

ON APPLICATION OF EMULSIFIED LIQUID FUELS FOR COMBUSTION CONTROL

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Introduction

The objective of the theoretical research summarized herein is to compare combustion performances of pure-fuel and emulsified-fuel drops. Based on general thermodynamic considerations, it is anticipated that addition of a volatile liquid component to a heavy hydrocarbon fuel in the form of dispersed droplets allows one to control parent drop combustion by decreasing the amount of fuel vapor accumulated between the flame and the drop surface and displacing the flame closer to the surface. As a consequence, more intense interphase fluxes can occur, affecting the parent drop lifetime and pollutant emission [1]. When the temperature of bubble nucleation in emulsion is lower than the hydrocarbon boiling temperature, bubble growth around the dispersed liquid droplets may result in parent drop disruption ('microexplosion') [2]. If, additionally, the volatile liquid component exhibits exothermic decomposition or reacts exothermically with the fuel, parent drop microexplosion can be significantly enhanced. Drop microexplosion facilitates mixing of fuel with oxidizer that is important for propulsion applications.

Formulation

The mathematical model is aimed at better understanding of the encountered phenomena. The model considers a spherical parent drop

of heavy hydrocarbon fuel with initially uniformly dispersed droplets of a volatile liquid component. Parent drop evolution is assumed to be continuous (without disruption) at constant ambient pressure, i.e., instantaneous variation of drop volume due to growth of vapor bubbles or thermal expansion of liquid is adopted. The set of governing partial differential equations describes transient heating of the multi-phase drop interior and transient heat and mass transfer in the multi-component gas-phase ambience. All physical properties are taken temperature and pressure dependent. In general, a number of chemical reactions in both gas and liquid phase are taken into account. The effect of Laplace pressure at curved liquid-gas interfaces is also incorporated.

As an example, liquid alkane (*n*-heptane, *n*-tetradecane, or *n*-hexadecane) and concentrated aqueous solution of hydrogen peroxide (HP) were considered as heavy hydrocarbon fuel and volatile liquid component, respectively. The dual-fuel system of this sort has been proposed as a candidate for advanced air-breathing propulsion [3]. To simulate combustion of such a composite drop in air, a thermodynamic problem of vapor-liquid equilibrium for the system *n*-tetradecane – wa-

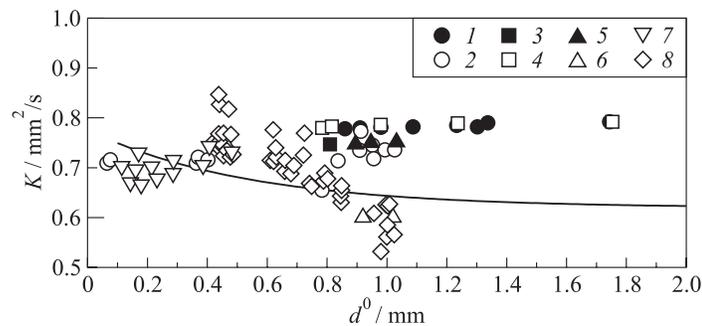


Figure 1 Comparison of predicted (curve) and measured (symbols) dependencies of *n*-heptane combustion constant on the initial drop diameter. Experimental data: 1 — Okajima and Kumagai (1975), 2 — Hara and Kumagai (1994), 3 — Mikami *et al.* (1994), 4, 5 — Kumagai *et al.* (1971), 6 — Jackson *et al.* (1992), 7 — Monaghan *et al.* (1968), and 8 — Jackson & Avedisian (1994)

ter-HP-air has been addressed [4]. The vapor-liquid equilibrium relations were derived for the wide range of temperature and total pressure relevant to propulsion applications. Characteristic decomposition time of HP in aqueous solution has been estimated as a function of temperature.

Model Validation for Pure Hydrocarbon Drop

Curve in Fig. 1 shows the predicted dependence of the combustion constant of *n*-heptane drops on the initial drop diameter. In the calculations, the combustion constant is determined as the slope of the drop-surface regression curve when quasi-steady gasification is attained. Symbols in Fig. 1 represent experimental data obtained both under microgravity conditions (for drops of diameter exceeding 0.4–0.5 mm) and normal gravity conditions (for drops of diameter less than 0.4–0.5 mm). Clearly, the model correlates satisfactorily with the measurements within a wide range of initial drop sizes.

Comparison of Combustion Performances of Pure-Fuel and Water-in-Oil Emulsion Drops

First, consider some distinctive features of emulsion drop combustion on the example of a water-in-oil emulsion drop. The main distinctive feature of the emulsion drop gasification is the existence of a relatively long (up to 50% of the drop lifetime) period of drop expansion due to formation of vapor bubbles in parent drop interior. The predicted overheat of vapor bubbles attains 100–150 K. Figure 2 shows typical predicted surface regression curves for a burning 95% (wt.) *n*-tetradecane–5% (wt.) water drop (solid curve) and pure *n*-tetradecane drop (dashed curve) 30 μm in diameter under similar initial conditions. Contrary to the pure-fuel drop, there is no evidence of the quasi-static d^2 -law for the water-in-oil emulsion drop. Gasification of the emulsion drop exhibits a fast stage of surface regression after passing the maximum in the ‘ d^2 -time’ curve. The combustion constant at this later stage in the drop lifetime is about a factor of 2 higher than that for a pure-fuel drop. Within the present concept of continuous drop evolution, this stage can be conditionally treated as the microexplosion stage.

Thermodynamic Properties of Aqueous Solutions of Hydrogen Peroxide

To efficiently replace water by concentrated aqueous solution of HP in water-in-oil emulsion, one has to know characteristic properties of HP solutions. Total pressure $P(x, T)$ of the binary two-phase system HP – water can be modeled based on the expression [4]:

$$P(x, T) = \left[\left(\frac{T}{\alpha(x)} \right)^{1/8} - A(x) \right]^8$$

$$\alpha(x) = 3.4679 \cdot 10^{-7}(1 - x) + 3.7642 \cdot 10^{-7}x \quad (1)$$

$$A(x) = 12.4575(1 - x) + 12.5302x$$

where T is temperature (in K), x and $1 - x$ are the molar fractions of HP and water in solution, respectively, and P is in atm. This expression does not incorporate the ideal-gas approximation and is applicable within the entire temperature range where each of the solution components exists in both liquid and gas phases. Based on this expression and activity coefficients (see [4]), gas-phase composition can be readily obtained. Figure 3 shows the predicted dependencies of HP mole fraction in gas phase on the HP mole fraction in aqueous solution at $T = 423$ K. Note that in [4], HP is considered without kinetic issues of its stability in terms of liquid- and gas-phase decomposition and other chemical transformations. This is acceptable if the local characteristic time of attaining the conditional thermodynamic equilibrium (at “frozen” chemical composition of the solution) is less than the characteristic times of chemical relaxation. The probability of violation of this condition increases with temperature.

Liquid-Phase Decomposition of Hydrogen Peroxide

Hydrogen peroxide and its aqueous solutions are very complex substances in terms of physical and chemical properties, in particular, chemical kinetics. Aqueous solutions of HP exhibit electrolytic properties. Apart from neutral molecules and radicals, aqueous solutions of HP contain solvated ions. There are still many unresolved problems related, in particular, to chemical kinetics, especially at temperatures considerably exceeding normal temperature.

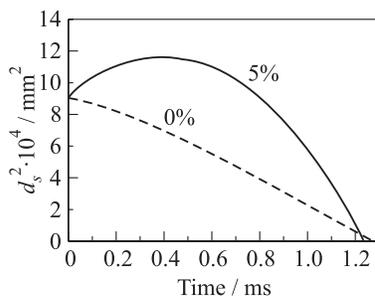


Figure 2 Predicted surface regression curves for a burning 95% (wt.) *n*-tetradecane – 5% (wt.) water emulsion drop (solid curve) and pure *n*-tetradecane drop (dashed curve) under similar initial conditions ($T_0 = 1200$ K, $p_0 = 1$ bar)

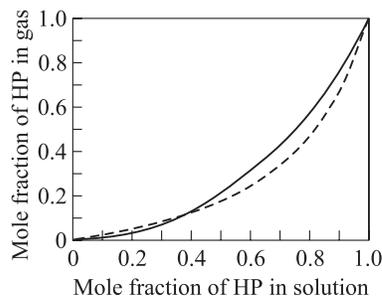
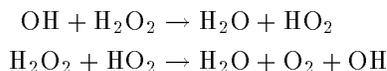
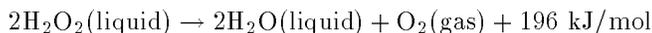


Figure 3 Predicted dependencies of HP mole fractions in gas phase on the HP mole fraction in aqueous solution at $T = 423$ K. Solid curve — Eq. (1), dashed curve — ideal solution approximation

Chemical bonds in the HP molecule are very strong therefore thermal dissociation of the molecule in the gas phase is negligibly small even at 1000 K. Decomposition of HP in aqueous solutions is closely connected with chain reactions involving active radicals. One of chain reaction mechanisms is:



The rate of HP decomposition according to this mechanism depends on the rate constants of both reactions and radical concentrations. The latter are dependent of the competition between the processes of radical formation and removal in other reactions. The combination of these two reactions results in exothermic reaction of HP decomposition:



Exothermic decomposition of HP and availability of additional oxygen is expected to intensify emulsion drop combustion due to both faster drop disruption and faster gas-phase ignition. Based on the analysis of

the chain mechanism of HP decomposition, two estimates of the characteristic decomposition times have been obtained. The first estimate is based on the hypothesis of radical formation in the dissociation reaction of HP with no effect of impurities. The second, more realistic, estimate is based on the radical formation due to charge exchange reactions between iron ions and solvated ions of radicals. It is shown that available experimental data for HP decomposition time under conditions when impurities are present in trace amounts agree satisfactorily with the second estimate at temperatures up to 100 °C.

The use of concentrated aqueous solution of HP rather than pure water, other conditions being equal, results in intensification of emulsion drop gasification and faster growth of vapor bubbles caused by HP decomposition. These effects are more pronounced when more concentrated and less purified aqueous solutions of HP are used.

Gas-Phase Decomposition of Hydrogen Peroxide

Faster gas-phase ignition of a fuel drop in air in presence of gas-phase HP was demonstrated computationally in [5] for *n*-heptane drops. Figure 4a shows predicted time histories of maximum temperature for an *n*-hexadecane drop in air (1) and in air with 10% (vol.) HP vapor (2) under conditions relevant to detonation initiation by a strong shock wave (pressure of 30 atm, temperature of 1500 K). Clearly, without HP, the ignition delay exceeds 100 μ s, while addition of HP results in decreasing the ignition delay by more than an order of magnitude. Figure 4b indicates that, without HP, a drop simply evaporates, while with HP, an *n*-hexadecane drop burns with the combustion constant of about 0.8 mm²/s.

Concluding Remarks

The paper describes the mathematical model of emulsified-fuel drop combustion and the results of its implementation. The model has been validated against available experimental data for combustion of pure-hydrocarbon fuel drops. It has been shown that mechanical mixing of a hydrocarbon fuel with concentrated aqueous solution of hydrogen peroxide allows one to efficiently control droplet combustion performance.

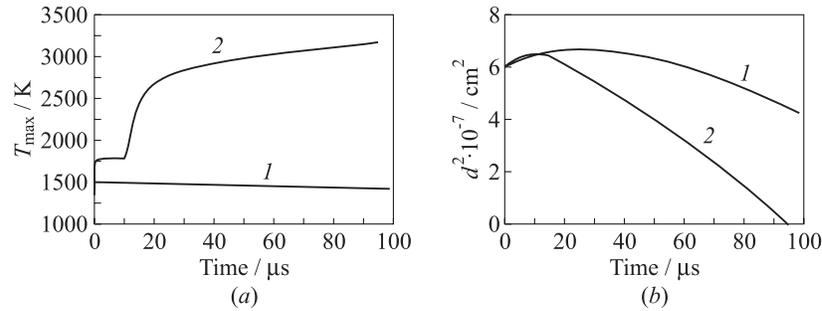


Figure 4 Predicted time histories of maximum temperature (a), and drop diameter squared (b), for an *n*-hexadecane drop in air (1) and in air with 10% (vol.) HP vapor (2) under conditions relevant to detonation initiation by a strong shock wave (pressure of 30 atm, temperature of 1500 K). Initial drop diameter is 8 μm

Acknowledgments

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