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INCREASE IN THE RATE OF FUEL COMBUSTION ON ADDITION OF NANOSIZED CARBON PARTICLES

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Nanosized carbon fuel additives were formed by ultrasonic crushing of graphitized films or by subjecting ethanol to an electric discharge. The obtained specimens of fuel were tested on a setup for rapid adiabatic compression. Under conditions of ultrasonic dispersion, a wide spectrum of particle sizes was observed, and their influence on the characteristics of combustion turned out to be insignificant. When ethanol was treated by an electric discharge, spherical or plane carbon nanoclusters and various transient shapes, as well as liquid components, were synthesized. The resulting fuel displayed a substantial increase in the rate of combustion.

Keywords: *hydrocarbon fuel, electric discharge treatment, nanocarbon clusters, setup for rapid adiabatic compression.*

Introduction. In order to improve the commercial properties of fuels, they are often supplemented with additives in the form of particles of ultradisperse materials. For example, additions of a nanodisperse aluminum powder make it possible to obtain a prospective solid rocket fuel, since with these additives the rate of combustion increases by an order of magnitude (as compared with compositions involving aluminum particles of micron size) [1]. Dispersion of aluminum in a liquid fuel decreases the ignition delay by 30%, with the heat transfer through particles and additional energy release during their combustion being considered as the main mechanisms of efficient combustion [2]. Nanoparticles of other metals too are used as combustion catalysts [3].

A fuel is also admixed with nanosized carbon additives, for example, fullerenes C_{60} and C_{70}, which have already become marketable [4]. Additions of carbon nanotubes also increase the efficiency of combustion [5]. Graphene particles of size 200–500 nm increase the rate of combustion by a factor of 1.7, which is attributable to the high thermal conductivity and emissivity of graphene, as well as to the absence of a solid phase in the combustion products [6].

In our experiments we investigated the influence of nanosized carbon additives, obtained by different methods, on the rate of fuel combustion. Ethanol C_2H_5OH was selected as a model fuel, because it is widely used as a biofuel [7]. An analysis of the obtainable fuel suspensions was made with the aid of a JEM100CX transmission electron microscope (TEM) and a LEO1455VP scanning electron microscope (SEM). Specimens were prepared by applying a drop of suspension to a mesh covered by a Formvar film (for TEM) or to a plane substrate (for SEM) and were dried at room temperature over the next 24 h.

Fuel. Nanosized Solid Additives. Several techniques were used to synthesize nanosized carbon additives to a fuel.

Technique A. Fuel A was produced by depositing graphitized films from a CH_4/He mixture onto a nickel surface in a gas discharge [8]. Thereafter, the films were separated from the substrate by etching in hydrochloric acid (HCl), washed with distilled water, dried, and dispersed in ethanol by treating in an ultrasonic bath (RK103M of Bandelin Company) for 1 h. As is seen from Fig. 1, the particles have different shapes and a marked spread in the size, hence the fuel was additionally cleaned of the largest particles by passing it through a filter paper.

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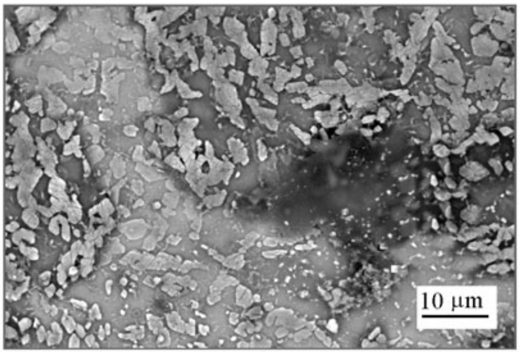


Fig. 1. Ultradispersed particles of fuel suspension A (SEM image).

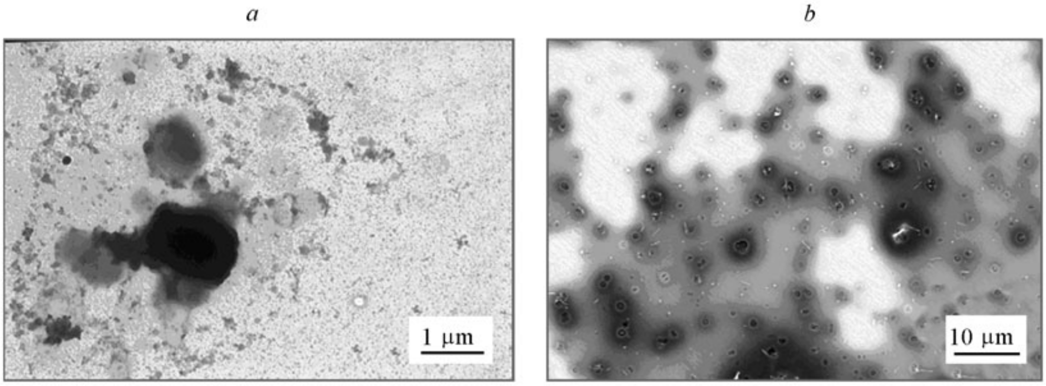


Fig. 2. Solid-phase carbon structures formed on electric-charge treatment of ethanol in fuel B and obtained with the aid of TEM (a) and SEM (b).

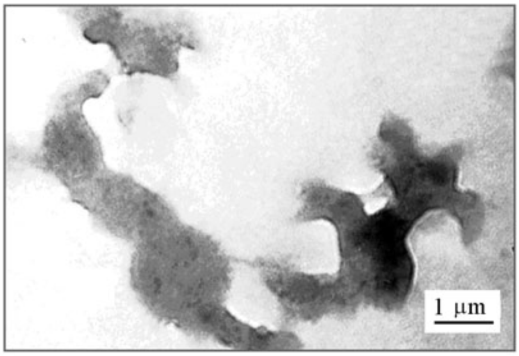


Fig. 3. Solid phase in fuel D (TEM image).

Techniques B and D. Nanosized particles were synthesized during the exposure of ethanol to an electric d.c. discharge. The cathode electrode made from the 12Kh18N10T stainless steel was mounted at a distance of several millimeters above the ethanol surface, whereas the anode was put deeper into the ethanol. The gas volume of the reactor was filled with argon. On supply of voltage of 1000 V to the electrodes, a gas discharge was developed between the cathode and the liquid phase surface and, depending on the intensity of current, plasma synthesis of various particles occurred. A typical time of treating 10-ml specimens was approximately 1 h.

It is seen that in fuel B produced after treating ethanol with a current of 1–2 mA, different-structure clusters of size of up to 1 μm were synthesized (Fig. 2). Planar structures appear in fuel D when ethanol is treated by a high current of approximately 10 mA (Fig. 3).

Technique C. A pair of stainless steel electrodes with an interelectrode gap of 1–10 mm was immersed into ethanol at a depth of 1 cm, and a d.c. voltage of 1000 V was applied to them. In the zone between the electrodes,

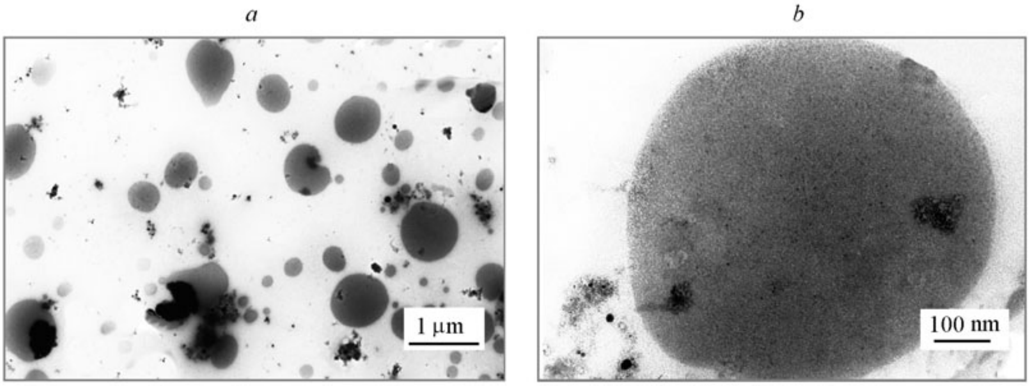


Fig. 4. Solid phase (a) and a carbon cluster (b) in fuel C (SEM image).

the supply of a high-voltage initiating pulse caused the formation of gas bubbles which consisted of ethanol vapor and the products of its decomposition through which a quasi-stationary discharge was initiated. Under these conditions, the discharge current varied within 20–50 mA. In this high-current regime, the formation of a certain amount of soot-like particles was observed; they were removed by filtering as in the case of fuel A. After the electric discharge treatment, clusters of predominantly spherical shape and submicron size were detected in fuel C (Fig. 4a). On higher magnification, the point structure of their surface can be seen (Fig. 4b).

In our case, the recovery of solid particles occurs due to a relatively high specific power density of about 10 W/cm^3 of the discharge in ethanol vapors. Here, a chain mechanism of formation of radicals that leads to the formation of linear macromolecules and solid phase nuclei can take place [9]. Particles can also be formed via nucleation and polymerization by way of successive addition of acetylene (C_2H_2) fragments [10], which is usually the case where there is an excess of hydrogen and which is confirmed by the presence of C_2 dimer lines in the spectrum of a similar weak-current hydrocarbon plasma [11].

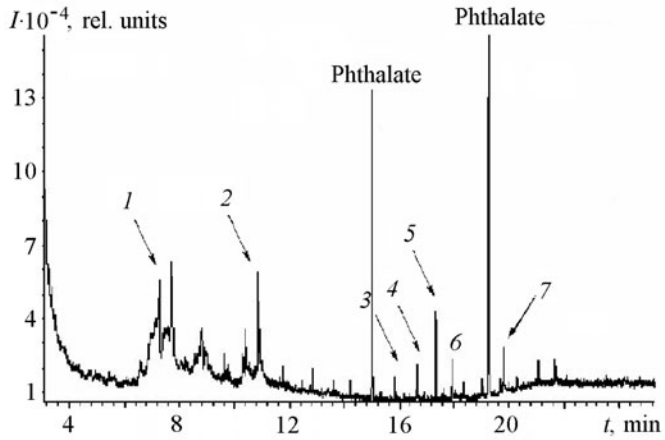
The obtained specimens of fuel were transparent yellowish suspensions which, being illuminated by a laser beam, displayed the Tyndall effect, that is, the side visibility of the beam because of light scattering on the nanoparticles. Since in the course of time, the colloid solution develops aggregation, which leads to an increase in the size of particle agglomerates and their sedimentation, tests on the setup for rapid adiabatic compression were conducted not later than several days after the suspension was obtained.

Fuel. Liquid Synthesized Products. In the case of electric discharge treatment, the fuel, apart from solid particles, contains liquid synthesized compositions, which are detected by the chromatography and mass spectrometry methods. Stream chromatography with the aid of a "Crystal-2000M" for all types of fuel revealed the presence of a certain amount of higher components after electric discharge treatment.

When heavier components are recorded in a fuel, an Agilent 7890A gas chromatograph with an Agilent 5975C Inert mass-selective detector operated in the regime of ionization by an electron shock with an energy of 70 eV; it was tuned to a maximal sensitivity to the substances detected. The basic parameters of the device are given below. An HP-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm) was led directly into the ion source of the mass spectrometer. A computer system with the ChemStation program provided continuous recording, conservation, and processing of all mass spectra obtained by the chromatography program. In preparing specimens, dichloromethane (99.9%) was used as a solvent: 0.1 μl of the substance under study was dissolved in 0.5 μl of dichloromethane.

Parameters of chromato-mass-spectrometry:

Initial temperature of the column	80°C
Exposure	2 min
Heating rate	10°C/min
Final temperature of the column	300°C
Injector temperature	250°C
Detector temperature	280°C
Helium speed	1 ml/min



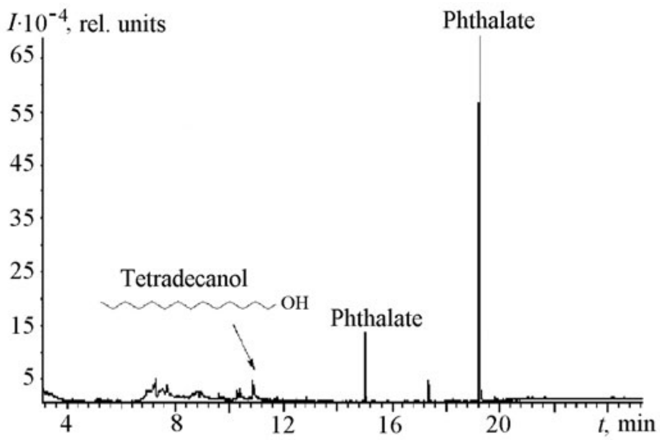


Fig. 5. Chromatogram of a specimen of ethyl alcohol treated by technique B: 1) 3, 3 dimethylbutyl-1-amine; 2) tetradecanal; 3) hexyltetraglycol; 4) dibutyl ester of cebacic acid; 5) N-phenylnaphthalen-1-amine; 6) pentaethylene glycol; 7) octaethylene glycol.

Fig. 6. Chromatogram of a specimen of ethyl alcohol treated by technique C.

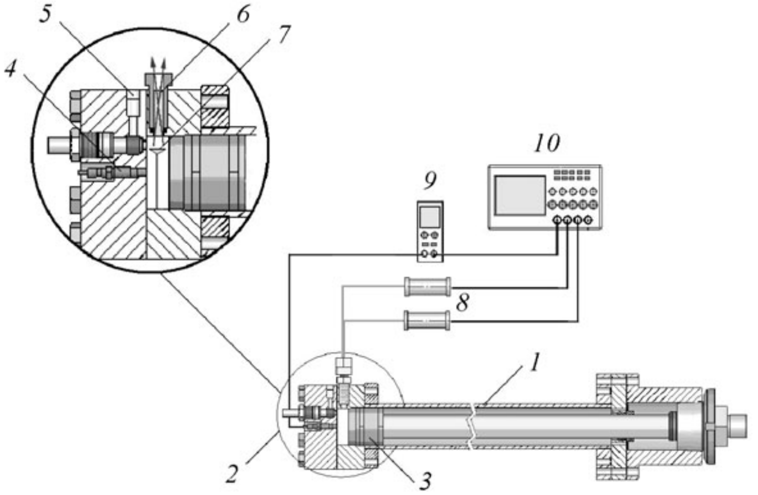


Fig. 7. Setup for rapid compression and schematic diagram of measurements: 1) compression cylinder; 2) test chamber; 3) piston; 4) pressure gauge; 5) valve; 6) quartz window; 7) metal bowl; 8) photomultipliers; 9) charge amplifier; 10) digital oscilloscope.

Volume of injection	1 μl
Injection	without flow division

As a result of the chromato-mass-spectrometric analysis, it was established that the treatment of the ethyl alcohol by technique B (Fig. 5) results in the formation of glycols, a complex acid, and an aldehyde. Compounds of glycol series were also detected in the specimen obtained by technique D. Tetradecanol $CH_3–(CH_2)_{12}–CH_2–OH$ was detected, in particular, in specimen C (Fig. 6). Some of the substances detected related to artefacts: amine was formed as a result of the seeping of atmospheric air into the reactor, whereas phthalates got inside the solution during sampling (it is planned to eliminate these impurities by altering the reactor construction).

Thus, in our case, the electric-discharge synthesis of intermediate ethanol compounds proceeds with the formation of molecules predominantly in the form of linear chains of carbon atoms.

Setup for Rapid Compression. The characteristics of combustion of synthesized fuels were investigated with the aid of a setup for rapid adiabatic compression [12], the schematic diagram of which is presented in Fig. 7. The

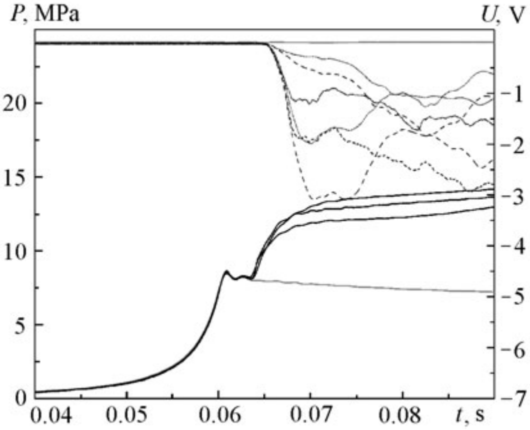


Fig. 8. Pressure in the combustion chamber *P* (solid lines) and glow *U* (of the signal from a photomultiplier) as a function of time at wavelengths 308.9 nm (dashed lines) and 431.5 nm (dotted lines).

test chamber was equipped with: a Kistler 6031U18 high-temperature piezoelectric pressure gauge (4) connected with a Kistler 5015A charge amplifier (9), a valve for evacuation and inflow of gas mixture (5), and a quartz window (6) that provides access for optical measurements. A dual fiber-optic cable is used to transfer light radiation from the interior of the chamber to photometric devices (8). All signals are recorded with the aid of a multichannel storage oscilloscope (10).

In the experiments, the compression cylinder was filled with air up to atmospheric pressure, and a specimen of liquid fuel was placed in a metal bowl (7) (see Fig. 7) put into the combustion chamber. The quantity of fuel was calculated on the basis of the stoichiometric ethanol/air relationship at the given atmospheric pressure, temperature, and moisture content of air. In the course of each experiment, the change in the pressure in the combustion chamber caused by compression and ignition of fuel, as well as the glow within the chamber, was recorded. As photometric devices, two photoamplifiers were used, before whose photocathodes narrow-band interferential filters transmitting radiation with wavelengths λ = 308.9 nm and λ = 431.5 nm were placed. These wavelengths correspond to transitions between the energy levels of excited OH (A2Σ – X2Π) and CH (2Δ – 2Π) molecules, with the former being the basic intermediate radicals in the chemical reactions during the self-ignition of mixture and the latter being the intermediate radicals in the reactions of the formation of combustion products. Three criteria were used to measure the time of mixture induction: the pressure increase in the chamber due to the mixture ignition and the appearance of glow within the chamber at two wavelengths. The moment of stopping of the piston group was adopted as the inception of the reading of time, which corresponded to the maximal pressure and temperature of mixture in the combustion chamber.

Results and Discussion. During the preparatory testings, we determined the parameters at which the self-ignition of a fuel (ethanol) occurs, as well as the repeatability of experimental results. It was found that the original fuel ignites spontaneously at degrees of fuel compression above 27:1. In this case, at the end of the compression stroke, the pressure in the chamber attains 8.5 MPa and the temperature amounts to 980 K (estimates based on the adiabaticity of the process). The signals from the pressure gauge and PMs recorded in the course of a series of four experiments are depicted in Fig. 8 where the gray lines correspond to the signals in the experiment without a fuel. It was established in the course of experiments that the maximal pressure in the chamber as a result of fuel compression is reproduced with an accuracy of 3.5% and the ignition delay, with an accuracy of about 5%. Thus, we may state that the given procedure will make it possible to carry out a comparative analysis of the fuel properties of different specimens of a liquid fuel if the resulting effect exceeds the 5-% level.

Figure 9a presents the results of a comparative analysis of self-ignition and combustion of specimens A (dashed line) and B (dotted lime) relative to the original specimen 0 (solid line). The experiments were run in the course of one day and under identical initial conditions. The delay in self-ignition and the maximum level of pressure in the chamber are identical within the procedure error for all specimens. However, in the case of combustion of specimen B, the rate of pressure rise in the chamber is much higher as compared with the original fuel 0 and sample A. This can be associated with the more intense evaporation of sample B.

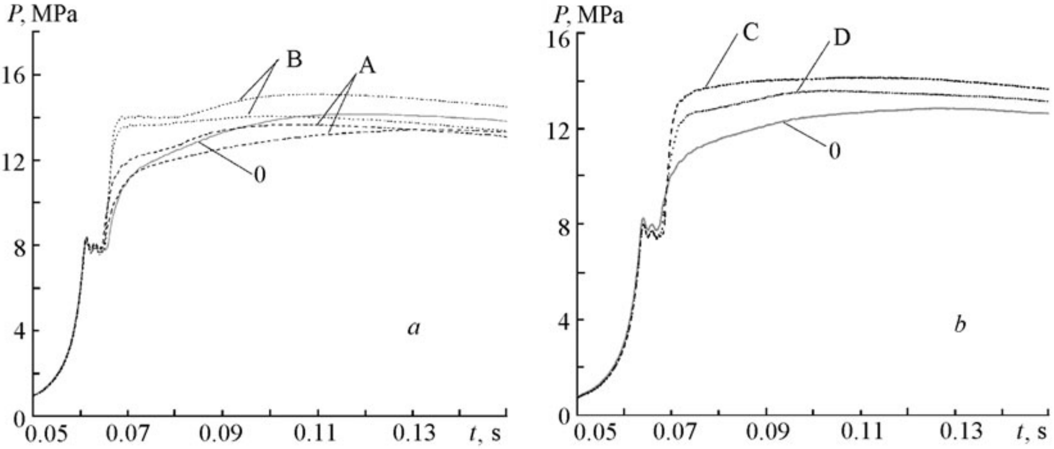


Fig. 9. Pressure P as a function of time t in the combustion chamber on compression of air, self-ignition, and combustion of specimens A and B (a), C and D (b); 0, pure ethanol.

In the next series of experiments we investigated specimens C and D. The results of measurements are presented in Fig. 9b. As with the previous specimens, the delay in self-ignition lies within the limits of the error of the method, which points to the fact that the delay in self-ignition after fuel compression depends on the ethanol evaporation rate. However, during the subsequent combustion of samples C and D, the pressure in the chamber increases more rapidly as compared to the original fuel. As is seen, the level of specimen C is approximately 10% higher than that of specimen 0.

As is seen from the experimental data, the rate of fuel combustion after electrical discharge treatment can increase substantially. There are several plausible explanations for the effect observed. The dynamics of combustion experiences the effect from both liquid synthesized substances and solid nanoparticles. Liquid light fractions can accelerate the evaporation of fuel during its combustion in a bowl. Some components synthesized by an electric discharge, e.g., tetradecanol, have a higher enthalpy in comparison with the original ethanol [13], and during combustion they produce a higher thermal effect.

Various mechanisms of combustion acceleration for solid particles can be considered. In our experiments, synthesized particles are predominantly represented by porous clusters composed of chain structures. Their influence on the fuel combustion rate can manifest itself as acceleration of heterogeneous reactions on the developed solid surface of nanoparticles as compared to purely gas-phase combustion. However, since the material of the particles can contain uncontrolled impurities, for example, of metals sputtered by the electrodes, the catalytic mechanism of the accelerated combustion must also be taken into account.

In order to make a more distinct separation of the above-mentioned factors, it is necessary to carry out experiments on combustion of a fuel under conditions of diffuse injection on a setup for rapid compression. It is also necessary to investigate specimens of fuels after their long storage in order to determine the factor of sedimentation of solid particles.

It should be noted that in future modification of bioethanol seems to be imperative, because its production in a pure state is nonprofitable (see, e.g., [14]); therefore, only ethanol with improved characteristics will turn out to be competitive as an additive to a traditional fuel.

It is of interest to estimate the magnitude of additional energy expenditures on electric discharge treatment of a fuel as compared to the own calorific value of the latter. For example, for technique C of obtaining a fuel at an electric discharge power of about 1–10 W, with the heat of combustion of ethyl alcohol assumed to be equal to 27.2 MJ/kg (without expenditures on evaporation of inherent water), the fraction of the additional energy input equals several percent.

Conclusions. The dynamics of pressure increase on combustion of ethanol preliminarily treated by electric discharge can be improved by the formation of both nanosized carbon solid particles and liquid synthesized substances.

Catalytic heterogeneous reactions on the surface of solid nanoparticles can be an important mechanism underlying the improvement of the rate of combustion. Liquid volatile fractions can ensure accelerated evaporation of a fuel.

The power expenditure on electric discharge treatment for obtaining a positive effect amounts to approximately 100 W·h/liter, which is acceptable for special kinds of fuels, for example, in high-speed energy-intensive plants and flying vehicles.

NOTATION

I, intensity of a signal from a chromatograph, rel. units; *P*, pressure, MPa; *t*, time, min; *U*, signal from a photomultiplier, V.

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