Obtaining nano-disperse soot from orthoxylene by the high-voltage AC plasma torch

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Abstract. The article deals with the synthesis of fullerene-containing soot using high-voltage AC plasma torch. The plasma torch consists of three electric arc channels with three graphite rod electrodes. Orthoxylene vapors are fed into the arc zone of the plasma torch, and argon is used as a protective gas. In the plasma torch orthoxylene decomposes under the action of an electric arc. The produced soot contains 5.4\% $C_{60}$ fullerene and 1.6\% $C_{70}$ fullerene.

1. Introduction
Plasma torches are used for a wide range of chemical applications. They can be used for the processing of toxic compounds [1], gasification of solid carbonaceous substances to produce synthesis gas [2], natural gas reforming [3], production of oxide materials [4], as well as the production of carbon materials [5]. One of the urgent tasks of plasma chemistry is fullerenes obtaining. Fullerenes have a large number of unique properties. Currently, the derivatives are being investigated in medicine [6] and agro-chemistry [7]. The main method of obtaining fullerenes is the evaporation of graphite electrodes by the action of an electric arc [8].

On the installation [9] the plasma formed by arc discharge by evaporation of graphite rods in the helium atmosphere, that is, the unit operation is based on a modified Kretschmer method. A distinctive feature of the installation compared to most of the devices used is the use of AC arc. The symmetrical arrangement of the electrodes allows to achieve up to 100\% transformation of the electrode material into fullerene soot. The chamber in which the synthesis takes place is cooled by water, and two pairs of graphite electrodes have an automatic feed system (stepper motor connected to the control unit). The control unit regulates the flow of the rods so that the arc current remains constant (with an accuracy of 2–3\%). The power of each pair of electrodes is 25 kW. At a pressure of 120 kPa, the content of all fullerenes was 12 wt.% of total soot mass. With increasing pressure, the content of fullerenes decreased and reached 7.5 wt.% at a pressure of 360 kPa.
With the use of resistive heating and an electric arc, the installation works to increase the efficiency of obtaining fullerenes [10]. The experimental setup consists of a water-cooled chamber and two 6 mm electrodes. One of the electrodes was made movable and provided a constant distance between the electrodes during the arc discharge. The operating pressure of the plant is 200 Torr in helium atmosphere, and the operating current is 150 A. In addition, one of the electrodes was heated resistively at 4.5, 7.5 and 11 V during the start and combustion of the arc discharge. However, when using resistive heating, the fullerene content in soot decreased from 6 to 2.8%, but the total soot yield increased.

The electric arc reactor used to produce fullerene soot was described in [11]. This reactor can stabilize arc parameters (current, interelectrode distance, electrode feed rate) and keep them at a constant level during electrode evaporation. Composite graphite rods doped with potassium carbonate were used to form fullerene-containing soot. The use of potassium is explained by the low ionization potential in the carbon-containing plasma, which contributes to more efficient formation of large carbon clusters. At the same time, with an increase in potassium content, the yield of higher fullerenes increases from 1 to 12 wt.%. It was also found that the optimal partial pressure of helium is $2 \times 10^4$ Pa, also that fullerenes are not formed if the distance from the arc to the cooled surface is less than 1 cm and the yield of fullerenes is maximum when this distance is 4 cm).

2. Experimental part

To determine the specific surface area and porosity of highly dispersed solids or systems with developed porosity are used adsorption isotherms. The most often for this applies the Brunauer–Emmett–Teller (BET) theory [12].

According to the BET equation, adsorption ($a$) of a substance on the surface is related to the vapour pressure ($p$) of the same substance above the surface:

$$a = \frac{a_m c \left( \frac{p}{p_0} \right)}{1 + (C-1) \left( \frac{p}{p_0} \right) \left[ 1 - \left( \frac{p}{p_0} \right) \right]^C}$$

where $a$ – adsorption value, mole·m$^{-2}$; $a_m$ – adsorption value at full monolayer filling, mole·m$^{-2}$; $p/p_0$ – ratio pressure in the system to the condensation pressure; $C$ – the ratio of the adsorption equilibrium constants in the first layer and the condensation constant.

Micromeritics ASAP 2020 was used to analyze the surface area and porosity of solid materials. Technical characteristics of the system are presented in table 1.

| Parameter                                      | Value                  |
|------------------------------------------------|------------------------|
| Specific surface area measurement range (m$^2$·g$^{-1}$) | from 0.01 to 4000     |
| Pore diameter measuring range (nm)             | from 2 to 100          |
| Specific pore volume measuring range (cm$^3$·g$^{-1}$) | from $2 \times 10^{-4}$ to 2.00 |

Studies of soot and extracted product samples were carried out on a TESCAN VEGA3 SBH EMS at the engineering centre in SPSIT (table 2).
Table 2. Specifications of the EMS TESCAN VEGA3 SBH.

| Parameter                      | Value                                      |
|--------------------------------|--------------------------------------------|
| Resolution (nm)                | 3 at 30 (kV)                               |
|                                | 8 at 3 (kV)                                |
| Magnification                  | from 4.5 to 1 000 000                       |
| Electronic gun                 | tungsten heated cathode with thermionic     |
| emission                       |                                            |
| The working value of the vacuum in the chamber (Pa) | less 9·10⁻³ |
| Image size (pixels)            | from 512×512 to 8192×8192                  |

IR-spectra were recorded on a spectrometer Shimadzu IRTracer-100, provided by the engineering centre SPSIT (table 3).

Table 3. Main characteristics ShimadzuIRTracer-100.

| Parameter                      | Value                                      |
|--------------------------------|--------------------------------------------|
| Interferometer                 | Michelson type with a dip angle of 300     |
| Spectral range                 | (7800–350 cm⁻¹; 12500–240 cm⁻¹)            |
| Resolution                     | 0.25; 0.5; 1; 2; 4; 8; 16 cm⁻¹ (middle and far infrared range) |
|                                | 2; 4; 8; 16 cm⁻¹ (near infrared range)     |
| Ratio signal/noise             | 60000: 1 and higher (4 cm⁻¹, 1 min., 2200 cm⁻¹, peak to peak) |

A spectrophotometer from the SPbSU analytical laboratory was used, the main technical characteristics of which are given in table 4.

Table 4. The main characteristics of the spectrophotometer.

| Parameter                      | Value                                      |
|--------------------------------|--------------------------------------------|
| Spectral range (nm)            | 190–1100                                   |
| Wavelength setting accuracy (nm)| ± 0.5                                      |
| Optical density range          | -0.3–3.0 A                                 |
| Optical layout                 | dual beam                                  |

Determination of the qualitative composition of the ortho-xylene extract was carried out on a MALDI-TOF Shimadzu Biotech Axima Resonance mass spectrometer of the St. Petersburg State University Resource Center (table 5).

Table 5. Technical characteristics of a mass spectrometer MALDI-TOF Shimadzu Biotech Axima Resonance.

| Parameter                      | Value                                      |
|--------------------------------|--------------------------------------------|
| Range (m/z⁻¹)                  | 1–120000                                   |
| Mass accuracy (ppm)            | Better 3                                   |
| Resolution (FWHM)              | Better 8000                                |

3. Electric arc pyrolysis of hydrocarbons

The experimental setup consists of the following parts: plasma torch, power supply system, cooling system, gas supply system, a diagnostic chamber for studying the process. The plasma torch is made of steel in the form of two perpendicularly intersecting cylinders (figures 1–2). The system is equipped
with sensors for monitoring gas flow and electric current parameters. The electrode system of the plasma torch consists of three interchangeable rod graphite electrodes with fluoroplastic insulators at the base (figure 3). A protective gas (argon) is supplied to the bases of the electrodes; a mixture of plasma gas with ortho-xylene vapour is supplied at some distance from the ends of the electrodes. Electrodes are located at three ends of the plasma torch case. The water cooler is installed at the outlet of the electric arc channel.

![Figure 1. Plasma Torch.](image1)

![Figure 2. Appearance of installation (without a refrigerator).](image2)

![Figure 3. Experimental setup. 1 – electric arc channel; 2 – electrode; 3 – PTFE insulator; 4 – electric arc trajectories; 5 – water cooler.](image3)

In all experiments, argon was fed in the area of the electrodes with a total mass consumption \( G_{Ar/e} = 3 \, \text{g} \cdot \text{s}^{-1} \). Also, argon was supplied in the arc combustion zone with a consumption of \( G_{Ar/b} = 0.5 \, \text{g} \cdot \text{s}^{-1} \) (table 6).
Table 6. Experimental conditions

| №  | Electrode | Hydrocarbon | Consumption of hydrocarbon (g·s⁻¹) | Uab (V) | Ubc (V) | Uac (V) | I (A) | P (kW) |
|----|-----------|-------------|------------------------------------|--------|--------|--------|-------|--------|
| 1  | Graphite  | orthoxylene | 0.05                               | 132    | 144    | 187    | 31.7  | 7.4    |

4. Results and discussion

For soot single point method and the BET method determined the specific surface area. According to the single point method, this characteristic of soot is 58.7 m²·g⁻¹, and according to the BET method, 60.4 m²·g⁻¹. The total pore volume ($P/P_0 = 0.98$) equal to 0.253 cm³·g⁻¹ was calculated. The average BET pore width is 16.7 nm. The total volume and total area in the pores of 0.183 cm³·g⁻¹ and 37.760 m²·g⁻¹, respectively, were calculated using the DFT method. Figure 4 shows the nitrogen adsorption isotherm of a soot sample.

![Figure 4. Isotherm of adsorption of fullerene-containing soot.](image)

Micrographs of extract from soot were obtained (figure 5) and elemental analysis was performed by the EDX method.

![Figure 5. Micrographs of soot extract (magnification ×17000 and ×102000, respectively).](image)
EDX shows the following elemental composition of the extract: 96.4% carbon and 3.6% oxygen (absorbed and surface groups).

The IR-spectrum of the extract from soot (Figure 6) allows us to conclude that there are various polycyclic aromatic hydrocarbons (naphthalene, phenanthrene, fluorene, benzpyrene etc.).

![IR spectrum of the extract from sample 5. C_{Ar} – aromatic carbon ring; \nu – valence, \delta – deformation (ip – planar, oop – out-of-plane, \gamma – skeletal vibrations).](image)

**Figure 6.** IR spectrum of the extract from sample 5. C_{Ar} – aromatic carbon ring; \nu – valence, \delta – deformation (ip – planar, oop – out-of-plane, \gamma – skeletal vibrations).

Soot samples were subjected to extraction with o-xylene (magnetic stirring/ultrasonic bath at room temperature for one hour). The spectrum is shown in figure 7.

![Electronic spectrum of extract from soot (dilution 100x). Marked peak related to fullerene C_{60}.](image)

**Figure 7.** Electronic spectrum of extract from soot (dilution 100x). Marked peak related to fullerene C_{60}.

MALDI-TOF the mass spectrum of the extract from soot No. 5 is shown in figure 8.
Figure 8. Mass spectrum of the extract from the soot sample.

The mass spectrum shows the presence of fullerene $C_{60}$ (intense peaks 720 and 721 m/z from $[C_{60}]$, as well as general peaks (720 – 12·2x) m/z from $[C_{60} –2x]$). There is a group of peaks 398 and 375 m/z, corresponding to polycyclic aromatic hydrocarbon – avalon $C_{32}H_{14}$. Peaks 292–298 m/z may refer to poly methyl derivative of tetragen a (benzanthracene) or similar compounds. A small group 512 amu, stands out, presumably, from the tetramer of naphthalene $[C_{40}H_{32}]$.

According to electron spectroscopy, the content of fullerenes in soot was estimated. The following formulas were used to estimate the concentration of fullerenes [13] (mg/l):

$$C(C_{60}) = 13.1 \cdot (D_{335.7} – 1.81 \cdot D_{472.0}),$$

$$C(C_{70}) = 42.5 \cdot (D_{472.0} – 0.0081 \cdot D_{335.7}).$$

Comparative results are presented in table 7.

### Table 7. Processing of electronic spectra of extracts for fullerene content.

| № | $D_{335.7}$ | $D_{472}$ | $C(C_{60})$ (mg/l) | $C(C_{70})$ (mg/l) | Dilution | $\omega(C_{60})$ (%) | $\omega(C_{70})$ (%) | Ratio $C_{60}$/$C_{70}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.49 | 0.04 | 5.42 | 1.62 | 100 | 5.42 | 1.62 | 3.36 |

5. Conclusions
Nanocarbon material with submicron particle sizes was obtained by the method of plasma oxygen-free pyrolysis of hydrocarbons (orthoxylene). The produced soot contained particles of graphite (about 60%) and amorphous carbon (33%), as well as light fullerenes in amounts up to 7%. It can be assumed that this method can be applied as a cheap and effective method for the synthesis of fullerenes.

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