

Modeling of Low-Temperature Oxidation and Combustion of Droplets

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Presented by Academician A.A. Berlin April 12, 2016

Received June 20, 2016

Abstract—Key features of radiation extinguishing of spherical hot flame around a single droplet with its subsequent low-temperature oxidation and combustion under microgravity conditions—a phenomenon discovered in experiments onboard the International Space Station—have been reproduced using the mathematical model of droplet combustion and detailed kinetic mechanism of *n*-heptane oxidation and combustion. It has been demonstrated that experimentally observed repeated temperature flashes were blue flame flashes, and their duration was determined by the hydrogen peroxide decomposition time. In addition to this phenomenon, calculations predict the existence of new modes of low-temperature oxidation and combustion of droplets without the hot flame stage. In such modes, the basic reaction is concentrated very close to the droplet surface, and fuel vapor reacts in it only partially.

DOI: 10.1134/S0012501616100018

A new, previously unobserved phenomenon of radiation extinguishing of spherical hot flame around single droplets of hydrocarbon fuel (*n*-decane or *n*-heptane) with their subsequent low-temperature oxidation and combustion under microgravity conditions has been reported [1–3]. The corresponding flame extinguishment experiment (FLEX) was carried out onboard the International Space Station (ISS), and calculations with analysis of this phenomenon have also been presented in the cited works. The low-temperature droplet oxidation observed in the FLEX experiments was sometimes accompanied by repeated temperature jumps.

In the present work, based on the previously developed mathematical model of combustion of droplets [4] and detailed kinetic mechanism (DKM) of oxidation and combustion of *n*-heptane [5], we reproduced all key features of this phenomenon and predicted the existence of new modes of low-temperature combustion of droplets without the hot flame stage.

The spherically symmetric model of oxidation and combustion of droplets [4] is based on nonstationary differential equations of conservation of matter and

energy in the liquid and gas phases at variable thermo-physical properties. In the problem setting, the concept of multicomponent diffusion in the gas phase was used. The model has been constructed for microgravity conditions and constant pressure in the gas–droplet system. An important advantage of the DKM used [5] is that it describes both the multicomponent oxidation with “cool” and “blue” flames and the high-temperature combustion of *n*-heptane and does not require additional tests. The key prerequisite of the model is that, despite differences in physical nature between the self-ignition of a homogeneous combustible mixture and the combustion of droplets under low-temperature oxidation conditions, the chemical kinetics of both processes, being universal, is similar.

The spark ignition used in the experiments [1–3] was modeled in calculations by surrounding the droplet by a thin spherical layer with high temperature (2000 K), which leads to the appearance of hot flame.

The only change in the model [4] and in the DKM [5] was that the radiation of the soot formed in combustion was taken into account. To consider the radiation, into the equation of conservation of energy in the model [4], a negative source was introduced:

$$-\sigma S_{\text{rad}} Y_c \rho T^4,$$

where σ is the Stefan–Boltzmann constant, Y_c is the mass fraction of soot (soot is denoted as C and is modeled by equivalent gas with a molecular weight of 12 kg/kmol), ρ is the gas density, T is the gas tempera-

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Macrokinetic mechanism of soot formation at a pressure of 0.1 MPa

No.	Reaction	A [L, mol, s]	E/R [K]
1	$C_2H_2 + C_2H_2 \rightarrow C + C + C_2H_4$	2.0×10^{16}	40000
2	$C + CO_2 \rightarrow CO + CO$	1.3×10^{15}	40000
3	$C + H_2O \rightarrow CO + H_2$	1.3×10^{15}	40000

A is the preexponential factor, E is the activation energy, R is the gas constant in the Arrhenius equation for the reaction rate constant.

ture, $S_{\text{rad}} = 6/d_s \rho_s$ is the specific surface of the mass unit of soot particles (here, d_s is the particle size, and ρ_s is the soot density). If we take $d_s \sim 1$ nm and $\rho_s \approx 2000$ kg/m³, then $S_{\text{rad}} \approx 3 \times 10^6$ m²/kg. To take into account radiation, a simple macrokinetic mechanism of soot formation (table) was introduced into the DKM [5]; this mechanism was suggested and verified in [6], where acetylene C_2H_2 was used as a soot precursor.

Figure 1 shows an example of calculation of the combustion of a *n*-heptane droplet of initial diameter $D(0) = D_0 = 2.8$ mm in an unconfined air atmosphere at initial temperature $T(0) = T_0 = 293$ K and initial pressure $P = 0.1$ MPa; the maximum gas temperature T_{max} in the vicinity of the droplet, the reduced droplet surface area D^2/D_0^2 , and normalized concentrations of OH, $C_7H_{15}O_2H$, and H_2O_2 (here, I_m is the mass frac-

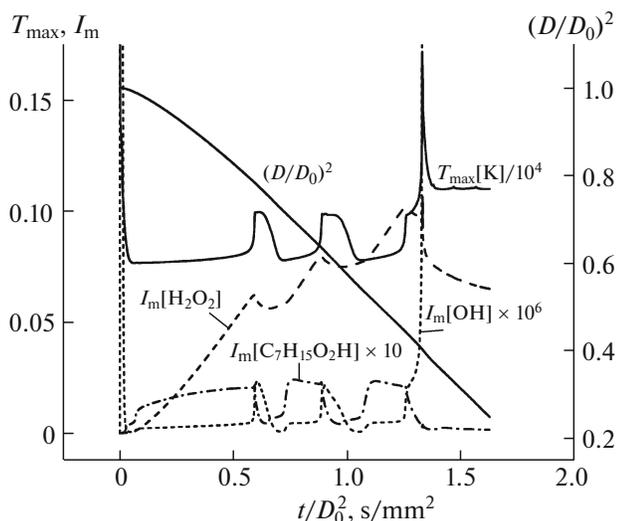


Fig. 1. Calculated maximum gas temperature T_{max} in the vicinity of the *n*-heptane droplet, reduced droplet surface area D^2/D_0^2 , and normalized concentrations of OH, $C_7H_{15}O_2H$, and H_2O_2 as a function of reduced time t/D_0^2 for combustion in air.

tion of a given component in the gas phase with respect to the initial droplet mass) as a function of reduced time t/D_0^2 are shown. To illustrate the process in more detail, the curves in Fig. 1, were limited by time $t = 12.74$ s ($t/D_0^2 = 1.63$ s/mm²).

In full accordance with [1–3], the maximum temperature T_{max} of the gas around the droplet gradually decreases as a result of energy loss by radiation, which leads after a time to the extinguishment of high-temperature hot flame and the establishment of “cool flame combustion” (according to the terminology in [1–3]). In fact, the cool flame combustion mode is a low-temperature oxidation reaction at $T \approx 770$ K with a triple stepwise increase in temperature (flashes) to $T \approx 1000$ K with its subsequent decrease to the initial level and even with one high-temperature flash to $T \approx 1750$ K (short-term hot flame flash). It should be noted that, despite the apparent constancy of T_{max} in the time intervals between the flashes, the average temperature of the gas gradually increases due to exothermic oxidation reactions. In the course of this process, the droplet diameter is continuously reduced. Figure 1 also shows that the normalized concentrations of OH, $C_7H_{15}O_2H$, and H_2O_2 are a nonmonotonic function of time, following the nonmonotonic change in T_{max} .

Detailed analysis of calculation results showed that the flashes on the temperature curve emerge because of the periodic decomposition of hydrogen peroxide—branching leading to the formation of hydroxyl radicals, i.e., due to “blue flames” [7]. When the hydrogen peroxide decomposition was excluded from the DKM, the calculation gave roughly constant maximum temperature $T_{\text{max}} = 763$ – 769 K during the entire process of low-temperature oxidation of the droplet. Thus, the above-mentioned experiments [1–3] have revealed a new specific feature of blue flames: they can be multiple.

Changing modeling conditions, a $T_{\text{max}}(t)$ function with one short cool flame flash on the temperature curve of oxidation at low temperatures can be obtained.

For example, going from the problem with spark ignition of the droplet in air to the problem with droplet self-ignition leads to a new (not observed experimentally so far) low-temperature combustion mode of the droplet.

Let us consider the self-ignition and low-temperature oxidation of the *n*-heptane droplet with the initial diameter $D_0 = 0.7$ mm in air at $T_0 = 600$ – 800 K and $P = 0.1$ MPa. The calculated $T_{\text{max}}(t)$ dependences for these conditions are shown in Fig. 2 by solid curves. Judging from the stepwise change in the maximum temperature of the gas at time moment $t \sim 0.16$ s at $T_0 = 750$ K and $t \sim 0.25$ s at $T_0 = 700$ K, multistage self-ignition of the droplet occurs in this range of start-

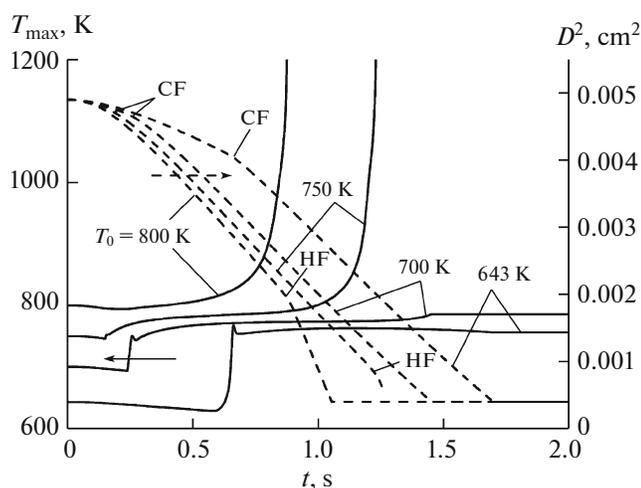


Fig. 2. Calculated maximum gas temperature T_{\max} in the vicinity of the *n*-heptane droplet and the squared diameter D^2 of the droplet as a function of time at different initial temperatures: 643, 700, 750, and 800 K at $P = 0.1$ MPa. CF and HF are the moments of appearance of cool and hot flame, respectively.

ing temperatures. However, at $T_0 = 700$ K transition to hot flame at time moment $t \sim 1.45$ s is terminated because of the disappearance of the droplet, whereas at $T_0 = 643$ K after short-term appearance of cool flame at time moment $t \sim 0.67$ s, the low-temperature oxidation of the droplet is observed, like in the case of spark ignition. The corresponding calculated time dependences of the squared droplet diameter $D^2(t)$ are shown in Fig. 2 by dashed curves. The arrows labeled by CF and HF indicate the moment of appearance of cool and hot flames, respectively. The slope of the $D^2(t)$ curves at these points increases jumpwise.

Figure 3 shows the time course of the oxidation of the *n*-heptane droplet at $T_0 = 643$ K after a single cool flame flash, as the curves of the maximum gas temperature T_{\max} , the D^2/D_0^2 ratio, and OH, $C_7H_{15}O_2H$, H_2O_2 , H_2O , and C_7H_{16} concentrations. The low-temperature oxidation rate constant, determined from the slope of the $D^2/D_0^2(t)$, is 0.358 mm²/s. This value is very close to the corresponding values in Fig. 1 for spark ignition. It should be noted that the presence and accumulation of *n*-heptane C_7H_{16} are evidence of the reaction incompleteness in the gas phase and retention of some amount of the starting fuel after the end of the process.

For the same calculation, Fig. 4 shows radial distributions of temperature in the gas–droplet system at different moments of time; the zero radius $R = 0$ corresponds to the droplet center, and the dashed line shows the initial temperature distribution with a jump from the temperature of the liquid (293 K) to the temperature of air (643 K) at the droplet surface $R = R_0 =$

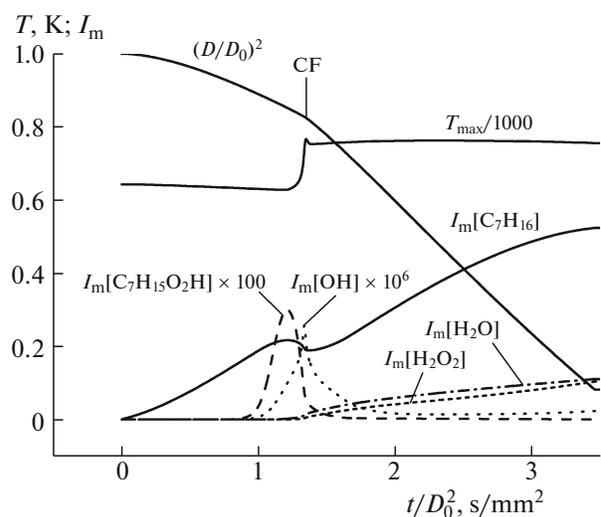


Fig. 3. Calculated maximum gas temperature T_{\max} , reduced droplet surface area D^2/D_0^2 , and normalized concentrations of OH, $C_7H_{15}O_2H$, H_2O_2 , and H_2O as a function of reduced time t/D_0^2 for self-ignition of the *n*-heptane droplet of initial diameter $D_0 = 0.7$ mm in air at $T_0 = 643$ K and $P = 0.1$ MPa.

$D_0/2$. It is seen that, after droplet self-ignition, the maximum gas temperature remains roughly constant, ~ 770 K. The temperature maximum is located very close to the droplet surface, at a distance of about $\sim 2R_0$, which distinguishes the cool flame combustion of the droplet from its high-temperature combustion where hot flame is at a distance of $\sim 8R_0$ from the droplet surface [8]. Figure 4 also shows that a heat wave

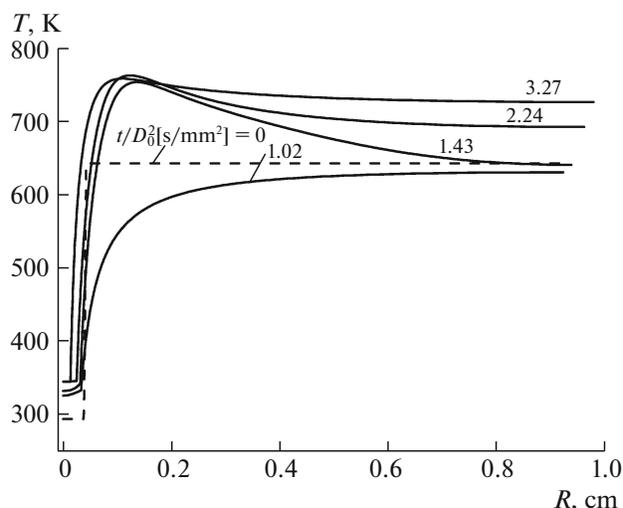


Fig. 4. Calculated radial distributions of temperature at different reduced times t/D_0^2 for the self-ignition of the *n*-heptane droplet in air: $T_0 = 643$ K, $P = 0.1$ MPa, and $D_0 = 0.70$ mm.

propagates away from the droplet, which gradually increases the ambient gas temperature.

Thus, our calculations reproduce all key features of “cool flame combustion” of *n*-heptane droplets observed in the experiments onboard the ISS [1–3] upon high-temperature (hot) flame extinguishment caused by radiation loss. The calculations enable the conclusion that the observed low-temperature combustion of *n*-heptane droplets is not actually cool or blue flame combustion. Both the cool and blue flames are short-term stages of reaction acceleration (the duration of these stages is determined only by the decomposition time of the corresponding peroxides) during which the temperature jump is observed. The calculations demonstrate the possibility of appearance of multiple blue flames revealed in the space experiment, which has not been previously observed. In addition, the calculations predict the existence of new modes of low-temperature combustion and oxidation of droplets without the hot flame stage. In such modes, the basic reaction is concentrated very close to the drop surface, while fuel vapor in it reacts only partially.

ACKNOWLEDGMENTS

We thank V.S. Posvyanskii for help with performing the calculations.

Studies were carried out in the framework of the “Zarevo” space experiment.

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Translated by G. Kirakosyan