The object of research is the mechanisms of synthesis of nanocarbon structures in the process of electric high-voltage breakdown of hydrocarbons. The problem to be solved is the purposeful synthesis of various types of nanocarbon with small losses of raw materials.

Mechanisms of nanocarbon formation in the process of high-voltage electric breakdown of hydrocarbons have been established. It is shown that a high-voltage breakdown leads to a cascade of chemical transformations. As a result of transformations, lower gaseous hydrocarbons are formed due to the destruction of molecules and higher ones – as a result of polymerization, and as a result of dehydrocyclization and polymerization with the participation of metal catalysts – various carbon nanostructures. The possibility of targeted synthesis of fullerene-like structures, nanotubes with diameters from 10 to 50 nm, nanofibers, and films is demonstrated. Experimental studies have confirmed that the qualitative and quantitative composition of nanocarbon can be varied in a wide range. With an increase in the number of carbon atoms or the number of C–C bonds in the raw material molecules, other things being equal, the practical yield of solid nanocarbon increases. It was determined that the synthesis of structured nanocarbon from a mixture of hydrocarbon gases, formed as a result of high-voltage breakdown of liquid hydrocarbons, actively occurs on the nickel-chromium catalytic surface. An increase in the area of the catalytic deposition surface leads to an increase in the yield of nanocarbon. The study of the ability of the obtained nanocarbon samples to absorb electromagnetic radiation confirmed the potential of the method of high-voltage breakdown of hydrocarbons for the synthesis of materials that weaken electromagnetic radiation at a frequency of 25 to 38 GHz. The greatest weakening is observed for samples consisting mainly of carbon nanotubes and nickel nanoparticles.

Keywords: synthesis of nanocarbon, high-voltage breakdown of hydrocarbons, mass yield of the product, electromagnetic properties

1. Introduction

The term “nanocarbon” is a rather broad research concept that combines various structures of carbon with nanometer dimensions. For materials science, nanocarbon and related nanotechnologies are one of the most promising areas of research. For example, the development of elements of microcircuits with characteristic dimensions of about units and tens of nanometers qualitatively changes the electronics of phenomena and transfers it to a new area – nanoelectronics, which requires the creation of appropriate materials [1–3]. The construction of powerful and efficient electrochemical devices (batteries, supercapacitors) is also currently based on the use of nanocarbon [4–6]. Features of the structure and surface morphology of carbon nanomaterials make them very attractive for catalysis [7, 8]. The application of nanocarbon in biotechnology and medicine [9–11], in construction [12] is promising. Thus, the creation of new materials with functional properties that significantly exceed the properties of modern ones or have unique combinations of properties that cannot be obtained in existing materials, is an urgent need of science and technology. In this regard, carbon nanomaterials have great prospects due to the diversity of their structure [13, 14]. The prospect of using carbon nanomaterials is determined by their thermal and chemical stability, high strength, microhardness, developed specific surface area. In addition, the new composite properties of materials and coatings obtained on the basis of nanocarbon have unique electromagnetic and tribological properties.

2. Literature review and problem statement

Currently, the following are recognized as successful methods of nanocarbon synthesis.

The method of chemical vapor deposition from the gas phase (Chemical Vapor Deposition, CVD) is known and successfully developed since 1990s. The method is used mainly for applying ultra-thin coatings on the surface. Recently, the absolute advantage of this method has become the use of...
of natural ingredients to obtain transitional nanostructures. The scientific community has come to the conclusion that the technology of nanocarbon production based on fossil fuels will not be sustainable, but the authors admit that nanomaterials obtained on the basis of natural ingredients are inferior in quality, purity, and crystallinity of samples [15]. At the same time, the authors of [16] emphasize the importance of the morphology of the volume and surface of derivatives for the implementation of the chemical deposition method. On the one hand, this enables the precise creation of nanomaterials, and on the other hand, it makes the stage of preparation of derivative materials for synthesis very difficult and expensive.

As for the synthesis of nanocarbon by this method, the observation of the growth of carbon nanotubes, for example, showed that the mechanism is extremely sensitive to each parameter, such as the carbon precursor, the metal catalyst, the size of the derived particles, temperature, and pressure. Changing any of these parameters leads to the formation of nanocarbon in critically different directions. Catalysis is the mainstay of the synthesis of nanocarbon by the CVD method, the authors of the review [16] conclude that an important need today is the need for materials for the development and research of catalysts. The main challenge is still the task of reducing the synthesis temperature to room temperature with the help of a precisely selected substance, which could reduce the activation energy of the reactions of the formation of nanomaterials.

Methods of laser ablation are thoroughly discussed in review articles [17, 18]. It is shown that laser technologies allow selective heating and efficient synthesis of nanotubes and nanofilms. The laser ablation method is primarily used for the production of single-layer carbon nanotubes with an adjustable diameter and is determined by such parameters as the reaction temperature, inert gas flow rate, etc. Although this method is more complex and expensive than chemical vapor deposition, it can produce carbon nanotubes of higher quality. A fundamentally unsolvable problem of the synthesis of nanomaterials by this method is the low utilization rate of raw materials, and, accordingly, a very small mass yield of the desired product.

The exfoliation method – mechanical separation of three-dimensional materials, such as graphite, allows obtaining graphene in the form of two-dimensional layers [19], but this very successful and low-cost method is intended exclusively for obtaining layered nanocarbon structures. In addition to the well-known method of obtaining graphene, used by the 2010 Nobel laureates K. Novosyolov and A. Geim, there are a large number of other techniques, and their number continues to grow. However, it is already clear that the basic methods are the deposition of graphene films from the gas phase and the method of liquid phase exfoliation. At the same time, it can be argued that the method of deposition from the gas phase is being developed primarily for use in electronics, and the process of liquid phase exfoliation can already be considered as the basis for the organization of mass production of layered graphene particles of modifying agents.

The method of chemical reduction of carbon oxides [20] (Reduction of Carbon Oxides) is based on the reduction of carbon oxides to nanotubes on a mixture of metal catalysts and is very successful in this. The fact that it becomes possible to convert the greenhouse gas CO₂ into nanocarbon with the help of this method and significantly reduce the carbon load on the environment has become especially important recently. But a significant drawback is an extremely low productivity and a naturally limited range of synthesized products. The efficiency of catalysts undoubtedly plays a key role in reduction reactions. However, the catalysts themselves have a negative impact on the environment, thus limiting the environmental effect of large-scale CO₂ processing. The next direction in the development of the carbon oxides recovery method is to investigate the lifetime and reusability of the catalyst materials to make this technology more economical and environmentally viable.

All of the above methods of synthesis of nanomaterials have been verified by the scientific community under laboratory conditions but require complex equipment and a multi-stage technological process for their industrial implementation. That is why so far, they have not become common in the large-scale production of nanocarbon materials. This limits the multi-ton application of nanocarbon in industry and restrains the economic effect of its use. Therefore, the problem of developing new, high-performance, and energy-efficient, as well as the development of existing methods of nanocarbon synthesis is urgent. There are a number of requirements for nanocarbon synthesis methods that are potentially suitable for industrial use:

- a diverse qualitative composition of the resulting nanocarbon powder mixtures;
- the possibility of controlling the phase and (or) component composition of nanocarbon powder mixtures;
- high productivity of the method;
- low specific energy costs and raw material costs;
- high environmental friendliness of the method.

All this gives reason to assert that it is expedient to conduct a study that considers the purposeful synthesis of nanocarbon by means of high-voltage breakdown of liquid and gaseous hydrocarbons.

High-voltage breakdown of dielectric liquids, as a phenomenon of a sharp increase in current in the medium that occurs when an electric voltage higher than the critical voltage is applied to it, has been actively studied since the middle of the last century. Initially, high-voltage breakdown of dielectric liquids was associated exclusively with the study of electrical insulating properties of materials and lightning protection of objects. The breakdown of liquid media is actively used to develop methods of high-energy impact on substances in order to change their properties.

High-voltage breakdown of water is actively discussed as the most traditional medium for the implementation of discharge-pulse technologies. In [21], the electrical characteristics of water breakdown are considered, and the effect of electrode geometry and voltage polarity on high-voltage breakdown is reported. But the authors see the future use of high-voltage breakdown exclusively as a tool for crushing solid bodies in an aqueous environment. According to the authors of [22], the change in electrical conductivity of tap, distilled, and lake water in the direction of increase during electric discharge is caused by the formation of water bubbles and the structuring of water molecules. The authors also put forward a rather controversial scientific hypothesis that electrical conductivity can serve as a criterion for evaluating the efficiency of the electrohydraulic processing process.

The review [23] considers the influence of the conductivity of aqueous solutions on the critical current density in the discharge channel and the breakdown voltage. Thus, great success has been achieved in the field of high-voltage breakdown of water, the understanding and use of plasma-chemical transformations of water molecules during
breakdown is rapidly developing. Other fluids remain beyond the scope of the wide-scale interest of materials scientists. Nevertheless, plasma-chemical processes in various liquid media are a promising source of materials with unique properties. It is important to note that the electrical equipment for high-voltage breakdown of liquid media has long since reached the industrial level and allows for high-voltage breakdown in a wide range of liquids.

The method based on the synthesis of carbon nanostructures from carbon-containing plasma, which is formed as a result of high-voltage breakdown of hydrocarbons, has great potential. It was previously shown [24, 25] that a wide range of allotropic forms of carbon is formed as a result of the electric discharge effect on liquid hydrocarbons. At the same time, the structural and phase state of nanocarbon is largely determined by the dynamics of plasma-chemical and thermodynamic processes occurring during their synthesis. This determines the possibility of targeted production of various forms of nanocarbon. In [24], it was observed that the yield of nanocarbon powder increases as the length of the hydrocarbon chain of the raw material increases. In this case, both solid phase nanocarbon with an amorphous structure and gaseous products are formed. Gaseous products, in turn, contain both hydrogen and lower hydrocarbons with varying degrees of saturation of carbon bonds. In the same work, an attempt was made to describe the process of destruction of n-hexane under the action of an electric discharge.

The mechanisms of the formation of various carbon nanostructures in the process of high-voltage electric breakdown of hydrocarbons have not yet been determined. Descriptions of known methods of synthesis of carbon nanomaterials do not reveal the yield of nanocarbon in the proposed technologies. The practical application of various types of nanocarbon is limited due to the low productivity of methods, low yield, and high cost of nanocarbon, which are associated with low product yield.

The problem to be solved is the purposeful resource-saving synthesis of various types of nanocarbon in the processes of electric high-voltage breakdown of hydrocarbons.

### 3. The aim and objectives of the study

The purpose of this work is to improve the method of targeted synthesis of various types of nanocarbon in the processes of electric high-voltage breakdown of hydrocarbons. This will make it possible to use the nanocarbon synthesis method in industry.

To achieve the goal, the following tasks were set:
- to determine the mechanisms of formation of various types of nanocarbon in the processes of high-voltage breakdown of liquid hydrocarbons;
- to investigate samples of nanocarbon synthesized in the processes of high-voltage breakdown of liquid and gaseous hydrocarbons;
- to analyze the mass yield of nanocarbon from hydrocarbons.

### 4. The study materials and methods

The object of our research is the mechanisms of synthesis of nanocarbon structures in the process of electric high-voltage breakdown of hydrocarbons.

The main hypothesis of the research is the reduction of raw material losses as a result of the processing of gases produced in the process of electric breakdown of liquid hydrocarbons, and the use of catalytic surfaces for the deposition of nanocarbon.

The experiment was carried out on the installation described in [26]. As a result of previous experiments, it was observed that the removal of the mixture of gases formed as a result of high-voltage breakdown from the working area of the reactor is a necessary action to ensure stable conditions for high-voltage processing of liquid hydrocarbons. Therefore, the installation was supplemented with a device for electric discharge treatment of gases that are formed as a result of high-voltage breakdown of hydrocarbon liquid.

The breakdown of the gases formed was carried out with the same frequency as the breakdown of the liquid, other parameters of the gas breakdown were fixed and did not change during the experiment. After the electric discharge activation of the gas mixture, deposition of solid nanocarbon took place on the walls of the container (quartz glass) or on a metal catalytic substrate, which was heated to 1200 K. In this way, the deposition of nanocarbon, which was formed from the mixture of hydrocarbon gases activated by a high-voltage breakdown, took place.

Liquid hydrocarbons were used as raw materials for nanocarbon synthesis. In particular, alcohols (ethanol, butanol), alkanes (pentane, hexane), cycloalkanes (cyclopentane, cyclohexane) and a mixture of hydrocarbons (kerosene TS-1) were subjected to high-voltage breakdown. This choice was made on the basis of the following considerations. Cyclopentane and cyclohexane have a similar skeletal formula, the carbon atoms in their molecules are in a state of sp3 hybridization, but they differ in the number of carbon atoms. Cyclohexane and hexane, in turn, have the same number of carbon atoms in the sp3-hybridization state, but differ in their structure and the number of C–C and C–H bonds. Ethanol and butanol molecules have different numbers of carbon atoms but are similar in skeletal formula and contain one oxygen atom. The role of oxygen in intermediate plasma chemical reactions is still uncertain from the point of view of the possible formation of liquid and gaseous carbon compounds. Molecules of benzene and cyclohexane have the same number of carbon atoms and structure but differ in the degree of hybridization of carbon atoms in the molecules.

The energy of a single pulse, with the help of which liquid breakdown was carried out, was varied in the range from 10 to 110 J. This was ensured by changing the charging voltage and capacity of the capacitor bank in the range of 15...35 kV and 0.05...250 μF, respectively. The total energy consumption for high-voltage breakdown of hydrocarbon liquid for all modes of high-voltage breakdown was fixed at the level of 1.35 MJ, the mass of raw materials processed with the help of high-voltage breakdown was constant for all processing modes.

To maintain the stable nature of the breakdown when changing the parameters of the power unit, the width of the interelectrode annular gap between the disc anode and the wall of the cylindrical discharge chamber (cathode) was changed, and the treatment of organic liquids was carried out under oscillating modes of the breakdown. Liquid and gaseous hydrocarbon processing products were weighed on a FEN-300 laboratory balance and studied by electron transmission and raster microscopy methods using Hitachi H-800 and LEO Supra 50VP electron microscopes.
5. Results of research on the synthesis of nanocarbon in the processes of high-voltage breakdown of liquid and gaseous hydrocarbons

5.1. Results of studying the mechanisms for the formation of various types of nanocarbon in the processes of high-voltage breakdown of liquid hydrocarbons

To estimate the amount of energy affecting a hydrocarbon molecule in a high-voltage breakdown channel, we shall assume that all stored energy is used to break chemical bonds. The energy in a single high-voltage pulse with an electric capacity of capacitors of 0.25 μF and a charging voltage of 30 kV is 112 J, the volume of liquid processed in one pulse is approximately 10^−3 dm^3. Thus, for one pulse, energy of about 400 kJ/mol is released in the working medium. This means that for one impulse in a hydrocarbon molecule, it is possible to homolytically break only one C–C bond (bond energy 339 kJ/mol) or one or two C–H bonds (bond energy 238 kJ/mol).

The rupture of these bonds leads, on the one hand, to the appearance of lower hydrocarbons – gases, and on the other – to the appearance of chemically active fragments – dissociates, which take part in various transformation reactions. In graphite- or fullerene-like nanomaterials, Carbon is in a sp^2-hybridized state. Then, in order to explain the possible mechanisms of formation of graphite- or fullerene-like nanomaterials, it should be assumed that the bulk of chemically active fragments are unsaturated hydrocarbons with different lengths of the carbon skeleton. This assumption is based on the data of chemical and mass spectral analysis of the formed gases and solid phase products, respectively [28].

The formation of nanocarbon can be carried out as a result of a huge number of chemical reactions known to organic chemistry. The most well-known and widely used reaction for the formation of an aromatic compound is the Zelinsky-Ka- 

zansky reaction – the thermal cyclotrimerization of acetylene, which proceeds on a coal catalyst with the formation of benzene (an aromatic hydrocarbon). Further polymerization of aromatic rings can be carried out thanks to the diene synthesis discovered by Diels and Adler (Fig. 1, b).

According to the Gay-Lussac and Ostwald rule, in any chemical process, the most stable state of the system does not first appear, but the least stable, closest in terms of energy to the initial state.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Melting/boiling point, K</th>
<th>Component of structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>C_{14}H_{10}</td>
<td>218/342</td>
<td>Graphite</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>C_{12}H_{10}</td>
<td>96/279</td>
<td>Fullerenes</td>
</tr>
<tr>
<td>Indene</td>
<td>C_{6}H_{8}</td>
<td>206/182</td>
<td>Fullerenes</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C_{10}H_{8}</td>
<td>80/218</td>
<td>Graphite</td>
</tr>
<tr>
<td>Pyrene</td>
<td>C_{9}H_{8}</td>
<td>156/303</td>
<td>Graphite</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C_{14}H_{10}</td>
<td>101/340</td>
<td>Graphite</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>C_{16}H_{10}</td>
<td>111/375</td>
<td>Fullerenes</td>
</tr>
<tr>
<td>Fluorene</td>
<td>C_{14}H_{10}</td>
<td>116/295</td>
<td>Fullerenes</td>
</tr>
<tr>
<td>Chrysene</td>
<td>C_{18}H_{12}</td>
<td>255/448</td>
<td>Graphite</td>
</tr>
</tbody>
</table>

If there are a number of relatively stable intermediate states between the initial and final states of the system, they will successively replace each other in the order of a step change in energy. This “rule of step transitions” or “law of sequential reactions” also corresponds to the principles of thermodynamics since there is a monotonous change of energy, taking successively possible intermediate values, from the initial state to the final state.

The presence of intermediate compounds during the high-voltage breakdown of hydrocarbon liquids is confirmed both by gas chromatography data [31] (Fig. 2) and by the results of measuring their refractive indices (Table 2). From the above chromatograms, one can see that the intermediate products of the high-voltage breakdown of liquid hydrocarbons differ depending on their saturation. The nature of the intermediate products indicates that dehydrogenation processes mainly occur in benzene (an aromatic hydrocarbon). Further polymerization of aromatic rings (formation of new C–C bonds) may be the cause of a high concentration of diphenyl in the treated liquid.
In hexane, the range of possible reactions is wider – dehydrocyclization with the formation of benzene, breaking of C–C bonds with the formation of aromatic compounds (toluene, phenylethane, styrene). Thus, the high-voltage breakdown of liquid alkanes (sp³-hybridization of carbon atoms) leads to the formation and consolidation of arenes (sp²-hybridization of carbon atoms), as well as polymerization.

Additional confirmation of the presence of polyaromatic compounds dissolved in the treated liquids (after filtering to remove nanocarbon that has already formed) is a slight increase in their refractive indices (Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Composite material</th>
<th>Refractive index before breakdown</th>
<th>Refractive index after breakdown</th>
<th>Possible nanocarbon formation process</th>
<th>Decay constant of C–C bonds at 1073 K, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>1.3832</td>
<td>1.3841</td>
<td>Destruction-dehydrocyclization-polymerization</td>
<td>18</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.4261</td>
<td>1.4296</td>
<td>Destruction-dehydrocyclization-polymerization</td>
<td>1.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.5008</td>
<td>1.5037</td>
<td>Destruction-dehydrocyclization-polymerization</td>
<td>0.001</td>
</tr>
</tbody>
</table>

**Fig. 2.** Chromatograms of samples of hydrocarbon liquids after high-voltage breakdown [31]: a – benzene; b – hexane
From Table 2, it follows that the refractive index of the treated hexane undergoes the smallest change. In this case, the decay constant of C–C bonds is of the greatest importance, which indicates that the processes of destruction of C–C bonds with the predominant formation of gaseous hydrocarbons prevail in hexane. In benzene, the molecule of which is the most stable under high-voltage breakdown conditions (the value of the homolytic bond breakdown constant in Table 2), the increase in the refractive index can be explained by the presence of soluble products of the dehydrogenation and polymerization processes.

In cyclohexane, the increase in the refractive index is due to the course of dehydrogenation processes and the formation of aromatic structures. However, part of the C–C σ-bonds in alkanes and cycloalkanes due to the higher breaking energy, compared to the breaking energy of π-bonds in arenes, can be preserved in the process of high-voltage breakdown of hydrocarbons, which causes the formation of sp²/sp³-nanocomposites. Depending on the ratio of sp² and sp³-hybridized carbon atoms, the products can be both diamond-like and graphite-like. At the same time, one of the possible mechanisms for the formation of nuclei of diamond-like structures is the synthesis of a multiple adamantane radical, which occurs by joining two-dimensional carbon radicals to a dehydrogenated cyclohexane molecule. An analogy of this synthesis is also found in the substantiation of the mechanism of nanodiamond formation during the explosion of a mixture of explosive substances (trinitrotoluene, TNT, benzotrifuroxan) [32].

### 5.2. Results of investigating nanocarbon samples obtained in the processes of high-voltage breakdown of liquid and gaseous hydrocarbons

Nanocarbon samples obtained by high-voltage breakdown of hydrocarbons differ in the degree of hybridization of carbon atoms in the molecule. In order to compare their structural state and morphological features, two liquid hydrocarbons with the same number of carbon atoms closed in a ring – benzene and cyclohexane – were treated. Benzene C₆H₆ is an arene characterized by sp²-hybridization of carbon atoms, cyclohexane C₆H₁₂ belongs to the class of cycloalkanes characterized by sp³-hybridization of carbon atoms.

Raman spectroscopy studies have shown that the products of electric discharge treatment of these hydrocarbons are typical amorphous carbonaceous materials. Table 5 gives data on the parameters of Raman scattering (RA) spectra of nanocarbon, which was synthesized from benzene and cyclohexane. Table 3 shows that the I_D/I_G is sufficiently large, and the size of Lₐ does not exceed 45 nm, which is characteristic of amorphous materials. It is important to note that the I_D/I_G and Lₐ values practically do not depend on the type of raw material.

### Table 3

<table>
<thead>
<tr>
<th>Hydrocarbon raw materials</th>
<th>G-band</th>
<th>D-band</th>
<th>I_D/I_G</th>
<th>Lₐ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Center, cm⁻¹</td>
<td>FWHM, cm⁻¹</td>
<td>Center, cm⁻¹</td>
<td>FWHM, cm⁻¹</td>
</tr>
<tr>
<td>Benzene C₆H₆</td>
<td>1555</td>
<td>75</td>
<td>1553</td>
<td>101</td>
</tr>
<tr>
<td>Cyclohexane C₆H₁₂</td>
<td>1555</td>
<td>60</td>
<td>1348</td>
<td>59</td>
</tr>
</tbody>
</table>

Note: Center is the position of the maximum, FWHM is the width at half height, I_D/I_G is the ratio of the integrated intensities of the D- and G-bands, Lₐ is the particle size along the graphene plane; standard band positions for graphite D – 1350 cm⁻¹, G – 1581 cm⁻¹.
atoms remain covalently unsaturated and, therefore, can form C–H bonds. This hypothesis is in good agreement with the mechanism of abiogenic formation of carbonaceous minerals discussed in [33].

Table 4

The elemental composition of the material obtained in the process of high-voltage breakdown of cyclohexane

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Purification conditions</th>
<th>Atomic ratio C:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No purification</td>
<td>1.93:1</td>
</tr>
<tr>
<td>2</td>
<td>Annealing at 400 °C</td>
<td>3:1</td>
</tr>
<tr>
<td>3</td>
<td>Annealing at 1000 °C</td>
<td>37:1</td>
</tr>
</tbody>
</table>

The final product of electrical breakdown of a mixture of hydrocarbon gases formed during the processing of liquid hydrocarbons is nanocarbon in the form of carbon 3D structures and a significant number of carbon nanotubes (Fig. 4). It is worth noting that the active synthesis of fibrous nanocarbon from a mixture of hydrocarbon gases was observed mainly on the nickel-chromium catalytic surface, while nanofilms were formed on quartz glass.

The decomposition of hydrocarbon radicals on a metal catalyst proceeds in several stages. First, dissociative adsorption occurs on the surface of the metal catalyst with the formation of methyl radical CH$_3$–Me and atomic carbon. Then, a dehydrogenation reaction (breaking of C–H bonds) of the methyl radical occurs sequentially, leading to the formation of C–Me atomic carbon on the surface of the metal. Carbon atoms on the metal surface, depending on the degree of hybridization and the type of catalyst, can go into one of two possible states – structured carbon nanoparticles or amorphous carbon. In the second case, the so-called blocking of the catalytic surface occurs, since active centers on the surface are not released in this case, and the further course of chemical transformations becomes impossible. After the effect of electric breakdowns, active radicals are deposited on the nickel-chromium catalytic surface in the form of nanotubes.

![Fig. 4. Electron microscopic images of nanocarbon obtained during the treatment of gases produced during the high-voltage breakdown of liquid cycloalkanes: a – on a nickel-chromium catalytic surface; b – quartz glass](image)

The result of high-voltage breakdown of hydrocarbons, depending on the raw material and the deposition surface, can be different types of nanocarbon (Table 5).

Table 5

Samples of nanocarbon obtained as a result of high-voltage breakdown of hydrocarbons

<table>
<thead>
<tr>
<th>No.</th>
<th>Carbon source</th>
<th>Structural state of synthesized nanocarbon</th>
<th>Micrographs of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kerosene TC–1</td>
<td>Amorphous nanocarbon</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>2</td>
<td>Gas formed by high-voltage breakdown of cyclohexane</td>
<td>Nanocarbon films</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexane</td>
<td>Fullere-like structures of nanocarbons</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>4</td>
<td>Gas formed during the high-voltage breakdown of kerosene TS-1 (substrate – nickel/chromium)</td>
<td>Carbon nanotubes+Ni</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>5</td>
<td>Hexane</td>
<td>Amorphous nanocarbon</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>6</td>
<td>Gas formed during high-voltage breakdown of ethanol (substrate – nickel/chromium)</td>
<td>Carbon nanotubes+Ni</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>7</td>
<td>Cyclohexane+ferrocene</td>
<td>Amorphous nanocarbon composite+Fe</td>
<td><img src="image" alt="Image" /></td>
</tr>
</tbody>
</table>

The prospects for the practical application of various types of nanocarbon obtained by high-voltage breakdown of hydrocarbons are interesting. On the example of various synthesis products, which are briefly described in Table 5,
the characteristics of attenuation of electromagnetic radiation by screens based on the obtained materials were investigated. The amount of attenuation was recorded as the ratio of the average powers of the waves falling on the screen and passing through it over the period.

The studied materials are radio-absorbing to one degree or another in the wave frequency range from 25 to 38 GHz (Fig. 5).

![Fig. 5. Attenuation of electromagnetic radiation by nanocarbon materials obtained by high-voltage breakdown of hydrocarbon liquids and gases](image)

The greatest attenuation of electromagnetic radiation in this frequency range was shown by the sample, the material of which was synthesized from the gas formed during high-voltage breakdowns of ethanol.

**5.3. Results of the analysis of mass yield of nanocarbon**

The method of high-voltage breakdown of hydrocarbons to obtain nanocarbon is relatively simple to implement. In [26], the basics of a continuous, waste-free electric discharge technology for obtaining nanocarbon are considered. The difference between this technology and the previously proposed electric discharge methods is the application of the flow mode, the working fluid circulates in a closed hydraulic system. The proposed technological scheme ensures the rapid removal of synthesized carbon nanostructures from the plasma region, which prevents their destruction and re-entry into the discharge zone. The technology is complemented by the devised procedure of separation, purification, and enrichment of nanocarbon materials, which are in the form of soluble and insoluble parts in the treated organic liquid.

Work [26] reports an original sequence of operations for obtaining carbon nanomaterials. This sequence includes the stage of separation of the obtained nanomaterial into various allotropic forms of carbon or composites by the methods of centrifugation, magnetic separation, filtration, and high-voltage electrophoresis. Next, the stage of further purification and enrichment of the obtained materials by chemical methods is provided. At the same time, the development of the method involves increasing its efficiency, namely the determination of modes of high-voltage breakdown of hydrocarbons, which ensure the maximum degree of processing of carbon raw materials with minimal energy consumption.

As discussed above, during the high-voltage breakdown of hydrocarbons, the destruction of molecules and splitting of hydrogen atoms occurs, while as a result of plasma-chemical reactions, carbon is formed in the solid phase in various allotropic forms: \( C_2H_6 \rightarrow nC + 0.5kH_2 \). For the theoretical calculation of the maximum mass of nanocarbon \( m \), which can be obtained as a result of the high-voltage breakdown of a carbon liquid, the molar masses of the raw material \( M=12n+k \) and the product \( M'=12n \) were calculated. Then for the mass of raw material \( m' \), the maximum possible mass of obtained carbon is \( m = \frac{m'M'}{M' + k} = \frac{m'}{12n + k} \). By relating the mass of liquid solid phase carbon obtained after breakdown treatment to the theoretically possible, the practical yield of the product is obtained.

The practical yield of nanocarbon \( (\gamma) \) was determined not only by the results of processing the liquid but also by the results of processing the resulting gas mixture. Thus, it was calculated by experimentally determining the mass of the product obtained directly from the liquid \( (m''\gamma) \) and adding the mass of the product obtained with the help of high-voltage breakdown of the gases formed \( (m''\gamma) \): \( \gamma = \gamma' + \gamma'' \). In the extreme case, when all the processed hydrocarbon liquid is converted into solid phase carbon, the practical yield is determined by expression:

\[
\gamma'' = \frac{m''\gamma}{m'} \left( 1 + \frac{k}{12n} \right) \frac{m''\gamma}{m'} .
\]

It was this expression that was used for the final calculations.

Table 6 gives the results regarding the practical yield of nanocarbon obtained under the specified conditions during the high-voltage breakdown of liquid and gaseous hydrocarbons.

<table>
<thead>
<tr>
<th>Hydrocarbon raw materials</th>
<th>Chemical formula</th>
<th>Solid nanocarbon yield from liquid, %</th>
<th>Solid nanocarbon yield from gases, %</th>
<th>Total yield of solid nanocarbon, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>1.21</td>
<td>25.0</td>
<td>26.2</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>C₅H₁₂</td>
<td>3.3</td>
<td>18.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₀</td>
<td>5.0</td>
<td>8.5</td>
<td>12.0</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>C₇H₁₄</td>
<td>6.1</td>
<td>13.9</td>
<td>20.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>12.6</td>
<td>8.8</td>
<td>21.4</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>12.2</td>
<td>7.8</td>
<td>20.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>14.4</td>
<td>15.1</td>
<td>29.5</td>
</tr>
<tr>
<td>Kerosene TS-1</td>
<td>C₇₂H₁₅</td>
<td>18.0</td>
<td>9.7</td>
<td>27.7</td>
</tr>
</tbody>
</table>

It was established that with an increase in the number of carbon atoms in the raw material molecules, other things being equal, both the weight of the carbon product...
obtained from the liquid and its practical yield increase. At the same time, for an equal number of carbon atoms, the yield is greater from raw materials whose molecules have a greater number of C–C bonds. For the investigated series, this situation corresponds to pentane-cyclopentane and hexane-cyclohexane pairs, for which a greater number of bonds reflects the presence of a cycle in the structure of cycloalkane molecules.

The results of the practical yield of nanocarbon, obtained during the high-voltage breakdown of hydrocarbons with the use of catalysts (Table 7), showed a significant increase in the yield of nanocarbon.

### Table 7

<table>
<thead>
<tr>
<th>Hydrocarbon raw materials</th>
<th>Chemical formula</th>
<th>Nanocarbon yield from liquid, %</th>
<th>Nanocarbon yield from gases without metal catalyst, %</th>
<th>Nanocarbon yield from gases (catalyst – nickel), %</th>
<th>Total nanocarbon yield (catalyst – nickel), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>12.2</td>
<td>25.0</td>
<td>51.5</td>
<td>62.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>14.4</td>
<td>15.1</td>
<td>50.3</td>
<td>64.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₉H₁₈</td>
<td>14.4</td>
<td>15.1</td>
<td>50.3</td>
<td>64.7</td>
</tr>
</tbody>
</table>

It can be assumed that an increase in the area of the catalytic surface and the choice of catalysts will lead to a further increase in the yield of nanocarbon from gaseous hydrocarbons.

### 6. Discussion of results of the nanocarbon synthesis research

Our experimental studies confirm the theoretically determined mechanisms of nanocarbon synthesis from liquid and gaseous hydrocarbons (Table 7). The results of the experiment indicate intensive formation of lower gaseous hydrocarbons as a result of destruction (rupture of C–C bonds). High-voltage breakdown in the generated gases leads to the deposition of carbon radicals on the catalytic surfaces.

The possibility of targeted synthesis of various types of nanocarbon as a result of high-voltage breakdown of hydrocarbons is shown. The key to targeted synthesis is the choice of liquid hydrocarbon – raw material. The resulting carbon material has a high adsorption activity (Table 4). The results of the study of attenuation of electromagnetic radiation by various samples of nanocarbon (Fig. 5), synthesized in the process of high-voltage breakdown of hydrocarbon liquids and the resulting gases, show the prospects of the method for obtaining composite materials for attenuation of electromagnetic radiation.

In the synthesis of nanocarbon from the gases formed, the choice of catalyst plays a key role (Fig. 4, Table 5). The yield of nanocarbon from gases exceeds the yield from liquid by 1.5 (kerosene) to 20 times (ethanol) (Table 6). This is related to the structure of the ethanol molecule – C₂H₅OH. The destruction of the molecule leads to the formation of gaseous molecules that contain C₂. And these are the components of carbon nanotubes. Kerosene molecules contain a fairly large number of carbon atoms. Their destruction and dehydrogenation lead to the synthesis of nanocarbon from liquid, the mass output of which is close to the output from the formed gases (Table 6). The use of catalysts (Table 7) leads to a several-fold increase in the yield of nanocarbon.

Determining the mechanisms of nanocarbon synthesis makes it possible to purposefully obtain the desired type of material. The synthesis of nanocarbon from the gases produced, as well as the choice of the catalyst and the increase in the area of the catalytic surface, lead to a reduction in the loss of raw materials. This allows the use of an improved method of synthesis of nanocarbon in industry.

The exfoliation method [19] makes it possible to obtain only graphene, the method of chemical reduction of carbon oxides [20] – only nanotubes, laser ablation methods [17, 18] nanotubes or nanofilms, etc. Information about the mass output of the target product is not given in the analyzed works. Instead, the method of high-voltage breakdown of hydrocarbons allows simultaneously obtaining different types of nanocarbon, which differ in the degree of hybridization of carbon atoms and the structural state depending on the raw material. The yield of the target product from gaseous hydrocarbons increases due to the activation of gases by high-voltage breakdown and the formation of active radicals interacting with the catalyst.

A feature of the proposed method is the possibility of regulating the yield of nanocarbon. For example, the use of cycloalkanes as raw materials leads to the synthesis of mainly fullerene-like structures, and ethanol to nanotubes. At the same time, the technological equipment remains unchanged. It should be noted that a necessary part of the synthesis remains the stage of separation of the obtained nanomaterial into various allotropic forms of carbon or composites by the methods of centrifugation, magnetic separation, filtration and high-voltage electrophoresis, and the stage of further purification and enrichment of the obtained materials by chemical methods.

A promising direction for advancing our studies is the synthesis of nanocarbon from raw materials, the molecules of which contain more than 7 carbon atoms. There are no natural and technical limitations in conducting such research and, in fact, in the implementation of the method of nanocarbon synthesis by high-voltage breakdown of liquid and gaseous hydrocarbons.

### 7. Conclusions

1. High-voltage breakdown of hydrocarbon liquids leads to a cascade of chemical transformations. There is a synthesis of solid nanocarbon and intensive formation of lower gaseous hydrocarbons as a result of destruction. The mechanism of synthesis of nanocarbon from liquid hydrocarbons is the processes of dehydrocyclization and polymerization. The synthesis of nanocarbon from gaseous hydrocarbons occurs as a result of dehydrogenation with the participation of metal catalysts.

2. It was established that nanocarbon obtained as a result of electric breakdown of hydrocarbons consists mainly of one type (amorphous carbon, fullerene-like carbon struc-
tures, carbon nanotubes with a diameter of 10 to 50 nm, nanofibers, or films). All obtained nanocarbon samples absorb electromagnetic radiation at a frequency from 25 to 38 GHz. The greatest attenuation of the signal is observed for samples consisting mainly of carbon nanotubes and nickel nanoparticles.

3. With an increase in the number of carbon atoms or C–C bonds in molecules of liquid hydrocarbon – raw material, other things being equal, the practical output of solid nanocarbon from liquid increases. The yield of nanocarbon from gases is many times higher than that from liquid. An increase in the area of the catalytic surface leads to an increase in the release of nanocarbon from gases.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

References