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Surface Temperature and Time-Dependent Measurements of Black Liquor Droplet Combustion

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Black liquor droplets, initially 1–3 mm in diameter, were burned while simultaneously measuring surface and internal temperature, mass loss, and diameter to gain insight into the physical processes of single droplet combustion. Data were collected by weighing a droplet hanging on a thermocouple wire within a heated furnace. Two-color images of the droplet were obtained to determine a surface temperature and particle size. The data suggest that models of droplet combustion should treat drying, devolatilization, and char oxidation as occurring simultaneously, though typically in different regions of the particle. Isothermal models should be avoided as temperature differences in excess of 300 K exist between the surface and interior, with larger gradients along the surface. Droplet swelling increased at lower ambient temperatures, and is greater for softwood than hardwood liquors. Additional unidentified factors also influence swelling, meaning it is still highly unpredictable and may be a function of initial droplet shape, size, and chemical composition. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1926–1931, 2008
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Introduction

Single-droplet combustion behavior largely dictates the conversion processes in the upper furnace of a recovery boiler. Several investigators report interesting and insightful data related to single-droplet combustion, including swelling, mass loss, and internal temperature obtained simultaneously.[1] Droplet swelling,[2–7] mass loss,[8] internal temperature,[9] and off-gas composition[10–13] have also been measured independently. One investigation measured internal temperature and off-gas composition simultaneously.[14] The available data are useful for understanding black liquor combustion, but attempts to model the process using the existing information have proven inadequate at predicting parameters such as swelling, temperature, and reaction time. Additional insights are needed, particularly regarding the relationship between temperature and swelling, which by nature requires simultaneous measurements. Surface temperature and its relationship with internal temperature have not yet been measured for burning black liquor droplets. A recent modeling effort[15] noted that temperature gradients within the droplet are important in predicting transport mechanisms, but to date the magnitude of these gradients is not known. Simultaneous measurement of droplet size, surface temperature, internal temperature, and mass loss in addition to spatially-resolved images of reacting black liquor droplets promises to provide new insights into the phenomena involved in black liquor reactions and combustion.

The single droplet combustion process

Black liquor droplet combustion and gasification includes four overlapping stages: drying, devolatilization, char oxida-

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tion, and inorganic smelt coalescence. In gasification applications, the term pyrolysis sometimes substitutes for devolatilization. However, in this work devolatilization describes this process for both gasification and oxidation.

Drying involves the transport of free and chemisorbed water from the droplet and generally occurs under heat-transfer-controlled conditions, meaning the rates of vaporization depend strongly on the gas temperature, but weakly on local gas moisture content. As used here, the term "chemisorbed" refers to both hydrates and other forms of chemically-bounded water molecules in the complex organic/inorganic mixture. Droplets usually swell about 50% in diameter during drying.[16] The size and transport properties of the droplet result in steep concentration and temperature gradients, with the center of the droplet commonly still drying as the surface begins thermal decomposition (devolatilization).

During devolatilization, droplets swell substantially, with diameters commonly increasing by more than a factor of three (relative to initial diameter) and causing volumes to change by a factor of 30. Swelling, combined with water and volatiles loss causes density to change by over a factor of 100. The condensed-phase, carbon-containing product of devolatilization is char, which occurs in the droplet in combination with the residual inorganic material. Black liquor chars exhibit extremely high porosity (90–99%) at their peak diameters. Devolatilization yields are usually 80–85% of organic dry mass.

As char burns, the inorganic alkali salts coalesce in a process driven by surface tension forces and characterized by diameter reductions as dramatic as are the increases during devolatilization. This process is called smelt coalescence. These smelt reactions include carbonate and sulfate decomposition reactions at successively higher temperatures, respectively, and salt reactions with char leading to significant changes in particle mass based on inorganic transformations.[2]

Specific objective

The objective of this work is to obtain a comprehensive set of data describing black liquor droplet combustion including internal temperature, surface temperature, swelling, and mass loss, all as functions of time under systematically varying conditions of gas temperature and composition. By so doing, the distinguishing aspects of black liquor combustion would be highlighted.

Experimental Method

The experimental setup illustrated in Figure 1 includes 1–3 mm droplets suspended on a 0.25 mm diameter bead of a cantilevered type K or S bare thermocouple. The thermocouple reports to a wireless data logger sampling at 100 Hz to record internal temperature. A mass balance with 0.1 mg resolution monitored the weight of this subsystem. The high viscosity of the liquor ensured that the thermocouple was near the center of the droplet at the start of an experiment, but due to dramatic shape and size changes during combustion the bead position changes. The measurement from the thermocouple is therefore referred to as an internal rather than a center temperature.

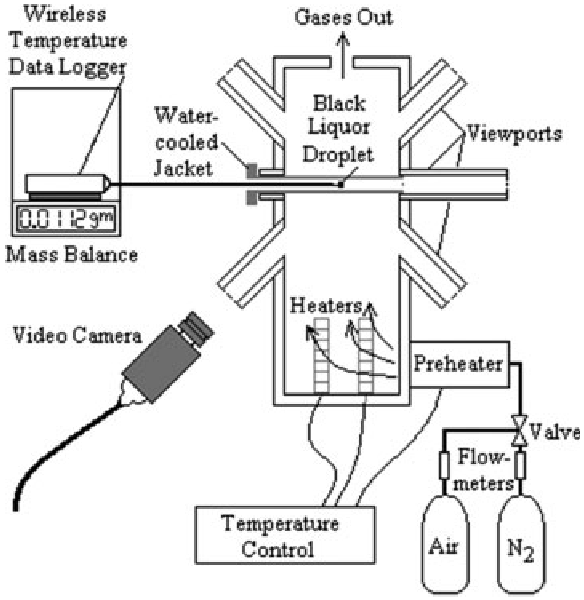

Figure 1. Equipment setup for simultaneous measurement of mass loss, diameter, and internal and surface temperatures during black liquor droplet combustion.

The refractory reactor includes three orthogonal viewport pairs intersecting at the location of the suspended droplet. One of the six viewports provides access for the cantilevered thermocouple. Air or nitrogen with a superficial velocity of 0.5–1 m/s flows upward through the reactor, preheated to 973, 1073, or 1173 K. A water-cooled jacket shields the thermocouple probe and droplet until the beginning of the experiment, marked by withdrawing the shield.

The droplets experience a relatively uniform convective heating but a nonuniform radiant heating. This is at least qualitatively similar to the industrial process in which droplets fall onto a burning char bed.

A digital video camera measures droplet size and surface temperature (30 fps, 2 ms exposure) through one of the viewports. The computer clocks of the camera, mass balance, and wireless data logger are synchronized as closely as possible to combine the data.

The camera system used was a 10-bit RGB CCD camera, the same system described and analyzed in detail by Svensson et al.[17] Surface temperature was calculated from the images using a broadband two-color method with an assumption of gray emissivity. The camera was fitted with two IR filters to ensure only visible radiation was detected. In the visible spectrum, there is essentially no spectral variation in emissivity whereas there are large spectral variations in the IR, as documented by Bernath et al.[18] Size measurements from the average of two orthogonal measurements provided equivalent diameter data, with highly irregular shapes being omitted. Numerous experiments where only swelling data were collected were completed with a Redlake MotionScope camera at 60 fps.

Five different liquors were used, all adjusted with water to 70% dry solids. The results presented in this article are for three liquors, the compositions of which appear in Table 1.

Table 1. Elemental Analysis prior to Dilution of the Liquors Used in This Work

Element (% mass)	Liquor Softwood A	 Softwood/ Hardwood D	 Softwood/ Hardwood E
C	35.6	38.6	37.5
H	3.34	3.52	3.63
O	36.6	Unknown	Unknown
S	4.06	3.47	3.92
Na	18.8	Unknown	Unknown
K	1.50	Unknown	Unknown
Cl	0.10	Unknown	Unknown
Dry Solids %	95	70	77

Results and Discussion

Swelling

Droplet swelling was quantified by calculating the ratio between the maximum and initial diameters as observed in videos of combusting droplets. The three liquor types shown in Table 1 were heated in nitrogen or air at 973 or 1073 K, giving 12 different conditions for swelling with results shown in Figure 2. Each condition was repeated from 6 to 15 times. The error bars shown correspond to two standard deviations and demonstrate the high degree of variability. A regression analysis shows that temperature and liquor type are significant factors with greater than 95% confidence despite the high variability. The effect of reduced gas temperature is increased swelling, and the softwood liquor swelled more than the softwood/hardwood blends. It also appears in Figure 1 that the reducing environment caused greater swelling but this cannot be proven statistically from the data obtained in this work. Possible causes of unexplained variation are the initial shape of the droplet (which is not perfectly spherical) and compositional variation between droplets.

Overlap of combustion stages

Internal droplet temperatures as a function of time at three different gas temperatures appear in Figure 3. Consider first the 973 K furnace temperature case in which the heat transfer to the droplet is lowest. Temperatures begin at 300 K and increase linearly until reaching the boiling point where drying suppresses further increase. This drying stage is clearly visible in the temperature data where the temperature remains constant at 400 K for over a second. After drying, the temperature increases during devolatilization and then even more rapidly during combustion reaching a peak value and then cooling. As the furnace gas temperature increases, heat transfer to the droplet increases and the processes require less time. Additionally, they appear to overlap making it difficult to distinguish them as sequential and separate. This is an indication that the temperature of the droplet is not as uniform at higher heating rates creating portions of the droplet which are still drying whiles others are devolatilizing.

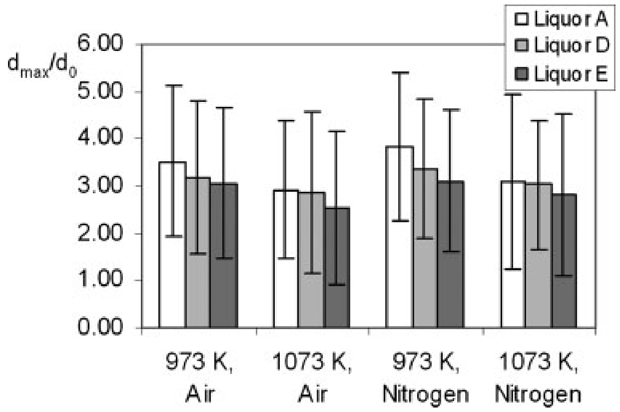

Figure 2. Swelling data for three liquor types in air and nitrogen environments at 973 and 1073 K.

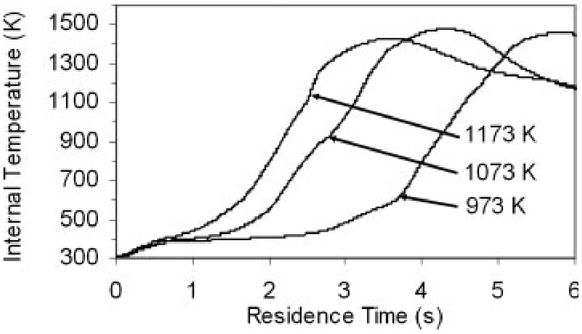

Figure 3. Internal temperature data for droplets of liquor E burned in air.

Evidence of the nonuniform reaction process is clear when viewing video images. A sequence of images of an 18.6 mg droplet with an initial diameter of 3 mm burning in air at 973 K appears in Figure 4. The images begin 0.866 s after exposure of the droplet to the furnace environment. Images appear at 0.1 s intervals over a time period of 1.1 s. In the first image, a bright edge, indicating high temperature and oxidation, occurs at the bottom right and top left edges of the droplet. The bottom right edge of the droplet has dried and devolatilized enough to oxidize while the surface at the center of the image is still drying or devolatilizing. The time from the beginning of combustion at one point on the surface until the entire surface is reacting is ~0.4 s. In repeated experiments, the bottom or upstream side of droplets consistently ignites first, presumably due to greater rates of heat and mass transfer associated with the thinner boundary layers in this location. The evidence seen in the video images and temperature data illustrate the need for a model that allows drying, devolatilization, char oxidation, and smelt coalescence to occur simultaneously as done elsewhere in the literature.[15]

Surface temperature measurement

An example of temperature and emissivity contours obtained from two-color images of a burning black liquor droplet 1.266 s after being exposed to air at 973 K appears in Figure 5. This result is from the same droplet as shown in Figure 4. The surface temperature of luminous regions is initially 1300–1400 K. Just prior to the entire particle surface reacting, the temperature on the surface becomes nonuniform, with hot sections as shown reaching over 1700 K while

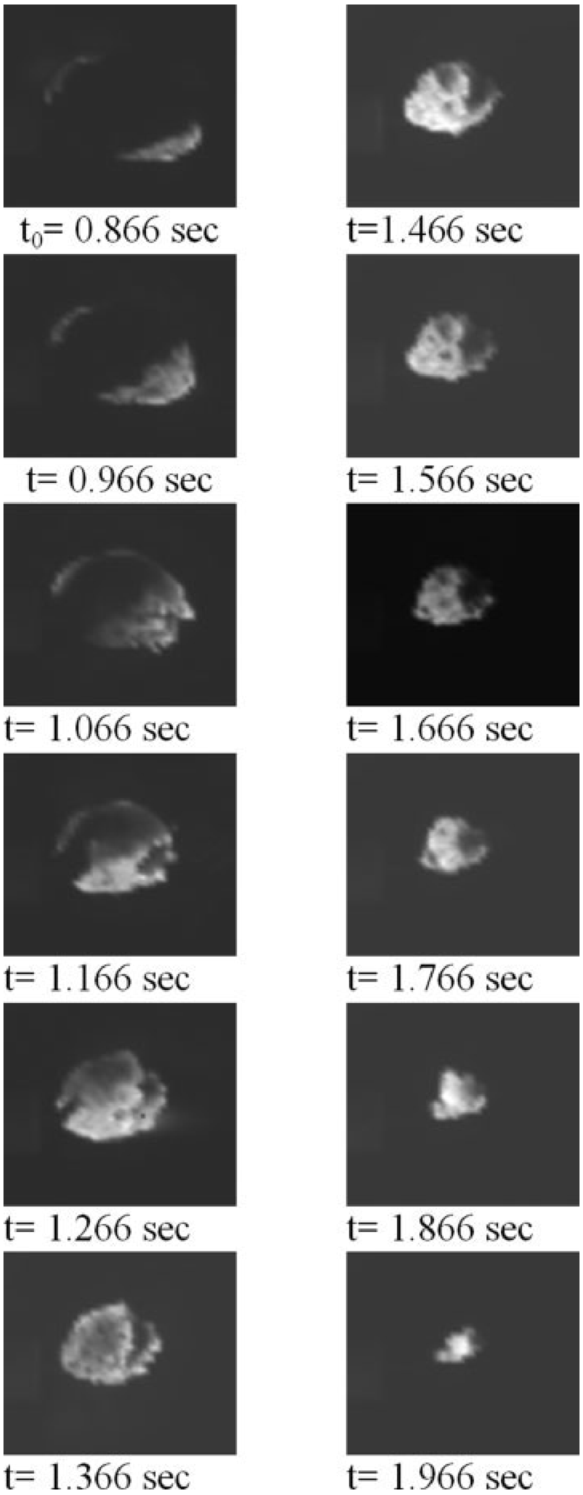

Figure 4. Images from a burning droplet of liquor E showing the progression of the reacting area beginning in the right edge of the droplet.

Air temperature was 973 K. Initial droplet mass was 18.6 mg. Initial droplet diameter was 3 mm.

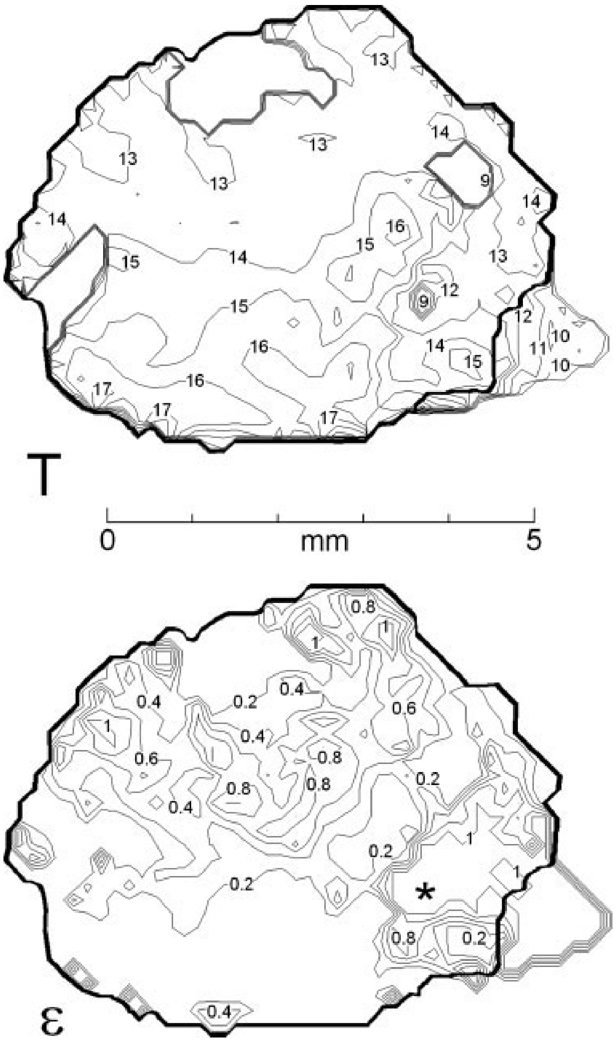

Figure 5. Surface temperature and emissivity data at 1.27s for the data set shown in Figures 4 and 7.

Temperature contour lines have 100 K increments and are labeled in units of 100 K. Emissivity contours in increments of 0.2 are also shown. Note that generally higher temperatures occur at the bottom of the droplet, and that low temperature (<900 K) and high emissivity (0.8–1) occur at the location indicated by the asterisk. The heavy black line is the droplet edge, data outside of which are from a soot flame.

other locations are as low as 1300 K. The low emissivity values at the bottom of the droplet may indicate a lack of carbon in this region, and is consistent with the bright white color of completely burned out black liquor char or smelt (predominantly sodium salts). This region ignited first and is therefore further progressed in char oxidation. Occasionally, dark regions appear on the surface of the particles where it appears that a crevice has opened in the surface and the oxygen-deprived region inside cannot react. In these areas, the emissivity is close to one as would be expected for a cavity.

The images also show radiating clouds,[19] which appear to be soot forming from reacting volatiles. When these clouds move between the particle and the camera, the temperature appears to be lower and the emissivity increases. The effect of soot between the particle surface and camera is to decrease the indicated temperature. It would appear from the

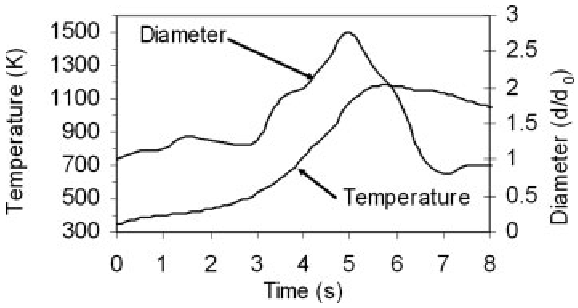

Figure 6. Simultaneous diameter and internal temperature data for a droplet of liquor E burned in 973 K air.

images that after ignition, devolatilization is still occurring and that the temperature of locations where devolatilization is occurring is lower than regions of char oxidation.

Comparing one frame to the next, which are 1/30 s apart, large fractions of the particle surface appear to change temperature significantly (200–300 K) between frames. In some cases, the temperature at every point on the particle drops, whereas in other cases a distinct region of the particle increases. It is not clear what causes these rapid apparent temperature changes. In cases where the entire particle temperature appears to change, it seems likely that a blockage of light is created by soot or gases which cause the measurement method to see a lower temperature. Another possibility is transient fluctuations in oxygen availability at the surface or the periodic release of pockets of gas from within the particle. These seem to be the more likely cause of local hot spots.

Simultaneous data

Figure 6 shows simultaneous diameter and internal temperature data for another droplet of liquor E burned in 973 K air. The slow internal temperature rise and relatively flat diameter change during the first 2 s indicates the drying stage. The steep rise in diameter from 3–5 s indicates that large amounts of swelling occur during devolatilization. The latter stages of combustion exhibit large decreases in diameter characteristic of smelt coalescence during late char burnout.

Figure 7 shows simultaneous data that corresponds to the results shown in Figures 4 and 5. Based on the swelling data from other droplets (such as that shown in Figure 6), a small amount of swelling occurred prior to the diameter data shown but could not be recorded in this data set because the surface temperature method requires the light to be emission from the particle, not reflection. Without an external light source, the droplet could not be seen clearly prior to ignition.

The lack of a plateau in the internal temperature data from 0 to 0.5 s indicates that drying overlaps with devolatilization. The rapid increase in temperature and decrease in mass that follows is indicative of devolatilization.

As discussed in connection with Figure 4, ignition occurs before devolatilization is complete with the first luminous images occurring at 0.766 s. The start of char oxidation corresponds closely to the point of largest diameter with those portions of the droplet which are burning decreasing in size. Char oxidation spreads across the particle, causing increased luminous area from 0.766 to 1.2 s. Devolatilization appears to end when the entire surface ignites. From ~1.2–2.1 s, the average surface temperature and internal temperature continue to increase while the size of the droplet decreases. The peak surface and internal temperatures occur at the same time, ~2.1 s, which is after the particle has coalesced and decreased in size to approximately one third of the maximum diameter. After this time, the smelt flows along the thermocouple wire causing a sharp decrease in surface temperature. A small amount of carbon remains producing a measurable surface temperature. The internal temperature moves slowly toward equilibrium with the furnace temperature. Changes in the mass measurement after the surface temperature signal ends most likely indicate oxidation of sulfide, and experimental uncertainty (which includes changes in buoyancy forces on the particle and thermocouple wire).

The surface temperature data is the average of all irradiating locations on the droplet. As was mentioned above, the image appeared brighter and large portions of or the entire image became brighter or darker between images collected. This results in the rapid fluctuations in the surface temperature data seen in Figure 7. These data show that during oxidation, temperature differences of 300 K or more exist between the droplet interior and surface. The magnitude of the difference decreases slowly as the internal temperature rises more rapidly than the surface temperature.

Conclusions

Black liquor droplets were burned in an optically accessible furnace while internal and surface temperature, mass loss, and diameter were simultaneously measured.

The results of this work lead to the following conclusions:

1. Swelling of single droplets ranged from 2.5 to 3.5 times the original diameter. Swelling variability was large, perhaps due to nonuniform heating and varying initial shape or composition but the cause is not well understood.

2. Swelling of a single droplet was higher at lower gas temperature (973 versus 1073 K) and was higher for the softwood liquor tested than the softwood/hardwood liquors. Swelling also appeared higher under inert (nitrogen) conditions than in air but this was not statistically significant.

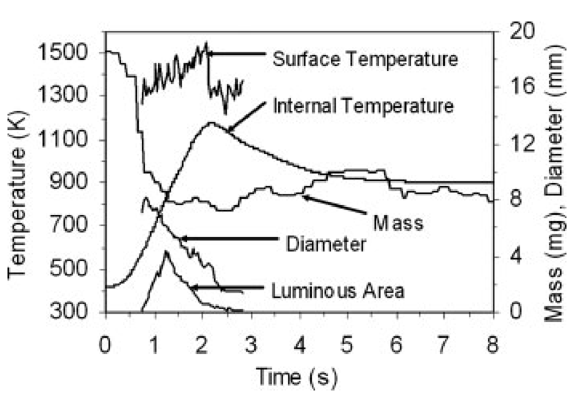

Figure 7. Simultaneous measurements of mean surface and internal temperature, mass loss, and diameter for a droplet of liquor E burning in air.

This data is for the same droplet shown in Figures 4 and 5.

3. Drying, swelling, devolatilization, and ignition do not occur uniformly around the droplet. Gas flow relative to the droplet produces an oxygen rich side, which ignites prior to the remaining particle and reaches higher temperatures sooner due to higher oxygen availability.

4. Large temperature differences on the order of hundreds of Kelvins exist between the surface and interior of combusting droplets.

5. There are three-dimensional effects during combustion resulting in temperature gradients on the droplet surface and between the surface and interior.

6. Surface temperature measurements of holes in the droplet surface show the interior is at times cooler and oxygen depleted.

These conclusions indicate that accurate single droplet combustion model should incorporate routines for simultaneous drying, devolatilization, char oxidation, and inorganic reaction, commonly in different regions of the particle.

Further work needs to be done to determine the mechanism of swelling such that predictive models of this phenomenon can be designed. This would be a valuable contribution to the ability to model single droplet combustion.

Acknowledgments

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