

Soot and Fullerenes Formation in the Premixed Benzene-Oxygen Mixture in Electric Field at Low Pressure

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Abstract

Influence of the direct electric current of different polarity on flame forms, soot yield, parameters of soot samples micro crystals (L_a , L_c and d_{002}) and soot particles sizes in intensity range from 0.5 to 20 kV at electrode systems «needle-plane» at combustion of benzene-oxygen mixture at the ratio C/O = 1.0 with addition of 10% volume of argon at pressure 40 Torr was investigated. It was found that at positive polarity action of electric field rises to such a degree that at $U \geq 10$ kV it leads to flame extinction. It is shown that maximum decrease in soot yield is observed at negative polarity. It was found that intensity range of electric field in which soot yield was 10 % more soot yield without applying electric field. It was shown that parameters of soot micro crystals on average remain constant irrespective of intensity and polarity. Fullerenes C_{60} , C_{70} and PAH were identified in the extracts of soot samples by the method of IR-spectroscopy.

Introduction

The electric field influence on the processes of hydrocarbon combustion is of great importance for managing chemical synthesis and soot formation control concerning ecology. It is stated, that even electric field of low intensity has significant influence on the combustion kinetics.

Influence of the applied electric field on nucleation of soot particles, their growth in the zone of pyrolysis and sedimentation was also investigated. The rate of formation of soot particles depends on both polarity and the value of ionic stream through the zone of pyrolysis. Positive ions act as nuclei for formation of soot particles, and negative charges, apparently, do not act as nuclei, but tend to reduce soot formation by neutralization of positive ionic nuclei [1]. From the detailed analysis of the soot particles sizes, carried out by electron microphotography it was established that the sizes of particles with a diameter of 50 nanometers, obtained in the experiments without the application of electric field, decreased to 10

nanometers in diameter when applying an electric field of several kV [1]. Thus, as is shown in the work [2, 3], with increase in the value of applied pressure, soot particles become more homogeneous.

Of great interest is the use of low temperature of soot forming flame for obtaining various polycyclic aromatic hydrocarbons (PAH) with a number of valuable properties [3] of soot with the definite structural parameters [2] and fullerenes [4, 5]. Application of electric field to soot formable flame allows carrying out the management of chemical synthesis, regulating the process of soot formation and creating a high-temperature level for the yield of fullerenes.

It is known, that the electric field influences the processes of nucleation and growth of soot particles and as a rule soot particles have mainly positive charge in the flame [1, 6, 7]. According to the ionic theory of soot formation which was enough fully studied by H.F. Calcote et al. [8, 9] such ions as $C_nH_n^+$ are active centers for growth of soot particles this fact significantly influences the kinetics of soot formation under the effect of an external electric field. At the earliest stages of soot formation all soot particles get a charge. The size and mass of a soot particle are determined by the time of staying

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in the combustion zone, which can be changed by applying an electric field [1]. At voltage of an electric field of 200 kV/m and higher evolution of Joulean heat becomes comparable with heat evolution on account of a chemical reaction thereby increasing the flame temperature to 1800°C and higher [10] and creating more optimum conditions for fullerene formation [11].

The aim of this research work was to determine the effect of parameters of a constant electric field - values of the applied voltage, polarity on the form

of a flame, the yield and structural characteristics of formed soot particles, fullerenes and PAH.

Experimental

Investigations were carried out in the combustion of premixed mixture of benzene vaporous with oxygen at atomic ratio C/O = 1.0 with adding 10 % volume of argon, at pressure P = 40 Torr on the experimental plant, whose principal scheme is given in the fig. 1.

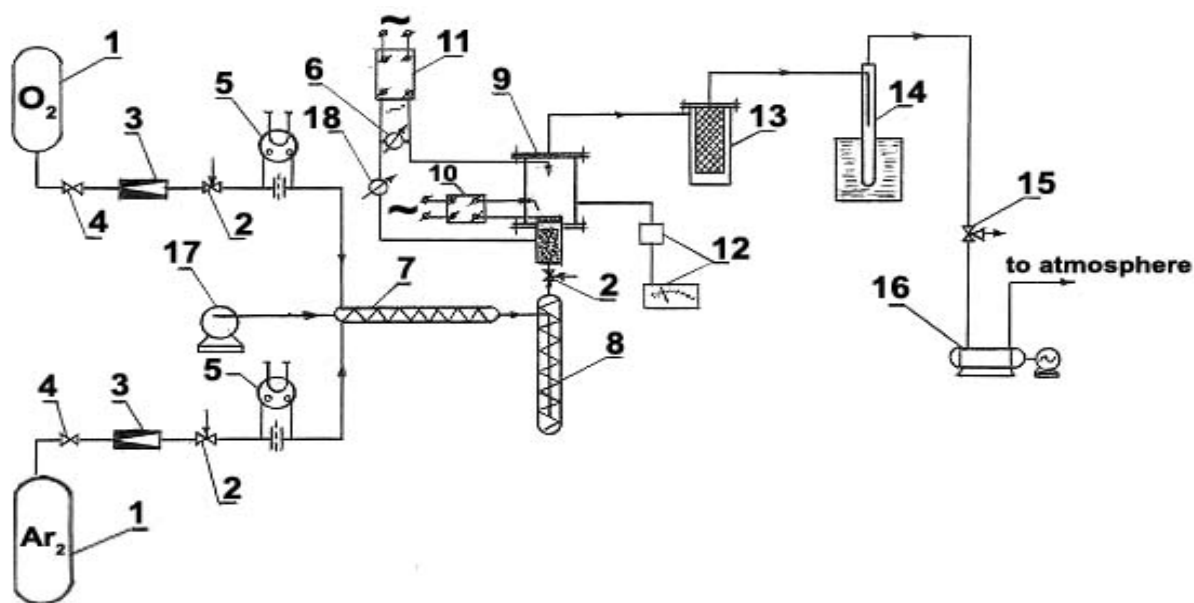


Fig. 1. The scheme of experimental plant: 1 - receiver; 2 - batcher- crane; 3 - reducer; 4 - crane; 5 - consumption indicator; 6 - kilo voltmeter C 50; 7 - evaporator-mixer agitator; 8 - vapour overheater buffer capacity; 9 - burning equipment from quartz glass; 10 - high-voltage electric fuser of alternating current; 11 - high-voltage source of constant current BV-9,0-1,5; 12 - vacuumeter VDG-1; 13 - filter - soot collector; 14 - low-temperature catch tank; 15 - three-throw crane; 16 - vacuum pump VN-2MG; 17 - batcher of electromechanical pump liquid batcher; 18 - microampere meter M95.

Benzene was introduced with a dozator in quantity $q = 1\text{ml/min}$. In benzene vaporization volume consumption of vaporous was $Q_1 = 250\text{ cm}^3/\text{min}$. Volume flow rates of oxygen and argon, made up $Q_2 = 758\text{ cm}^3/\text{min}$ and $Q_3 = 101\text{ cm}^3/\text{min}$, respectively the feeding path of a gas mixture was heated, that excluded condensation of benzene vaporous. Heat temperature of the evaporator and buffer vessel was equal to, $T = 473\text{ K}$. Overpressure of vaporous – gaseous mixture in the buffer vessel, which was equal to, $P_{\text{over}} = 97.5\text{ Torr}$, allowed equally supplying the mixture into the burner. The rate of supplying a gas mixture in the burner was $V = 18.4\text{ cm/s}$, that created stable combustion with the maximum temperature in the flame $T = 1200\text{ K}$ and with a flame front separation from the burner of 0.5

cm. The temperature on the flame height was measured using Chromel – alumel thermocouple and “Promin” pyrometer. The duration of one experiment was $t = 20\text{ minutes}$. Soot was collected in the filter of soot collector. Glass fabric was used as a filtering material. The filter of soot collector was heated to the temperature of 100° , that excluded the water vapours condensation, formed during combustion. After the end of a cycle of soot combustion, soot was taken from the burner unit, the filter – soot collector, was weighed and analyzed on an JEM-100CX electronic microscope at acceleration voltage of 100 kV, diffractometer DRON – 3M (CuK_α - radiation, $\lambda = 1.54051\text{ \AA}$, at intensity of 1000 impulse/s, $U = 30\text{ kV}$, $I = 20\text{ mA}$, soot mass $m_s = 0.5\text{ g}$). To identify fullerenes and

PAHs soot in the amount of $m_s = 100$ mg was subjected to cool extraction in the medium of benzene during 72 hours, then the obtained extract was investigated using IR- Fourier spectrometer, produced by "PERKIN ELMER".

To study the effect of an electric field on the flame, we chose an electrode system "needle-flat surface" with interelectrode distance $L = 18$ cm, located in the burner unit of quartz glass (Fig. 2).

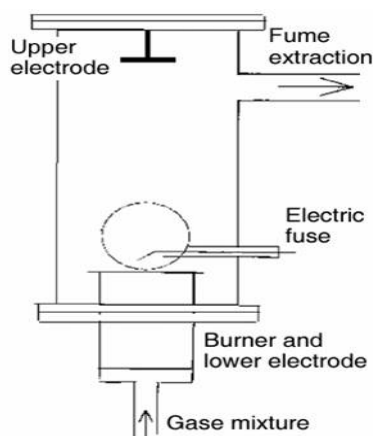


Fig. 2. The burner scheme and photograph

Discussion of results

Fig. 3 presents the effect of an electric field on the flame form.

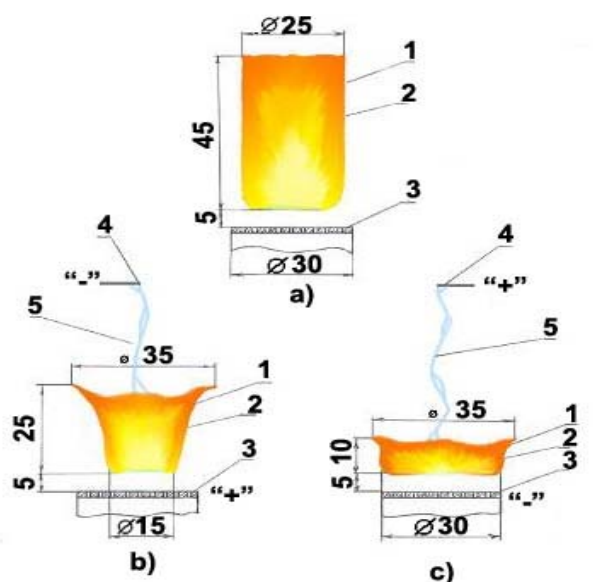


Fig. 3. The format and the sizes of a flame: a) without applying electric field; b) negative polarity electric field application, $U = 10$ kV; c) with applying electric field of positive polarity, $U = 10$ kV; 1 - front of flame; 2 - average luminous zone; 3 - burner; 4 - upper needle electrode; 5 - luminous cord of glow discharge

The burner was chosen as a flat surface electrode.

Constant high voltage U of negative ("minus" on an electrode "needle") or positive ("plus" on an electrode "needle") polarity in the range from 0.5 to 20 kV was applied to the needle electrode that was placed in the upper part of burner unit. As a result of applying a longitudinal electric field, negative or positive crown discharge, which influenced the flame, was created.

Influence of electric field on flame was observed visually, beginning with $U \geq 1.35$ kV - for negative polarity, and with $U \geq 3.0$ kV- for positive polarity. This influence was expressed in compression, fluctuation, extending and flattening of the flame, in its transformation to a tulip-like form and other phenomena. In the absence of an electric field, the flame steadily burned, without fluctuation, had the form of a cylinder (according the form of the burner) with parameters: $d = 2.5$ cm, height of a luminous zone $h = 4.5$ cm, distance from burner $\delta = 0.5$ cm when applying an electric field by voltage, $U = 10$ kV and higher, the upper part of flame front became a wave (see Fig. 3), following wave-like effect of a luminous twisting cord of the glow discharge on it, but the distance from the burner remained constant.

For positive polarity, starting with $U \geq 10$ kV, the action of an electric field on the flame, intensified to such a degree that resulted in the extinction of the flame. That is, under the action of an electric field, positive ions and neutral particles were carried out of the front of the flame to the pre-flame zone and to a negative electrode - a burner, extinguishing the flame. At reverse polarity, flame extinction didn't occur, that again indirectly confirms the primary value of positive ions in the organization of combustion process [6, 7].

As is known, by applying an electric field on the flame it is possible, in certain limits, to control the yield of soot. Investigations of the influence of an electric field on the yield of soot showed, that in a range of voltage from 1.2 to 1.35 kV, irrespective of polarity, the soot yield is 10% higher than the soot yield obtained without applying an electric field (Fig. 4). In other cases, the soot yield was less than soot yield without application of an electric field. The maximum decrease of the soot yield at voltage of 100 kV/m was: at negative polarity - 40%, at positive polarity - 25%. At diffusion combustion of acetylene in the atmosphere at 100 kV/m the maximum decrease in soot yield was: at negative polarity - 75%, at positive polarity - 65% and excess of soot yield without applying an electric field wasn't observed [8]. So, during combustion of benzene preliminary mixed with oxygen at the determined ratio of C/O oxidation of soot particles at low pressure occurs to less extent than in diffusion flame during combustion in the atmosphere.

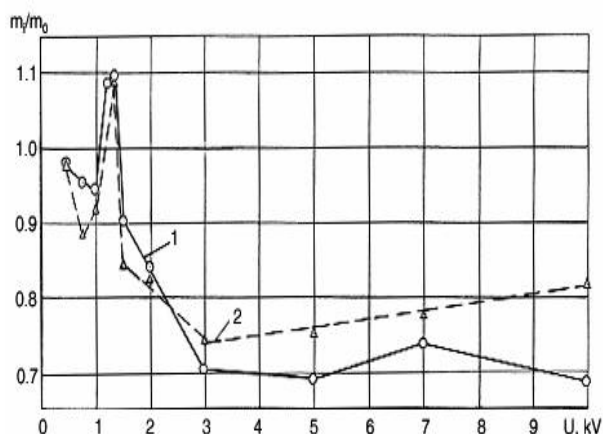


Fig. 4 Dependence of m_i/m_0 on applied voltage and polarity: 1 - negative polarity; 2 - positive polarity; m_0 - specific soot yield without field, mg/ml; m_i - specific soot yield in i - experiment with field application, mg/ml

As known, that soot particles are the set of crystallites, which has the form of soot package. Parameters of soot package such as: L_a – the width of soot package, L_c – height of soot package and d_{002} – interlayer distance were determined using X-ray structural analysis. It was determined, that, irrespective of the value of applied voltage and polarity under these experimental conditions, the height of the package soot $L_c = 10.43 \dots 11.85 \text{ \AA}$ and interlayer distance $d_{002} = 3.56 \dots 3.8 \text{ \AA}$ change a little, and the width of the package soot L_a is inclined to increasing.

The increase in L_a occurs as a result of the building up of polycyclic structures with side

chains. [12]. After yield of polycyclic aromatic hydrocarbons when being extracted in the medium of benzene, the value L_a decreases, resulting in the formation of compounds with higher content of carbon atoms similar to graphite, Table 1. The obtained soot represents a chaotic set of separate crystals consisting of three flat parallel lattices of carbon atoms.

The analysis of the obtained soot samples micro photos showed, that the obtained soot was a polydisperse substance, and the form of particles is close to spherical (Fig. 5). Average arithmetic weighed diameter of soot particles d_{av} , maximum d_{ax} and minimum in sizes are given in Table 2.

Table 1
X-ray structural analysis of the sample particle

U, kV	Polarity	$L_a, \text{ \AA}$	
		Before extraction	After extraction
0	-	62.98	40.51
0.5	$\bar{\pi}$	87.2	49.38
1	$\bar{\pi}$	56.88	43.63
1.35	$\bar{\pi}$	51.6	45.41
2	$\bar{\pi}$	54.16	40.65
5	$\bar{\pi}$	81.04	49.45
10	$\bar{\pi}$	86.95	43.63
15	$\bar{\pi}$	56.88	37.81
20	$\bar{\pi}$	45.64	56.88
0.5	\pm	62.93	42.13
1	\pm	56.58	53.98
1.35	\pm	63.25	47.33
2	\pm	51.71	47.26
5	\pm	51.6	47.33
7	\pm	56.76	40.62
10	\pm	75.57	49.35

The electric field contributes to the growth of the sizes of soot particles due to the change of the time of their staying in the zone of growth. At positive polarity more intensive growth of the sizes of soot particles takes place. However, the longer time of soot particles in combustion zone and in the zone under the effect of an electric field leads to oxidation of soot particles. This process intensifies with the increase in voltage being applied, which is exhibited in the reduction of average sizes of soot particles. This phenomenon is not observed at negative polarity and, formed soot particles, are carried away from the flame zone and the zone under the electric field. Oxidation of formed aggregates is not observed, and, with the increase in a applied voltage, their systematic growth takes place.

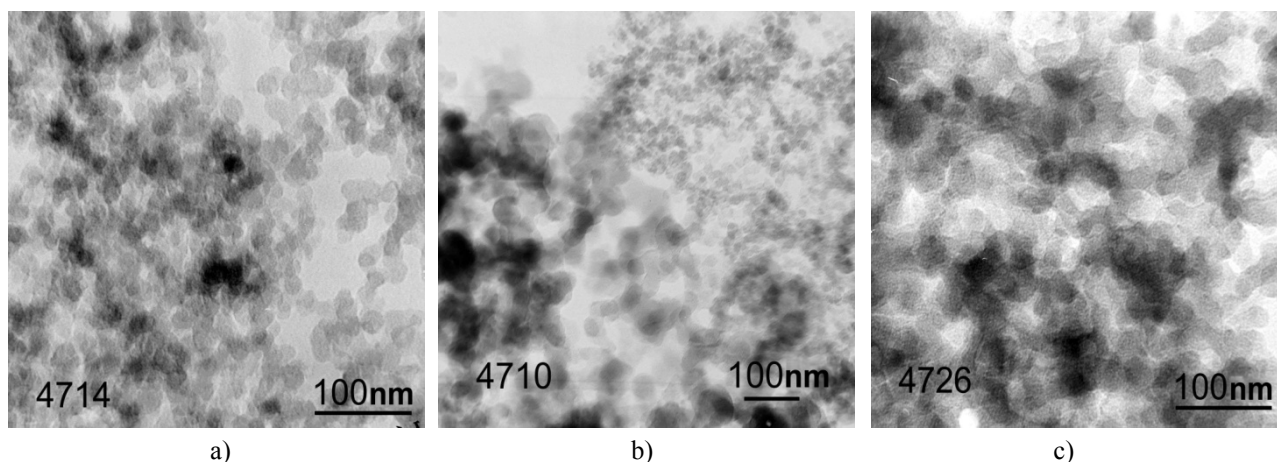


Fig. 5. Soot samples microphotographs at negative polarity: a) $U = 0$ kV, b) $U = 1$ kV, c) $U = 10$ kV

Table 2

The size of soot particles depending on the applied voltage and polarity

U, kV	The size of soot particles, $d, \text{\AA}$					
	Polarity					
	negative			positive		
	$d_{av.}$	d_{max}	d_{min}	$d_{av.}$	d_{max}	d_{min}
0	172	225	112	172	225	112
1	173	314	78	228	333	115
5	175	262	98	213	345	69
10	189	267	111	208	364	121
20	191	306	141	164	281	108

IR-spectroscopic investigation of soot extracts obtained by the method of cool extraction in the medium of benzene, showed presence of fullerenes C_{60} ($\lambda - 528, 577, 1183, 1429 \text{ cm}^{-1}$) and C_{70} ($\lambda - 458, 535, 565, 578, 642, 674, 795, 1134, 1414, 1430, 1460 \text{ cm}^{-1}$) (Fig. 6). To identify fullerenes C_{60} and C_{70} we combined standard spectrum with the spectra, obtained in the given work. Fig. 6 shows wave numbers characterizing only fullerenes C_{60}

and C_{70} . Values of reference and experimental wave lengths for fullerenes C_{70} and C_{60} are compared in the table. 3. With the increase in electric field voltage of negative polarity up to 200 kV/m, the percent value of fullerenes in the extract grows. In addition to fullerenes in the extract there were identified polycyclic aromatic hydrocarbons shown in Table 3.

Table 3

Comparison of experimental and reference wave length of spectra of fullerenes and PAHs

Fullerens	Extract, λ, cm^{-1}	Reference, λ, cm^{-1}
C_{60}	528, 578, 1183, 1429	528, 577, 1183, 1429
C_{70}	457, 538, 563, 578, 679, 798, 1136, 1414, 1430, 1460	458, 535, 565, 578, 642, 674, 795, 1134, 1414, 1430, 1460
PAHs		
Pyrene	711, 755, 842, 1183	710, 750, 840, 1190
Fluoranthene	618, 755, 775, 827	615, 750, 775, 825
Coronene	543, 842, 1314	545, 850, 1313
Anthatrene	690, 775, 880	690, 762, 877
1,12 - benzperylene	755, 775, 817, 842	645, 750, 765, 817, 845

Conclusions

The results of experiments have shown that in external electric field influence on soot forming flame one may change shapes and sizes of a flame, influence the stability of combustion, produce an effect on mass yield of soot, sizes of particles and also create conditions for the yield of fullerenes.

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Received 23 August 2011