A STUDY OF PREMIXED AND STRATIFIED CHARGE COMBUSTION OF CH$_4$/H$_2$/AIR AND H$_2$/AIR MIXTURES UNDER CONSTANT VOLUME CONDITIONS

A thesis submitted in fulfilment of the requirements for the degree of

MASTER OF ENGINEERING (Mechanical)

by

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To Mum and Dad
The aim of this research was to conduct fundamental charge stratification studies in a constant volume combustion chamber using hydrogen/methane/air and hydrogen/air mixtures. Charge stratification allows the benefits of a rich, or richer, mixture at initiation to be combined with the benefits of a lean overall mixture. Thus benefits can be achieved in terms of combustion efficiency and/or emissions. The investigation was divided into two main sections; the first dealing with the hydrogen enrichment of methane and the second, the reduction of nitric oxide emissions when burning hydrogen only in air.

The aim of the first section was to determine the improvements to the combustion characteristics of methane that could be achieved through the homogeneous (pre-mixed) and heterogeneous (stratified charge) addition of hydrogen. The parameters measured were the peak pressure and time to peak pressure while the proportion of hydrogen added was varied. The aim of the second section was an attempt to reduce the concentration of nitric oxide formed during the combustion of hydrogen/air mixtures through the use of charge stratification. The proportion of the hydrogen injected was varied along with the ignition delay in order to alter the level of stratification. The concentration of nitric oxide in the exhaust gases was measured using a mass spectrometer. In addition to the above, optical probes were used to investigate flame propagation and to determine the cause of the 'double hump' pressure trace.

For all investigations a cylindrical constant volume combustion chamber of internal volume 2.06 litres was used and the stratified charge was created by injecting pure hydrogen through the core of a specially modified spark plug. Investigations were carried out to improve the level of stratification of the injected hydrogen along with the accuracy of test mixture creation.

The results from the first section of this investigation indicate that the addition of hydrogen is a very efficient way of improving combustion characteristics. In particular, significant improvements were observed in the ignition delay and rate of pressure rise leading to higher peak pressures and reduced times to peak pressure. Further benefits
were achieved through the use of a stratified charge. Similar improvements to homogeneous charges were observed whilst using up to ten times less hydrogen.

The second section indicated that the use of a stratified charge is an effective means for reducing the emissions of nitric oxide. Maximum reduction of nitric oxide (30%) was achieved when igniting the stratified mixture with a minimum ignition delay after the end of injection. An increasing ignition delay leads to a less stratified region and nitric oxide levels tending to homogeneous values. Much work is still required in the area of stratified charge formation and initial results indicate that further improvements could be achieved.

In conclusion, this project has indicated that the use of hydrogen enrichment could pave the way for the general acceptance of alternative transport fuels, including hydrogen itself and that the charge stratification concept remains one of the most promising alternatives available for meeting the anticipated environmental and legislative requirements of the future.

Publications arising from this work:

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Ramon Brown and Steve Pearce, my fellow members of the 'Green Team' for their ever present advice and encouragement.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric oxide</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Oxides of nitrogen (NO + NO₂)</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CH₃</td>
<td>Methyl radical</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen atom</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen atom</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen atom</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxide</td>
</tr>
<tr>
<td>M</td>
<td>Unspecified collision partner</td>
</tr>
<tr>
<td>SOₓ</td>
<td>Oxides of sulphur</td>
</tr>
<tr>
<td>UHC</td>
<td>Unburnt hydrocarbons</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>O₃</td>
<td>Ozone</td>
</tr>
<tr>
<td>λₜₜₚₚ</td>
<td>Light wavelength</td>
</tr>
</tbody>
</table>

- \( x \) Proportion of hydrogen in fuel
- \( \lambda \) Relative air/fuel ratio
- \( P_{\text{max}} \) Peak pressure (absolute)
- \( t_{\text{max}} \) Time to peak pressure (after ignition)
- \( p \) Pressure
- \( V \) Volume
- \( n \) Number of moles
- \( R \) Universal gas constant
- \( T \) Temperature
- \( E \) Activation Energy
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CHAPTER 1 INTRODUCTION

1.1 ALTERNATIVE FUELS

1.1.1 Introduction

Since the energy crisis of the 1970's energy conservation has been a matter of worldwide concern [1]. Alternatives are increasingly being sought to the world's rapidly diminishing resources of fossil fuels, in particular oil. In recent years, alternative fuels for reciprocating engines have received much attention due mainly to the increasing world price of crude oil, the need for self sufficiency, a desire to use only renewable energy sources and a requirement to reduce atmospheric pollution [2].

Concern for the environment has lead to stringent limits being placed on the emissions resulting from the combustion of fossil fuels. The depletion of the ozone layer and global warming ('greenhouse effect') can be directly related to the rapidly growing use of the internal combustion engine for transportation. The current transport industry produces such harmful emissions as unburnt hydrocarbons (UHC’s), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), oxides of nitrogen (NO\textsubscript{x}), oxides of sulphur (SO\textsubscript{x}), airbourne lead and particulate matter such as soot.

Hydrogen is seen as the energy carrier of the future as it can be produced from water using primary energy sources (e.g. solar energy) and is very clean burning with NO\textsubscript{x} being the only major pollutant when burnt in air [3]. Much technology is still required before the widespread use of hydrogen will become a reality. In the interim alternative fuels such as alcohols (methanol, ethanol, butanol), ethers (MTBE, ETBE) and gaseous fuels (methane, propane) are being investigated [1]. Methane is very promising and currently enjoys significant worldwide usage in the form of CNG (compressed natural gas) [1]. Its continued development should see its popularity increase. The fuels that are of interest in the work described in this thesis are methane and hydrogen.

1.1.2 Methane

Methane (CH\textsubscript{4}) is the lowest order hydrocarbon fuel and is an odourless, colourless, non-
toxic gas at room temperature and pressure. The largest source of methane in the world is natural gas [4], which is typically 80-90% methane with the remainder consisting of small quantities of ethane, propane, butane, hydrogen, hydrogen sulphide and carbon dioxide. The exact composition is not constant and can vary from source to source. Natural gas is usually found in deposits associated with oil fields, although recently it has been found by itself in locations where oil would not be expected. Other sources include that from coal seams (93-95% CH₄), coal gas (30% CH₄, 50% H₂) and bio-gas (65% CH₄, 35% CO₂). Coal gas is produced by heating coal to 1000-1300°C in the absence of air. The by-product of the process is low grade coke. With the widespread introduction of natural gas this process has become almost obsolete and is now primarily used in the production of high grade coke for steel making where the gas is a by-product. Bio-gas is the most ecologically promising for the future. It is produced during the anaerobic decomposition of organic material and waste by naturally occurring bacteria. This process has been implemented successfully in sewerage plants and has the added benefit of reducing useless and potentially damaging waste. This technology is still to be used in a large scale production facility.

Natural gas use in the world will increase as reserves of liquid hydrocarbons are depleted. Along with its natural abundance a number of countries already have in place large distribution infrastructures for natural gas. As of August, 1995, 1,107 natural gas vehicle fuelling stations were operating in the United States, the number having tripled since 1991 [5]. The Gas Research Institute (GRI) recently (April, 1997) released a report indicating that with adequate technology advances, natural gas will play a major role in an increasingly competitive energy mix well into the next century. It is projected that gas demand by natural gas vehicles (NGV) will reach 633 quadrillion Joules (10¹⁵) by 2015. The total transportation gas demand is projected to grow from 739 quadrillion Joules in 1995 to 1688 quadrillion Joules in the same period. Accordingly, worldwide NGV demand is expected to increase to 2.6 million vehicles in the year 2000 from the 1 million currently in use [5].

As a gaseous fuel for internal combustion engines, methane enjoys such benefits as more homogeneous mixture formation leading to better combustion and lower emissions. As it does not require any fuel enrichment during cold starting or in transient operating conditions, CO production is considerably reduced [1]. Because of the higher H/C ratio,
methane combustion produces 25% less CO$_2$ than gasoline for the same engine efficiency. But the extra displacement of air when employing conventional external mixture formation techniques leads to lower volumetric efficiencies and a consequent reduction in engine power outputs. This can be overcome by the use of direct injection into the cylinder after inlet valve closure. Methane is more difficult to ignite than gasoline, has a relatively low flame speed and a narrow range of flammability (Table 1.1) [6]. These characteristics can lead to significant quantities of unburned hydrocarbons and other by-products of combustion being released into the atmosphere.

1.1.3 Hydrogen

There is considerable interest in hydrogen as a fuel for the present and the future. It has the potential to eliminate the present day reliance upon petroleum based fuels and to reduce vehicular pollution due to its clean burning properties [7]. It is seen as the energy carrier of the future because it can be produced from water using primary energy sources, such as wind, solar, tidal and hydroelectric power. This means that hydrogen is a renewable secondary energy source.

At present, the commercial production of hydrogen worldwide is derived almost completely from non-renewable sources. Processes such as solar photo-electrolysis are laboratory rather than commercial processes at present. The major resources used for the production of hydrogen are oil (50%), natural gas (30%) and coal (10%). At present steam reforming of natural gas is the cheapest method due to natural gas's low price. In this reaction, natural gas and steam are passed over a fire-bed catalyst at temperatures of 650-700°C to produce mixtures of hydrogen and carbon monoxide. Unwanted carbon monoxide is converted to carbon dioxide and hydrogen in a further reaction ('shift-reaction') and then the CO$_2$ is removed by scrubbing. Electrolysis of water also sees significant commercial use especially in countries with excess hydroelectric power. This is accomplished by passing a DC current between two electrodes immersed in an electrolyte which usually contains potassium hydroxide. The limiting factor in this process is the price of electricity and the means by which it is produced.
Table 1.1 Selected Properties of Various Fuels [8]

<table>
<thead>
<tr>
<th>Property</th>
<th>Gasoline</th>
<th>Methane</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 0°C and 101.3 kPa, kg/m³</td>
<td>~ 750</td>
<td>0.72</td>
<td>0.09</td>
</tr>
<tr>
<td>Boiling point at 101.3 kPa, °C</td>
<td>~ 40</td>
<td>-162</td>
<td>-253</td>
</tr>
<tr>
<td>Vapour Pressure at 0°C, bar</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diffusion velocity in air, m/s</td>
<td>-</td>
<td>0.0051</td>
<td>0.020</td>
</tr>
<tr>
<td>Specific calorific value (fuel), MJ/kg</td>
<td>44.0</td>
<td>50.0</td>
<td>120.0</td>
</tr>
<tr>
<td>Spec. calorific value (air/fuel mix), MJ/m³</td>
<td>3.22</td>
<td>2.97</td>
<td></td>
</tr>
<tr>
<td>Theoretical air requirement, kg air/kg fuel</td>
<td>14.8</td>
<td>17.2</td>
<td>34</td>
</tr>
<tr>
<td>Ignition Temperature, °C</td>
<td>280 - 400</td>
<td>650</td>
<td>560</td>
</tr>
<tr>
<td>Limits of flammability in air, vol. %</td>
<td>0.6 - 8</td>
<td>5.3 - 15</td>
<td>4.0 - 77</td>
</tr>
<tr>
<td>Limits of detonability in air, vol. %</td>
<td>1.1 - 3.3</td>
<td>6.3 - 14</td>
<td>18.3 - 59</td>
</tr>
<tr>
<td>Burning velocity in air, m/s</td>
<td>0.37 - 0.43</td>
<td>0.37 - 0.45</td>
<td>2.65 - 3.25</td>
</tr>
<tr>
<td>Quenching distance in air, mm</td>
<td>2.00</td>
<td>2.03</td>
<td>0.64</td>
</tr>
<tr>
<td>Minimum ignition energy in air, mJ</td>
<td>0.24</td>
<td>0.29</td>
<td>0.02</td>
</tr>
<tr>
<td>Octane number, RON</td>
<td>91 - 96</td>
<td>120</td>
<td>low/high*</td>
</tr>
</tbody>
</table>

* low using RON method of determination.

Hydrogen occurs naturally in negligible quantities on Earth and is very chemically active readily forming compounds with many other elements. As a gaseous fuel, hydrogen displays many of the same advantages (homogeneous mixture formation) and disadvantages (low volumetric efficiency) as methane. The only harmful substances emitted from an engine operating on hydrogen are oxides of nitrogen (NOₓ) and in some cases extremely small traces of hydrogen peroxide (H₂O₂). The wide limits of flammability of hydrogen (Table 1.1) allow the use of very lean operating mixtures leading to high thermal efficiencies and low peak cycle temperatures which help to reduce NOₓ emissions substantially. The high thermal efficiency arises from an increase in the ratio of specific heats (γ) of the charge becoming closer to that of air (γ = 1.4), lower heat loss to the engine coolant and reduced dissociation [7]. Hydrogen has a very high flame speed and good ignitability. The higher flame speed helps to maintain as close to constant volume combustion as possible at lean operating conditions while the low ignition energy helps in the rapid initiation of a stable, self-sustaining flame kernel.
thereby reducing cyclic variations. Hydrogen also has a low quenching distance and high spontaneous ignition temperature which help to resist knocking.

### 1.2 HYDROGEN ENRICHMENT

Although hydrogen is seen to be the most promising alternative to petroleum based fuels, there are still many problems to be overcome before it will see widespread use in internal combustion engines. These include irregular combustion processes (backfire, auto-ignition, engine knock), low power due to the hydrogen displacement of air and the aforementioned manufacturing and distribution problems. Therefore in the short-term the addition of hydrogen to other fuels in order to exploit its benefits is seen as an intermediate step towards its introduction.

Hydrogen, when added to virtually any homogeneous air-fuel mixture, can accelerate its combustion. By virtue of its excellent combustion characteristics the addition of hydrogen leads to a reduction in ignition delay and an increase in the burning velocity. This also means that the lean limit of operation for the fuel can be significantly extended. Thus the addition of a small amount of hydrogen to methane should overcome its slow burning characteristics and lead to more efficient burning, therefore reducing emissions.

Karim et al. [9] showed that the performance of a single cylinder spark ignition engine fuelled with methane could be significantly improved through the addition of hydrogen to form a homogeneous, gaseous fuel. In particular, improvements to power output, work production efficiency and emissions were observed while permitting operation at overall leaner mixtures throughout.

Although the amount of hydrogen added to the methane varies from programme to programme, the most commonly used mixture typically consists of 15% hydrogen by volume of fuel. Methane with this level of hydrogen enrichment is commonly called 'Hythane'.
1.3 LEAN BURN AND CHARGE STRATIFICATION

1.3.1 Lean Burn Engines

Running an engine with a lean mixture has many advantages in terms of efficiency and emissions. But research into this area has invariably lead to three main problems arising:

- ignition of a lean mixture is considerably more difficult than a stoichiometric one, which can lead to misfire.
- cyclic variation is increased leading to a decrease in engine performance
- burning velocity can be reduced to the point where combustion is not complete when the exhaust valve opens.

In addition to these problems is the level of exhaust emissions. In a conventional engine the main pollutants produced are UHC's, CO and NO\textsubscript{x}. In most modern engines these are removed through the use of a three-way catalytic converter. This device requires the engine to be run at exactly stoichiometric conditions, thus a lean burn engine cannot use a three-way catalyst because the excess oxygen in the exhaust would make the reduction of NO\textsubscript{x} impossible. However, this is generally not a large problem as NO\textsubscript{x} levels are significantly reduced in a lean burn engine due to the lower temperatures present. What is a problem is that levels of UHC's and CO can be increased. Systems have been produced to reduce these emissions although the catalytic converter is generally simpler and cheaper. It is mainly for this reason that the lean burn engine has not been adopted in the past [10].

1.3.2 Charge Stratification

A method to retain the best features of a lean burn engine while eliminating the problems of poor ignition, cyclic variation and slow burning is the technique of charge stratification. Charge stratification involves the creation of a heterogeneous charge within the combustion chamber or, more specifically, a region of richer mixture around the initiation point of combustion. In practice this can be achieved in two ways. The first is to have a pre-chamber in which combustion is initiated and then spreads to the main chamber. The second method (utilised in this investigation) is to use a single
combustion chamber which contains a lean mixture and then create a fuel rich charge around the ignition source by localised fuel injection.

The theory behind charge stratification is that the overall characteristics of a particular explosion are in the main determined by the conditions present at its initiation. Thus the benefits of a rich, or richer, mixture at initiation could be combined with the benefits of a lean overall mixture. A lean mixture near the walls reduces UHC production from wall quenching since the fuel concentration is lower and improves part load fuel economy as for the lean burn engine, but the richer mixture near the plug improves ignitability (less misfire) and reduces the ignition delay (time between firing of spark and pressure rise). This helps reduce the overall tendency of a lean burn engine to produce high levels of UHC’s (due to reduced burning velocity) and CO which could then be further treated by an oxidation catalyst. NO\textsubscript{x} levels are generally lower than a conventional engine due to the reduced flame temperature.

The concept of charge stratification was clearly identified in the 1970’s. But only one engine employing this technique has been put into large scale production. For a short time in the early 1980’s Honda produced their CVCC (compound vortex controlled combustion) engine. It was developed in order to meet stringent new Californian emission regulations, but when legislative changes eased the impact of these, the CVCC became uneconomical due to its increased manufacturing costs over a conventional engine.

In spite of its increased design and construction costs the charge stratification concept remains one of the most promising alternatives available for meeting the anticipated environmental and legislative requirements of the future.

1.4 AIM OF INVESTIGATION

1.4.1 Introduction

The overall purpose of this research is to investigate the fundamental theory of charge stratification. In particular, its application to the hydrogen enrichment of methane for
improved performance and the reduction of nitrogen oxide when burning hydrogen in air. Both investigations will utilise a constant volume combustion chamber and the stratified charge will be created by injecting hydrogen around the spark plug electrodes prior to ignition.

1.4.2 Hydrogen Enrichment of Methane

The first part of the research programme involves investigating the fundamental combustion characteristics and mechanisms involved when burning hydrogen enriched methane in a constant volume combustion chamber with and without charge stratification. The following areas are to be investigated:

1. To study the effect that hydrogen enrichment has on the combustion characteristics of methane.
2. To determine how effects vary with level of hydrogen enrichment.
3. To investigate whether further improvements can be achieved through the use of charge stratification.
4. To investigate flame propagation using optical methods.

By adding hydrogen to methane under charge stratification conditions it is hoped to achieve similar results to the pre-mixed ‘lythane’ case while using significantly less hydrogen. As initiation reactions are most important, hydrogen in this region will play a more important role than that in latter stages of combustion. In this manner emissions could be reduced by using an overall lean charge (leading to a reduction in NOx) whilst retaining the combustion stability/reduced ignition delay of a richer mixture.

1.4.3 Nitrogen Oxide Reduction Using Charge Stratification

The second part of the research programme investigates the formation of nitrogen oxide when burning homogeneous and heterogeneous mixtures of hydrogen and air. The following areas are to be investigated:

1. To study the trends associated with the formation of NO from the combustion of
homogeneous hydrogen/air mixtures.

2. To determine the effect of charge stratification on the formation of NO.

3. To investigate the effects of varying the proportion of hydrogen injected and variations in the ignition delay period.

It is hoped to significantly reduce the amount of NO produced by using a stratified charge while retaining the combustion characteristics of a homogeneous charge.
CHAPTER 2  COMBUSTION THEORY

2.1 INTRODUCTION

The study of combustion theory is large and very complex and as such a large number of publications have been written on its many areas. The following section is intended to give the reader a brief insight into the areas relevant to the research presented in this thesis. It is hoped that this will help to explain the phenomena detailed in later sections. In particular, the reaction mechanisms for hydrogen, methane and nitric oxide production will be reviewed along with a brief description of flame propagation. For further information on these and other topics the reader is directed to the many excellent publications referred to below.

2.2 REACTION MECHANISMS

2.2.1 Introduction

Although the final products of a fuel-oxidiser flame are easily determined, the mechanisms by which they are formed are not i.e. the reactions that lead from the reactants to the products. The main problem is in determining which of a number of possible processes is actually occurring. This involves obtaining experimental evidence of the production and consumption of various products and from this determining the various rates of reaction. From these a reaction mechanism is proposed. This is of course an extremely complicated process and even the simplest of flames are still not well understood. In this thesis a brief summary of the many proposed reaction mechanisms are given for the oxidation of hydrogen and methane. It is hoped this will give an insight into the combustion processes involved.

2.2.2 Hydrogen-Oxygen Reaction Mechanism

While the H\textsubscript{2} - O\textsubscript{2} reaction mechanism is the most researched and well understood, it is still very complicated. If all considerations are taken into account, over fifty equations can be derived [11], fortunately with careful simplification this number can be significantly reduced. The H\textsubscript{2} - O\textsubscript{2} reaction is not only important for the combustion of
hydrogen in air but also forms an integral part of the CH₄-O₂ reaction and indeed all other hydrocarbon reactions. Below is a summary of the most important reaction stages.

Initiation when burning hydrogen in air occurs by the following reactions:

\[
\begin{align*}
H₂ + M &\Leftrightarrow 2H + M \quad (2.1) \\
H₂ + O₂ &\Leftrightarrow HO₂ + H \quad (2.2)
\end{align*}
\]

where M is some unspecified collision partner (e.g. a gaseous molecule or wall) which stabilises the new molecule by removing energy from it. The dissociation energy of hydrogen is less than that of oxygen so the chain initiation is most likely related to the thermal decomposition of hydrogen (reaction 2.1). These two reactions provide the H-radicals required for the following mechanisms:

\[
\begin{align*}
H + O₂ &\Leftrightarrow OH + O \quad (2.3) \\
O + H₂ &\Leftrightarrow OH + H \quad (2.4) \\
OH + H₂ &\Leftrightarrow H₂O + H \quad (2.5)
\end{align*}
\]

which help to form the radical pool of H, O and OH required for the attack on the CH₄ molecule when burning methane in air. Reactions 2.3 and 2.4 are of the chain branching type which experience an exponential growth in the reaction rate as a result of the multiplication of the primary propagating species [12]. Reaction 2.3 is the most effective of the chain branching reactions, and in stoichiometric hydrocarbon-air flames at atmospheric pressure accounts for approximately 80% of the oxygen consumption [13]. At fuel lean conditions, processes involving the HO₂ radical can also become important [12] e.g.

\[
\begin{align*}
OH + HO₂ &\Leftrightarrow H₂O + O₂ \quad (2.6) \\
H + HO₂ &\Leftrightarrow H₂ + O₂ \quad (2.7)
\end{align*}
\]

The radicals produced can also undergo various recombination reactions involving a third body resulting in termination of the process. These include:

\[
H + H + M \Leftrightarrow H₂ + M \quad (2.8)
\]
\[ \text{O} + \text{O} + \text{M} \Leftrightarrow \text{O}_2 + \text{M} \quad (2.9) \]
\[ \text{H} + \text{O} + \text{M} \Leftrightarrow \text{OH} + \text{M} \quad (2.10) \]
\[ \text{H} + \text{OH} + \text{M} \Leftrightarrow \text{H}_2\text{O} + \text{M} \quad (2.11) \]

2.2.3 Methane-Oxygen Reaction Mechanism

Much research has been conducted on the reaction mechanisms of methane but it is by no means well understood. Although the final products are easily determined, the mechanisms by which they are formed are not. Methane also exhibits certain oxidation characteristics which are different from all other hydrocarbons [13]. The bond energy of the first C-H bond is kilocalories more than the remainders. Thus methane's ignition energy is higher than that of other hydrocarbons. The mechanism described below is a summary of that proposed by Fristrom and Westenberg [11]. The process can be divided into three main processes; CH\(_4\) consumption, H\(_2\)O and intermediates formation and the CO - CO\(_2\) reactions.

1. Methane Consumption - The following reactions provide the initial attack upon methane with 2.12 being the fastest and most important especially at fuel lean conditions [14]:

\[ \text{CH}_4 + \text{OH} \Leftrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (2.12) \]
\[ \text{CH}_4 + \text{H} \Leftrightarrow \text{CH}_3 + \text{H}_2 \quad (2.13) \]
\[ \text{CH}_4 + \text{O} \Leftrightarrow \text{CH}_3 + \text{OH} \quad (2.14) \]
\[ \text{CH}_4 + \text{M} \Leftrightarrow \text{CH}_3 + \text{H} + \text{M} \quad (2.15) \]

At fuel rich conditions 2.13 will probably predominate due to the larger H-radical concentration. 2.14 is the slowest and probably accounts for only a small amount of the CH\(_4\) disappearance. The radical pool required for these processes is supplied by reactions 2.3 - 2.5. The thermal decomposition of methane (reaction 2.15) is the most important for the radical-poor initiation process and strongly influences the ignition of methane [15].

2. H\(_2\)O and Intermediates Formation - One major source of H\(_2\)O, which forms throughout the reaction zone, is reaction 2.12. The other is from the following possible
reaction sequence:

\[
\begin{align*}
\text{CH}_3 + \text{O}_2 & \Leftrightarrow \text{H}_2\text{CO} + \text{OH} \quad (2.16) \\
\text{H}_2\text{CO} + \text{OH} & \Leftrightarrow \text{HCO} + \text{H}_2\text{O} \quad (2.17) \\
\text{HCO} + \text{OH} & \Leftrightarrow \text{CO} + \text{H}_2\text{O} \quad (2.18)
\end{align*}
\]

One CO molecule is produced by the reactions 2.16 to 2.18 for every CH\textsubscript{3} radical consumed, which in turn correspond to one CH\textsubscript{4} molecule. This has been experimentally demonstrated during the early stages of reaction before the onset of a CO loss reaction. Some doubt still exists though about the exact mechanism by which CH\textsubscript{3} is converted to CO.

3. Carbon Monoxide-Carbon Dioxide Reactions - Two possibilities for the disappearance of CO are:

\[
\begin{align*}
\text{CO} + \text{O}_2 & \Leftrightarrow \text{CO}_2 + \text{O} \quad (2.19) \\
\text{CO} + \text{OH} & \Leftrightarrow \text{CO}_2 + \text{H} \quad (2.20)
\end{align*}
\]

but reaction 2.19 is generally discounted due to its very low reaction rate in favour of 2.20.

The reactions given above are for a fuel lean system. Flames rich in CH\textsubscript{4} are found to produce significant quantities of C\textsubscript{2}-hydrocarbons, introducing substantially more reactions. However, this is beyond the scope of this thesis and the above is hoped to provide enough information so that the effects of hydrogen enrichment can be understood.

2.2.4 Hydrogen Enriched Methane

For burning of mixtures containing hydrogen and methane the initial stages of the process are the most critical in determining the overall combustion characteristics. As the dissociation energy for methane decomposing into a methyl radical and a hydrogen radical (439 kJ/mol) is almost identical to that of molecular hydrogen (436 kJ/mol), chain initiation can be related to the following reactions:
\[ H_2 + M \rightleftharpoons 2H + M \quad (2.1) \]
\[ CH_4 + M \rightleftharpoons CH_3 + H + M \quad (2.15) \]

Use of the Arrhenius equation shows the rate of methane dissociation (2.15) to be almost $10^3$ times that of hydrogen dissociation (2.1) which would infer that the effects of hydrogen were negligible. However, as both the above reactions are in a state of partial equilibrium any subsequent reactions which act as a sink for their products can considerably increase the overall reaction rate. The main reaction responsible for this is:

\[ H + O_2 \rightarrow OH + O \quad (2.3) \]

which although slow consumes $10^{12}$ times more H-radicals than reaction 2.15 produces. Thus reactions 2.1 and 2.15 are displaced towards their products increasing the reaction rate. In addition, as reaction 2.1 produces only H-radicals, its rate is further increased. The methyl radical produced in 2.15 is far less reactive than H and hence its concentration may increase, leading to less displacement of the equilibrium and consequently less H production. The overall reaction rate is very sensitive to reaction 2.3 due to its chain branching nature, thus a small increase in its rate accelerates the whole reaction. Therefore the presence of small amounts of hydrogen at initiation gives the reaction 2.3 a considerable head start by forming the radical pool required for attack on the hydrocarbon at an earlier stage. Reaction 2.3 is also accelerated at lean conditions due to excess O$_2$ being present.

Thus for a stratified charge and overall lean conditions the high concentrations of hydrogen and oxygen around the spark kernel serve to further accelerate the formation of the radical pool required. At rich conditions the effect is reduced due to H-radical recombination.

### 2.3 FORMATION OF NITRIC OXIDE

#### 2.3.1 Introduction

Oxides of nitrogen, NO$_x$ (NO, NO$_2$) are formed when combusting any fuel in air under
favourable conditions. In particular, the high combustion temperatures experienced in an internal combustion engine promote their formation. Nitric oxide, NO, is the most predominant oxide formed and is a major component of photochemical smog. NO\textsubscript{x} also exhibits the undesirable effect of forming dilute nitric acid in the lungs which can exacerbate respiratory problems [16].

### 2.3.2 Formation Conditions

As stated above nitric oxide is formed during the peak combustion temperatures experienced in the combustion chamber. The formation of nitric oxide proceeds less rapidly than the initial combustion reactions resulting in a time delay. For this reason local nitric oxide formation occurs in the post flame gases and increases in concentration with time after combustion until the temperature of the combustion gases begins to drop. Due to its high temperature dependence, nitric oxide formation ceases early in the expansion stroke. At this point the formation of nitric oxide is frozen and peak-temperature chemical-equilibrium nitric oxide levels are not achieved. The time available before expansion occurs (residence time) is therefore an important factor in determining the emissions from an engine.

The varying residence times of the mixture in different sections of the combustion chamber cause a concentration gradient of nitric oxide to form. This effect is further increased by the temperature gradient also formed in the chamber. The gases at the point of ignition have the most reaction time available and also experience the highest temperatures. The combination of these two conditions results in the formation of the highest concentration of nitric oxide, decreasing towards the far end of the chamber.

Nitric oxide formation is also highly dependant upon the concentration of oxygen in the combustion products [16]. For this reason nitric oxide levels are generally low in fuel-rich mixtures increasing to a maximum with approximately 10% excess air. A further increase in excess air causes a drop in nitric oxide concentration as the associated drop in combustion temperature offsets the increasing oxygen and nitrogen availability. This interaction is illustrated in Figure 2.1 which presents nitric oxide concentration versus equivalence ratio for a series of times following combustion.
2.3.3 Reaction Mechanism

The reaction and formation of nitric oxide is best explained by the widely accepted Zeldovich mechanism [17] given by the following equations:

\[ \text{O} + \text{N}_2 \rightleftharpoons \text{NO} + \text{N} \]  
(2.21)

\[ \text{N} + \text{O}_2 \rightleftharpoons \text{NO} + \text{O} \]  
(2.22)

The reaction rates for these two processes are very temperature dependant and decrease rapidly with a drop in temperature. To satisfy chemical equilibrium, it would be expected that the NO concentration would decrease during the expansion stroke of an engine due to the falling temperatures [18]. This has however, been shown experimentally not to be the case. Lavoie et al. [19] extended the Zeldovich mechanism by adding the reaction:

\[ \text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H} \]  
(2.23)

which would not normally be expected to be competitive with atom-molecule reactions.
such as 2.21 and 2.22. But under fuel rich mixture conditions with relatively low concentrations of O and O$_2$ for participation as reactants in 2.21 and 2.22 it could become dominant.

### 2.3.4 Reduction of Nitric Oxide Using Charge Stratification

Charge stratification reduces the formation of nitric oxide by replacing almost all the elements in the charge with elements of lesser nitric oxide producing air-fuel ratios i.e. rich or lean conditions. Thus the charge propagates from a rich mixture at ignition, which is low in O$_2$ and O (low NO production), to a lean mixture which having less fuel burns at a lower temperature (low NO production) [20]. Therefore, although the overall equivalence ratio would remain unchanged, the concentration of nitric oxide should be significantly reduced.

![Figure 2.2](image)

**Figure 2.2** Benefits of charge stratification on nitric oxide formation.

The benefits of charge stratification were demonstrated by Blumberg _et al_ [20, 21] using a computer model, the results of which are shown in Figure 2.2. This shows the percentage reduction in NO versus overall equivalence ratio, $\Phi$ (stoichiometric air-fuel
ratio divided by the actual), hence $\Phi < 1$ represents lean conditions. This is for linear stratification (constant concentration gradient) and the numbers in brackets represent the maximum and minimum equivalence ratios. Differing levels of exhaust gas recirculation (EGR) are also displayed which helps to further reduce the temperature of the charge. From these idealised results it can be seen that the use of a stratified charge is most significant at equivalence ratios close to stoichiometric. Indeed, the use of charge stratification with very lean mixtures could in fact increase the concentration of nitric oxide.

### 2.3.5 Photochemical Smog

The major harmful effect of nitric oxide is its tendency, along with other compounds, to form photochemical smog in the presence of sunlight. This problem was identified during the 1960’s in California. The effects of photochemical smog are eye and respiratory irritation, reduced visibility and damage to plant life. Nitric oxide, a primary pollutant, undergoes the following reactions to form various secondary pollutants. Firstly, it is oxidised to form nitrogen dioxide [12]:

$$2\text{NO} + \text{O}_2 \Rightarrow 2\text{NO}_2 \quad (2.24)$$

This initiates a chain reaction involving ozone where $\text{NO}_2$ is photodissociated by the absorption of solar radiation ($\lambda < 398\text{nm}$) to produce ground-state oxygen atoms:

$$\text{NO}_2 + \text{hv} \Rightarrow \text{NO} + \text{O}^3\text{P} \quad (2.25)$$

$$\text{O}^3\text{P} + \text{O}_2 + \text{M} \Rightarrow \text{O}_3 + \text{M} \quad (2.26)$$

$$\text{O}_3 + \text{NO} \Rightarrow \text{O}_2 + \text{NO}_2 \quad (2.27)$$

establishing the overall equilibrium:

$$\text{NO}_2 + \text{O}_2 \Leftrightarrow \text{NO} + \text{O}_3 \quad (2.28)$$

### 2.4 FLAME PROPAGATION

#### 2.4.1 Introduction
This section will briefly discuss the propagation of a combustion wave through an explosive gas when ignited by a spark. The spark produces a heat source as well as atoms and free radicals which may act as chain carriers in the subsequent reaction [22]. The flow of heat and chain carriers from the ignition source flow to the adjacent layer of gas. This initiates a chemical reaction so that the layer itself becomes a source of heat and chain carriers capable of initiating a chemical reaction in the next adjacent layer. This process continues producing a zone of burning which propagates through the explosive mixture. This zone is referred to as the combustion wave.

The combustion wave can accelerate by two mechanisms. The first, and predominant, mechanism is the increase in reaction probability with temperature according to exponential (Arrhenius-type) functions of the form $e^{-E/RT}$. This self-acceleration is of high order and allows each layer to activate the adjacent layer while still retaining enough heat to go to completion itself. The second mechanism is the increase of free-radical concentration by chain-branching type reactions. But this only becomes significant in certain cool flames.

For a more detailed description of the complex subject of flames and combustion the reader is referred to references [11, 12, 22 and 23].

### 2.4.2 Flame Structure

The temperature profile, intermediate and product concentration through the cross-section of a flame increase smoothly from the initial to final state while the reactants show a corresponding decrease (Figure 2.3). An element of flowing gas can receive heat by one of two mechanisms; from chemical reactions occurring within it or by conduction from the hot gases ahead of it. These two mechanisms occur to varying degrees within two distinct regions. The first is termed the preheat or preflame zone and an element of gas passing through it gains heat by conduction faster than it loses it because the gradient is steeper on the high temperature side. Upon entering the second region, which is termed the reaction zone, the opposite occurs and the heat loss exceeds the heat gain. However, at this stage the reaction rate has increased sufficiently that a significant
amount of heat is produced by this mechanism. The temperature continues to increase until a constant value is reached when all the reactants have been consumed and the reaction ceases. The reactants display opposite but parallel behaviour with the initial consumption of fuel due to diffusion into the flame front followed by subsequent consumption by chemical reaction. A third region can also be termed the post-flame or product zone.

![Flame zones showing reactant and product concentrations.](image)

**Figure 2.3** Flame zones showing reactant and product concentrations.

### 2.4.3 Flame Propagation

Propagating flames are subject to a number of factors that effect their progress. When propagating along a horizontally mounted cylinder the gases are subject to a buoyancy effect which causes the hot burnt gases to rise to the top of the cylinder. These rising hot gases remove heat from the bottom of the flame and add it to the top. This causes a difference in the flame temperature and hence the rate of reaction between the top and bottom of the tube. Thus the flame front distorts into a ‘hook’ shape as depicted in Figure 2.4. The difference between upwards and downwards propagation is shown in Figure 2.5. Due to the effects of gravity, the stream tubes for the former case open up well ahead of the flame front so the transport of gases to the wall takes place ahead of the thermal gradient of the flame. Thus, the velocity gradient at the flame surface is
decreased resulting in less flame stretch. The opposite is true for the latter case and hence its limits of flammability are decreased [22].

Figure 2.4  'Hook' shaped flame front (buoyancy effect).

Figure 2.5  Upwards and downwards flame propagation.
When the gas in a cylinder, closed at one end and open at the other, is ignited at the closed end the unburnt gas flows from the wave towards the open end. Under these conditions the flow generally becomes turbulent and continuously accelerates. The combustion wave in a closed vessel displays different behaviour as shown in Figure 2.6. The gas is ignited at the top and initially propagates as a hemisphere until it reaches the walls of the vessel where it assumes an increasingly planar shape as it progresses to half way along the cylinder. By this process the unburnt gas is forced into the lower half of the vessel, but as this mass is ultimately distributed evenly throughout the volume, the mass flow begins to reverse itself. From approximately the halfway point on the flame front becomes increasingly conical in shape until it reaches the end of the cylinder.

Figure 2.6 Combustion wave in a closed vessel.

2.4.4 Constant Volume Combustion

Combustion inside a constant volume vessel causes a rise in pressure and temperature along with induced mass flow. What is particularly relevant is the formation of a temperature gradient in the burned mixture which effects nitric oxide formation as discussed in section 2.3.2. This is best explained by considering the initial and final stages of combustion (see Figure 2.7). At the point of ignition the gas burns at an almost constant pressure, \( P_i \) and is then compressed back to almost its original volume by the subsequent combustion of the rest of the gas. The work required to compress this portion of gas exceeds the expansion work because the pressure steadily increases during combustion from \( P_i \) to \( P_e \), where the initial expansion occurred at \( P_i \). By comparison, the last portion to burn is initially compressed as the pressure rises from \( P_i \) to \( P_e \) then expands on burning at \( P_e \) to approximately its original volume. This latter work of expansion is larger than the former work of compression and thus the gas that burns last loses some of its energy while the gas that burns first gains energy. The overall result is a
temperature gradient, that rises from the last portion burnt to the first portion burnt, which can amount to several hundred degrees centigrade [22].

**Figure 2.7**  Constant volume combustion.
CHAPTER 3  DESCRIPTION OF APPARATUS

3.1 INTRODUCTION

In order to investigate the influence on combustion of hydrogen enrichment of methane and possible nitrogen oxide reduction using charge stratification an apparatus was required that would enable:

- accurate gas mixtures of hydrogen/methane/air to be prepared.
- gas mixtures to be combusted under constant volume conditions.
- a stratified charge to be created in the combustion chamber.
- analysis of the exhaust gases to determine NO concentration.

The apparatus utilised for this project was in some cases modified from that used by previous researchers and in other cases purpose designed and built. A schematic and photographic layout of the apparatus is shown in Figures 3.1 and 3.2.

Figure 3.1  Experimental apparatus layout.
Figure 3.2
Schematic layout of test apparatus.

- TEST MIXTURE
- INJECTION MIXTURE
- INJECTOR
- SPARK PLUG
- COIL
- TIMING BOX
- 12V
- PIERZO AMP
- OSCILLOSCOPE
- VACUUM PUMP
- COLD TRAP
- ELECT. CABLING
- VENTING PIPE
- MAIN PIPING
- DRY AIR
- MASS SPECTROMETER
- TO DIFFUSION PUMP
- VACUUM PUMP

Chapter 3 Description of Apparatus
3.2 CONSTATE VOLUME COMBUSTION CHAMBER

3.2.1 Combustion Chamber Design

The constant volume combustion chamber (Figure 3.3), or bomb, used for this work was the same as that used by Robinson [24] with a few modifications to enable investigations to be conducted with optical probes. The bomb was constructed from 304L stainless steel in order to comply with all the requirements for the combustion work and mass spectrometric sampling. The latter requires that the surface be corrosion resistant and very clean thus minimising any surface absorption of gases which could lead to contamination when sampling. The internal dimensions are similar to those used by Damiano [10] who calculated that a minimum diameter of 50mm was required in order to effectively eliminate wall quenching effects. He then increased the diameter to 100mm as it was feared ionisation probes could obstruct the flame path. A length of 275mm was used giving an internal volume of 2.059 litres (including crevice volumes from valves, spark plug and thermocouple probe). The vessel was constructed according to BS 5500: 1991 and the bomb pressure tested to 70 bar. The bomb has a flanged joint at one end for internal access. Mounted in the centre of the flange are the thermocouple, pressure transducer, inlet/outlet and sampling valves. All these positions have been recessed so that the bottom edge of the fittings fit flush with the inside surface of the flange to minimise any crevice volumes. A modified spark plug was located with a similar recess in the opposite end of the bomb.

Sealing of the flanged end of the bomb was achieved through the use of a conflat seal. This is a metal to metal seal and consists of a copper gasket which is crushed between two knife edges machined into the mating surfaces. This type of seal is widely used in all vacuum applications and is far superior to the O-ring seal used by Damiano. All threads were sealed using teflon thread tape and swagelok fittings were used for all attachments. Stainless steel Whitey 60 series valves were used for evacuating and filling the bomb as they use O-ring seals which give excellent performance at elevated temperatures. A stainless steel Nupro bellows sealed valve was used for sampling which eliminates air entrainment when operated.

The bomb, as used by Robinson, was modified through the placement of eleven optical
probe housing mounts along the length of the bomb. These were sealed using modified conflat seals and copper gaskets. When the optical probes were not in use M8 bolts were used to seal the holes. When carrying out the optical probe analysis the inside of the bomb was sprayed matt black using high temperature paint to minimise internal reflections. Mass spectrometer analysis was not carried out when conducting studies using the optical probes.

![Figure 3.3 Constant volume combustion chamber (exploded view).](image)

### 3.2.2 Pressure and Temperature Measurement

A K-type thermocouple mounted in the flange of the bomb was used to measure the initial temperature of the combustion mixture. Other thermocouples were mounted on the outer surface of the bomb and on the sampling valve. The initial pressure in the bomb was measured using an Airflow DB-1 Digital Barometer. This instrument has a resolution of 1 mbar and a pressure range of -1000 to +1999 mbar absolute. This allowed the bomb to be filled between each explosion to an accuracy of ±0.5% of the reading. The Digital Barometer was mounted after the main isolating valve to protect it
from the high pressures created during combustion. Thus the extra volume of the connecting passages was allowed for when calculating equivalence ratios.

The pressure rise during combustion was measured using an AVL 8QP 500c piezoelectric pressure transducer mounted in the flange of the bomb and sealed with a copper gasket. This was connected via a piezo channel charge amplifier to a Hewlett Packard 54602A Oscilloscope where the information was captured and then downloaded to a PC using HP Scopelink software for further analysis (Figure 3.4). The transducer arrangement was calibrated using a Barnet Instruments Industrial Deadweight Tester, modified by Trolove [25].

![Figure 3.4 Data acquisition and injection/ignition control equipment.](image)

### 3.2.3 Heating

To minimise gas entrainment on the surface of the bomb and to eliminate any condensation of water, the bomb and associated valves were required to be heated to approximately 120°C. This was achieved through the use of electrical resistance heating cable. The bomb’s outer wall was maintained at a constant 120°C giving an initial gas temperature of approximately 95°C. The bomb was wrapped in glass fibre insulation and an outer layer of aluminium foil (Figure 3.5).
3.3 **FUEL INJECTOR ASSEMBLY**

3.3.1 **Injector Assembly**

A stratified charge was created inside the bomb by injecting pure hydrogen through a specially modified spark plug. The injector assembly (Figure 3.6) chosen for this testing was that used by Damiano [10]. This consisted of a Bosch gasoline fuel injector, part number 0 280 150 201 (Specifications in Table 3.1), connected to a non-return valve. The non-return valve prevented combustion gases entering the injector and damaging the sealing surfaces.

<table>
<thead>
<tr>
<th>Operating Voltage</th>
<th>12 V DC with 6 Ω resistor in series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve Lift</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Gasoline Flowrate at 300 kPa</td>
<td>236 cm³/min with valve permanently open</td>
</tr>
<tr>
<td>Maximum Opening Time</td>
<td>1.8 ms</td>
</tr>
<tr>
<td>Maximum Closing Time</td>
<td>0.9 ms</td>
</tr>
</tbody>
</table>

**Table 3.1** Specifications of Bosch gasoline injector.

The duration of injection was controlled by a specially built timing control system which supplies the injector with 12 V DC through a 6 Ω resistor. This allowed the injector pulse to be varied from 1 - 1000 ms (see section 3.4.2). The gas to be injected was supplied via a pressure regulator which allowed the injection pressure to be varied from 3.4 bar (non-return valve cracking pressure) to 15 bar.
Robinson [24] discovered that at operating temperatures above 5 bar small amounts of hydrogen would leak through the injector. To overcome this a valve was placed between the non-return valve and the modified spark plug to prevent leakage into the bomb. This was necessary to prevent contamination of the exhaust gases while sampling with the mass spectrometer as this could take 20-30 minutes in which time significant amounts of hydrogen would otherwise enter the bomb.

![Figure 3.6 Injector assembly.](image)

### 3.3.2 Modified Spark Plug

A modified spark plug (Figure 3.7) has been developed in the department over the last seven years which allows a stratified charge to be formed in the combustion chamber by injecting gas through the central core [10, 24, 26, 27]. This method if required, would allow the installation of the modified plug into a standard automotive test engine without the need for major modifications to the cylinder head. The arrangement as used by Robinson [24] was based on a Champion N16YC spark plug. This was selected as it is a ‘hot’ type plug (the ceramic insulator has a smaller contact area with the body for reduced heat loss) and has a longer threaded section. Four Ø1.5mm holes were drilled into the plug body at 90 degree intervals around the circumference of the threaded section which aligned on the inside surface with the base of the ceramic insulator (Figure 3.8). A 1/8” stainless steel capillary tube was welded to a steel collar that had a recess machined on the inside surface. This collar was then screwed on to the threaded section of the spark plug using thread tape to form a seal.
Through the use of Schlieren photography it was discovered that this arrangement tended to produce a jet of hydrogen down the centre of the bomb rather than the desired localised ‘puff’ in the region of the spark plug. In view of this, the spark plug was further modified in an attempt to reduce the efflux velocity of the injected hydrogen. The ceramic insulator and electrode were removed to allow the use of a lathe to gradually increase the internal diameter of the plug towards the opening. The ceramic insulator was replaced with two layers of heat shrink and sealed at the base using Loktite 401 (cyanoacrylate ester). The electrode was reattached using ‘easyflow’ and the spark gap set to 1mm. Misfire with methane was found to be a problem when using the manufacturers suggested spark gap. Finally, the number of holes around the plug’s circumference was increased from four to six to reduce any pressure drop and lower the influx velocity. These modifications were very successful and led to a more localised region of stratified charge being formed in the combustion chamber. The spark plug/collar assembly was installed into the bomb using an annealed copper gasket to form a seal.
3.4 IGNITION SYSTEM

3.4.1 General Description

The ignition spark was provided by a single 12V DC Lucas SP12 automotive coil energised by a 12 V Exide Marine Battery. An earthed stainless steel mesh was placed around the high tension lead from the coil to the spark plug to help prevent any interference from the high voltage ignition spike affecting the oscilloscope.

3.4.2 Ignition and Injection Timing

A new timing control system was designed and built in the department to replace that used by Damiano [10] and Robinson [24]. The previous timing box was deemed inadequate as it relied on 6V DC relays for switching which Robinson had found had a number of inherent problems. The most common, were the shortening or lengthening of the injector pulse, caused by interference from the ignition coil and straying from the preset values.

The new timing system was a solid state device consisting of a switching box connected to a 286 PC. The switching box contained two transistors which controlled the 12 V
power supply to the injector and coil. The switching of the transistors was controlled by the PC. A program (see Appendix B) written in C accepted the injector duration and ignition delay as inputs and then sent the required commands to the transistors upon triggering by a keypress. Injection duration and ignition delay could be varied from 0-1000 ms in 0.1 ms steps.

3.5 GAS MIXING RIG

3.5.1 Mixing Vessels

Two stainless steel pressure vessels (Figure 3.9), as designed and constructed by Robinson [24], were used for the creation and storage of the mixtures required for combustion and injection. Test mixtures were formulated in the larger of the two which has an internal volume of 10.88 litres. The injection mixture vessel has an internal volume of 2.63 litres and was used to store the pure hydrogen for the injector. Both vessels were designed to BS 5500:1991 and are rated to a maximum operating pressure of 20 bar gauge. This pressure allowed a complete test series of 12 explosions to be completed on one fill. As a precaution against accidental ignition of the vessels contents they are both fitted with burst discs. These consist of a 0.3mm thick aluminium disc clamped in place by a burst nozzle and sealed with O-rings.

Figure 3.9 Gas mixing equipment (Baratron pressure transducers on right).
3.5.2 Pressure and Temperature Measurement

Mixtures were created using the method of partial pressures (Section 5.3.2). Two MKS Instruments Baratron pressure transducers mounted on a switching valve between the test and injection vessels were used for this purpose. These were capacitance type manometers and worked on the principle of the capacitance varying with the distance between two metal plates. Thus the flexing of a diaphragm with pressure increase caused the capacitance to change. The first was a Type 622A and measured in the range 0 - 1000 torr (mmHg) with an accuracy of ±0.25% of reading. The second was a Type 102A with a range of 0 - 20000 torr and an accuracy of ±0.5% of reading. Both were attached to the rig with stainless steel Cajon 8 VCR fittings which feature a metal gasket sealed between two highly polished metal beads. The pressure transducers were connected to a Type PDR-C-2C two-channel power supply/readout. This unit displayed the pressure reading on a digital readout, allowed the use of setpoints and was pre-calibrated for different units of pressure. These units always gave a linear reading so all that was required was that the zero be set before use by evacuating to a pressure of $10^{-3}$ torr.

The temperature inside the test and injection vessels was measured with K-type thermocouples connected to a Yokogawa digital thermometer.

3.5.3 Gas Supply

All the gases used during the test program were supplied from high pressure gas cylinders connected to the rig. The gases and their various compositions are shown in Table 3.2.

3.6 VACUUM PUMPS

3.6.1 Description

Two rotary vacuum pumps connected in parallel were used to evacuate the combustion chamber and mixing vessels. The first, an Hitachi 3VP-C (50 litre/min), was used as a roughing pump for initial evacuation down to a pressure of approximately 100 mbar. The second pump, a Japan Electron Optics JR-150 (75 litre/min), was then used in
parallel with the first pump to further reduce the vacuum to $10^{-3}$ torr while increasing the pumping speed. This method meant that only the first pump was exposed to the majority of the combustion products which may cause contamination. Edwards Supergrade A vacuum pump oil was used as it offers minimum back streaming and gives an excellent ultimate vacuum. For the mass spectrometer work both pumps were connected in series with cold traps to stop vapourised oil back streaming into the bomb. These were surrounded with liquid nitrogen during operation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Dry Air</td>
<td>BOC Gases Christchurch</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Zero Grade - 99.995% minimum</td>
<td>BOC Gases Ltd NZ</td>
</tr>
<tr>
<td></td>
<td>Oxygen &lt; 5ppm</td>
<td>Analytical Services Laboratory</td>
</tr>
<tr>
<td></td>
<td>Carbon Monoxide &lt; 0.5 ppm</td>
<td>Lower Hutt</td>
</tr>
<tr>
<td></td>
<td>Carbon Dioxide &lt; 1 ppm</td>
<td>Wellington</td>
</tr>
<tr>
<td></td>
<td>Hydrocarbons &lt; 2 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Moisture &lt; 0.2 g/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Instrument Grade - 99.99% minimum</td>
<td>BOC Gases Christchurch</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Special Gas - 99.7% minimum</td>
<td>BOC Gases Laboratory Wgttn</td>
</tr>
<tr>
<td>NO/NO$_2$</td>
<td>Calibration Gas - 2500 ppm NO ± 50 ppm</td>
<td>BOC Gases Ltd Australia</td>
</tr>
<tr>
<td>Methane</td>
<td>Scrubbed Biogas -</td>
<td>Christchurch City Council</td>
</tr>
<tr>
<td></td>
<td>Methane - 86.3%</td>
<td>Sewerage Treatment Plant</td>
</tr>
<tr>
<td></td>
<td>Carbon Dioxide - 12.4%</td>
<td>Bromley, CHCH</td>
</tr>
</tbody>
</table>

Table 3.2 Gas compositions.

3.6.2 Vacuum Measurement

Rough vacuum was measured using the DB1 Digital Barometer which gave a pressure reading from atmospheric down to 0 mbar absolute. Medium vacuum was then measured using a TC-1A thermocouple gauge connected to a MKS Instruments Type 286 thermocouple gauge controller.
3.7 MASS SPECTROMETER AND VACUUM SYSTEM

3.7.1 Introduction

The mass spectrometer and associated vacuum system (Figures 3.10 & 3.11) used for this project was essentially the same as that developed and used by Robinson [24] with minor alterations to the sampling system to allow continuous sampling at pressures near atmospheric.

Figure 3.10 Mass spectrometer assembly (front view).

Figure 3.11 Mass spectrometer assembly (rear view).
3.7.2 Mass Spectrometer

The mass spectrometer utilised was a Spectramass Dataquad DAQ200/DXS Quadrupole mass spectrometer which comprised of two main components; the analyser head and the control unit [28]. The analyser head contains the ion source, quadrupole analyser and the detector plates (Figure 3.12).

The ion source consists of a high energy electron beam which is produced within the ionisation chamber by a filament. This beam bombards the molecules in the sampling chamber exciting them to higher energy levels. When the energy reaches what is termed the ionisation potential of the molecule, an electron is ejected and a positive ion is produced. If the electron energy is further increased then the molecule will fragment into smaller positive ions of various masses. These ions are then accelerated and focused into the quadrupole analyser section by electrostatic plates.

The quadrupole analyser section consists of four stainless steel parallel rods of circular cross section. A negative and positive radio-frequency potential and superimposed DC potential are applied to opposing rods to produce a radio-frequency field. Ions upon entering this field are caused to oscillate. Depending on certain parameters, only ions within a discreet mass range will perform oscillations of stable amplitude. These are collected at the opposite end of the analyser while ions outside this range become unstable and are ejected. In this way the rod assembly acts as a mass to charge ratio (m/e) filter.

The ion detector determines the number of molecules in the substance of a particular m/e by measuring the ion current. As this current is very small it is first amplified using an electron multiplier and then measured by what is usually termed a Faraday plate collector.
The control unit houses the microprocessor and software, quadrupole power supply, keyboard and visual display unit. Outputs are provided for a printer and RS 232C interface.

<table>
<thead>
<tr>
<th>Mass range</th>
<th>1 - 200 amu (atomic mass units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>10% valley between adjacent peaks of equal height throughout the mass range</td>
</tr>
<tr>
<td>Min. detectable partial pressure</td>
<td>2 x 10^{-11} torr (Faraday cup detector)</td>
</tr>
<tr>
<td>Min. detectable total pressure</td>
<td>1 x 10^{-11} torr</td>
</tr>
<tr>
<td>Max. operating pressure</td>
<td>1 x 10^{-4} torr</td>
</tr>
<tr>
<td>Number of filaments</td>
<td>two</td>
</tr>
</tbody>
</table>

Table 3.4 Spectramass Dataquad DAC 200/DXS specifications [29]

3.7.3 Vacuum System

As the mass spectrometer operates at a maximum pressure of 1 x 10^{-4} torr an ultra low vacuum system is required for operation. This system is made up of a number of components described below:

a) Main Chamber - This component was designed by Robinson [24] to house the Dataquad analyser head and is manufactured from 304L stainless steel. All internal surfaces were finished as smooth as possible to reduce the possibility of trapping condensable and ‘sticky’ vapours. Attached to this were the gas sampling inlet flange, ionisation gauge and isolation valve. All seals were the high vacuum metal to metal conflat type arrangement. The ionisation gauge was removed for this research project as it tended to release large amounts of contaminants, when operated, which could effect results. The Dataquad has built in pressure measurement and safety features which eliminate the need for a separate gauge. The main vacuum chamber was isolated from the cold trap and diffusion pump by a bellows sealed Varian 951-5027 right angle valve. This eliminated the possibility of contaminating the chamber with diffusion pump oil and/or water vapour during startup and shutdown. A bellows sealed valve eliminated air entrainment during operation. This whole assembly was covered in aluminium foil and could be heated continuously at 400°C by a high temperature heating cable.
b) Liquid Nitrogen Cold Trap - Water vapour and oil that backstreams from the diffusion pump was condensed by a liquid nitrogen reservoir. This consisted of a stainless steel canister which was suspended inside a larger container which was in line with, and attached to, the diffusion pump. The internal canister was supported so as to allow for thermal expansion and to minimise heat gains from ambient air in order to reduce nitrogen boil-off. A tube at the top of the trap was used for filling.

c) Diffusion Pump - A Varian Type 0188 diffusion pump was bolted to the bottom of the cold trap assembly. The temperature of the oil heater was controlled using a 0 - 240V variable power supply. Care was taken not to overheat the oil or expose it to oxygen when hot as it could crack and become ineffective.

d) Backing Pump - A Varian SD200 rotary vacuum pump was connected to the exhaust port of the diffusion pump. The evacuated products were vented outside the laboratory via a 1” diameter plastic tube. Edwards Supergrade A mechanical pump oil was used.

e) Liquid Nitrogen Filling Controller - An automatic filling system allowed the vacuum rig to be maintained unsupervised for periods of up to 48 hours. The current through a transistor mounted inside a copper tube on the boil-off pipe of the cold trap changed with temperature. This was monitored by a control box and a relay was triggered when the temperature increased to a threshold value. This relay activated a 12V DC solenoid that supplied air at 0.4 bar gauge to the dewar causing liquid nitrogen to be pumped into the cold trap. When the trap overflowed the transistor is cooled and the filling is stopped. The transistor then warmed slowly aided by the thermal conductance of the copper tubing until the threshold value is reached again and the cycle is repeated.

3.7.4 Sampling System

A continuous sampling system, developed by Ahuja [30], was utilised to sample the exhaust from the combustion chamber into the mass spectrometer. This system allowed sampling at near atmospheric pressure and therefore negated the need to partially evacuate the combustion chamber as with the direct sampling system used by Robinson.
[24]. Only a brief description will be given here as the development of the system used is detailed in Ahuja [30]. Figure 3.13 shows a schematic layout of the sampling system. The sample at atmospheric pressure passes through capillary, $C_1$ ($\varnothing 0.254\text{mm}, L=1\text{m}$) to the reservoir which is connected to the sample bypass pump (Japan Electron Optics Laboratory Co. Ltd., JR-150; speed 75 l/min) via the bypass valve. The reservoir is also connected to the mass spectrometer by capillary, $C_2$ ($\varnothing 0.178\text{mm}, L=1\text{m}$). By altering the bypass valve the sampling pressure in the mass spectrometer analyser chamber can be varied from $10^{-8}$ to $10^{-5}$ torr.

![Figure 3.13 Schematic layout of continuous sampling system.]

If a gas sample consisting of a mixture of gases is introduced to a mass spectrometer and undergoes a transition from viscous to molecular flow at some point, mass fractionation of the sample will occur. If the velocity at this point is too low then the fractionated gas may back diffuse changing the sample composition in the mass spectrometer. Therefore, the particular diameters and lengths of capillary were chosen in order to ensure that the transition from viscous to molecular flow occurs in $C_2$ and that the velocity is sufficient to prevent back diffusion of the fractionated gas.

### 3.8 OPTICAL PROBES

#### 3.8.1 Introduction

In order to track the path of the flame front as it propagates along the length of the combustion chamber some type of probe was required. Previous researchers [24, 27] in this department had used ionisation probes with some success but had found that they were prone to interfering with each other if placed too close together. With this in mind it was decided to use optical probes as it was hoped that a number of probes could be
placed near the ignition end of the bomb. Optical probes have the advantage that their signals do not interfere with each other and if the field of view is small then they can produce a very discreet signal.

![Optical probe housing (exploded and cutaway)](image)

**Figure 3.14** Optical probe housing (exploded and cutaway).

### 3.8.2 Probe Housing

If a discreet signal is required from an optical probe then the field of view must be decreased. This is achieved in practice by constructing a channel in the path of the light entering the housing which only allows light rays from certain angles to pass through it. For this application a $\varnothing 1\text{mm} \times 40\text{ mm}$ hole was used to limit the field of view to three degrees. The inside of this hole was sand blasted in order to try and reduce the chance of stray light rays being reflected along its length. An optical window was placed at the end of this hole and sealed using copper gaskets and RTV. This isolated the photodiode from the combustion chamber. An infrared plastic photodiode (Radio Spares BPW34) was used to detect the light from the flame front. This consists of a $7\text{mm}^2$ planar silicon PIN photodiode housed in a two pin epoxy package. These were chosen for their low noise, high speed and high spectral sensitivity (Table 3.3). The photodiodes were mounted into nylon caps which screw into the top of the probe housings. The probe housings (Figure 3.14) were constructed from steel and screwed into special mounts along the length of the bomb (section 3.2.1). Two configurations were used; in the standard configuration all eight probes were equispaced along the length of the bomb and in the alternate configuration seven of the probes were clustered around the spark plug end of the bomb.
to give greater accuracy at initiation with the eighth at the far end. Sealing was achieved through the use of modified conflat seals.

<p>| | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Peak wavelength</td>
<td>850 nm</td>
</tr>
<tr>
<td>Responsivity</td>
<td>0.62 A/W</td>
</tr>
<tr>
<td>Rise/fall time</td>
<td>20 ns</td>
</tr>
<tr>
<td>Acceptance angle</td>
<td>120°</td>
</tr>
<tr>
<td>Dark current (max.)</td>
<td>30 nA</td>
</tr>
<tr>
<td>Noise equivalent power</td>
<td>$4.1 \times 10^{-14}$ W/√Hz</td>
</tr>
<tr>
<td>Power dissipation</td>
<td>150 mW</td>
</tr>
</tbody>
</table>

Table 3.3 Photodiode BPW34 technical specifications.

3.8.3 Signal Processing

The photodiodes were connected via twisted pair cabling (to eliminate interference) to an eight channel photodiode amplifier designed and built in the department. The gain for each channel was varied so that the maximum signal was just under the limit of 5 volts. The output from the amplifier was connected to a Boston Technology PC30 sixteen channel (200 kHz) analogue to digital high speed data acquisition board mounted in a 486 PC. The output from the photodiodes and the piezoelectric pressure transducer with time were then captured using data acquisition software and stored as a data file. This was then analysed later using the graphically based DADiSP software.
CHAPTER 4  CALCULATIONS AND CALIBRATIONS

4.1 STOICHIOMETRIC AIR/FUEL RATIO

4.1.1 Methane/Air Mixtures

The stoichiometric burning of methane in air can be represented by the following equation (ignoring the negligible quantities of CO₂ and Ar in air):

\[
\text{CH}_4 + 2[\text{O}_2 + 79/21\text{N}_2] = \text{CO}_2 + 2\text{H}_2\text{O} + 158/21\text{N}_2
\]  

(4.1)

The percentage composition of methane in the mixture on a volumetric basis can be calculated by dividing the number of moles of methane by the total number of moles in the mixture:

\[
\%\text{CH}_4 \text{ in mixture (stoic.)} = \frac{1}{1 + 2 + 158/21} = 9.50\% 
\]  

(4.2)

The stoichiometric air/fuel ratio is given by:

\[
\left[ \frac{n_{\text{air}}}{n_{\text{fuel}}} \right]_{\text{stoic.}} = \frac{2 + 158/21}{1} = 9.524 
\]  

(4.3)

The equivalence ratio, \( \lambda \), is defined as the actual air/fuel ratio divided by the stoichiometric air/fuel ratio:

\[
\lambda = \frac{\left[ \frac{n_{\text{air}}}{n_{\text{fuel}}} \right]}{9.524} 
\]  

(4.4)

4.1.2 Hydrogen/Air Mixtures

The equation for stoichiometric burning of hydrogen in air is shown below:

\[
2\text{H}_2 + [\text{O}_2 + 79/21\text{N}_2] = 2\text{H}_2\text{O} + 79/21\text{N}_2
\]  

(4.5)

From this the percentage composition of hydrogen in a stoichiometric mixture can be calculated as 29.58%, leading to an air/fuel ratio of 2.381.
4.1.3 Hydrogen/Methane/Air Mixtures

The equation for burning a stoichiometric mixture of hydrogen/methane in air depends on the proportion of hydrogen, \( x \) in the fuel. The two separate equations for methane in air and hydrogen in air are:

\[
(1 - x)\text{CH}_4 + 2(1 - x)[\text{O}_2 + 79/21\text{N}_2] = (1 - x)\text{CO}_2 + 2(1 - x)\text{H}_2\text{O} + 2(1 - x)79/21\text{N}_2 \tag{4.6}
\]

\[
2x\text{H}_2 + x[\text{O}_2 + 79/21\text{N}_2] = 2x\text{H}_2\text{O} + x79/21\text{N}_2 \tag{4.7}
\]

These two equations can then be combined to form the equation for burning a mixture of \( x \) % hydrogen and \((1 - x)\) % methane in air:

\[
(1 - x)\text{CH}_4 + 2x\text{H}_2 + (2 - x)[\text{O}_2 + 79/21\text{N}_2] = (1 - x)\text{CO}_2 + 2\text{H}_2\text{O} + (2 - x)79/21\text{N}_2 \tag{4.8}
\]

The percentage fuel in the mixture at stoichiometric is given by:

\[
\% \text{ fuel in mixture (stoic.)} = (1 + x) / (1 + 79/21 + (2 - x)(1 + 79/21)) \tag{4.9}
\]

The stoichiometric air/fuel ratio is given by:

\[
[n_{\text{air}}/n_{\text{fuel}}]_{\text{stoic.}} = (2 - x)(1 + 79/21) / (1 + x) \tag{4.10}
\]

4.2 MASS SPECTROMETER CALIBRATION

4.2.1 Introduction

In order to get quantitative readings from a mass spectrometer it must be calibrated. This can be achieved by either a relative or absolute method. The relative method relies on the fact that the relationship between the volume fraction of a component in the gas mixture and the characteristic peak height (partial pressure detected by mass spectrometer) can be assumed to be linear. Therefore a change in peak height can be
directly related to a change in component concentration [31]. Due to tuning effects on absolute intensities of a spectrum, it is an advantage to express a peak relative to a reference peak which is constant.

The second method requires an accurate gas mixture in which the absolute concentration of the gas to be measured is known. Alternatively a pure sample could be used. Thus the instrument’s sensitivity to that particular ion can be found. The sensitivity is pressure dependant so a calibration curve must be prepared by sampling the calibration gas over a range of pressures.

The calibration procedure used in this investigation utilised both relative and absolute methods as detailed below.

### 4.2.2 Calibration Theory

As the aim of this investigation was to determine the amount by which nitric oxide could be reduced by using a stratified charge it was necessary to accurately measure the concentration of nitric oxide in the exhaust. When burning hydrogen in air the products expected in the exhaust are un-reacted nitrogen, unburnt hydrogen & oxygen, water, nitrogen dioxide and nitric oxide. These six products along with their respective cracking patterns are shown in Table 4.1. A gas’s cracking pattern is the mass numbers that will be detected by the mass spectrometer when the gas is ionised i.e. when nitrogen is ionised it will produce ions of mass 28 \((N_2^+)\) and 14 \((N^+)\). The mass numbers shown in *italics* are unique to that particular component and can therefore be used to give an accurate measure of its concentration. As can be seen mass number 30, which is representative of nitric oxide, also appears in the cracking pattern of nitrogen dioxide. Fortunately, as has been shown by previous researchers, the amount of nitrogen dioxide produced in the exhaust is very small (≈ 1% of the nitric oxide concentration). Therefore the concentration of nitric oxide in the exhaust can be determined with very little error by measuring the peak at mass 30.
As was stated in section 4.2.1 it is desirable to express a peak relative to a reference peak. The reference gas chosen in this case was nitrogen as it remains almost constant before and after combustion as only a small amount (~1%) is consumed in the formation of nitric oxide. Also a calibration gas of NO in N\textsubscript{2} was already available. By sampling this gas the sensitivity could be determined as follows:

\[
\text{sensitivity} = \frac{\text{actual ratio of NO} / \text{N}_2 \text{ in calibration gas}}{\text{ratio of measured peak heights} \ 30 / 28 (\text{NO} / \text{N}_2)} \quad (4.11)
\]

The test mixture is then sampled before ignition to determined the concentration of nitrogen it contains which is assumed to remain constant after combustion. The exhaust is sampled and the ratio of the peak heights 30 and 28 calculated which in turn is multiplied by the sensitivity to determine the actual ratio of NO to N\textsubscript{2}. The concentration of nitric oxide in the exhaust can then be determined by simply multiplying this ratio by the initial concentration of nitrogen.

### 4.2.3 Calibration Gases

Two calibration gases were required as the concentration of nitrogen in the initial test mixture and nitric oxide in the exhaust gas had to be determined. As noted above the department already had a high accuracy calibration gas containing 2520 ppm ± 50 ppm nitric oxide with a balance of nitrogen. This concentration of NO was chosen as it is in the region of expected concentrations in the exhaust gas (0 - 5000 ppm). A second calibration gas (total pressure ≈ 1500 mbar) containing nitrogen, oxygen and hydrogen (components of the test mixture) was therefore created using the 1000 torr Baratron

<p>| | | | |</p>
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<thead>
<tr>
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<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>28</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>32</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>18</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>NO</td>
<td>30</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>44</td>
<td>32</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 4.1: Cracking patterns for the exhaust gases when burning hydrogen in air.
pressure transducer (Section 3.5.2) in a specially built three litre stainless steel vessel. The high accuracy mixture was prepared in much the same way as the test mixtures (Section 5.3) but with special attention paid to flushing of the vessel and supply lines with each gas. A bellows sealed metering valve was used for fine control and to eliminate valve entrainment. Temperature compensation was carried out using a K-type thermocouple. The relative proportions of each gas were chosen, as above, to be similar to those in the test mixture i.e. 30% H₂, 55% N₂ and 15% O₂.

4.2.4 Calibration Procedure

As the mass spectrometer's sensitivity to particular ions can alter with sampling pressure, it is necessary to calibrate at the same pressure that will be used for testing. Initially, the calibration gas was sampled over a range of pressures (1 x 10⁻⁷ to 5 x 10⁻⁵ torr) to produce a calibration curve. The calibration curve for a hydrogen, oxygen and nitrogen mixture is shown in figure 4.1. As can be seen, the ion ratios tended to show greater variation at low and high sampling pressures. A sampling pressure range of 1.0 x 10⁻⁵ to 2.0 x 10⁻⁵ torr was chosen as the calibration curve was relatively flat over this range meaning that changes in pressure would alter the sensitivity very little. Also, the higher the sampling pressure the greater the accuracy as the percentage error in each reading is minimised. The calibration curve for NO/N₂ was also found to be relatively constant over this range.

Before and after each test session the calibration gases would be sampled to determine the relevant sensitivities as these would vary from day to day.

When sampling the exhaust gases from the bomb it was found that the relative concentration of nitric oxide detected would increase to a maximum and then proceed to decrease with time. Figure 4.2 shows this trend with the peak height reached approximately 2-3 minutes after sampling commenced which in turn began about 30 - 60 seconds after the end of combustion. It is postulated that the initial increase in concentration is due to the nitric oxide being absorbed into the walls of the sampling chamber and the connecting capillaries. As the walls become saturated the detected concentration increases until the actual value is reached. The consequent decrease is then caused by the nitric oxide degrading to form nitrogen dioxide which is a continuing process. In view of this, special care was taken to ensure minimum time between the end
of combustion and admission of the exhaust gases into the mass spectrometer to minimise any degradation of the nitric oxide formed.

Figure 4.1 Variation of N$_2$/O$_2$/H$_2$ ion ratios with pressure.

Figure 4.2 Variation in relative nitric oxide concentration with time.
CHAPTER 5  EXPERIMENTAL PROCEDURE

5.1 INTRODUCTION

A test programme was developed in order to achieve the aims of the investigation as detailed in section 1.4. The test programme undertaken was divided into three main parts:

1. Hydrogen Enrichment of Methane
2. Stratified Charge Nitric Oxide Reduction
3. Flame Propagation Visualisation

This chapter details the procedures specific to these three parts along with general methods used for preparation of gas mixtures and their subsequent combustion. In total 1220 individual explosions were carried out during testing.

5.2 TESTING PROGRAMME

5.2.1 Hydrogen Enrichment of Methane

The first part of the test programme was divided into three sections:

1) Baseline Testing - Tests with pre-mixed methane/air mixtures were carried out in order to determine a reference point by which to compare the later tests using hydrogen enrichment. The overall charge relative air/fuel ratio of the mixtures was varied from $\lambda = 0.9$ to 1.5 (10.4% to 6.5% methane in air). As with all the tests in this part of the programme the initial pressure in the bomb before combustion was maintained at 1500 mbar absolute and the temperature at 25°C. Pressure traces were recorded along with the peak pressure ($P_{\text{max}}$) and time to peak pressure ($t_{\text{max}}$). Tests: 156.

2) Homogeneous Charge - Pre-mixed mixtures of hydrogen/methane/air were then used to determine the effect of hydrogen addition on the combustion properties of methane. The overall equivalence ratio was varied from $\lambda = 1.0$ to 1.3 as this research was mainly concerned with increasing efficiency and decreasing emissions when
utilising lean burn (λ > 1.0). The level of hydrogen enrichment was varied from 5 - 30% by volume of the fuel. This range was chosen to encompass the fuel commonly termed 'Hythane', which consists of 15% hydrogen by volume. As with the baseline testing pressure traces, $P_{\text{max}}$ and $t_{\text{max}}$ were recorded. Tests: 240.

3) Stratified Charge - The third section involved stratified or heterogeneous mixtures of hydrogen in pre-mixed methane/air mixtures. As with the homogeneous charges, the overall equivalence ratio was varied from $\lambda = 1.0$ to 1.3. However the amount of hydrogen added was reduced to 0 - 5% of the fuel. Hydrogen was injected through the spark plug with the level of stratification being controlled by varying the ignition delay after the end of injection. The ignition delay was varied in the time range 20-150ms in order to maximise $P_{\text{max}}$ and minimise $t_{\text{max}}$ for each test condition. Hydrogen was supplied to the injector at a pressure of 4.5 bar. This enabled injection to be achieved in under 100ms while producing a localised puff around the spark plug, in comparison to a jet flow observed with higher injection pressures. Tests: 204.

5.2.2 Stratified Charge Nitric Oxide Reduction

The second part of the test programme was divided into two sections:

1) Baseline Testing - As with the methane testing baseline tests were carried out in order to determine a reference point for further research. The relative air/fuel ratio of the hydrogen/air mixtures was varied from $\lambda = 1.0$ to 4.0 (29.6% to 9.5% hydrogen in air). For the hydrogen/air testing the initial pressure in the bomb before combustion was maintained at 1200 mbar absolute and the temperature at 95°C to minimise gas absorption on the interior surfaces. Pressure traces were recorded along with the peak pressure and time to peak pressure. The exhaust gases were then sampled using the mass spectrometer and the concentration of nitric oxide (NO) and oxygen ($O_2$) measured. Tests: 200.

2) Stratified Charge - The second section involved a proportion of the hydrogen being injected through the spark plug before ignition to form a stratified charge. The equivalence ratio for all of the stratified charge tests was kept constant at $\lambda = 1.2$ as this produced the highest concentrations of nitric oxide as determined with the baseline
testing. The proportions of hydrogen injected were 10, 20, 35 and 50% and the level of stratification was controlled by varying the ignition delay from 0 to 150ms (8 - 10 steps) after the end of injection. Hydrogen was supplied to the injector at a pressure of 8.5 bar. This allowed injection to be completed in under 300ms. As above, the pressure trace was recorded along with the concentration of nitric oxide. Tests: 350.

5.2.3 Flame Propagation Visualisation

The final part of the testing programme was divided into six sections. For each section the optical probes were mounted in both the standard and alternate configurations (Section 3.8.2). For the first four sections a methane/air mixture of equivalence ratio, $\lambda = 1.0$, was used with the orientation of the bomb and probes being varied:

1) Bomb mounted horizontally with probes at top to obtain initial propagation data.
2) Bomb mounted horizontally with probes at bottom to determine if flame is propagating with a 'hook' shape (effect of buoyancy).
3) Bomb mounted horizontally with probes at side to check symmetry of flame front.
4) Bomb mounted vertically to eliminate buoyancy effects with probes at side and spark plug at top (downward propagation).

For the last two sections pre-mixed and stratified hydrogen/methane/air mixtures were employed with an overall equivalence ratio of $\lambda = 1.0$ and 5% hydrogen addition by volume of fuel.

5) Bomb mounted horizontally with probes at top. Pre-mixed hydrogen/methane/air.
6) Bomb mounted horizontally with probes at top. Stratified hydrogen/methane/air, 4.5 bar injection pressure, 100ms ignition delay after the end of injection.

Tests: 70
5.3 **TEST MIXTURE PRODUCTION**

5.3.1 **Introduction**

All of the gas mixtures used in the testing programme were formulated by the method of partial pressures using the gas mixing rig and Baratron pressure transducers. The mixtures were then stored in the test mixture vessel until required. An EXCEL spreadsheet was used to determine the required filling pressures for each mixture.

5.3.2 **Method**

Using the method of partial pressures, first a final target pressure was selected, which in general was the maximum operating pressure of the vessel (20 bar). If, for example, a mixture of 10% methane in air was required then the partial pressure of methane required was 10% of the final target pressure (2 bar). The vessel was filled to this pressure with methane and then filled to the final target pressure with air. This of course, assumes that the temperature remains constant during the filling process which does not occur in practice so corrections have to be made.

The method used to formulate mixtures was as follows:

- The test mixture vessel was evacuated using the rotary vacuum pumps to a pressure of $10^{-3}$ torr.

- The vessel was flushed with hydrogen or methane (depending on what mixture was required) to a pressure of 1.5 bar absolute and then re-evacuated. This procedure was used to remove any unwanted molecules from the vessel and associated pipe work.

- The EXCEL spreadsheet was used to calculate the partial pressure, $P_1$, of hydrogen or methane required using the target final pressure, $P_2$. The vessel was then filled to $P_1$ and allowed to stabilise for 10-15 minutes at which point the pressure and temperature inside the vessel were recorded as $P_1$ and $T_1$. The target pressure was then recalculated using $P_1$ as it invariably differed from that originally predicted.
• All the pipe work used to fill the vessel was then vented to atmosphere, evacuated, flushed with air and then re-evacuated to $10^3$ torr to remove any traces of the fuel.

• The vessel was filled with air as close as possible to the recalculated target final pressure, $P_2$. As the temperature inside the vessel rose as it was filled, due to the compression of the gases, the pressure would subsequently drop as it cooled again. Therefore, additional air had to be added to compensate for this (see section 5.3.3 for details on this calculation).

• Once the temperature of the mixture had suitably stabilised, the mixture composition (volumetric basis) was calculated by dividing the fuel's partial pressure by the temperature corrected final pressure. The final equivalence ratio was then calculated allowing for gas composition.

• For homogeneous mixtures of hydrogen/methane/air the fuel (hydrogen/methane) was pre-mixed using the injection mixture vessel. This was done to increase the accuracy as a mixture of 5% H$_2$ and 95% CH$_4$ and air at $\lambda = 1.3$ would require a hydrogen partial pressure of 73 mbar (20 bar total pressure). As this is a very low pressure compared to the absolute error of the pressure transducer, the percentage error would be correspondingly high. The fuel mixture was allowed to settle overnight before being used to fill the test mixture vessel to the required partial pressure as with standard hydrogen or methane mixtures.

5.3.3 Temperature Correction

If a vessel of constant volume, $V$, containing $n_1$ moles of gas A at pressure, $P_1$, and a temperature, $T_1$, is filled with $n_2$ moles of gas B to a pressure of $P_2$ the temperature will increase to $T_2$ due to the compression of gas A. As the vessel cools and the temperature decreases the pressure will also drop as the volume and total number of moles ($n_1 + n_2 = n_T$) are constant ($pV = nRT$). If the pressure and temperature are known then the number of moles can be calculated at any time. Unfortunately, due to the limitations of the available equipment, the temperature and pressure could not be measured when they were rapidly changing. This left two choices, the first of which involved waiting for the
temperature to drop to \( T_1 \) and then adding a small amount of gas B to bring the pressure up to that desired. The mixture could then be calculated using:

\[
\frac{n_1}{n_2} = \frac{P_1}{(P_2 - P_1)} \tag{5.1}
\]

This unfortunately takes a very long time due to the decreasing heat transfer rate as the gases temperature approaches that of the surroundings.

The second, and preferred, method involved the use of a simple calculation to correct for the gas's elevated temperature. The vessel was filled as before but is only left long enough for the temperature to drop to within 1-2°C of \( T_1 \) at which point the intermediate values, \( T_i \) and \( P_i \), are recorded. These values were used to predict the final pressure, \( P_2 \), at temperature, \( T_1 \), using the perfect gas equation:

\[
\frac{P_2 V}{n_2 RT} = \frac{P_i V}{n_i RT_i} \tag{5.2}
\]

Cancelling like terms gives:

\[
\frac{P_2}{T_i} = \frac{P_i}{T_i} \tag{5.3}
\]

Rearranging 5.3:

\[
P_2 = \frac{T_i}{T_1} P_i \tag{5.4}
\]

From \( P_2 \) the extra gas B required to reach the desired equivalence ratio could be calculated by finding the difference between the predicted \( P_2 \) and the target final pressure. Once this amount was added, equation 5.4 could be used again to check that the corrected pressure is exactly that required.

### 5.4 INJECTOR CALIBRATION

#### 5.4.1 Introduction
Before beginning the charge stratification tests it was required that the injector be calibrated. This was achieved by injecting pure hydrogen into the bomb, recording the pressure and temperature changes, then calculating the number of moles injected by using the ideal gas equation.

**5.4.2 Calibration Method**

A series of calibration curves were developed for different injection pressures by varying the duration of injection. The injector supply pressure was set using the 20000 torr Baratron pressure transducer as the gauge on the pressure regulator was found to be in error by 0.5 bar. The pressure before and after injection inside the bomb was measured using the 1000 torr Baratron pressure transducer in order to increase accuracy over the DB-1 digital barometer. The bomb was filled with air to approximately 1300 mbar so that the pressure after injection would be close to 1500 mbar. Once stabilised the initial temperature and pressure were recorded. 5 - 10 injection pulses were then fired depending on the duration of injection. The final temperature and pressure were recorded and used to calculate the number of moles injected for a single firing. As the pressure gauges were mounted outside the bomb for their protection during combustion, the extra volume due to pipe work had to be allowed for when performing this calculation.

The resulting calibration curves were then used to set the injection duration for a required amount of hydrogen. Through subsequent calibrations at weekly intervals these curves were found not to vary.

**5.5 COMBUSTION PROCEDURE**

**5.5.1 Introduction**

As the procedure for combustion is essentially the same for all parts of the test programme, the procedure for the hydrogen enrichment of methane will be detailed in its entirety with any changes listed for the stratified charge nitric oxide reduction and flame propagation studies.
5.5.2 Hydrogen Enrichment of Methane

a) Homogeneous Charge:

- The bomb is vented to atmosphere then evacuated using the rotary vacuum pumps to $10^{-3}$ torr.

- The bomb is flushed with pre-prepared mixture to a pressure of 1500 mbar and then re-evacuated to eliminate any contaminants in the bomb.

- The bomb is filled with pre-prepared mixture to a pressure of 1500 mbar and left to stabilise for 10 minutes while either heated or cooled to a temperature of 25°C. Fine adjustments to the internal pressure can be made using the metering valve.

- When initial temperature is reached the bomb isolation valve is closed and the ambient temperature, internal temperature and pressure recorded. The oscilloscope is reset and placed in ‘run’ mode.

- The ground switch on the piezo charge amplifier is pressed and then ignition is initiated by a key-press on the controlling PC. Peak pressure and time to peak pressure are recorded from the oscilloscope and the pressure trace down-loaded to a computer hard disk for further analysis.

b) Stratified Charge:

- While being evacuated, the injector isolation valve is left open to remove any hydrogen trapped between it and the injector. This, along with the hydrogen supply valve, is closed during filling and stabilisation to stop small traces of hydrogen leaking through the injector. As before, the bomb is filled to a pressure of 1500 mbar and left for 10 minutes.

- The injector duration and ignition delay are entered into the controlling computer. The injector supply pressure is set to 4.5 bar using the regulator and Baratron pressure
transducer.

- Once the bomb’s temperature has reached 25°C the main valve is closed and the hydrogen supply and injector isolation valves are opened. The piezo charge amplifier’s ground switch is pressed and the oscilloscope reset. The injection and ignition are then activated by a key-press. The injector isolation valve is then closed and the data recorded as before.

5.5.3 Stratified Charge Nitric Oxide Reduction

As stated above the combustion procedure for part two is based on that of part one with the only major differences being the initial pressure and temperature conditions of 1200 mbar and 95°C and an injector supply pressure of 8.5 bar. Once ignition has occurred the injector isolation valve is closed and the sampling valve to the mass spectrometer is opened. The gas analysis then begins (Section 5.6). When this is completed the bomb is evacuated and recharged as above.

5.6 GAS ANALYSIS

Analysis of the exhaust gases from the combustion chamber were carried out using a Spectramass Dataquad mass spectrometer (Section 3.7). At the beginning and end of each test series (ten explosions) the mass spectrometer is calibrated (Section 4.2) and the test mixture analysed. The procedure for analysing a sample is as follows:

- The bypass valve is fully opened and the mass spectrometer left to evacuate for 5 - 10 minutes (this is usually done while evacuating and recharging the combustion bomb in between tests) until a total pressure of approximately $1.0 \times 10^8$ torr is reached. The background spectrum is then recorded by printing the partial pressures for masses 18 (water), 28 (nitrogen), 30 (nitric oxide) and 32 (oxygen).

- After ignition has occurred the sampling valve on the combustion bomb is opened to allow a small proportion of its contents to be drawn into the mass spectrometer. The desired sampling pressure (usually around $1.4 \times 10^{-3}$ torr) is then set by closing the bypass valve (approximately 8.5 turns from fully open) while monitoring only mass 0
(total pressure) at a precision of zero to ensure a quick response.

- Once the desired sampling pressure has been reached masses 18, 28, 30 and 32 are monitored at a precision of 4° which ensures high accuracy. Once the mass ratio of nitric oxide over nitrogen (30/28) has reached a maximum the values are recorded.

- The sampling valve is then closed, the bypass valve fully opened and the mass spectrometer allowed to re-evacuate ready for the next test.

The procedure for analysing pre-prepared test mixtures is identical to that above apart from the masses monitored which include 2 (hydrogen).

5.7 FLAME PROPAGATION

Four different probe/combustion chamber orientations were used in order to determine whether buoyancy effects were significant. The first three involved a horizontally mounted combustion chamber with the probes mounted along its length on the top, side and bottom. For the fourth test the combustion chamber was mounted vertically with downward propagation. The effects of pre-mixed and stratified hydrogen addition were investigated using the standard horizontal combustion chamber orientation with the probes mounted along the top.

Once the bomb’s orientation and optical probes had been installed in the desired configuration, the procedure for combustion proceeded as outlined in section 5.5.2. Before ignition was triggered the desired sampling rate, duration and number of channels was entered into the data acquisition program. The sampling rate used was 20,000 Hz for nine channels (eight optical probes and the pressure transducer). The sampling duration was set to 2 seconds. This allowed time for both sampling and ignition to be triggered manually in sequence as the equipment had no provision for automatic triggering. The data was then saved to file for further analysis using the graphically based DADiSP software and the bomb evacuated and recharged for the next test.

*The precision can be varied from 0 - 5 and determines the accuracy with which an ions partial pressure is measured. The higher the precision, the greater the number of scans made at each mass number. But consequently more time is required for each scan.*
CHAPTER 6 HYDROGEN ENRICHMENT OF METHANE

6.1 INTRODUCTION

This chapter details and discusses the results obtained during investigation of the hydrogen enrichment of methane. The results for stratified charge nitric oxide reduction are detailed in the following chapter. The main focus of this work was to determine what improvements to the combustion characteristics of methane could be achieved through the addition of hydrogen. In particular, the characteristics to be observed were the peak pressure, \( P_{\text{max}} \) and time to peak pressure, \( t_{\text{max}} \). \( P_{\text{max}} \) represents the power available from the fuel during an explosion. \( t_{\text{max}} \) determines the efficiency of the combustion as the shorter the time to \( P_{\text{max}} \), the closer it is to constant volume combustion in an engine and thus, less time is available for heat loss. Two methods of hydrogen enrichment were also to be investigated; pre-mixed charge (homogeneous) and stratified charge (heterogeneous). The experimental work was conducted as three separate test series:

a) Baseline testing - to establish a standard set of results for the combustion of methane in air by which to compare the hydrogen enriched results.

b) Pre-mixed charge testing - to determine the combustion characteristics of a homogeneous hydrogen/methane/air mixture.

c) Stratified charge testing - to investigate the possible improvements over a pre-mixed hydrogen/methane/air mixture that can be achieved through the use of a hydrogen stratified charge.

These three test series will each be discussed separately. Each test point represents the average of 10-12 individual explosions requiring approximately 6 hours of testing.

6.2 BASELINE TESTS

6.2.1 Introduction

Initial testing began by exploding mixtures of methane/air to determine baseline data for
the experimental test rig. This would then be used later to compare with the data acquired for hydrogen enrichment. As detailed in Section 5.3 mixtures of methane and air were prepared with relative air/fuel ratios, \( \lambda \) in the range 0.9 - 1.5. As with all testing detailed in this chapter the initial charge temperature and pressure were 25°C and 1500 mbar respectively.

### 6.2.2 Discussion

The peak pressure and time to peak pressure with varying \( \lambda \) is illustrated in Figure 6.1. As expected, the maximum peak pressure was observed with a stoichiometric (\( \lambda = 1.0 \)) mixture of methane/air. \( P_{\text{max}} \) decreases rapidly with rich mixtures (\( \lambda < 1.0 \)) and displays a corresponding but less rapid decrease for increasingly lean mixtures (\( \lambda > 1.0 \)). These observations compare well with the limits of flammability, 5.3% - 15.0%, which equate to a relative air/fuel ratio range of 1.85 - 0.60. Peak pressure is directly related to flame temperature which in turn is related to relative air/fuel ratio. In a fuel rich system there is insufficient air for complete oxidisation of the fuel so the energy released is less. In a fuel lean system there is less energy available and the excess air must be heated to the temperature of the products, thus using extra energy and lowering the overall temperature. The time to peak pressure displayed similar but opposite characteristics to \( P_{\text{max}} \) with a varying relative air/fuel ratio. Minimum \( t_{\text{max}} \) was achieved slightly lean of stoichiometric indicating a possible erroneous reading and increased for both \( \lambda < 1.0 \) and \( \lambda > 1.0 \) as expected. The time to peak pressure is inversely proportional to the flame speed which is also dependant upon the relative air/fuel ratio.

The repeatability of results was determined by preparing and testing three methane/air mixtures at the same relative air/fuel ratio. The results were very encouraging with the peak pressure and time to peak pressure variance within 2%. As this research was mainly concerned with increasing efficiency and decreasing emissions the remainder of the testing was carried out with lean mixtures (\( \lambda \geq 1.0 \)). Rich mixtures generally only display benefits in terms of outright performance (power output).
6.3 PRE-MIXED CHARGE TESTS

6.3.1 Introduction

The second test series involved homogeneous hydrogen enrichment of methane/air mixtures. Pre-mixed hydrogen/methane/air mixtures were prepared with relative air/fuel ratios defined as the overall charge air/fuel ratio divided by the overall stoichiometric air/fuel ratio as detailed in Section 4.1.3. The proportion of hydrogen added to the fuel was defined on a volumetric basis and varied from 5 - 30%. It was chosen to define the amount of hydrogen on a volumetric basis rather than a mass basis as the test mixtures were formed using the method of partial pressures (Section 5.3) which was based on volumes. A volumetric basis had also been used by previous researchers in this area [32]. This range of hydrogen enrichment was selected to encompass the proportion used in 'hythane' which typically consists of 15% hydrogen by volume of fuel. The overall relative air/fuel ratio was varied in the range 1.0 to 1.3 in steps of 0.1.

6.3.2 Discussion

As with the methane/air mixtures, the hydrogen enriched mixtures displayed the same
overall trend of decreasing peak pressures with increasing relative air/fuel ratios (Figure 6.2). This can be explained by the same reasoning as in Section 6.2. The main observation to be made is the increase in $P_{\text{max}}$ with addition of hydrogen while maintaining a constant relative air/fuel ratio. As previously, this would normally be explained by an increase in the available energy of the charge. But as illustrated in Figure 6.3 the energy content of the fuel actually drops as the proportion of hydrogen added to the methane is increased. This occurs because although the specific calorific value of hydrogen is higher than methane (120 MJ/kg and 50 MJ/kg respectively) its density is eight times less (0.09 kg/m$^3$ compared to 0.72 kg/m$^3$). Thus, the increased $P_{\text{max}}$ cannot be attributed to an increase in fuel energy content but rather to an improvement in one or more of the combustion parameters associated with a flame propagating in a constant volume combustion chamber. The improvement in $P_{\text{max}}$ over that for pure methane was approximately proportional to the amount of hydrogen added for each relative air/fuel ratio indicating that the effects of hydrogen addition were more significant for lean conditions. At $\lambda = 1.3$ with 30% hydrogen enrichment $P_{\text{max}}$ improved by 14%. However, for the same proportion of hydrogen at $\lambda = 1.0$ the improvement to $P_{\text{max}}$ was only 4%.

![Figure 6.2 Peak pressures for homogeneous CH$_4$/H$_2$ mixtures.](image-url)
An explanation for the increase in $P_{\text{max}}$ can perhaps best be explained by investigating the variance in the time to peak pressure with hydrogen enrichment. From Figure 6.5 it can be seen that the general trend of increasing $t_{\text{max}}$ with relative air/fuel ratio is present as for methane/air mixtures. As for $P_{\text{max}}$, an improvement is observed with the addition of hydrogen resulting in a decrease in $t_{\text{max}}$. Once again this improvement is approximately proportional to the amount of hydrogen added to the methane and becomes more
significant as the relative air/fuel ratio increases. The percentage improvement to $t_{\text{max}}$ is illustrated in Figure 6.6. The reduction in $t_{\text{max}}$ for 30% hydrogen enrichment ranged from 25% ($\lambda = 1.0$) to 33% ($\lambda = 1.3$).

![Figure 6.5](Image)

**Figure 6.5** Time to peak pressure for homogeneous methane/hydrogen mixtures.

![Figure 6.6](Image)

**Figure 6.6** Reduction in time to peak pressure with homogeneous hydrogen enrichment.
The time to peak pressure is a function of two combustion parameters; ignition delay and flame speed. If these particular properties of hydrogen are investigated (Table 1.1) it can be noted that they are significantly better than those for methane. Hence, it could be assumed that the addition of hydrogen to methane would improve these particular characteristics. Also, as shown in Sections 2.2.3 and 2.2.4 the initial decomposition of methane is very dependant upon the attack by H, O and OH radicals. The rate of this initial breakdown of the CH₄ determines the ignition delay. The addition of hydrogen helps to quickly establish this pool of radicals thus reducing the delay. Excess oxygen helps to accelerate the reactions responsible for the radical formation therefore explaining the increased improvements at lean conditions. Karim et al. [9] observed that the addition of hydrogen to methane speeds up the rate of initiation of propagating flames over the whole combustible mixture range and that once a flame kernel is initiated the apparent rate of flame propagation is increased very significantly.

![Representative pressure traces for homogeneous methane/hydrogen mixtures (λ = 1.2).](image)

Representative pressure versus time traces for homogeneous charges with increasing hydrogen addition are detailed in Figure 6.7. It can be clearly seen that the addition of hydrogen to a pre-mixed charge improves the rate of pressure increase for all stages of combustion. These characteristics agree with those observed by Karim et al. [9] and
indicate that the overall characteristics of a particular explosion are significantly affected by what occurs at its initiation.

The enhancement of the rates of flame initiation and subsequent flame propagation reduces the ignition lag and combustion period in spark ignition engines which lead to noticeable improvements in the combustion process and engine performance [1].

6.4 STRATIFIED CHARGE TESTS

6.4.1 Introduction

The third test series in the programme utilised the technique of charge stratification for the hydrogen enrichment of the methane/air charge. Thus, a heterogeneous charge was produced inside the combustion chamber. The stratified charge was created by injecting hydrogen through the core of a specially modified spark plug (Section 3.3.2). An injector supply pressure of 4.5 bar was chosen to enable injection to be achieved in a time of under 100ms. This was desirable, as the longer the injection duration, the more time was available for mixing of the injected hydrogen with the pre-mixed methane/air charge in the combustion chamber. Thus, the charge would become less stratified and the results would start tending towards those for a homogeneous charge. The behaviour of this injected fuel flow was investigated with the aid of Schlieren photography (Appendix C). This confirmed that a supply pressure of 4.5 bar produced a localised puff around the plug, in comparison to a jet flow, observed with higher injection pressures.

As with the pre-mixed charge investigation, the relative air/fuel ratio was varied in the range $\lambda = 1.0$ to $\lambda = 1.3$. Once again the relative air/fuel ratio was defined as the overall charge air/fuel ratio divided by the overall stoichiometric air/fuel ratio. Pre-mixed methane/air mixtures were prepared with particular proportions so that the required hydrogen/methane/air ratios would result after injection within the bomb just prior to combustion. The aim of using a stratified charge was to try to achieve similar improvements to pre-mixed hydrogen enrichment while using significantly less hydrogen. Therefore the amount of hydrogen added was reduced to 1.5 - 5% of the fuel by volume.
6.4.2 Ignition Delay

Before testing commenced a brief investigation was carried out to determine the effects of ignition delay. The ignition delay is defined as the time delay period after the end of injection before ignition was initiated. A minimum ignition delay was found for each air/fuel ratio below which the mixture failed to ignite. The minimum ignition delay (time to form an ignitable mixture) was observed to increase with the volume of hydrogen injected and the enrichment of the overall charge. Further, for each test condition, an optimum ignition delay producing the most rapid combustion could be found. Varying the ignition delay primarily effected $t_{\text{max}}$ and to a lesser extent $P_{\text{max}}$. In view of this a rough optimisation was carried out for each test condition to find the ignition delay which gave the best results in terms of minimum $t_{\text{max}}$ and maximum $P_{\text{max}}$. This optimum ignition delay varied in the time range 20 - 150ms.

6.4.3 Discussion

Once again the general trends of decreasing $P_{\text{max}}$ and increasing $t_{\text{max}}$ with increasing relative air/fuel ratio were present. But the effect of hydrogen enrichment on $P_{\text{max}}$ was not as clear as with homogeneous charges. 5% hydrogen addition by stratified charge displayed similar increases in peak pressure to those achieved with 30% pre-mixed addition at $\lambda = 1.0$ decreasing to 10% at $\lambda = 1.3$ (Figures 6.8 and 6.2), i.e. the absolute pressure increase was almost constant and appeared to be independent of $\lambda$. 2.5% enrichment behaved almost identically to a pure methane/air mixture producing a similar curve profile to 5% (absolute improvement in $P_{\text{max}}$ did not increase with $\lambda$ as with premixed addition of $H_2$). In contrast, the peak pressures measured for 1.5% hydrogen addition tended to fluctuate from greater to less than $P_{\text{max}}$ for 0%. No discernible trend could be identified and when repeated the same results were encountered. It is postulated that the low volume of hydrogen injected meant that the injector's opening and closing dynamics became significant and affected the actual amount of hydrogen injected. In summary, these results indicate that the peak pressure is a function of the overall combustion process rather than just the initial stages. Thus, with richer mixtures significant improvements (compared to the premixed results) were observed, but as the overall mixture became leaner the relative improvements did not continue to increase (in contrast to the premixed case). This was due to the latter parts of the mixture to be burnt
being significantly leaner and consequently slower burning and containing less energy.

Figure 6.8  Peak pressures for heterogeneous methane/hydrogen mixtures.

Figure 6.9  Time to peak pressure for heterogeneous methane/hydrogen mixtures.
By the use of a stratified charge, levels of time to peak pressure enhancement similar to those obtained with homogeneous hydrogen/methane/air mixtures were achieved with the addition of significantly less hydrogen. These results are illustrated in Figure 6.9. As an example, the injection of 1.5% hydrogen resulted in similar $t_{\text{max}}$ values as 10% hydrogen addition in a pre-mixed charge. In contrast to the homogeneous charge, the decreases in $t_{\text{max}}$ were not proportional to the amount of hydrogen injected. Injection of 1.5% hydrogen showed the best relative improvements with a 12% decrease in $t_{\text{max}}$ at $\lambda = 1.0$ compared with 20% for 5% enrichment (Figure 6.10). The latter being roughly similar to a 30% homogeneous charge. Likewise, 2.5% hydrogen produced $t_{\text{max}}$ values similar to a 20% pre-mixed charge. These results appear in the main to agree with the theories postulated in Section 2.2.4. In particular, that hydrogen enrichment of methane mainly serves to enhance the combustion initiation process resulting in a reduction in the ignition delay. The mechanism behind this is the same as for a homogeneous charge, i.e. the earlier formation of the radical pool required for the attack upon the CH₄ radical. Further proof of this mechanism is given in Figure 6.11 which contains representative pressure traces for pre-mixed and stratified charges (5% hydrogen enrichment, $\lambda = 1.2$) compared with that for a pure methane/air mixture. As noted previously the addition of hydrogen in the pre-mixed charge improves the rate of pressure increase for all stages of combustion. However, for the stratified charge, the initial rate of pressure increase is greatly improved for approximately the first 50ms after ignition. Once the richer stratified region of hydrogen is burnt, the rate of pressure rise then returns to that which is similar to a pure methane charge. This clearly illustrates that the reduction in ignition delay is effected by the addition of hydrogen. Representative pressure traces for varying levels of heterogeneous hydrogen enrichment ($\lambda = 1.2$) are shown in Figure 6.12. As above, the reduced ignition delay is obvious along with the only slight increase in peak pressure over zero hydrogen enrichment.

The reason for the improvements in $t_{\text{max}}$ not being proportional to the amount of hydrogen injected is probably due to the dynamics of the stratified charge. The injection of a greater amount of hydrogen requires that the injector be left open for a longer period of time. This of course allows more time for the injected hydrogen to mix with the surrounding charge. Therefore, the concentration of hydrogen around the spark plug for 5% injection is not twice that for 2.5% but rather some lower value due to the extra mixing time available. Increasing the supply pressure in the injector would allow shorter
injection times for greater volumes but as observed during Schlieren photography testing this results in the production of a very turbulent jet. This would mean even greater mixing and consequently less stratification.

**Figure 6.10** Reduction in time to peak pressure with stratified hydrogen enrichment.

**Figure 6.11** Representative pressure traces - methane and methane/hydrogen mixtures (5% hydrogen enrichment, $\lambda = 1.2$).
Figure 6.12  Representative pressure traces - heterogeneous methane/hydrogen mixtures ($\lambda = 1.2$).
CHAPTER 7  NITRIC OXIDE REDUCTION USING CHARGE STRATIFICATION

7.1  INTRODUCTION

In this chapter the results of the nitric oxide reduction investigation will be presented and discussed. The primary aim of this work was to determine the benefits that could be achieved in terms of nitric oxide emissions through the use of a stratified hydrogen/air mixture. The proportion of hydrogen injected and the ignition delay were varied to alter the level of stratification in the combustion chamber. It was hoped to reduce the nitric oxide concentration in the exhaust gases while retaining or improving the combustion characteristics of a hydrogen/air mixture. As with the hydrogen enrichment of methane research, the peak pressure, $P_{\text{max}}$, and time to peak pressure, $t_{\text{max}}$, were recorded as a measure of combustion performance. In addition to this the nitric oxide concentration in the exhaust was measured using a mass spectrometer. The experimental work was conducted as two separate test series:

a) Baseline testing - to establish a standard set of results for the combustion of hydrogen in air and to determined the relative air/fuel ratio at which nitric oxide emissions are a maximum.

b) Stratified charge testing - to investigate the possible improvements over a premixed hydrogen/air mixture that can be achieved through the use of a stratified charge.

These two test series will each be discussed separately. Each test point represents the average of 10-12 individual explosions requiring approximately 6 hours of testing.

7.2  BASELINE TESTS

7.2.1  Introduction

The initial test series was carried out using homogeneous mixtures of hydrogen and air to determine the relative air/fuel ratio that produces the maximum level of nitric oxide and
the corresponding concentration of NO produced. As detailed in Section 5.3 mixtures of hydrogen and air were prepared with relative air/fuel ratios, \( \lambda \) in the range 1.0 - 4.0. As with all testing detailed in this chapter the initial charge temperature and pressure were 95°C and 1200 mbar respectively.

### 7.2.2 Discussion

The measures of combustion performance, \( P_{\text{max}} \) and \( t_{\text{max}} \) are represented in Figures 7.1 and 7.2 respectively. As expected the peak pressure achieved decreased as the relative air/fuel ratio increased as discussed in Section 6.2.2. Likewise the time to peak pressure increased with relative air/fuel ratio. It is interesting to compare the \( t_{\text{max}} \) for hydrogen/air to that of methane/air mixtures. As predicted by hydrogen's significantly higher flame speed the times are greatly reduced for similar relative air/fuel ratios.

![Figure 7.1](image-url)  
**Figure 7.1**  
Peak pressure for homogeneous hydrogen/air mixtures.

While analysing the exhaust gases for NO the concentration of oxygen was also recorded as shown in Figure 7.3. At stoichiometric (\( \lambda = 1.0 \)) the oxygen concentration in the exhaust approached 0% indicating that all the available \( O_2 \) was consumed during combustion. As the relative air/fuel ratio increased the oxygen also increased reaching
16% at $\lambda = 4.0$. This was as expected because lean mixtures do not contain enough fuel to react with all the available oxygen.

**Figure 7.2**  
Time taken to reach peak pressure for homogeneous hydrogen/air mixtures.

**Figure 7.3**  
Oxygen concentration in exhaust gases for homogeneous hydrogen/air mixtures.
Figure 7.4 shows the variation in nitric oxide concentration with relative air/fuel ratio in parts per million (ppm). Starting at stoichiometric the NO concentration increases rapidly reaching a maximum value of 4800 ppm at $\lambda = 1.2$. It then decreases at a similar rate until $\lambda = 2.0$ at which point it asymptotically approaches a value of 150 ppm. As discussed in Section 2.3.2 nitric oxide formation is highly dependant upon the concentration of oxygen in the combustion products reaching a maximum with approximately 10% excess air. For a further increase in available air the benefit of excess oxygen is offset by a consequent drop in combustion temperature. As seen in Figure 7.3 the available oxygen in the exhaust increases with relative air/fuel ratio.

![Figure 7.4](image_url)  
**Figure 7.4** Nitric oxide concentration in exhaust gases for homogeneous hydrogen/air mixtures.

What is of particular note is the rate by which the amount of nitric oxide formed decreases for relative air/fuel ratios rich and lean of $\lambda = 1.2$. As stated above once the relative air/fuel ratio has reached $\lambda = 2.0$ the nitric oxide concentration has dropped to negligible amounts and only decreases slightly with any further increase in relative air/fuel ratio. Similarly, at $\lambda = 1.0$ (no mixtures rich of stoichiometric were tested) the NO concentration has dropped from 4800 ppm to 2500 ppm. This trend forms the basis of the theory that nitric oxide formation should be reduced through the use of a stratified charge (Section 2.3.4). By injecting a proportion of the hydrogen at ignition a region
richer than $\lambda = 1.2$ will be formed around the spark plug while the rest of the combustion chamber will contain a mixture leaner than $\lambda = 1.2$. As can be seen in Figure 7.4 both these regions should produce lower concentrations of NO. Thus the overall NO concentration in the exhaust gases should be reduced while the overall relative air/fuel ratio remains at the maximum NO producing relative air/fuel ratio of $\lambda = 1.2$.

7.3 STRATIFIED CHARGE TESTS

7.3.1 Introduction

The second test series investigated the benefits that could be achieved through the use of a stratified charge as discussed in Section 7.2.2. As with the hydrogen enrichment of methane work the heterogeneous charge was created by injecting a proportion of the hydrogen through the core of a specially modified spark plug (Section 3.3.2). All of the test mixtures were prepared for an overall relative air/fuel ratio of $\lambda = 1.2$ after injection. Robinson [24] had conducted tests using a leaner mixture ($\lambda = 3.0$) but had found that the concentration of NO in the exhaust actually increased. From Figure 7.4 it can be seen that at $\lambda = 3.0$ the level of NO produced is very low. By injecting pure hydrogen around the spark plug the local relative air/fuel ratio will decrease towards a higher NO producing relative air/fuel ratio thus increasing the proportion of nitric oxide in the exhaust. The proportion of hydrogen injected was defined on a volumetric basis and varied from 10 - 50% of the overall hydrogen. Previous work by Robinson [24] had indicated that the greatest benefits were achieved with approximately 20% hydrogen injection.

In contrast to the methane work, an injector supply pressure of 8.5 bar was used. Although this tended to produce a 'jet' or plume of hydrogen along the centre of the combustion chamber rather than the desired localised 'puff', it was deemed necessary in order to reduce injection times. Using a supply pressure of 4.5 bar (as for the methane work) an injection duration of 870 ms was required for 50% hydrogen. This duration would have allowed too much time for mixing to occur thus lowering the level of stratification. It was also found that a certain amount of turbulence was required in order to form an ignitable mixture. These problems could have been overcome through the use of a high flow rate/low velocity injector but this was outside the scope of the project.
7.3.2 Ignition Delay

Other than the proportion of hydrogen injected, the other variable was the ignition delay period after the end of injection. The ignition delay period directly controls the level of stratification in the combustion chamber, as the longer the delay, the more time is available for mixing. The delay was varied from 0 - 150 ms. Robinson [24] had found that igniting before the end of injection could produce a further reduction in nitric oxide. But it was also found that the last portions of hydrogen injected were not being burnt (thus simulating the burning of a leaner mixture) which is inefficient. Therefore the minimum delay period was restricted to 0 ms.

When the proportion of hydrogen injected was increased to 50%, difficulty was encountered when trying to achieve reliable ignition with short delays (see Section 6.4.2). Delay periods of 10 and 20 ms produced many misfires and 0 ms was found to be almost impossible to ignite. This was most probably due to the region around the spark plug being beyond the rich limit of flammability for hydrogen i.e. >77% H₂. Therefore a minimum ignition delay period was necessary in order to achieve a flammable mixture and ensure positive ignition.

7.3.3 Discussion

The peak pressures measured for the stratified charge tests appeared to be independent of the proportion of hydrogen injected and the ignition delay. No discernible trends were present with \( P_{\text{max}} \) remaining constant apart from the odd fluctuation. It is assumed therefore that peak pressure is a function of overall energy content of the fuel rather than initiation conditions. This result agrees with that found with the hydrogen enrichment of methane.

In contrast the time to peak pressure displayed significant variation with both the proportion of hydrogen injected and the ignition delay (Figure 7.5). The overall trend, independent of the hydrogen fraction, was of decreasing \( t_{\text{max}} \) with a reduction in ignition delay. The average time reduction for all hydrogen fractions was from 14.5 ms (for a homogeneous mixture) to 10 ms (using a 10 ms ignition delay). Interestingly, \( t_{\text{max}} \) for
10% and 35% hydrogen increased from 10 ms to 0 ms delay after initially displaying a downward trend. This could be due to the mixture immediately around the spark plug being too rich (slower flame speed) with no ignition delay therefore effecting the early stages of combustion. The other major trend observed was of increasing $t_{\text{max}}$ with increasing hydrogen proportion. This is perhaps surprising as it was found during the hydrogen enrichment of methane work (Section 6.4.3) that increasing the proportion of hydrogen injected served to reduce $t_{\text{max}}$. But it was also noted that the reduction in $t_{\text{max}}$ was not proportional to the amount of hydrogen injected. Rather the relative improvement in $t_{\text{max}}$ was observed to decrease with increasing hydrogen injection. It is therefore postulated that there is an optimum proportion of hydrogen injection in terms of reducing $t_{\text{max}}$. Once this point is reached any further increase in the proportion of hydrogen injected only serves to decrease the local relative air/fuel ratio ($\lambda < 1.0$) leading to a slower flame speed and consequent reduction in $t_{\text{max}}$.

![Figure 7.5](image.png)

**Figure 7.5** Effect of ignition delay on time to peak pressure for stratified hydrogen/air mixtures.

As stated previously, the nitric oxide concentration measured was taken as the peak value recorded. Figures 7.6 - 7.9 represent the nitric oxide concentration vs ignition delay for injected hydrogen proportions of 10, 20, 35 and 50% respectively. The overall trend, independent of hydrogen proportion, was a decreasing nitric oxide concentration in the exhaust gases with a reduction in ignition delay. This agreed with the theory, as the shorter the ignition delay, the greater the level of stratification and hence the greater the
volume of low NO producing mixture. Although the relationship was not proportional, the trend demonstrated in each case was similar, with the NO curve split into three distinct areas; from 100 to 60 ms the NO concentration decreased at a slow but steady rate, from 40 - 20 ms the rate of decreasing concentration increased reaching a maximum, and from 20 - 0 ms the rate of decrease began to drop again.

Figure 7.6 Nitric oxide concentration with varying ignition delay (10% hydrogen injection).

Figure 7.7 Nitric oxide concentration with varying ignition delay (20% hydrogen injection).
Figure 7.8 Nitric oxide concentration with varying ignition delay (35% hydrogen injection).

Figure 7.9 Nitric oxide concentration with varying ignition delay (50% hydrogen injection).

The upper bound on the x-axis of each of the figures represents the NO concentration recorded for an infinite ignition delay (in reality a delay of 10 minutes was used) or homogenous mixture. This method was used rather than a pre-mixed mixture to allow for any inconsistencies in the injection process. In each case the NO concentration tends towards this value with increasing ignition delay as would be expected. With increasing
injected hydrogen proportion the ignition delay required to reach the homogeneous NO concentration also increases. This is because the larger volume of hydrogen injected takes longer to mix and form a homogeneous mixture.

The results of the nitric oxide reduction work are summarised in Figure 7.10 where the maximum reduction of NO vs fraction of hydrogen injected is shown. The maximum percentage reduction of NO (30%) is achieved by injecting 20% of the total hydrogen. For injected proportions less and greater than this the reduction decreases. Robinson [24] found similar results to this, but with a more consistent decrease for greater fractions, unlike the inconsistently low value for 35% H₂ injection found here. The overall trend is best explained through two observations. Firstly, as the hydrogen fraction is increased the relative air/fuel ratio of the pre-mixed hydrogen/air mixture increases and the volume of pure hydrogen injected increases. Therefore theoretically the level of stratification should increase leading to greater volumes of low NO producing relative air/fuel ratio. But secondly, as the hydrogen fraction increases so does the time required for injection which in turn allows more time for mixing to occur. Thus greater regions of high NO producing relative air/fuel ratio will form. The maximum reduction of NO is therefore a trade off between these two conflicting phenomena. This is a function of the apparatus and procedure adopted. It would be further compounded in an engine with a high level of turbulence present.

![Figure 7.10](image)

**Figure 7.10** Maximum reduction of nitric oxide concentration in exhaust gas.
Figures 7.11 - 7.14 contain representative pressure traces with varying ignition delay periods after the end of injection for each of the hydrogen fractions tested. As indicated in Figure 7.5 the time taken to reach maximum pressure decreased with a reduction in ignition delay. What is interesting to note is that for each of the four hydrogen fractions the initial rate of pressure rise for the homogeneous case is greater than for some or all of the stratified charge cases. Secondly, the initial rate of pressure rise decreases with increasing hydrogen fraction. This can be clearly seen in Figures 7.13 and 7.14 where the pressure trace for the homogeneous mixture is above all of the other traces for the first 6 ms after ignition. These observations seem to contradict those found for the hydrogen enrichment of methane (where the greatest improvement was observed at initiation when a stratified charge was utilised) but it must be remembered that the proportion of hydrogen injected for this second section is far greater and that hydrogen is already present. It is therefore assumed (as stated previously) that as the hydrogen fraction is increased, the local air/fuel ratio around the spark plug becomes richer leading to a reduction in flame speed. But the later stages of combustion are faster due to the local air/fuel ratio being closer to stoichiometric (maximum burning velocity) leading to an overall increase in flame speed. This agrees with the theories postulated above.
Chapter 7  Nitric Oxide Reduction Using Charge Stratification

Figure 7.12  Representative pressure trace (20% hydrogen injection).

Figure 7.13  Representative pressure trace (35% hydrogen injection).
Figure 7.14  Representative pressure trace (50% hydrogen injection).
Chapter 7  Nitric Oxide Reduction Using Charge Stratification
CHAPTER 8 FLAME PROPAGATION VISUALISATION

8.1 INTRODUCTION

The aim of this investigation was, firstly, to determine the effect of hydrogen enrichment and charge stratification on the mixture flame speed at various intervals during the combustion process along with any observable buoyancy effects. The second aim was to investigate the phenomenon, which will be discussed in depth later in this chapter, of the 'double hump' pressure trace. Eight optical probes were mounted in various configurations along the length of the combustion chamber and utilised to detect the flame front during combustion.

For all of the flame propagation work a methane/air mixture was used along with small amounts of hydrogen enrichment as a pure hydrogen/air mixture burns with a flame invisible to the optical probe detectors. The relative air/fuel ratio was kept at $\lambda = 1.0$ for all tests (including those using hydrogen enrichment). The initial charge temperature and pressure were 25°C and 1500 mbar respectively.

8.2 OPTICAL PROBE INVESTIGATION

8.2.1 Introduction

For each explosion the voltage output from each optical probe was recorded against time along with the associated pressure trace. The resulting data was then analysed graphically using DADiSP software. A sample output from a probe along with the corresponding pressure trace is shown in Figure 8.1. The time at which the flame front reached the position of the probe was determined by subtracting the time of ignition (measured at the second spike on the probe output) from the time where the probe output begins to decrease. As can be seen, the output from a probe produces a very discreet and clear signal. Also of note is the observation of a second peak after the initial one. It is postulated that this is due to post-flame reactions or reflection as it occurs after peak pressure is achieved. Each test point is the average of 5-10 explosions.
8.2.2 Discussion

The initial tests in this section involved determining the effect that hydrogen enrichment and a stratified charge had on the flame front velocity, the results of which are shown in Figure 8.2 which is a plot of time versus displacement. Therefore, the lower the gradient the greater the velocity and an increase in gradient represents a deceleration in flame front speed. The overall trend observed was of a gradually accelerating flame front until a point approximately 140mm along the combustion chamber was reached. At this point the flame front suddenly decelerates and continues to do so gradually until the end of the chamber is reached*. The possible reasons for this occurring are discussed below in Section 8.3. As expected, and in agreement with the pressure traces, the homogeneous hydrogen enriched methane/air mixture ($\lambda = 1.0$, 5% H$_2$) displays a constant relative increase in flame front velocity throughout all stages of combustion over the methane/air mixture ($\lambda = 1.0$). This observation is easily explained by hydrogen's higher flame speed over methane's.

* The time taken to reach the end of the chamber was not recorded from a probe but rather taken as the time at which maximum pressure was achieved. As such, it may not give a true representation of the flame position with time, but should be very similar.
In contrast to the pre-mixed case some interesting trends were observed with the use of a stratified charge. During the initial stages of combustion the flame front velocity of the stratified charge was very similar to that of the pre-mixed charge and in fact slightly slower, although this difference seems negligible. What is significant is the flame front velocity upon reaching the position 140mm along the chamber. Whereas the flame front velocities for the pre-mixed methane/air and hydrogen/methane/air mixtures displayed a sudden decrease at this point, the velocity of the stratified charge flame front remains almost constant before smoothly decreasing upon nearing the end of the chamber with a similar velocity to the pre-mixed cases. This sudden change in relative flame front velocities between the pre-mixed and stratified charges occurs in the time range 30 - 55 ms after ignition and results in the peak pressure being reached in a reduced time period. This observation compares well with the pressure traces represented in Figure 6.11. As can be seen, the stratified charge pressure trace shows a relative increase in rate of pressure change over the same approximate time range as above before reverting to a similar rate of pressure change as in the pre-mixed case.

![Flame Front Displacement vs. Time](image)

**Figure 8.2** Flame front displacement with time ($\lambda = 1.0$, 5% hydrogen).

Therefore the results of the optical probe investigation agree with those discussed in Section 6.4.3. But what is of particular note is the fact that the effects of the stratified
charge extend to 140 - 170mm along the length of the combustion chamber. This agrees with the results of the Schlieren photography where it was found to be very difficult to produce a very localised region of hydrogen by injection.

8.3 'DOUBLE HUMP' PHENOMENON

8.3.1 Background Theory

Throughout the experimentation carried out by Damiano[10], Barth[27] and Robinson[24] using the constant volume bomb for combustion analysis, an interesting characteristic has been observed for the rate of pressure rise. Each of the above experimenters observed an initial increase in the rate of pressure rise as would be expected (the mixture does not burn at a constant rate as the expansion of the burnt gases causes the pressure to rise and thus the burning velocity to increase). This was then followed by a momentary decrease and subsequent increase until maximum pressure was reached. This phenomena has been termed 'double hump' after the characteristic shape of the pressure versus time plot.

Damiano observed this effect for both homogeneous and heterogeneous mixtures of methane and oxygen. He postulated that this effect was due to the flame front changing from three-dimensional to two-dimension propagation. Initially the flame propagates as a hemi-sphere until it reaches the wall of the combustion vessel at which point it assumes an increasingly planer shape as it travels linearly along the length of the bomb. During the initial three-dimensional propagation the rate of pressure rise is a function of the flame front area. On reaching the wall this area is significantly reduced and hence the rate of reactant consumption would decrease. This, coupled with the increased area for heat loss (reaction rate is dependant on temperature according to the Arrhenius Factor $e^{-E/RT}$) to the walls of the bomb, could explain the double hump phenomena. The hemispherical flame front has a lower surface to volume ratio than the cylindrical volume behind the planer flame front.

Barth found that the 'double hump' effect was more pronounced for homogeneous than heterogeneous mixtures of methane and air. The effect also became less pronounced as the combustion rate increased, but was always present. He suggested that the double
hump was due to the shape of the flame front altering as it approached the end of the constant volume bomb (see Figure 2.6). After reaching the wall the flame propagates with a planer front. Initially it is convex in shape due to the viscous drag exerted by the walls of the bomb. As the flame approaches the end of the bomb its profile flattens out and then becomes increasingly concave (or cone shaped). This effect is caused by the increasing pressure ahead of the flame. Barth believed that the drop in the rate of pressure increase may have been caused by the temporary reduction in flame front area as the flame profile changed from convex to concave. The reduction in flame front area would cause less mass to be burnt per unit of time.

Robinson performed similar experiments to the above using hydrogen-air mixtures. Although he also encountered the double hump phenomenon it was generally not observed for homogeneous mixtures. He proposed that the double hump was related to the level of charge stratification present in the vicinity of the spark plug after injection. As the rate of reaction is dependant upon the mixture strength (a stoichiometric mixture burns faster than a lean mixture), Robinson suggested that initially the flame travels with a high velocity through the rich stratified region and upon reaching the overall lean mixture slows down. A small level of charge stratification may have been occurring around the spark plug due to leakage or trapped hydrogen which would explain the effect occurring for homogeneous mixtures. He also observed that for faster burning mixtures the double hump was less obvious or absent.

Another factor that may explain the phenomenon is that of the buoyancy effect. When a flame propagates horizontally (along a horizontally mounted bomb), the buoyancy of the hot burnt gases causes them to rise to the top of the cylinder. These rising hot gases remove heat from the bottom of the flame front and add it to the top. This causes a difference in the flame temperature and hence the rate of reaction between the top and bottom of the bomb. Thus the flame front distorts into a 'hook' shape (see figure 2.4). This hook shape would lead to an increasing flame front area and thus increased area for heat transfer.

Two factors may point to heat transfer being a major factor in the formation of the double hump. Firstly, both Damiano and Robinson noticed that the double hump became less significant as the combustion rate increased. An increase in combustion rate would
allow less time for heat transfer to the walls of the bomb. Secondly, during its propagation the flame front's surface to volume ratio changes significantly thus affecting its heat transfer properties.

8.3.2 Discussion

The results of the investigation into buoyancy effects utilising the four optical probe orientations are shown in Figure 8.3. No significant difference in trends could be discerned between the four plots indicating that if buoyancy effects were present they were insignificant. As mentioned above the overall trend was of a gradually accelerating flame front velocity until a point 140mm along the chamber was reached at which point a sudden flame front deceleration was observed. The time after ignition at which this sudden deceleration occurred (≈40ms) was found to correspond almost exactly with the point of inflexion on the pressure trace representing the formation of the 'double hump'. Referring to Figure 8.2 the point of inflexion also corresponded to the time at which the deceleration of the flame front occurred for both the pre-mixed and stratified charges. But as discussed above the transition point for the stratified charge was much smoother. This agrees well with the observation that the 'double hump' was less obvious and in some cases unidentifiable when using a stratified charge (see Figure 6.11).

The fact that the point of deceleration is occurring approximately 140mm along the length of the chamber from the spark plug would tend to discount Damiano's theory that the 'double hump' is caused during the transition from three-dimensional to two-dimensional propagation. Theory dictates that this would occur at around 50mm as this is when the initial hemispherical combustion wave would contact the walls of the bomb and begin the transition. Further investigations into this were carried out through the use of a longer combustion chamber (500mm) with the same diameter. The 'double hump' was still present and occurred at approximately the same point in time during the combustion process thus confirming the above observations. Robinson's theory that some form of charge stratification is responsible for the 'double hump' can also be discounted due to the observation that it is still present when using homogeneous mixtures of methane/air. As the injector was disconnected this would eliminate the possibility of any hydrogen leakage around the spark plug. Also, as noted above, any buoyancy effects appear to be insignificant.
To understand what is occurring in the combustion chamber to cause the apparent decrease in flame speed we must first differentiate between the flame front velocity and the burning velocity. The flame front velocity is the speed of the propagating flame measured by an observer who is stationary with respect to the combustion chamber. The burning velocity is the speed observed when stationary with respect to the unburnt gas mixture. The flame propagation measured by the optical probes (Figure 8.3) indicates the flame front velocity and the sudden deceleration observed is best explained by looking at the mass flow rate. Initially during the combustion process much of the unburned gas is compressed into the opposite end of the chamber from the point of ignition, but this mass must ultimately be redistributed over the entire volume [22]. Thus the mass flow reverses itself on further burning resulting in a net flow in the opposite direction to the path of the flame. The cone shape results from the viscous drag at the walls causing the velocity in the centre to be the greatest. An observer stationary with respect to the combustion vessel therefore witnesses a decrease in flame velocity even though the burning velocity with respect to the unburnt gas may be constant or accelerating. It is assumed that the burning velocity does continue to accelerate as all the local conditions (higher pressure and temperature, increased turbulence) favour this.
Therefore the mass of fuel burnt per unit of time should also increase. As the combustion pressure is proportional to the mass of fuel burnt the decrease in the flame front velocity should not effect it.

Pressure effects ahead of and behind the flame front were investigated by mounting an extra pressure transducer at the front of the combustion chamber next to the spark plug. It was postulated that the increased pressure ahead of the flame front and consequent redistribution could be causing the 'double hump'. It was found that the point of inflexion and the peak pressure were occurring at the same time for both transducers with the only difference being an increased pressure at the opposite end from initiation which was as expected (Figure 8.4).

![Figure 8.4](image.png)

Figure 8.4 Comparison of front and end mounted pressure transducers.

This leaves Barth's theory that the 'double hump' phenomenon is caused by the shape of the flame front altering as it approaches the end of the chamber. The most significant fact in favour of this theory is the position along the chamber at which the 'double hump' is occurring. Referring back to Figure 2.6 it can be observed that the transition from the initially convex flame front to a concave (or cone shaped) profile occurs at
approximately the half way point. This compares well with the displacement of 140mm (total chamber length = 240mm) at which the point of inflexion occurs. The temporary reduction in flame front area during the transition from convex to concave profile leads to a decrease in the *burning velocity* and hence the mass of fuel burnt per unit time drops. This in turn causes a temporary decrease in the rate of pressure increase resulting in the 'double hump' pressure trace. The addition of hydrogen serves to increase both the flame front and burning velocities leading to a shorter transition time and hence a smaller reduction in the rate of pressure increase.
CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

9.1.1 Hydrogen Enrichment of Methane

The experimental work conducted showed the addition of small volumes of hydrogen (5-30% by volume of fuel) to be a very effective means of improving the combustion characteristics of methane. In particular, significant improvements were observed in the ignition delay period and rate of pressure rise leading to higher peak pressures and reduced times to peak pressures. The level of combustion enhancement was found to be proportional to the amount of hydrogen added when using a pre-mixed charge.

Further benefits were achieved through the use of a stratified charge. Similar improvements to homogeneous charges were observed whilst using up to ten times less hydrogen. In particular, it was demonstrated that a stratified charge could significantly improve methane's relatively slow flame speed during the initial stages of combustion leading to reduced times to peak pressure. Therefore, leaner mixtures could be used to reduce emissions whilst minimising any loss of performance. In contrast to the pre-mixed case the level of relative combustion enhancement was observed to decrease with increasing amounts of hydrogen enrichment. In addition, a minimum ignition delay after the end of injection was observed, below which the mixture would not reliably ignite due to the localised mixture being too rich. This affected the maximum level of stratification obtainable.

9.1.2 Nitric Oxide Reduction using Charge Stratification

For hydrogen/air mixtures with relative air/fuel ratios near stoichiometric the use of charge stratification was found to be an effective means of reducing the concentration of nitric oxide. The maximum attainable percentage reduction in nitric oxide at the greatest NO producing air/fuel ratio of \( \lambda = 1.2 \) was found to be 30%.

The two variables investigated were the fraction of hydrogen injected and the ignition delay after the end of injection which controls the level of stratification inside the
combustion chamber. The general trend observed was that maximum nitric oxide reduction occurred at delay times close to the end of injection. This resulted in the initial stages of combustion occurring under rich conditions and the later stages under lean conditions, both of which are ideal for producing low levels of nitric oxide. With an increasing ignition delay NO levels would tend to that for a homogeneous charge. In addition, an injected hydrogen fraction of 20% was found to produce the maximum reduction in nitric oxide concentration. A consequent increase or decrease in the hydrogen fraction resulted in greater levels of NO production.

As with the hydrogen enrichment of methane the use of a stratified charge was found to enhance the overall combustion characteristics. In particular, the time taken to reach maximum pressure reduced with a decrease in ignition delay. The peak pressure was observed to be largely independent of hydrogen fraction and/or ignition delay and remained relatively constant for all test conditions.

9.1.3 Flame Propagation Visualisation

Through the use of optical probes the homogeneous addition of hydrogen to methane was found to increase the velocity of the flame front throughout the complete combustion process. In contrast, the use of a stratified charge was observed to increase the flame front velocity over only a small portion of the combustion process where a sudden deceleration usually occurs. Thereby the effects of this deceleration are reduced. Interestingly, this occurs at a position just over halfway along the length of the combustion chamber indicating that the injected hydrogen 'puff' is not fully localised.

The sudden deceleration of the flame front coincides with the 'double hump' observed in the pressure trace. By altering the orientation of the probes and the combustion chamber any buoyancy effects were found to be insignificant. Also the displacement along the combustion chamber at which the 'double hump' occurs discounts the theory that it is caused by the transition from three-dimensional to two-dimensional flame propagation. It is therefore postulated that the 'double hump' phenomenon arises during the transition from an initially convex flame front to a concave (or cone shaped) profile which occurs just over halfway along the chamber. This transition is caused by a reversal in the mass flow which is initially moving away from the point of ignition, but later moves back
towards it again. This reversal causes the sudden decrease in the flame front velocity relative to the combustion vessel but the actual burning velocity (relative to the unburnt mixture) should continue to accelerate or remain constant. What does cause a decrease in the burning velocity, and subsequently the rate of pressure increase, is the temporary reduction in the flame front area during the transition in flame front profile. This leads to the 'double hump' pressure trace. Hydrogen's superior flame speed over methane results in higher flame front and burning velocities during this transition and therefore minimises any effects. This also explains the reduction in the magnitude of the 'double hump' when utilising a stratified charge.

9.2 RECOMMENDATIONS

9.2.1 Further Research and Suggested Modifications

The research undertaken, due to its fundamental nature, has created scope for further study. In particular, the creation and consequent nature of the stratified charge deserves further investigation. The initial investigation of the injected hydrogen indicated that it was not as localised or concentrated as intended. Also, in order to increase the volume of hydrogen injected, the injection duration had to be increased allowing more time for dispersion of the cloud. The use of a more sophisticated injector would allow the shape and location of the injected fuel to be varied and its consequent effects on the combustion characteristics and emissions to be determined.

Many of the improvements to the equipment, as suggested by Robinson, were implemented and as such the apparatus was found to be very suitable for the work carried out. As stated above a low flow-rate high volume injector with a variable nozzle would allow greater control over the stratified charge.

The effects of hydrogen enrichment on other fuels such as methanol, petrol and diesel could be investigated to determine whether similar benefits to methane could be achieved. The conditions inside an internal combustion engine could be further simulated by operating at higher pressures, using a smaller volume more appropriate to studies at top dead centre and generating turbulence in the combustion chamber.
Ultimately the techniques investigated in this thesis should be applied to an internal combustion engine.
REFERENCES


25 Trolove H.P. *Calibration of Piezoelectric Pressure Transducers.* Final year project No.37, Department of Mechanical Engineering, University of Canterbury, 1991.


27 Barth M. *Investigation into the Combustion of Methane-Air-Mixtures Enriched with Hydrogen.* Diplomarbeit, Universitat Stuttgart (Research conducted at the University of Canterbury), 1993.


Figure A.2
Test mixture and injection vessels.

NOTE 1: MACHINES SHOWN ON PAGES OF TUBE TO MOUNT END CAP AGAINST FOR AN INTERFERENCE FIT.
RETAI SHARP EDGES TO FACILITATE WELDING.

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MECHANICAL ENGINEERING DEPARTMENT

STAINLESS STEEL MIXING VESSELS

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<td>1/4&quot; 1/8 OD DRILL</td>
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DRAWN: l \ n i n g h o n d | ORG NO: M.J
DATE: 9/15/93
Figure A.3

Optical probe mounts.

SECTION AA

WELD DETAIL

-PRESSURE TEST TO 60 bar

1. STAINLESS STEEL BOMB MODIFICATIONS
2. STAINLESS STEEL BOMB

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MECHANICAL ENGINEERING DEPARTMENT

Scales: 2:3

ALL DIMENSIONS IN MILLIMETERS

ITEM DESCRIPTION
1. GASKET - NON-ALLOY COPPER 20
2. OPTICAL PROBE MOUNT - 304L SS. 17
3. STAINLESS STEEL BOMB 1

CHECK: DHM 1ST MPR: 1/34-03A
DATE: 16/09/96

DRG No: 134-03A
APPENDIX B

PROGRAM LISTING FOR INJECTION/IGNITION CONTROLLER

#include "upph.h"
#include <stdio.h>
#include <conio.h>

#define IOADDR 0x232 /* IO address of board */
#define INJ_REG 01 /* Register used for injection time from trigger */
#define IGN_REG 03 /* Register used for ignition time from trigger */
#define TRUE 1
#define FALSE 0
#define CLOCK 5

/* Prototyping declarations */
void main(void);
void load_upp_program(void);
void set_up_upp(void);
void input_data(void);
void ready_sety_go(void);
void port_test(void);
void shut_down(void);
void screen_setup(void);
void input_data_int(void);

/* Global defines */
int Error = FALSE;
int inj_time = 100;
int ign_delay = 100;

/* Main subroutine*/
void main(void)
{
    set_up_upp();
    while(ign_delay!=0)
    {
        screen_setup();
        input_data();
        ready_sety_go();
    }
    shut_down();
}

/* main() */
void shut_down(void)
{
    UPPIntEnableWrite(IOADDR,1,0x00); /* Disable all interrupts */
    UPPIntEnableWrite(IOADDR,2,0x00);
}
UPPIntEnableWrite(IOADDR,3,0x00);
UPPStop(IOADDR);
UPPContactEnable(IOADDR,0x00); /* Tristate all UPP lines */
}/* shut_down */

#endif

/* Do all the initialisation associated with setting up the UPP and its ports */
void set_up_upp(void)
{
    UPSStop(IOADDR);
    load_upp_program();
    UPPIntEnableWrite(IOADDR,1,0x01); /* Disable all interrupts */
    UPPIntEnableWrite(IOADDR,2,0x00); /* except bit one */
    UPPIntEnableWrite(IOADDR,3,0x00);
    UPPDataDir(IOADDR,0x000e); /* Set port direction 1=output*/
    UPPContactEnable(IOADDR,0xff); /* Enable the correct port lines 1=enable */
    UPPLPortDir(IOADDR,2,0x01); /* output */
    UPPWriteData(IOADDR,CLOCK,20); /* 10,000 counts equals 200ms */
}/* sep_up_upp */

void input_data_int(void)
{
    scanf("%d",&inj_time);
    scanf("%d",&ign_delay);
    UPPWriteData(IOADDR,INJ_REG,inj_time);
    UPPWriteData(IOADDR,IGN_REG,ign_delay);
}/* input_data_int */

/* Get valid data from user and the write to UPP */
void input_data(void)
{
    int correct_range=FALSE;
    float inj_timef =0.0,
           ign_delayf =0.0;

while(!correct_range)
{
    /* Get timing values from user, values in ms */
    gotoxy(28,5);
    scanf("%f",&inj_timef);
    gotoxy(28,6);
    scanf("%f",&ign_delayf);

    /* Check to see if entered values are in the valid range */
    if((inj_timef>0.98)&&(inj_timef<1001)&&(ign_delayf>0.98)&&(ign_delayf<1001))
    {
        correct_range=TRUE;
    }
    else
    {
printf("Incorrect range.....Please reenter");
}

/* Calculate the integer values to put into the UPP register */
inj_time=(int)(50*inj_timef);
ign_delay=(int)(50*ign_delayf);

/* Write data into the UPP registers */
UPPWriteData(IOADDR,INJ_REG,inj_time);
UPPWriteData(IOADDR,IGN_REG,ign_delay);
}*/

void screen_setup(void)
{
    clrscr();
go toxy(20,1);
printf("Bomb Ignition/Injection program V1.00
");
go toxy(2,5);
printf("Enter injection duration---->");
go toxy(2,6);
printf("Enter ignition delay---->");
}/* screen_setup */

void ready_sety_go(void)
{
printf("Press any key to initiate test
");
/* Wait for that keypress */
while(!kbhit())
{
}
getch();

/* Start up the UPP and trigger the event */
UPPStart(IOADDR);
delay(10);
UPPWritePort(IOADDR,2,1);
delay(10);
UPPWritePort(IOADDR,2,0);

/* Inform user of what has happened, wait for user input before continuing */
printf("Test completed\n");
printf("Press any key to continue\n");
getch();
}/* ready_sety_go */

void load_upp_program(void)
{
    /*
Port 2 is used to output a signal which triggers the event
*/
UPPLoadProgram(IOADDR,&pwc_tpc);
} /* load_upp_program */
C.1 Introduction

The technique known as Schlieren photography originated in Germany for the detection of inhomogeneous regions in optical glass. In addition it allows the observation of gas flows, air motion past aerofoils and convection of transparent and colourless gases. All of these phenomena involve changes of refractive index which can be visualised or photographed by using Schlieren methods which depend on the effects of the refractive index on the transmission of light [24].

Schlieren photography was utilised on order to determine the size and distribution of the hydrogen injected through the core of the modified spark plug. In addition, it allowed the effects of any further modifications to the spark plug to be investigated.

C.2 Equipment

A typical Schlieren arrangement is shown in Figure C.1. The light source, $S$, is placed at the focal point of the concave mirror, $M_1$, so that the working section is illuminated by a parallel beam of light. The second concave mirror produces an image of the source in it’s focal plane at which point a knife edge, $K$, is utilised to control the light intensity. A focusing lens, $L$, is used to give an image of the working section on the screen or photographic plate, $Q$.

The test section used consisted of a specially built rectangular perspex container with the same internal dimensions as the stainless steel combustion chamber. Two 6" diameter concave mirrors, a variable width knife edge and a focusing lens were mounted on optical benches. An Optical Works Ltd. argon jet light source was used both as a constant low level light source during set up and to produce a high intensity light pulse of 0.2 microseconds for taking still photographs. A remote triggering box was used to fire the light source at a preset delay (0 - 999ms) after the beginning of injection which was in turn controlled via its own timing box. Initially video work was carried out followed by stills.
photography utilising a NIKON F3 camera with the lens removed. For a complete description of setup and operating procedures the reader is referred to Robinson [24].

![Diagram](image)

Figure C.1 Schematic of typical Schlieren apparatus layout (refracted rays shown dotted) [24].

C.3 Results

The initial video work was used to determine the effects of the modifications carried out on the spark plug. The area of the annulus at the end of the spark plug was increased by removal of the insulation and machining of the core. This led to a reduction in the exit velocity of the injected hydrogen leading to the formation of a localised 'puff'. The spark plug modified in this way was used for the hydrogen enrichment of methane investigation.

Figure C.2 shows a series of stills taken at increasing time intervals from the beginning of injection. The injection pressure and duration (4.5 bar and 20ms respectively) correspond to 2.5% hydrogen enrichment of a methane/air mixture (overall air/fuel ratio, \( \lambda = 1.1 \)). The length of the test section visible in the photographs is 120mm (total test section length = 240mm) with the spark plug mounted in the middle of the left side. As can be observed, the use of the core-modified spark plug and an injector supply pressure of 4.5 bar results in the formation of a very localised puff of hydrogen around the point of ignition. Even 55ms after the end of injection the injected hydrogen is still contained within the first quarter of the combustion chamber. In addition, although turbulent mixing is occurring the level of
air entrainment in the injected hydrogen appears to be low. Hence the need for a significant delay period after the end of injection before an ignitable mixture was formed.

The Schlieren photographs corresponding to the conditions utilised for the reduction of nitric oxide when burning hydrogen/air mixtures is represented in Figure C.3. The spark plug utilised for these tests did not have its annulus enlarged and the injector supply pressure was increased to 8.5 bar as greater amounts of hydrogen were required to be injected in similar time periods. In contrast to that for the lower injection pressure, the region of injected hydrogen is large and forms a 'column' reaching up to halfway along the combustion chamber. This observation agrees with that found from the optical probe investigation (Section 8.2.2). Also, any buoyancy effects appear to be minimal.

Due to the highly turbulent nature of the injected hydrogen there appears to be significant levels of air entrainment thus explaining why the mixture could be ignited at ignition delays down to and including the end of injection. The disadvantage of this is that the concentration gradient between the rich injected hydrogen and the leaner pre-mixed hydrogen/air mixture is low. This is not as favourable for the reduction of nitric oxide as a steep gradient because there is a greater volume of intermediate air/fuel ratios which are high NO producing. From the photographs we can also observe that after a delay of 90ms the injected hydrogen has almost totally diffused into the surrounding mixture. This agrees well with the results in Figure 7.6 (10% hydrogen enrichment) whereby the level of nitric oxide formed approaches that for a homogeneous mixture at delays of 100+ ms.

*The downward trend displayed in some of the photographs is actually an upward trend due to the buoyancy of hydrogen in air. The observed inversion is due to the method of Schlieren photography which results in an inverted image.*
Figure C.2  Schlieren photographs of injected hydrogen. Time increments after beginning of injection corresponding to 2.5% hydrogen enrichment of methane/air mixture ($\lambda = 1.1$). Injector pressure and duration 4.5 bar gauge and 20ms respectively.
Figure C.3  Schlieren photographs of injected hydrogen. Time increments after beginning of injection corresponding to 10% hydrogen fraction. Injector pressure and duration 8.5 bar gauge and 55ms respectively.