Measurement of the Burning Rate and Ignition Delay for Various Hydrocarbon Fuel Droplets using Photothermal Ignition of Aluminum Nanoparticles

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Abstract
Combustion of a wide range of hydrocarbon fuel droplets has been achieved through photoignition (PI) utilizing sub milligram of aluminum nanoparticles (Al NPs). For diesel fuel, a reliable ignition was made possible by mixing a solid oxidizer with the Al NPs. PI offers a fast (<5 ms) gasless reaction, a high ignition temperature (>2000 K), and a relatively short total ignition duration (80-200 ms). Droplets with a diameter of 1.4±0.1 mm were suspended from a 0.15 mm quartz fiber, then ignited through PI and in a few cases with a Ni-Cr heating wire. The burning rate constant $K$ for ethanol, heptane, n-dodecane, kerosene (RP-2), Fischer–Tropsch synfuel (FT), and diesel #2 was found to be 0.83±0.01, 0.95±0.01, 0.90±0.01, 0.77±0.02, 0.99±0.01 and 0.71±0.05 mm²/s, respectively. PI also allows the evaluation of ignition delays via high-speed imaging of the luminous flame. Ignition delays as short as 50 ms were observed, which are much smaller than those achieved by conventional ignition methods at atmospheric pressure (>400 ms). The dramatically shorter ignition delay may be explained in part by the extremely fast local heating effect (estimated to exceed $10^5$ K/s) and the high burning temperature of Al NPs in the vicinity of the droplet.

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Introduction

When studying combustion characteristics of liquid rocket fuels, it is customary to either investigate the combustion of liquid fuel droplets or the combustion of fuel sprays. However, the two are closely related to each other, as in a typical rocket combustion chamber, where the burning of droplets, droplet clusters, and fuel sprays occur simultaneously. The study of droplet burning is mostly focused either on single suspended droplets or free droplets, usually in a free fall. In either case, the conditions regarding the combustion of a single fuel droplet deviates from what is expected in typical liquid rocket engines (LRE’s). This not only concerns the chamber pressure and temperature usually being much lower in a typical droplet study, but also the droplet ignition process and the related transient effects such as temperature ramp up, which is much slower than what takes place in LRE’s. As a result, reported values of combustion parameters such as the burning rate constant and the ignition delay time obtained under typical experimental conditions may not entirely represent the combustion processes in LRE’s. However, studying droplet combustion behavior provides a platform to fundamentally characterize the burning characteristics of fuels.

The burning of a single fuel droplet involves evaporation of the fuel at the surface of the droplet, which leads to a diffusion flame to form around the droplet as the fuel vapor reacts with the surrounding air. While in LRE’s the flame regime encompasses the entire spray [1], characterizing the burning of single droplets is required to assist with the modeling of such sprays [2]. Specifically, the fundamental processes that occur during the burning of individual droplets are pertinent to understanding combustion dynamics for multiphase reactive systems that are prone to self-excited combustion instabilities [3, 4].

Another objective of this work was to study possible effects of a faster and hotter ignition approach on the combustion characteristics of suspended hydrocarbon fuel droplets. Photoignition (PI) was selected as an alternative ignition method because it is much faster than any conventional approach in droplet ignition, as will be described later in this paper. Another advantage of PI is the ease of its application for sub-scale test rocket engines at elevated pressures, as has been demonstrated recently [5].

Substantial experimental work has been devoted to the ignition of single droplets [6] and fuel sprays [7], as well as ignition delay in past decades [8-12]. However, a systematic study to correlate the stated combustion parameters for rocket relevant fuels using this ignition approach is yet to be reported. The present experimental study has been focused on the burning characteristics of various hydrocarbon fuels to quantify changes in important combustion metrics related to combustion dynamics. The objective of this study is to determine the burning rate constant and ignition delay of different hydrocarbon fuel droplets under ambient conditions ignited by PI.

It should be mentioned that this work is the first part of a larger project investigating the effects energetic fuel additives have on the combustion dynamics of hydrocarbon fuels at elevated pressures. By quantifying the burning rate constant $K$ and the ignition delay of these hydrocarbon fuel droplets under ambient conditions, a baseline is created to compare against fuel additive data.

Experimental Details

In order to investigate various combustion characteristics of hydrocarbon fuels, the suspended droplet approach was implemented. A fuel droplet with a nominal size of 1.4±0.1 mm was suspended from a 0.15 mm uncoated quartz fiber (see Fig. 1), from Polymicro Technologies Inc. The droplets were first produced using a hypodermic needle and then mechanically transferred to the fiber. In order to increase the surface tension of the fuel droplet on the fiber, a bead was generated at the end of each fiber through a heating process using an oxy-propane torch once the polymer coating of the fiber was chemically removed. Each quartz fiber was used for a set of 10-15 identical experiments in order to generate statistically reliable data. The fiber was flame treated with a butane torch and mechanically cleaned in between tests as needed.

The burning of the fuel droplet was captured by a high-speed camera, model Phantom v7.1 from Vision Research Inc., imaging at 1,000 fps. In order to provide the proper contrast between the liquid droplet and background for image processing, a cluster of adjustable intensity white light emitting diodes (LED’s) was implemented for sufficient backlighting to create shadowgraph images of the droplet burning process. A dual-band bandpass filter, Semrock FF01-433/530-25, was placed in front of the camera in order to limit the spectral spread of light reaching the high-speed camera during the burning of fuel droplets. The backlight was turned off during the evaluation of the droplet ignition delay time in order to observe the appearance of the flame that was indicative of the initiation of droplet combustion.

Ignition System

For ignition, two different methods were implemented for the suspended droplets experiments, a conventional Ni-Cr heating wire and the PI system, which was the main ignition method in this work. To the best of our knowledge, this is the first use of PI for the ignition of fuel droplets. PI, also known as flash ignition, takes advantage of photothermal heating from a Xe-
flash and subsequent ignition of energetic nanostructures, in this case aluminum nanoparticles (Al NPs).

Unless otherwise stated, a miniature PI source designed to work for a millimeter size fuel droplet was used for the experiments reported this study. This ignition system consisted of Xe-flash lamp, a photo-ignitable solid fuel mixture, and a transparent substrate to hold the fuel and protect the flash bulb from burning particles. The entire assembly was positioned directly underneath the droplet at a distance of ~7 mm, as shown in Fig. 1. The light source for PI was a compact Xe-flash lamp with a flash duration of ~1 ms and an energy output of ~1.4 J per flash. In order to achieve a relatively small ignition plume (~10 mm in size) that produced little or no gas, 0.3±0.2 mg of 18 nm Al NPs were implemented as the energetic fuel for PI. Upon activating the Xe flash, micron size burning aggregates of Al NPs are ejected from the glass substrate, initiating the combustion of the droplet.

PI has a few characteristics that sets it apart from other droplet ignition methods. Generally, PI is fast acting (<5 ms) and has a short total duration (<250 ms) compared to traditional droplet heating methods (>0.5 s) and the typical burn duration of a droplet (>1.5 s). More specifically, PI of Al NPs takes place in the solid phase and at a high temperature (>2000 K) [5] with a temperature ramp up on the order of 10^4 K/s [13]. It also involves a burning process that produces no gas, which means any pressure wave that may be generated during the ignition of Al NPs minimally disturb the fuel droplet, as seen by the high-speed imaging. Instead, PI produces numerous burning particles that rapidly surround the droplet and ignite pockets of combustible mixtures that may exist locally around the droplet. The fast moving burning particles significantly increase the chance of a successful ignition, making PI quite suitable for hard-to-ignite fuels such as rocket grade kerosene (RP-2) and diesel fuel.

Results and Discussion
The image processing method presented in Sevilla et al. [14] was developed to track the droplet diameter regression throughout its burning by fitting an ellipse around the droplet boundary. Example images demonstrating the diameter tracking of an ethanol droplet is shown in Fig. 2(a), which is designated by the red ellipsoid outline of the droplet in each image.

By properly tracking the droplet diameter regression, the average burning rate constant \( K \), given by

\[
K = \frac{d}{dt} \left( \frac{d_{eqvs}}{2} \right)^2, \tag{1}
\]

was calculated using the well-established D^2 law for burning fuel droplets [15]. For this study, the diameter used in the \( K \) calculation was the droplet diameter associated with the equivalent volume of a sphere as described by Struk et. al. [16]. This equivalent diameter can be written as

\[
d_{eqvs} = 2a^{2/3}b^{1/3}, \tag{2}
\]

where \( a \) and \( b \) are the semi-major and minor axis lengths of the fitted ellipse.

Utilizing this equivalent diameter, \( K \) was then determined using 70% of the data centered around the midpoint of the droplet burning event, as shown by the darker line in Fig. 2(b). This reduced the variability in the calculation of \( K \) due to any transient startup behavior immediately following ignition, as well as the end of the droplet lifetime when the droplet size became on the order of the quartz fiber.

Pure Hydrocarbon Fuel Droplet Baseline Results
A series of 10-15 droplet burning tests for the hydrocarbon fuels have been performed to produce statistically reliable data for \( K \). A major objective of this study was to quantify and minimize the uncertainty in the \( K \) values, generating a robust baseline for burning
rates of various hydrocarbon fuels. To quantify the uncertainty of $K$ values, the Student’s $t$-distribution for small sample size [17] was implemented to provide a 95% confidence interval on the reported values. A summary of these results is presented in Table 1.

Table 1 shows the experimental burning rate constants and ignition delays for fuel droplets that were ignited by PI. RP-2 and diesel #2 have the lowest average values of $K$, while Fischer–Tropsch synfuel (FT) has the highest. Also, the burning rate constant for ethanol was the same for both PI and ignition through a Ni-Cr heating wire ($0.83 \pm 0.02 \text{ mm}^2/\text{s}$), which indicates that PI is a viable method for initiation of combustion in fuel droplets.

Specific examples of the droplet diameter regression for n-dodecane and heptane are shown in Figs. 3(a) and 3(b), respectively. Similar to the droplet burning for ethanol, the droplet regression for these hydrocarbon fuels are mostly linear across the range that was used for the $K$ calculation. However, less volatile fuels such as diesel #2 have a noticeable non-linear startup transient immediately following ignition, most likely associated with heating of the liquid fuel before the quasi-steady droplet burning phase begins. Hence, this justifies calculation of the burning rate constant based on the middle section of the droplet burning event as described previously. The experiments have yielded burning rate constants with very low statistical uncertainties, which provide a reliable baseline for discerning small changes in droplet burning rates for future studies.

Ignition delay was another parameter of interest in this study, and unlike the burning rate, it is not as easy to come up with a measured value through conventional ignition methods such as heating by a Ni-Cr wire. The problem is associated with the relatively slow heating process and the interference from the luminous background in most cases. The subjective definition of the ignition delay time is another matter, where most generally it is defined as the time interval from introducing the droplet to a hot environment to the point that the combustion of the droplet is established [6].

While the time from introducing the droplet to a hot environment applies to conventional methods involving furnace heating, it does not directly apply to the PI process. Instead, the activation time of the Xe-flash was chosen as the beginning of the ignition process ($t = 0 \text{ ms}$), followed by the appearance of burning Al NPs surrounding the droplet within ~5 ms. For most hydrocarbon fuel droplets, two-stage combustion is observed where the first visible flame, here referred to as the "initial flame", peaks within 60-120 ms for different fuel droplets. This is shown in Fig. 4(c), while still a few burning NPs may be present around the droplet, as seen within the field of view of the high-speed camera. For most fuels, the initial luminous flame gradually diminishes, or even disappears in some cases within another 50-100 ms, eventually returning as the "primary flame" that is generally more luminous in most cases and remains visible as long as the fuel droplet burns.

Figure 4 shows snapshots from a high-speed movie for the ignition and burning of a heptane droplet. The first frame in Fig. 4 indicates the peak of the Xe-flash at $t = 0 \text{ ms}$, where its high luminosity saturates the pixels of the image sensor within the entire field of view. It should be noted that most burning particles in Figs. 4(b) and 4(c) are by far much smaller than the droplet, i.e., $<< 1 \text{ mm}$, but the out-of-focus particles in the image appear to be much larger than their actual size. Though the exact timing of the stated flames are somewhat subjective, their presence is unmistakable by the growing luminosity in the cases where flames are observed. In Table 1, the last column shows the estimated time of the initial flame for each fuel except for ethanol. The reported values are the best estimate and they clearly show relatively short ignition delays compared to what has been reported in the literature [6]. A more detailed investigation of ignition delays for hydrocarbon fuel droplets is underway and will be reported subsequently.

The values of ignition delays obtained through the application of PI are substantially lower than the values that have been reported for these fuels utilizing conventional ignition methods [6], presumably due to the ignition method that was employed in each case. The large reduction in the ignition delay for PI may be explained in part by the extremely fast local heating effect (estimated to exceed $10^5 \text{ K/s}$) and the high burning temperature of Al NPs ($> 2000 \text{ K}$) in the vicinity of the droplet. While the initial results indicate that the ignition method may have a sizable effect on the ignition delay and possibly some other combustion properties of a fuel droplet, a detailed experimental work on the effect of ignition method on the combustion characteristics of fuel droplets is needed to properly address these issues.

Conclusions

In the present experimental study, the burning characteristics of various suspended hydrocarbon fuel droplets have been investigated utilizing photoignition (PI) of aluminum nanoparticles for the first time. PI is a fast acting (<5 ms), hot burning (> 2000 K) ignition method with a relatively short burn duration (< 150 ms). The burning rate constant, $K$, for ethanol, heptane, n-dodecane, kerosene (rocket grade), Fischer–Tropsch synfuel (FT), and diesel #2 ignited with PI was found to be $0.83\pm0.01$, $0.95\pm0.01$, $0.90\pm0.01$, $0.77\pm0.02$, $0.99\pm0.01$ and $0.71\pm0.05$
mm$^2$/s, respectively. For these fuels, $K$ was determined through high-speed imaging of the burning droplets at 1,000 fps, with the droplet diameter automatically tracked throughout the fuel burning process using edge-detection software. The study of the various fuel droplets yielded burning rate constants with a maximum uncertainty of 0.02 mm$^2$/s, with the exception being diesel #2 that had an uncertainty of 0.05 mm$^2$/s. Also, investigation of the high-speed images for fuel ignition by PI provided a lower and upper limit of ~50 to ~250 ms for the ignition delay of the various hydrocarbon fuel droplets. These values are generally much shorter than the reported ignition delays for similar size droplets using conventional ignition methods at ambient pressure (typically > 400 ms), which may be explained in part by the extremely fast local heating effect (estimated to exceed $10^5$ K/s) and the high burning temperature of Al NPs in the vicinity of the droplet. Quantification of the droplet burning rate constant $K$ and the ignition delay for these fuels provides a baseline for the continuation of this project that will be focused on the effect of different solid additives on the combustion characteristics of liquid hydrocarbon fuels.

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Nomenclature

- $a$: semi-major axis length
- $b$: semi-minor axis length
- $d_{eqv}$: droplet diameter with the equivalent volume of a sphere
- $d_0$: initial droplet diameter
- $K$: burning rate constant

References

**Figure 1.** Schematic layout of the suspended droplet experiment test facility consisting of the high-speed imaging configuration and the photoignition system.

**Figure 2.** Time sequence of the droplet diameter edge detection for the burning ethanol droplet and (b) the corresponding normalized droplet diameter regression. The burning rate constant $K$ is determined using 70% of the data around the midpoint as depicted by the darker line.

**Figure 3.** Normalized droplet diameter regressions for (a) n-dodecane and (b) heptane.
Figure 4. A time sequence of specific burning events for a heptane droplet, demonstrating (a) the Xe-flash light covering the entire field of view, (b) burning Al NPs surrounding the droplet, (c) the initial flame clearly visible, (d) the initial flame almost disappearing, and (e) the primary flame gradually appearing. The framing rate for this time sequence was 1,000 fps and the exposure time was ~0.98 ms.