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Study of the concentration effect and structure of multilayer spherical carbon nanoclusters on the carrying capacity of alternative fuels

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Abstract

The paper presents the results of tribological studies of the influence of nanoscale additives on the properties of ethanol and biodiesel fuels. The non-monotonic extreme nature of the dependence of the carrying capacity of liquid fuels on the content of nanoscale particles is revealed; this indicator changes most maximally in the region of ultra-low concentrations of nanoparticles (several ppm).

The possibility of improving the synthesis and modification of carbon spheroidal nanoclusters by conducting high-frequency high-voltage synthesis in various organic solvents has been shown, which allowed to increase significantly the set of starting materials for the synthesis with the inclusion of various elements in the structure of CNSs. In order to increase the yield of carbon nanospheres during synthesis in the liquid phase, a reactor with a given angle of the interelectrode space was made for the first time for use in the synthesis process of "Jacob's ladder".

Chemical analysis and structural studies of synthesized samples of nanoscale objects of different chemical structures were carried out using IR and Raman spectroscopy, and electron microscopy.

For the first time, the hypothesis proposal has been made that individual carbon nanoparticles, obtained by high-voltage high-frequency plasma-chemical synthesis, which appear as spheroidal objects in electron microscopic images, are actually twisted coils of linear chain molecules of the polyyne type – carbynes.

Keywords: fullerene-like carbon nanoparticles, plasma discharge, high-voltage high-frequency plasma chemical synthesis, carrying capacity, alternative fuels.

Introduction and literature review

In addition to the main function of motor fuels – the ability to transform the chemical energy accumulated in them into thermal and mechanical work of engines, they must provide high lubricating properties [1].

According to the generally accepted definition, "the lubricating properties of fuels and lubricants are their ability to reduce friction and wear of contact surfaces moving relative to each other when a load is applied to the friction pair."

In modern internal combustion engines running on liquid fuels (gasoline, diesel and jet), fuel acts as a lubricant for plunger pumps, injector elements and other parts of the fuel supply control equipment. The condition of this equipment determines fuel consumption, reliability, service life and functional suitability of the engines as a whole.

Therefore, the problem of assessing the anti-wear properties of modern motor fuels (both traditional hydrocarbon and biofuels) is very important for developing the composition of fuels, creating new anti-wear additives, and recommendations for their use.

The final, most reliable tests of batches of motor fuels for compliance with anti-wear properties before their practical implementation are carried out on real engines. However, this requires significant consumption of motor fuel (tens of tons) and is long-term.

For screening non-engine assessment of anti-wear properties of liquid motor fuels at the initial stages, more than 10 tribological testing methods are used in world practice [2–3]. These methods differ in friction contact schemes, friction pair materials, test time and load. When conducting tribological tests, the anti-wear properties of diesel fuels are characterized by the values of the following indicators: friction coefficient, average diameter of wear spots (under selected standardized conditions), as well as by the value of the bearing capacity (critical load before seizure).

In our studies, the impact of nanoscale additives on the anti-wear properties of biofuels was assessed by the change in bearing capacity.

The bearing capacity of fuels determines the range of loads at which, under given standard conditions, the fluid friction mode is implemented until the fluid layer ruptures and metal contact of friction surfaces occurs with their microdamage - burrs.

The characteristic of bearing capacity for a liquid is, in its physical content, analogous to the corresponding characteristic of dynamic strength for solids; they both reflect the ability of materials to resist external loads on them.

Carbon nanospheres (CNSs) ideally have a structure in the form of concentric fullerene-like shells. In addition to the six-membered C_6 rings, the shells also include C_5 and C_7 rings [4].

But in real spherical carbon nanoobjects, the regular shell spherical structure is disrupted; they consist of individual graphene fragments – petals.

Currently, various methods for the synthesis of CNSs have been developed: pyrolytic deposition from the gas phase, hydrothermal synthesis, template synthesis. However, despite the significant number of publications on the synthesis methods of carbon nanospheres, they mainly concern large-sized nanospheres. The number of publications on the synthesis of CNSs with sizes smaller than 100 nm is very limited [5].

The main methods for obtaining such nanospheres are arc discharge between carbon electrodes in the gas phase, as well as in a liquid, for example, in water or benzene, the particle size in this case is 5–100 nm [6]. High-temperature annealing of detonation nanodiamonds creates spheroidal particles with well-defined shells and a narrow size distribution of 2–10 nm [7].

There is no commonly accepted model for the primary structure of individual spherical nanoparticles at the moment. Most researchers who have obtained CNSs by thermal transformation of nanodiamonds [8] believe that individual nanoparticles that form spheroidal agglomerates consist, in turn, of multilayered partially closed defective graphene shells – petals of irregular shape, the interplanar distance between which is ~ (0.332±0.001) nm (the interplanar distance of graphite is 0.3354 nm). In the middle of the particle there is a disordered core. It is believed that this core is in a liquid state [9].

In the previous stages of our research, the modification of carbon nanospheres was carried out by treating the mixed synthesis product (in the form of carbon black) with various chemical reagents and subsequent isolation of the desired target nanoparticles by extraction in various solvents, filtration and vacuum distillation of solvents [10]. The structure and size of the nanoobjects selected for further research were controlled using SEM and TEM electron microscopy and Raman scattering spectroscopy.

We have improved the synthesis and modification of carbon spheroidal nanoclusters - high-frequency high-voltage synthesis was carried out in various organic solvents. This allowed us to increase significantly the set of starting materials for the synthesis of CNSs with the inclusion of atoms of various elements in the structure.

Purpose

The aim of the work is to develop methods for the synthesis of nanosized objects with different chemical structures and to identify the mechanisms of action of small concentrations of nanoclusters on the magnitude of the carrying capacity of individual liquid substances and practically important liquid petroleum products.

Results

Brominated CNSs were obtained by a one-step synthesis from solutions of bromo- and fluorocarbons in hydrocarbon solvents without using an additional CNSs halogenation step.

The synthesis of carbon nanomaterials in the liquid phase is carried out using dielectric liquids. These can be organic solvents, as well as liquid gases (nitrogen, argon, helium). During these processes, a suspension of individual nanoparticles with a defined spatial structure, as well as associates of such nanostructures, is formed in the liquid. The content of various modifications of individual nanoparticles, their sizes and the sizes of associates of these objects depend on the energy conditions of the arc discharge process and on the liquid in which the synthesis takes place.

Plasma-chemical liquid-phase synthesis of carbon nanoparticles was carried out in a glass reactor. The plasma discharge in aliphatic and aromatic solvents was generated by a bipolar power source - a high-voltage high-frequency generator using tungsten open electrodes. The electrodes were placed in the volume of liquid - the starting material. The frequency of the voltage pulses was 25 kHz. The generator voltage $U = 4$ kV.

Also, to increase the yield of carbon nanospheres during liquid-phase synthesis, a reactor with a given angle of the interelectrode space was first made for use in the Jacob's ladder synthesis process.

plasma-chemical liquid-phase synthesis modes for the production of spheroidal carbon nanomaterials was carried out using individual hydrocarbon compounds in the liquid state (hexane, octane, benzene, bromomethane), mixtures (hexane with bromomethane), and fluorocarbon derivatives.

The synthesis products were isolated from the liquid phase by centrifugation (30 min at 4000 rpm). Then the powders were additionally dried in vacuum and fractionated by extraction in low-boiling solvents and filtered on filters with a pore diameter of 250 nm and the solvent was distilled off.

Electronic images of the CNSs samples are shown in Fig. 1. High-resolution microscopic images of the CNSs were obtained using a JEOL JEM-2100F transmission electron microscope (TEM) with an electron accelerating voltage of 200 kV. For this, carbon nanosphere samples were dispersed in a dimethyl ketone medium using an ultrasonic disperser, and then applied to a special substrate.

The obtained carbon nanomaterials are spheroidal nanoparticles with sizes of ~ 10–30 nm with a complex hierarchical structure.

We were the first to propose the hypothesis that individual carbon nanoparticles obtained by high-voltage high-frequency plasma-chemical synthesis, which appear as spheroidal objects in electron microscopic images, are actually twisted coils of linear chain molecules of the polyyne type - carbynes.

This opinion is confirmed by in particular, the results of IR spectroscopic analysis of these materials. Their IR spectra (Fig. 2) show a rather intense band at 1737 cm^{-1}, which is characteristic of linear carbynes with double cumulated bonds =C=C=C=C=C=, and is absent in the spectra of cyclic molecules of the benzene type.

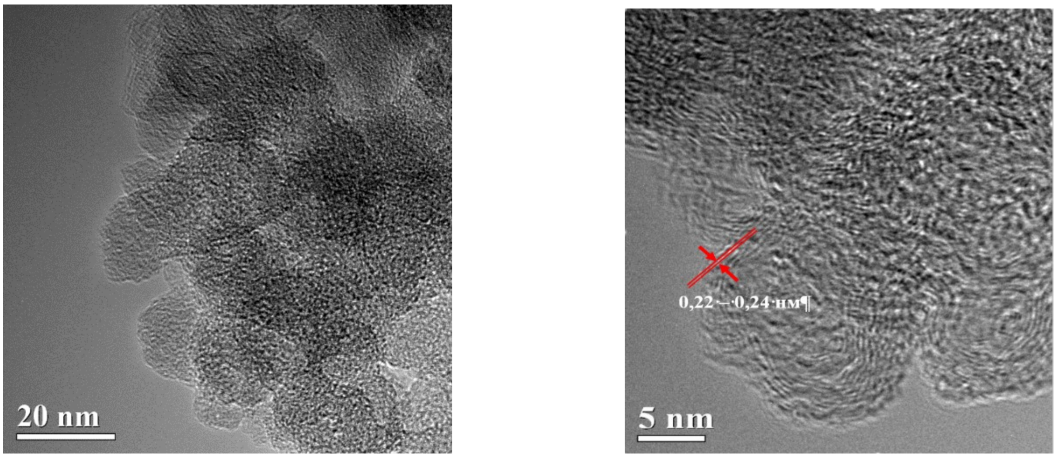

Fig. 1. TEM image of carbon nanospheres

Fig. 1 presents the results of the study of the structure of the synthesized compounds by transmission electron microscopy. The synthesized nanospheres of the type consist of carbyne threads woven into a ball with a diameter of 2.2 - 2.4 nm, which coincides with the diameter of the polycumulene chain. Indeed, the absorption band at 1737 nm present in the IR spectra of the obtained nanocarbon compounds is present in the IR spectrum of polycumulenes and is not observed in the spectrum of graphene.

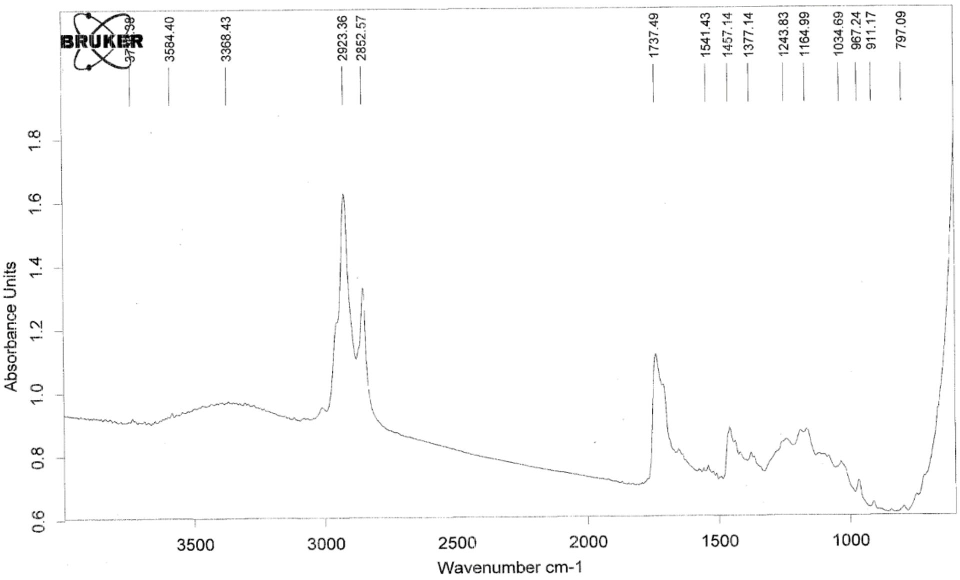

Fig. 2. IR spectrum of carbon nanospheres

To identify the structural features, degree of ordering, and homogeneity of the obtained carbon materials, laser Raman spectroscopy was used.

Raman spectroscopic studies of samples of synthesized nanomaterials were carried out at the V.E. Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine (senior scientific collaborator Kolomys O.F.).

Raman spectra were recorded in a wide range of wavenumbers at 150–3500 cm^{-1} using a LabRAM laser spectrometer (Yobin Yvon) with a 632.8 nm He-Ne laser excitation line.

Raman spectroscopy is one of the vibrational spectroscopy methods that does not require the destruction of samples for analysis and is widely used in the study of various allotropic modifications of carbon. A characteristic feature of the Raman spectra of carbon materials is the presence of a G-band at 1500–1600 cm^{-1}. The vibrations that are reflected in the spectrum by the G (graphite) - band are considered to be associated with vibrations of carbon atoms in the plane of graphene cycles (tangential vibrations).

Depending on the structural perfection and curvature of such layers, the G-band can vary in frequency and shape. In the spectra of pure graphite, it has a narrow and undivided shape due to the symmetry and unstrained state of the bonds between carbon atoms in the flat graphene layers of this material.

In the Raman spectra of onions (spheroidal multilayer carbon clusters), in addition to the band characteristic of vibrations of sp^2-bonds in ordered carbon materials, a band also appears at about 1320 cm^{-1}. The intensity of the band at 1320 cm^{-1} may be different in magnitude compared to the intensity of the band at a frequency 1590 cm^{-1}.

The Raman-active oscillation bands at a frequency 1590 cm^{-1} are usually designated G (graphite) - band, and the band at 1320 cm^{-1} is designated as D (disorder) - band. The D (disorder) - band is due to various structural defects and limited crystallite sizes, i.e. it is associated with the disordering of carbon nanomaterials. The intensity of this band characterizes the defectivity, i.e. the degree of symmetry violation of the ideal graphite layer with sp^2-hybridization of carbon atoms. Therefore, the ratio of the intensities of the D/G bands characterizes the relative content in the studied sample of the amount of materials with disordered and ordered structures.

The presence of these two bands in the Raman spectrum of a chemical substance is a kind of characteristic mark that indicates the content of carbon with sp^2- and sp^3-hybridization in the substance, that is, carbon nanomaterials with a spheroidal shell structure.

Below are the Raman scattering spectra (Fig. 3) of bromine-containing carbon nanoclusters, which we obtained by the method of plasma-chemical synthesis in the liquid phase.

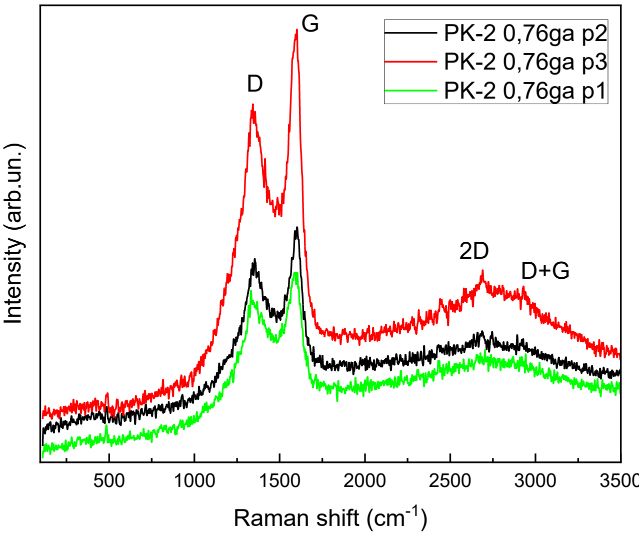

Fig. 3. Raman spectrum of carbon nanoclusters obtained by plasma-chemical synthesis of bromine-containing hydrocarbons in the liquid phase

The presence of two characteristic vibration bands in the Raman spectra of the products synthesized by us (at about 1500 cm^{-1} and 1300 cm^{-1}) is confirmation that spheroidal carbon nanoparticles were indeed obtained using the plasma-chemical synthesis method.

Tribological studies of the effect of small concentrations of nanoparticles in liquid motor fuels

The comparison of the bearing capacity of fuels was determined on a four-ball tribometer by the magnitude of the critical load according to the ASTM D2783 method [11].

This indicator represents the maximum value of the axial load, up to which there is no metal contact and no scoring during sliding friction of standardized metal balls made of steel ShKh15 (microhardness 64-66 HRC, hardness parameter Ra < 0.25 μm, ball diameter – 12.7 mm) in test liquid medium. Test conditions: rotation speed of the upper loaded ball relative to three stationary balls – 1500 rpm, temperature 20 °C, test time – 10 s. At each load, at least three tests were performed.

Fig. 4 shows that the carrying capacity of ethanol is changing non-monotonically with increasing concentration of bromine-containing CNSs.

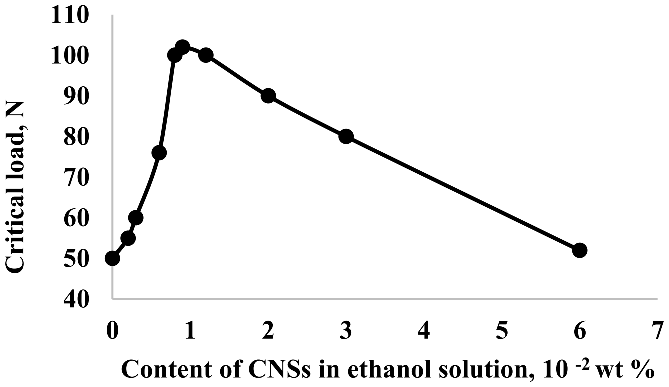

Fig. 4. Non-monotonic dependence of the carrying capacity of ethanol solutions on the concentration of bromine-containing CNSs

The critical load value for blended biodiesel fuel (80% commercial petroleum diesel fuel DSTU 7688:2015 + 20% ethyl esters of vegetable oils) at different concentrations of spheroidal carbon nanoclusters is shown in Fig. 5.

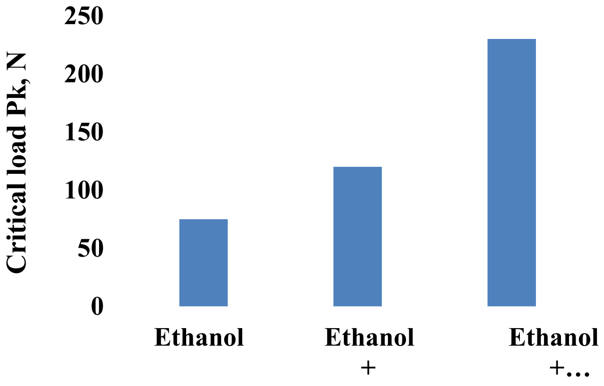

Fig. 5. Maximum increase in the carrying capacity of ethanol fuel by additives of bromine- and fluorine-containing carbon spheroidal nanoclusters (at optimal concentrations in the range of 10^{-4}-10^{-3} % by weight)

The critical load value for blended biodiesel fuel (80% commercial petroleum diesel fuel DSTU 7688:2015 + 20% ethyl esters of vegetable oils) at different concentrations of spheroidal carbon nanoclusters is shown in Fig. 6.

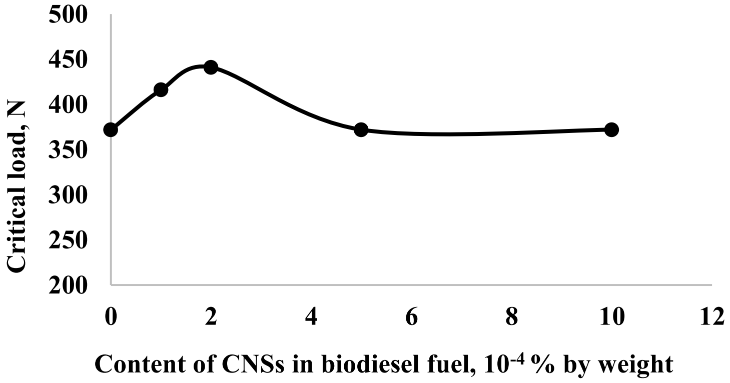

Fig. 6. Effect of carbon bromine-containing nanospheres on the carrying capacity of blended biodiesel B20 (80% diesel fuel + 20% ethyl esters)

According to the results of tribological studies, the concentration dependences of the bearing capacity of ethanol solutions and biofuels on the content of nanoparticles - carbon nanoclusters and metal complexes - are of an extreme nature.

The maximum effect of increasing the critical load index is observed in the range of small concentrations of nanoclusters in solutions (less than 10^{-2} % by weight).

The magnitude of the effect of increasing the carrying capacity for a given solution depends on the polarity (polarizability) of the nanoparticles. The most significant increase in the carrying capacity of ethanol solutions (by 2–3 times) was observed for fluorine-containing carbon nanospheres.

Conclusions

1. The chemical analysis of the synthesized samples and structural studies using IR and Raman spectroscopy, electron microscopy confirms the formation of nanosized objects of different chemical structure (carbon spheroidal nanoclusters).
2. Tribological studies of the influence of nanoscale additives on the properties of ethanol solutions and biodiesel fuels were conducted. It was shown that the introduction of small concentrations (several ppm) of nanoscale additives allows to increase the carrying capacity of biofuels by 2–3 times. A non-monotonic extreme nature of the dependence of the carrying capacity of liquid fuels on the content of nanoscale additives was revealed; this characteristic changes most maximally in the region of small concentrations of nanoparticles, when the concentration threshold values are exceeded, the efficiency of the action of nanoparticles decreases.
3. The extreme non-monotonic nature of the dependence of solution parameters on the concentration of nanoparticles is explained by the formation of regions of heterogeneity in solutions.

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Полункін Є.В., Плескун С.М. Дослідження концентраційного впливу та структури багатошарових сферичних карбонових нанокластерів на величину несучої здатності альтернативних палив

В роботі показано результати трибологічних досліджень впливу нанорозмірних присадок на властивості етанольних та біодизельних палив. Виявлено немонотонний екстремальний характер залежності несучої здатності рідких палив від вмісту нанорозмірних часток; найбільш максимально цей показник змінюється в області надмалих концентрацій наночастинок (декілька ppm).

Показано можливість вдосконалення синтезу та модифікацію карбонових сфероїдальних нанокластерів шляхом проведення високочастотного високовольтного синтезу в різних органічних розчинниках, що дозволило значно збільшити набір вихідної сировини для синтезу з включенням атомів різноманітних елементів в структуру КНС. Для збільшення виходу карбонових наносфер при синтезі в рідинній фазі вперше був зроблено реактор з заданим кутом міжелектродного простору для використання в процесі синтезу «драбина Якоба».

Проведено хімічний аналіз та структурні дослідження синтезованих зразків нанорозмірних об’єктів різної хімічної будови методами ІЧ- та КР- спектроскопії, електронної мікроскопії.

Вперше висунуто припущення, згідно якого окремі карбонові наночастинки, які отримували високовольтним високочастотним плазмохімічним синтезом, що в електронномікроскопічних зображеннях виглядають як сфероїдальні об’єкти, в дійсності є скрученими клубками лінійних ланцюжкових молекул поліінового типу – карбінів.

Ключові слова: фулереноподібні карбонові наночастки, плазмовий розряд, високовольтний високочастотний плазмохімічний синтез, несуча здатність, альтернативні палива