Detailed modeling of an isolated, ethanol droplet combustion under microgravity conditions

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Abstract

Simulations of ethanol droplet combustion in microgravity have been conducted using a transient, finite-element, reactive flow model that includes a detailed description of gas-phase chemical kinetics and transport as well as non-luminous radiation. The results of the simulations are compared with a wide range of experimental data available in the literature. The experimental targets included ground-based, suspended droplet experiments, drop-tower experiments, and space-based experiments from the Fiber-Supported Droplet Combustion-2 project. The presented model is shown to reproduce closely nearly all aspects of ethanol droplet burning phenomena, such as droplet burning history, average burning rates, radiative extinction behavior, and kinetics of water accumulation in the liquid phase. Both the experimental and computational results reported in the present study suggest that for ethanol droplets burning in air at 1 atm, the radiative extinction diameter has a value of \( \frac{1}{110} \text{ mm} \). © 2003 The Combustion Institute. All rights reserved.

Keywords: Droplet combustion; Microgravity; Ethanol

1. Introduction

Understanding the liquid-ethanol combustion process has significant industrial and fundamental implications. Ethanol has been considered as a motor fuel since the early days of automobiles. In recent years, the use of ethanol as a fuel additive has been stimulated by the Clean Air Act Amendments of 1990 [1,2], which require utilization of re-formulated and oxygenated gasoline to reduce carbon monoxide and volatile organic compound emissions. Ethanol currently contributes \( \sim 1\% \) of the total highway fuel market in the United States [3]. Until recently, the primary component in oxygenated fuels was methyl tertiary butyl ether (MTBE). However, it has been reported to contaminate groundwater, which subsequently has led to strong interest in banning the usage of MTBE. With the phase-out of MTBE, ethanol remains one of the most favorable oxygenate additives. In addition to the conventional internal combustion engine applications, there are possibilities of ethanol usage in fuel cells, both as feed-stock for on- and off-road hydrogen re-formers and as a direct fuel with specially-developed, high-temperature polymer electrolytes [3]. Unlike gasoline, ethanol is produced from bio-mass, a renewable energy source. In addition, while the applications of fuel ethanol are mainly focused on the environmental aspects, ethanol also improves fuel octane number and can serve as a gasoline extender.

From a fundamental point of view, ethanol represents one of the simplest liquid fuels, with properties similar to those of practical liquid fuel blends. Additionally, its gas-phase oxidation chemistry is relatively simple and has been extensively studied [4-9].
These factors make ethanol a valuable target for fundamental droplet combustion studies and model validation that can ultimately lead to a better understanding of practical liquid fuel combustion processes. Liquid ethanol is also readily soluble in water, and, similar to methanol [10-13], is able to absorb water vapor from the gas phase. Ethanol-water mixtures are known to exhibit a non-ideal (azeotropic) behavior, a property of potential interest to liquid hazardous waste incineration applications [14,15]. Finally, ethanol has unusual sooting characteristics that have not received much attention in the literature. As an oxygenate, ethanol is considered to be essentially a non-sooting fuel at normal conditions. At elevated pressures (starting from as low as 2 atm of air), however, an ethanol droplet flame has been shown to form soot profusely [16]. Therefore, ethanol can also be used for studying sooting phenomena in general and the effect of pressure on soot formation during droplet combustion in particular.

One of the first quantitative data sets describing the burning of an isolated, ethanol droplet was reported in the classic work of Godsave [17]. Later, Kumagai and co-workers [18,19] performed the first microgravity ethanol droplet combustion experiments using drop-tower facilities. Droplet burning histories, average burning rates, and flame diameters were reported for isolated, ethanol droplets burning in air at 1 atm. Initial droplet diameters covered the range of $0.7-1.7$ mm, and the observation time was $1$s. Lee and Law [12] studied combustion of small $(\sim 200 \, \mu m)$, free-falling methanol and ethanol droplets. The experiments were carried out in the post-burning region of a laminar flat flame at temperatures of $1050 \, K$. The authors reported droplet burning histories and time-resolved, integral, liquid-phase water mass fractions. Based on the analysis of their data, Lee and Law concluded that the effect of gas-phase water condensation on ethanol gasification was smaller compared to that of methanol. Colantino and Nayagam [20] measured radiative emission during microgravity droplet combustion using the NASA 2.2 s drop-tower facilities. Their experiments were conducted with methanol, ethanol, and $n$-heptane droplets burning in air at 1 atm. The radiative-emission intensities of the burning droplets were recorded with two wide-angle radiometers. Due to the limited zero-gravity time available, only initial parts of the burning history for two large ($2.5$ and $2.65$ mm) ethanol droplets were obtained.

The number of modeling studies that have specifically considered isolated, ethanol-droplet combustion is rather limited. Puri and Libby [21] presented a numerical model for steady-state, one-dimensional, droplet combustion with a special emphasis on an accurate description of the gas-phase transport processes. Gas-phase chemistry was described with an infinitely fast, single-step reaction leading to the equilibrium composition of water-gas products, CO, CO$_2$, H$_2$, and H$_2$O. The authors performed calculations for several liquid fuels, including ethanol. The predicted burning rates for an ethanol droplet were in very good agreement with the experimental data of Kumagai and co-workers [18]. More recently, Filho [22] reported a simplified, analytical, steady-state, droplet-burning model that accounted for the temperature dependence of the molecular transport coefficients and non-university Lewis numbers. Again, the results for several fuels inclusive of ethanol were reported. The agreement with the experimental data of Kumagai and co-workers [18,19] was shown to be rather poor, and the author attributed it to over-estimation of flame temperatures caused by a simplified description of gas-phase combustion kinetics. It should be emphasized, however, that neither of these modeling studies considered the effects associated with gas-phase radiative heat transfer and water condensation on the droplet surface, important issues identified in the modeling work reported here.

2. Experimental

Microgravity ethanol droplet combustion experiments have recently been performed aboard the STS-94/MSL-1 Shuttle mission within the Fiber-Supported Droplet Combustion-2 (FSDC-2) program [24]. This paper presents the first summary of all of the FSDC-2 experiments performed using ethanol and an ethanol-4% water mixture as fuels.

All experiments were carried out in the Glovebox (MGBX) facility using the FSDC-2 experimental apparatus. Liquid fuel was contained in modified, airtight, commercial syringe cartridges. To operate the experiment, the fuel cartridge was screwed into the base of the experiment module. The crew turned a plunger screw, forcing fuel through two opposed, hypodermic needles to the deployment site on a silicon fiber located between the needles and perpendicular to them. After the fuel coalesced into a droplet of the desired size, the needles were slowly retracted to minimize contact of the liquid with the needle surfaces. The stretched droplet was then deployed by rapidly retracting the needles into the bottom of the chamber. Motions of the deployed droplet were allowed to dampen before the igniter was energized. Actuation of the igniter system lifted a replaceable hot igniter into place on one side of the droplet (parallel to the fiber), approximately 3.5 mm from the fiber, and simultaneously provided electric current to the igniter. When the crew operator detected ignition visually, the igniter button was released, automati-
cally retracting the igniter wire assembly to the bottom of the test chamber. Imaging data were provided by two video views, a back-lit view of the droplet and, a perpendicular view of the flame. The video camera for the droplet view was attached to the Glovebox microscope. The second video camera, with a view essentially orthogonal to the microscope, recorded the droplet, the fiber, and the flame. All of the data were recorded using three 8-mm VCRs.

The taped camera images were analyzed in this laboratory using microcomputer-based imaging analysis systems. The data-reduction techniques that were utilized have been described elsewhere by Struk et al. [24]. Each droplet-combustion test occurred at pressures of 0.996–1.107 bar, oxygen mole fraction 0.204–0.222, and relative humidity of 39 to 46% of the SpaceLab environment. Both pure ethanol and 96% ethanol-4% water droplets were studied; the initial droplet diameter ranged from ~2.5 to 6 mm.

3. Droplet-combustion model

The numerical modeling of spherically-symmetric, liquid droplet combustion was performed by solving the following gas-phase conservation equations of mass, species, and energy:

\[ \frac{\partial \rho_g}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \rho_g \nu_g \right) = 0 \]  

(1)

\[ \rho_g \frac{\partial Y_g}{\partial t} + \rho_g \nu_g \frac{\partial Y_g}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \rho_g \nu_g \right) = \omega_{g,i} \]  

(2)

\[ \rho_g C_{p,g} \frac{\partial T_g}{\partial t} + \rho_g C_{p,g} \nu_g \frac{\partial T_g}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \lambda_g \frac{\partial T_g}{\partial r} \right) - \rho_g \sum_{i=1}^{n} (Y_{g,i} V_{r,i} C_{p,g,i}) \frac{\partial T_g}{\partial r} - \sum_{i=1}^{n} \omega_{g,i} H_{g,i} = \nabla \cdot q_R \]  

(3)

where \( t \) is the time; \( r \) the radial coordinate; \( \rho_g, T_g, C_{p,g}, \) and \( \lambda_g \) the density, temperature, constant-pressure heat capacity, and thermal conductivity, respectively, of the gas mixture; \( \nu_g \) the radial fluid velocity; \( Y_{g,i}, V_{r,i}, \omega_{g,i}, C_{p,g,i}, \) and \( H_{g,i} \) the mass fraction, diffusion velocity, gas-phase mass-production rate, constant-pressure heat capacity, and enthalpy, respectively, of the \( i \)-th gaseous species; and \( n \) the number of gaseous species. The term \( q_R \) appearing in Eq. 3 is the heat flux due to the non-luminous radiative heat transfer.

In the liquid phase, the following equations were applied:

\[ \frac{\partial \rho_l}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \rho_l \nu_l \right) = 0 \]  

(4)

\[ \rho_l \frac{\partial Y_{li}}{\partial t} + \rho_l \nu_l \frac{\partial Y_{li}}{\partial r} - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_l \frac{\partial Y_{li}}{\partial r} \right) = 0 \]  

(5)

\[ \rho_l C_{p,l} \frac{\partial T_l}{\partial t} + \rho_l C_{p,l} \nu_l \frac{\partial T_l}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \lambda_l \frac{\partial T_l}{\partial r} \right) \]  

(6)

where \( Y_{li} \) is the mass fraction of the \( i \)-th species in the liquid phase, and \( \nu_l, D_l, \rho_l, C_{p,l}, T_l, \) and \( \lambda_l \) the flow velocity, effective diffusion coefficient, mass density, constant-pressure heat capacity, temperature, and thermal conductivity, respectively, of the liquid phase.

The boundary conditions included application of zero gradients in the center of the droplet,

\[ \frac{\partial Y_{g,i}}{\partial r} |_{r=0} = \frac{\partial T_g}{\partial r} |_{r=0} = 0 \]  

(7)

and gas ambient conditions at \( r = \infty \),

\[ Y_{g,i} |_{r=\infty} = Y_{g,i}^\infty T |_{r=\infty} = T\infty, \]  

(8)

where \( Y_{g,i}^\infty \) is the mass fraction of the \( i \)-th species in the ambient environment, and \( T\infty \) the temperature of the ambient environment. In addition to the boundary conditions at \( r = 0 \) and \( r = \infty \), the temperature continuity and conservation of mass and energy across the liquid-gas interface were considered:

\[ (T_g = T_l) |_{r=r_p} = r_p, \]  

(9)

\[ \frac{dr_p}{dt} = \left( v_g - (v_g - v_l) \frac{\rho_l}{\rho_g} \right) |_{r=r_p}, \]  

(10)

\[ \left( D_l \frac{\partial Y_{li}}{\partial r} - (v_g - v_l) \frac{\rho_l}{\rho_g} (Y_{li} - \epsilon_i) \right) |_{r=r_p} = 0 \]  

(11)

\[ \left( \lambda_l \frac{\partial T_l}{\partial r} - \lambda_g \frac{\partial T_g}{\partial r} - \rho_g (v_g - v_l) \sum_{i=1}^{n} \epsilon_i L_i + q_R \right) |_{r=r_p} = 0, \]  

(12)

where \( r_p \) is the droplet radius, \( L_i \) the latent heat of the \( i \)-th species in the liquid phase, and \( \epsilon_i \) the fractional gasification rate of the \( i \)-th species in the liquid phase, defined as

\[ \epsilon_i = \frac{m_i}{\sum_{i=1}^{n} \tilde{m}_i}. \]  

(13)

In Eqs. 12 and 13, \( m \) is the total mass-gasification rate, \( \tilde{m}_i \) the mass gasification rate of the \( i \)-th species in the liquid phase, and \( n_i \) the number of species in the liquid phase equal to 2 (i.e., ethanol and water) in
the present study. Besides the main liquid component, ethanol, the presence of water in the liquid phase was also considered, both as an initial liquid-mixture component and as an absorbed gas-phase combustion product. The system of Eqs. 1 through 12 is closed with the ideal-gas equation of state, along with the density \( \rho_1 = \rho_c (Y_c, T) \), and equilibrium vapor-pressure correlations for non-ideal ethanol-water liquid mixtures. Detailed gas-phase kinetics of ethanol oxidation was described with the reaction mechanism of Norton and Dryer [7], which consists of 142 reversible reactions of 33 species. As will be discussed in the next section, the predicted droplet-flame structure and the burning history were relatively insensitive to the existing uncertainties in the gas-phase chemistry. The gas-phase-diffusion and heat-conduction terms in Eqs. 2 and 3 were evaluated using TRANLIB [31], and the properties for the transport-data calculation were taken from the Sandia database [31] and the compilation of Reid et al. [32]. The vapor pressure at the surface of a bi-component ethanol-water droplet was calculated using the vapor-pressure data for the individual compounds and the standard NTRL correlation for ethanol-water mixtures [32] from Kurihara and co-workers [33]. The temperature-dependent latent heats for ethanol and water were taken from Daubert and Danner [34], and the excess-volume equation of states [32] from Kurihara and co-workers [33]. The standard NTRL correlation for ethanol-water mixtures [31] and the compilation of Reid et al. [32]. The vapor pressure at the surface of a bi-component ethanol-water droplet was calculated using the vapor-pressure data for the individual compounds and the standard NTRL correlation for ethanol-water mixtures [32] from Kurihara and co-workers [33]. The temperature-dependent latent heats for ethanol and water were taken from Daubert and Danner [34], and the mixture liquid density appearing in Eqs. 4 through 6 was computed from the correlations for pure compounds [34] and the excess-volume equation of Bai et al. [35]. Droplet ignition was initiated by imposing the gas-phase temperature profile, which approximated a thermal ignition source, similar to the one used previously [13,29]. Equations 1 through 6, along with the boundary conditions 7 to 12, were solved with the transient, moving-mesh, finite element code described in detail by Cho et al. [25]. This approach has been successfully applied previously to the problems of methanol and methanol-water [13,26–28], n-heptane, and n-heptane-n-hexadecane droplet combustion. All computations were performed on a Pentium III-class Linux workstation.

4. Treatment of non-luminous radiation

In the majority of the previous liquid- and solid-particle combustion modeling efforts [36–38] that have attempted to include radiative heat transfer, the spherically-symmetric formulation presented by Viskanta and Merriam [39] has been utilized. Viskanta and Merriam offered a set of analytical equations expressing the radiative heat-transfer rate terms as functions of local temperature and gas optical thickness, \( \tau(r) = \int_0^r \kappa_p \, dp \), where \( \kappa_p \) is the Plank-mean coefficient. While most of the studies based on Viskanta and Merriam [39] also relied on the assumption of the spatially-uniform \( \kappa_p \), the original description [40] was somewhat unclear on whether this assumption is required for the use of their formulation. During the course of the present study, we have re-examined the original source of the formulation by Viskanta and Merriam, an early analytical development by Kuznetsov [40]. First, we have confirmed that the formulation of Viskanta and Merriam [39] is indeed an approximation valid only for the constant \( \kappa_p \) and therefore cannot be used for the general case when \( \kappa_p \) varies with the radial distance \( r \). Next, after re-evaluation of Kuznetsov’s work and elimination of several typographical errors in his publication, we have arrived at a set of exact, analytical equations applicable to the general case of the arbitrary radial distribution of the Plank-mean coefficient. The resulting equations describing the divergence of the radiative heat flux, \( \nabla \cdot q_R \), in Eq. 3, are given below:

\[
\nabla \cdot q_R = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 q_R \right) = 2 \sigma_p \kappa_p(r) T_s^4 (2 \tilde{T}^4 - g_1 - g_2),
\]

where

\[
g_1 = \int_1^\infty \exp \left[ - \frac{\mu^2}{\kappa_p} \left( \sqrt{u^2 + \tilde{p}^2 (1 - \mu^2)} \right) - 1 d\mu, \right.
\]

\[
g_2 = \frac{1}{\tilde{\tau}} \int_1^\infty \frac{K(\tilde{\tau}, \tilde{\rho} \tilde{p}) \tilde{p} T_s^4 (\tilde{\rho} \kappa_p (\tilde{\rho}) d\tilde{\rho},
\]

\[
K(\tilde{\tau}, \tilde{\rho}) = \int_{|\tilde{\tau} - \tilde{\rho}|}^{|\tilde{\tau} + \tilde{\rho}|} \exp \left[ - \frac{|\tilde{\tau}^2 - \tilde{\rho}^2|}{2z^2} \kappa_p \left( \sqrt{u^2 - \phi(\tilde{\tau}, \tilde{\rho}, z)} \right) du \right] \frac{dz}{z},
\]

\[
\phi(\tilde{\tau}, \tilde{\rho}, z) = \frac{1 + \tilde{\rho} - z)(\tilde{\tau} + \tilde{\rho} + z)(\tilde{\tau} - \tilde{\rho} + z)(\tilde{\tau} - \tilde{\rho} - z)}{4z^2},
\]

\[
\sigma_{\text{SB}} \text{ is the Stefan-Boltzmann constant, } \tilde{T} = \frac{T_s}{T_s, \tilde{\rho} = \kappa_p \tilde{\tau}}, \text{ and } \tilde{r} = r/lp.
\]
The first term in Eq. 14 is associated with the heat loss due to radiation, and the \( g_1 \) and \( g_2 \) terms represent the re-absorption of radiation from the particle surface and the gas-phase, respectively. Clearly, the radiation from the droplet surface, i.e., the surface and the gas-phase, respectively. Clearly, the energy balance on the droplet surface in Eq. 12 is given by

\[
q_{\text{r}}|_{r=r_p} = \sigma_B T_l^4 \left( 1 - 2 \int \rho \bar{r} \left( \frac{\bar{r}}{r_p} \right) \frac{\bar{T}}{T_l} \psi(\bar{r}) \, d\bar{r} \right),
\]

where

\[
\psi(\bar{r}) = \int \frac{1}{\sqrt{\bar{r}^2 - 1}} \exp \left[ - \int \frac{\bar{r}_p \sqrt{\bar{r}^2 + \bar{r}_p^2 - z^2}}{\sqrt{\bar{r}^2 - \bar{r}_p^2 + 1}} \, dz \right] \, dz.
\]

While Eqs. 14 and 19 involve two-dimensional integration, these integrals are well-defined and can be evaluated efficiently, as opposed to the use of costly discretizations needed for the direct solution of the radiative-transfer equation with a discrete ordinate method [41]. It is also worthwhile to point out that, although it was not attempted in the present study, Eqs. 14 through 19 can be trivially extended to account for non-gray effects using, e.g., the spectral-line-weighted sum of the gray-gases model [42]. The local values of \( \kappa_\rho \) in the present calculations were computed from the individual contributions of CO, CO\(_2\), and H\(_2\)O, as reported by Marchese and Dryer [28].

5. The effect of variations in liquid-phase density

As can be seen, Eqs. 4 through 6 include convective terms associated with the liquid-flow-velocity, \( v_l \). A rigorous multi-dimensional treatment of liquid-phase flow was not attempted in the present work, and, as will be discussed in the next section, liquid-phase flow effects on liquid mass and thermal transport were accounted for via effective, empirical, transport corrections. In the present section, we also considered a radial convective liquid-flow velocity component in the governing equations solely for the purposes of assessing the importance of the effects associated with changes in the local liquid-phase density. From Eq. 10, the effective burning rate, \( K_{\text{ov}} \), has contributions from two sources,

\[
K_{\text{ov}} = - \frac{d(d_p^2)}{dt} - 8 r_p \frac{dr_p}{dt} = K_1 + K_2,
\]

where \( d_p \) is the droplet diameter, \( K_1 = - 8 r_p \left( v_g - v_l \frac{\rho_g}{\rho_l} \right) \) is associated with the actual liquid-mass gasification. Following Eq. 4, the expression for \( K_1 \) can be rewritten as

\[
K_1 = - \frac{8}{\rho_l \rho_p} \int_0^{r_p} \frac{\partial \rho_l}{\partial t} \, dr
\]

\[
= - \frac{8}{\rho_l \rho_p} \left( \int_0^{r_p} \frac{\partial T_l}{\partial t} \, dr + \sum_{i=1}^{m} \int_0^{r_p} \frac{\partial Y_{li}}{\partial t} \, dr \right),
\]

distinguishing the contributions due to the changes in local liquid-phase temperature (thermal contraction/expansion) and in composition (due to water dissolution in the liquid phase in the case of ethanol droplet). To clarify the importance of the effects associated with changes in liquid-phase density, a series of model exercises were carried out. Figure 1 compares the results of two test calculations for a 3-mm ethanol droplet burning in air at 1 atm. In the first case, the computations were performed using the complete set of equations presented in the previous sections. In the second case, \( v_l \) was set to zero in the corresponding equations while retaining the functional dependencies of the liquid-phase density on local temperature and composition. Shown on the top panel of Fig. 1 is the comparison of evolution of normalized, droplet diameter-squared and the instantaneous burning rate. It is clear that the results are affected by variations in liquid density. These effects, however, are primarily confined to the duration of the initial droplet heat-up when an increase in droplet diameter due to thermal expansion results in large negative values of \( K_{\text{ov}} \). After the initial heat-up period is over, the contribution of \( K_1 \) to the total effective burning rate approaches zero and becomes much less important than that from the actual liquid-gasification rate, \( K_2 \). The contribution of \( K_1 \) becomes competitive again (but to a lesser extent) only around the point of extinction, when the gasification rate ceases, while an increase in liquid-water content and subsequent cool-
droplet burning is established, it has very little “memory” of the initial transient, heat-up period (as long as the ignition energy does not over-drive the process). In all FSDC microgravity droplet-combustion experiments, ignition is initiated by a non-symmetric source, and spherical symmetry is not established until a short time later in the process. However, the numerical test presented here supports the idea that experimental burning histories can still be compared with uni-dimensional-model results by matching the quasi-linear parts of the curves, and detailed resolution of the initial heat-up period is not required. Second, the presence of $v_i$ terms in the governing equations does not affect significantly the model results relevant to the present study. Consequently, these terms were ignored in the following analysis (to reduce numerical stiffness).

6. Treatment of liquid transport

The extent of water absorption and its effect on both the quasi-steady burning rate and flame-extinction phenomena are strongly influenced by liquid mass-transport [13,43]. The liquid mass Peclet number,

$$
P_{e_{\text{lm}}} = r_p \frac{d r_p}{d t} D_l = \frac{1}{8} \frac{d (d_p^2)}{d t} \frac{D_l}{D_t} = \frac{1}{8} \frac{K_p}{D_t}. \tag{22}
$$

is normally used to characterize the effects of the liquid-phase transport. If the liquid mass Peclet number is low, the condensed water is preferentially transferred into the droplet interior, resulting in a higher degree of water accumulation in the liquid phase. If, on the other hand, the Peclet number is high, only a thin, surface boundary layer containing water is formed, without significant water penetration into the droplet interior. Consequently very little water accumulates in the liquid phase over the droplet-burning time. In the calculations, the burning rate $K_b$ is obtained as part of the solution, but the “effective liquid diffusivity”, $D_l$, has to be provided as the model input parameter. In the absence of internal liquid motion, the liquid transport is controlled by molecular diffusion, and the value of molecular diffusivity of water in ethanol appears to be $\sim 1 \times 10^{-5}$ mm$^2$s$^{-1}$ [44]. Based on the data that will be reported in the following sections, this value of $D_t$ would correspond to $P_{e_{\text{lm}}}$ of $\sim 5 \times 10^2$ for a 3-mm ethanol droplet burning with an average $K_b$ of $0.4$ mm$^2$s$^{-1}$. This, in turn, would imply a high-Peclet-number regime, or the diffusion limit [45], with very little water accumulation in the liquid phase. However, the available experimental evidence [11,12], as well as

![Fig. 1. Model predictions for a 3-mm ethanol droplet burning in air at 1 atm, illustrating the effect of variations in liquid-phase density. Top panel: evolution of droplet diameter-squared and instantaneous burning rate; bottom panel: instantaneous burning rate and integrated liquid-water mass-fraction plotted as functions of the extent of burning, $1 - (d/d_0)^2$. Solid lines represent computations based on the full system of Eqs. 1 through 12; dotted lines correspond to the solution with $v_i$ set to zero (see text).](image-url)
extensive asymptotic [45] and numerical [13] analysis of methanol droplet combustion, has suggested that the transport of water in the liquid phase is characterized by the low Peclet number regime (convection, or well-mixed, limit [45]). The enhancement of flow motion in the droplet interior originates from a number of sources, including interfacial effects between liquid and gas phases (thermal and solutal Marangoni effects [46–49]), interaction between needles and the droplet during deployment, droplet motions relative to the local gas-phase environment, and the presence of gaseous bubbles within the liquid interior as a result of droplet growth and deployment. Under combustion conditions, tethering filaments and the associated interfacial surface tension effects can also induce significant internal circulation. Considering physical and chemical similarities between ethanol and methanol as well as the fact that the same method of droplet generation and deployment was used for both ethanol and previously analyzed methanol [27] droplets in the FSDC-2 program, it is reasonable to expect similar convective enhancement of diffusive liquid-transport by internal liquid-phase motions in the case of ethanol droplets. Furthermore, inspection of video records from the FSDC-2 program shows rapid bubble circulation inside burning ethanol droplets, thus providing additional, direct evidence of internal liquid motion. In the previous methanol droplet combustion modeling studies [13,27,28], the effective liquid diffusivity was empirically increased to address the effect of internal liquid motion. The detailed discussion justifying this approach is given by Marchese and Dryer [13]. In the present study, we have followed the same approach, and the value of the effective liquid diffusivity $D_l$ for the baseline simulations was assigned by analogy with the previously studied methanol cases [13,27]. It is important to emphasize, however, that the effective liquid diffusivity is the only empirical parameter in the present study; the rest of the model remains as detailed and uncompromised as possible, with no other parameters treated as adjustable quantities.

To elucidate the choice of $D_l$ adopted in the present study, a number of parametric sensitivity calculations were performed, as discussed below. Figure 2 shows the model predictions for a 3-mm ethanol droplet burning in air at 1 atm. Inspection of this figure indicates that the present baseline choice of $D_l$ corresponding to $Pe_{l,m} \sim 0.6$ results in a near “convection limit” of droplet burning, and a further decrease of $Pe_{l,m}$ does not have a significant effect on the droplet-burning history or water accumulation in the liquid phase. As can also be seen in Fig. 2, the uncertainty in $Pe_{l,m}$ within a factor of 2 of the baseline case does not affect the predicted droplet-burning history, resulting in virtually the same burning rate and extinction diameter. An increase of $Pe_{l,m}$ by an order of magnitude, on the other hand, initiates transition to “diffusion limit” burning, drastically reducing the rate of water dissolution. At $Pe_{l,m} \sim 18$, the system approaches the result when water condensation is turned off completely in the simulation. The results presented in Fig. 2 also exhibit an interesting feature, namely, there appears to be an acceleration of droplet burning (increase in the burning rate) at the end of the process for the cases with little or no water absorption (high liquid-mass Peclet numbers). This behavior is caused by the fact that the chosen initial droplet diameter is relatively large, and the radiative heat losses, being a strong function of the droplet size [28], contribute significantly in the beginning of the process. With liquid-fuel consumption, the droplet size becomes smaller and the influence of radiation decreases, resulting in accelerated burning. This phenomenon is not observed for the high-$Pe_{l,m}$ cases, since the burning acceleration is hindered by increasing water content in the liquid phase.

To further illustrate the choice of effective $D_l$, a number of model runs were performed at the condi-
tions studied experimentally by Lee and Law [12]. As was mentioned in the Introduction, Lee and Law investigated droplet burning and temporal liquid-water accumulation in the post-combustion gases of a laminar premixed flame. Figure 3 displays the comparison of their experimental data and the present model predictions for the case of a "wet" environment, i.e., when water vapor was present in the ambient atmosphere as one of the combustion products of a CH$_4$/O$_2$/N$_2$ laminar, premixed flame. As shown in the top panel of Fig. 3, the evolution of diameter-squared with time is well reproduced in the simulations. It is also clear that the burning history is not very sensitive to the $P_{e_{l,m}}$ for the entire range of experimental observations. Shown on the bottom panel of Fig. 3 is the comparison of the computed liquid-water mass fraction with the experimental measurements. As can be seen, the baseline choice of $D_v$, which corresponds to $P_{e_{l,m}} \sim 1.1$ for this case of $K_b = 0.8$ mm$^2$ s$^{-1}$, agrees reasonably well with the experimental results. A further decrease of $P_{e_{l,m}}$ shows only moderate improvement of the agreement, and the predicted changes are likely to be less than the uncertainties in the estimated ambient conditions (gas-phase composition and the temperature) and the actual experimental measurements. An increase of $P_{e_{l,m}}$ toward the diffusion limit, on the other hand, leads to the drastic departure of the model predictions from the experimental data. Therefore, it can concluded that the results of Lee and Law also support the low-$P_{e_{l,m}}$-regime of droplet burning, indicating that in these experiments, substantial internal liquid-phase motions existed.

An important observation that can be made based on the computational results presented in Fig. 2 is that the rate of water accumulation in the liquid phase is substantially smaller for the ethanol droplets as compared to the previously-studied methanol cases [13]. The same conclusion was also reached by Lee and Law [12], based on their experimental results. As discussed next, detailed analysis of the model predictions indicates that low rates of water accumulation in the liquid phase for the ethanol droplets are caused by non-ideal (azeotropic) behavior of liquid ethanol/water mixtures. As was noted previously, ethanol forms an azeotrope with water at 4% of water by mass. This implies that at this composition of ethanol/water liquid mixture, the total vapor pressure of liquid components near the droplet surface goes through a maximum, as opposed to the behavior of ideal mixtures described by Raoult’s law (Fig. 4).

Once the level of liquid water at the droplet surface reaches the azeotropic value, further water condensation becomes constrained. To illustrate this phenomenon, an additional model run was performed where the azeotropic vapor-pressure correlation [32] was replaced with Raoult’s law (Fig. 4) for ideal
mixtures. Figure 4 displays the comparison of the results from this test run and the baseline model calculations for combustion of a 1-mm ethanol droplet in air (1 atm). The apparent burning history and the evolution of the instantaneous burning rate shown on the top panel of Fig. 5 are very close for both cases during most of the burning duration. Near the completion of combustion, however, the calculations based on Raoult’s law show significant deviations from the $d^2$ law, followed by earlier extinction with a much larger extinction diameter as compared to the baseline case. This behavior is very typical of the extinction phenomenon caused by water accumulation in the liquid phase [13]. Indeed, as can be seen on the bottom panel of Fig. 5, the calculations based on Raoult’s law exhibit a larger water-condensation rate (i.e., smaller water fractional-gasiﬁcation rates) and result in greater liquid-water mass-fraction.

As was mentioned above, the FSDC-2 experiments involved both pure ethanol and 96% ethanol-4% water mixture droplets. Figure 6 shows the comparison of the model results obtained for the cases of 1- and 3-mm initial droplet sizes with both pure ethanol and ethanol-4% water mixtures. Although the 4% water addition to the initial droplet has a noticeable effect on droplet-burning behavior, the changes in the main observables are relatively small for both droplet sizes, i.e., the observed average burning rate decreased by ~2%, and the extinction diameter increased by 20%. As will be shown in the following sections, these differences appear to be well within the experimental scatter of the FSDC-2 data, and therefore, pure ethanol and ethanol-4% water data can essentially be used collectively.

7. Uncertainties in gas-phase chemistry

To elucidate the influence of the existing uncertainties in the gas-phase reaction chemistry, the model predictions based on the reaction mechanism of Norton and Dryer [7], the baseline of the present study, were compared with the results obtained using another recently published reaction set [8]. The results of this comparison are presented in Fig. 7 for a 1-mm ethanol droplet burning in air (1 atm). As
shown on the bottom panel of Fig. 7, the predicted flame structures appear to be very similar. The predicted maximum flame temperatures at 0.47 s after ignition differ by about 27 K. The main differences appear to be for water, carbon monoxide, and hydrogen profiles in the pyrolysis region of the flame, which are caused by the additional uni-molecular decomposition pathways included in the mechanism of Marinov [8]. The model based on this mechanism also displays a slightly higher degree of water accumulation (Fig. 7, top panel) due to greater water concentrations near the droplet surface. Nonetheless, as can be seen from the predicted burning-rate profiles, the observed variations do not have a significant effect on droplet-burning history and extinction behavior. On the other hand, the mechanism of Norton and Dryer has been shown to yield better agreement with species measurements in an atmospheric flow-reactor [7] and is more compact than the reaction set of Marinov, which contains 383 reactions of 57 species. The Norton and Dryer mechanism [7] was therefore chosen as a baseline throughout the present study. Further refinement of the kinetics [9] will certainly be necessary for future efforts in which we plan to incorporate soot-precursor kinetics and a soot-formation sub-model.

8. Results

8.1. Burning histories

Due to the high cost of space-based experiments, the FSDC-2 data were restricted to the relatively large initial droplet sizes starting from ~2 mm for which the burning histories cannot be followed in full using the drop-tower facilities on the ground. Here, the drop-tower data of Kumagai and co-workers [18,19] were used for smaller droplet comparison. Figure 8 shows the comparison of model predictions and the experimental data for the burning histories with the initial droplet sizes ranging from ~1 to 6 mm. As can be seen, the model shows an overall good agreement with the experiments. For the small, unsupported droplet results [19] shown on the top panel of Fig. 8, the model closely follows the experimental points during the entire observation time. The FSDC-2 data for intermediate-size droplets (2.79 and 3.41 mm) depart from the model predictions during the later parts of burning histories. The inspection of experimental curves and the original video recordings indicated that during the periods in question, the droplets were engaged in oscillatory motion along the supporting fiber. This motion likely induced a forced convective flow around the droplet, enhancing the droplet-burning rates [50]. Shown on the bottom panel of Fig. 8 are the data for the largest droplet experiment conducted in FSDC-2 (d0 = 5.8 mm). The experiment exhibited an early extinction, with very little change in diameter. (Note that for emphasis, the bottom panel is scaled differently from the rest of the Fig. 8.) As can be seen, the model captures the observed behavior.

8.2. Average burning rates

The average droplet-burning rates are compiled in Fig. 9 as a function of the initial droplet size. For consistency with the experimental definition, the model-predicted, average burning rates were obtained from the linear fits to the computed evolution of \( \frac{d^2}{dt^2} \) with time. Clearly, the experimental data exhibit relatively large scatter. Nonetheless, the model appears to provide a good description of the data, both in terms of the general trend and quantitative agreement. As will be discussed in the following sub-sections, the observed decrease in the average droplet-burning rate is mainly caused by the influence of non-luminous, radiative heat losses that be-

Fig. 7. Comparison of model predictions based on the reaction mechanism of Norton and Dryer [7] (solid lines) and Marinov [8] (dotted lines) for a 1-mm ethanol droplet burning in air at 1 atm. Top panel: evolution of droplet diameter-squared and instantaneous burning rate; bottom panel: flame structure at 0.47 s after ignition.
come more pronounced at larger droplet sizes [28]. The predictions of simplified, steady-state models [21,22] are also shown in Fig. 9. Since neither of these models includes radiative heat losses, their predicted burning rates are independent of the initial droplet size.

8.3. Flame diameters

The flame diameters in the FSDC-2 experiments were determined from the visual observations of flame intersections with the supporting filament. The obtained information is rather limited, due to the difficulties caused by the weak, visible luminosity of ethanol flames, and consequently is subject to large uncertainties. The evolution of normalized flame diameter (flame stand-off ratio) for the 2.9-mm ethanol droplet is presented in Fig. 10. Also shown on this figure are the drop-tower data of Hara and Kumagai [19] for a 0.92-mm droplet, as well as the predictions of the present model and the models of Puri and Libby [21] and Filho [22], discussed in the previous section. Throughout the comparisons, the computed flame diameter was defined as the location of the maximum flame temperature. The present detailed, transient model predictions are very close to each other for both droplet sizes and are in a good agreement with the FSDC-2 data (i.e., 2.9-mm droplet). In
addition, the fully-transient model also captures the shape of the experimental curve. The data of Hara and Kumagai [19] appear to be below the present model predictions for the corresponding droplet size. It should be pointed out that the flame positions in the experiments of Hara and Kumagai were obtained based on the visible radiation from the images of unsupported burning droplets and are likely to have even greater uncertainty than the FSDC-2 data. The model of Filho [22] significantly over-predicts all the data, which is very typical of simplified, quasi-steady or transient theories. The predictions of Puri and Libby [21] agree very well with the results of Hara and Kumagai [19]; however, their model was calibrated against these data.

8.4. Extinction behavior

As shown in Fig. 8, larger droplets display early extinction. The extinction diameters obtained for the entire ethanol droplet data set from FSDC-2 are presented in Fig. 11. The model performs very well in reproducing the complex extinction behavior observed in the experiments. Analysis of the model predictions indicates that, for the droplets of < 3 mm in diameter, extinction is mainly caused by water accumulation in the liquid phase. However, the predicted extinction diameters are very small (over a factor of 2 less than those observed for the methanol droplets of the same initial size [27]). Such values cannot be fully resolved in the FSDC-2 experiments, because the predicted extinction diameters are of the same order as the size of the ceramic tethering bead (Fig. 11) embedded in the supporting filament to prevent the droplet from sliding along the fiber. As the initial droplet size approaches ~ 4 mm, both the model and the experimental data follow a sharp, nearly discontinuous increase in the extinction diameter, indicative of radiative extinction. At even larger initial droplet sizes, the value of the extinction diameter asymptotically approaches the value of the initial droplet diameter, i.e., the limiting situation when no burning takes place.

During the FSDC-2 experiments, some of the large droplets that burned and underwent extinction were subsequently re-ignited. This procedure was repeated until the droplet was fully consumed. Also shown in Fig. 11 is the sequence of re-ignition and extinction events calculated for the largest initial droplet size studied (5.8 mm). The droplet re-ignition was simulated by imposing the gas-phase temperature profile that imitated the igniter wire while retaining the liquid- and gas-phase composition produced from the previous burn, followed by extinction and subsequent vaporization periods. As can be seen, the model closely follows the sequence of re-burns reported in the experiments. To further illustrate the effect of radiative heat losses on the burning behavior of large droplets, the following numerical test was performed. For the largest droplet (5.8 mm), an additional model run was carried out, with the radiative heat losses turned off. As a result, no extinction was observed; instead, the burning proceeded at a very high rate close to that of a 1-mm droplet.

Successful prediction of droplet extinction behavior due to radiative heat losses demonstrated above gives indirect evidence of the adequacy of the radiative heat transfer model used in the present study. To further address this point, the model predictions were compared with the direct measurements of total radiant emission, $Q_{\text{rad}}$, by Colantonio and Nayagam [20]. Figure 12 displays the experimental data against the model predictions for two ethanol droplets burning in air at 1 atm. The limited observation time in the 2.2-s drop-tower did not permit sufficiently resolved burning histories for relatively large droplets (2.5 and 2.65 mm) considered in the experiments. Therefore, a large portion of the observed burning history may still be affected by three-dimensional, transient, post-ignition processes that are not accounted for in the uni-dimensional numerical model. The modeling results shown in Fig. 12 indicate that the entire experimental observation period resides over times when the initial, radiant-emission changes are responding primarily to the initial, transient, in-flame development. The burning reaches a quasi-steady regime when $Q_{\text{rad}}$ is approximately at its peak value; after that, radiant emission starts to decline following the decrease of the droplet (and flame) size. Clearly, the model performs reasonably well in capturing the initial increase in total radiant emission and matches very closely the experimental values reported at the Fig. 11. Droplet extinction diameter as a function of the initial droplet size for ethanol and ethanol/water droplets burning in air at 1 atm.
end of the observation period when three-dimensional, post-ignition effects are expected to be minimized.

9. Summary

A comprehensive model of ethanol-droplet burning in microgravity is presented and thoroughly validated. The model predictions for various droplet-combustion characteristics (burning rate, extinction diameter, flame diameter, liquid-water accumulation, flame radiant emission) are in very good agreement with the experimental data obtained within the FSDC-2 program [23], as well as with other available literature data [12,19,20]. The model supports the observation of Lee and Law [12] that the burning of ethanol droplets is less affected by water-vapor condensation as compared to the previously studied methanol cases [13]. Analysis of the model predictions suggests that azeotropic behavior of ethanol-water mixtures restricts the amount of water that can be absorbed by the droplet. The experimental and numerical results of the present work also suggest that, for ethanol droplets burning in air at 1 atm, the radiative extinction diameter has a value of \( \sim 4 \) mm.

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