

Lecture 13. Soot formation at combustion of hydrocarbons

The purpose of the lecture: to familiarize students with the process of soot formation during the combustion of hydrocarbons, the structure and properties of soot particles.

Expected results: students getting information about the soot formation process, structure and parameters of soot particles.

The relevance of the study of soot formation is associated with:

- the fact that soot is the target product;
- environmental aspects of the process;
- the release of smog, visibility, engine operation due to soot deposits on the walls of the combustion chamber.

During combustion, the temperature at which soot particles are formed is 1500-2500 K, but also much lower. Soot particle formation time t - milliseconds.

The soot particles formed are characterized by the following values:

- soot particle volume Φ cm³/cm³
- the number of soot particles N (cm⁻³)
- particle size, d .

The form of soot particles is spherical or close to it. $d \approx 200-300$ Å ~ 1 million atoms C. Aggregation occurs through straight or side chains.

Soot formation during low-temperature methane combustion

Soot formation is an important and constantly studied aspect of combustion. Despite numerous studies in a wide range of parameters, there is still little information on soot formation during low-temperature combustion of hydrocarbons at temperatures $T = 900-1200$ K. The effect of preheating of the combustible mixture is poorly studied, although, apparently, it can be one of the parameters for controlling the completeness combustion and properties of soot formed. In connection with the foregoing, it is of interest to study soot formation during low-temperature combustion of methane ($T = 1200$ K), determine the physicochemical characteristics of soot, and also highlight the determining process parameters.

Typically, soot is formed at $T = 1600-1800$ K. The preheating of the combustible mixture contributes to a decrease in this temperature; therefore, it is convenient to study the process in a two-section separately heated reactor.

To study the soot formation in a flame of a rich methane-oxygen mixture, a flame stabilization technique in a two-section separately heated reactor was used. In the first section, the mixture of methane with oxygen was heated, and in the second, a flame was ignited and stabilized, which is isolated from the pre-flame zone due to the fact that the flow rate in the narrow jumper connecting the first and second sections is many times higher than the flame speed stabilized in the second section.

The resulting soot mixture through the exhaust pipe enters the soot collector made of carbon fabric, which allows you to separate the soot from gaseous products. To prevent water condensation, the soot collector was heated to 423 K.

The experiments were carried out at atmospheric pressure and a change in the temperature of the first T_1 section from 723 to 873 K, and in the second $T_2 = 973-1223$ K. Contact time $t = 2.5-10.2$ s, the ratio of CH₄:O₂ components varied from 1.5:1 to 2:1. To measure T_2 , a chromel-alumel thermocouple ($d = 50$ mm) was used, placed in a thin quartz case to prevent radical recombination. Two more thermocouples were introduced outside the reactor to determine the temperature of both sections. The thermocouple readings were recorded by KSP-4 potentiometers (accuracy class 0.25).

The soot samples obtained were analyzed by gravimetric and X-ray diffraction methods, as well as by EPR spectroscopy. Gravimetric analysis by the Pregl method of carbon black samples

obtained at low temperature showed the content of carbon, hydrogen and oxygen 90.06; 3.17 and 6.77 %, respectively. In soot obtained at high temperature, the carbon content is usually 96-99 %. The carbon balance was calculated from the results of chromatographic analysis and the mass of the carbon black obtained. The total conversion of methane is 93-95 %, and the yield of solid carbon product (soot) reaches 25%.

The external surface for surfactants is 50 m²/g, and the adsorption surface (for nitrogen adsorption) is 53 m²/g, and since the roughness coefficient is close to unity, this carbon black can be classified as smooth.

Due to the fact that the obtained samples had a complex phase composition, an X-ray quantitative phase analysis was used according to the technique previously used for natural carbon-containing objects. The analysis of diffraction spectra (DRON-1.5 with modified collimation, CuK_α radiation) of all the soot studied represents a superposition of three X-ray amorphous phases: an oxygen-containing O phase, characterized by the position of 002 peaks at $\theta_1 = 3.7^\circ$, a Boghedov or hydrocarbon B phase with $\theta_2 = 9.4-10^\circ$ and a prographite crystalline G phase with $\theta_3 = 12^\circ$. A comparative analysis showed that the diffraction spectra of the studied carbon blacks significantly differ from industrial samples of carbon black and, above all, by the presence of O and B phases in them. On the other hand, the composition and quantitative ratio of X-ray phases turn out to be close to natural coal formations - anthracites. A quantitative analysis revealed a close composition of all the soot studied, with the content of the O phase ranging from 12 to 14%, the B phase from 27 to 31% and the G phase from 57 to 60%. The diffraction coefficient characterizing the phases, $M = 63-75\%$.

The results of x-ray analysis of soot samples are given in table 13.1. The values of the coherent scattering region L_a , L_c and the values of d_{002} characterizing the structure of the carbon black packet of which the sample particle is composed are calculated from the X-ray diffraction pattern. Here, L_a is the diameter of the carbon black package, L_c is its height and d_{002} is the distance between two adjacent layers in the carbon black package.

Table 13.1.

The results of x-ray analysis of soot samples

T_2 , K	t, s	L_a , A	L_c , A	d_{002} , A	Number of flat lattices	Type of sample
973	7	54	15,5	3,64	4	Soot
1003	7	50,7	22	3,62	6	
973	7	42,7	24,3	3,55	7	Pyrocarbon

The resulting low temperature soot has a large amount of volatiles. When extracting the studied soot, it was found that from 20 to 30% of the substance passes into the extract. From the data of chromatographic group analysis it follows that the extract contains up to 70% polyaromatic hydrocarbons, up to 17% resins, 10-11% asphaltenes and 1-2% paraffinic and naphthenic hydrocarbons.

The resulting carbon blacks were studied by ESR. In the table 13.2 shows the heights of the peaks h and the mass of the sample R of soot and pyrocarbon. Evacuation of samples weakly affects the width of the ESR signals. The volume of samples for analysis is the same for all samples. Soot deposits on the walls of the upper part of the second section of the reactor are pyrocarbon (1-3%), which has a more ordered structure of flat lattices than soot.

Table 13.2.

The results of ESR analysis of soot samples

Material type	T_2 , K	h , mm	P , mg	h/P , mm/mg
soot	963	158	2,13	74,178

	1193	430	9,0	47,77
pyrocarbon	963	115	2,42	47,52
	1193	11	10,13	1,067

With increasing temperature of the second section of the reactor, the number of unpaired electrons in soot decreases sharply. So, when T_2 changes from 1193 to 963 K, the concentration of unpaired electrons decreases by more than 1.5 times. In the case of pyrocarbon, the number of radicals under the same conditions drops by almost 45 times. With an increase in the reactor temperature by 230 K, a more crystalline structure forms, accompanied by a decrease in the concentration of defects, and in the case of pyrocarbon this decrease is more drastic.

Literature

1. Henning B. Soot Formation in Combustion: Mechanisms and Models. Springer London, Limited, 2011. – p. 606.
2. Bockhorn H. Soot Formation in Combustion: Round Table Discussion / Ed. Heidelberg Springer Verlag, 1994.
3. Mansurov Z.A. Combustion, Expulsion and Shock Waves. Vol.48, №5, P. 561-569, 2012.