# Detonation Characteristics Of Dimethyl Ether, Methanol and Ethanol Air Mixtures

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## 1 Introduction

Dimethyl-ether (DME), methanol and ethanol are liquid fuels widely used for industrial applications. In recent years there has been an increased interest in the use of these and other renewable fuel sources for automotive and power generation applications. Very little explosion safety data is currently available for these fuels, especially detonation cell size data. Detonation cell size is used to characterize the detonability of a fuel-air mixture at a given initial temperature and pressure. The detonation cellular structure is associated with the average spacing between triple-points on the detonation front. The triple-point trajectories are recorded on a soot foil traversed by a steady detonation wave. Detonation cell size data was reported for DME-oxygen [1] and methanol-oxygen [2] but no data exists for fuel-air mixtures. The detonation characteristics of DME-air, methanol-air and ethanol-air mixtures, initially at atmospheric pressure and a temperature range of 298K to 373K, were investigated in this study. Experiments were performed in a heated detonation tube where detonation initiation was achieved by two methods; via flame acceleration through a series of orifice plates placed in the first half of the tube, and via a short acetylene-oxygen driver with only a few orifice plates. The detonation cell size was obtained using the classic soot foil technique. Accurate quantitative numerical simulation of the three-dimensional detonation structure is not possible at this time. The steady one-dimensional detonation structure, commonly referred to as the ZND model, can be obtained using detailed chemical kinetics [3]. The ZND reaction zone length, obtained using existing chemical kinetics in the literature, is calculated and compared with the experimentally measured cell size.

## 2 Experimental Details

Figure 1 shows a schematic of the heated detonation tube that was used for the investigation. The detonation tube was composed of two 3.1m long, 10cm inner-diameter, sections mated by a pair of flanges and sealed with a metal spiral gasket. The flanges and tube section heaters were independently controlled. The tube was equipped with eight ionization probes for measuring the flame time-of-arrival. The detonation cellular structure was captured on a 0.62m long soot foil that covered the full inner-circumference of the tube. The foil was located at the end of the tube where a steady detonation was present. The 0.65 mm (0.025 inch) thick aluminum foil was cleaned and then soot covered using a kerosene lamp. Mixtures were prepared by the method of partial pressures inside of a heated mixing chamber equipped with a motor driven stirrer. The constituents were mixed for 20 minutes and then

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transferred through 1.27cm diameter trace heated tubing. After the mixture transfer the detonation tube was vented to atmospheric pressure. Due to the low vapour pressure of methanol and ethanol at 303K and 310K these mixtures could not be prepared at sufficiently high pressure in the mixing chamber, instead they were prepared at atmospheric pressure in the preheated detonation tube. The mixture constituents were added to the tube and circulated externally from the detonation tube through trace heated 1.27 cm diameter tubing using a bellows pump for four tube volumes. In this configuration combustion was initiated by an automobile spark plug mounted on the end of the detonation tube.

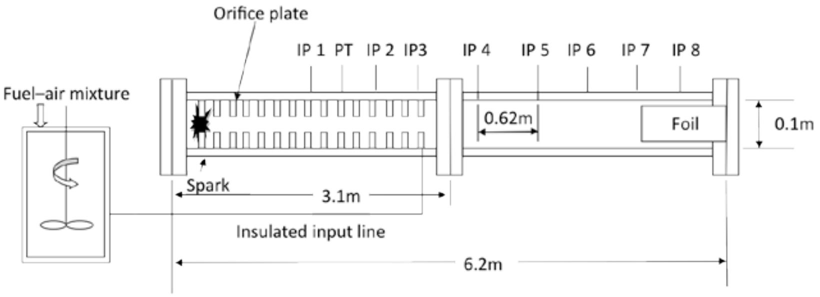

Figure 1. Schematic showing the mixing chamber and orifice plate laden detonation tube.

For most tests the first half of the tube contained orifice plate obstacles spaced at the tube diameter to promote flame acceleration leading to DDT. The second half of the tube was free of obstacles. For less reactive mixtures a gas driver was used to initiate prompt detonation initiation. Only three orifice plates were uses and a small pre-chamber, not shown in Fig. 1, was installed on the outside of the ignition endplate. The pre-chamber contained two electrodes that were connected to the automotive spark system. Premixed acetylene-oxygen was injected into the pre-chamber flushing out the test mixture. The amount of driver gas that entered into the detonation tube is governed by the driver load-time. For most tests a 0.2s driver load-time was used. For these tests the detonation tube was first filled with the test mixture to 98kPa absolute, followed by an additional 4kPa of driver gas. Compared to the orifice plate configuration the gas driver initiated detonation closer to the ignition end and since DDT happened in the smooth tube it permitted the widening of detonability limits. A longer 0.5s driver was used to test near the detonability limits, this data is not as trust worthy since the cell size approaches the tube diameter.

# 3 Chemical Kinetic Analysis

The one-dimensional detonation structure was obtained using Shepherd's publically available ZND code [3] and the chemical kinetic mechanism developed at Princeton University [4], and modified by Zhao et al. [5]. The code was used to obtain the reaction zone temperature profile for DME-air, methanol-air and ethanol-air mixtures. The calculated ZND detonation structure of DME-air varies greatly with composition. The temperature profile in the reaction zone for a typical fuel rich DME-air mixture at 298K is provided in Fig. 2. The reaction zone length is typically defined by the distance between the shock wave and the point of maximum heat release rate, i.e., the location of the maximum temperature gradient. Figure 3 shows the temperature gradient behind the lead shock wave for fuel-rich DME-air mixtures at 373K. As shown in Fig. 3, for fuel-rich DME-air mixtures (stoichiometric is 6.54%) at 298K and 373K two peaks are observed in the temperature gradient. As a result two reaction zone lengths can be defined, a similar finding was reported in [1] for DME-oxygen mixtures. The authors correlated the double peak with a dual-cellular detonation structure, typically observed in fuel nitrogen-dioxide mixtures [6]. For lean mixtures only a single peak exists, and for near stoichiometric mixtures a second less pronounced peak forms ahead of the main peak. For rich mixtures, as the DME concentrations increases the amplitude of the prominent second peak decreases and becomes insignificant for a 13.5% DME mixture. The calculated reaction zone lengths as a function of DME concentration at 298K and 373K is summarized in Fig. 4.

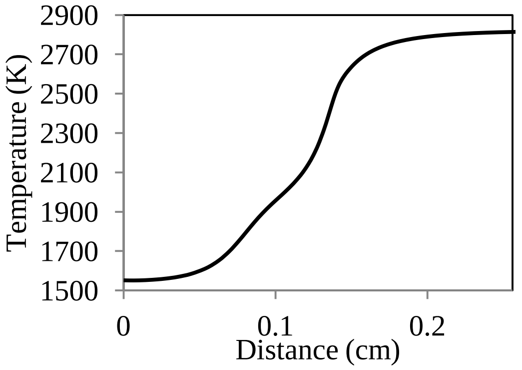

Figure 2. Temperature within ZND detonation reaction zone for 9.0% DME at 298K.

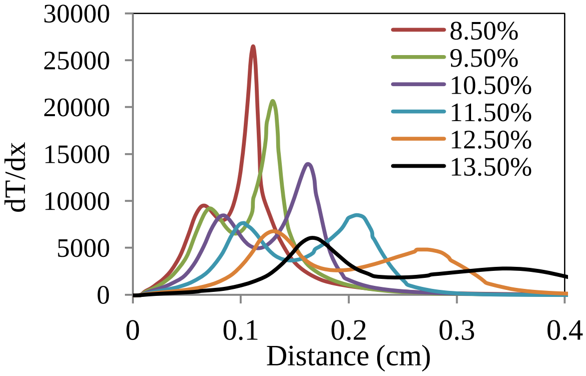

Figure 3. ZND temperature gradient within the reaction zone for DME-air at 373K

The characteristics of the ZND detonation structure of ethanol-air varied over a range of concentrations. Figure 5 shows the progression of the temperature gradient behind the shock as the concentration of ethanol is increased from stoichiometric, i.e., 6.54% ethanol. Only one peak is visible in the profile near the stoichiometric composition. As the ethanol concentration is increased the magnitude of the peak decreases and the profile widens, eventually forming a trough (local minimum). This trough in the peak of the temperature gradient profile is obtained at concentrations between 10.5% and 11.0% ethanol, beyond these concentrations the shape of the curve displayed a single maxima. This creates a shift in the reaction zone length between 10.5% and 11.0%. The existence of a minimum over such a small range of concentrations is most likely due to inaccuracies in the chemical kinetics mechanism.

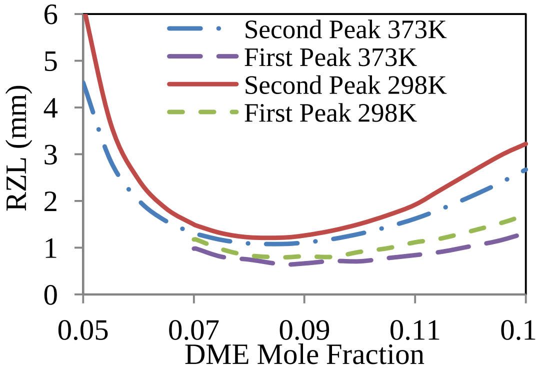

Figure 4. Calculated ZND reaction zone length (RZL) for DME-air mixtures at 298K and 373K

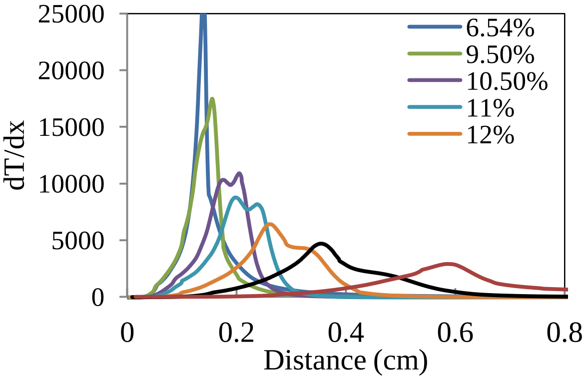

Figure 5. ZND temperature gradient within reaction zone for ethanol-air at 373K for rich mixtures.

The ZND detonation structure of methanol-air exhibits a smooth single peak heat release profile behind the shock wave, which results in a single reaction zone length value for each condition.

## 4 Experimental Results

The detonation cell structure for fuel-air mixtures is typically classified as "irregular." This makes interpretation of the soot foil imprint very difficult due to the presence of a range of cell sizes associated with substructure. Substructure refers to fine cell structure that is imbedded within the dominant cells. Normally the length-scale of the substructure increases through the cells, finer at the start of the cell where neighboring transverse waves collide. The average cell size represents an important parameter that controls most detonation phenomena. The average cell size can be obtained based on a collection of cells identified on the soot foil. In the present study the "dominant mode" method was used to analyze the detonation cellular structure. This technique places emphasis on prominent, long continuous triple-point trajectories. In this technique the cell size is based on the average transverse distance between adjacent dominant trajectory lines. The cellular structure for the DME-air, although fairly regular, was found to contain significant substructure. Selecting strong triple point trajectories was very subjective, creating uncertainty in the measurement of dominant cells at both 298K and 373K. Figure 6 shows a typical foil obtained from experiments with the selected dominant triple point trajectories sketched in with white dashed lines. The dominant triple-point lines are more pronounced than the substructure that includes short lived lines within the dominant bands. Although these substructure triple-point trajectories are well defined they tend to meander as they split and merge with adjacent lines. The substructure observed for these fuels can be considered atypical because their length scale does not vary significantly through the cell. Ng et al. [1] observed a similar cell structure for DME-oxygen mixtures and proposed that for fuel rich mixtures the dual-cellular structure is due to the double energy release predicted by the ZND model.

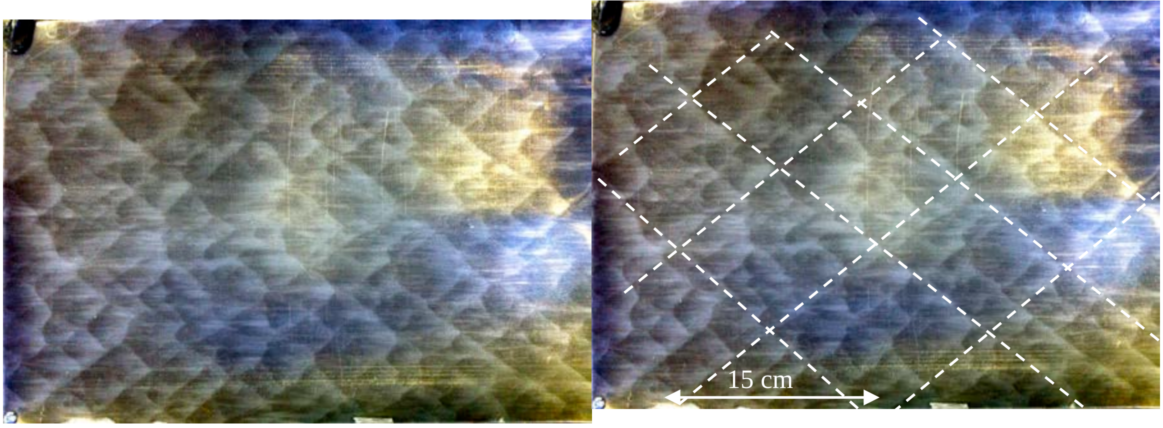

Figure 6. Soot foil for 6.5% DME at 298K showing dominant triple-point trajectories

Figure 7 shows the measured average cell size for DME-air mixtures obtained using the dominant trajectory method, defined as large cells, as well as the average size of the smaller cells that make up the substructure. There is no distinction made for the orifice plate and gas driver small cell data in Fig. 7 and subsequent figures. The error bars represent the standard deviation of the measured triple-point trajectory line spacing for the large cell size data. The error bars do not account for uncertainty associated with choosing the dominant lines. Also shown in Fig. 7 is the scaled reaction zone lengths (RZL) obtained by multiplying the calculated ZND reaction zone length provided in Fig. 4 by a scaling factor *A*. The value of *A* is chosen such that the stoichiometric ZND data point is anchored to the measured stoichiometric cell size data point. To reflect the possibility of a dual-cellular structure the RZL corresponding to the first and second reaction rate peaks were scaled with the dominant cell data (*A*=78 and 92 in Figs. 7a and b) and the smaller cell data (*A*=33 in Figs. 7a and b), respectively. Also shown in Fig. 7 is the scaled RZL using the second reaction zone peak anchored to the stoichiometric small cell size data (*A*=23 in Figs. 7a and b). Interestingly the small cell size data is better fit with the scaled RZL from the second reaction zone peak. This observation, along with the fact that small cells are observed for lean mixtures, where only a single RZL exists in the ZND model, is an indication that the existence of the two peaks in the heat release rate is inconsequential to the detonation cell structure. Cell size measurements at 373K showed only a small decrease compared to the 298K data, e.g., compare values in Figs. 7a and b.

Knystautas et al. [7] determined experimentally that the DDT limit in a smooth tube corresponds to the composition where the cell size equals the tube diameter, i.e., $\lambda/d=1$. It is also known that the detonation *propagation* limit in a smooth tube is characterized by a single head spin, where $\lambda/d=\pi$. The size of the small cells in Fig. 7 approaches the tube diameter of 100 mm at the limits, so $\lambda/d\rightarrow 1$.

Note for these limit mixtures there are only three cells across the foil so the cell structure can be slightly influenced by the boundary condition. Also for the limit mixtures the larger dominant triple point trajectory line spacing approaches roughly half the tube circumference of 314 mm and therefore approaches the $\lambda/d=\pi$ limit. Due to the lack of detailed instrumentation the exact nature of the transition to detonation phenomenon with the gas driver is difficult to ascertain. Based on the size of the small cells being roughly equal to the tube diameter, it appears that DDT occurs in the test gas in the smooth part of the tube, in which case the larger cells play no role in the transition process.

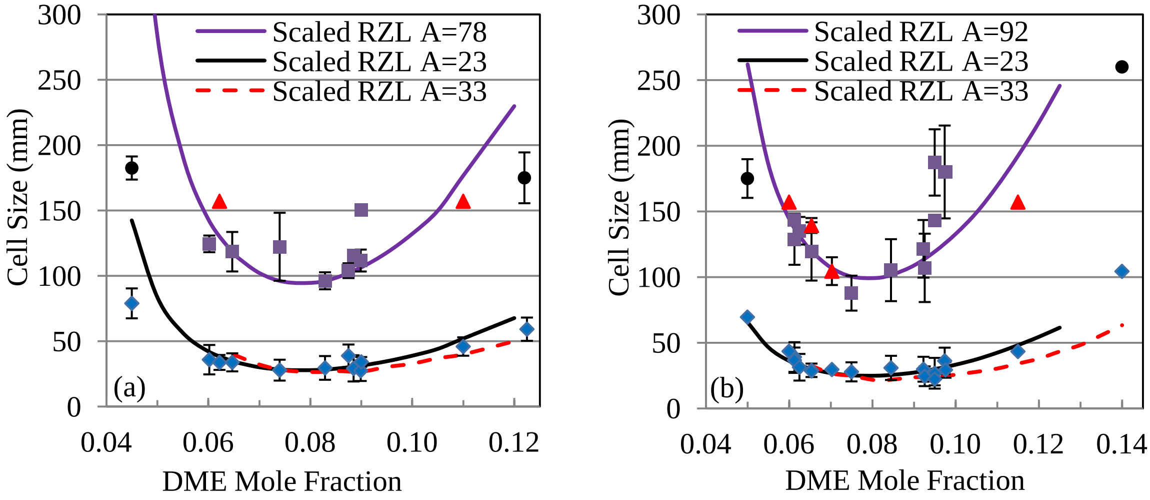

Figure 7. Measured cell size and scaled reaction zone length for DME-air at a) 298K and b) 373K. Small cells - ♦; large cells: orifice plate - ■, 0.2 second gas driver -▲, 0.5 second gas driver - ●

Experiments performed with ethanol-air and methanol-air mixtures conducted at 303K with the orifice plates were enhanced by additional experiments performed at 310K using the gas driver. The small increase in temperature, and corresponding vapor pressure, allowed for richer mixtures to be tested without any significant change in chemical reactivity. The measured cell size at 303/310K is presented in Figs. 8a and 9a. Note, the scaled RZLs were calculated at 303K. The shift observed in the methanol-air RZL at 10.5% in Fig. 8b is due to the double peak in the temperature gradient observed in Fig. 5. Similar to that observed for DME, the cell size measurements for both fuels at 373K show only a slight decrease in size compared to cell measurements at 303/310K. The value of the proportionality constants for the ethanol-air, e.g., $A$=23 and 26, are similar to the value of 23 obtained for the smalls cells in the DME tests at 298K and 373K. Whereas, for the methanol the value of the proportionality constant is about twice the value obtained for the ethanol and DME mixtures. The most striking observation is that for both fuels there is very little change in the cell size with concentration, for both initial temperatures, in contrast to the scaled RZL that shows a modest increase on the rich side. It is not clear if this disagreement is due to inaccuracies in the kinetic mechanism for rich mixtures or due to experimental error. Experimental issues related to mixture preparation can be ruled out for tests performed at 373K where the mixture is prepared in the mixing chamber which is uniformly heated. The measured cell size at the lean and rich limits is only about half of the tube diameter. Evidence for dual cell sizes for ethanol and methanol, similar to that found for DME, is very weak. However, the relatively small size of the cells compared to the tube diameter at the limits would indicate that perhaps there is a second larger cell scale.

## 5 Conclusions

The calculated DME-air reaction zone structure shows a double peak in the heat release which corresponds to the appearance of a "weak" double cell structure captured on soot foils. The cell size measurements for methanol and ethanol are insensitive to mixture composition compared to predicted ZND reaction zone length predictions.

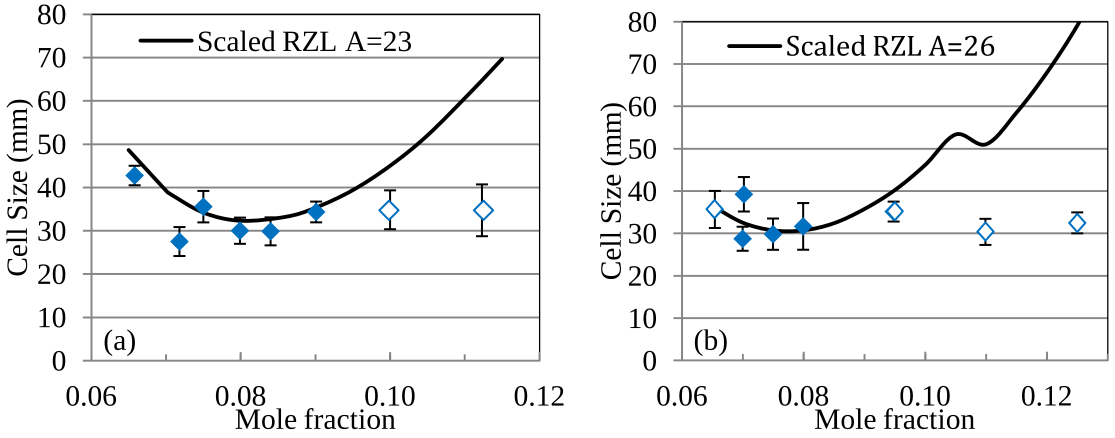

Figure 8. Experimental cell size and scaled reaction zone length for ethanol-air at a) 303/310K and b) 373K. Closed symbol – orifice plates, open symbol – 0.2 second gas driver

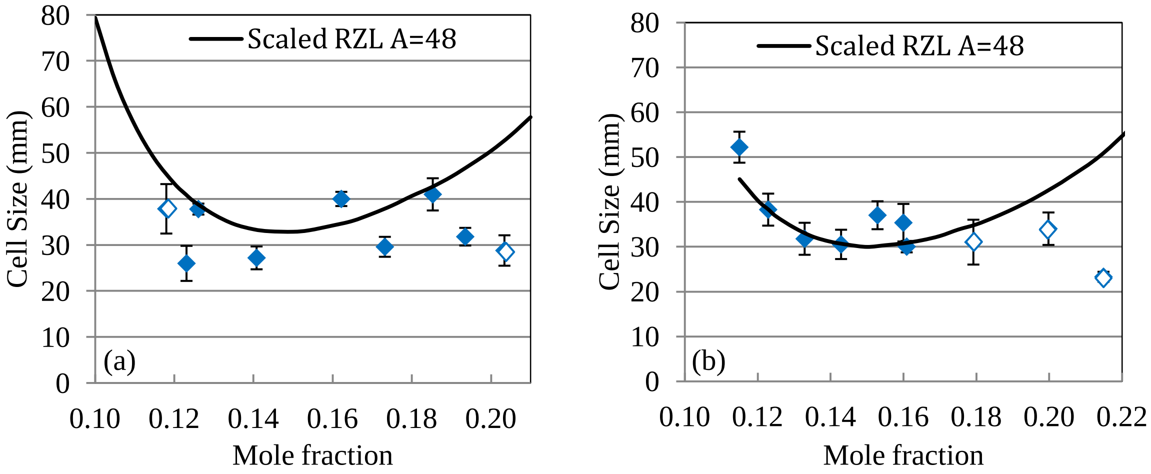

Figure 9. Measured cell size and scaled reaction zone length for methanol-air at a) 303/310K and b) 373K. Closed symbol – orifice plates, open symbol – 0.2 second gas driver

## References

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