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# The Role of Chain Processes in Cool Flames and Soot Formation#

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| Article info | Abstract |
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| | The 125th anniversary of Academician N.N. Semenov, the great natural scientist of the 20th century, is a significant event for the world scientific community. With his discoveries and tireless scientific, organizational, pedagogical, and social activities, he made an invaluable contribution to the formation of chemical physics and to the development of physics, chemistry, and biology. Nobel Prize laureate, academician N.N. Semenov played a huge role in the creation of the Department of Chemical Kinetics and Combustion of the Al-Farabi Kazakh National University and the Institute for Problems in Combustion. Contacts with the disciples of Academician N.N. Semenov made it possible for the researchers of the Institute for Problems in Combustion to discuss their candidate and doctoral dissertations at the seminars of the Institute of Chemical Physics in Moscow. With the support of N.N. Semenov, Ya.B. Zel'dovich, and A.G. Merzhanov, All-Union Symposia on Combustion and Explosion (1980 in Alma-Ata) and on Structural Macrokinetics (1984 in Alma-Ata) were organized. The article provides an overview of the author's works on studying the structure of the front of cool flames of diethyl ether and butane, the preflame zone of normal propane flames, and soot formation during combustion of hydrocarbons. The phenomenology, kinetics and mechanism of soot formation, and the influence of various factors on the formation of polycyclic aromatic hydrocarbons, carbon nanotubes, fullerenes, graphene, and soot are considered. |

## 1. Introduction

In the introduction to the collective monograph "Chemical Kinetics and Chain Reactions" [1], dedicated to the 70th anniversary of Academician N.N. Semenov, it is noted that N.N. Semenov showed what a great role in the chemical process plays the formation of chemically active intermediate atoms, radicals and relatively atoms, radicals, and relatively stable compounds. N.N. Semenov drew the attention of scientists to the role of labile particles, which revolutionized the thinking of chemists and forced them to consider many complex chemical processes differently.

N.N. Semenov has always paid great attention to the creation and application of the most modern physical methods for the study of chemical processes, realizing that this is a necessary condition for penetrating the essence of a chemical phenomenon [2, 3].

The present article gives a brief review of the author's works in the field of studying the structure of the cool flame front, the pre-flame zone of hydrocarbon flames based on data on the distribution of H atoms and peroxide radicals in the flame front, oscillatory cool flame oxidation, and soot formation in fuel-rich flames.

## 2. Low-temperature zone of the hydrocarbon flames. Cool flames

When studying the structure of the flame front, the nature of the distribution of atoms, radicals, and stable intermediates in the pre-flame low-temperature zone of the normal flame front and the front of stabilized cool hydrocarbon flames.

In [4] G.I. Ksandopulo together with his collaborators under atmospheric conditions studied a pre-mixed close to stoichiometric (4.2% propane) propane-air flame. Hydrogen atoms and peroxide radicals were detected and profiles of their concentration in the flame front were obtained. The maximum concentration of hydrogen atoms is fixed near the luminous zone behind the flame front and reaches a magnitude of $1.7 \cdot 10^{17}$ cm$^{-3}$.

The presence of such high concentrations of hydrogen atoms in the glow zone can lead to their diffusion into a fresh mixture and cause chain nucleation and continuation reactions at temperatures close to the initial temperature of the gas mixture. One of the results of such reactions may be the formation of peroxide compounds and radicals:

$$H + O_2 + M \rightarrow HO_2 + M; \qquad (1)$$
$$RH + H \rightarrow R + H_2;$$
$$R + O_2 \rightarrow RO_2;$$
$$H + R \rightarrow R_1 + R_2;$$
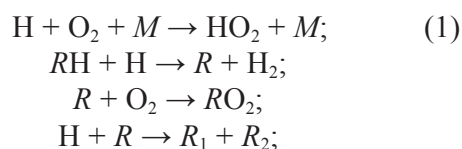
In accordance with the above scheme of reactions, radicals can be detected at the sampling point, as well as due to the reaction (1) occurring on the glass of the cooled finger of the Dewar vessel. The profile of the concentration of peroxide radicals in the cool and hot zones of the flame front with a maximum value of $6 \cdot 10^{14}$ cm$^{-3}$ in the hot zone (+1 mm) was obtained.

The presence of peroxide radicals in the cool zone of the flame front indicates an intense reaction in the pre-flame zone, the peculiarity of which is that it is detected in an area where the temperature increase of the initial gas mixture is only 10–50 °C.

The shape of the electron paramagnetic resonance (EPR) spectra of peroxide radicals frozen out of the cool zone of the flame front corresponds to the shape of the total spectrum of HO$_2$ and $RO_2$ radicals. In the spectra of radicals frozen out of the hot zone (starting from the point $z = 0.1$ mm), the appearance of another well-resolved line is detected, which indicates the freezing of at least three types of radicals.

## Non-isothermal cool diethyl ether flames

Temperature and peroxide radical profiles were obtained when studying two-stage (12.5% and 18% ether) and one-stage (32% ether) cool flames of diethyl ether with air stabilized on a flat burner [5]. A method of cool flame stabilization at a given distance from the burner matrix was developed, which allowed us to study the effect of the heated matrix surface.

Comparison of the EPR spectra of samples taken from the luminous zone located at different distances from the matrix indicates that in the case when the flame front is closer to the matrix, a line-splitting characteristic of HO$_2$ radicals is observed in the EPR spectrum, and indicates the overlap of two types of radicals.

Figure 1 shows the profiles of the concentration and temperature of peroxide radicals in the front of a two-stage flame of diethyl ether (18% ether), from which it can be seen that the maximum concentration of radicals is in the front of the cool flame and is $30.0 \cdot 10^{13}$ cm$^{-3}$, which is 6 times more than in the front of the blue flame. This distribution of the concentration of radicals is apparently because radicals with a small molecular weight are formed behind the cool flame front, the freezing temperature of which is lower than the temperature of liquid nitrogen.
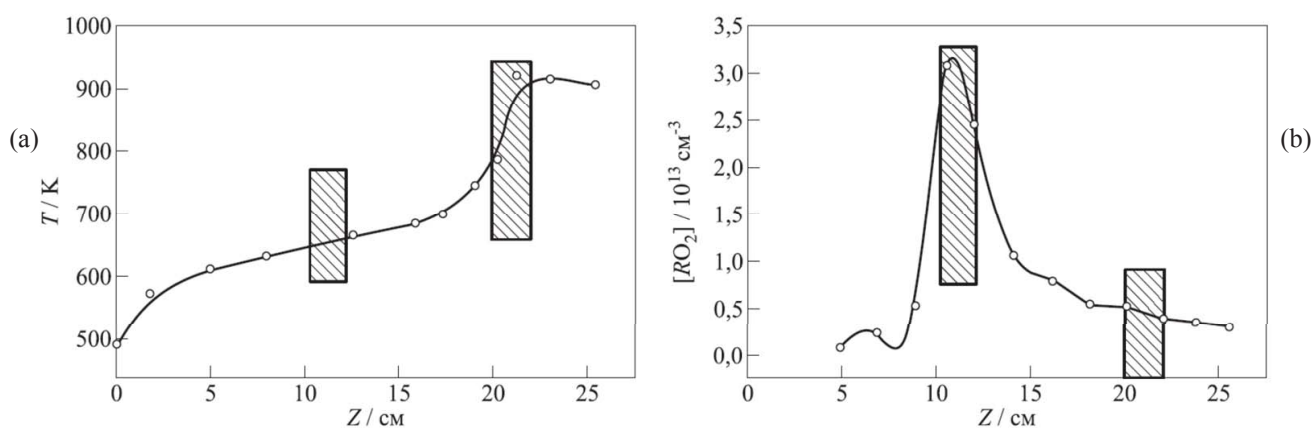


Fig. 1. Profiles of temperature (a) and concentration (b) of peroxide radicals. The shaded areas correspond to the fronts of cool and blue flames [5].

In the one-stage ether-rich (32% ether) flame, the maximum concentration of peroxide radicals is $8.1 \cdot 10^{13}$ cm$^{-3}$, and in the two-stage (12.5% ether), it is $7.0 \cdot 10^{12}$ cm$^{-3}$ [5].

## 3. Determination of the concentration of hydrogen atoms using the radical capture method

Earlier, G.I. Ksandopulo and his co-workers [6] detected hydrogen atoms in the low-temperature zone of hot flames by the loss of tetrafluorodibromoethane, which was introduced as an additive in the initial mixture. There are no data on the direct detection of H atoms in cool hydrocarbon flames, although their presence can be expected. Apparently, this is due to the high reactivity of hydrogen atoms and their relatively low concentration, due to which, at large distances from the sampling zone to the detection site, H atoms either have time to recombine on the sampling walls or react with unreacted oxygen or with other compounds almost inactivation-free. For the detection of hydrogen atoms in stabilized cool flames, it seems inexpedient to introduce jointly an inhibitor additive with the combustible mixture, since thermal decomposition reactions of the inhibitor are possible at preheating temperatures.

In connection with the above, the method of radical capture with additive feeding immediately after sampling was used for the detection of H atoms [7]. To detect H atoms, a method combining the radical capture method [8, 9] and additive feeding near the sampling point was used. Carbon tetrachloride was used as an additive for capturing H atoms followed by determining the concentration of chlorine ions by amperometric titration [10]. The installation consists of a CCl$_4$ vessel, a CCl$_4$ heating furnace, a quartz probe for sampling from the flame, a capillary for feeding CCl$_4$ and a trap for freezing the sample. The diameters of the hole and the probe and capillary are the same and equal to 70 microns. Freezing was carried out with liquid nitrogen. Based on the optimization of experimental conditions, the supply of CCl$_4$ was carried out at a furnace temperature of 520 K and constant stirring; the sampling time is 1 h, the volume of the sampled sample is 0.2–0.3 ml. In the obtained sample after defrosting, using the method of amperometric titration, the concentration of chlorine ions was determined, which is equal to the concentration of H-atoms:

$$C_{\text{H}} = \frac{C_{\text{Cl}}}{\text{ЭCl A(H)} 100} \cdot 6{,}023 \cdot 10^{23}.$$

Then the concentration of hydrogen atoms was found in 1 s at the sampling point according to the formula:

$$[\text{H}] = \frac{C_{\text{H}}}{Q\tau},$$

where [H] is the concentration of H-atoms, particle/cm$^3$; $Q$ is the probe throughput, cm$^3$/s; $\tau$ is the sampling time, s.

When studying the cool flames of hexane and butane, hydrogen atoms were found, the concentration of which reaches $10^{11}$–$10^{12}$ cm$^{-3}$. To assess the role of hydrogen atoms in low-temperature hydrocarbon conversion processes, let us compare the interaction rates of the initial hydrocarbon with the peroxide radical and the hydrogen atom:

$$R\text{H} + \text{H} \xrightarrow{K_1} R + \text{H}_2 ;$$

$$R\text{H} + RO_2 \xrightarrow{K_2} R + R\text{OOH} .$$
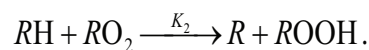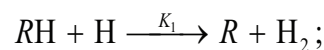
The kinetic data of these reactions are taken from the review [11] for a temperature of 600 K corresponding to our experimental conditions, the value of RO$_2$ corresponds to the concentration of peroxide radicals in a cool flame of diethyl ether (see Fig. 1) at a temperature of 600 K [5]:

$$\frac{W_1}{W_2} = \frac{K_1[\text{H}]}{K_2[RO_2]} =$$

$$= \frac{3{,}1 \cdot 10^{14} e^{-35600/(R \cdot 600)}}{3{,}2 \cdot 10^{11} e^{-68900/(R \cdot 600)}} \frac{1{,}4 \cdot 10^{11}}{2{,}2 \cdot 10^{14}} = 4{,}8 \cdot 10^2 .$$

As can be seen, despite the fact that the concentration of hydrogen atoms is 1000 times less than the concentration of peroxide radicals, fuel conversion reactions involving H-atoms proceed 480 times faster. This fact is convincing proof of the correctness of the assumption about the significant role of hydrogen atoms in cool-flame oxidation reactions, put forward by G.I. Ksandopulo and his colleagues [6, 12].

It should be noted that a joint examination of the temperature profiles and concentrations of hydrogen atoms and peroxide radicals leads to the conclusion that there is a narrow subzone in the pre-flame region adjacent to the luminous zone of
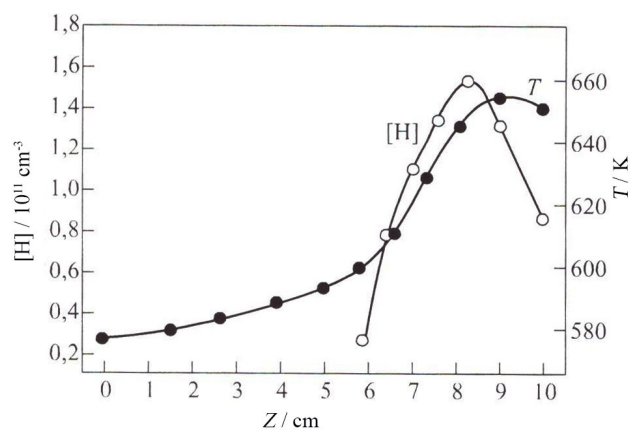
Fig. 2. Profiles of temperature and hydrogen atom concentration: $T_1$ = 443 K; $T_2$ = 730 K; $C_4H_{10}$ : $O_2$ = 1 : 2 [7, 13].

cool flame, which is determined mainly by the reactions of hydrogen atoms and a wider subzone, where reactions involving less active radicals, including peroxide radicals, are significant [7, 13].

Figure 2 shows the profiles of temperature and concentration of hydrogen atoms in the front of a flat cool flame of butane. It can be seen that the maximum concentration of H-atoms is somewhat ahead of the maximum temperature.

## 4. Oscillatory mode of cool hydrocarbon flames

Various modes of low-temperature oxidation of hydrocarbons are known – modes of stable, damped oscillations and stationary cool flames [5, 9, 14–17]. There is no doubt that the general scheme of oxidation in all modes of cool flames is represented by the same reactions, free radicals and stable intermediates, It is natural to assume that both in the mode of stationary cool flames and in the mode of oscillations, radicals play an essential role. In the oscillatory mode, the detection and study of radicals by the EPR method is hampered by the inertia of the method.

In [15, 16], differential thermocouples were used to detect fluctuations in the concentration of radicals during cool-flame oxidation of propane in the oscillation mode. The oscillations were recorded by a thermocouple probe, which consisted of two chromel-alumel thermocouples ($d$ = 0.005 mm) located at a distance of 9 mm from each other. The thermocouple probe was moved along the axis of the second section of the reactors. The surfaces of the thermocouples were previously passioned with ethyl ether of orthosilicic acid. A multichannel loop oscilloscope H 117 recorded temperature

fluctuations. The design of the thermocouple made it possible to register the temperature at two different points simultaneously, and by the phase shift on the oscillogram, the flame propagation velocity could be calculated. In the study of butane oxidation, a modified two-section reactor was used, where a flat perforated plate [15] replaced the bridge connecting the two sections. Such a reactor can be called a flat flame reactor.

The studies were carried out in a two-section pyrex reactor with an internal diameter of 62 mm, separated by a perforated pyrex plate. The length of the first section $l_1$ = 300 mm, the second $l_2$ = 100 mm. The experiments were carried out at $T_1$ = 468–568 K and $T_2$ = 533–583 K with a contact time of $\tau$ = 33.2 s and a component ratio of $C_4H_{10}$ : $O_2$ = 1 : 2.

Visual observations carried out in the dark for a pale blue glow of low intensity show that the flame front is a horizontally arranged disc 1–2 mm thick, the spread of which is complex. A flat faintly luminous disk moves from top to bottom with acceleration to a certain point, then there is a change in the direction of movement, while the shape of the luminous zone changes, which is half of the pseudo sphere with an axis coinciding with the axis of the second section of the reactor. The explanation of such a complex movement of the flame front is based on the assumption that initially there is an accumulation of intermediate compounds to a certain critical concentration, upon reaching which a reaction of degenerate branching with heat release occurs, leading to the appearance of a flame front. Since the flame propagation velocity is higher than the linear velocity of the oxidizing mixture, it begins to spread towards the fresh mixture.

In order better to understand the nature of oscillatory processes, it is advisable to study the behavior of radicals. Since the use of the EPR method for these purposes is impossible due to its inertia, we used the differential thermocouple method to study the behavior of radicals. The thermocouple probe for determining the presence of radicals in the reaction zone consisted of three chromel-alumel thermocouples ($d$ = 0.005 mm), separated at the same level. One of them was intended for temperature registration, and the other two included differentially – for registration of radicals. One of the thermocouples included was differentially coated with LiCl solution in ethyl alcohol. The experiments were carried out at $T_1$ = 443–493 K, $T_2$ = 650–720 K and the contact time $\tau$ = 50–130 s. The composition of the mixture ($C_4H_{10}$:$O_2$ = $P$) varied from $P$ = 0.5 to 4 after 0.5 units.
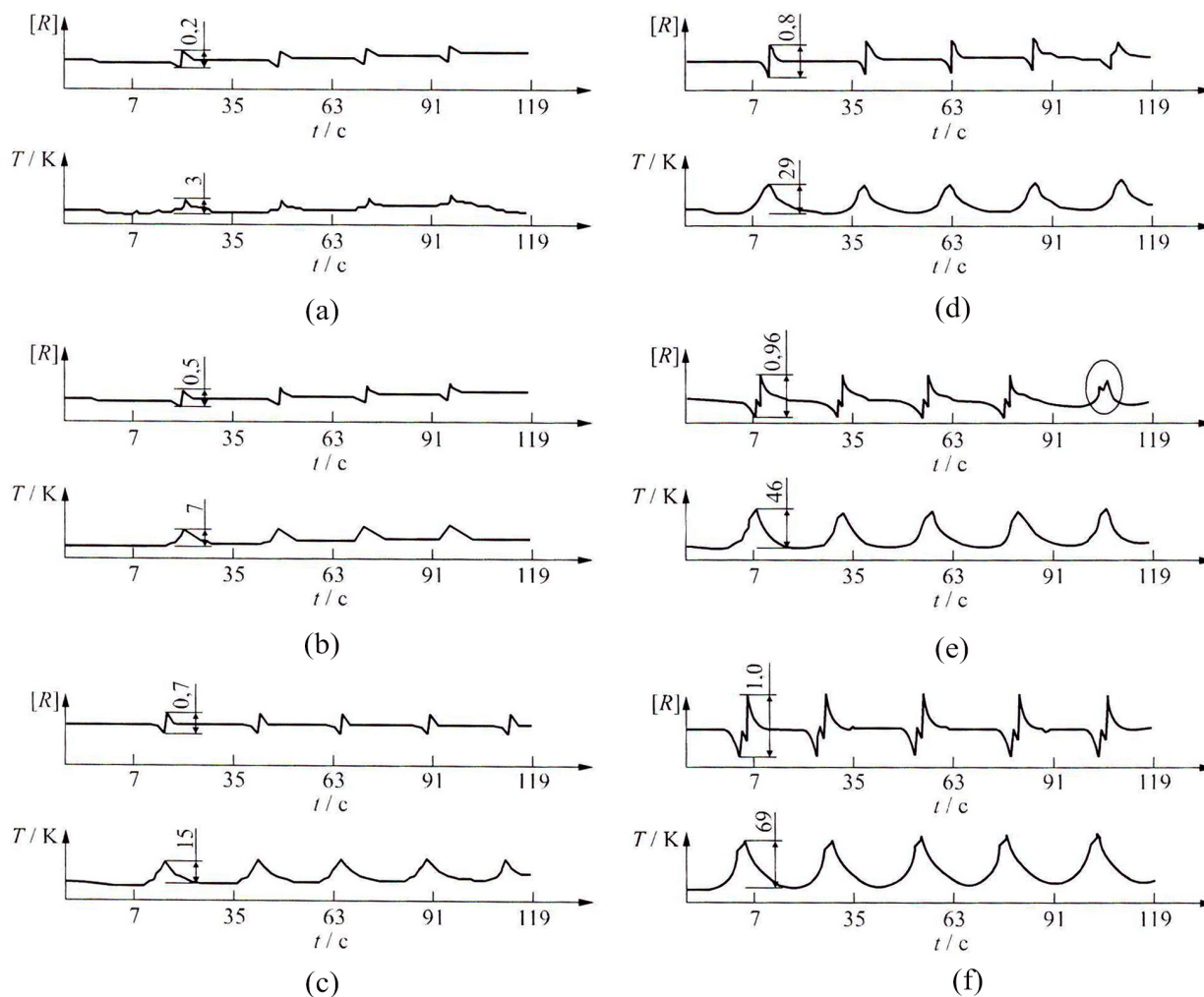
Fig. 3. Time histories of temperature and radical concentration in the mode of steady-state oscillations along the axis of the second section of the reactor ($T_1$ = 453 K, $T_2$ = 673 K, $\tau$ = 60 c. ($C_4H_{10}$ : $O_2$ = 1 : 2) [16]: (a) $x$ = 5 cm; (b) 6; (c) 7; (d) 8; (e) 9; (f) x = 10 cm.

Figure 3 shows the oscillograms of temperature changes and the concentration of radicals at various points in the second section of the reactor. Since the flame front occurs in the upper part of the reactor, and the disappearance of luminosity is observed at $x$ = 5 cm, the change in temperature and concentration of amplitude radicals on the oscillograms gradually decreases to zero with a simultaneous change in the waveform. At $x$ = 5 cm, the amplitude of temperature fluctuations is approximately 3 K, and fluctuations in the concentration of the thermocouple probe are not detected in this case (see Fig. 3, a).

The presence of local minima on the curve of changes in the concentrations of active particles can be explained by the desorption of particles previously sorbed on the junction surface of a thermocouple treated with LiCl. To confirm this assumption, an experiment was carried out in which

a differential thermocouple was heated (up to the approaches of the flame front) to the temperature of the flame front. When the thermocouple is heated by electric current, the signal changes qualitatively (see Fig. 3, d, oval), minima disappear and two clearly defined maxima are observed, i.e. E., as expected, when the thermocouple is heated, particles desorption occurs from the surface of the thermocouple.

The desorption of some compounds that appear to be present in the reaction mixture in front of the flame front ($C_4H_{10}$, $O_2$, $N_2$) has been evaluated, the desorption of which leads to a negative value of the differential thermocouple readings. According to estimates (using the value of the adsorption heat of 10–20 kcal/mol), the signal decrease should lie within 2–7 K, which is in good agreement with the experiment.
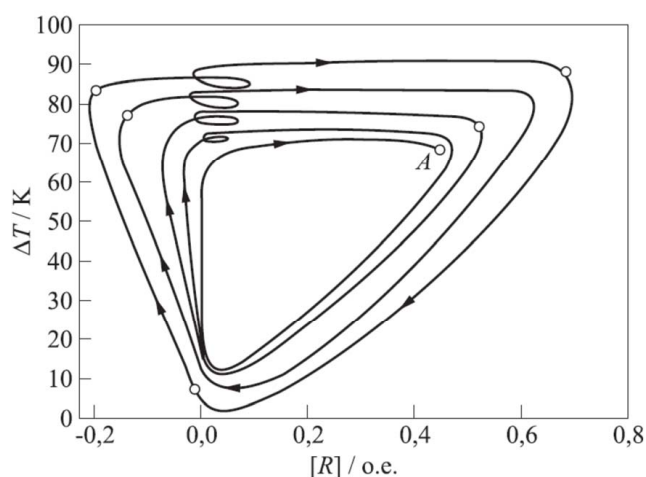
Fig. 4. Phase portrait of butane oxidation in the mode of damping oscillations [7, 17].

The phase portrait of the system in the coordinates "reduced temperature – relative concentration of radicals" in the case of stable oscillations or a limit cycle is a closed curve of complex shape (Fig. 4). With unchanged parameters, the system in the mode of stable oscillations passes sequentially all the points of this closed curve arbitrarily long clockwise.

The phase trajectory of the system, when damped oscillations occur in it, is a set of complex curves. Figure 4 shows several curves along which the system moves. With each cycle, the area covered by the curve narrows and transforms into point A. Point A is the stationary state of the system when the flame has stabilized after a series of successive oscillations. Note that Fig. 4 does not depict all the cycles through which the system

passes as it approaches the stabilized flame. Thus, relative measurements of the concentration of radicals in various modes of cool-flame oxidation of butane were carried out. It is established that in the oscillatory mode of cool flame oxidation of butane, a periodic change in the concentration of radicals is observed due to the periodic propagation of the flame front through the combustible mixture. As a result of studies of oscillatory processes during butane oxidation, it is shown that the propagation velocity of a cool flame varies along the length of the reactor and passes through the maximum. It should be noted that such studies are more convenient to conduct in a heated flat flame reactor.

## 5. Soot formation in combustion processes

### Cool-flame soot formation during hydrocarbon combustion and the structure of the flame front

Cool flames, as is known [14], are realized in the temperature range of 500–800 K for long-chain hydrocarbons and 800–1200 K for methane. Soot formation is often observed at the upper temperature boundary of cool flames, but due to the difficulty of studying such flames, it is always possible to get out of the soot formation mode by changing experimental conditions. At the same time, soot formation has never been considered as a transitional phenomenon between cool and hot flames, and low-temperature soot formation itself has not been studied in detail.

In [18], Wagner and his collaborators emphasize that the properties of "cool sooty flames" differ from the properties of hot flames and have common features with the pyrolysis of aromatic

**Table 1**
Extraction of soot obtained at low-temperature combustion of methane and propane (the mass of extracted soot is 1 g; flow rate of methane is 2000 cm³/min; and flow rate of propane is 1600 cm³/min) [20, 21]

| Sample number | $O_2$ consumption, cm³/min | $T_1$, K | $T_2$, K | Weight of dry residue, mg | Dry extract yield, % |
|---|---|---|---|---|---|
| Methane | | | | | |
| 1 | 1150 | 832 | 873 | 223.1 | 22.31 |
| 2 | 1150 | 832 | 873 | 214.0 | 21.40 |
| 3 | 1150 | 832 | 1023 | 177.4 | 17.74 |
| 4 | 1400 | 298 | 289 | 301.5 | 17.74 |
| Propane | | | | | |
| 5 | 2450 | 423 | 773 | 502.5 | 50.25 |
| 6 | 2450 | 423 | 873 | 410.2 | 41.02 |
| 7 | 2450 | 423 | 973 | 220.0 | 22.00 |

compounds. It is pointed out the need for a detailed study of "cool-flame soot particles" to understand the nature and mechanism of low-temperature soot formation. A.A. Mantashyan and co-workers previously observed soot formation during cool-flame oxidation of propane-oxygen mixture in the range of 720–800 K, where soot emission is recorded [19].

***Formation of polycyclic aromatic hydrocarbons in low-temperature sooty flames***

The table shows data on the extraction of soot formed from methane and propane flames [20, 21]. While the highest amount of PCAH of methane soot is 22.31%, in propane soot it is 50.25%. In addition, the table shows that the reactor temperature at which the maximum PCAH content is observed decreased by 100 K during the transition from the methane flame to the propane flame, with a significant decrease in $T_1$. The considered data suggest that in the low-temperature combustion mode of methane and propane, the precursors of soot are PCAH.

When extracting the soot (carbon black) obtained, it was found that from 20% to 30% of the substance passes into the extract. The chromatographic group analysis data shows that the extract contains up to 70% polyaromatic compounds, up to 17% resins, 10–11% asphaltenes and 1–2% paraffin and naphthenic hydrocarbons.

Based on the data presented above, a diploma for the discovery "The phenomenon of low-temperature cool-flame soot formation" #243 from 11.06.2002 [22] was obtained.

Flame can be considered as a chemical reactor for the synthesis of target products. The main feature of processes based on technological combustion is that the target product is formed as a result of the combustion reaction, which proceeds spontaneously at high temperatures at high velocity without energy input from outside, i.e., due to its own heat release. With the development of nanotechnology, new problems of synthesizing nanomaterials in the combustion mode arise.

Soot formation, which is characteristic of fuel-rich flames, is important in connection with environmental problems and the production of various materials used as a filler [23]. Recently, the study of the mechanism and kinetics of soot formation has intensified in connection with the production of alternative fuels from plant raw materials. It is important to know the general regularities of fuel transformation into soot particles regardless of the fuel molecular weight. To date, considerable experimental material on soot formation processes has been accumulated and various phenomenological models have been proposed [23–25]. In spite of this, there are still many uncertainties in the mechanism of soot formation. Even in simple cases, for example, the homogeneous pyrolysis of hydrocarbons, there is no complete understanding of the process, because it is associated with a large number of fast, parallel reactions leading to the formation of a solid phase – soot particles (for example, the conversion time of methane with a molecular weight of 16 a.m.u. to soot particles with a molecular weight of over $10^6$ a.m.u. is $10^{-4}$–$10^{-2}$ s). It should be noted that these fast reactions occur in a flow, i.e., with intense transport of particles with a parallel increase in their molecular weight [23, 25, 26].

It should be noted that the study of soot formation in the last 40 years mainly concerned environmental problems related to air pollution during the use of various fuels. It is known that soot affects the optical properties of the atmosphere, the global climate and human health. However, with the development of nanoscience, combustion came to be considered as a method of synthesizing nanomaterials.

Is there a connection between chain reactions and nanochemistry? Obviously, the basis and driving force of these two phenomena is the participation of free radicals or defects in the case of solid-phase reactions. Thus, the formation of nanoparticles from atoms is characterized by the concept of self-assembly. Self-assembly (self-organization) is the spontaneous process of forming spatial or temporal structures from individual components' of highly non-equilibrium open systems. Bottom-up synthesis of nanomaterials is a striking example of rapid chain reactions of nanoscale particle formation. The growth of a carbon black nanoparticle to 50 nm – which is 1 million carbon atoms – takes only $10^{-3}$ s, i.e., the chain reaction of polymerization proceeds at an enormous rate.

## 6. Fullerene formation in a flame

Fullerenes $C_{60}$ and $C_{70}$ were identified in 1985 and obtained in macroscopic quantities in 1990, in both cases by arc-discharge evaporation of graphite [27]. Fullerene ions were detected in flames in 1987, and in 1991, $C_{60}$ and $C_{70}$ were extracted in significant amounts from flames and spectroscopically identified.
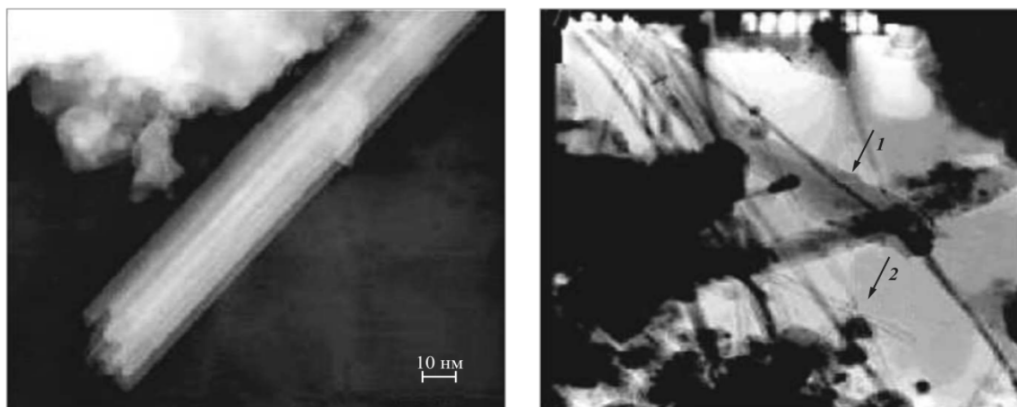
Fig. 5. Electron microscopic images of the sample: 1 – carbon nanotubes; 2 – in a carbon shell [30].

Howard obtained significant amounts of $C_{60}$ and $C_{70}$ in pre-mixed laminar soot-forming flames of benzene and oxygen at low pressures [28].

These data became the basis for the development of an alternative method for producing fullerenes in the hydrocarbon combustion mode. The studies were performed during the combustion of a premixed $C_6H_6/O_2/Ar$ flame for the conditions corresponding to the maximum yield of fullerenes. Processing of the experimental data on determining the yield of fullerene $C_{60}$ revealed the advantage of the ring electrode compared to the needle electrode and showed that the highest yield of fullerene $C_{60}$ (~ 15%) was observed when it was located in the middle part of the flame (L = 4 cm) [7, 29].

## 7. Formation of carbon nanotubes in the flame

The most promising method for the production of carbon nanotubes (CNTs) is the flame method. When the flame is used to synthesize carbon nanoparticles, part of the fuel is used to heat the mixture and part is used as a reagent, which makes this method more economical compared to the methods based on electricity, hydrocarbon pyrolysis, or graphite arc evaporation.

In [30] the results of a diffusion propane-oxygen planar flame stabilized on a burner with counter flows at atmospheric pressure are presented. Two counter flows formed a flat flame. The flame was surrounded by an external flow of nitrogen from the burner matrices. A catalyst solution $(Fe(CO)_5$ or an alcohol solution of nickel nitrate) was sprayed with an ultrasonic atomizer and fed through a metal nozzle into the flame on the fuel side. The resulting products were deposited on the reactor walls and trapped in liquid nitrogen traps. The temperature in the reactor was measured with a thermocouple and in the flame with an Iron Ultimax pyrometer.

Figure 5 shows that the samples contain agglomerates of soot, among which there are metallic particles. It was found that under certain experimental conditions it is possible to form well-ordered bundles of carbon nanotubes with a diameter of 20–30 nm.

## 8. Formation of a superhydrophobic carbon surface in the flame

An experimental study of soot deposition on a substrate of silicon and nickel during combustion of the propane-oxygen mixture was carried out [31]. Figure 6 shows a photo of the experimental setup and a liquid drop on a superhydrophobic surface.

When a drop of water was applied to the disk, which was kept in the flame for 4 min, the surface of the disk revealed hydrophobicity, and the hydrophobicity was very stable. The external contact angle (see Fig. 6) was in the range 152.4°–157.1° for all cases. The same drops of water were applied to the hydrophilic surface of silicon, which has an external contact angle of 50.1°.

To reveal the effect of the electric field on the hydrophobicity or hydrophilicity of the resulting soot surface, studies with electric field exposure were carried out. When an electric field was applied, soot with a wetting angle > 170° was obtained.

In [32] the synthesis of graphene layers in the benzene-oxygen flame at low pressure was studied. The studies showed that the formation of the graphene layers takes place in the pre-sintered zone, as well as at atmospheric pressure. Figure 7 shows the Raman spectra characterizing the car-
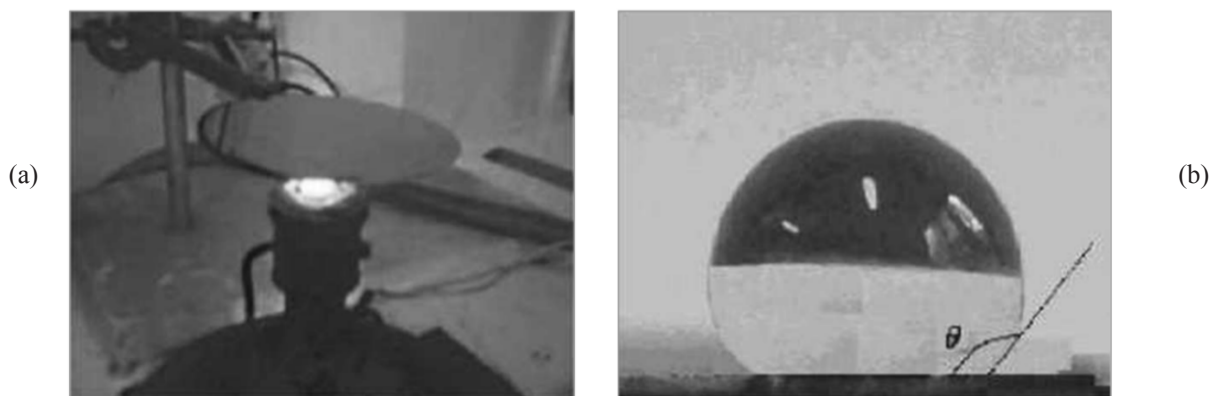
Fig. 6. Photograph of the experimental setup (a) and a liquid drop on the superhydrophobic surface (b) [31].
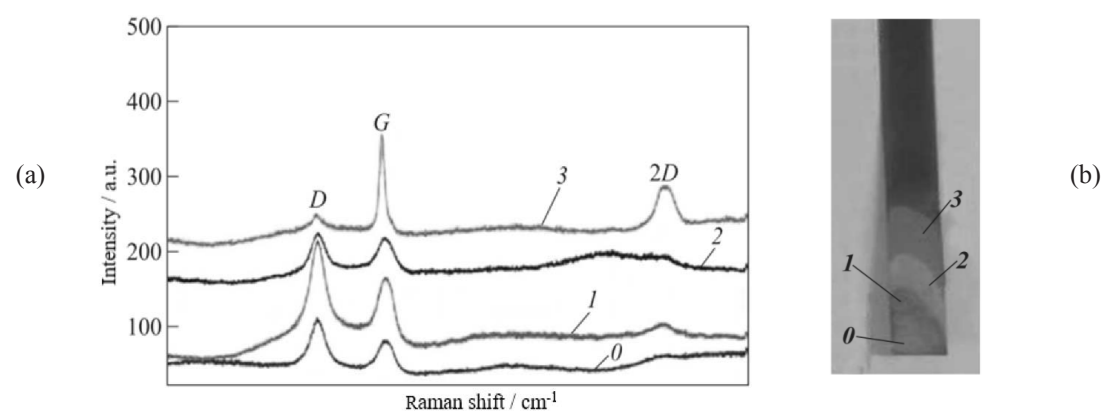


Fig. 7. Raman spectra of carbon structures in the zones of the surface layer (a) and a photograph of the nickel substrate (b) with the indication of the zones formed in the surface layer at low pressure.

bon structures forming on the nickel plate in zones 0, 1, 2 and 3 (Fig. 7, b). In zones 0, 1, and 2 an amorphous carbon structure and graphene layers are synthesized in zone 3. The zone of graphene formation at low pressure is more expanded than at atmospheric pressure. Above zone 3 the soot structure is formed (see Fig. 7 b).

## 9. Phenomenology soot formation

It is known that the formation and synthesis of fullerenes in the traditional method of arc evaporation of graphite and in flames are carried out at pressures below 40 Torr [27, 28, 33]. In [26, 34] experiments were carried out at 40 Torr. The formation of fullerenes occurs at low pressures, and here it is important to consider the steric factor. It should be taken into account that the formation of such a graceful molecule as $C_{60}$ requires the necessary spatial orientation of two $C_{30}$ molecules. There are various models of $C_{60}$ fullerene formation, one of which is realized by the zip-mechanism [35].

The necessary condition for such a mechanism is low pressures. With increasing pressure, i.e. with the transition to atmospheric and higher pressure, where triple collisions prevail, which complicates the formation of fullerenes and single-layer graphenes, the coagulation of PCAH with the formation of soot clusters occurs [36, 37].

Earlier, Bockhorn in 1994 [38] proposed a phenomenological scheme for the reaction of soot formation in homogeneous mixtures of premixed flames, where the intermediate products are PCAH. The sequence of formation of combustion products in fuel-rich flames was shown: CO, $H_2$, $H_2O$, aliphatic hydrocarbons, aromatics with the increasing number of rings, up to coronene, then nucleation of soot particles and their growth to the size of 50 nm.

Taking into account the new data PCAH can be considered as the basis for the formation of fullerenes and graphenes in the flame as precursors to the formation of soot particles. We developed a complete scheme of soot formation [36, 37].
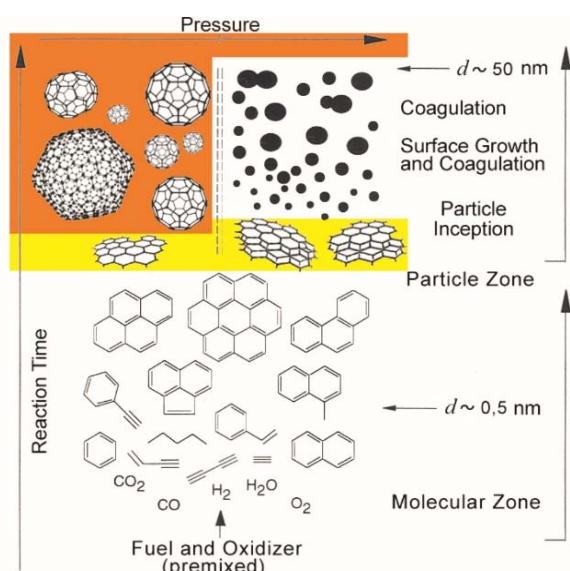
Fig. 8. Scheme of soot formation in a fuel-rich flame [36, 37].

Figure 8 shows the scheme of soot particle formation, supplemented by the stages of formation of fullerenes and graphenes. As shown in the scheme, at low pressures single-layered graphenes are formed, and at atmospheric pressure – multilayered ones.

A scheme for the formation of fullerenes, graphenes and carbon black in rich hydrocarbon flames has been developed, taking into account the pressure. It can be assumed that the synthesis in a flame of fullerenes, graphenes and carbon nanotubes is an alternative technology to the existing methods of synthesis in an electric graphite arc.

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