Available online at www.sciencedirect.com
ScienceDirect
*Mendeleev Commun.*, 2011, **21**, 31–33
Mendeleev Communications

# High-speed colour cinematography of the spontaneous ignition of propane–air and *n*-pentane–air mixtures†

**Nikolai M. Rubtsov,*[a] Boris S. Seplyarskii,[a] Kirill Ya. Troshin,[b] Georgii I. Tsvetkov[a] and Victor I. Chernysh[a]**

[a] *Institute for Structural Makrokinetics and Problems of Materials Science, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 495 962 8025; e-mail: nmrubtss@mtu-net.ru*
[b] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2011.01.013

**The spatial development of spontaneous ignition in propane–air and *n*-pentane–air mixtures depends on the state of the reactor surface, namely, an ignition initial centre originates at the reactor surface, and then the flame front propagates from the centre into the bulk with a normal velocity corresponding to the reactor walls temperature and gas mixture composition.**

Data on the spatial development of spontaneous ignition (SI) in combustible gases at contact with a heated surface are of practical and scientific interest for the use of hydrocarbons as fuels in engines and other power devices. The experimental investigation of fuel ignition is usually performed under static conditions when the test mixture is heated with reactor walls. The SI of $2H_2 + O_2$ mixtures at low pressures (~1 Torr) in the vicinity of a lower self-ignition limit is considered homogeneous over the reactor volume.[1] However, the probability of ignition origination near the reactor surface increases with the total pressure of a gas mixture due to an increase in the time of warming up of gas because thermal diffusivity decreases with pressure. It means that, with raising pressure, a one-dimensional problem on SI passes on to the problem on ignition with a heated surface.[2–4]

The data on spatial development of ignition of combustible gases are presented in the literature. The spatial development of ignition in dichlorosilane–oxygen mixtures at 4–500 Torr and 300–400 K was studied[5] using high-speed shlieren cinematography. The SI was shown to originate with the participation of adsorbed active centres at the reactor surface.

Previously,[6] we explored the spatial development of SI in the stoichiometric mixtures of hydrogen, methane and isobutylene with oxygen at total pressures of 10–100 Torr and initial temperatures of 750–1000 K by high-speed colour cinematography. The features of the spatial development of ignition in a branched chain gaseous reaction are determined by the relation of characteristic times of chemical reaction at the temperature of hot walls and the time of warming up of a gas mixture, as well as by the state of the reactor surface. Numerical modeling[6] revealed that the increase in the reaction rate of chain origination allows one to observe a transition from volume ignition to surface ignition both for diffusive and kinetic areas of chain termination. The flux of active centres from the surface provides the non-uniform development of SI in the reactor volume. According to experimental data,[6] homogeneous SI of hydrogen oxidation can be observed only for low pressures (< 10 Torr of $2H_2 + O_2$) in the vicinity of a lower self-ignition limit. However, the ignition of hydrocarbon–oxygen mixtures at the lower limit (~70 Torr) always originates at the reactor surface.

Taking into account the time of warming up is principal as it provides other dependence of induction period on the characteristic size of a system. For example, the maximal measured induction period in SI of $2H_2 + O_2$ mixtures at pressures close to 1 atm is ~30 s.[7] We will estimate the time of warming up of the mixture using the relation $t \approx r^2/2D$, where $r$ is the characteristic size (cm), $D$ is the diffusivity ($cm^2\ s^{-1}$) being close to thermal diffusivity, and $t$ is time (s). For $r = 6$ cm and atmospheric pressure that corresponds to the described[7] experimental conditions, we get $t \sim 36$ s at $D \approx 1.0\ cm^2\ s^{-1}$.[8] Thus, ignition occurs under conditions of non-uniform warming up.

As distinct from experimental conditions in ref. 7, where the reactor was filled with a gas mixture before it was immersed in a hot liquid, in the procedure described in ref. 9 a gas mixture from a buffer volume was allowed to bleed into a heated and pumped reactor to a total pressure of 1 atm. Due to a sharp difference in pressure convective gas fluxes occurred in the reactor leading to reduction of time of an establishment of homogeneous temperature distribution.

By means of the direct measurements[9] of temperature at the centre of the reactor (10 cm in diameter and 10 cm in length) with thin 25 μm thermocouples at atmospheric pressure and 800–980 K it was shown that the time of warming up of a gas mixture does not exceed 3 s. It is much less than the time obtained with the formula considering only conductive heat exchange.

A platinum layer on the reactor surface exhibits a promoting action on the hydrogen oxidation reaction,[10] that is caused by heterogeneous development of reaction chains.[11] The occurrence of these heterogeneous reactions also enhances the probability of spontaneous ignition of a gas mixture at a surface. Hence, the state of the reactor surface is another factor that influences the uniformity of ignition.

This work is aimed at the experimental determination of the place of origination of initial centres of ignition and investigation of the spatial development of ignition in propane–air and *n*-pentane–air mixtures by high-speed colour cinematography.

The experiments were carried out with stoichiometric propane–air and *n*-pentane–air mixtures and a rich propane–air mixture at 600–800 K and atmospheric pressure. A heated stainless steel horizontally placed cylindrical reactor (25 cm in length and 12 cm in diameter) equipped with demountable covers and an optical window in one of the covers was used in the experiments. The design of the heater provided a uniform temperature distribution in

† The electronic version of this article includes video clips for Figures 1(*b*), 2(*a*) and 3(*b*). To view the clips, please follow the instructions in the captions to Figures 1–3.

the reactor volume, which was controlled with a movable thermocouple placed at the reactor surface. Combustion was recorded by means of a Casio Exilim F1 Pro colour high-speed digital camera (300–1200 frames per second), sensitive over the spectral range of 420–740 nm. The pumped and heated reactor was filled with the gas mixture from a buffer volume to atmospheric pressure. An electromagnetic valve was used to open and close gas lines. At the moment of the valve opening, a light-emitting diode was turned on; its flash was recoded by the camera. It allowed us to determine the induction period of SI from a shot sequence for each separate ignition with high accuracy.

Before each experiment, the reactor was pumped out to $10^{-1}$ Torr. Total pressure in the reactor was controlled with a vacuum gauge, and the pressure in the buffer volume, with a manometer. Chemically pure gases were used.

The pressure during combustion was recorded by a pressure transducer. From the time dependence of the visible radius of a spherical flame $R(t)$, the normal flame velocity $Un = [\mathrm{d}R(t)/\mathrm{d}t]/\varepsilon_T$ was calculated. The value of $\varepsilon_T$ was determined from the maximal pressure of combustion $P_b$:[2]

$$P_b/P_0 = 1 + \gamma(\varepsilon_T - 1), \quad (1)$$

where $P_0$ is the initial pressure and $\gamma$ is the ratio of specific heats ($\gamma = 1.2$).[2]

In preliminary experiments, it was revealed that the spontaneous ignition temperature of stoichiometric hydrocarbon–air mixtures at atmospheric pressure is ~25 K lower in a reactor washed with warm distilled water than in the reactor that was not washed with water after ignition. This result means that the regularities of spontaneous ignition at atmospheric pressure depend on the surface state of reactor walls.[11]

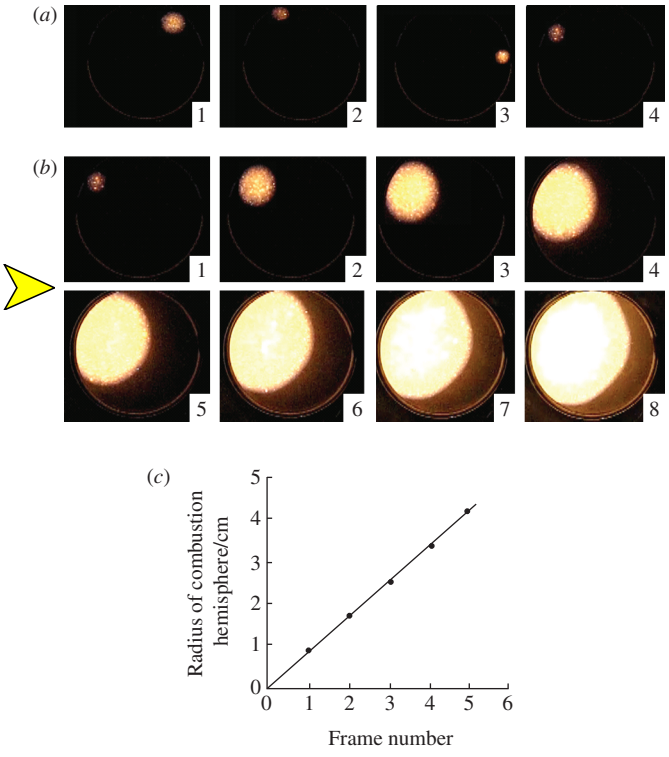


**Figure 1** (*a*) Video images of the initial centres of spontaneous ignition in stoichiometric *n*-pentane–air mixtures in four consecutive experiments at wall temperatures of (1) 650, (2) 643, (3) 645 and (4) 649 K. (*b*) Sequences of video images of the spatial development of ignition in stoichiometric *n*-pentane–air mixture at the reactor wall temperature of 649 K. (*c*) The time dependence of the hemispherical flame visible radius of stoichiometric *n*-pentane–air mixture corresponding to (*b*). 600 shots per second, $P = 1$ atm. A video clip for Figure 1(*b*) is acceptable in the electronic version of this article. To start playback of the video, please click on any image of Figure 1(*b*).

All experiments on the high-speed registration of spontaneous ignition testified to the fact that an initial centre of ignition originates at the reactor surface; in each subsequent experiment under the same conditions, the site of origination of the initial centre varies [Figure 1(*a*)]. Bright points in Figure 1 are caused by the emission of hot soot particles in the flame zone.

Before each experiment, the reactor was washed by warm distilled water as the chemical activity of various sites of surface changes from one ignition to another.[11,12] Note that, at the initial stages of combustion, the development of the initial single centre leads to propagation of the flame front of a hemispherical shape. Hence, the velocity of flame propagation can be determined directly from the experimental sequences of video images. It is obvious that the observed pattern of combustion origination corresponds to a regime of ignition with a heated surface.[2–4] The basic feature of ignition is that it occurs at separate surface sites at a uniform temperature of the reactor surface. The sequences of video images of spatial development of ignition in a stoichiometric *n*-pentane–air mixture at the reactor walls temperature of 649 K corresponding to the development of initial centre presented in Figure 1(*a*) are presented in Figure 1(*b*). The hemispherical flame front develops from the initial centre of ignition; then, the front becomes asymmetric as new ignition centres occur. In these series of experiments, the induction period was > 7 s; therefore, the uniform warming up of a gas mixture in accordance with direct measurements[9] was almost provided for, because the fast bleeding-in reduces the time of warming up of a gas mixture (see above). Therefore, combustion originates at the surface of the steel reactor even under conditions of almost homogeneous warming up of a gas mixture.

As can be seen in Figure 1(*b*) the flame front has a hemispherical shape; the time dependence of the flame radius can be easily estimated [Figure 1(*c*)]. The experimental value of $\varepsilon_T$ is 3.35; then, the normal flame velocity $Un = [\mathrm{d}R(t)/\mathrm{d}t]/\varepsilon_T$ determined from the change of visible radius of a spherical flame [Figure 1(*c*)] using equation (1) is 150 cm $s^{-1}$ in good agreement with published data.[13]

The spatial development of ignition in rich propane–air mixtures (12.3% $C_3H_8$ in air) at pressures of 0.65–0.69 atm was investigated. Induction periods in rich mixtures are as long as tens of seconds;[14] therefore, the uniformity of warming up of a gas mixture is attained. In Figure 2, the sequences of video images of development of the initial centres of ignition corresponding to induction periods of 12.6, 23.7 and 43.2 s are exhibited. The increase in induction periods was provided by decreasing the total pressure of a gas mixture from 0.69 to 0.65 atm. As can be seen in Figure 2, the ignition of a rich mixture also originates at the reactor surface. Note that, in three consecutive experiments (Figure 2), the initial centres of ignition originate at different sites of the reactor surface. The initial centres of ignition originate at the surface both when the reactor surface is treated with hot distilled water (Figure 1) and when it is not treated (Figure 2); *i.e.*, the process of ignition at atmospheric pressure begins with appearance of an initial centre at the surface independently of the surface state, self-ignition in the volume is not observed anyway.

Experiments with rich mixtures demonstrate the possibility of multicentric surface ignition [see Figure 2(*b*)]. Blurring of the flame front and bright points round the basic image (Figure 2) are caused by the occurrence of a nonuniform thin soot film on the optical window upon combustion of the mixture.

There are chemically active surface sites, which are capable to initiate ignition in the combustion of stoichiometric hydrocarbon–air mixtures at higher temperatures. Figure 3 manifests the sequences of video images of the spatial development of ignition in stoichiometric *n*-pentane–air mixture at reactor wall temperatures of 652 and 653 K with induction periods of 4.2 and

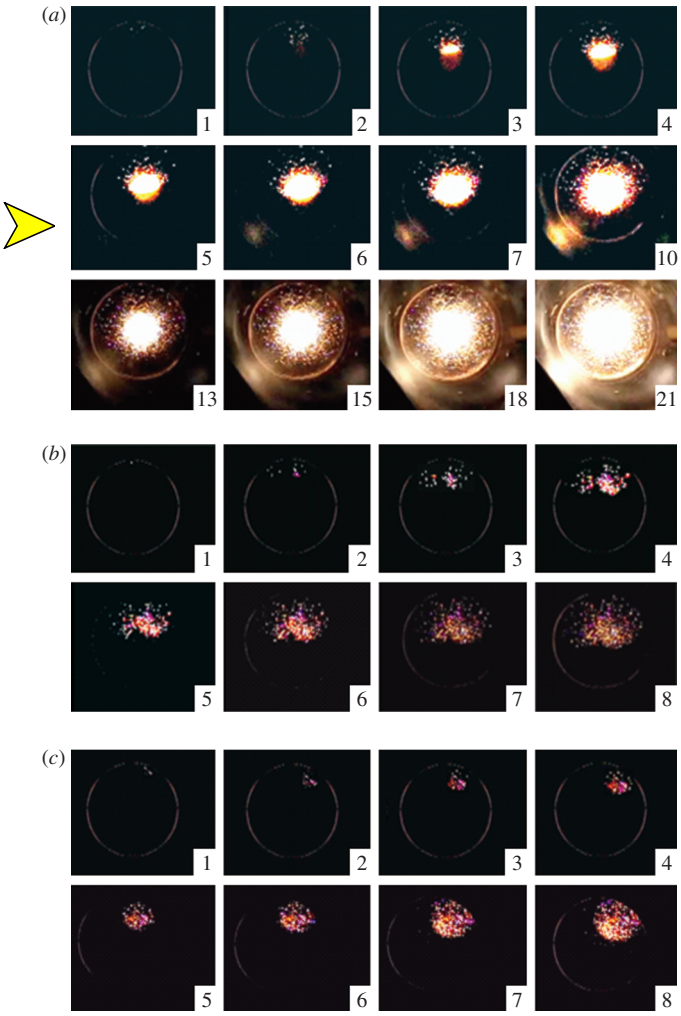


**Figure 2** Sequences of video images of development in time of the primary ignition centres of a rich 12.3% propane–air mixture at induction periods of (*a*) 12.6 s ($P$ = 0.69 atm, $T$ = 763 K), (*b*) 23.7 s ($P$ = 0.67 atm, $T$ = 737 K) and (*c*) 43.26 s ($P$ = 0.65 atm, $T$ = 716 K). 600 shots per second. A video clip for Figure 2(*a*) is acceptable in the electronic version of this article. To start playback of the video, please click on any image of Figure 2(*a*).

3 s, respectively. Initial ignition centres can occur independently in the immediate vicinity of each other, as well as be widely separated.

Thus, the ignition of the investigated hydrocarbon–air mixtures at atmospheric pressure begins with the appearance of an initial centre at the most chemically active site of surface which initiates the propagation of hemispherical flame front with the normal velocity corresponding to the temperature of the reactor walls and gas mixture composition; *i.e.*, the process includes the stages of warming up, local ignition and flame propagation. Therefore, the process consists in ignition with chemically active heated surface.

The results of this work should be taken into account in the interpretation of experimental data on spontaneous ignition at elevated pressures, in particular, at the third self-ignition limit of hydrogen oxidation.[7] It is possible to assume that the latter occurs within the regime of ignition with chemically active heated surface, *i.e.*, has a localized character and demands other approach for the explanation of regularities observed.

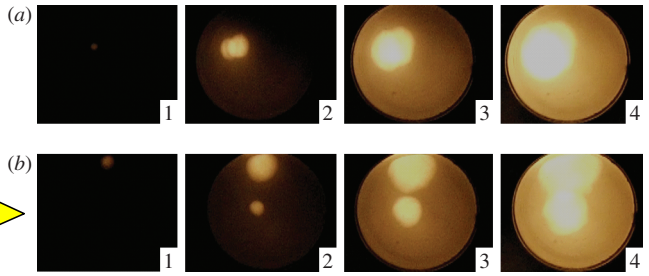


**Figure 3** Sequences of video images of the spatial development of ignition in a stoichiometric *n*-pentane–air mixture at reactor wall temperatures of (*a*) 652 and (*b*) 653 K. 600 shots per second. $P$ = 1 atm. A video clip for Figure 3(*b*) is acceptable in the electronic version of this article. To start playback of the video, please click on any image of Figure 3(*b*).

We are grateful to Professor V. V. Azatyan (Institute for Structural Macrokinetics and Materials Science, RAS) and Professor A. A. Borisov (N. N. Semenov Institute of Chemical Physics, RAS) for useful discussions.

This work was supported in part by the Russian Foundation for Basic Research (project nos. 08-03-01034-a, 09-03-00622-a and 10-08-00305-a).

## References

1 N. N. Semenov, *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (*On Some Problems of Chemical Kinetics and Reactivity*), Academy of Sciences of the USSR, Moscow, 1958, p. 685 (in Russian).

2 Ya. B. Zel'dovich, G. A. Barenblatt, V. B. Librovich and D. V. Machviladze, *Matematicheskaya teoriya rasprostraneniya plameni* (*Mathematical Theory of Flame Propagation*), Nauka, Moscow, 1980 (in Russian).

3 D. A. Frank-Kamenetsky, *Diffusiya i teploperedacha v khimicheskoi kinetike* (*Diffusion and Heat Transfer in Chemical Kinetics*), Nauka, Moscow, 1967 (in Russian).

4 A. G. Merzhanov and B. I. Khaikin, *Teoriya voln goreniya v gomogennykh sredakh* (*Theory of Combustion Waves in Homogeneous Media*), ISMAN RAS, Chernogolovka, 1992 (in Russian).

5 V. P. Karpov, N. M. Rubtsov, O. T. Ryzhkov, S. M. Temchin and V. I. Chernysh, *Archivum Combustionis*, 1995, **15**, 25.

6 N. M. Rubtsov, B. S. Seplyarskii, V. I. Chernysh and G. I. Tsvetkov, *Mendeleev Commun.*, 2009, **19**, 346.

7 V. A. Poltorak and V. V. Voevodsky, *Zh. Fiz. Khim.*, 1950, **24**, 299 (in Russian).

8 *Tablitsy fizicheskikh velichin* (*Tables of Physical Values*), ed. I. K. Kikoin, Atomizdat, Moscow, 1976, p. 1007 (in Russian).

9 A. A. Borisov, V. G. Knorre, E. L. Kudryashova and K. Ya. Troshin, *Khim. Fiz.*, 1998, **17**, 80 [*Chem. Phys. Rep.* (*Engl. Transl.*), 1998, **17**, 105].

10 V. V. Azatyan, J. I. Pyatnitskii, N. A. Boldyreva and T. M. Shaprinskaya, *Khim. Fiz.*, 1988, **7**, 235 (in Russian).

11 V. V. Azatyan, *Zh. Fiz. Khim.*, 1998, **72**, 1998 (*Russ. J. Phys. Chem.*, 1998, **72**, 2096).

12 V. V. Azatyan, G. A. Arutyunyan and Z. G. Dzotsenidze, *Zh. Fiz. Khim.*, 1987, **61**, 3151 (*Russ. J. Phys. Chem.*, 1987, **61**, 3227).

13 M. G. Zabetakis, *Washington U.S. Dept. of the Interior, Bureau of Mines, Bulletin 627*, 1965.

14 B. Lewis and G. Von Elbe, *Combustion, Explosions and Flame in Gases*, Academic Press, New York, London, 1987.

*Received: 23rd March 2010; Com. 10/3494*