Synthesis of carbon nanotubes in arc plasma from liquid hydrocarbons

B A Timerkaev¹, G R Ganieva²
¹General Physics Department, Kazan National Research Technical University – KAI, 420111, K. Marx St., 10, Kazan, Russia
²Kazan Federal University, 420008, 18 Kremlyovskaya Str., Kazan, Russian Federation

btimerkaev@gmail.com

Abstract. In the presented research the experimental setup is proposed and the new method for the multilayer carbon nanotubes synthesis from liquid hydrocarbons is described. The systematic studies of the drowned electric arc interaction in the hydrocarbon feedstock with hydrocarbon molecules were carried out to obtain atomic carbon. The resultant product in the carbon black form was analysed through the electron microscope. It is shown that much carbonaceous deposits on the cathode are contained in carbon nanotubes.

Due to the rapid nanotechnology development, the search for ways to produce various shapes of carbon nanostructures for nowadays is the urgent task. The search for new methods of growing cheap carbon nanotubes in simple and reliable ways is relevant for researchers and manufacturers as well. Among the countless methods of obtaining carbon nanotubes by synthesis methods, it is particularly meaningful to single out arc synthesis, laser ablation, chemical vapour deposition and electrolytic synthesis [1-6].

In this paper, we propose the technique for obtaining carbon nanotubes from a heavy hydrocarbon feedstock using an arc discharge. Studies in this direction were carried out in the following works [7-12], in which certain results on the production of single-walled carbon nanotubes were achieved. The presented study is a continuation of these studies and focuses on the multilayer nanotubes production, which are very valuable as the structural materials elements for many industries. In order to study the drowned arc discharge plasma effects on heavy hydrocarbon raw materials the experimental setup was created, which includes a ceramic vessel with hydrocarbon feed, connecting wires, a high-current electrical source power, and measuring instruments (Figure 1).

Before the experiment begins, the ceramic container 1 is placed in a fume hood. Voltage is applied to the electrodes 2, which are located at some depth in the fuel oil, is consumed from the power source 4. As for the electrodes material, copper was used with a 5 mm diameter. The arc is ignited by direct electrodes contact, which after the arc ignition are moved at a certain distance, so that the arc does not fade. At the same time, the steady arc discharge burning occurs. The current and voltage are measured using an ammeter 5 and a voltmeter 6, respectively.

Under the electric arc influence on hydrocarbon raw materials, the complex hydrocarbon molecules decomposed into simple fractions. Owing to the high arc temperature, the pressure, which is able to support the plasma region with in the hydrocarbonaceous raw material is created. The area edges are
in contact with fuel oil. Subsequently the high temperature, high-boiling complex hydrocarbons fractions are in the plasma region and under the fast electrons action then high-energy ions are broken into small fractions.

![Figure 1. The installation scheme. 1 – ceramic container with hydrocarbon feedstock; 2 – copper electrodes; 3 – connecting wires; 4 – power supply; 5 – ammeter; 6 – the voltmeter; 7 – ballast resistance; 8 – standpoint; 9 – key.](image1)

When an electric arc discharge in the hydrocarbon fluid at a certain depth is created, the electric arc burns in hydrocarbon steam evaporated in the discharge region from the inner surface of the gas-vapour bubble. In the electric arc, drowned in the fuel oil, the pressure is set, which corresponds to the arc immersion depth. When the arc burns in fuel oil, the electric arc channel will be filled with hydrocarbons’ gases and steams of very different fractions, among which are numerous gasoline and other light fractions, which partly dissolve in the fuel oil. That fuel oil part that directly contacts the arc will be in the boiling state, supplying various oil fractions to the discharge area. Surface boiling and relatively low fuel oil thermal conductivity prevent the fuel oil main mass and its coking from overheating. Hydrocarbon molecules, being in the electric discharge region, will be opposed by fast electrons and discharge ions, as well as by activated atoms and molecules of hydrocarbon gases. Due to the high temperature, the formed gases and steams leave the discharge area quickly.

As the experiment’s result, the carbon build-up on the copper electrodes is formed. In comparison with the anode, a greater soot growth on the cathode is observed. The carbon growths formed during the electrodes experiment were analysed by means of an electron-scanning microscope, the images of which are presented in the Figures 2.1-2.3. Electron microscopic soot analysis showed that the deposits contain much carbon nanotubes (fibres) of different length and structure. Nanostructures formed in a chaotic order in the tightly intertwined threads form.

![Figure 2.1. Electron microscopic carbon deposits image on the anode. Magnification 70000x.](image2)

![Figure 2.2. Electron microscopic carbon deposits image on the anode. Magnification 125000x.](image3)
Since nanotubes are twisted together, it can be assumed that they have a complex structure. In Figure 2.3, we can see multi-layered nanotubes of the “Russian matryoshka” type. The nanotube is 44.04 nm in diameter, a nanotube similar to it, which is inside, is 18.46 nm in diameter.

![Figure 2.3. Electron microscopic carbon deposits image on the anode. Magnification 260000x.](image)

Consequently, the carbon nanotubes production from liquid hydrocarbons makes it possible to obtain nanostructures in a good amount. The average single-walled nanotubes diameter ranges from 11.81 nm to 18.46 nm, the multi-layered diameter is from 25.72 nm to 111.2 nm. The average nanotubes length is of several micrometres. It is surprising to increase the carbon nanotubes diameter to 100 nm, while the initial single-walled carbon nanotubes diameters are 10-20 nm. Thus, the method for growing sufficiently thick multi-layered nanotubes has been found.

References
[1] Slovetskii DI Plasma-chemical processing of hydrocarbons: current status and prospects Proceedings of The 3rd international Symposium on theoretical and applied plasma chemistry 2002 vol 1 pp 55-58
[2] Foster L. Nanotechnology. Science, innovation and opportunities / Moscow: Technosphere. 2008 353 P
[3] Peshnev B V Filimonov A S AbuD O Nikolaev A I Technology of production of carbon-based materials from the electrocracking paste. Moscow 2013 Proceedings of Conference 35 P
[4] Rakov E.G. Methods for obtaining carbon nanotubes / Uspekhi Khimii. 1999 pp 41-54
[5] Timerkaev B.A., Galeev I.G., Ziganshin D.I., Gismatullin N.K., Takhautdinov R. Sh., Mukhamedzyanov R.B. The method of producing soot containing fullerenes and nanotubes from gaseous hydrocarbon feedstock. (11) 2 531 291 RU, 20 10 2014
[6] Starostin V.V. Methods and materials of nanotechnology / Publishing: Binom: Laboratory of Knowledge. 432 P
[7] Ganieva G R Timerkaev B A Plasmachemical decomposition of heavy hydrocarbons Petrochemicals Publishing(MIAK "Nauka / Interperiodica") 2016 vol 9 pp 1-5
[8] Timerkaev B.A., G.R. Ganieva, I. G. Galeev, N. K. Gismatullin, D. I. Ziganshin. Decomposition of heavy hydrocarbons in a recessed arc. Bulletin of KSTU. A.N. Tupolev, №4, 2012 pp 184-188
[9] Ganieva G R Timerkaev B A Plasmachemical effect of recessed micro-arc discharge on liquid hydrocarbons / VI All-Russian scientific-technical conference "Low-temperature plasma in the processes of deposition of functional coatings" Kazan 2014 pp 196-199
[10] Ganieva G R Timerkaev B A Electrical microdischarges in liquids and prospects of their
application in plasma chemistry May-June 2014 Journal of Engineering Physics and Thermophysics Minsk vol 87 №3 pp 677-681

[11] Ganieva GR Timerkaev BA Plasmachemical processing of raw liquid hydrocarbons by sunk microarc- discharge IOP Conference Series: Materials Science and Engineering 012009 2015 vol 86

[12] Ganieva G R Timerkaev BA Decomposition of heavy hydrocarbons in argon arc with the sunken electrodes VII Conference on Low Temperature Plasma in the Processes of Functional Coating Preparation IOP Publishing Journal of Physics: Conference Series 669 2016 012061