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Carbon nanotubes formation in the decomposition of heavy hydrocarbons creeping along the surface of the glow discharge

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Abstract. The possibility of heavy hydrocarbons decomposition in the plasma of the creeping glow discharge in a magnetic field is investigated. An electron microscopic analysis of carbon deposit on the electrodes and the walls of the discharge chamber, and gas chromatographic analysis formed in the course of the experiment is carried out. The grown carbon nanotubes have a length of about 6,17µm and a diameter of about 18nm.

1. Introduction
A high degree of disequilibrium is established in the glow discharge caused by a large detachment of the electron temperature from the gas one. Despite the fact that the temperature of the electrons in the glow discharge reaches many hundred thousands of degrees, the discharge itself is cold, and the gas temperature is only slightly different from ambient. In other words, in the glow discharge the electric field energy is transferred mainly to the electrons, which in elastic collisions with neutral particles do not practically lose their energy. Inelastic collisions, depending on the situation, can lead to the excitation of atoms or either ionization or to bonds rupture in the molecules. For the conversion of new hydrocarbon the bonds break between atoms is of particular attraction. The attractiveness of gas discharges for new compounds was confirmed in [1-4]. Modern hydrodynamic theory of such discharges is described in [5-6]. It is easy to provide selectivity of the reaction in the glow discharge by changing the reduced electric field. In this case there is no heating of the hydrocarbon mixture unlike thermal cracking. However, the organization of heavy hydrocarbons interaction with a glow discharge is not an easy task, as the glow discharge burns in a rarefied gas, but heavy hydrocarbons are in a liquid phase. The glow discharge arranged near the liquid surface practically does not interact with this fluid. In order to ensure the best possible interaction of the glow discharge with liquid hydrocarbons we decided to use a magnetic field.

2. A theoretical basis
The behavior of charged particles in the electric and magnetic fields is studied in details. As is known, an electric current in the gas is caused by the electrons and ions drift. Since opposite charged particles move in opposite directions in the electric field then the Lorentz force is routed in the same direction

for all of them. By selecting the appropriate direction of the electric and magnetic fields, the discharge side of the deflection surface of the liquid hydrocarbons can be achieved.

Let us analyze the physical processes occurring in the glow discharge in a magnetic field near the surface of the liquid hydrocarbons. First, we estimate the mean free path of electrons by the formula $\lambda = 1/\sigma n$, where σ - the cross section area, $n = p/kT$ - the concentration of particles in the gas, p - pressure, T - the temperature of the gas, k - Boltzmann constant. For estimations let us assume that the pressure is 10 Torr, the temperature is 500 K, $\sigma = 7 \cdot 10^{-20}$ m^2. Then the mean free path of electrons would be 0.074 mm and the potential drop in the positive column at this pressure corresponds to 10 V/mm. Thus, the mean free path of electron energy will be 0.74 eV, and the average velocity of the electron on the mean free path (i.e. the speed of the drift in the direction of the electric field) will be equal to $0.16 \cdot 10^6$ m/s. At such speeds, the Larmor motion is of 1.5 microns. Therefore, if an electron in such magnetic fields begin its movement under the influence of an electric field, it will drift in the direction perpendicular to both the electric and magnetic fields. At the same time in such magnetic fields Larmor radius of the ions would be of 1 mm, and the ions in the mean free path will not have time to feel the effect of the magnetic field. This means that the electrons will carry out this difficult drift toward the surface of the liquid, and will also pull the plasma ions there. The discharge will be pressed against the liquid surface, i.e. will creep along the surface of the liquid. Therefore, this type of discharge can be called "creeping" discharge. The electrons of the discharge will effectively attack the surface of the liquid decomposing molecules of liquid hydrocarbons into lighter fractions. Due to the interaction with the plasma heavy hydrocarbon molecules can break off the liquid surface which will also be attacked by plasma electrons. Thus, creeping discharge is ideal for the interaction of the glow discharge with liquid hydrocarbons.

3. Experiment

For the experimental investigation of the glow discharge characteristics in the vicinity of the surface of the liquid hydrocarbon raw material in a magnetic field an experimental setup has been developed and constructed which consists of a vacuum system, electric power supply, the reaction chamber, as well as measuring and control instruments. Schematic diagram of the experimental setup is shown in Figure1.

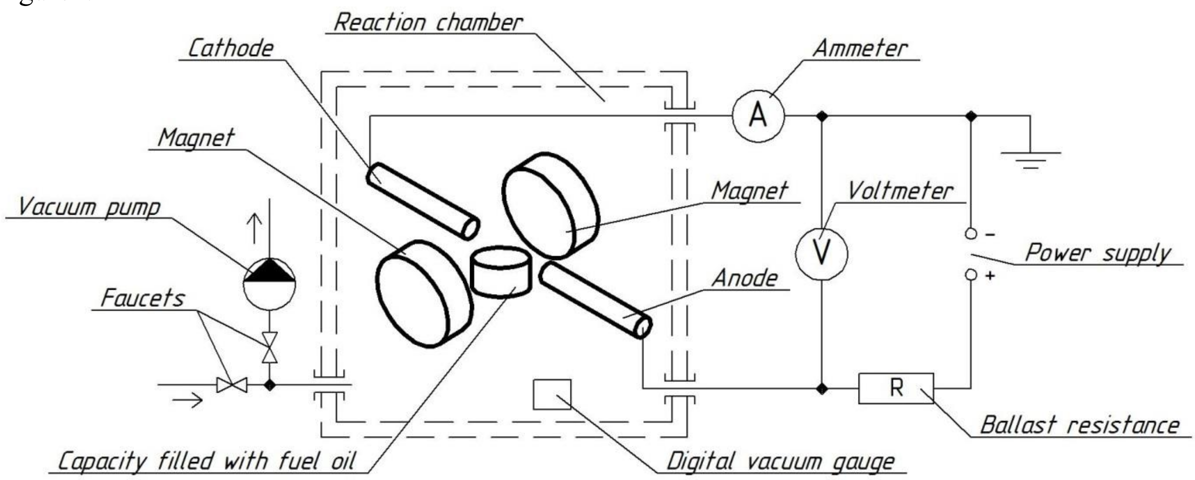

Figure 1. Schematic diagram of the experimental setup.

After loading all the necessary elements in the reaction chamber, the air is evacuated to a pressure of 1 Torr and is filled with argon to a pressure of 30 Torr. A glow discharge is energized and ignited on the electrodes. Gradually, adjusting the voltage, the current and the magnetic field the discharge with a creeping form is being achieved. During the experiment, the fuel oil in the tank turns into white gas-steam phase. This gas-vapor mixture is a product of decomposition of heavy hydrocarbons and a gaseous hydrocarbons and light oil. As chromatographic analysis shows, in the mixture of the gas-vapor phase of fuel oil decomposition products there are hydrogen, acetylene, methane, ethane, propane, butane, as well as a whole bunch of gasoline range. When the discharge burns, the carbon black is gradually formed on the electrodes. Whereas a portion of carbon atoms is directed to a cathode, and a part to the anode. The structure of the cathode carbon black differs from the carbon black structure on the anode.

4. Investigation of carbon black formed on the electrodes

Investigation of carbon black formed on the electrodes was carried out by the electron microscope AURIGA CARL ZEISS. In the presented electron micrographs of carbon black from the cathode (Figure 2-3) an ideal carbon nanotube length of about 6,17 μm and a diameter of about 18nm are seen.

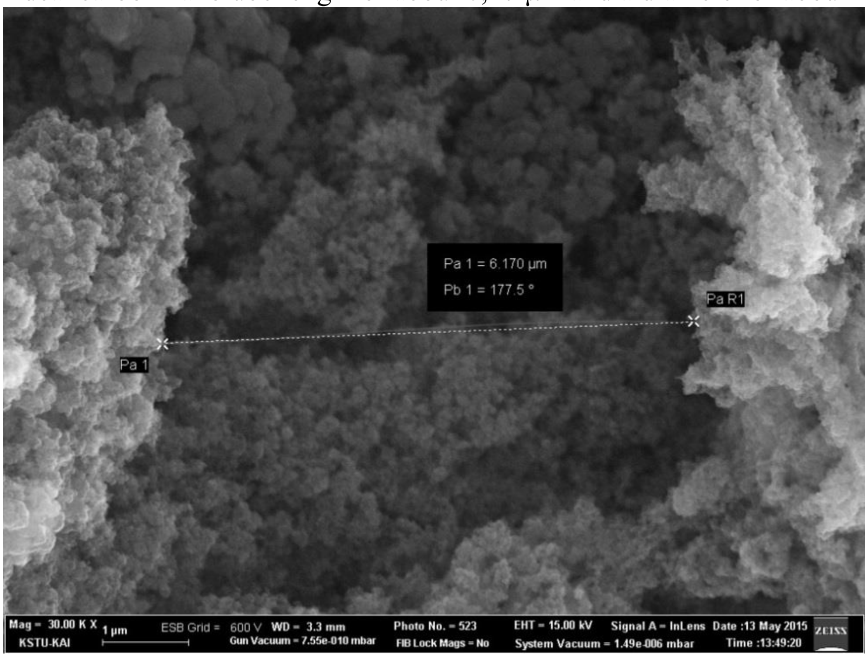

Figure 2. The length of the nanotubes 6,17μm.

Figure 3. The diameter of the nanotubes about 18nm.

5. Conclusion

The From the research it follows that creeping glow discharge allows to make the deepening of fuel oil, the waste oil refining and oil sludge up to 100 percent. For the processing of 60 grams of fuel oil it requires about 0.2 kilowatt-hours of electricity (it is about 1 gram of fuel oil per minute when the power is 200 W). The target products of processing of heavy hydrocarbons are volatile and light oil fractions, as well as carbon nanotubes and a wide range of fullerene.

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