An experimental study of exhaust hydrocarbon emissions from a spark ignition engine

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AN EXPERIMENTAL STUDY OF EXHAUST HYDROCARBON EMISSIONS
FROM A SPARK IGNITION ENGINE

by

N. M. M. Lambert

A Masters Thesis
Submitted in Partial Fulfilment of the Requirements
for the Award of
Master of Philosophy of Loughborough University of Technology

May 1986

Supervisor: Professor J.C. Dent, Ph.D., C.Eng.

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SUMMARY

The control of hydrocarbon emissions from spark ignition engines is important and there is a need for a better understanding of the mechanisms contributing to this source of emissions.

The absorption/desorption mechanism is believed to be a significant contributor to hydrocarbon emissions. The aim of the project has been to validate the absorption/desorption model experimentally.

Modelling studies predict that sufficient fuel vapour is absorbed into the cylinder wall oil film on the compression and early firing strokes with subsequent desorption late in the expansion stroke to seriously affect hydrocarbon emissions in the exhaust, as temperatures are too low for adequate oxidation.

The experimental investigation which follows develops a method to allow accurate measurement of hydrocarbon specie levels in the exhaust of a spark ignition engine. The object of the experiment was to detect and measure differences in hydrocarbon levels for two fuels, Iso-octane and Iso-pentane, at identical engine conditions and therefore establish whether the absorption/desorption effect is significant to hydrocarbon emissions. The theory behind this relies upon the varying solubilities of both fuels in a given oil with temperature which should reflect a varying base fuel hydrocarbon emissions level for each fuel if absorption/desorption is in fact taking place.

Samples of exhaust were taken from a Ricardo-hydra test engine and analysed chromatographically. Experimental results (which compare favourably with prediction from modelling studies) indicate about 30
percent of total hydrocarbons are due to the absorption/desorption mechanism.

In conclusion, the results suggest that the solubility of the fuel in the engine oil has a significant effect on hydrocarbon levels in the exhaust.
ACKNOWLEDGEMENTS

I would like to thank my research supervisor, Professor J.C. Dent, for his advice and guidance throughout the course of this work.

My thanks are also expressed to the technician staff of the Mechanical Engineering Department with special thanks to Mr. G. Manship, Mr. S. Line and Mr. S. Taylor who struggled to build equipment with limited resources.

I wish to express my sincere thanks to colleagues and friends whose assistance has helped the completion of this thesis.

Appreciation is also due to the Shell Oil Company and the Chemical Engineering Department of Loughborough University of Technology for the loan of equipment vital to this project.

Finally I must acknowledge the financial help of the Ford Motor Company who have made this research possible.
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CHAPTER 1

LITERATURE SURVEY
CHAPTER 1

LITERATURE SURVEY

Introduction

The gasoline engine is a major source of air pollutants and the problem has been tackled so that emissions are minimised in both the cylinder and subsequently through suitable after treatment of the exhaust gases.

The three independent sources of air pollutants include:

(1) Crankcase blowby
(2) Evaporative emissions
(3) Exhaust emissions

This report is concerned only with the third case and specifically with unburned exhaust hydrocarbons.

It is now generally accepted that the main sources of unburned hydrocarbons from spark ignition engines are:

(1) Flame quenching at the walls of a combustion chamber.
(2) Unburned fuel in the various trapped volumes inside the combustion chamber (ie. top piston land, around spark plug and ring crevices).
(3) Gas phase quenching when the engine is running under extreme conditions of stoichiometry.

(4). Absorption/desorption in the cylinder lubricating oil films and surface deposits

The first three are fairly well understood and documented[1-9],[13],[15],[21]. The absorption/desorption process being a relatively new concept very little literature has been published. Combustion test data[23],[24],[27],[28] and mathematical modelling[10],[26] suggest the possibility of the absorption/desorption mechanism being a significant source of unburned hydrocarbons. Consequently the need for a representative experimental method to support the theoretical evidence.

Discussion of the various investigations which follow will be focussed mainly on the absorption/desorption source and so most literature cited will be confined to this area.
1.1 The Effect of Quench Layers and Crevices On Hydrocarbon Emissions

Quench layers are believed to be regions of unburned fuel, close to the walls of the combustion chamber, owing to the flame quenching short of the combustion wall. Crevices or trapped volumes can be defined as any volume into which the flame cannot propagate.

Lorusso et al[1] used a gas sampling valve in the combustion wall of a spark ignition engine to sample hydrocarbons near the wall over a wide range of engine operating conditions. Experimental results suggested that quench layer hydrocarbons contributed no more than 3 - 12 percent of the total hydrocarbons observed in the exhaust and therefore indicated that the other sources :- ring-crevice storage, absorption-desorption and surface deposits were more important. Figure(1.1) shows volumetric concentration in parts per million (ppm) at the cylinder wall for various hydrocarbon species at different crank angles. It can be seen that there is a low level of quench layer hydrocarbons at 40 degrees crank angle which represents the actual contribution due to quench layers. The rising portion of the hydrocarbon concentrations after 40 degrees is believed to result from convection of unburned material into the sampling zone from sources other than wall quenching(i.e., ring crevices, oil films, etc).

Recent combustion bomb experiments by Adamczyk et al[2] have supported the theoretical results of Westbrook et al [3] showing that wall quench hydrocarbons are extensively burned after the time of flame quenching at the walls. Furthermore, the exhaust hydrocarbons under stoichiometric conditions are shown to be 95 percent fuel molecules with few product gases present, indicating little exposure to high temperature oxidation processes. Adamczyk et al[2] also demonstrated the significance of crevices as a source of hydrocarbons but conclude that with rich mixtures(equivalence ratio of 1.4) and for a clean vessel, storage volumes and wall- quenching cannot account wholly for all the exhaust hydrocarbons.
Daniel and Wentworth[4] presented evidence to show that wall quenching is the fundamental source of exhaust hydrocarbon emissions from a spark ignition engine, but further work[5] since then has pointed to the existence of a special case of the quench phenomenon which is now understood as the "crevice effect". Wentworth[5] showed that by using the sealed ring-orifice(SR-O) design which minimised the crevice effect, exhaust hydrocarbon concentrations were reduced significantly. In the SR-O design the piston and top compression ring in an engine are modified to virtually eliminate the crevice between the top land and the cylinder wall, and at the same time, seal the combustion chamber at the top compression ring. Wentworth[6] gives extensive details of the SR-O design. Experiments by Wentworth[5] with a single cylinder engine showed that small crevices formed by the piston, bore and top compression ring were responsible for at least half of the exhaust hydrocarbon emissions in a clean engine for most conditions of speed and load. Further work by Wentworth[6] confirmed the importance of the piston crevice volume effect on exhaust hydrocarbon emissions. Experiments were carried out using a revised design of spark ignition engine piston having a much narrower top land and reduced hydrocarbon levels by about 50 percent on the production design. These results demonstrated the sizeable reductions in exhaust hydrocarbon emission that are possible when the piston-bore-ring crevice volume is essentially eliminated.

Daniel[7] analytically modelled the effect of engine variables on exhaust hydrocarbon emissions to compare quench layer and crevice volume sources. The data, Figures(1.2) & (1.3), indicate that crevice volume sources produce much greater changes in unburned hydrocarbons than quench layer sources for all engine variables considered. This lends further weight to the belief that quench layers are an insignificant source to exhaust hydrocarbons.

Weiss and Keck[8] carried out a time resolved study of the unburned hydrocarbons in the cylinder of a spark ignition engine and considered just two sources of hydrocarbons: quench layers and
crevice volumes. For the purposes of comparison samples of hydrocarbons were collected from both the cylinder, using a needle valve, and the exhaust. Models were developed for predicting hydrocarbons from both quench layers and crevice volumes. The data presented concluded, that of the two sources considered crevice volumes were the only significant contributor to exhaust hydrocarbons. Quench layer hydrocarbons mixing with the burned gas were shown to be completely oxidised due to the sufficiently high temperatures prior to blowdown.

Single-Pulse sampling valve measurements of wall layer hydrocarbons in a combustion bomb by Adamczyk et al[9], have shown that less than 10 percent of tail pipe emissions can be attributed to the quenching process. Propane and air were used as the fuel and oxidiser with a fuel/air equivalence ratio of 0.9. The sharp drop in propane concentration coupled with the sharp rise in propane oxidation products supports the theory that the flame quenches short of the combustion wall. Residual Propane in the wall quench layer is free to diffuse into the hot bulk gas forming intermediate products which are then consumed about 4 milliseconds after flame arrival.

The results, Figure(1.4), show how the Propane concentration changes with distance from the wall, where increasing the sampled mass(which is effectively sampling at an increasing distance from the wall) causes hydrocarbons to diminish. For a short time after flame arrival, up to about 200 milliseconds, the decrease in Propane concentration with increasing distance from the chamber wall is quite marked. However at about 400 milliseconds there is only a relatively small change in concentration with distance from the wall. This higher Propane concentration - above exhaust concentration - could be attributed to material diffusing into the wall region from a source such as a crevice or even desorption from an oil layer. The measurements suggest that the adjustment of hydrocarbon level in the quench layer could be controlled by crevice volumes. It is also indicated that a fraction of the exhaust background hydrocarbon level may arise from a residual of the quenching process. Moreover through
measurement of the hydrocarbon concentration of the residual gases. Daniel and Wentworth[4] established that a significant proportion of the quench zone hydrocarbons may be recycled within the engine.
1.2 The Effect of Engine Variables On Hydrocarbon Emissions

The effects of engine variables on exhaust hydrocarbons have been investigated both through mathematical modelling[10],[7] and experiments[11],[12]. Lavoie et al[13] analysed these effects through modelling and experimental methods in terms of ring crevice and wall quench hydrocarbon contributions. Predicted and experimental data compared well for hydrocarbons versus indicated specific fuel consumption, indicated mean effective pressure, compression ratio and exhaust gas recirculation (EGR) but poor correlation was shown for hydrocarbons versus coolant temperature, engine speed and equivalence ratio (rich). Owing to the discrepancies between the models and experiment it was concluded that further work was necessary to elucidate the processes of wall quenching, ring crevice storage and blowby effects.

A single cylinder engine study was carried out by Wentworth[14] (using a sealed ring - orifice piston[6] as described earlier) to quantify the effect of combustion chamber surface temperature on exhaust hydrocarbon concentration. Figure(1.5) shows the relationship between exhaust hydrocarbon emissions and cylinder surface temperature. Simultaneous measurements of combustion chamber surface temperatures and exhaust hydrocarbon concentrations in a single cylinder spark ignition engine showed that about 43 percent of the drop in hydrocarbon level was due to increased surface temperature. After considering the way in which other engine variables (such as pressure, engine speed, turbulence etc.) may affect the hydrocarbon level no satisfactory explanation was found for the other 57 percent drop.

Engine variable effects on exhaust hydrocarbon composition were investigated by Daniel[11] using a single cylinder engine with Propane as the fuel. It was found that an engine variable effect observed at one air-fuel ratio, ignition timing combination was not
necessarily directionally the same as that observed at another air-fuel ratio, ignition timing combination. The data showed that:

(1) the minimum total hydrocarbon concentration was obtained at a lean air-fuel ratio

(2) retarding the timing reduced the total hydrocarbons

(3) increasing engine speed reduced hydrocarbons generally

(4) increasing the compression ratio increased the total hydrocarbons

(5) increasing the exhaust back pressure decreased the total hydrocarbons

(6) increasing the temperature decreased the total hydrocarbons

Figures (1.6) - (1.12) clearly indicate the above effects.

For all engine variables the concentration of Propane found in the exhaust behaved in the same way, directionally, as the total hydrocarbon concentration. However Daniel's experiments failed to show the relative importance of the engine variables which affect both the amount and composition of the exhaust hydrocarbons. Additionally the data did not indicate how fuel and non fuel hydrocarbons may be affected differently by changes in the proportion of total hydrocarbons exhausted.

Namazian and Heywood[15], using a single cylinder square piston engine, demonstrated that unburned hydrocarbons bleeding out of the top ring gap can affect exhaust hydrocarbon emissions and that the location of the ring gap with respect to the spark plug and exhaust valve is important. The square-cross-section engine was fitted with two parallel quartz glass walls which permitted optical access to the entire cylinder volume. In this way gas flow into and away from the top ring gap could be photographed and details of the flow examined
closely. The test results showed that for the spark plug located near the exhaust valve, placing the top ring gap 90 degrees away produced lowest emissions. A gap too close to the exhaust provides an easy path for trapped hydrocarbons to exit. Placing the gap 180 degrees away maximised hydrocarbons. In general, the closer the plug was to the exhaust valve the lower were the hydrocarbon emissions. The authors[15] believed that this may have been because of the greater residence time for hydrocarbon burn-up and the selective exhausting process of the cylinder. Lowest emissions were obtained with dual ignition, and ring gap position had little effect in that case. Experiment therefore confirmed that crevice gases constitute a major source of unburned hydrocarbon emissions as well as a significant loss in power and efficiency.
1.3 The Effect of Fuel Composition on Exhaust Hydrocarbons

Dishart and Harris[16] conducted exhaust emission measurements using gasolines of varying aromatic and olefin content in a variety of vehicle types and concluded that no significant changes in total hydrocarbons in the exhaust would result from changes in gasoline hydrocarbon composition. In contrast R.D. Fleming[17] later found that fuel composition does affect exhaust emissions from a spark ignition engine. In the investigation[17] a single cylinder research engine was run on three pure hydrocarbons found primarily in commercial fuels, namely a paraffin(2,2,4-trimethylpentane), an olefin(2,4,4-trimethylpentene-2) and an aromatic(metaxylene). The exhaust samples were analysed for carbon monoxide, carbon dioxide, hydrogen, nitrogen oxides, aldehydes and hydrocarbons. A detailed study was made on the post combustion reactions for each fuel from the analysis of the exhaust products.

Amongst the three fuels which Fleming[17] assessed, it was found that the paraffin fuel gave the highest total hydrocarbons in the exhaust while the aromatic produced the highest base fuel hydrocarbon level in the exhaust. Infact for the same conditions the base fuel level for the aromatic was three times that for the paraffin. This was expected since the ring structure of aromatics is quite stable producing less decomposition than for the case of the paraffin. From this Fleming concluded that as aromatic content in fuel is increased, the hydrocarbon mole fraction of aromatic in the exhaust that represents unburned fuel increases.

An explanation for the discrepancy between Dishart and Harris and Fleming's conclusions may be offered in terms of the fuel blends used in the experiments. Dishart and Harris used complex fuel blends made up of various hydrocarbons while Fleming kept to single component fuels and simple two component mixtures of pure hydrocarbons. It is therefore theorized that any isolated component effect on emissions, in a complex fuel blend, is likely to be masked by effects from the
other components within that blend. For this reason it is suggested that Fleming's method of investigating each component's effect on hydrocarbons in isolation is the most practical method of assessment rather than the global method adopted by Dishart and Harris.
1.4 Deposit Formation - Its Effect Upon Hydrocarbons

Published experimental data on deposit formation as a source of exhaust hydrocarbons is scarce. Although combustion chamber deposits are known to increase exhaust hydrocarbon emissions the relative contributions of deposits from various parts of the chamber still requires further investigation. Wentworth[18] performed experiments to assess the significance of wall deposits on exhaust hydrocarbons at various locations in an engine. It was found that deposits exhibit a location effect and therefore contribute different increments to exhaust hydrocarbon concentration.

Data[18] was collected for deposits at various locations in the chamber and indicated that the average hydrocarbon concentration increase, 25 ppm, was more than 10 times the smallest increase, proving that deposit location has considerable influence on the contribution that deposits make to exhaust hydrocarbon concentration. Generally it was found that deposits in the vicinity of the exhaust valve produced greater hydrocarbon increases than for any other location in the combustion chamber. The reason for this was assumed to be due to the direction of swirl induced by the intake charging process, so that hydrocarbons clinging to the wall surfaces somewhat "upwind" of the exhaust valve would most likely be exhausted.

It is stressed that deposits are not the only source of hydrocarbon emission which might exhibit location effects. Hydrocarbons originating at different portions of clean wall surfaces, as well as hydrocarbons originating in different portions of crevice, may contribute different increments to exhaust hydrocarbon concentration because of their particular location in the combustion chamber. Jackson et al[19] also studied the effect of combustion chamber wall deposits on exhaust hydrocarbons experimentally and concluded that the accumulation of deposits in both a single cylinder and multi-cylinder engine, Figure(1.13), caused a significant increase in
exhaust hydrocarbon content. Therefore it appears that engine deposit condition is an important factor which cannot be neglected in making long term comparative tests or in establishing absolute levels of exhaust hydrocarbon emission from engines.
1.5 The Effect of Oil Layers on Hydrocarbon Emissions

There is increasing evidence to suggest that cylinder oil layers in spark ignition engines could be a significant source of exhaust hydrocarbons.

Haskell and Legate[20] first theorized that the effect of oil on exhaust hydrocarbon concentration could be due to momentary absorption of fuel vapour into the oil film coating the combustion chamber wall. Moreover, it was suggested that the decrease in hydrocarbon concentration resulting from increased coolant temperature[14] was due to decreasing solubility of fuel in the oil film. The effect of the absorption/desorption phenomenon on exhaust hydrocarbons was extensively modelled by Dent and Lakshminarayanan[10] and compared with existing experimental data. The predictions of the model compared favourably with engine experiments(Lavoie et al [13] and Lavoie and Blumberg[21]) for different engine variables apart from exhaust gas recirculation(EGR).

In contrast the predicted data presented by Lavoie et al[13] generally fell short of the experimental data for hydrocarbons versus coolant temperature, engine speed and rich equivalence ratios. The absorption/desorption mechanism assessed in Reference [10] has essentially accounted for these discrepancies between experiment and model. Dent and Lakshminarayanan[10] conclude that the two major sources of hydrocarbon formation are crevice volumes and cyclic absorption/desorption. The process of absorption and desorption of fuel vapour into the oil film layer is illustrated diagrammatically in Figure(1.14). It has been theorized that transfer of fuel vapour across the oil film layer is by molecular diffusion and a linear concentration gradient in the oil has been assumed. An effective penetration depth, the controlling factor of this mechanism, has also been assumed. It is dependent upon the following parameters:

(1) The fuel/oil combination (ie., the Henry Constant for the
particular combination will affect the solubility of the fuel in the oil and so affect the amount of absorption taking place).

(2) Engine speed (ie., Since fuel/oil absorption and desorption is time dependent engine speed will be inversely proportional to the penetration depth).

(3) Engine load (ie., The rate at which fuel is transferred into the oil is controlled by cylinder pressure. The higher the cylinder pressure the greater the absorption rate).

(4) Coolant temperature (The Henry Constant of the fuel in the oil falls - while solubility increases - with increasing coolant temperature. This results in less absorption of fuel into the oil).

All the variables discussed above have been shown to effect the level of hydrocarbon emissions in the exhaust[10],[13],[11].

The effect of varying wall temperature on hydrocarbon emissions, Figure(1.15), is primarily due to variation of Henry Constant and variation of oil viscosity with temperature. In addition increasing wall temperature reduces gas density in the trapped volumes and so decreases crevice mass contribution to hydrocarbon emissions. The importance of absorption/desorption as a significant source of hydrocarbons is compared to ring crevice contribution. Experimental data[13] are also shown in the figure for comparison. It is evident that for relatively high coolant temperatures, such as 360 K and above, the model proposes that the absorption/desorption mechanism accounts for at least 50 percent of the total hydrocarbons in the exhaust.

Figure(1.16) indicates the instantaneous level of hydrocarbons in the oil layer with crank angle for the first engine cycle. Early in the induction stroke, when cylinder pressure is sub-atmospheric, a low
level of hydrocarbons (fuel vapour) are found dissolved in the oil layers. This hydrocarbon level increases with the compression and expansion strokes reaching a maximum shortly after top dead centre (TDC) where cylinder pressure is also at a maximum. This level diminishes as cylinder pressure falls finally reaching a minimum at the end of the exhaust stroke. The trend with cylinder pressure is to be expected since absorption and desorption are related directly to the Henry Constant and the mass transfer conductance[10]. The quantity of fuel vapour remaining in the oil at the end of the cycle is dependent upon the period of the cycle (ie., engine speed) and the thickness of the oil film. This residual of fuel at the end of the first cycle forms the initial condition for the next cycle which generates a slightly greater fuel residual and for subsequent cycles there is a build up of fuel mass in the oil film, Figure(1.1), until an equilibrium state is reached where absorption/desorption fluctuates about a steady periodic level. Also shown, Figure(1.1), is the variation of net hydrocarbons desorbed after oxidation with crank angle which demonstrates the cyclic nature of the mechanism. It is seen that desorption starts about 90 degrees after top dead centre (ATDC) on the expansion stroke and increases rapidly to reach a maximum at about BDC. This behaviour is due to three factors. Firstly the oil film temperatures are below 1100 degrees K and therefore oxidation of the desorbed hydrocarbons is negligible. Secondly, the surface area for desorption increases as the expansion proceeds, and finally the decrease in cylinder pressure during expansion causes an increase in the Henry Number which results in an increased desorption rate. Beyond bottom dead centre during the exhaust stroke desorbed hydrocarbons decrease because of the reducing surface area for desorption.

The model[10] discussed above has two limitations. Firstly it assumes a uniform oil film thickness on the cylinder wall surface. Oil film thickness on the piston ring has been measured during an engine run by Keiichiro Shin et al[22] and it was found that with standard ring arrangements the thickness of oil formed on the top ring was appreciably smaller than the theoretical value. This was attributable
to the inadequate supply of lubricating oil to the ring. Therefore
since the absorption/desorption mechanism is dependent on oil film
thickness\cite{23,24} the magnitude of this effect predicted by the
model\cite{10} would be lower in value (i.e. less than the 50 percent
indicated). Secondly the engine lubricant was assumed to be squalane
since data was readily available for Henry Constants for various
paraffins dissolved in squalane over a range of temperatures\cite{25}. n-
Octane was used as the fuel and its Henry Constant in squalane found
by extrapolation of data given by Chappelow \& Prausnitz\cite{25}. It was
accepted that the process of extrapolation is prone to error and that
the use of n-Octane as the fuel instead of Iso-octane (which is more
representative of commercial fuel) could introduce error due to their
differing solubilities.

Carrier et al\cite{26} also investigated this cyclic effect of the
absorption/desorption mechanism by theoretical modelling. The model
was intended to approximate duplicate the hydrocarbon
absorption/desorption effect in the oil film layer on the cylinder
wall of a reciprocating piston engine. It was found to be consistent
with experimental data\cite{11,13,21} demonstrating the
absorption/desorption effect on hydrocarbons, which decrease with
increasing engine speed, as shown in Figures\\(1.18\) \& \(1.20\). It is
also indicated that first cycle absorption (Figure\(1.19\)) is greater
than the absorption/desorption of a steady periodic
level (Figures\(1.18\) \& \(1.20\)). At the same time it was shown that
first cycle desorption was less than the absorption/desorption of a
steady periodic level.

The model\cite{26} revealed that solubility increases with pressure in the
cylinder. Although the model had considered the reciprocating nature
of the piston engine it had ignored flow within the oil film, the
combustion event was taken as instantaneous and the variability of
Henry's Constant with pressure was also ignored. The model was
concerned with total hydrocarbons rather than the discrete
components, so no predictions could be made on how the various
hydrocarbon specie were being affected.
The effect of oil layers on hydrocarbon emissions has been investigated by Kaiser et al [23]. Measured amounts of oil were placed on the piston of a CFR engine fuelled on Propane, and Iso-octane. It was evident(Figure(1.21)) that when fuelled on Iso-octane, measured quantities of oil added to the engine cylinder produced proportional increases of the base fuel in the exhaust hydrocarbons. When the engine was fuelled on Propane, base fuel concentration in the exhaust hydrocarbons was significantly lower than in the Iso-octane case. In fact in the Propane fuelled case the hydrocarbon distribution was essentially constant with or without oil added, indicating that burning up of the oil itself was not contributing to the higher base fuel hydrocarbon level when running on Iso-octane.

It was found by Kaiser et al[23] that the exhaust hydrocarbons (base fuel) increased with increase in the volume of oil deposited on the piston. The temperature dependence of fuel/oil solubility was also demonstrated, higher temperatures producing lower levels of base fuel hydrocarbons. The effect of oil temperature on solubility and diffusion rate of the fuel in the oil was not assessed because of unknown surface temperatures and loss of oil from the cylinder. However it was concluded that the principle source of increase in hydrocarbon concentration was the dissolving of the fuel into the oil layer during compression, with subsequent release into cooling burned gas during the expansion stroke.

Adamczyk and Kach [24] studied the problems of absorption/desorption using low solubility oils. A combustion bomb was used to show how hydrocarbon emissions vary with 5 different oils in ascending order of Henry Constant (squalane, a synthetic motor oil, a petroleum-based motor oil, a polypropylene oxide oil and a polypropylene-polyethylene oxide copolymer oil) in combination with 3 different fuels (Ethane, Propane and Butane). Glycerol of higher Henry Constant than the oils was also studied with Propane as the fuel. The experimental results showed that hydrocarbon emissions varied in direct proportion to the quantity of oil present in the bomb, to the initial fuel.
concentration and to the solubility of the specific fuel in the oil layer (Figures 1.22 & 1.23). Not surprisingly, increasing the wall temperature decreased the hydrocarbon emission. In conclusion the results indicated that the oil layers do significantly increase the hydrocarbon emission and that this increase is extremely dependent on the specific fuel/oil combination. The primary hydrocarbon emission from the exhaust was found to be unreacted fuel.

Kaiser et al [27] demonstrated the effect of oil layers on the hydrocarbon emissions generated during closed vessel combustion. This was done by analysing, chromatographically, the exhaust gas from a combustion bomb generated with and without the presence of oil. Five fuels (Methane, Ethane, Propane, n-Butane and Hydrogen) and three oils (a synthetic motor oil, a petroleum based motor oil and a diffusion pump fluid) were used at a variety of fuel/air equivalence ratios. The results showed that for an equivalence ratio of 0.9, the higher the carbon number of the fuel the greater the hydrocarbon emissions (i.e. hydrocarbons of higher molecular weight are more soluble in oil than those of lower molecular weight).

Figure 1.24 illustrates this effect clearly. The experiments indicated that the exhaust hydrocarbon concentration was made up of at least 95 percent of base fuel at fuel lean conditions and was proportional to the amount of oil in the bomb and the solubility of the specific fuel in the oil. However for rich conditions, equivalence ratio greater than one, hydrocarbon emissions were very much greater and made up of less than 1 percent of base fuel. The reason for this was shown to be due to degradation of the oil into lighter hydrocarbons which was dependent on equivalence ratio and fuel type. From the data it was evident that both crevice volumes and the absorption/desorption mechanism play an important part in exhaust emission generation and that post desorption oxidation is minimal.

A further combustion bomb study of fuel-oil solubility and hydrocarbon emissions from oil layers was carried out by Adamczyk and Kach [28]. The bomb study estimated the solubility of four fuels
Methane, Ethane, Propane and n-Butane) in squalane over a range of temperatures (298 K - 382 K). All experiments were performed at a fuel-lean equivalence ratio of 0.9. It was shown, Figure(1.25), that hydrocarbons vary inversely with Henry Constant over an order of two magnitude change in the value of Henry Constant. This trend is to be expected since solubility varies inversely to Henry Constant. Methane with the greatest Henry Constant is the least soluble of all the fuels and n-Butane possessing the lowest Henry Constant is the most soluble of the four fuels tested. Note that, although the data for n-Butane at room temperature (the unfilled diamond shaped points) do not lie on a straight line through the other data, the difference between the straight line and this data was believed to indicate an inconsistency in the value for Henry Constant for n-Butane in Squalane reported by Chappelow & Prausnitz[25]. Appropriate extrapolation of this data[25] for a room temperature condition yielded a new value of Henry Constant for n-Butane giving the flagged points in Figure(1.25) which lie directly on the plotted data line. It has been demonstrated that the absorption/desorption of fuels into oil layers can occur on engine time scales and can significantly increase the hydrocarbon emission from a homogeneous charge engine. The results indicated that the magnitude of the exhaust hydrocarbon emissions from a non-degrading oil layer during clean combustion are directly related to the solubility of the fuel in the oil. However the study did not show the direct relationship between the magnitude of the oil layer hydrocarbon emissions and fuel-oil solubility.
Expand plot of hydrocarbon species, CO₂, CO, and O₂ concentrations measured near the time of flame arrival at the sampling valve location for $\phi = 0.9$, baseline engine conditions. Species concentrations are plotted versus the time after flame arrival, $\Delta t$ and crank angle degrees ATDC. Sample mass per cycle, $\Delta m = 7.6 \times 10^{-6}$ g. Symbols with downward arrow represent values at or below the detection limit.

Ref. [1]
Variations in unburned propane due to flame quenching with engine variable changes

Variations in unburned propane due to chamber crevices with engine variable changes

Ref. [7]
Propane Concentration as a Function of Sampled Mass at 15, 80, 170 and 400 msec after peak pressure. [Ref. 9]
The effect of average surface temperature on exhaust hydrocarbon concentration-varying coolant temperature [Ref. 14]
Effect of air-fuel ratio on total hydrocarbon concentration

Fig. 1-6
TOTAL CARBON - PPM C₆

Effect of ignition timing on total hydrocarbon concentration

Fig. 1-7
TOTAL CARBON - PPM C₆

Effect of engine speed on total hydrocarbon concentration

Fig. 1-8

Effect of air-flow rate on total hydrocarbon composition

Fig. 1-9

Ref. [11]
Fig. 1·10

Effect of compression ratio on total hydrocarbon concentration

Fig. 1·11

Effect of exhaust back pressure on total hydrocarbon concentration

Fig. 1·12

Effect of coolant temperature on total hydrocarbon concentration

Ref. [11]
The Effect of combustion chamber deposit accumulation on exhaust hydrocarbon concentration

[Multi-cylinder engine]

Ref. [19]

Fig. 1.13
TEMPERATURE AND CONCENTRATION GRADIENTS WITHIN THE ENGINE

Ref. [10]
CALCULATED AVERAGE WALL TEMPERATURE (°K)

TEST CONDITIONS
ENGINE SPEED: 1250 RPM
LOAD: 380 kPa (IMEP)
SPARK: 20° BTDC
Φ: 0.9
SHROUDED VALVE
FUEL: ISO-Octane

EFFECT OF COOLANT TEMPERATURE ON HC EMISSIONS
Ref. [10]
Figure 1.16: Fuel content of oil layers variation with crank angle. Ref. [10]

Figure 1.17: Stabilisation of fuel quantity in oil layers at 300°C coolant temperature. Ref. [10]
$0.8(7/2) < T_1 < 1.2(7/2)$ for several values of $T$ (corresponding to $n = 1000, 2000, 3000, 4000$ rpm)

the value of $\Delta f$ is presented as a function of $T_1$, where $\Delta f$ is the total amount of gas taken into the liquid over the entire absorption portion of a steady periodic cycle (or, equivalently, the total amount of gas discharged from the liquid over the entire desorption portion of the cycle).

For fixed values of $T_1$ examined, the $(\Delta f)_{\text{absorption}}$ of the first cycle exceeds $(\Delta f)$ of steady periodic operation.

Fig. 1.18

$[T \text{ IS PERIODIC TIME OF CYCLE}]$

$T \propto \frac{1}{\text{ENGINE SPEED}}$

Fig. 1.19

$0.8(7/2) < T_1 < 1.2(7/2)$ for the same value of $T$ adopted in Fig. 1.18, the value of $\Delta f$ is presented as a function of $T_1$, where $(\Delta f)_{\text{absorption}}$ is the total amount of gas discharged from the liquid over the entire desorption portion of the first cycle. For fixed values of the $T_1$, $T_1$ examined, the $(\Delta f)_{\text{absorption}}$ of the first cycle is smaller than $(\Delta f)$ of steady periodic operation.

Fig. 1.20

Ref. [26]
Exhaust hydrocarbon concentration as a function of time after the engine begins to fire (\(T_{\text{coolant}} = 320^\circ K\)). The amount of oil (a synthetic motor oil of SAE grade 5W20) added to the engine cylinder is noted on each curve. Data are presented for propane and isooctane fuels.

Ref. [23]
Hydrocarbon emissions as a function of the weight of oil present in the reactor for five oils and glycerol.

**Fig. 1.22**

Increase in the % of initial fuel remaining in the burned gas caused by the addition of 0.21 gm of each oil. Data were obtained with ethane, propane and butane as fuels.

**Fig. 1.23** [H_f is Henry Constant for fuel in squalane]

Ref. [24]
Increase in the percentage of initial fuel remaining in the burned gas caused by addition of 0.14 gm of oil A to the plate as a function of Henry's Constant (H_r) relative to that of n-butane dissolved in squalane (H_{n-butane}/H_r). The data were obtained using \( \phi = 0.9 \) fuel-air mixtures of ethane, propane, or n-butane ignited at 300 kPa.

Ref. [27]
Increase in the percentage of initial fuel remaining in the burned gas caused by the addition of 0.21 g of squalane to the reactor as a function of Henry's constant from Reference [28]. The data were obtained for $\phi = 0.9$ fuel-air mixtures of methane, ethane, propane and $n$-butane from 24.7 C to 109 C.
CHAPTER 2

EXPERIMENTAL METHOD
CHAPTER 2

EXPERIMENTAL METHOD

2.1 Introductory Account

The design of the experiment including the development of a suitable gas chromatographic technique accounted for the major expenditure of effort in the project. The final experimental method decided upon was arrived at through a combination of previous experimental work[8],[11],[17],[27] and trial and error.

Since information available on this type of work was limited various methods were tried before arriving at a satisfactory solution. However only the method adopted is discussed here.

A Ricardo Hydra single cylinder engine with a fuel injected, twin cam cylinder head was used to generate the exhaust gas required. Fuel injection with intake air heating was employed to provide a homogeneous air/vapour charge to the engine. For fixed engine conditions exhaust samples were collected in a heated, semi-evacuated, 5 litre flask. During the collection period the flask pressure increased from about 160 mmHg at 195 degrees C to about atmospheric pressure at a slightly increased temperature of about 200 degrees C. The hot exhaust gases entering the flask were responsible for this slight increase in temperature.

An internal standard, normal-Hexane(approximately 100 milligrams) was added to the flask, by syringe injection, which was then pressurised to about 1300 mmHg with nitrogen, and the mixture then allowed to settle for approximately 2 hours. About 6 samples from the flask were then passed via a heated sample line through the chromatograph and indications of specie concentration were given on an electronic 3390 A Hewlett Packard integrator[4.5]. These results were then passed to a computer which gave the various hydrocarbon specie concentrations
in PPM C and PPM Hexane. For details see Appendix(F).

For set conditions, Appendix(A), the engine was run on two fuels of differing molecular weight namely, Iso-pentane of molecular weight 72 and Iso-octane of molecular weight 114. The results of the specie PPM C counts for the two fuels was then compared and conclusions drawn. These results are discussed in Chapter[5].

An exhaust gas analyser[4,6] from the Analytical Development Company was used for measuring air/fuel ratio from the engine by the use of Spindt's method [29] although a measured method, Appendix(E), using the Alcock airflow meter[4,2] and fuel burette was also employed to act as a check. To ensure the same percentage excess air was present for both the fuels all tests were run at the same equivalence ratio.
2.2 A Typical Engine Test

When changing fuels, the engine was allowed to run on the new fuel for about ten minutes purging the old fuel from the system. On completion of this run the oil was changed and the engine was run once again (for about ten minutes) on the new fuel before an actual test was carried out. This ensured that the engine and system were thoroughly purged of any traces of the old fuel.

When running on Iso-pentane the fuel pump was cooled in a refrigerated water bath to inhibit vapour lock (i.e. Iso-pentane has a low vapour pressure). Since the inlet air was heated to about 38 degrees C the adverse effect of lower fuel temperature on fuel/air mixing was adequately compensated for.

The gas analyser[4.6] was allowed at least 1 hour to warm up and stabilise. This allowed the heated pump and lines feeding the hydrocarbon analyser to reach a steady temperature and also ensured that the flame ionisation detector in the hydrocarbon analyser was producing a steady base signal. This was important since the air/fuel ratio could have been adversely affected. All analysers (CO2, CO, O2 and hydrocarbon [4.6]) were then calibrated using standard gas mixtures. The oil and water heaters for the engine were switched on and the thermostats adjusted to the planned running temperatures. However since the heaters were of limited capacity it was not always possible to reach these planned running temperatures before starting the engine.

The 5 litre flask was purged with air for about half an hour and repeatedly evacuated and filled with nitrogen until all traces of contaminant were removed. Finally the flask was evacuated to a pressure of about 160 mmHG leaving it ready to accept an engine sample. The evacuated pressure was recorded. However after purging, a sample from the flask was always run through the chromatograph at low attenuation to check the purity level. This is the flask hydrocarbon
base level as shown in Figures(2.2) & (2.3). The flask was only evacuated ready for an engine sample when the level of impurity was acceptable. This level was normally set at about 20 area counts but higher levels were sometimes tolerated, about 100 area counts[4.5], where peaks appeared well away from those of interest. In other words it was ensured that the retention times of the impurity peaks did not overlap or coincide with the peaks of interest in an engine sample.

The fuel pump (pump pressure set to 30 psi) and electronic ignition were then switched on, the ignition timing manually set to about 12 degrees BTDC and the fuelling( ie. quantity of fuel fed to injectors) set, from a potentiometer, to give a rich mixture on start up. Throttle and speed control potentiometers were adjusted to minimum position and when the dynamometer ready light illuminated, the engine was ready to be started.

The dynamometer used to motor the engine applies load only when the speed has exceeded approximately 550 RPM. When this state has been reached the engine speed, load, ignition timing and fuelling were all adjusted together to bring the engine to its set operating conditions. The air temperature was thermostatically controlled by a heater in the inlet to the induction system but to avoid damage to the element was not turned on until the engine was running. However for the 1000 rpm tests, Appendix(A), the engine was motored with the air heater on for at least 10 minutes before each test. The reason for this was to prevent possible fuel condensate developing on the cylinder walls which would quickly go into solution with the oil consequently masking the absorption/desorption effect during steady state running. During normal engine running the air heater compensated for any air temperature fluctuations in the test cell.

The speed,1000/2000 RPM, was set and held steady, to within 3 RPM, by a throttle feedback control system while the required load, 14.3/19 NM, was applied by the dynamometer to the engine. The load varied(up to 2 NM for the 19 NM case) according to the engine coolant
temperature and the fuel type. It was found that when running at 1000 RPM, Appendix(A), the load of approximately 14 NM, could be kept to within 0.1 NM for varying coolant temperature (90 – 200 degrees F) with the slight penalty of about 5 percent fluctuation in the airflow to the engine as compared with 3 percent for the 2000 RPM case. The air/fuel ratio was checked continually by monitoring the levels of oxygen, carbon monoxide, carbon dioxide and hydrocarbons from the gas analyser and the airflow from the Alcock flow meter. Adjustments were made at the fuelling potentiometer followed by further adjustment of the throttle potentiometer to compensate for the change in airflow which normally accompanied any change in the fuelling. Sometimes it was necessary to repeat this procedure to maintain the planned running conditions. A measured method was finally used to give an estimate of air/fuel ratio. This was done by recording the time taken to use a fixed volume of fuel from the fuel burette, Figure(4.5), and recording the manometer reading on the airflow meter. However this figure was usually lower (ie. richer) than that from the analyser, usually by about a quarter of an air/fuel ratio. This discrepancy was accounted for in terms of air leakage into the inlet manifold bypassing the air flow meter in the measured method. For this reason the analyser figure was always taken as the more accurate. Calculations for Spindt's[29] and the measured method are given in the program listing, Appendix (E).

When all engine conditions had been reached and were steady a filtered sample from the engine was introduced into the 5 litre flask shown in Figure(2.1). At this point the pressure in the flask was approximately atmospheric. Once all settings had been recorded the engine was switched off but the oil and water pumps were left on to keep the residual temperature to a safe level.
2.3 Exhaust Sample Analysis

The sample, at about 240 degrees C, was collected in the flask and subsequently cooled to the flask temperature of about 195 degrees C. Once in the flask the sample from the engine was left to stabilise for 1/2 an hour and then temperature and pressure readings were taken. The mass of exhaust sample in the flask was calculated from the equation of state for an ideal gas\(^2.5\) using temperature and pressure readings before and after introduction of the sample.

Since the Internal Standard method\(^2.5\) was used, a small amount of Hexane (the internal standard) weighed accurately, was added by hyperdermic syringe to the flask. Nitrogen was added to pressurise the flask usually to about 400 mmHG above atmospheric pressure and was accompanied by a temperature rise of approximately 5 degrees C, increasing the flask temperature to about 200 degrees C. This was attributed to the swirling and turbulent action of the nitrogen as it entered the flask subsequently increasing the convective heat transfer from the walls to the contents of the flask. However when equilibrium had been restored the temperature usually fell back to normal, 195 degrees C. The nitrogen also served to dilute the exhaust sample keeping the water in the vapour state and inhibiting further chemical reactions both within the mixture and with the flask wall. The flask was pressurised to allow transfer of the sample from the flask to the chromatograph by pressure difference alone therefore avoiding the need for pumping between the two stations. The final mixture comprised approximately 50 percent nitrogen and 50 percent of sample by mass. The mixture was then allowed to settle for 2 hours. Schematic details of the sample flask system are given in Figure(2.1).
2.4 Chromatographic Method

The Internal Standard method used for the analysis of the exhaust gas, is an extremely flexible method and renders actual sample size unimportant. The feature was invaluable since in this project it was difficult to sample the same mass of gas each time. This meant that the actual mass sampled in the test loop, Figure(2.1), was irrelevant. In addition to this it is not necessary that the weight of internal standard for both the calibration and engine sample mixtures be the same. However it is desirable for the two weights to be comparable. It is necessary that the internal standard chosen should not be present in the sample and should elute both distinctly and centrally amongst the components of interest and be of similar concentration to those components. Through running continual chromatographs from the engine it was established that the hydrocarbon, n-Hexane, did not appear in the chromatograms and lay somewhere near the centre of the hydrocarbon spectrum that was of interest.

Before sampling through the chromatograph all flows were recalibrated (ie. the carrier nitrogen, hydrogen and air for the FID flame) and the unit was left for at least an hour for flows and temperatures to stabilise. The Hewlett Packard integrator[4.5] was zeroed and the various settings were adjusted appropriately (ie., attenuation, chart speed, area rejection, threshold etc). The chromatograph was then ready to accept a sample from the flask. A low sample flow was allowed to bleed through the sample test loop via heated interconnecting lines. When the flow was sufficient the sample loop valve was switched over and at the same time the integrator plot sequence was initiated. According to the nitrogen flow rate a few seconds were allowed for the sample to be swept out of the loop before switching the valve back to the fill position. The sample flow from the flask was then cut off by closing valve D. See Figure(2.1) for details.
The sample passed through the chromatograph, usually about 4 minutes, and a chromatogram with a component area table was produced by the integrator. For a typical chromatogram of an exhaust sample (engine fuelled on Iso-pentane), see Figure (2.2). Since the integrator only produces area counts for given components these figures were passed to a data reduction program yielding specie values for PPM C and PPM Hexane. A computer program was written to handle this data and a listing of the program is given in Appendix (F). The program actually gives PPM C values for Methane and Ethane combined, Propane, n-Butane, Iso-pentane, n-Hexane and Iso-octane, the most significant pure hydrocarbons which appear in the chromatographic table. For chromatographic conditions see Appendix (B).
2.5 Calibration procedure

In the procedure adopted all hydrocarbon components of interest were calibrated against an internal standard, n-Hexane. An example of such a chromatogram is given in Figure(2.3). The objective was to get a relative response factor for each component against n-Hexane. The relative response factor of a given component is equal to the ratio of its detector response factor to that for the internal standard, which can be expressed as:

\[
R.R.F = \frac{\text{Component R.F.}}{\text{I.S. R.F.}} \tag{1A}
\]

\[
R.R.F = \frac{\text{AC} \times \text{M I.S.}}{\text{MC} \times \text{A I.S.}} \tag{1B}
\]

Where

- \( R.R.F. \) is the relative response factor of the component
- \( AC \) is area count of component from integrator
- \( MC \) is mass of component
- \( A \text{ I.S.} \) is area count of internal standard
- \( M \text{ I.S.} \) is mass of internal standard
- \( \text{R.F.} \) is detector response factor
- \( \text{I.S. R.F.} \) is internal standard response factor

The 5 litre flask was preheated to about 195 degrees C to ensure that all components vaporised completely. The flask was purged with air first and then nitrogen and a base line run was made to test the contents for purity. The purging technique is described in...
Chapter[4.1]. An example of a base line chromatogram is given in Figures(2.2) & (2.3) and for an acceptable level of purity should indicate no run peaks stored. The flask was left in a slightly pressurised state in readiness to accept the calibration mixture. The pressure was noted.

A known percentage mixture of the liquid components including the internal standard was prepared (ie. Iso-pentane, n-Hexane and Iso-octane) and a weighed amount added by injection to the flask. Further details on the preparation of this mixture are given in Chapter[3]. The total mass was also calculated by partial pressures (a mercury manometer was used to measure pressure in the flask but since the quantity added was so small, about 50 mg, this method was not as accurate as direct measurement but did serve as a rough check). The other gaseous components (Methane, Ethane, Propane, n-Butane) were then injected in larger quantities one at a time, and the masses added calculated from the partial pressure law. These components had to be added in larger quantities to ensure a reasonable degree of accuracy, since the partial pressure law was the only method available for calculating their masses. However since the main area of interest was in the base fuel hydrocarbon levels, inaccuracies of about 10 percent in the lighter hydrocarbons were relatively unimportant. The masses of the various components have been calculated from:

\[
\text{Mass comp.} = \frac{P \cdot V}{R \cdot T} \quad (2)
\]

Where

- \(P\) is the partial pressure of the component gas or vapour
- \(V\) is the volume of the flask
- \(R\) is the characteristic gas constant
- \(T\) is the flask temperature
The average gas constant for the vaporised mixture is calculated from the various mass fractions present:

\[ R = X_1 \cdot R_1 + Y_2 \cdot R_2 + Z_3 \cdot R_3 \]  

Where

\( R_1, R_2 \) and \( R_3 \) are the characteristic gas constants and \( X_1, Y_2 \) and \( Z_3 \) are the mass fractions.

\( R \) is the average gas constant for the mixture.

and

- \( n\text{-Hexane}(\text{internal standard}) = 1 \)
- \( \text{Iso-pentane} = 2 \)
- \( \text{Iso-octane} = 3 \)

Since the percentage content of the liquid mixture was known the individual component masses including the standard were calculated from the liquid sample mass added to the flask (liquid sample mass was weighed using a micro-balance).

Since it was only the ratio of component mass to internal standard mass that was actually required in the relative response factor (R.R.F.) calculation, the R.R.F.'s for the two liquid components Iso-pentane and Iso-octane were calculated directly from the mass fractions of the components. (ie. there was no need to use the component masses calculated from the partial pressure law).

\[ \text{R.R.F. Liquid Component} = \text{MFR} \times CR \]  

(4)
Where

MFR is the internal standard to component mass fraction ratio
CR is the component to internal standard area count ratio

For example:

For Iso-octane

\[
MFR = \frac{X_1}{Z_3}
\]  
\(\text{(5)}\)

For Iso-pentane

\[
MFR = \frac{X_1}{Y_2}
\]  
\(\text{(6)}\)

However since the internal standard mass was needed to calculate the R.R.F.'s for the gaseous components this liquid mass calculation had to be performed.

Once all components had been added the flask was pressurised with nitrogen and left for two hours to allow stabilisation of the mixture. Six to eight samples were then taken from the flask and chromatographed giving average values for the component area count ratios. The area count for a given component is the figure appearing under "area" in the chromatogram table, Figure(2.3).

These figures are used to calculate the R.R.F.'s of the various components as shown in equation (1) above.
2.6 Data Reduction

It has already been stated that due to the nature of the method used it was necessary to utilise a micro computer for the final handling of the data. The electronic integrator merely produces chromatograms indicating hydrocarbon concentrations in terms of area counts and so would not perform this exercise. Details of the integrator's function are given in Chapter[4.5].

A computer program was developed to handle the data (ie. area counts, pressures, temperatures and masses) from the system. See program listing, Appendix (F), for details. The relative response factors calculated beforehand were written into the program as constants but were revised from time to time to allow for slight changes in chromatographic conditions (ie. bleeding away of material in columns, changing sensitivity of detectors etc). As already explained an internal standard was added to each flask sample and similarly as for the calibration procedure average area count ratios (that is number of area counts for a component divided by number of area counts for the internal standard) were obtained for a series of chromatographic runs. From these area ratios and previous data the percentage of each component by weight was calculated from:

\[
MC = \frac{AC \times 1}{A \times R.R.F} \times \frac{M \times I.S. \times 100}{I.S. \times R.R.F \times MS} \quad (7)
\]

And

\[
PPM(Hexane) = \frac{MC \times SMW \times 10000 \times N}{CMW \times 6} \quad (8)
\]
Where

MC is the percentage mass of the component
AC is the area count of the component
MS is the mass of the sample in the flask
M I.S. is the mass of the internal standard
A I.S. is the area count of the internal standard
SMW is the sample molecular weight
CMW is the component molecular weight
N is the number of carbons in the component molecule

Clearly

\[
PPM \text{C} = 6 \times PPM(\text{Hexane}) \quad (9)
\]

PPM C levels for Methane and Ethane were given as a combined figure under Methane. This was because Methane and Ethane elute so close to each other it was not possible to separate them without going to much longer columns and or chromatographic temperatures below 0 degrees C. Since primary interest was in base fuel PPM C levels, and Methane/Ethane PPM C levels were not particularly significant to overall PPM C levels, there was little justification for the additional expense of fitting the features mentioned above. Since the relative response factors for Methane and Ethane were not significantly different the combined PPM C level was very similar in magnitude to the sum of the individual PPM C levels. For typical PPM C levels see Appendix(D).
EXHAUST MANIFOLD TO ATMOS WHEN PURGING

I MERCURY SAMPLE TUBE

EXHAUST VALVE

N.B. ALL LINES HEATED UNLESS STATED OTHERWISE

TO HYDROCARBON = NOx ANALYSERS

TO O2, CO, CO2 ANALYSERS

WATER TRAP

FLASK SAMPLING SYSTEM

Fig. 2.1
TYPICAL GAS CHROMATOGRAM
(EXHAUST SAMPLE)

ENGINE FUELLED WITH ISO-PENTANE

BASE FUEL

INTERNAL STANDARD (HEXANE)

RUN # 421  DEC/04/95  16:18:06

<table>
<thead>
<tr>
<th>AREA</th>
<th>AREA TYPE</th>
<th>% AT HT</th>
<th>AREA %</th>
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<td>0.418</td>
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<tr>
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<td>0.303</td>
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</tr>
<tr>
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<td>4212</td>
<td>2.947</td>
<td>0.058</td>
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</tr>
</tbody>
</table>

TOTAL AREA= 4863888
MUL FACTOR= 1.8640E+00

Fig. 2.2
### Calibration Chromatogram

#### Chemicals Present
- Methane: 0.71 g/mL
- Propene: 0.89 g/mL
- Butane: 0.96 g/mL
- Iso-Pentane: 1.19 g/mL
- Hexane: 2.11 g/mL
- ISO-Octane: 3.69 g/mL

#### Peak Areas

<table>
<thead>
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<th>Area Type</th>
<th>Area (g/mL)</th>
<th>Area %</th>
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<tr>
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<td>15.44%</td>
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</table>

**Total Area:** 6.7199E+07

**Mul Factor:** 1.3000E+08

---

**RUN #: 186**

**BASE RUN**

---

**RUN #: 188**

**TOTAL AREA:** 6.7199E+07

**Mul Factor:** 1.3000E+08

---

**Fig. 2.3**
CHAPTER 3

EXPERIMENTAL ACCURACY AND IDENTIFICATION OF HYDROCARBONS - DISCUSSION
CHAPTER 3

EXPERIMENTAL ACCURACY AND IDENTIFICATION OF HYDROCARBONS - DISCUSSION

3.1 Experimental Accuracy

3.1.1 General Note

During both calibration and engine sampling it was important to keep liquid additions to the flask to a minimum not only to give comparable concentrations to those in an engine sample but to maintain a homogeneous mixture both within the flask and the test loop, Figure(2.1). That is the flask mixture was assumed to be of identical component concentration as a sample in the chromatographic test loop. This assumption was not unreasonable since sample area count ratios for the base fuel component were to within 1 percent for a given flask mixture. Both Fleming[17] and Daniel and Wentworth[4] emphasise the importance of dilution and thorough mixing of the exhaust sample before any measurements are taken if serious error is to be avoided. The work in this project has met both these conditions.

3.1.2 Engine Conditions

Great effort was made to keep air/fuel ratio to within set limits from one test to another. However this was difficult for coolant temperatures above 185 degrees F. Generally air/fuel ratio was kept to within about 0.2 of an air/fuel ratio for a given set of engine tests. Inlet manifold air temperature was maintained to within 1/2 degree C so did not constitute a serious source of error. An effort was made to keep airflow approximately the same for each test, differences not amounting to more than 5 percent. To avoid excessive residual gas dilution of the intake mixture and subsequent spurious
effects on hydrocarbon emissions, a normal consequence of four-stroke cycle engine operation at high intake manifold depressions[4][30], the intake manifold depression on the Ricardo engine was maintained at a low value of about 4 in.Hg for all engine tests. Coolant and oil temperatures, monitored by thermocouple, were kept to within 2 percent of the planned values by means of a feedback loop system.

3.1.3 Hydrocarbon Mass Calculation
(by the Weighing Method)

The method of weighing liquid samples in order to obtain their mass maybe justified by the following argument. Since it was required that small quantities of liquid samples must be added to the flask to stay within other constraints it was found that samples of around 50 mg could be weighed to within 1/2 mg on a microbalance which is to within 1 percent. However evaluation of mass of this magnitude by the partial pressure method proved to be very inaccurate even when using an inclined water manometer. This was due to small temperature changes within the flask producing pressure fluctuations of about 50 percent of the partial pressure to be measured. Consequently the weighing method was adopted as the most accurate.

The accuracy of the weighing method was checked quite simply by the following procedure. A syringe filled with a paraffin hydrocarbon, n-Hexane, and an empty phial were weighed separately. About 50 mg of the hydrocarbon were transferred from the syringe to the phial and both items were weighed once again. The changes in weight of both items compared to within 1/2 mg. This process was repeated three times to ensure repeatability of the accuracy. The calibration mixture of Iso-pentane,n-Hexane and Iso-octane was made up using the weighing method. An empty bottle was weighed first, a quantity of n-Hexane added, the bottle and its contents weighed again and the weight of n-Hexane added found by subtraction. Similarly quantities of Iso-pentane and Iso-octane were added to the bottle and their masses obtained. It should be noted that immediately after the n-
Hexane was added the bottle was sealed with a screw top and rubber septum. All further additions, and subsequent withdrawals for calibration analysis, were made through the septum, therefore preventing any loss of the mixture from the bottle due to evaporation.

It was found by experiment that during calibration tests changes in relative concentrations of components to internal standard can seriously effect the relative response factors of those components. For this reason it was ensured that the relative concentrations of Iso-pentane and Iso-octane to n-Hexane in the calibration mixture was comparable with that of a typical engine sample.
3.2 Identification of Hydrocarbons

Before any measurement of hydrocarbon levels could be made each hydrocarbon specie of interest had to be identified first.

Since the engine was run on pure fuels (Iso-octane and Iso-pentane) it was not necessary to fractionate the sample as is sometimes done when running on blended fuels[17] (i.e., in the case of gasoline which has a broad band of hydrocarbons, fractionating allows separation of species of high molecular weights from those of low molecular weights). Hydrocarbon identification was made by repeatedly running typical engine samples through the chromatograph and establishing a pattern of the various species and their concentrations. In the case of the special fuels (i.e., Iso-octane and Iso-pentane) the most prominent peak after the internal standard was the base fuel. According to theory each hydrocarbon will elute from the column at a different time so retention time maybe used as a method of identification of the various components of interest.

For a given flask mixture the base fuel peak was confirmed by adding a small quantity of the fuel hydrocarbon to the flask and then noting the change to the chromatogram. In both cases identification of the base fuel was made when the peak increased in size in proportion to the amount added to the flask with no change to any of the other components in the chromatogram. It was established by comparing chromatograms for the two fuels (Iso-pentane and Iso-octane) that no other peaks or components of appreciable concentration eluted at the same time as the base fuels. This meant that to a good approximation base fuel peak area counts could be taken to represent the total concentration of the base fuel in the exhaust sample.

To facilitate better separation of the other species of interest two
metre column lengths were used in the chromatograph. Prior to this 0.9 metre length columns were used giving very poor separation of the lighter components (Methane, Ethane, Propane and n-Butane). However since these components were in considerably lower concentration than the base fuel identification was more difficult.

The same method as used for the base fuels was adopted to identify the retention times or positions in the chromatogram of the lighter components. However it could be argued that these peaks, believed to represent the lighter components, were made up of other components not identified in the chromatogram with similar or identical retention times. If this was the case then there would have been some evidence of partial separation when changing from 0.9 metre to 2 metre length columns. In fact there was none so it was reasonable to suppose that the retention times of those peaks of interest did in fact correspond to those components alone and no others.

Since all components present in significant quantities were identified the method was checked by comparing the sum of the hydrocarbon specie levels in PPM C from the chromatographic technique to the total PPM C from the hydrocarbon analyser. After allowing for the low levels of unidentified hydrocarbons in the chromatographic analysis the two methods compared to within 5 percent.
CHAPTER 4

EXPERIMENTAL EQUIPMENT
CHAPTER 4

EXPERIMENTAL EQUIPMENT

Photographic Plates (4.1), (4.2), (4.3) & (4.4) illustrate: The Sampling Flask System, Engine with Fuel and Air Intake Systems, The Control Panel and finally The Gas Analyser and Chromatograph with Integrator respectively. The general schematic, Figure (4.1), shows the position of all equipment used in the experiment. The arrows indicate the direction of flow of fuel, air, exhaust and data through the system.

4.1 Sampling Flask System

The diagrammatic layout of the flask and interconnecting lines are shown in Figure (2.1). All interconnecting lines were heated to approximately 150 degrees C unless stated otherwise. The flask, which sits inside an insulated box - not shown in Figure (2.1), was heated by an electrical ring oven to about 200 degrees C. Stainless steel tubing was used throughout to minimise surface reaction effects with the sample. All pipework and valves, including the flask, coming into contact with the sample were cleaned thoroughly with Iso-pentane to remove deposits which may have contaminated the sample during a chromatographic test. Although inline filters, shown in Figure (2.1), take out the small particles from the sample before it enters the flask, deposits still tended to form on the inside of the flask after about 10 fillings. For this reason the cleaning process was repeated several times throughout the experimental work in order to keep contaminant levels to a minimum.

In the early stages of the work a 1/2 litre flask was used for the
collection of exhaust samples. However it was found that the capacity was too small to mask engine transient effects on the exhaust products therefore producing inconsistent results. For this reason a 5 litre pyrex flask was finally chosen giving the desired averaging effect on exhaust composition transients.

It was found that continual changes of pressure and temperature had a fatigue effect on the flask finally leading to an implosion of the flask while evacuating the contents. Consequently for future experiments of this nature a stainless steel flask would be a safer and more adequate enclosure.

A - I represent shutoff valves - Figure(2.1).

During purging air is admitted to the flask via screw top, position (1) illustrated in Figure(2.1), and finds its way out via valve I and the test loop. In this manner both the flask and the test loop were purged of impurities. Air was used because it is cheaper than nitrogen and was therefore normally left on overnight to purge the flask thoroughly of the old sample. Finally the air was flushed out with nitrogen using the filling and emptying technique already described[2.2]. The contents of the flask were chromatographed to check for impurities and then evacuated to around 150 mmHg ready to accept an engine sample.

It is well known that hydrocarbon concentration varies with distance along the exhaust pipe and also with engine crank angle[4]. The sample size should therefore be large and its collection as close to the exhaust valve as possible to mask transient effects. In this project the exhaust products were sampled about an inch away from the exhaust valve and passed via a stainless steel tube through a fine gauze filter and then a 1 micron paper filter. The isolation valve A was kept closed until the engine had run up to speed which prevented unwanted products from entering the filters during start up.
When engine conditions were steady and the air/fuel ratio was correct the sample flow was diverted to the flask via valves C and D until flask pressure had equalled exhaust pressure, usually about 5 mmHg gauge. At this point valves C and D were closed and the sample was left to settle in the flask before adding the internal standard.

When the flask sample was ready for chromatographing, valves D and F were opened allowing a low flowrate of sample through the test loop to atmosphere. The test loop was then switched into the carrier circuit of the gas chromatograph and left for a few seconds in this position to ensure that the loop had been swept clear of the sample. During this short period the sample flow escaped directly to atmosphere until the test loop valve was switched back refilling the test loop once again ready for the next chromatographic run.
4.2 Air Intake System

All diagrammatic details of the system and airflow route are shown in Figure (4.2).

An Alcock viscous air flow meter with inclined manometer was used for monitoring the air flow into the engine. The Viscous Flow air meter contains a Meter Element which is a honeycomb of long, narrow triangular passages. Within the working range, the flow through these passages is viscous and the resistance of the element is, therefore, directly proportional to the velocity. The air enters through a cleaner and then passes through the meter element, which is made up of alternate layers of flat and corrugated strip metal wound upon a core. Even very irregular flow, as produced by a single cylinder engine without any smoothing, does not cause significant error.

The air was channelled by means of a flexible hose from the flow meter to the filter body, Figure (4.2). Since the Viscous Flow air meter contained a cleaner, the filter element normally housed in the filter body was dispensed with. This had the advantage of avoiding an unnecessary pressure drop along the inlet tract. An electric element housed in the filter assembly was used to heat the air before it entered the following section of the inlet tract in order to assist in fuel vaporization.

The throttle was of the butterfly type and control was affected by a pulley wheel and cable system linked to the throttle spindle. The cable was connected to an electro-mechanical solenoid which was operated from the control panel according to load and speed demand. The throttle spindle was sealed with an '0' ring which prevented unwanted air leaks into the system.

The plenum chamber assisted in dampening pressure fluctuations due to the reciprocating nature of the engine. The chamber also housed a mercury thermometer, used to monitor air temperature and a
thermocouple for maintaining the temperature to the demand level during running of the engine.

The two injectors were positioned opposite each other just after the plenum chamber and inclined at an angle of about 20 degrees to the horizontal against the direction of air flow. The location and angle of the injectors were chosen to create a more uniform fuel distribution across the airstream and so assist in both fuel vaporization and fuel/air mixing.

Once the air had entered the injector section it was constrained to follow two separate routes isolated from each other. The injectors were operated by electro-mechanical solenoids triggered by a rotating disc mounted on the end of the inlet camshaft. The disc had a slot which covered and uncovered a photo-electric cell. The signal was then fed to the injection timing box which fired the two injectors.

The two independent injector airflow routes, shown in Figure(4.2), communicate separately with the two straightner tubes which were included to assist in fuel mixing. The two independent flows enter the induction manifold and feed the two inlet valves inside the engine cylinder head.
4.3 Fuel System

The fuel system network, Figure(4.3), was designed with the intention of using it as a multi-fuel system since it was required that the engine should be run on three different fuels namely, gasoline, Isopentane and Iso-octane. The system was fabricated to meet the engine requirements and supply the injectors with sufficient fuel at 30 psi. It was also important that the fuel was free from air and vapour pockets.

A burette was used for measuring fuel flow and details of the calculations are given in Appendix(E). A Bosch electric fuel pump with pressure regulator was used for feeding the fuel under pressure (30 psi) to the injectors.

In the early stages of the work when setting up and commissioning the engine and equipment it was both convenient and more economical to run on gasoline rather than a pure hydrocarbon fuel. For this reason the system was designed to cater for the use of gasoline as well as the special fuels.

The schematic in Figure(4.3) is fairly self explanatory but will be discussed briefly. When the engine was to be run on gasoline stop cock B was closed to isolate the special fuels tank from the system and breather C was then opened to allow trapped air to escape as the system was being filled with the fuel. Stop cock A was opened allowing the filtered fuel to fill the system. Fuel was then fed under pressure to the injectors by means of a Bosch electric fuel pump. The pump delivered a constant flow at a given pressure, the excess fuel being fed back to the suction side of the pump via the pressure relief valve also used to set the fuel pressure of 30 psi. A pressure gauge monitored the fuel pressure.
When changing over to run the engine on either of the special fuels stop cock A was closed and the residual gasoline remaining in the system was drained via plug C. Breather C was then closed and stop cock B was opened to allow the new fuel to fill the system. Normally the engine was run for a few minutes on the new fuel before changing the oil for a fresh set of tests. This allowed the old fuel to be flushed out of the system completely.

When running on Iso-pentane the fuel pump was semi immersed in a refrigerated water bath to prevent fuel vapour forming in the suction line leading to vapour lock and subsequent overheating of the pump.
4.4 Gas Chromatograph (G.C.)

A Pye Unicam series 104 gas chromatograph was used in the experiments.

The G.C. was fitted with dual heated flame ionisation detectors (FIDS) and dual columns. The dual column system compensates for effects due to small changes in the chromatographic condition so that both columns are affected similarly. The unit was equipped with an ionization amplifier, a detector oven controller and an oven programmer. A mixture of hydrogen and air was used for the FID flame and nitrogen was used as the carrier gas. The object of a G.C. is to separate the various components of a given sample, quantitatively. The columns perform the function of separation with subsequent detection and measurement by the FID's and ancillary equipment.

The sample was carried from the test loop and through the column by the carrier gas. The components in the sample were separated according to their boiling points, the lighter hydrocarbons eluting from the column first. The FID's operate on the principle that the electrical conductivity of a gas is directly proportional to the concentration of charged particles within the gas. The sample component contained in the effluent gas from the column is mixed with hydrogen and burned in air. As the sample enters the flame a percentage of the molecules are ionized forming positive and negative ions and free electrons. The extent of the ionization depends on the nature of the compound and the temperature of the flame (dependent on the ratio of hydrogen/air/carrier gas).

The sample is passed through one of the columns and it is the difference in levels of ions between the two columns that is measured. These ions give rise to a voltage which is amplified by the ionization amplifier and then fed to the integrator for further data handling. For chromatographic conditions see Appendix (B).
4.5 Electronic Integrator

The Hewlett Packard integrator is responsible for turning voltage levels fed from the chromatograph into area counts corresponding to PPM C levels. A fast sampling method was used to transform the voltage levels into area counts which were finally produced in a graphical plot against time. The various peaks which appear in the plot or chromatogram quantitatively represent components of the chromatographed sample as shown in Figures (2.2) & (2.3). The retention time of each peak appears in the chromatogram indicating the relative elution times of the components making up the sample. Finally a table is printed out indicating retention times, area counts and other relevant details for each component appearing in the chromatogram.

Before a sample is passed through the chromatograph the controlling parameters for the integrator need to be entered which are the following:

(a) Zero - The integrator base zero level is set by means of a control potentiometer on the amplifier of the chromatograph. This in effect adjusts for any slight differences in base voltage levels between the two FID's. It also allows setting of the plot baseline to any position between the left margin (-6) and the right margin (100). The value entered is a set percentage of full scale. In the sample analysis it was found that the default value of zero was convenient which sets the plot baseline approximately 1.3 cm. from the left edge of the paper.

(b) Attenuation (ATT) - This level is set from the integrator to ensure that peaks appearing in the chromatogram remain within scale. It sets the maximum signal voltage at full-scale deflection on the recording paper. However the area count is totally independent of attenuation changes on the integrator. The signal voltage level to
the integrator, which must not exceed it's range of 1 volt, is attenuated appropriately on the ionisation amplifier of the chromatograph. For the analysis attenuation was set to ensure that the peaks appeared clearly in the chromatogram and during measurement was set to a value of 4 which corresponds to a maximum signal voltage at full scale deflection of 16 mv.

(c) Chart speed (CHT SP) - This controls paper advance speed in cm./min, helping visual identification of the various peaks. A value is chosen to give the clearest chromatogram (for the analysis a value of 2 was chosen).

(d) Peak width (PK WD) - This controls selectivity in distinguishing peaks from noise or each other by filtering data sufficiently to improve the apparent signal-to-noise ratio. Successful use of PK WD requires just enough filtering to eliminate noise from being interpreted as peaks, but not enough to distort chromatographic information. The value used, 0.01, was obtained by measurement of the time width (in minutes) at half-height of the narrowest (fastest) peaks of interest. Therefore peaks having values less than this figure were ignored.

(e) Threshold (THRSH) - THRSH's function is to remove from the signal any information the integrator should not consider significant. A reasonable choice for THRSH (one insuring adequate peak detection without too much sensitivity to noise or trace impurities) is a value between the auto-THRSH (value determined by the integrator from the signal), and the value used for ATT that plots the smallest peaks of interest so as to be at least 1 mm. in height, as measured from their starting points. If the auto-THRSH value itself is used, some noise may be mistaken for peaks. The value for THRSH chosen in the analysis varied from 0 to 2 (ie. 1mv - 4mv) depending on the type of chromatographic run (ie. baseline run, calibration or exhaust sample run).

(f) Area rejection (AR REJ) - Peaks with areas less than the value
for AR REJ, are discarded. Values represent area counts (1 area count = 0.125 microvolts·sec.). In the analysis no area rejection was necessary and the default value of zero was used.

Typical experimental values for the above parameters are given in Figures (2.2) & (2.3). When all input parameters had been entered the integrator was put into start mode and at the same instant the test loop valve was switched from fill to inject. When all peaks of interest had emerged the integrator was put into stop mode and a chromatographic table was printed out. The integrator was then re-zeroed ready for the next sample.
4.6 Exhaust Gas Analyser

The system is designed to sample and measure the concentrations of carbon monoxide, carbon dioxide, oxygen, NOX and hydrocarbons in engine exhaust and includes filters, a heated sample line with proportional temperature control, a cooling unit and pumps. The CO, CO2 and O2 analysers are supplied by a sampling system which passes the gas through a cooler unit. The hydrocarbon and the NOX analysers are supplied by a heated sampling system and are completely separate and independent apart from their zero grade and span gas supplies.

The five analysers incorporated in this system are discussed briefly:

(a) Carbon monoxide and carbon dioxide analysers are of the infra-red type manufactured by The Analytical Development Company Limited. Measurement uses an infra-red absorbing technique and the analyser is a non-dispersive double beam unit in which the gas to be measured is passed through an optical cell, either continuously or as a static sample. The gas is not affected by the measurement and may be recovered if desired. The analyser output meter is calibrated in terms of gas concentration, but this type of instrument operates as a comparator: the calibration is not absolute, but is established by standardising with a known gas mixture at one point on the calibrated scale. The unit is zeroed using clean air. The infra-red detector is of the Luft-type which receives low energy infra-red radiation from a simple hot wire source in the analyser, but, because it is filled with a pure sample of the type of gas to be measured, can respond only to energy in that region of the infra-red spectrum corresponding to the absorption band peculiar to that gas. When the gas to be measured enters the analyser it passes through a cell in the path between the radiating source and the detector and, according to the concentration present, absorbs some radiation and thus reduces the level of energy reaching the detector. It is this change of energy which is amplified to give the analyser output signal.
The infra-red radiation source consists of a heated wire in a quartz tube mounted in the source block, which is located at the opposite end of the optical bench to the detector. Radiation from the source is reflected within the mounting block and passes out of a symmetrical pair of rectangular apertures into the analysis tube set. This comprises of a pair of tubes which are internally highly polished and gold plated to ensure high transmission of radiation into the detector cells. One tube is used for the gas to be measured, whilst the opposite tube is used for reference, and is usually filled with dry air. The sample cell may be divided by windows into various lengths, to give different ranges of sensitivity, the unused sample cells generally being flushed with a non infra-red absorbing gas such as oxygen or nitrogen, or gas free of the component being measured, for example, fresh air for carbon monoxide analysers.

(b) NOX analyser (BOC special gases) - The heart of the Luminox 201B chemiluminescent analyser is the chemiluminescent gas phase reaction between ozone and nitric oxide. The reaction produces light measured by a photomultiplier tube and is proportional to the nitric oxide concentration. The Luminox 201B operates at low pressure in order to maximise the light output from the chemiluminescent reaction and allows wet sample gas to be analysed without the need to maintain the entire pipework system at 70 degrees C or more. Calibration is again performed by standardising with a known gas mixture.

(c) Hydrocarbon analyser (Analysis Automation Limited model 523) detects and measures hydrocarbons utilising a flame ionization detector (FID). A small, continuous flow of sample gas is burnt in a polarised hydrogen flame. During the combustion process compounds containing carbon-hydrogen bonds form ions; a potential is applied between the flame and a collector electrode causing migration of the ions to the electrode. The resulting ion current is related to the concentration of hydrocarbon in the sample. This signal is amplified and displayed by the electronics module of the analyser. Calibration is by a standard propane/air mixture. On start up the unit needs to
be left for about half an hour to allow the oven to reach its set
temperature about 150 degrees C. When the flame is lit the unit is
left for a further half hour to allow stabilisation of the FID base
level. The analyser is then zeroed and calibrated before commencing
measurement of a sample.
4.8 Injection System

Injection of the fuel was electronically actuated by solenoid valves housed in each of the two injectors. The solenoids were fired from a manual fuel injection unit which was fed with cam pulses and a 12 volt supply. The quantity of fuel injected was controlled manually by a potentiometer mounted on the injection unit. Injection occurred at half engine speed or every time a cam pulse was fed to the injection unit.
4.7 Ignition System

A lumenition and coil combination were used to generate a spark at the plug. Engine position was monitored by photoelectric cells triggering on TDC and 2 degree slots cut into a disc bolted to the flywheel. A photoelectric cell which picked up on a slot machined in another disc, fixed to the inlet camshaft, indicated the position in the engine cycle. The TDC, 2 degree and cam slot pulses were fed to a timing box which allowed timing adjustment in increments of 2 degrees BTDC using a thumb wheel. When engine position corresponded to the thumb wheel setting on the timing box the lumenition was switched on, which in turn switched off the coil producing a spark at the plug.
PLATE 4.1  FLASK SAMPLING SYSTEM  (FLASK INSIDE BOX)
PLATE 4.2
ENGINE WITH ANCILLARY EQUIPMENT
PLATE 4.4 GAS ANALYSER AND CHROMATOGRAPH
Fig. 4·1
Fig. 4.2
CHAPTER 5

GENERAL DISCUSSION OF RESULTS AND CONCLUSIONS
GENERAL DISCUSSION OF RESULTS AND CONCLUSIONS

5.1 Discussion of Results and Figures

The raw test data for the experimental results discussed in this Chapter can be found in Appendices (H) & (I).

It was noted that whenever the engine was run on a different fuel, accompanied by an oil change, traces of the old fuel would still appear in the exhaust. These traces are illustrated in the chromatogram shown in Figure (2.2) where Iso-pentane is the base fuel and a trace level of iso-octane has appeared at a retention time of 3.98 minutes. Note the two peaks that appear immediately before and after the internal standard at 2.09 minutes and 2.70 minutes respectively. These were identified as impurities in the internal standard of less than 1 percent concentration and therefore ignored in the calculations. Baseline conditions were set so that peak area counts above about 50 would register as a peak.

These fuel traces were small but well within the detector range of the chromatograph. To identify the source, these residual traces were monitored during the tests when the engine was fuelled first with Iso-octane and then with Iso-pentane. The traces for these tests are shown in Figure (5.1), where successive engine tests have been plotted against fuel trace levels for both Iso-pentane and Iso-octane fuels. Engine conditions were the same for both the fuels.

The Iso-pentane curve indicates that when the fuel was switched from Iso-pentane to Iso-octane, traces of Iso-pentane appear but rapidly
decrease to zero as the number of engine tests increase. On the other hand the Iso-octane curve indicates greater traces which decrease more slowly than those for the Iso-pentane. This suggests that the traces of the old fuel were in fact present in the engine oil and not in the test fuel. If these traces had been present in the test fuel then a constant hydrocarbon trace level would have been expected throughout the tests but clearly this is not the case. For the first test the concentration of Iso-pentane is about 5 percent of that of Iso-octane when running on Iso-octane and Iso-pentane fuels respectively. Again this demonstrates the higher solubility of Iso-octane in oil than Iso-pentane, and suggests that each fuel trace is being gradually desorbed out of the oil as the number of tests increase for a given fuel. The results of Figure (5.1) illustrate the desorption part of the mechanism well.

Mathematical models [10],[13] and experimental results [24],[11],[14] have shown that hydrocarbon levels decrease with increasing coolant temperature. Theory suggests that an increase in wall temperature is accompanied by a thinner cylinder wall oil film and a higher Henry Constant for the oil. This leads to lower fuel/oil absorption rates and therefore lower hydrocarbon levels. This trend consistent with Figure(5.2) (speed 2000 RPM and load 19 NM) indicates a 20 percent difference in base fuel hydrocarbon levels for Iso-octane and Iso-pentane fuels emphasising the effect of iso-octane's higher fuel/oil solubility. However this difference is not entirely due to the absorption/desorption mechanism. The importance of trapped volumes as a hydrocarbon source has been stressed in other studies[13],[2]. It has been shown that base fuel hydrocarbon levels produced as a result of trapped volumes are about 10 percent greater for Iso-octane than for Iso-pentane fuel for the same engine conditions. A derivation of this is given in Appendix (G). It follows that any absorption/desorption effect should show up on top of this 10 percent. Therefore assuming other sources such as surface deposits to contribute equal amounts of hydrocarbons for both fuels, Figure (5.2), only a 10 percent difference in base fuel hydrocarbon levels could be attributed to the absorption/desorption effect.
It is well known that total hydrocarbons are dependent on engine speed and load[10],[13],[11],[21] but experimental work in this project has indicated that the difference between base fuel hydrocarbons for Iso-octane and Iso-pentane is also dependent on load and speed. Figure(5.3) shows the effect of a lower speed of 1000 RPM and load of 14.3 NM on the base fuel hydrocarbon levels for the two fuels plotted against coolant temperature. It is clear that the difference in base fuel hydrocarbons, about 40 percent, is much greater than that shown in Figure(5.2). However since trapped volumes account for a 10 percent difference in hydrocarbon levels, only a 30 percent difference can be attributed to the absorption/desorption effect. In addition the absolute base fuel hydrocarbon levels for the two fuels are also greater than those shown in Figure(5.2) by about 1000 PPM C for Iso-octane and about 500 PPM C for Iso-pentane. This is consistent with theory[10],[13] which suggests that lower speeds allow more time for absorption/desorption to take place (ie., increasing hydrocarbons), and lower loads lead to lower exhaust temperatures which produces less oxidation of desorbed hydrocarbons in the expansion stroke (ie., increasing hydrocarbons). In order to demonstrate the well known speed effect on base fuel hydrocarbons the engine was run on Iso-octane at 2000 RPM and the same load of 14.3 NM. The result, shown as the dotted line in Figure(5.3), indicates how base fuel hydrocarbons fall with increasing speed. These data shown in Figures(5.2) & (5.3) clearly show the relationship between the magnitude of the oil layer hydrocarbon emissions and fuel/oil solubility[24],[27] not assessed in Adamczyk and Kach's bomb study[28].

To give another dimension to the engine test data it has been displayed in terms of Henry constant shown in Figures(5.4) & (5.5). Henry's Constant for a solute in a particular solvent is defined as the partial pressure of the solute divided by the mole fraction of the solute. Henry's constant is a measure of solute/solvent solubility such that the greater the Henry's Constant the lower the solubility. In the investigation the solute is the fuel and the
solvent is the engine oil. Since no literature on the Henry Constants of Iso-pentane and Iso-octane in the engine test oil was available, an experiment using a chromatographic technique, was carried out, Appendix(H), to determine the Henry Constants of Iso-pentane, n-Hexane and Iso-octane in the engine test oil for various coolant temperatures. The results shown in Figure(H.5), illustrate that for a temperature of 350 degrees K, Iso-octane is about 8 times as soluble in the engine oil as Iso-pentane. It should be noted that as Henry Constant increases fuel/oil solubility falls. In Figure (5.4) the range of engine coolant temperatures have been displayed in terms of reciprocal of Henry constant for both the fuels on a common data line. The results illustrate both the higher solubility of Iso-octane in oil than Iso-pentane for the same coolant temperature and the consequent effect of fuel/oil solubility on base fuel hydrocarbon emissions.

A similar but steeper trend is shown in Figure (5.5) for a lighter speed and load combination. The Henry Constants for both fuels are unchanged to those of Figure (5.4) but the lower speed gives more time for fuel/oil absorption and the lighter load leads to lower exhaust temperatures which produces less oxidation of desorbed hydrocarbons in the expansion stroke. The combined result of lower speed and lighter load has increased base fuel hydrocarbons for Iso-octane by about 1000 PPM C and Iso-pentane by about 500 PPM C with other engine conditions essentially constant.

Although it has been assumed that deposits would not contribute significantly to the base fuel hydrocarbon levels it is quite possible that they may have had an irregular effect on the results. Wentworth[18] proved that deposit location has considerable influence on the contribution of deposits to exhaust hydrocarbon concentration. Experimental evidence[18] showed that deposits placed at specific points on the surfaces of the combustion chamber and piston crown produced increases in hydrocarbons of the order of 100 PPM C. It was found that deposits in the vicinity of the exhaust valve produced greater hydrocarbon increases than for any other location in the
combustion chamber. However if the deposits were to cover the entire combustion chamber, as in a running engine, the hydrocarbon levels due to deposits could be much higher. The deposits could be responsible for an irregular effect on the base fuel hydrocarbons producing a scatter on the results. This could be a feasible explanation for much of the scatter present in the engine test data - Appendix(I).

Shinn and Olson[31], investigating factors affecting unburned hydrocarbons, were forced to abandon early experiments with a CFR engine due to poor repeatability which was attributed to cyclic variations of the engine. Although the authors of the paper[31] were aware of the presence and formation of chamber deposits due to condensation of fuel vapour on the walls the effects of these deposits on exhaust hydrocarbons was not realised. However in this project deposit formation was minimised by motoring the engine until warm before carrying out an engine test. This prevented the condensation of fuel on cold wall surfaces which would lead to higher wall deposits. It has been assumed that whatever deposits may contribute to hydrocarbon emissions, on average they contribute equal amounts to the base fuel hydrocarbon levels for the two fuels. It is also possible that the position of the top piston cylinder ring gap, believed to be a controlling factor in hydrocarbon emissions[15], could have affected the scatter in the data - Appendix(I). Further details of this effect may be found in the literature survey - Chapter[1].

The Dent & Lakshminarayanan[10] model has predicted that about 50 percent of total hydrocarbons in the exhaust are due to the absorption/desorption effect (n-Octane as the fuel). Experiment has shown about 30 percent due to this mechanism but it has only considered the absorption/desorption effect in terms of the difference shown between the two levels of base fuel hydrocarbons for Iso-octane and Iso-pentane. This does not represent the total isolated effect of the mechanism on exhaust hydrocarbons for either Iso-octane or Iso-pentane fuel. For instance if Iso-pentane was
replaced by a fuel with very low solubility in oil (i.e. Propane) any difference in base fuel hydrocarbons between this fuel and Iso-octane (less unequal contributions from other sources such as trapped volumes) would essentially represent the entire absorption/desorption contribution for Iso-octane. A fuel such as Propane would be a good choice since it produces comparatively low increases in exhaust hydrocarbons due to oil layers in the cylinder of a spark ignition engine [23]. Consequently the absorption/desorption effect on hydrocarbon emissions could be even more significant than found in this work. In addition to this the model has several limitations which could also help to account for the discrepancy. Firstly the model assumes a uniform oil film thickness on the cylinder surface[22] and secondly the Henry Constant for the fuel/oil combination was estimated from extrapolation of data (known to be prone to error) given by Chappelow & Prausnitz[25].

Consequently considering the limitations of both the model and experiment, the presented results compare favourably with those predicted by the model.
5.2 Conclusions

The differing effect of conditions inside the engine for the two fuels was not investigated in detail since it was assumed that surface deposits, quench layers etc. made an equal contribution to the hydrocarbon emissions for both fuels. However a brief mathematical analysis, Appendix(G), has shown that hydrocarbon levels produced as a result of crevice volumes are about 10 percent greater for Iso-octane than for Iso-pentane fuel for the same engine conditions. Therefore any absorption/desorption effect must appear on top of this 10 percent difference.

Since the object of the experiment was to assess the significance of the absorption/desorption effect in a running engine surface deposits would therefore be encountered. The differing effect of these surface deposits on exhaust hydrocarbons for the two fuels has not been assessed experimentally. However experimental evidence [18] suggests that deposit formation upon the surfaces of both the cylinder head and piston crown, especially in the vicinity of the exhaust valve, can increase hydrocarbon emissions in the exhaust. It was found that increases of about 200 PPM C would not be uncommon from an engine having surface deposits. However it is difficult to say how hydrocarbon species would be affected by deposit formation within the Ricardo engine. It may be concluded that there was some increase in base fuel hydrocarbons due to surface deposits within the combustion chamber for the two fuels Iso-octane and Iso-pentane. It is probable that surface deposits could have had an irregular effect on hydrocarbon emissions accounting for the highly scattered data. However it is assumed that the difference between base fuel hydrocarbon emissions due to surface deposits for the two fuels is not significant.

Since quench layers are closely controlled by molecular diffusion effects and these depend on molecular weights, there would have been
a difference in hydrocarbon contributions for the two fuels, Iso-octane and Iso-pentane, due to this source. However since quench layer sources are considered to be small[1],[2],[9],[3] compared to other sources such as ring crevices, absorption/desorption and deposits their contribution to the difference in hydrocarbon levels for the two fuels would be insignificant. Therefore, apart from the 10 percent due to crevice volumes, any difference in base fuel hydrocarbon levels between the two fuels has been attributed to the absorption/desorption mechanism. This was not unreasonable in the light of the fact that hydrocarbon sources such as those already mentioned were thought to remain fairly unchanged for all the experiments, and therefore to make the same sort of contribution towards hydrocarbon emissions for the two fuels. The only parameter to have been significantly changed was engine coolant temperature, in order to show the temperature dependence of the fuel solubility effect in the oil.

The data indicate a small difference in hydrocarbon levels for the two fuels, about 400 PPM C at 2000 RPM (varies according to coolant temperature), Figure(5.2), for fixed engine conditions but half of this difference (200 PPM C) is due to crevice volumes. Consequently only 200 PPM C can be attributed to the absorption/desorption mechanism. However this effect is shown more markedly, about a 900 PPM C difference in base fuel hydrocarbons, Figure(5.3), when running at 1000 RPM and a comparatively light load of 14.3 NM. In contrast to the 50 percent indicated in the model[10] experiment has shown that about 30 percent of total hydrocarbons in the exhaust are due to the absorption/desorption mechanism. Two reasons are suggested for the 20 percent discrepancy. Firstly experiment has not assessed the total effect of absorption/desorption on exhaust hydrocarbons and secondly the model makes certain assumptions which could have exaggerated the predicted absorption/desorption effect on hydrocarbon emissions.

The absorption/desorption mechanism has been shown to be a
significant source of hydrocarbons for higher molecular weight fuels, such as Iso-octane and therefore gasoline. Further work could be addressed to synthetic fuel blends and their combined effect with alternative engine oils.

It should be noted that only those hydrocarbon species making a significant contribution were identified and measured. In the future it may become necessary to consider how low hydrocarbon concentrations (about 50 PPM C) are affected by the absorption/desorption mechanism.
SPEED 2000 RPM
EQUVALENCE RATIO 0.9

LEGEND
■ ISO-OCTANE
☐ ISO-PENTANE

Fig. 5.1
SPEED 2000 RPM
EQUIVALENCE RATIO 0.9
LOAD 19 NM MBT

LEGEND
- ISO-OCTANE
- ISO-PENTANE

Fig. 5.2
SPEED 1000 RPM
EQUIVALENCE RATIO 0.9
LOAD 14.3 NM MBT

LEGEND

- ISO-OCTANE
- ISO-PENTANE

Fig. 5.3
SPEED 2000 RPM
EQUIVALENCE RATIO 0.9
LOAD 19 NM MBT

LEGEND
■ ISO OCTANE
□ ISO-PENTANE

Fig. 5.4
SPEED 1000 RPM
EQUIVALENCE RATIO 0.9
LOAD 14.3 NM MBT

LEGEND
■ ISO OCTANE
□ ISO-PENTANE

Fig. 5.5
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APPENDIX (A)

Engine Test Conditions:

- Air temperature: 38 degrees centigrade
- Coolant temperature: variable (95 - 200) degrees F
- Oil temperature: 115 degrees F
- Engine speed: 2000 RPM & 1000 RPM
- Engine load: 19 NM & 14.3 NM
- Spark timing: MBT
- Air flow: 0.35 kg/min approx.
- Fuel flow: 0.02 kg/min approx.
- Fuel pressure: 30 psi.
- Equivalence ratio: 0.9
APPENDIX (B)

Chromatographic Data:

- Oven temperature: 60 degrees C isothermal
- Detector temperature: 100 degrees C
- Carrier (N2) flowrate: 45 ml/min
- N2 pressure: 60 psi.
- Hydrogen flowrate: 45 ml/min
- Air flowrate: 500 ml/min
- Chromatograph type: Pye Unicam
- Column type: 2 metres * 0.125 O.D. stainless steel packed with 5% OV-1 on diatomite M-AW. 80-100 mesh.
- Integrator type: 3390 A Hewlett Packard
### Engine and General Specification:

<table>
<thead>
<tr>
<th>Type</th>
<th>Gasoline Ricardo Hydra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cylinders</td>
<td>1</td>
</tr>
<tr>
<td>Bore</td>
<td>80.26 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>88.9 mm</td>
</tr>
<tr>
<td>Swept volume</td>
<td>450 ml</td>
</tr>
<tr>
<td>Maximum speed</td>
<td>90 rev/sec</td>
</tr>
<tr>
<td>Maximum power</td>
<td>15 kw</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>11 : 1</td>
</tr>
<tr>
<td>Valve arrangement</td>
<td>twin overhead camshaft, vertical valves</td>
</tr>
<tr>
<td>Fuelling</td>
<td>petrol injection, 12 volt Bosch pump feeding twin injectors, injector type: Bosch 0280 150 151</td>
</tr>
<tr>
<td>Cooling</td>
<td>closed circuit system with heat exchanger.</td>
</tr>
<tr>
<td>Lubrication oil</td>
<td>82.5 % Mid-east base oil 15.5 % Additive packing 2 % Viscosity improver Viscosity grade 20/40</td>
</tr>
<tr>
<td>Special Fuels</td>
<td>Iso-pentane : Research Analar Grade minimum assay 99 % contains 1 % n-pentane. Iso-octane : Shell Research Grade</td>
</tr>
</tbody>
</table>
APPENDIX (D)

Typical PPM C Levels (2000 RPM at 19 NM load):

Fuel Iso-octane

- Methane & Ethane: 180 to 420 PPM C
- Propane: 180 to 240 PPM C
- n-Butane: 360 to 540 PPM C
- Iso-pentane: Approx. 5 PPM C
- n-Hexane: Negligible
- n-Heptane: Negligible
- Iso-octane: 2400 to 3500 PPM C

Fuel Iso-pentane

- Methane & Ethane: 420 to 570 PPM C
- Propane: 240 to 270 PPM C
- n-Butane: 100 to 140 PPM C
- Iso-pentane: 2400 to 3200 PPM C
- n-Hexane: Negligible
- n-Heptane: Negligible
- Iso-octane: Approx. 40 PPM C
APPENDIX E - CALCULATION OF AIR/FUEL RATIO

APPENDIX F - DATA REDUCTION PROGRAM
LIST
10 REM PROGRAM TO CALCULATE
20 REM AIR/FUEL RATIO FROM
30 REM EXHAUST GAS COMPOSIT.
40 REM USING SPINDTS EQUATNS.
50 REM AND ALSO FROM AIR/FUEL
60 REM MEASUREMENTS
62 REM
63 REM FF=FUELFLOW INTO ENGINE
66 REM CALC.FROM FUEL TIME
67 REM (KG/ENGINE CYCLE)
68 REM FM=FUEL.FLOW INTO ENGINE
69 REM CALC.FROM SPINDTS EQUAT
70 REM & MEAS.AIR FLOW
72 REM (KG/ENGINE CYCLE)
75 HOME
80 PRINT "INPUT ATM.P (MM HG)";
90 PRINT " & TEMP (DEG.C)."
100 INPUT P,T
102 PRINT "INPUT TYPE OF FUEL :"
103 PRINT "TYPE 1 FOR ISO-OCT."
104 PRINT "TYPE 2 FOR ISO-PENT."
105 INPUT AA
106 IF AA = 1 THEN 5000
107 IF AA = 2 THEN 5010
110 PRINT "INPUT AS PERCENTAGE";
120 PRINT ": O2, CO2, CO, & HC"
130 INPUT O2,C2,CO,H
140 PRINT "INPUT AIR FLOW IN NO.
OF DIVS";
150 PRINT " & FUEL TIME (SECS)"
160 INPUT V,F1
170 IF V = 0 THEN 450
175 REM CALC.AIR DENSITY
176 REM (KG/M3)
180 R1 = P / 750 * 100000 / 288.8
4 / (T + 273.15)
181 REM CALC.MEAS.AIR FLOW
182 REM A1(KG/MIN)
183 REM SCALE FACTOR=.475
184 REM PROD.OF SCALE FACTOR
185 REM AND NO.OF DIVS GIVES
186 REM AIRFLOW(FT3/MIN)
190  AI = V * R1 * .475 * .305 * .305 * .205
192  REM CALC.MEAS.FUEL FLOW
193  REM .(KG/MIN)
194  IF AA = 2 THEN 202
195  REM FUEL BURETTE - 32CC
196  REM REL.DENS.OCTANE = .703
197  M1 = .082 * .703 * 60 / F1
200  GOTO 210
201  REM REL.DENS.FENTANE = .626
202  M1 = .082 * .626 * 60 / F1
203  REM CALC.FUEL MASS(KG/CYCLE)
205  FF = M1 / 1000
207  REM CALC.MEAS.A/F RATIO
210  Z = AI / M1
220  PRINT ""
230  PRINT "MEASURED AIR FLOW = ".
240  PRINT AI;" (KG/MIN)"
245  A1 = AI / 1000
250  PRINT "MEASURED FUEL FLOW = ".
260  PRINT M1;" KG/MIN"
265  M1 = M1 / 1000
270  PRINT "AIR/FUEL RATIO = ";Z
272  PRINT "AIR FLOW KG/CYCLE = ";A1
274  PRINT "FUEL MASS(KG/CYCLE) F
275  REM CALC.A/F RATIO FROM
276  REM SPINDTS' EQUATIONS
280  IF O2 > 60 GOTO 440
290  R = C0 / C2
300  O = O2 / C2
310  F = (C0 + C2) / (C0 + C2 + H)
320  C = (C2 + C0 + H) / (8.63 + .
325  S78 * C2 - .422 * O2 + .784 *
329  C0 + 1.206 * H)
330  REM CALC.A/F RATIO
335  REM SPINDTS'EQUAT.A/F
340  A = F * (11.492 * C * ((1 + R)
345  / 2 + O) / (1 + R)) + 120 *
349  (1 - C) / (3.5 + R))
350  REM CALC.FUEL FLOW FROM
355  REM SPINDTS'EQUAT.A/F
356  REM RATIO & MEAS.AIRFLOW
FM = A1 / A
PRINT ""  
PRINT "EXHAUST COMPOSITION : "
PRINT "OXY = ";O2; " (%)"
PRINT "CO2 = ";C2; " (%)"
PRINT "CO = ";CO; " (%)"
PRINT "HC = ";H; " (%)"
PRINT "A/F RATIO = ";A
PRINT "FUEL FLOW FROM SPINDTS "
PRINT " = ";FM; " KG/CYCLE"
PRINT "C = ";C
PRINT "(1-C)/C = ";(1 - C) / C
REM ROUTINE TO CALCULATE AVERAGE MOLECULAR WT. OF FLASK SAMPLE BY MOLAR BALANCES
A = H / (6 * CO)
B = C2 / CO
C = O2 / CO
D = 1 + B + 6 * A
REM DEFINE MOLAR EQTS.
A1 = (U * A) / D
A2 = (U * B) / D
A3 = U / D
A4 = (U * C) / D
A5 = (W + W * B + X * A) / D
A6 = (Y + J * B + G * A + U * C) / D
E = A1 + A2 + A3 + A4 + A5 + A6
F = 86 * A1 + 44 * A2 + 28 * A3 + 32 * A4 + 18 * A5 + 28 * A6
M = F / E
GC = 9.314 / M
PRINT "AV. MOL. WT. EXHAUST = " ;M
PRINT ""  
PRINT "GAS CONST. = ";GC
PRINT ""  
GOTO 110
STOP
REM SUBPROGRAM SPECIFYING VARIOUS CONSTANTS FOR OCTANE AND PENTANE
REM USED IN THE MOLECULAR WEIGHT CALCULATION.
U = 8
5001 W = 9
5002 X = - 2
5003 Y = 8.5
5004 J = 12.5
5005 G = - 1
5006 GOTO 110
5010 U = 5
5011 W = 6
5012 X = 1
5013 Y = 5.5
5014 J = 8
5015 G = 0.5
5016 GOTO 110
APPENDIX F

LIST

10 HOME
15 PRINT "DATA REDUCTION PROGRAM"
20 REM DATA REDUCTION PROGRAM
30 REM CALCULATES HYDROCARBON
32 REM COMPONENT CONC.IN FLASK
33 REM SAMPLE USING SAMPLE AREA

34 REM RATIOS & RESPONSE FACT.
35 REM ALSO CALCULATES
36 REM HYDROCARBON COMPONENT
37 REM RESPONSE FACTORS FROM
38 REM KNOWN MASS CONC.
39 REM AND AREA RATIOS
50 REM CONSTS.
60 REM MOL.WTS.
62 REM NOS.IN BRACKETS REFER
63 REM TO NO.OF CARBONS IN
64 REM HYDROCARBON COMPONENT
65 REM (IE.(1) - METHANE)
70 MW(1) = 16
80 MW(2) = 30
90 MW(3) = 44
100 MW(4) = 58
110 MW(5) = 72
120 MW(6) = 86
130 MW(7) = 100
140 MW(8) = 114
150 REM GAS CONSTS.
160 R(1) = 0.5196
170 R(2) = 0.2771
180 R(3) = 0.189
190 R(4) = 0.1433
200 R(5) = 0.1155
210 R(6) = 0.0967
220 R(7) = 0.0831
230 R(8) = 0.0729
260 PRINT ""
270 PRINT "INPUT NO.COMPONENTS";

280 INPUT Y
290 PRINT ""
300 PRINT "DO YOU WISH TO RECALIBRATE?"
302 PRINT "(IE.TO OBTAIN NEW RESPONSE FACTORS)"
303 PRINT "YES=2,NO=1"
310 PRINT ""
320 INPUT Z
330 IF Z = 1 THEN 890
335 REM INPUT CALIB.DETAILS
340 PRINT "INPUT FLASK TEMPS."

78
350 PRINT ""
360 FOR N = 1 TO Y
365 IF N = 7 THEN 400
370 PRINT ""
380 PRINT "T":N;"=";
390 INPUT T(N)
400 NEXT N
410 PRINT ""
420 PRINT "INPUT PARTIAL PRESSURES"
430 FOR N = 1 TO Y
435 IF N = 7 THEN 470
440 PRINT ""
450 PRINT "P":N;"=";
460 INPUT P(N)
470 NEXT N
480 PRINT ""
510 HOME
520 REM CALCS
530 FOR N = 1 TO Y
535 IF N = 7 THEN 550
550 NEXT N
560 FOR N = 1 TO Y
565 IF N = 7 THEN 580
570 M(N) = 0.726E-3 * P(N) / (R (N) * (T(N) + 273))
580 NEXT N
590 PRINT ""
600 FOR N = 1 TO Y
605 IF N = 7 THEN 620
610 PRINT "P":N;"=";P(N)
620 NEXT N
630 PRINT ""
640 FOR N = 1 TO Y
645 IF N = 7 THEN 660
650 PRINT "M":N;"=";M(N)
660 NEXT N
670 PRINT ""
680 REM CONTINUE STATEMENT
690 INPUT "TO CONTINUE TYPE 1";Z

700 HOME
710 REM INPUT CALIB.AREA RATIOS
720 PRINT ""
730 PRINT "INPUT CALIB.AREA RATIOS"
740 PRINT ""
750 FOR N = 1 TO Y
755 IF N = 7 THEN 780
760 PRINT "CALIB.AREA RATIO ";N;
" = ";
770 INPUT CR(N)
780 NEXT N
790 FOR N = 1 TO Y
795 IF N = 7 THEN 810
800 RF(N) = CR(N) * M(6) / M(N)
810 NEXT N
820 PRINT ""
830 PRINT "RESPONSE FACTORS ARE:"

840 FOR N = 1 TO Y
845 IF N = 7 THEN 860
850 PRINT "RF ";N;" = ";RF(N)
860 NEXT N
861 PRINT ""
870 GOTO 950
880 REM ENTER RESPONSE FACTORS
890 RF(1) = 1.1582
895 RF(2) = .9
900 RF(3) = .9023
910 RF(4) = .8626
920 RF(5) = 1.18
930 RF(6) = 1
935 RF(8) = 1.1704
940 PRINT ""
945 INPUT "TEST NO. = ";TN
950 PRINT "ENTER TYPE OF FUEL USED"

960 PRINT "1 FOR OCTANE"
970 PRINT "2 FOR PENTANE"
980 INPUT Z
990 IF Z = 1 THEN 1020
1000 A$ = "ISO PENTANE"
1010 GOTO 1040
1020 A$ = "ISO-OCTANE"
1030 REM CALC.SAMPLE & I.S. WT
1040 HOME
1045 INPUT "ATMOS.PRESS. (MMHG) = ";AF
1050 INPUT "ENTER SAMPLE GAS CON ST. ";RS
1060 INPUT "ENTER SAMPLE P/PRESS MMHG ";PS
1070 INPUT "ENTER SAMPLE TEMP DE ";C ";ST
1080 INPUT " ENTER IS WT. IN KG ";IS
INPUT "AIR MASS(KG/CYCLE)"=
PRINT "FUEL MASS(KG/CYCLE)"
PRINT "FROM AFR CALC. = ";
INPUT FM
REM CALC. SAMPLE MOL.WT.
MS = 8.314 / RS
REM CALC. SAMPLE WT.
SW = ((0.726E - 3) * PS) /
( RS * (ST + 273))
REM CALC. I.S.WT.
PRINT ""
PRINT "ENTER SAMPLE AREA RATIOS:" 
PRINT "SAMPLE AREA RATIO ...
FOR N = 1 TO Y
IF N = 7 THEN 1205
PRINT "SAMPLE AREA RATIO ";
N;" = "
INPUT SR(N)
NEXT N
FOR N = 1 TO Y
IF N = 7 THEN 1230
C(N) = (SR(N) * IS) / (RF(N) * SW)
PM(N) = C(N) * MS * N * (1E + 6) / (6 * MW(N))
NEXT N
IF Z = 1 THEN L = 8
IF Z = 2 THEN L = 5
FL = C(L) * SW
PT = PM(1) + PM(2) + PM(3) +
PM(4) + PM(5) + PM(8)
FO = FL * (AM + FM) / SW
D = FO * 100 / FM
TL = 7.814E - 8 * AP * FL
REM PRINT OUT MASS FRACTI
HOME
PRINT A$,"TEST ";TN
FOR N = 1 TO Y
IF N = 7 THEN 1300
PRINT "MASS FRACT. ";N;" = ";
C(N)
1300 NEXT N
1320 FOR N = 1 TO Y
1325 IF N = 7 THEN 1340
1330 PRINT "PPM(HEX) COMP. "; N; " = "; PM(N)
1340 NEXT N
1342 PRINT "TOTAL PPM HEX = "; PT
1343 PRINT "TOTAL PPM C = "; (6 * PT)
1345 PRINT "SAMPLE WT. = "; SW; " KG"
1350 PRINT "FLASK FUEL MASS = "; FL; " KG"
1360 PRINT "FUEL OUT = "; FO; " KG/CYCLE"
1370 PRINT "TEST LOOP FUEL MASS = "; TL; " KG"
1380 PRINT "FUEL OUT AS % OF FUEL IN = "; D
APPENDIX (G)

THE EFFECT OF CREVICE VOLUMES ON BASE FUEL HYDROCARBON EMISSIONS FOR ISO-OCTANE AND ISO-PENTANE

The following derivation shows the expected difference in base fuel hydrocarbon emissions for the two fuels, Iso-octane and Iso-pentane, due to trapped volumes alone. The trapped volume considered is that between the piston and cylinder wall but the derivation would apply equally well to other crevice volumes within the combustion chamber.

From the equation of state:

\[(P \cdot V_c/T_w) = (m_t \cdot G/M)\] (1)

Where

- \(P\) is the cylinder pressure
- \(T_w\) is the wall temperature
- \(m_t\) is the trapped mass
- \(G\) is the gas constant
- \(M\) is the average molecular weight
- \(V_c\) is the crevice volume
Clearly

\[ mt = (ma + mf) = mf(\frac{ma}{mf} + 1) \]  \hspace{1cm} (2)

\[ M = \frac{ma \cdot Ma + mf \cdot Mf}{ma + mf} \]

\[ = \frac{(ma/mf) \cdot Ma + Mf}{(ma/mf + 1)} \]  \hspace{1cm} (3)

Where

- \( ma \) is the trapped air mass
- \( mf \) is the trapped fuel mass
- \( Ma \) is the molecular mass of air
- \( Mf \) is the molecular mass of the fuel

The crevice volume, \( Vc \), will be the same for both fuels. For a given wall temperature with other engine conditions remaining constant for both the fuels, it follows that the cylinder pressures for both cases will also be about the same.

It follows from (1)

\[ (mt \cdot G/M)_0 = (mt \cdot G/M)_p \]  \hspace{1cm} (4)
Where the suffixes:

\( o \) denote iso-octane

\( p \) denote iso-pentane

By appropriate substitution of equations (2) and (3) into (4) the expression becomes:

\[
mfp \times \left[ \frac{(ma/mfp)+1}{(ma/mfp) \times Ma + Mfp} + 1 \right]^2 = mfo \times \left[ \frac{(ma/mfp)+1}{(ma/mfo) \times Ma + Mfo} + 1 \right]^2
\]

Therefore the trapped fuel mass ratio for iso-octane and iso-pentane is given by:

\[
\frac{mfo}{mfp} = \frac{\left[ \frac{(ma/mfp)+1}{(ma/mfp) \times Ma + Mfp} + 1 \right]^2 \times \left[ \frac{(ma/mfo) \times Ma + Mfo}{(ma/mfp) \times Ma + Mfp} + 1 \right]^2}{\left[ \frac{(ma/mfo)+1}{(ma/mfo) \times Ma + Mfo} + 1 \right]^2 \times \left[ \frac{(ma/mfp)+1}{(ma/mfp) \times Ma + Mfp} + 1 \right]^2}
\]

Stoichiometric air/fuel ratios for:

Iso-octane = 15.05
Iso-pentane = 15.25

Since all tests were carried out at an equivalence ratio of approximately 0.9 for both fuels then:

A/F ratio of iso-octane = 16.72
A/F ratio of iso-pentane = 16.94
Molecular mass of:

\[
\begin{align*}
\text{Air} & = 29 \\
\text{Iso-pentane} & = 72 \\
\text{Iso-octane} & = 114
\end{align*}
\]

Substitution of these figures into equation(5) gives:

\[
m_{fo} = 1.09 \times m_{fp}
\]  \hspace{1cm} (6)

At given conditions where the engine is run at fixed speed, load, water temperature and equivalence ratio for Iso-octane and Iso-pentane:

(1) Iso-octane emissions should be about 9 percent greater than those of Iso-pentane due to crevice volumes alone.

(2) Any absorption/desorption effect should show up on top of this 9 percent.

In order to give a more conservative estimate to the absorption/desorption effect this figure of 9 percent has been rounded up to 10 percent. The extra 1 percent would help to allow for any other small hydrocarbon sources which may also contribute unequal levels of hydrocarbons for the two fuels.
APPENDIX (H)

HENRY CONSTANT TEST

H.1 Introduction

Henry Constants at three different temperatures (61, 42 and 91 degrees C) have been determined for Iso-octane, n-hexane and Iso-pentane in the oil used in the engine tests from chromatographic measurements[33]. For temperatures lying between and slightly outside of those just defined, Henry constants are found by interpolation and extrapolation of the curves, Figure (H.5), respectively.

The chromatographic technique was originally suggested by Martin[32]. Prausnitz et al[33] have made use of this technique to find low pressure solubilities of five light hydrocarbons in three heavy paraffin solvents in the temperature region 30 - 200 degrees C. The same method has been adopted to find the solubilities of Iso-octane, n-hexane and Iso-pentane in the engine test oil. Although n-hexane was not used as an engine test fuel it has been used as a solute in the Henry constant experiment to yield a more complete map of solubilities versus temperature, Figure (H.5).

H.2 Experimental

Measurements were made with a Pye Unicam gas chromatograph fitted with two metre coiled glass capillary columns. Acid-washed diatomaceous earth material (Chromosorb P) of mesh number 100/120 was used as solid support. The solutes, Iso-pentane, n-hexane and Iso-octane were obtained from Fisons chemicals and purities exceeded 99.9 percent. The common solvent was the engine test oil. Nitrogen was
used as the carrier gas; the flow rate was maintained at about 25 cc. per minute and accurately measured with a bubble flow meter.

Prior to loading the columns, solvent and solid support were weighed separately. The solvent made up about 8 percent of the mixture. Isopentane was added to dissolve the solvent and then slowly evaporated to allow uniform coating of the solid support. Columns were first weighed empty and then again after loading to establish the weight of the solvent present. Solute samples injected into the chromatograph had a volume of approximately 0.3 microlitres each and air gas samples about 1/2 cc. each. The flame ionisation detector signal was recorded on the strip chart of a Hewlett Packard integrator.

H.3 Data Reduction

Henry's Constant, H, for a solute in a particular solvent is defined by

\[ H = \frac{P}{X} \]  \hspace{1cm} (1)

Where \( P \) is the partial pressure of the solute and \( X \) is its mole fraction. Henry's Constant maybe obtained from the chromatographic partition coefficient [32] according to

\[ H = \frac{RT}{BM} \]  \hspace{1cm} (2)

Where \( T \) is the column temperature, \( R \) is the gas constant amd \( M \) is the molecular weight of the solvent (ie. engine test oil). The approximate composition of the engine oil was 82.5 percent Mid-East base oil, 15.5 percent additive packing and 2 percent viscosity improver. More detailed information of the oil composition, not
available, was required to assess the molecular weight of the oil. The molecular weight of the engine oil was assumed to be the same as that for squalane (i.e. 422). The plots shown in Figures (5.4) & (5.5) are in terms of the reciprocal of Henry constant which is linearly dependent on the molecular weight of the oil (see equation (2)). The actual value for molecular weight is unimportant since it is only the trends that are of interest in Figures (5.4) & (5.5).

The partition coefficient, B, is defined as the ratio of the mass of solute per gram of solvent to the mass of solute per cc. of gas at column temperature. For a given system, B, is related to peak retention time, tr, by

\[
B = (tr - tm) \frac{V}{W}
\]

Where \( tm \) is the peak retention time of an essentially insoluble gas (air), sec.; \( V \) is the flow rate of carrier gas at column outlet pressure and temperature, cc. per sec.; and \( W \) is the weight of solvent in the column, grams.

The pressure correction factor, \( j \), is given by

\[
j = \frac{1.5(P^2_{in}/P^2_{out} - 1)}{(P^3_{in}/P^3_{out} - 1)}
\]

Where \( P_{in} \) is the pressure at the inlet of the column and \( P_{out} \) is the pressure at the outlet of the column.

A schematic of the apparatus is shown in Figure (H.1) and tabulated data is found in Table (H.1). Chromatograms for the three fuels (Iso-pentane, n-Hexane and Iso-octane) at the three temperatures (61, 42 and 91 degrees C) are given in Figures (H.2), (H.3) & (H.4). The
average peak retention time was found from three chromatograms for each fuel/temperature setting but for simplicity only one chromatogram per fuel/temperature combination is shown in the Figures.
Gas chromatographic apparatus

Ref. [33]

Fig. H·1
CHROMATOGRAMS
(WITH ELUTION TIMES)

COLUMN TEMPERATURE  42°C

2.01 MIN.
ISO-PENTANE

5.85 MIN.
n-HEXANE

13.62 MIN.
ISO-OCTANE

Fig. H.2
CHROMATOGRAMS
(WITH ELUTION TIMES)

COLUMN TEMPERATURE 61°C

Fig. H·3
CHROMATOGRAMS
(WITH ELUTION TIMES)

COLUMN TEMPERATURE 91°C

1.04 MIN.
ISO-PENTANE

1.79 MIN.
n-HEXANE

3.14 MIN.
ISO-OCTANE

Fig. H·4
USING MOL. WT. OF SQUALANE FOR ENGINE OIL

![Graph](image-url)

**Legend**
- ■ ISO-PENTANE
- □ ISO-OCTANE
- ◇ N-HEXANE

**Fig. H.5**
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HENRY CONSTANT TEST DATA
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APPENDIX (J)

THE SOLUBILITIES
OF ISO-OCTANE AND ISO-PENTANE IN SQUALANE

The following discussion indicates the reasons behind using Iso-octane and Iso-pentane as fuels in an engine test to demonstrate the significance of the absorption/desorption effect. Figure (J.1) shows data from Reference [25] displayed as lines of constant temperature in the variation of Henry's Constant for a range of paraffins dissolved in Squalane. It should be noted that the greater the Henry constant for a given paraffin/oil combination the lower the solubility is of the paraffin in the oil. Since modelling [26],[10] and experiment [23],[24],[27] have indicated the fuel/oil solubility dependence of the absorption/desorption mechanism the work in this thesis has aimed to use this characteristic to show the relative significance of this mechanism on exhaust hydrocarbons.

The requirement was to run an engine on two fuels whose solubilities in oil differed appreciably and thereby determine the magnitude of the absorption/desorption effect from differences in exhaust hydrocarbons measured for the two fuels. Since the choice of fuels was subjected to other constraints such as availability, octane number and more importantly a criterion to keep the fuel system of the engine unchanged, two liquid fuels were finally chosen, Iso-octane and Iso-pentane.

It is evident from Figure (J.1) that the Henry Constant for Iso-pentane is at least a factor of ten greater than that for Iso-octane depending on temperature. Therefore providing that hydrocarbon contribution from other sources, such as crevices and deposits, remain approximately the same for both fuels any difference in
exhaust hydrocarbons between Iso-octane and Iso-pentane for a given set of engine conditions could be attributed to the absorption/desorption effect. However it was found that this assumption was not entirely correct and details of this are given in Appendix(G).
VARIATION OF HENRY'S CONSTANT FOR RANGE OF PARAFFINS DISSOLVED IN SQUALANE (C₃₀H₆₂).
DATA FROM REF. [25]

Fig. J.1