Isolated Alkane Droplet Combustion in Microgravity: “Cool Flames”

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Flame Extinguishment (FLEX) Experiment Program has been conducting isolated droplet combustion experiments aboard the International Space Station (ISS) with an overall goal to determine and analyze burning behavior, limiting oxygen index, and extinction mechanisms as a function of fuel, drop diameter, pressure, oxygen index, and dilution (using various diluents, including helium, nitrogen, and carbon dioxide). In recent experiments anomalous combustion of n-heptane droplets are observed; high temperature combustion followed by radiative visible extinction and a transition to a second stage (‘cool flame’) burn characterized by loss of visible flame emission. In the cool flame regime the droplet regression continues eventually resulting in extinction diameters characteristic of diffusive extinction. Experimental examples of the two stage burning and extinction characteristics of isolated n-heptane droplets under microgravity conditions are presented and analyzed numerically using a novel spherically symmetrical droplet combustion code that includes full two-stage detailed chemical kinetics, multi-component transport, and spectral radiative interactions. Simulations are presented for a wide range of droplet sizes as well as different diluents. Radiant heat loss from the larger diameter cases results in the transition to the “cool-flame” configuration. Simulations further show that ambient diluent conditions and initial droplet sizes that favor enhanced radiative heat loss transition from a high temperature combustion stage to a “low temperature” diffusive combustion stage and continues to diffusive extinction. Numerical results are analyzed in detail to identify key controlling experimental parameters and detailed kinetic properties that result in the noted observations. Special attention is given towards identifying the dominant kinetic pathways responsible for the cool diffusion flame behavior as well as extinction. Predictions are found to be in good qualitative agreement with the experimental measurements. The generic character of these results as they pertain to other alkanes-fuels will also be discussed.

1. Introduction

Since 2009, the Flame Extinguishment (FLEX) Experiment has been conducting isolated droplet combustion experiments aboard the International Space Station (ISS). The overall goal of these experiments is to determine and analyze burning behavior, limiting oxygen index, and extinction mechanisms as a function of fuel, drop diameter, pressure, oxygen index, and dilution (using various diluents, including helium, nitrogen, and carbon dioxide) [1]. Unique to microgravity experiments is the ability to study a wide range of initial drop diameters so as to characterize both radiative and diffusive extinction phenomena. In the first phase of the program, methanol was utilized to obtain data on a non sooting fuel which absorbs combustion products over its burning history, notably water [1, 2]. More recently, the study of hydrocarbons was initiated using n-heptane as the fuel. In the case of methanol,
classical diffusive and radiative extinction phenomena are observed, and a detailed numerical analysis of the results has recently appeared [2]. In the $n$-heptane experiments, radiative heat loss from larger diameter, ignited droplets results in cessation of classical (high temperature) droplet combustion behavior at a relatively large droplet size. In contrast to the classical radiative extinction observed with methanol, a transition to a second stage of low temperature constant burning rate behavior characterized by loss of visible flame emission follows; indicating an anomalous combustion characteristic. In this second stage the droplet continues to undergo rapid and apparent quasi-steady vaporization without the presence of a visible flame. This second stage burning and droplet regression continues, eventually resulting in diffusive extinction at a finite drop size that then apparently experiences additional time-dependent evaporation into the surrounding environment. This dual mode of combustion is only observed for sufficiently large initial droplet diameter; at smaller droplet diameters, classical single stage burning and high temperature diffusive extinction occur.

Dual-mode combustion as evidenced by two different burning rates has been reported and studied in the past for fuel droplets [3, 4] composed of two components of widely different saturation temperatures (e.g. heptane/hexadecane, methanol/dodecanol). In these studies, the two stage combustion process was attributed to liquid phase “batch-like” distillation with the initial lighter component vaporization supporting the initial first stage flame, and the heavier component supporting the second stage flame. Both stages produced traditional, high temperature, visible flames. Dual-mode combustion has not been observed for single component liquid fuel droplets previously – to our knowledge, the possibility of a low temperature, diffusive burning configuration has never been proposed or hypothesized.

Since the accidental discovery by Sir Humphery Davy in 1810 and the coining of “Cold Flames” by Harry Julius Emeléus in 1928, premixed “Cool Flames” have intrigued researchers. Classically, premixed “Cool Flames” undergo transient laminar propagation, with multiple occurrences potentially leading to a hot flame propagation. Bradley and coworkers [5] studied cool flame and second-stage ignition phenomena in a vertical flow reactor arrangement during the oxidation of acetaldehyde and propionaldehyde. They obtained a “Cool Flame” (pale blue, ~ 425°C) and a second-stage flame (deeper blue, ~ 690°C) by increasing the oxygen concentration. They further conducted mass spectrometry to determine the kinetic processes responsible for the flames. Fairlie et al. [6, 7] studied “Cool Flames” and oscillatory flames for a premixed propane-oxygen system under microgravity conditions. Their study involved both experimental and numerical aspects. The onset, spatial growth and stability of the “Cool Flame” was attributed to the interaction between the elementary reactions rates governing the negative temperature coefficient (NTC) and the temperature field controlled by thermal diffusion to the reaction wall. Foster [8] and Pearlman [9] conducted additional numerical studies on “Cool Flame” configuration and formation at terrestrial, partial and near-zero gravity condition. They simulated the same unstirred reactor system as that of Fairlie and co-workers. Moriue et al. [10] utilized the tethered droplet configuration to experimentally measure the ignition delays of “Cool Flame” and hot flame for single $n$-decane, $n$-dodecane, $n$-tetradecane and $n$-hexadecane droplets in a multiphase system. The “Cool Flame” was triggered by inserting the droplet in a temperature controlled furnace and observing the flames by Michelson interferometry.

In very recent work emerging from FLEX, Nayagam et al. [11] analyzed the observed dual-stage combustion of $n$-heptane droplets onboard the ISS. Measured droplet burning rates and extinction diameters were not only utilized to extract effective heat release, overall activation energy and pre-exponential factor, but to specifically relate them to low-temperature, oxidative reaction chemistry. Their analysis concluded that the temperature during the second stage burn ranged in between 1000 – 1400K assuming a 50% heat release rate. They however suggest that if the second stage combustion is indeed a “Cool Flame” then the cool flame chemistry taking place would have to sit at the position of the maximum reaction rate in the NTC curve and will therefore have a flame temperature of ~ 700 K with heptylketoperoxide, formaldehyde and alkenes being the major reaction products instead of H$_2$O, CO$_2$ and CO.
It is well known [12] that premixed n-heptane-air, low and intermediate temperature chemistry involves the reactions of n-heptyl radicals, R, with molecular oxygen, O$_2$, (see Figure 1). The addition/isomerization/further addition of O$_2$ and the thermodynamic reversibility RO$_2$ and QOOH formation are responsible for “cool flame”, i.e. negative temperature coefficient (NTC) kinetic behavior, eventually leading to “hot ignition”. However, the observed low temperature diffusive burning of n-heptane droplets seems incongruous with this low temperature oxidation chemistry which requires (at least partial) premixedness. This seeming dilemma stimulated the present numerical studies on the dual mode of combustion observed for large sized spherosymmetric n-heptane droplet burning under the microgravity conditions of the FLEX experiments.

Simulations are conducted to elucidate the influence of the coupled physico-chemical processes that triggers the observed dual-mode behavior. Simulations were conducted using a recently developed, one-dimensional, spher-o-symmetric, transient combustion model [13]. The predictions from the model is compared against the recent ISS n-heptane droplet experiments [1]. Predictions from the model were found to compare favorably with the experimentally measured droplet and flame diameter evolution. Special attention is given to delineate whether the observed flames result from classical NTC, “Cool Flame” kinetic behavior or are other driving factors responsible for the dual-mode/two stage combustion process. Using the model, special attention is given to elucidating the effects of different atmospheric condition (CO$_2$, He) and initial droplet sizes on predicted behavior. Finally, the prospects that similar behavior will be observed with other large carbon number n-alkane droplets are discussed.

2. Mathematical Model

The mathematical model employed in this current work is a transient, spher-o-symmetric droplet combustion model featuring detailed gas phase kinetics, spectrally resolved radiative heat transfer and multi-component gas phase transport. Details of the model have been reported in some of our recent publications [2, 14]. A brief description of the model is provided here. The model comprises of species conservation for each of species considered and energy conservation in both the phases. Species and energy conservation equations for the control volumes in both phases are:

\[
\frac{\partial}{\partial t}\int_{\Omega_i} y_i \rho r^2 dr + \frac{\partial}{\partial r}\int_{\Omega_i} y_i \rho r^2 dr + y_i(\rho u - \rho \dot{r}) r^2 \bigg|_{r_i}^{r_f} = -y_i \rho V_i r^2 \bigg|_{r_i}^{r_f} + \int_{r_i}^{r_f} \omega_i r^2 dr
\]

\[
\frac{\partial}{\partial t}\int_{\Omega_i} (h\rho) r^2 dr + \frac{\partial}{\partial r}\int_{\Omega_i} h\rho r^2 dr + h(\rho u - \rho \dot{r}) r^2 \bigg|_{r_i}^{r_f} = -q r^2 \bigg|_{r_i}^{r_f}
\]

\[
\sum_{i} y_i = 1
\]

where, $y_i$ = mass fraction, $\rho$ = mass density, $r$ = radius, $u$ = bulk fluid velocity, $\dot{r}$ = velocity of the control volume boundary, $V_i$ = diffusion velocity, $\omega_i$ = rate of species production due to chemical reaction, $h$ = enthalpy per unit mass and $q$ = heat flux. The heat flux $q$ represents contributions from diffusive and radiative heat transport. Three channels of diffusive heat transfer are considered, thermal conduction, enthalpic transport via species diffusion and Dufour effect where heat flow is established due to gradients in composition. The equation for the diffusive heat flux is given as:

\[
q_{diff} = \sum_{iS, gas} h_i \rho y_i V_i - \lambda \nabla T_g - p \sum_{iS, gas} \theta_i d_i
\]

where, $\lambda$ is the thermal conductivity, $T_g$ is the gas temperature, $p$ is the thermodynamic pressure, $\theta_i$ is the thermal diffusion coefficient expressed as $\theta_i = D_y \chi_j$. $D_y$ is the diffusion coefficient and $\chi_j$ is the thermal diffusion ratio. $d_i$ is the thermodynamic driving force and is expressed in the form of Stefan-Maxwell equation.
In the model the radiative heat flux is expressed in the following form:

\[ \nabla \cdot \bar{q}_{rad} = \int_0^\pi a(\eta, \bar{r}) \left( 4\pi I_\gamma(\eta, \bar{r}) - \frac{\int I(\eta, \bar{r}, \omega)d\omega}{4\pi} \right) d\eta \]  

where, \( I \) is the radiative intensity, \( \eta \) is the radiative path length and \( \omega \) is the solid angle. For convenience the radiative flux term is only shown for a single wavelength.

Equations at the liquid-gas interface arise either through satisfaction of thermodynamic constraints or conservation of material fluxes:

\[ y_i (\rho u - \rho \dot{r}) = -y_i \rho V_i \]  

\[ \sum_{i \text{liquid}} h_{\text{vap},i} \left[ y_i (\rho u - \rho \dot{r}) + y_i \rho V_i \right] = -q \]  

\[ \sum_{i \text{gas}} y_{i,\text{gas}} = 1, \quad \sum_{i \text{liquid}} y_{i,\text{liquid}} = 1, \quad \text{and} \quad T_\varepsilon = T_\gamma \]

\[ x_{i,\text{gas}} p = x_{i,\text{liquid}} \gamma_i(T, x_{j,\text{gas}}) p_{\text{vap},i}(T) \]

where, \( h_{\text{vap},i} \) = enthalpy of vaporization, \( p \) = system pressure, \( T \) = temperature, \( x_i \) = mole fraction, \( \gamma_i \) = activity coefficient and \( p_{\text{vap},i} \) = vapor pressure of the \( i \)th component in its pure state. The symbols ‘+’ and ‘-’ denote location in the gas and liquid phase, respectively. The heat flux \( q \) at the interface has contribution from chemical enthalpy of diffusing species, thermal conductive heat transport, radiative heat transport and Dufour effect.

In the model, the volume boundaries are defined to coincide with the liquid–gas interface, and the far field (two hundred times the initial droplet diameter) boundary is well defined using Dirichlet conditions and remains fixed in the simulations. The Dirichlet conditions imposed on the far-field are of fixed ambient composition and temperature (298 K). The inner most liquid node is centered at the origin, providing the required no-flux condition.

3. Results and Discussion

Unlike conventional droplet combustion where the combustion process is strictly due to the high temperature chemical kinetics process due to the dual stage nature of the observed combustion phenomena a detailed \( n \)-heptane chemical kinetics model is used [15, 16] in the present study. The detailed \( n \)-heptane chemical kinetics model consists of 1038 species and corresponding 2739 reaction steps. To keep the chemical kinetics numerically tractable for spatio-temporal simulations the detailed chemical kinetics model was reduced employing the path flux analysis method (PFA) [17]. For the mechanism reduction in addition to the high temperature kinetics special attention was given to the low and intermediate temperature regime so that the entire temperature range (low temperature, NTC, high temperature) can be captured with sufficient resolution. The reduced mechanism consisted of 128 species and 565 elementary reaction and is essentially identical to the one used in [18]. As shown in Figure 2, the reduced mechanism with 128 species is sufficiently comprehensive to reproduce the low temperature and NTC region for both shock tube ignition delay and flow reactor oxidation. In addition the prediction from the reduced mechanism is in fairly good agreement with the experimental measurements. All the droplet combustion simulation presented in this current study is conducted with this reduced mechanism unless otherwise noted and will be referred to as the “detailed” model.

To get insight into the anomalous dual stage burning characteristics and hence affirm the combustion regime simulations were conducted with two chemical kinetics model, a “detailed” chemical kinetics model and a high temperature \( n \)-heptane chemical kinetic model [19] separately. It should be noted that
the “high temperature” model of Chaos et al. was specifically developed for high temperature oxidation and did not include any low and intermediate temperature reaction pathways. Figure 3 shows the predicted droplet diameter, burning rate, flame diameter and peak gas temperature evolution from both these kinetic models and compares them to the experimental measurements [1]. The experimental conditions are \( d_0 = 3.91 \text{ mm}, 0.21 X_{O_2}, 0.79 X_{N_2}, \) one atmosphere pressure and is referred to as the base case. It can be seen that the predictions from the two kinetic models are distinctively different. The “high temperature” model predicts extinction of the droplet at a large droplet size due to radiative heat losses [2, 20] associated with the larger droplet size. After extinction the droplet is predicted to undergo evaporation in the quiescent environment, which is evident in the droplet diameter regression and burning rate evolution (Figure 3 a and c). Consistently the flame diameter evolution predictions with “high temperature” model shows a abrupt decrease corresponding to the flame extinction. In the simulations the peak temperature is utilized as the flame position marker as has been done some of our previous work. [2, 13]. As a consequence the flame diameter shows continuing evolution even after extinction. The “detailed” model shows significantly different combustion characteristics and captures the experimental observation qualitatively. The “detailed” model indicates that following the visible flame extinction which corresponds to the typical radiative extinction the droplet transitions to a second stage combustion where droplet diameter regresses at a significantly higher rate suggesting higher burning rate. In addition the “detailed” model predicts extinction towards the end of the second stage burn. During this second stage the flame diameter is found to be significantly smaller, locating itself very close to the droplet surface. Due to the large radiative heat loss (Figure 4) the flame positions itself closer to the droplet surface to compensate and sustain continuous burning. It can be seen that during the second stage the flame temperature is significantly lower and has a value of \( \sim 750 \text{K} \) (Figure 3 d). The predictions from the “detailed” model are very similar to the “high temperature” model in the first stage only difference being the temporal location of the transition. In comparison to the experiments the “high temperature” model shows an earlier extinction of the visible flame in contrast the “detailed” model predicts the transition to occur slightly later and is in good agreement with the experiments. Even though the “detailed” model qualitatively captures the experimental measurements, the second stage burning rate is significantly over predicted and vice versa for the extinction diameter. The predicted extinction diameter was found to be \( \sim 0.35 \text{ mm} \) being smaller by a factor of 3.5 than the experiment.

The integrated heat generation (\( Q_{\text{generation}} \)) and losses due to radiation (\( Q_{\text{radiation}} \)) and conduction (\( Q_{\text{conduction}} \)) are presented in Figure 4 for the base case. It can be seen that the integrated heat generation has a very sharp rise during ignition which also decreases very rapidly as a somewhat quasi-steady diffusion flame structure is established. The decrease in \( Q_{\text{generation}} \) after ignition is also a consequence of the increasing radiative loss \( Q_{\text{radiation}} \) during the first stage of the burn when the flame radius is still increasing (Figure 3). At the same time the conductive heat losses is also substantial. In this first stage of combustion the radiative heat loss is almost a factor of \( \sim 2 \) higher than the conductive losses. It can be clearly seen that the transition to the second stage occurs when the summation of the heat loss terms are close to the heat generation. As significant heat loss dominates the combustion process the flame positions itself close to the droplet surface for compensation as it is evident in Figure 3. During this second stage \( Q_{\text{Generation}} \) is approximately \( \sim 17 \text{ W} \), which is \( \sim 11\% \) of the first stage generation. It is interesting to note that during the second stage the dominant heat loss term switches from being radiation to conduction.

Figure 5, 6 and 7 summarizes the influence of initial droplet size, carbon-dioxide and helium concentration on the dual stage “Cool Flame: behavior. The influence of initial droplet shows that as the initial droplet diameter increases an earlier transition to the second stage takes place. This further enforces the fact that the radiative heat loss plays a dominant role in this transition. To study the influence of radiative effects on the combustion characteristics, simulations were conducted for ambience containing increasing CO_2 concentration since CO_2 is a radiatively participating medium. An initial droplet diameter of 3.0 mm was so chosen as in ambient air it did not show a two stage “Cool Flame” combustion characteristics. The influence of \( CO_2 \) concentration in the ambient is summarized in Figure 6. An increase
in the CO\textsubscript{2} concentration in the ambient readily triggered the “Cool flame” combustion. The “Cool Flame” behavior cannot only be triggered by radiative heat loss but rather any enhanced heat loss mechanism. Figure 7 which summarizes the effect of increasing helium in the ambient shows that increasing the diffusive heat loss but increasing the helium concentration to promote increasing diffusive heat loss initiates the “Cool Flame” combustion.

4. Concluding Remarks

\textit{n}-heptane droplet combustion under microgravity conditions has been successfully simulated using a recently developed transient spherosymmetric droplet combustion model. The simulation showed unique two stage “Cool Flame” like combustion behavior for large sized droplets. Unlike classical “Cool flames” these two stage combustion initiates at the high temperature combustion and then transitions to the “Cool flame” combustion process. The predictions from the simulations were found to be in good qualitative agreements with the experimental measurements The simulation results further indicated that heat losses initiates the two-stage behavior. Providing ambience that accentuates heat loss has the potential to initiate the two stage burning.

Acknowledgements

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References

[16] \url{http://www-cmls.llnl.gov/data/docs/science_and_technology/chemistry/combustion/nc7_2b_mech.txt}.
Fig. 1. Schematic of the kinetic scheme [15] of the oxidation reactions at high and low temperature. An inset of flow reactor reactivity measurements showing the high, intermediate and low temperature oxidation regimes.
Fig. 2. Comparisons of predicted and measured a) ignition delay time for stoichiometric n-heptane at 1, 13.5 and 30 atm respectively. The experimental ignition delay measurements at 13.5 atm are that of Ciezki and Adomeit [21].  b) flow reactor oxidation data for n-heptane for conditions of 8.0 atm, 0.3 mole% carbon, $\phi = 1.0$ at 1.0 s residence time, inset; change in temperature due to chemical heat release $\Delta T$. Predictions using both the full and reduced mechanisms are shown.
Fig. 3. Measured and predicted evolution of: a) droplet diameter, b) burning rate, c) flame radius and d) peak gas temperature for a $n$-heptane droplet in ambient air ($d_o = 3.91$ mm, 0.21 $X_{O_2}$, 0.79 $X_{N_2}$, one atmosphere pressure). The experimental data are that of [1]. The flame radius experimental data contains measurement from both a color camera (Color) and low light UV (LLUV) camera. Predictions are shown with both the detail chemical kinetics model and the high temperature $n$-heptane model of Chaos et al. [19].
Fig. 4. Total heat generation, radiative and conductive heat losses for a \( n \)-heptane droplet undergoing two stage combustion in air \((d_0 = 3.91 \text{ mm}, 0.21 X_{O2}, 0.79 X_{N2}, \text{ one atmosphere pressure})\).
Fig. 5. Numerically predicted evolution of: a) droplet diameter; b) burning rate; c) flame standoff ratio; d) peak gas temperature for $n$-heptane droplet combustion having different initial droplet diameter (0.21 $X_{O_2}$, 0.79 $X_{N_2}$, one atmosphere pressure).
Fig. 6. Numerically predicted evolution of: a) droplet diameter; b) burning rate; c) flame standoff ratio; d) peak gas temperature for a $n$-heptane droplet in different ambient carbon-dioxide mole fractions ($d_o = 3.0$ mm, $0.21 X_{O_2}$, noted $X_{CO_2}$, balance $X_{N_2}$, one atmosphere pressure).
Fig. 7. Numerically predicted evolution of: a) droplet diameter; b) burning rate; c) flame standoff ratio; d) peak gas temperature for a $n$-heptane droplet in different ambient helium mole fractions ($d_0 = 3.0$ mm, $0.21X_{O_2}$, noted $X_{He}$, balance $X_{N_2}$, one atmosphere pressure).