Procedure

To calculate the flame speed in each event, a high-speed video of chemiluminescence was taken during ignition using a Photron FASTCAM SA5 high-speed 8-bit camera. Most events were recorded at 4000 frames per second (fps), although a few slow, dim flames were recorded at 3000 or 2500 fps to increase image intensity. The videos were then imported into MATLAB as grayscale bitmaps for analysis.

For each frame of a given run, edges in the image were identified using the 'edge' function in MATLAB, which takes the grayscale bitmap as input and returns a binary image of the same size with 1s where an edge is detected, which is where the intensity gradient between neighboring pixels exceeds a specified threshold. Where an edge is detected, the pixels appear white, while all others are black. Within the 'edge' function, the Canny method is used to minimize noise by implementing both a high and low threshold to identify edges, so that the intensity gradient must fall between them for edge identification. The upper threshold is specified by a function dependent on the frame number *f* in the run, $T_H = 0.35\left(\frac{f^2}{F^2}\right)$, in which *F* is the total number of frames in the run. The lower threshold in each frame is $T_L = 0.4(T_H)$. The quadratic threshold function was found to identify edges reliably for a wider range of equivalence ratios than a linear threshold function, and where both produced a coherent flame speed, the difference in flame speed calculated by each model was less than 2%. Variation was also tested in the case that less than all of the frames from the video were used in the run, which also varies the gradient thresholds. When only two-thirds of the frames were used, a difference greater than 2% was only made in a few of the runs at the lowest flame speeds. For Ethane at 1 ATM, the maximum difference at ϕ = 0.7 was a 2.64% increase, and the maximum difference at ϕ = 1.7 was a 13.7% decrease, and the second largest difference at this equivalence ratio was a 2.74% increase. At all other equivalence ratios, the differences in flame speed calculated when using only two-thirds of the videos' frames compared to using all of them were less than 2%.

The center of the flame was initially calculated as the geometric center of the spark, which usually appeared in the first few frames. In some instances, the initial center was input manually using the center of the electrodes, where the spark was expected to have been. Subsequent centers were derived from the geometric center of the identified flame front in the previous frame to have any edges. In a few videos, there were blank frames immediately following the spark, and in these frames, the flame center was inherited from the previous frame. This approach provides a more accurate average flame radius than keeping a fixed center, and it accounts for the upward motion of the flame due to buoyancy.

When imported, each raw frame was stored in a vector *imageData*; after edges were identified using the intensity gradient thresholds, a new image *edgeData* was defined; an example of each appears in Figures 1a and 1b, respectively. Though the flame front is clearly visible in *edgeData*, there are also other edges caused by noise in the flame, reflections off the vessel walls, and the electrodes that make the average flame radius difficult to calculate. To isolate the flame front, a five-step algorithm was used for each frame. First, the distance from the center and the angle around the circle were calculated for each edge point, and the points were then sorted by angle into wedges of approximately one eighth of a radian each. Second, an initial approximation to the flame front was stored in a vector *outers* containing the distance to the outermost point in each wedge, and another vector *diffOuters* contained the differences between values in *outers* for each pair of adjacent wedges around the circle. Third, the initial approximation of the flame front was improved using the assumption that the flame front must be smooth. Due to the difficulty in isolating the flame front near the often much clearer edges of the electrodes in the image, the smoothness threshold in each wedge in the arcs from $-\pi/6$ to $\pi/6$ and $5\pi/6$ to $7\pi/6$ was generously defined as half the corresponding *outers* value, and all points in these wedges were discarded in the fourth step of the algorithm. Elsewhere around the circle, a smoothness threshold was defined to be one twentieth of the corresponding *outers* value. If a value of *diffOuters* exceeded this threshold, points within the latter wedge were searched for values that did not exceed this threshold. This was done in case the flame front was present in that wedge, but was not the outermost point, as in the case of a wedge in which there was a reflection off the vessel wall. If no such points were found, a new point was chosen to replace the *outers* value in the latter wedge that was no further from the adjacent *outers* point than two standard deviations of the *diffOuters* vector. This procedure continued around the circle until a pass through all wedges was made without any adjustments. In the last part of the algorithm, all pixels in *edgeData* not within 2% of the points in *outers* were set to black, and this image was stored in *frontData*, as in Figure 1c. The average flame radius was calculated from the remaining edge points.

The observed flame speed was extracted from the plot of average flame radius versus time, which included a near-linear section when the flame is expanding before reaching the walls of the vessel. Because a constant-volume vessel was used, some runs produced trends that looked slightly more logistic than linear, and in these cases the maximum slope was approximated by taking the slope of the portion of the data consisting of at least 25 data points that showed the steepest slope to a naked-eye analysis. The amount of variation using wider ranges in these cases was investigated, and it was found that, in runs with higher equivalence ratios, the calculated flame speed varied by more than 10% when the smaller range was used compared to the full range from the time of the spark until the flame hit the wall. In these cases, we interpret the deceleration as the flame approaches the wall to be an effect of changing pressure in the constant-volume container, irrelevant to the application. The initial acceleration may be caused by positive feedback of the flame burning faster as it grows in light of the higher mixing ratios. In this case, it may be most relevant to use the slower initial flame speed, but for consistency with other runs, only the maximum slope was considered. Time was converted from frames to seconds using the frame rate of the camera during the run, and distance was converted from pixels to centimeters using the usually clearly-identified edges of the electrodes of known outer diameter 0.500 inches. Depending on the resolution, this distance was found to correspond to 62-69 pixels with an inherent uncertainty of 2.9-3.2%, assuming accuracy to within 2 pixels.

Finally, the laminar flame speed was derived from the observed flame speed using the ratio of densities method. Using assumptions of ideal gases, the ratio of densities is reduced to the ratio of the initial to the adiabatic flame temperature. For all runs, the initial temperature was assumed to be 300K and the air molar ratio of nitrogen to oxygen was assumed to be 3.76. An online calculator using Cantera software was used to compute the adiabatic flame temperature.

Results

The flame speed data collected showed similar trends to that found in previous literature, though values were notably lower than found in these works. Figure 1a below shows the average flame speed measured over three trials for methane at a range of equivalence ratios and pressures. Figure 1b shows the corresponding results from [citation] for methane at 1 atm. Figure 2 compares similar data for ethane, and Figure 3 for dimethyl ether. The error bars show one standard deviation of the variation in the laminar flame speed between the three trials.

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