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Establishment of features of unstable flame propagation using 3D optical spectroscopy and color speed cinematography

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Features of combustion in flame cells caused by hydrodynamic instability were experimentally established. It was found that each flame cell represents a separate chemical reactor; the process of complete chemical transformation occurs in the cell.

In the absence of special conditions, the processes of gas-phase combustion occur under non-stationary currents, density and pressure fluctuations; *i.e.*, these have a non-steady character.[1] For example, according to Landau,[2] a flat flame front is unstable from the hydrodynamic point of view. The aim of this work was to consider gaseous combustion in non-stationary and unstable regimes. These unstable modes can be classified as diffusional-thermal, hydrodynamic and thermoacoustic ones. Diffusional-thermal instability is observed in flames, in which $\mathrm{Le} \neq 1$ (Lewis's number $\mathrm{Le} = D/\alpha$, where D is the diffusion coefficient of the component determining combustion velocity, and α is the heat diffusivity coefficient). This instability results in the existence of cellular flames in lean hydrogen mixtures.[3–5]

Hydrodynamic instability is connected with a difference in the density of the burned-down and initial flammable gas caused by thermal expansion of products; this can lead to the occurrence of cellular structures on a flame front (FF) under certain conditions.[6–8]

Thermoacoustic instability is caused by a feedback between the non-stationary mode of combustion and the acoustic modes of reactor. The criterion of origination of this instability is obtained by Rayleigh, who established that acoustic fluctuations are sustained if the maximum of heat is transferred to the fluctuating gas at the time of its maximum compression.[9]

The knowledge of chemical transformations in the course of unstable combustion is a problem for both the combustion theory advancement and practical applications to combustion intensification and explosion safety. Experimentally, this problem is solved for diffusional-thermal instability[10] under conditions of zero gravity in International Space Station (ISS). It was shown for the first time by Ronney that in lean hydrogen–oxygen mixtures under conditions of zero gravity separate isolated motionless combustion cells arise, *i.e.* separate chemical reactors occur in the combustible environment.[10] Earlier, Zeldovich theoretically predicted[4] that the steady heat and mass conservation equations admit a solution corresponding to a stationary spherical flame, though the same equations in planar geometry provide a solution in the form of a propagating wave. Indeed, in the simplest case of spherical geometry, the solution to steady, free convection diffusion equations for temperature T and chemical species C, $\nabla^2 T = 0$ and $\nabla^2 C = 0$, has the form $c_1 + c_2/r$, where c_1 and c_2 are constants. This form reflects the fact that T and Y are bounded as $r \to \infty$. For cylindrical and planar geometry, the forms are $c_1 + c_2 \ln r$ and $c_1 + c_2 r$, respectively, which are unbounded as $r \to \infty$. Therefore, a spherical flame is admitted, but not a flame cylinder solution.

Direct verification of the hypothesis of Landau was performed by Clanet and Searby.[11] The flat FF shape was kept by means of imposing an acoustic field. Growth rate of two-dimensional perturbations in time was observed after switching off the acoustic field. This experiment illustrates very important interrelation of the major factors causing flame instability, namely, hydrodynamic and thermoacoustic ones.[9]

In this work, by the example of combustion of *n*-pentane–air mixtures, both the spatial distribution of unstable FF and the features of chemical transformation in the flame in a constant volume bomb are established by optical 3D spectroscopy and color high-speed cinematography. The experiments were performed under conditions when the spherical shape of a flame front transforms to unstable flat one after contact of FF with reactor walls.[†]

Before each experiment, the reactor was pumped out with a 2NVR-5D fore vacuum pump. Pressure in the reactor was controlled with a vacuum gauge. Gaseous *n*-pentane from Merck, CO_2 and CCl_4 were chemically pure. Carbon tetrachloride was

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[†] Experiments were carried out in a stainless steel cylindrical reactor 25 cm long and 12 cm in diameter supplied with removable covers and an optical window at the end face (Figure S1, Online Supplementary Materials).[12] The electrodes of spark ignition were placed at the center of the reactor. A previously prepared gas mixture was admitted into the reactor up to a necessary pressure; then, a spark discharge (1.5 J) was triggered. Ignition and FF propagation were detected with an optical 3D spectrometer (hyper spectrometer) and a Casio Exilim F1 Pro color high-speed camera (frequency of shots, 600 s^{-1}). A video file was stored in a computer memory and its time-lapse processing was performed.[13] The 3D spectrometer[14] detected both a narrow strip on the test object (a spatial coordinate) and a spectral wavelength with a two-dimensional optical detector array. The data from the optical detector array were stored in a computer memory with a 300 Hz frequency. The speed video filming of combustion and 3D spectrophotometry were carried out simultaneously.

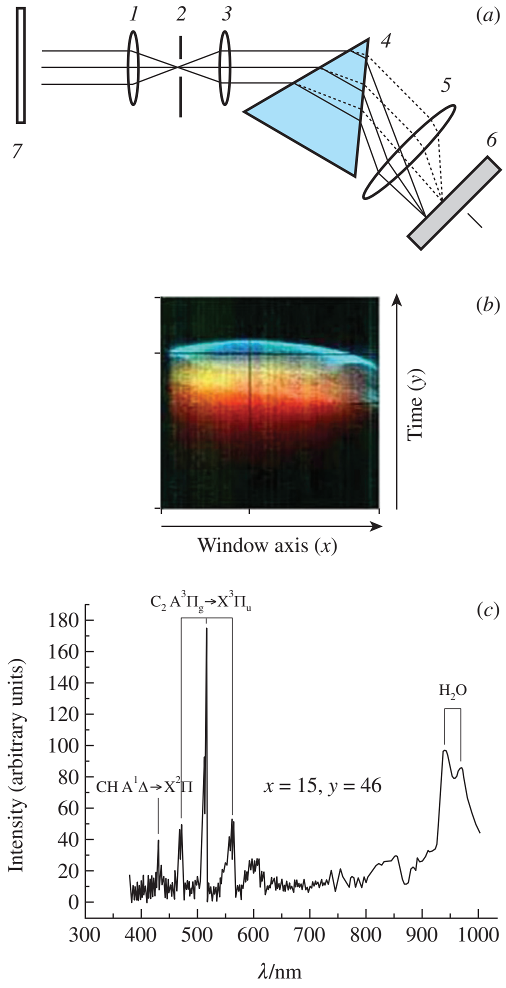

Figure 1 (*a*) Obtaining of 3D spectra. Paths of light beams in a hyper spectrometer: (*1*) entrance lens, (*2*) diaphragm with a slit, (*3*) collimator, (*4*) dispersing element, (*5*) projective lens, (*6*) two-dimensional optical detector array and (*7*) the line of the image formed by a narrow slit of diaphragm. (*b*) Hyperspectral data (hypercube). (*c*) Emission spectrum of stoichiometric mixture of *n*-pentane with air + 10% CO_2 + 1% CCl_4 at 1 atm, in each pixel of the hypercube, depending on the place on the strip and time.

used as an inhibitor of hydrocarbon combustion.[5] The process of hyperspectral recording of a combustion process is shown in Figure 1.[14]

Experiments in the reactor were performed at atmospheric pressure with previously prepared stoichiometric mixtures of *n*-pentane with air and carbon dioxide (CO_2). CO_2 additives made up to 10% and CCl_4 additives made up to 2%. In Figure 2, certain frames of high-speed filming of FF propagation in *n*-pentane–air mixtures in the presence of 10% CO_2 and 1% CCl_4 are presented, from the moment of initiation of the stationary spherical FF propagation until its contact with reactor inner surface. Further FF propagation occurs in the cylindrical part of the reactor in the direction toward the end faces. Upon transition to the combustion in cylinder, cellular combustion proceeds in agreement with published data.[13] Indeed, at a stage of spherical FF propagation, the FF radius grows so quickly that instabilities do not have time to develop; FF is unperturbed.[15] At propagation stage along the cylinder, unstable flat flame arises as the theory predicts.[2] This instability manifests itself in the formation of cellular structures on FF. Formation of cells is characteristic of a certain extent of dilution with inert additive – in fast-burning mixtures (not diluted with inert gas) flame cells do not occur. In the flames of the mixtures diluted with argon, cellular structures do not move in space; thus, the cell size slowly grows.[13] With an increase in the extent of dilution of the stoichiometric mixture by additives of CO_2 and CCl_4 instead of argon, cellular structures move in the direction of gravity (Figure 2, see also ref. 13).

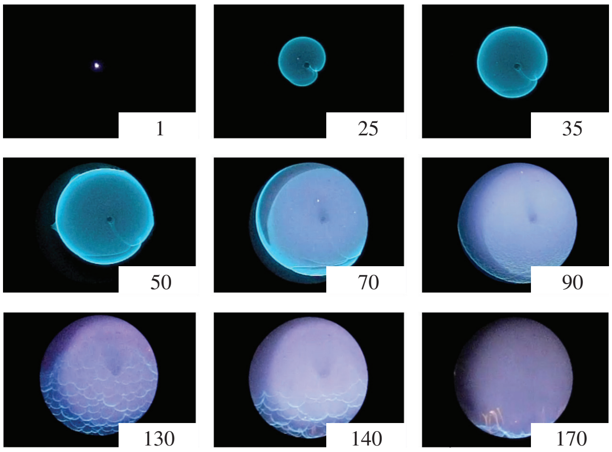

Figure 2 Speed filming of the process of FF propagation in a stoichiometric mixture of *n*-pentane with air + 10% CO_2 + 1% CCl_4 at 1 atm in a stainless steel reactor with a frequency of shots 600 s^{-1}. The figure on a shot corresponds to the number of a frame in high-speed video.

We will specify that one cannot expect the occurrence of both thermal diffusion instabilities (there is no significant distinction in transfer coefficients) and thermoacoustic ones (the velocity of FF is comparably small, and sound vibrations are missing[16]) in stoichiometric flames. Thus, the cellular combustion mode is caused by the gas dynamic instability peculiar to flat flames.[2,13]

The typical frame characterizing cellular combustion of *n*-pentane is presented in Figure 3(*a*). In Figure 3(*b*), the hypercube for this image along a vertical axis is given, and Figure 3(*c*) shows a fragment of this hypercube on which the points of spectral analysis are specified. The spectra recorded from the border and from internal area of one of flame cells are given in Figure 4. Since the mixture contains an inhibitor (CCl_4), the intensity of combustion is lower than that without an inhibitor; accordingly, the heat release is comparably small, therefore 'hot' lines of Na and K atoms, which are usually observed in flame emission spectra, are missing.[5] The spectra obtained agree with literature data and contain the bands of active intermediates and products of hydrocarbon oxidation.[5] These are CH ($A^1\Delta$–$X^2\Pi$) at 431 nm, C_2 (A^3P_g–X^3P_u) (1–0, 0–0 and 0–1 transitions) in a range of 470 to 570 nm[17] and emission bands of water vapor near 950 nm [for example, (1,2,0), (3,0,0)[18]]. Note that CH and C_2 bands belong to the zone of intense chemical transformation (FF zone),[5] and emission bands of water vapor, to the zone of emission of combustion products.

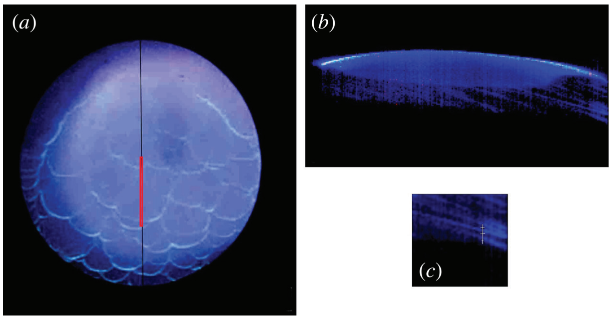

Figure 3 (*a*) Video frame of the cellular combustion of stoichiometric mixture of *n*-pentane with air + 10% CO_2 + 1% CCl_4 at 1 atm, the spatial interval x = 0–200 in which the spectra were recorded is marked by vertical line, (*b*) the hyper spectral image (hyper cube) for better allocation of flame cells and (*c*) the allocated fragment of Figure 3(*b*).

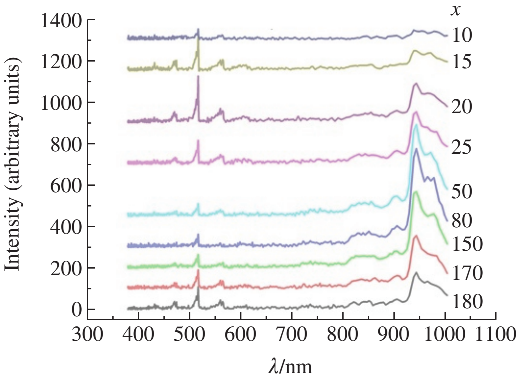

Figure 4 Spectra of combustion of *n*-pentane–air mixture + 10% CO_2 + 1% CCl_4 at 1 atm along a window axis [along the vertical line in Figure 3(*a*)], t = 210 ms from the initiation impulse.

Therefore, by the ratio of intensity of the bands of C_2 radicals to those of water molecules in the spectra, it is possible to make a qualitative conclusion specifying which zone of combustion characterizes the spectrum: FF zone (the zone of intense chemical transformation) or the zone of reaction products. If the relative intensity of C_2 bands considerably exceeds the relative intensity of water vapor bands, the emission spectrum mainly corresponds to FF zone; if the ratio of intensities is inverse, the spectrum belongs to reaction products.

The scanning of emission spectra of the flammable mixture along a window axis, namely, along the coordinate from top to down in the certain interval marked in Figure 3, is shown in Figure 4. The intensities of spectral bands along a window axis change in opposite directions: while relative intensity of C_2 bands has a maximum at x = 20 and 180 (x is the relative spatial coordinate), the intensity of H_2O bands at the same x has a minimum. It means, first, that combustion is nonuniform in space; otherwise, the intensities of C_2 and H_2O spectral bands would both increase or decrease smoothly; *i.e.*, 3D spectroscopy allows us to observe combustion cells in the same way as high-speed filming (Figure 2).

Second, the fact that the intensity of C_2 bands has a maximum at the same values (x = 20 and 180) at which the intensity of H_2O bands has a minimum, means that, at these x values, light is emitted mainly from the FF zone. At the x values at which the ratio of intensities of C_2 and H_2O bands is inverse, light is emitted from the zone of reaction products. It follows from the above that 3D spectroscopy allows us to establish that combustion cells (Figure 3) represent separate chemical reactors; in each of them the process of complete chemical transformation occurs.

Previously it was shown[10] that diffusional-thermal instability in lean hydrogen–oxygen mixtures under conditions of zero gravity manifests itself in the occurrence of separate isolated motionless combustion cells, *i.e.*, separate chemical reactors in the combustible environment. Here, by means of both 3D optical spectroscopy and color high-speed filming, the features of combustion in flame cells caused by hydrodynamic instability were experimentally established for the first time.

Thus, in a combustion cell caused by the instability of any nature (thermal diffusion, hydrodynamic and thermoacoustic ones), the complete cycle of chemical transformations characteristic of the given combustion process occurs.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.11.029.

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