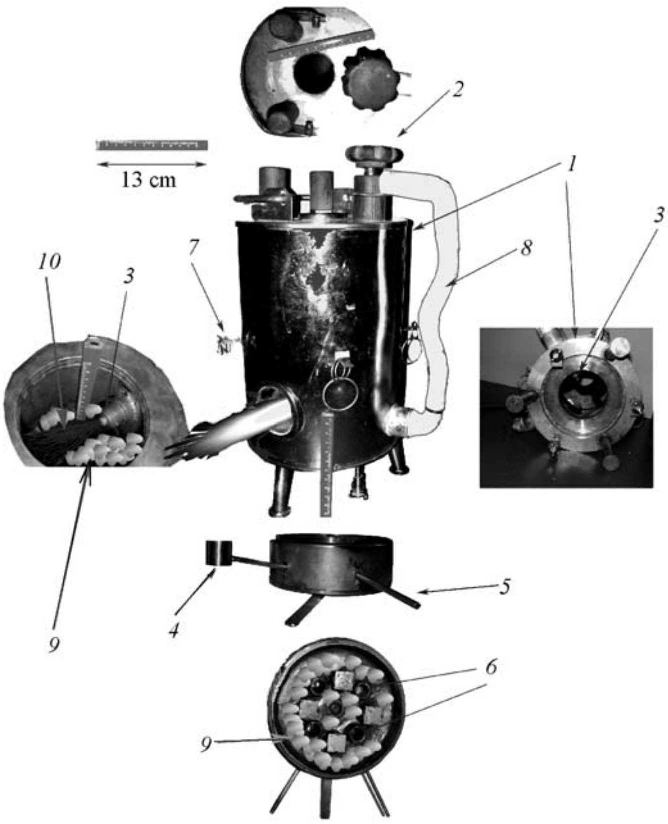

Fig. 2. Basic structural assemblies of the burner-demonstrator: 1) double case with water; 2) hole for pouring water; 3) nozzle with dry strongly superheated vapor; 4) straw oil leak; 5) spare fuel drain; 6) holes for drawing-in air from below; 7) vapor pressure control valves; 8) superheated steam line; 9) straw oil vapors and hydrocarbon aerosol formed in the regime of combustion with oxygen deficiency; 10) primary vapor jet.

tages of the developed self-contained power supply burner are the unnecessary continuous watch, fire safety, the possibility of burning a wide gamma of off-grade fuels, low cost, long service life, multifunctionality.

Trial experiments were also performed on portable burners-demonstrators for burning other off-grade fuels: used crankcase oil, crude oil, water-coal fuel, etc. Used oil caught fire, but this combustion was unstable. Technical crankcase wastes contain a large amount of foreign impurities, including metal ones. Moreover, the oil contains water because of the tosol that gets into it, or for some other reason. Water is distributed over the oil very nonuniformly. Apparently, because of the above factors the combustion process is accompanied by a high emission of black smoke and an acrid smell. It is quite possible to separate water from oil, as well as to create a more homogeneous consistency of oil. But another problem arose: carbonization of the metal walls of the combustion chamber. On the bottom of the furnace, a "coke pie" grew rapidly (in our experiments in about 15 min). There was no external flame, and combustion occurred inside the furnace itself. In principle, the device can burn crankcase wastes, but further design development and selection of "its own" regime parameters for energy-efficient and ecologically clean burning of such "heavy" fuel are required.

The content of water in the crude oil is much larger than in the crankcase technogenic waste. The combustion here was even more unstable, but the carbonization was much slower; it lasted for about 30 minutes in our case. Similar difficulties arose also in burning water-anthracite fuel.

Unfortunately, the available database on the physicomechanical processes of combustion of "poor" fuels in the presence of large concentrations of H_2O molecules does not permit developing, on a new scientific basis, burners with optimized design and regime parameters. Since in the given design of the burner the main medium carrying the fuel

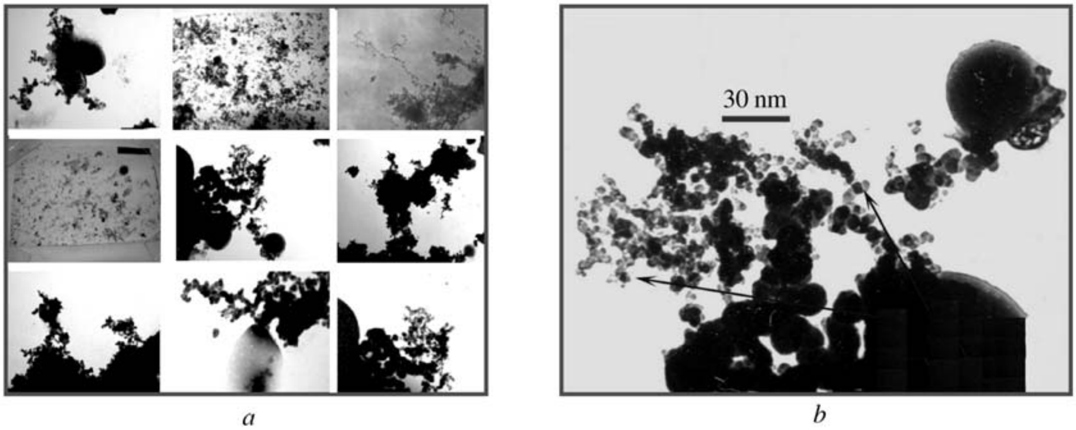

Fig. 3. Electron-microscope photographs of various types of soot particles: a) various soot particles of the fractal type; b) enlarged electronic photograph of an aerosol particle of size about 200 nm on whose surface a settled fractal consisting of catalytic soot particles of size about 5 nm is seen.

pyrolysis products into the zone of mixing with the external oxidizer (air) is water vapor, the problem on the kinetics of water decomposition on clusters of the soot formed has to be solved. Recent theoretical studies in the area of water decomposition on the surfaces of nanosized particles have shown that water can already decompose effectively on the surfaces of such particles at a temperature as low as ~1000°C, and not like in the homogeneous case at ~2000°C [7]. For this reason, the whole of the kinetics of the processes proceeding with superheated steam and nanoparticles in the mixing zone in the burner requires taking into account the heterogeneous processes on aerosol particles. Of particular interest are also the catalytic processes that can proceed on nanosized particles of soot or hydrocarbons. With such an approach the most important characteristic of products in the combustion zone must be the size distribution function of nanoparticles, the time of their formation, etc. [8, 9].

To solve successfully the posed problem, one has, in the first place, to:

a) study the processes of ignition and combustion of the hydrocarbon aerosol fuel in a medium consisting of water vapor molecules at high temperatures (determine the role of the OH radical in the surface aerosol reactions and the decomposition efficiency of H_2O molecules on the surfaces of cluster particles with a size of a few nanometers, establish the parameters of the appearance of stable combustion conditions in the soot-vapor system, and make a quantitative estimate of the concentrations of harmful gaseous and condensed combustion products formed by burning the primary fuel);

b) carry out a substantiated choice and optimization of the design and regime parameters of the burner for a number of "heavy" fuels in order to realize a radically new technology by the burning of off-grade fuels and combustible wastes.

Fundamental Investigations of the Processes of Nanocluster Initiation of Combustion of Off-Grade Hydrocarbon Fuels. *Experimental study of the processes of soot-vapor combustion.* The two-phase soot-vapor flame is a complex physicochemical phenomenon, and various methods are required to gain an insight into it. Figure 2 shows the basic structural assemblies of the burner-demonstrator. Primary consideration is given to the elements where mixing of the vapor stream with the vapor-soot mixture formed by the incomplete combustion of the straw fuel occurs. In our investigations, a broad spectrum of diagnostics is used [10]. They can conventionally be subdivided into three categories: 1) contact methods — ceramic capillary vacuum samplers for particles of size from 3 nm to 2 μm; multiposition vacuum samplers for particles from 10 nm to 5 μm in size; inertial samplers for particles of size up to 100 μm; a nephelometer of up 10^9 particles/cm^3; a fast condensation enlarger of clusters; an aerosol counter for determining the spectrum of particles by size with a diameter greater than 0.3 μm; 2) optical methods — composite video photography combined with microthermocouple measurements; high-speed photography of up to 12,000 frames per second; photography with interference filters; equipment for measuring the laser scattering by aerosols; an interference portable spectrometer with an output to a photomultiplier; a time-of-flight nephelometer with a resolution of 10^{-3} s; 3) physical methods — a generator of a narrow stream of soot particles; a portable measuring complex; an ultraviolet lamp for

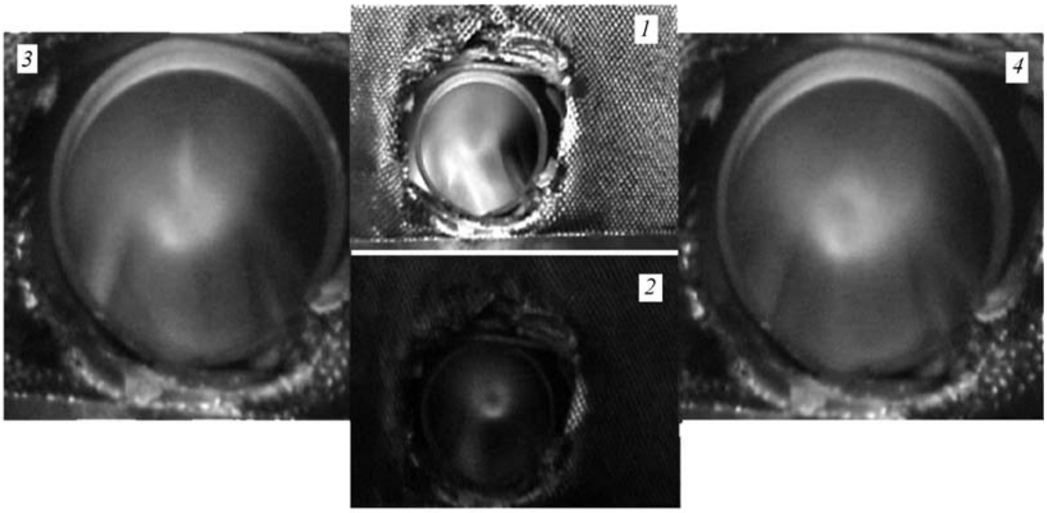

Fig. 4. Spectral measurements of the flame luminosity with the use of optical and interference filters: 1) flame imaged by a wide-band filter in the red region of the spectrum; 2) same, in the ultraviolet region of the spectrum at the initial stage of ignition; 3, 4) luminescence in the ultraviolet region in different regimes of stationary combustion.

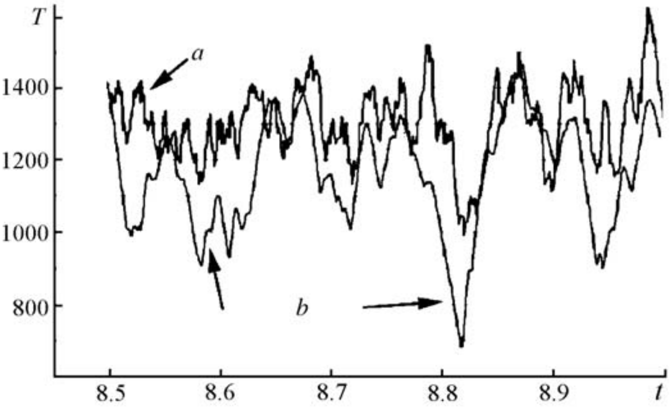

Fig. 5. Pulsation regime of luminescence of the chosen part of the flame (a) and microthermocouple measurements of the temperature pulsation in this part (b). T, ^{o}C; *t*, s.

model action on water vapors; a high-sensitivity fast barometric recorder; optical microscopy of high-temperature filters with particles; an infrared imager with accessory silicon lenses with image enlargement up to ×40 and with a frequency up to 10 frames per second.

Methods for sampling aerosols from the flame. One of the most important problems is the development of methods for sampling aerosols from the flame where the concentration of particles can be of the order of 10^{12}–10^{13} particles per 1 cm^3. We used a vacuum multiposition sampler equipped with an additional connector for the setting of a photodiode under the transparent substrate and a tube with adapters for connecting to the vacuum system.

Principal Fundamental Results Obtained. *Detection of soot nanometer particles in the flame.* With the aid of transmission electron microscopes various types of sooty particles were obtained (Fig. 3). The particles shown in the photograph were sampled in the mixing region of the water vapor and the fuel. In the figure, the arrows indicate catalytic nanosoot particles with a high gradient of the electron-microscopic contrast. This points to the existence of a typical layer structure in catalytic soot particles observed by many authors [8]. From the electron-microscopic data it follows that in the presence of "large particles" (fractions of micrometers) fractal type particles consisting of primary

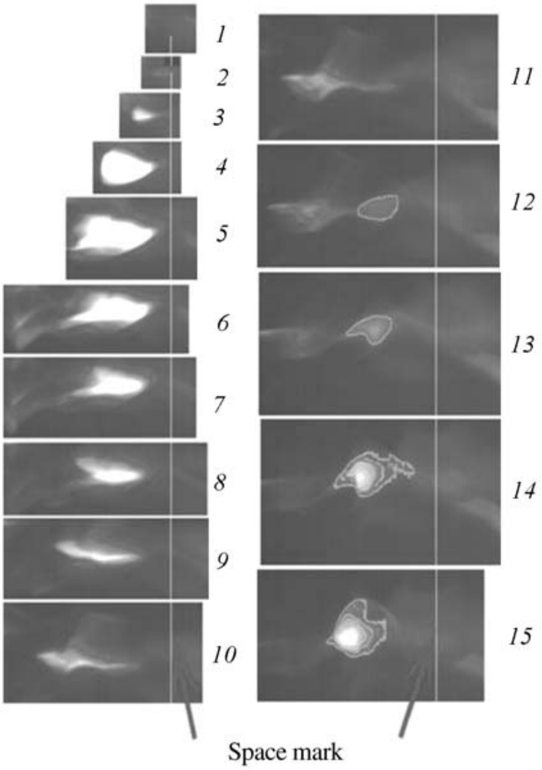

Fig. 6. Pulsation regime of combustion and after-combustion of aerosols at the boundary between the vapor jet and the cloud of soot particles: 1–15) video frames of different formats taken at 1μs intervals; white line — fixation of the initial center of ignition for all frames.

particles of the nanometer range are always present in the bulk. This is the first important result for understanding the specific features of the operation of the given device.

OH radical detection in the ultraviolet region. According to the working hypothesis tested by us, nanosoot particles can precisely be the centers of higher catalytic activity of water vapor decomposition with the appearance of the chemically active OH radical. The luminescence of this radical is in the near ultraviolet region, which is registered experimentally. Figure 4 shows images of the jet flame in the frontal plane in the visible and ultraviolet regions (the annular structure of the OH radical luminescence around the vapor jet is seen). This is the second important result.

Pulsating combustion of the soot-vapor jet. Microthermocouple measurements of pulsations of the temperature and luminosity of the part of the jet in which the thermocouple was set point to the existence of correlations between the temperature and the luminosity (Fig. 5). High-speed photography with a great enlargement of the mixing zone in the burner-demonstrator have made it possible to reveal a number of specific features of the process of burning soot particles in the medium of the external oxidizer in the presence of the vapor phase (Fig. 6), in particular, its pulsating character. The pulsating combustion of the soot-vapor jet can also be observed from the analysis of the time scan of aerosols with recording on a photoelectric counter of the "AZ-6" type with induced fast pumping of air samples from the jet directly through its counting volume. This is the third important result.

Spectrum of acoustic pulsations of the jet. Important information about the processes in the jet is given by the acoustic method. It is known that sound analyzers are often used in investigating the specific features of the operation of burners of various types. On the basis of the data on the pulsating character of the ignition process in a vapor-soot highly turbulent jet, obtained previously by high-speed photography, we stated the problem of determining the maximum frequencies in the sound spectrum as a reflection of such processes. The sound channel of signal reception from the jet consists of a detector microphone, an A-D converter, and a computer recording line. The signal transduction linearity of the chance is adjusted and calibrated by means of an audio-frequency generator. Fundamental harmonics are recorded by an oscilloscope and a web-camera. Measurements of the spectrum of acoustic pulsations of the jet per-

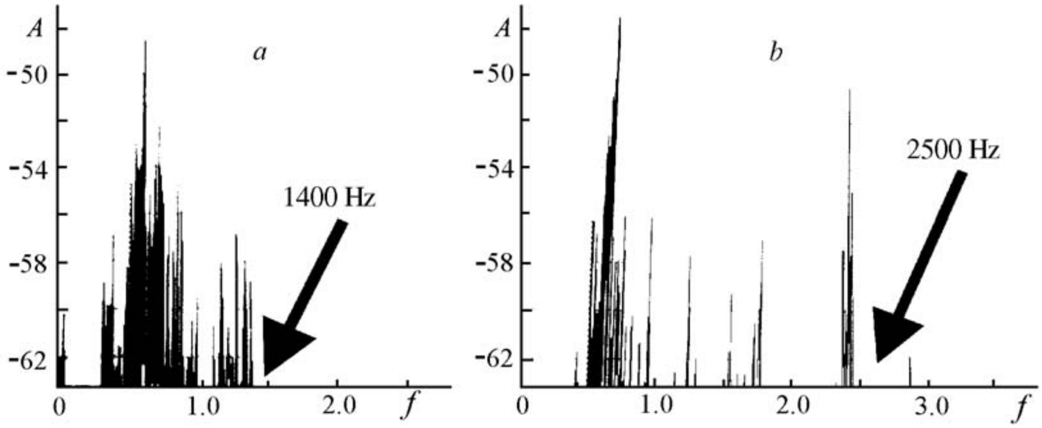

Fig. 7. Measurements of acoustical frequency spectra in high- (a) and low-temperature (b) flames.

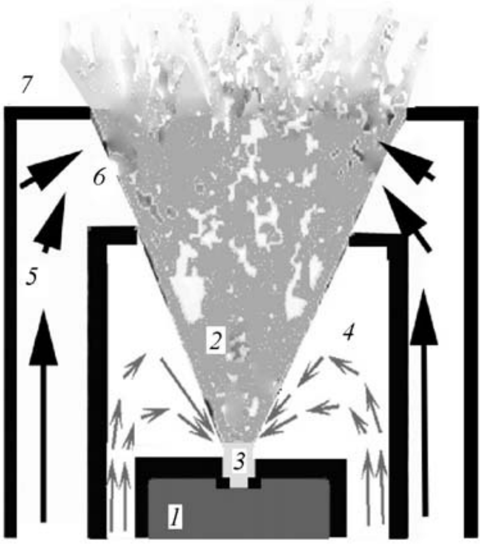

Fig. 8. Basic diagram of the processes in the burner: 1) saturated vapor; 2) superheated vapor; 3) laminar outflow zone of the jet; 4) first flow of the smoke-gas mixture of evaporated fuel; 5) mainstream flow of the smoke-gas mixture from the fuel; 6) zone where the mainstream flow of the smoke-gas mixture goes into the central vapor-gas stream with soot nanoclusters; 7) interaction of the flame with the external atmosphere and the additional oxidizer.

mitted extracting fundamental harmonics at frequencies of 800–1000 Hz in all regimes of combustion (Fig. 7). The maximum edge of the frequency spectrum for a low-temperature jet is 1400 Hz (see Fig. 7a), and for a high-temperature jet an intense new harmonic at 2500 Hz appears (see Fig. 7b). This agrees with the measured video data on the combustion process inside the jet on scales of a few millimeters. This is the fourth important result.

Mathematical Modeling of the Processes of Soot-Vapor Combustion. Conceptually, the burner under consideration realizes the following basic processes: 1) the hydrocarbon fuel is subjected to pyrolysis until a smoke-gas mixture appears over its surface; 2) air and superheated water vapor are supplied into the burner at a pressure; 3) a flow of the smoke-gas mixture is directed into the main zones of laminar outflow of the vapor jet so that at the exit from this zone pulsating combustion arises (Fig. 8). Note that in all reactions of combustion of hydrocarbon fuel systems the following basic gaseous products of combustion reactions are released: H_2O, CO, and CO_2, and intermediate radicals, among which the most important for the complete cycle of initiation of combustion is the OH radical. The experiments performed have shown that high concentrations of OH radicals are formed by the heterogeneous-catalytic

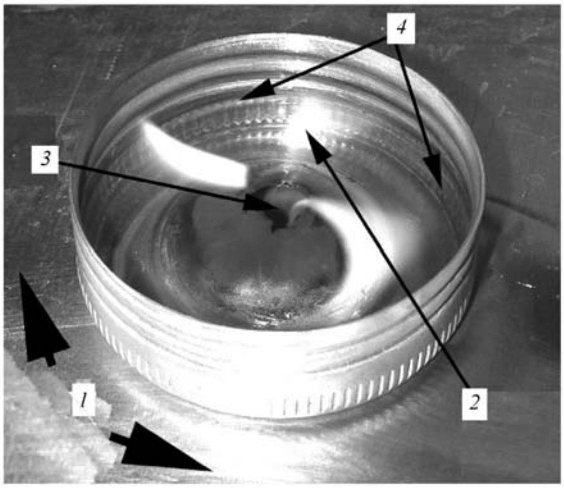

Fig. 9. Model device for demonstrating the mixing at the base of the vapor jet: 1) top view of the steel vessel containing superheated vapor, the vessel diameter is 2 cm; 2) burning front of straw oil vapors contracting towards the vapor jet axis; 3) hole out of which the superheated steam jets vertically upwards; 4) grooves around the circumference of the vessel filled with straw oil.

decomposition of water molecules on soot nanoclusters at the base of the pulsating combustion jet. To understand and realize the mechanism of nanocluster initiation of the process of combustion of hydrocarbon fuels, we consider two main stages in mathematical modeling: 1) the process of formation of small hydrocarbon (soot) nanoparticles is described with the help of the classical Bekker–Frenkel–Zel'dovich theory of nucleation [11], whose application permits determining the limits where the process of formation of nanosoot catalysts begins; 2) the process of growth of nanosoot particles is calculated by the Smoluchowski coagulation scheme [12], which makes it possible to correctly forecast the spectrum of the size distribution of particles from nanoparticles to micron fractal-soot particles (see Fig. 3a). In so doing, nanometric particles continue to play the role of a catalyst in the decomposition of water to OH radicals. Particles of larger sizes serve as the main sink for the reaction of hydrocarbons with OH radicals on the surface of these particles with a release of the major portion of combustion reaction heat.

Our experiments have shown that in using the nucleation theory it is necessary to feed the smoke-gas mixture into the burner at a temperature T_1 determined from the expression

$$R_{\text{cat}} = \frac{2\sigma v}{k\gamma\,(T_1 + T_2)\,B\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}. \tag{1}$$

The mathematical expression (1) follows from the Thomson formula [13] and permits determining the temperature ratio between the superheated steam (T_2) and the smoke-gas mixture (T_1) fed into the burner with the aim of obtaining soot particles of a given size initiating the combustion process before the formation of a high-temperature flame.

From the experimental results it has been established that: 1) the centers of increased catalytic activity in combustion of hydrocarbon fuels are soot nanoclusters of size $R_{\text{cat}} \approx$ 3–5 nm; 2) the smoke-gas mixture in the form of an aerosol haze over the fuel surface appears at a decomposition temperature of 400–650°C (for all practically important fuels); 3) the temperature of the superheated steam T_2 should be 150–200°C lower than the temperature of the smoke-gas mixture T_1 fed into the burner. The formation of nanocluster soot particles takes place in the zone of laminar outflow of the vapor jet when the vapor is mixed with the aerosol particles of the smoke-gas mixture. Their maximum concentration is achieved at the outlet from the laminar zone. It is here that the primary flame of pulsating combustion is formed, in which intense gasification of carbon (soot) occurs. Then a secondary high-temperature flame arises, in which CO aerosols and soot particles are practically absent and where other gases (e.g., synthesis gas) burn out. Directional feeding into the burner (to the base of the vapor jet) of a smoke-gas mixture containing also soot primary aerosols promotes intensive formation of soot clusters of the nanometer range in a certain zone.

Figure 9 shows the specially designed simplified "open" model of the main unit of the burner. The aim is to obtain direct photodata, including those obtained with the use of a high-speed cine camera, on the features of the interaction between the vapor jet and the primary flame. It is seen that the main feature of the given process is the pulling of the primary flame into very narrow zones at the base of the vapor jet, which determines many features of the process investigated by us.

Soot formation before the intense combustion zone. We used the computing algorithm of [11] that shows at what temperatures and at what quantity of water vapor with a given temperature soot clusters of certain sizes can be introduced into the flame zone. Taking into account that the heterogeneous catalysis of water decomposition on the surface of soot particles is a function of their size, we carried out preliminary calculations of these processes of aerosol formation in the low-temperature zone by this algorithm. The calculations are based on the main postulates following from the classical theory of homogeneous formation and coagulation and condensation processes of disperse particle growth. The estimates made show that the size of the critical nucleus (according to the classical theory) is less than 0.2 nm. Such a small value means that practically immediately the main process forming the spectrum of the size distribution of particles will be coagulation, and not nucleation [14]. Under such conditions, for a more rigorous description of the processes of condensed phase formation the modified Smoluchowski coagulation equation [12]

$$\frac{dn_l}{dt} = \frac{1}{2} \sum_{l=i+j} a_{ij}K_{ij}n_i n_j - n_l \sum_{i=1}^{\infty} a_{li}K_{li}n_i + \beta_{l+1}n_{l+1} - \beta_l n_l \, . \tag{2}$$

Physically, Eq. (2) represents the description of three processes: molecular growth, molecular evaporation, and coagulation. The classical nucleation theory ignores the coagulation processes (i.e., the collision of particles with one another and not only with vapor monomers). At characteristic coagulation constants $K = 10^{-8}$–10^{-9} cm^3/s and concentrations of nuclei from $n = 10^{15}$–10^{18} 1/cm^3, the characteristic time of the coagulation process equals $1/Kn$ and is less that 1 μs. The order differences between the coagulation time and the residence time of particles in the flame lead in experiments to the formation of a fine fraction of particles with an average size from 0.05 to 0.3 μm and a dispersion parameter of the log normal size distribution function of particles σ_g = 1.3–1.8. In so doing, larger values of σ_g are observed mainly only in the case of prolonged keeping of aerosols in the air ducts or at fast "hardening" by the external air [15]. The approximation of the calculations has shown that the "primary" spectrum of the size distribution of particles can be given with fair accuracy by the equation

$$n\,(j,\, t) = \frac{1}{j}\,\frac{N}{\ln \sigma \; 3\sqrt{2\pi}} \exp\left(-\frac{\ln^2 (j/j_g)}{18 \ln^2 (\sigma)} \right). \tag{3}$$

Under Brownian coagulation conditions,

$$K_{ij} = K_0\,(i^{1/3} + j^{1/3}) \left(\frac{1}{i^{1/3}} + \frac{1}{j^{1/3}} \right). \tag{4}$$

To solve the Smoluchowski equation, we used the generalized equations for the first and the second moments of the size distribution function of particles. For the total concentration of particles in time, we obtained the expression

$$\frac{N\,(t)}{N_0} = \frac{1}{1 + \left[1 + \exp\,(\ln^2 \sigma_0) \right] K N_0 t}\,, \tag{5}$$

closely resembling the traditional solution of the Smoluchowski equation. The solution for the second moment has the form

$$\ln^2 \sigma = \frac{1}{9} \ln \left[2 + \frac{\exp\,(9 \ln^2 \sigma_0) - 2}{1 + \left[1 + \exp\,(\ln^2 \sigma) \right] K N_0 t} \right]. \tag{6}$$

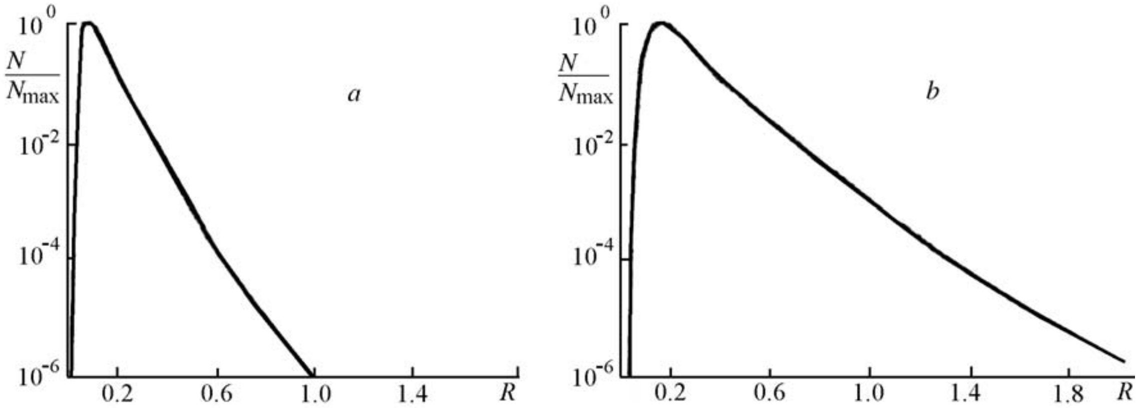

Fig. 10. Calculated spectra of the size distribution of particles depending on the characteristic time of the coagulation process: a) 1 μs; b) 0.5 s.

Using the known relation for the variation coefficient in the log normal distribution

$$\alpha = \sqrt{\exp(\ln^2 \sigma_g) - 1}\ , \tag{7}$$

these formulas can be simplified:

$$\frac{N(t)}{N_0} = \frac{1}{1 + \left[1 + (\alpha^2 + 1)\right] K N_0 t}\ , \tag{8}$$

where

$$\alpha = \left\{\left[2 + \frac{(\alpha_0^2 + 1)^2 - 2}{1 + \left[1 + (\alpha_0^2 + 1)\right] K N_0 t}\right]^{1/9} - 1\right\}^{1/2} . \tag{9}$$

As a result of the calculated numerical data processing, we proposed simpler empirical formulas for determining the characteristic relaxation times of the spectra of the size distribution of particles:

$$\sigma_{g+} = (\sigma_{g0} - \Delta)\,(K N_0 t + 1)^{-0.37} + \Delta\ ,\quad \sigma_{g-} = (\sigma_{g0} - \Delta)\,(K N_0 t + 1)^{-1.38} + \Delta\ . \tag{10}$$

Note that the obtained formulas are only used at $K N_0 t \geq 1$; this complies with the physical meaning of the problem — to perform, on average, at least one collision act for all particles of the spectrum. The results of the calculations were compared for both types of the formulas. The empirical formulas (10) describe the process more validly at ultrahigh supersaturations. With the aid of the methods described above, one can obtain data on the spectra of the distribution of fine soot particles inside the burner, and then, upon mixing with the external oxidizer (air), carry out calculations for their burning in the flame. In many cases, in practice, the so-called asymptotic spectrum of the size distribution (self-sustaining spectrum) arises (Fig. 10) [16]. In fact, this means that although the average size of the size distribution of particles does increase with time, its relative halfwidth (or the ratio of the second distribution function moment to the first one) goes to stationary values. Knowledge of this fact makes it possible to discriminate in the soot-vapor combustion system several characteristic times and apply in each time interval asymptotic solutions for proximate evaluation of the processes in the burner. For example, in the region where the primary soot flame is formed, asymptotic methods can be used with certainty, and characteristic sizes of particles for the main fraction of the soot-organic aerosol component can be obtained. We shall call the main fraction the particles of the order of fractions of a micron containing more than 99.9% of the total condensed mass. They are the basic material for combustion in the presence of a sufficient quantity of oxygen. Such prepared mass of the combustible material is reburned, as a

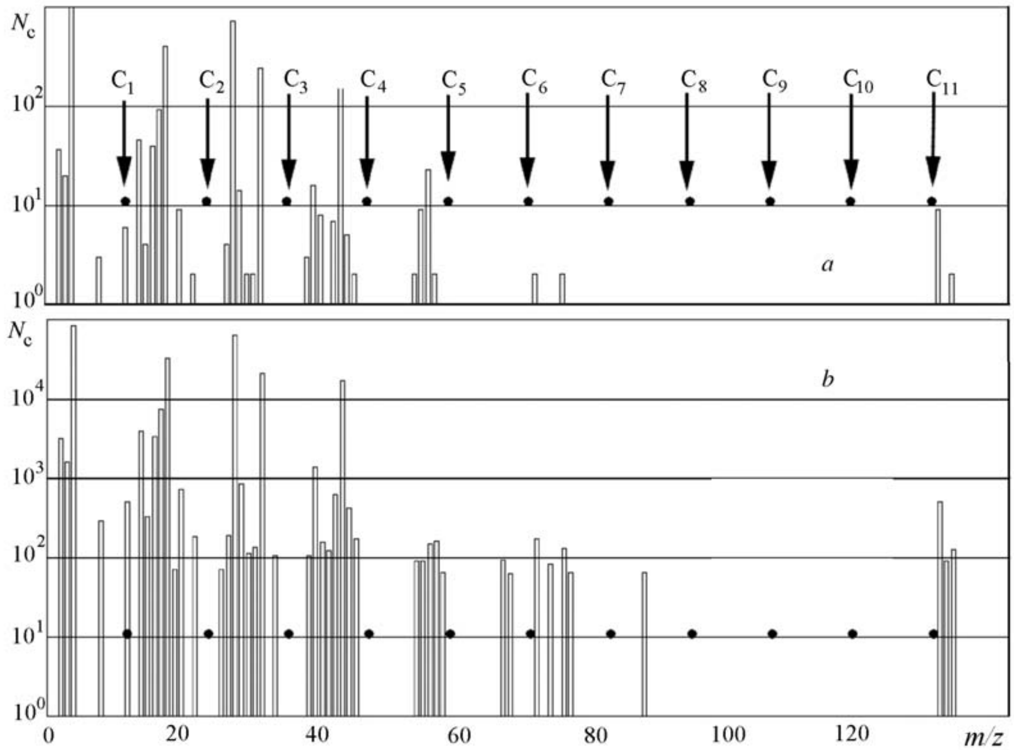

Fig. 11. Mass-spectroscopic spectra recorded in extracting the vapor-gas phase over the coal surface depending on the carbon particle temperature: a) 50°C; b) 80°C.

rule, in conventional (not vapor) burners. In our case, however, intense mixing occurs in the high-turbulence zones created by the vapor jet itself ejecting under pressure into the atmosphere. In so doing, the residual saturated vapors and the aerosol are cooled sharply again to induce the secondary process of formation of aerosols with a supersmall critical nucleus, that is, in the coagulation regime of its growth. The calculated numerical estimates and the first direct calculations by the complete system of Smoluchowski equations show that precisely secondary supersaturations that are so large enable small nanoparticles to appear among large particles of the primary fraction. After this the catalytic process of formation of OH radicals sharply intensifies, leading to the ignition of the mixture of micron particles and their complete burning. From the viewpoint of this theory, it is very important to know the time of relaxation of a broad spectrum of aerosols to the self-sustained value, in other words, how fast the small clusters will settle on the large ones and cease to be catalytically active.

It has been established by video observations of vapor flames in different regimes of combustion that before the maximum luminosity zone in the flame, darker zones are present. It is supposed that the main condensation and coagulation growth of nanoparticles occurs exactly in these zones. When a certain size and a certain specific surface of the condensed phase in the flow are attained, the heterogeneous reactions lead to fast heating of the flame (according to our measurements, to a temperature from 800°C in the dark regions to 1600°C in the lighter regions) (Fig. 6).

Figure 11 shows the obtained mass-spectroscopic spectra recorded in extracting the vapor-gas phase over the surface of coal as one of the most complex kinds of organic fuel. From the graph it is seen that the hydrocarbon components appear in the vapor phase at extremely low (for combustion) temperatures (up to 100°C). At the same temperatures they are represented by a large number of nuclei consisting, at a minimum, of C_1–C_{11} carbon atoms. A change in the heating of the coal surface from 50 to 80°C leads therewith to an increase in the size of such nuclei by more than an order of magnitude. This example shows that in considering the conditions for the initiation of nanocluster combustion, one can easily see that the process (the formation of the spectrum of catalytically active nanoparticles) begins at very early temperature stages of combustion. The authors wish to thank associates of the Novosibirsk State University A. E. Zarvin, V. V. Kalyada, N. G. Korobeishchikov, and M. D. Khodakov for assistance in performing the experiment, assistance in the operation of modern equipment, and discussing the results.

Conclusions. We have performed experiments on burning such off-grade fuels as straw oil, hydrocarbon fuel, crankcase wastes, crude oil, etc. in the laboratory burner.

The application of optical spectroscopy in the near UV and IR regions, as well as in the visible region of the spectrum, has made it possible to obtain information on the physicochemical processes in flames of different scales with a time resolution of no less than 10 ms and video framing of about 1 ms. Analysis of the acoustic spectrum in high and low frequencies has also revealed the specific features of the time processes in the microflares inside the flame.

The question on the kinetics of soot clusters at the earliest stages of the process has been investigated in the first approximation. Mathematical modeling of the processes of formation of nanoparticles on the basis of modified Smoluchowski equations has shown that the decomposition of water on the surfaces of carbon particles (1–5 nm) can already be effective at a temperature of about 1000^{o}C in the mixing zone (in accord with the recent works), and not as in the homogeneous case at 1500–2000^{o}C. When a certain size and a certain specific surface of the condensed phase in the flow are attained, the heterogeneous reactions lead to a fast heating of the flame (according to the measurements made, to a temperature from ~800^{o}C in the dark regions and to ~1600^{o}C in the lighter regions).

The scientific and technical results obtained are the basis for creating a promising class of self-contained burners of off-grade fuels with a high energy efficiency and ecological harmlessness.

NOTATION

A, relative amplitude of the acoustic signal; a_{ij}, collision efficiency coefficients; B, reference constant characterizing the pressure of saturated vapors of the hydrocarbon fuel at a given temperature; C_{1-11}, carbon masses of registered clusters; f, frequency of the measurable acoustic signal, kHz; k, Boltzmann constant; K, coagulation constant; K_{ij}, collision coefficients; m, mass of the hydrocarbon cluster, amu; N, concentration of aerosol and soot particles, cm^{-3}; N_c, number of registered clusters in the mass-spectrometer; N_0, initial concentration of aerosol particles, cm^{-3}; N_{max}, maximum concentration of soot and aerosol particles in the size distribution spectra, cm^{-3}; n, concentration of nuclei; n_i, concentration of clusters consisting of i, j, or l molecules or atoms; R, radius of soot and aerosol particles, cm; R_{cat}, radius of the soot clusters, cm; T_1, temperature of the smoke-gas mixture, ^{o}C; T_2, temperature of superheated vapor, ^{o}C; t, time, s; z, cluster charge, electron charge units; v, molecular volume of the condensing molecule, cm^3; β_j, coefficients taking into account molecular evaporation of a molecule of mass j from the cluster surface; Δ, asymptotic width of the self-sustained coagulation spectrum of the size distribution of particles at a free molecular coagulation constant equal to 1.32 [14, 15]; γ, stoichiometric coefficient of the ratio of the quantity of fuel to the quantity of air upon the appearance of the smoke-gas mixture; σ_s, surface tension coefficient of water, erg/cm^2; width of the spectrum of the size distribution of particles; σ_0, at the initial instant of time; σ, at the current instant of time; σ_g, for log normal distribution. Subscripts: cat, catalytic cluster; 0, value of a quantity at the initial instant of coagulation; i, j, or l, quantized numbers; max, maximum concentration of aerosol particles in their size distribution; c, carbon cluster; g, half-width of the log normal spectrum of the size distribution of a part of aerosols; s, surface tension pertaining to the surface of critical-size aerosol particles.

REFERENCES

1. *Power Strategy of Russia for the Period until the Year 2030.* Approved by the decree of the Russian Federation Government No. 1715 of 13.11.2009.
2. S. L. Klimov, E. G. Gorlov, G. N. Delyagin, et al., *Water-Coal Fuel and Prospects of Its Use in the Electrical and Heat Power Engineeirng in Russia*, Central Scientific-Research Institute of Economics and Scientific-Technical Information of Coal Industry, Moscow (2001).
3. V. I. Kormilitsyn and É. Ya. Ismailov, Fire decontamination of mazut- and oil-polluted waters of power plants, *Ross. Khim. Zh.*, No. 6, 67–68 (1997).
4. E. G. Gorlov, Composite water-containing fuels from coals and oil products, *Khim. Tverd. Topl.*, No. 6, 50–61 (2004).

5. G. S. Khodakov, E. G. Gorlov, and G. S. Golovin, Suspension coal fuel, *Khim. Tverd. Topl.*, No. 6, 15–31 (2005).
6. M. S. Vigriyanov, V. V. Salomatov, and S. V. Alekseenko, A means of soot-free combustion of fuel, Patent 2219435 of the Russian Federation, published on 20.12.2003.
7. P. T. Radulovic and L. D. Smoot, Chapter 1, in: L. D. Smoot (Ed.), *Fundamentals of Coal Combustion: For Clean and Efficient Use*, Elsevier Science Publishers, The Netherlands (1993), Funded by ACERC.
8. P. A. Tesner (G. N. Makarov Ed.), *Kinetics of Formation of Pyrocarbon* [in Russian], MKhTI, Moscow (1980).
9. P. Ya. Pokhil, A. F. Belyaev, Yu. V. Frolov, et al., *Combustion of Powdery Metals in Active Media* [in Russian], Nauka, Moscow (1972).
10. S. É. Pashchenko and K. K. Sabel'fel'd, Atmospheric and technogenic aerosol, in: *Kinetic, Electronic-Probe, and Numerical Methods of Investigation* [in Russian], Pts. I and II, Nauka, Novosibirsk (1993).
11. Ya. I. Frenkel', *Kinetic Theory of Liquids* [in Russian], Nauka, Leningrad (1975).
12. M. Smoluchowski, Three papers on the diffusion, Brownian motion, and coagulation of colloid particles, in: *Brownian Motion* [in Russian], Collected papers, Fizmatgiz, Moscow (1936), pp. 332–415.
13. H. Tomino, I. Kusaka, and K. Nishioka, Interfacial tension for small nuclei in binary nucleation, *J. Cryst. Growth*, **113**, 633–636 (1991).
14. V. M. Voloshchuk and Yu. S. Sedunov, *Coagulation Processes in Disperse Systems* [in Russian], Gidrometeoizdat, Leningrad (1975).
15. A. G. Sutugin, É. I. Kosev, and N. A. Fuks, Formation of condensation, finely dispersed noncoagulated aerosols, *Kolloidn. Zh.*, **33**, No. 4, 585–591 (1971).
16. T. G. Daniel, A stochastic analysis of the homogeneous nucleation of vapor condensation, *J. Chem. Phys.*, **74**, No. 1, 661–678 (1981).