Peculiarities in formation of smoke aerosol dispersion structure at thermal decomposition of coniferous wood. 1. Variations of combustion sample masses

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A series of smoke experiments in the Big Aerosol Chamber (BAC) on studying the dynamics of variations of smoke aerosol polarization characteristics was conducted; their microphysical changes in the process of relaxation and disintegration were estimated. It has been shown that the specificity in formation of the fine-dispersed smoke component depends not only on the mass of a coniferous wood sample, but also on the residence time of the aerosol-gas mixture inside the thermal decomposition chamber (TDC) (muffle furnace). The increase of sample masses leads to growing "coagulation" losses of small particles ($r < 0.2$ microns). The active formation of the moderate-dispersed fraction favors more effective cleaning of the air medium from finely dispersed aerosols, including the nanometer range of the particle size. Particles of pyrolysis smoke generated at low temperatures ($T \sim 300$°C) represent mainly aerosols, which poorly absorb the visible radiation. Estimations show that the values of a real part of the refractive index n vary within 1.52–1.58. In this case, the sought minimum of the regularizing functional is commonly achieved at values of the imaginary part of the complex refractive index $\chi \sim 0.001$.

Introduction

In the process of thermal decomposing of the biomass from forest fires and peat bog, abnormally high concentrations of finely dispersed aerosols and aerosol-forming components (AFC) are carried away in the atmosphere. During fire-dangerous seasons (May–September) in the regions adjacent to the boreal forest zone, the smoke anomalies usually are scattered along complex trajectories of air mass motion. Based on data of long-term observations, significant variations of the atmospheric optical parameters during the above-mentioned period, including the anomalous spectral behavior of the aerosol extinction coefficient β_e, km^{-1}, and, as a consequence, optical weather instability were recorded.[1,2]

The carry-over of the thermal decomposition products in the regions of Western Siberia has sometimes such scales, that they influence the efficiency of the convective rise of aerosol fractions into the free atmosphere.[3] Therefore, the studying of the peculiarities in formation of microstructure and optical characteristics of smokes is an object of instrumental investigations for a long time.[1–5]

Earlier, a considerable attention has been given[6] to methodical problems of organization of laboratory experiments in BAC, methods of spectronephelometer calibration, and synchronization of the measured data.

A series of simultaneous experiments has made it possible to study general dynamics in smoke aerosol polarization characteristics, to assess some microstructural variations in the course of their relaxation and decay. These experiments have shown an urgent need for preliminary processing of the measurements and separating out the optimal time scale for synchronization of data, participating in solution of the inverse problem of aerosol light scattering. An allowable measurement error was estimated for obtaining information on microstructural variations of smokes. Methods for evaluating the mean-effective refractive index were developed.

When analyzing data of some experiments, it was noted that the level of accumulation and the efficiency of sink of smoke particles of the accumulation fraction depend on the state of the medium, in which the particles occur when escaping the thermal decomposition chamber (TDC) (muffle furnace). Therefore, this paper presents the results of experiments, which characterize in more detail the regularities in formation of smoke aerosol size spectra at their transition from muffle furnace to the BAC.

Experimental procedure

As the initial information in the optical diagnostics of microstructural variations, data on polarization components of the coefficient of directed light scattering of wooden smokes $\beta_s^\theta(\lambda)$, measured in the controlled conditions with the use of the polarization nephelometer, were used. The measurements were carried out at five scattering angles: $\theta = 15$; 45; 110; 135; and 165° and nine wavelengths λ in the range ~ 0.44–0.69 μm. Thus, to determine the microstructural parameters of smoke in one of (conditional) points of the process of

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smoke state variation, 90 values of polarization components of the directed light scattering coefficient were successively measured in the automated regime. The regime of recording the light scattering parameters was computer-controlled, based on the developed algorithm with file-by-file storage of optical data from different experiments. The full cycle of measurements considering all angles and wavelengths took 8–9 minutes; therefore, the smoothing and matching of the measured data was required.

In the BAC experiments, the smokes were first generated in the TDC of muffle furnace, which had the form of a parallelepiped ($10 \times 16 \times 32$ cm) with ~5 liter volume.

When decomposing wood in the pyrolysis regime, the access of oxygen to the heating zone was limited by a closed door of the muffle furnace. To eliminate the occurrence of fire in the TDC at high temperatures (about 600°C and higher), the door of the muffle furnace was closed tightly. Therefore the smoke mixture, before passing from TDC of muffle furnace to BAC through the channels of reduced power, was retained in TDC for some time in the heating zone. Thus, the products of decomposition interacted with each other not only at higher temperature than in BAC but also at higher concentration of particles in the aerosol-gas mixture (AGM).

At lower temperatures (~300°C), the probability of the combustion regime with fire decreased significantly, that made an easier output of the AGM from TDC to the BAC, that is, reduced time, if necessary, of AGM stay inside the TDC. At increased delivery of the dispersed mixture from TDC to BAC, the AGM concentration decreased in a local volume and in flows carried out from TDC to BAC. The indicated peculiarities of the mechanism of dispersed mixture generation affected the qualitative character of the retrieved smoke aerosol size spectra.

Discussion of results

Figure 1 shows the transformation of smoke microstructure during the pyrolysis depending on different masses M of the decomposable wood (pine), as well as estimates of values of the particle complex refractive index obtained from inversion of data of the optical experiment.

As it is seen in Fig. 1*a*, the increase of the mass of coniferous samples at the initial stage leads to the broadening of the smoke particle size spectrum and the shifting of the right-hand boundary of size spectrum r_2 to the values of ~2 μm. The volume of the moderate- and coarse-dispersed particles increases considerably. At the same time, the fraction of fine particles ($r < 0.15$ μm) steadily decreases.

Such transformation of the particle size distribution is in agreement with the model estimates obtained earlier,[7] from which it follows that the reduction of relative concentration of small particles ($r \sim 0.5$–0.15 μm) in the analyzed smokes can be due to a stronger intensity of their transition to the medium-size interval caused by increasing efficiency of the coagulation process.

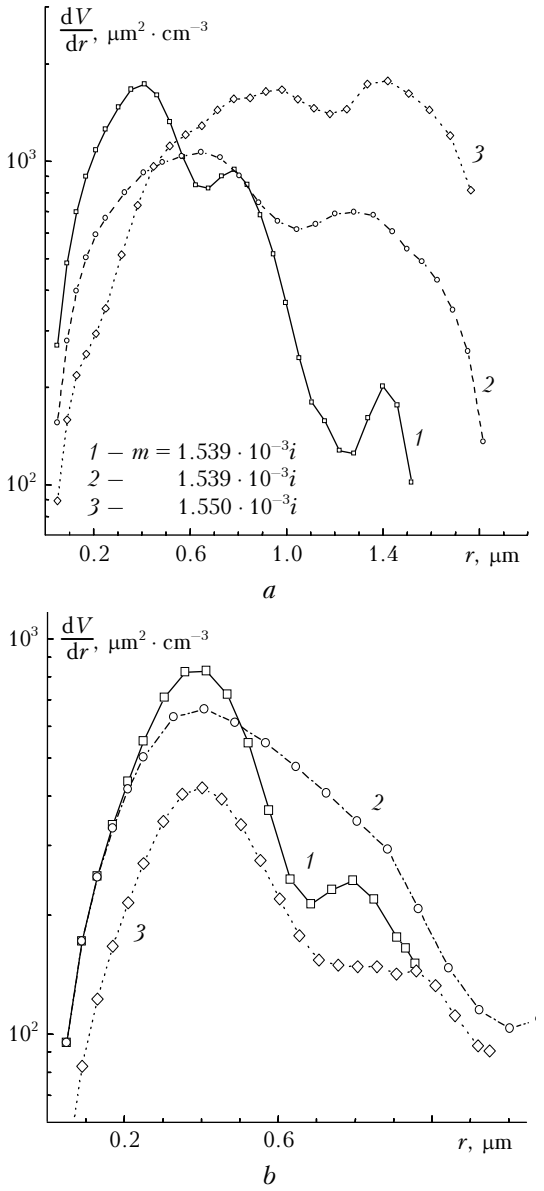

Fig. 1. Distribution of particle volumes over radii in the pyrolysis smokes: initial (after 25–30 min of scattering in BAC); M = 250 (*1*); 500 (*2*); 750 g (*3*) (*a*); at the same initial masses (according to the numbering of curves) after 15 (*1*); 12 (*2*); and 20 hours (*3*) from the beginning of the process (*b*).

As the mass of wood samples inside the thermal decomposition chamber increases, the emission of aerosol-forming compounds grow. As a consequence, at a reasonably limited volume of TDC, the concentration of a finely dispersed component increases, which favors the efficiency of the particle coagulation process.

The coagulation activation of small particles results in their enlargement, the decrease of relative aerosol content in the given particle size range, and the increase in the adjacent (moderate-dispersion) range. As a result, the smokes with the lowered concentration

of fine particles ($r < 0.1$ μm) are formed at the transition of the dispersed mixture from TDC to BAC. The shift in the size distribution density of fine particles on the whole to the right (Fig. 1*a*) can be interpreted as a consequence of their limited inflow from the range of extremely fine particles ($r < 0.03$–0.05 μm) because of their coagulation.

The retrieved qualitative pattern of the smoke particle size spectrum transformation, based on the inversion of nephelometric data, suggests that the pyrolysis regime of wood decomposition has an insufficient (for self-conservation of the spectrum form) generation efficiency of particles of the nanometer size ($r \sim 0.005$–0.05 μm). As a whole, the growth of the sample mass results in the increase of the smoke mixture concentration inside TDC and favors the effective formation of larger particles: $r \sim 0.4$–1.2 μm for $M \sim 500$ g and $r \sim 1.2$–2.2 μm for $M \sim 800$ g and more.

The laboratory experiments with pyrolysis smokes also demonstrate that the smoke particle size distribution strongly depends both on the concentration of AGM and the duration of its existence in the concentrated form in the local volume of TDC.

At subsequent stages of the smoke life (Fig. 1*b*), in spite of significant differences in initial spectra, more effective sedimentation of larger smoke particles on the chamber walls and in the channels of AGM motion makes the spectral shapes more close. The residual fraction of smoke particles for samples with different initial masses is more localized in time in the 0.2–0.6 μm range, that is seen from the comparison of curves *2* (12 hours) and *3* (20 hours) in Fig. 1*b*.

Time dynamics of smoke microstructure in the process of pyrolysis is shown in detail in Fig. 2 in variations of size distributions of the total geometric cross section of particles, retrieved from spectral nephelometric measurements.

As an example, the results are given for thermal decomposition of a pine sample of a large mass ($M \approx 750$ g), that makes it possible to observe the transformation of smoke aerosol microstructure in a wide range of the particle size spectrum. In the initial period of filling up the smoke chamber, a deficit of small particles is seen in the distribution of dS/dr (curve *1*), which is replenished during the next hour (curve *2*). At subsequent stages of smoke life in the BAC (curves *3*, *4*), the particle size spectrum gradually becomes more narrow as a result of effective sink of the largest particles. The particles of moderate- and coarse-dispersed fractions for a long time ($t \sim 20$ hours) are traced in the reconstructed spectra, however, the main contribution to coefficients of aerosol extinction and scattering is given by the particles with $r \sim 0.2$–0.5 μm.

Despite considerable differences in the sample masses (250, 500, and 750 g), durations of the aerosol-gas mixture existence inside the thermal decomposition chamber, in the initial spectra, estimated values of the complex refractive index (CRI) of smoke particles vary insignificantly. The values of the refractive index real part fall mainly in the range ~1.54–1.56. Estimates of the imaginary part χ of CRI obtained for all stages of smoke development practically coincide and are equal to ~0.001.

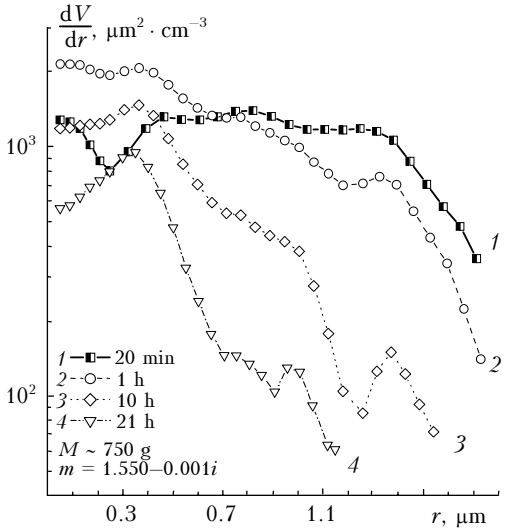

Fig. 2. Variation of probability density function of total cross section of smoke particles dS/dr during the first 22 hours after pyrolysis decomposition of coniferous wood sample ($M = 750$ g).

The results of direct numerical simulation of all parameters of aerosol light scattering, based on the retrieved parameters of the smoke aerosol microstructure, have shown, in particular, that for pyrolysis smokes the single scattering albedo Λ is close to 1 (between 0.94 and 0.95). Thus, the particles of pyrolysis smoke, generated at low temperatures of decomposition of coniferous wood samples ($T \sim 350$°C), are the aerosols weakly absorbing the visible radiation.

Based on the retrieved data on the dispersed structure of pyrolysis smokes, we have obtained estimations of time variability of the integral parameters: the number density $N(t)$, total cross section $S(t)$, and the volume $V(t)$ of particles, from which the variation of mean-effective smoke particle size $r_{\text{eff}}(t) = 0.75V(t)/S(t)$ was estimated (Fig. 3).

It is evident that mean size of smoke particles in the polydispersion ensemble varies with time in the range from 300 to 700 nm.

For standard atmospheric hazes this size spectrum is intermediate between the fine and coarse aerosol fractions. The estimates given in Fig. 3 support the conclusion that spectra gradually approach each other (Fig. 1*b*) at final stages of the smoke development. With increasing weight of samples the time of spectra relaxation grows, the value of $r_{\text{eff}} \sim 0.3$ is accomplished at increasing time intervals of spectra development (as the mass increases).

The obtained estimates have shown that high concentration of moderate smoke particles in air can provide for an effective sink on their surface of particles with $r < 0.1$ μm.

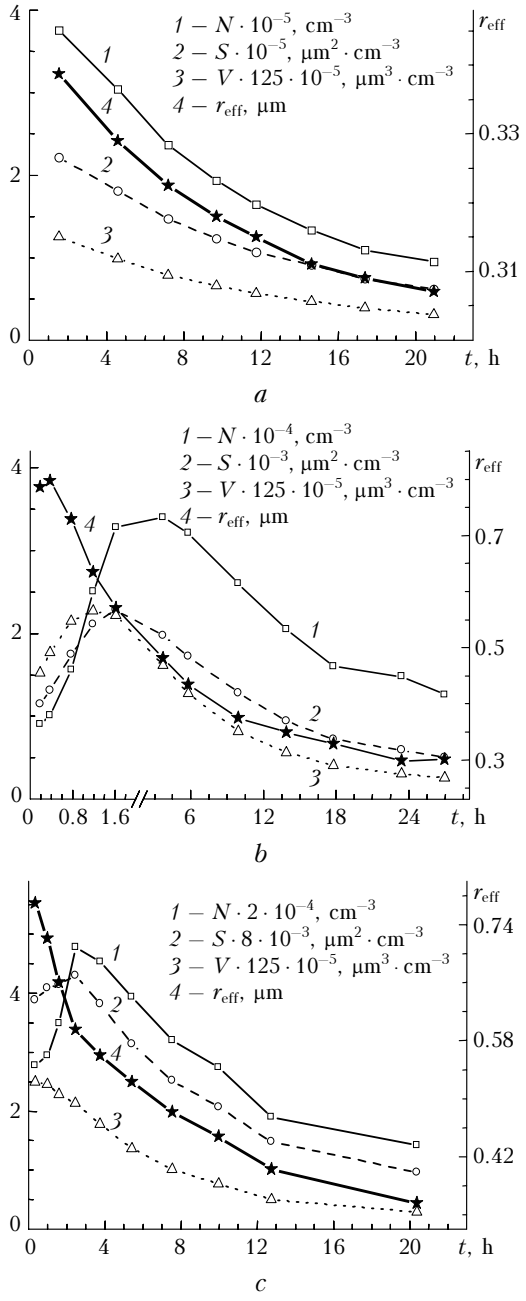

Fig. 3. Time dynamics of the integral volume V, cross section S, number density N, and effective size r_{eff} of smoke particles, calculated from results of nephelometric measurements: at M = 250 (*a*); 500 (*b*); 750 g (*c*).

Conclusion

The BAC experiments have shown that due to high concentration of products of thermal decomposition, the smoke particle size distribution depends essentially both on the aerosol-gas mixture concentration and on the lifetime in the concentrated form inside the local volume of TDC.

The growth of relative proportion of particles of moderate and coarse fractions at increasing masses of burned samples increases the "coagulation" losses of small ($r < 0.2$ μm) particles, the relative concentration of which in the size spectrum of smoke particles noticeably tends to decrease.

The particles of pyrolysis smoke, generated at low temperatures of coniferous wood decomposition ($T \sim 350$°C) is represented by aerosols weakly absorbing the visible radiation. The estimates have shown that values of the real part of the refractive index vary in the range ~ 1.52–1.58. The obtained estimates for the imaginary part of the complex refractive index at all stages of smoke development coincide closely and are equal to ~0.001.

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