DETONATION CHARACTERISTICS OF DIMETHYL ETHER, METHANOL AND ETHANOL AIR MIXTURES

by

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Abstract

The detonation characteristics of dimethyl ether-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, 6.1m long with an inner-diameter of 10cm. Transition to detonation was achieved for fuel-air mixtures by spark ignition and subsequent flame acceleration using orifice plate obstacles in the first half of the tube, and via a gas driver with a short orifice plate obstacle section. Cell width measurements were obtained using the soot foil technique for fuel-air mixtures inside the detonation limits. The measurements show that dimethyl ether-air, methanol-air and ethanol-air mixtures are less “sensitive” to detonation than propane-air and ethane-air mixtures, but more sensitive than methane-air mixtures, within the tested temperature range. Soot foil records also indicated the presence of substantial cellular substructure for all three fuel-air mixtures. One-dimensional detonation reaction zone length calculations were performed and fit with the measured cell width using a simple linear correlation, which resulted in an accurate representation of the data. The correlation proportionality constants for dimethyl ether-air, methanol-air and ethanol-air were obtained for the dominant cellular structure as well as the substructure. The values obtained for the substructure are comparable to values reported in the literature for typical hydrocarbons.
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Nomenclature and Greek Symbols

AProportionality Constant
ANSIAmerican National Standards Institute
BRBlockage Ratio
cSpeed of Sound
CJChapman and Jouget
C_{p}Specific Heat constant pressure
C_{v}Specific Heat constant volume
DDiameter
d_{c}Critical Tube Diameter
DDTDeflagration-to-detonation transition
defDeflagration
detDetonation
DMEDimethyl ether
E_{a}Activation Energy
E_{c}Critical Energy
hEnthalpy
IPIonization Probe
kRatio of Specific Heats
l_{i}Induction length
M Mach Number
PPressure
PTPressure Transducer
qHeat Release
\( \bar{q} \)  Rate of Heat Release

\( R \)  Universal Gas Constant

\( s \)  Entropy

\( T \)  Temperature

\( u \)  Velocity

\( V \)  Voltage

\( ZND \)  Zeldovich, vonNeuman and Doring

\( \delta \)  Reaction Zone Length

\( \Delta q \)  Heat of Reaction

\( \lambda \)  Cell Width

\( \rho \)  Density

\( \sigma \)  Reaction Progression

\( \bar{\sigma} \)  Rate of heat release for reactants

\( \tau \)  Induction Time

\( Y \)  Adiabatic index

\( \phi \)  Equivalence Ratio
Chapter 1

Introduction

1.1 Project Overview

This study involved measuring the detonation characteristics of fuel-air mixtures at atmospheric pressure and elevated temperatures. Dimethyl-ether (DME)-air, methanol-air and ethanol-air mixtures were considered in this investigation, along with propane-air mixtures, which served as a baseline case for comparison with the three other fuel-air mixtures. DME (CH$_3$OCH$_3$), methanol (CH$_3$OH) and ethanol (C$_2$H$_5$OH) are all chemically similar alcohol compounds widely used for industrial applications. In recent years there has been an increase in interest to use these and other renewable fuel sources in the automotive industry. As applications for these and other renewable fuels are developed an infrastructure to transport and store these fuels will have to be developed, or have the existing infrastructure adapted and expanded. Very little explosion safety data is currently available for these fuels; the potential harm due to detonation of these fuels, within storage infrastructures, is high due to the extremely destructive energy release associated with detonation.

The project was carried out in a number of phases. Experiments were carried out in a tube filled with the test mixture and ignited at one end. Initially the flame velocity profile down the length of the tube was determined as the fuel concentration was varied, with the first half of the tube containing orifice plate obstacles to promote deflagration-to-detonation transition (DDT). The orifice plate obstacles section was then shortened and detonation was initiated quickly in a very reactive gas cloud formed at the ignition end of the tube, i.e., a gas driver. The lean and rich
limits of detonability for the fuel-air mixtures were determined using both the orifice plate obstacle section and the gas driver. The effect of varying the initial temperature on the detonation limits was also determined. The final phase of the study was to collect detonation cell width data for each fuel-air mixture at two initial temperatures within the detonability limits.

The most significant deliverable of this study is the detonation cell width data. Comparing the measured cell width to published data for common hydrocarbon fuels allows for the detonability, or the fuel-air mixtures sensitivity to detonation, to be evaluated for explosion safety purposes.

1.2 Literature Review

Very little explosion safety data is currently available for DME-air, methanol-air and ethanol-air mixtures. Limited detonation cell size data exists for these fuels, typically with oxygen; this section provides a brief overview of available literature.

1.2.1 DME

Tieszen et al. [1] performed a study on a broad range of gaseous hydrocarbon-air detonations; only one cell size measurement was reported as 30mm for stoichiometric DME-air at 1atm and 373K. Mogi et al. [2] performed experiments with DME-air at 1atm and 298K; no cell size data was collected however, detonation velocity and pressure were collected within the detonability limits for two different detonation tubes. Ng et al. [3] performed detonation experiments where cell size was collected for DME-oxygen mixtures at 298K and initial pressures within the range of 2-30kPa. For fuel-rich mixtures they reported that the detonation cellular structure consisted of two characteristic scales, corresponding to the calculated double peak in the one-dimensional
detonation reaction zone. They also observed substantial cellular substructure for fuel-lean mixtures that was attributed to detonation wave instabilities.

### 1.2.2 Methanol

Eaton et al. [4] performed experiments at initial pressures of 2-30kPa for a range of methanol-oxygen mixtures at 298K, cell size measurements were made and the smallest cell size was found to correspond to an equivalence ratio of 1.4. Irregularities in soot foils were reported and were attributed to detonation instabilities for methanol-oxygen mixtures. The cell size data showed that methanol-oxygen was more sensitive to detonation than methane-oxygen at similar conditions, but less sensitive than hydrogen-oxygen.

### 1.2.3Ethanol

Roy et al. [5] performed a study on a broad range of heterogeneous mixture detonations, including ethanol-oxygen mixtures. Detonability limits for a 36mm diameter tube were found for ethanol-oxygen mixtures at 1atm and 298K, however no cell size measurements were made.
Chapter 2

Detonation Theory

This chapter covers the relevant theory pertinent to the research covered in later chapters.

2.1 Introduction

A detonation wave is a supersonic combustion wave consisting of a shock wave supported by energy release in a trailing reaction zone. The shock wave raises the pressure and temperature of the mixture, which initiates chemical reaction. The energy release from the chemical reaction supports the lead shock wave. Once reaction is complete, at the end of the reaction zone, chemical equilibrium is achieved. A detonation wave in a fuel air mixture typically propagates at a velocity on the order of 2000 m/s, and has an associated pressure rise of approximately 2.0 MPa. However, the characteristics of a detonation wave are dependent on the initial thermodynamic conditions and the energy release of reactants and therefore vary greatly. For example, a detonation wave in an acetylene-oxygen mixture at stoichiometric and standard conditions travels at approximately 2430 m/s, and has a pressure rise of 3.5 MPa.

2.2 Detonation Structure

2.2.1 Chapman and Jouguet (CJ) Theory

Chapman [6] and Jouguet [7] independently theorized that detonation waves did not have a finite thickness structure, i.e., they presumed all the energy release from chemical reactions occurred instantaneously at the shock wave. Their calculations, based on this assumption, were supported
by experimental data available at the time. Detonation values such as peak pressure and wave
velocity, agree with CJ values since the theory is based solely on the chemical energy release.
The basic thermodynamic model involves the balancing of mass, momentum and energy across a
control volume, the rate of reaction is not considered in the model. The control volume encloses
the detonation wave, where the inlet to the control volume consists of fresh mixture travelling at
the detonation wave velocity and the outlet flow velocity is relative to the detonation wave, which
is shown in Figure 2.1.

\[ P_1, \rho_1, T_1 \xrightarrow{u_1} u_2 \xrightarrow{P_2, \rho_2, T_2} \]

Figure 2.1: Reactants entering and products exiting a detonation wave with energy release
occurring instantaneously contained within a control volume.

Applying conservation of mass

\[ \rho_1 u_1 = \rho_2 u_2 \] (2.1)

Applying conservation of momentum

\[ P_2 - P_1 = \rho_1 u_1 (u_1 - u_2) \] (2.2)

Applying conservation of energy (adiabatic, negligible potential energy change)

\[ \frac{u_1^2}{2} + h_1 = \frac{u_2^2}{2} + h_2 \] (2.3)

Assuming a perfect gas

\[ P = \rho RT \] (2.4)
The enthalpy is defined as:

\[ h = h_f^0 + C_p(T - T^0) \]  
(2.5)

Where \( T^0 = 0K \)

Therefore equation 2.3 becomes:

\[ \frac{u_1^2}{2} + C_{p_1} T_1 + q = \frac{u_2^2}{2} + C_{p_2} T_2 \]  
(2.6)

Where \( q \) is the chemical energy per unit mass:

\[ q = h_{f_1}^0 - h_{f_2}^0 \]  
(2.7)

By combining equations (2.1) and (2.2), the Rayleigh equation is obtained:

\[ \frac{p_2}{p_1} = - \left( \frac{\rho_2 u_2^2}{\rho_1} \right) \frac{p_1}{\rho_2} + \left( 1 + \frac{\rho_2 u_2^2}{\rho_1} \right) \]  
(2.8)

Combining equations (2.2) and (2.6) yields:

\[ C_p T_2 - (C_p T_1 + q) = \frac{1}{2} (P_2 - P_1) \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \]  
(2.9)

Assuming the specific heat remains constant across the wave:

\[ k_1 = k_2 = k \]  
(2.10)

After some algebraic operations equation (2.9) yields the so-called Hugoniot equation:

\[ \left( \frac{k}{k-1} \right) \left[ \left( \frac{\rho_1}{\rho_2} \right)^{\frac{2}{k-1}} - 1 \right] - \frac{\rho_1 q}{\rho_1} = \frac{1}{2} \left( \frac{P_2}{\rho_1} - 1 \right) \left( 1 + \frac{\rho_1}{\rho_2} \right) \]  
(2.11)

Where the energy term is equal to the ratio of energy release to initial sensible energy:

\[ \frac{\rho_1 q}{\rho_1} = \frac{a}{RT_1} = \frac{(k-1)q}{c_v T_1} \]  
(2.12)

The CJ state is represented by the point at which the Rayleigh line is tangent to the Hugoniot curve, see Figure 2.2; this also represents the point of minimum entropy increase across the wave.
It can also be shown that the flow at the end of the reaction zone (outlet of the control volume) is choked. The velocity at the CJ state can then be determined directly by equating the pressure ratio for the Rayleigh line and the Hugoniot curve and using the fact that:

$$\bar{q} = \frac{q}{c_1^2}$$  \hspace{1cm} (2.13)

The following expression is obtained:

$$\frac{\rho_1}{\rho_2} = \frac{1}{k+1} \left( k + \frac{1}{M_1^2} \right) \pm \sqrt{\left( \frac{1}{M_1^2} \right)^2 - \frac{(k^2-1)2\bar{q}}{M_1^2}}$$  \hspace{1cm} (2.14)

This expression provides two possible end states for a given detonation Mach number. The unique CJ state, corresponding to the tangency condition, is obtained by setting the square root term equal to zero:

$$\frac{1}{M_{\text{CJ}}^2} = (k^2 - 1)\bar{q} \left\{ 1 + \frac{1}{(k^2-1)\bar{q}} \pm \sqrt{1 + \frac{2}{(k^2-1)\bar{q}}} \right\}$$  \hspace{1cm} (2.15)

Again there are two possible solutions, a deflagration and detonations state. These two states can be seen graphically in Figure 2.2, represented by the tangency of the Rayleigh line and the Hugoniot curve. The detonation state, relevant to this study, is characterized by a density and pressure rise.
Figure 2.2: The two possible solutions for the Rayleigh line lying tangent to the equilibrium Hugoniot curve adapted from Ciccarelli et al. [8]

The CJ theory is excellent for calculating detonation pressure and velocity, however since it does not take into account the time dependent chemical reactions it cannot predict the detonation wave internal structure. Therefore another model, which takes into account the thickness of the detonation, is required.

2.2.2 Zeldovich, von Neumann Doring Detonation Reaction Zone

Zeldovich, vonNeuman and Doring (ZND) independently developed a one dimensional detonation wave model that takes into account the finite reaction zone length. This detonation
model consists of three sections; a planar front shockwave, a planar inviscid reaction zone, and a CJ plane, as shown in Figure 2.3.

![Diagram of ZND detonation model]

**Figure 2.3: ZND detonation model, adapted from Ciccarelli [9]**

Immediately behind the shockwave, at the beginning of the reaction zone is an induction zone, where the temperature and pressure remain constant. Moving along the reaction zone the temperature increases until the final CJ state is achieved [10]. Figure 2.4 shows a typical plot of temperature and the derivative of temperature with respect to distance through the detonation wave. Note, the temperature gradient in the reaction zone is proportional to the rate of heat release. The point of maximum temperature change represents the location of maximum energy release and is used to define the induction zone length, $l_i$ in Figure 2.4.
The temperature and the flow velocity through the reaction zone can be obtained by the method described by A. Higgins [12]. Assume steady state flow, over a constant cross-sectional area. The left boundary of the control volume used in the analysis is located immediately after the shock wave and extends into the reaction zone, as shown in Figure 2.5. All the properties behind the shock wave can be determined by calculating the CJ detonation velocity and then by using the normal shock wave relations.

\[ P_I, \rho_I, T_I \xrightarrow{U_I} \text{Reaction Zone} \xrightarrow{x} P_x, \rho_x, T_x \]

Figure 2.5: The reaction zone directly behind the shock, known as the von Neumann state.

Figure 2.4: Typical plot of temperature and time derivative of temperature behind the shock for 28.6% acetylene, acetylene-oxygen detonation at standard conditions [11]
Applying the steady conservation of mass:

\[ d(\rho u) = 0 \]  \hspace{1cm} (2.16)

Applying conservation of momentum:

\[ d(\rho + \rho u^2) = 0 \]  \hspace{1cm} (2.17)

Applying conservation of energy, similar to equation (2.3), where the subscript \( x \) refers to the parameter value in the reaction zone at a distance \( x \) from the shock wave:

\[ \frac{u_1^2}{2} + h_1 = \frac{u_x^2}{2} + h_x \]  \hspace{1cm} (2.18)

Where the enthalpy, \( h_x \), consists of the sensible heat less the amount of energy released by that point:

\[ h_x = c_p T_x - \sigma(x)\Delta q \]  \hspace{1cm} (2.19)

Where \( \sigma \) corresponds to the reaction progresses, \( \sigma = 0 \) when only reactants are present, \( \sigma = 1 \) when only products are present, \( \Delta q \) is the heat of reaction and defined as:

\[ \Delta q = h_{f_A}^0 - h_{f_B}^0 \]  \hspace{1cm} (2.20)

where \( h_{f_A}^0 \) is the enthalpy of formation corresponding to the reactants, and \( h_{f_B}^0 \) corresponds to products. Note this is a simplified global reaction, i.e. the reactants proceed directly to products without intermediate steps.

Re-arranging equations (2.16-2.19):

\[ T(x) = \frac{1}{c_p} \left( h_1 + \sigma(x)\Delta q + \frac{1}{2} (u_1^2 - u(x)^2) \right) \]  \hspace{1cm} (2.21)

Where:

\[ h_1 = c_p T_1 - \sigma(0)\Delta q \]  \hspace{1cm} (2.22)
Since \( \sigma(0) = 0 \) the following equation provides an expression for the temperature profile in the reaction zone:

\[
T(x) = \frac{1}{c_p} \left( C_p T_1 + \sigma(x) \Delta q + \frac{1}{2} (u_i^2 - u(x)^2) \right) \quad (2.23)
\]

In order to obtain the temperature profile from equation (2.23) an expression relating the velocity and progress variable is required.

The ideal gas law in differential form:

\[
\frac{dp}{p} = \frac{d\rho}{\rho} + \frac{dT}{T} \quad (2.24)
\]

The speed of sound:

\[
C^2 = \left( \frac{\partial p}{\partial \rho} \right)_s = \gamma RT \quad (2.25)
\]

Using equation (2.16-2.20, 2.24, 2.25) and noting \( M = \frac{u}{c} \), a differential expressions for the change in velocity is developed:

\[
d\frac{u}{u} = \frac{\Delta q}{C_p T} \left( \frac{\sigma dx}{u} \right) \quad (2.26)
\]

Where \( \sigma \) is the reaction progress variable. An Arrhenius expression can be used to express the global heat release rate into the flow (reactants proceed to products):

\[
\dot{\sigma} = k (1 - \sigma) \exp \left( -\frac{E_a}{R T} \right) \quad (2.27)
\]

So that the rate describes the reaction of a particle in the flow:

\[
\frac{d\sigma}{dx} = \frac{1}{u} \dot{\sigma} \quad (2.28)
\]

The final equation for velocity including equation 2.28 becomes:

\[
\frac{du}{dx} = \frac{\Delta q}{C_p T} \frac{\sigma}{1 - M^2} \quad (2.29)
\]
Equation (2.29) represents change in flow velocity with distance in the reaction zone for a reaction with a known rate constant $k$ and activation energy, $E_a$, in 2.27. Equations (2.23, 2.27, 2.29) are solved simultaneously to obtain the temperature profile, $T(x)$, in the reaction zone, a detailed reaction mechanism can be included by considering species conservation equations, requiring elementary reaction equations.

### 2.2.3 Actual detonation waves

Actual detonation waves are very three-dimensional in structure and are highly time dependent. A representation of the actual structure can be seen in Figure 2.6, a schlieren image of a detonation wave moving from left to right obtained by Austin et al. [13]. The front does not consist of a planar lead shock wave; it is actually made up of three different shock waves, i.e., referred to as the Mach stem, the transverse wave and the incident shock. The common point for all three waves is known as the triple point. The detonation front consists of a collection of triple points that propagate transversely over the front as it moves forward. The transverse waves are clearly seen extending back from the triple points into the products.

![Image of a detonation wave](image)

**Figure 2.6:** Schlieren image of a detonation wave front propagating from left to right in $2\text{H}_2-\text{O}_2-3.5\text{N}_2$, at 20kPa [13], the top left corner of the box contains the triple point.
Figure 2.7 from Gavrikov et al. [15] shows the detonation front at four different times. The sketch shows two adjacent triple points on their way to collision as well as the forward moving shock waves and the corresponding reaction zones. Truncated transverse waves are also shown in the sketch. The two triple points trace out a diamond shape cell that bounds a shock wave followed by a reaction zone. In the first half of the cell the shock wave is strong and is referred to as a Mach stem. As the Mach stem progresses it decays in strength and the reaction zone length increases. This weakening wave becomes the incident shock, in the second half of the cell. By the end of the cell the incident shock completely decouples from the reaction zone to form a shock followed by a deflagration. At the end of the cell the transverse waves extending back from the triple point collide, creating a local explosion that generates a strong Mach stem with a short reaction zone. The triple point collision allows for a new cycle of shock decay to begin, and the release of energy associated with each collision allows for the propagation of the next set of waves. The continuous decay, collision and re-initiation of the waves allows the global detonation to propagate, and is the driving factor behind the detonation. It also creates a highly time dependent system. For example, the shock wave within the cell does not propagate at the constant CJ velocity; it fluctuates between 1.6 times the CJ velocity, at the start of the cell, to about 0.6 times the CJ velocity at the end of the cell. However, the average propagation of the detonation wave matches the CJ velocity since momentum and energy is always conserved [14].
Figure 2.8 adapted from Lee [17], shows triple point interactions over the entire detonation wave. As the triple points propagate they collide with adjacent triple points and are forced in opposing directions until they collide with another set of triple points. Traced out triple point trajectories over time create a fish scale pattern, where each scale is known as a cell (as discussed above). The cell width, $\lambda$, represents the average triple point spacing over the detonation front, or equivalently the average transverse spacing between parallel triple point trajectories. The cell width represents the characteristic detonation wave chemical length scale [16], which is an important parameter pertaining to detonability.
Figure 2.8: Time-lapse triple point trajectories resulting in cellular pattern, E represents a triple point collision location, the transverse spacing from collision locations is designated by λ, adapted from [17].

2.2.4 Detonation Cell Irregularity and Substructure

A detonation wave by nature is an unstable phenomenon. Even for the simplified one-dimension ZND structure the coupling between the shock wave and the reaction zone is nonlinear. In a time dependent calculation this coupling results in an oscillatory behavior of the detonation wave velocity, or the corresponding shock pressure, about the CJ value [18]. This nonlinear coupling is associated with the exponential dependency of the reaction rate with temperature (governed by
shock wave) as provided in the Arrhenius form of the reaction rate, i.e., $exp(-\frac{E_A}{RT})$. There is a critical value of the activation energy, $E_A$, above which the well-behaved oscillation in the detonation velocity becomes highly irregular in nature and includes the generation of multiple frequency modes [18].

In two and three-dimensions this unstable coupling is responsible for the generation of transverse waves, and the corresponding cellular structure that is always present in a detonation wave. In detonation waves, the varying degrees of instability within the reaction zone leads to varying degrees of regularity in the cellular structure. Just like in one-dimensional detonations the activation energy is one of the key parameters governing this instability, in general the larger $E_A$ is, the more unstable the system [19]. Detonation waves characterized by an unstable system have a highly irregular cellular structure, whereas detonations that exhibit a stable system have a more regular cellular structure [19].

Triple point trajectories can be captured for a detonation wave via the soot foil technique [20]. This technique involves coating a metal sheet with carbon soot that is placed inside of a detonation tube with the soot covered side facing inwards. After the detonation wave passes by the foil a cellular pattern is scribed onto the foil. The mechanism by which the triple points scrapes the soot off the foil is not know, however the technique offers a simple way to visualize the cells. Figure 2.9 from Strehlow [21] shows examples of unrolled soot covered foils inscribed with cellular detonation structure; the four foils show varying degrees of regularity.
Figure 2.9: Soot covered foil showing classic detonation cell structure with varying degrees of regularity, from Strehlow [21], A) very regular, C$_2$H$_4$+3O$_2$+75%Ar, P=100mm Hg, B) regular, 1.26H$_2$+O$_2$+40%Ar+16%N$_2$, P=150mm Hg, C) irregular, 2H$_2$+O$_2$, P=125mm Hg, D) very irregular, CH$_4$+2O$_2$, P=50mm Hg.

Strehlow [21] and Libouton et al. [22] suggested that four classifications of cell regularity exist, examples of sketched cellular structures corresponding to the four classifications are shown in Figure 2.10. Fuel-air mixtures most commonly display irregular and very irregular cellular structure [23]. The regularity of the cellular structure is characterized by the uniformity of the cell width, or equivalently the lateral distance between parallel triple point lines, as well as the presence of “substructure.” Substructure refers to triple point lines associated with transverse waves that are fairly weak that play no role in the propagation of the detonation wave, typically the triple point trajectories are not parallel to the principle lines, or they abruptly start or end, as shown in Figure 2.9 C.
Figure 2.10: Variation of cell irregularity: a) very regular, b) regular, c) irregular, d) very irregular [22]

Fine-scale substructure commonly accompanies irregular, and highly irregular mixtures, e.g., fuel-air mixtures commonly exhibit fine-scale substructure [23]. Fine-scale substructure is identified as very small cells, or tightly packed triple point trajectories, that appear inside the large dominant cells but do not persist or continue along the entire foil. The fine structure is evident in Figure 2.9 C and D, and clearly shown in Figure 2.10 d. These small cells are due to local shock velocities inside a detonation cell being much higher than the CJ velocity, as discussed in section 2.2.3, i.e., the locally overdriven detonation exhibits triple point trajectories similar to the global detonation wave. An overdriven detonation wave is one that propagates at a velocity above the CJ value. As discussed earlier the local shock velocity within a detonation cell typically decreases from a maximum value of about 1.6 times CJ at the start of the cell, immediately following the collision of transverse waves, to about 0.6 times the CJ velocity by the end of the cell [14]. For detonations that display very irregular cell structure the maximum velocity can be significantly higher than 1.6 times the CJ value at the start of the cell. And
typically very small cells are observed at the beginning of the large cell, further along as the shock velocity decreases, the size of these fine cells increases, see Figure 2.10d. By mid-span of the cell, where the local shock velocity is roughly CJ, the substructure disappears due to the weakening of the triple points [24].

2.2.5 Cell Width Measurement

Reading soot foils is very subjective so the method used to identify the cells needs to be established up front. There are two main ways of measuring cells, and each can give a different value for λ. The preferred method as stated by Moen et al. [20] is the dominant mode method. In this method the cells are measured by identifying the most dominant parallel triple point bands that have high contrast. By choosing this method it ensures that substructure isn’t mistaken as dominant cells, and there is less subjectivity compared to the second method that involves choosing individual cells. Figure 2.11, taken from Moen et al. [20], shows how cell structure can be irregular, but by using the dominant mode method it is possible to reduce uncertainty.
Figure 2.11: Dominant parallel bands within irregular structure [20]

### 2.3 Cell Width and Detonation Limits

The cell width is a dynamic parameter and represents the characteristic length scale of a detonation wave; therefore many studies have included measurements of cell width as a way of quantifying mixture sensitivity or detonability [10, 14, 15, 16, 20, 25]. It has been shown that the larger the cell width the more energy is required to directly initiate a spherical detonation wave [26]. The critical energy $E_c$, is the minimum energy required to instantaneously initiate a detonation in a reactive medium. Any energy level below the critical energy will result in a deflagration [26]. Lee et al. [26] derived a simple relation between cell width and critical energy, where $E_c$ is proportional to $\lambda^3$. 

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For a fuel-oxidizer mixture the cell width will change in relation to initial conditions such as mixture composition, initial temperature and pressure. Cell width as a function of composition for hydrogen-air mixtures from Ciccarelli et al. [25] is shown in Figure 2.12. For a particular mixture and set of initial thermodynamic conditions the smallest cell width typically corresponds to a slightly rich mixture. The cell width increases in size as the detonation limits are approached producing a classic U-shape curve. The cell width curve is steeper on the fuel-lean side compared to rich side. The detonability limits are defined as the minimum and maximum concentrations of fuel that can propagate a detonation in a fuel-oxidizer mixture. These detonation limits are dependent on the boundary conditions of the constraining apparatus. Peraldi et al. proposed that the detonation propagation limit in a circular cross section tube corresponds to a cell width equal to the tube diameter [27]. A single head spin detonation [26], which will be described later, corresponds to a cell width on the order of the circumference of the tube, \( \lambda = \pi D \), and is considered marginal since the detonation wave is supported by the boundary conditions of the apparatus.
2.3.1 Cell width relation to Reaction Zone Length

Detailed ZND reaction zone length calculations have been reported in many studies [15]. For hydrogen oxidation the energy release is governed by 23 reactions and 11 different species that make up the chemical kinetics. By simultaneously solving the steady conservation equations, including conservation of species, in small steps behind the shock it is possible to determine the characteristics of the reaction zone [10], as covered in section 2.2.2. There are multiple approaches to defining the reaction zone length, common definitions include the distance behind
the shock to the point where flow Mach number reaches 0.75, where the temperature gradient is a maximum [16], and where the reactant consumption reaches 0.5 or 0.9 [15]. A standard definition for reaction zone length is important for correlating the reaction zone length with the experimental cell width. The most common definition for the reaction zone length is the distance from the shock to the point of maximum temperature gradient; this corresponds to the point of maximum heat release rate [16].

The cellular structure, and hence the cell width, is based on the multi dimensional nature of the detonation wave, whereas the ZND detonation model is strictly one-dimensional. The ZND model takes into account the chemical reaction that occurs behind a shock wave, so on average it provides a rough measure of the chemical length scale for a true detonation wave. Despite the fundamental difference of the two parameters, relating the two can be useful and there have been many studies that relate the experimental cell width to calculated reaction zone length [10, 15, 16, 20, 25, 28]. The simplest method involves using a linear relationship between the cell width and the reaction zone length. Equation 2.30 provides the correlation between the cell size, \( \lambda \), and the reaction zone length \( \delta \) with a proportionality constant, \( A \). The proportionality constant is obtained by arbitrarily matching the experimental cell width and the calculated reaction zone length at the stoichiometric condition [16]. Using the proportionality constant method a strong correlation has been found for hydrogen, hydrogen sulfide, and many hydrocarbons [10]. Figure 2.12 shows a fit for hydrogen-air, with \( A \) equal to 51 [25].

\[
\lambda = A \times \delta
\]  
(2.30)
2.3.2 Dual Cellular Structure

Dual cellular detonation structures have been shown to exist in a limited number of fuel oxygen mixtures, e.g., nitromethane-oxygen [29]. Dual cellular structures consist of large cells with much smaller cells inside of them, an example of which from Joubert et al. [30] is shown in Figure 2.13. Fuel-air mixtures commonly exhibit cellular substructure consisting of smaller cells as covered in section 2.2.4, however a dual cellular structure is a completely different phenomenon.

![Image](image)

Figure 2.13: Soot covered foil exhibiting dual cellular structure in H\textsubscript{2}-(NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4}) mixtures at P=1bar and \(\phi=1.2\) [30]

Dual cellular structures have been linked to the specifics of the chemical energy release rate inside the reaction zones of detonations [31]. When the chemical energy is released in two steps of very different characteristic times, as illustrated in Figure 2.14 from Joubert et al. [31], the
resulting detonation will show a dual cellular structure. The first chemical energy release step is associated with an initial maximum in the heat release rate and is associated with the small cells. The second chemical energy release step is the second maximum in the heat release rate and is associated with the larger cells. The correlation of the two different induction lengths i.e. reaction zone lengths, to the two characteristic cell sizes has been shown to be valid by Sturtzer et al. [29].

Figure 2.14: Temperature and time derivative of temperature behind the shock showing two steps of very different characteristic times, for an H$_2$-NO$_2$/N$_2$O$_4$, detonation at $\varphi = 1.5$ and standard conditions [31]. $\tau_{i1}$ shows the first induction length, the $\tau_{i2}$ shows the second induction length.
2.3.3 Single Head Spin

As mentioned in section 2.3 the detonability limits are approached for a particular apparatus when the cell width approaches the size of the tube. One type of marginal detonation is the spin detonation. A single head spin detonation occurs when only a single strong triple point exists. When only a single triple point is present, triple point collisions cannot occur; therefore the triple point travels in a single continuous path. The path of the triple point trajectory on the tube inner-surface appears helical because the triple point is traveling along the circumference of the tube simultaneously to the detonation front moving forward. Soot foil records of a single head spin detonation display banding, as opposed to the classic cellular pattern, due to the helical trajectory of the triple point. Shown in Figure 2.15, from Schott [32], is a typical soot foil record of a single head spin detonation. The single head spin detonation is considered a limiting case for steady detonation propagation in a tube with a circular cross section. It is not considered to be self-sustained since it relies on the coupling of the chemical reaction with the tube acoustic resonance.

![Figure 2.15: Typical soot covered foil showing banding from a single heat spin detonation in 6.7C_2H_2 + 10O_2 + 83.3Ar [32].](image)
Chapter 3

Apparatus and Procedure

This chapter covers the experimental apparatus and procedures used to perform experiments presented in this report. All experiments were performed in the Explosion Physics and Prevention Laboratory, at Queen’s University. Photographs of the apparatus can be found in Appendix D.

3.1 Detonation Tube

The apparatus consisted of the detonation tube, the mixing chamber, and the data acquisition system. The mixing chamber and detonation tube are shown schematically in Figure 3.1.

![Figure 3.1: Mixing chamber and detonation tube equipped with extended orifice plate obstacle section and showing possible ionization probe (IP) locations](image)

The detonation tube consisted of two mated 316 stainless steel tubes, both 3.05m long with inner diameters of 10cm and wall thicknesses of 1.91cm. The tubes were connected with standard
1500 class ANSI flanges with a spiral metal gasket between them. Mating 1500 class ANSI endplates closed off the tube. Two versions of the ignition endplate were used; one was equipped with an external compartment, while the other was equipped with a mounting hole for a standard automobile engine spark plug.

Eighteen 1/2 inch – 20 threaded holes were located at the top of the tube at an equal spacing of 3.05cm to allow for instrumentation. Instrumentation along the tube consisted of eight ionization probes to allow for flame time of arrival measurement, two PCB Piezotronics piezoelectric pressure transducers (PCB model 113A22 and 113A26) to measure detonation pressure, and a strain gauge type pressure transducer (Omega model PX219-015A5V) to measure mixture fill pressure. The pressure transducer calibration procedure and measurement uncertainty are located in Appendix C. Orifice plate obstacles were positioned every 10cm for the first 3.05m of the detonation tube. The orifice plates had an outer diameter equal to the inner diameter of the detonation tube and a central hole with a diameter of 7.55cm. The blockage ratio (BR) of the orifice plate was 0.43, defined as the ratio of the cross-sectional area of the tube blocked by the obstacle to the tube cross-sectional area.

### 3.2 Mixing chamber

The mixing chamber was a 30litre pressure vessel used for preparing air-fuel mixtures. It was ASME certified to a maximum allowable working pressure of 3.4MPa at 425K and included a rupture disk rated for 3.74MPa at 425K. The body of the mixing chamber was a 50cm long cylinder with a diameter of 25cm; it was capped at each end with a 2:1 elliptical head. The top cap was connected to a second cylinder that was 5cm long with a diameter of 15cm; a 300-class ANSI flange capped the second cylinder. The inside of the mixing chamber contained an
impeller for mixing the gas components. A Parr Instruments rotating sealing gland assembly allowed the impeller to be rotated via a pneumatic motor mounted on top of the mixing chamber.

3.3 Heating System

3.3.1 Detonation Tube Heating

The detonation tube was equipped with a custom heating system from Cooper Heat Inc. The system consisted of a master controller, a slave power distribution unit, junction boxes, heater elements, and insulation. The master controller consisted of four Honeywell UNC 2000 Mini-Pro digital temperature controllers and one Fuji electric PXV3-RAY2-4V temperature controller for monitoring and controlling the five control zones. The control zones consisted of two zones for the tube sections and three zones for the flange sections of the apparatus. The slave unit consisted of a power transformer, zone conductors, current switches, and ground fault interrupter modules, which communicated with the master controller via a 24VDC signal. Two junction boxes were used for power distribution. The slave unit supplied power to the junction boxes and the junction boxes distributed power to the heater elements. The heater elements consisted of nichrome wire woven through ceramic beads, which were grouped into rectangular pads or lines for wrapping the detonation tube.

The two control zones for the pipe sections of the tube each consisted of 16, 60V heater pads, which were connected into eight parallel circuits. Each flange section control zone consisted of two, 80V heater pads connected in parallel. All sections of the tube were wrapped in two layers of Kawool to reduce heat loss and promote temperature uniformity along the tube. To monitor the temperature of each control section a K-type thermocouple was placed between a central
heating pad and the tube and connected to a master controller. As well, multiple thermocouples were arrayed along the tube for manual temperature monitoring. The heating system was also equipped with a ground fault detection system that monitored for contact between the heating elements and the tube and would cut power in the case of a short.

### 3.3.2 Mixing Chamber Heating

The mixing chamber was wrapped with 3 OMEGA FGS102-100 240V high temperature heater tapes and insulated with standard fiberglass insulation. OMEGA CN-302-K-F digital temperature controllers individually controlled the heating tapes; K-type thermocouples were placed between the heating tapes and the mixing chamber to relay data back to the controllers.

The piping that connected the mixing chamber to the detonation tube was trace heated with two OMEGA FGS102-100 240V high temperature heater tapes, which were individually powered by POWERSTAT Variable Autotransformers. The temperature of the two heater tapes were monitored manually by a K-type thermocouple located at the junction of the two lines and the temperature was adjusted by varying the voltage of the power supply.

### 3.3.3 Mixing in the tube

For some experiments the detonation tube was fitted with a circulation line for preparing mixtures directly in the tube. The circulation line was attached at the far ends of the detonation tube to allow complete circulation. The circulation line was trace heated with a Wrap-On Company 31024 pipe heating cable, which kept the mixture in the line heated to approximately 303K. A
Thomas 917CA22F bellow pump was used for circulating the test mixture through the detonation tube and the circulation line.

**3.4 Ignition System**

Combustion was initiated by a standard automobile ignition system, powered by an OMRON 12VDC power supply and triggered via LabVIEW.

For the orifice plate obstacle experiments an automobile spark plug was connected to the ignition system and threaded into the endplate of the tube to initiate combustion of the test mixture directly.

**3.4.1 Gas Driver**

For the gas driver experiments the endplate of the detonation tube was replaced by a flange with a built in chamber, the altered apparatus is shown in Figure 3.2.

![Figure 3.2: Mixing chamber and detonation tube equipped with gas driver and shortened orifice plate obstacle section](image-url)
The gas driver chamber contained two electrodes that were connected to the ignition system and optimally spaced to produce the longest possible spark discharge. The driver gas mixture consisting of acetylene and oxygen was mixed on the fly via a custom piping system shown in Figure 3.3. The acetylene flowed through a ¼ inch tube that was inserted into a ½ inch tube that carried the oxygen. The coaxial flow mixed the two gas streams very effectively. The acetylene-oxygen mixture was injected into the driver chamber via a side port. The spark initiated combustion of the acetylene oxygen mixture rather than the test mixture directly. Attached to the end flange was a shortened obstacle section consisting of 3 orifice plates, identical to those used in the 3.05m obstacle section shown in Figure 3.1.

![Figure 3.3: Acetylene and oxygen mixing system](image)

### 3.5 Gases and Fuels

The gases used in the experiments; dry air, acetylene, propane and oxygen were commercial grade standard gases. The purity of the fuels used in testing is shown in Table 3.1.

**Table 3.1: Purity of Liquid Test Fuels**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>99.8%</td>
</tr>
<tr>
<td>Anhydrous Ethyl Alcohol</td>
<td>100%</td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>99.5%</td>
</tr>
</tbody>
</table>
All gases were transported via a piping system shown schematically in Figure 3.4. The gas lines were seamless stainless steel tubing with an outer diameter of \( \frac{½}{inch} \) or \( \frac{¼}{inch} \), and a wall thickness of 0.049 inch. All connections and junctions were made with Swagelok compression fittings. The system was connected to an Edwards RV5 two-stage rotary vane vacuum pump.

![Figure 3.4: Piping schematic](image)

### 3.6 Control and Data Acquisition System

#### 3.6.1 Control System

The system was equipped exclusively with pneumatically actuated ball valves, all the pneumatic valve actuators were opened and closed by three-way solenoid valves that were controlled by a computer. LabVIEW version 10.0f2 was used in conjunction with two National Instruments USB-6525 data acquisition cards. The NI cards each had 8 digital outputs and 8 analogue inputs. The digital outputs were used to control the 13-solenoid valves. The solenoid valves were powered by a National Instruments PS-16 24VDC power supply.
3.6.2 Data Acquisition

Flame time of arrival and pressure time histories were recorded via LabVIEW through a National Instruments PCI-6133 card and a BNC-2110 connector block. Two analogue inputs were used for recording the voltage signals from the ionization probes. Four other analogue inputs were used to record the voltage signals generated by the piezoelectric pressure transducers; two measuring detonation pressure and two measuring fill pressure.

3.6.3 Ionization Probes

Flame time of arrival was tracked using ionization probes mounted in the detonation tube instrumentation ports. The ionization probes consisted of 2 electrically isolated electrodes 1.6mm in diameter spaced approximately 4.5mm apart and protruding approximately 15mm into the tube. They were connected to an electrical circuit shown in Figure 3.5. As the flame passed between the two electrodes, the circuit between the two probes closed due to ions in the flame. The closed circuit resulted in a voltage drop along a resistor that was measured and recorded in LabVIEW. The circuit was connected to a Systron RS320-2C power supply producing a voltage potential of 270VDC.

![Figure 3.5: Ionization probe electrical circuit](image.png)
3.6.4 Soot Foils

Cell width data was collected using the soot foil technique as discussed in section 2.2 Chapter 2. Sheets of 0.55mm thick aluminum sheet metal were used to produce the foils. The aluminum was cut into 30.48cm by 55.88cm rectangles and rolled into cylinders. The resulting cylinder had a 9.7cm diameter, when inserted into the detonation tube it nearly covered the entire circumference of the 10cm diameter tube. Prior to being inserted into the detonation tube the foils were cleaned and “smoked.” A kerosene lamp was used to produce soot. The foils were positioned vertically above the lamp flame and capped at one end such that it filled with smoke resulting in a thin soot coating. The foil was filled with smoke for approximately 1.5 minutes, then rotated and held over the lamp for an additional 1 minute to ensure a uniform soot covering, see Figure 3.6. Post combustion, the soot foil was removed from the detonation tube, spread out flat and sprayed with a clear acrylic to protect the inscribed detonation cellular pattern from the elements. The cell width was then measured and recorded.

Figure 3.6: Aluminum foil coated with soot
3.6.4.1 Cell Width Measurement

The technique used to measure cell width was the dominant mode method. In this method, the cells are measured by finding the most dominant parallel bands that have high contrast. Using this method introduces less subjectivity in choosing “cells,” as discussed in section 2.2

3.7 Procedure

Procedures for performing experiments varied depending on the type of test. The main test variables included the system temperature, the ignition method, and the phase of the fuel, e.g. liquid or gas. For all tests, the pattern of preparation was similar.

Initially, all the gas bottles were opened to allow gas to flow through the lines leading from regulators to the piping system, to insure only pure gas was present in the lines. The piping system was then evacuated, typically to a pressure of 0.25kPa but never greater than 0.5kPa. The mixture was prepared using the method of partial pressures, by first adding the liquid fuel and then dry air. The mixture was then stirred for 15-20 minutes using the impeller to produce a homogenous mixture. While mixing, the piping system and the detonation tube were evacuated to a pressure of 0.25kPa but never greater than 0.5kPa. Once mixing was complete, the mixture was loaded into the detonation tube via the injection line, filling the detonation tube until the pressure rose above atmospheric. The excess mixture inside the detonation tube was then vented out until the tube reached local atmospheric pressure. The mixture resided in the tube for no longer than one-minute while test parameters such as temperature and pressure were recorded and then ignition was initiated via LabVIEW. Due to the limited range of the mixing chamber pressure transducer and the volume and pressure of the detonation tube, only one test per mix
could be performed. Post combustion the entire system, including the mixing chamber and detonation tube, were purged with compressed air before a vacuum was pulled.

### 3.7.1 Testing Procedure for Special Cases

For tests performed at elevated temperatures, the detonation tube was pre-heated to a uniform temperature $\pm 5^\circ$C. The mixture was loaded into the detonation tube via the injection line (which was trace heated and insulated leading from the mixing chamber to the detonation tube) allowing the mixture to be pre-heated to the required temperature before entering the detonation tube.

For tests using a liquid fuel, the liquid was injected directly into the mixing chamber and stirred for 7 minutes, then allowed to sit for an additional 7 minutes to ensure that the pressure fluctuations due to condensation or evaporation of the fuel within the mixing chamber had ceased. If the fuel had a low vapor pressure at room temperature, the mixing chamber would be pre-heated to a uniform temperature to allow for rich mixtures to be created.

For tests using the gas driver ignition system, the detonation tube was filled to approximately 98kPa with the test mixture and an additional 4kPa of driver gas, for a 0.2s driver (the time refers to the duration that the acetylene and oxygen flowed into the tube), further details on driver lengths are found in Appendix A. The final pressure before ignition within the detonation tube would be approximately local atmospheric pressure.

For fuels with very low vapor pressure the mixture was made inside the detonation tube. For these mixtures the liquid fuel was injected directly into the preheated detonation tube and circulated using the bellow pumps for 7 minutes, then allowed to sit for an additional 7 minutes to confirm that the pressure was not fluctuating. The dry air was then added to the mixture inside.
the detonation tube to achieve approximately atmospheric pressure and the mixture was then circulated for four detonation tube volumes (approximately 40 minutes) to ensure uniformity.

For tests that involved cell width measurement, the soot foil was placed inside the detonation tube on the opposite side of the ignition end. The soot foil was removed post combustion but prior to tube purging to insure the soot was not displaced or damaged by compressed air or any combustion products, e.g. soot, water vapor.

Tests performed under special conditions are listed below.

- Methanol and ethanol at 303K, mixtures were prepared in the detonation tube for orifice plate obstacle tests.
- Methanol at 310K, mixtures were prepared in the heated mixing chamber at a temperature of 333K for gas driver tests.
- Ethanol at 310K, mixtures were prepared in the detonation tube for gas driver tests.
- Methanol and ethanol at 373K, mixtures were prepared in the heated mixing chamber at a temperature of 333K for orifice plate obstacle tests and gas driver tests.
Chapter 4

Chemical Kinetic Analysis

The one-dimensional detonation structure was obtained using Shepherd’s publically available ZND code [33] and the chemical kinetic mechanism developed at Princeton University [34], and modified for DME by Zhao et al. [35]. The code was used to determine the reaction zone length and to obtain the temperature profile within the reaction zone for DME-air, methanol-air and ethanol-air mixtures.

4.1 DME-Air Mixtures

The calculated ZND detonation structure of DME-air varies greatly with composition. The temperature and the gradient of temperature (proportional to the heat release rate) with respect to distance in the reaction zone of a 9% DME-air mixture at 298K are provided in Figure 4.1. For DME-air two peaks were observed in the temperature gradient for mixtures above 6.54% DME at 298K and 373K.
Figure 4.1: Temperature and temperature gradient along ZND detonation structure at 9.0% DME and 298K

The distance and magnitude of the peaks in the temperature gradient change over a range of DME-air concentrations. Figure 4.2 shows the temperature gradient behind the shock for rich concentrations of DME (note, a stoichiometric mixture has a DME concentration of 6.54%). For lower DME concentrations the first peak was significantly smaller in magnitude than the second peak, as the concentration of DME was increased the magnitude of both peaks decreased; however the second peak decreased more quickly. At 11.5% DME the two peaks were approximately the same magnitude, beyond this concentration the first peak was larger and the second peak continued to decrease in size and become less pronounced.
Figure 4.2: ZND temperature gradient within reaction zone for DME-air at 373K for select rich mixtures

Figure 4.3 shows the disappearance of the double peak as the DME concentration is reduced for mixtures near stoichiometric. At 7.5% DME a clear double peak is evident, as the concentration of DME decreased the first peak became less pronounced and disappeared at 6.54% DME.
Figure 4.3: ZND temperature gradient within reaction zone for DME-air at 373K for select mixtures near stoichiometric

The reaction zone length was defined as the distance from the shock to the point of maximum heat release rate, i.e., maximum temperature gradient. Over a range of DME-air mixtures two different values of the reaction zone length could be obtained depending on which peak in the temperature gradient is chosen. Figure 4.4 shows the calculated reaction zone lengths for DME-air at 298K and 373K for both peaks. The minimum values were found to correspond to slightly rich mixtures, i.e., approximately 8.0% DME at 298K and 373K. Moving away from 8% DME the reaction zone length increased creating the classic U-shaped curve in a plot of reaction zone length versus fuel concentration. The size of the calculated reaction zone length decreased by approximately 17% and 12%, as the temperature was increased from 373K to 298K, corresponding to the first peak and second peaks respectively.
4.2 Methanol-Air Mixture

The ZND detonation structure of methanol-air exhibited a standard one-peak heat release profile behind the shock. Figure 4.5 shows the calculated reaction zone length for methanol-air at 298K and 373K. The minimum values were found to correspond to approximately 15.0% methanol at 298K and 373K, slightly rich relative to the stoichiometric concentration of 12.3%. The reaction zone length was calculated to be approximately 6.0% smaller at 373K, compared to 298K, for stoichiometric methanol-air. The effect of initial temperature is more significant for rich mixtures.
Figure 4.5: Calculated ZND reaction zone length for methanol-air mixtures at 303K and 373K

4.3 Ethanol-Air Mixtures

The characteristics of the ZND detonation structure of ethanol-air varied over a range of concentrations. Figure 4.6 shows the progression of the temperature gradient behind the shock as the concentration of ethanol is increased from stoichiometric. One sharp peak was visible in the profile near the stoichiometric composition of 6.54% ethanol. As the concentration of ethanol was increased the magnitude of the peak decreased and the profile widened, eventually forming a trough (local minima). This trough in the peak of the temperature gradient profile was obtained at concentrations between 10.5% and 11.0% ethanol, beyond these concentrations the shape of the curve displayed a single maxima. The local minima created a shift in the reaction zone length. The existence of a minimum over such a small range of concentrations is most likely due
to inaccuracies in the chemical kinetics mechanism, and suggests that the two peaks in the heat release rate evident in DME-air mixtures may be caused by similar inaccuracies.

Figure 4.6: ZND temperature gradient within reaction zone for ethanol-air at 373K for select rich mixtures

Figure 4.7 shows the calculated reaction zone lengths for ethanol-air at 293K and 373K. The shift in the magnitude of the reaction zone length at approximately 11.0% ethanol corresponds to the shift in the absolute location of the peak in the heat release profile, as previously discussed. The minimum values were found to correspond to approximately 7.5% ethanol at 293K and 373K. For stoichiometric ethanol-air the reaction zone length was calculated to be approximately 19% smaller at 373K compared to 293K. The effect of initial temperature is more significant for rich mixtures.
Figure 4.7: Calculated ZND reaction zone length for ethanol-air mixtures at 293K and 373K
Chapter 5

Experimental Results

This chapter contains experimental data from the various phases of this project. Flame acceleration, detonation limits and cell size for fuel-air mixtures of DME, methanol and ethanol are presented. Experimental results for each fuel-air mixture have been divided into tests performed with the orifice plate obstacle section to promote deflagration-to-detonation transition and tests performed with the gas driver section. Tests were performed at 1 atmosphere and at a range of temperatures between 298K and 373K.

5.1 DME–Air Mixtures

5.1.1 Orifice Plate Obstacle Initiation System

The detonation limits for DME-air were determined at 298K and 373K by using the orifice plate obstacle section to initiate a detonation wave. Measurements were made of flame acceleration in the obstacle laden first half of the tube and constant velocity detonation propagation in the smooth second half of the tube. Propagation of a detonation wave was confirmed by a velocity near the theoretical CJ detonation velocity and the appearance of detonation cells on the soot foil. Figure 5.1 shows the measured flame and detonation velocities along the length of the tube for different DME-air mixtures at an initial temperature of 298K. For mixtures near stoichiometric (6.54% DME), DDT occurred early in the obstacle section achieving velocities on the order of 1400m/s in the last part of the obstacle section. Once the detonation left the obstacle section, at a distance of 3.1m, it quickly accelerated to a velocity on the order of 1800m/s. For mixtures near the upper and lower limits flame acceleration was less pronounced and DDT occurred near the
end of the obstacle section. For mixtures outside the detonation limits the flame accelerated in the first section to a velocity under 1000m/s and then decelerated upon exiting the obstacle section into the smooth wall tube section. Figure 5.2 shows the flame velocity down the length of the detonation tube for mixtures at 373K, characteristics of acceleration are similar to those observed in the tests conducted at 298K.

Figure 5.1: Flame/Detonation velocity along the detonation tube for DME-air at 298K using the orifice plate obstacle section
The average flame/detonation velocity measured at the end of the tube as a function of the DME concentration at 298K, along with the theoretical CJ detonation velocity, is shown in Figure 5.3. The lean and rich detonation limits were found to be 6.0% and 9.0% DME based on the sharp drop off in velocity beyond those concentrations, which indicated a failure to detonate. Figure 5.3 shows the measured detonation velocities agree very well with the theoretical CJ velocities.
Figure 5.3: Detonation limits for DME-air at 298K using the orifice plate obstacle section

The detonation velocities measured for all DME concentrations were slightly lower at 373K as shown in Figure 5.4, compared to those measured at 298K. The detonation limits were found to be slightly wider at the higher temperature. For tests at 373K the upper limit was determined to be 9.75%, which is an increase from 9.0% DME at 298K, while the lower limit remained constant at 6.0% DME.
5.1.2 Gas Driver Initiation System

Experiments performed using the orifice plate obstacle section were repeated with the majority of the obstacle section removed and the end flange replaced with a gas driver to initiate prompt detonation initiation. Details on the driver gas calibration are provided in Appendix A. The detonation limits for DME-air using the gas driver were determined by measuring flame velocity in the smooth detonation tube. Figure 5.5 shows the measured flame and detonation velocity along the length of the tube in different DME-air mixtures at an initial temperature of 298K. For mixtures near stoichiometric conditions initial flame velocities near the exit of the gas driver were on the order of 1600m/s, within 1m detonation velocities were achieved, approximately 1800m/s, and remained nearly constant along the rest of the tube. For mixtures outside the detonation limits two modes of detonation failure were observed, sustained detonation failure and failure to transition to detonation. In the case of sustained detonation failure, initial flame velocities near
the exit of the gas driver were on the order of 1400m/s, within 1m detonation velocities were achieved. At approximately 2.5m along the tube flame deceleration began and continued until steady deflagration flame velocities were achieved. For this mode of failure it is believed that the driver produced an overdriven detonation wave that survived up to 2.5m and then failed as the detonation wave decayed with distance. For mixtures that fail to transition to detonation, initial flame velocities in the driver gas were on the order of 800m/s, followed by prompt deceleration to a low constant velocity. In this mode a detonation does not form in the driver gas due to the low reactivity of the driver gas diluted by the test gas. The final velocities of the two failure modes were similar and ranged from 200m/s to 600m/s, well below the CJ detonation velocity. Figure 5.6 shows flame velocities in the detonation tube for mixtures at 373K, characteristics of acceleration are similar to those observed in the tests conducted at 298K, except only one failure mode was present, failure to transition to detonation.

![Figure 5.5: Flame/Detonation velocity along the detonation tube for DME-air at 298K using the 0.2s gas driver](image-url)
5.1.3 Orifice Plate Obstacle Section and Gas Driver Detonation Comparison

The average flame/detonation velocity measured near the end of the tube as a function of the concentration of DME at 298K for experiments using the orifice plate obstacle section and the gas driver are shown in Figure 5.7. Also shown in Figure 5.7 is the theoretical CJ detonation velocity. Using the gas driver the rich detonability limit increased from 9.0% to 11.0% DME, while the lean limit remained unchanged at 6.00% DME. Figure 5.7 shows the measured detonation velocities agree very well with the theoretical CJ detonation velocities.
Using the gas driver the limits of detonability were determined at 373K, the orifice plate limits and the gas driver limits are shown in figure Figure 5.8. The lean limit of detonability decreased from 6.00% to 5.75% DME, while the rich limit increased from 9.75% to 12.5% DME using the gas driver. Figure 5.8 shows the measured detonation velocities agree very well with the theoretical CJ velocities.
Figure 5.8: Detonation limits for DME-air at 373K using the orifice plate obstacle section and the gas driver

A summary of the detonation limits at 298K and 373K for orifice plate obstacle and gas driver experiments are provided in Table 5.1.

**Table 5.1: Detonability Limits of DME-Air**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Orifice Plate Obstacle Section</th>
<th>Gas Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lean limit (%DME)</td>
<td>Rich Limit (% DME)</td>
</tr>
<tr>
<td>298</td>
<td>6.00%</td>
<td>9.00%</td>
</tr>
<tr>
<td>373</td>
<td>6.00%</td>
<td>9.75%</td>
</tr>
</tbody>
</table>
5.1.4 Reaction Zone Length and Cell Size

The soot foil technique, described in section 2.2.5, was used to analyze detonation cellular structure and to measure the detonation cell width via the dominant mode method, for mixtures within the detonation limits. The cellular structure, although fairly regular, was found to contain significant substructure and selecting strong triple point trajectories was very subjective creating significant uncertainty in the measurement of dominant cells at both 298K and 373K. Figure 5.9 shows a typical foil obtained from an experiment performed with 6.5% DME at 298K. The same foil is shown in Figure 5.10 with the selected dominant triple point trajectories sketched in with white dotted lines. Note, the dominant lines are more pronounced on the actual foil compared to that seen in the photo. The abundance of short lived triple point trajectories can be seen within the dominant bands, which is typical for all concentrations. The non-dominant triple point trajectories form a set of smaller cells, a sample of which is shown in Figure 5.10.
Figure 5.9: Soot covered foil for 6.5% DME at 298K
Figure 5.10: Soot covered foil with dominant triple point trajectories and smaller cells sketched, 6.5% DME at 298K

Figure 5.11 shows the measured cell size, from orifice plate obstacle and gas driver experiments at 298K. The error bars shown for the measured cell size represents the standard deviation of the measured cells at a particular concentration, and do not include the uncertainty associated with the selection of the dominant triple point trajectories. The experimental data in Figure 5.11 includes the average cell width obtained using the dominant trajectory method, as well as the average size of the small cells. Also shown in Figure 5.11 are the scaled ZND reaction zone lengths based on the two peaks in the DME heat release rate profile (see Figure 4.2 and Figure 4.3). The ZND data is scaled and anchored to the measured cell size data at stoichiometric
conditions. To reflect the possibility of a double cell structure the reaction zone length corresponding to the first and second reaction rate peaks were scaled with the dominant cell and the smaller cell data, respectively. The corresponding proportionality constants are 78 and 33. Using the more dominant second peak to scale the small cell data, also shown in Figure 5.11, resulted in a proportionality constant of 23.

![Graph showing experimental cell size and scaled reaction zone length for DME-air at 298K.](image)

**Figure 5.11**: Experimental cell size and scaled reaction zone length for DME-air at 298K. The detonability limits using the orifice plate obstacle section and the gas driver section are shown as vertical dashed lines.

Small and large cells were evident at all concentration within the detonability limits, the scaled reaction zone lengths fit well to the experimental data. Cell size was collected using a 0.5s driver as indicated by the solid circles in Figure 5.11 and as well as in the 373K data provided in Figure 5.12. The stronger driver was able to detonate mixtures outside of the detonability limits.
obtained using the 0.2s gas driver, this allowed for cell size measurements to be taken within a greater range of mixtures.

Cell size measurements at 373K showed only a small decrease in size compared to cell measurements obtained at 298K, as can be seen by comparing values in Figure 5.11 and Figure 5.12. The 373K ZND data is scaled and anchored to the measured cell size data at stoichiometric conditions; this gives a proportionality constant of 92 for the large cells and 23 for the small cells using the second peak and a value of 33 using the first peak. The proportionality constants of 23 and 33 for the smaller cells are consistent with the values obtained at 298K, however the value of 92 for the larger cells is larger than the value of 78 obtained at 298K.

Figure 5.12: Experimental cell size and scaled reaction zone length for DME-air at 373K. The detonability limits using the orifice plate obstacle section and the gas driver section are shown as dashed lines.
5.2 Methanol–Air Mixtures

5.2.1 Detonability Limits

The detonation limits for methanol-air were obtained at 303K and 373K by using the orifice plate obstacle section. Flame acceleration and detonability limit data using the orifice plate section are provided in Appendix B.

The detonation limits for methanol-air using the gas driver were determined at 310K and 373K. Tests were performed at a slightly higher initial temperature (310K compared to 303K) to compensate for the low vapor pressure of methanol. The slightly higher temperature does not have a significant effect on the detonation cell width. The higher temperature allowed for higher concentration mixtures of methanol to be tested. Flame acceleration data using the gas driver is provided in Appendix B.

5.2.2 Orifice Plate Obstacle Section and Gas Driver Comparison

The average flame/detonation velocity measured near the end of the tube as a function of the concentration of methanol, along with the theoretical CJ detonation velocity are shown in Figure 5.13, for experiments using the orifice plate obstacle section at 303K and experiments using the gas driver at 310K. Using the gas driver the rich detonability limit increased from 19.4% to 21.0% methanol, while the lean limit decreased from 12.3% to 10.4% methanol at 310K. Figure 5.13 shows the measured detonation velocities agree very well with the theoretical CJ detonation velocities.
Figure 5.13: Detonation limits for methanol-air using the orifice plate obstacle section at 303K and the 0.2s gas driver at 310K

Using the gas driver the limits of detonability were determined at 373K, the orifice plate limits and the gas driver limits are shown in Figure 5.14. The rich detonability limit increased from 16.3% to 23.0% methanol, while the lean limit remained unchanged at 11.5% methanol, at 373K. Detonations did occur beyond the lower limit in isolated tests, however the results were not reproducible and therefore 11.5% was taken to be the limit for the tube at 373K.
A summary of the detonation limits at 303K, 310K and 373K for orifice plate obstacle and gas driver experiments are shown in Table 5.2.

**Table 5.2: Detonability Limits of Methanol-Air**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Orifice Plate Obstacle Section</th>
<th>Gas Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lean limit (%)</td>
<td>Rich Limit (%)</td>
</tr>
<tr>
<td>303</td>
<td>12.3%</td>
<td>19.4%</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>11.5%</td>
<td>16.3%</td>
</tr>
</tbody>
</table>

**Figure 5.14:** Detonation limits for methanol-air at 373K using the orifice plate obstacle section and the 0.2s gas driver
5.2.3 Reaction Zone Length and Cell Size

Similar to DME detonations the cellular structure was found to contain significant substructure, and selecting strong triple point trajectories was very subjective. Figure 5.15 shows a typical foil obtained for a 12.6% methanol mixture at 303K.

![Soot Foil with triple point trajectories sketched, 12.6% methanol at 303K](image)

Figure 5.15: Soot Foil with triple point trajectories sketched, 12.6% methanol at 303K

Figure 5.16 shows the measured cell size, from orifice plate obstacle experiments at 303K and gas driver experiments at 310K, the scaled ZND reaction zone length was calculated at 303K. The scaled ZND data is anchored to the measured cell size data at stoichiometric conditions for the large cells; this gives a proportionality constant of 111 for large cells and 48 for small cells at 303/310K.
Figure 5.16: Experimental cell size and scaled reaction zone length for methanol-air at 303/310K. The detonability limits using the orifice plate obstacle section and the gas driver section are shown as dashed lines.

Cell size measurements at 373K showed little change in size compared to cell measurements at 303/310K, as can be seen by comparing values in Figure 5.16 and Figure 5.17. The scaled ZND data is anchored to the measured cell size data at stoichiometric conditions; this gives a proportionality constant of 147 for large cells and 48 for small cells.
Figure 5.17: Experimental cell size and scaled reaction zone length for methanol-air at 373K. The detonability limits using the orifice plate obstacle section and the gas driver section are shown as dashed lines.

5.3 Ethanol–Air Mixtures

The detonation limits for ethanol-air were determined at 303K and 373K by using the orifice plate obstacle section. Flame acceleration and detonability limit data using the orifice plate section are located in Appendix B.

The detonation limits for ethanol-air using the gas driver were determined at 310K and 373K. Tests were performed at a slightly higher initial temperature (310K compared to 303K) to
compensate for the low vapor pressure of ethanol. The slightly higher temperature does not have a significant effect on the detonation cell size. The higher temperature allowed for higher concentration mixtures of ethanol to be tested. Flame acceleration data using the gas driver is located in Appendix B.

5.3.1 Orifice Plate Obstacle Section and Gas Driver Comparison

The average flame/detonation velocity measured at the end of the tube as a function of the concentration of ethanol, along with the theoretical CJ velocities are shown in Figure 5.18 for experiments using the orifice plate obstacle section at 303K and experiments using the gas driver at 310K. The small variation in temperature allowed for an increased range of mixtures to be tested while allowing for results to be directly compared. Using the gas driver the rich detonability limit increased from 8.5% to 11.0% ethanol, while the lean limit remained unchanged at 6.0% ethanol and 310K. Figure 5.18 shows the measured detonation velocities agree very well with the theoretical CJ detonation velocities.
Figure 5.18: Detonation limits for ethanol-air using the orifice plate obstacle section at 303K and the 0.2s gas driver at 310K

Using the gas driver the limits of detonability were determined at 373K, the orifice plate limits and the gas driver limits are shown in Figure 5.19. The rich detonability limit increased from 8.5% to 13.0% ethanol, while the lean limit remained unchanged at 6.5% ethanol, at 373K. Detonations did occur beyond the lean limit in isolated tests, however the results were not reproducible and therefore 6.5% was determined to be the limit for the tube at 373K.
Figure 5.19: Detonation limits for ethanol-air using the orifice plate obstacle section and the 0.2s gas driver at 373K

A summary of the detonability limits at 303K, 310K and 373K for orifice plate obstacle and gas driver experiments are shown Table 5.3.

Table 5.3: Detonability Limits of Ethanol-air

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Orifice Plate Obstacle Section</th>
<th>Gas Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lean limit (%)</td>
<td>Rich Limit (%)</td>
</tr>
<tr>
<td>303</td>
<td>6.0%</td>
<td>8.5%</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>6.5%</td>
<td>8.5%</td>
</tr>
</tbody>
</table>
5.3.2 Reaction Zone Length and Cell Size

Similar to the DME foils the cellular structure was found to contain significant substructure, and selecting strong triple point trajectories was very subjective, this created significant uncertainty in the measurement of dominant cells at 303K, 310K and 373K. Figure 5.20 shows a typical foil at 373K; the abundance of small cells can be seen within the large cells, which is typical for all concentrations.

![Figure 5.20](image)

**Figure 5.20: Soot covered foil with triple point trajectories sketched, 9.48% ethanol at 373K**

Figure 5.21 shows the measured cell size, from orifice plate obstacle experiments at 303K and gas driver experiments at 310K. Small cells were measured within the detonability limits and the size of the cells remained approximately constant for all concentrations. The scaled ZND data is anchored to the measured cell size data at stoichiometric conditions; this gives proportionality constants of 57 and 23 for large and small cells respectively.
Figure 5.21: Experimental cell size and scaled reaction zone length for ethanol-air at 303/310K. The detonability limits using the orifice plate obstacle section and the gas driver section are shown as dashed lines.

Cell size measurements at 373K showed a slight decrease in size compared to cell measurements at 303/310K, as can be seen by comparing values in Figure 5.21 and Figure 5.22. The ZND data is anchored to the measured cell size data at stoichiometric conditions; this gives proportionality constants of 67 and 26 for the large and small cells respectively. The shift in the reaction zone length at approximately 10.5% ethanol is due to the shift in the heat release profile as discussed in section 4.3.
Figure 5.22: Experimental cell size and scaled reaction zone length for methanol-air at 373K
Chapter 6

Discussion

This chapter discusses the interpretation of soot foil records from Chapter 5, compares the detonation structure to the characteristics of the ZND model from Chapter 4 and compares the measured cell size to data available in the literature.

6.1 ZND Reaction Zone Calculations

The reaction zone length was calculated for all fuel-air mixtures. The reaction zone length at stoichiometric conditions for DME-air, methanol-air and ethanol-air were found to be 1.29mm, 0.80mm and 1.39mm, respectively at 373K. These reaction zone lengths are all smaller than the reaction zone length for stoichiometric propane-air (1.63mm) but bigger than the reaction zone length for ethylene-air (0.45mm) two standard hydrocarbon-air mixtures for which cell size data was reported by Tiesszen et al. [1]. Therefore DME-air, methanol-air and ethanol-air mixtures should be less sensitive to detonation than ethylene-air mixtures (methanol-air being the most sensitive and ethanol-air being the least sensitive) but still more sensitive to detonation than propane-air mixtures.

The calculated reaction zone length was smaller as the temperature was increased at stoichiometric conditions. For a temperature increase from 298K to 373K, DME-air and methanol-air showed a reaction zone length reduction of 12% and 6% respectively, which is less than the reduction in propane-air of 24% [1], but more than the reduction in ethane-air at 2% [1]. Ethanol-air showed a reaction zone length reduction of 19%, which is less than propane-air at
24%, but more than methane-air at 14% [1], when the temperature was increased from 298K to 373K. Therefore DME-air, methanol-air and ethanol-air mixtures should be less sensitive to temperature changes than propane-air mixtures, but more sensitive than ethane-air mixtures. Ethanol-air mixtures, being the most sensitive, should also be more sensitive to temperature changes than methane-air mixtures.

The temperature and gradient of temperature profiles with respect to distance behind the shock were modeled for mixtures near stoichiometric, methanol-air mixtures were found to have a standard single peak in the heat release rate, similar to that observed in typical hydrocarbon fuels. DME-air showed what appeared to be a double peak in the heat release rate over a limited range of concentrations, and for ethanol-air a double peak was observed over a very narrow range of mixtures, as discussed in Chapter 4.

Two peaks in the heat release rate have previously been attributed to two exothermic reaction steps during the chemical energy release process for large molecule decomposition, most notably in nitromethane-oxygen (NM-O₂) mixtures [29] and hydrogen nitrogen dioxide (H₂-NO₂) mixtures [31]. This two stage heat release process resulting in a double peaked heat release rate for NM-O₂ mixtures and H₂-NO₂ mixtures has been shown to produce a dual cell structure detonation [29], [31], as discussed in section 2.3.2. Also a dual cellular detonation structure was reported for DME-oxygen mixtures by Ng et al. [3], for a range of equivalence ratios at low pressure. Chemical kinetic modeling of DME-air mixtures exhibit what appears to be a two-stage heat release process, similar to that obtained by Ng et al. [3]. However, the characteristic shape and size of the ZND reaction zone for both DME-air and ethanol-air mixture are not the same as those found in dual cell structure mixtures. The most noticeable difference being that the relative
size of the peaks in DME-air change, as shown in Chapter 4, while for NM-O\textsubscript{2} mixtures and H\textsubscript{2}-NO\textsubscript{2} mixtures the first peak is always larger [29, 31]. The relative lengths of the two reaction zones are also not typical of a dual cell structure. For the NM-O\textsubscript{2} and H\textsubscript{2}-NO\textsubscript{2} mixtures the relative sizes are at least one order of magnitude different [29], whereas for the DME-air in the present study, the peaks are typically separated by a factor of two as discussed in Chapter 4. This strange behavior in the temperature profile brings into question the accuracy of the kinetic mechanism used to model the DME-air and ethanol-air reactions, and suggests that the dual peak may not be linked to a dual cellular detonation structure.

6.2 Detonation Limits

The detonability composition limits for fuel-air mixtures were obtained using two different methods to promote deflagration-to-detonation transition as discussed in Chapter 3. It was found that for DME-air, methanol-air and ethanol-air, at all temperatures tested the limits of detonation were found to be wider using the gas driver than the orifice plate obstacle section. It was also found that for most conditions the limits of detonation were wider as the temperature was increased.

The limits of detonability are governed by the size of the apparatus. For mixtures approaching the limit the transverse size of the apparatus begins to influence the detonation cell structure, and cell width measurements can be affected. As a consequence, near limit cell widths are not reported. Once the cell size is larger than the constraint the detonation tends to fail. In the experiments using the orifice plate obstacle section the lateral constraint is associated with the orifice plates. The inner-diameter of the orifice plate obstacles was 7.55cm; therefore once cells
approached this size a sustained detonation was not able to propagate through the obstacle section. Once the failed detonation wave exited the obstacle section as a decoupled shock wave and trailing flame, although the tube diameter was 10cm, the flame could not re-accelerate within the smooth section leading to detonation initiation. The gas driver used a shortened obstacle section to promote deflagration to detonation transition, however these experiments were not limited by the orifice plate size due to the more reactive driver gas used, as explained in detail in Appendix A. The driver gas, consisting of an acetylene-oxygen mixture, has a cell size much smaller than any of the three fuel-air mixtures that were evaluated. Due to the small cell size of the driver gas detonation initiation readily occurred and was able to propagate through the shortened orifice plate section. Once the detonation exited the shortened orifice plate section it initiated detonation in the test mixture. Therefore, the apparatus constraint relevant for tests using the gas driver is the 10 cm detonation tube diameter. As a result, test mixtures with a cell size approximately 30% larger should detonate using the gas driver, as compared to those using the orifice plate obstacle section. As a result, detonations were achieved in less reactive mixtures using the gas driver. The limits determined by the gas driver are seen as the true limits of detonability for the detonation tube.

6.2.1 DME-Air Mixtures

At 298K and 373K detonation composition limits for DME-air mixtures were wider using the gas driver. The rich limit increased more dramatically than the lean limit; this is due to the fact that the cell size increases more rapidly on the lean side than the rich side with change in composition. Using both the orifice plate obstacle section and the gas driver section the limits of detonability were wider at 373K, than at 298K, this is due to cell size and the reaction zone length decreasing
as temperature is increased. Over the temperature range of 298K to 373K the detonability range was increased by 1.75% DME using the gas driver, which indicates that the temperature dependence of DME-air mixtures over this range of temperatures is not significant.

6.2.2 Methanol-Air Mixtures

Methanol-air was found to have the largest detonability range of the three fuel-air mixtures tested in this study; this is in agreement with the findings that methanol-air had the smallest calculated reaction zone length. As seen in Table 5.2 at the lower and higher temperatures, detonation composition limits were found to be wider using the gas driver compared to the obstacle section, which is expected. However, with the orifice plate obstacle section the rich limit of detonability decreased from 19.4% to 16.3% as the temperature was increased, this is surprising since the calculated reaction zone length decreased in size, and therefore the limit should have increased or at least remained constant. A similar anomalous trend was observed using the gas driver, the lean limit increased from 10.4% to 11.5% with an increase in temperature. Many repeat tests were performed to confirm these limits; the reason for these anomalies could not be determined.

6.2.3 Ethanol-Air Mixtures

Ethanol-air mixtures were found to have the smallest detonability range of the three fuel-air mixtures tested in this study, this agreed with the findings that ethanol-air had the largest calculated reaction zone length. At 298K and 373K detonation composition limits were wider using the gas driver, the rich limit increased more dramatically than the lean limit, which is to be
expected. Ethanol-air mixtures showed very little sensitivity to temperature changes, which is surprising since the calculated reaction zone length showed the largest change over the temperature range. Ethanol-air mixtures actually showed an increase in the lean detonability as the temperature was increased using both the orifice plate obstacle section and the gas driver. The change was approximately 0.5%, which is within experimental uncertainty for the mixture composition, which is covered in Appendix C.

6.3 Cell Size Measurement

A limited number of experiments were performed with propane-air at 1atm and 298K to obtain cell size data to compare with data in the literature and for comparison with the alcohol data obtained in this study. Figure 6.1 shows cell size measurements from the present study and the scaled ZND reaction zone length for propane-air mixtures, along with cell size data from Knystautas et al. [36]. Figure 6.1 shows good agreement between cell width measurements from the present study and those from Knystautas et al. [36]. There is a fairly good match between the data and the scaled ZND reaction zone length for lean mixtures. However, the cell size data deviates from the reaction zone length curve on the rich side, a common finding for smaller hydrocarbons [17]. The measured cell size for propane-air at stoichiometric conditions was found to be 52mm, which is within error of the 50mm value reported by Tiesszen et al. [1]. The reaction zone length and the resulting proportionality constant, A, (25), are also in good agreement with data from Tiesszen et al. [1] that reported a proportionality constant of 23.
Figure 6.1: Experimental cell size and scaled reaction zone length for propane-air at 298K, using the 0.5s driver, and cell width measurements from Knystautas et al. [36] for propane-air mixtures at 293K and 101.3kPa.

Soot foil records for propane-air tests indicated the existence of similar detonation cellular structure and substructure to the three fuel-air mixtures tested in this study. Figure 6.2 shows that both dominant parallel bands and substructure consisting of short lived triple point trajectories were evident; this was typical of all tested concentrations.
Ethanol-air at stoichiometric conditions showed smaller cells, 91mm, than methanol-air, 105mm, or DME-air, 119mm at 298/303/310K. These cell sizes are larger than propane and ethane at 50mm, but smaller than methane at 305mm [1]. Therefore DME-air, methanol-air and ethanol-air mixtures are less sensitive to detonation than propane-air and ethane-air mixtures, but more sensitive than methane-air mixture at 298/303/310K, this same trend was also apparent at 373K.

The stoichiometric cell size for DME-air at 298K is much larger than the 30mm value reported by Tiesszen et al. [1]. In the present study the small cells were found to be 34mm at this condition, which is within error of the finding by Tiesszen et al. It appears that Tieszen et al. did not take
note of the larger cells due to their limited testing that included only a single mixture composition.

The change in cell size due to temperature at stoichiometric conditions varied between fuels tested. Ethanol-air showed the largest reduction in cell size, 23%, as the temperature was increased from 298K to 373K. This agreed with the high sensitivity to temperature that was shown in the calculated reaction zone length. Methanol-air showed little variation in cell size, i.e., 5%, as the temperature was increased from 303K to 373K. This variation makes it less sensitive to temperature changes than methane-air at 15%, but more sensitive than ethane-air at 4%. DME-air cell size showed very little, to no change over the temperature range of 298K to 373K at stoichiometric conditions.

The cell sizes near the rich and lean limits of detonability for each set of fuel-air mixtures; DME-air, methanol-air and ethanol-air were similar. The cell size was consistently less than half the foil width, which indicates that at least two cells across the foil were always present when measurements were taken. In nearly all cases the cell size near the rich limit was larger than the cell size near the lean limit. This was likely due to the cell size increasing more rapidly on the lean side, and therefore making it difficult to obtain a soot foil measurement near the actual limit on the lean side. On the rich side the cell size increased less rapidly making it easier to obtain soot foil records near the true detonation limit.

The reaction zone length was correlated to the measured cell size using a proportionality constant A, as discussed in section 2.3.1. For the large cells, the constant A was determined for DME-air, methanol-air and ethanol-air mixtures to be 78, 111 and 57 respectively at 298K. These values of
A, are larger than that obtained for smaller hydrocarbons such as propane and ethane, with values of 23 and 11 respectively at 298K [1]. This trend is repeated at 373K. The proportionality constant was calculated for small cells in DME-air, methanol-air and ethanol-air mixtures to be 23, 48 and 23, respectively at 298K. These values agree much better with the values for propane, 23, and ethylene, 34, [1].

6.3.1 Cell Irregularity

DME-air mixtures exhibited fairly regular cellular structure, however substructure was found to be abundant at all concentration within the detonability limits. The dominant bands method was used to measure cell size and to differentiate substructure from dominant cells. The large cells are defined by strong triple point trajectories that survive along the entire foil, the substructure is composed of triple point trajectories that meander, split, merge or die off. Figure 6.3 is a close up photo showing a single cell on a typical foil. The larger cell is full of substructure, the uniformity and apparent size of the substructure is not typical of fine-scale substructure, as defined in section 2.2.4. The uniformity of the substructure between the identified dominant bands could explain the dual cellular structure reported by Ng et al. [3], however there are a number of differences between the substructure seen in this study and small cells shown in classic dual cell structure detonations. The clearest difference is the relative size of large and small cells, in classic dual cell structure detonations the cells are orders of magnitude different, whereas in DME-air mixtures the measured large cells are only about three times the size of the small cells. Also in classic mixtures with a dual cellular detonation structure small cells are only evident when a double peak in the heat release rate exists, in DME-air mixtures the same substructure was
evident in all DME-air mixtures within the detonability limits. However, a single peak in the heat release rate was only obtained for rich mixtures.

Figure 6.3: Single cell containing small cells/substructure for 6.47% DME at 298K, the detonation propagates from left to right

Methanol-air and ethanol-air mixtures also exhibited significant substructure at all mixture compositions as discussed in Chapter 5. Comparing soot foil records from all three fuel-air mixtures, it is clear that the substructure evident in DME-air is similar to the substructure evident in methanol-air and ethanol-air mixtures. However, ethanol and methanol do not display a double peak in the heat release rate. This suggests that although the substructure evident in these fuel-air mixtures is not typical of fine-scale substructure it should not play a significant role in detonation phenomena. This assertion can only be proven with additional testing.
6.3.2 Near limit cellular structure

Experiments with DME-air mixtures were performed with a driver strength of 0.75s to extend the detonability limits and determine the characteristics of marginal detonations for the apparatus. These cell sizes were not reported due to the likelihood of the detonation being overdriven at the soot foil due to the large driver gas slug. A foil obtained for a mixture in the extended DME-air lean detonability limit is shown in Figure 6.4. Two strong triple points traveling initially in opposite directions, eventually colliding on the diametrically opposite side of the tube and then changing direction, dominate the cellular structure. The two associated triple point trajectories form one large cell that extends the full width of the soot foil. In Figure 6.4 the top of the cell is cropped by the finite width of the soot foil, which is just slightly narrower than the circumference of the tube. The substructure inside the large cell varies in size and aspect ratio, and therefore is less uniform and is larger in size than the substructure evident in mixtures closer to stoichiometric conditions.
The soot foil obtained for the richest mixture in the extended rich limit is provided in Figure 6.5. A single major triple point characterizes the 12.9% DME mixture. The main triple point trajectory, traveling from the middle of the left side of the foil upwards to the right, shows high contrast and a substantial thickness as it propagates and is sustained along the entire foil. One other strong triple point exists, traveling from the top left corner towards the bottom right corner, which could show the formation of a single large cell, however the triple point does not appear to continue on the top of the foil once it reaches the bottom at just over half way. This foil could be considered a single head spin, due to the single dominant triple point. The single-head spin represents the ultimate limit for detonation propagation in a round tube. The other triple point trajectories observed on the foil are disorganized and short lived. The main difference with the
cellular structure observed in the 4.5% DME mixture near the lean limit is that the observed substructure is significantly smaller near the rich limit.

Figure 6.5: Soot covered foil, 12.9% DME at 298K, the detonation propagated from left to right.
Chapter 7

Conclusions and Recommendations

This research investigated the detonability characteristics such as detonation cell width and detonation limits, for various alcohol fuel-air mixtures at 1atm and at a range of temperatures. One-dimensional ZND reaction zone length calculations were performed and applied to aid in the interpretation of detonation structure, and to correlate the calculated reaction zone length to the measured cell width. Experiments performed in this study have shown that transition to detonation was achieved for fuel-air mixtures both through spark ignition and subsequent flame acceleration in extended orifice plate obstacles, and through direct initiation using a gas driver and a shortened orifice plate obstacle section. DME-air, methanol-air and ethanol-air mixtures experienced an increase in their limits of detonability when the gas driver was used, compared to the orifice plate section, since direct detonation initiation allowed for mixtures with cells larger than the orifice plate obstacles to propagate a sustained detonation. By increasing the initial temperature of the detonation tube detonation velocities for the three fuel-air mixtures have been shown to decrease. A small increase in the limits of detonability for DME-air, methanol-air and ethanol-air, where evident over the temperature range of 298K to 373K, however it has been shown that these fuel-air mixtures were not greatly affected by temperature over this range.

Soot foil records indicated that DME-air, methanol-air and ethanol-air detonations exhibited significant substructure, which were more orderly than typical hydrocarbon fine-scale substructures and could be mistaken for a dual-cellular structure, however strong evidence existed to support the theory that the small cells were not associated with a dual-cellular structure in any of the fuel-air mixtures. A linear correlation between the reaction zone length and the measured
cell size was developed that resulted in an accurate representation of the data. Proportionality constants for DME-air, methanol-air and ethanol-air were calculated for the substructure, i.e., smaller cells, that resulted in values comparable to typical hydrocarbons. Cell size measurements have indicated that DME-air, methanol-air and ethanol-air mixtures have very similar cell sizes. Based on the larger dominant cells the three alcohols are less sensitive to detonation than propane-air and ethane-air mixtures, but more sensitive than methane-air mixture within the temperature range of 298K to 373K. However, based on the smaller cells the three alcohols have a similar sensitivity to detonation as propane.

A number of future studies into DME-air, methanol-air and ethanol-air detonations would be very worthwhile. For instance, investigation into the failure modes of the three fuel-air mixtures would be an excellent continuation of this research since classic limit detonation structure such as spin detonations were not plainly evident. Also, detonation tests where an established cell size criterion should be performed in order to determine if the large or small cells govern the detonation phenomenon. For example, it has been established that a detonation wave will transmit from a tube into an unconfined volume if the tube accommodates at least thirteen cells [17]. This so-called critical tube diameter experiment could be carried out with the alcohols from the present test to determine if the smaller cells govern the transmission phenomenon. Beyond the fuels tested in this study a continuation of research into renewable fuels is extremely worthwhile and necessary for the future large-scale adoption of any prospective alternative fuel.
Appendix A

Gas Driver Calibration

The gas driver was used to initiate the detonation wave in a number of experiments. The physical specifications of the gas driver are covered in Chapter 3; this appendix discusses gas driver calibration and analysis in order to optimize the driver strength.

Minimizing Overdriven Detonations

The driver was calibrated by varying the acetylene oxygen mixture concentration and by varying the driver gas load time; note the strength of the driver is governed by how much driver gas is injected. The gas driver mixture composition was chosen to produce the highest initial wave velocity exiting the gas driver and entering the detonation tube for a set driver gas loading time. The driver length used to measure cell size was selected to be the shortest possible, corresponding to the shortest driver gas loading time that reproducibly initiated a detonation wave. It was important to use a short driver so that the detonation was not overdriven; overdriven detonation waves have a smaller cell size than a CJ detonation wave.

The driver loading time, which corresponded to the volume of driver gas (acetylene-oxygen) used to initiate detonation, was varied between 0.2s and 0.75s to analyze the possibility of overdriving a detonation. The larger the driver intake time the more driver gas was used in the experiment, however the final pressure inside the detonation tube was always kept constant at 1atm. It was found that larger driver times correlated with higher initial velocities and in some cases higher velocities near the end of the detonation tube. Figure A.1 shows typical initial velocity profiles
for tests performed at three driver strengths with identical initial stoichiometric DME-air conditions. For this stoichiometric mixture all three drivers produced a CJ detonation by the middle of the tube. This is expected since a stoichiometric mixture is the most reactive mixture and therefore there is less of a transition from the driver to the test gas. For mixtures near the detonation limits the stronger driver produced an overdriven detonation at the end of the tube. Variability in the initial velocity was due to the high detonation velocity of stoichiometric acetylene-oxygen, approximately 2430 m/s, compared to 1821 m/s for the DME-air mixture. When more driver gas is injected, more of the test gas is purged from the driver end of the tube increasing the ratio of driver gas to test gas in the driver end of the tube. This translates into a higher initial velocity at the beginning of the tube.

Figure A.1: Flame/Detonation velocity along the first half of the detonation tube for DME-air at stoichiometric conditions, 298K and varying driver strengths
Gas Driver Analysis

The gas driver gas dynamics were analyzed by using two pressure transducers, one located inside the driver chamber and one located at 30cm from the driver endplate of the detonation tube. The goal was to determine the characteristics of combustion within the driver chamber and at the driver end of the detonation tube.

The driver strength was found to affect the rate of pressure rise inside the gas driver chamber. Figure A.2 shows a typical pressure trace for a short driver and a long driver. Experiments that used a short driver started with a gradual increase in pressure followed by a slight drop in pressure leading to a very rapid rise; see Figure A.2a. The initial slow rise in pressure is associated with the propagation of the flame through the driver chamber. The absence of a sharp pressure rise, associated with a strong shock wave, indicates that a detonation does not form in the driver chamber. The drop in pressure occurs when the flame leaves the chamber, and the rapid rise in pressure is associated with the pressure pulse associated with DDT in the tube that is transmitted back into the chamber. Experiments that used a long driver showed a very slow pressure rise followed by a sharp increase in pressure corresponding to the passage of a detonation wave. The pressure profile observed in Figure A.2b is characteristic of a detonation wave. The short duration of the slow pressure rise, associated with flame propagation, is an indication that transition to detonation occurred very quickly, possibly inside the driver chamber. This is consistent with a much higher concentration of driver gas, i.e., more of the test gas is purged from the driver chamber.
Figure A.2: Experimental combustion pressure for DME-air at stoichiometric conditions, 298K. a) 0.2s driver, b) 0.5s driver

Table A.1 shows the measured peak pressure inside the gas driver chamber and at 30cm from the gas driver exit, inside the detonation tube. The measured pressure inside the chamber was above the calculated CJ pressure, 3.5MPa for stoichiometric acetylene-oxygen at standard conditions. The expected pressure rise for detonation initiation inside the gas driver chamber was 8.75MPa due to a shock reflection multiplier of 2.5. The measured pressure profile and peak value indicated that detonation initiation occurred inside the chamber only for the 0.75s driver. The pressure recorded in the tube indicated that the driver strengths of 0.2s and 0.5s resulted in a CJ detonation wave at 30cm, and a driver strength of 0.75s produced an overdriven detonation wave.
Table A.1: Combustion Pressure for stoichiometric DME-air at standard conditions varying the driver strength

<table>
<thead>
<tr>
<th>Driver (s)</th>
<th>Chamber PT</th>
<th>Tube PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>4.2</td>
<td>3.6</td>
</tr>
<tr>
<td>0.5</td>
<td>4.8</td>
<td>3.6</td>
</tr>
<tr>
<td>0.75</td>
<td>6</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Detonation Initiation Modes**

Based on the driver chamber pressure measurements, a 0.75s driver produces a detonation wave in the chamber. The detonation wave enters the detonation tube and is transmitted into the test mixture. For the 0.2s and 0.5s driver the pressure recorded at 30cm in the detonation tube indicated two modes of detonation initiation, prompt versus delayed, dependent on the volume of driver gas used.

In the case of prompt initiation, it is assumed that the driver section and the shortened orifice plate section are filled with driver gas. Figure A.3 shows a step-by-step process of prompt detonation initiation. The loading of the driver gas mixture produces a turbulent flow within the driver chamber; the ignition of the mixture then forms a turbulent flame. The acceleration of the turbulent flame causes a shockwave to form ahead of the flame and induces a flow in the unreacted gases. The flow of the gases forms a jet as they exit the driver chamber and enter into the detonation tube. When the turbulent flame and shock wave reach the jet, a flame jet is formed and a hot jet exits the driver chamber. Prompt detonation initiation then occurs in two possible modes, hot jet initiation or shock reflection initiation. In hot jet initiation the high temperature flame directly initiates a detonation, at a point source, and a spherical detonation propagates.
radially outwards. In shock reflection initiation the shock wave preceding the flame reflects off the sidewall of the tube, which causes a high pressure, which initiates a detonation. The result of either point source detonation is steady detonation propagation within the tube with strong shock oscillations behind it due to the detonation originating via a spherical detonation and the resulting transverse shockwaves associated with shock reflection.
Figure A.3: Prompt detonation initiation of the driver gas. 1: Flame acceleration, 2: Flame jet, 3: Hot jet initiation, 4: Shock reflection detonation, 5: Detonation Propagation

In the case of delayed initiation, it is assumed that the driver chamber and the shortened orifice plate section contain a mixture of the driver gas and the test gas. Figure A.4 shows a step-by-step process of delayed detonation initiation. The initial acceleration and propagation of the flame
occurs similarly to the case of prompt detonation initiation, until the flame jet is formed. When the flame jet exits the driver chamber hot jet or shock reflection initiation does not occur since the mixture of driver gas with test gas is less sensitive to detonation than pure driver gas. Since detonation does not occur initially the shock wave quickly decouples from the flame. The flame accelerates through the shortened obstacle section until it forms a new shock wave. This shock wave initiates detonation by reflecting off of an orifice plate obstacle resulting in a high pressure. The result of the point source detonation is steady detonation propagation within the tube with shock oscillations behind and shockwaves due to flame acceleration ahead of it.
Figure A.4: Delayed Detonation initiation of the driver gas. 1: Flame acceleration, 2: Flame jet, 3: Flame shock decoupling, 4: Detonation initiation on an obstacle, 5: Detonation Propagation

An example of a prompt and a delayed detonation initiation pressure trace are shown in Figure A.5. For delayed initiation the pressure rises slowly, this is due to a series of decoupled shock
waves reaching the pressure transducer early on, the sharp rise in the pressure is due to the eventual arrival of the detonation wave front, as is illustrated in Figure A.4, parts 4 and 5. For prompt initiation a sharp rise in the pressure indicates the detonation wave front passes by, without being preceded by any shock waves. Smaller peaks behind the initial pressure rise are also evident; these are attributed to the strong transverse shock waves following the detonation.

![Figure A.5: Pressure trace at 12in from driver exit varying the driver strength to produce 1: Delayed, 2: Prompt; detonation initiation in 14% methanol-air at standard conditions](image)

Figure A.5: Pressure trace at 12in from driver exit varying the driver strength to produce 1: Delayed, 2: Prompt; detonation initiation in 14% methanol-air at standard conditions
Appendix B

Additional Results

This appendix provides detailed results from experiments summarized in Chapter 6.

Methanol-Air Mixtures

Orifice Plate Obstacle Section

Figure B.1 shows the measured flame and detonation velocities along the length of the tube in different methanol-air mixtures at an initial temperature of 303K. Initial flame velocities approximately 1m from the spark plug were on the order of 800m/s for all mixtures. For mixtures that achieved detonation, acceleration within the orifice plate obstacle section varied depending on mixture composition, richer mixtures exhibited higher rates of acceleration. Final velocities within the orifice plate section ranged between 1200m/s and 1600m/s. Once a detonation left the obstacle section, at a distance of 3.1m, it quickly accelerated to a velocity on the order of 1800m/s. For mixtures outside the detonation limits flame velocities in the orifice plate section reached approximately 1000m/s, upon exiting the obstacle section flame deceleration occurred and constant velocities were achieved on the order of 400m/s. Figure B.2 shows flame/detonation velocities in the detonation tube for mixtures at 373K, characteristics of acceleration were similar to those observed in the tests conducted at 303K, except some tests which failed were able to achieve velocities on the order of 1200m/s before decelerating.
Figure B.1: Flame/Detonation velocity along the detonation tube for methanol-air at 303K using the orifice plate obstacle section

Figure B.2: Flame/Detonation velocity along the detonation tube for methanol-air at 373K using the orifice plate obstacle section
The average flame/detonation velocity measured at the end of the tube as a function of the concentration of methanol at 303K; along with the theoretical CJ velocities are shown in Figure B.3. The detonation limits were determined to be 12.3% and 19.4% methanol based on the sharp drop off in velocity beyond those concentrations, which indicates a failure to detonate. Figure B.3 shows the measured detonation velocities agree very well with the theoretical CJ velocities.

![Graph showing detonation limits for methanol-air at 303K using the orifice plate obstacle section](image)

**Figure B.3:** Detonation limits for methanol-air at 303K using the orifice plate obstacle section

The detonation velocities measured for all methanol concentrations were slightly lower at 373K, as shown in Figure B.4, compared to those measured at 303K. The detonation limits were found to be narrower at the higher temperature. The lean detonability limit decreased from 12.3% to 11.5% methanol, while the rich limit decreased from 19.4% to 16.3% methanol at 373K. Detonations did occur beyond the upper limit in isolated tests, however the results were not reproducible and therefore 16.3% was determined to be the limit for the tube at 373K.
Gas Driver

Figure B.5 shows the measured flame and detonation velocities along the length of the tube in different methanol-air mixtures at an initial temperature of 310K. For mixtures within the detonability limits, the initial flame velocities, near the exit of the gas driver, ranged from 1300m/s to 1700m/s. Within 2m of the gas driver flame velocities approached 1800m/s and remained nearly constant along the rest of the tube. For mixtures outside the detonation limits two modes of detonation failure existed, sustained detonation failure and failure to transition to detonation. In the case of sustained detonation failure, initial flame velocities near the exit of the gas driver ranged from 1300m/s to 1700m/s and within 1m detonation velocities were achieved. At approximately 2.5m along the tube flame deceleration began and continued until steady deflagration flame velocities were achieved. For mixtures experiencing a failure to transition to
detonation, initial flame velocities ranged from 600m/s to 1000m/s, flame deceleration occurred immediately until approximately constant velocities were achieved. The final velocities of the two failure modes were similar and ranged from 200m/s to 800m/s, well below detonation velocities. Figure B.6 shows flame velocities in the detonation tube for mixtures at 373K, characteristics of acceleration are similar to those observed in the tests conducted at 310K, except initial flame velocities can be observed as high as 2000m/s.

![Graph showing flame velocities in the detonation tube for mixtures at 373K](image)

Figure B.5: Flame/Detonation velocity along the detonation tube for methanol-air at 310K using the 0.2s gas driver
Figure B.6: Flame/Detonation velocity along the detonation tube for methanol-air at 373K using the 0.2s gas driver

**Ethanol-Air Mixtures**

**Orifice Plate Obstacle Section**

Figure B.7 shows the measured flame and detonation velocity along the length of the tube in different ethanol-air mixtures at an initial temperature of 303K. Initial flame velocities approximately 1.75m from the spark plug were on the order of 900m/s for all mixtures. For mixtures that achieved detonation, acceleration within the orifice plate obstacle section varied depending on mixture composition, the highest acceleration being evident in mixtures slightly richer than stoichiometric (6.54% ethanol). Final velocities within the orifice plate section approached 1400m/s. Once a detonation left the obstacle section, at a distance of 3.1m, it quickly
accelerated to a velocity on the order of 1800m/s. For mixtures outside the detonation limits flame velocities in the orifice plate section were not able to achieve velocities above 1000m/s, upon exiting the obstacle section constant velocities were achieved on the order of 400m/s. Figure B.8 shows flame/detonation velocities in the detonation tube for mixtures at 373K, characteristics of acceleration were similar to those observed in the tests conducted at 303K, except initial velocities varied between 700m/s and 1000m/s and some tests which failed were able to achieve velocities on the order of 1400m/s before decelerating.

![Flame/Detonation velocity along the detonation tube for ethanol-air at 303K using the orifice plate obstacle section](image)

**Figure B.7: Flame/Detonation velocity along the detonation tube for ethanol-air at 303K using the orifice plate obstacle section**
Figure B.8: Flame/Detonation velocity along the detonation tube for ethanol-air at 373K using the orifice plate obstacle section.

The average flame/detonation velocity measured at the end of the tube as a function of the concentration of ethanol at 303K, along with the theoretical CJ velocity, is shown in Figure B.9. The lower detonation limit was determined to be 6.0% ethanol based on the sharp drop off in velocities beyond this concentration, which indicates a failure to detonate. At 303K it is not possible to produce higher concentration mixtures of ethanol than approximately 8.5% at 1 atm. Since 8.5% ethanol is within the detonability limits at 303K, ethanol does not have a traditional rich detonability limit at this temperature. Further tests of ethanol-air mixtures at slightly higher temperatures (310K) were performed and are reported on in section 5.3.1. Figure B.9 shows the measured detonation velocities agree very well with the theoretical CJ velocities.
The detonation velocities measured for all ethanol concentrations were slightly lower at 373K, as shown in Figure B.10, compared to those measured at 303K. The detonation limits were also found to be narrower at the higher temperature. For tests at 373K the lean limit was determined to be 6.5%, which is an increased from 6.0% ethanol at 303K, the rich limit was determined to be 8.5% ethanol. Detonations did occur beyond the lean limit in isolated tests, however the results were not reproducible and therefore 6.5% was determined to be the limit for the tube at 373K.
Figure B.10: Detonation limits for ethanol-air at 373K using the orifice plate obstacle section

Gas Driver

Figure B.11 shows the measured flame and detonation velocities along the length of the tube in different ethanol-air mixtures at an initial temperature of 310K. For mixtures within the detonability limits, the initial flame velocities, near the exit of the gas driver, ranged from 1200m/s to 1600m/s. Within 2m of the gas driver flame velocities approached 1800m/s, and remained nearly constant along the rest of the tube. For mixtures outside the detonation limits two modes of detonation failure existed, sustained detonation failure and failure to transition to detonation. In the case of sustained detonation failure, initial flame velocities near the exit of the gas driver were on the order of 1400m/s, within 1m detonation velocities were achieved. At approximately 2.5m along the tube flame deceleration began and continued until steady deflagration flame velocities were achieved. For mixtures experiencing a failure to transition to
detonation, initial flame velocities were on the order of 1200m/s flame deceleration occurred immediately until approximately constant velocities were achieved. The final velocities of the two failure modes were similar and on the order of 400m/s, well below detonation velocities. Figure B.8.12 shows flame velocity in the detonation tube for mixtures at 373K, characteristics of acceleration are similar to those observed in the tests conducted at 310K, except only one failure mode was present, failure to transition to detonation.

![Flame/Detonation velocity along the detonation tube for ethanol-air at 310K using the 0.2s gas driver](image)

Figure B.11: Flame/Detonation velocity along the detonation tube for ethanol-air at 310K using the 0.2s gas driver
Figure B.8.12: Flame/Detonation velocity along the detonation tube for ethanol-air at 373K using the 0.2s gas driver
Appendix C

Uncertainty Analysis

The sensitivity of the strain-gauge pressure transducers were determined using a two-point calibration. The pressure transducers were connected directly to a vacuum pump and the transducer voltage reading was recorded. This value is assumed to correspond to 0kPa, the vacuum pump specifications indicates 1.5x10\(^{-3}\)Torr. The pressure transducer was then exposed to atmospheric pressure and the voltage was recorded. The atmospheric pressure in the room was assumed to be comparable to the pressure reported by the weather network for Kingston at that time. The accuracy of the pressure transducers used for measuring fill pressure in the mixing chamber and in the detonation tube were 0.25% full scale, this equated to 1.034kPa and 0.26kPa for the mixing chamber and the detonation tube respectively. The mixture composition reported within this study is dependent on the pressure readings in the mixing chamber and is based on the method of partial pressures, from equation B.1.

\[
[fuel] = \frac{P_f - P_i}{P_f} \tag{B.1}
\]

Where \([fuel]\) is the concentration of fuel, \(P_f\) is the fuel pressure, \(P_i\) is the initial pressure after vacuum and \(P_F\) is the final pressure. The final pressure in the mixing chamber was nominally 310kPa and the maximum pressure after vacuum was 0.25kPa, therefore for an example mixture of 6.5% fuel, 20.4kPa of fuel would need to be added. The total uncertainty associated with the mixture composition is given in equation B.2.

\[
DT = \left(\frac{DP_f + DP_i}{P_f + P_i}\right)^2 + \frac{DP_F}{P_F} \tag{B.2}
\]
Where DT is the total uncertainty, and DP is the uncertainty based of the pressure measurement. The uncertainty associated with each pressure measurement is 1.034kPa; for the example of a 6.5% fuel concentration mixture the uncertainty is shown in equations B.3-4.

\[
DT = \left( \frac{1.034 + 1.034}{20.4 + 25} \right) + \frac{1.034}{310} \tag{B.3}
\]

\[
DR = 0.10kPa \tag{B.4}
\]

Based on the total pressure being 310kPa the example mixture composition has an uncertainty of 0.033%.

The final fill pressure of the detonation tube was dependent on the atmospheric pressure, since the tube was overfilled and allowed to vent. Since the atmospheric pressure varied day to day by much more than the uncertainty associated with the pressure transducer the filled pressure in the detonation tube has an uncertainty of approximately 2kPa.

The uncertainty associated with velocity measurements are based on the measurement of flame time of arrival. The largest source of uncertainty came from manually determining the time for the voltage drop from the signal recorded on the data acquisition system. Figure C.1 shows an example voltage output recorded by LabVIEW, each the voltage drop corresponds to the flame propagating past an ionization probe. A standard method was developed to ensure consistency when measuring the instantaneous flame time of arrival however repetition in the measurement of a number of time of arrival signals was shown to produce an uncertainty of approximately ±0.11% in the final calculated velocity of approximately 1800m/s.
Figure C.1: Voltage drop associated with flame time of arrival for measuring flame velocity, in 6.5% DME at 298K using a 0.2s gas driver

The detonation limits were determined by the presence of two consecutive tests that failed to detonate, and the presence of two consecutive tests that detonated at the next composition interval. The unsteady nature of a detonation leads to inherent uncertainty associated with the limits of detonability, in many instances detonations were evident beyond the limits of detonability, but were not reproducible; therefore it was the intention to state the limits, as limits for repeatable detonability for the apparatus. If the uncertainty associated with the mixture composition is taken into account the uncertainty associated with the limits of detonability is ±0.11% in addition to size of the composition interval approximately 0.5%, leading to a total uncertainty of approximately ±0.61%.
The measurement of cell widths contained significant uncertainty; the uncertainty is due to the cells varying in size, the appearance of substantial substructure and the interpretation of dominant cells. The uncertainty of cell width measurements shown in Chapter 5 are based on the standard deviation of the sample of cells measured for a particular foil. If no error bars appeared on a cell width measurement then the sample of cells measured was below 3, therefore the standard deviation was not a useful measurement.
Appendix D

Apparatus Photos
Figure D.1: Detonation tube
Figure D.2: Gas driver chamber, with spark ignition at front and input line underneath
Figure D.3: Insulated mixing chamber
Figure D.4: Ceramic bead heating pad
References


[9] Ciccarelli G., Combustion Dynamics, MECH 832 Class Note, Department Mechanical and Material Engineering, Queen’s University, 2011

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[28] J. L. CARD, flame acceleration and Deflagration-to-detonation Transition studies in Fuel – Air Mixtures at Elevated Temperatures and Pressures, Queen’s University, July 2004


