EXPERIMENTAL SHOCK TUBE STUDY OF IGNITION PROMOTION FOR METHANE UNDER ENGINE RELEVANT CONDITIONS

BY

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ABSTRACT

The ignition delay time of methane and various methane-additives mixed homogeneously with air has been measured experimentally using a reflected shock technique for pressures from 16 to 40 atm and temperatures from 950 to 1400K.

A non-constant-specific-heat model has been developed for calculating initial experimental conditions. A good agreement has been found between the model and the experimental results.

The ignition delay time measured in the current study has been found to depend strongly on temperature and moderately on pressure, and is significantly different from that reported by previous workers whose experiments have been conducted at lower pressures. Empirical equations correlating the ignition delay time with the initial temperature, pressure and fuel concentration have been obtained based on the experimental results.

Hydrogen and DME (dimethyl ether) have been investigated for their efficiencies as ignition promoters for methane under engine relevant conditions. A prominent reduction of the ignition delay has been found for methane with 35% hydrogen added. With 15% hydrogen addition, the promotion effect is mainly evident at low pressures. DME has been found to cause moderate reduction on the ignition delay of methane.

Computational results using detailed reaction mechanisms have shown disagreements with the current experimental measurements. Further tuning of the mechanisms has been suggested for high-pressure methane ignitions.

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NOMENCLATURE

- C_p Specific heat at constant pressure, kJ/kmol.K
- e Total energy, J/kmol
- Ea Activation energy, kJ
- h Enthalpy, kJ/kmol
- Ma Mach number
- P Pressure, Pa or atm
- Pr Prandtl number
- R Gas constant, kJ/kmol.K
- Re Reynolds number
- S Entropy, kJ/kmol.K
- T Température, K
- t Time, s, ms or µs
- u Velocity component in x direction
- v Velocity component in y direction
- W, U Velocity, m/s
- [Xi] Concentration of Species Xi, mol/cm³
- y Mole fraction
- γ Specific heat ratio
- μ Viscosity, kg/m.s
- v Kinematic viscosity, m²/s
- v_i Stoichiometric coefficient
- ρ Density, kg/m³
- τ Ignition Delay, μs
- Φ Equivalence ratio

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CHAPTER I

Natural-gas-fueled internal combustion engines have been undergoing a fast development in recent years. They offer an attractive combination of reduced engine emission and lower fuel cost. The wide availability of natural gas makes it an ideal alternative fuel that provides practical solutions to the increasingly restrictive emissions control requirement. A more recent step is to use natural gas (NG) in heavy-duty diesel engines. The high pressure direct injection technique (HPDI) developed by Westport Innovations Inc. (WII) has made it possible to achieve a significant reduction of the NO_x and particulate emissions by running the engine on natural gas while maintaining the performance and efficiency of a conventional diesel engine.

A major problem associated with the natural gas direct injection system comes from the poor compression ignitability of natural gas, or, more precisely, of methane, which is a major component of natural gas. So far the HPDI system has to use a pilot diesel fuel to ignite natural gas. This impairs a further reduction of engine emissions and increases the system complexity as well as the cost.

Early research on methane ignition indicates that the ignition delay of methane can be reduced by blending it with some other active gaseous fuels. Experiments conducted by Oppenheim and Chan [1], Frenklach and Bornside [2], Lifshitz et al. [3, 4] have all shown significant promotion effects on the ignition of methane by mixing additives such as hydrogen and propane at low pressures. This provides the possibility to run a diesel engine on natural gas enriched by ignition promoters eliminating the dependence on the pilot fuel or other extra ignition sources.

Despite many previous efforts to measure the ignition delay of methane at low pressures and high temperatures, the ignition delay time at engine-like conditions, (which incorporate high pressures and low temperatures), remains uncertain. This was the incentive to carry out the current experimental studies on measuring the ignition delay of methane and methane-additives under conditions that are directly engine-relevant, so as to find out the most suitable ignition promoter for NG engine applications.

For a homogeneously charged spark ignition NG engine, on the other hand, we need to prevent autoignition, which may lead to a problem called engine knock. This also requires comprehensive information on the variation of the ignition delay for methane

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with respect to different pressures and temperatures as well as fuel concentrations. Especially, we need to find the limit of strong ignition, which is an explosive combustion at a relatively high temperature generating rapid pressure increase that may damage the engine.

A shock tube, which is an efficient and reliable instrument for measuring ignition delay, has been used in the current study. The merits of using a shock tube instead of other combustion devices come from its close-to instantaneous pressure and temperature rises which minimize the effects of heating process. The constant initial conditions obtained behind the reflected shock wave make it easy to detect the variation of pressure or temperature caused by an ignition. Another merit of using a shock tube is that the experimental conditions in the shock tube can be calculated with a good reliability by using the measured shock velocity. The method provides a practical solution to the problem of accurately measuring the temperature within a very short residence time.

CHAPTER II

2.1 Introduction

Shock wave research and shock tube development have been receiving sustained interest in various scientific disciplines for more than half a century. Besides use in studying supersonic and hypersonic aerodynamic problems, this instrument also provides a cheap, reliable method to obtain instant high-enthalpy reservoirs for studies of high-temperature chemical reaction phenomena such as combustion.

When it comes to measuring ignition delay time, the shock tube is one of the most widely used instrument. The merit of an 'instantaneous' rise of pressure and temperature minimizes the effects of heating process as inherent to other instruments and thus makes the experimental results more accurate.

Measuring the rapid temperature change in combustion devices such as internal combustion engines remains a difficult engineering problem. In a shock tube experiment, the temperature can be calculated from the shock propagation velocity, which can be measured with high accuracy. The shock tube is also capable of achieving temperatures and pressures similar to those found in internal combustion engines, (typically from 900 to 1200 K and 20 to 70 atm).

In the study described in this thesis, a shock tube is used to investigate ignition delay times for various gaseous fuel-air mixtures at pressures from 16 to 40 atm and temperatures from 950 to 1400 K. It is necessary for us to understand the nature of the shock tube working under such conditions so that the uncertainty of the experimental conditions can be found and minimized. The primary purpose of this chapter is to discuss shock tube modeling and problems associated with its application as well as to compare the model with the experimental results.

2.2 Background

2.2.1 Shock Tube

A schematic of the shock tube and its working principle is shown is figure 2.1.

A shock tube is a device in which a high-pressure driver gas and a low-pressure driven gas are separated by one or two diaphragms. When the diaphragms burst, a shock wave is

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generated. The shock wave, which is a high-enthalpy compression wave with its local Mach number higher than one, travels downstream into the driven gas causing a pressure and temperature jump across the shock front. A contact surface that separates the driver gas from the driven gas follows the incident shock wave and travels at a lower speed. At the same time, a rarefaction fan composed of a series of expansion waves fans out into the upstream driver gas.



Fig. 2.1 Shock tube working principle. (a) Initial state: the high-pressure driver gas is separated from the low-pressure driven gas by the diaphragm. (b) An incident shock wave forms right after the bursting of the diaphragm. (c) The shock wave reflects from the end of the driven section (d) The shock wave passes through the contact surface.

The shock wave, upon reflection from the end wall of the shock tube, interacts with the driven gas set to move by the incident shock and brings it to a stop. The static high-temperature and high-pressure reservoir generated behind the reflected shock wave can be readily used for studies of various purposes.

Under ideal conditions as we will explain later, the pressure and temperature in the experimental area can be kept constant until the arrival of the reflected rarefaction fan.

2.2.2 Normal Shock Relations

A normal shock is a shock wave with its front normal to the direction in which it travels. We consider a normal shock wave propagating into an undisturbed fluid with velocity $U_{1.}$. The pressure, density, and temperature of the fluid ahead of the shock are P_a , ρ_a , and T_a , and those behind the shock are P_b , ρ_b , T_b . The velocity behind the shock wave is $U_{2.}$ By switching from laboratory coordinates to shock fixed coordinates, we bring the wave to rest as illustrated in figure 2.2. This stationary shock sees the undisturbed gas approaching with velocity U_a and the gas behind it travels at a velocity U_b , where $U_a=U_1$ and $U_b=U_1-U_2$.



Fig. 2.2 Moving shock and equivalent stationary normal shock

Applying a control volume analysis across the shock and neglecting viscous effects and body forces we can write one-dimensional continuity, momentum and energy equations as:

$$\rho_a U_a = \rho_b U_b \tag{2.1}$$

$$P_{a} + \rho_{a} U_{a}^{2} = P_{b} + \rho_{b} U_{b}^{2}$$
(2.2)

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$$h_a + \frac{1}{2}U_a^2 = h_b + \frac{1}{2}U_b^2.$$
(2.3)

With the ideal gas assumption, we can also have the equation of state

$$\frac{P}{\rho} = RT.$$
(2.4)

For given initial conditions ahead of the shock front, we can solve Eqs. (2.1) - (2.4) to get P_b, ρ_b , T_b and U_b. For a constant specific heat ratio $\gamma = c_p/c_v$, the solution is most conveniently written in terms of the Mach numbers.

$$Ma_{b}^{2} = \frac{1 + \frac{\gamma - 1}{2}Ma_{a}^{2}}{\gamma Ma_{a}^{2} - \frac{\gamma - 1}{2}}$$
(2.5)

$$\frac{\rho_b}{\rho_a} = \frac{(\gamma + 1)Ma_a^2}{a + (\gamma - 1)Ma_a^2}$$
(2.6)

$$\frac{P_b}{P_a} = 1 + \frac{2\gamma}{\gamma + 1} (Ma_a^2 - 1)$$
(2.7)

$$\frac{T_b}{T_a} = 1 + \frac{2(\gamma - 1)}{(\gamma + 1)^2} \left(\frac{1 + \gamma M a_a^2}{M a_a^2}\right) (M a_a^2 - 1)$$
(2.8)

Here Ma_a and Ma_b are local Mach numbers ahead and behind the shock wave. The Mach number is defined as Ma = u/a and a is the local sound speed given by

$$a = \sqrt{\gamma RT}.$$
(2.9)

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2.2.3 Pressure Distribution in Shock Tube and Tailored Interface

In laboratory coordinates the incident shock travels at a constant velocity U_1 . The corresponding Mach number is Ma₁. The Mach number and pressure of the flow behind the shock wave according to Eqs (2.5) and (2.6) - denoted as U_2 and P_2 - are constant. Since no velocity jump is allowed across the contact surface to satisfy continuity, U_2 equals the velocity U_3 with which the contact surface moves. Also, there is no pressure variation across the contact surface so that $P_2=P_3$ as shown in figure 2.1 (c). After the shock wave reflects from the end wall, it travels first into the driven gas and then crosses the contact surface entering the driver gas. The pressure of the driven gas is boosted by the reflected shock to P_5 , which is the desired experimental pressure. The pressure behind the reflected shock in the driver gas is denoted as P_6 as illustrated in figure 2.1 (d).

Hurle and Gayden [30] discussed three possible situations that may occur after the reflected shock crosses the contact surface depending on the difference between P_5 and P_6 . They are under-tailoring, over-tailoring, and tailoring.

1) Under-tailoring

When P_5 of the driven gas is lower than P_6 of the driver gas, we have under-tailoring. As shown in figure 2.3 (a), the pressure jump across the contact surface will form a secondary shock wave, which travels back into the driven gas and further increases its pressure and temperature. The contact surface, due to this favored pressure gradient, will further move ahead until the pressure of P_5 adjusts enough to balance P_6 .

2) Over-tailoring

If P_5 is higher than P_6 , we will have over-tailoring. In such a case, an expansion wave will be generated from the contact surface and travels towards the end of the driven section. Meanwhile, the contact surface will bounce back when the driven gas expands to reduce P_5 .

3) Tailored-interface

When P_5 exactly equals P_6 , we have a tailored-interface condition. When such a condition is obtained, only Mach waves are generated when the shock passes the contact surface.

The pressure and temperature in the experimental area will be kept constant until the arrival of the reflected rarefaction fan. The experimental time can thus be significantly increased.



Fig. 2.3 Three possible situations after the reflected shock wave travels across the contact surface: (a) under-tailoring; (b) over-tailoring; (c) tailored interface.

If we assume the same composition for both driver and driven gas with constant specific heat ratio γ , from equation (2.7) we can calculate the pressure behind the shock wave. In a real experiment, the initial temperatures for the driver and the driven gases are usually the same (T₁=T₄). The expansion of the driver gas reduces its temperature from T₄ to T₃, while the incident shock wave raises the driven gas temperature from T₁ to T₂. Since the local sound speed is proportional to the square root of the temperature if R and γ are constant, with the condition T₂>>T₃, we must have a₂>a₃. Thus it is reasonable to get Ma₅<Ma₆ for the same reflected shock velocity. (In most cases, the reflected shock velocity does vary across the contact surface. However, the change compared with the

change of sound speed is small, so we can still get a higher Mach number for the shock wave traveling in the driver gas than in the driven gas). Since initially we have $P_3 = P_2$, after the passage of the shock, there will be $P_6 > P_5$.

The above analysis shows that we will always end up with an under-tailored condition if the same gas is used in both the driver and the driven sections. In order to achieve a balance between P_5 and P_6 , it is necessary to increase the sound speed on the driver gas side so that we can reduce the Mach number properly for the equivalent end pressure. In the current experiment, we mix helium, whose gas constant and specific heat ratio is much higher, with air to get the desired sound speed. Calculations are needed to decide the proportion of the two gases, as a function of different incident shock speed, in order to achieve a tailored interface.

2.3 Experimental Apparatus

A schematic of the experimental apparatus is shown in figure 2.4. The bore of the shock tube used in the current study is 0.059 m. The lengths of the driver and driven section are 3.18 meters and 4.25 meters respectively. The device has been designed and tested to work under a maximum pressure of 200 atm [5], which is equivalent to the pressure achieved when a stoichiometric methane-air mixture with an initial pressure of 95 atm burns to completion at constant volume (see appendix E for details).



Fig. 2.4 Schematic of the shock tube and attached equipment

The initial pressure in the driver section is measured with an Eclipse static pressure transducer, and that in the driven section is measured by an Auto Tran vacuum sensor. A series of five PCB 112B11 piezoelectric pressure transducers with a minimum response time of 3 microseconds are flush mounted along the driven section of the shock tube. They are used to measure the passage time of the shock wave and the associated pressure rise. The incident shock velocity is calculated from the measured time for the shock passing each sensor and the distance between the sensors.

A double diaphragm technique [5] is used to guarantee the diaphragms burst at the desired pressure as shown in figure 2.5. An intermediate flange is placed between the driver and driven sections. A piece of diaphragm is inserted between the intermediate plate and the driver and driven sections respectively. When charging the driver section, first open the intermediate valve and charge the driver and small chamber simultaneously to a pressure P_{gap} (P_{gap} < P_4). Then the intermediate valve is closed and the driver pressure is further raised to P_4 . To trig a shock, the release valve is opened and the pressure in the small chamber drops quickly. The increased pressure difference causes the diaphragms to burst consecutively.



Fig. 2.5 Double diaphragms

In the current experiment, we mix helium and air in the driver section in order to achieve tailored interface conditions. Details of calculating the initial helium concentration in the driver gas with respect to different experimental conditions will be provided in the following section.

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2.4 Shock Tube Modeling

2.4.1 Ideal Model

For high temperatures it is necessary for the shock calculation model to incorporate nonconstant specific heat. The model accepts initial experimental conditions -namely P_1 , T_1 , P_4 , T_4 - to calculate the pressure and temperature behind the reflected shock. The model also predicts the concentration of helium in the driver gas for tailoring conditions. Another function of the model is to estimate the experimental time given the shock tube geometry and initial conditions.

1) Normal Shock Relations with Non-constant Specific Heat

For non-constant specific heat, the simple normal shock relations – Eqs. (2.5) to (2.8) – can no longer be used. Taking the specific heat C_p as a function of temperature, we rewrite the energy conservation (Eq (2.3)):

$$\int_{Tref}^{T_a} C_p(T) dT + U_a^2 = \int_{Tref}^{Tb} C_p(T) dT + U_b^2$$
(2.10)

or

$$U_{b} = (U_{a}^{2} + \int_{Tb}^{Ta} C_{p} T dT)^{\frac{1}{2}}$$
(2.11)

where T_{ref} is the arbitrary reference temperature usually taken to be 298K. From Eq. (2.1), we have

$$\rho_b = \frac{\rho_a U_a}{U_b}.$$
(2.12)

Using the momentum conservation equation, we can solve for P_b .

$$P_{b} = P_{a} + \rho_{a} U_{a}^{2} - \rho_{b} U_{b}^{2}.$$
(2.13)

It is not possible get a direct analytical expression for states behind the shock wave. One can iterate with guessed temperatures and solve Eqs (2.11) - (2.13) to get P_b and ρ_b behind the shock and check the result with the ideal gas law.

We abandon the specific heat ratio and Mach number here for the reason that little simplification can be obtained when assuming a non-constant specific heat.

2) Coordinates Transformation

The shock relations stated above are only valid for stationary shock wave. When doing a shock tube calculation, we need to transfer from the laboratory-fixed coordinates to the shock-fixed coordinates.

First, we look at the incident shock wave. The incident shock wave travels into a stationary driven gas. Assume this incident shock wave travels at velocity W_1 . The observer in laboratory-fixed coordinates sees the gas behind the incident shock moving at velocity U_2 as shown in figure 2.6. In shock-fixed coordinates, the shock wave sees the driven gas approach at velocity U_a and leave at U_b . So we have $U_a=W_1$, and $U_b=W_1-W_2$.



Fig. 2.6 Coordinates transformation for an incident shock wave: (a) laboratory-fixed coordinates; (b) shock-fixed coordinates.

Secondly, we look at the reflected shock. The reflected shock wave travels in a fluid with velocity U_2 caused by the incident shock (see figure 2.7). Its absolute velocity before crossing the contact surface is W_5 . The gas behind the reflected shock is at rest so that $U_5 = 0$. Upon transformation, the velocity in which the driven gas moves towards the shock front is $U_a = W_5 + U_2$. Behind the shock wave, the velocity $U_b = W_5 - 0 = W_5$.



Fig. 2.7 Coordinates transformation for a reflected shock wave: (a) laboratory-fixed coordinates; (b) shock-fixed coordinates.

A similar transformation can also be applied after the reflected shock wave crosses the contact surface, for which we change W_5 into W_6 and replace U_2 with U_3 .

3) Calculate Incident Shock Velocity from Initial Pressure Ratio

In the ideal model, we assume no momentum or energy loss due to viscous effects and also no throttling caused by the burst diaphragm. We also neglect heat transfer to the wall of the shock tube due to the very short over-all experimental time and high Reynolds number. The adiabatic inviscid expansion of the driver gas from P_4 to P_3 satisfies isentropic flow conditions. The expansion wave travels at the local sound speed and causes a small but continuous disturbance behind it. In wave-fixed coordinates, we denote the pressure and velocity change behind the wave with dU, dP and d ρ respectively as shown in figure 2.8.



Fig.2.8 Property variations across an isentropic wave in wave fixed coordinates

For a small value of dP and dU, we can assume the flow to be steady state, for which the steady flow continuity and momentum equations are

$$\rho a = (\rho + d\rho)(a + dU) \qquad (2.14)$$

$$P + \rho U^{2} = (P + dP) + (\rho + d\rho)(U + dU)^{2}.$$
 (2.15)

Rearranging and eliminating high-order terms, we get

$$\rho \, dU = -ad\,\rho \tag{2.16}$$

and

$$-dP = 2a\rho dU + a^2 d\rho.$$
^(2.17)

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Substituting Eq. (2.16) into Eq. (2.17), we obtain a simple relation between dP and dU.

$$-dP = a\rho dU. \tag{2.18}$$

For the driver gas, we can reasonably assume a constant specific heat ratio because of its low temperature so that the isentropic flow relations are

$$\frac{dP}{P} = \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \frac{2\gamma}{\gamma - 1} \frac{da}{a}$$
(2.19)

and

$$P = \frac{a^2 \rho}{\gamma}.$$
 (2.20)

Using Eqs. (2.19) and (2.20) to eliminate P in Eq. (2.18), we get an important relation that is valid for any arbitrary isentropic wave:

$$d(a + \frac{\gamma - 1}{2}U) = 0, \qquad (2.21)$$

or

$$\lambda = a + \frac{\gamma - 1}{2}U = const.$$
(2.22)

We will come back to equation (2.22) later when we discuss the method of characteristics. For now, we use equation (2.21) to derive an expression for the velocity of contact surface U₃. Integrating Eq. (2.21) from a₄ to a₃ we get

$$U_{3} = \frac{2}{\gamma - 1} (a_{4} - a_{3}).$$
(2.23)

For isentropic flow,

$$\frac{P_{3}}{P_{4}} = \left(\frac{T_{3}}{T_{4}}\right)^{\frac{\gamma}{\gamma-1}} = \left(\frac{a_{3}}{a_{4}}\right)^{\frac{2\gamma}{\gamma-1}}.$$
(2.24)

Substituting equation (2.23) into equation (2.24), we obtain an expression for U_3 in terms of the pressure ratio and the initial sound speed of the driver gas:

$$U_{3} = \left[1 - \left(\frac{P_{3}}{P_{4}}\right)^{\frac{\gamma_{drv} - 1}{2\gamma_{drv}}}\right] \frac{2a_{4}}{\gamma_{drv} - 1}.$$
(2.25)

Meanwhile, the pressure and velocity behind the incident shock wave, P_2 and U_2 , must equal P_3 and U_3 . With a given initial condition P_1 , P_4 and T_1 , T_4 , a calculation for the incident shock velocity can be accomplished with an iterative method illustrated by the flowchart in figure 2.9.



Fig. 2.9 Solution procedure for the incident shock velocity

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4) Predict Helium Concentration in Driver Gas

For different experimental conditions, the helium concentration in the driver gas should be varied in order to achieve a tailored interface. Iteration with different initial helium concentrations is necessary to find the point where the calculated P_5 equals P_6 . This procedure is shown in figure 2.10.



Fig. 2.10 Solution procedure for tailored interface conditions

5) Experimental Time

In designing a shock tube experiment, it is essential to know the maximum experimental time that can be obtained. If a tailored interface is established, the contact surface separating the driver gas from the driven gas will stay still and conditions in the experimental area can be kept constant until the arrival of the reflected rarefaction fan. For this reason, we need to calculate the velocity of the rarefaction fan to decide when its leading edge starts to enter the experimental region, whose border is defined by the location of the contact surface.

In the current model, we use the method of characteristics to accomplish this task (see appendix A for details). The method of characteristics can tell us the location of any isentropic expansion wave that composes the rarefaction fan in space at a given time. With this information, we can evaluate the velocity field as well as the pressure distribution of the driver gas at any moment of interest. We define the experimental time as the duration between the reflection of the incident shock wave from the end wall to the moment when the leading edge of the rarefaction fan reaches the contact surface.

However, the isentropic assumption is only valid before the reflected rarefaction fan makes contact with the reflected shock wave. Since the shock wave is not isentropic, we can not apply the method of characteristics further. Early research indicates that the contact will slightly weaken and deflect both of these waves. We thus assume the leading edge of the rarefaction fan will maintain its speed after it travels into the region behind the reflected shock. The assumption gives us a conservative estimate of the experimental time as shown in figure 2.11. The formula is given by

$$t_{\exp} = t_{shock} - t_{ref} + \frac{x_s - x_c}{\left(\frac{dx}{dt}\right)_{\lambda,shock}}$$
(2.26)

Here t_{shock} means the time when the rarefaction fan hits the reflected shock wave; t_{ref} represents the time when the incident shock wave reflects from the end wall; x_c is the location of the contact surface while x_s is the position of the shock front; $(dx/dt)_{\lambda.shock}$ is the velocity of the leading λ wave when it hits the reflected shock.



Fig.2.11 Model prediction of the experimental time. X axis represents length scale, y axis represents time scale.

2.4.2 Model Results and Comparisons

1) Calculated Pressure Distribution and Wave Velocities

Figure 2.12 shows a model-predicted pressure distribution in the shock tube. Each line represents a snapshot at a particular moment listed in the legend. The time is set to 0 immediately after the diaphragm bursts. The time here is in milliseconds.



Figure 2.12 Pressure distribution in the shock tube at different moments. Initial conditions: $P_1 = 1$ atm, $P_4 = 77$ atm, $T_1 = T_4 = 298$ K. Driver gas – air, driven gas – 99.9% helium.

The driver section is on the left-hand side of the plot while the driven section is on the right-hand side. For the plotted case, the driver gas is air and the driven gas is nearly pure helium (99.9%). The initial pressure ratio is 77 and the calculated incident shock velocity is 1168 m/s. The calculated temperature behind the reflected shock is 1563 K. This is the strongest shock wave given by the model for which tailored interface conditions can be established. Higher incident shock velocities can still be achieved with higher initial pressure ratios at the expense of a reduced experimental time due to the occurrence of under-tailoring.

From the graph we can see that initially the driver and driven sections with different pressures are separated by the diaphragm at about 3.18 meters measured from the end of the driver section. Shortly after the diaphragm bursts, the incident shock wave travels to the right and raises the driven gas pressure behind it. Meanwhile, a smooth expansion occurs in the driver gas backing towards the end of the driver section. It takes the incident shock wave nearly 3.8 ms to reach the end wall of the driven section and reflect. The pressure behind the reflected shock wave is slightly lower than the initial pressure of P_4 in the driver gas. The calculation ends when the reflected shock wave makes contact with the leading edge of the expansion wave at about 6.6 ms.

Figure 2.13 illustrates the variation of positions of shock wave, contact surface and a series of expansion waves versus time with the same experimental conditions mentioned above. In the x-t plot, the slope of the curve reveals the velocity. It can be seen that the shock wave travels at a constant speed to the end of the driven section, then reflects at a slower velocity due to its traveling against the flow moving in the opposite direction. After passing the contact surface the shock velocity increases a little bit but is still a constant until it hits the leading rarefaction wave. The contact surface, following the incident shock, travels to nearly 30 cm from the end wall where it is stopped by the reflected shock. For tailoring conditions, the contact surface stays there until the arrival of the rarefaction fan.



Figure 2.13 Positions of shock wave, contact surface and rarefaction fan versus time. Numbers in the legend are values of λ or β that characterize the expansion waves; x_s denotes shock positions and x_c denotes contact surface positions.

On the other hand, the leading rarefaction wave travels back to the end of the driver section at the local sound speed, then reflects and speeds up in the flow moving in the same direction. At about 6.6 ms, it hits the reflected shock. We extend the line from this point to the contact surface in order to estimate the experimental time. The final experimental time calculated in this way is 3.8 ms.

2) Comparisons with Experimental Results

Passage of an incident shock wave is recorded by the pressure transducer sampling at a rate of 166.7 KHz. The distance of each sensor measured from the exit of the driver section is plotted with the time when the incident shock is recorded. The slope of a linear fit to the measurements gives the incident shock velocity as shown in figure 2.14. It is encouraging to find that for all the experiments, the measured incident shock velocities are constant (the coefficient of determination, r^2 , for the least square fit by a linear correlation is always higher than 0.995). This is very important to both the shock calculation and the establishment of desired experimental conditions.



Fig. 2.14 Measured incident shock displacement versus time. The slope shows the incident shock velocity. Solid line: linear curve fit for the measurements. Symbol: measured shock passage time at each sensor. r^2 for this case is 0.9999.

Figure 2.15 shows the calculated incident shock velocity versus measured incident shock velocity with the same initial pressure ratio and helium concentration.



Fig. 2.15 Comparison of measured and calculated shock velocities for the same initial pressure ratio. Solid line: calculated velocities. Symbols: measurements. Dotted line: least square fit of measurements.
It can be seen that for all these cases the results from the model slightly over-predict the incident shock velocity. The reason for the lower value of the experimental incident shock velocity is that in the model, we assume no loss at the driver section; the expansion from P_4 to P_3 is isentropic. However, in reality, the inner diameter of the burst diaphragm is always smaller than the inner diameter of the tube, which causes a significant throttling loss when a high-speed flow passes through. Also there are losses due to viscous effects along the whole driver section. The least square fit of the measurements shows that the difference caused by the loss increases with an increasing initial pressure ratio as well as with an increasing incident shock velocity.

Figure 2.16 compares the reflected shock velocity obtained from both experiments and the model for the same incident shock velocity.



Fig. 2.16 Comparison of measured and calculated reflected shock velocities for the same incident shock velocity. Solid line: calculated velocity. Symbols: measured velocity. Dashed line: least square fit of measurements.

We find that the reflected shock velocity predicted by the model is slightly lower than the measurements. The difference increases with increasing incident shock velocity.

The disagreement could be mainly attributed to the attenuation of the flow velocity behind the incident shock that increases the reflected shock velocity in the laboratoryfixed coordinates as well as to the increasing error of the measured reflected shock velocity.

Finally, we checked the calculated experimental time using measurements for the same initial pressure ratio and helium concentration. The calculated experimental time is slightly shorter than the measurements, which is due to the 'conservative' estimation explained above.



Fig. 2.17 Comparison of measured and calculated experimental time.

2.4.3 Modified Model

In the modified model, which is currently being used for experimental calculations, we input the measured incident shock velocity and calculate conditions behind the reflected shock accordingly. The measurement of the incident shock velocity, as we will show later, can be quite accurate.

Modifications have been made to the conservation equations to take into account the throttling loss at the exit of the driver section. Variations in driver gas properties brought about by throttling can cause corresponding changes in tailoring conditions as well as the calculated experimental time.

First, we make an assumption that flow out of the driver exit is in steady state. This is close to experimental observation in which we find the pressure at the first sensor 0.5 meter downstream of the diaphragm is a constant until the arrival of the rarefaction fan. Second, we assume the expansion ahead of the broken diaphragm in the driver section is still smooth and isentropic so that the method of characteristics can be applied within this area. We consider a control volume involving the flow ahead of and behind the diaphragm (see figure 2.18).



Fig. 2.18 Control volume analysis for the throttling loss at the exit of the driver section. We assume the flow property variation across the diaphragm occurs within a very short distance so that the total length of this control volume can be neglected when compared with the driver and driven section lengths. The areas of the inflow and outflow for the control volume are the same, so mass conservation remains unchanged from Eq. (2.1)

$$U_a \rho_a = U_b \rho_b \tag{2.27}$$

Also, we assume the process is adiabatic and no work has been done by or to the control volume. The steady flow energy equation remains the same as Eq. (2.3).

$$h_a + \frac{1}{2}U_a^2 = h_b + \frac{1}{2}U_b^2.$$
(2.28)

For momentum conservation, we need to take into consideration the head loss caused by throttling, for which we introduce a loss coefficient K and assume the loss is proportional to the kinetic energy of the flow downstream so that we have

$$P_{a} + \rho_{a} U_{a}^{2} = P_{b} + \left(1 + \frac{1}{2}K\right) \rho_{b} U_{b}^{2}.$$
(2.29)

We also know that the upstream flow satisfies isentropic relations:

$$\frac{P_a}{P_4} = \left(\frac{T_a}{T_4}\right)^{\frac{\gamma}{\gamma-1}} = \left(\frac{\rho_a}{\rho_4}\right)^{\gamma}.$$
(2.30)

The incident shock velocity can be obtained from measurements. Hence, the flow properties behind the incident shock, i.e., Ub, Pb are known. Recalling the discussion of the isentropic expansion in the previous section, we know that the velocity at any point can be related with the pressure ratio so that

$$U_{a} = \frac{2a_{4}}{\gamma - 1} \left[1 - \left(\frac{P_{a}}{P_{4}} \right)^{\frac{\gamma - 1}{2\gamma}} \right].$$
(2.31)

Replacing the pressure ratio with the temperature ratio by using Eq. (2.30), we rewrite Eq. (2.31) as

$$U_{a} = \frac{2a_{4}}{\gamma - 1} \left[1 - \left(\frac{T_{a}}{T_{4}}\right)^{\frac{1}{2}} \right].$$
 (2.32)

Substituting Eq. (2.30) and Eq. (2.32) into the continuity equation and applying the ideal gas law, we obtain an expression for down stream temperature

$$T_{b} = \frac{U_{b}P_{b}(\gamma - 1)}{2a_{4}\rho_{4}R} \left[1 - \left(\frac{T_{a}}{T_{4}}\right)^{\frac{1}{2}}\right]^{-1} \left(\frac{T_{a}}{T_{4}}\right)^{\frac{-1}{\gamma - 1}}.$$
(2.33)

Here, R is the gas constant of driver gas. Substituting Eqs. (2.32) and (2.33) into Eq. (2.28) and assuming constant specific heat, we get

$$c_{p}T_{4}x + \frac{2a_{4}^{2}}{(\gamma-1)^{2}} \left[1 - x^{\frac{1}{2}}\right]^{2} - c_{p}\frac{U_{b}P_{b}(\gamma-1)}{2a_{4}\rho_{4}R} \left[x^{\frac{1}{\gamma-1}} - x^{\frac{\gamma+1}{2(\gamma-1)}}\right]^{-1} - \frac{1}{2}U_{b}^{2} = 0 \qquad (2.34)$$

where x is the temperature ratio $x=(T_a/T_4)$. Here the only unknown is x, for which we can solve by iteration so that the value of T_a can be found. Once T_a is known, other properties can be solved easily with isentropic relations and conservation equations from (2.27) to (2.29).

Finally, we solve the momentum equation for the loss coefficient K. The calculated K remains constant as long as the flow across the diaphragm is steady. This is true until the arrival of the reflected rarefaction fan. The velocity of the leading edge of the rarefaction fan after leaving the control volume above can be obtained by calculating the velocity of a sound wave traveling in the flow of driver gas moving at the constant velocity U_3 . We apply the method of characteristics up to the exit of the driver section. The model predicts the total experimental time, as illustrated in figure 2.19.



Fig. 2.19 Estimation of the experimental time using the modified model

It is worthwhile to point out that the value of K calculated in this way represents the overall non-isentropic effect on the driver gas including friction and throttling losses. It depends strongly on the burst condition of the diaphragm, which may vary with different designs, materials and machining accuracy. For the current experiment the value of K is found mostly between 0.2 to 1 and has an average of 0.4.

The initial helium concentration in the driver gas and the incident shock velocity predicted by the modified model for tailoring conditions are compared with the experimental results for the same initial pressure ratio in figures 2.20 and 2.21.



Fig.2.20 Model prediction of the helium fraction in the driver gas for tailoring conditions with the given initial pressure ratio. Solid line: model with throttling effects (K=0.4). Dotted line: model without throttling effects (K=0). Symbols: experiments in which tailoring conditions have been achieved.



Fig.2.21 Model prediction of the incident shock velocity for the given initial pressure ratio. Solid line: model with throttling effects (K=0.4). Dotted line: model without throttling effects (K=0). Symbols: measurements.

It can be seen that by taking into consideration the throttling effects, the agreement between the model and the experimental measurements has been improved. The procedure for applying the modified model can be illustrated by the flowchart shown in figure 2.22.



Fig. 2.22 Procedure of applying the modified model

2.5 Uncertainty of Experimental Conditions

Before we move on to reach any conclusions from our experiments, it is essential for us to find the uncertainty of our shock wave calculation and measurements and to take whatever measures possible to reduce the error.

The incident and reflected shock wave velocities are calculated by dividing the distance between 2 sensors by the measured time duration for the shock wave to pass between them. The sampling rate of PCB pressure transducers is set at 166.67 kHz, which converts to 6 microseconds for each sample; so the uncertainty of our time measurement is $\pm 6 \ \mu s$. We estimate the uncertainty of the length measurements to be 0.2% of the overall length plus the radius of the pressure transducer. The calculated uncertainty (see appendix B for details) for the incident shock velocity is about 0.31% and that for the reflected shock is 2.2%. The corresponding uncertainty for temperature T₅ is 5 to 7 K for the current experimental range. It increases to 9 to 13 K when the reflected shock velocity is also used in the calculation. However, the value is still small compared with T5 that is usually over 1000K.

Since we do not have independent verification of experimental temperatures, we use measured pressures and velocities to check our calculations.

Figure 2.23 is a comparison between calculated and measured pressures behind the reflected shock - P_5 . The error in pressures measured by PCB transducers is roughly 5%. The plot demonstrates a good agreement between the calculations and the measurements although the least square fit of measured pressures shows a slight bias towards under-prediction at the high pressures.



Fig. 2.23 Comparison of measured and calculated pressures behind the reflected shock for the same incident shock velocity. Solid line: calculated pressure. Symbols: measured pressure. Dashed line: least square fit of measurements.

As we have shown in the previous section, the measured reflected shock velocity is generally higher than calculated for the same incident shock speed. To establish the

extent to which this difference is going to affect calculated temperature, we modified the model and input both measured incident and reflected shock velocities. We compared the results with model predictions by using only measured incident shock velocities. The comparison is shown in figure 2.24.





The difference between calculated temperatures, ΔT , using the two aforementioned methods increases with an increasing incident shock velocity. The biggest gap appears at the highest initial temperature, for which it is nearly 37 K. For the majority of the temperature range the differences are less than 25K.

2.6 Reflected Shock Boundary Layer Interaction

One famous phenomenon observed in shock tube experiments is reflected shock/wave boundary layer interaction [6,7,11]. In the aforementioned one-dimensional model used for shock calculations, we always assume uniform inflow/outflow velocity profiles. This is certainly valid for the incident shock wave, which travels into a gas at rest. However, for the reflected shock, which travels in a flow set in motion by the incident shock, the velocity profile of the incoming flow is no longer uniform due to the viscous effects near the wall of the shock tube. Figure 2.25 illustrates the velocity profile of the incoming flow in reflected-shock fixed coordinates.



Fig. 2.25 Velocity profile of the incoming flow in reflected-shock-fixed coordinates.

The flow velocity at the wall is the same as the wall velocity. For shock-fixed coordinates, the wall moves at the reflected shock velocity W_5 . The velocity of the main stream is the sum of the flow velocity behind the incident shock and the velocity of the reflected shock.

It has been observed by early researchers [9,10] that the interaction between the reflected shock and the boundary layer may cause the boundary layer to separate with separation bubble producing a shock bifurcation at the foot of the reflected shock (see figure 2.26). Holder [11] in his shock tube experiment observed a stream of cold gas along the side wall penetrating into the hot gas behind the reflected shock and meeting the end plate of the driven section. The phenomenon was believed to relate directly with the reflected shock/boundary layer interaction.

There are two possible influences that may be brought about by this non-uniform velocity profile of the incoming flow based on the above observations. The first is direct cooling of the hot gas close to the end wall by the cold flow emerging from the bifurcated shock foot. Since we define the experimental time starting from the shock wave reflection from the end wall of the driven section, and the observed ignition actually starts very close to the end wall, we need to examine the time when the gas starts to change the temperature

at this crucial area and make sure that the temperature is not significantly reduced before ignition. The second is that the boundary layer thickness may grow to such an extent that the uniform flow assumption becomes no longer valid. Our entire calculation of experimental conditions behind the reflected shock need to be reevaluated for such a condition.



Fig. 2.26 Bifurcated foot of the reflected shock in shock-fixed coordinates

Mark [9] developed a simple model for the reflected shock – boundary layer interaction. The model was extended by Davies [6] to calculate the time required for the emerging cooling flow from the reflected shock bifurcation foot to reach the end wall. In the Mark and Davies model, the boundary layer in the path of the reflected shock is taken to be a layer of gas of unspecified thickness 't' at wall temperature and having the wall velocity with the pressure equal to free stream value. The observed flow separation at the shock foot is explained as the boundary layer being brought to rest by the reflected shock in shock-fixed coordinates. It has been shown by Mark that for air, the stagnation pressure for incident shock Mach number ranging from 1.8 to 16 is less than the pressure behind the normal shock. Instead, it gathers under the shock foot growing as the reflected shock travels upstream and causes bifurcation of the shock to form forward and backward limbs denoted by OA and OB as shown in figure 2.26.

Part of the main flow outside the boundary layer is turned to pass through the forward limb and then further compressed by the backward limb. Experimental observations reveal that the flow direction is turned parallel to the main stream flow behind the reflected shock after emerging from the two oblique shocks. It can be shown that this

flow, with its velocity faster than the flow velocity behind the normal shock, has an absolute velocity towards the end wall.

For a flow passing an oblique shock, the normal shock relation can still be valid if we choose to use the velocity component normal to the shock front. The velocity component parallel to the shock front will not be affected after passage as illustrated in figure 2.27.



Fig. 2.27 Oblique shock wave and equivalent normal shock wave

It can be shown that the following relations hold for a perfect gas passing an oblique shock.

$$\frac{\rho_1}{\rho_2} = \frac{(\gamma + 1)Ma_a^2 \sin^2 \beta}{1 + (\gamma - 1)Ma_a^2 \sin^2 \beta}$$
(2.35)

$$\frac{P_2}{P_1} = 1 + \frac{2\gamma}{\gamma + 1} \left(M a_a^2 \sin^2 \beta - 1 \right)$$
(2.36)

$$\frac{T_2}{T_1} = 1 + \frac{2(\gamma - 1)}{(\gamma + 1)^2} \left(\frac{1 + \gamma M a_a^2 \sin^2 \beta}{M a_a^2 \sin^2 \beta} \right) \left(M a_a^2 \sin^2 \beta - 1 \right)$$
(2.37)

where Ma_a is the flow Mach number ahead of the oblique shock and β is the angle between moving direction of the incoming flow and the shock front. The Mach number behind the shock wave is given by:

$$Ma_{b}^{2}\sin^{2}(\beta-\theta) = \frac{1+\frac{\gamma-1}{2}Ma_{a}^{2}\sin^{2}\beta}{\gamma Ma_{a}^{2}\sin^{2}\beta-\frac{\gamma-1}{2}}.$$
(2.38)

Also the deflection angle θ can be calculated from

$$\tan\theta = 2\cot\beta \left[\frac{Ma_a^2 \sin^2\beta - 1}{2 + Ma_a^2 (\gamma + \cos 2\beta)} \right].$$
 (2.39)

Returning to the bifurcated foot of the reflected shock, we can calculate the flow properties after passing two oblique shocks (OA and AB), however we need to calculate the angles with respect to the moving direction of the incoming flow so that the oblique shock relations, Eq. (2.35) to (2.39), can be applied. In the Mark and Davies model, two assumptions have been made to calculate these angles. First, the pressure under the triangle OAB is assumed the same as the stagnation pressure. Second, the flow leaves the rear limb AB having the same pressure as that behind the normal shock. Since we have already assumed the temperature of the boundary layer is the wall temperature, we can obtain the local sound speed and, from that, the local Mach number for the boundary flow. The stagnation pressure can be calculated by the Rayleigh supersonic pitot formula.

$$\frac{P_{st,bl}}{P_a} = \frac{\left[\frac{\gamma+1}{2}Ma_{bl}^2\right]^{\frac{\gamma}{\gamma-1}}}{\left[\frac{2\gamma}{\gamma+1}Ma_{bl}^2 - \left(\frac{\gamma-1}{\gamma+1}\right)\right]^{\frac{1}{\gamma-1}}}.$$
(2.40)

Here, $P_{st,bl}$ is the stagnation pressure and P_a is the pressure of the boundary layer flow, which is assumed the same as that of the main flow; Ma_{bl} is the boundary layer (wall) Mach number. Once we know the stagnation pressure, with assumption 1, the angle β or COA of the forward limb (see figure 2.28) can be calculated from Eq. (2.36).



Fig. 2.28 Mean flow passing through two oblique shocks. Ma represents the local Mach number of the flow.

$$Ma_{a}^{2}\sin^{2}COA = \frac{(\gamma+1)\frac{P_{st,bl}}{P_{a}} + (\gamma-1)}{2\gamma}.$$
(2.41)

The flow direction after passing the forward limb is given by

$$\frac{\tan(COA - COB)}{\tan(COA)} = \frac{(\gamma - 1)Ma_a^2 \sin^2 COA + 2}{(\gamma + 1)Ma_a^2 \sin^2 COA}.$$
(2.42)

Also the flow Mach number between two limbs is obtained using Eq. (2.38).

$$Ma_{x}^{2}\sin^{2}(COA - COB) = \frac{(\gamma - 1)\frac{P_{st,bl}}{P_{a}} + (\gamma + 1)}{2\gamma \frac{P_{st,bl}}{P_{a}}}.$$
(2.43)

The flow Mach number Ma_5^* after passing the rear limb can be obtained from Ma_x and $(P_5/P_{st.bl})$ in similar equations.

$$Ma_{5}^{*2}\sin^{2}(DAB - DAC') = \frac{(\gamma - 1)\frac{P_{5}}{P_{st.bl}} + (\gamma + 1)}{2\gamma \frac{P_{5}}{P_{st.bl}}}.$$
(2.44)

Finally, the absolute velocity with which the cooling flow approaches the end wall is given by $(U_5^*-W_5)$, where U_5^* denotes the relative velocity of the flow emerging from AB.

It is shown by the model that before the reflected shock passes the contact surface, the flow temperature of driven gas after being compressed by two oblique limbs is very close to the temperature in the main flow. However, after the shock passes the contact surface and traveling into the driver gas, the temperature of the flow emerging from the bifurcated foot is much lower than the temperature in the experimental area.

Despite the obvious crudeness of this model, it is observed by Mark and later researchers that the 'model provided a most useful and sometimes surprisingly accurate description of the bifurcation phenomenon' [6]. The predicted cooling flow velocity has been verified by the heat transfer experiment conducted by Davies.

We use Davies' model to calculate the flow velocity after passing the bifurcation foot in the current experiments so that we can evaluate the time for the cooling gas to reach the end wall. We compare it with previously calculated experimental time for various initial conditions. The result is shown in figure 2.29.

It can be seen that for an incident shock velocity higher than 1030m/s, the cold gas passing the bifurcation foot is able to reach the end wall prior to the arrival of the rarefaction fan. The experimental time for those cases could be shorter than that predicted before. The temperature of this stream is much lower than the main flow temperature (around 266-269K for the current experimental range), and increases slightly with a decrease of the incident shock velocity.



Fig. 2.29. Comparison of the time for the cooling gas to reach the end wall with calculated experimental time versus the incident shock velocities. Time starts from the shock reflection at the end wall. Dotted line: experimental time. Solid line: time for the cooling gas to reach the end wall. Driver gas: Helium mixed with air. Driven gas: air.

We also calculated the boundary layer thickness of the flow behind the incident shock using a numerical model (see appendix D for details). It is found that for the current experimental range, the boundary layer thickness does not bring a significant effect on the one-dimensional shock tube model.

2.7 Contact Surface Instability

Another factor that contributes to the premature termination of constant conditions in the experimental area is contact surface instability. Lapworth [7,8] reported the duration of constant temperature behind the reflected shock is much shorter than the duration of constant pressure when hydrogen is used to drive nitrogen in his shock tube experiment. A similar phenomenon has been reported by Lapworth and Townsend for their helium-nitrogen system. The problem is examined by Bird et al [14] and is attributed to the

instability of a "shocked" contact surface– a contact surface through which a shock has passed - that causes cooling of the hot gas.

Taylor [15] discussed the stability of an interface between two fluids of different densities when the two fluids are accelerated in a direction perpendicular to their interface. He used the velocity potential to show that the rate of development of the instability is proportional to

$$\sqrt{\frac{\rho_{2-}\rho_1}{\rho_2 + \rho_1}} \tag{2.45}$$

where ρ_1 and ρ_2 are the densities of the two fluids.

Markstein [16] developed Taylor's analysis and applied it to a 'shocked' contact surface in a shock tube experiment. The result is an expression for the velocity field for the disturbance flow, which has the form

$$u(x, y) = UkA \frac{(\rho_5 - \rho_6)}{(\rho_5 + \rho_6)} e^{k(\pm x + iy)}.$$
(2.46)

Here, U is the velocity difference between reflected shock and the driver gas behind the reflected shock; k equals $2\pi/\lambda$ where λ is the wavelength of the disturbance of the interface. ρ_5 and ρ_6 are the densities of driven and driver gas behind the reflected shock, and A is an amplitude factor. It is interesting to notice that the sign of the perturbation velocity depends on (ρ_5 - ρ_6). Davies [6] used this analysis to show that for a helium-nitrogen system neutral stability happens when M₁=3.56 so that $\rho_5=\rho_6$ and u vanishes. For any Mach number higher than that, the perturbation flow will move towards the driven gas and change the constant conditions there. A calculation using the current shock tube model shows that for our helium-air system, within the entire experimental range (M₁<3.5), we have $\rho_5 > \rho_6$ which means the perturbation always propagates towards the driver side. The contact surface instability should not affect the experimental conditions for the current study.

CHAPTER III

3.1 Introduction

Accurate measurements of the ignition delay for natural gas under engine-relevant conditions provide important information to obtain an optimal control for a natural-gas-fueled engine. For a direct injection natural gas engine, the ignition delay determines directly the injection advance. On the other hand, for a homogeneously charged spark ignition engine, a short ignition delay that leads to an autoignition may result in engine knock and thus must be avoided.

Historically, the study of the ignition for methane – a major component of natural gas – has enjoyed wide attention. However, despite many experiments measuring the ignition delay for methane in air or oxygen, there are surprisingly few published for high pressure (P>15 atm) and low temperature (T<1400 K) methane ignition, on which engine designers' interests are focused. A simple extrapolation of empirical equations derived from low-pressure high-temperature experiments generates dubious and usually inaccurate results.

The lack of experimental data in this area also affects the applicable range of chemical kinetics, which have been developed to match experimental measurements.

A primary purpose of the current project is to measure the ignition delay for methane under engine-relevant conditions and to correlate the ignition delay with key environmental parameters such as temperature and pressure.

It is the author's hope that the results of the present study may serve as a guide to understanding ignition in natural gas engines as well as provide help in extending the reaction mechanism for high-pressure methane ignition.

3.2 Background

3.2.1 Oxidation of Methane

Among the hydrocarbons, methane is the one of the more "inactive" fuels. The energy required to break the primary C-H bond in methane is 439.3 kJ/mole, which is significantly higher than longer-chain hydrocarbons.

Glassman [29] divided the mechanism for methane oxidation into two regimes of temperature with respective dominant kinetics. The slow reaction speed of methane may be mainly attributed to the following:

1) Slow chain initiation.

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The major initiation steps for methane oxidation are:

$$CH_4+O_2 => CH_3+HO$$
 (low temperature) (3.R1)

$$CH_4+M \Rightarrow CH_3+H+M$$
 (high temperature) (3.R2)

The high C-H bond energy of methane prevents these steps from proceeding rapidly especially at low temperatures.

2) At high temperature (1000K or above), the equilibrium of an important chain propagating step, i.e.,

$$CH_3+O_2 \Leftrightarrow HO+H_2CO$$
 (3.R3)

shifts strongly towards the reactants and the overall reaction to form formaldehyde and hydroxyl can not proceed.

3) Another major oxidation destruction path of the methoxy radical, i.e.,

$$CH_3+O_2 => CH_3O+O$$
 (3.R4)

is highly endothermic requiring large activation energy, and thus, quite slow for a chain step.

 In the presence of high concentration of CO formed by precursory chain propagation steps, reactions

$CH_4+OH->CH_3+H_2O$

and

CO+OH->CO₂+H

(3.R5)

(3.R6)

0

compete for hydroxyl radicals. Since reaction (3.R5) is faster than reaction (3.R6), the net result of this competition is the reduction of the fuel consumption rate.

3.2.2 Previous Work

Experimental studies on methane-air/methane-oxygen autoignition have been reported by Lifshitz et al. (1971), Grillo and Slack (1976), Seery and Bowman (1970), Tsuboi and Wagner (1974), Hidaka et al. (1978), Oppenheim and Cheng (1984), Cowell and Lefebvre (1987) etc. Among these studies, the shock tube was used as the primary experimental instrument because of its instantaneous temperature and pressure rise that minimizes the effects of heating process. Other methods, such as rapid compression machines or heated air experiments by Cowell and Lefebvre [18], are also used in ignition measurements.

The criteria that define the onset of ignition vary from sudden changes of temperature and pressure to the appearance of certain radical peaks as well as the variation of density of the mixture. Zhou and Karim [19] examined the different criteria numerically using a detailed reaction mechanism, and found little difference among different criteria used for ignition delay at low temperatures (<1100K), but relatively large scatter for higher temperatures. The criteria based on the sudden changes in pressure and temperature are recommended for the reason that the ignition delay time measured by such methods always lies in the middle of the results obtained using different criteria. Furthermore, temperature and pressure are the most readily measurable parameters, and are thus considered more reliable. In reality, rapid change in temperature is usually more difficult to measure than that of pressure because of the short residence time. The response of pressure-measuring instruments available in the market is usually much faster than that of most instruments that measure temperature.

The measured ignition delay is often correlated with pressure, temperature and reactant concentrations using global reaction formulas. It is worthwhile to point out that even the simplest combustion reaction will involve dozens of intermediate species and hundreds of

forward and backward reaction steps. It is far too complicated to be represented by any one step reaction mechanism. However, empirical equations do provide valuable information to both the development of detailed reaction mechanism and practical engineering applications by establishing how the ignition-delay time changes with the variation of system parameters.

In its general form, the rate of a chemical reaction is expressed as

$$\omega = k \prod_{i=1}^{n} [X_i]^{v_i}, \qquad (3.1)$$

where $[X_i]$ is the concentration of reactant i raised to the power of its stoichiometric coefficient v_i . k is the reaction rate constant, which is given by the Arrhenius expression

$$k = A \exp\left(-\frac{E}{RT}\right) \,. \tag{3.2}$$

Here A is the Arrhenius constant, E is a global activation energy, and R is the universal gas constant. For an empirical expression of the reaction rate, stoichiometric coefficients in Eq. (3.1) are replaced by empirical coefficients to fit experimental measurements. For an air/oxygen-fuel reaction system, the empirical expression becomes

$$\omega = k[oxygen]^{-b}[fuel]^{-a} p^{-m}, \qquad (3.3)$$

where a, b and m are empirical coefficients; p is the mixture pressure in atm. The unit for concentrations of oxygen and fuel is mol/cm^3 . The ignition delay time is considered proportional to the inverse of the initial reaction rate and is given by the general form

$$\tau = A \exp\left(\frac{E}{RT}\right) [oxygen]^{a} [fuel]^{b} P^{m} T^{n-a-0.5}, \qquad (3.4)$$

where $T^{0.5}$ comes from the molecular collision theory. The last term ($T^{n-a-0.5}$) of equation (3.4) is usually neglected unless one is working with a wide temperature range [20].

The most common form of the empirical equation for a methane-air/oxygen system thus becomes

$$\tau = A \exp\left(\frac{E}{RT}\right) [O_2]^a [CH_4]^b P^m.$$
(3.5)

The empirical coefficients from previous studies, along with their experimental conditions are tabulated in table 3.1. These coefficients are achieved normally by fitting experimental data using regression methods.

	Pressure	Temperature	a	b	m	А	Ea	Experimental
	(atm)	(K)						Method
Seery and	1.5-4	1300-1900	0.4	-1.6	0	7.65E-12	215	Shock tube
Bowman	·							Premixed
Lifshitz et	2-10	1500-2150	0.33	-1.03	0	3.62E-08	195	Shock tube
al.								Premixed
Tsuboi and	2-3	1200-2100	0.32	-1.02	0	2.50E-09	222	Shock tube
Wagner								Premixed
Cheng and	1-3	1100-2200	0.48	-1.94	0	1.19E-12	194	Shock tube
Oppenheim								Premixed
Walker et	1.5-15	?	0.33	-1.05	0	2.21E-08	189	Shock tube
al.								Premixed
Grillo and	1-6	1640-2150	0.33	-1.03	0	4.40E-09	219	Shock tube
Slack								Premixed
Hidaka et	0.47-0.74	1800-2500	0.37	-0.64	0	4.54E-04	149	Shock tube
al.								Premixed
Cowell and	7-10	<1000	-	-	-1	1.99E-01	105	Heated Air
Lefebvre			0.19					Non-premixed

Table 3.1. Experimental conditions and empirical coefficients for previous work measuring the ignition delay of methane

The calculated ignition delay is in microseconds. Other units are: kJ/mol for Ea, K for T, mol/cm³ for [CH₄] and [O₂], and kJ/mol.K for the gas constant R.

Clearly, there is a lack of data in the literature for low temperatures and high pressures that one would expect in an engine environment.

It is interesting to compare the ignition delay time calculated from all these equations to see how they agree with each other. In figure 3.1, calculated ignition delay times are shown in an Arrhenius plot (log τ versus the inverse of temperature) within their respective temperature ranges for a pressure of 2 atm and an equivalence ratio of 1.



Fig. 3.1 Ignition Delay of a stoichiometric methane-air mixture calculated using different empirical equations for an initial pressure of 2 atm

At this low pressure, different empirical equations show relatively good agreement with each other. However, when trying to extrapolate these equations to low temperature and high pressure conditions close to that of engine environments, we find a big scatter of calculated ignition delay time as shown in figure 3.2, where the initial pressure has been raised to 30 atm.

It is obvious that using these empirical equations out of the scope where they are derived generates unreliable results.

The lack of experimental results for the ignition delay of CH_4 -air mixture at engine relevant conditions is what has activated the experiments to be decided herein.



Fig. 3.2 Ignition Delay of a stoichiometric methane-air mixture calculated using different empirical equations for an initial pressure of 30 atm

Using the shock tube introduced in the previous chapter, we have conducted a series of ignition experiments for methane and air premixed inside the driven section of the shock tube with desired equivalence ratio. A 20-30 minute relaxation time is given before each experiment to allow complete mixing of fuel and air. Various experimental temperatures and pressures have been obtained by changing the initial driver and driven pressures and helium concentrations according to calculations using the method introduced in chapter II.

3.3 **Results and Discussions**

3.3.1 Pressure History of Methane Self-ignition Process

The pressure histories detected at the end wall of the shock tube behind the reflected shock wave for initial pressures from 16 to 40 atm are shown in figures 3.3 to 3.6. The experimental temperature covers a range from 1000 to 1400 K. Below 1000 K, we find that either the ignition delay exceeds the maximum experimental time or the pressure variation may be too weak to be detected by the pressure sensor due to a slow combustion. In either event, for these conditions, we are unable to measure ignition delay with the present system.

It can be seen that the pressure trace is a flat curve initially after the reflection of the shock wave. After a short delay time, the pressure starts to rise, which is an indication of the beginning of ignition. The ignition delay time is then defined for our study as the time duration from the shock reflection to the time when the maximum curvature on the pressure trace is found. This criterion has also been used by early researchers including Frenklanch and Bornside [2].



Fig. 3.3 Pressure history of a stoichiometric methane-air mixture ignition process ($P_{ini} = 16\pm 2 \text{ atm}$)



Fig. 3.4 Pressure history of a stoichiometric methane-air mixture ignition process ($P_{ini} = 23\pm 2$ atm)



Fig. 3.5 Pressure history of a stoichiometric methane-air mixture ignition process ($P_{ini} = 30\pm 2$ atm)



Fig. 3.6 Pressure history of a stoichiometric methane-air mixture ignition process ($P_{ini} = 40\pm2$ atm)

For temperatures between 1000 to 1200K, methane ignition causes a mild pressure rise and a clearly distinguished pressure peak. This is especially prominent for relatively low initial pressures (P<23) but less so for higher pressures. The slope of the pressure rise grows steeper with the increase of temperature. At the same temperature the increase is sharper for a higher initial pressure than that for a lower one.

A noticeable change of the ignition pattern occurs when the temperature is raised to around 1250 K. The ignition becomes less ordered. Specifically, we no longer see a unique maximum in pressure. In some cases, a sharp, secondary pressure peak whose magnitude can usually exceed the first one starts to appear.

With further increase of temperature to over 1300K, strong ignitions, which are characterized by a sudden increase of pressure followed by violent pressure oscillations, are found. The peak pressure of such an ignition may be 1.5 to 2 times higher than that of the mild ignition, and has a maximum value up to 100 atm. The blast wave formed by this sudden pressure jump traveling at a very high velocity may catch up with the reflected shock wave, and form a detonation front that propagates downstream supersonically.

It is noticeable that the change from weak to strong ignition happens within a short temperature range. There is no obvious variation of the magnitude of peak pressure as the temperature approaches the strong ignition limit. Similar observation of this discontinuity is reported by Chang and Oppenheim [1] as well as by Fieweger et al. [21] in their respective studies, which we will discuss in the following section.

3.3.2 Strong Ignition Limit

The mild ignition observed at a low temperature is considered to be an autoignition that originates from one or several hot spots in the experimental area and proceeds inhomogeneously. In a spark ignition engine such an ignition, which evolves primarily into a deflagration causing only mild pressure rise, is not commonly termed knock [23]. It is, rather, the appearance of a strong ignition that brings a sudden and big jump of the pressure, which may quickly damage the engine.

Oppenheim and Cheng [1] discuss strong ignition based on their study of methane/hydrogen-air mixture ignition at low pressures. They attribute the cause of strong ignition to coherence in the exothermic processes, which quickly produces a sufficiently strong power per unit mass to generate a blast wave. They further relate this

coherence with the standard deviation of the temperature field during the induction period, the heat release of reactions, the reaction rate, and also a critical value of $(\partial \tau / \partial T)_p$. It should be mentioned that the coherence of the exothermic processes is not exclusively decided by temperature and pressure; factors such as shock wave / boundary layer interaction can also influence the appearance of strong ignition provided that they change the homogeneity of the reactive mixture.

Figure 3.7 shows P-T conditions where strong and mild ignitions are measured in the current experiment.



Fig. 3.7 Measured strong ignition limit for stoichiometric methane-air mixtures at pressures from 16 to 40 atm. Symbols: diamonds - mild ignition, squares - strong ignition.

The fact that the observed temperature limit for strong ignition decreases with an increase of pressure is readily explained. The high energy released per unit volume mixture at high pressure increases the possibility of generating a blast wave – the indication of a strong ignition.

Different ignition patterns from mild to strong ignition recorded in the present study are given in figure 3.8.



Fig. 3.8 Mild to strong ignition – 4 different ignition patterns

Fieweger et al. [22] study the transitions from mild ignition to strong ignition of several different hydrocarbons at high pressure. They find a detonation-like pressure jump following the initial gradual pressure increase caused by deflagration at high temperature. The pressure wave and the heat release generated by the initial deflagration travels backward to the end wall with a velocity faster than the flame front. The temperature and pressure of unburned gas at the end wall are increased more or less uniformly by this compression wave, which leads to a simultaneous combustion that generates a strong ignition. If the initial ignition is sufficiently slow, the raised temperature may not be high enough to induce a second explosion at the end wall and all the unburned gas is consumed by the deflagration process. In this case, we end up with a mild ignition that may not cause a knock problem when occurs in a spark-ignition engine. In the present study, two strong-ignition patterns – strong ignition with or without obvious pre-

deflagration - are found at nearly the same temperature range. This may be related to the difference in positions where ignitions start. If the ignition starts very close to the end wall, the compression happens so quickly that it can hardly be distinguished from the subsequent strong ignition. Otherwise, the compression process takes longer time and we can observe a clear mild pressure rise before the occurrence of a secondary explosion.

3.3.3 Ignition Delay of Methane at High Pressure

Figures 3.9 and 3.10 are Arrhenius plots showing the changes of measured ignition delay with respect to initial temperature at different pressures. The equivalence ratios here are 1 and 0.7 respectively.



Fig. 3.9 Measured ignition delay time of stoichiometric methane-air mixture at different pressures. Symbols: squares -16 atm, diamonds -30 atm, circles -40 atm. Solid lines are the least square fits to the experimental measurements.



Fig. 3.10 Measured ignition delay time of lean methane-air mixture at different pressures (Φ =0.7). Symbols: triangles – 16 atm, diamonds – 30 atm, circles – 40 atm. Solid lines are the least square fits to the experimental measurements.

An obvious disagreement can be seen between the present results and those shown in figure 3.2 using previous empirical equations. The ignition delay time obtained in the current study for high pressures is significantly shorter than that from early low-pressure experiments.

We now discuss three factors that are considered as major contributors to the ignition delay time according to the global reaction mechanism: temperature, pressure and fuel/oxidizer concentrations.

1) Temperature

Temperature is the most important factor that determines the ignition delay. It can be seen that the ignition delay time increases dramatically with the decrease of temperature. In most of the previous work on global reaction rates, the activation energy is assumed to be a constant. The Arrhenius plot of ignition delay is then a straight line with its slope revealing the global activation energy. At high temperature and low pressure, this value is

found to be approximately 180-220 kJ/mol as reported by many previous workers [1,3,23]. However, by scrutinizing the activation energy obtained in early experiments, one may find a clear trend of it decreasing in magnitude as the experimental temperature is reduced, e. g., Cowell and Lefebvre [20]'s experiment conducted at low temperature (<1000 K) and moderate pressure (7-10 atm) yields Ea=105 kcal/mol. Zhou and Karim [19] use detailed mechanism to simulate the ignition process of methane and suggest using 3 different values for activation energy in different temperature ranges in their conclusions. In the present results, it is found that the measured ignition delay time at given pressure is not fit well with a straight line in the Arrhenius plot. This is especially true for high-pressure stoichiometric mixtures where the trend line follows a reversed 'S' curve. Similar curves are found in high-pressure shock tube ignition tests for high-order hydrocarbons by Fieweger et al. [22]. The range (roughly 1100K to 1200K) where ignition delay time shows less sensitivity to the change of temperature is not very prominent for lean mixtures, whose curves are more straight than are those of stoichiometric mixtures.

2) Pressure

In most of the previous work, pressures are either sub-atmospheric or slightly higher than 1 atm. The pressure effect is usually neglected. Cowell and Lefebvre investigate the ignition delay of methane in heated-air flow from 7 to 10 atm, and find that it is proportional to the inverse of pressure.

Figure 9 and 10 shows an obvious reduction of ignition delay time from 16 to 30 atm, but the difference diminishes when the pressure is further increased to 40 atm. Also the ignition delay does not change significantly for different pressures when the temperature is high. In terms of kinetics, this may suggest a shift of dominant reactions in an ignition process when the temperature changes from low to high, and the low temperature mechanism is more pressure-sensitive than the high temperature one.

3) Concentrations of Fuel and Oxidizer

Increase of reactant concentration increases the possibility for inter-molecular collisions, and thus the chance for the reaction to take place. In the fuel-air reaction system for a

given pressure and temperature, the concentration of fuel and oxidizer can be varied with different equivalence ratios.

In figures 3.11 and 3.12, stoichiometric results at a given pressure are compared with lean and rich results to show the effect of equivalence ratio on ignition delay. It can be seen that at 16 atm, a lean mixture generates a slightly longer ignition delay at high temperature; the difference increases sharply when the temperature decreases. However, with an increase of pressure, the ignition delay time of the lean mixture moves closer to the stoichiometric one. At P=40 atm, it even cross the stoichiometric line at low temperatures. With the same pressure, a rich mixture shows a significantly longer ignition delay as the stoichiometric one.



Fig. 3.11 Comparison of ignition delay for lean and stoichiometric methane-air mixtures at 16 atm. Symbols: squares – lean (Φ =0.7), diamonds – stoichiometric (Φ =1). Splines are used to show the trend of change.



Fig. 3.12 Comparison of ignition delay for lean, rich and stoichiometric methane-air mixtures at 40 atm. Symbols: squares – lean (Φ =0.7), diamonds – stoichiometric (Φ =1), triangles – rich (Φ = 1.3). Splines are used to show the trend of change.

3.3.4 Correlation Equations

An empirical equation has been derived using the linear regression method based on the present experimental results

Clearly, the activation energy of the methane-air ignition process can not be represented by a simple constant. It is observed that the activation energy is close to a third order polynomial within the experimental range in the Arrhenius plot. Also, the pressure dependence drops with the increase of temperature. The modified Arrhenius-type equation is thus given by

$$\tau = A \exp\left(\frac{Ta}{T}\right) CH_4 P^m (P)^{\frac{n}{T}}$$
(3.6)

where Ta is the activation temperature given by the equation

$$Ta = a \left(\frac{1}{T}\right)^2 + b \left(\frac{1}{T}\right) + c.$$
(3.7)

The global activation energy Ea is related to Ta by the universal gas constant R

$$Ea = Ta \times R. \tag{3.8}$$

The concentration of oxygen is absorbed in $[CH_4]^m$ for a given equivalence ratio for an air-fuel reaction system.

A, a, b, c and m are empirical coefficients that are determined experimentally as listed in table 3.2:

Coefficients	Ф=1	Ф=0.7
A, μ s.(cm ³ /mole) ^m (atm) ^{T/n}	1.20E-17	1.24E+14
a, K ³	9.71E+10	4.46E+10
b, K ²	2.46E+8	-1.06E+8
с, К	2.20E+5	1.04E+5
m	1.52	4.44
n, K	-2.41E+3	-6.03E+3

Table 3.2 Empirical coefficients for the ignition delay of methane obtained in the current study

The equation has been found being able to fit the experimental results reasonably well. Overall changes of ignition delay with respect to pressure and temperature for stoichiometric and lean mixtures are presented in figures 3.13 and 3.14. It can be seen that both surfaces turn upward steeply with decreasing temperature and pressure. Also, the difference between the lean and stoichiometric surface (shown in figure 3.15) shrinks as the temperature and pressure increase.



Fig. 3.13 Ignition delay of a stoichiometric methane-air mixture by equation (3.6) (Φ =1)



Fig. 3.14 Ignition delay of a lean methane-air mixture by equation (3.6) (Φ =0.7)


Fig. 3.15 Difference between lean and stoichiometric mixtures for ignition delay time

It's interesting to notice that unlike the equation presented by Cowell and Lefebvre, the coefficient for the fuel concentration - m- obtained by us is negative, which suggests that ignition delay time may be shorter for lean mixtures at certain conditions.

3.3.5 Comparisons of Experimental and Computational Results

A computer model incorporating detailed reaction mechanism has been developed to simulate the ignition process in the shock tube. The initial condition behind the reflected shock is modeled as an adiabatic and constant volume one. Gasdynamic effects brought about by heat release and shock wave boundary layer interaction are neglected in the current model. The methane-air kinetic mechanism is taken from GRI-Mech (version 3.0) [31]. That generates 53 intermediate species and 318 reaction steps. Chemkin-II (version 1.6) developed by Kee et. al. [32] of the Sandia National Laboratory is used as the mechanism interpreter. The differential equations in the model are solved using LSODE (1987 version) [33]. The same pressure criterion is used to define the onset of the ignition. The computational results are plotted in figure 3.16 together with the experimental measurements.



Fig. 3.16 Comparison of computational results with experimental measurements for the ignition delay of stoichiometric methane-air mixture. Symbols: squares – 16 atm, diamonds – 30 atm, circles – 40 atm. Solid lines: computational results.

It can be seen that within the current experimental range, the mechanism largely overpredicts the global activation energy, which leads the calculated curves to be steeper than the experiments. The calculated ignition delay at high temperature is shorter than the measurements, while at low temperature the calculation predicts a significantly longer ignition delay than what we have observed experimentally. However, despite the obvious disagreement between model predictions and experimental results, the mechanism does indicate correctly a diminishing pressure effect. Notice that the difference between 16 and 30 atm given by the model is of more than 2 times that between 30 and 40 atm.

Results from the above comparison suggest that detailed kinetics, which have been tuned to match experimental measurements obtained for low-pressure, high-temperature ignitions do not necessarily work well when applied at high-pressure and lowtemperature conditions. Further tuning of the mechanism is needed to match the current experimental results.

CHAPTER IV

4.1 Introduction

A major problem associated with using natural gas as a fuel for compression ignition engines comes from its very long ignition delay time at engine relevant conditions. Different strategies involving injection with a pilot fuel, using a spark plug or glow plug, etc., are being developed to address this problem. An alternative, and possibly preferable approach for engine makers, is to blend natural gas with some other active gaseous fuel, known as an ignition promoter, to shorten the ignition delay time. This would make it possible to run a diesel-based engine on natural gas without making major modifications to engine components.

Although promotion for natural gas/methane ignition has been a subject of study in the field of combustion for some time, there are few publications revealing the behavior of ignition promoter under diesel engine conditions, which requires high pressure (20-70 atm) and low temperature (900 - 1200 K). Clearly, the efficiency of an ignition promoter will be significantly different under these conditions compared to that at low pressure and high temperature as are found in many experiments. Furthermore, the way in which the promoter and the fuel is introduced into the combustion chamber, i.e. homogenous charge or direct injection, can also play an important role in the ignition progress, and consequently, the ignition delay time. With direct injection ignition is a more complicated process in which transport phenomena of two different fuels have to be taken into consideration.

In the current study, we have carried out literature researches as well as conducted experiments to investigate efficiencies of different promoters for a high-pressure low-temperature methane-air reaction system. The objective is to find out possible candidates for natural gas engine applications.

Meanwhile, gasdynamic features of ignitions with and without promotion have be studied. The strong ignition limit, which is fuel dependent, has been explored for its close relationship with engine knock problems.

4.2 Background

4.2.1 Mechanism of Ignition Promotion

Frenklach and Bornside [2] study the detailed chemical kinetics of methane ignition based on their shock tube experimental results. They find that the oxidation of methane during the induction period (ignition delay) proceeds through three distinct phases: initiation, determined by decomposition and H-abstraction reaction of methane; oxidation of methyl radicals by molecular oxygen; and oxidation of CH_3 by HO_2 radicals and, to a less extent, O and OH radicals.

For methane-air reactions without promotion, the large energy required to break the C-H bond in a methane molecule makes the initiation process slower than that of other hydrocarbons. Also the high activation energy and highly endothermic nature of the methyl-oxygen reaction makes this chain step quite slow.

In general, there are two major mechanisms in terms of shortening the reaction time. The first one is the thermal promotion, which can be achieved by quickly oxidizing the promoter to release energy to increase the mixture temperature. Since the reaction time is a strong function of temperature, the higher the temperature the shorter the subsequent reaction time. The second mechanism is through adding extra active species (radicals) at the chain initiation and propagation stages to speed up the chain reaction. These species are generated by fast promoter decomposition at the beginning of the reaction. The second mechanism is found especially effective in a nonbranched system [24]. The ignition delay time in such a system may be reduced by several orders of magnitude through decomposition of the additive. However, it only weakly affects branched systems.

For most ignition promoters, both of the mechanisms are involved simultaneously. Zamansky and Borisov [24] use heat balance equation for the molecular reaction to show that for a typical reaction system, purely thermal promotion can show its effectiveness only when the concentration of the promoter is higher than 20-30% with respect to the fuel, while it only takes 0.6% of the fuel concentration for a chain-initiation promoter to show significant effects. As the conclusion of this estimation, they suggest the initial radical concentration provided by the promoter to be 0.5-5% with respect to the total fuel for a chain-thermal promotion and 20-30% for a pure thermal promotion.

4.2.2 Previous Work

Comprehensive studies of various ignition promoters for methane have been reported by Zamansky and Borisov [24], as well as by Golovitchev and Chomiak [25]. Additives discussed in their studies include hydrogen, high-order hydrocarbons, nitrocompound, hydrogen peroxide, ozone, and dimethyl ether.

1) Hydrogen

a) Efficiency of Hydrogen in Homogeneous System

Chen and Oppenheim investigate the ignition delay time of methane-hydrogen-oxygen mixtures diluted with argon using a reflected shock technique. The experimental conditions cover temperatures from 800 to 2400 K and pressures from 1 to 3 atm. A generalized Arrhenius type empirical equation is obtained by fitting experimental data with a non-linear regression method for both methane and hydrogen. It is observed that the global activation energy of the mixture is proportional to the ratio between concentration of CH_4 and H_2 . Their proposed expression for ignition delay time of methane-hydrogen mixtures is

$$\tau = \tau_{CH_4}^{(1-\varepsilon)} \tau_{H_2}^{\varepsilon} \tag{4.1}$$

where ε is the mole fraction of hydrogen in the total fuel. The correlation incorporates the expression for both the ignition delay for methane, τ_{CH4} , and the ignition delay for hydrogen, τ_{H2} , which come from their respective correlation equations with a general formula

$$\tau = A[fuel]^{x}[O_{2}]^{y} \exp(E/RT)$$
(4.2)

The empirical coefficients x, y, A, E are listed in table 4.1.

	x	У	Α	E (kJ/mole)
CH ₄	0.48	-1.94	$1.19E^{-12}$	194.0
H ₂	0.145	-0.56	1.54E ⁻⁴	71.9

Table 4.1 Correlation coefficients for methane and hydrogen ignition delay by Oppenheim et al. Here, T is the initial temperature in K and R is the universal gas constant in kJ/mol. concentrations of reactants are in mol/cm³, which can be calculated from the initial partial pressure and temperature.

The ignition delay time calculated according to above equations for a premixed methanehydrogen-air reaction system is shown in figure 4.1.



Fig.4.1 Comparison of ignition delay time for stoichiometric methane-air mixture using Oppenheim's equation with different hydrogen concentrations at 1 atm.

It can be seen that at 1 atm and 1000 K, with 15% methane replaced by hydrogen, the ignition delay time predicted by equation (4.1) is 4 times lower than the promotion free mixture, while it is less than 2 times lower when the temperature exceeds 1500 K. Further reduction can be achieved with higher concentrations of hydrogen. With 35% hydrogen added at 1000K the predicted ignition delay is reduced by nearly an order of magnitude compared with that of pure methane.

b) Efficiency of Hydrogen in Diffusive System

The monotonic increase of promotion with increasing hydrogen concentration found in Oppenheim's experiment is not observed in the study carried out by Fotache et al. [18]. They test the ignition temperature of hydrogen enriched methane by heated air using a variable-pressure counter-flow facility. Unlike the shock tube experiment aforementioned, Fotache's experiment is designed to study the non-premixed diffusive system. Besides finding a substantial decrease of ignition temperature by adding H_2 to the jet flow of fuel composed of methane and nitrogen, they have also observed three distinct regimes of promotion efficiency in terms of hydrogen concentration in the fuel.

- Hydrogen-assisted ignition regime, for hydrogen concentration below 6-7%, in which the ignition of methane is facilitated by the hydrogen addition. But by replacing methane with nitrogen on the fuel side makes the hydrogen fail to ignite.
- Transition regime (7 to 30% hydrogen concentrations). In this regime the reduction of ignition temperature grows with increasing hydrogen concentration. Unlike in the hydrogen-assisted regime, replacing methane with nitrogen reduces the ignition temperature of hydrogen.
- Hydrogen-dominated regime, for hydrogen concentrations in excess of 30%, in which the ignition temperature converges to nearly 934 K despite the further increase of hydrogen proportion in the fuel.

An analysis of the system response curve reveals that in the first and second regimes, the thermal feedback plays an important role in the ignition process while the third regime is mainly dominated by the kinetics.

The residence time in their experiment is 10-100 ms, which is much longer than that of shock tube experiments. Residence time in the latter is usually less than 10 ms. The largest reduction brought about by hydrogen addition occurs when the hydrogen concentration is under 15% of the total fuel. Above that, little further reduction can be achieved even by increasing the hydrogen proportion over 35%.

The dominant ignition chemistry involved in the reactions is discussed in the same paper. The difficulty of methane ignition is largely attributed to the competition between a major chain branching reaction

$$CH_3 + HO_2 \Longrightarrow OH + CH_3O \tag{4.R1}$$

and the recombination step

$$CH_3 + CH_3 + (M) => C_2H_6 (+M).$$
 (4.K2)

(1 0 0)

The direct result of this competition is that the chain branching efficiency is weak, and the thermal feedback is required to speed up the forward reaction to achieve ignition. However, the appearance of hydrogen in the system yields extra H radicals through the reaction with OH radicals coming from fuel decomposition.

$$OH + H_2 => H + H_2O$$
 (4.R3)

This reaction is highly exothermic and the H radical generated is more active than the CH_3 radical generated in the initiation stage of methane oxidation.

$$OH + CH_4 \Longrightarrow CH_3 + H_2O \tag{4.R4}$$

The oxidation process can be greatly facilitated by hydrogen addition for the above reasons. However, it is obvious that the reaction (4.R3) must compete with reaction (4.R4) for OH radicals. Moreover, the H radical may recombine with methane to form methyl

$$H + CH_4 \Longrightarrow CH_3 + H_2 \tag{4.R5}$$

Reactions (4.R4) and (4.R5) are the main reasons why significant inhibitive effect is found by methane on hydrogen ignition in homogenous system where abundant CH_4 is available to scavenge the H radicals. While in the diffusion system, as pointed out by Fotache et al., the higher diffusivity of hydrogen might help to separate its stoichiometric line from that of methane in the flow. In practice, using the counter flow facility, the stoichiometric location of hydrogen air mixture moves slightly towards the oxidizer side

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while that for methane is closer to the jet side. The separation yields a more dramatic promotion effect due to the partial de-coupling of hydrogen oxidation from reactions with methane. The role played by hydrogen is thus, partially, a pilot fuel in the diffusive system.

The pressure effect on ignition delay time from 0.2 to 8 atm was also studied in the Fotache's experiment. It is found that the ignition temperature decreases with the increasing pressure, while the difference due to the variation of the hydrogen concentration in the fuel become smaller at the same time.

c) Autoignition of Hydrogen at High Pressure

The existence of three explosion limits of hydrogen from classical hydrogen ignition theory indicates the peculiar nature of its oxidation rate which, unlike most other fuels, does not increase monotonically with temperature. The autoignition characteristics of hydrogen at high pressure are believed to relate directly to its behavior as an ignition promoter in the current experiment.

Gordon et al. [31] in their early shock tube study find that for pressures above 2 atm, the explosive mode of various hydrogen-oxygen-diluent systems can be found only when the temperature behind the reflected shock wave reaches over 1100 K. A similar observation is made by Voevodsky and Soloukhin [32], who report only weak ignition, or deflagration, could be established when the temperature is lower than the observed explosion limit.

Cain [26] investigates spontaneous ignition of hydrogen at pressures between 35 and 70 bars with a free piston compressor driven by compressed air. Hydrogen is mixed with oxygen and diluted with helium in the driven section. A computer model incorporating a hydrogen-oxygen reaction mechanism and gasdynamic features of compression process has been compared with experimental result, and good agreement has been reported. It is found that the spontaneous ignition (strong ignition according to his definition) happens during compression at a temperature well above that at which the third limit is normally placed. The measured and calculated temperature for this critical point is 1150 K and is insensitive to pressure. His study of the mechanism shows that at high pressure, the long induction periods of HO_2 and H_2O_2 retard the ignition until the temperature exceeds 1150

K, after which the rate of breakdown of H_2O_2 into OH is sufficient to initiate explosion. In terms of ignition delay time, their calculated values for stoichiometric H_2 - O_2 mixtures diluted by 30% helium at an initial temperature of 1100, 1200 and 1300 K are 770, 150, and 38 µs respectively. It is noticeable that the value at 1100K is much larger than that reported by Oppenheim whose experiment concentrates on low-pressures.

2) Higher-Order Paraffins

The effectiveness of higher-order paraffins such as ethane and propane on the ignition delay of methane have been studied in order to understand the difference in ignition characteristics between methane and natural gas.

Frenklach and Bornside conduct series of shock tube experiments on CH_4 -O₂-Ar mixtures with propane added. They find that the addition of a relatively small amount of propane is able to affect methane oxidation due to an increased amount of CH_3 radicals and H atoms brought about by propane decomposition. Specifically, within their experimental range from 1300 to 1600 K, 20% propane additive (with respect to methane) reduces the ignition delay by about a factor of 5, while the global activation energy remains unchanged.

Lifshitz and coworkers have reported from their early work the "unexpected result" that hydrogen is less efficient than propane in terms of promoting methane ignition. They rationalize this "singular" result by making the following assumptions: 1. The two ignition reactions (i.e., that of the additive and that of methane) are completely uncoupled. 2. The shortening of the induction time of methane is merely an outcome of the heat released by the ignition of the additive. The heat of combustion of propane (488 kcal/mol) is almost 8.5 times that of hydrogen (58 kcal/mol). Therefore, propane releases more heat and raises the reaction mixture to a higher temperature for the same volume percent addition.

These assumptions may not be completely correct from the viewpoint of kinetics, but the fact that heat addition plays an important role for promoters like hydrogen and propane has been confirmed both experimentally and computationally [2].

3) Nitrocompounds

Nitrocompounds, such as NO_x , $C_3H_7ONO_2$, $C_2H_5NO_2$, CH_3ONO_2 , are believed to be among the most effective ignition promoters [24]. These compounds work by quick decomposition via breaking of O-N bond or via fission of C_2H_5 radical to form H atoms as well as NO_2 or NO to enhance branching.

Dabora [24] use a reflected shock technique to measure the ignition of methane-air mixture with 0.12% NO₂ additive and achieve a 2-3 times shorter ignition delay. However, the restrictive requirement of limiting NO_x in engine emission clearly discourages using any of these compounds in practical engine applications.

4) Dimethyl Ether (DME)

Dimethyl ether has been used as an ignition promoter for methanol-fueled diesel engine by Karpuk et al. [25]. Its efficiency as a promoter for methane ignition has been explored numerically by Golovitchev and Chomiak. It is found that the initial reaction of DME at the presence of oxygen evolved into generating high concentration of H_2O_2 radicals, which, together with formaldehyde, CH_2O , are effective branching intermediates. The numerical simulation incorporating a detailed mechanism for methane and DME oxidation shows that by adding 5% DME, the ignition delay time of methane-air mixture at 40 atm can be reduced by about 5 times for a initial temperature at 1000K.

It should be pointed out that the vapor pressure of DME is low ($P_{sat} < 5$ atm). When mixed with methane, its partial pressure must be maintained lower than P_{sat} to prevent it from condensing. For a pressurized bottle of methane whose initial pressure is about 100 atm, the DME additive can not exceed 5% by volume.

Despite all aforementioned studies, we find an obvious lack of experiments on promoting methane ignition under high-pressure and low-temperature conditions, which are engine relevant. This motivated us to conduct experimental studies that can lead to results for direct engine applications.

4.3 **Results and Discussions**

4.3.1 Efficiency of Ignition Promotion for Hydrogen

The ignition delay times for 15% and 35% hydrogen balanced by methane (with respect to the total fuel) at 16 and 40 atm are shown in figures 4.2 and 4.3.



Fig. 4.2 Measured ignition delay time of methane with 0%, 15% and 35% hydrogen added at 16 \pm 2 atm Symbols: Diamonds – hydrogen free, triangles – 85% CH₄ 15% H₂, squares – 65% CH₄ 35% H₂. All tests are done for stoichiometric fuel-air mixture without dilution. Splines are used to indicate the trend of change.

It is clear that the reduction of ignition delay time given by hydrogen additive is much less dramatic than that predicted by equation (4.1). For an initial pressure of 16 atm and initial temperature around 1050 K the measured ignition delay with 35% hydrogen additive is only 3 times less than that of pure methane. The ratio reduces to about 2 when the initial temperature rises to 1350 K. At this pressure, it is found that the reduction achieved by adding 15% hydrogen is fairly close to that by 35% hydrogen addition. This confirms the observation in Fotache's experiment that by adding extra hydrogen the ignition temperature levels off as the system approaches a hydrogen-dominated regime. It is observed that at low temperatures, the ignition delay time of methane with 15% hydrogen additive deviates from that of 30% line and approaches that of pure methane.

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Fig. 4.3 Measured ignition delay time of methane with 0%, 15% and 35% hydrogen added at 40 \pm 2 atm a. Symbols: Diamonds– hydrogen free, Triangles– 85% CH₄ 15% H₂, squares – 65% CH₄ 35% H₂. All tests are done for stoichiometric fuel-air mixture without dilution. Splines are used to indicate the trend of change.

When the pressure is raised to 40 atm, the trend of measured ignition delay of methane without promotion is a reversed 'S' shape in the Arrhenius plot. From 1100 to 1200 K the ignition delay time is mostly insensitive to the variation of temperature. Below this temperature, it rises sharply. It is interesting to find that the trendline of the ignition delay time of methane with 15% hydrogen merges with that of pure methane for most of the temperatures range. The promotion effect of hydrogen does not appear until the temperature drops below 1030 K, from where an increasing reduction effect starts to show up. At the same time, prominent reduction can still be observed through the entire experimental temperature range for 35% hydrogen added.

For a given induction time of 2 ms, adding 35% hydrogen at 16 atm brings the ignition temperature down from 1080K to 1020 K, while at 40 atm the same amount of hydrogen will lower the ignition temperature by nearly 75 K to 975 K. This is significantly less than the over 200K reduction found in Fotache's experiment with the same amount of hydrogen added. This is likely due to differences in the ignition mechanisms between diffusive and homogenous ignition processes.

The obvious inefficiency of hydrogen in promoting methane ignition at high pressures can be rationalized in light of the chemical kinetics described earlier in this section. The abundance of CH_4 in a high-pressure stoichiometric homogenous methane/air system effectively impairs the formation of active H radical pools. Meanwhile, reaction (4.R2) as a major chain termination step, can be greatly facilitated with the high concentration of third bodies.

The noticeable increase of promotion efficiency with 35% hydrogen addition for temperatures over 1150 K agrees well with the results of Cain [26]. The dramatic increase of decomposition rate of HO₂ and H₂O₂ above 1150 K triggers the explosive mode with a significant ratio of thermal feedback that instantaneously promotes the ignition of the system. The precondition for this mechanism to work is that the system must have a high concentration of hydrogen initially, i.e., the system is in a hydrogen-dominated regime. For lower hydrogen concentration, formation of HO₂ and H₂O₂ radicals could be strongly influenced by the methane oxidation reactions, which possibly accounts for the small reduction in ignition delay found with 15% hydrogen added to the system.

Although the high pressure reduces the efficiency of hydrogen as an ignition promoter, it also results in an overall reduction of ignition delay time of the methane/methane-additive system as shown in figure 4.4.

The weakened promotion given by the additive is effectively compensated by the increasing overall reaction rate due to the higher concentration of all reactants.



Fig. 4.4 Measured ignition delay time of methane at 16 ± 2 , 30 ± 2 and 40 ± 2 atm with 35% hydrogen added. Symbols: diamonds - 16 ± 2 atm, triangles - 30 ± 2 atm, squares - 40 ± 2 atm. All tests are done for stoichiometric fuel-air mixture without dilution. Splines are used to indicate the trend of change.

4.3.2 Comparisons of Experimental and Computational Results

Numerical simulations incorporating detailed reaction mechanisms for both methane and hydrogen oxidation have been carried out for comparisons to these experiments. The CH_4 - H_2 -air kinetic mechanism is taken from GRI-Mech (version 3.0) [31]. That generates 53 intermediate species and 318 reaction steps. Chemkin-II (version 1.6) developed by Kee et. al. [32] of the Sandia National Laboratory is used as the mechanism interpreter. The differential equations in the model are solved using LSODE (1987 version) [33]. The condition in the experimental zone of the shock tube is modeled to be adiabatic and constant-volume. Gasdynamic effects induced by heat release and shock wave boundary layer interaction are neglected here. The onset of ignition is defined to be at the time when the maximum curvature on the P-t curve is found.

The calculated results are plotted in Figures 4.5 to 4.6 together with the experimental measurements.



Fig. 4.5 Comparison of computational results using detailed reaction mechanism and experimental measurements for P=16 atm. Lines represent computational results. Symbols represent experimental measurements: diamonds H₂ free, triangles – 85% CH₄ 15% H₂, squares - 65% CH₄ 35% H₂.

It can be seen that within the whole experimental range, the current mechanism largely over-predicts the global activation energies, which leads the calculated curves to be steeper than those of measured in the Arrhenius plots. The calculations intersect with the measurements at medium temperatures from 1100K to 1200 K. It under-predicts the ignition delay at high temperature by 4 times but over-predict it at low temperature by almost an order of magnitude. Moreover, the change of ignition delay time yielded by the mechanism in Arrhenius plot is nearly a straight line rather than a reversed S curve as shown by the experiments. Although there is an obvious disagreement between the computational and the experimental results, it is interesting to find that the mechanism shows a separation of reduced ignition delay time between 15% and 35% hydrogen addition for temperatures higher than 1100K, which is also observed in the experiments (more obvious at higher pressure).



Fig. 4.6 Comparison of computational results using detailed reaction mechanism and experimental measurements for P=40 atm. Lines represent computational results. Symbols represent experimental measurements: diamonds H_2 free, triangles – 85% CH₄ 15% H_2 , squares - 65% CH₄ 35% H_2 .

4.3.3 Efficiency of Ignition Promotion for DME

Shown in figures 4.7 and 4.8 are measured ignition delay time with 5% DME added at 16 and 30 atm respectively.

The results are rather disappointing when compared with Golovitchev's numerical model, which predicts a strong reduction for methane ignition delay by adding 5% DME for temperatures below 1200K. For the current experiments, DME shows only moderate effects on reducing the ignition delay of methane at high and low temperatures, and even a modestly inhibitive effect at around 1100 K. Further studies are considered necessary for the mechanism to involve DME and methane oxidations at high pressure.



Fig. 4.7 Measured ignition delay of methane with 5% DME added at $P=16\pm 2$ atm. Symbols: diamonds – DME free, squares – 5% DME 95% CH₄ All tests are done for stoichiometric fuel-air mixture without dilution. Splines are used to indicate the trend of change.



Fig. 4.8 Measured ignition delay of methane with 5% DME added at $P=30\pm2$ atm. Symbols: diamonds – DME free, squares – 5% DME 95% CH₄ All tests are done for stoichiometric fuel-air mixture without dilution. Splines are used to indicate the trend of change.

4.3.4 Strong Ignition Limit of Methane with Additives

Three distinctive ignition patterns for methane and methane-additives (i.e., mild ignition, transition from mild to strong ignition and strong ignition) are observed in the current study as shown in figure 4.9.



Fig. 4.9 Pressure histories of methane and methane-hydrogen ignition processes showing 3 distinctive ignition patterns ($P = 16 \pm 2$ atm): a. mild ignition with unique pressure peak; b. transition from mild to strong ignition; c. strong ignition causing sharp pressure rise and violate oscillation.

Additional hydrogen is found not only to shorten the ignition delay time of methane, but also to promote the entire combustion process. The peak pressure for methane – hydrogen mixture ignition is noticeably higher than that for pure methane ignition due to the faster reaction speed.

The changes of strong ignition limit by ignition promoters have been measured and shown in figure 4.10. It is found that an addition of 15% or 35% hydrogen to methane significantly reduces the strong ignition limit. Also, the pressure dependence of the strong ignition limit becomes more prominent for higher hydrogen fractions in the fuel. By increasing the pressure from 15 atm to 40 atm, we lower the strong ignition limit by nearly 200 K with 35% hydrogen added to methane. With the same pressure increase, the change of strong ignition limit for 15% hydrogen addition is just slightly over 100 K.



Meanwhile, 5% DME causes virtually no change to the strong ignition limit of pure methane at both high and low pressures.

Fig. 4.10 Strong ignition limit for methane with different hydrogen concentrations for pressures from 16 to 40 atm. Symbols represent experimental measurements. Solid line – strong ignition limit for methane with 35% and 15% hydrogen additions. Dashed line – measured strong ignition limit for pure methane and methane with 5% DME.

However, upon comparison with other conventional fuels whose strong ignition limits are usually less than 1000 K, we find that methane, even enriched with hydrogen, has the highest strong ignition limit, making it a safe and stable fuel for IC engines, and indicates the potential for increased thermal efficiency by rising IC engine compression ratios.

CHAPTER V

5.1 Conclusions

5.1.1 Shock Tube and Modeling

- 1) A one-dimensional model using non-constant specific heat for the shock tube calculation has been built up and modified according to experimental results.
- Comparisons between model predictions and experimental measurements have been carried out. The model has shown good agreement with the experimental results.
- 3) The uncertainty of the experimental temperature has been investigated. It is found that the uncertainty for calculated temperature is 5 to 7 K by using measured incident shock velocity and 9 to 13 K by using both measured incident and measured reflected shock velocities.
- 4) Disturbing effects for the constant experimental conditions resulting from the reflected shock/boundary layer interaction and the contact surface instability have been investigated numerically. The boundary layer cooling flow is found to shorten the experimental time for an incident shock velocity higher than 1020 m/s. The contact surface instability is found to have no significant effect on the current system.

5.1.2 Ignition Delay of Methane under Engine-Relevant Conditions

- Previous studies on methane ignition delay have been reviewed. The empirical equations derived in early experiments are found not suitable for use outside their respective experimental ranges.
- 2) High-pressure shock tube experiments on methane-air ignition have been carried out for temperatures from 1000 to 1400K and pressures from 16 to 40 atm with different equivalence ratios. Significant differences have been found between the current study and previous work due to the difference in experimental conditions.

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- A modified Arrhenius-type empirical equation for the measured ignition delay of methane has been derived assuming a non-constant global activation energy and variable pressure effects.
- 4) The effects on ignition delay of pressure, temperature, and concentrations of reactants are discussed based on the experimental measurements. The ignition delay of methane has been found to increase strongly with temperature and to decrease with pressure.
- 5) The strong ignition limit of methane-air mixture has been measured. It has been found to decrease with increasing pressure.
- 6) A computer model incorporating detailed reaction mechanism to simulate the ignition process in the shock tube has been compared to the current experiments. Disagreements have been found. Further tuning of the mechanism is suggested in order to match the experimental results.

5.1.3 Ignition Promotion for Methane under Engine-Relevant Conditions

- 1) A literature review on methane ignition promotion has been carried out. Mechanisms involving different promoters in various reaction systems have been discussed.
- 2) The efficiency of hydrogen at promoting methane autoignition for pressures from 16 to 40 atm has been investigated with a reflected shock technique. Hydrogen concentrations are selected at 15% and 35% with respect to the total fuel. It is found that at high pressure, the efficiency of hydrogen as an ignition promoter is much lower than that reported by previous work at low pressure.
- 3) Disagreement between the model prediction using the latest elementary chemical kinetic mechanism for methane-hydrogen-air reaction and experimental results has been found. The model largely over-predicts the global activation energy for the experimental conditions.

- 4) Efficiency of 5% DME in promoting methane ignition has been investigated in the current shock tube experiment. DME has been found to have a limited effect in promoting methane ignition within the experimental range.
- 5) Gasdynamic features associated with strong and mild ignition for different methaneadditive ignition processes have been examined. Hydrogen addition has been found to lower the strong ignition limit of methane, while 5% DME addition makes no change to the limit.

5.2 Problems with Current Experimental Apparatus and Shock Tube Upgrades

At low temperatures, an autoignition in the experimental region of the shock tube results in a deflagration and all the mixture is consumed slowly by a propagating flame front without generating a strong pressure rise. The detection of such a mild ignition by pressure transducers is sometimes difficult especially when it comes to determining the onset of the ignition process.

On the other hand, light emission associated with an ignition can be detected readily even if the ignition is a very weak one. The current experimental range can be extended by adding light detecting devices to the shock tube to help in observing low temperature ignitions. Also, the results achieved from the optical access can be used as an independent verification of the ignition delay time measured currently by using only pressure signals.

As a part of the future plan, with the help of more sophisticated optical devices, we hope to observe the combustion process directly in the shock tube. It will greatly facilitate our study of natural gas direct injection as well as many other combustion systems.

Lower temperature also means longer ignition delay time. Besides maximizing the experimental time by obtaining tailored interface, we can also extend it by increasing the length of the shock tube. Optimization is needed to find the best proportion between the driver and the driven section for a given total length of the shock tube.

5.2.1 Design of Shock Tube Optical Access

The working principle of the optical access being designed currently is shown in figure 5.1.

The optical access includes a quartz window, which can be mounted on a through hole on the shock tube to allow light emissions to be transmitted and also to withstand the highest pressure and temperature in the shock tube during ignition tests. The signal is picked up by an optical fiber mounted right behind the quartz window and conducted to a photomultiplier. The function of the photomultiplier is to amplify the received light signals and to convert them into standard electric signals with corresponding characteristic frequencies. A bandwidth filter is then used to filter out signals of unwanted frequencies and leave only those in which we are interested. Finally the signal is transferred into the data acquisition system and stored in a computer.



Fig.5.1 Schematic of the shock tube optical access system

As a part of the optical access, the quartz window is to be designed in such a way that it can be easily fitted in and/or removed from the existing pressure taps on the driven section of the shock tube. No significant variation of the present configuration of the shock tube is necessary. The window should have a good transmittance value so that interesting bandwidths can be readily detected by the optical instrument installed behind it.

First we need to calculate the maximum pressure in the driven section in order to decide the thickness of the quartz window. For a high-temperature ignition the process goes so fast that a detonation occurs, which ignites all the mixture at the end of the driven section almost simultaneously. In such a case, the driven has little time to expand because of the extremely fast rate of combustion. The process can be modeled as an adiabatic constantvolume combustion problem. The maximum pressure is calculated from the adiabatic flame temperature and the known initial pressure and temperature using the ideal gas law. The adiabatic flame temperature of the mixture can be calculated by the conservation of energy. A general equation for the combustion of CH_4 in air/oxygen can be written as

$$CH_4 + a_1O_2 + a_2N_2 \rightarrow bCO_2 + cH_2O + dCO + eO_2 + fH_2 + gN_2 + hNO + qCH_4.$$
 (5.1)

For this equation, we assume the initial mole number for methane is 1. Three dissociation reactions, which happen simultaneously, are

$$2CO_2 \Leftrightarrow 2CO + O_2 \tag{5.2}$$

$$2H_2 O \Leftrightarrow 2H_2 + O_2 \tag{5.3}$$

$$N_2 + O_2 \Leftrightarrow 2NO.$$
 (5.4)

Eqs (5.2) - (5.4) have their own equilibrium constants, which are functions of the reaction temperature and pressure, determining the final composition of the products. A computer model has been built to solve Eqs. (5.2)-(5.4) simultaneously and to iterate with temperature T to satisfy the energy conservation based on Eq (5.1) (See appendix E for details).

The condition in the experimental region is modeled as constant volume so that the ideal gas law simplifies to:

$$\frac{P_5}{T_5} = \frac{P_{flame}}{T_{flame}}.$$
(5.5)

The maximum initial pressure P_5 is set to be 95 atm. The initial temperature T_5 is decided by the maximum experimental temperature reached so far, which is about 1500 K. The adiabatic flame temperature is found to be from 3072 K (with 3 dissociation reactions) to 3324 K (complete reaction) under these initial conditions. (In a real shock tube experiment, the short residence time prevents the system from reaching complete equilibrium, so that the real temperature should lies between the equilibrium temperature and the complete reaction temperature.). The calculated maximum pressure using Eq. (5.5) is 210 atm at the end of the driven section.

The thickness of the quartz window is obtained by an empirical equation designed specifically for calculating the rupture pressure of a quartz plate. For a plate with a clamped edge, the equation is

$$P = 2.28S_{\rm max} \frac{t^2}{r_0^2},\tag{5.6}$$

where S_{max} is the maximum tensile stress, (with a safety factor of 10, this value is approximately 4.8×10^6 Pa); 'r_o' is the unsupported disc radius which is determined by the radius of the pressure tap (3 mm), and t is the disc thickness. Substituting the maximum pressure from the above calculation we get a minimum window thickness of 4.19 mm. Considering the load is a shock rather than a steady one, we apply an extra safety factor of 2 on the base of 4.19 mm, which makes the final window thickness 8.38 mm.

From the average transmittance curve for fused quartz we found that a quartz window is very effective in transmitting light in the visible as well as parts of the infrared ranges. For a 10 mm thick window, the transmittance is nearly 90% for wavelengths from 270 nm to 2.5μ m. This is ideal to detect CH and OH emissions whose wave lengths are 432 nm and 307 nm respectively. But the transmittance drops quickly outside this range. This

makes a quartz window much less efficient in transmitting CO_2 emission at 4.2µm (the value of transmittance ranges from 50% to 10% depending on the type of the quartz).

5.2.2 Length Calculation for Increasing Experimental Time

The variation of the experimental time with respect to different driver and driven section lengths is shown in figure 5.2. The initial pressure ratio for this case is 35 and the incident shock velocity is 890 m/s, which represents conditions of a low-temperature experiment.

The lower-left corner of the mesh is the current shock tube length (3.086m driver section and 4.255m driven section).





It is interesting to find that the experimental time can be increased almost linearly with extra-length added to the driver section. By adding 2 meters to the driver section and keeping the current driven length, we increase the experimental time by nearly 2 times. However an extra length to the driven section decreases the experimental time, especially

when the driver section is long. It is understandable that for a long driven section the incident shock wave takes a longer time to travel to the end wall, while the average velocity of the reflected rarefaction fan is higher than that of the incident shock wave so that the absolute time from the shock reflection to the arrival of the rarefaction fan becomes shorter. For an extreme case of a very short driven section and a very long driver section, the reflected rarefaction fan may catch up with the incident shock wave before it reflects so that the experimental time drops to 0. The same trend is also observed for higher initial incident shock velocities within the current experimental range.

However, a long driven section does help to increase the distance between the end wall and the reflected-shock-stopped contact surface so that disturbances such as boundary layer cooling flow take longer to start affecting the end wall area. When choosing a new length for the shock tube, comprehensive considerations are necessary to reach an optimal solution for different experimental ranges.

5.3 Recommended Future Work

- 1) Complete the design and installation of the shock tube optical access to be used in future experiments.
- Use the shock tube to study the combustion process with natural gas direct injection or HPDI systems.
- 3) Further test the ignition promotion of premixed and non-premixed natural gas by using different additives.
- 4) Design a more sophisticated optical access and install image capture devices on the shock tube for a deeper study of various combustion phenomena.
- 5) Redesign major shock tube components (change the slot design of the diaphragm and change the driver and driven section lengths) to improve the repeatability and accuracy of experimental measurements as well as to broaden the experimental range.

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Appendix A

Method of Characteristics

A.1 Characteristics of Isentropic Wave

Equation (2.23) tells us that for any isentropic wave, the value of λ is constant. It does not vary in time or space with the movement of the wave provided that isentropic conditions are satisfied. In the shock tube experiment, isentropic expansion waves may travel in the same or opposite directions as that of the fluid. We'll treat these two situations separately.

A.1.1 Right Moving Wave

We define the positive flow direction being from left to right. A right moving wave travels in the same direction of the fluid. For a flow velocity U and local sound speed a, the absolute velocity of the wave is U+a. The wave causes a small disturbance of fluid properties behind it as shown in figure A.1.



Fig. A.1 Right moving isentropic wave: (a) laboratory-fixed coordinates (b) wave-fixed coordinates

First we transfer from absolute coordinates to wave fixed coordinates. Using the same approach solving the continuity and momentum equations as we have done before, we find that for the right moving wave, the characteristic value λ is as follows:

$$\lambda = a + \frac{\gamma - 1}{2}U = const. \tag{A.1}$$

We therefore call the right moving wave a λ wave and the velocity of such a wave in the absolute coordinates is

$$\left(\frac{dx}{dt}\right)_{\lambda} = U + a. \tag{A.2}$$

A.1.2 Left Moving Wave



Fig. A.2 Left moving isentropic wave. (a) laboratory-fixed coordinates (b) wave-fixed coordinates

We can deal with a left moving wave using a similar method. For this wave, we find its characteristic value, which we call it β , is given by

$$\beta = a - \frac{\gamma - 1}{2}U, \tag{A.3}$$

and the absolute wave velocity is

$$\left(\frac{dx}{dt}\right)_{\beta} = U - a. \tag{A.4}$$

We call this left-moving wave a β wave.

A.2 Description of Rarefaction Fan with λ and β .

For any isentropic wave, the value of λ or β remains the same as it propagates undisturbed along the flow field. The rarefaction fan being composed of a series of such expansion waves can be readily described by these elemental waves. Since any point in the rarefaction fan, such as its leading edge, has its unique characteristic value that does not change in time, we can locate such a point at any moment, by finding where in the flow field this characteristic value exists.

We first describe the velocity field of the fluid in terms of λ and β . With equation (A.1) and (A.3), it is easy to show

$$U = \frac{\lambda - \beta}{\gamma - 1} \tag{A.5}$$

and

$$a = \frac{\lambda + \beta}{2}.$$
 (A.6)

Substituting Eqs. (A.5), (A.6) into Eqs. (A.2) and (A.4), we rewrite the absolute propagation speed of the wave as

$$\left(\frac{dx}{dt}\right)_{\lambda} = B\lambda - A\beta \tag{A.7}$$

$$\left(\frac{dx}{dt}\right)_{\beta} = A\lambda - B\beta \tag{A.8}$$

where A= $(3-\gamma)/2(\gamma-1)$ and B= $(\gamma+1)/2(\gamma-1)$.

A.3 Numerical Scheme

We now discuss the transport of wave characteristics in a one-dimensional mesh space with respect to time.

A.3.1 Subsonic Flow

For a subsonic flow, the local sound velocity is higher than the flow velocity. For a flow traveling from left to right, the λ wave should propagate down-stream to the left and the β wave should move upstream to the right as shown in figures A.3 and A.4 respectively. For a certain node point i at time t, we need to find out the value of λ and β in the next time step, so that all other properties, such as flow velocity, can be calculated. A linear interpolation method, which has the first-order accuracy in both time and space, has been used here.



Fig. A.3 Time-space mesh for a subsonic λ wave

At certain time t, the characteristic λ at node points i and i-1 are denoted by λ_i and λ_{i-1} respectively. After a small time step Δt , these two λ waves move downstream to new locations, which are given by

$$x_{i-1}^{n+1} = x_{i-1} + V_{i-1}\Delta t \tag{A.9}$$

and

$$x_i^{n+1} = x_i + V_i \ \Delta t. \tag{A.10}$$

Here V is the absolute velocity of the λ wave; n denotes nth time step and i denotes ith node point. We can find the new value of λ_i at t+ Δt by interpolating between these two points.

$$\lambda_{i}^{n+1} = \lambda_{i}^{n} - \frac{V_{i} \Delta t}{x_{i}^{n+1} - x_{i-1}^{n+1}} (\lambda_{i}^{n} - \lambda_{i-1}^{n})$$
(A.11)

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Substituting Eqs. (A.9) and (A.10) into Eq. (A.11) and adopting an explicit 1^{st} order Euler's scheme to evaluate V_i and V_{i-1} at time t, we achieve

$$\lambda_i^{n+1} = \lambda_i^n + \frac{\frac{\delta x}{\Delta x}}{1 + (V_i^n - V_{i-1}^n)\frac{\Delta t}{\Delta x}} (\lambda_{i-1}^n - \lambda_i^n)$$
(A.12)

where

$$\frac{\delta x}{\Delta x} = \frac{\Delta t}{\Delta x} V_i = \frac{\Delta t}{\Delta x} \left(\frac{dx}{dt} \right)_{\lambda} = \frac{\Delta t}{\Delta x} \left[B \lambda_i^n - A \beta_i^n \right]$$
(A.13)

and

$$V_i^n = B\lambda_i^n - A\beta_i^n \tag{A.14}$$

$$V_{i-1}^{n} = B\lambda_{i-1}^{n} - A\beta_{i-1}^{n}.$$
 (A.15)

Substituting Eqs. (A.13), (A.14) and (A.15) into Eq. (A.12) and rearranging, we obtain a formula for the λ wave at point i and time t+ Δ t:

$$\lambda_i^{n+1} = \lambda_i^n + \frac{(A\beta_i^n - B\lambda_i^n)}{\frac{\Delta x}{\Delta t} + B(\lambda_i^n - \lambda_{i-1}^n) - A(\beta_i^n - \beta_{i-1}^n)} \left(\lambda_i^n - \lambda_{i-1}^n\right)$$
(A.16)

The analysis for a subsonic β wave is exactly the same as that for λ wave except that the β wave is evaluated from the down stream information. The schematic of the t-x mesh is shown in figure A.4. The expression for updating β (omitting the proof) is:
$$\beta_i^{n+1} = \beta_i^n + \frac{(B\beta_i^n - A\lambda_i^n)}{\frac{\Delta x}{\Delta t} + B(\beta_{i+1}^n - \beta_i^n) - A(\lambda_{i+1}^n - \lambda_i^n)} \left(\beta_{i+1}^n - \beta_i^n\right)$$
(A.17)



Fig. A.4 Time-space mesh for a subsonic β wave

A.3.2 Supersonic Flow

If a supersonic flow moves from left to right, for a λ wave the solution is exactly the same as that for the subsonic flow. However, for a β wave the situation is sonewhat different. Because the flow speed is higher than the local sound speed, no information can travel upstream from the right. We can only evaluate β from left of the node.



Fig. A.5 Time-space mesh for a β wave in a supersonic flow from left to right

The wave move from left to right with a velocity $(dx/dt)_{\beta}$ =U-a. Interpolation at point i and time t+ Δt yields

$$\beta_{i}^{n+1} = \beta_{i}^{n} + \frac{(B\beta_{i}^{n} - A\lambda_{i}^{n})}{\frac{\Delta x}{\Delta t} - B(\beta_{i}^{n} - \beta_{i-1}^{n}) + A(\lambda_{i}^{n} - \lambda_{i-1}^{n})} (\beta_{i}^{n} - \beta_{i-1}^{n})$$
(A.18)

On the other hand, if the supersonic flow moves from right to left as that shown in figure A.6, we have to rewrite the expression for the λ wave.



Fig. A.6 Time-space mesh for a λ wave in a supersonic flow from right to left

In summary, when the absolute wave velocity is positive, we evaluate the next time step with information coming from upstream; when the absolute wave velocity is negative, we use downstream information to predict the characteristic value at the next time step. With an explicit scheme, the CFL number, which is defined as $U\Delta t/\Delta x$ should always be less than one in order to achieve computational stability. Here, U is the velocity of the fluid or wave, Δt is the time duration in one time step, and Δx is the length between two consecutive nodes. This means the displacement of the fluid or wave in one time step can not exceed the size of a unit mesh. In our case, the maximum velocity occurs for a wave traveling in the flow direction. We can calculate the corresponding maximum time for each time step, which is given by

$$\Delta t_{\max} = \frac{\Delta x}{a + |U|} \tag{A.20}$$

A.4 Boundary Conditions

We apply the method of characteristics for driver gas expansion from the contact surface to the end of the driver section. The contact surface is moving at a constant velocity U_3 , which can be calculated by the method introduced in 2.4.1. At the contact surface we can calculate the value for λ and β as our right boundary condition (assuming the shock wave is traveling from left to right), with

$$\lambda_c = a_3 - \frac{\gamma - 1}{2} U_3 \tag{A.21}$$

and

$$\beta_c = a_3 + \frac{\gamma - 1}{2} U_3, \tag{A.22}$$

where a_3 denotes the local sound speed for the driver gas at the contact surface. The specific heat ratio γ for the driver gas is assumed constant. The location of the contact surface at any given time is calculated by

$$x_c = U_3 t. \tag{A.23}$$

At the end of the driver section, a wall condition applies. The velocity drops to zero so that

$$\lambda_{wall} = \beta_{wall} \tag{A.24}$$

where β can be evaluated from Eq. (A.18) as we do for any other node point. The initial condition for the rest of the gas inside the driver section can be obtained from $a=a_4$ and U=0. That gives

$$\lambda_{ini} = \beta_{ini} = a_4 \tag{A.25}$$

One extra initial condition we consider is choked flow at the exit of the driver section when the down stream flow is supersonic. According to nozzle flow theory, when the flow reaches the local sound velocity no further acceleration can be achieved unless we expand the flow area downstream of the choking point. We may or may not have choking when the diaphragm bursts depending on whether the flow is locally supersonic or subsonic. If the flow velocity U_3 is subsonic, free expansion is allowed from P_4 to P_3 . However, if U_3 is supersonic, we need to set the initial velocity at the exit of the driver section so that

$$U^* = a^*,$$
 ...(A.26)

where the asterisk denotes the diaphragm location. The initial condition tells us

$$\beta_0 = a_4, \tag{A.27}$$

where 0 denotes the location of the right boundary. According to Eq. (A.3), we solve for

$$a^* = U^* = \left(\frac{2}{\gamma + 1}\right)a_4. \tag{A.28}$$

Finally, we write the formula for λ and β at the choking point as

$$\lambda_0 = U^* - \frac{\gamma - 1}{2}a^* = \frac{1}{\gamma + 1}a_4 \tag{A.29}$$

and

$$\beta_0 = U^* + \frac{\gamma - 1}{2}a^* = a_4 \tag{A.30}$$

Appendix B

Uncertainty of Calculated Experimental Temperature

B.1 General Formula

The general formula of the uncertainty for a calculated value R, for which $R = f(x_1, x_2, ..., x_n)$, is

$$w_{R} = \left[\left(\frac{\partial R}{\partial x_{1}} \right)^{2} w_{1}^{2} + \dots \left(\frac{\partial R}{\partial x_{n}} \right)^{2} w_{n}^{2} \right]^{1/2}$$
(B.1)

where $w_1...w_n$ are the respective uncertainties of independent variables $x_1...x_n$.

B.2 Uncertainties for Measured Shock Velocities

The shock velocity is calculated from

$$U_{s} = X_{s} / t_{s}. \tag{B.2}$$

Here U is the velocity in m/s; X is the distance between first and last sensor in meters; t is the time duration for the shock wave to travel between the two sensors in seconds. We estimate the error of measured distance by the formula

$$w_{x} = 0.002X + 0.002. \tag{B.3}$$

The second term in Eq. (B.3) comes from the radius of the sensor.

The sampling rate of the PCB pressure transducers has been set at 166.667 kHz , which converts to 6 μ s/sample, so that the uncertainty of the time measurement is

$$w_t = 6E - 6.$$
 (B.4)

Substituting Eq. (B.2) into Eq. (B.1), the uncertainty of calculated velocity U is

$$w_{U} = \left[\left(\frac{1}{t}\right)^{2} w_{x}^{2} + \left(-\frac{x}{t^{2}}\right)^{2} w_{t}^{2} \right]^{1/2}.$$
 (B.5)

For the incident shock, x from the current sensor configuration is 3.493 m and x for the reflected shock it is 0.151m. A typical experimental value for the incident shock velocity is 1000m/s and that for the reflected shock velocity is 380m/s. Using Eq. (B.2), we calculate the time for the incident shock, which is 0.00349s, and that for the reflected shock is 0.000378s. Substituting Eqs. (B.3) and (B.4) into Eq. (B.5) and using estimated x, and t, we obtain uncertainties for the incident and the reflected shock velocity. For the incident shock, w_u is 3.09m/s or 0.309% with respect to the incident shock velocity. In the current model, the experimental temperature is a function of the shock velocity. Given the uncertainty of the shock velocity in shock fixed coordinates, we can calculate the uncertainty of calculated temperature using the incident shock velocity is 5 to 7 K. The uncertainty increases to 9 to 13 K when the reflected shock velocity is also used in the calculation.

Appendix C

C.1 PCB Pressure Transducer Calibration

The PCB pressure transducer mounted at the end wall of the shock tube has been calibrated using the following method.

First we disconnect the driver section from the driven section and put in a diaphragm separating the driver section from the intermediate plate (see figure C.1). The end plate is then moved from the end of the driven section to the outer side of the intermediate plate. That forms a small chamber between the end plate and the diaphragm.

Secondly, we charge the driver section with compressed air to a pressure P. The value of P can be read from the static pressure transducer mounted on the driver section (with an error range of 5%). We then charge the small chamber to the same pressure by quickly opening the valve connecting the driver section and the small chamber. The pressure detected by the PCB transducer is recorded during this charging process. For the same pressure P, this reading is a function of the charging speed, which can be varied by changing the opening speed of the intermediate valve.

Finally, we plot the peak value of the sensor reading with respect to the time it takes for the pressure in the small chamber to reach P. The value of P hardly changes before and after charging the chamber since the volume in the chamber is much less than that in the driver section. The variation of peak readings as a function of the charging speed or time t for the same P is shown in figures C.2. It is found that the relationship is nearly linear. We then extrapolate the line to t=0 which represents the instantaneous rise of pressure behind the shock wave. The final pressure/voltage ratio, which varies very little for Ps from 15 to 44 atm, is found to be 63.2 atm/volt. This value is used in the current study to convert the initial sensor reading to the final pressure.



Fig.C.1 Schematic of the experimental configuration for calibrating the PCB pressure transducer mounted on the endplate.



Fig.C.2 Calibration Chart for the PCB Pressure Transducer (P=15 atm). The y axis is the reading from the PCB pressure transducer. The x axis is the time for the pressure rise.

Appendix D

A Computer Model for 2-D Compressible Boundary Layer Flow

The Mark and Davies model does not tell us to what extent the cooling gas is going to affect the overall temperature inside the experimental area. The thickness of the boundary layer remains unspecified. We don't know yet what is the real shape of the flow towards the reflected shock and whether this non-uniform velocity profile leads to problems in our application of the one-dimensional shock model.

Since the boundary layer flow behind the incident shock can be either laminar or turbulent, we will treat these two situations separately. Although it is very possible that the flow may go through the transition from laminar to turbulent, which is a highly complicated problem, our single-status analysis here can serve as the upper and lower limits when estimating the boundary layer thickness.

A two-dimensional numerical simulation of the flow behind the incident shock wave propagating in the shock tube has been carried out for both laminar and fully developed turbulent cases.

D.1 Governing Equations for Laminar and Turbulent Compressible Flows

D.1.1 Laminar Flow

For a laminar flow, a 2-D thin-layer compressible-flow Navier-Stokes equation proposed by Takano [12] has been employed, which is written as follows

$$\frac{\partial Q}{\partial t} + \frac{\partial E}{\partial x} + \frac{\partial F}{\partial y} = \frac{\partial S}{\partial y} + S_s$$
(D.1)

where

$$Q = \begin{pmatrix} \rho \\ \rho u \\ \rho v \\ e \end{pmatrix} \qquad E = \begin{pmatrix} \rho u \\ \rho u^2 + P \\ \rho u v \\ u(e+p) \end{pmatrix} \qquad F = \begin{pmatrix} \rho v \\ \rho u v \\ \rho v^2 + P \\ v(e+P) \end{pmatrix} \qquad S = \begin{pmatrix} 0 \\ \mu u_y \\ \frac{4}{3} \mu v_y \\ \frac{4}{3} \mu v_y v + \mu u u_y + kT_y \end{pmatrix}$$
(D.2)

The source term S_s for this laminar flow is 0.

Here t represents time, u and v are velocity components in x and y direction, μ is the viscosity coefficient and k is the heat conductivity. The pressure P is related with total energy e by

$$P = (\gamma - 1)[e - \frac{1}{2}\rho(u^2 + v^2)] = \rho RT$$
(D.3)

 μ and k are related by the equation

$$\frac{c_p \mu}{k} = \Pr = \frac{c_p}{(c_p + 1.25R)}$$
(D.4)

where Pt is the Prandtl number, c_p the specific heat and R the universal gas constant. The no-slip and constant temperature boundary conditions have been applied to the wall of the shock tube. The left boundary is a uniform flow behind the incident shock and the right boundary is a free inflow.

D.1.2 Turbulent Flow

For the turbulent flow, a modified k- ε model embedded into the laminar model has been used. Two extra equations have been added to equation (D.2) to calculate the turbulent kinetic energy and its dissipation rate. Eq. (D.2) then becomes

$$Q = \begin{pmatrix} \rho \\ \rho u \\ \rho v \\ \rho h \\ k \\ \epsilon \end{pmatrix} E = \begin{pmatrix} \rho u \\ \rho u^{2} + P \\ \rho uv \\ \rho uv \\ \rho uh \\ 0 \\ 0 \end{pmatrix} F = \begin{pmatrix} \rho v \\ \rho uv \\ \rho v^{2} + P \\ \rho vh \\ 0 \\ 0 \end{pmatrix} S = \begin{pmatrix} 0 \\ (\mu + \mu_{t})u_{y} \\ \frac{4}{3}(\mu + \mu_{t})v_{y} \\ (\mu_{t} + \frac{HT}{c_{p}})(\frac{1}{\phi}(\rho h)_{y} - \frac{h}{\rho}\rho_{y}) \\ (\mu + \mu_{t}/\sigma_{\epsilon})k_{y} \\ (\mu + \mu_{t}/\sigma_{\epsilon})\epsilon_{y} \end{pmatrix}$$
(D.5)

where k is the turbulent kinetic energy and ε is the dissipation rate of the turbulent kinetic energy. h is the total enthalpy given by

$$h = c_p T + \frac{1}{2} (u^2 + v^2);$$
 (D.6)

HT is the heat transfer coefficient in Eq. (D.1). σ_k and σ_{ϵ} are empirical coefficients taken to be 1.0 and 1.3. The turbulent viscosity μ_t is calculated from

$$\mu_t = C_{\mu} \rho \frac{k^2}{\varepsilon} \tag{D.7}$$

where C_{μ} is another coefficient equals 0.09 for a fully developed turbulent flow. For a viscous sublayer very close to the wall, the law of the wall applies. This layer is defined by

$$30 < \frac{yU_{\tau}}{v_{lam}} < 100 \tag{D.8}$$

where y is the perpendicular distance from the wall and U_{τ} is resultant friction velocity. In this region we know that

$$\frac{\tau}{\rho} = U_{\tau}^2 = \sqrt{C_{\mu}}.$$
(D.9)

Here, τ is the wall shear stress. The wall skin friction factor, s, which is defined by

$$s = \frac{\tau}{\rho V^2} \tag{D.10}$$

in which V is the fluid speed, is determined from the formula

$$\sqrt{s} = \frac{\kappa}{\ln(1.01 + E \operatorname{Re}\sqrt{s})} \tag{D.11}$$

where κ , the Kaman constant, is equal to 0.435, E, the wall roughness parameter, usually be set to 9.0 for smooth walls, an Re, the local Reynolds number, which is defined by the formula

$$\operatorname{Re} = \frac{V_{y}}{v_{lam}}.$$
(D.12)

For a given velocity and location, we can calculate, with some iterations, the value of s from Eq. (D.11) to solve for the wall shear stress in Eq. (D.10). Once τ is solved, we can get U_{τ} easily using Eq. (D.9) so that we can decide whether or not the fluid is in the sublayer defined by Eq. (D.8). If this is true, we can apply the law of the wall, which gives the turbulent kinetic energy and its dissipation rate by following formulas.

$$k = \frac{\tau}{\rho \sqrt{C_{\mu}}} \tag{D.13}$$

$$\varepsilon = \frac{0.1643}{\kappa} \frac{k^{1.5}}{y}.$$
 (D.14)

For a turbulent flow, we need to add source terms for k and ε , which are given by the general formula

$$S_s = S_c - S_l \phi \tag{D.15}$$

where ϕ represents k or ε .

For k source term:

1

$$S_c = \mathbf{v}_t \rho G \tag{D.16}$$

$$S_L = C_D C_\mu k \rho / v_t \tag{D.17}$$

where G is the turbulent generation rate given by

$$G = \left(\frac{\partial u}{\partial y}\right)^2 \tag{D.18}$$

for a 2D boundary layer flow.

For ε source term:

$$S_c = C_{\mu} C_D \rho k C_{1\varepsilon} G \tag{D.19}$$

$$S = C_{2\varepsilon} C_{\mu} C_{D} \rho k / v_{t}$$
 (D.20)

where $C_{1\epsilon}$ and $C_{2\epsilon}$ are also empirical coefficients set to be 1.44 and 1.92 respectively.

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D.2 Numerical Schemes

To solve equation (1), the splitting technique of finite difference method proposed by Takano has been adopted. Eq. (D.1) has been divided into three independent sub-equations.

$$\frac{\partial Q}{\partial t} + \frac{\partial E}{\partial x} = 0 \tag{D.21}$$

$$\frac{\partial Q}{\partial t} + \frac{\partial F}{\partial y} = 0 \tag{D.22}$$

$$\frac{\partial Q}{\partial t} - \frac{\partial S}{\partial y} = 0 \tag{D.23}$$

and in case of turbulence

,

$$\frac{\partial Q}{\partial t} - S_s = 0. \tag{D.24}$$

A second order Crank-Nicolson scheme is used to solve x-direction convection and ydirection diffusion. The y-direction convection term is solved using Beam-Warming scheme introduced by Pullian and Chaussee [13] for improving the numerical stability. A fourth order Rungae-Kutta scheme is used to solve the turbulent source term. For the first three schemes, a subroutine is written to solve the tri-diagonal matrix composed of flux jacobians using Thomas algorithm.

D.3 Computational Mesh

A 40x80 uniform mesh is generated for the laminar flow, and a 40x120 mesh is used for calculating the turbulent flow. Geometry of the computational domain is obtained from the current shock tube with selected length scales. Takano used transformation method to convert a uniform mesh to a non-uniform mesh to increase the resolution close to the wall. However, the transformation is not used in the current simulation because it leads to stability problems.

Since the observed ignition starts near the end wall of the driven section, we run our calculation up to the time when the reflected shock reaches 12 cm away from the end wall or roughly 0.43 ms after the passage of the incident shock. For a typical case, the calculated boundary layer thickness is a function of time for both turbulent and laminar flow as plotted in figure D.1.



Fig. D.1 Calculated boundary layer thickness versus time using laminar and turbulent models.

The boundary layer is defined as a layer of flow close to the side wall of the shock tube with it velocity less than 99% of the mean stream velocity. Two cases have been tested

for different initial conditions. The first one comes from a typical shock tube experiment whose initial pressure in the driven section is 5 psi and incident shock velocity is 1000 m/s. The Reynolds number of the flow behind the incident shock is 2.099×10^6 , which is well above the transitional condition for a pipe flow. It can be seen from the plot that the boundary layer thickness given by the turbulent model is much larger than that calculated from the laminar model due to the presence of turbulent viscosity. In reality, for a flow of such a large Reynolds number, the transition from laminar to turbulent happens within a very short distance, so presumably the real flow condition is closer to the line given by the full turbulent model. At a very low initial pressure, as in the second testing case, where the laminar equation can be confidently applied (Re<2300 for the pipe flow), the calculation shows a much thicker laminar boundary layer. The velocity profile of the laminar boundary is largely different from that of the turbulent boundary layer, which has a much fuller shape as illustrated in figure D.2.



Fig. D.2 Velocity profiles of laminar and turbulent boundary layers at 0.43 ms after the passage of the incident shock wave (or for the reflected shock to reach 12 cm from the end wall). The incident shock velocity for both cases is 1000m/s. The initial driven pressure for the turbulent model is 5 psi and that for the laminar model is 0.005 psi.

It is more meaningful for us to compare the displacement thickness of the laminar and turbulent boundary layer given their different shapes. The definition of the displacement thickness is

$$\delta^* = \int_0^\delta \left(1 - \frac{u}{u_e} \right) dy \tag{D.25}$$

where δ is the boundary layer thickness, u is the local velocity in the boundary layer and u_e is the free-stream velocity. At the same location as that in figure D2, the displacement thickness of the turbulent boundary layer is 0.75 mm, while that of the laminar boundary layer is 2.3 mm. The corresponding area ratio between displaced boundary layer and entire pipe cross section is 5% for the turbulent flow and 15.4% for the laminar flow.

Also revealed by the simulation is a phenomenon called thermal suction. This appears when a constant temperature boundary layer is applied to the wall of the shock tube. Since the wall temperature is much lower than the inner flow temperature, quick cooling happens close to the wall, which generates a pressure drop. The effect, when applied to the region behind the reflected shock, is beneficial because the pressure gradient between the inner and outer layers of the flow prevents the disturbing boundary layer stream from mixing quickly with the hot core of gas in the experimental area.

The simulation, although still a crude one, shows us that when the flow behind the incident shock is laminar, which may happen for very low initial pressure, the boundary layer thickness is much larger than that of the high pressure turbulent flow as we have in the current study. For the latter, we can likely neglect the boundary layer thickness in our calculation, especially for the region close to the end wall of the driven section.

Appendix E

A Computer Model for Calculating Adiabatic Flame Temperature for Methane-Air/Oxygen Reaction with Dissociation

E.1 Methodology

In reality, no chemical reaction can go along a single direction to a completion. There are always backward reactions that involve product recombination or dissociation. The equilibrium point at which the forward and backward reactions reach a balance shifts with the variation of temperature. This causes a corresponding change of final product compositions, and further affect the equilibrium temperature as well.

We now start to build a computer model for calculating the reaction temperature for methane oxidization at equilibrium. For a closed system the first law of thermodynamics tells us that there is no enthalpy loss, which means that that the total enthalpy of the products should be the same as that of the reactants at the beginning of the reaction no matter how the reactions take place. For ideal gases, enthalpies are only functions of T. Our final solution of T should, thus, satisfies the enthalpy conservation. While the final composition, which is decided by equilibrium constant K of reactions involved, is also a function of T. We thus start our calculation from guessing the final temperature. We use guessed T to calculate the product composition, then use the energy conversation to check the correctness of our guess and go iteration reguessing T until the conservation equation is balanced. The flowchart illustrating this procedure is shown in figure E.1.



Fig.E.1 Solution procedure for calculating the equilibrium temperature with dissociation

E.2 Reaction Equations

A general equation for the combustion of CH₄ in air/oxygen can be written as

$$CH_4 + a_1O_2 + a_2N_2 \rightarrow bCO_2 + cH_2O + dCO + eO_2 + fH_2 + gN_2 + hNO + qCH_4$$
 (E.1)

Here, we assume the initial mole number for methane is 1. For a given air/fuel ratio, denoted as λ , the mole number for oxygen a_1 is 2λ . If the oxidizer is air, we need to add nitrogen so that the coefficient a_2 equals to 7.52 λ , otherwise, a2 is just 0 for oxygen.

Three dissociation reactions, which happen simultaneously, are given by

$$2CO_2 \Leftrightarrow 2CO + O_2$$
 (E.2)

$$2H_2O \Leftrightarrow 2H_2 + O_2$$
 (E.3)

$$N_2 + O_2 \Leftrightarrow 2NO.$$
 (E.4)

E.2.3 Computer Model

In the current program, we use the concept of finite difference method to discrete single reactions. Instead of calculating all those reactions simultaneously, we can calculate one reaction at one step and use the calculate results to update the product composition. The next reaction happens on the basis of the previous one. After several iterations, we should see the final composition converges to a steady value, which is the solution for the equilibrium composition.

We start our calculation from assuming a complete reaction. We now discuss the product composition of methane combustion according to 3 different cases: a) fuel lean, b) fuel rich, and c) stoichiometric.

For the fuel lean case, the only products for this complete reaction are CO₂, H₂O, and excessive O₂ and N₂. Given λ , we can easily find their mole numbers by Eq. (1). It turns out that for 1 mole of CH₄ in the initial reactants the coefficients for the products are: 1 for b, 2 for c, (2 λ -2) and 7.52 λ for e and g. All other coefficients are 0.

For the fuel rich case, we have some excessive fuel in the products. Similar analysis shows that the system should end up with λ moles of CO₂, 2λ moles of H₂O, 7.52 moles of N₂ and (1- λ) mole of CH₄. Again, other coefficients in Eq. (E.1) are set to be 0.

When the initial mixture is stoichiometric, for a complete combustion, no excessive oxygen or methane can be found in the products. This case can be combined into either the rich or the lean case by setting the value of λ to be 1.

The total mole number of the products is achieved by summarizing all the coefficients of the products and mole composition of a certain product i is just y_i =mole_i/mole_{total}.

We then start to guess a temperature T, and find equilibrium constants for reactions (E.2) to (E.4) from the thermodynamic table [27]. Assuming the initial total mole number of all products is M_{total} , and mole numbers of reactants and products is M_a , M_b , M_c and M_d . At the state of equilibrium, ε moles of reactant 'a' have dissociated, so that the final mole fractions become:

$$y_a = \frac{M_a - \varepsilon}{M_{total}^{n+1}}$$
(E.5)

$$y_b = \frac{M_b - \frac{\varepsilon}{v_a} v_b}{M_{total}^{n+1}}$$
(E.6)

$$y_{c} = \frac{M_{c} + \frac{\varepsilon}{v_{a}}v_{c}}{M_{total}^{n+1}}$$
(E.7)

$$y_{d} = \frac{M_{d} + \frac{\varepsilon}{v_{a}}v_{d}}{M_{total}^{n+1}}$$
(E.8)

where

$$M_{total}^{n+1} = M_{total} + \frac{\varepsilon}{\nu_a} (\nu_c + \nu_d - \nu_a - \nu_b); \qquad (E.9)$$

 ν denotes stoichiometric coefficients. The equilibrium constant K is related to reactant fractions by

$$K = \frac{y_c^{\mathbf{v}_c} y_d^{\mathbf{v}_d}}{y_a^{\mathbf{v}_a} y_b^{\mathbf{v}_d}} \left(\frac{P}{P_o}\right)^{\mathbf{v}_c + \mathbf{v}_d - \mathbf{v}_a - \mathbf{v}_b}$$
(E.10)

where P is the total pressure and P_o is a reference pressure. When K is known, substituting Eqs. (E.5) to (E.8) into Eq. (E.10), the degree of reaction ε can be calculated using an iterative method.

We do this procedure from Eqs. (E.2) to (E.4) iteratively and update the product composition for each step. Finally, the equilibrium composition converges. The total enthalpy is calculated by

$$h_{total} = \sum M_i h_i \tag{E.11}$$

where M_i is the mole number of the ith product and h_i is its specific enthalpy at T.

E.2.4 Computational Results

We calculate the adiabatic flame temperature of methane-air mixture as a function of λ . The initial temperature of reactants is set to be 1500 K so that it matches the highest initial temperature behind the reflected shock wave achieved so far in our current experiment. The initial pressure is 95 atm. The result is plotted in figure E.2. We can see that the highest temperature appears for a stoichiometric mixture, for which T is 3072 K with 3 dissociation reactions. The peak value increases to 3324K when assuming complete reaction without dissociation. We use this temperature to calculate the corresponding maximum pressure in the experimental area.



Fig. E.2 Calculated equilibrium temperature as a function of λ . Solid line: complete reaction. Dotted line: with 3 dissociation reactions.

Appendix F

Thermodynamic Properties for Driver and Driven Gases in the Shock Tube

F.1 Specific Heat

The specific heat calculated from following equations is in kJ/kmol.K unless otherwise specified *.

The specific heat for oxygen and nitrogen is calculated using empirical equations listed in the table in Van Wylen and Sonntag's thermodynamic book.

Cp for O₂

$$Cp_{02}=37.432+0.020102\tau^{1.5}-178.57/\tau^{1.5}+236.88/\tau^2$$
(F.1)

Cp for N₂

$$Cp_{N2} = 39.060 - 512.79/\tau^{1.5} + 1072.7/\tau^2 - 820.40/\tau^3$$
(F.2)

Here τ is defined by T/100

Cp for air

$$Cp_{air}=0.21Cp_{O2}+0.79Cp_{N2}$$
 (F.3)

For temperatures below 298.15K, Cp_{air} is taken as a constant that equals 29.09. The specific heat for methane and hydrogen is calculated using empirical equations provided by Spencer et al..

Cp for H₂

$$Cp_{H2} = 4.186(6.947 - 0.2 \times 10^{-3} \text{T} + 0.4808 \times 10^{-6} \text{T}^2)$$
(F.4)

Cp for CH₄

$$Cp_{CH4} = (4.171 + 14.450 \times 0.001T + 0.267 \times 1e - 6T^{2} - 1.722 \times 1e - 9T^{3}) \times 4.186$$
(F.5)

Cp for He

Cp for helium is taken as a constant since the temperature for the driver gas is low.

$$Cp_{He}=20.81$$
 (F.6)

Cp for driver gas

Denote the helium fraction in the driver gas as Xhe, Cp for the driver gas is then

$$Cp_{drv} = XheCp_{He} + (1-Xhe)Cp_{air}$$
(F.7)

Cp for mixed fuel

For a mixture of CH_4 and H_2 , denote the mole fraction of H_2 with respect to the total fuel as ξ . Cp for the fuel can be written as

$$Cp_{fuel} = \xi Cp_{H2} + (1-\xi)Cp_{CH4}$$
(F.8)

Cp for driven gas

Denote the equivalence ratio in the driven gas as Φ . Cp for the driven gas is given by

$$Cp_{drn} = Cp_{fuel}\zeta/(\zeta+1) + Cp_{air}/(1+\zeta)$$
(F.9)

where ζ is the fuel/air ratio given by

$$\zeta = 0.21 \Phi / (0.5 \xi + 2(1 - \xi)). \tag{F.10}$$

F.2 Enthalpy

Enthalpy is calculated by integrating CpdT from 298.15K to the experimental temperature.

The enthalpy calculated from following equations is in kJ/kmol unless otherwise specified.

h for O₂

$$h_{O2} = 3743.2\tau + 0.80408\tau^{2.5} + 35714.0/\tau^{0.5} - 23688.0/\tau - 23911.058$$
(F.11)

h for N₂

$$h_{N2} = 3906\tau + 102558/\tau^{0.5} - 107270/\tau + 41020/\tau^2 - 39677.027$$
(F.12)

h for air

$$h_{air} = 0.21h_{O2} + 0.79h_{N2} \tag{F.13}$$

h for He

$$h_{\rm He} = 20.81(T - 298.15)$$
 (F.14)

h for driver gas

h _{drv} =h _{He} Xhe+h _{air} (1-	(Xhe) ((F.15))
uiv	/	·	

h for CH₄

 $h_{CH4} = 4.186 (4.171T + 14.450 \times 10^{-3}T^{2}/2 + 0.267 \times 10^{-6}T^{3}/3 - 1.772 \times 1e - 9T^{4}/4) - 7889.34$ (F.16)

h for H₂

$$h_{\rm H2} = 4.186 \ (6.947 \text{T} - 0.2 \times 10^{-3} \text{T}^2/2 + 0.4808 \times 10^{-6} \text{T}^3/3) - 8559.44$$
(F.17)

h for mixed fuel

$$h_{\text{fuel}} = \xi h_{\text{H2}} + (1 - \xi) h_{\text{CH4}} \tag{F.18}$$

h for driven gas

$$h_{drn} = [h_{fuel} \zeta / (\zeta + 1) + h_{air}] / (1 + \zeta)$$
(F.19)

F.3 Molecular Weight (denoted by M, unit kg/kmol) Molecular weight for driver gas

$$M_{drv} = 28.97(1 - Xhe) + 4.003Xhe$$
 (F.20)

Molecular weight for driven gas

$$M_{dm} = \{\zeta[2\xi + 16(1-\xi)] + 28.97\}/(1+\zeta)$$
(F.21)

* Cp and h used in the conservation equations are base on per kilogram. We need to convert Cp or h based on per mole calculated using above equations into the correct unit by dividing it with the molecular weigh.

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Append	ix G									
List of E	lxperiments	ul Conditio	ns and Re	sults						
File No.	P1	P4	He%	Vi	۷r	Tcal	Pcal	Pmea	Tau	1000K/T
35%H2 1	6 atm									
278	6.3	315	94.5	946.30	375.60	1029.09	15.49	16.81	1924.00	0.97
202	6.8	306	95	959.50	375.60	1049.19	17.44	16.75	1398.00	0.95
210	5.5	319	95.4	969.00	387.20	1064.07	14.54	14.68	1188.00	0.94
195	4.7	249	98.5	1009.00	387.20	1126.11	14.02	13.94	1086.00	0.89
211	5.4	324	96.5	1028.00	387.20	1157.57	17.07	17.00	936.00	0.86
* 213	5 D	310	97.5	1042.00	393.20	1179.25	16.43	16.11	852.00	0.85
* 212	5.1	316.2	97	1051.00	393.20	1194.46	17.21	16.88	840.00	0.84
* 214	4.8	326.4	98.5	1085.60	399.50	1250.06	17.78	16.86	522.00	0.80
* 196	4.7	305.5	66	1120.00	391.20	1307.71	19.06	14.83	396.00	0.76
* 197	4	280	66	1130.00	393.20	1324.70	16.65	14.93	348.00	0.75
* 198	4	320	<u> 99.9</u>	1141.00	412.60	1343.50	17.12	17.01	324.00	0.74
Pure CH4	t 16 atm									
288	6.2	297	<u> </u>	931.00	359.50	1023.00	15.60	16.21		0.98
#304	E	E	E	940.00	E	1034.00	14.10	14.00	1542.00	0.97
289	9	300	93	944.10	359.50	1043.00	15.80	16.31	3108.00	0.96
228	5.8	290	96	961.00	375.60	1070.06	15.89	16.21	1998.00	0.93
221	5.5	330	97.5	973.00	381.30	1088.71	15.64	15.17	2100.00	0.92
229	5.6	308	96.5	00.666	375.60	1129.46	17.23	16.52	1836.00	0.89
# 241	7.2	432	98	1001.20	370.10	1129.00	18.00	17.60	1320.00	0.89
232	9	300	6.66	1002.00	393.20	1133.59	18.61	18.59	1638.00	0.88
336	4.5	292.5	96.7	1035.80	381.30	1185.00	16.00	15.00	1368.00	0.84
222	5.5	330	97.5	1040.00	393.20	1195.87	19.09	17.45	1434.00	0.84
223	4.8	336	98.5	1073.00	412.60	1250.35	18.27	17.76	954.00	0.80
#224	4.5	337.5	66	1100.70	399.50	1295.65	18.41	16.52	1026.00	0.77
* 225	4.2	327.6	6.66	1106.50	405.90	1305.48	17.45	18.48	504.00	0.77
* 231	4	320	6.66	1117.00	405.90	1322.85	17.07	17.14	600.00	0.76
* 227	4.1	336.2	6.66	1137.00	412.60	1357.59	18.43	18.07	414.00	0.74
* 230	3.95	335.8	<u> 99.9</u>	1146.60	419.40	1374.43	18.19	17.86	444.00	0.73
Pure CH ²	4 23 atm									
239	0	405	95.5	953.00	370.10	1057.09	24.01	22.46	2100.00	0.95
240	8.5	425	96	980.40	375.60	1099.66	24.70	23.76	1698.00	0.91

2	6.8	408	95	981.30	370.1	1098.00	20.60	20.60	1560.00	0.91	
	7.8	429	97	1009.00	399.50	1144.90	24.70	23.92	1164.00	0.87	
	5.7	387.6	<u> 6</u> .66	1009.90	412.60	1143.00	24.00	24.00	1026.00	0.87	
	7.2	432	86	1044.00	370.10	1202.06	25.26	23.98	1023.00	0.83	
	6.7	435.5	98.5	1069.00	399.50	1242.05	25.15	24.05	794.00	0.81	
	5.7	387.6	<u>99.9</u>	1092.00	412.60	1281.48	22.81	22.75	624.00	0.78	
ღ	6.5	520	99.8	1113.60	412.60	1315.00	24.90	23.10	534.00	0.76	
9	5.9	442.5	<u> 6</u> .66	1126.00	419.40	1338.28	25.77	24.93	480.00	0.75	
4	5.6	476	<u>99.9</u>	1140.00	412.60	1363.80	25.39	25.42	462.00	0.73	
4 DME	. 15 atm										
	5.9	318	<u> </u>	961.50	370.10	1043.00	17.20	17.27			
	7.3	328.5	93.5	925.60	364.70	990.05	18.71	18.05	4512.00	1.01	
	6.3	315	92.1	930.00	370.10	00.766	16.60	17.34	4746.00	1.00	
	9	315	92.6	942.50	354.46	1015.00	16.50	17.54	2688.00	0.99	
	5.9	318.6	<u> </u>	952.50	375.60	1027.00	17.20	17.64	1998.00	0.97	
_	6.3	315	95	961.50	370.10	1043.33	18.13	17.66	2304.00	0.96	
	5.5	319	94.3	978.40	375.60	1066.00	17.30	17.72	2286.00	0.94	
	5.55	305.25	96	991.10	387.20	1088.23	17.49	17.29	2448.00	0.92	
	5.7	313.5	96	994.30	381.30	1093.14	18.14	17.41	2622.00	0.91	
	5.4	324	67	1028.00	399.50	1146.08	19.00	18.88	1260.00	0.87	
	4.7	305.5	98.5	1053.60	399.50	1185.97	17.77	17.45	1056.00	0.84	
	3.95	308.1	99.9	1055.80	393.20	1189.48	15.02	15.79	912.00	0.84	
	4.1	307.5	99.5	1102.20	412.60	1264.41	17.68	17.51	738.00	0.79	
2	3.95	335.75	99.9	1140.20	426.60	1328.04	18.80	19.42	288.00	0.75	
e CH4	30atm										.
	13.6	584.8	94	919.70	335.60	1006.36	32.56	32.87	2508.00	0.99	
	11.9	571.2	93.2	945.70	364.73	1043.00	32.20	33.30	2166.00	0.96	
	11.3	542.4	95	951.50	354.50	1054.78	30.00	30.03	1464.00	0.95	
	11.3	542.4	95	956.00	375.60	1061.71	30.44	30.03	1260.00	0.94	
	10.4	551.2	96.5	991.70	370.10	1117.44	31.28	31.11	1080.00	0.89	
	9.8	568.4	97.5	1018.90	370.10	1160.76	31.95	31.89	1050.00	0.86	
	8.7	548.1	98.5	1047.40	375.60	1206.97	30.78	30.78	888.00	0.83	
80	9.3	548.7	<u>99.9</u>	1057.80	399.50	1224.03	33.87	31.55	552.00	0.82	
63	10	600	<u>99.9</u>	1067.10	393.20	1239.40	38.70	35.90	534.00	0.81	
55	8	544	99.4	1085.80	412.60	1270.56	31.46	31.39	384.00	0.79	
4	7.5	562.5	98.7	1105.70	399.00	1301.00	32.20	31.90	570.00	0.77	
8	6.5	500.5	66	1107.30	399.50	1304.00	28.00	27.10	546.00	0.77	

0.76 0.75 0.75		0.98	0.95	06.0	0.92	0.92	0.88	0.84	0.83	0.83	0.78	0.75		0.97	0.95	0.93	0.88	0.85	0.80	0.78	0.66					0.97	0.95	0.95	0.94	0.89	0.85	0.79
474.00 468.00 426.00		2172.00	1226.00	1026.00	1974.00	1500.00	00.066	552.00	582.00	930.00	528.00	486.00		3246.00	1128.00	1152.00	1044.00	768.00	642.00	408.00	6.00					1908.00	1296.00	1212.00	1338.00	1260.00	966.00	558.00
31.02 28.20 30.77		39.40 40.40	39.00	39.80	39.76	39.95	41.00	39.75	38.38	40.00	38.60	37.02		31.36	29.89	28.78	30.47	28.96	26.44	30.53			30.20	29.10	29.20	29.30	29.00	29.60	29.10	29.30	28.20	29.60
31.69 29.40 30.64	38.60	39.30 38.70	38.20	40.20	42.23	41.87	43.50	41.01	39.60	40.60	40.55	41.38		31.90	32.20	30.70	31.70	30.60	31.90	31.50	44.20		31.60	30.80	31.70	31.00	31.60	31.10	31.10	30.50	29.90	30.70
1307.85 1335.00 1339.82	1026.00	1025.00	1050.00	1114.00	1083.57	1089.48	1140.00	1196.68	1201.41	1208.00	1289.90	1336.56		1033.00	1057.00	1080.00	1137.00	1179.00	1250.00	1281.00	1522.00		1009.00	1001.00	1047.00	1033.00	1054.00	1055.00	1064.00	1120.00	1177.00	1268.00
387.20 393.20 433.90	364.73	370.10 370.10	370.10	375.62	354.50	335.60	381.30	387.20	399.50	E	375.60	344.70		359.50	370.10	331.10	375.60	375.60	375.60	405.90	967.90		349.54	359.50	364.70	335.56	351.60	370.00	364.70	356.80	375.60	393.20
1107.40 1125.40 1126.60	934.70	935.7U 936.90	950.50	991.70	970.10	973.90	1007.60	1041.00	1044.00	1050.00	1097.30	1124.70		948.60	964.50	979.20	1015.70	1041.90	1085.60	1104.20	1241.60		925.20	933.50	950.10	940.10	954.50	955.00	960.80	996.60	1032.10	1087.10
99.9 99.9 99.9	93.2 00.7	93.5 93.2	93.5	95	95	95	96.5	97.7	98.3	92.9	99.9	99.9		92.9	93.3	94.3	95.5	96.8	97.6	99.1	99.2		93.2	92	92.8	93.5	93.4	<u> </u>	93.5	95.1	97	98.7
554.8 500.5 560	680.8 705	cu/ 680.8	681.1	704	720	735	731.5	731.6	768.4	584.2	780	712.5		584.2	585.6	555	566.5	552	552.5	560	600		578.1	590	581.4	575	582.4	583	588.5	570	546	555
7.6 6.5 7	4 40 atm 14.8	15 14.8	13.9	12.8	15	14.7	13.3	11.8	11.3	12.7	10	9.5	30 bar	12.7	12.2	11.1	10.3	9.2	8.5	ω	8	atm	12.3	11.8	11.4	11.5	11.2	11	10.7	9.5	8.4	7.4
* 254 * 333 * 253	Pure CH 391	403 369	368	370	#276	#271	275	#270	* # 264	* 286	* 262	* 272	35% H2	286	285	283	282	* 281	* 280	* 287	* 279	DME 30	418	306	308	417	310	307	305	303	* 302	* 301

0.79 0.78	01.0					0.91	0.91	06.0	0.88	0.84	0.83	0.81	0.80	0.76		0.91	0.76	0.88	0.77	0.74	0.88	0.93	0.89	0.75	0.77	0.87	0.84	0.89	0.95	0.97		0.87	0.84	0.81	0.81
558.00 636.00	00.000					1746.00	2976.00	1152.00	1170.00	978.00	792.00	552.00	702.00	462.00		1560.00	552.00	942.00	546.00	522.00	1830.00	1230.00	1098.00	468.00	570.00	00.066	1368.00	1596.00	1026.00	2466.00		2022.00	1482.00	1158.00	984.00
29.10 28.10	20.10	17.30	16.70	15.70	17.40	17.10	17.10	16.70	16.60	15.10	16.00	16.40	16.30	16.70		20.60	20.40	27.30	27.10	34.10	35.10	35.10	34.40	28.20	31.90	24.00	15.00	27.70	39.00	40.40		15.80	16.60	17.80	16.10
30.80 30.50	00.00	17.60	17.20	16.30	17.50	17.40	17.30	16.50	16.20	15.90	16.30	16.30	16.50	17.30		20.60	20.50	27.80	28.00	35.80	35.90	36.30	35.20	29.40	32.20	24.00	16.00	27.80	38.20	38.90		15.30	16.90	17.90	15.70
1269.00 1281.00	00.1021	1072.00	1111.00	1049.00	1083.00	1099.00	1097.00	1108.00	1140.00	1187.00	1202.00	1242.00	1252.00	1311.00		1098.00	1310.00	1139.00	1304.00	1353.00	1139.00	1073.00	1129.00	1335.00	1301.00	1143.00	1185.00	1127.00	1050.00	1029.00		1148.00	1192.00	1239.00	1241.00
393.20 303.20	07.000	364.73	364.70	359.50	387.18	359.50	381.31	975.60	399.50	397.40	381.30	393.20	387.18	415.00		370.10	399.00	375.60	399.50	393.20	364.70	375.00	364.70	393.20	399.00	370.00	381.30	381.30	370.10	370.10		375.62	387.18	387.20	399.47
1087.50 1004 70	01.4001	968.60	994.10	953.60	976.00	987.70	984.80	992.10	1012.00	1041.70	1050.10	1075.10	1080.80	1115.70		981.30	1110.70	1007.50	1107.30	1136.20	1007.00	965.50	1000.70	1125.40	1105.70	1009.90	1035.80	999.40	950.50	936.90		996.10	1022.60	1050.30	1051.50
98.7 08 6	0.00	95	94.6	95	95	95	95	94.6	96.2	96.7	97.2	98.3	98.8	99.1		95	99.5	95.7	66	99.8	95.5	94.7	95.5	6.66	98.7	95.5	96.7	97	93.5	93.2		96	67	97	98
555 525 6	77.0	344.4	324	300	300	300	307.4	324	325	292.5	315	315	306.6	320	0	408	376	510	500.5	616	627	630	627	500.5	562.5	452.6	292.5	461.1	681.1	680.8	7)	306	318.5	326.4	294
7.4	16 atm	6.15	5.4	9	9	9	5.8	5.4	5	4.5	4.5	4.2	4.2	4	14 Different F	6.8	4.7	8.5	6.5	7.7	1	12.6	1	6.5	7.5	7.3	4.5	8.7	13.9	14.8	an 16atm (0.	5.1	4.9	4.8	4.2
* 304	15% H2	321	314	405	407	405	322	316	313	337	312	* 311	*339	*318	Pure CF	325	*326	327	*328	*329	#330	331	332	*333	*334	335	336	364	368	369	CH4 Lei	348	387	363	347

0.76 0.73 0.73		0.94	0.93	0.92	0.92	0.92	0.90	0.87	0.85	0.81	0.77	0.72		0.98	0.96	0.95	0.93	0.89	#DIV/0!	0.80	0.77	0.74	0.71		1.01	0.92	0.87	0.83	0.80	0.78	0.77	1.02
690.00 696.00 606.00		4620.00	2154.00	1422.00	1392.00	1362.00	1464.00	1146.00	1092.00	822.00	714.00	448.00		1728.00	1668.00	1548.00	1416.00	1050.00	1068.00	798.00	694.00	534.00	456.00			2088.00	1014.00	978.00	720.00	624.00	612.00	2640.00
16.00 16.20 16.20		32.00	33.00	32.20	32.20	31.40	32.80	31.80	31.20	31.10	31.40	32.40		39.90	38.80	38.60	39.30	37.90	38.50	40.40	39.60	39.00	40.10			38.80	39.10	39.20	38.60	37.00	38.50	34.40
15.50 16.70 16.80		32.10	32.40	31.90	31.90	31.30	31.30	30.70	31.00	31.70	31.70	32.90		39.70	39.00	38.70	39.90	38.50	39.30	0.00	39.10	40.40	41.20		39.80	38.00	39.60	40.50	39.90	37.30	38.10	35.30
1310.00 1312.00 1369.00		1060.00	1073.00	1082.00	1082.00	1091.00	1111.00	1144.00	1178.00	1232.00	1293.00	1393.00		1019.00	1041.00	1048.00	1080.00	1126.00	00.0	1256.00	1291.00	1346.00	1406.00		992.00	1083.00	1148.00	1205.00	1243.00	1282.00	1295.00	982.00
399.00 m 381.30		370.10	370.10	364.73	349.54	370.10	343.96	375.62	375.62	370.10	399.47	399.47		370.10	370.10	349.54	354.46	370.10	373.76	393.23	405.91	375.62	419.44		349.50	370.10	387.18	381.31	399.47	405.90	393.23	349.54
1091.40 1094.10 1124.90		341.80	949.90	955.80	955.70	961.50	973.80	993.90	1014.20	1046.60	1081.70	1138.10		915.70	929.90	934.10	954.50	983.10	1019.50	1060.60	1080.90	1111.70	1145.30		898.60	986.40	1028.40	1064.90	1088.30	1112.30	1120.30	06.606
99.9 т 99.5		93.2	93.4	<u> </u>	93.5	93.8	94	95	96	97	98.5	<u>99.9</u>		92.6	92.9	93.2	93.5	94.5	96.5	3 8	98.5	66	<u>99.9</u>		92.5	94.5	96.5	98	98.5	6.66	99.9	93.5
296 m 288	.7)	571.2	573.3	576.3	576.3	577.7	577.5	562.6	552	559	546	560	0.7)	688	069	705.6	710	687.5	069	689	686	069	688	1.3)	680	687.5	069	689	686	627.8	627.8	705
3.7 1 4	n 30 atm (C	11.9	11.7	11.3	11.3	10.9	10.5	9.7	9.2	. 8.6	7.8	7	an 40 atm (16	15	14.7	14.2	12.5	11.5	10.6	9.8	9.2	8.6	:h 40 atm (⁻	17	12.5	11.5	10.6	9.8	8.6	8.6	40 atm 15
346 364 * 365	CH4 lea	356	358	357	355	354	353	352	351	359	350	*349	CH4 Le	389	388	378	377	376	375	374	* 373	* 372	*,371	CH4 Ric	390	383	382	381	* 380	* 385	* 379	15% H2 404

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704 94.8 989.10 364.73 1104.00 38.70 38.60 1164.00 0.91 712.4 94.5 975.60 375.62 1083.00 39.80 1164.00 0.92 711.1 96.5 1017.10 355.62 1083.00 39.80 31.60 1164.00 0.92 701.1 96.5 1017.10 359.52 1148.00 39.80 37.40 1074.00 0.87 702 99.9 1117.00 364.73 1228.00 39.740 1074.00 0.87 581 99.9 1117.00 364.73 1228.00 39.740 1074.00 0.81 581 99.9 1117.00 364.73 1228.00 39.70 0.74 581 99.9 1140.50 419.44 1353.00 38.40 840.00 0.74 664 99.9 1140.50 419.44 1353.00 38.50 166.00 0.09 700 95.5 910.70 38.74 138.50 <th>14.6</th> <th>715.4</th> <th>94</th> <th>947.00</th> <th>381.30</th> <th>1038.00</th> <th>38.80</th> <th>39.50</th> <th>1614.00</th> <th>0.96</th>	14.6	715.4	94	947.00	381.30	1038.00	38.80	39.50	1614.00	0.96
7712.494.5975.60375.621083.0039.8038.601164.000.927701.196.51017.10 359.52 1148.00 39.80 37.40 1074.00 0.90 7701.896.51017.10 359.52 1148.00 39.80 37.40 1074.00 0.87 770297.81042.80 381.31 1189.00 41.50 40.90 960.00 0.84 58199.91117.00 364.73 1228.00 39.70 38.40 840.00 0.81 58199.91117.00 405.90 1313.00 35.90 35.00 578.00 0.76 58199.91117.00 405.90 1313.00 35.90 35.00 578.00 0.76 58199.91117.00 405.90 1313.00 35.90 35.00 578.00 0.76 58199.91117.00 405.90 1313.00 35.20 36.20 578.00 0.76 58199.91117.00 405.90 313.00 37.40 37.60 196.00 0.76 66499.91117.00 364.73 1283.00 37.60 1966.00 1.00 668.392.5941.60 38.20 38.20 38.50 1650.00 1.00 70094.5954.10 364.73 1038.00 37.20 1986.00 1.00 7159592.00 381.31 1019.00 38.70 37.20 1966.00 <	ന	704	94.8	989.10	364.73	1104.00	38.70	37.30	4803.00	0.91
701.1 96 993.20 381.31 1110.00 37.70 36.10 1158.00 0.90 7 701.8 96.5 1017.10 359.52 1148.00 39.80 37.40 1074.00 0.87 7 702 97.8 1042.80 381.31 1189.00 41.50 40.90 960.00 0.84 581 99.9 1117.00 405.90 1313.00 35.90 37.40 1074.00 0.81 581 99.9 1117.00 405.90 1313.00 35.00 38.40 840.00 0.74 581 99.9 1117.00 405.90 1313.00 35.90 37.40 1074.00 0.74 564 99.9 1140.50 419.44 1353.00 38.20 38.60 0.74 664 99.9 1140.50 344.75 973.00 37.40 37.60 103 6690.6 93.2 94.05 38.20 38.50 1650.00 1.03 700 93.5	~	712.4	94.5	975.60	375.62	1083.00	39.80	38.60	1164.00	0.92
	ო	701.1	96	993.20	381.31	1110.00	37.70	36.10	1158.00	06.0
770297.81042.80381.311189.0041.5040.90960.000.845682.5981066.70364.731228.0039.7038.40840.000.81558199.91117.00405.901313.0035.9035.00578.000.8166499.91117.00405.901313.0035.9035.00578.000.767668.392.8910.70344.75973.0037.4036.000.748669.693.2929.00350.351000.0038.2038.501056.001.037669.693.5941.60381.311019.0038.2038.501650.001.007690.993.5941.60381.311019.0038.2037.201986.000.96770094.5954.10364.731038.0036.9037.201140.000.96770295.51006.60393.231128.0039.571140.000.96870298.51069.10393.201189.0040.8038.76702.000.84770099.51105.10419.401220.0039.7639.200.960.96770298.51069.10399.471220.0039.7639.200.900.74770299.51105.10419.401338.0039.7039.200.900.997 <td< td=""><td>-</td><td>701.8</td><td>96.5</td><td>1017.10</td><td>359.52</td><td>1148.00</td><td>39.80</td><td>37.40</td><td>1074.00</td><td>0.87</td></td<>	-	701.8	96.5	1017.10	359.52	1148.00	39.80	37.40	1074.00	0.87
5 682.5 98 1066.70 364.73 1228.00 39.70 38.40 840.00 0.81 8 581 99.9 1117.00 405.90 1313.00 35.90 35.00 578.00 0.76 1 664 99.9 1140.50 419.44 1353.00 38.20 36.90 578.00 0.76 1 668.3 92.9 1140.50 419.44 1353.00 38.20 36.20 468.00 0.74 1 668.3 92.8 910.70 344.75 97.30 37.40 37.60 1986.00 1.03 1 699.6 93.2 929.00 350.35 1000.00 38.20 38.50 1650.00 1.03 1 690.9 93.5 941.60 381.31 1019.00 38.20 38.50 1660.00 0.96 1 700 94.5 954.10 364.73 1038.00 39.70 39.60 846.00 0.96 1 702 95	2	702	97.8	1042.80	381.31	1189.00	41.50	40.90	960.00	0.84
3 581 99.9 1117.00 405.90 1313.00 35.00 578.00 0.76 7 664 99.9 1140.50 419.44 1353.00 38.20 36.00 578.00 0.76 7 668.3 92.9 1140.50 419.44 1353.00 37.40 37.60 468.00 0.74 7 669.6 93.5 910.70 344.75 973.00 37.40 37.60 1986.00 1.03 7 690.9 93.5 941.60 381.31 1019.00 36.90 37.20 1986.00 1.03 7 700 94.5 954.10 364.73 1038.00 36.70 37.20 1986.00 0.96 715 95 992.00 387.18 1108.00 39.70 39.60 846.00 0.96 702 95.5 1006.60 393.23 1128.00 39.70 39.60 846.00 0.96 8 702 95.5 1066.60 393.20	ы	682.5	86 86	1066.70	364.73	1228.00	39.70	38.40	840.00	0.81
3 664 99.9 1140.50 419.44 1353.00 38.20 36.20 468.00 0.74 m 910.70 344.75 973.00 37.60 1986.00 1.03 929.00 350.35 1000.00 38.20 38.50 1.03 1.03 668.3 93.5 941.60 381.31 1019.00 38.20 38.50 1.03 0.03 6690.9 93.5 941.60 381.31 1019.00 36.70 37.50 1986.00 0.96 700 94.5 954.10 364.73 1038.00 36.70 37.20 1140.00 0.96 704 95.5 1006.60 393.23 1128.00 39.70 39.60 846.00 0.99 702 95.5 1066.60 393.23 1128.00 39.70 39.60 846.00 0.99 702 95.5 1066.10	~	581	<u> 6</u> .66	1117.00	405.90	1313.00	35.90	35.00	578.00	0.76
m 344.75 973.00 37.40 37.60 1986.00 1.03 .9 699.6 93.2 929.00 350.35 1000.00 38.20 38.50 1650.00 1.03 .7 699.6 93.5 941.60 381.31 1019.00 36.90 37.20 1986.00 1.00 .7 690.9 93.5 941.60 381.31 1019.00 36.70 37.20 1986.00 1.00 .7 690.9 93.5 941.60 381.31 1019.00 36.70 37.20 1986.00 0.09 .7 700 94.5 954.10 364.73 1038.00 36.70 37.20 1986.00 0.96 .715 95 992.00 387.18 1108.00 39.70 39.60 37.50 1056.00 0.96 .7 702 97.5 1060.60 393.20 1189.00 40.80 38.70 702.00 0.84 .7 702 98.5 1069.10 399.47 <td>~</td> <td>664</td> <td>99.9</td> <td>1140.50</td> <td>419.44</td> <td>1353.00</td> <td>38.20</td> <td>36.20</td> <td>468.00</td> <td>0.74</td>	~	664	99.9	1140.50	419.44	1353.00	38.20	36.20	468.00	0.74
.3 668.3 92.8 910.70 344.75 973.00 37.40 37.60 1986.00 1.03 .9 699.6 93.2 929.00 350.35 1000.00 38.20 38.50 1650.00 1.00 .7 690.9 93.5 941.60 381.31 1019.00 36.90 37.20 1986.00 1.00 .7 700 94.5 954.10 364.73 1038.00 36.70 37.20 1140.00 0.96 .7 700 94.5 954.10 364.73 1038.00 36.70 37.20 1140.00 0.96 .715 95 992.00 387.18 1108.00 39.70 37.50 1056.00 0.90 .702 95.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.90 .702 97.5 1050.30 393.20 1189.00 40.80 38.70 702.00 0.84 .702 99.5 1069.10 399.40 <td< td=""><td>lε</td><td></td><td></td><td></td><td>-</td><td></td><td></td><td></td><td></td><td>-</td></td<>	lε				-					-
(3) 699.6 93.2 929.00 350.35 1000.00 38.20 38.50 1650.00 1.00 .7 690.9 93.5 941.60 381.31 1019.00 36.90 37.20 1986.00 0.98 .7 700 94.5 954.10 364.73 1038.00 36.70 37.20 1140.00 0.98 .7 700 94.5 952.00 387.18 1108.00 39.70 37.20 1140.00 0.96 .8 704 95.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.90 .7 702 97.5 1060.60 393.23 1128.00 39.60 37.50 1056.00 0.90 .7 702 97.5 1060.60 393.20 1189.00 40.80 38.70 702.00 0.84 .7 702 99.5 1069.10 399.47 1220.00 39.40 264.00 0.84 .7 704 99.9	с.	668.3	92.8	910.70	344.75	973.00	37.40	37.60	1986.00	1.03
.7 690.9 93.5 941.60 381.31 1019.00 36.90 37.20 1986.00 0.98 700 94.5 954.10 364.73 1038.00 36.70 37.20 1986.00 0.98 715 95 952.00 387.18 1108.00 39.70 39.60 846.00 0.96 .8 704 95.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.89 .7 702 97.5 1060.60 393.23 1128.00 39.60 37.50 1056.00 0.89 .7 702 97.5 1050.30 393.20 1189.00 40.80 38.70 702.00 0.84 .8 702 98.5 1069.10 399.47 1220.00 39.70 39.20 0.84 0.84 0.06 .8 700 99.5 1105.10 419.40 1280.00 38.60 39.00 0.82 .701 99.9 1139.50 484.00	<u>.</u>	699.6	93.2	929.00	350.35	1000.00	38.20	38.50	1650.00	1.00
700 94.5 954.10 364.73 1038.00 36.70 37.20 1140.00 0.96 .8 715 95 992.00 387.18 1108.00 39.70 39.60 846.00 0.90 .8 704 95.5 1006.60 393.23 1128.00 39.60 346.00 0.90 .7 702 97.5 1056.30 393.20 1189.00 40.80 38.70 702.00 0.84 .8 702 98.5 1069.10 399.47 1220.00 39.70 39.20 39.70 39.20 0.84 .8 702 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 .7 704 99.9 1139.50 484.00 1338.00 38.60 198.00 0.75	2	60.9	93.5	941.60	381.31	1019.00	36.90	37.20	1986.00	0.98
715 95 992.00 387.18 1108.00 39.70 39.60 846.00 0.90 .8 704 95.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.90 .7 702 97.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.89 .8 702 97.5 1050.30 393.20 1189.00 40.80 38.70 702.00 0.84 .8 702 98.5 1069.10 399.47 1220.00 39.70 39.20 390.00 0.82 .700 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 3 704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75		200	94.5	954.10	364.73	1038.00	36.70	37.20	1140.00	0.96
.8 704 95.5 1006.60 393.23 1128.00 39.60 37.50 1056.00 0.89 .7 702 97.5 1050.30 393.20 1189.00 40.80 38.70 702.00 0.84 .8 702 98.5 1069.10 399.47 1220.00 39.70 392.00 0.84 .8 702 98.5 1165.10 419.40 1220.00 39.70 392.00 0.82 .700 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 .704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75	_	715	95	992.00	387.18	1108.00	39.70	39.60	846.00	0.90
.7 702 97.5 1050.30 393.20 1189.00 40.80 38.70 702.00 0.84 .8 702 98.5 1069.10 399.47 1220.00 39.70 392.00 0.84 .8 702 98.5 1105.10 419.40 1220.00 39.70 39.20 390.00 0.82 .700 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 3 704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75	œ	704	95.5	1006.60	393.23	1128.00	39.60	37.50	1056.00	0.89
.8 702 98.5 1069.10 399.47 1220.00 39.70 39.20 390.00 0.82 700 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 3 704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75	2	702	97.5	1050.30	393.20	1189.00	40.80	38.70	702.00	0.84
1 700 99.5 1105.10 419.40 1280.00 40.50 39.40 264.00 0.78 3 704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75	8.	702	98.5	1069.10	399.47	1220.00	39.70	39.20	390.00	0.82
3 704 99.9 1139.50 484.00 1338.00 38.90 38.60 198.00 0.75		200	99.5	1105.10	419.40	1280.00	40.50	39.40	264.00	0.78
	m	704	6.66	1139.50	484.00	1338.00	38.90	38.60	198.00	0.75

* Strong Ignition # Doubtable Results (Incomplete bursting of diaphragm etc.)