The use of a volatile liquid fuel to reduce cold-start emissions from a spark ignition engine

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THE USE OF A VOLATILE LIQUID FUEL TO REDUCE COLD-START EMISSIONS FROM A SPARK IGNITION ENGINE

by

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A Master’s Thesis submitted in partial fulfilment of the requirements for the award of Master of Philosophy of the Loughborough University

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Abstract

As traffic density increases, there is growing urgency to reduce its polluting effect. Catalysts fitted to new vehicles, with spark ignition engines, are highly efficient at controlling harmful emissions once they have reached operating temperature. However, during a cold-start the catalyst is initially inactive, just when engine-out emissions are at their highest, mainly due to the fuel-rich mixtures used for reliable starting and good driveability, particularly at low ambient temperatures. As the population of vehicles fitted with catalysts grows, the significance of this cold-start and warm-up period of operation will increase.

The performance of a modern 4-valve engine has been studied, when fuelled on conventional gasoline, to gain an improved understanding of the emissions formation during cranking and starting over a range of ambient temperatures from \(-7^\circ\text{C}\) to \(+49^\circ\text{C}\). This showed that, even with a constant supply of fuel and air to the engine, the mixture burned within the cylinder was considerably different to the supply mixture and changed continuously during the early stages of engine operation. It is the control of the gas-phase mixture within the cylinder that determines the starting and emissions behaviour of the engine.

When fuelled on a single-component liquid fuel, with low boiling point, engine starting was rapid and robust at all temperatures tested. Good control of in-cylinder fuel-air ratio development, together with lean-of-stoichiometric operation, resulted in reduced unburned hydrocarbons and carbon monoxide over a 60 second period from ‘fuel-on’. There was, however, an increase in oxides of nitrogen which requires further investigation. Fuel enrichment was not required for starting, even at sub-zero temperatures.

The possibility of using such a fuel for the start-up period of operation, before reverting back to the engine’s primary fuel supply, needs further investigation to determine its viability.
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Publication from this Work

The following written publication and conference presentation arose from this work:-

P Cardani, M Brunt and A Scarisbrick, "The Use of a Volatile Liquid Fuel to Reduce Cold-Start Emissions from a Spark-Ignition Engine", to be presented at Autotech 97, 4 - 6 November 1997, National Exhibition Centre, Birmingham, UK.
## References

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Notation

TDC  top dead centre
BDC  bottom dead centre
FID  flame ionisation detector
HC   hydrocarbon
CO   carbon monoxide
CO₂  carbon dioxide
NOₓ  oxides of nitrogen
ppm  parts per million
SER  supply equivalence ratio
COVₘᵢₑᵖ  coefficient of variation of imep
COV₂₅  COVₘᵢₑᵖ of 25 cycles from second positive imep cycle
COV₅₀  COVₘᵢₑᵖ of 50 cycles from second positive imep cycle
COV₂₀₀ COVₘᵢₑᵖ of cycles 50 to 250
COVₛₛ  COVₘᵢₑᵖ of last 200 of the 1200 cycles recorded
imep  indicated mean effective pressure
FTP  Federal test procedure
CFD  Computational fluid dynamics
RON  Research octane number
RVP  Reid vapour pressure
DI   Driveability index
CNG  Compressed natural gas
OEM  Original Equipment Manufacturer
TWC  Three-way catalyst
LEV  Low emission vehicle
ULEV Ultra low emission vehicle
CEC  Co-ordinating European Council
1. Introduction

Pollution in general, and air pollution in particular, continues to cause concern throughout the developed world with the road transport sector, which continues to grow unabated, being targeted with ever increasing demands for lower emissions of harmful pollutants. The spark ignition gasoline engine is the most common form of vehicle power unit in most parts of the world, particularly within the passenger car market, and it is the exhaust emissions from this type of engine with which this thesis is concerned.

All vehicles using this type of engine, and complying with the most severe current emissions legislation, are fitted with the so called three-way catalyst. This type of catalyst is very efficient at reducing harmful emissions when it has reached working temperature. However, in order to meet the most stringent proposed legislative levels, it is recognised that there are certain operating conditions which require improved emissions control.

Transient operation of the engine is one such condition where emissions can be significant, due to the difficulty in maintaining the stoichiometric air-to-fuel ratio required by the catalyst for optimum efficiency. These mixture ratio excursions result in catalyst 'break-through' and significant increases in tailpipe emissions. During the legislative drive cycles, however, it is the cold-start and warm-up period which has the most significant influence on overall mass emissions and will often determine whether a vehicle succeeds in meeting the required limits.

There is debate as to whether the legislative drive cycles truly represent 'real world' driving conditions. However, it is generally agreed that, as the vehicle population with catalysts fitted increases, it is the cold-start and warm-up period which is going to be the most significant for the release of noxious pollutants to the atmosphere. As a significant proportion of vehicle operation is short journeys with stop-start driving, particularly in urban areas, when engine and catalyst temperatures remain below their
optimum, it is essential that additional ways of dealing with these emissions during this period are found.

In order to meet the severest future emission standards there is a need to reduce cold-start hydrocarbon and carbon monoxide emissions by approximately 90 percent, compared to that produced with conventional underfloor three-way catalyst technology. This required reduction will be even more demanding if the proposals for sub-zero test temperatures are adopted.

At the time of starting a cold engine the catalyst is virtually inoperative and the emissions pass through the exhaust as though no catalyst was fitted, except for some early retention of heavy hydrocarbon molecules which are later desorbed. These emissions are potentially higher than on earlier technology vehicles, where there could be no reliance on a catalyst to ensure the vehicle met the legislative limits. It is these relatively uncontrolled emissions during engine cranking, starting and the very early stages of fired operation, that the research reported here addresses.

1.1 Objectives of the Research

It was an objective of the work to gain a better understanding of how these start-up emissions were generated and what might be done to reduce them. Whilst most current effort concentrates on ‘cleaning-up’ the emissions once produced within the engine, it was intended to seek further ways of reducing their production at source.

It was required to gain a better understanding of what causes high emissions of HC and CO during the cold-start and early warm-up period when fuelled on ‘conventional’ gasoline and what might be done to reduce them. The effect of start temperature and the supplied fuel-air ratio on these emissions was of particular interest.
Initial experiments on a reference gasoline fuel, particularly at low temperatures, clearly indicated the damaging effect that mixture enrichment, which was necessary for starting reliability and subsequent driveability, had on the emissions of unburnt hydrocarbons (HC) and carbon monoxide (CO). It was, therefore, an objective to investigate how this mixture enrichment could be reduced or eliminated whilst maintaining ‘start quality’.

A survey of published work showed that little had been done on the use of alternative fuels to reduce emissions during the initial cold-start period of operation. After starting, the engine could revert back to operation on conventional gasoline. It was therefore intended to select a suitable ‘alternative’ fuel and investigate its potential benefit during a cold-start and its ability to meet the research objectives described here.

As catalyst light-off times are progressively reduced the significance of the initial engine-out emissions will increase. It was therefore an objective to concentrate the emissions measurements and analysis over a 60 second period from when the fuel was first supplied to the engine.

1.2 Work Programme

To enable the objectives of the research to be met, it was necessary to follow a programme of work to develop an appropriate test facility and procedures which are described fully in section 5. An existing engine test bed with motoring dynamometer was used by the author as the basis for the test facility. Having completed the commissioning of this facility a cold chamber containing the test engine was designed and built to enable cold-starts to be made, under controlled conditions, down to sub-zero temperatures. Considerable attention was given to designing a suitable raw exhaust gas sampling system and ensuring that existing analysers were fully calibrated and in reliable working order. The engine was instrumented for the measurement of numerous temperatures and pressures whilst the installation of a cylinder pressure
transducer and high-speed data acquisition system allowed combustion analysis to be carried out.

A study of the engine calibration strategy and an interface with the engine's management system was necessary to enable revisions to the start-up calibration to be made. This allowed fixed engine operating conditions to be maintained during the start and warm up, so that fuel effects could be distinguished from engine effects and to enable changes to be made to the start-up fuel-air ratio supplied to the engine.

Test procedures were developed which gave acceptable repeatability of emissions and overcame the difficulties associated with starting an engine at sub-zero temperatures with high degrees of fuel enrichment.

1.3 Overview of the Thesis

Section 1 has described the background to the cold-start emissions problem, explained what the main objectives of the thesis were, and given a brief summary of the work carried out by the author in order that these objectives could be met.

Section 2 describes the requirements for successful starting on conventional gasoline and of the mechanisms which affect the formation of HC and CO. A description is given of how the legislation has changed over the years, with significant progress being made in reducing the main pollutants, but with new challenges emerging, especially as the population of vehicles fitted with catalysts increases. The section closes by recognising that there are now other toxins and reactive species being emitted which must be regulated.

Section 3 describes a variety of techniques that are being evaluated as potential solutions to the cold-start emissions problem. Most of these aim to achieve faster catalyst light-off, whilst others attempt to reduce the emissions during the time that
the catalyst is inoperative. The section concludes with a review of what is being done to develop 'conventional' three-way catalysts.

Section 4 introduces the concept of using an 'alternative' fuel for the cold-start and early warm-up period whilst the catalyst is inactive. It gives the advantages of gaseous fuels and vaporised fuels before explaining the choice of a liquid fuel of high volatility, which was to give the possibility of eliminating, or at least reducing, the mixture enrichment required for starting on conventional gasoline. Other objectives of the work, such as improving the in-cylinder air-fuel ratio control, are introduced in this section.

Section 5 describes the engine test facility, including the cold chamber, which was designed and built to enable start-up tests at sub-zero temperatures. The test procedure of starting the engine at a fixed speed and load with constant air-fuel ratio and fixed ignition timing is described, together with the precautions needed to ensure reliable data. The section concludes with the data reduction and analysis methods used.

Section 6 introduces and discusses the most significant results. The emissions and combustion characteristics of starting on reference fuel and isopentane at different supply equivalence ratios and temperatures are presented. These illustrate the potential advantage of using a highly volatile fuel even when comparison is made under unfavourable conditions. The section concludes with a small number of results from tests to investigate the effect of ignition timing on the start-up and emissions and also from conventional cranked starts, using the manufacturer's standard calibration.

Section 7 is a summary of the main findings of the research. These are presented as statements highlighting the more significant observations which were discussed in detail in section 6.

Section 8 gives the conclusions of the thesis and closes with suggestions for further work.
2. Factors Affecting Cold Starting and Emissions

2.1 Introduction

The following sections describe the main requirements for the successful starting of a conventional spark-ignition gasoline engine and how these and other mechanisms can result in excessive emissions of pollutants, particularly as temperatures are reduced.

2.1.1 Fuel Vaporisation

It is a primary requirement, for reliable initiation of combustion within the cylinder of a spark ignition engine, that an air-fuel mixture ratio within the vapour’s flammability limits is provided at the spark plug gap. The ignition range for gasoline is generally between about 7:1 and 20:1 by mass\(^{(1)}\), although some engines may be able to start with air-fuel ratios outside these limits. In one study\(^{(2)}\), where the mixture ratio was measured at the spark plug, it was found that the upper limit on this ratio for successful first-fire appeared to be near to 35:1. The ease with which this vapour mixture can be produced depends on the distillation characteristics of the fuel used and, particularly during cold starting, the fuel's volatility becomes increasingly important. In this situation it is the low boiling point components in the fuel which are most significant\(^{(1)}\). These are characterised by such parameters as the Reid Vapour Pressure (RVP) and the temperature at which ten and fifty percent of the fuel evaporates (T10 and T50). The RVP is a measure of the fuel's vapour pressure as determined by ASTM Procedure D 323\(^{(3)}\).

Modifying a gasoline's distillation characteristic can have a large impact on HC emissions. Gething\(^{(4)}\) used the driveability index (DI), which is normally used as a measure of how smoothly a vehicle responds to throttle changes during warm-up, as a measure of the overall distillation characteristic. The DI is defined as \((1.5 \times T10) + (3 \times T50) + T90\), where T10, T50 and T90 are the temperatures at which 10, 50, and 90 percent of the gasoline evaporates. It was found that reducing this index decreased HC emissions particularly in the first phase (cold transient) of the legislative FTP
cycle. More recent work has also shown that driveability and hydrocarbon emissions appear to be linked, although CO and NO\textsubscript{x} showed no correlation with the fuel composition\textsuperscript{(5)}. The tailpipe HC emissions were greater with high DI fuel even after the engine had warmed up, but the effect was most pronounced when the engine was cold.

Takeda et al\textsuperscript{(6)}, when comparing three gasolines with different distillation characteristics, found it was the T50 in particular that had a significant effect on the engine starting and HC emissions. Their unique measurements quantified the mass of liquid fuel retained on the port and cylinder walls and showed that this was least for the low T50 fuel. As a consequence of this reduced surface build-up during starting, less fuel was required to produce stable combustion and lower HC emissions resulted.

When an engine is cold it can be difficult with conventional gasoline to achieve even the leanest ignitable air-fuel ratio. Under these circumstances an excess of fuel is supplied to ensure that there are sufficient light-end components available for rapid formation of an ignitable gas-phase air-fuel ratio at the spark plug gap. This is essential for fast reliable engine starting and subsequent stable idling and good driveability. According to Shayler et al\textsuperscript{(2)}, at 16°C, only 25 to 30 percent of the injected fuel is in vapour form inside the cylinder during the first few cycles of cranking. At -20°C, this proportion falls to less than 10 percent. Mixture preparation during this cranking / first-fire period is absolutely crucial to the production of unburnt hydrocarbons. Boam and Finlay et al\textsuperscript{(7)} found that, when supplying the engine with vaporised fuel instead of liquid fuel, the running-engine hydrocarbon levels were obtained from the first turn of the engine.

The importance of good mixture preparation, in reducing HC emissions, has also been demonstrated by comparison of results from a single-cylinder engine when supplied with fuel either from a conventional port fuel injector, or from a fuel vaporiser and mixing unit. When the ambient temperature was lowered from 24°C to -7°C the HC emissions increased by 54 percent when using the port fuel injector, but only by 19 percent for the premixed charge. Speciation measurements showed that both fuelling
systems resulted in similar masses of light alkanes in the exhaust gases, but port injection caused a higher mass of heavy components. This, it was concluded, was evidence that incomplete vaporisation of the fuel, with port fuel injection, was a major contributor to high HC emissions\(^8\).

New evidence of inadequate mixture preparation during the first-fire period has been obtained with unique in-cylinder filming. This revealed diffusive burning during the first two cycles when starting a port-injected 4-valve engine\(^9\). It was concluded that inadequate vaporisation during cold-starting caused poor mixture preparation. The diffusive burning was indicated by a strong red flame which progressively changed to blue during the third and later cycles as piston speed and temperature increased giving rise to improved mixture homogeneity.

### 2.1.2 Cold-Start Fuelling

The consequence of a rich fuel-air mixture, during cold starting and warm-up, is a large increase in the emissions of carbon monoxide (CO) and unburnt hydrocarbons (HC). Even well developed cold-start calibrations can give rise to an initial high rise in HC emissions, due to misfire, caused by the short-term drop below the lower rich misfire limit. This rise, however, may be of less consequence than a calibration which risks a lean mixture situation, in which the potential misfiring can produce even more severe HC emissions. This balance between lean and rich limits places very exacting demands on the calibration strategy and the control system in keeping the emissions to a minimum, particularly as the start and warm-up period is a highly transient process.

Current engine starting strategies initially inject approximately five times the required fuel for a room temperature start\(^{10}\), followed by lower, but still richer than stoichiometric, levels during warm-up. On starting, the air flow is initially low and fuel evaporation is poor, leading to a large fraction of this fuel remaining as a liquid film on the port walls, the intake valve and in the cylinder\(^{11}\). CO emissions are a function of the air-fuel ratio and increase almost linearly for mixtures richer than
stoichiometric. Due to the inherently poor mixture preparation during cold starting, the cylinder is initially filled with an inhomogeneous charge which can give rise to localised rich pockets of vapour. These rich pockets give rise to high CO emissions, even in a cylinder with an initially lean overall air-fuel ratio. The HC emissions will also rise due to the oil film adsorption/desorption effect, which is described in more detail in section 2.1.3, as well as the poor air-fuel ratio control which exists under these starting conditions.

Estimates of the fuel utilisation have been made from in-cylinder gas sampling during cranking\(^{(2)}\). In these experiments the mixture was analysed for light, medium and heavy components. The results indicated that, at \(-20^\circ\mathrm{C}\), only 25 percent of the light fraction and just a few percent of the medium and heavy components contributed to the gas-phase mixture. The remainder of the fuel was unaccounted for, supporting the view that accumulation of liquid fuel in the intake port seriously impedes the formation of an ignitable mixture at the spark plug gap. The injectors must, therefore, supply a large excess of fuel to ensure that sufficient light ends are available at the spark source to form an ignitable mixture. This process is difficult enough at moderate temperatures; at very low temperatures it becomes a challenging control problem to balance the requirements for good starting without the penalty of unacceptable emissions. Furthermore, it has been estimated that, at cranking speeds, up to 16 percent of the cylinder charge is lost to blowby. This is considered to be a further major source of unaccounted fuel\(^{(10)}\) and further explains the need for excess fuel during the start-up process.

Using an analytical engine Takeda et al\(^{(6)}\) were able to quantify the following fuel fractions, of the total injected, on a cycle-by-cycle basis in a firing engine: 1) minimum required fuel, 2) intake port wall wetting fraction, 3) cylinder wall wetting fraction, 4) the burned fuel and 5) the engine-out HC emissions. From their analysis of the first three cycles after a cold start they deduced that most of the injected fuel adheres to the intake port and cylinder wall. This fuel is carried over to the next cycle thus reducing the fuel requirement of that cycle. They conclude that, because of the
large quantity of fuel that is carried over, the precise control of the air-fuel ratio is
difficult, which results in high HC emissions.

Other results supporting this conclusion come from filming the in-cylinder fuel flow
during a fixed speed and load start-up\textsuperscript{(12)}. This showed that, as well as strip-
atomisation of the fuel film by the intake flow, the fuel film was squeezed between the
intake valve and seat at valve closing which formed large droplets, estimated at about
1\text{mm} in diameter. There was also a liquid film distributed on the intake valve and
head region. It was noted that the thick film around the valve area survived
combustion and was carried over to the next cycle. This carry over process occurred
for approximately 60 seconds into the warm-up period.

The importance of the backflow of hot gases into the intake port during valve overlap
was recognised by Cheng et al\textsuperscript{(13)}. They described how this flow broke up any liquid
film around the valve as it opened and how it influenced the temperature of the gas
and walls, which had a major influence on the fuel vaporisation process.

The remainder of section 2.1 describes other important influences on the fate of the
fuel as it passes through the engine. These determine whether it is converted into
useful energy, oxidised after the main combustion process, or emitted from the engine
as a pollutant.

### 2.1.3 Oil Film Effects

The dissolving of unburned fuel into the oil film present in the combustion chamber,
followed by its return into the bulk gases as the cylinder pressure reduces during the
expansion stroke, has become known as the oil film absorption/desorption process and
has been shown to contribute significantly to the hydrocarbon emissions.

Heywood\textsuperscript{(14)} reports on experiments where the unburned hydrocarbon levels increased
in proportion to the amount of oil deposited on the engine piston crown. By analysis
of the HC species it was established that the increase was due to fuel species and not
oil oxidation products. Further tests using propane instead of iso-octane gave no increase in HC emissions, thus demonstrating that it is the fuel solubility in the oil which drives the absorption/desorption process. The reduced HC emissions often reported for engines fuelled on natural gas\textsuperscript{15} is attributed to the fact that methane, which is a major component of natural gas, has a low solubility in oil\textsuperscript{16}.

As temperature is reduced the oil film viscosity increases, which means that less oil and fuel drains back to the sump and hence the potential for higher desorption exists. The initial oil film thickness will also be greater at lower temperatures, leading to higher masses of absorbed fuel. The solubility and diffusion rates will be significantly affected by the influence of temperature on the oil film, as well as by the characteristic of the fuel. Trinker et al\textsuperscript{17} found that, in general, the solubility of a fuel increases with its carbon number; the solubility of aromatic compounds being very much higher than that of the paraffins.

Weaving and Pouille\textsuperscript{18} reported research on a single cylinder engine, where the effect of the fuel's solubility in oil, (a function of Henry's constant), on the hydrocarbon emissions was determined. Comparison was made between iso-octane, which has a high solubility and isopentane, which has low solubility and gave lower HC emissions. Further evidence of this effect was obtained by the reduction in HC emissions which occurred when the cylinder wall temperature was raised. The effects of the cylinder wall temperature are discussed further in section 2.1.5.

2.1.4 Oil Temperature

Hydrocarbon emissions gradually reduce to a stable level when an engine is operating under steady-state conditions. Even when cold-start enrichment has ceased and the air-fuel ratio is constant this effect is still apparent. Whilst some of this effect is no doubt due to improved vaporisation and, therefore, improved combustion, a significant contribution has been shown to be due to the relatively slow warm-up process of the lubricating oil\textsuperscript{19}, which can take four times as long as the engine coolant to reach a stable temperature. This is attributed to the absorption of the fuel.
vapour by the lubricating oil when the piston is near TDC and its desorption near BDC. This effect decreases with increasing temperature and hence the amount of fuel which escapes the primary combustion process is reduced.

2.1.5 Coolant Temperature

Early work on the sources of unburned HCs suggested that the flame was quenched as it approached the relatively cool wall of the combustion chamber. This quench layer is not exhausted, as was initially assumed, but is mostly oxidised by the rapid mixing and post-flame reactions that occur in the cylinder of an engine at normal running temperatures. Under cold-start conditions, however, when the coolant and wall temperatures are low, the quench layer is thicker and, therefore, less likely to be completely consumed. The work of Boam and Finlay et al(7), where tests were carried out with the coolant pump disconnected and also with no coolant, confirms this effect. Their results showed a significant decrease in unburned HC, demonstrating a strong dependence of the emissions on cylinder wall temperature and hence coolant temperature. Their results from work with a rapid compression machine showed that, whilst at normal engine temperatures and with strong mixture motion wall quench layers are largely consumed in the post-combustion reactions, at low wall temperatures quench could be a very significant source of HC emissions.

Tests on a single cylinder research engine, operating at 1500 rev/min and 3.8 bar IMEP, showed that when the coolant temperature was raised from 66°C to 108°C the HC emissions were reduced by about 30 percent when operating on a 91 RON gasoline(20). Tests on isopentane, which was used to eliminate liquid fuel and oil layer effects, showed a far lower reduction. Speciation results showed that the higher temperature produced a higher percentage of partial combustion products and a decreased percentage of fuel hydrocarbons, particularly the higher molecular weight components.

There is considerable interest in open-valve fuel injection timing in order to reduce cylinder port wall-wetting, which occurs particularly when the engine is cold. With
this strategy the effect of coolant temperature becomes significant, particularly when the fuel droplets are large. In one set of experiments, with large droplets, there was a 50 percent increase in the HC emissions when injecting onto an open valve, with the coolant temperature at 30°C, compared to closed-valve injection timing\(^{21}\). Small droplets, however, produced no increase. At 89°C coolant temperature droplet size had little effect on the emissions.

2.1.6 Air Inlet Temperature

Air temperature affects both mixture preparation through its influence on fuel evaporation and charge reactivity through its effect on charge temperature at the end of compression. Boam et al\(^7\) carried out tests, at a constant ignition setting, with air intake temperatures of 20°C and 40°C, where they eliminated the effect of air temperature on mixture preparation by operating on a fully vaporised fuel. Their results gave only small reductions in unburned HC, although they believe the increased reactivity would have allowed the ignition to be retarded slightly, which would have resulted in a further reduction.

Results from modelling of the intake port mixture formation process indicate that air temperature has only a limited influence on fuel droplet and liquid film vaporisation\(^{22}\). The model showed that, even though heat transfer from the air to the droplets increased with increasing air temperature, the vapour mass fraction showed only a small change and the wall-film vapour generation increase was almost negligible. This is attributed to the low temperature differential between the ambient air and the boiling point of the fuel. The other heat transfer driving forces are the thermal conductivity, which is low for air, and the Reynolds number, which is limited due to the small droplet size.
2.1.7 Fuel Temperature

The temperature of the fuel will directly influence the degree of vaporisation which takes place. As already described, the characteristics of the fuel will determine how easily this vaporisation process occurs. Clearly, lowering the fuel temperature will reduce the fraction of liquid fuel that can vaporise and hence a greater excess of fuel will be required to ensure that a flammable vapour/air mixture is rapidly available at the spark plug.

Ohyama et al\(^{(11)}\) describe how there is insufficient time for mixture formation in a cold engine and that vaporisation does not reach a state of equilibrium. As the rate of vaporisation is influenced by the difference between the instantaneous partial pressure and the partial pressure in the vicinity of the fuel film or droplet, it can be increased by raising the temperature of the intake air and/or fuel. It is therefore important to ensure good heat transfer to these fluids, particularly when engine temperatures are low.

As indicated in section 2.1.6, it is difficult to influence the vaporisation process by increasing the air temperature, however, the initial fuel temperature has a significant effect. This is mainly as a result of the increased fuel-vapour flow caused by increased droplet vaporisation. It is suggested that pre-injection fuel heating could be an effective method of improving the mixture formation process resulting in reduced emission levels, particularly during cold starting\(^{(22)}\).

It has been estimated that only about 10 to 20 percent of the total fuel vapour is derived directly from the injector spray, even in a warm engine, the remainder coming from the dominating wall-film evaporation process\(^{(22)}\). Since heat from the intake air is negligible, it is important to ensure good heat transfer to the fuel film by raising wall temperatures.
2.1.8 Crevice Effects

A further important source of unburned HCs are the crevice volumes found within the combustion chamber of the engine\(^{22}\). The most significant crevices are those of the top piston land and ring pack, whilst others include spark plug threads and the gap around the centre electrode, head gasket recesses and crevices around valve heads. All these crevices act as potential storage areas for unburned mixture, which may not be accessible to the advancing flame front and will, therefore, contribute to unburned HC emissions. In the same manner as with the fuel desorption process, some post flame oxidation will occur when falling cylinder pressure allows the release of this unburnt mixture back into the combustion chamber.

Experiments with a significantly reduced piston top land and special top ring seal\(^{7}\) resulted in a 30 percent reduction in unburned HC levels shortly after a cold-start from 20°C. Clearly, the size of these crevices, particularly those of the piston, will depend on engine temperature, therefore, this source of emissions can be higher under cold-start conditions and can increase with decreasing temperature. Experiments have shown there is an optimum top land width that ensures the advancing flame front can penetrate the crevice and consume the unburnt fuel\(^{24}\). Engine tests showed a reduction in HC emissions of 35 to 50 percent with a power loss of 0.5 to 1.5 percent and a 1 to 3 percent increase in fuel economy.

Computer modelling, to predict trends in engine component heat transfer rates and temperatures during engine warm-up, has shown that the thermal capacitance of the block is much larger than that of the piston and, therefore, reductions to the piston thermal capacity would reduce the time taken for the temperatures to equilibrate. This would ensure a rapid reduction of the piston / liner crevice volume during the warm-up period with consequent reductions in HC emissions\(^{25}\).

The potential of the crevices to contribute to engine-out HC emissions is well illustrated in the analysis of Cheng et al\(^{26}\). They calculate that 9 percent of the fuel in the cylinder, at a typical warmed-up part load condition, escapes combustion each
cycle. Of this fuel they estimate that 5.2 percent is due to the crevice effect, which accounts for 38 percent of the engine-out HC emissions. The next largest contributor is the in-cylinder liquid fuel effect at 20 percent, followed by the oil film and deposit effects at 16 percent each, and the quench and valve leakage effects at 5 percent each. They conclude that in a cold engine the fuel escaping combustion would be higher due to the cold crevices and oil layer, with much more liquid fuel entering the cylinder.

2.1.9 Other Effects

The process of fuel absorption into the oil film, and subsequent desorption, has already been described. It is perhaps not as well recognised that this process can also occur with porous combustion chamber deposits. Harpster et al\(^{(27)}\) carried out experiments which showed a 25 percent increase in the unburned hydrocarbons, when operating an engine with combustion chamber deposits, compared to the deposit-free result. They also found that the effect depended on the fuel structure and therefore this interaction needed to be considered in the development of reformulated gasolines if emission levels were to be maintained for the life of the vehicle. They also recognised the possibility that these deposits could fill crevice volumes and therefore reduce the amount of fuel escaping combustion. Clearly these deposits would also have an effect on the chamber temperature which could further influence the hydrocarbon oxidation process.

A certain amount of leakage occurs past the nominally closed exhaust valve during compression and the early part of the combustion process\(^{(23)}\). Boam et al\(^{(7)}\), however, found this insignificant in a new engine but concluded that it could cause an increase in unburned HC emissions as an engine ages.

2.2 Significance of the Cold-Start Period

All of the above factors have the potential to significantly increase the emissions of unburned HC, particularly under cold-start conditions. Most of them will also have an increasing effect with decreasing temperature. Significant increases in CO will also
be exhibited, not only when rich fuel-air ratios are required for starting, but also when cold operation affects the cylinder-to-cylinder distribution and where poor mixture preparation gives rise to areas of rich mixture within individual cylinders\textsuperscript{(28)}. When this stratification occurs high CO emissions can result, even when the overall engine air-fuel ratio is nominally stoichiometric.

In order that vehicles with three-way catalysts meet future stringent Californian legislation, cold-start emissions must be eliminated\textsuperscript{(29)}, since these emissions can contribute up to 70 percent of the HC and CO tailpipe emissions from an FTP test. Although three-way catalysts have become an essential component in the overall control of these emissions, it is unfortunate that they do not operate immediately during the crucial cold-start operating mode, but require a finite period of time, which depends on engine running conditions, to reach their operating temperature. The significance of the cold-start period is therefore evident and the need to research ways of both improving the catalyst light-off characteristics or other after-treatment techniques, as well as reducing engine-out emissions, has become increasingly urgent. It should also be remembered that, even if enrichment time is short, closed loop stoichiometric control is not possible until the oxygen sensor in the exhaust gas stream has reached its working temperature: Even when the sensor is electrically heated this can take 20 to 30 seconds, although fast warm-up sensors are being developed\textsuperscript{(30)}.

Figure 1\textsuperscript{(31)} shows the tailpipe HC emissions during the early stages of an FTP75 test cycle. This illustrates, not only how reducing test temperature increases the emissions of HC, but also how it is this early stage of the test which can determine whether a vehicle passes or fails. As can be seen, 78 percent of the cumulative HC emissions are emitted during the first 200 seconds of a 2447 second test. The lack of catalyst activity during this early phase of the test cycle is illustrated in Figure 2\textsuperscript{(32)}, where the HC emissions are shown both from the tailpipe and directly out of the engine. For the first 30 seconds the two levels are identical, with the tailpipe emissions only reducing significantly after about 60 seconds into the test.
Whilst most of the emphasis has been on developing systems that ensure compliance with the emissions standards, it is generally recognised that 'real world' driving can be under considerably different conditions from those of the simulated drive cycles which are used in the legislative tests. The EEC test temperature in particular is unrealistic when compared to the year average ambient temperatures across Europe which are much lower\(^{33}\). This has led to vehicle manufacturers designing fuelling strategies where issues such as driveability and startability take precedence over emissions when operating at temperatures outside the legislative limits. Consequently at low temperature the emissions allowed into the environment can be very high due to the large amounts of fuel enrichment used. Even when the catalyst has reached light-off temperature these excessive mixture strengths prevent conversion, unless secondary air is supplied to the exhaust gases to ensure the required oxidising environment\(^{34}\). There is an urgent need to find ways of reducing or eliminating the necessity for these rich fuel calibrations at all temperatures and of ensuring rapid catalyst heating.

Fuel management is clearly crucial during the cold-start and early warm-up period which makes it essential that particular care is given to the calibration of the critical pre-catalyst-light-off-period and this must include attention to every engine cycle if large excursions in unburned HCs are to be avoided\(^{35}\).

### 2.3 Changing Legislation

Much of the impetus for the extensive research into engine pollutant formation, so far described, has come about as a result of the ever increasing severity of the imposed legislation. The control of vehicle exhaust emissions, by the setting of standards to which vehicle manufacturers had to comply, began in the 1960s in California, where a combination of climate and topography, in certain urban areas, was creating severe episodes of photochemical 'smog'. Since these early days of regulation the limits have become progressively more severe, with the California Air Resources Board (CARB) leading the rest of the world with its 'technology-forcing' emissions limits. Table 1 shows the United States Federal and California light duty (FTP-75) emissions
standards, where it can be seen that very demanding standards have been established for the 1990s and beyond.

Table 1 US Federal and California light duty emissions standards (FTP75), g/mile

<table>
<thead>
<tr>
<th>Year</th>
<th>HC/NMOG</th>
<th>CO</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Federal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1966 (Typical pre-control)</td>
<td>10.6</td>
<td>84</td>
<td>4.1</td>
</tr>
<tr>
<td>1983</td>
<td>0.41</td>
<td>3.4</td>
<td>1.0</td>
</tr>
<tr>
<td>1994 (Tier 1)</td>
<td>0.25</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2004 (Tier 2)</td>
<td>0.125</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td>California</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>0.25</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>1994 (TLEV)</td>
<td>0.125</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>1997 (LEV)</td>
<td>0.075</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td>1997 (ULEV)</td>
<td>0.04</td>
<td>1.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

NMOG Non-methane organic gas (sum of non-oxygenated and oxygenated HCs)
TLEV Transitional low emission vehicle
LEV Low emission vehicle
ULEV Ultra low emission vehicle

To illustrate the progress that has been made, the above table includes typical emissions for a pre-control vehicle. It can be deduced that current conventional vehicles are now producing only two percent of the HC, four percent of the CO and ten percent of the NOx emitted from pre-control vehicles. Despite this significant achievement, the ULEV requirements mean these figures must be reduced to 0.4, 2 and 5 percent of the HC, CO and NOx emitted by these 1960s vehicles.

To further illustrate the changes that have taken place, Heywood(36) quotes typical HC emissions of 11 g/mile for a pre-control vehicle and 3 and 0.3 g/mile for the engine emissions and tailpipe emissions of a current US vehicle. These figures are approximately 9, 3 and 0.3 percent respectively of the fuel used (25 miles/US gallon.
= 120 g/mile HC), which represent a highly significant improving trend. A lot of the early improvements gave significant benefits in fuel consumption but, unfortunately, the three-way catalyst fitted to current vehicles, so necessary for the lowest emissions, does no useful work and results in a loss of fuel economy.

Although these improvements are significant, they have all come about with development under 'warm' ambient conditions. As temperature is reduced it is seen that the emissions reduction, in comparison to pre-catalyst vehicle designs, has not been as great. Vehicle tests have shown a three to four fold increase in CO emissions as temperature is reduced from 24°C to -7°C (37).

It is generally understood that meeting the ULEV standards will require an approximate reduction of 90 percent in cold start HC and CO emissions, compared to conventional underfloor three-way catalyst (TWC) technology. This difficult target will be even more challenging if the -7°C CO test, already adopted by the Environmental Protection Agency (EPA) and CARB on current vehicles, is required for ULEV.

The legislative limits for Europe are shown in Table 2. These levels have developed in response to the changes being introduced in the US, with the stage 2 levels being considered equivalent to TLEV. Furthermore, there are proposals to modify the test cycle by removing the unmeasured 40s idle period, as well as the possibility of a lower test temperature being required. The potential influence of these changes has been investigated by Laurikko (38), who found that at 20°C there was little effect when the 40s idle period was included, but at -7°C and -20°C there were substantial changes, particularly in the CO emissions, which were most significant for the large vehicle tested.

It is also likely that Europe will retain the inclusion of methane in the measurements, making it even harder to meet stage 3 standards, since the conversion of methane by current three-way catalysts is generally very poor (39). If all the proposed changes are
implemented, it is likely that the European stage 3 emissions challenge will be at least as severe as the Californian ULEV requirements.

Table 2 European emissions legislation for light duty gasoline vehicles, gm/km

<table>
<thead>
<tr>
<th></th>
<th>HC + NOₓ</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1 (1992/1993)</td>
<td>0.97</td>
<td>2.72</td>
</tr>
<tr>
<td>Stage 2 (1995/1996)</td>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>Stage 3 (1999/2000)*</td>
<td>0.05</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*proposal of the FRG Environmental Protection Agency

2.4 Catalyst Population Effects

The significance of cold start emissions is growing with the increasing population of catalyst-equipped vehicles. Figure 3\(^{(40)}\), for example, shows how the distribution of total emissions of CO and HC for cold and hot engines, during typical Danish town driving conditions, varies with the number of vehicles fitted with catalytic converters. For the case of a vehicle population with no catalysts fitted the cold engine emissions contribute approximately 26 percent of the total, whereas when all vehicles have catalysts this contribution will increase to 60 percent, even though the overall emissions will be reduced by approximately 50 percent.

As traffic density increases and roads become more congested, traffic speeds will decrease with more stop-start and short journey driving occurring. As a consequence, the amount of cold engine emissions will increase and their contribution to the total will become even more significant. This further emphasises the need to find ways of controlling these emissions if 'conventional' engines are to remain viable.
2.5 Unregulated Emissions

Automotive fuels and the products of their combustion are composed of many different species of HC, all of which have a different reactivity and smog-forming potential, as well as a toxicity and likely detrimental effect on health. There are a number of currently unregulated pollutants which are being targeted for reduction, due to their suspected adverse affect on public health and/or the environment, such as formaldehyde, 1,3 butadiene, benzene and toluene.

Regulation of the reactivity of HC species has already begun in the US, along with limits for some of the known toxins. This has become more important with the introduction of ‘clean’ and alternative fuels. These fuels can often reduce overall mass emissions but may burn to emit higher proportions of the more toxic or reactive species. An example of this is the higher emissions of aldehydes from methanol-burning engines to those burning conventional gasoline.

Both the fuel properties and the exhaust emissions control devices can have an effect on the speciated emissions and the ozone-forming potential (OFP). In the case of gasoline fuels, catalysts with higher conversion rates, such as those which are close-coupled to the engine, can reduce alkenes and aromatics, which have a high OFP\(^{41}\). With deterioration of the catalyst, non-methane organic gas (NMOG) increases, but the OFP decreases slightly because of an increase in alkanes. With regard to gasoline fuel compositional effects on ozone-forming potential, an effective decrease can be made by reducing the aromatic content of the fuel, whilst reducing the T90 lowers the NMOG emissions. Other research has shown that high aromatic levels in typical European fuels give rise to increased emissions of the non-regulated volatile organic compounds (VOC) such as benzene, ethyl benzene, toluene and xylene. 1,3 butadiene levels in exhaust were similarly dependant upon fuel olefin levels\(^{42}\). This increase in VOC emissions is considered to lead to greater severity of photochemical smog events and to an increased evidence of pollution-related cancers.
Natural gas, a fuel of particular interest in the US, has been shown to have a number of considerable potential benefits in terms of reductions in key toxic emissions. Wallace et al\(^{(43)}\) found that there was no detectable 1,3 butadiene in the tailpipe emissions of a bi-fuelled engine running on natural gas; acetaldehyde was reduced by 94 percent, benzene by 89 percent and formaldehyde by 39 percent, compared to measurements made for gasoline operation. Furthermore, the grams ozone/grams NMOG were reduced by 81 percent with natural gas. Carbon dioxide, another currently unregulated pollutant, was reduced by 23 percent.

Apart from the fuel and emissions control system effects, the operating condition of the engine will have an important influence on the speciated emissions. The cold start and warm-up phases have considerable influence on the species distribution in the exhaust gases. Kubo et al\(^{(44)}\) investigated the HC species emissions during starting and found that the main engine-out components during warm-up were the unburned fuel species and the reaction products, which consist of the C\(_2\) to C\(_4\) olefins, methane and acetylene. They found that the percentage contribution of the olefins increased with warm-up and, since these components have high reactivity factors, it follows that the specific reactivity of the exhaust gases increased during this period. The catalyst conversion efficiency of these species during the warm-up process is also described. Their results showed that the olefins passed straight through the catalyst before light-off, whereas the conversion efficiency of the alkylbenzenes was nearly 100 percent between 50 and 90°C.

The increase in specific reactivity during the warm-up period is confirmed by the work of Kaiser et al\(^{(45)}\), who draw the following conclusions: 1) The species distribution and the atmospheric reactivity of the HCs vary with time after cranking. Thus, if time to catalyst light-off is decreased to reduce the total emissions, the reactivity may also change significantly; 2) changing the engine operating conditions can alter the species distribution, reactivity and time dependence of the HC emissions and; 3) changing operating conditions to reduce total HC emissions may increase the reactivity of these emissions for photochemical smog formation, partially counterbalancing the advantage gained from the lower total emissions. It was
observed that, with a conventional starting calibration, the exhaust was initially enriched in light fuel alkanes and depleted in heavy aromatics. The light alkanes fell rapidly whilst the lower vapour pressure aromatics increased over 50 seconds. These results indicated the early retention of low vapour pressure components in the intake manifold and exhaust system. It is the light alkane components, such as butane and isopentane, which vaporise rapidly and provide the initial fuel to start the engine.

A further study\(^{(46)}\) showed that the initial reactivity was low during starting and increased as the engine warmed up. The results also suggested that faster catalyst light-off can reduce tailpipe reactivity as well as HC mass. It is also reported that the optimum conversion efficiency to minimise exhaust reactivity was 95 percent and that higher efficiencies actually increased reactivity by as much as 50 percent. Formaldehyde was a particular concern when the catalyst operated at high efficiencies.

The effect of cold start enrichment had a significant effect on reactivity. It was found that the equivalence ratio affected both specific reactivity, OFP and toxic air pollutant mass. The exhaust specific reactivity decreased at rich air-fuel ratios and during misfire because NMOG species increasingly resembled those of the fuel. While NMOG mass was found to be at a minimum near the lean limit, minimum OFP and toxic levels were found near to stoichiometric air-fuel ratios. During the first half-minute of a cold-start 75 percent of the HCs were attributed to unreacted fuel. This level dropped to less than 60 percent after one minute, whilst the steady state level was 53 percent.

2.6 Concluding Remarks

This section has introduced the need for reducing emissions from spark ignition engines, particularly during the cold-start period, when the catalyst is inoperative. Factors which affect the starting process, such as fuel vaporisation and supply mixture enrichment, have been described, as well as other mechanisms which contribute to pollutant formation. A résumé of emissions legislation development has been given
and concern for unregulated emissions has been highlighted. The following section
details some of the many technologies which are currently being evaluated as
potential solutions to the cold-start emissions problem.
3. Potential Solutions

3.1 Introduction

A cure for cold-start emissions would be a catalyst which was fully functional as soon as the engine started. This means it would be at working temperature, together with the ability of the engine to run under closed-loop stoichiometric control, as soon as the engine is cranked. Significant research is currently being carried out to approach this ideal solution, or provide alternative means to control the high cold-start HC and CO emissions, at least to levels which enable compliance with the most stringent proposed legislation.

Possible technologies can be broadly classified as either 'active' or 'passive'. In an active system the engine is required to operate, for a short period of time, in a different non-standard mode\(^{(36)}\). An example of this would be exhaust gas ignition, where the engine runs very rich, thus producing hydrogen in the exhaust system, which is then burnt with extra air provided by an air pump. The heat from this combustion is used to quickly light-off the catalyst. The concern with these systems, although very effective, is their durability and reliance on careful control. An example of a 'passive' system would be a close-coupled catalyst relying on heat from the exhaust and a low thermal inertia manifold to obtain effective operation.

The following describes some of these active and passive components and systems, which are currently being investigated:-

3.1.1 Electrically Heated Catalysts

These active systems have had significant development and consist of an electrically heated metal foil or extruded substrate, which can be battery and/or alternator powered, but may need a second battery to provide sufficient energy\(^{(47)}\). The electrically heated catalyst is usually combined with a close coupled or starter catalyst, which in turn is fitted close to the main converter in a 'cascade' system.
Secondary air injection may also be required\textsuperscript{(48)} to ensure that an adequate oxidation environment exists within the catalyst during the enrichment period. Hadded et al\textsuperscript{(29)} found that for large high performance vehicles power requirements in excess of 4 kW and up to 15 seconds pre-cranking heating was required for adequate cold-start performance.

A more recent report\textsuperscript{(49)} describes the test results from a 3 litre, 4-cylinder, 4-valve engine, which successfully met both ULEV and Stage 3 limits, when using an electrically heated catalyst system. They stress that such a system is not an add-on solution, but part of a complete exhaust and electronic system, which must be tailored to individual vehicle applications. The vehicle tested had a system comprising the following:

- close-coupled converter
- reduced exhaust thermal loss upstream of catalyst
- increased cold start idle speed and/or idle air flow
- retarded ignition during cold start
- reduced warm up and acceleration enrichment
- secondary air into the manifold for first 50 seconds to achieve \textit{Lambda} = 1

The catalyst was heated for 16 seconds at 1 kW and the emissions during the first 125 seconds of the EC and FTP tests were found to be similar. Even with this heated system the authors make the point that 70 to 80 percent of the HC in the FTP test are emitted during the first acceleration between 20 and 32 seconds into the test. For the European test 50 percent of the emissions are emitted during the first ‘hill’ and the other 50 percent during the second ‘hill’.

### 3.1.2 Ignition Retard

Ignition retard, as mentioned above, is already used as a method for improving the heat input to the catalyst. By delaying combustion, higher temperatures exist at exhaust valve opening. However, this method is now being developed with extremely retarded timings, so that burning takes place well into the exhaust stroke\textsuperscript{(50)}. The
technique is to start the engine conventionally and then, as soon as combustion is established, retard the ignition significantly. If this is combined with a close-coupled catalyst then light-off can be achieved very rapidly. Clearly this method relies on very precise engine management and must not be compromised by excessive early emissions or durability issues.

3.1.3 Insulated Exhausts / Manifolds

Hadded and Stokes et al\(^{(29)}\) found that, even when an electrically-heated catalyst (EHC) is used with pre-crank heating, its volume may only be sufficient to control the first 20s idle of the FTP cycle. During the first 70s of the test most of the heat from the exhaust gases is lost in heating the manifold and downpipes. It is, therefore, important to minimise these heat losses so that the power requirements of the EHC can be minimised.

Methods of conserving the exhaust thermal energy in order to reduce catalyst light-off time are being developed. Double-walled air-gap exhaust downpipes are one effective method of reducing heat loss, which has been shown to be important in reducing cold-start HC emissions during the FTP test\(^{(51)}\). Close-coupling the catalyst to the manifold, which is described further in section 3.2, is another way of ensuring maximum heat transfer from the hot exhaust gases to the catalyst.

3.1.4 Burner-Heated Catalyst

In this system an external fuel burner with dedicated air, fuel and ignition system provides a very large heat input to the catalyst front face, thus providing very fast light-off. Unlike EHCs, power consumption is not an issue and a 10 to 15 kW burner has a negligible impact on fuel economy during the emissions test\(^{(52)}\). The design of these systems is still providing technical challenges, particularly with regard to their durability, reliability and safety. In an FTP test Hepburn et al\(^{(53)}\) found that catalyst light-off occurred after 15 seconds instead of 50 seconds and the HC emissions were
reduced by 60 percent. Provided the thermal shock from the burner does not affect the catalyst, the ready supply of heat energy means the catalyst can be mounted underfloor well downstream from the engine and hence protected from thermal degradation.

3.1.5 Exhaust Gas Ignition

As with burner-heated catalysts, described above, the exhaust gas ignition (EGI) system uses energy derived from the vehicle's fuel. However, with this system it is an indirect process using exhaust gases from an engine calibrated to run very rich. This rich calibration produces significant hydrogen in the exhaust which, together with an additional supply of air, provides an easily ignitable mixture within a chamber directly in front of the catalyst. The heat thus generated is then used to rapidly heat the front face of the catalyst ensuring a very rapid light-off\(^{(54)}\). The key to this technology concerns the method of making this combustible mixture, which must be ignitable within two seconds of starting the engine.

Under normal cold starting, exhaust gases are cold and non-reacting, consisting mainly of CO and unburned HCs. It was found, however, that if the engine was run at an equivalence ratio of 1.5 then sufficient hydrogen was generated to produce an ignitable exhaust gas even when cold. For reliability this ratio was increased to 1.75, which gives an initial CO content of approximately 8 percent. As soon as a reliable flame is established in the afterburner, the calibration is returned to a more normal air-fuel ratio. Catalyst light-off is claimed to occur in 20 seconds, compared to over 100 seconds for the underfloor catalyst without EGI.

At the time of the report, the adverse effects of running with such an excessively rich mixture had not been fully investigated. It is common knowledge that, under normal circumstances, the use of these low air-fuel ratios would cause heavy engine deposits, rough running with poor performance and high fuel consumption. It remains to be seen what adverse effects, if any, there are from using this new technology. Clearly,
the benefits in reduced emissions are substantial, with claims for reductions in HC, CO and NO\textsubscript{x} of 76, 85 and 54 percent respectively, for the bag 1 results from the FTP test. A further benefit of EGI is easier packaging, since close-coupling of the catalyst is unnecessary. The secondary air pump, however, which must supply an air flow rate approximately the same as the engine idle rate, is larger than that required for normal secondary air duties.

3.1.6 Engine Preheaters

If an engine is preheated before it is started, the fuel vaporisation process is improved and the need for mixture enrichment is reduced. This has a direct effect on lowering cold-start emissions and also, indirectly, through changes in other mechanisms, such as crevice effects and fuel absorption/desorption in the oil layer. The increase in initial combustion and exhaust temperatures will also be of benefit in reducing the light-off time of the catalyst and the time to closed loop operation of the engine. A number of countries with cold climates use electrical engine block heaters, which are mains powered and switched on some time before a journey is made. These devices, however, were intended for providing instant passenger compartment heating and windscreen defrosting and not for emissions control. Work carried out in Sweden\textsuperscript{55}, however, has shown how they can benefit the environment through reduced pollution under cold-start conditions. FTP tests were carried out at +22°C and -2°C on a number of California certified vehicles, both with and without electrical block heaters of 0.5 kW rating. The results showed that the low temperature tests, without block heaters, produced three times more CO than at +22°C and nearly double the HC. When a heater was used for approximately 3 hours before starting, the engine block temperature increased to around 40°C and the HC and CO emissions were the same, or lower, than when starting at +22°C without preheating. The NO\textsubscript{x} levels for the first kilometre, however, increased by a factor of two.

An alternative technology, which removes the need for an external power supply and significant preheating time, is the heat battery\textsuperscript{56}. This is a latent heat store device
which can very rapidly supply an initial power of 50 to 100 kW. It functions by accumulating the waste heat of the engine and preserving it, with highly efficient insulation, ready for the next time the engine is started. It is claimed that with just 30 seconds of engine heating the tailpipe emissions of CO are reduced by up to 50 percent and HC by 30 percent in the first bag of the FTP test.

3.1.7 Hydrocarbon Adsorber

This technology uses a zeolite material to adsorb HC emissions during the cold-start period. The retained hydrocarbons are then released when the catalyst has reached a sufficient temperature for efficient oxidation. The advantage of such a system is that no additional energy is required for its operation, but obviously it is only suitable for HC control. The suitability of the adsorption/desorption characteristics of the existing trapping materials and lack of stability at high temperatures is still a concern, as is the difficulty of complying with on-board-diagnostics (OBD).

Three systems are described by Kollmann et al\(^{(57)}\); an adsorber coated substrate (ACS), an advanced adsorber system (AAS) and a hydrocarbon trap (HCT). The ACS is the simplest and consists of an adsorbing material in front of, or together with, the catalytic coating. The advantage of such a system is that no changes in the exhaust layout are required and no additional features such as controller, air supply, electricity or fuel are needed. In the AAS, the adsorber is placed between the first catalyst and the underfloor catalyst, but parallel to the exhaust system. During cold start the exhaust flow is directed initially through the adsorber for the first few seconds. The adsorber, with its trapped HCs, is then isolated from the system for the next few seconds to keep it cool and to allow the main catalyst to heat up. A valve arrangement then allows partial flow through the main system, and through the adsorber, to enable purging. This purging may be assisted with an additional air supply. The final system is the HCT, consisting of charcoal or other adsorbent material. It is positioned parallel to the rear silencer to keep it cool, due to its low thermal tolerance. The advantage of this system is that it remains cool until the normal TWC is at operating temperature and so no desorption takes place during the cold start period. After the catalyst has
reached light-off temperature, a valve opens and the high back pressure of the adsorber causes the gases to pass through the normal silencer system. The desorbed gases are drawn back to the engine under manifold vacuum for consumption and final clean up by the hot catalyst. Measurements with the HCT system gave better results than ULEV, but the ACS system suffered from desorption occurring before the catalyst was fully operational. This system, however, would be the most cost effective and, therefore, merits further development.

3.1.8 Exhaust Storage

A Swedish manufacturer is developing a system where the total exhaust flow during the first 30 seconds after a cold start is stored in a flat 100 litre PVC bag housed in the boot of the car. Once the catalyst is working effectively the emissions are returned to the engine for recombustion and final treatment by the catalyst. It is claimed to be the nearest thing yet achieved to developing a near-zero emissions vehicle. For the production version it is anticipated that the bag in the boot will be replaced by two smaller bags in the rear wheel arches. Pressure sensors ensure that the bag pressure does not become excessive.

3.1.9 Fuel Vaporisers

The importance of good fuel vaporisation for effective cold starting, with minimum emissions, has already been discussed. The use of vaporising aids such as coolant and electrically-heated manifolds are commonplace. These have mostly been used in the past for achieving good mixture distribution to aid starting, driveability and economy, rather than emissions. The use of exhaust heat during warm-up, to assist vaporisation, has also been extensively used, as well as occasional attempts to produce systems which vaporise the entire charge. These latter systems were developed, however, in an attempt to improve the lean running ability of the engine, rather than improving its cold starting. They were unsuccessful, largely due to their damaging effect on engine volumetric efficiency and power. A resurgence of interest is now
apparent in the use of these concepts, primarily to reduce emissions during the start-up process, where the effect on engine breathing is unimportant. Unfortunately, the coolant and exhaust do not warm up rapidly enough to be of much assistance in the task of controlling start-up emissions and, therefore, attention has turned to electrical heating.

An experimental electrical device for producing vaporised gasoline, described by Boyle et al\(^{59}\), was installed in the intake system of three port-injected gasoline engines. Compressed air was also used to aid the vaporisation process and typical results are shown in Figure 4. With this system the engine was started with an air-fuel ratio close to stoichiometric giving a significant improvement in HC emissions. During the first 60 seconds of operation, the area under the HC trace, which equates closely to the mass emissions of HC, was reduced by approximately 45 percent, when prevaporised gasoline was used, whilst the stabilised HC emissions level was reduced by 20 percent.

Heated pintle-type fuel injectors have also been used, but these took two minutes for the fuel to reach the required temperature of 49°C, which was considered too long\(^ {60}\). Computational fluid dynamics (CFD) analysis led to the conclusion that it was fuel vapour, having a low thermal conductivity, which was acting as insulation and preventing the required heat transfer to the fuel.

Another vaporiser, designed around a diesel engine glow plug as a heat source and with air assistance through manifold depression, shows similar results\(^ {61}\). This system was designed to achieve good atomisation, without heating, after the cold start period and complete vaporisation, with heating, for starting and idling. It was estimated that at 1500 rev/min road-load only 20 to 30 percent of the fuel was totally vaporised, the remainder persisting in a finely atomised liquid state. The presence of droplets was due to the limited heated surface, together with a four-fold increase in the mass of fuel delivered during each injector pulse. However, using the vaporiser, the engine started at close-to-stoichiometric conditions and the HC emissions were
reduced by 50 percent during the first 60 seconds, compared to the optimised start-up calibration using liquid fuel.

A method of assisting the fuel vaporisation process, by recirculating a quantity of hot exhaust products back into the cylinder late in the inlet stroke, is described by Gardiner et al\textsuperscript{(62)}. Clearly this is only of benefit if combustion has already occurred during the starting process so that heat is available to assist further vaporisation. They claim reductions in the required fuel enrichment which reduces the CO and HC emissions. Additional reductions in HC emissions result as the gases which are recirculated are those containing the highest concentrations from the crevices and cylinder surfaces.

### 3.1.10 Air-Assisted Injection

In addition to the systems described above, where air is used together with a heat source, there are systems being developed which rely purely on air interacting with the fuel from the injector for good atomisation\textsuperscript{(63)}. The greater the degree of atomisation, the easier it is for the fuel to vaporise and the better the air/fuel mixture distribution within the engine. These systems are likely to be simpler and less costly than heated vaporisers and may form part of a system which gives adequate control of start-up emissions. The simplest air-assisted injection utilises the pressure difference between the atmosphere and the intake port, whilst the more complex systems use air pressure from an auxiliary pump. The fuel droplet Sauter mean diameter (SMD) has been measured as 320\textmu m, 50\textmu m and 10\textmu m from conventional, manifold pressure-assisted and pump-assisted injection respectively\textsuperscript{(6)}. It was reported that, in the first engine cycle after a cold start, the HC emissions were reduced by 80 percent compared with conventional injection. Figure 5 shows the reduction in HC emissions during the first 20 seconds of a cold start and the similarity between this and the fully vaporised results shown in Figure 4 is evident.
Achleitner et al\textsuperscript{(64)} claim that air assisted injectors are a very effective means of ensuring good mixture preparation, particularly for engine starting and during the warm-up phase. They claim that, with a fast burning combustion chamber, the smaller fuel droplets from the air assisted injectors allowed injection onto an open inlet valve, even with a cold engine. This produced less wall wetting, thus allowing a leaner calibration, resulting in a reduction in CO and HC emissions. They claim a reduction in HC, CO and NO\textsubscript{x} of about 45, 60 and 48 percent respectively, during an FTP75 test cycle when injecting with air assistance onto an open inlet valve and with retarded spark timing. The lean calibration was also beneficial in reducing the catalyst light-off time.

\subsection*{3.2 Three-Way Catalyst Development}

Although there has been significant progress in all of the above technologies, none of them removes the need for the catalyst, which continues to be developed, not only as part of an overall system, but also to reduce or remove the necessity for additional emissions control components. Precious metal loading and formulation developments have resulted in considerable reductions in the light-off temperature. The coatings are expensive, however, and obviously a balance has to be achieved between performance and cost.

Current emphasis appears to be on close-coupling of the catalyst to the engine. This entails mounting the catalyst as close to the exhaust ports as durability and packaging will allow, thus ensuring maximum heat transfer efficiency from the exhaust gases to the catalyst brick. The catalyst may even become an integral part of the exhaust manifold\textsuperscript{(65)}, but ensuring the catalyst survives in such a hostile environment and continues to remain effective for the required legal lifespan is a major technical challenge. The common noble metals used in catalysts are platinum, palladium and rhodium. Platinum and rhodium deteriorate considerably more than palladium, which is the preferred noble metal for high temperature HC conversion and, therefore, more suited to close-coupling. Summers et al\textsuperscript{(66)} investigated the use of a 0.5 litre close-
coupled palladium catalyst, bolted directly to the manifold and acting as a light-off catalyst, to get heat rapidly to a 1.5 litre underfloor palladium catalyst, mounted in the standard OEM position. The manifold catalyst was heavily loaded, at 10.6 grams palladium/litre, but enabled the vehicle, with a 2.5 litre engine, to meet the demanding ULEV standard without the need for secondary air or a double-walled, heat-insulated exhaust system. The use of the manifold catalyst was also found to be of benefit in dampening the modulation of the air-fuel ratio seen by the underfloor catalyst and also in reducing extreme lean excursions during transient operation. The point is made, however, that the success of this combination of catalysts and loadings will depend upon the fuel used and the non-methane fraction of the exhaust gases.

Clearly, there is considerable scope for continued development of three-way catalysts and systems, which will certainly be of major benefit, at least in the short term, whilst the more advanced alternative technologies mature. It is worth emphasising that, at high HC catalyst conversion efficiencies, a small increase in efficiency can be very significant. For example, going from 96 to 97 percent efficiency, reduces tailpipe HC emissions by 25 percent. This also illustrates the significance of ensuring close control of the air-fuel ratio which must remain within one percent of the stoichiometric ratio for the catalyst to remain effective\(^{(67)}\).

Recent results\(^{(68)}\) confirm that the combination of close-coupled and underfloor catalyst offers the best combination of fast light-off and optimum packaging; the most significant recent development being the use of highly loaded palladium catalysts, which have superior performance to equally costly platinum/rhodium catalysts. Because of the relatively low cost of palladium, it is possible to use high loadings in three-way catalysts and data shows light-off being achieved in 23 seconds, as the air-fuel ratio approaches stoichiometry. It is demonstrated that it is possible to achieve ULEV on existing production vehicles after engine ageing with such an advanced palladium catalyst. The authors conclude that both future European and US legislation can be met with such passive catalyst technology. It is, however, emphasised that a suitable engine start calibration must be used.
3.3 Closure

From what has been described in Section 3, it is evident that technology is currently available to potentially meet the most stringent proposed legislative emission levels for the majority of engine/vehicle applications. However, there is still considerable concern for the aged performance of some of these systems, as well as their complexity and cost.

Fast catalyst light-off is the likely key to this technology, together with other strategies, depending upon the engine/vehicle characteristics, such as thermal control of manifolds and pipes, secondary air injection and improved transient air-fuel ratio control. Such a ‘total system’ approach based around an EHC, is described by Hadded et al\(^{69}\) for achieving ULEV and Stage 3 emissions legislation. Summers et al\(^{66}\) report success in attaining ULEV levels on a smaller engine by the use of a highly loaded palladium close-coupled manifold catalyst and underfloor catalyst, with further improvements in HC/CO emissions and improved driveability by the use of secondary air injection and a double-walled exhaust system.

Whilst these and other reported systems show measurable success, it is clear that the required levels are only being reached with considerable effort. Indeed Austin et al\(^{70}\) suggest that the compliance of larger vehicles is highly uncertain unless natural gas is used. Under current regulations, however, full-range manufacturers can avoid compliance with ULEV on all but their smallest vehicles. With the possibility of this changing in the future and the current emphasis in Europe on testing at significantly lower temperatures, with emissions measured from ‘key-on’ instead of after a period of idling, the demands for longer term solutions is becoming more severe.

There is little doubt that future engine generations will have lower base level emissions through improved combustion system designs and improved fuel formulations. The use of alternative fuels, as a means of reducing emissions, will also continue to develop, except that storage and other problems of some of the more promising fuels remain an issue, particularly where they are used as primary supplies.
Having reviewed the technology, currently under development or investigation, which offers a potential solution to the cold-start emissions problem, it was noted that one area where comparatively little work had been done was in the use of alternative fuels for the cold-start period, whereby at some suitable point after the engine had started the fuel supply would revert back to the conventional gasoline system. This strategy reduces many of the drawbacks of some alternative fuels, such as low energy density/bulk storage difficulties, safety concerns, reduced power and vehicle range. Work has been done on the use of alternative fuels as starting aids at low temperature, such as the use of dimethyl ether for starting methanol fuelled engines\(^{(71)}\), but these have not been carried out with emissions reduction as a main objective.

Whilst a complete cold-start strategy would not be feasible, within the time constraints of the project, a decision was made to select a potentially suitable fuel and investigate its performance during the cold-start and early warm-up period. This selection procedure is the subject of the next section.
4. Selection of Cold-Start Fuel

4.1 Introduction

Whilst a vehicle using an alternative fuel for the cold-start period would correctly be described as dual-fuelled, it would only be required for the period it takes for the TWC system to reach sufficient conversion efficiency to control the initially high HC and CO emissions after a cold start. For a vehicle with high engine-out emissions this may have to be for as long as it takes the TWC system to reach its fully heated conversion potential, which could be a number of minutes. For a well developed engine or one with a control system constrained, for example, only by the exhaust gas oxygen sensor delay, the period of alternative fuel use may only be a number of seconds. It is, therefore, clear that the quantity of start-up fuel required and storage (and/or generation) capability will vary, but it is anticipated that this would only be a small percentage of the vehicle's main fuel storage capacity.

4.1.1 Gaseous Fuels

The best fuel would be one which remains in a gaseous state throughout the induction process of the cold engine. Quader\textsuperscript{72} demonstrated that when propane was used the starting equivalence ratio remained constant for all ambient temperatures between $+30^\circ$C and $-30^\circ$C, whereas for gasoline the ratio varied by a factor of 5 (from an approximate stoichiometric mixture at $21^\circ$C to a very rich 3:1 A/F ratio at $-29^\circ$C). Also the time to first-fire remained constant for propane, regardless of temperature, whereas for gasoline the time increased significantly with decreasing temperature.

Tests carried out using two fast response HC probes, installed in a specially adapted spark plug, sampling from two different positions within the combustion chamber, enabled the degree of stratification and vaporisation to be determined\textsuperscript{73}. Natural gas was used to simulate a perfectly vaporised fuel and to serve as a baseline. With this fuel the readings from both probes were similar, indicating that the charge within the chamber was perfectly mixed. When fuelling on gasoline with conventional injection
onto a closed valve, however, there was considerable difference in the readings. This difference was even greater when injection was onto an open inlet valve, which was explained as being due to the lack of fuel residence time on the back of the hot valve, which normally assists vaporisation, and the lack of turbulence which is created as the inlet valve opens and reverse flow into the manifold occurs. From these results it was concluded that fuel-air charges, considered to be homogeneous, can in fact be highly stratified at the time of ignition. Clearly these effects will be exacerbated when the engine is cold and will increase the HC and CO emissions, particularly during the early cycles of operation.

By using a suitable gaseous fuel, the problem of ensuring adequate fuel vaporisation is removed and it should be possible to reliably start and run the engine with good driveability at equivalence ratios which, apart from any delay in exhaust gas oxygen sensor functionality, will allow immediate closed-loop control. This has the twofold advantage of eliminating the additional HC/CO penalty of cold-start enrichment and also of allowing the catalyst to reach its maximum conversion potential in the shortest possible time.

Even though very fast initiation of closed-loop control should be possible, the catalyst will still require a finite time to light-off and attain significant conversion efficiency. Therefore, if a ‘clean burning’ fuel could be used for this short period of inactivity, a further significant reduction in emissions could be secured.

Hydrogen is probably the ‘cleanest’ potential gaseous fuel. It contains no carbon and, therefore, any HC or CO emissions could only be generated from other sources, such as the lubricating oil. There is still some concern regarding NOx production, but this needs further investigation. It has been concluded that hydrogen vehicles are less energy efficient than either gasoline or natural gas vehicles(74), but the lean-burning capability of hydrogen is well recognised(75), which could make it attractive as a potential start-up fuel if not a primary fuel(76). In the work of Fulton et al(77) it was indicated that, by using hydrogen for the cold-start period and for supplementing the exhaust gases to increase the heat to the catalyst, a reduction in CO and NOx of 21
percent and 33 percent respectively was possible during a cold-start legislative test. They claim that the significance of the result was that only 1.8 percent of the fuel consumed during the tests was in the form of hydrogen, therefore, with this technology the main drawback of size, weight, complexity and cost of hydrogen storage could be reduced.

Compressed natural gas (CNG), although not as 'clean' as hydrogen, is currently receiving considerable attention as a vehicle fuel, both for dedicated and bi-fuel use. However, whilst engine-out emissions have been shown to be lower for CNG, the tailpipe total HC emissions can be higher\(^{78,43}\). This is due to the difficulty that current catalysts have in oxidising methane\(^{79}\), which is the primary constituent of natural gas. There is also recognition that the air-fuel ratio must be very closely controlled at all times to obtain maximum conversion efficiency\(^{80,81}\). For regulations which only limit non-methane hydrocarbons then CNG fuelling can show significant benefits.

Several reports have been given of the advantages of operation on CNG during cold-starting\(^{16,82}\). In one series of tests it was shown how the HC and CO emissions from a gasoline-fuelled vehicle increased by 210 and 400 percent respectively during the first phase of the FTP75 drive cycle, when the temperature was reduced from 25°C to 0°C. However, when operation was on CNG the emissions at -15°C were lower than at 25°C\(^{83}\). Gaseous fuels do not require fuel enrichment at low temperature, which explains most of this improvement\(^{84}\).

Results published by the Southwest Research Institute\(^{85}\), where tests were carried out on a 3/4 ton pick-up truck, compare emissions during an FTP test at 24°C and -7°C for a dual-fuelled 5.7 litre V8 GM engine, running first with gasoline and then with natural gas during starting and whilst the catalyst reached operating temperature, after which it reverted back to gasoline-only operation. This ‘CNG start - gasoline run’ strategy showed a reduction in emissions from the baseline gasoline operation, especially at -7°C. Operation at this sub-zero temperature doubled the HC and CO emissions when using gasoline but levels remained the same as at 24°C, when running
with CNG for starting or dedicated CNG. No recalibration of engine management systems was carried out for this work.

Liquid petroleum gas (LPG), consisting of the three and four carbon atom hydrocarbons such as propane, butane and propene, is mainly used in locations where it is favourably taxed. However, it is now recognised as another potential ‘clean’ fuel, mainly due to its gaseous state. An example of its environmental advantage is demonstrated by the results from a bi-fuelled vehicle operating on LPG during the European test cycle\(^86\). These results showed a reduction in CO and HC of 65 and 40 percent respectively compared with unleaded reference fuel operation. When the temperature was lowered from 25°C to -5°C the reduction was approximately 90 percent for both emissions.

4.1.2 Vaporised Fuels

Any liquid fuel, conventional or ‘alternative’, must vaporise and mix with air before combustion will occur. The term vaporised fuel is used here to describe fuels which are more completely vaporised than in conventional systems before being inducted by the engine. These systems, which have been described in section 3.1.9, normally supply additional heat to the fuel and improve its atomisation, both of which assist the vaporisation process.

Considerable work has been done over the years using vaporised gasoline as a means of extending the lean limit of combustion and also for reducing cold-start emissions. Boyle et al\(^{59}\) demonstrated reliable starting at 20°C without enrichment using standard injectors incorporating heating elements and air assistance. They demonstrated significant reductions in mass emissions, although found it essential to maintain a stoichiometric mixture ratio whilst starting.

The benefits and feasibility of maintaining fuel vaporisation at lower temperatures need to be investigated. It is predicted that, as the temperature is reduced, it will
become increasingly difficult to prevent fuel condensation. At some point it may become necessary to introduce a degree of enrichment in order to maintain reliable starting and driveability.

4.1.3 High Volatility Liquid Fuels

Having considered the use of gaseous fuels and vaporised conventional gasoline, it was decided that, in order to avoid hardware changes and the need for two fuel systems, the research would be based on a liquid fuel that could be relatively easily handled and supplied to the engine with the existing standard fuel system. Whilst a 'clean-burning' fuel was desirable, this was not considered paramount. What was considered essential was a fuel that gave potential for eliminating, or reducing, the mixture enrichment required for starting on conventional gasoline.

If immediate operation at a stoichiometric air-fuel ratio were possible this would not only be of direct benefit in reducing engine-out emissions, but would also ensure that the three-way catalyst, which requires that combustion is at a close-to-stoichiometric air-fuel ratio, could operate at maximum efficiency as soon as it had reached operating temperature. This would remove the need for a secondary air injection system to add oxygen to the exhaust gases during periods of fuel enrichment.

Even with rapid light-off catalysts and secondary air injection, a sensor is required to control the amount of oxygen in the exhaust gases to ensure optimum conversion efficiency. Although exhaust gas sensors are now electrically heated, they still require time to become operational, as described in section 2.2. Therefore, before optimum control and conversion efficiency is achieved, there is a potential for high emissions, particularly during the cold-start when fuel enrichment is used. Even with the best technology there will be a control delay which, as will become clearer in later sections, is exacerbated when using conventional gasoline. However, if an oxidising environment in the exhaust gases could be maintained, by using a suitable alternative fuel for starting and early warm-up, then this problem would be removed.
Initial results using CEC reference fuel (RF-08-A-85), which is a full boiling range unleaded gasoline consisting of a mixture of hydrocarbons, showed that its inherently wide range of boiling points was detrimental to the control of in-cylinder air-fuel ratio during starting and warm-up, as explained in subsequent sections. It was, therefore, required that the fuel to be investigated should not only possess sufficient volatility, but also be a pure substance with a single boiling point.

How the fuel’s solubility in oil can contribute significantly to hydrocarbon emissions, through the absorption/desorption process, particularly when temperatures are low and oil films are thick and viscous was described in section 2.1.3. It has been found that the solubility of fuel in oil increases with carbon number, therefore, it was anticipated that a highly volatile fuel might help reduce this HC forming process, since carbon number reduces as the volatility increases. A possible further benefit of using a single component fuel is that it could make it easier in the future to design a fuel/oil combination that reduces the solubility effect, particularly at low temperatures.

Of the single component fuels readily available, which remain liquid at normal room temperatures, isopentane, with a low boiling point of 27.9°C, was selected. This fuel, which is representative of the light-ends in conventional gasoline, was fairly easy to store and handle and also had a relatively high octane value. This high value was considered important as, when an engine first turns during cranking, the manifold pressure is initially atmospheric and there is a risk of detonation during this first high load cycle. Also, as temperatures rise during warm-up, a single component fuel would increase the possibility of detonation if it had an inadequate octane value. A brief specification for isopentane and the baseline reference gasoline is given in Appendix 1.

Further incentive for using isopentane was given by the results of work using Interferometric Laser Imaging for Droplet Sizing (ILIDS), which had been used for the first time in a firing engine to investigate the evaporation of fuel droplets. Isopentane, iso-octane and xylene, three single component fuels, representing the
light-end, mid-range and heavy ends of gasoline, were investigated. The results showed that isopentane evaporated fully very early in the induction stroke, whereas the iso-octane persisted longer and the xylene persisted towards the end of the compression stroke. It was suggested that during a cold-start there was little evaporation of middle or heavy end components from the inlet port wall film prior to inlet valve opening.

Other results that showed the potential of isopentane came from the work of Moran\textsuperscript{(88)} who modelled the behaviour of a typical gasoline in the inlet manifold of an engine. The gasoline was ‘approximated’ by seven components where the smaller quantities were lumped together for simplicity. The results showed that isopentane, representing the lightest gasoline fraction, had completely vaporised at a distance of 0.2 m along the manifold whereas Heptane, a heavier component, was less than 40 percent vaporised.

The difficulty of controlling the in-cylinder equivalence ratio with conventional gasoline was noted from recent results described by Skippon et al\textsuperscript{(89)} where a differential infra-red absorption technique was used to monitor the transient evolution of the vapour phase directly within the cylinder of an engine. They compared the performance of a full boiling range gasoline with that of single component fuels representing the light end, mid-range and heavy ends of typical gasoline. When the fuel was shut-off to the running engine the in-cylinder ratio rapidly reduced to zero with isopentane, whereas there was a delay of some 20 cycles when fuelled on gasoline. They concluded that very little fuel was stored in the wall film reservoir when the lighter component fuels were used whereas it was considerable for the heavy ends. Although these results were for a fuel shut-off transient, the excellent air-fuel ratio response demonstrated for isopentane was expected to be of direct benefit during cold starting.

A considerable amount of work has been done establishing the relationship between starting temperature and emissions when using liquid fuels. Most of this, however, has been carried out, using the manufacturer’s standard calibration and cold-start
strategy, on vehicles not intended for European stage 3 or ULEV compliance. The calibrations, in many instances, were optimised for high quality starting and driveability rather than emissions. This is due to recognition that, to-date, it has been possible to let the catalyst take care of any problems the calibration may cause in terms of emissions. It was, therefore, intended to show the effects of temperature on emissions, using conventional unleaded reference gasoline and isopentane, where some attempt was made to remove the effect of the calibration.

4.2 Closure

Having selected isopentane, as the highly volatile liquid fuel to be compared with reference gasoline, it was necessary to develop suitable test procedures and experimental facilities to ensure the objectives described in section 1.1 could be met. This is the subject of the next section.
5. Experimental

5.1 Introduction

The facility had to provide the capability of starting the engine at a fixed speed and load with a constant supply equivalence ratio and fixed ignition timing. During each three minute test the emissions were to be measured, with particular emphasis on the first sixty seconds from the start of fuel injection. Cylinder pressure data was also required during this period to determine the 'quality' of the start, as well as for comparing the burning characteristics of the reference fuel with the isopentane.

The main variables in the experiments were the supply equivalence ratio and the start temperature. The supply ratio was held constant at any desired value by making changes to the manufacturer's standard calibration through a computer interface with the engine's management system. The start temperature was varied by flushing chilled coolant through the engine which was housed in an insulated chamber.

5.2 Facility

5.2.1 Test Engine and Dynamometer

The gasoline spark ignition engine, used for the research, was a modern 1.8 litre four-valve unit, as described in Appendix 2. It was coupled to a Brush DC motoring dynamometer through an in-line, four-speed gearbox and remote, air-actuated clutch. Fourth gear, which provided direct one-to-one drive, was used for the work described here. The standard vehicle exhaust system was used, including the standard three-way catalyst and muffler, but some slight changes to pipework length downstream of the catalyst were necessary to fit the system in the cold chamber.

The dynamometer had fixed speed control capability whilst a throttle actuator allowed fixed throttle position control. There was no provision for fixed torque control. The engine management system was interfaced with a PC fitted with a Ford SPB (special prototyping board). This allowed changes to be made to the standard engine
calibration settings, such as fuelling and ignition timing, as well as monitoring and acquiring data from the engine sensors and interrogating software variables.

5.2.2 Instrumentation

Airflow was measured using a calibrated output from the standard engine hot-wire air mass flow sensor. Fuel flow was measured by a 'Litre Meter', consisting of a pelton wheel, whose instantaneous frequency of rotation was sensed and output as a voltage. The calibration curve for the air mass flow sensor was provided by the engine manufacturer, whilst the fuel flow meter was calibrated by flowing test fuel through the meter, over a range of flows, and weighing the fuel collected over a fixed time period. The specific gravity of the reference fuel, used in the tests reported here, was measured over a range of temperatures to allow fuel flow to be converted to a mass basis. The calibrated output from these sensors was logged on computer, together with the other instrumentation data.

Number one cylinder of the engine was fitted with an uncooled flush-mounted Kistler 6125A piezoelectric pressure transducer. The signal from this, after conditioning by a Kistler Type 5011 charge amplifier, was logged on a PC at one degree crank-angle intervals using a Metrabyte DAS50 data acquisition card. At this resolution the first 1200 consecutive cycles could be recorded which provided pressure data for the complete three minute test at 800 rev/min. An AVL 364 optical encoder provided crank-angle and trigger pulses for the combustion analysis system, whilst a separate magnetic pick-up sensing flywheel teeth provided engine speed information. Engine TDC (top dead centre) position was confirmed from examination of the motored cylinder pressure trace, with adjustment through software, for the thermodynamic loss angle.

Type 'K' mineral insulated thermocouples, of 1 mm diameter, were used to measure various temperatures, which included the following:-

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• Oil: Sump
• Fuel: Supply at fuel meter
    Injector rail
• Air: Intake duct (near OEM standard position)
    Intake manifold (close to No.4 port)
• Coolant: Inlet to engine
    Outlet from engine
    Engine jacket (No.1 cyl)
    Chilled coolant store
• Metal: Engine block surface (No.1 cyl)
• Exhaust: Manifold gas (close to each port)
    Pre and post catalyst gas
    Catalyst bricks

A Transinstruments one bar strain gauge type transducer was used to measure inlet manifold absolute pressure. An IML strain gauged torque shaft and sixty tooth wheel, with magnetic pick-up, were used for torque and dynamometer speed measurement, whilst the flywheel ring gear and a magnetic pick-up, fitted to the gearbox bell-housing, were used to detect engine speed. Air-fuel ratio was measured by an NTK MO-1000 meter and sensor fitted in the exhaust downpipe close to the manifold.

5.2.3 Exhaust Gas Measurement

Raw exhaust gases from the engine were sampled from the catalyst housing just upstream of the front brick. The gases passed through the cold chamber, via a one metre heated line controlled to 190°C, to prevent condensation of heavy molecules, to a five-way solenoid-controlled distribution manifold. From here, a second 5 metre heated line took a sample of the gases to the Horiba MEXA-8420 FID HC analyser via a heated filter, which was also controlled to 190°C. A 5 metre unheated line took another sample of gases from the distribution manifold to a refrigeration and condensate removal unit, before passing to the Horiba MEXA non-dispersive infra-red
CO and CO₂ analysers, the paramagnetic O₂ analyser and the chemiluminescent NOₓ analyser. The analysers, which were calibrated using standard reference gases and a Signal Model 821 gas divider, were zeroed and spanned before each test and then again afterwards to ensure there had been no signal drift. A schematic of the test installation is given in Appendix 3.

5.2.4 Cold Chamber and Chiller Unit

The engine is housed within a cold chamber, constructed of 150 mm thick polystyrene panels covered in galvanised steel sheet. The chamber was designed as compact as possible to reduce the cooling duty requirements and cost, whilst still giving reasonable interior access for engine fitting and maintenance. Triple glazed observation windows were fitted and two doors give front and rear access to the chamber. The dynamometer is outside the chamber, with the engine driveshaft passing through the chamber wall and sealed with brush rubbing strips. A high capacity CO₂ dump system for fire protection within the chamber was installed, as well as a gas detection system to shut the rig down should a flammable vapour develop.

The chiller unit is housed separately, alongside the cold chamber. This unit contains the refrigeration plant which provides a 300 litre store of chilled coolant which can be routed to the engine coolant jacket and/or the air cooling system. This 50/50 ethylene glycol/water reservoir can be chilled down to -29°C overnight, ready for flushing through the engine block and air chiller unit to provide rapid cooling to the desired temperature, as described in more detail in section 5.3.6.

The design and development of the cold chamber took longer than anticipated due to difficulties achieving sufficiently stable low temperatures. The main problem was the considerable heat transfer through the floor, which could not be efficiently insulated due to the chamber having to be designed and built around an existing engine and test-bed. There was insufficient time or resources to remove the engine and pallet but,
with the addition of extra insulation and development of the chilling procedure, the desired minimum temperature of -7°C was achieved. This temperature was required as it is likely to be demanded in future emissions legislation.

A further measure to reduce temperature was the addition of flexible ducting to direct chilled air locally onto the engine. In particular, this was concentrated on the sump to speed the temperature reduction of the oil, which was the slowest fluid to change temperature. The engine sump oil level was reduced to a minimum to assist this process. This slow temperature change has been noted by other researchers\(^\text{90}\), who suggest that the slow temperature change of the lubricating oil may be the limiting factor in the rate at which an engine warms up and combustion stabilises.

5.3 Test Procedures

5.3.1 Introduction

Whilst there is considerable published data on the effects of reduced temperature on emissions from gasoline engines, such as the work of Laurikko\(^\text{38}\), it was evident from the data available that there was a need for more direct comparative emissions data between fuels, from engines operating under conditions where the 'confounding' influence of calibration strategies could be removed. Much of the reported work uses results from engines operating under the manufacturer's standard calibration, which may not have been fully optimised for emissions and might easily be improved upon. It was, therefore, an objective of this work that the emissions would be quantified, during the first few minutes from cranking and starting, with the engine operating with a fixed supply equivalence ratio (SER).

Of the published results reviewed, where it was attempted to make comparisons between fuels with fixed fuelling calibrations, these were invariably with a constant injector pulsewidth which kept the fuel supplied to the engine nominally constant. Whilst this has some merit, it was considered that a better comparison could be made...
if the air-fuel ratio was held constant, particularly as the work was concerned with the start-up process which is highly transient.

With a fixed injector pulsewidth no account is taken of the reduction in volumetric efficiency which occurs as the engine starts and warms-up. This is caused by the charge heating effect and reverse flow of hot burned gases and results in a decreasing air-fuel ratio. As a result of this, and other effects on the air flow, there can be considerable changes in the air-fuel ratio supplied to the engine which can have a significant influence on the emissions produced, thus making it difficult to determine whether changes are due to fuel or calibration effects. The steady-speed tests described in the next section were, therefore, made with a fixed SER.

5.3.2 Constant-Speed Tests

The majority of tests were at a constant speed of 800 rev/min and a load giving approximately 0.45 bar manifold absolute pressure at the start of fuel injection. These conditions were chosen partly as being representative of engine idle conditions, but also to remain within certain operational and equipment constraints. The ignition timing was held constant at 20° BTDC and the sequential fuel injection, which was onto a closed valve, was timed at 88° BTDC during the exhaust stroke.

Clearly these conditions are significantly different to starting an engine in a vehicle when, for example, the manifold pressure would initially be at atmospheric pressure, the cranking speed lower and the engine management system would be varying the amount of fuel delivered during the start-up transient. However, the simulated start-up gives a precisely controlled and repeatable procedure, which maintains the fundamental characteristics of the mixture preparation process in the start-up transient\(^{(01)}\) whilst separating the effects of the management system from effects due to the physical properties of the fuel.

The engine speed was held constant by the dynamometer control system, whilst the manifold absolute pressure was set by making use of the engine idle speed controller,
which is normally used to maintain a calibrated idle speed. This was achieved by making various calibration changes to the engine management system, which effectively allowed the idle speed controller to be used as a throttle, capable of giving a limited range of manifold pressures. This method of load control was developed for a number of reasons. Firstly, the test bed throttle actuator exhibited a high degree of hysteresis and stiction, making it difficult to adjust precisely and repeatably. Secondly, the fine ‘air bleeding’ ability of the throttle by-pass allowed simple adjustment for day-to-day variations in ambient conditions. This method also avoided having to ‘peg’ the throttle actuator in a fixed position or entering the cold chamber to make adjustments.

To perform a test the dynamometer was first started and held at a fixed speed of 800 rev/min. The engine ignition was then activated, but the injectors left inoperative, whilst the clutch was engaged to set the engine rotating. As soon as speeds had stabilised the injectors were enabled and the engine allowed to fire and run. During the three minute operating period the test bed, engine management and combustion data logging systems acquired data for subsequent analysis.

Prior to each test run the engine was conditioned to the desired temperature and the required supply equivalence ratio programmed into the engine management system. The emissions analysers were zeroed and spanned before each test and checked for drift at the end.

5.3.3 Standard Calibration Starts

A limited number of normal starts were carried out, where the engine was cranked and started with its starter motor, using a standard vehicle battery kept outside the cold chamber and fully charged to ensure repeatable cranking performance. For these tests the standard engine strategy and calibration were used. The standard calibration adjusts the ignition, fuelling and other variables, such as engine speed, during
cranking, starting and warming-up, depending upon a number of factors, such as coolant and air temperature and time since start.

5.3.4 General Procedures

Prior to each test the condition of the battery was checked to ensure that it was adequately charged. This was considered important, even for the constant speed tests where battery power was not required for cranking, since, if the voltage level were to drop significantly, it could affect the injector pulse performance, particularly during the early stages of operation. Since it was the start performance which was of particular importance, it was essential that the injectors delivered the required amount of fuel, so that any unexpected changes in air-fuel ratio could not be attributed to the fuel supply system.

As a further precaution against variation in the fuel supplied by the injectors during their first few strokes, the fuel system was primed, to build up any lost pressure in the fuel rail, by activating the fuel pump a number of times before every test. In addition, the engine's adaptive fuelling strategy was reset before each test to ensure this would have no effect on repeatability.

To ensure optimum performance the spark plugs (details in Appendix 2) were changed approximately every 15 and 25 tests when operating on reference fuel and isopentane respectively. The longer change interval when using isopentane was due to the reliable service that the plugs gave when running on this fuel. Even this longer change interval was pessimistic, as the plugs never showed significant deposits when removed. When the engine was run very rich, provided the engine was run fuel-lean after the test, as described in the next section, any plug fouling was soon cleared. When the plugs were used with reference fuel, however, whilst not giving any major problems, they showed visible sooting. It is recognised, however, that mixture settings were generally richer when running on reference fuel and it is possible that a period of operation at a higher load after each test may have prevented this.
5.3.5 Engine Purging

Considerable difficulty was initially experienced in ensuring there was no response from the analysers to residual gases prior to each engine start. Tests showed that the sample line was readily cleared of gases with the standard analyser purge system, so the cause lay in the engine and/or exhaust system. It was interesting to note that the problem was most acute when the engine was operated on reference fuel under fuel-rich conditions. When running on isopentane any residual gases were easily purged from the system if the engine was briefly run after each test at a fuel-lean setting. This indicated that it was the heavier molecules of the reference fuel which were being retained somewhere in the system and clearly required significant heat and oxygen to ensure their successful oxidation and removal.

A review of other researchers' work showed that this was a common problem and required the installation of a compressed air line, to both the inlet and exhaust manifolds, to enable purging with air at all times when not testing. It was still necessary to ensure that after each run the engine was operated at a fuel-lean setting and then motored with the purge air circulating until residuals were reduced to a low level.

5.3.6 Engine Temperature Conditioning

For tests at sub-zero temperatures, the chiller unit was left in the 'chilled store' mode overnight to reduce the coolant reservoir to its minimum temperature of -29°C. The following morning the appropriate fuel tank would be installed and pre-test checks carried out. The chamber would then be closed and the engine cooled with mains water, to achieve the lowest possible block temperature, before flushing with chilled coolant. This coolant was also circulated through the air chiller unit to lower the air temperature.

An example of this process is given in Figure 6, where data was logged after the block temperature had been reduced, from 25°C to 20°C, with mains water. The rapid
drop in jacket temperature, and resulting rise in chilled coolant temperature, can be seen after 125 seconds. The block temperature fell at a slower rate, to a minimum of -12°C, before rising again at a similar rate to the jacket temperature. The other fluid temperatures followed this trend, but at slower rates, before converging towards the end of the test.

The rate at which the oil temperature reduced, being the slowest to change, was subsequently improved so that all temperatures were generally within 4°C by the end of conditioning. The chilled store temperature was only reduced to -26°C for the results described here. When this was taken to its lowest temperature of -29°C it was possible to achieve a test temperature of -9°C +/- 2°C for some tests. Less severe test temperatures were generally achieved by reducing the time that the chilled coolant was flushed through the engine and then waiting until temperatures converged and stabilised. To achieve higher temperatures the chamber was heated, by running the engine, to a temperature above that required and then leaving it to soak down to the required test temperature. By varying the chilled coolant flush time, engine running, air-cooling and soak time, it was possible to achieve a range of temperatures.

When the engine and fluids were at the desired temperature, the chiller unit was put in the 'engine run' mode which connected the engine's cooling circuit to an external Bowman heat exchanger. The engine was then ready to be started, during which time the air chiller unit would remain operational, thus reducing the rate at which the engine and fluids warmed up. During the majority of tests the engine's thermostat remained closed, which meant there was no flow through the Bowman heat exchanger.

The temperature development of the engine and fluids, during a cold-start using isopentane, is shown in Figure 7. The engine jacket and block were at -11.5°C when the engine was started, whereas the other fluid temperatures were slightly higher. After approximately 5 seconds the engine was motored, when it will be seen that the fuel temperature, measured in the rail, increased by a few degrees. The injectors were not operating at this stage, so this was presumably due to the fuel pump charging the
fuel rail with fuel from the filter housing, which was at a higher temperature. This was despite the precaution of priming the fuel circuit prior to the test. After this initial rise the fuel temperature remained fairly constant for the remainder of the test, only rising by a further one or two degrees.

The port air temperature also increased, but to a lesser extent than the fuel, as soon as motoring started, as warmer air from the surroundings was induced. Once the engine was firing the air temperature only increased by about 4°C during the remainder of the test. The sump oil temperature, which initially continued to fall in the early stages of the test, due to its high thermal capacity, only changed by about 2°C throughout the test. The largest temperature change, as expected, occurred with the jacket and block temperatures. The block temperature, after an initial slow response to the start of combustion, increased at a slightly slower rate than the jacket temperature, which increased by a steady 10°C per minute after an initial small peak in temperature when the engine first fired.

5.3.7 Fuel Handling

Separate portable 11.4 litre fuel tanks were used for the reference and isopentane fuels. For safety reasons these were generally kept outside the building in a purpose-built fuel store and only installed in the cold chamber when required. They were topped up from single 200 litre barrels of each fuel, which were the sole supply sources for the duration of the work.

Precautions were taken with the reference fuel to ensure that all containers were kept sealed when not transferring fuel. When the fuel tank was installed in the chamber it was only vented to atmosphere just prior to the test. These precautions were taken to ensure that as little as possible of the fuel light-ends were lost, thus ensuring consistent engine start performance.

The isopentane storage barrel was designed for high pressure, whereas the fuel tanks were not. Due to the low boiling point of this fuel, therefore, it was necessary to leave
the tank vented to atmosphere at all times, to avoid any risk of rupturing the tank. Since the fuel was a pure compound any loss from the tank would have no effect on engine start performance.

Each series of tests was designed to minimise the number of times fuels had to be changed, but when it became necessary, considerable purging with the new fuel was carried out at medium engine speed and load. However, as described elsewhere, it was noted on occasion that this purging procedure may not have been entirely satisfactory, as it appeared that some residual fuel was 'hanging-up' and affecting the engine's start performance. It was generally possible to detect when a problem existed and additional purging could be carried out. At least one reference found in the literature described using nitrogen to ensure total purging of the fuel system, so this may not be an unexpected difficulty, but it was too late to apply the procedure to this work.

5.4 Data Reduction and Analysis

5.4.1 Exhaust Emissions Time-Alignment

The emissions concentration data were time-aligned before analysis. This was necessary to take account of the delay between the sample gas appearing at the exhaust port and arriving at the analyser. This delay is due to the transition time of the gas in the exhaust and sample line, which depends on the volume of the system and the flow rate from the engine. Having arrived at the analyser there is a further delay due to the instrument's response time.

A number of methods were investigated to measure these delays, which included introducing calibration gases into the system, at various points, and noting the response times to both rising and falling gas levels. The method selected, however, was that of causing an emission event from the engine, over one or two cycles, by interrupting the spark to two cylinders simultaneously and monitoring the time taken for each analyser to respond. The equivalence ratio was set to give easily detectable changes in the relevant gas levels. This procedure was carried out at the same speed
and load as used for testing, thus creating a similar exhaust flow. This was done a number of times, at different equivalence ratios and an average response time determined for each analyser.

5.4.2 Exhaust Mass Emissions

Although concentrations of raw gas emissions were measured, it was the mass emitted which was of most significance. In order to minimise the task of converting from a volume to a mass basis, for which exhaust mass flow rate was required, it was considered adequate to use a relative scale of mass as it was a comparison between fuels that was required.

As the engine speed and throttle were fixed, with the air inlet temperature and air-fuel ratio supplied to the engine nominally constant, then the exhaust flow rate was also constant. Therefore, a measure of the mass of each gas component produced was determined by integrating the concentrations produced in each test for a period of 60s from fuel-on. To allow the mass of HC produced to be compared between fuels the isopentane integrated values were corrected to allow for the fuel’s different molecular weight. It should be remembered that these are only relative mass units for each gas and, therefore, different gases cannot be compared. For example, the mass of HC (measured in HC mass units) cannot be compared with the value for the mass of CO (measured in CO mass units).

5.4.3 The Start of Combustion

The net imep for the first 1200 consecutive engine cycles, which covered the complete three minute test, was calculated from the raw pressure data. The cycle-by-cycle imep was used to determine when combustion commenced. However, it was often difficult to establish this, particularly when using reference fuel. Even when first-firing could be detected, the pressures produced contributed little useful work. It was, therefore,
decided that a more precise indicator of successful combustion initiation would be the first cycle to produce a positive imep.

The fuel-on cycle number was subtracted from the number of this first positive imep cycle to give the number of cycles in which no substantial combustion occurred. This not only gave a measure of the speed with which the fuel formed a combustible mixture, but also quantified the fuel passing through the engine unburned and causing high HC emissions.

The determination of the fuel-on cycle was made by inspection of the pressure data. This decreased when fuelling commenced, due to latent heat effects and changes in the charge specific heat ratio.

5.4.4 Pressure Development

The combustion characteristics of the two fuels were compared by analysing the cumulative pressure rise due to combustion, instead of the more normal mass fraction burned, as explained in detail in section 6.9.1. This pressure rise, due to combustion, was calculated by subtracting the pressure rise due to piston motion from the total pressure rise. A full derivation of this is given in Appendix 4.

5.4.5 COV of IMEP

Any measure to reduce emissions must not degrade the quality or stability of the combustion to an extent which might adversely affect such factors as starting reliability and speed, idle stability and refinement, or cause hesitation and stalling or other driveability malfunctions. A measure of the combustion stability is often given by the coefficient of variation in imep\(^{(14)}\), which is the standard deviation in imep divided by the mean imep and expressed as a percentage:

\[
COV_{\text{imep}} = \left( \frac{\sigma_{\text{imep}}}{\text{imep}} \right) \times 100
\]
This parameter defines the cyclic variability in indicated work per cycle and it is often considered that the limit for good driveability is 10 percent. This limit and the use of the COV$_{\text{imep}}$ are generally applied to steady-state testing and not to highly transient processes, such as starting. It was believed, however, that it would indicate differences in the quality of the combustion between the two fuels during different phases of the start and warm-up process. The phases to be assessed were described as 'start-up', 'early running', 'warming-up' and 'steady-state', with each phase consisting of a different group of consecutive cycles from the 1200 logged for the complete test.

When a low value of the first positive imep cycle occurred it often had an excessive influence on the magnitude of the COV$_{\text{imep}}$ at start-up and was, therefore, disregarded in this analysis. In addition, the point in the engine cycle at which fuelling commenced was not closely controlled, so it was possible that the first-fired cycle may not have received a full charge of fuel and was, therefore, unrepresentative. The COV$_{\text{imep}}$ calculations, therefore, started with the second positive imep cycle.

The COV$_{25}$ and COV$_{50}$ defined the COV$_{\text{imep}}$ of the first 25 and 50 cycles, from the second positive imep cycle respectively, and characterised the start-up and early running phases. The COV$_{200}$ analysed cycles 50 to 250 and represented the warming-up phase, whilst the COV$_{\text{ss}}$ represented the steady-state period and used the last 200 of the 1200 cycles recorded.

### 5.4.6 Calculation of Air-Fuel Ratio

In addition to measuring the air-fuel ratio with the NTK sensor, it was also calculated by exhaust gas analysis. This was done to confirm the accuracy of the NTK meter and the emissions analysers. The exhaust analysis was made using the well known Spindt method$^{(92,93,94)}$ which uses an oxygen balance for the estimation of the mass of air in the charge. Since the oxygen was measured using a paramagnetic analyser, which inherently has a slow response, this method can give errors when used in transient
testing. Consequently, during the highly transient in-cylinder air-fuel ratio development phase just after starting, there were differences in the absolute values measured by the NTK sensor and calculated by the Spindt method. Also, if analyser saturation occurred, the absolute level of the HC emissions could not be determined, giving a further source of error. However, as the test proceeded the agreement between the two methods typically improved to better than one percent, giving reasonable confidence that the analysers were functioning correctly. An example of the correlation between the two methods, during a typical start and warm-up, is shown in Figure 8 for a test on reference fuel. In this instance there was no analyser saturation and the ratio calculated by the Spindt method was higher than for the NTK, particularly during the early stages of the test. The average level of the supply equivalence ratio, described in the next section, is also shown.

5.4.7 Equivalence Ratio

The stoichiometric air-fuel ratios for the reference and isopentane fuels are 14.15 and 15.33 respectively. To allow for this difference all data has been compared, where appropriate, on a fuel-air equivalence ratio basis ($\phi$). This is the actual fuel-air ratio divided by the stoichiometric fuel-air ratio:

$$\phi = \frac{(f/a)_{\text{actual}}}{(f/a)_{\text{stoich}}}$$

The equivalence ratio based on the measured fuel and air masses delivered to the engine intake port will be described as the supply equivalence ratio (SER) to distinguish it from the in-cylinder gas phase fuel-air ratio or the fuel-air ratio measured by the NTK sensor in the exhaust, which may be considerably different at any instant in time, as seen in Figure 8.

The difference in the ratio measured by the NTK sensor and the SER was of significant interest in this work. The determination of the SER, by measuring the supplied fuel and air masses, proved unsuccessful due to problems with the fuel flow
meter. This gave poor repeatability and an output which appeared affected by the fuel pump priming and feeding the fuel rail, which did not necessarily correspond to fuel being supplied to the engine.

As described in section 5.2.1, the engine management system was interfaced with a PC that allowed data to be acquired from engine sensors as well as calibration changes. In this way it was possible to monitor the output from the hot-wire air flow meter and also determine the scheduled fuel injected per cycle. This data was converted to flow rate units, for the fixed speed condition of 800 rev/min, from which the air-fuel ratio was calculated.

A check on the accuracy of the derived ratio was made by comparing this with measurements from both the NTK sensor and from exhaust gas analysis. These measurements were made under warmed-up steady-state conditions and, therefore, should be the same as the supplied ratio. Differences, however, were apparent which may have been due to a number of reasons. It is unknown to what accuracy the manufacturers calibrate the injectors or airflow meter or whether fuel temperature has any significant effect. The injectors will certainly not have been calibrated for use with isopentane, which could explain some of the discrepancy when operating on this fuel. Obviously any malfunction of the injectors or other hardware would also cause errors.

Ideally, the individual injectors should have been calibrated off the engine, with both fuels, over a range of temperatures. Time did not allow for this and, as absolute accuracy was not considered essential, a calibration was performed by making further measurements, over a wide range of air-fuel ratios, under warmed-up steady-state conditions. An average ratio, from the NTK sensor and exhaust gas analysis, was compared with the value derived from the management system data. In this way linear correlations were produced for the two fuels, as shown in Figures 9 and 10. All ratios subsequently calculated from the management system data were corrected according to these linear relationships. No account was taken of any combustion inefficiency or change in fuel temperature.
5.5 Closure

Up to this point the background to the cold-start emissions problem, together with the potential solutions, have been described. It has been explained that the objective of this thesis was to further the understanding of the combustion and emissions formation process during starting and to investigate the potential of using a highly volatile fuel for reducing emissions during this period of operation. This section described the experimental facility, test procedures and how the resulting data was analysed. It now remains for the following sections to present and discuss the most significant results, before concluding and suggesting what further work might be done to confirm the benefits of this technology and develop it into a viable solution.
6. Test Results

6.1 Introduction

All results presented in Figures 7 to 78 inclusive are from tests at a constant speed of 800 rev/min and 0.45 bar manifold absolute pressure, whilst those in Figures 79 to 85 are from standard calibration starts, as described in section 5.3.3.

From the considerable amount of data obtained, those presented in Figures 11 to 14 illustrate the significant potential advantage of cold-starting the engine on a highly volatile fuel such as Isopentane. Although there are differences in the start temperatures and supply equivalence ratios (SERs) for the two fuels, the response characteristics are fairly typical for the wide range of SERs and start temperatures investigated.

From the development of HC and CO concentrations, shown in Figure 11, a number of significant differences in the performance of the two fuels can be seen. With reference fuel there is a rapid rise in HC (shown as REF HC) beyond 7000 ppm, which saturates the analyser. This continues for a number of seconds before it reduces rapidly to about 3000 ppm and then immediately rises again to a second smaller peak, after which it gradually reduces to 2500 ppm as the test proceeds. The CO (shown as REF CO) remains close to zero for the period of time that the HC is at its highest peak and only starts to rise significantly when the HC starts rising towards its second peak. The CO levels then continue to rise, at a reduced rate to a maximum of 8.5 percent, whilst the HC levels fall. The CO and HC levels have not stabilised by the end of the three minute test.

In contrast, when the engine is started on isopentane, the HC level (shown as ISO HC), whilst still showing two low peaks of 1600 and 1400 ppm, always remains significantly lower than for reference fuel and reaches a stable value of 950 ppm before the end of the test. The CO (shown as ISO CO) exhibits little delay in rising rapidly to its steady-state level of less than one percent.
Figure 12 shows the very different development characteristics of the NO\textsubscript{x} concentrations for the two fuels under these operating conditions. The reference fuel result shows that relatively little NO\textsubscript{x} is produced whilst the HC levels are at their saturation value. Once the HC starts to fall so the NO\textsubscript{x} rapidly rises to a peak of 1000 ppm, corresponding to the HC reaching its first minimum. The NO\textsubscript{x} level then rapidly falls, whilst the HC rises to its second peak and then reduces, at a lower rate, to a relatively stable value of 80 ppm as the HC continues to decrease. The isopentane result shows a much earlier and significantly lower peak of 620 ppm, which initially reduces to a minimum of 350 ppm before increasing for the remainder of the test to significantly higher values than for reference fuel. The lean supply ratio for isopentane is probably the cause of the considerable instability in the NO\textsubscript{x} output compared to the reference fuel result, which was for a significantly richer supply ratio.

For completeness, the CO\textsubscript{2} concentration is shown in Figure 13. Again the reference fuel emissions show a delay in development before rising, at first rapidly and then more gradually, to a peak at about 20 seconds. The level then reduces and does not show signs of stability until near the end of the test. The isopentane CO\textsubscript{2} emissions, by contrast, exhibit rapid attainment of a stable but higher value.

The bar chart in Figure 14 shows these fuel characteristics in terms of the mass emissions produced by the engine in the first 60 seconds of the test from the start of fuelling. The HC mass was reduced by more than 66 percent when using isopentane (the absolute value cannot be determined due to the brief saturation of the analyser when using reference fuel) and the CO mass by 81 percent. The NO\textsubscript{x} mass emissions, however, increased by 55 percent.

The following sections present results from tests, under varied conditions, intended to assist in furthering an understanding of the mechanisms involved in the emissions produced by the engine when starting on these two fuels, and to quantify the benefits of starting the engine on a highly volatile single component fuel in place of conventional gasoline.
6.2 Effect of Air-Fuel Ratio on Emissions

It is known that air-fuel ratio has a significant effect on engine-out emissions. In order to confirm the expected trends on emissions when the air-fuel ratio is varied and to make comparisons between the behaviour of the two fuels, tests were carried out at the same speed, load and spark timing as used for the start tests but with measurements made under steady-state conditions. The engine was fully warmed-up for the reference fuel tests but held at a steady and lower temperature for the tests on isopentane. This was necessary to prevent vapour-lock and fuel starvation which can occur with this fuel at normal running temperatures.

The results from these tests are presented in Figure 15 for isopentane and Figure 16 for reference fuel. Also included in these plots of emissions concentrations is the COVimem to indicate the quality of combustion for a given equivalence ratio.

The resulting trends were as expected for both fuels, with a peak in CO₂ of 14 percent for reference fuel and 13 percent for isopentane occurring at the stoichiometric ratio. NOₓ peaked on the lean side of this ratio, where combustion temperatures are highest. The considerable difference in peak NOₓ concentration of 2600 ppm for reference fuel and 1900 ppm for isopentane is most likely due to the differences in operating temperature for the two tests, since NOₓ levels are strongly dependant upon combustion temperature as well as equivalence ratio. The CO follows the same trend for both fuels, reducing rapidly to low levels as the equivalence ratio decreases towards the stoichiometric value.

The HC levels were similar, but slightly lower, for the isopentane fuel over most of the equivalence ratio range tested, reaching a minimum for both fuels at a ratio of 0.9. The lower levels cannot be explained by the lower temperature during the isopentane test as this would have tended to increase these emissions. It is believed that these lower levels are due to differences in reaction kinetics between the two fuels and other effects, such as the lower solubility of isopentane in lubricating oil which reduces the effect of the adsorption/desorption process known to contribute to HC emissions.
From the HC and COV\textsubscript{imp} characteristic it is clear that both fuels were tending towards the lean limit of operation at an equivalence ratio of around 0.8. The upturn in HC and COV\textsubscript{imp} noted during these and other tests was found in general to be more rapid with reference fuel. On the other hand, at the rich limit, which was not reached in this instance for the reference fuel, the isopentane exhibited a sharp increase in HC emissions and rapid deterioration of combustion quality, whereas reference fuel tended to be more tolerant to these levels of excess fuel.

6.3 Reference Fuel - Temperature Effects

6.3.1 CO Emissions (reference fuel)

The engine was started on reference fuel at temperatures varying from -7°C to +49°C. The resulting CO emissions for the first 60s from fuel-on at each temperature are shown in Figure 17. Despite the fixed SER of 1.44, the significant differences in engine-out emissions indicate that conditions within the engine cylinder are considerably different. Since CO is highly dependant upon air-fuel ratio, it is apparent from the comparatively low initial CO at low temperature that the engine is operating on a fuel-air mixture which is considerably weaker than at the higher temperatures. This temperature effect results in mass emissions which are 2.6 times greater at 49°C, the highest temperature tested, compared to those at -7°C.

As the temperature was lowered, the time taken for the engine to fire increased, which explains the delay in CO formation, since this will only be formed when combustion occurs. Clearly the mass emissions difference would have been lower, but still substantial, had measurement been compared over a time period from first-firing instead of from fuel-on. The period from fuel-on was chosen, however, due to the significance of this period on HC emissions, which is described later, and also because future legislative testing is likely to include this event. As can be seen in Figure 17, this delay in CO formation results in considerable differences in the concentration levels after 60s. These differences reduce to less than 5 percent by the
end of the 3 minute test when temperatures are more closely matched but still increasing.

These results support the assumption that, as the temperature is raised, the rate of fuel vaporisation increases and port and wall wetting decreases, resulting in faster development of an ignitable mixture at the spark plug. However, even when the start of combustion was rapid, at the higher temperatures tested, there were still marked differences in the rate of CO production, indicating that either the fuel was still not being fully vaporised and burnt, or it was being lost elsewhere, such as in the blow-by gases. Inaccuracies in the fuel metering system may also have accounted for some of the differences\(^{(95)}\).

6.3.2 HC Emissions (reference fuel)

The corresponding HC emissions concentrations are shown in Figure 18. As with the CO, there are significant differences in the emissions produced, depending on the temperature at the start, despite the same nominal supply equivalence ratio. At -7°C, the lowest temperature tested in this series of experiments, the emissions were highest over the first 60s due to the significant period of time it took for the engine to start. This resulted in fuel being passed through the engine unburned, thus saturating the analyser until combustion occurred. This is similar to the findings of other research which included results from operation on propane. Even with this gaseous fuel, measurements with fast response instrumentation revealed a brief peak in the HC emissions\(^{(96)}\).

As the start temperature increased the engine fired earlier, but it was not until 18°C that analyser saturation was avoided. However, even at this relatively high temperature, an initial peak in the emissions still occurred, indicating that the engine start was still not rapid enough. It was not until temperatures over 40°C were reached that this initial peak was no longer evident. This showed that considerable heat energy was required, at this SER, to ensure that the reference fuel was sufficiently
vaporised to obtain rapid firing and control of HC emissions to their minimum steady-state value. Only the tests above 30°C reached their steady-state value before the end of the 60s period. On a mass basis the emissions at 49°C, the highest temperature tested, were reduced by significantly more than 60 percent of the mass at -7°C, although because of analyser saturation the exact value is indeterminate, as explained earlier.

The high initial peak in unburned HCs is similar to that reported by Edward et al\textsuperscript{(97)}, who carried out similar emissions measurements during cold starts at temperatures between 5 and 10°C. They concluded that the number of unfired cycles, when fuel is being injected into the engine, could have a substantial effect on the HC emissions during the first minute of running.

6.3.3 NO\textsubscript{x} Emissions (reference fuel)

Figure 19 shows the corresponding NO\textsubscript{x} concentrations which also exhibit considerable variation with start temperature. The delay in rise in concentrations for the low temperature tests are again attributable to the delay in the start of combustion.

For a fixed equivalence ratio NO\textsubscript{x} generally increases with combustion temperature. The rapid rise and fall in values recorded during the start tests suggest there is another more dominant effect. Referring back to the results presented in section 6.2, it can be seen in Figure 16 that, for a fixed temperature, NO\textsubscript{x} is also highly dependant upon equivalence ratio. The concentration rises to a peak just lean of the stoichiometric ratio before falling to low levels as the mixture becomes richer. It is believed that it is this mechanism, of in-cylinder equivalence ratio varying over a range from weak to rich, despite a constant supply ratio, which is dominating the start process.

Figure 20 shows how the NO\textsubscript{x} mass emissions decrease with increasing temperature, implying that the average equivalence ratio being burned in the cylinder is becoming richer with increasing start temperature due to improved mixture vaporisation. The
mass emissions, for the first 60 seconds from fuel-on, reduced by 65 percent when the start temperature was increased from -7°C to +49°C. It is uncertain whether the high reading at 18°C is a genuine effect or due to measurement error. NO\textsubscript{x} is very sensitive to changes in equivalence ratio and therefore liable to considerable variability as temperature and spatial variations of in-cylinder mixture strength occur during the start process.

NO\textsubscript{x} is also sensitive to humidity and no correction was made for this, partly because no suitable measurement system was available that could withstand the extreme conditions in the cold chamber, and also because when this work started NO\textsubscript{x} was not of significant interest. This was because most reported work indicated that as temperature reduced the mass emissions of NO\textsubscript{x} would also reduce. However, these results were generally over longer periods of operation than reported here, or during tests where emission measurements were not made from the time of fuel-on, but at some later point when the engine had already started warming up. Clearly if the very early stages of emissions formation are being investigated, as in this work, then it is the equivalence ratio change which has the dominant effect on the NO\textsubscript{x} formation and not the combustion temperature.

6.3.4 In-Cylinder Air-Fuel Ratio (reference fuel)

Evidence of slow development of in-cylinder air-fuel ratio, for the fixed supply equivalence ratio of 1.44, is shown in Figure 21 where measurements from the NTK sensor, during the first 60s of the test, are shown for each start temperature. It is not possible to determine the ratio for the first firing cycles due to delays in the gas reaching the sensor and in the response of the sensor itself. It should also be remembered that the exhaust gas from all four cylinders is being measured, so no differentiation between cylinders is possible. It is clear, however, that the initial burning is at considerably weaker ratios than the supply ratio.
Similar differences between the exhaust based equivalence ratio and the supplied ratio were noted by Quader et al during tests on a single cylinder engine with port fuel injection at -7°C (8). This was most significant when using a high T90 fuel, which indicated that not all the supplied fuel was being burned in the combustion chamber under these low temperature conditions. They speculated that vaporisation was incomplete and that liquid fuel was being trapped in the piston top land crevice and probably getting past the piston with the blow-by gases. This possible route for the fuel has already been mentioned in section 6.3.1, where the CO development was described. In this current work no attempt was made to account for this 'lost' fuel and no analysis of the sump oil was made. However, it did not appear to be heavily contaminated with fuel, as would be expected, when considering that at -7°C there was a considerable difference between the in-cylinder and the supply ratios, which lasted for more than 30 seconds. Clearly some of the fuel in the oil would vaporise and be fed back to the intake of the engine, but there is some doubt that this is the complete explanation.

Figure 22 shows how the time to reach 90 percent of the SER varies with starting temperature. The start process is a highly variable process and inevitably there is considerable scatter in the data points, however the trends of increasing time for air-fuel ratio development, with decreasing temperature, can be clearly seen. For an SER of 1.4 it takes approximately six times longer to reach this 90 percent point at -5°C than it does at 50°C.

As expected, if the curve for the SER of 1.4 is ignored, there is also evidence of reducing time with increasing SER. This is due to a greater quantity of fuel light ends being supplied with each injection stroke and it is this light fraction which is so vital for providing a flammable mixture for early combustion. Why the 1.4 SER data goes against this trend is unclear. It is possible that the rich limit is being approached which, whilst giving faster starting, could be producing poorer overall combustion quality which would begin to suppress the rate at which the temperature rose within the cylinder and hence reduce the vaporisation rate of the denser fuel molecules.
6.3.5 IMEP Development (reference fuel)

The imep development clearly indicates the delay in the start of combustion as shown in Figure 23 for the 1.44 SER series of tests. It also shows how the imep development is retarded by the colder temperatures which correspond to the slow development of in-cylinder mixture ratio.

As described in section 5.4.3, much of the analysis has been based on the first cycle to produce a positive imep. It can be seen, from the small fluctuations in imep below zero, that there is some burning, at the coldest temperatures tested, over a number of cycles prior to this. However, once a positive imep has been achieved, there is no evidence of misfire (as defined by the imep dropping below zero) except in the 5°C test, where one cycle did misfire. Generally though, once significant positive imep had been established, there was a period of combustion instability and partial burns which decreased as time, temperature and the in-cylinder equivalence ratio increased. For the tests at temperatures above 30°C the imep development was rapid and achieved stability within approximately 20 cycles.

The corresponding torque development for the test at -7°C is shown in Figure 24. When the clutch was engaged at approximately 6 seconds the engine speed increased to match that of the dynamometer. The motoring torque then steadily decreased, from approximately -70 Nm, as the friction reduced, with a slight disturbance at approximately 10 seconds as fuelling commenced. At approximately 21 seconds measurable combustion occurred with a small sharp increase in torque and a number of partial burns. This corresponds with the early fluctuation in imep seen in the -7°C trace of Figure 23 between cycles 70 and 80. After a few cycles combustion was more sustained and the torque increased rapidly to almost positive values. This corresponds to the high rise in the imep just after the 80th engine cycle. The torque continued to rise at a steady rate, for approximately 15 seconds, as the in-cylinder fuel-air ratio increased. The rate of increase then settled to a lower value as the reduction in friction with rising temperature became the dominant effect.
At both the point of initial combustion, and during the second change in rise rate of the torque, there was a period of significant engine instability. The first period was clearly due to instability as combustion developed. The second period, however, may have been exaggerated by the control response characteristics of the dynamometer, as indicated by the fairly uniform decay rate in the speed signal from 35 to 45 seconds.

6.3.6 Effect of Engine Cooling (reference fuel)

In order to investigate the effect of engine cooling on the starting performance with reference fuel, two cooling strategies were used which gave different warm-up rates. The results from these tests will be described as fast and slow-warm. The fast-warm strategy, which was the normal strategy for most tests, gave a rise in cooling jacket temperature of approximately 10°C/min, whereas the slow-warm strategy reduced the jacket temperature rapidly to -9°C once firing had commenced and then held it virtually constant for the duration of the test. Both tests started from an ambient temperature of 12°C and with an SER of 1.16.

The HC and CO concentrations, from fuel-on, over the complete tests are shown in Figure 25, where considerable differences in the emissions generation can be seen. Both exhibit the characteristic of delayed firing with fuel passing through the engine unburnt and briefly causing the analyser to saturate. The rapid fall in HC is delayed by the slow-warm strategy, after which there is a slow increase in level. This increase is likely to be due to increased flame quenching and other effects, due to a decrease in cylinder wall temperature, caused by the jacket temperature reduction from 12°C at the start to -9°C. Although the jacket temperature was rapidly reduced to -9°C and held virtually constant for the test, the cylinder wall temperature would have continued to fall during the test. The HC from the fast-warm strategy, however, continued to fall throughout the test after the initial small second peak which occurred at about 40 seconds. This significant result emphasises the need for rapid engine warming if engine-out HC emissions are to be reduced to their lowest possible levels.
The CO levels remain close to zero whilst combustion is delayed then display the expected characteristic of slowly rising towards their stable values. The difference between the two strategies is substantial. The slow-warm strategy causes the CO to continue to rise at virtually the same slow rate for the complete test. Even by the end of the test it has not reached the level achieved by the fast-warm strategy which is virtually stable. The absence of an initially higher rise rate in the CO level, as exhibited by the fast-warm strategy, corresponds to the slow-warm strategy's absence of a second peak in the HC emissions, which was exhibited by the fast-warm strategy at 40 seconds.

Figure 26 shows the NO\textsubscript{x} concentrations during the slow and fast-warm tests. Both traces show a delay in output followed by a rapid rise as combustion proceeds with the slow-warm strategy lagging and not reaching as high a peak as the fast-warm strategy. The fast-warm strategy then shows a rapid reduction in levels as the in-cylinder equivalence ratio becomes richer. This is followed by a slow increase in levels as the combustion temperature begins to dominate the process. In contrast, the slow-warm strategy shows a continuing, gentle decrease from the peak level for the duration of the test. This is caused by the dominating influence of the slow in-cylinder air-fuel ratio development, which is gradually becoming richer and suppressing the formation of NO\textsubscript{x}.

The imep development from fuel-on is shown in Figure 27, where it can be seen that the fast-warm strategy gives a fairly rapid development after firing commences. The slow-warm strategy, however, exhibits considerable misfiring and partial burning during its imep development. Stable values in the imep are not achieved until approximately half-way through the test.

The air-fuel ratio, as measured by the NTK sensor, is shown in Figure 28 and shows a continuous reduction throughout the test, for both strategies, as the in-cylinder ratio develops towards the supply equivalence ratio. The slow-warm strategy causes a noticeably slower development, which corresponds to the slow development in CO concentration. Although the two levels are still converging at the end of the test, there
is still a considerable difference between the two levels with the slow-warm strategy remaining at a weaker level.

The results from the cooling tests have been summarised in the bar charts of Figure 29. The top chart shows the COV_{imep} for the various stages of the tests, where the significant effect of overcooling the engine on combustion stability during starting and warm-up is very evident. The COV_{25}, which was already poor at 47 percent, was over 4 times worse in the slow-warm test. By the end of the test, although significantly improved, there was still a difference in COV_{ss} of 69 percent.

The effect of the different strategies on mass emissions is shown in the middle bar chart. The slow-warm strategy produces the highest HC mass emissions. The absolute value of the increase cannot be determined, due to analyser saturation in the early stages of the tests. The CO mass is reduced by 64 percent by the slow-warm strategy, due to the longer period of operation at weak equivalence ratios, whilst the NO_x is increased by 22 percent.

The final bar chart shows how the slow-warm strategy required 9 more injections of fuel before a positive imep was produced and then misfired 15 times, compared to only once for the fast-warm strategy. The slow development of the in-cylinder equivalence ratio is shown by the time taken to reach 90 percent of the SER, which was nearly 3 times as long as for the fast-warm strategy. The firing spread time, (described in section 6.9.2), which was nearly double that of the fast-warm strategy, indicates that the mixture preparation and distribution to the cylinders was inferior.

6.4 Isopentane - Temperature Effects

6.4.1 CO Emissions (isopentane)

For this series of tests the engine was started on isopentane at an SER of 1.07 at temperatures ranging from -10°C to +26°C. The resulting CO emissions for the first 60s from fuel-on at each temperature are shown in Figure 30. Care should be taken
when comparing these results with those of reference fuel (SER = 1.44) due to the considerable difference in equivalence ratios. However, they are typical of the differences encountered during much of the testing, which was for a wide range of equivalence ratios and temperatures. These will be reported in later sections.

The first significant difference to note is that there was no noticeable delay in the start of combustion even at the lowest temperature tested. The CO levels rose immediately from the start of fuel-on. Even at -10°C the CO developed immediately and was comparable to the characteristic shown by the reference fuel at the much higher temperature of 49°C.

The sub-zero tests showed an unexplained further rise in CO at temperatures below about -5°C. This can be seen in the trace for the -10°C test where the CO increases after about 15s, having apparently stabilised prior to this. The CO then shows significant variability before reducing back to stable levels after about 60s and then remaining constant to the end of the test. Generally the CO levels achieved stable levels within about 10s of starting.

The tests at 18°C and 26°C were made at the same equivalence ratios, so it must be concluded that the somewhat lower levels of CO recorded were caused by either inaccurate mass air measurement by the hot-wire airflow meter or from inaccuracies in the injector pulsewidth, which may not have matched that demanded by the control system.

In contrast to starting on reference fuel, where CO mass emissions increased by a factor of 2.5 when going from the lowest to the highest test temperature, isopentane fuelling resulted in the opposite effect of approximately halving the mass emissions. If the possible inaccuracies described above had not occurred, it is believed that the mass emissions would not have changed significantly with change in temperature.
6.4.2 HC Emissions (isopentane)

The corresponding HC emissions concentrations are shown in Figure 31. In contrast to reference fuel, any initial peak exhibited, was only of a low value, and at all the usable equivalence ratios investigated, never approached analyser saturation levels. Apart from the -10°C test, where HC emissions rose to a second peak in a similar manner to the CO described above, the levels generally stabilised fairly rapidly, giving further evidence that the equivalence ratio within the cylinders was also rapidly becoming stable. Although comparing results at different supply equivalence ratios, it should be noted that the HC emission levels from all the isopentane tests are of the same relatively low order as the stable values reached by the highest temperature reference fuel results.

In order to attempt an explanation for the appearance of an HC peak in some of the isopentane tests, the combustion data from these runs was analysed in detail. This will be described in Section 6.4.5.

6.4.3 NO\textsubscript{x} Emissions (isopentane)

The NO\textsubscript{x} emissions concentrations from the isopentane tests are presented in Figure 32, where it will be apparent that, unlike for reference fuel, any peak in concentrations is brief and, with the exception of the -10°C test, rapidly settles to a nominally stable value. There was a tendency, however, for the levels to rise slightly beyond the 60s point up to the end of the three minute test.

These results support the theory that the in-cylinder equivalence ratio rapidly increases to that of the SER and that any tendency for the NO\textsubscript{x} concentration to rise beyond this point is due to an increase in the combustion temperature and not to any significant change in the in-cylinder air-fuel ratio.
6.4.4 In-Cylinder Air-Fuel Ratio (isopentane)

Whilst reference fuel showed a strong dependence on temperature and SER for the time it took the measured exhaust gas to indicate that 90 percent of the SER had been reached (Figure 22), the same is not the case for isopentane, as Figure 33 demonstrates. Here, the time taken to reach 90 percent of the SER has been plotted against temperature for all temperatures and supply equivalence ratios tested (SER = 0.72 to 1.59). As can be seen, apart from the numbered outlyers, all times were generally within 2.5 seconds, regardless of temperature or SER.

The numbered outlyers are from a consecutive series of tests on isopentane, made after tests had been completed on reference fuel. Whilst significant purging was carried out before measurements were made, it seems that some residual fuel may have remained. With each successive cold start the time to reach 90 percent of the SER continued to reduce. This indicated that purging of some heavier fractions, which may have been trapped at some point in the fuel system, was continuing even after some considerable time. This is an area for further investigation as the reverse was also found to be the case, but to a lesser extent, when changing from isopentane to reference fuel.

6.4.5 IMEP Development (isopentane)

When using isopentane fuel, the imep developed to close-to-stable conditions within one or two engine cycles. This is shown in Figure 34 over the range of temperatures from -10°C to +26°C. This characteristic is similar to that reported by Fox et al. for operation on pre-vaporised fuel using an electrically-heated and air-assisted injector. Their results were for a stoichiometric supply ratio with engine operation at 900 rev/min and 1 bar intake pressure. It was observed that, even without enrichment, the engine fired at the first cycle with minimum imep fluctuation. This should be compared with the performance of the reference fuel shown in Figure 23, which was described in Section 6.3.5. This shows a high degree of variability in imep, compared with the isopentane, except at the highest temperatures tested where similarities are
beginning to emerge. Clearly even at -10°C, the coldest temperature tested, the vaporisation of the isopentane is extremely rapid and provides a flammable mixture within only a few cycles.

This rapid development of the in-cylinder mixture ratio to flammable values clearly contributes to the high degree of control of the initial HC concentrations compared to the results from reference fuel. The amount of unburned fuel passed through the engine because of slow initial combustion is very small and the in-cylinder ratio rapidly equates to the supply ratio, thus making the control of air-fuel ratio a much less demanding process.

The start-up process has been studied on a cycle-by-cycle basis to try and understand why the initial HC emission for isopentane still exhibits a small peak under some operating conditions. The pressure development for the -10°C test, which showed a peak in the HC emissions, is shown in Figure 35, where the first few consecutive fired cycles are shown. Cycles 13 and 14 are motoring cycles, whilst cycle 15 is the first fired cycle which is clearly a partial burn and only develops pressure very late in the cycle. Cycles 16 and 17 show that burning is now well established with strong pressure development. Figure 36 shows the peak pressure detail of cycles 13, 14 and 15 in more detail. The reduction of pressure in cycle 14, from that of the motored cycle, is due to the latent heat effect of the first injection of fuel and changes in the specific heat ratio as the charge changes from air to air-fuel mixture. The pressure is further reduced in the first half of cycle 15, due to continuing fuel injection, prior to a late burning of the charge which raises the pressure above the motoring pressure. Clearly all the fuel from the non-burning cycle 14 is available to contribute to HC emissions, whilst a substantial fraction of charge from the partial burning cycle 15 can also pass unreacted to the engine exhaust. Not all the fuel from an unburned cycle will pass through the engine, since some will be retained within crevices and oil film layers, whilst a further fraction will be lost in the blow-by gases, particularly in the early stages of the start process when piston and ring clearances are at their greatest due to the low temperatures.
In contrast to the -10°C results, the tests at 18°C and 26°C showed no peak in the HC emissions concentration at the start of combustion. The first few cycles were, therefore, studied in a similar manner to attempt an explanation. The pressure data for the test at 26°C is shown in Figure 37. In this instance the first cycle to burn was also the first cycle in which fuel was supplied. Therefore, there were no complete cycles of unburned fuel to contribute to an HC peak. Furthermore, this first burning cycle was a relatively strong cycle compared to the first burning cycle of the -10°C test, which would help keep the early emissions under control.

Care is needed when drawing conclusions from these results, since combustion data was only taken from one cylinder, whilst the emissions were an average from all cylinders combined. It should also be remembered that the injectors were enabled at an unknown position of the engine, which could vary the first cylinder to fire from test to test. It is not known whether this also has the potential to supply an underfuelled cycle, which may have been mistaken for a partial burn. The time of injection enablement was also not closely controlled and, in this series of tests, varied by up to about 15 cycles. Clearly, this affects the time the engine remains motoring and hence the degree of heating due to the compression effect. In general though, it was noted that the motoring pressure had stabilised at the time of injection so it is believed that these effects will have been of secondary importance.

6.5 Reference Fuel V Isopentane

6.5.1 First Positive IMEP Cycle

The number of cycles to the first positive imep cycle for reference fuel is shown in Figure 38 against temperature of starting. For each equivalence ratio it can be seen that the sensitivity to temperature increases as temperature is reduced and there is a temperature at which the number of cycles begins to rise rapidly. The greater the equivalence ratio, the lower this temperature becomes.
The number of cycles taken for a range of SERs at -5°C and 20°C is shown in Figure 39, where it can be seen that the number of cycles increases rapidly at supply equivalence ratios leaner than about 1.9 at -5°C and 1.1 at 20°C. These results show similar trends to those reported by Shayler et al\(^{(99)}\), where model predictions were compared to experimental data at different temperatures, for the variation in number of injector pulses to first fire against injector pulsewidth.

To ensure a calibration which guarantees a rapid start and minimises the fuel passing through the engine unburned, the ratio should be controlled to remain well to the rich side of these transition points. However, if excessively high ratios are used the speed of starting will not be enhanced but there will be a greater risk of high CO and HC immediately after the engine has fired.

These data well illustrate the compromises and trade-offs that have to be made between start quality and emissions when designing a fuelling strategy for a multi-component fuel such as gasoline. It is clearly a hard task to ensure a robust yet ‘clean’ start at a single start temperature, let alone one that is successful under all potential ambient conditions and in an engine that, once fired, will begin a relatively long transient heating process where temperatures change continuously.

To contrast the performance with reference fuel, the number of cycles to the first positive imep for isopentane, at all temperatures and equivalence ratios tested, is shown in Figure 40. In these tests the engine fired in less than 5 cycles, regardless of temperature and SER. This lack of sensitivity to temperature and SER, within the range tested, indicates that an isopentane fuelling strategy would be easier to design for reliable starting and good emissions control.

6.5.2 Exhaust Temperature Development

As well as establishing the first cycle to reach a positive imep, the exhaust temperature was recorded to further illustrate the progression from engine motoring to
firing. An example of this, when operating on reference fuel, is given in Figure 41 for a sub-zero test at an SER of 1.44. The engine was motored approximately 7 seconds after the start of data logging which, as can be seen, caused the exhaust temperatures to rise due to the compression effect. When the injectors were activated, at 10.3 seconds, the rate of temperature rise reduced due to the latent heat effect of the fuel. At this relatively lean equivalence ratio and low ambient temperature, it took approximately 10 seconds of motoring, with fuel injection, before number 3 cylinder fired well before the other cylinders. This cylinder invariably fired first, when operating on reference fuel, for reasons which are discussed later in section 6.9.2. The other cylinders then fired approximately 2 seconds later when, although difficult to see in this graph, number 4 cylinder fired second but then subsequently misfired. Once combustion was under way, the temperatures increased rapidly to their stable values; number 1 cylinder reaching 400°C approximately 12 seconds after first firing.

Figure 42 shows the equivalent results for a sub-zero ambient test fuelled on isopentane at an SER of 0.9. The most significant difference is the immediate firing of all cylinders as soon as the fuel was injected at 8.6 seconds. The temperature rise time to 400°C was similar to the reference fuel result, with number 1 cylinder taking 11 seconds. The rate may have been marginally faster due to a higher in-cylinder ratio despite a leaner SER.

Although motoring started at similar ambient temperatures, for the two tests, combustion began at a significantly lower temperature on isopentane, due to this fuel’s ability to readily vaporise and create a flammable mixture at the spark plug, which gave less time for compression heating to take effect. The ability of isopentane to rapidly fire and burn without misfire, even at cold temperatures, contributes to the fuel’s relatively clean starting characteristic and the engine’s ability to run at lean ratios results in low emissions during warming-up.
6.5.3 HC Mass Emissions

The HC mass emissions for the two fuels over a range of temperatures, at both lean and rich supply equivalence ratios, are shown in Figure 43. Although the equivalence ratios are not the same for the two fuels, particularly on the rich side of stoichiometric, they were chosen for their usability over a reasonably wide range of temperatures, whilst demonstrating differences between 'rich' and 'weak' mixture starts. Clearly the need to run at considerably higher ratios at sub-zero temperatures was necessary for reference fuel, to obtain a successful start within a realistic time, whereas isopentane reliably started at all ratios near to stoichiometric.

The curves for the isopentane show that HC mass emissions are fairly insensitive to both temperature and SER. There is a tendency for the mass to increase with higher equivalence ratios and lower temperatures but it is in marked contrast to the reference fuel which shows a strong response to both equivalence ratio and temperature.

Due to saturation of the analyser for some of the tests on reference fuel, the exact mass emissions is indeterminate. However, since the saturation was only brief, the results correctly rank the tests and have, therefore, been included. These saturated results are indicated on the Figure. It is interesting to note that, at temperatures below about 30°C, all the lean starts on reference fuel saturated the analyser, whereas the rich starts did not do this until approximately sub-zero temperatures were reached. Clearly the rich setting would be beneficial at temperatures below about 30°C but at higher temperatures the lean setting results in lower HC emissions. It should also be noted how the emissions from the two fuels converge to closer levels above this threshold temperature of approximately 30°C.

6.5.4 CO Mass Emissions

The corresponding CO mass emissions for the two fuels are shown in Figure 44, where it can be seen that the low levels at the lean settings were similar for both fuels. At the rich equivalence ratios considerable mass emissions occurred, as was expected,
due to the sensitivity of CO to ratios richer than stoichiometric. The most significant difference between the two fuels is the manner in which the reference fuel gives rise to rapidly increasing CO mass with increasing temperature, whereas isopentane levels appear to fall slightly. The reference fuel performance can be explained by the fact that, as the temperature rises the degree of fuel vaporisation increases and, therefore, for a fixed SER, the in-cylinder ratio increases. If this in-cylinder ratio becomes richer than stoichiometric it will give rise to increasing levels of CO.

The fact that levels do not increase for isopentane supports the belief that the fuel is readily vaporised at these temperatures and burning at ratios close to the SER. A possible explanation for the reduction in CO, apart from inaccuracies in fuel metering, is that as temperatures rise the degree of oxidation during the combustion process and post-combustion oxidation in the cylinder and exhaust port improves. These mechanisms reduce the amount of incomplete combustion and consequently reduce the levels of CO produced.

At the rich equivalence ratios tested, the mass emissions of CO for the two fuels were of a similar order at sub-zero temperatures. Assuming there was complete vaporisation of the isopentane and negligible error in fuel metering, this implies that, at these low temperatures, the reference fuel was actually burning at an equivalence ratio closer to the 26 percent lower SER of the isopentane.

6.5.5 NO\textsubscript{x} Mass Emissions

Mass emissions of NO\textsubscript{x} are presented in Figure 45 where, in general, the isopentane is shown to produce larger amounts at both equivalence ratios. The effect on NO\textsubscript{x} of burning at ratios close to stoichiometry has already been shown in Figure 15 to produce close to peak concentrations. Clearly the isopentane is burning at ratios close to this peak and hence producing high NO\textsubscript{x} mass emissions.
The divergence of the NO\textsubscript{x} mass emissions for the two equivalence ratios of the reference fuel, at a temperature of approximately 20°C, can be explained by the fact that the lean setting provided an in-cylinder equivalence ratio which stabilised close to the lean-of-stoichiometric SER and was predominantly affected by combustion temperature. This caused the mass emissions to increase with increasing temperature. The rich setting test, however, continued with increasing fuel vaporisation and was dominated by a transition from lean-to-rich in-cylinder ratios. This caused a subsequent reduction in the NO\textsubscript{x} mass emissions, despite the increasing temperature.

6.5.6 COV of IMEP and Starting Performance

The coefficient of variation of imep (COV\textsubscript{imep}), which was defined in section 5.4.5, has been plotted for the tests described above at the two equivalence ratios for each fuel. These are shown in Figures 46 to 49 where the COV\textsubscript{25}, COV\textsubscript{30}, COV\textsubscript{200} and COV\textsubscript{ss} have been plotted against temperature for each SER. As described in section 5.4.5, these COVs broadly describe the quality of the four stages of engine operation defined as ‘start-up’, ‘early running’, ‘warming-up’ and ‘steady-state’ respectively.

Figure 46 shows the performance of isopentane at the lean equivalence ratio of 0.98. As can be seen, for all start temperatures, the COV\textsubscript{imep} generally reduced as the engine warmed-up, except for the sub-zero temperature starts, where it can be seen that the COV\textsubscript{200} rises to similar levels as the COV\textsubscript{25}. This deterioration in combustion quality shortly after starting has already been mentioned in connection with the emissions in Section 6.4.1, where it was noted that the CO concentrations exhibited a period of instability shortly after the start at -10°C.

The apparent improvement in start performance at low temperature is unexpected. For example, the COV\textsubscript{25} at 5°C was approximately 8 percent compared to 17.5 percent at 22°C. Some of this effect may be due to lack of repeatability caused by differences in time of injector enablement, which has already been discussed. In
general the COV reduced with time until a stable value of less than 5 percent was recorded.

The COV at the richer SER for isopentane of 1.07 shown in Figure 47 was significantly better than at the weak setting. All COV values were generally better than 3 percent over the slightly reduced temperature range of these tests. The COV\textsubscript{ss} was particularly good at less than 1 percent. The COV\textsubscript{200} again showed the tendency, described above, to deteriorate to similar levels as the COV\textsubscript{25} at sub-zero temperatures but, at these levels of COV, all the results are subject to repeatability errors and definite conclusions are difficult.

The lean test on reference fuel, with an SER of 0.98, showed significant COV, as can be seen in Figure 48. Due to this lean setting, tests could only be carried out over a restricted temperature range, hence the minimum temperature was only 10°C. The COV\textsubscript{25} was the most susceptible to this lean setting, giving a value of around 400 percent at the lowest temperature tested. Once combustion had started, however, the COV reduced rapidly, but was still around 100 percent at 10°C for the COV\textsubscript{50}. The COV\textsubscript{ss} showed a consistently low value, well below 10 percent, at all temperatures. This again indicated how the combustion process develops and improves over a considerable period of time for this multi-component fuel.

Finally, Figure 49 shows the result for the test on reference fuel at an SER of 1.44. The COV levels are significantly lower than at the leaner setting, with the COV\textsubscript{ss} now below 1 percent and the COV\textsubscript{200} below 5 percent throughout the temperature range. The COV\textsubscript{25}, which reflects start quality, goes from a high of over 50 percent at 5°C down to a more acceptable value of under 10 percent at temperatures greater than about 30°C. The COV\textsubscript{25} improves at temperatures of less than 5°C, which again may seem unexpected and could be due to repeatability effects. However, some of this is due to the very first cycle to burn, which may or may not be the first cycle to have fuel supplied, as described earlier for isopentane, when considering the possible reasons for a peak in the HC concentrations. At colder temperatures there is less likelihood of the first-fuelled cycle burning. Some of the fuel from this cycle is therefore available.
for the next cycle, which if it fires, is likely to produce a high imep cycle which will contribute to a low value of COV_{25}.

The data of Figure 50 is a comparison of the starting performance of the two fuels at conditions which gave the closest similarity in HC mass emissions. Both tests were from 40°C and with an SER of 0.98. Although the engine fired rapidly on both fuels, as indicated by the low number of cycles to the first positive imep cycle, the COV_{25} for isopentane was 82 percent lower than that of the reference fuel. It is clear from the time taken to reach 90 percent of SER, which was 29s for reference fuel and only 2s for isopentane, that even at these relatively high temperatures the reference fuel vaporisation process is slow and the engine is starting and continuing to run on mixtures considerably leaner than the SER. This lean running is obviously a contributory factor to the high initial COV_{imei}. As the engine warms the COV_{imei} improves, as indicated by the low values of 4.3 for the COV_{200} and 2.4 for the COV_{ss}. These values, however, are still 93 and 73 percent higher than for isopentane, again illustrating the high quality starting potential of isopentane.

It should be noted, however, that at these conditions there is a penalty, during the first 60 seconds from fuel-on, of over 40 percent higher CO and NO_x emissions from isopentane. Again the lower CO of the reference fuel can be explained by the lean in-cylinder equivalence ratio caused by the slow vaporisation process. The isopentane, at 0.98 SER, will be burning with an equivalence ratio just lean of stoichiometric and will, therefore, as described earlier, be producing peak NO_x concentrations. The reference fuel, however, burning at considerably leaner in-cylinder ratios at this time will be holding NO_x output to lower levels.

6.5.7 Lean Starting at -9°C on Isopentane

Even at -9°C and a lean SER of 0.98 the engine started easily on isopentane. In order to contrast this performance with that of reference fuel under favourable conditions, the data from a start at the relatively high temperature of 20°C and with an SER of
1.28 was chosen. Even at this temperature the engine had to be supplied with a mixture considerably richer than for starting on isopentane to ensure firing occurred in a similar number of cycles.

The results from this test are presented in the bar chart of Figure 51, where the mass emissions for the first 60s from fuel-on are given, together with the COV values for the various stages of the start-up and the number of cycles to the first positive imep cycle. As can be seen, even at this adverse temperature of -9°C with a lean mixture, isopentane gave a mass reduction in HC of 35 percent and a CO reduction of 77 percent, when compared with reference fuel. Due to the lean-of-stoichiometric equivalence ratio for the isopentane the NO\textsubscript{x} mass increase of 39 percent was not unexpected. As explained previously, this ratio is close to that which produces peak NO\textsubscript{x} concentrations.

All the COVs for isopentane operation were better than 3 percent, which implies that the quality of the start is robust and resistant to misfire. In contrast to this, the COV\textsubscript{25} and COV\textsubscript{50} for reference fuel were 16 and 14 percent respectively, implying a poorer quality start with greater susceptibility to misfiring and stalling. As the engine warmed up, however, the trend began to reverse, with the COV\textsubscript{200} and COV\textsubscript{SS} showing a 9 and 62 percent improvement over isopentane. This is due to the in-cylinder gas-phase ratio changing from lean to rich as the engine warms up and is able to burn more of the supplied fuel. This rich operation is clearly beneficial to the quality of the combustion and is reflected in the stable COV\textsubscript{SS} of less than 1 percent by the end of the test.

Figure 52 shows the mass emissions for isopentane operation at equivalence ratios close to stoichiometric. Whilst the NO\textsubscript{x} is relatively constant, there does appear to be a peak at a ratio close to 0.98. This would support part of the reasoning, described above, for the relatively high levels of NO\textsubscript{x} compared to reference fuel. The CO and HC masses generally increase with increasing ratio.
Because of these characteristics, it would seem beneficial to operate at the leanest ratio in order to hold the emissions to a minimum. However, from the COV of imep for these ratios, given in Figure 53, it can be seen that the stability of combustion deteriorates markedly at some value leaner than 0.98. Therefore, the penalty of aiming for the absolute minimum emissions could be an unreliable start prone to misfire and hesitation, which, in extreme cases, could actually cause an increase in the emissions of HC and CO. From the above it would appear that the optimum ratio for isopentane, to ensure reliable robust starting with low emissions, is just weak of stoichiometric at 0.98. Due to the low sensitivity of isopentane to differences in start temperature this optimum should be good for all temperatures within the range investigated.

6.6 Fuel Comparison at Optimum SER

In order to further illustrate the potential benefits of starting on isopentane at two extremes of temperature, data was analysed from tests at -5°C and +20°C. To ensure a good basis for comparison, a single optimum SER of 0.98 was used for isopentane at both temperatures, for the reasons described above, whereas for reference fuel data from tests at ratios of 2.71 at -5°C and 1.28 at 20°C was used. The higher ratio of 2.71 for reference fuel was chosen as the leanest setting which would give a start with a COV$_{25}$ of less than 10 percent, whilst the lower ratio of 1.28 for the 20°C test was selected to give a minimum COV$_{25}$.

The results from these tests are given in the bar charts of Figure 54, where it will be seen that at both temperatures the starts on isopentane, with the same SER, took 1 cycle to produce a positive imep, whereas the reference fuel start took 4 cycles at 20°C and 10 at -5°C.

Inspection of the COVs at -5°C for isopentane, which were all below 5 percent, again illustrates the benefits of this fuel during all stages of the start and warm-up. The start on reference fuel was also good, with low values of 5.9 percent for the COV$_{25}$.
and 4.43 percent for the COV₃₀. There was a severe deterioration in combustion with reference fuel during the later stages of the test, as shown by the high values of 54 percent for the COV₂₀₀ and 129 percent for the COV₅₅. This is not unexpected at the high SER used, which, although giving a rapid start, would soon have caused high in-cylinder ratios, which reached close to the rich limit as the test progressed. Some of this will have contributed to the high levels of HC and CO mass shown and in a practical fuelling calibration would have necessitated the reduction of the SER as the warm-up progressed, requiring difficult compromises between keeping the combustion process robust and reliable, for good customer perception of quality, as well as ensuring that emissions were kept to their lowest levels for compliance with legislation. Once again the penalty of running on a ratio close to stoichiometric at -5°C is seen for the isopentane NOₓ level, which is close to a factor of 7 higher than the rich-burning reference fuel.

With reference fuel at 20°C the reverse of the above occurs in the change of COV with time. It is clear from the COV₂₀₀ of 2.3 percent and COV₅₅ of 0.66 that running on reference fuel at an SER of 1.28 produces an in-cylinder ratio which, as it develops towards the SER, is close to optimum for combustion stability. However, during the start and early cycles the combustion is inferior, with a COV₃₅ of 16 percent and a COV₅₀ of 14 percent. Again, this shows the difficult task which is necessary to hold a multi-component fuel, with a wide range of boiling points, at optimum conditions in an engine which is undergoing a thermal transient. For these tests the engine was held at nominally constant conditions of load and speed. If the engine were to undergo a change of condition, such as an acceleration, during this already transient thermal period, then it can be appreciated that the optimisation of the fuelling calibration becomes a very difficult task.

The isopentane results also show a change in COV with time at 20°C but these changes are small compared to the reference fuel results. The COV is less than 6 percent throughout the test. It is this low value of COV, with little extreme variation in value during warm-up, which could make the optimisation of the start and early warm-up fuelling calibration an easier task if operating on a fuel such as isopentane.
The mass emissions benefits of operating on isopentane at 20°C are shown in this comparison with reference fuel to be a reduction in HC and CO of 43 and 91 percent respectively. The disadvantage of this lean setting for isopentane, over this 60s starting and warming period, is a 1.5 times increase in the NOₓ mass emissions.

6.7 Fuel Comparison at Equal SER

Due to the many criteria that could be used for selecting the SER at which the two fuels are compared, a further comparison was made, this time at equal equivalence ratios rather than the optimum as used above. The ratio selected was 1.1 and again temperatures of -5°C and +20°C were compared. This comparison is shown in the bar charts of Figure 55 where the mass emissions, COVs and number of cycles to first positive imep are given for the two fuels at each of the two temperatures.

It is clear from the -5°C results that the performance of isopentane operation has deteriorated from when using the ‘optimum’ ratio. Whilst the start and warm-up stability is generally better than that of the reference fuel, the COV₂₅ and COV₅₀ are now both over 10 percent, which is considered beyond that desirable for good combustion stability. Furthermore, the CO emissions are now 800 percent and the NOₓ 35 percent higher than for reference fuel. The HC emissions, however, still show a reduction of over 68 percent compared to those produced by reference fuel.

It is suspected that the deterioration in start quality on isopentane is due to the use of a higher than optimum SER, causing locally rich regions within the cylinder that are close to the rich limit and causing poor combustion stability. Although vaporisation is still likely to be fairly complete, it is possible that, at these low temperatures, it is occurring later in the cycle giving less time for uniform mixing and distribution throughout the cylinder, hence creating the possibility of an unfavourably rich pocket of mixture at the spark plug at the time of ignition.
It is worth comparing the results for the isopentane at this rich SER with those presented earlier for the SER of 0.98 at -5°C. The penalty of running at this higher ratio is a 14 and 382 percent increase in HC and CO mass respectively with a reduction in NO\textsubscript{x} of 34 percent. The combustion stability, as indicated by the COV\textsubscript{25} has also degraded by a factor of approximately 3.5.

Whilst the engine started rapidly at -5°C on isopentane, it took 192 cycles for the reference fuel to produce a positive imep cycle. Clearly, this is an unrealistic number of cycles for any practical purpose, as it would take approximately 30 seconds to start the engine at 800 rev/min.

At 20°C both fuels gave rapid starting with the 1.1 SER, taking 5 and 3 cycles to produce a positive imep for reference and isopentane fuels respectively. The COV\textsubscript{ss} for both fuels was only 1 percent, showing that this SER eventually produced an optimum in-cylinder ratio for both fuels. The quality of the start on isopentane was excellent, with all COVs below 5 percent. The reference fuel by contrast had a poor start quality, with a COV\textsubscript{25} of 32 percent and a COV\textsubscript{50} of 24 percent. It did rapidly stabilise during warm-up, however, showing a COV\textsubscript{200} of 6 percent. The mass emissions benefit from isopentane fuelling at 20°C was a reduction in HC and NO\textsubscript{x} of 26 and 21 percent respectively. The CO mass, however, was 4 times higher than for the reference fuel at these conditions.

Again, comparing the isopentane performance at an SER of 1.1 with that at the optimum ratio for the 20°C tests, it will be seen that the penalty of using the higher equivalence ratio was an increase in HC and CO of 10 and 858 percent, whilst the NO\textsubscript{x} reduced by 30 percent. The starting quality, as measured by the COV\textsubscript{25}, improved by 29 percent.
6.8 Effect of SER on Isopentane Performance

In order to better understand the performance characteristics of operating on isopentane fuel, the results were analysed over a wide range of equivalence ratios. The variation in mass emissions with equivalence ratio for the two temperatures of -5°C and 20°C are presented in Figures 56 and 57 respectively. The similarity in trends between these results and those presented in Section 6.2 for the warmed-up, steady-state concentrations data is apparent.

6.8.1 HC Mass Emissions

The HC mass emissions are fairly constant and, at similar levels for the two temperatures, near to the stoichiometric ratio. At both temperatures there is a relatively sharp increase in levels as the equivalence ratio goes leaner than about 0.9 or richer than about 1.2. Clearly, there is only a fairly narrow band in which it is safe to operate if high HC output is to be avoided. This, however, is not a major problem with isopentane fuelling because, as has already been demonstrated, in contrast to reference fuel, there is no need for significant changes in equivalence ratio for different operating temperatures.

6.8.2 CO Mass Emissions

As expected, CO mass is low at ratios lean of stoichiometric and progressively increases with increasing ratios. Clearly, the ability of isopentane to successfully start at all temperatures, within the range tested, gives the possibility of starting at ratios close to stoichiometric, which will minimise the emissions of CO.

6.8.3 NOx Mass Emissions

The NOx peaks around the stoichiometric point and then falls to low levels as the equivalence ratio tends towards the lean or rich limits of operation. This characteristic
may give the biggest challenge to a good engine calibration, since starting near the stoichiometric ratio, whilst keeping HC and CO to a minimum, will generate potentially high NO\textsubscript{x} emissions.

Starting at rich-of-stoichiometric equivalence ratios would keep both HC and NO\textsubscript{x} low but the penalty then would be high CO. Starting lean of stoichiometric has potential for keeping all three pollutants to low levels but operation very close to the lean limit would be required, particularly at the coldest temperatures, with considerable risk of a heavy HC penalty if errors in the control occurred.

6.8.4 COV of IMEP

Figure 58 shows how the COV of imep varies with the equivalence ratio for isopentane at -5°C. This indicates a fairly narrow range of equivalence ratios for which the best start quality will be achieved. The possibility of operating lean, as described above, would clearly put this potentially excellent start performance at risk, as well as giving the potential for high HC emissions. It may be possible to keep all pollutants low if some degradation of start quality could be tolerated. From a purely subjective point of view, it was noted during some of the many tests made that, although the engine appeared quite ‘lumpy’ when starting and running under certain conditions with isopentane, it rarely resulted in any significant emission penalty, unlike when using reference fuel.

At 20°C, as seen in Figure 59, there was a larger range of equivalence ratios, with low COVs, than at -5°C giving greater scope for achieving a ‘safe’ calibration. However, the results still exhibited the same sharp rise in COV at the lean ratio of around 0.9. The rich limit in this instance was at the higher value of about 1.55, as opposed to 1.1 for the -5°C tests. Whilst the engine was able to start and run successfully at lean conditions, even when the ratio was below 0.9 and the COV was very high, the engine would not start and run at rich ratios greater than 1.55, although it did generally fire on the first injection. This ratio marked a very sharp ‘cut-off’ point between starting
successfully with less than 10 percent COV and refusing to start. This rich mixture limit explains the difficulties encountered when attempting conventional cranked starts using the manufacturer's standard calibration. The SER was clearly too rich for running on isopentane under certain conditions. These tests are described more fully in section 6.11.

To show the relationship between HC, COV of imep and equivalence ratio more clearly, the data from the 20°C tests have been plotted in Figure 60. This shows the risk of a rapid rise in HC if the ratio becomes much richer than about stoichiometric. Leaning the mixture will keep the HC low over a considerable range of ratios, but will cause the combustion stability to deteriorate rapidly. This again demonstrates the possible need to accept some deterioration in start quality to provide a 'safe' low emission calibration.

6.9 Combustion Characteristics

6.9.1 Pressure Development

Pressure data from test runs at 18°C were analysed to determine differences in the combustion characteristics between the two fuels. The normal practice of computing mass fraction burned values was not considered appropriate in this work, as it assumes that all the induced fuel is burned\(^{(100)}\), which is clearly not the case during a cold start. In this instance the pressure rise due to piston motion was subtracted from the total pressure rise, to allow the pressure rise due to combustion alone to be obtained. The cumulative pressure rise due to combustion, which has the shape of the normal mass burn fraction curve, was also computed. An example of such data for a test on reference fuel is shown in Figure 61. From the pressure rise due to combustion it was possible to determine the combustion duration by establishing the crank angle degrees between the point at which the curve first showed a positive pressure to the point when it returned to zero. The number of degrees to reach the peak of this curve and then to return to zero was also determined. These two values which, for convenience, will be described as the 0 to 50 percent and the 50 to 100 percent combustion
duration, enable differences in burning rates during the first and second halves of the burn period to be determined. Test data from starts at an equivalence ratio of 1.28 for reference fuel and 0.98 for isopentane were used, these being optimum ratios for the reasons described earlier.

Pressure data at four different stages during the start and warm-up period were analysed to determine changes in the combustion characteristics with time. These four different stages can broadly be described as ‘start-up’, ‘early running’, ‘warming-up’ and ‘steady-state’. Cycles 2, 25, 200 and 1200 have been chosen as representative of these four periods. Considerable cyclic variation in combustion data occurs during cold operation and particularly during the first fired cycles. The data presented, therefore, have been selected as representative from the many data sets analysed.

Figure 62 shows the second cycle, where the most significant difference between the performances of isopentane and reference fuel can be seen. The isopentane readily burns during these early start-up cycles, whereas the reference fuel exhibits very slow partial burns during this period.

The 25th cycles (numbered 47 and 48 in the isopentane and reference fuel group of cycles respectively), together with their neighbouring cycles, are shown in Figure 63. This illustrates the higher variability and slower burns of the reference fuel. It also shows clearly how the isopentane has a significantly faster flame initiation during these early cycles; the pressure rise being noticeable very soon after ignition at 340°.

Comparison of Figure 64, showing the 200th and neighbouring cycles (numbered 272 and 273 in the isopentane and reference fuel group of cycles respectively), with Figure 63 shows how these ‘warming-up’ cycles exhibit less cyclic variability and greater similarity. It is now noticeable that, whilst the reference fuel’s early burning speed is increasing to become closer to that of the isopentane, the burn rate of the isopentane is becoming slower towards the end of combustion.
Finally, Figure 65 shows the 1200th cycle, representing the 'steady-state' case. The two fuels are now similar in performance (despite the large difference in supply equivalence ratios) which can also be seen from the pressure curves in Figure 66. The early burn rate is now very similar, whilst the later stages again exhibit isopentane producing a slower burn.

Figure 67 shows consecutive pressure cycles for reference fuel combustion, from the last motoring cycles to the last cycle used in the calculation of the COV$_{25}$, together with the 1200th and last cycle measured. There is a considerable degree of cyclic dispersion with a significant number of slow burning cycles, including the first cycle to fire, giving late pressure development with low peaks. The maximum HC emissions will obviously come from those cycles with fuel supplied but no burning, followed by the late burning weak cycles, which, although receiving a full supply of fuel, are only able to burn part of it, mainly because of poor fuel vaporisation.

The pressure development for similar cycles from isopentane combustion is shown in Figure 68. The cyclic dispersion is lower than for reference fuel with fewer late burning cycles and the first cycle to fire is a well developed high peak cycle. The fast-burning first-fired cycle with its high peak pressure will speed the input of heat energy to the engine and benefit the combustion of subsequent cycles, thus reducing the amount of unburned HC emissions.

The above data are summarised in Figure 69 showing the total combustion duration, the 0 to 50 percent and the 50 to 100 percent combustion periods, together with the crank angle position of peak pressure for the 2nd, 25th, 200th and 1200th cycles. The bar chart of the total combustion duration clearly shows how the total burn period for the two fuels becomes closer with time due to the reference fuel's increasing burn rate, whilst the isopentane rate remains substantially constant, particularly over the early part of the test. This increasing reference fuel burn rate is due to the increasing in-cylinder, gas-phase, fuel-air equivalence ratio which occurs as temperature increases and fuel vaporisation improves.
Comparison of the 0 to 50 percent and 50 to 100 percent bar charts clearly illustrates that, whilst differences are significant during the early cycles, the largest differences occur for the latter part of the combustion process, where reference fuel burns considerably slower than isopentane during the early cycles, but then rapidly increases to rates giving a final burn period slightly faster than the isopentane. Again this is likely to be due to the increasing in-cylinder mixture strength which, not only becomes more favourable from cycle-to-cycle, but also within each individual cycle, which might explain the increasingly rapid final burn period.

The final bar chart compares the crank angle positions of maximum pressure. This shows a fairly constant angle for isopentane throughout the test, whereas the reference fuel exhibits significant variability. In general the peak pressure increased with time during the start and warm-up and advanced closer towards TDC. The very early timing of the 2nd cycle for reference fuel was due to partial burning, which resulted in a cylinder pressure only slightly higher than that of a motored cycle. This can be seen in Figure 70.

The data presented are for different equivalence ratios for the reasons already described. Results for tests at similar supply equivalence ratios exhibited similar trends during the early stages but with larger differences. The latter stages, however, showed less correlation which was likely to be due to the considerably different in-cylinder, gas-phase, fuel-air equivalence ratios despite the same supply equivalence ratios.

6.9.2 Mixture Distribution

A measure of the quality of the fuel-air mixture preparation and distribution is the time taken between the first and last engine cylinders to fire, with the shortest time indicating the best quality. With cold start tests, using the reference fuel in particular, it was often difficult to determine the exact point of first-firing due to weak burns which were difficult to detect. It was, therefore, considered that the time for the
exhaust gas to reach a temperature of 80°C, as indicated by the thermocouple in each
exhaust port, might be a more reliable indicator. Tests showed that the first cylinder
to fire was most often the first cylinder to reach 80°C, but this was not always the
case, especially if firing was immediately followed by one or more misfires. It is
believed, however, that it was more indicative to use a detection technique which
indicated mixture distribution quality by the speed with which all cylinders begin
burning strongly, rather than just firing. In view of this, it was considered that the
time to reach 80°C, which was easily measured, would be a good indicator of mixture
quality and distribution.

The results from this analysis are shown in Figure 71, where the time between the first
and last cylinder to fire has been plotted against temperature of start for the two fuels.
Two equivalence ratios have been given for reference fuel as this is more sensitive to
changes in ratio than isopentane, which retains a fairly constant time over the
temperature range at all usable ratios. As can be seen, the reference fuel exhibits a
fairly steeply rising characteristic with decrease in temperature which is reduced in
level with an increase in ratio. The difference in times for the fuels decreases as the
temperature increases.

The difference in times for all tests has been plotted in Figure 72 against SER.
Although the range of ratios is smaller for isopentane, the fuels are compared over
their usable ranges. There is a greater scatter of results for reference fuel and the
repeatability at any ratio is not as good as for isopentane. The average time for
isopentane from all the data is 0.19s, which is significantly lower than the 0.76s
average for reference fuel. Data from tests with the isopentane at higher ratios would
have given increasingly longer times. However, at ratios above about 1.55 the engine
would not continue to run, even though it may have initially fired on all cylinders and
produced an exhaust gas temperature greater than 80°C. These data, therefore, are not
considered to fall within the usable range, as mentioned above, and have been
excluded from the analysis.
Figure 73 shows the results for the tests at sub-zero temperatures only and shows a tendency for the isopentane time to increase and spread with increasing ratio and decrease with the reference fuel. At high equivalence ratios the times for the reference fuel are similar to those for isopentane. The need to keep ratios low for isopentane and high for reference fuel for best mixture preparation and distribution, particularly at low temperature, can be seen from these data.

Finally, as a further measure of the distribution quality, an analysis was made of the number of times each cylinder reached 80°C first. If the supply and distribution of air-fuel mixture to each cylinder was perfect then the number of times each cylinder fired first, or reached 80°C, would be a random process. Figure 74 shows the percentage of times that each cylinder reached 80°C first for all test temperatures and SERs and clearly indicates the poor mixture distribution for both fuels at these engine conditions.

There are obviously other influencing factors which could give an incorrect indication of poor distribution, such as one cylinder having a greater spark energy, or a directional external cooling fan causing differences in the vaporisation process between ports. However, the fact that the fuels behaved differently suggests that these effects are likely to be of secondary significance.

From this analysis it can be seen that for reference fuel the distribution was biased very strongly towards number 3 cylinder, which reached 80°C first in over 70 percent of the tests, whereas the other cylinders were fairly evenly matched at around 10 percent. With isopentane the offset was towards number 4 cylinder, which reached 80°C first in only 7 percent of the tests, whereas the other cylinders gave values between 27 and 38 percent of the tests. The fact that both fuels had similarly low values for number 4 cylinder could indicate that this cylinder was receiving less fuel due to poor injector matching or a malfunction.

In conclusion, taking all the above data into consideration, it is considered that isopentane fuelling gives better mixture preparation and distribution, which is as
expected due to the ease with which this fuel vaporises thus ensuring thorough mixing with the induced air and the best chance of equal delivery to the cylinders.

6.10 Ignition Timing

All the tests described so far were made at a fixed ignition timing of 20° BTDC. In order to investigate the effect that different ignition timing might have on the start-up process, a short series of tests was carried out on the two fuels over a range of timings.

The mass emissions results for isopentane, at an SER of 0.98 and a temperature of 18°C, are shown in Figure 75, where it can be seen that only the NOx changes significantly, showing a strong linear increase with increasing ignition advance. The CO, as expected for this lean setting, is at low levels which only increases very slightly with advancing ignition. The HC mass is generally fairly constant with a small peak at about 25°. From these tests it would seem that the optimum timing for lowest emissions at these conditions is 10° BTDC. However, at retarded timings the quality of the combustion deteriorates, as can be seen in Figure 76, where at 10° advance the COV25 is about 17 percent. The best quality start would be at the most advanced timing of around 40 where all the COVs are well below 5 percent. The best COVss was at 20° BTDC.

These results go against the expectation that the lowest COV25 would be achieved with retarded timing, which gives longer time for the in-cylinder fuel to vaporise and mix with the air, which would also be at a higher temperature\(^{[10]}\). From this evidence it would seem that the best ignition timing strategy would be one which starts advanced, to ensure a good quality robust start, and then rapidly retards to around 15° BTDC once combustion is under way, thus ensuring lowest emissions during the early stages of warm-up with acceptable combustion stability. Further testing at other temperatures and equivalence ratios is required to confirm this.
Similar trends were found when using reference fuel at an SER of 1.16 and a temperature of 20°C, although in this case there was more evidence of increasing HC mass with retarded timing, as seen in Figure 77. This is as expected since there is less time for the complete charge to burn in the cylinder, although this will be balanced to some extent by more heat being available in the exhaust which will assist post-combustion oxidation.

The COV$_{25}$ for the reference fuel was highly variable, as can be seen in Figure 78 but, as with isopentane, the lowest COVs were at advanced timings. Again, initial starting would appear best with an advanced timing but with less need to change to retarded settings as combustion progresses, since the NO$_x$ is already at a comparatively low level and the HC would increase with retard. As with isopentane, the best timing for the COV$_{SS}$ was around 20° BTDC.

### 6.11 Standard Calibration Starts

A number of conventional starts, where the engine was started on the starter motor and allowed to idle, using the manufacturer's standard calibration, were carried out on the two fuels over a range of temperatures. Typical emissions when operating on reference fuel at -2°C are shown in Figure 79. Although there is no saturation of the analyser, the HC levels remain high, although decreasing, for a considerable period before stabilising towards the end of the test. The very high SER is evident from the CO levels, which saturate the analyser after a very rapid rise at the start of the test. Even at the end of the test the CO is at a high but stable level, indicating the continued use of a significantly rich air-fuel mixture to maintain driveability. Even with a high SER the COV$_{25}$ was poor at 35 percent.

There are no data presented for isopentane at sub-zero temperatures as the engine would not run at these conditions using the standard calibration. The very high SER used at sub-zero temperatures is clear from the CO results for the reference fuel and, as already mentioned in previous sections, isopentane combustion deteriorates rapidly at equivalence ratios greater than about 1.55. It is likely that the standard calibration
ratio is significantly higher than this, with the inevitable consequence that the rich limit is exceeded. Analysis of the combustion data revealed that, even under these adverse conditions, the engine initially fired for the first 1 or 2 cycles.

The engine operated satisfactorily on isopentane with the standard calibration at higher ambient temperatures. An example of a test at 17°C is shown in Figure 80 where the initial peak in the HC indicates that the SER is still too high for this fuel, which is confirmed by the high COV$_{25}$ of 55 percent. This start, however, is better than that shown for reference fuel at the similar temperature of 16°C in Figure 81, where the engine fired immediately but then misfired for a number of cycles before stabilising. This caused very high HC emissions, which saturated the analyser and contributed towards the poor COV$_{25}$ of 58 percent. Once combustion was underway, the levels dropped rapidly but remained at higher levels than for the isopentane test.

In most of the cases where a successful start occurred, on either fuel, it was noted that initial firing was rapid followed by one or more misfires. These misfires are clearly undesirable for minimum emissions and low COV$_{25}$ but are probably inevitable under some conditions if the desired speed of starting is to be achieved. Under these misfire conditions it was noted that high initial emissions were more likely when fuelling on reference fuel than with isopentane, probably because the isopentane was firing on the first-fuelled cycle whereas the reference fuel was not.

At high temperature, where the standard calibration injects less fuel, the isopentane produces only a very low initial HC peak, as shown in Figure 82, where the data is for a test at 33°C. Although the HC emissions are controlled, the COV$_{25}$ was 70 percent, indicating a poor quality start. This may be due to the initial retarded ignition timing of 10° BTDC for the standard calibration, which, as described in section 6.10, can give increasing combustion instability. The data in section 6.10 were, however, for a lower temperature and equivalence ratio so comparison is difficult.

At a comparable temperature of 28°C the reference fuel still saturates the analyser for some considerable time at the start, as shown in Figure 83. The fuelling may have been slightly different for this test, as the temperature was slightly lower, but it is typical of the response on this fuel. The COV$_{25}$ was also high at 68 percent. It is
surprising that the emissions and stability were so poor at this comparatively mild condition. It is possible that the standard calibration was not optimum for this fuel or temperature.

The start process, which is highly transient and subject to many influencing factors, is not highly repeatable and many tests are required to establish trends. The above tests were relatively few in number and therefore results need to be interpreted with caution. However, sufficient tests were made to conclude that if the start was successful, then isopentane fuelling was unlikely to produce the same extreme high levels of HC emissions, during the early start period, so often seen when fuelling on reference fuel.

An example of a relatively poor start on isopentane is shown in Figure 84 where the HC emissions showed a considerable spike due to the non-optimised and excessive SER. In this instance misfiring occurred, after a start which was not immediate, thus giving rise to a very high COV₂₅ of 99 percent which was the highest of all the tests made on both fuels. However, even under these very poor start conditions the HC emissions were still well below saturation level. A similarly poor start on reference fuel would almost certainly have given rise to far higher levels.

An example of the potential for reducing the start-up emissions is given in the bar chart of Figure 85, where the mass emissions and COVs are compared for the two fuels at a temperature of approximately 16°C and using the standard calibration. The quality of the starts are similarly poor for both fuels, with the COV₅₀ and COV₅₅ worse for isopentane. This is as expected for isopentane at such a high SER and with retarded ignition timing. However, despite the high COVs, isopentane still showed a reduction in HC mass emissions of more than 46 percent and a reduction of 23 percent in CO over the 60s period from fuel-on. The NOₓ mass increased by 54 percent, which was higher than expected for such a high SER. Low oxygen availability at this high ratio would not be favourable for NOₓ production. However, it should be remembered that these are only relative mass units to allow comparisons between the fuels.
7. Summary of Results

The previous section described and discussed the test results in detail. It is the intention of this section to bring together all the main findings of the research, in summary form, before the more formal conclusions are made in the next section.

7.1 Reference Fuel

- When starting on reference gasoline, at a fixed supply equivalence ratio (SER), there was a considerable delay as the in-cylinder fuel-air equivalence ratio developed.

- In the early stages of this development the in-cylinder ratio was too weak to start the combustion process and raw fuel was expelled from the engine, giving rise to very high HC emissions.

- As the ratio developed to within the flammability limits, combustion started. However, the initial operation was at a lean ratio, with misfiring and partial burning, giving rise to high emissions.

- The speed with which the in-cylinder ratio developed could be increased by either increasing the SER (up to a certain limit) or increasing the start temperature.

- Starting on reference fuel, at a lean SER of 0.98 and 10°C, produced a COV\textsubscript{25} of nearly 400 percent, but a COV\textsubscript{55} of better than 10 percent, thus providing further evidence of a slowly improving in-cylinder ratio which increases with increasing temperature.
• When the reference fuel SER was increased to a rich 1.44 the COV$_{25}$ reduced considerably to approximately 50 percent at 5°C and less than 10 percent at temperatures over 30°C.

• When starting at -5°C with an SER of 1.4 it took six times longer for the in-cylinder ratio to reach 90 percent of the SER than it did at +50°C.

• When the start temperature was increased from -7°C to +49°C, with an SER of 1.44, the CO mass emissions increased by a factor of 2.6, whereas the HC and NO$_x$ masses reduced by over 60 and 65 percent respectively.

• Below a certain temperature the number of cycles, before a positive imep was produced, increased rapidly. This threshold temperature was reduced by increasing the SER.

• Conversely, at a fixed temperature, there was a threshold SER at which leaner ratios caused a rapid increase in the number of cycles before starting and increased the fuel passing through the engine unburned. Substantially richer ratios did not increase the starting speed but produced higher post-combustion HC and CO emissions.

• To ensure reliable starting, within a realistic time, it was necessary to use considerably higher SERs when using reference fuel, particularly at sub-zero temperatures. Isopentane, however, produced rapid starting at all SERs close to stoichiometric.

• The HC mass emissions from reference fuel operation were sensitive to changes in both the start temperature and the SER, whereas for isopentane operation there was little change. The difference in HC mass emissions for the two fuels became less with increasing temperature.
7.2 Isopentane

• When fuelling with isopentane there was little delay of in-cylinder fuel-air ratio development, which gave rapid combustion and little unreacted fuel passed through the engine, thus giving lower HC emissions.

• Starting was successful with lean-of-stoichiometric equivalence ratios at all temperatures tested, resulting in low CO and HC mass emissions. Starting was achieved within 5 engine cycles at all temperatures and SERs.

• At a lean SER of 0.9 isopentane gave a COV$_{25}$ and a COV$_{SS}$ of less than 10 percent at 10°C, indicating a favourable, fully developed, in-cylinder ratio which changed little with increasing temperature.

• Although reducing CO and HC emissions, the NO$_x$ emissions increased. This was due to the higher oxygen availability and higher flame temperatures which occur at lean-of-stoichiometric ratios.

• The following observations were made during a series of tests (1.07 SER) where the start temperature ranged from 26°C to -10°C:-

> Even at -10°C the CO increased rapidly and stabilised within approximately 10 seconds of starting. This rise characteristic was comparable to fuelling on reference fuel (1.44 SER) at +49°C.

> The CO mass emissions reduced when temperature was increased, unlike for reference fuel which showed a significant increase.

> Even when a peak occurred in the HC concentration, it was small and never approached analyser saturation level.
\[ \text{NO}_x \] concentration tended to increase with increasing temperature, indicating that the in-cylinder ratio was close to the SER and that it was temperature, rather than fuel-air ratio, dominating its formation.

The time taken to reach 90 percent of the SER was generally within 2.5 seconds regardless of temperature or SER.

The imep developed to close-to-stable conditions within one or two engine cycles. This ensured that fuel passing through the engine unburned was minimal and that HC emissions were well controlled.

- When starting at both -5°C and 20°C the HC mass increased fairly rapidly as the SER was reduced beyond about 0.9 or increased beyond about 1.2. The CO mass was low, as expected, when lean of stoichiometric. Therefore, for the lowest CO and HC emissions, the equivalence ratio should be set just lean of stoichiometric.

- Care needs to be taken with calibrations lean of stoichiometric, however, since there was a sharp deterioration in the combustion stability when going leaner than about 0.9 SER. If some deterioration in start quality was acceptable there would be further scope for emissions reduction.

- At -5°C there was a very sharp transition, at an SER of 1.55, from successful engine starting, with a COV of less than 10 percent, to a refusal to start.

- The optimum SER for isopentane starting was 0.98. This gave the lowest HC and CO emissions whilst retaining a good start quality.
7.3 Optimum Supply Equivalence Ratio

- Tests at -5°C, with optimum SERs (reference fuel 2.71, isopentane 0.98), showed that starting on isopentane:
  - Reduced HC emissions by over 79 percent
  - Reduced CO emissions by 92 percent
  - Increased NO\textsubscript{x} emissions by 671 percent
  - Reduced COV\textsubscript{25} by 44 percent
  - Reduced number of cycles to first positive imep cycle by 90 percent

- Tests at 20°C, with optimum SERs (reference fuel 1.28, isopentane 0.98), showed that starting on isopentane:
  - Reduced HC emissions by 43 percent
  - Reduced CO emissions by 91 percent
  - Increased NO\textsubscript{x} emissions by 143 percent
  - Reduced COV\textsubscript{25} by 65 percent
  - Reduced number of cycles to first positive imep cycle by 75 percent

7.4 Equal Supply Equivalence Ratio

- Tests at -5°C, with equal SERs of 1.1, showed that starting on isopentane:
  - Reduced HC emissions by over 68 percent
  - Increased CO emissions by 800 percent
  - Increased NO\textsubscript{x} emissions by 35 percent
  - Reduced COV\textsubscript{25} by 29 percent
  - Reduced number of cycles to first positive imep cycle by 98 percent
• Tests at 20°C, with equal SERs of 1.1, showed that starting on isopentane:-
  
  Reduced HC emissions by over 26 percent  
  Increased CO emissions by 408 percent  
  Reduced NOx emissions by 21 percent  
  Reduced COV25 by 88 percent  
  Reduced number of cycles to first positive imep cycle by 40 percent  

• Comparison of results for isopentane, at -9°C and a lean SER of 0.98, with reference fuel, at 20°C and a rich SER of 1.28, still showed significant benefits. HC and CO masses were reduced by 35 and 77 percent respectively, whilst the COV25 was less than 2 percent, which was 88 percent lower than for reference fuel.

• The COVss, however, was over 1.5 times higher than for reference fuel, but still better than 2 percent. As expected, there was a significant increase in NOx mass emissions, which was nearly 40 percent higher.

• The closest HC mass emissions were produced during tests with SERs of 0.98 and a start temperature of 40°C. At these conditions, the isopentane COV25 was 82 percent lower than for reference fuel and the time to reach 90 percent SER was only 2 seconds for isopentane, compared to 29 seconds for reference fuel. The CO and NOx emissions, however, were both 40 percent higher when operating on isopentane.

• Fuelling with isopentane at warmed-up steady-state conditions produced slightly lower HC concentrations at most equivalence ratios. The lean limit of operation was increased but the rich limit was reduced.
7.5 Combustion Analysis

- At a start temperature of 18°C, and with optimum SERs, the burn rate of reference fuel was considerably slower than isopentane during the early cycles, but increased to similar levels as the test progressed. The isopentane burn rate was substantially constant during starting and early running.

- The biggest difference between the burn rates of the two fuels occurred during the 50 to 100 percent burn periods, when reference fuel was considerably slower during the starting and early cycles, but rapidly increased to levels slightly faster than isopentane.

- The position of maximum pressure was relatively constant for isopentane, but varied significantly for reference fuel throughout the test. In general the peak pressure position moved towards TDC as the test progressed.

7.6 Mixture Distribution

- The time between the first and last cylinder to fire during starting on reference fuel increased with reducing temperature for a fixed SER. The time between firing reduced with increasing SER.

- Mixture distribution was poor, at the conditions tested, for both fuels but was best when fuelled with isopentane.

- For the best mixture preparation and distribution, when operating on reference fuel, the SER needed to be high. When using isopentane, however, the best performance was with low SERs.
7.7 Ignition Timing

- The NO\textsubscript{x} mass emissions showed the strongest dependence on ignition timing, increasing significantly with increasing advance when starting with isopentane at 18°C (0.98 SER)

- At this temperature and SER the best timing for lowest emissions was 10° BTDC, however, combustion quality deteriorated at this retarded timing (COV\textsubscript{25} = 17 percent).

- The mass emissions, when starting on reference fuel at 20°C (1.16 SER), showed similar trends, apart from there being a greater change in HC emissions, which increased with ignition retard. Again, the best combustion stability was at advanced timing.

7.8 Standard Calibration Starts

- When fuelling on isopentane, at sub-zero temperatures, the engine would not crank-start to idle using the starter motor because the rich limit for this fuel was exceeded by the manufacturer’s standard calibration.

- The engine started successfully on isopentane at higher temperatures. However, the SER was still excessive and caused a peak in the HC emissions, although the mass emissions were still lower than when starting on reference fuel. This demonstrated the tolerance of isopentane operation to a calibration for which it was not developed, provided the rich limit was not exceeded.

- When starting at 16°C on isopentane, even with the excessive SER of the standard calibration, HC and CO mass emissions were reduced by over 46 percent and 23 percent respectively compared to reference fuel. NO\textsubscript{x}, however, was increased by 54 percent.
All references to mass emissions in the above summary apply to the 60 second period of operation from fuel-on.

7.9 Closure

The use of isopentane has demonstrated how a volatile fuel can make an engine easier to start, quicker to warm-up and use less fuel with lower HC and CO emissions, particularly at low temperature. However, there are potential problems with high fuel volatility, not least of which is the contribution this can make to evaporative losses. Indeed, the volatility of gasoline has been severely restricted in recent years, in order to control the hydrocarbons emitted in this manner, despite the need for light fuel fractions to ensure easy starting. The sophistication and efficiency of the evaporative loss systems now used to control these emissions have also improved since their inception and it is anticipated that these will be able to handle any additional losses that might arise from the start-up fuel, which would only be used at relatively low temperatures.

Another potential problem with fuels of high volatility is the risk of vapour lock within components of the fuel system, such as the fuel pump and rail. This is normally attributed to the very lightest components, added to conventional gasoline to give good starting, such as butane, which boils at -5°C. Isopentane has a considerably higher boiling point and would only be used at relatively low temperatures for starting, so fuel restriction due to vapour lock is less likely.

Although no specific tests were carried out to investigate the possibility of vapour lock, it will be recalled from section 6.2 that a steady-state test could not be carried out at normal coolant temperature due to fuel starvation. The length of time that the engine was allowed to run from starting was considerable, however, and no problems were encountered when the fuel was used just for the start and early warm-up period.
Clearly though, this is an area for further work and the design of a fuel system and storage for the start-up fuel will have to consider this aspect with care.
8. Conclusions and Suggestions for Further Work

8.1 Conclusions

The work of this thesis has provided a better understanding of the emissions generation process during engine starting and the early stages of warming-up, particularly at low temperatures. The potential benefits of starting the engine on a single-component liquid fuel with a low boiling point has been investigated.

The use of such a hydrocarbon fuel, for the starting and early running period, is seen as a potential method for reducing the HC and CO emissions that are generated during this critical period of operation. It has been explained how tailpipe emissions are high during this period, due to the fuel-rich mixture used for fast reliable starting and good driveability, at a time when the catalyst has not reached its working temperature and is, therefore, ineffective. The significance of developing methods to control this period of high emissions is becoming greater as the vehicle population, with catalysts fitted, increases.

As the development of catalysts progresses, with reduced light-off times and other technologies, the very early cycles of engine operation during starting are becoming increasingly significant. Most of the published work considers the first few minutes of starting, or the operation over the early phases of the legislative drive cycles, where the quality of the start and the resulting emissions depend upon the sophistication of the manufacturer's engine calibration. The work described in this thesis was particularly concerned with the mixture formation and combustion characteristics during the starting process and the emissions generated during a 60 second period from the start of fuelling. To reduce the effect of changes, caused by the engine's standard calibration or changes in operating conditions, and help identify the effects of the fuel used, the engine was started, at a fixed speed and load, with the air-fuel ratio and ignition timing held constant.

The results showed how a multi-component gasoline, with a wide range of boiling points, made it difficult to ensure that no fuel passed through the engine unburned,
because of low mixture flammability, during engine cranking and starting. The work also showed how a conventional gasoline caused the in-cylinder fuel-air ratio to undergo a complex transient development process even under relatively steady operating conditions.

The levels of emissions generated are highly dependent on the fuel-air ratio burned in the cylinder, which means this must be carefully controlled. This task is made difficult by the rapidly changing conditions in the engine cylinders during starting and warming-up, caused by the properties of conventional gasoline. This control becomes increasingly onerous if changes in engine operating conditions occur during the warm-up period.

Having selected a single component hydrocarbon fuel, with a low boiling point, for the starting and early warming-up period, it was found that the high volatility of this liquid fuel ensured rapid starting with little fuel passing through the engine unburned during the crucial early stages before and after combustion initiation. The pure nature of the fuel ensured that the in-cylinder equivalence ratio stabilised very rapidly to the steady-state condition. This behaviour was close to how a gaseous fuel, perhaps the most ideal, was expected to behave but without the need for a special fuelling system.

A fuel-rich mixture was not required for successful cold starting on such a fuel, even at low temperatures. Indeed the work showed that a slightly lean-of-stoichiometric equivalence ratio was best for ensuring that the CO mass emissions were kept to low levels. The HC rapidly stabilised to close-to-normal running levels when other mechanisms of HC formation started to dominate, such as crevice effects and the oil adsorption/desorption process.

Whereas the supplied equivalence ratio, at any particular temperature, was critical with reference fuel to ensure a good quality start, this was not the case when fuelling on isopentane. For this fuel a single lean-of-stoichiometric supply equivalence ratio could be used over a wide range of starting temperatures, giving improvements in both the quality of the start and lower levels of HC and CO emissions. This gives
potential for reducing cold-start development times, as well as improving the quality of the calibration.

This lean-of-stoichiometric equivalence ratio, as well as reducing the light-off time, should also be close to the ideal for maximum three-way catalytic conversion of the exhaust gases. If this were not the case, it could be adjusted to a value around the stoichiometric point with little effect on emissions or combustion quality.

Starting the engine under lean mixture conditions has highlighted a possible future challenge of finding ways of reducing the NO\textsubscript{x} emitted under these conditions. In the majority of tests it was found that, whilst lean-mixture starting reduced CO and HC emissions, the NO\textsubscript{x} levels increased to levels higher than when starting on reference fuel with a high equivalence ratio. Current fuel-rich starting calibrations do not favour NO\textsubscript{x} formation, particularly at low temperatures.

Much of the literature reviewed either ignored NO\textsubscript{x} or reported little effect when starting at low temperatures. Clearly, if lean-mixture starting becomes a possibility, then the significance of NO\textsubscript{x} formation during this process will increase. The current methods of reducing NO\textsubscript{x}, such as exhaust gas recirculation, are not appropriate during starting because of their detrimental effect on combustion quality. Whether sufficient control can be gained through ignition timing is a subject for future work and is discussed further in section 8.3.

8.2 Summary of Main Conclusions

When using reference fuel:-

• The delay from fuel-on to the start of combustion increased and subsequent initial burning was less complete, as ambient temperature or SER was reduced. This resulted in unburned fuel passing through the engine.
• The significance of the HC from this source, relative to the total emitted, will increase as the catalyst light-off time continues to be reduced.

• The in-cylinder fuel-air ratio development was highly transient, despite the fixed engine operating conditions and constant supply equivalence ratio. This characteristic increases the required complexity of cold-start fuel calibrations.

When using isopentane:

• The high volatility of the fuel ensured rapid starting and essentially complete combustion, even at sub-zero temperatures, with little unburned fuel passing through the engine.

• Because isopentane is a single component fuel, the in-cylinder fuel-air ratio rapidly stabilised at the temperatures tested. This gives potential for less complex cold-start fuel calibrations, whilst maintaining good control of emissions.

• Mixture enrichment was not required. Lean-of-stoichiometric fuel-air mixtures gave rapid and robust starts, even at -10°C, resulting in significant reductions in CO and unburned HC.

• Starting with a lean mixture increased emissions of NO\textsubscript{x} during the 60 second period of operation from fuel-on. The significance of this will increase as catalyst light-off times are reduced.

8.3 Suggestions for Further Work

Whilst it was necessary to operate the engine with a fixed fuel-air ratio and ignition timing, to help understand the mechanisms occurring during the starting process, a full working start-up calibration on isopentane should now be developed to enable the maximum benefit to be determined. The conventional cranked starts, with the
manufacturer's standard calibration, showed potential at 'normal' temperatures, even though the calibration had not been designed for this fuel. Having developed the optimum calibration the fuels should be compared in vehicle trials, both over standard legislative drive cycles and in driveability assessments.

As part of this calibration work, the effect of ignition timing and other variables on the NO\textsubscript{x} formation will be determined. The significance of the NO\textsubscript{x} formation was not anticipated when this work started and clearly this warrants further investigation. The results reported here showed the strong influence that ignition timing had on this pollutant and how, for lowest starting emissions, the ignition was best retarded. This timing, however, was detrimental to combustion quality and, therefore, some compromise will be necessary. The absolute mass levels of NO\textsubscript{x} were not measured but, even if these are not found excessive by today's standards, it is certain that reductions will be required in the future.

The fact that the start quality was best at advanced timings, particularly for isopentane, was surprising, since timings closer to TDC would be expected to give more time for the vaporisation process to take place and, therefore, assist combustion. The subsequent mixing process would also be improved, since the air in the cylinder would be at a higher temperature due to the increased pressure. Further tests are required to see if this result occurs at other temperatures and supply ratios. An explanation of this apparent discrepancy could be beneficial even for current engine strategies, as these use early ignition retard, not for improved vaporisation, but to assist the catalyst light-off process.

The experiments should be repeated on a range of single component fuels, with different boiling points and vapour pressures, to establish the optimum volatility. The results from these tests should be compared with those obtained using a fuel vaporiser which ensures full vaporisation of the fuel before injection. Electrical fuel vaporisers, operating with conventional gasoline, are a possible future technology, but their control of emissions at low temperatures needs further assessment. Fuels with a limited number of components may also be worth investigating, as well as full-boiling
range fuels, which should include summer and winter grades. This work should ideally be carried out on a single-cylinder engine to remove the influence of mixture distribution and other inter-cylinder effects.

Emphasis should remain on the very early stages of the start and warm-up, due to the increasing significance of this period of operation, as already explained. During this period the effects of the fuel components in conventional gasolines, which boil at the higher temperatures, will become of increasing importance. Whilst these 'heavy' components are required for good vehicle and refinery economy, as well as ensuring the fuel has a high energy density, they are clearly undesirable during cold engine operation. The effect of reducing these higher boiling point components and the end-point temperature needs further investigation.

The use of a single component fuel gives greater possibility for designing an oil/fuel combination which significantly reduces the adsorption/desorption effect. Whilst considerable work has been done in gaining an understanding of this process, oil formulations do not seem to have changed significantly as a result. Using a single component fuel for starting gives renewed incentive for further investigation of this potential benefit.

As described in section 6.3.4, it was unclear whether the difference between the supplied and burned fuel quantities could all be accounted for by the mass of fuel passing the piston with the blow-by gases. A carefully designed set of experiments are, therefore, required to further investigate this phenomena.

The fact that conventional gasoline is composed of many different hydrocarbons means that the combustion products also contain many different species, all having a different reactivity and toxicity. Therefore, it is important that an understanding be gained of how the start and warm-up process influence these and what effect the use of a highly volatile or other starting fuel may have on them.
Finally, whilst this work was primarily concerned with gaining a better understanding of the emissions and combustion processes during cold starting, the practicalities and costs of using a dedicated start-up fuel should be considered. Questions of hot-fuel handling, storage and evaporative losses of the start-up fuel need addressing, as well as how the system could be purged and primed ready for each start, if a single fuel system were to be used. Could the fuel be generated on-board from the primary fuel or could use be made of the vapours stored in the carbon canister of the evaporative loss system?
References


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(Reference Fuel)
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REFERENCE FUEL (1.44 SER = 9.8 AFR)

Start Temp, °C
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- **COV$_{25}$** - 25 CYCLES FROM 2ND +VE IMEP CYCLE
- **COV$_{50}$** - 50 CYCLES FROM 2ND +VE IMEP CYCLE
- **COV$_{200}$** - 200 CYCLES FROM LAST CYCLE IN COV 50
- **COV$_{SS}$** - LAST 200 CYCLES IN TEST
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WOUlD NOT RUN AT HIGHER RATIOS
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Appendix 1

Fuel Specification

**Reference Fuel** (CEC Legislative Fuel RF-08-A-85)

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<td>- 10% v/v at</td>
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<td>- Saturates</td>
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<td>Data taken from certificate of analysis no. 74706</td>
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**Isopentane**<sup>(89)</sup>

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<td>Net heat of combustion</td>
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### Appendix 2

**Test Engine Details**

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<tr>
<td>Maximum Power:</td>
<td>86.5 kW at 5750 rev/min</td>
</tr>
<tr>
<td>Maximum Torque:</td>
<td>158 Nm at 4500 rev/min</td>
</tr>
<tr>
<td>Torque at 1500 rev/min:</td>
<td>139 Nm</td>
</tr>
<tr>
<td>Displacement:</td>
<td>1796 cc</td>
</tr>
<tr>
<td>Bore:</td>
<td>80.6 mm</td>
</tr>
<tr>
<td>Bore / Stroke ratio:</td>
<td>0.915</td>
</tr>
<tr>
<td>Valvetrain:</td>
<td>DOHC</td>
</tr>
<tr>
<td>Combustion Chamber:</td>
<td>Pent-Roof 4-Valve</td>
</tr>
<tr>
<td>Compression Ratio:</td>
<td>10:1</td>
</tr>
<tr>
<td>Configuration:</td>
<td>4-Cylinder, In-Line</td>
</tr>
<tr>
<td>Fuel System:</td>
<td>Sequential Multipoint Fuel Injection</td>
</tr>
<tr>
<td>Ignition:</td>
<td>Distributorless Programmed Electronic</td>
</tr>
<tr>
<td>Oil:</td>
<td>Esso SAE 10W/30 (Ford AL 3612)</td>
</tr>
<tr>
<td>Spark Plugs:</td>
<td>Motorcraft Platinum AYRF 22PP Gap 1.3 mm</td>
</tr>
</tbody>
</table>
Appendix 3: Test Installation
Appendix 4

Calculation of Cumulative Pressure Rise Due to Combustion

This calculation is based on the method used by Rassweiler and Withrow for determining the mass fraction of the charge burned and is described by Stone et al.\(^{102}\)

The pressure rise during a crank angle interval $\Delta \theta$ is:

$$\Delta p = \Delta p_c + \Delta p_v$$

where $\Delta p_c$ is the pressure change due to combustion and $\Delta p_v$ is the pressure change due to piston motion.

As the engine turns, the crank increments from angle $\theta_{i-1}$ to $\theta_i$:

Now $\Delta p_v = p_{(i-1)} (V_{(i-1)/V_{(i)}}^n - 1)$

and $\Delta p = p_{(i)} \cdot p_{(i-1)}$

$$\therefore p_{(i)} \cdot p_{(i-1)} = \Delta p_c + p_{(i-1)} (V_{(i-1)/V_{(i)}}^n - 1)$$

$$\Delta p_c = p_{(i)} \cdot p_{(i-1)} (V_{(i-1)/V_{(i)}}^n - 1)$$

As combustion does not occur at constant volume it has to be referenced to a common value. In this instance the clearance volume was used, i.e. $V_{360}$.

$$\therefore \Delta p_{c\text{(ref)}} = \Delta p_c \cdot (V_{(i-1)/V_{360}})$$

Therefore the cumulative pressure rise due to combustion:

$$= \sum \Delta p_{c\text{(ref)}}$$

The summation in this instance was made over the period from spark time ($\theta = 340^\circ$) to $\theta = 450^\circ$.

A value of 1.3 was selected for the polytropic index which ensured that the combustion pressure was zero prior to spark time.