European Conference on Computational Fluid Dynamics
ECCOMAS CFD 2006
P. Wesseling, E. Oñate, J. Périaux (Eds)

OXIDATION AND COMBUSTION OF FUEL-RICH *N*-BUTANE–OXYGEN MIXTURE IN A STANDARD 20-LITER EXPLOSION VESSEL

Sergey M. Frolov*, Valentin Ya. Basevich*, Victor A. Smetanyuk*, Andrei A. Belyaev*, and Hans J. Pasman†

*Semenov Institute of Chemical Physics, Department of Combustion and Explosion
4, Kosigin Street, Moscow 119991, Russia
e-mail: smfrol@chph.ras.ru

†Delft University of Technology, Faculty of Applied Sciences, Department of Multi Scale Physics
Lorentzweg, 1, 2628 CJ Delft, The Netherlands

Key words: Fuel-Rich *n*-Butane–Oxygen Mixture, Mixture Preparation, Flammability, Self-Ignition, Computational Fluid Dynamics, Explosion Hazards

Abstract. *Experiments on forced ignition of extremely fuel-rich n-butane–oxygen mixture with the equivalence ratio of 23 in the standard 20-liter spherical vessel at elevated initial pressure (4.1 bar) and temperature (500 K) reveal the nonmonotonic influence of the forced ignition delay time on the maximum explosion pressure and the maximum rate of pressure rise. The objective of the study reported herein is better understanding of test mixture oxidation and combustion in the 20-liter explosion vessel by means of mathematical modeling of the accompanying phenomena. It is shown that several temporally and spatially coupled phenomena could take place simultaneously in the experiments. These are mixing caused by oxygen injection to n-butane, forced ignition, flame propagation, preflame oxidation, heat transfer, and natural convection. Based on the CFD simulations of the mixing process and natural convection of the ignition kernel, as well as on the analysis of the detailed reaction mechanism of n-butane oxidation, laminar flame propagation, and self-ignition, possible explanations for the phenomena observed in the experiments have been suggested. The results of the study indicate that apparently inflammable mixtures can nevertheless become hazardous depending on the mixture preparation procedure and forced ignition timing.*

1 INTRODUCTION

For testing flammability of homogeneous and heterogeneous reactive mixtures a standard spherical 20-liter explosion chamber is usually used (Fig. 1). According to the standard requirements, the vessel *1* is connected via a fast acting valve *2* with a pressurized 0.6-liter storage canister *3* to inject the reactants. When one is interested in mixture flammability at elevated temperatures, the explosion chamber is electrically heated. At elevated initial temperatures, premature ignition can occur prior to the forced ignition of the mixture, which imposes certain limitations on the range of applicability of the standard procedures. In view of it, new approaches have been suggested recently to overcome the limitations. For example, a new mixture preparation method was established in [1]. A fuel–oxygen mixture was prepared by fast injection of oxygen from the pressurized canister to the explosion vessel filled with fuel. The mixture was ignited in the vessel center after different delay times (from several seconds to 1400 s) after completion of oxygen injection. Using this method, the authors of [1] have observed the influence of the forced ignition delay time (IDT) on the explosion pressure p_{exp} and the maximum rate of pressure rise $(dp/dt)_{\text{max}}$.

The influence of the forced IDT on the explosion parameters of the fuel-rich 78% C_4H_{10} + 22% O_2 mixture (further referred to as the test mixture) is illustrated by Fig. 2 [1]. The explosion pressure ratio p_{exp}/p_0 (where p_0 is the pressure in the vessel after completion of oxygen injection) was shown to increase with increasing IDT to a maximum at an IDT of 40 s. After the maximum, the explosion pressure ratio dropped with increasing IDT, reached a minimum at an IDT of 360 s and rose again to a second maximum at an IDT of 1020 s. The $(dp/dt)_{\text{max}}$ roughly followed a similar trend. Starting from about 1220 s, the test mixture self-ignited, which is indicated by open symbols in Fig. 2.

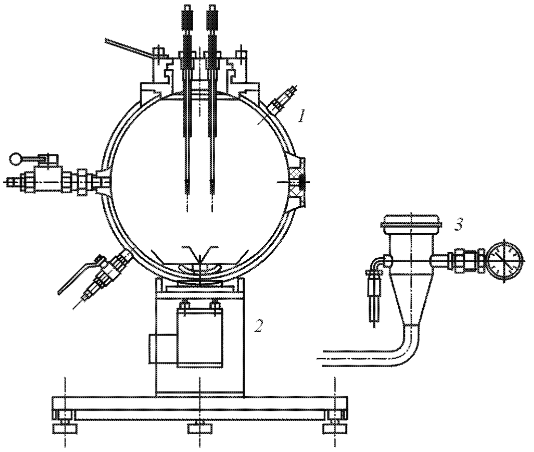


Figure 1: Standard 20-liter explosion sphere: *1* — explosion sphere, *2* — fast acting valve, and *3* — storage canister

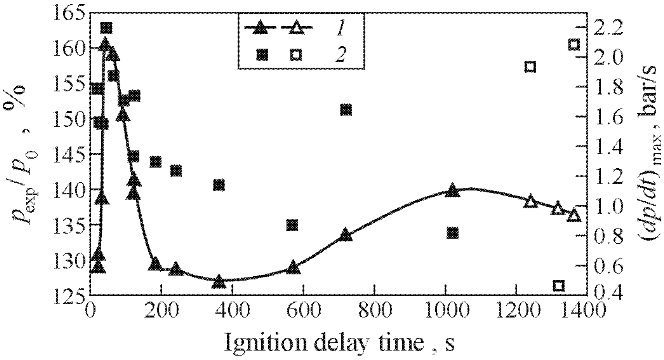


Figure 2: Measured explosion pressure p_{exp} (*1*) and maximum rate of pressure rise $(dp/dt)_{\text{max}}$ (*2*) as a function of forced ignition delay time in the fuel-rich 78% C_4H_{10} + 22% O_2 mixture at $p_0 = 4.1$ bar and $T_0 = 500$ K [1]. Closed symbols are related to forced ignition, open symbols to self-ignition

This behavior was explained in [1] by preflame reactions in the mixture. Although there were some indications of the validity of this implication, further studies of the phenomena detected in [1] were required. In [2], multidimensional CFD simulations of the mixing process in the 20-liter vessel have been performed using air as a test gas. It was shown that the thermochemical conditions at the ignition site could be affected in the long run by the residual gas coming from the manifold between valve *2* and vessel *1* after injection termination. Thus in addition to preflame reactions in the vessel, imperfect mixing of reactants could be another reason for the phenomena observed in [1]. In general, several temporally and spatially coupled phenomena could take place simultaneously in experiments [1]. These are mixing, forced ignition followed by flame propagation, preflame oxidation, heat transfer, and natural convection. The objective of the study reported herein is better understanding of the oxidation and combustion of the test mixture in the 20-liter explosion vessel by means of mathematical modeling of the phenomena.

2 THERMODYNAMIC CALCULATIONS

The test mixture containing 78% C_4H_{10} and 22% O_2 corresponded to the equivalence ratio of $\Phi = 23$, i.e., it was extremely fuel-rich. The mean molecular mass of the test mixture was 52.3767 kg/kmol. Tables 1 and 2 show the results of thermodynamic calculations for the test mixture at $p_0 = 4.1$ bar and $T_0 = 500$ K using the thermochemical code TDS [3]. Presented in the tables are the thermodynamic temperature *T*, density r, pressure *p*, molecular mass m, and species mole fractions at constant-pressure (HP-problem) and constant-volume (UV-problem) combustion of the test mixture at $p_0 = 4.1$ bar and $T_0 = 500$ K.

Table 1: Thermodynamic temperature, pressure, density, molecular mass, and species mole fractions (in %) at constant-pressure combustion (HP-problem) of the test mixture at $p_0 = 4.1$ bar and $T_0 = 500$ K

T, K	p, bar	r, kg/m^3	m, kg/kmol	Gaseous species					Soot
				H_2	CH_4	H_2O	CO	CO_2	
911.63	4.1	0.9508	10.361	32.16	19.43	6.12	1.42	0.58	40.28

Table 2: Thermodynamic temperature, pressure, density, molecular mass, and species mole fractions (in %) at constant-volume combustion (UV-problem) of the test mixture at $p_0 = 4.1$ bar and $T_0 = 500$ K

T, K	p, bar	r, kg/m^3	m, kg/kmol	Gaseous species					Soot
				H_2	CH_4	H_2O	CO	CO_2	
1049.42	25.47	5.2341	10.792	30.11	22.31	5.61	2.40	0.53	39.03

According to Table 1, if the test mixture would be flammable, the combustion temperature in the constant-pressure flame could be equal to 911.63 K. According to Table 2, constant-volume combustion of the test mixture would result in the maximal thermodynamic temperature and pressure equal to 1049.42 K and 25.47 bar, respectively, i.e., the thermodynamic pressure ratio could be p_{max} / p_0 = 6.21. The equilibrium combustion products could contain much (about 39%) soot and 61% gaseous species, most of which are hydrogen (about 30%) and methane (about 22%). The maximal pressure ratios measured in [1] were considerably less (~ 1.6) than the thermodynamic pressure ratio (6.21), which was the indication of incomplete oxidation of the test mixture. Among possible reasons of incomplete oxidation could be imperfect mixing of *n*-butane with oxygen and flame quenching caused by radical recombination on suspended and deposited soot particles, buoyancy effects, and heat loss. The effects produced by these imperfections are discussed below.

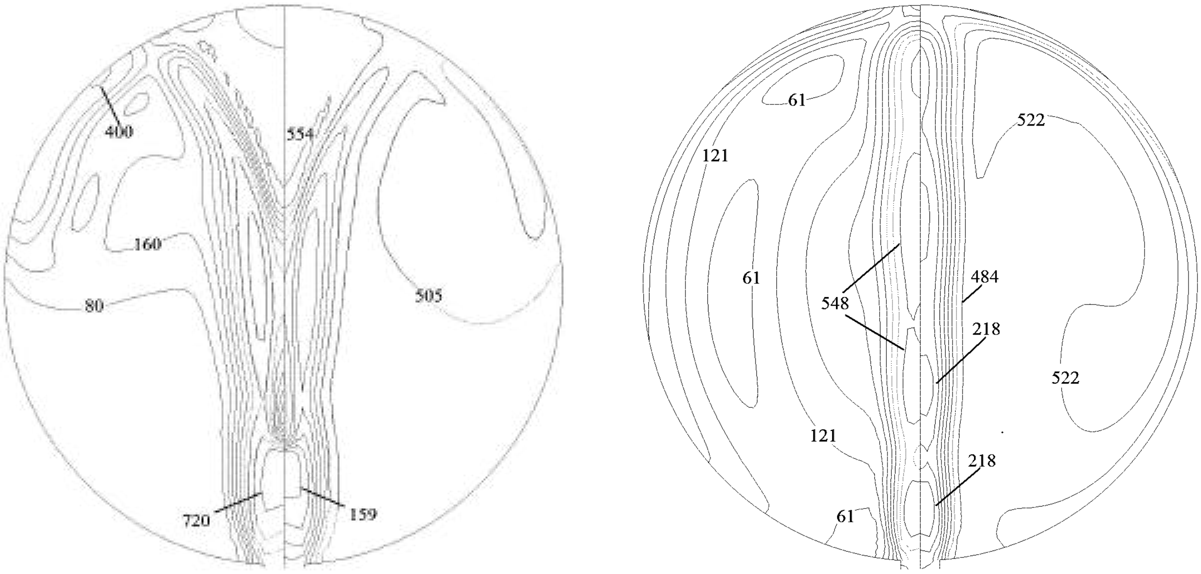
3 MIXTURE PREPARATION

To understand the mixing dynamics of oxygen and *n*-butane in the 20-liter explosion vessel, 2D and 3D RANS-based simulations were performed using AVL SWIFT code [4]. In the calculations, the flow dynamics in the oxygen canister, in the manifold connecting the canister and the vessel, and in the vessel itself were simulated. After valve closing, only the dynamics of the flow in the vessel and in the manifold section downstream from the valve was considered. The geometrical dimensions of the units in Fig. 1 were taken as close as possible to the design drawings. The radius of the vessel was taken equal to 168.4 mm. The canister was modeled as a cylinder 100 mm high and 87.4 mm in diameter. The diameter and length of the manifold connecting the valve and the vessel were taken 25.4 and 200 mm, respectively. All rigid walls of the volume were kept at constant temperature of 500 K. The initial temperature of oxygen and *n*-butane were also taken equal to 500 K to fit the experimental conditions of [1]. The turbulence model used in the simulations was the $k-e$ model. The duration of oxygen injection was varied from 10 to 12 ms depending on the required experimental value of the final pressure of the mixture in the 20-liter vessel.

Two-dimensional calculations were made at grids containing 20,000–30,000 cells with a variable time step to keep a number of iterations within a SIMPLE algorithm between 20 and 30. Typically, the CPU time required for one computational run did not exceed 20 hours. Three-dimensional calculations were made at grids containing 200,000–300,000 cells and were used only for validating the results of 2D calculations at the initial stages of oxygen injection.

Figures 3*a* and 3*b* show the initial period of oxygen injection into the 20-liter vessel in terms of oxygen mass fraction and temperature distributions at time instants of 2.3 and 5.5 ms after starting the injection. The starting shock wave caused by a high initial pressure ratio (21 bar / 0.4 bar = 52.5) between the canister and the vessel was rather strong and resulted in high local flow velocities, which at time t = 2.3 ms exceeded 700 m/s in the jet core and attained 400 m/s in the near-wall regions of the vessel. Due to expansion, the oxygen temperature in the jet at t = 2.3 ms was as low as 160 K. Due to shock compression, the *n*-butane temperature at t = 2.3 ms increased locally to about 550 K. Clearly, oxygen injection in experiments [1] led to a considerable mixture stratification in terms of velocity, temperature and composition.

Figure 4 compares the predicted turbulent velocity in the vessel center with the root-mean-squared values of two pulsating velocity components measured in [1] using Laser Doppler Anemometry. It is seen that at $t > 0.1$ s, the predicted and measured results correlate



(*a*) (*b*)

Figure 3: Calculated isolines of the velocity vector length (in m/s, left hemisphere) and temperature isotherms (in K, right hemisphere) at injection of pressurized oxygen into a vessel filled with *n*-butane at time (*a*) 2.3 ms and (*b*) 5.5 ms after valve opening. Initial oxygen pressure is 21 bar. Initial *n*-butane pressure is 0.4 bar. Injection duration is 0.0117 s. The interval between the isolines is uniform

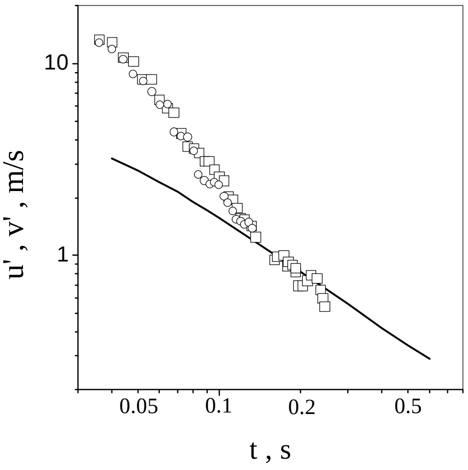
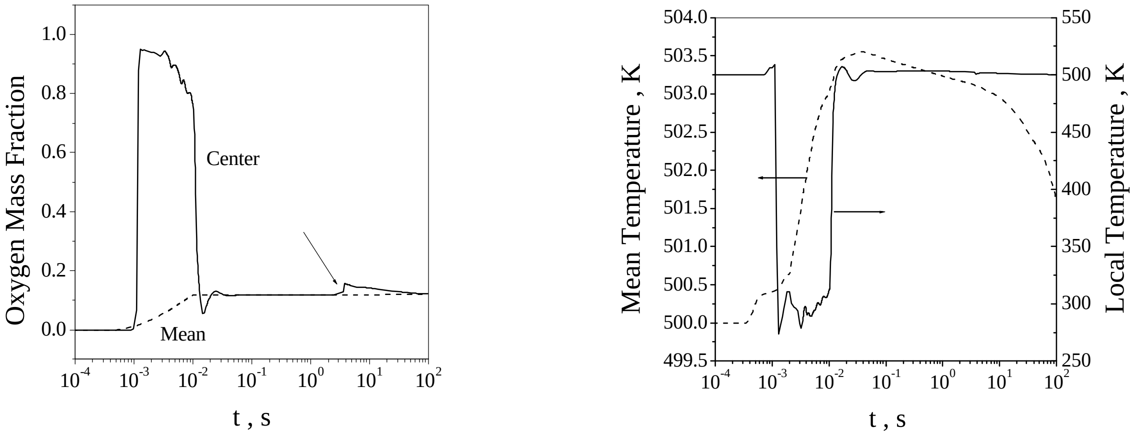


Figure 4: Comparison of predicted and measured [1] root-mean-squared velocity fluctuations u' and v' in the vessel center. Initial oxygen pressure is 21 bar. Initial *n*-butane pressure is 0.4 bar. Injection duration is 0.0117 s

reasonably well with each other and the turbulence in [1] was isotropic at least at $t > 0.04$ s. At the initial injection stage, the discrepancy between the predicted and measured data is observed, which could be attributed to some differences in the experiments and simulations. In the experiments, the turbulence measurements were made with the ignition electrodes near



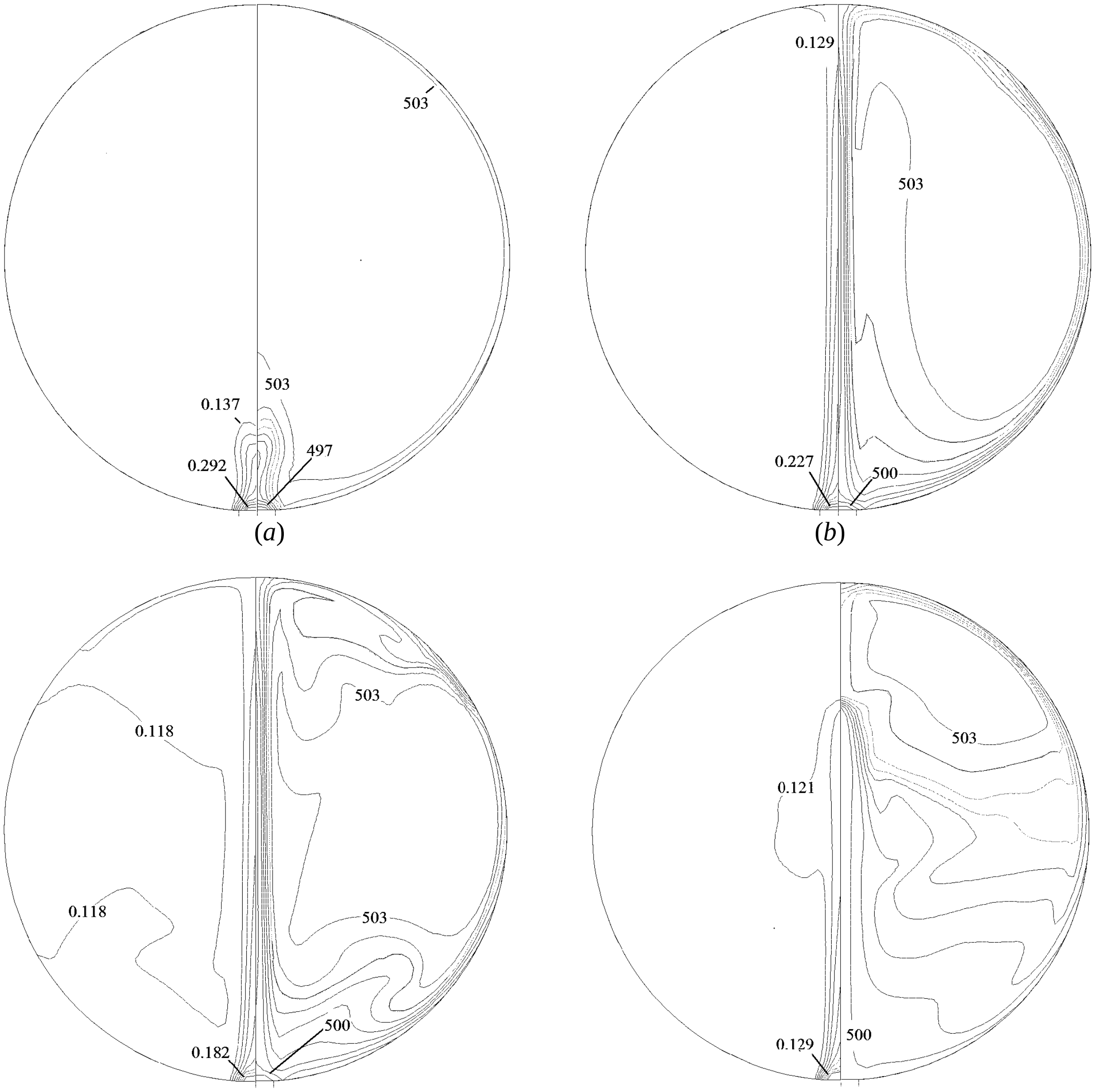
(*a*) (*b*)

Figure 5: Calculated time histories of (*a*) oxygen mass fraction and (*b*) temperature in the 20-liter vessel. Solid curves correspond to local instantaneous values at the ignition site (vessel center). Dashed curves correspond to mean values. Initial oxygen pressure in the canister is 29.67 bar. Initial *n*-butane pressure in the vessel is 3.2 bar. Injection duration is 0.01 s

the vessel center causing faster turbulence decay (see Fig. 1), while in the calculations the electrodes were absent. In addition, the $k-e$-model used in the simulations could underestimate the turbulence decay rate.

Solid curves in Fig. 5 show the predicted time histories of oxygen mass fraction (Fig. 5*a*) and temperature (Fig. 5*b*) in the vessel center (ignition site) up to t = 100 s. For the sake of comparison, the time histories of mean oxygen mass fraction and mean temperature in the vessel are shown by the dashed curves in the same figures. In the computational runs relevant to Fig. 5, the oxygen injection period terminated at about t = 0.01 s. During injection, the oxygen mass fraction and temperature at the ignition site attained the values of 0.95 and 275 K, respectively. However, shortly after injection termination, the oxygen mass fraction and temperature attained the values of 0.117 and 500 K close to the corresponding mean values. Nevertheless, starting from t = 3 s, one can observe the deflection of the local oxygen mass fraction from the mean value in Fig. 5*a* (shown by arrow). The growth of the oxygen mass fraction in the vessel center continued till t = 3.8 s, when it attained a value of 0.16, and then turned to decrease gradually to the mean value of 0.117 at about t = 100 s.

The reason for the elevated values of the oxygen mass fraction in the vessel center at $3 < t < 100$ s is evident from Fig. 6 showing the calculated isolines of the oxygen mass fraction (left hemisphere) and temperature (right hemisphere) at time (*a*) 3 s; (*b*) 10; (*c*) 20; and (*d*) 100 s after injection termination. It is seen that at t = 3 s the mixing in the bulk of the vessel had been already completed. However, at this time there was still a portion of oxygen stagnated in the manifold at the instant of valve closing. This residual oxygen spread slowly along the injection axis. At time of about 3 s, the mass fraction of oxygen started to increase in the vessel center due to arrival of the residual oxygen from the manifold.



(*a*) (*b*) (*c*) (*d*)

Figure 6: Calculated isolines of oxygen mass fraction (left hemisphere) and temperature (right hemisphere) at time (*a*) 3 s; (*b*) 10; (*c*) 20; and (*d*) 100 s after injection. Initial oxygen pressure is 29.67 bar. Initial *n*-butane pressure is 3.2 bar. Injection duration is 0.01 s. The interval between the isolines is uniform

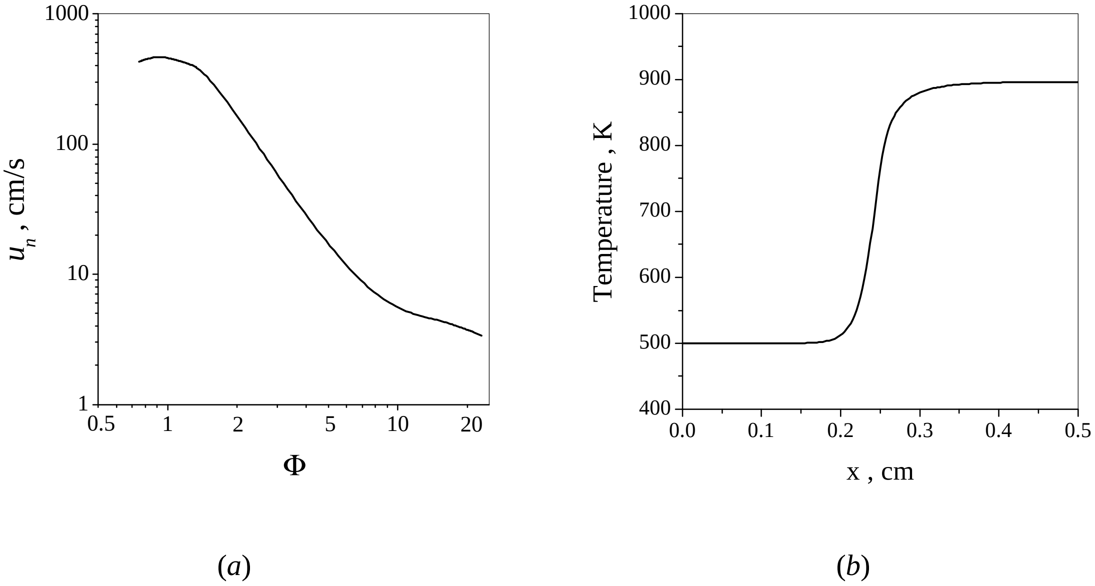
Thus, the CFD simulation of the mixing process in the 20-liter vessel provided a possible explanation for the local maximum of explosion pressure at about $t = 40$ s in Fig. 2. This could be a result of ignition of a less fuel-rich (and therefore more reactive) *n*-butane–oxygen mixture than the test mixture with $\Phi = 23$.

4 LAMINAR FLAME PROPAGATION IN TEST MIXTURE

To estimate the reactivity of the test mixture in terms of the laminar burning velocity and the self-ignition delay, a detailed reaction mechanism of *n*-butane oxidation developed and validated recently by the authors [5] was used. The mechanism contained 288 reversible elementary reactions and 54 species and was capable of simulating reasonably well both low- and high-temperature self-ignition of *n*-butane. At low temperatures and high pressures, this mechanism provided the parametric domain with the negative temperature coefficient of the reaction rate correlating well with experimental data [6]. It is worth mentioning however that this mechanism did not include reactions responsible for soot formation.

Figure 7*a* shows the predicted laminar burning velocity in the *n*-butane–oxygen mixture as a function of the equivalence ratio Φ under initial pressure and temperature conditions relevant to Fig. 2. The laminar burning velocity was calculated using the laminar flame code [7] assuming adiabatic walls and neglecting radiation heat loss. It is seen from Fig. 7*a* that the test mixture with Φ = 23 exhibited a laminar burning velocity u_n of 3.4 cm/s at T_0 = 500 K and p_0 = 4.1 bar, which was by two orders of magnitude less than the value of u_n for the stoichiometric *n*-butane–oxygen mixture at similar initial conditions (458 cm/s).

Figure 7*b* shows the calculated temperature profile in the laminar flame at Φ = 23. The temperature in the flame increased from $T_0 = 500$ K to about 896 K. The predicted flame temperature was somewhat less than the thermodynamic value of 911 K (see Table 1). The arising discrepancy was evidently caused by the lack of thermodynamic equilibrium at short



(*a*) (*b*)

Figure 7: (*a*) Predicted laminar burning velocities of *n*-C_4H_{10}–O_2 mixtures as a function of equivalence ratio Φ at T_0 = 500 K and p_0 = 4.1 bar; (*b*) Calculated temperature profile in the *n*-C_4H_{10}–O_2 laminar flame at $\Phi = 23$ at T_0 = 500 K and p_0 = 4.1 bar

distances behind the flame front shown in Fig. 7*b*. In the calculations relevant to Fig. 7*b* up to 200 grid nodes were used. The CPU time required for obtaining the steady-state solution at Φ = 23 was about 50 hours at Pentium IV.

The results of calculations presented in this Section indicate that the test mixture in experiments [1] was flammable indeed.

5 SELF-IGNITION OF TEST MIXTURE

As follows from Tables 1 and 2 oxidation and combustion of the test mixture should be accompanied by considerable soot formation. Under extremely fuel-rich experimental conditions [1], the contribution of chain termination reactions at soot particles deposited on the vessel walls and suspended in the mixture could be significant. In experiments [1], the existence of soot deposits on the vessel walls could be caused by incomplete air-blast removal of particles formed in previous tests. As for the origin of suspended soot particles in the vessel volume, they could be blown in the volume from the vessel walls by a strong starting shock wave (see Section 2), or could form in the mixture during the induction period according to a low-temperature mechanism of soot formation [8].

To model test mixture self-ignition at the conditions relevant to Fig. 2, the detailed reaction mechanism of *n*-butane oxidation [5] was used. Due to the lack of reliable information on kinetics of low-temperature heterogeneous reactions on the surface of soot particles, it was assumed that the most important chain termination reactions were represented by two overall, quasi-volumetric, monomolecular reactions [9]:

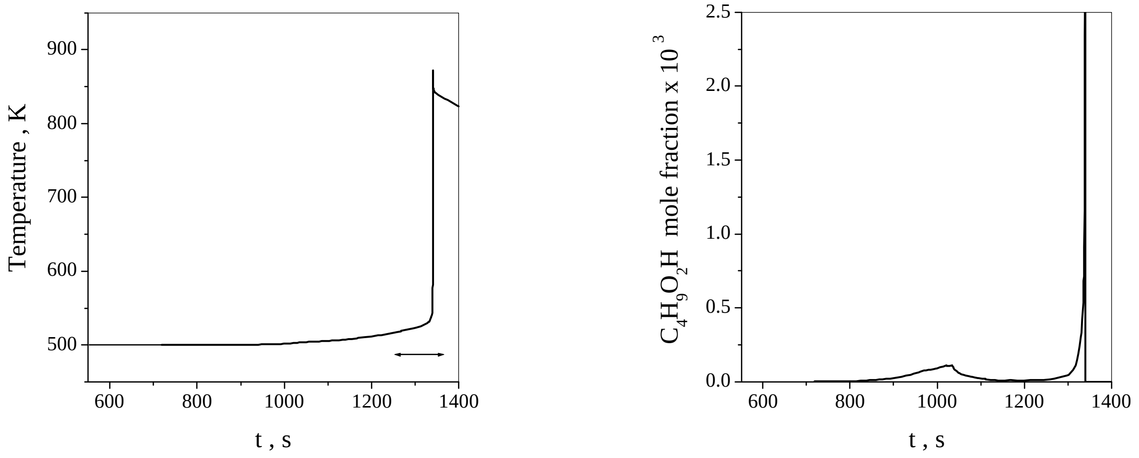
$$C_4H_9O_2H \rightarrow C_4H_{10} + O_2 \tag{1}$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 \tag{2}$$

The effective activation energies E_1 and E_2 of reactions (1) and (2) were taken zero, while the corresponding preexponential factors were taken equal to $k_1 = k_2 = k = 80$ s^{-1}. Figure 8*a* shows the results of calculations for the test mixture. The heat transfer coefficient in the calculations was taken equal to 0.615 W/m^{2}K. The arrow shows the experimentally measured self-ignition delays in [1].

It is seen from Fig. 8*a* that the predicted and measured ignition delays correlate well with each other. Note that the assumed value of k = 80 s^{-1} seemed quite reasonable for the problem under study. The calculations revealed the existence of a cool-flame stage during test mixture oxidation. The temperature curve in Fig. 8*a* exhibits a staged behavior with the first stage attributed to cool flame and the second to hot explosion. Figure 8*b* shows the corresponding time histories of butyl hydroperoxide mole fraction in the test mixture, which exhibits two stages of peroxide accumulation and decomposition at 800–1100 s and at 1200–1340 s, corresponding to the cool flame and hot explosion stages.

It is worth noting that the origin of cool flame (t = 1000 s) coincided well with the second maximum of the explosion pressure in Fig. 2. At the cool-flame stage of hydrocarbon oxidation, the mixture reactivity is known to increase considerably [10]. Therefore the second maximum at the explosion pressure curve could be explained by faster flame propagation in the test mixture at its ignition during the cool-flame conversion.



(*a*) (*b*)

Figure 8: (*a*) Predicted temperature history in the 78%C_4H_{10} +22%O_2 test mixture in the course of self-ignition at T_0 = 500 K and p_0 = 4.1 bar (arrow shows the experimental self-ignition delay); (*b*) Predicted time history of butyl hydroperoxide mole fraction in the test mixture

6 EFFECT OF BUOYANCY

Slow burning mixtures are known to exhibit a strong influence of buoyancy effects [10]. Figure 9 shows the results of CFD simulations of upward natural convection of the hot ignition kernel in the gravity field. In this example, the mixture was ignited 10 s after termination of oxygen injection. These calculations were aimed at estimating the characteristic times taken for the kernel to reach the upper wall of the vessel and to cool down to the wall temperature. Combustion reactions in these calculations were not activated for the sake of simplicity.

It follows from Fig. 9 that the entire process of flame kernel dissipation took 1–2 s. If one takes into account that in actual experiments [1] the flame kernel moved upward along the massive electrodes, no wonder that combustion in the experiments [1] was incomplete and the maximal explosion pressure $p_{\exp} / p_0$ did not exceed a value of about 1.6 instead of the thermodynamic value of 6.21.

7 DISCUSSION AND CONCLUSIONS

Experimental studies [1] of constant-volume combustion of the extremely fuel-rich 78% C_4H_{10} + 22% O_2 mixture (an equivalence ratio of 23) in the standard 20-liter vessel at elevated initial temperature (500 K) and pressure (4.1 bar) resulted in some unexpected phenomena, which needed explanation. Contrary to a standard testing procedure, a fuel–oxygen mixture in [1] was prepared by fast injection of oxygen from the pressurized canister to the explosion vessel filled with fuel. The mixture was ignited in the vessel center after

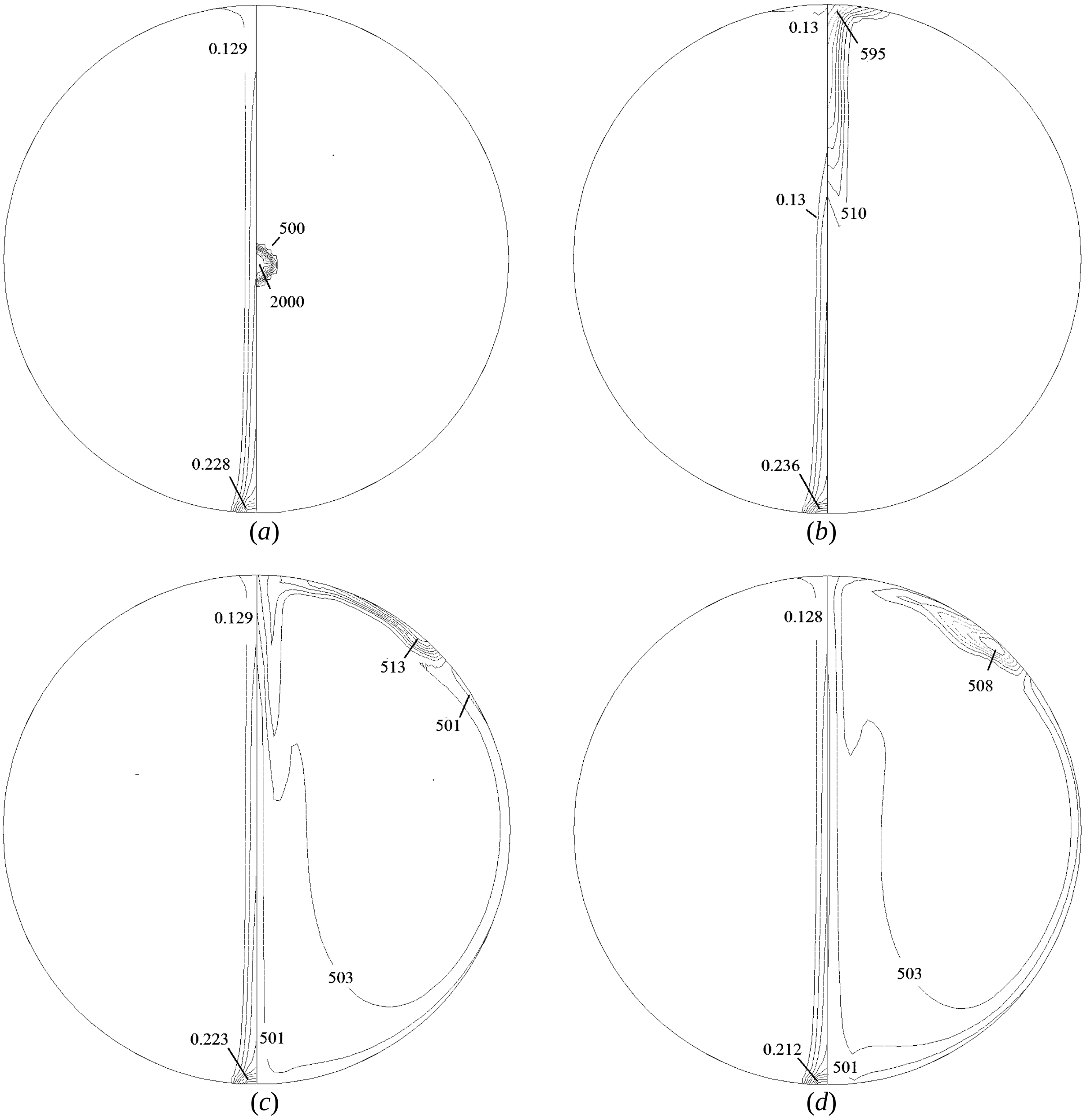


Figure 9: Calculated isolines of oxygen mass fraction (left hemisphere) and temperature (right hemisphere) after ignition of test mixture in the vessel center 10 s after termination of oxygen injection: (*a*) ignition completion; (*b*) 0.3 s; (*c*) 1; and (*d*) 2 s. Initial oxygen pressure in the canister is 29.67 bar. Initial *n*-butane pressure in the vessel is 3.2 bar. Injection duration is 0.01 s. The interval between the isolines is uniform

different delay times (from several seconds to 1400 s) after completion of oxygen injection. It was found in [1] that the forced IDT affected considerably the explosion pressure and the maximum rate of pressure rise (see Fig. 2). The explosion pressure ratio was shown to increase with increasing IDT to a maximum at an IDT of 40 s. After the maximum, the explosion pressure ratio dropped with increasing the IDT, reached a minimum at an IDT of 360 s and rose again to a second maximum at an IDT of 1020 s. Starting from about 1220 s, the test mixture self-ignited.

Based on the CFD simulations of the mixing process and natural convection of the ignition kernel, as well as on the analysis of the detailed reaction mechanism of *n*-butane oxidation, laminar flame propagation, and self-ignition, possible explanations for the phenomena observed in [1] can be suggested.

The test mixture was found to be flammable. At the initial conditions of [1], the mixture exhibited the laminar burning velocity of about 3.4 cm/s and the thermodynamic temperature of combustion products of 911.63 K. Self-ignition of the test mixture exhibited a two-stage behavior with a cool flame and hot explosion arising at about 1000 and 1300 s, respectively, after oxygen injection termination. Since the burning velocity of the test mixture was very low, its combustion in the vessel after forced ignition was highly affected by buoyancy. According to the estimations, the buoyant flame kernel could dissipate completely during 1–2 s after ignition due to the contact with massive electrodes and the upper wall of the vessel. As a result, combustion of the test mixture in [1] was always incomplete: a maximal explosion pressure ratio was only ~1.6 instead of the thermodynamic value of 6.21. Thus, the behavior of the explosion pressure ratio curve in Fig. 2 could be explained primarily by the variation of the laminar burning velocity in the test mixture with increasing the IDT. Keeping in mind the buoyant flame quenching in 1–2 s after ignition, one could expect that a higher explosion pressure ratio be attained at a higher burning velocity.

The mixture preparation procedure used in [1] implied a possibility of obtaining excessive (as compared to the mean value) oxygen concentration at the ignition site at a time between 3 and 100 s after injection termination. A higher oxygen concentration in a fuel-rich mixture implied a higher burning velocity (see Fig. 7*a*). This could be a reason for the first maximum at the explosion pressure curve of Fig. 2, obtained at an IDT of about 40 s. Further temporal relaxation of the oxygen mass fraction in the vessel center to the mean value (see Fig. 5*a*) resulted in decreasing the burning velocity and the maximal explosion pressure to the minimal value at an IDT of about 360–400 s.

The subsequent increase in the maximal explosion pressure with the IDT exceeding 360–400 s could be explained by the growing influence of preflame reactions leading to formation of various intermediate combustion products including alkyl peroxides. As mixture reactivity is known to increase due to these processes, the laminar burning velocity in the preconditioned test mixture should also increase. Thus, the second maximum of the explosion pressure in Fig. 2 arising at an IDT of 1000 s could be explained by faster flame propagation in the test mixture at its forced ignition during the cool-flame conversion. Further decrease of the maximal explosion pressure at IDT exceeding 1000 s could be explained by lower reactivity and exothermicity of the test mixture. As a matter of fact, cool-flame conversion results in release of up to 7%–10% of available chemical energy in the test mixture. Therefore, both the combustion temperature and the laminar burning velocity of the mixture passed through cool-flame oxidation should decrease. Forced ignition of such a mixture then should result in a lower explosion pressure.

Self-ignition of the test mixture at time exceeding 1220 s could be expected to result in the third prominent maximum at the pressure ratio curve of Fig. 2, caused by volumetric hot explosion (see Fig. 8*a*). However the corresponding curve in Fig. 2 does not seem to have it. It could be expected that at t = 1220–1380 s hot explosion in experiments [1] occurred locally in exothermic centers and therefore the resultant explosion pressure was still lower than at forced ignition. This implication is substantiated by the highest maximum rates of pressure rise relevant to self-ignition (see Fig. 2). Nevertheless, to verify this implication, further experimental and computational studies are required.

In general, the results of the study clearly indicate that apparently inflammable mixtures can nevertheless become hazardous depending on the mixture preparation procedure and forced ignition timing.

ACKNOWLEDGEMENTS

The work was partly supported by the Russian–Dutch Research Cooperation project No. 046.016.012 and Russian Foundation for Basic Research projects 05-08-50115a and 05-08-33411a.

REFERENCES

[1] A. A. Pekalski, E. Terli, J. F. Zevenbergen, S. M. Lemkowitz, and H. J. Pasman, Proceedings of the Combustion Institute, **30**, 1133–1139 (2005).

[2] V. A. Smetanyuk, A. A. Skripnik, S. M. Frolov, and H. J. Pasman, In: *Nonequilibrium Processes*. Vol. 1: Combustion and Detonation. Ed. by G. D. Roy, S. M. Frolov, and A. M. Starik, Moscow, Torus Press, 37–43 (2005).

[3] S. B. Victorov, Proc. 12th International Detonation Symposium, ed. by J.M. Short and J. L. Maienschein, CD-ROM, San Diego, CA (2002).

[4] SWIFT Manual 3.1, AVL AST, AVL List GmbH, Graz, Austria (2002).

[5] V. Ya. Basevich, A. A. Belayev, and S. M. Frolov, *Rus. J. Chemical Physics* (2006, accepted).

[6] R. Minetti and R. Sochet, *Combustion and Flame*, **96**, 201 (1994).

[7] A. A. Belyaev and V. S. Posvianskii, In: *Algorithms and Codes*. Information Bulletin of USSR Foundation of Algorithms and Codes. No. 3, 35 (1985).

[8] H. Bohm, D. Hesse *et al.*, Proceedings of the Combustion Institute, 403 (1988).

[9] V. N. Kondratiev and E. E. Nikitin, *Kinetics and Mechanism of Gas-Phase Reactions*, Moscow, Nauka (1974).

[10] A. S. Sokolik, *Self-Ignition, Flame, and Detonation in Gases*, Moscow, USSR Acad. Sci. Publ. (1960).