Discharge creeping along the surface in the process for producing nanomaterials

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Abstract. In this paper, we propose a new principle of assembling carbon nanoparticles in the plasma of a glow discharge creeping along the surface. In this paper, it is shown that carbon nanoparticles (fullerenes and nanotubes), as well as light fractions of oil, can be produced by means of a glow discharge on the surface of the fuel oil. Single-walled carbon nanotubes of about 10 μm in length were obtained.

1. Introduction
The organization of the interaction of a glow discharge with dielectric liquids causes certain difficulties due to the fact that the plasma of a glow discharge always deviates upward, and the liquid is always at the bottom. Therefore, there must be a force of a different nature, which exceeds the strength of Archimedes and presses the plasma to the surface of the liquid. As such a force can act as an Ampere force, which acts on the current of a glow discharge in a magnetic field. In the presence of a magnetic field of the corresponding direction, the plasma of a glow discharge can be pressed against the surface of the liquid. Since the directions of motion of electrons and ions in a glow discharge plasma are opposite, the directions of action of the Lorentz force on them will have the same direction. The discharge will run near the surface. In this paper, we studied the characteristics of such a discharge, which we called a "creeping discharge".

A new principle of assembling carbon nanoparticles in the plasma of a glowing discharge is proposed. Electrons accelerated in a strong electric field and directed by the action of the Lorentz force to the surface of a hydrocarbon feedstock are capable of breaking hydrocarbon molecules into constituent elements. Thus, after the action of high-energy electrons on molecules of liquid hydrocarbons, both atomic carbon and hydrogen appear, as well as a great variety of the results of their synthesis. Including volatile and light hydrocarbons. Going through the plasma of a glow discharge they continue to be bombarded with electrons, enriching the elemental composition of the products of decomposition of hydrocarbons. At the same time, carbon atoms in a glow discharge acquire a charge and are directed to the electrodes, where, basically, the synthesis of carbon nanomaterials occurs. The processes of the action of electric discharges on hydrocarbons were previously studied in [1-8].
2. Experiment

The schematic diagram of the experimental setup is shown in Figure 1. The installation includes: an adjustable high-voltage power supply, a block of ballast resistances, a measuring equipment, a vacuum system, a reaction chamber, an electrode system, a working fluid reservoir, magnets.

![Schematic diagram of the installation.](image)

Figure 1. Schematic diagram of the installation.

Before the beginning of the experiment, a vacuum is created in the flask by means of a pump to a value of 2 Torr. Then a voltage is applied to the electrodes, which is increased until the discharge appears. The magnetic field presses the discharge to the surface of the fuel oil, and the discharge, as it were, spreads on the surface of the fuel oil. In the course of the experiment, the black oil in the tank begins to intensively transform into a gas vapor phase of white color. That is, electrons accelerated in a strong electric field acquire sufficient energy to break up the hydrocarbon atoms into their constituent elements. Thus, after the action of high-energy electrons, molecules on liquid hydrocarbons appear as atomic carbon, hydrogen, and also a great variety of the results of their synthesis. Including volatile and light hydrocarbons. Going through the plasma of a glow discharge they continue to be bombarded with electrons, enriching the elemental composition of the products of decomposition of hydrocarbons. At the same time, carbon atoms in a glow discharge acquire a charge and are directed to the electrodes, where, and mainly, the synthesis of carbon nanomaterials occurs. Due to the conversion of fuel oil during the experiment into the gas-vapor phase, the pressure in the flask gradually increases. On the rate of increase in pressure, one can judge the intensity of the process of conversion of fuel oil into light and volatile fractions. For this, it is necessary to know the composition of the gaseous phase, the increment in pressure, and the mass of carbon nanomaterials formed on the electrodes. It is also necessary to weigh the fuel oil before and after the experiment. With a discharge power of the order of 150 W for 10 minutes, the pressure in the chamber rises to 100 Torr.

The glow discharge arising between the electrodes, judging from the current-voltage characteristic, is a hindered glow discharge. The current-voltage characteristic of the discharge is shown in Figure 2. It is seen that even at sufficiently high currents the discharge remains volumetric with a voltage of the order of 800 V. This is most likely due to the action of the magnetic field on the discharge. The Lorentz force, which acts on the discharge electrons, additionally expands the current region and does not allow the discharge to be contrapulated.

For a visual demonstration of the "creeping discharge on the surface," Figure 3 shows a photograph. In this case, a ceramic substrate was used as a dielectric, by which the discharge "floats".
In the case of the interaction of a "creeping discharge" with hydrocarbon raw material, the color of the discharge became yellow-orange.

3. Study of samples of soot formed
During the experiment with hydrocarbon raw materials, carbon black formed on the electrodes, in which, as further studies have shown, large numbers of fullerenes are contained. To extract fullerenes from soot, the Soxhlet apparatus was used. The obtained extract was studied by infrared spectroscopy.

It is known that, the lower the symmetry of fullerene, the more absorption frequencies we can observe. Because of the high symmetry of the C60 molecule, only 4 absorption peaks appear in the IR spectrum at 1429, 1183, 577 and 528 cm\(^{-1}\) and a width varying in the range 3-10 cm\(^{-1}\). The lower the symmetry of fullerene, the greater the absorption frequencies, respectively, in the C70 molecule, 11: 1460, 1430, 1414, 1134, 795, 674, 642, 578, 565, 533 and 458 cm\(^{-1}\) are observed.

The IR absorption spectra of higher fullerenes are more complex than those of C60 and C70 molecules. The absorption bands of the C76 molecule correspond to wavelengths of 230, 286, 328, 350, 378, 405, 455, 528, 564, 574, 642, 709, 768 nm. In the absorption spectrum of the C84 molecule, the bands 280, 320, 380, 393, are singled out. 476, 566, 616, 668, 760 and 912 nm.

With this process, the discharge power is about 300 watts.

4. Results
A new type of discharge with an increasing volt-ampere characteristic, which is called a "creep-discharge discharge," is studied. Surface discharging on the surface is ideal for organizing the
interaction of a discharge with a dielectric surface. As an example, the interactions of such a discharge with a ceramic surface and a fuel oil surface have been studied. It follows from the conducted researches that such a discharge is suitable for creating technologies for the synthesis of carbon nanoparticles, gasification of coal, as well as for deepening the processing of fuel oil and oil sludge. The target products of processing heavy hydrocarbons are volatile and light oil fractions, as well as carbon nanomaterials.

References
[1] Timerkaev B A, Sofronitskiy A O and Andreeva A A. Carbon nanotubes formation in the decomposition of heavy hydrocarbons creeping along the surface of the glow discharge. 2016 Journal of Physics: Conference Series, Volume 669, conference 1, 012062. doi:10.1088/1742-6596/669/1/012062
[2] Timerkaev B A, Andreeva A A and Sofronitskiy A O. Discharge creeping along the surface in the process of cleaning and strengthening of the materials surface. 2017 Journal of Physics: Conference Series, Volume 789, conference 1, 012063. doi:10.1088/1742-6596/789/1/012063
[3] Sadikov K G, Sofronitskiy A O and Dautov I G. Functional plasma sprayed coatings on magnesium ceramic substrates. 2017 Journal of Physics: Conference Series, Volume 789, conference 1, 012043. doi:10.1088/1742-6596/789/1/012043
[4] Timerkaev B A, Ahmetov M M, Zalyaliev B R, Petrova O A and Israfilov D I. Longitudinal distribution of electrical parameters in normal glow discharge. 2014 Journal of Physics: Conference Series, Volume 567, conference 1, 012036. doi:10.1088/1742-6596/567/1/012036
[5] Saifutdinov A, Timerkaev B, Zalyaliev B. Control of the glow discharge parameters at low pressures by means of a transverse supersonic gas flow. 2016 High Temperature 54 669
[6] Galeev I G and Asadullin T Ya. Obtaining fullerene-containing soot during combustion of gaseous hydrocarbons in an external electric field. 2016 Journal of Physics: Conference Series, Volume 669, conference 1, 012016. doi:10.1088/1742-6596/669/1/012016
[7] Galeev I G and Asadullin T Ya. The magnetic field application for the gas discharge plasma control in processes of surface coating and modification. 2017 Journal of Physics: Conference Series, Volume 789, conference 1, 012003. doi:10.1088/1742-6596/789/1/012003
[8] Galeev I G and Asadullin T Ya. Improving of stability of the volumetric glow discharge in the gas flow. 2017 Journal of Physics: Conference Series, Volume 789, conference 1, 012012. doi:10.1088/1742-6596/669/1/012012