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**Berlin Institute of Technology  
(TU Berlin)**

**Prof. Dr. Frank Behrendt**  
Fakultät III: Prozesswissenschaften,  
Institut für Energietechnik

Chair Energy Process Engineering and  
Conversion Technologies for  
Renewable Energies (EVUR)  
Fasanenstr. 89  
10623 Berlin

**Contact**  
info@flame-structure-2014.com  
frank.behrendt@tu-berlin.de

Berlin Institute of Technology • Fasanenstr. 89 • 10623 Berlin

Institute of Combustion Problems  
**Z. Mansurov**  
172, Bogenbai Batyr St.  
050012, Almaty, Republic of Kazakhstan

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### **Confirmation of paper submission**

**Name:** Z. Mansurov  
**Email:** zmansurov@kaznu.kz  
**Co-author:** -  
**2nd co-author:** -  
**3rd co-author:** -  
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# MECHANISM OF SOOT AND NANOMATERIALS FORMATION IN FLAME

Z. Mansurov

Institute of Combustion Problems, 172, Bogenbai Batyr St., 050012, Almaty, Republic of Kazakhstan

Email: zmansurov@kaznu.kz

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## Abstract

The seventieth anniversary of Professor Jürgen Warnatz is an important event for the scientific community of investigators of chemical kinetics and computation of combustion. It should be noted his brilliant research in the field of combustion, particularly in the chemical kinetics reactions. His manuscript «Combustion» with co-authors is a handbook for specialists in the field of combustion and under my supervision was translated to Kazakh. Professor J. Warnatz contributed great to development of combustion processes modeling and education of scientists from various countries, including Kazakhstan.

The general scheme of conversion of hydrocarbon fuels with new experimental data on the formation of fullerenes and graphenes taking into account the pressure effect is proposed for the fuel-rich flames. It is shown that the formation of fullerenes is important to the corresponding spatial orientation of PAH, possible at low pressures. The formation of hydrophobic soot surface on silicon and nickel substrates during combustion of propane-oxygen flame was studied. It is established that the hydrophobic properties are due to the presence of soot particles in the form nanobeads.

**Keywords:** Soot, nanomaterials, fullerene, graphene, hydrophobic.

## 1. Introduction

Simultaneously with the soot formation, fullerenes and nanotubes are formed by the mechanism competing with the mechanism of soot formation. A knowledge of the conditions and mechanisms of formation of soot, fullerenes, and nanotubes in a flame allows one to change the combustion such that soot particles, fullerenes, or nanotubes are predominately formed.

At the present time a large number of experimental data on the processes of soot formation have been accumulated and different phenomenological models have been proposed [3, 4]. However, the mechanism of soot formation is imperfectly understood yet. This is explained by the fact that even in simple cases, such as the homogeneous pyrolysis of hydrocarbons, this process includes a large number of rapid simultaneous reactions leading to the formation of a new solid phase – soot particles (e.g., the time of transformation of methane with a molecular mass of 16 a.m.u into the soot with the molecular mass more than  $10^6$  a.m.u makes  $10^{-4}$ – $10^{-2}$ s).

Considerable interest of scientific and technical communities to study production processes, structure and properties of nanosized systems is caused by variety and uniqueness of their practical applications. The small size of structural components – typically up to 100 nm – determines the difference in the properties of nanomaterials from massive analogues. Flame is a self-sustaining sys-

tem in which hydrocarbons can be precursors of carbon nanomaterials, and the heat released during combustion, is a parameter of the process control. It is known that PAH are nucleation centers of forming soot i.e. PAH can be converted into either soot or fullerenes. The formation of CNTs occurs in diffusion flames from the fuel side and is initiated by transition metals particles.

The  $C_{60}$  and  $C_{70}$  fullerene ions were detected in flames in 1987 and identified by the mass-spectrometry method [5]. Howard et al. [6] have obtained large amounts of  $C_{60}$  and  $C_{70}$  in laminar premixed soot forming flames of benzene and oxygen at low pressures. Unlike the evaporation of graphite, in the fullerenes formed in flames the ratio  $C_{70}/C_{60}$  changes from 0.26 to 8.8 (in the case of evaporation of graphite, this ratio changes from 0.02 to 0.18).

The original results on development of carbon nanomaterials of different functional application which were obtained at the Institute of Combustion Problems are presented in the article:

- Formation of soot and synthesis of fullerenes in flame;
- Formation of carbon nanotubes in flames;
- Formation of the hydrophobic soot in hydrocarbon flames;
- Formation of layered graphene films in the flames.

## 2. Formation of soot and fullerenes in flame

The formation of fullerenes occurs at low pressures, and corresponding space orientation which requires the account of steric factor is important here.

It should be noted, that formation of such elegant molecule of  $C_{60}$  requires the necessary space orientation of two molecules of  $C_{30}$ . There are different formation models of fullerenes  $C_{60}$  one of which is carried out by zipper-mechanism.

Low pressures are the necessary conditions of such mechanism. With increasing of pressure, i.e., transition to the atmospheric and above, where triple collision take place and coagulation of PAH occurs, with formation of soot clusters. Howard has shown that the maximum of fullerene formation shifted to the right relative to the maximum of soot formation. At detailed examination by him the formation of fullerenes from benzene flame is shown that there is the second maximum at a distance of 70 mm from matrix of burner [6].

These data become the basis for development of alternative method for obtaining of fullerenes in the regime of hydrocarbons combustion.

A series of experiments on the study of the yield of fullerenes in a premixed benzene-argon-oxygen flame exposed to a longitudinal electric field under the conditions of a dark discharge, a corona discharge, and a glow discharge [4, 7] at  $C/O = 1.0$ ,  $P = 40$  torr, a benzene-flow rate  $Q_1 = 250$  cm<sup>3</sup>/min, an oxygen-flow rate  $Q_2 = 758$  cm<sup>3</sup>/min, an argon-flow rate  $Q_3 = 101$  cm<sup>3</sup>/min (10% of the combustion-mixture volume),  $V = 18.4$  cm/s.

It has been stated that the negative polarity of the upper electrode is more favorable for the fullerene formation as compared to the positive one. The investigations carried out under the conditions where the upper electrode was positioned directly above a flame have shown that, in this case, the yield of fullerenes increases. The influence of the type of an electrode and the height of its position above a flame on the formation of fullerenes was investigated for determining the conditions providing their maximum yield. Electrodes in the form of a needle and a ring were used. The investigations were carried out at a negative polarity of the upper electrode under the conditions where  $U_H = 7$  kV,  $H = 1-9$  cm (with a step of 1 cm). A glow discharge appeared independently of the type of an electrode at different heights of its disposition above the flame. In this case, the average temperature of the flame increased to  $T = 1200$  °C (without a field, this temperature was equal to  $T = 950$  °C).

Thus, it has been stated that the yield of fullerenes increases under the action of a glow discharge in the case where an electrode (a needle or a ring) is positioned directly above flame and that a maximum yield of fullerenes is attained with the use of a ring electrode placed

above the central region of the flame front. The maximum yield of the fullerene  $C_{60}$  was  $\beta = 15\%$  of the soot formed.

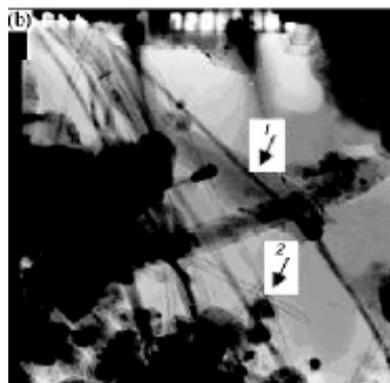
## 3. Formation of carbon nanotubes in flames

The most promising way to produce carbon nanotubes, according to Merchan-Merchan et al. [8], is the flame method. In the synthesis of carbon nanoparticles using flames, part of the fuel is consumed in heating of the mixture, and part is used as a reactant, which makes this method more cost-effective than methods based on the use of electricity, pyrolysis of hydrocarbons or arc evaporation of graphite.

The results of the study of a flat diffusion propane-oxygen flame stabilized on an opposed-jet burner at atmospheric pressure are presented in [7]. Two opposed flows formed the flat flame. The flame was surrounded by an external nitrogen flow supplied from the burner matrices. A solution of catalyst [ $Fe(CO)_5$  or an alcohol solution of nickel nitrate] was sprayed by an ultrasonic nebulizer and delivered through a metal nozzle into the flame from the side of the fuel.

The resulting products were deposited on the walls of the reactor and collected in traps with liquid nitrogen. The temperature in the reactor was measured by a thermocouple, and in the flame by an Iron Ultrimax pyrometer.

It is evident from **Fig. 1** that the samples contain soot agglomerates, among which metal particles are encountered. It was found that under certain experimental conditions, well-ordered bundles of carbon nanotubes 20–30 nm in diameter formed.



**Fig. 1.** Electron micrographs of samples: (1) carbon nanotube; (2) Ni in a carbon shell

## 4. Formation of hydrophobic soot in hydrocarbon flames

Low surface-energy materials like amorphous carbon (a-C) films are frequently used to modify surfaces in order to control their wettability. The nanobeads are morphologically similar to the carbon nanopearls synthesized by Levesque and co-workers [9] through acetylene dissociation at 700 °C on nickel catalyst nanoclusters. Puri et al. have determined new ways of the synthesis of carbon nanotubes in the fuel-rich diffusion flames, exposed to an electric field during 2-10 min, on superhydrophobic surfaces representing nanodimensional round amorphous carbon particles deposited on a silicon substrate [10].

The formation of hydrophobic soot surface on silicon and nickel substrates during combustion of propane-oxygen flame was studied [11]. It is stated that the hydrophobic properties are due to the presence of soot particles in the form nanobeads. The schematic diagram of the synthesis process is presented in Fig. 2 and Fig. 3 shows water droplets on superhydrophobic soot.

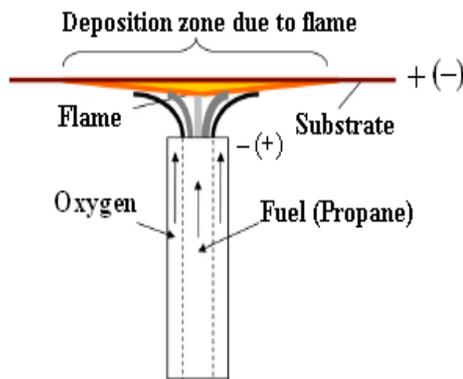


Fig. 2. Schematic diagram of the synthesis process

Studies have shown that carbon deposits on the plates different in the morphological structure of deposited particles in different zones. In the central and middle zone long chains of individuals formed in the form nanobeads 15-30 nm without applying an electric field, and 40-50 nm with an electric field. In the outer zone, regardless of the conditions of combustion, there are coagulated aggregates of soot particles with sizes 30-50 nm.

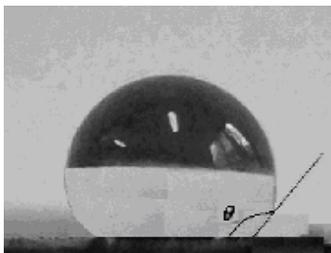


Fig. 3. Water droplets on superhydrophobic soot

The results for the exploration of the soot formation of hydrophobic surfaces on silicon substrates and nickel during combustion of propane oxygen flame are listed. The distance from the burner matrix and the substrate was varied, the exposure time and the influence of the electric field of different polarity and voltage. It is shown that at the exposure of more than 4 minutes the soot with hydrophobic properties is formed and a division of the soot surface area occurs. The application of an electric field narrows the soot deposition on the substrate and in diameter of 2.5-3 cm from the centre; the soot super hydrophobic surface with a wetting angle of more than 170° is formed.

## 5. Formation of a layered graphene in the flames

The study of the formation of layered graphene films was carried out in the propane-oxygen flame under the following conditions: flow rate of propane – 219.1 cm<sup>3</sup>/min, the flow of oxygen – 381.2 cm<sup>3</sup>/min, corresponding to the ratio of C / O = 0.86.

The studies were carried out both with the addition of argon in benzene-oxygen mixture in an amount of 300-650 cm<sup>3</sup>/min and without argon. As catalytic substrates used plates made of copper and nickel, are placed in the fire.

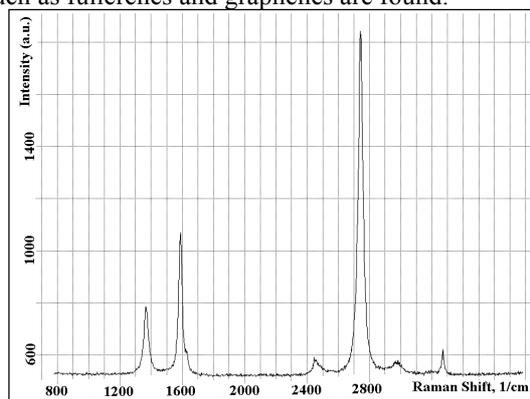
Varied range of residence time of the substrate in the flame: 5, 10, 20, 30, 40, 60 seconds, 5 and 10 minutes, the angle varied substrate relative to the vertical axis of the flame:  $\alpha = 0, 30, 45, 60, 85^\circ$ . Flame temperature in the experiments was in the range 900-950°. Formed on the substrate samples were examined for particulate structures Raman spectrometer NTEGRA Spectra. Analysis of the results of synthesis of graphene layers in the flame at low pressure and with addition of benzene showed that in the pressure range of 40-100 Torr one- to three-layer graphene sheets on nickel substrate are formed, which is characterized by the intensity ratio  $I_G/I_{2D} \leq 1.3$  [10]

At a pressure of 55 Torr preferential formation of a single layer graphene is observed, its characteristic Raman spectra was shown in Fig. 4.

## 6. Mechanism of soot formation in rich flames

The flame front structure of soot formation flames can be considered in close connection with mechanism of fuel conversion. A scheme that suggested by Bockhorn [11] in 1994 is known, where polycyclic aromatic hydrocarbon (PAH) are precursors of soot particles.

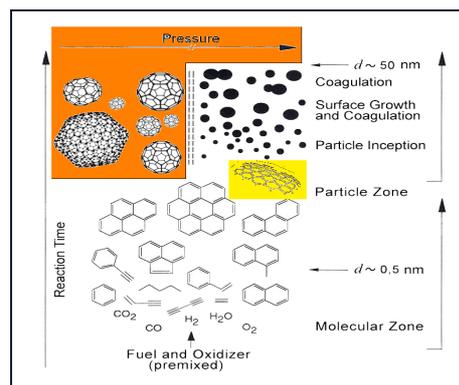
Since then, in rich fuel flames the nanosized particles such as fullerenes and graphenes are found.



**Fig. 4.** Raman spectra of single-layer graphene samples obtained with the addition of benzene to  $C_4H_{10}/O_2$  flame on a nickel substrate at a pressure of: 55 Torr ( $I_G/I_{2D} = 0.58$ )

The fullerenes formation is generally observed at pressures below 60 Torr, because for fullerenes formation is necessary an adherence of steric spatial factor, but in flames at atmospheric pressure this factor is prevented by triple collisions. Therefore, the pressure coordinate can be introduced to the general scheme for soot formation. At low pressure the formation of fullerenes from polycyclic aromatic hydrocarbon (PAH) is occurred, but with pressure increase the polycyclic aromatic hydrocarbon (PAH) are coagulates to soot particles. From (PAH) follows the graphene formation as intermediate product between PAH and soot particles, which is confirmed by the formation of multi-layered graphene films at atmospheric pressure and single-layered at the pressures below 60 Torr. On the basis of the data on synthesis of fullerenes, carbon nanotubes, superhydrophobic soot and graphene in the flame it is possible to modify the general scheme proposed by H. Bockhorn [11] for rich fuel flames, namely to make a pressure-coordinate, which allows the formation of fullerenes at low pressures, and soot at high pressures. In addition the scheme was completed by graphene formation as an intermediate product stage of graphene formation (**Figure 5**) [12].

Experimentally, the formation of graphenes is accompanied by the presence of soot deposits on nickel substrates, but, the obtaining of pure grapheme films without soot particles theoretically is possible and it is the work of our future investigations.



**Fig. 5.** Modified scheme for soot, fullerenes and graphene formation process in flames

## References

- [1] K.H. Homann and H. G. Wagner, Some aspect of soot formation, in: J. Ray Bawen (Ed.), Dynamics of Exothermicity (Combust. Sc. Techol. Book Series, Vol. 2), Carbon and Breach Publishers (1996), P. 151-184.
- [2] Z.A. Mansurov, Combustion, explosion and Shock Waves, 2005, 41(6), 727-744
- [3] P. Gerhardt, S. Löffler and K. H. Homann, Proc. 22<sup>nd</sup> Int. Symp. Combust., The Combustion Inst., Pittsburgh (1988), pp. 395-401
- [4] J.B. Howard, A. L. Lafleur and other, Carbon, 30, 1183-1201 (1992)
- [5] Z.A. Mansurov, Combustion, Explosion and Shock Waves. Vol.48, №5, P. 561-569, 2012.
- [6] W. Merchan-Merchan, A.V. Saveliev, L.A. Kennedy, Carbon 44 (2006) 3308–3314
- [7] Levesque A, Binh VT, et al. Thin Solid Films 2004; 464–465: 308 - 14.
- [8] Sayangdev Naha, Swarnendu Sen, Ishwar K. Puri, Carbon 45 (2007) 1696–1716.
- [9] Mansurov Z.A Advanced Materials Research Vol. 486 (2012) pp 134-139
- [10] Prikhodko, N.G., Lesbaev, B.T., Auelkhankyzy, M., Mansurov, Z.A. (2014) "Synthesis of Graphene Films in a Flame" Rus. J. of Phys. Chem. B, Vol. 8 (1), p. 61–64.
- [11] H. Bockhorn (ed). Soot formation in Combustion. Springer, Berlin / Heidelberg. 1994. P.4.
- [12] Mansurov Z.A. Journal of Materials Science and Chemical Engineering, 2014, 2, 1-6