

## HEAT AND MASS TRANSFER IN DISPERSED MEDIA

### PLASMA PYROLYTIC SYNTHESIS OF CARBON NANOSTRUCTURES IN A MIXTURE OF NITROGEN AND PROPANE-BUTANE

A. F. Bubljevskii, A. A. Galinovskii,  
A. V. Gorbunov, S. A. Zhdanok,  
L. I. Sharakhovskii, and A. L. Mossé

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*The results of experimental investigation of the parameters of gaseous-phase synthesis of carbon nanoparticles in atmospheric-pressure arc reactors operating with mixtures of nitrogen and hydrocarbon gases have been given. It has been revealed that, under the conditions studied, arc plasma synthesis makes it possible to synthesize highly dispersed carbon products with a content of fullerene phases of up to 15 wt.% and nanotubes to 3–5 wt.%.*

The basic method of synthesis of carbon nanotubes discovered in 1991 was the arc method, which is based on the evaporation of graphite in burning of a d.c. electric arc between carbon electrodes in the flow of helium or another inert gas. Subsequently this method gave way to a more productive laser-thermal method of evaporation of the graphite target (containing a catalyst, if need be) by a high-power scanning laser beam in a furnace with a temperature of 950–1200 K [1, 2].

However, increasing worldwide attention has been paid recently to the pyrolytic synthesis of nanotubes from gaseous hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_6\text{H}_6$ , and others) and from CO; preference is given to the catalytic variants of synthesis, which enable one to produce not only multilayer nanotubes but also single-layer ones with a fairly high yield. The synthesis of nanotubes is often accompanied by the formation of other forms of carbon: fullerenes, nanofibers, polyhedral particles, and amorphous soot, which determines the necessity of separating the nanotubes subsequently from the mixture. The pyrolysis of hydrocarbons in atmospheric-pressure arc plasmajet reactors can be an organic development of this method [3]. According to our evaluations, the plasma method may turn out to be the most promising, as far as both scaling for a high semicommercial output (up to 1–2 kg of carbon nanomaterials per hour) and the purity of the materials produced are concerned.

From certain physicochemical considerations, it is expedient to subdivide investigations of the plasma synthesis of carbon nanomaterials into two trends: 1) a purely pyrolytic process with the endothermic dissociation of a hydrocarbon raw material in an oxygen-free plasma based on inert gases or nitrogen; 2) a combined pyrolytic-oxidation process with an appreciable contribution of the exothermic reactions of hydrocarbons with the oxygen-containing gas of a plasma-generating mixture to the thermal balance. The first trend is characterized by the formation of such intermediate products, precursors to multiwalled carbon nanomaterials and fullerenes, as unsaturated hydrocarbons of the  $\text{C}_2\text{H}_2$  type, whereas the second trend is characterized by the presence of CO molecules — precursors to the formation of single-walled carbon nanomaterials — in the reaction zone.

Below, we give results of investigations of a pure pyrolysis with the use of nitrogen and propane-butane as plasma-generating gases. Nitrogen corresponded to the standard data of the supplier company and contained no less than 99 vol.% of the base material. Preliminary determination of the composition of propane-butane yielded the following concentrations (vol.%): methane  $\text{CH}_4$  — 0.6, propane  $\text{C}_3\text{H}_8$  — 72.5, *n*-butane  $\text{C}_4\text{H}_{10}$  — 12.2, isobutane  $\text{C}_4\text{H}_{10}$  — 9.0, and ethane  $\text{C}_2\text{H}_6$  — 5.6; the mean molecular weight was 47.2 g/mole.

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A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; email: fsp@hmti.ac.by. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 79, No. 2, pp. 3–9, March–April, 2006. Original article submitted May 5, 2005.

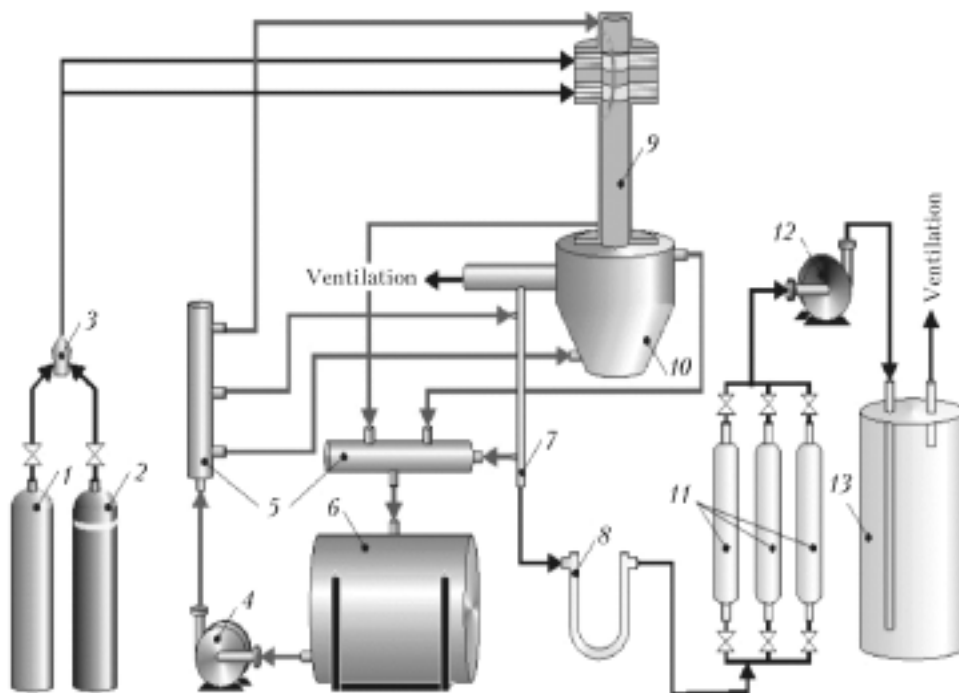


Fig. 1. Diagram of the setup for synthesis of carbon nanomaterials: 1) vessel with a liquefied propane-butane; 2) vessel with a compressed nitrogen; 3) gas mixer; 4–6) system of water cooling of the reactor; 7) sampler; 8) dry filter for separation of dispersed carbon products; 9) arc plasmatron; 10) quenching-absorption apparatus; 11–13) system of sampling for chromatographic analysis.

The investigations were performed on a setup with a d.c. plasmatron of a linear circuit (Fig. 1). The power supply with an open-circuit voltage of 860 V consisted of two series rectifiers connected on semiconductor diodes in a Larionov circuit. The arc current was stabilized by ballast resistors which could be shunted during the operation using conductors. The arc was fired by a high-voltage unit.

The optical-emission-spectroscopy method widely used for diagnostics of an arc plasma was employed for determination of the plasma parameters in synthesizing nanomaterials [4]. This method made it possible to find the component composition and the electron temperature. Spectral measurements were carried out using an SL40 spectrometer enabling us to record the radiation of plasma jets in the range 210–900 nm with the use of diffraction gratings with a density up to 1200 bars/mm.

Also, we performed differential calorimetric measurement of the reactor [5] on the basis of the stationary-heat-flux method. The voltage and current on the plasmatron arc, the mass flow rate and temperature of water supplied for cooling of the components of the setup, and the flow rates of plasma-generating gases were measured.

The regime parameters of the arc during the experiments were as follows:  $I = 123\text{--}275$  A,  $U = 140\text{--}330$  V, and  $N = 24\text{--}88$  kW. The quantity  $G_n$  could change 2.2 times, and  $G_{pr}$  could change more than 15 times. According to our evaluations, the rate of quenching of the pyrolytic gas in condensation of nanoparticles was  $10^5\text{--}10^6$  K/sec.

A representative analysis of nanostructures synthesized in a plasma reactor requires that the integral methods be primarily employed. For this purpose, we used a combination of physicochemical-analysis methods widespread in investigating nanomaterials [6, 7]: a) measurement of the specific surface by the BET (Brunauer–Emmett–Teller) method; b) x-ray phase analysis; c) Raman spectroscopy; d) IR spectroscopy; e) thermogravimetry (derivatographical analysis).

These methods, unlike, for example, transmission electron microscopy (TEM), ensure the possibility of obtaining reliable (averaged over a sample of 0.5–2.0 g) characteristics of a nanomaterial, which is equivalent to a set of  $10^{13}\text{--}10^{17}$  particles. The integral approaches were supplemented with local ones, i.e., with measurements using an EM-125 electron microscope ensuring a magnification of 100,000 times.

TABLE 1. Spectral Characteristics of the Arc Plasma of the Mixture of Nitrogen (47 wt.%) with Propane-Butane

Spectral interval, nm	Characteristic peaks of $\lambda$ , nm	Intensity $J$ , rel. units	Identification according to the literature sources [9–12]
353—360	356.1	656	CN
	358.6	1653	N <sub>2</sub>
375—389	385.3	1641	N <sub>2</sub>
	386.2	1526	CN
	387.1	1408	
	388.3	1215	
	410—422	415.2	614
463—474	420.1	484	CN
	468.0	1912	C <sub>2</sub> , C
502—517	469.4	1822	C <sub>2</sub>
	471.4	1805	
	473.4	1522	
	513.0	4070	Cu
	516.4	4093	C <sub>2</sub>
537—564	547.2	1541	C <sub>2</sub>
	550.0	1771	
	554.0	1965	
	558.5	2143	
	563.6	2041	
786—802	791.5	805	Cu

To more completely determine the influence of the synthesis conditions on the composition of the products formed, in addition to analyzing the dispersed solid phase, we studied the chemical component composition of the pyrogas at exit from the plasma reactor by the chromatographic method. Chemical investigation of the gas samples was carried out by the gas adsorption-chromatography method with the use of a heat-conduction detector and a plasma-ionization detector. The specimens of gases to be analyzed were headed from the sampling line of the plasma reactor to gas pipettes via a special filter with glass wool for separation of moisture and trapping of solid micro- and nanoparticles of soot. The error in determining the composition of the pyrogas was no higher than 5–7% for each ingredient.

Finally, we note that the selection of propane-butane as the raw material pyrolyzed in the plasmatrons was substantiated primarily in the context of thermodynamics. According to the thermodynamic calculations of the equilibrium composition, which preceded the experiment, propane-butane dissociates in the plasma to form, in the temperature range 3500–4500 K, concentrations higher than those of methane of such important (gaseous) particles as a carbon monomer and dimer (C and C<sub>2</sub>) — precursors to, respectively, carbon nanotubes and fullerenes of the C<sub>60</sub> type [6–8]. The calculation yields 3.5–3.6 vol.% C<sub>2</sub> and C for propane-butane and no more than 2.5–3.0 vol.% for methane.

Interpretation of the experimentally obtained plasma spectrum on the basis of the data from [9–12] for the mixture of propane-butane with nitrogen (47 wt.%) in one operating regime and the results of a thermodynamic calculation modeling this regime are given in Tables 1 and 2 respectively. The components whose concentrations exceed 10<sup>-2</sup> vol.% throughout the temperature range are indicated in Table 2. Hydrogen, nitrogen, carbon, and partially nitrogen-carbon or nitrogen-hydrogen-carbon compounds, not counting the copper line from the electrodes, are the most probable atomic-molecular plasma components in both cases. From the data of the thermodynamic calculation, at  $T = 4000$  K, the mixture is enriched with the components H (54 vol.%), H<sub>2</sub> (11.5 vol.%), N<sub>2</sub> (12 vol.%), C<sub>2</sub>H (6.13 vol.%), HCN (4.28 vol.%), CN (3.6 vol.%), C (3.15 vol.%), and C<sub>2</sub> (2.77 vol.%) to the greatest extent. From the spectral data, peaks with  $\lambda = 516.4$  and 513.0 nm, characteristic of C<sub>2</sub> and Cu, have the maximum relative intensity (about 4100 rel. units). Also, there are two intense N<sub>2</sub> bands (nearly 1650 and 1640 rel. units), one of which is adjacent to the CN band, and no less than three strong C<sub>2</sub> bands (with an intensity of ~1540–1910 rel. units). Also, a

TABLE 2. Thermodynamically Equilibrium Composition of the System Nitrogen (47 wt.%) + Propane-Butane Mixture at Different Temperatures ( $P = 0.1$  MPa, calculation using the CHEMKIN Program (Database chem. 05VERS))

Component	Concentration of the gaseous components (vol.%) at different temperatures (K)			
	1820	2000	3000	4000
H	$2.99 \cdot 10^{-2}$	0.115	10.3	54
H <sub>2</sub>	50	50.3	42.5	11.5
CH <sub>3</sub>	$6.97 \cdot 10^{-3}$	$8.05 \cdot 10^{-3}$	$10^{-2}$	$1.38 \cdot 10^{-3}$
CH <sub>4</sub>	0.582	0.179	$2.64 \cdot 10^{-3}$	—
C <sub>2</sub> H <sub>2</sub>	11.3	11.2	9.56	1.62
C <sub>2</sub> H <sub>4</sub>	0.109	$3.59 \cdot 10^{-2}$	—	—
C <sub>2</sub> H	—	$1.45 \cdot 10^{-3}$	0.802	6.13
HCN	7.38	8.22	10.7	4.28
C <sub>2</sub> N <sub>2</sub>	$6.66 \cdot 10^{-3}$	$1.11 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	$6.44 \cdot 10^{-2}$
C <sub>3</sub> H <sub>3</sub>	4.16	4.28	3.84	0.283
p-C <sub>3</sub> H <sub>4</sub>	$1.47 \cdot 10^{-2}$	$5.62 \cdot 10^{-3}$	—	—
C <sub>4</sub> H <sub>2</sub>	3.39	3.21	2.45	0.239
iso-C <sub>4</sub> H <sub>3</sub>	$5.19 \cdot 10^{-2}$	$5.83 \cdot 10^{-2}$	$7.3 \cdot 10^{-2}$	$5.01 \cdot 10^{-3}$
N <sub>2</sub>	22.9	22.3	19.4	12
CH <sub>2</sub>	—	—	$4.28 \cdot 10^{-3}$	$1.27 \cdot 10^{-2}$
CH	—	—	$2.77 \cdot 10^{-3}$	0.14
C <sub>2</sub> H <sub>3</sub>	—	—	$2.33 \cdot 10^{-3}$	—
C <sub>2</sub>	—	—	$1.17 \cdot 10^{-2}$	2.77
C	—	—	$9.48 \cdot 10^{-3}$	3.15
CN	—	—	0.218	3.6
C <sub>4</sub> H	—	—	$1.53 \cdot 10^{-2}$	$9.81 \cdot 10^{-2}$
N	—	—	—	$6.16 \cdot 10^{-2}$

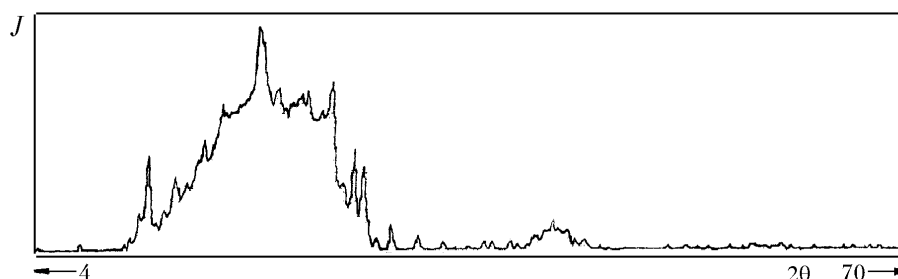


Fig. 2. X-ray diffraction pattern of PCS with nanomaterials.

contribution of the monomer C is possible for the band with a peak at 468 nm (467.9 nm [9]). The above data point to the substantial concentration of gaseous C and C<sub>2</sub> — the precursors to carbon nanotubes and fullerenes — in the plasma.

As the relation of the flow rates of propane-butane and nitrogen grows (above 2.1), the spectra acquire a non-discrete form which is characteristic of jets dusted with soot particles.

Measurement of the specific surface  $S$  of the obtained specimens of a plasmachemical dispersed carbon product — plasmachemical soot (PCS) — by the BET method has shown that its mass-mean dispersity  $d$  is 9.2 nm in

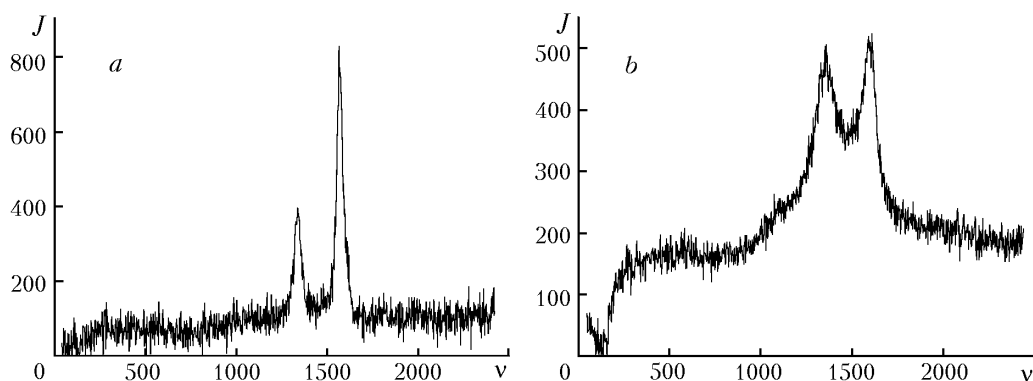


Fig. 3. Raman spectra of PCS (a) and the carbon-nanotube standard (b).

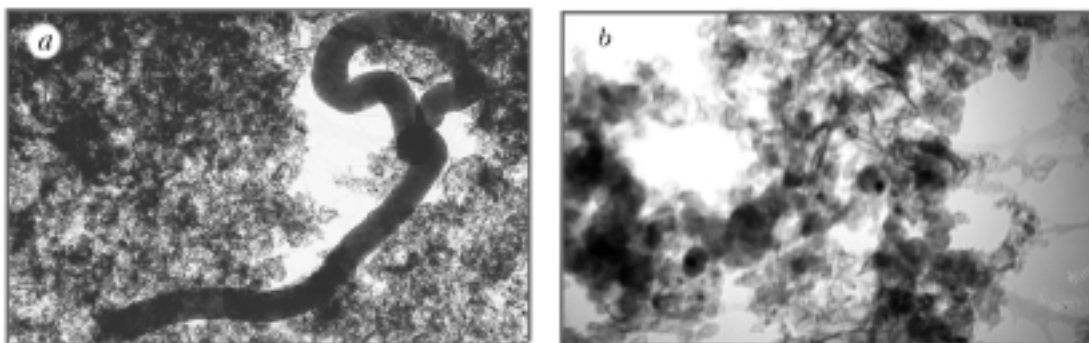


Fig. 4. Transmission electron microphotographs of the specimen of PCS with nanostructures.

rough calculation in the spherical approximation ( $d = 6 \cdot 10^{-3} / (\rho S)$  and  $S = 257 \text{ m}^2/\text{g}$ ). With allowance for the fact that typical (specially studied earlier in [13]) PCSs from a carbon raw material are characterized by values of  $S = 120\text{--}150 \text{ m}^2/\text{g}$ , this result is evidence in favor of the presence of structures (of the carbon-nanotube type) finer than regular quasi-spherical graphite particles in the synthesized PCS product. This is consistent with the data of [14, 15], where the increase from 190 to  $650 \text{ m}^2/\text{g}$  in  $S$  with growth in the fraction of the carbon nanotubes (with a diameter of 0.6–3.0 nm) in the soot product has been revealed with the example of the specimens of soot with carbon nanotubes, synthesized by catalytic pyrolysis of methane-hydrogen mixtures at 1270 K.

Figure 2 gives the data obtained in x-ray phase analysis of the synthesized specimens of soot with nanomaterials. In phase identification, we have used the data of the JCPDS International X-ray Phase Card Index. The results of the x-ray phase analysis of the PCS point to the presence of up to 20.5 wt.% of  $\text{C}_{60}$  fullerites, 10.3–32.5 wt.% of hexagonal graphite, and up to 2.8 wt.% of single-walled nanotubes in the material.

The data obtained by the Raman-spectrography method are given in Fig. 3. The Raman spectrum of the specimen yields two pronounced maxima in the region of the Raman shift ( $1300\text{--}1600 \text{ cm}^{-1}$ ), which is characteristic of single-walled carbon nanotubes. Thus, the reference tangential modes for the latter are observed in the regions of 1550, 1567, and  $1593 \text{ cm}^{-1}$  [1, 6]. The evaluations point to the presence of carbon nanotubes in an amount of up to 15 wt.% in the product. In such an evaluation, we allowed for the intensity of spectral lines and the exposure in irradiation of the soot with a monochromatic laser beam; the exposure was 140 sec for the PCS and 40 sec for the carbon-nanotube standard (with a 50% content of nanotubes).

The IR-spectroscopy data point to the presence of up to 24 wt.% of  $\text{C}_{60}$  and  $\text{C}_{70}$  fullerenes in the PCS.

The results of interpretation of thermogravimetric curves with construction of the histograms of the weight distribution of the components in the specimen have shown that the composition of the synthesized material includes 69 wt.% of highly volatile organic substances (from the unit of trapping of products in the plasma reactor), 27 wt.% of condensed carbon gasified, from the thermogravimetric data, in the range of about 550–600 K (here belong fuller-

TABLE 3. Composition of the Pyrolysis Gas (vol.%) in Operation with the Mixture of Nitrogen and Propane-Butane\* in the Arcing Regime:  $I = 275$  A,  $U = 307$  V, and  $N = 87.6$  kW; Samples with Quenching

Component	Sample No. 1	Sample No. 2	Mean Values
Acetylene C <sub>2</sub> H <sub>2</sub>	29.30	29.22	29.26
Methane CH <sub>4</sub>	2.62	2.46	2.54
Ethylene C <sub>2</sub> H <sub>4</sub>	2.58	2.48	2.53
Propane C <sub>3</sub> H <sub>8</sub>	<0.1	<0.1	<0.1
n-Butane C <sub>4</sub> H <sub>10</sub>	<0.1	<0.1	<0.1
Ethane C <sub>2</sub> H <sub>6</sub>	<0.1	<0.1	<0.1
Propylene C <sub>3</sub> H <sub>6</sub>	0.31	0.29	0.30
Isobutane C <sub>4</sub> H <sub>10</sub>	<0.1	<0.1	<0.1
Hydrogen H <sub>2</sub>	44.63	45.48	45.05
Oxygen O <sub>2</sub>	0.26	0.16	0.21
Nitrogen N <sub>2</sub>	20.31	19.91	20.11
Energy consumption, kWh/kg C <sub>2</sub> H <sub>2</sub>	5.7 (without allowance for the efficiency of the voltage source)		

\*Partial pyrolysis of liquid hydrocarbons (diesel fuel) was carried out in addition to the pyrolysis of the propane-butane gas material.

enes evaporated in the same temperature range [16]), 3 wt.% of single-walled carbon nanotubes, and 1 wt.% of multiwalled carbon nanotubes.

Figure 4 gives the data of the TEM of the synthesized PCS specimens; these data show the presence of carbon nanofibers (of thickness about 60 nm) in the specimens obtained in the plasma of the mixture of nitrogen and propane-butane and, probably, of multiwalled carbon nanotubes of thickness about 4–6 nm. On the two TEM photographs shown (a and b), the magnification is 29,000 and 100,000 times, respectively.

Table 3 gives the total chemical composition (determined by chromatography) of the pyrogas at exit from the reactor after quenching in liquid hydrocarbons at a temperature of 370–450 K for one arcing regime. A characteristic feature of the results of this analysis is the fairly high content of the precursor to carbon nanotubes and fullerenes: C<sub>2</sub>H<sub>2</sub> (of the order of 29 vol.%).

Thus, the experimental investigation of the process of gaseous-phase formation of carbon nanoparticles in atmospheric-pressure arc reactors operating with mixtures of nitrogen and hydrocarbon gases that was carried out has revealed a combination of the basic parameters of synthesis in different regimes (current, voltage, flow rate of the gases and their relation, enthalpy of the jet, etc.), for which the target product is formed in amounts sufficient for semicommercial production.

A complex physicochemical analysis of the obtained specimens of carbon nanomaterials by different methods has shown that arc plasma synthesis under the conditions studied (in particular, pressure  $\sim 10^5$  Pa and rate of quenching of the carbon-containing gas in condensation of nanoparticles  $10^5$ – $10^6$  K/sec) makes it possible to synthesize highly dispersed carbon products with a content of fullerene phases of up to 15–20 wt.% and carbon nanotubes up to 3–5 wt.%. The projected soot-containing-nanostructure output of the setup may attain 2 kg/h.

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## NOTATION

$d$ , mean-mass dispersity, nm;  $G$ , flow-rate of the gas, g/sec;  $I$ , current strength, A;  $J$ , spectral intensity, rel. units;  $N$ , power, kW;  $P$ , pressure, MPa;  $S$ , specific surface, m<sup>2</sup>/g;  $T$ , temperature, K;  $U$ , arc voltage, V;  $2\theta$ , diffraction angle, deg;  $\lambda$ , wavelength, nm;  $\nu$ , wave number, cm<sup>-1</sup>;  $\rho$ , density of the material, kg/m<sup>3</sup>. Subscripts: n, nitrogen; pr, propane-butane.

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