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OCTANE REQUIREMENT INCREASE ARISING FROM THE USE OF LEAD FREE FUEL

JAMIL AHMAD

Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

May 1989

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Summary

Lead in petrol has been identified as a health hazard and attempts are being made to create a lead-free atmosphere. Through an intensive study a review is made of the various options available to the automobile and petroleum industry. The economic and atmospheric penalties coupled with automobile fuel consumption trends are calculated and presented in both graphical and tabulated form.

Experimental measurements of carbon monoxide and hydrocarbon emissions are also presented for certain selected fuels. Reduction in CO and HC's with the employment of a three-way catalyst is also discussed.

All tests were carried out on a Fiat 127A engine at wide open throttle and standard timing setting. A Froude dynamometer was used to vary engine speed.

With the introduction of lead-free petrol, interest in combustion chamber deposits in spark ignition engines has been renewed. These deposits cause octane requirement increase or rise in engine knock and decreased volumetric efficiency. The detrimental effect of the deposits has been attributed to the physical volume of the deposit and to changes in heat transfer.

This study attempts to assess why leaded deposits, though often greater in mass and volume, yield relatively lower ORI when compared to lead-free deposits under identical operating conditions. This has been carried out by identifying the differences in the physical nature of the deposit and then through measurement of the thermal conductivity and permeability of the deposits. The measured thermal conductivity results are later used in a mathematical model to determine heat transfer rates and temperature variation across the engine wall and deposit.

For the model, the walls of the combustion cylinder and top are assumed to be free of engine deposit, the major deposit being on the piston head. Seven different heat transfer equations are formulated describing heat flow at each part of the four stroke cycle, and the variation of cylinder wall area exposed to gas mixture is accounted for. The heat transfer equations are solved using numerical methods and temperature variations across the wall identified. Though the calculations have been carried out for one particular moment in the cycle, similar calculations are possible for every degree of the crank angle, and thus further information regarding location of maximum temperatures at every degree of the crank angle may also be determined.

In conclusion, thermal conductivity values of leaded and lead-free deposits have been found. The fundamental concepts of a mathematical model with great potential have been formulated and it is hoped that with future work it may be used in a simulation for different engine construction materials and motor fuels, leading to better design of future prototype engines.

Key Words: ORI, Exhaust Emissions, Unleaded Deposit

ERRATA

Please note in order to attain consistency of SI units the following corrections are to be inserted:-

- Page 212, line 6 should read "manifold pressure 99.28 KPa and temperature 300° K".

  Line 7 should read "exhaust pressure 103.42 KPa" and "temperature 1389° K".

  Last line should read Tmixture = 333.6° K.

- Page 213, the following should read as:-

  V_1 = 0.559 M^3 U_1 = 10.76 KJ
  H_1 = 63.3 KJ V_2 = 6.20 x 10^{-2} M^3
  T_2 = 605.6° K P_2 = 1622.3 KPa
  U_2 = 125.6 KJ

- Page 214, the following should read as:-

  $V_3 = V_2$ = 6.20 x 10^{-2} M^3 U_3 = 1439.5 KJ
  P_3 = 8101.4 KPa T_3 = 2805° K
  V_4 = 55.9 x 10^{-2} M^3 T_4 = 1805.6° K
  P_4 = 586 KPa U_4 = 725.88 KJ

- Page 215, the following should read as:-

  P_5 = 103.42 KPa $T_4{}^1$ = 1261° K
  $U^1{}_4$ = ^{L}132.6 KJ U_5 = 111.8 KJ
  $V_4 = V^1{}_4$ = 2.15 M^3 $H^1{}_4$ = 575 KJ
  $P^1{}_4$ = 103.42 KPa T_5 = 1261° K
  V_5 = 55.9 x 10^{-2} M^3

  Line 11 should read: "Volume of gases left in the cylinder is 6.20 x 10^{-2} M^3."

- Page 216, Table 34
  Heading in second column should read : "Pressure KPa" and all the values in the column to be multiplied by a factor of 6.8948.
  Heading in third column should read: "Relative Volume M^3" and all values in the column to be multiplied by a factor of 3.531×10^{-2}".
  Heading in sixth column should read: "Temperature °K" and all values in the column to be multiplied by a factor of 5/9.

- Page 220, Table 35
  Heading in second column should read: "Gas Volume M^3" and all values in the column to be multiplied by a factor 3.531×10^{-2}.
  Heading in seventh column should read: "HM(KJ)" and all values in the column to be multiplied by a factor of 1.055.
  Heading in eighth column should read: "T (°K)" and all values in the column multiplied by a factor of 5/9.

- Page 221, the following should read as:-

  $V_2 = 55.9 \times 10^{-2}\ M^3$, $P_2 = 99.28$ KPa,
  $V_3 = 6.20 \times 10^{-2}\ M^3$, $P_3 = 1746$ KPa.

- Page 222, Table 36
  Heading in first column should read: "Pressure P(KPa)" and all values multiplied by a factor of 6.8948.
  Heading in second column should read: "Volume V(M^3) and all values in the column to be multiplied by a factor 3.531×10^{-2}.
  Heading in fourth column should read: "Temperature T(°K)" and all values in the column to be multiplied by a factor 5/9.

- Page 223, the following should read as:-

  $V_3 = 6.20 \times 10^{-2}\ M^3$, $P_1 = 8101$ KPa,
  $V_4 = 55.9 \times 10^{-2}\ M^3$, $P_2 = 586$ KPa.

- Page 224, Table 37
  Heading in first column should read: "Pressure P(KPa)" and all values to be multiplied by a factor (6.8948).
  Heading in second column should read: "Gas Volume V (M^3)" and all values to be multiplied by a factor (3.531×10^{-2}).
  Heading in fourth column should read: "Temperature (°K)" and all values to be multiplied by a factor (5/9).

- Page 239
  Heading in second volumn should read, the deposit surface temperature T_D (°K) and all the factors to be multiplied by a factor of 5/9 (°F -32).
  Heading in third column of the table should read, outside wall temperature Tow (°K) and all the values in the column to be multiplied by a factor of 5/9 (°F -32).
  Last line should read "equivalent to 43.36 KJ".

I DEDICATE THIS WORK

TO MY MOTHER and FATHER

Acknowledgements

I am indebted to several people for their generous assistance with this project, their contributions have been numerous and varied. It is hoped that this acknowledgement will partially express my sincere gratitude to:

My tutor, Dr.R.G.Temple, for his guidance and patient supervision throughout this project;

the staff of the Mechanical and Electronics workshop for their assistance with experimental equipment;

the post graduate students of the department for their contribution in creating a lively and cheerful atmosphere;

and most particularly to my parents and family who have borne the many inconveniences and trials of this long period with a minimum of complaint and maximum of understanding and support.

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INTRODUCTION

INTRODUCTION

Since the 1920's when combustion chamber deposits were first discovered by Lea and Friel (16), there has been widespread interest in the subject. Initially deposits were thought to be a mere nuisance that fouled the engine with soot and gum. Research in the first twenty years, since deposits were first discovered, was mainly based on testing the quantity of deposit produced from different fuels and motor oils. Later research was diverted to identifying and quantifying the effects of the deposit on the engine requirement of fuel quality. This led to expressing the harmful effects of the deposits in terms of octane requirement increase.

Recent research has been on the inducement of knock and mechanisms by which the deposits affect the engine. High speed photography has contributed significantly to the understanding of the knocking process (17).

During the 1960's and 1970's it became a popular belief that the detrimental effect of the deposits was due to the catalytic effect, volumetric effect and thermal effect. However further research showed the catalytic effect to be negligible. The octane requirement increase due to the volumetric effect could be easily classified but is not completely clarified. The thermal effect is even less understood than the volumetric effect.

There has been other work in this field relating to deposition mechanisms and composition of deposits. However a great deal of work still remains to be carried out in this important subject that costs the consumer millions of pounds per annum, in loss of engine efficiency. The increasing economic pressures to both the automobile and petroleum industry has led to the renewed interest in combustion chamber deposits and octane requirement increase (ORI).

In light of previous research the objectives of the present study are:

1. As octane requirement increase reduces engine efficiency,an economic assessment is required that incorporates both the cost of the fuel together with the decreased efficiency arising due to octane requirement increase arising from the use of that fuel.
2. To quantify the ORI attributed to the volumetric effect of the deposit and that attributed to the thermal effect.
3. Measurement of the thermal conductivity of the leaded and unleaded deposits under conditions resembling in situ measurements.
4. Chemical and physical analysis of leaded and unleaded deposits
5. The potential of any fuel is limited by the amount and type of emissions,irrespective of the ORI affect. Investigation with blends of Ethanol and petrol, employing a three - way exhaust catalytic convertor to determine the overall affect on hydrocarbon emissions.
6. As the combustion chamber deposits reduce heat flow, a theoretical study in the form of a mathematical model is desired, in order to assess the temperature profile in the deposit and the combustion chamber walls.

In this research the effects of the deposits have been approached from a much wider aspect than in the previous years, firstly due to different deposits arising from the use of leaded and lead-free fuel. Secondly an economic analysis is carried out that incorporates the different deposits produced and their financial impact. Six different optional proposals for reducing lead emissions were considered in the analysis and the conclusions reached were startling, as they showed the British Government's recent decision to promote the use of lead-free petrol of 98 RON to be both economically and environmentally disadvantageous.

Work using alcohols and other oxygenates by previous researchers in the department revealed some coincidental relevant findings. On stripping the engine after it had been run on alcohols and blends of alcohols, the engine was found to be completely free of any deposits. Alcohols therefore represent not only octane boosters for gasoline, but would also reduce ORI arising from deposits. Interest was drawn to alcohol blends as a method of reducing ORI. No assessments could be made as regards how quickly the deposit could be removed. Emission results with alcohol blends were obtained both with and without the use of a three-way catalytic converter.

In light of the problems associated with identifying the exact nature in which the generally believed thermal effect, affects ORI; thermal conductivities of both leaded and lead-free deposits were measured. Thermal conductivity of the leaded deposit was found to be 50% greater than that of the unleaded deposit. This work was followed by examination of deposits under the scanning electron microscope.This gave visual comparisons between leaded and lead-free deposits. No three layer stratum structure was found, as reported in some previous work. The photographs of the deposits also revealed the extent of porosity in the deposits. This work was followed by the measurement of permeability of the deposits, as this is thought to affect heat transfer out of the engine and no previous data relating to this property is listed.

Finally a mathematical model is developed that utilises the measured thermal conductivities and expresses the difference in heat transfer out of the engine walls and piston head, with a clean engine and compared with a case where a 0.5 mm deposit had accumulated on the piston head.

The mathematical model utilises Hottel charts which are based on the principle of combustion at constant volume, as is the case in extreme conditions of heavy knock. Pressures and temperatures have been calculated at every two degrees of the cycle. The heat transfer equations were developed by considering energy balances at various positions on and in the deposit wall composite.

CHAPTER 1

LITERATURE SURVEY

1.1 The Internal Combustion Engine

The two forms of internal combustion engines that exist today, the petrol engine and the diesel engine, occupy dominant roles as means of land transport, mainly because of the easy availability of the petrol and diesel fuel. The physical and chemical properties of the fuels have influenced the way the two engines have developed over the years into their present forms.

The difference (and the aspect with which we are presently concerned) between the two engines lies in the combustion of the respective fuels. In the diesel engine, the fuel is injected in the form of a spray. A flame starts inside the spray and travels rapidly through it. The combustible mixture in this case is heterogeneous and combustion has no definite starting or finishing point.

In the petrol engine the fuel and air are pre-mixed in the carburetor, this ensures that by the time the piston has compressed the mixture up to the stage when the spark is fired the combustible mixture is more homogeneous, and unlike the diesel, premixed combustion takes place across the chamber, starting always from the spark plug.

It was felt that this point of difference should be highlighted at the beginning of the study to explain briefly why the petrol engine knocks and the diesel engine does not, which is a point that underlies the whole field of study.

1.2 Hydrocarbon Combustion in Spark Ignition Engines

1.2.1 Constituents of Petrol

First of all before considering the combustion process let us consider the typical components of petrol:

				Boiling point
1.	Paraffins:	Pentane	C_5H_{12}	36°C
		Hexane	C_6H_{14}	69°C
		Heptane	C_7H_{16}	98°C
		Octane	C_8H_{18}	135°C
		Iso-Octane	C_8H_{18}	103°C
		Nonane	C_9H_{20}	155°C
		Decane	$C_{10}H_{22}$	173°C
2.	Olefins:	Olefins of similar boiling point as paraffins		
		Pentene	C_5H_{10}	30°C
		Hexene	C_6H_{12}	63°C
		Heptene	C_7H_{14}	93°C
3.	Aromatics	Benzene	C_6H_6	80°C
		Toluene	C_7H_8	110°C
		Xylene	C_8H_{10}	110°C
4.	Napthenes	Cyclopentane	C_5H_{10}	50°C
		Cyclohexane	C_6H_{12}	81°C
		Cycloheptane	C_7H_{14}	119°C

It can thus be seen that petrol contains hydrocarbons with varying proportions of carbon and hydrogen. The principal elements concerned in the combustion process include hydrogen, carbon, oxygen and, to some degree, sulphur (approx. 0.01%). Nitrogen, as the main constituent of air, is of interest particularly in relation to nitrogen oxide emissions.

1.2.2 Combustion Process

As mentioned earlier the combustible elements in fuels are predominantly carbon and hydrogen, with small amounts of sulphur, as the only other fuel element. Although liquid fuels are mixtures of complex hydrocarbon (37), for simplicity as in the past, it will be assumed that petrol average to the molecular formula of octane (C_8H_{18}) and in the case of complete combustion, the following equation shows the chemical reaction that takes place:

$$C_8H_{18} + 12.5O_2 + 47N_2 \rightarrow 8CO_2 + 9H_2O + 47N_2$$

As regards the physical process many theories have been set out to explain the process of combustion in petrol engines and a vast amount of experimental work has been carried out on the subject. For example, the methods employed include those of chemical analysis of the gases taken at different stages of the combustion process (18), cinematograph photographs, etc.(17). Whilst there is no clear understanding, or at least accepted explanation, it is felt that the explanation of R.H.Richards (38,39) is adequate and outlined here. When the electric spark occurs across the electrodes of the sparking plug it leaves behind a thin flame, this may be regarded as the starting point of the flame. This flame then spreads to the envelope of mixture that immediately surrounds it, at a rate that depends primarily upon the temperature of the flame front, and temperature and density of the surrounding mixture. There thus grows up, gradually at first, the rapidly enlarging flame which spreads through the combustion chamber. In theory the combustion products would be carbon dioxide and water, however, in practice, combustion is incomplete and carbon monoxide as well as CO_2 is produced, and some of the hydrocarbons remain unburnt. To a small extent nitrogen and oxygen also react under the high temperatures of the combustion chamber to form oxides of nitrogen. Also some of the intermediate products formed, in what is a complex process, may cause spontaneous ignition leading to detonation in the combustion chamber.

1.3 Detonation and the S.I. Engine

The mechanism of detonation is the setting up within the cylinder wall a pressure wave travelling at high speed (500m/s) compared to the normal flame front speed of 25m/s. By its impact against the cylinder walls, the pressure wave gives rise to a high pitched "ping" sound known more commonly as knocking or detonation (46).

The broad physical mechanism of the knocking phenomenon was postulated a long time ago and is basically, initially the same as the normal combustion of fuel in the engine, i.e. as the fuel and air mixture is ignited by the passage of a spark, a rapidly accelerating flame builds up spreading outward with great rapidity. If the mixture were at rest, the film of flame would travel in an unbroken front across the chamber. Due to high turbulence the film is fragmented. As the flame front advances the unburnt mixture, whose temperature is raised both by compression and by radiation from the advancing flame until the point arises when the remaining unburnt charge ignites spontaneously, this sets up a pressure wave, which passes through the burning mixture at very high speed, such that the impact against the cylinder walls, gives rise to a knocking sound as though the engine has been struck with a light hammer.

It is difficult to ascertain what proportion of the charge is detonated, but previous researchers have put the amount to at least 25% of the total charge(46).

Research(42) has shown that the process of combustion involves some extremely complex chemical reactions and that all sorts of products of partial combustion are formed. It is believed that these are transient only and thus become difficult to track and identify. It is thought that one or more of these transient products, which as a initiator sets off the charge, but no-one has yet been able to completely identify the transient products.

However, sampling tests have shown that with the use of lead anti-knocks, the concentration of peroxide radicals is reduced. When the more stable peroxides were tested(42) under laboratory conditions, they were found to be very pro-knock. This suggested that lead showed anti-knock properties by virtue of it suppressing the formation of peroxides.

A number of tests carried out by the National Bureau of Standards (40,41) showed very briefly, using high speed valves for sampling, that the knocking process occurred in a number of steps, figure 1.

a) Dark oxidation: This is the start of peroxide formation at a temperature of approximately 330°C.

b) Cool flames: As the temperature increases the forming of new compounds slows down and thermal decomposition becomes more important (peroxides converted to aldehydes, ketones and unsaturated hydrocarbons). Radiation accompanying the decomposition is a characteristic of formaldehyde.

c) Blue flames: As the temperature rises the concentration of predominantly hydrogen peroxide and formaldehyde rises to a very high level accompanied with a blue luminescence, resulting in substantial increases in the pressure.

d) Autoignition ((knock): As the temperature rises to approximately 600°C the reaction suddenly increases to a rapid speed as the hot flame commences, resulting in violent pressure waves being set up and causing knock.

This idea that simple radicals made up of hydrogen and oxygen touch off knock or autoignition is an intriguing one, but the fact that simple radicals (OH^-, HO_2^o, H^o) are important in the knock reaction is rather impressive.

The other theory concerned with knocking involves the formation of alkyl radicals by the reaction of alkyl molecules with oxygen (43,44,45).

$$R + O_2 \rightarrow R^* + HO_2^*$$

The alkyl radical may, amongst other things, react with a further molecule of oxygen to produce a peroxide radical

$$R^* + O_2 \rightarrow ROO^*$$

The peroxide radical may further react with a fuel molecule to produce hydro-peroxide radicals

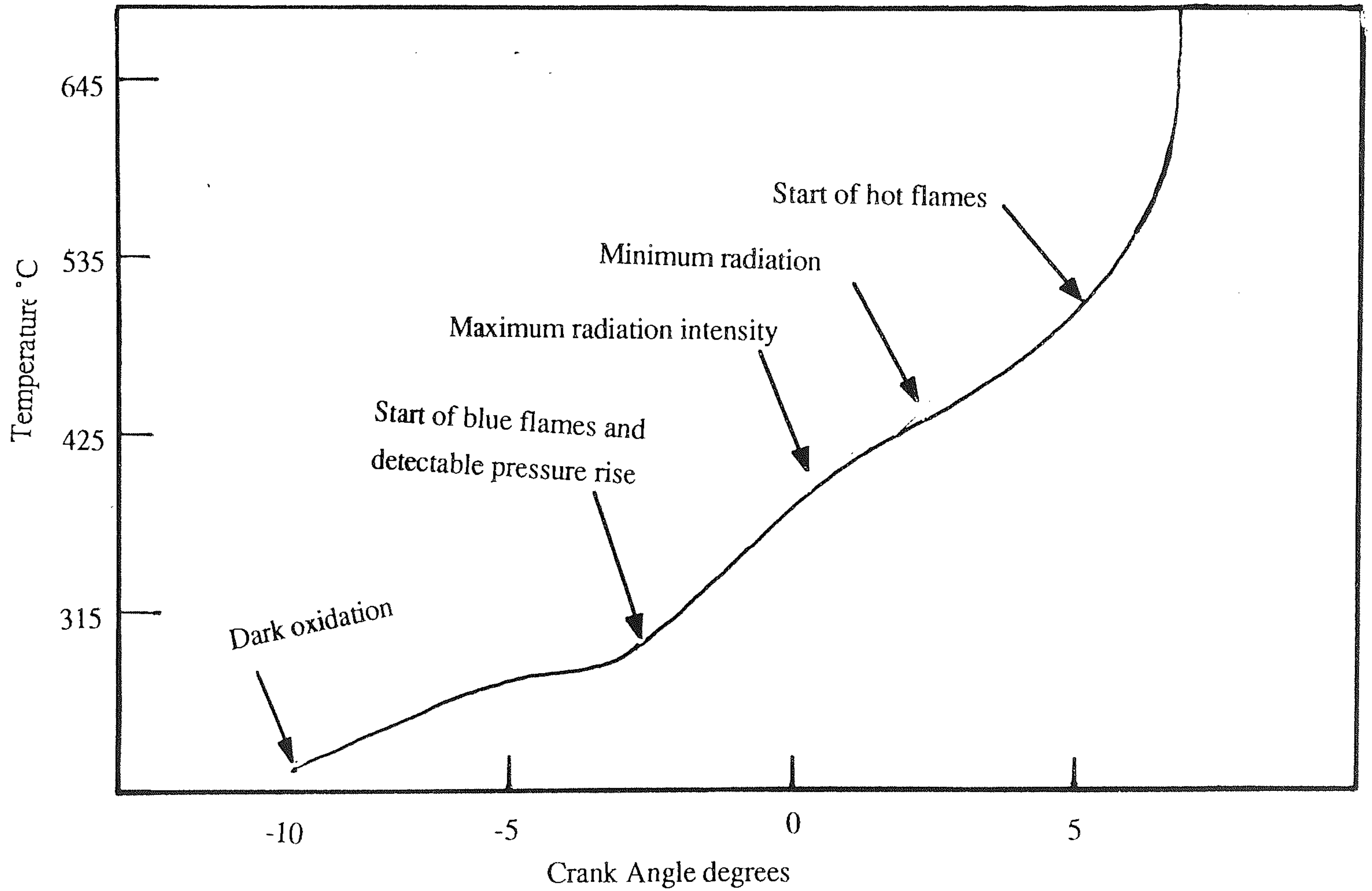


Fig 1 Temperature time curve for n-hexane Auto ignition conditions

$$ROO^{*} + R \rightarrow ROOH + R^{*}$$

followed by

$$ROOH \rightarrow \underset{\text{alkoxy radical}}{RO^{*}} + OH^{*}$$

Termination of the reactions occur by radical-radical interactions or destruction at the wall.

It is of course inevitable that alongside the reactions listed above there are many other reactions taking place simultaneously, for example, the radicals may isomarise, decompose or react to form complex intermediates (41) figure 1.

1.4 Compression Ratio and Engine Knock

An important factor in the efficiency of any given design of internal combustion engine is its compression ratio. Within certain overriding factors (e.g. friction and other energy losses and the requirements of gaseous emission control standards, which vary according to engine design), the higher the compression ratio the greater the power obtained and the better the fuel economy (46), as represented by the formula:

$$\frac{\text{net power output}}{\text{heat content of mixture}} = \text{efficiency} = 1 - \left(\frac{1}{r}\right)^{0.258}$$

The mixture in the furthest corner (known as the end gas) is subject to heating and compression for longer periods than any other location, particularly when the engine is under load. Under these conditions the end gas zone is brought to an abnormal state of partial oxidation and ignites at high speeds. This emits the vibrations which are heard as a familiar knocking noise. There is also, what is known as light knock or acceleration knock which is relatively harmless, but in a heavier and persistent form it not only reduces the efficiency and power output of the engine but can cause serious damage to pistons and cylinder heads, leading to engine failure(47,48). The other variety of knock, known as heavy knock or high speed knock, occurs at high speeds, i.e. 4-5000 rev/min. This is normally inaudible to the driver above the engine and road noise, but is the most dangerous form of knock because it may occur very rapidly in motorway cruising conditions, with the driver unaware until the point where the pistons melt and the engine may seize up.

1.5 Other Factors Affecting Knock

The problem of knock is important in spark-ignition engines for a number of reasons:

a) Design limitation in achieving maximum power output and efficiency.
b) Knock can cause engine damage under severe conditions.
c) The noise can cause apprehension to the motorist.

The factors that lead to knock can be due to either the fuel or the engine.

1.5.1 Sensitivity: The research method of octane number determination (see Section 1.7) rates a gasoline higher than the more severe motor method. The difference between the two methods is the measure of the sensitivity of the fuel to changes in operating conditions.

1.5.2 Octane Distribution: The importance of octane distribution in a fuel is that during full throttle accelerations there can be segregation of the high and low boiling components in the inlet manifold. This has the effect that, for a short period, only the lower boiling components of gasoline, that have been fully vapourised, go forward to some cylinders, while the high boiling materials still in liquid form hang back in the manifold. Since the lighter fraction mostly have a lower octane quality than the heavier components, transient knock can occur.

1.5.3 Ignition Timing: The tendency to knock increases as spark advance B.T.D.C. is increased. Although it is possible to make large changes in octane requirements by adjustment of the spark advance mechanism of a car, it must be borne in mind that maximum power is influenced significantly if the spark timing is moved too far from the optimum.

1.5.4 Temperature: Since detonation occurs in the last 25% of the mixture charge, thus the detonation depends on the degree of compression and heating which the unburnt gas mixture can endure, that is the chemical nature of the fuel, i.e. pre-flame oxidation. Secondly, we can also say that detonation will also be affected by the opportunities the unburnt mixture has for getting rid of heat which is being thrust onto it by the rapidly advancing flame front.

Increase in engine temperature, particularly the charge temperature, increases the tendency to knock.

1.5.5 Engine load Increasing the load raises the engine temperature and pressure. Normally the most severe condition would be at wide open throttle.

1.6 Engine Damage Due to Knock

Abnormal combustion which produces different forms of engine damage cannot be all associated with knock directly, because piston melting, inlet valve deformation, for example, can be associated with pre-ignition. However, often pre-ignition can arise due to knock. Also damage to the engine can occur due to lack of coolant and insufficient lubrication.

Erosion damage to piston head and cylinder head are examples of common damage when knocking has occurred, and these present the worst problems. Failure of piston ring lands, cylinder head gasket failure, spark plug failure, loosening of valve seat inserts and piston seizure, are also examples of different engine damage that have been associated with engine knock.

1.7 Petrol Quality and Octane Number

Petrol quality is often defined by its octane number which gives an indication of the degree to which a fuel resists knock. Based on the arbitrary scale where n-heptane has an octane number of zero, and iso-octane a value of 100.

The octane number of petrol is determined by using a variable compression ratio, single cylinder engine. The compression ratio is gradually increased until the point where knocking occurs. The octane number of the particular fuel is then equal to that of a mixture of n-heptane and iso-octane which produces the same results. There are two designated octane numbers specified by the Co-operative Fuel Research Committee (CORC) known as the research octane number and motor octane number.

i) Research Octane Number (RON)

This is determined as simulating acceleration from low speed - the condition from which audible knock occurs - and is carried out under the following conditions:

engine speed	600 rpm
air intake temperature	22°C
mixture temperature	not controlled
ignition advance	13°
coolant temperature	100°C

ii) Motor Octane Number (MON)

This simulates driving at high speeds - a condition in which the high temperature can cause the performance of fuels to degrade more than others and this can lead to high speed knock. This would naturally give a lower octane number; conditions as laid down by the CORC are:

engine speed	900 rpm
air intake temperature	38°C
mixture temperature	149°C

ignition advance	variable
coolant temperature	100°C

Both motor and research octane numbers, together with fuel sensitivity, are used to specify fuel quality at all conditions, because two fuels with the same RON may have very different MON, thus, the performance of each fuel will differ at high speeds(47).

The octane distribution through the boiling range of the fuel is also an important factor, as mentioned earlier. Fuel segregation may occur during wide open throttle acceleration with some fuels. A measure of research octane number of the lighter components (R_{100}) which boil off at 100°C, the front end octane number. The difference between this and the whole fuel research octane number is known as the R_{100} which is preferred to be as small as possible.

1.8 Organic Lead Compounds as Anti-Knock Additives

Anti-knock additives are used to achieve the required octane levels in commercial gasolines in the most economical way. The most widely used are the lead alkyls, such as tetraethyl lead (TEL) and tetramethyl lead (TML). Lead alkyls were first discovered as anti-knocks more than six decades ago, and because of their effectiveness for enhancing octane quality and economical advantages they have not yet been replaced. Though the amount of lead added as TEL and TML has over the years been progressively reduced. Currently in the U.K. it is not allowed to exceed a maximum limit of 0.15 g/l of petrol. With the use of lead alkyls, scavengers have also had to be used so as to avoid the collection of lead oxides and other compounds during combustion (see Section 1.13), but are removed with the exhaust. The most common scavengers used are mixtures of ethylene dibromide and ethylene dichloride and they function by forming volatile lead halides.

A typical composition of the lead antiknock fluid used in the U.K. is shown in the table below(41).

	composition % wt		Boiling point
TEL	lead alkyls	61.5%	200°C
	ethylene dibromide	17.9%	
	ethylene dichloride	18.8%	
	dye, diluent, inhibitor	1.8%	
TML	lead alkyls	50.8%	110°C
	ethylene dibromide	17.9%	
	ethylene dichloride	18.8%	
	dye, diluent, inhibitor	12.5%	

1.9 Other Properties of Lead in Petrol

Besides boosting octane quality of petrol, the lead in petrol also prevents or inhibits, for example, the valve recession. The lead helps by providing a protective and a lubricating film. Valve recession or erosion of valve seats (3,4) would otherwise allow combustion gases to leak away, thus resulting in the loss of compression. This problem can be eliminated when using unleaded petrol, by the use of aluminium cylinder heads and, in some cases, the valve seat inserts and the valve themselves are made from a harder material (29).

In contrast to its positive effect on engine performance, lead in petrol indirectly has some adverse effects on certain components of the car. The combustion products of lead alkyls (mainly lead oxide) tend to accumulate in the combustion chamber and cause fouling of spark plugs; to counteract this, scavengers are also added with lead alkyls. These convert the non volatile combustion products into more volatile chlorides and bromides of lead, which are carried out with the rest of the exhaust gases. Even with the use of scavengers the spark plugs do not last as long on leaded petrol as they do on unleaded, and if not properly serviced, this results in wastage of fuel (24,29).

On combustion, the scavengers used, also generate acids which have strong corrosive effects on iron and steel. They may also collect in the lubricating oil, resulting in corrosion of engine parts.

1.10 Why Lead Must be Eliminated From Petrol

There are two main reasons for reducing lead from petrol. Firstly, during the past 15-20 years there has been considerable concern over the health effects of lead emissions. Evidence linking lead exposure with low-level impairments of mental functioning in young children has been postulated (29-31). In fact, Yule et al found a lead-related average deficit of 7 I.Q. points in a group of London children, whose blood levels were not uncommon for urban areas (32).

It has been estimated that 70% of the lead used as an anti-knock additive is emitted as vehicle exhaust, the remaining 30% remains in the exhaust pipe and the engine. Lead emission from vehicle exhausts accounts for 90% of the air borne lead and 24 to 60% of the blood level of lead (32,33). Although the evidence linking health hazard to exhaust emissions has not been conclusively accepted, the government nevertheless, has decided to phase down the lead in petrol (34,35). The new lead level for premium petrol in Britain since January 1986, is 0.15 grams per liter. The first introduction of lead-free petrol was in July 1986.

The second reason why elimination of lead or phase down of lead is required, is over the acid rain pollution. West Germany, with its vast forestry, has taken the lead towards unleaded gasoline. All the new cars must be able to run on unleaded gasoline, the cars are also installed with a catalytic converter in the exhaust pipe. With leaded fuel the catalytic converters become poisoned and unable to function. The catalytic converters reduce oxides of nitrogen, while oxidising carbon monoxide and hydrocarbons (30,36). The concept of acid rain and its effect on trees and rivers is a subject that is causing increasing public concern.

1.11 Lead in Air

Nearly all the lead in the air in the U.K. comes from exhaust gases of petrol engines (30). In 1987 about 2.8 thousand tonnes of lead was used in petrol, of which approximately 70% (29) is thought to be released into the atmosphere; other researchers put this figure to 75% (2). In contrast, the annual emissions from major U.K. lead industries is very small(29).

The concentration of airborne lead in any locality depends on the amount of traffic and weather conditions. Nevertheless it is higher close to roads than the background values, and about 20% of the emitted lead is deposited within 100 metres of the road (30), where of course there would be additional depositions through re-suspension of lead from the road surface, including lead from contaminated motor oil. Lead which is not deposited in the immediate vicinity of the roads is transported in the air over considerable distances. It has been estimated by Chamberlin and others (29,30) that nearly half of the lead emitted is blown out to sea and the remainder deposited in the U.K. The fact that so much of the exhaust lead is blown out to sea and into other countries does not mean that the problem in Britain is reduced, because it may still enter the food chain.

1.11.1 Action in the U.K.

Towards then end of 1972 the British Government announced a maximum permitted lead level in petrol of 0.84 g/l. The objective was to bring the level of lead emissions to the level of 1971. But, coincidentally, at the time of this announcement market forces were keeping the lead content of petrol around this level anyway. The amount of lead emitted thus increased due to the increased car ownership, figure 2, and vehicle mileage. Over the years the lead content of petrol was further reduced as indicated in figure 3 and figure 4 , partly due to the pressure from other European countries to collectively reduce the lead content of petrol, hence reducing acid rain. As the various maximum permitted levels were reduced the amount of lead emission correspondingly decreased table 1.

In January 1986 the lead level was finally reduced to 0.15 g/l of petrol, and later in July 1986, due to EEC regulations, the sale of lead free petrol in Britain was introduced.

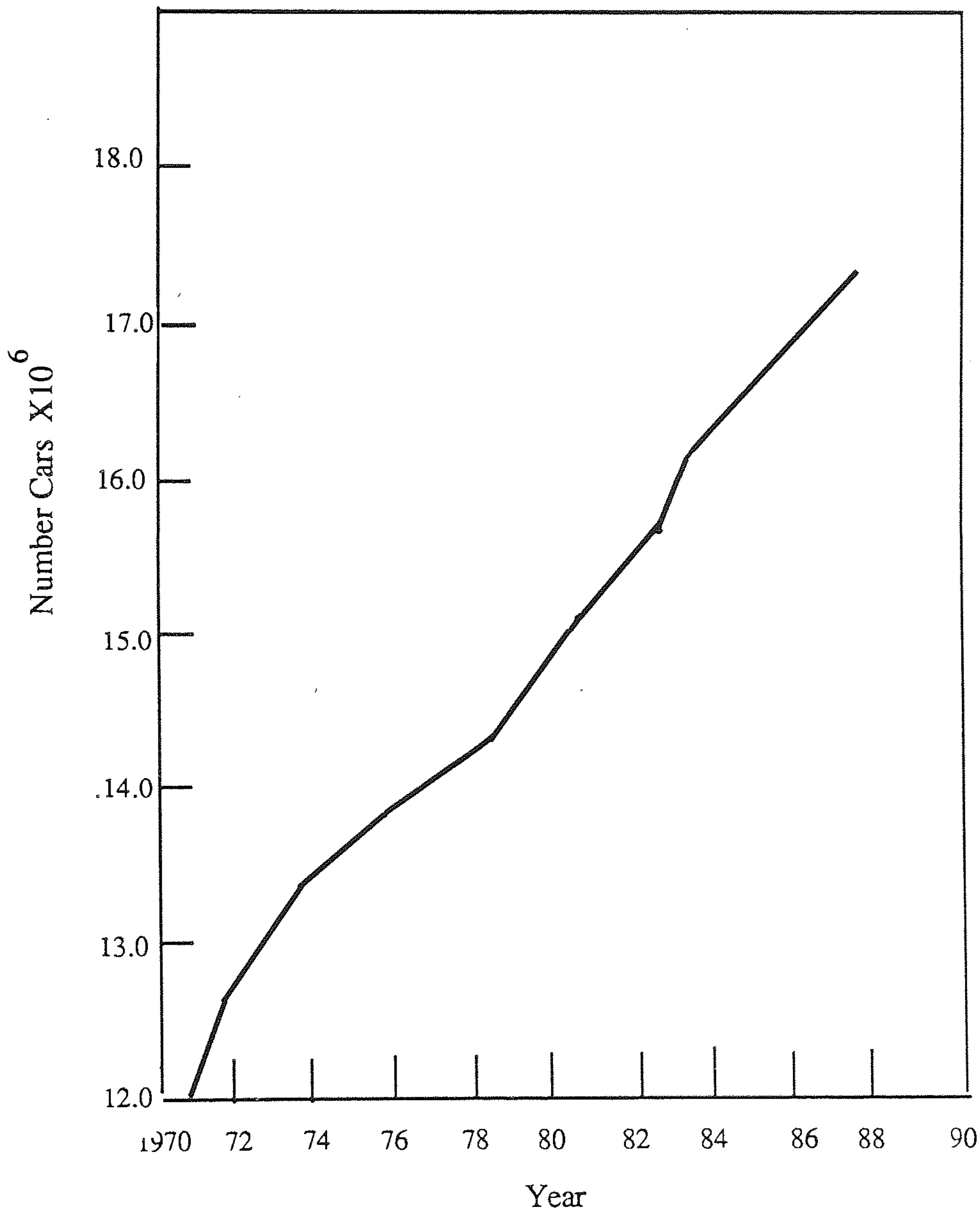
However, because of uncertainty due to economic factors and energy consumption, Britain is cautious and undecided as to its next stage of legislation concerning the lead content of petrol.

1.11.2 Lead Pollution from Road Vehicles(table 1)

Year	Thousand tonnes of lead emission (70% emission basis)	No.of cars X 10^6	Total No.of[(85)] vehicles X 10^6	Legal limit of lead g/l
1971(91)	7.3	12.062	15.478	0.84
1972	8.1	12.717	16.117	0.84
1973	8.4	** 13.497	17.014	0.84
1974	8.0	13.399	17.252	0.64 / 0.55
1975	7.4	13.517	17.501	0.55
1976	7.6	13.792	17.832	0.55 / 0.5
1977	7.4	13.800	18.200	0.5
1978	7.3	13.801	18.625	0.45
1979	7.3	14.307	19.210	0.45
1980	7.5	14.772	19.355	0.45
1981	6.7	14.942	19.770	0.40
1982	6.7	15.303	20.216	0.40
1983	6.8	15.543	20.773	0.40
1984	6.8	16.055	21.321	0.40
1985				0.40
1986				0.15
1987				0.15

** Contradiction in statistics of 1973 and 1974

Figure 2 Number of Cars on Great Britain
(NB not the total number of vehicles)



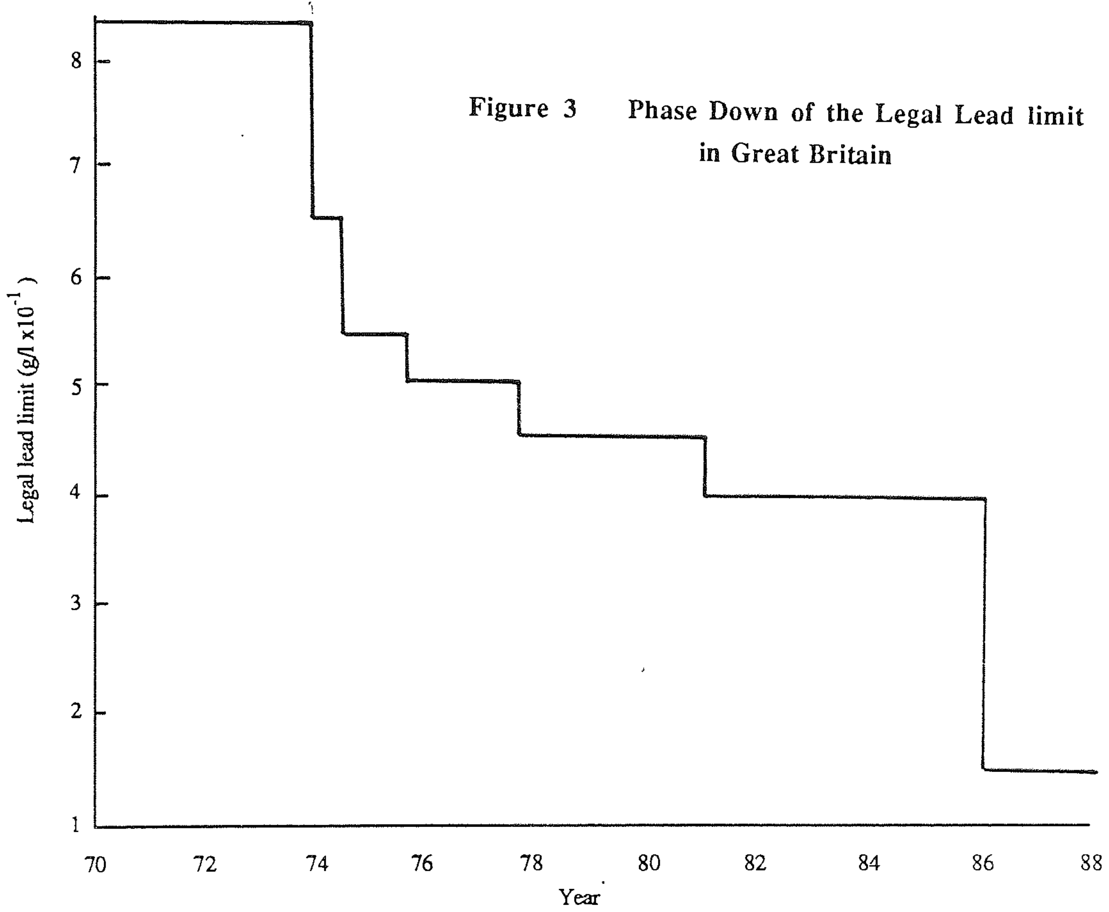
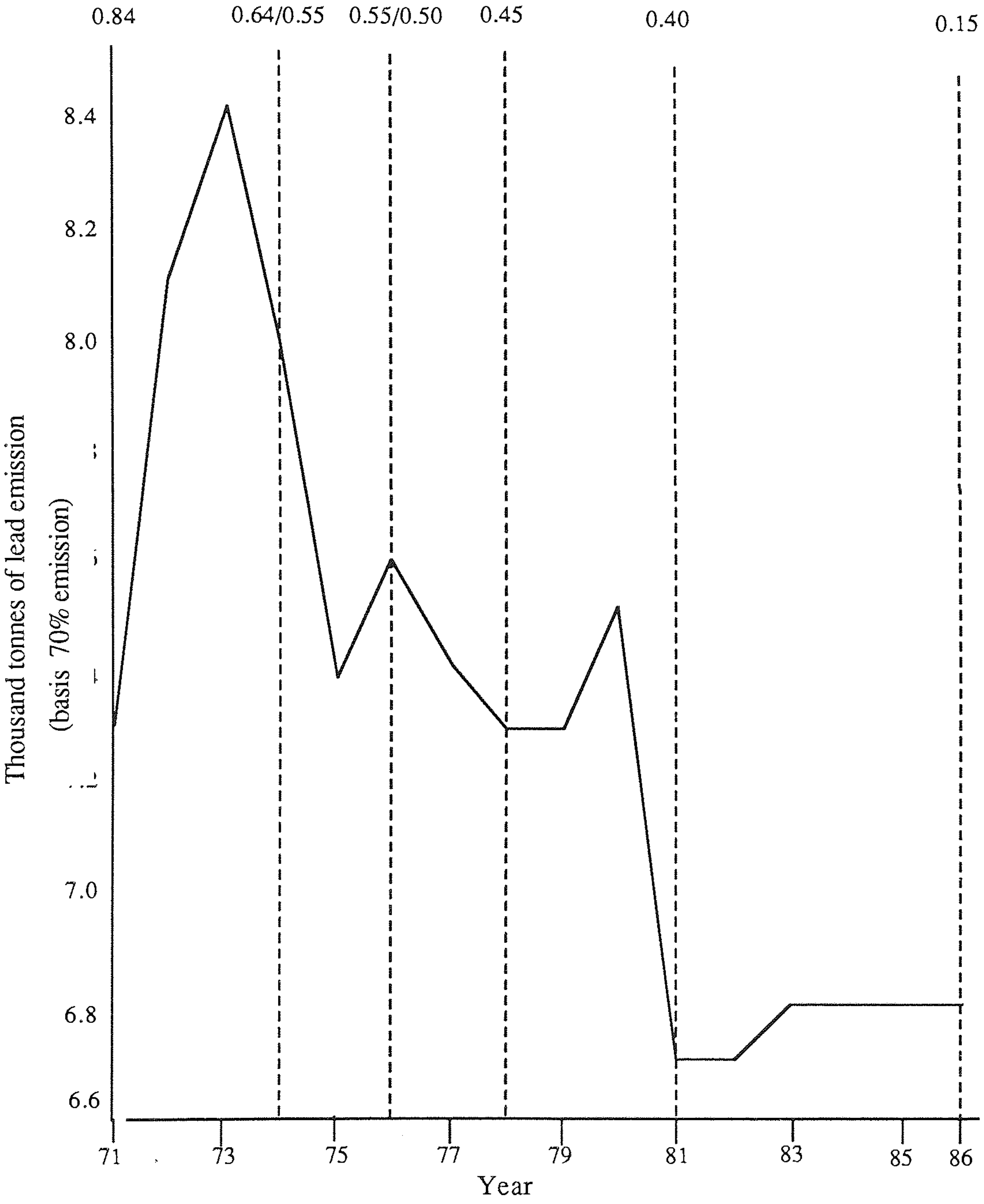


Figure 3 Phase Down of the Legal Lead limit in Great Britain

Figure 4 Lead Pollution from Road Vehicles



1.11.3 International Action to Reduce Lead in Petrol. Maximum Lead Content in Selected Countries.

Country(93)	g Pb / liter	Effective Date
Belgium	0.15	Jan. 1987
Canada	0.15	Jan. 1987
Denmark	0.15 (Reg) 0.15 (Prem)	July 1982 July 1984
EEC[a]	0.40 0.01	Jan. 1981 July 1989 (Pre ??)
Finland	0.15 (Reg) 0.15 (Prem)	Jan. 1985 Jan. 1986
France	0.40	Jan. 1981
Germany [b][c]	0.15 0.00	Jan. 1976 Jan. 1986
Italy	0.40	July 1981
Japan	0.02	Feb. 1975
New Zealand	0.45	Jan. 1985
South Africa	0.836	Current
Spain	0.65 (98 RON) 0.60 (96 RON) 0.48 (90 RON)	Jan. 1976
Sweden	0.15 (Reg) 0.15 (Prem)	Jan. 1980 July 1981
Switzerland	0.15 (Reg) 0.15 (Prem) 0.00 (Reg)	Jan. 1978 Jan. 1982 July 1986
U.K [d]	0.15	Jan. 1986
U.S.A [e]	0.29	Nov. 1982
U.S.A. [f] (California)	0.21	Oct. 1984

(a) EEC regulations state that any member state may enforce a lead content lower than 0.4 g/liter provided that it is not lower than 0.15.

(b) All new cars produced and sold are required to be equipped with exhaust catalytic converters and designed to run on lead-free petrol.

(c) Maximum lead level allowed in "leaded" petrol to remain at 0.15g

(d) From the conclusion of this current study it is recommended that U.K. at the least partly follow the German example.

(e) This represents a quarterly average allowed in all gasoline produced.

(f) This represents a quarterly average allowed in leaded gasoline only (N.B. lead-free gasoline excluded).

Not all countries regulate lead levels in petrol and no restrictions apply, other than commercial units, in Eastern Europe, South Africa, Middle East, Africa, Asia.

Other countries that regulate lead levels have been excluded in the above list due to them not being sufficiently industrialised nor contributing to air-borne lead significantly.

1.12 Alternatives to Lead

As mentioned earlier, efficiency of an engine can be improved with increasing octane quality and lead additives are used to maintain this quality. The obvious question arises whether there is some alternative additive which would resolve the problem. The search has gone on for many years, but up to date no commercially viable alternative has been found.

Recent research in this department, in the search for high octane components in particular, has revealed other compounds such as methyl tertiary butyl ether (MTBE), which are effective. MTBE was found to be an excellent octane improver, and in studies on of the petrol engine, was found to reduce HC and CO emissions. However, manufacture of ether compounds involves high expense and would not be a viable substitute in the near future.

Methanol and ethanol have also been considered as a replacement for the whole or part of conventionally blended petrol. While they have good anti-knock properties (26) and can be made easily (but perhaps expensively) they have other technical limitations and have a lower calorific value. Also their supply at present is limited.

The use of manganese as an additive to petrol has been studied for many years. But to sustain present octane quality it would have to be used in quantities that would be many times more toxic than lead. Also the combustion chamber deposits formed with manganese are much greater than with lead, because manganese cannot be scavenged as lead. This would result in increased octane requirement and emissions of hydrocarbons.

Iron carbonyl is yet another additive that has interested researchers because of its good anti-knock properties, but it appears to have the disadvantage of causing engine wear due to the formation of iron oxide particles in the combustion process.

Research for alternative additives will be in progress for many years to come but it seems unlikely on the information to date that an adequate alternative to lead as an additive can be developed for general use in the near future.

1.13 Combustion Chamber Deposits in Spark Ignition Engines

With the combustion of a petroleum fraction in an internal combustion engine, oxides of carbon and water are formed and heat is produced and thus work is done. If the fuel is incorrectly chosen or conditions of operations are not quite right, then some involatile debris or unburned material may remain in the combustion chamber and part of this debris will form combustion chamber deposit.

The objective of this research is to focus attention on the deposit occurring on the piston head. Deposits also occur at the inlet and exhaust manifold of the combustion chamber, but it is not within the scope of this research to discuss them in detail here, it is clear however that they all have a detrimental effect on the performance of the engine. The deposit occurring on the piston head shows the most significant effect and often, in the discussion of combustion chamber deposits, the phrase solely refers to the deposit on the piston head; this will also be the case in this study.

The combustion chamber deposits result in an increase in the octane requirement of the engine, fouling of spark plugs, valve gumming; resulting in the loss of up to twelve octane numbers (1,2,3,4), hence a loss of efficiency and power. In figure 5, we see that a deposit resulting in an octane requirement increase (ORI) of twelve leads to the reduction of compression ration by two. A decrease of compression ratio by two reduces the efficiency using the thermal efficiency equation :

$$E = 1 - \left(\frac{1}{r}\right)^{0.258}$$

E = thermal efficiency

r = compression ratio

$$E_{98} = 1 - \left(\frac{1}{9.7}\right)^{0.258}$$

$$E_{86} = 1 - \left(\frac{1}{7.8}\right)^{0.258}$$

$$\therefore \text{ efficiency loss } = \left(\frac{E_{98} - E_{86}}{E_{98}}\right)^{100} = 7.3\%$$

Past researchers have carried out vast amounts of work to reduce the quantity and to modify the chemical composition of the deposit, but nevertheless a great deal of work still remains. Special emphasis in this research has been placed on the physical nature of the deposits and measurements of the physical properties.

1.14 Formation of Combustion Chamber Deposits

The accumulation of combustion chamber deposits is the overall result of the formation of deposits and the removal of deposits. The formation of deposits has been studied (1-8) and it has been shown that when the engine is started with a clean combustion chamber, the high boiling point hydrocarbons condense on the walls and are not completely burnt before they become covered with a layer of condensed lead compounds. It is thought that initially lead oxide is deposited, but this is reacted upon by the acid products of combustion to form lead salts. These are mainly lead halides, since the low temperature favours this reaction more than the reaction between lead oxide and the oxides of sulphur. As the engine warms up, the high boiling point hydrocarbons would no longer condense but the lead salts continue to build up, thus increasing the thickness.

The deposit very quickly builds up, and owing to its thermal properties, heat transfer from the combustion chamber to the cooling water is reduced, thus resulting in an increased deposit surface temperature. With the elevated temperature the reaction between lead oxide and sulphur is favoured to form the non-volatile lead sulphate. The change in chemical composition from compounds of high volatility to compounds of lower volatility has been shown(19).

1.15 The Removal of Combustion Chamber Deposits

If the deposits were not somehow removed, soon the deposits would build up to a level on the piston head until no combustion could occur. In this section a review is made of the various processes that occur to limit the deposit.

1.15.1 Volatilization

The two scavengers used in leaded petrol are ethylene dibromide and ethylene dichloride, they convert the lead oxide to the corresponding lead halides which are volatile at normal combustion temperatures, to be removed with the exhaust gases.

Mikita and Sturgis (1) showed that lead oxide is first deposited on the combustion chamber walls prior to conversion to lead halides by the acid gases. This was demonstrated by running an engine alternately with a gasoline containing tetraethyl lead but without the scavengers, and then with the gasoline containing the organic halide scavengers only. The weight of the deposit accumulated in this manner was found to be similar to the weight of deposit from another test in which TEL and the scavengers were combined.

The extent to which the volatilization process affects deposit removal is dependent upon the engine operating conditions, since conditions which tend to produce higher combustion-chamber temperatures are more advantageous to the removal of deposits by this mechanism, by Mikita, Sturgis, Shore and Ockert (1,2). As deposits accumulate the change in chemical composition (7) is similar to the differences in the chemical composition of deposits which result from increasing combustion chamber wall temperatures. It was thus concluded that the thermal insulating effect of deposits causes a substantial increase in their surface temperatures as deposits build up.

If the engine is run intermittently, the above mechanism would of course be expected to be repeated each time the engine is started from cold. Thus it would consequently be expected that combustion chamber deposits would exhibit a stratified structure, with each stratum being separated by a carbon boundary. The thickness of each stratum would depend on the time the engine is run between starting and stopping, and changes in chemical composition would be expected to occur within each stratum as the total layer increases in thickness.

1.15.2 Flaking

As the deposit thickness increases, its insulating effect also increases, thus resulting in an increased deposit surface temperature, and temperature gradients are set up within the deposit. With these temperature gradients thermal stresses are set up, and when they exceed the adhesive strength of the structurally weakest layer, that is, the carbonaceous layer, flaking occurs. Any abnormal combustion giving thermal and mechanical shock accelerates the production of deposit flakes. It is interesting to note that once flaking has occurred down to the carbonaceous layer, there is less tendency for deposit accumulation in these regions. If the deposit is hard and brittle, flaking is facilitated, but oily deposits rarely flake, probably on account of the high adhesive forces in this type of deposit.

1.15.3 Flecking

Mikita and Sturgis (1) showed that when a lead salt, deposited on a metal surface, was brushed with a flame, tiny areas of the deposit surface were fused. On cooling, these contracted, ruptured the forces of adhesion and were consequently ejected. In flecking the particles are much smaller than in the flaking process and are broken away from the surface layer only. Flecking can also occur on very thin (4) deposit layers, whereas flaking only takes place after a rather thick deposit has built up.

1.15.4 Burning of the Deposit

Due to the high temperature involved, some of the carbonaceous material deposited on starting the engine may burn after the engine has been run for some considerable time.

1.16 The Adhesion of Deposit

It has been shown (1) that the deposited carbon content will increase the adhesive tendencies of the deposit, and these effects can be both physical and chemical in nature. For example, at high temperatures a chemical form of adhesion can take place. This is brought about by the oxidation of the carbonaceous film, the resultant oxidised hydrocarbon molecule acting as a link between the combustion chamber wall and the deposit. In addition, away from the wall the connecting molecule may utilize a similar mechanism to join the independent entities of the deposit together. Mikita and Sturgis reported that the most adhesive deposits are those containing carbonaceous material associated with a high percentage of oxygenated products, whilst deposits formed at lower temperatures are less adhesive in character.

1.17 Deposits from Leaded Fuel

Dumont reported that the introduction of 1.5g TEL/gal of fuel caused a four-fold increase in deposit weight over that of unleaded fuel. Doubling the TEL content to 3.0g/gal, had only negligible effect on the deposit weight. Deposit accumulation analysis through microscopy and x-ray diffraction showed deposit growth to occur in three phases, as outlined by Mikita and Sturgis.

Dumont also postulated three possible mechanisms by which combustion chamber deposits could increase octane requirements.

1. By occupying physical volume
2. By possessing an active surface-catalysis effect
3. Thermal insulation effect.

To actually experimentally separate the volume effect from the thermal insulation effect, Dumont coated the inside surface of a single cylinder engine with a dispersion of Teflon in water followed by a 672K fusion. The octane requirement increased in direct proportion to the thickness of the Teflon film, with 25% of the ORI due to the volume effect, 75% of the ORI due to the insulating effect.

Consistent with previous work, Dumont believed that the carbonaceous portion of the deposit depended on the type of crank case oil used and on the amount of oil reaching the combustion chamber surfaces. This lube-oil dependence was further confirmed in a comparison of ORI results between synthetic lube-oils (as a polyether and a polybutene, which gave low values of ORI) and conventional lube-oils (as heavy while oil and wastel B which gave high values of ORI) (9).

However, this lube-oil dominance of the carbonaceous portion of the deposit came into question as radiotracer experiments were used in engine research. The first radiotracer experiments performed on an engine deposit involved Pb_{210}, and was used to demonstrate that the new deposits will form at a more rapid rate on thick deposit surfaces than on thin surfaces or bare metal walls. Later P.C.White (10) reported C^{14} results using either labelled benzene or toluene as a fuel, and a synthetic polyglycol as a lubricant. Deposits from the piston crowns showed 70% of the activity of the fuel, demonstrating that the fuel, not the lube-oil, created the majority of the carbonaceous deposit. Similar results were obtained for toluene.

L.B.Shore and K.E.Ockert (2) performed ^{14}C studies on labelled fuel with an L-head CFR engine employing a high quality low-30 motor oil (12). They noted that nearly all the combustion chamber deposits came from the fuel. The conclusion for the research soon recognised that both lube-oil and fuels contribute to the carbonaceous portion of the deposit, though a correct selection of the lube-oil may reduce its contribution to the deposit, resulting in reduced deposits in total.

1.18 Deposits from Unleaded Fuels

With the recent interest in unleaded fuel, the deleterious effect of deposits on octane requirement increase has again become an issue, although it is difficult from both an economic and energy conservation stand point (Chapter 2) to produce high octane unleaded fuel.

Benson (12), in his work on lead-free deposits, noted that the ORI with unleaded fuel could be eliminated by removing combustion chamber deposits, with about two thirds of the ORI specifically caused by deposit accumulated in the end-gas region of the chamber. With reference to the mechanism suggested by Dumont, Benson stated that 10% of the ORI is due to the volume effect, and the other 90% probably due to the thermal effect.

In a study of the effect of lubricant and viscosity index improver on ORI, Bachman and Prestridge discussed physical and chemical characteristics of deposits formed within a 1975 model car, using commercial unleaded fuel (13). Electron microscopy indicated the carbon to be amorphous, extremely porous, and characterised by a heterogeneous granular structure. Heat capacity values were found to be within the range of 0.40 and 0.44 cal/g °C.

Nakamura and associates (14) discussed the relationship between combustion chamber deposits and octane requirement increase for Japanese cars of 4 and 6 cylinders. ORIs ranged from 3.5 to 11 octane units, corresponding to final octane requirements for 86.5 to 95.5 RON. With respect to the weight of the deposits, the authors reported between 0.15g and 2.07g per cylinder for four cylinder cars. No direct correlation between total deposit weight and ORI was found, nor was there a relationship between weight of a specific deposit and observed ORI. Very little other literature exists concerning the mechanism of formation of unleaded deposits and the complexity of predicting ORI.

1.19.1 Exhaust Emissions

The formation of smog is dependent on the amount and type of hydrocarbons evaporated and emitted from the vehicle fuel system and exhaust (51). Dishart (52) in his research, using a wide range of leaded gasoline, found that the aromatic content of the fuel is related to the aromatic compounds emitted in the exhaust. Dishart furthermore observed that as the branched paraffin content of the petrol increased, the amount of low molecular olefins emitted increased. These lower molecular weight olefins and the aromatics were found to be the more reactive hydrocarbons that contributed to the bulk of the photochemical reactivity. Olefin content of petrol however, had little effect on the photochemical reactivity. Dishart also noted that fuels containing a high percentage of aromatics usually contained a lower percentage of branched paraffins and vice-versa. Thus the end result is an insensitivity of the exhaust photochemical reactivity to changes in hydrocarbon composition since they are the practical high octane components available to today's refiners.

In unleaded gasoline compared with leaded gasoline, the aromatic content would be higher but without an accompanying decrease in the branched paraffin content, as in the case of leaded gasoline. Invariably the aromaticity of the exhaust is expected to increase while the amount of lower molecular olefins would not change, resulting in an increase of photochemical reactivity (53,54).

1.19.1 Polynuclear Aromatics

If aromatics are used to raise the octane number of unleaded petrol this will increase the amount of polynuclear aromatics in the exhaust (55-58).

Many studies have been carried out to determine the PNA emissions from engines, among which McKee and McMahon (59) made a survey of PNA emissions from vehicles and concluded that, as expected, the formation of PNA compounds in combustion or pyrolysis increased with increased aromatic content of the fuel. An interesting point to be noted however, is that lead in petrol was found by Jacob (60) to have virtually no effect on PNA emissions.

CHAPTER 2
ECONOMIC ANALYSIS

Economic Analysis of Lead in Petrol

2.1 Introduction

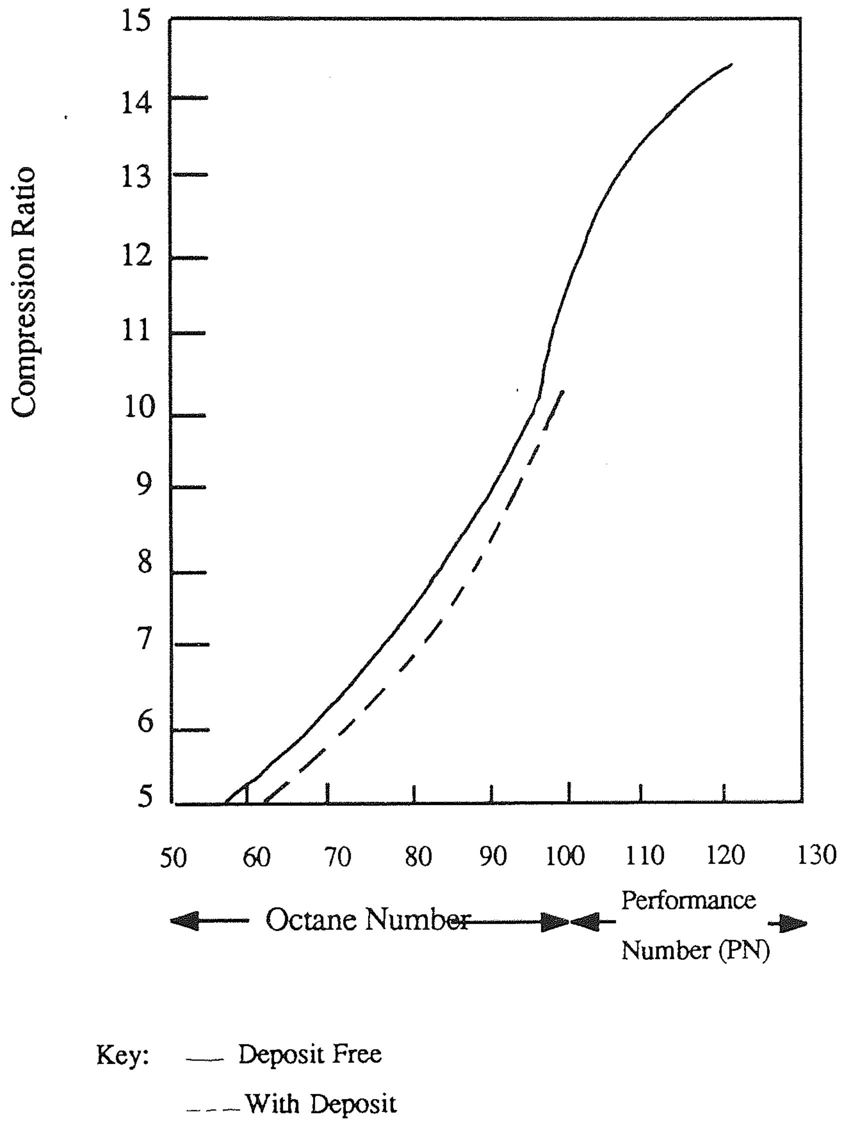
When provisions were being made in the UK for, a reduction in lead levels to 0.4 g/l of petrol, it was thought at the time that a threshold was being reached and any further reductions would result in costly changes at refineries. Also if the risk of abortive investment was to be avoided a decision was needed on the long term level of control before any change was made. However, the decision to implement lead levels of 0.4 g/l of petrol was carried forward and further, in January 1986, the lead level was reduced to 0.15 g/l of petrol, with no apparent effect to the consumer. It must be borne in mind that around December 1985 / January 1986, the price of crude oil collapsed from around $32 per barrel to as low as $12 per barrel. At the time of writing, the price of crude oil is still hovering around $19 per barrel. This collapse of crude oil price came at a crucial stage for the petroleum industry and consumers, because petrol pump prices were due to rise in any case, and the cost of reducing lead to the lower limit of 0.15 g/l would have raised it further. But as it was the crude oil market had been disturbed since the Gulf war started in 1980 and has now stabilised at a much lower level. In the event the price at the petrol pump came down.

With some EEC countries and the Americans reducing the level of lead to a stage of complete elimination - the automobile industry in Britain is now being asked to produce two different types of cars. With Britain ever trying to increase its export market, this is vital, because for cars exported to Japan, Germany and some states in the USA, it has become a statutory requirement that all new cars must be able to run on unleaded petrol. To enforce this the Governments of countries eliminating leaded petrol have introduced new legislation for lower exhaust emission. [A further measure has been undertaken so as to prevent people using the wrong fuel. The nozzles at the petrol pumps have been changed, so that the public owning new cars may not jeopardise the exhaust system that may have been installed in their cars].

In this respect, analyses of the costs to the motorist have been carried out for various options available. Also an energy analysis for the case of the refinement costs. Whatever the amount of ultimately permitted lead it is important to establish what octane quality at that lead level would be the optimum from a total energy point of view, having regard both to energy used in the refinery and fuel economy on the road. In practice however, having determined the optimum octane it may or may not be applied, due to wider economic or other reasons.

Below a lead level of 0.15 g/l of petrol it is assumed, that it becomes difficult to maintain the expected performance of the engine. Broadly speaking, the lower the lead level, the lower the optimum octane number, and a prohibitive expenditure of refinery energy would be needed to produce lead-free or nearly lead-free gasoline of satisfactory performance. Reductions in octane quality also have implications for motor manufacturers as vehicles with high octane requirements will not function satisfactorily on low octane fuel figure 5. Many existing cars will not function on fuel with 95 RON and any further reductions in RON would have to be very long term and introduced gradually over a number of years. This option has been suggested in the past (21) but its

Figure 5 Relationship between Octane Number and Compression Ratio with and without Deposit on Piston Head



implications were not fully explored. As mentioned in Section 1, the elimination of lead also results in valve seat recession. This is yet another reason why lead-free fuel can only be introduced gradually.

2.2 Previous Reports

Previous estimations of the cost of all options available have not been sufficiently reliable to give accurate predictions in terms of actual cost to the consumer. A recent report by the Select Committee on the European Communities (26) draws evidence from the Ministry of Transport and from the United Kingdom Petroleum Industry Association (UKPIA) in carrying out its proposals for the introduction of unleaded petrol. Though the report is very detailed and provides much useful data, it lacks in clarity in its final conclusion.

The report by the Royal Commission (22,23) again covers the problem in a very detailed manner providing a great deal of background information. This HMSS report looks at various options that are available but again falls short of drawing adequate conclusion from the data that is available. There are yet other publications (83,84) that view the problem from an industrialist point of view and look at refineries and the probable options of achieving unleaded fuel. Bonner and Moore Associates(83) in their study for removal of lead additives from gasoline have considered the problem by considering refineries of various sizes but their models of scaling are doubtful.

The list of reports on the economical analysis is in no way inexhaustive, but on the contrary it is felt that not enough literature on the subject has been supported, especially by the automobile industry. However, there is one other report by the Friends of the

Earth that must be mentioned here (21). Brian Price, in his report, looks at the issue totally from an energy standpoint of view and concludes that removal of lead will save the UK the equivalent of 500x103 tonnes of crude oil. But Mr. Price fails to recognise the capital investment required for the production of lead-free petrol, and secondly, he uses the basis of 95 RON instead of the present 97/98 RON petrol quality level, thus resulting in the loss of compression ratio and efficiency, which is not taken into account. In Mr.Price's calculations a large slice of the saving in favour of unleaded petrol is the increased mileage obtained with unleaded petrol.

With the literature in such disarray the author feels that a more precise analysis of the effects and economic penalties of lead in petrol is required.

2.3 Options for Further Reducing Lead Emissions

The options for further limiting lead emissions lie in either trapping lead by means of installing filters in exhaust systems, or in action to lower the lead level of petrol itself. One of the most important constraining factors is that any general requirement for vehicles to use lead-free or low-lead, low octane petrol can only be applied to vehicles designed to function on it. In fact it is believed that it could only be introduced on a phase basis by application to all new vehicles brought in to use for the first time after a certain date.

The following are accordingly long term options which have been considered and at present seem to be the only likely options:.

1. To maintain the present quality of petrol 98 RON and existing lead levels of 0.15g/l (base case).

2. To maintain the present quality of petrol and lead levels, and fit filters to all new vehicles, to remove a substantial proportion of the lead from the vehicle exhaust. (on the basis of development work to date an average of catchment efficiency of 60% is assumed, but higher efficiencies than this appear feasible)

3. To maintain the present quality of petrol (98 RON) by more severe refining processes while eliminating the use of lead compounds as anti-knock agents, for all new vehicles. During the introduction of lead-free petrol, the present petrol (98 RON with 0.15 g.l) would have to be still retained for existing vehicles until they are substantially phased out, say ten years. After this period it is anticipated that most petrol filling stations may find it uneconomical to market the leaded grade petrol.

4. To maintain the present quality of petrol (98 RON) by more severe refining processes and install three-way catalytic converters to all new vehicles, resulting in the lowering of all types of emissions from the exhaust.Phase period as mentioned in option 3

5. To lower the octane quality of petrol to 95 RON while eliminating the use of lead additives altogether but retaining the 98 RON and 0.15 g/l petrol for a similar period as mentioned in option three.

6. To lower the octane quality of petrol to 92 RON while removing lead additives, but again retaining the present fuel for existing vehicles.

2.4 Assumptions Underlying Options

It is assumed that in the case of each of the options they would be enforced by regulations from the governments; including perhaps the use of special fuel nozzles, as is practised in some other countries, also the colour of the petrol may also need to be changed.

In some of the options the question of how long supplies of existing petrol would or should be continued, would be a matter for commercial decision. Of course in these cases individual companies may decide to withdraw supplies of a certain type of petrol from some, but not all, filling stations, depending on whether it was thought practical to market leaded and unleaded petrol simultaneously.

It must also be stressed here, even though this factor will not be considered in this report - the new octane fuel (options 5 and 6), if introduced, should be allowed to have an attractive price differential, because it would be expected that many users of new vehicles with compression ratios at the higher end of the range would seek to improve performance by using premium fuel still available for existing vehicles.

For options 5 and 6 it is assumed that the emission of other obnoxious pollutants would remain at their present level or even be reduced, thus not justifying the use of catalytic converters (Figure 32). For options 3 and 4 it is believed that a price differential in favour

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Fig 6 Qualitative Representation of all Emissions for each option

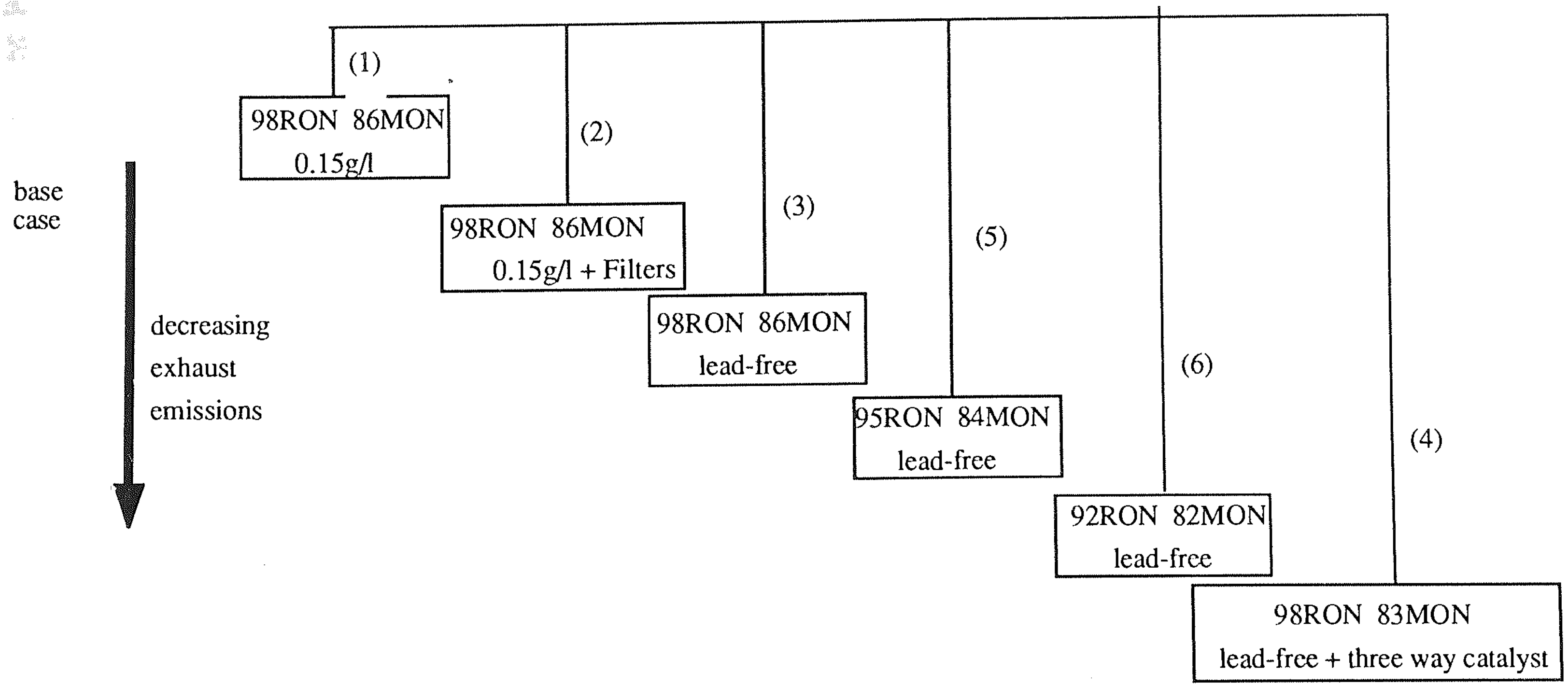
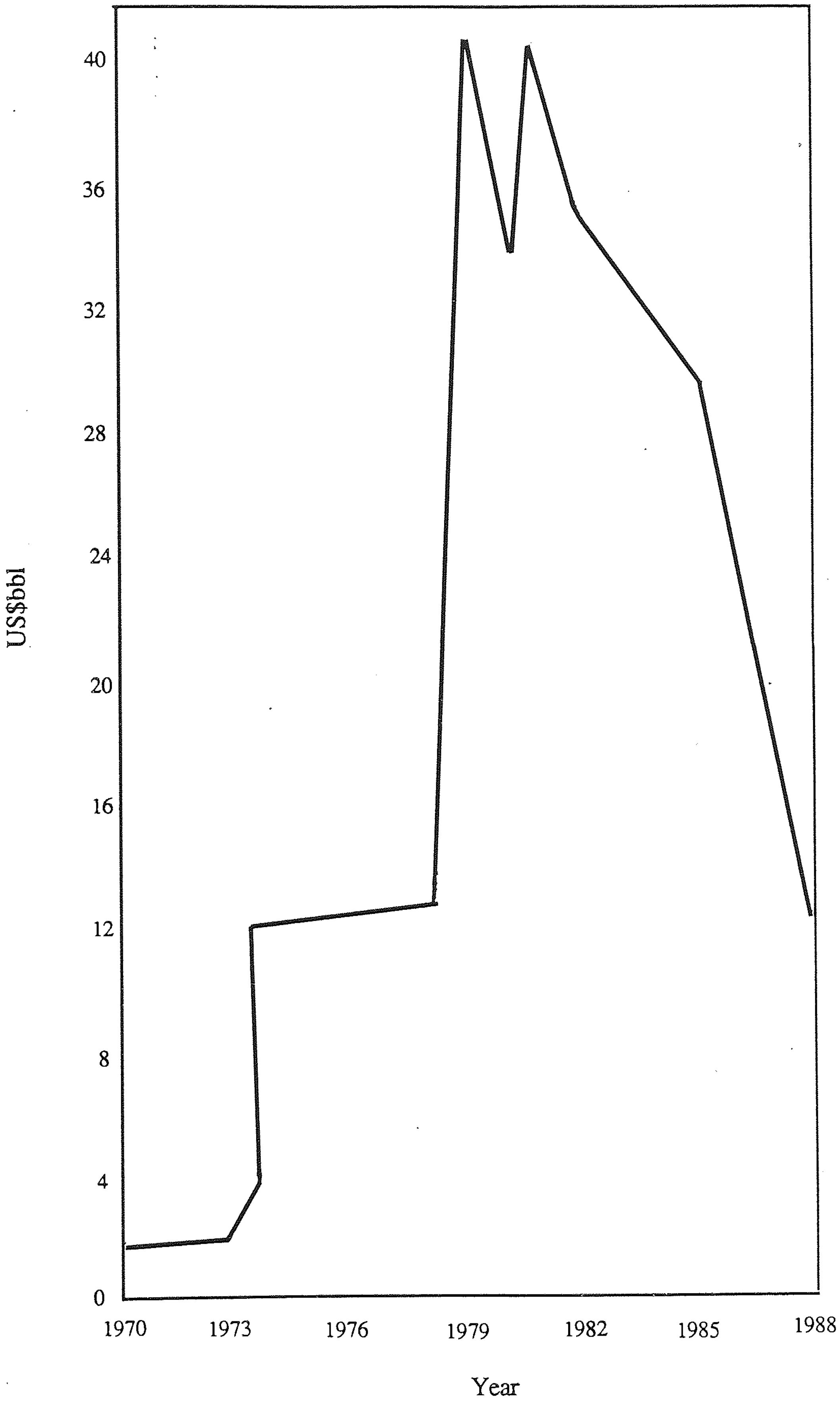


Figure 7 Crude Oil Prices



of lead-free petrol must exist or else the experience felt in the USA would also be encountered in Britain as well.

It must be emphasised here that though these options considered in the study have been viewed as alternatives to one another this need not be the case in practice. But for simplicity they will however be treated as alternatives, because otherwise if all combinations were considered the analysis would become extremely complex and very time consuming.

All the options presented are considered as long term options, not only in the sense of needing significant time to implement but also in the sense of representing a final solution. It must also be stressed that none of the options are seen to be a mere prelude to more drastic measures, for it is felt that further uncertainty in the policy will result in a sense of insecurity for both the automobile and the oil industry in Britain.

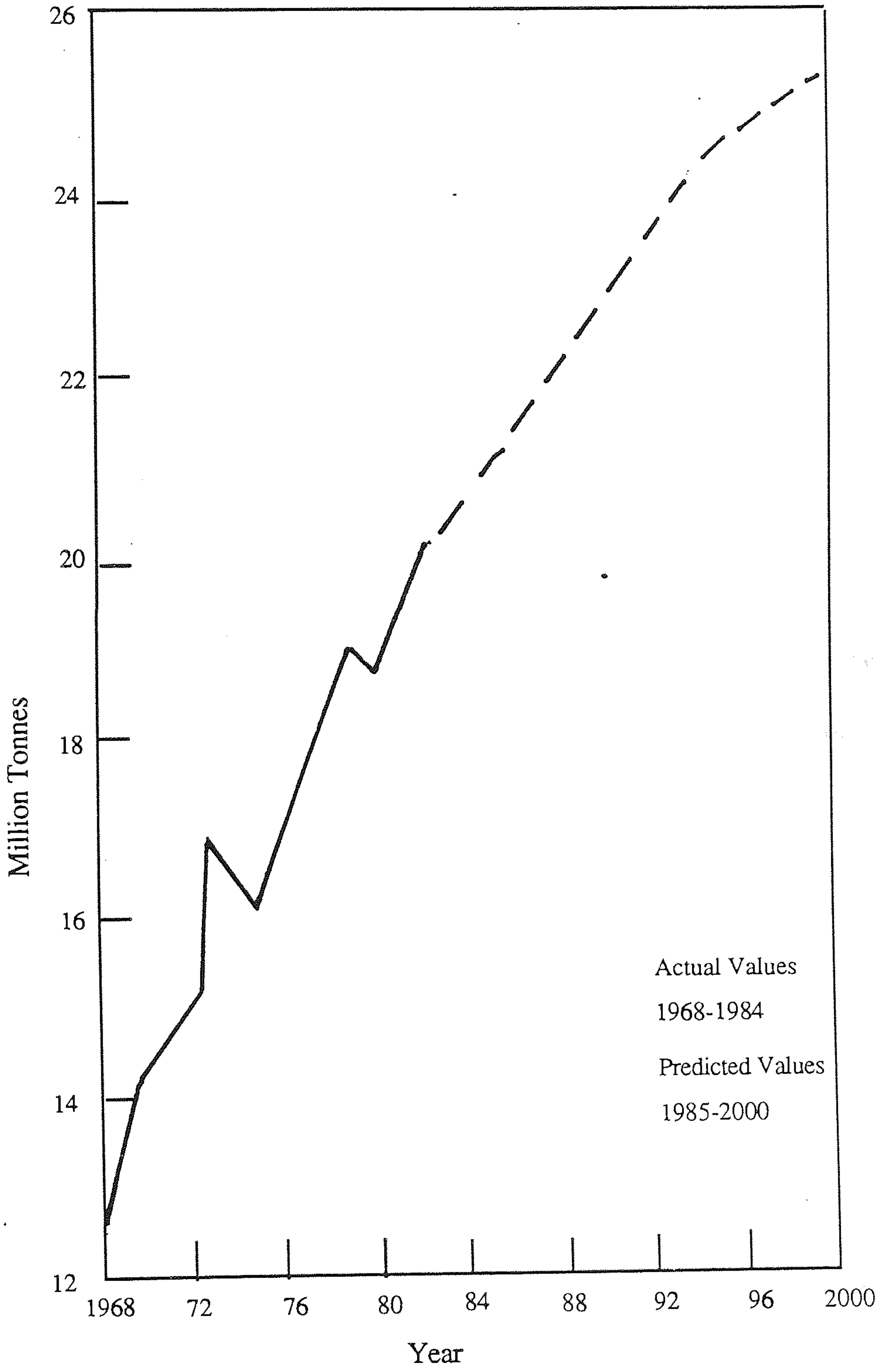
2.5 Criteria for Cost Estimation

Due to the limited financial data available concerning the production of gasoline, it was found very difficult to assess the capital investment impact on the petroleum industry for the various options that are available. Nevertheless, with existing technology it was reasonable to predict the costs to the individual motorist as regards expenditure incurred in the automobile industry.

Other countries have introduced the sale of lead-free petrol but it has been found that there is no exact similarity or analogy to be confidently made for the purposes of estimating the costs of eliminating lead. In Germany estimated costs for the change (from 0.4 g/l to 0.15 g/l) was only 1/3 of the actual cost that was eventually incurred, furthermore the oil industry claimed that this also led to an increase of 3% in imports of crude oil for refining into petrol. This wide difference is in some degree a reflection of the difficulties of identifying costs. Also UK estimates cannot be compared to those of Germany's, because Germany imports roughly 40% of the petrol as a finished product. Due to the lack of funds and time the author has not had the opportunity to visit other countries, but it is thought worthwhile to also mention in brief the situation as prevalent in the USA. The Environmental Protection Agency issued a report in 1976 on the impact of the USA regulations on lead additives and the estimated cost on USA refineries of producing only lead-free petrol by the year 1985. Again, as in Germany, there was no unanimity between Government and industry on the orders of costs incurred, and no straight analogy can be drawn to the case in the UK.

Costs have been estimated primarily in terms of 1987/88 prices with no allowance being made for inflation. With the track record of the oil industry Fig. 7 it is difficult to predict the price of petrol in the future, because advanced technology is developing in parallel to the depletion of natural resources. However it is thought necessary to assume some increase in real energy costs over the next 13 years or so. It is thought reasonable to assume that the rate of real increase in crude oil price between 1987 to 2000 would be likely to be in the region of 30% to 60%. In practice any such increase would be unlikely to take the form of a constant annual percentage increase. Nevertheless the related annual increases are approximately 2.2% to 4.0%, respectively. At first glance the predicted increases seems rather low, but consider an increases of 2.2% above the inflation rate then

Figure 8 Motor Gasoline Consumption in UK.



the increase is found realistic. Again there are other factors that may keep the price of crude oil down, for example Brazil is developing the use of gasohol. Such development could spread to other countries. In Pakistan for instance almost half of the privately owned cars have and are further being converted to run on pressurised natural gas.

In the light of the above considerations and many others it was thought that a related annual increase between 2.2% to 4.0% was realistic. Over a time span of 13 years one may ignore any temporary or short term political influences.

2.6 Costs to the Oil Industry

Consideration of the impact on the oil industry involves consideration of petrol consumption in future years Fig. 8. The consumption of petrol in future years is expected to increase at its present rate because it is thought that the present phase of changing social structure will continue, resulting in larger numbers of car owners and increasing at the present rate. After a period of 7 years (assuming the UK population being steady at 54 x 106) the percentage of private car ownership is likely to have risen to (19.25/54) x 100. After this period, with the increased price of crude oil, it is concluded that the rate of car ownership, and hence fuel consumption, will decrease.

In the past, in order to make an assessment, an initial assumption of a constant petrol consumption has been made to estimate the additional costs involved in producing this quantity of petrol. However, in this research an attempt has been made to also estimate any additional petrol consumption (i.e. loss of fuel economy) which might arise under the options due to lower engine performance.

Option 1: The present case would entail no further or extra costs than as envisaged in its present course. Although the petrol consumption would rise, this option will not involve any change from the present routine in terms of investment.

Option 2: Involves no penalty to the oil industry (as Option 1).

Option 3: Assuming the predicted investment for the change to be around £200 x 106 spread over 7 years(85), the cost of extra crude that would be required to produce lead-free petrol, with the introduction of this option as outlined in figure 2, would be £1454 million, resulting from a real increase of 30% over the period 1988-2000. A subsequent increase of £1680 Million equivalent to 60% increase in real price (based on 1988 price) table2.

Option 4: For this option the cost of installing a three-way catalyst would be met by the motor industry, thus resulting in the same costs as in Option 3.

Option 5: As seen from figure 9, the cost of producing 95 RON petrol lead-free is the equivalent of petrol with RON of 98 containing 0.15 g/l. But nevertheless (22,23) a reduction of 1 RON results in a loss of efficiency of roughly 1%. The choice of this option would result in a further consumption of crude oil by 3% overall, though this option would not result in an increased price per gallon of petrol.

Option 6: This option would require a reduction of crude consumption per unit volume by 3.2%, as compared to petrol containing 0.15 g/l with RON of 98. But without doubt there would be a reduction of mileage per gallon i.e. efficiency reduced by approximately 6%. The savings incurred by the oil industry, if consumption of petrol remained as forecasted in figure 8,this would be £808 x 10^6 for a real increase in crude of 2.2% per annum, 30% over the period 1988 to 2000. Over the same period with a 60% increase in real crude oil prices would be £1680 million table 3.

It is crucial to note that options 1, 2 and 5 would require non, or very little, alteration as far as the petroleum industry is be concerned. Options 3 and 4 would require the greatest amount of investment and increased cost to the oil industry. This would inevitably be passed on to the consumer in the end, but the values given represent what the nation as a whole would have to bear. The oil industry would no doubt favour Option 6, for it would entail less energy consumption per unit volume of petrol refined. It can be understood why some other countries have chosen this option.

2.7 Other Areas of Energy Consumption

The estimates to the petroleum industry do not cover all the additional energy costs which would arise. Additional fuel consumption would arise due to the employment of Options 5 and 6. In the analysis of cost to the oil industry Options 5 and 6 seemed the most promising, however due to the use of lower octane quality petrol, it leads to the use of engines with lower compression ratio and accordingly lower efficiency. Only when this is carried out can an assessment be made of total energy implications. The loss of 1% economy with a reduction of 1 RON from a petrol of 96 RON has been shown in the Rufit report (22,23). Of course this finding can only be proved with an engine that utilises the full quality of the fuel. This however does not actually appear to be the case at the present time and some waste of octane quality occurs due to variations in the octane requirements of particular engines. In this analysis it is assumed that there is full utilisation of fuel quality at all levels of RON values.

N.B

1. 1 barrel of petroleum $= \dfrac{\text{m3 0f petroleum}}{0.1589873}$

2. density of petroleum = 750Kg/m^3

   No. of barrel $= \dfrac{\text{Wt. in tonnes}}{0.75 \times 0.1589873}$

3. Average price of crude oil = \$19.00

4. \$1.77 = £1.00

5. (extra crude) (price/barrel)(%leadfree petrol)(price index)$(1.022)^n$ or $(1.040)^n$

   of all petrol sold

   $n = 0$ for 1988

   $n = 12$ for 2000

Table 2. Cost analyis of producing lead-free gasoline with RON of 98 as compared with gasoline of 98 RON containing 0.15 g/l of lead.

Year	Forecast of petrol consumption x 10^6 tonnes	Crude consumption x 10^6 tonnes	Extra consumption if all petrol was lead free x10^6 barrels	% of lead-free petrol sold of all petrol sold	Cost with annual increase of 2.2% \$ x 10^6	Cost with annual increase of 4.0% \$ x 10^6
1988	21.89	26.27	11.89	5	11.29	11.29
1989	22.35	26.82	12.15	10	23.59	24.01
1990	22.75	27.30	12.36	20	49.06	50.80
1991	23.17	27.80	12.59	30	76.60	80.72
1992	23.62	28.34	12.83	50	132.97	142.59
1993	24.02	28.82	13.05	70	193.52	211.17
1994	24.32	29.18	13.21	90	257.39	285.82
1995	24.65	29.58	13.39	95	281.46	318.05
1996	24.95	29.94	13.56	95	291.30	334.97
1997	25.17	30.20	13.68	95	300.35	354.45
1998	25.37	30.44	13.79	95	309.42	368.45
1999	25.62	30.74	13.92	95	319.21	386.79
2000	25.82	30.98	14.03	95	328.81	405.45
				TOTAL	2574.97	2974.56
				≡	£1454.78 x 10^6	£1680.54 x 10^6

Figure 9 Effect of Lead Content on Refinery Fuel Consumption (85)

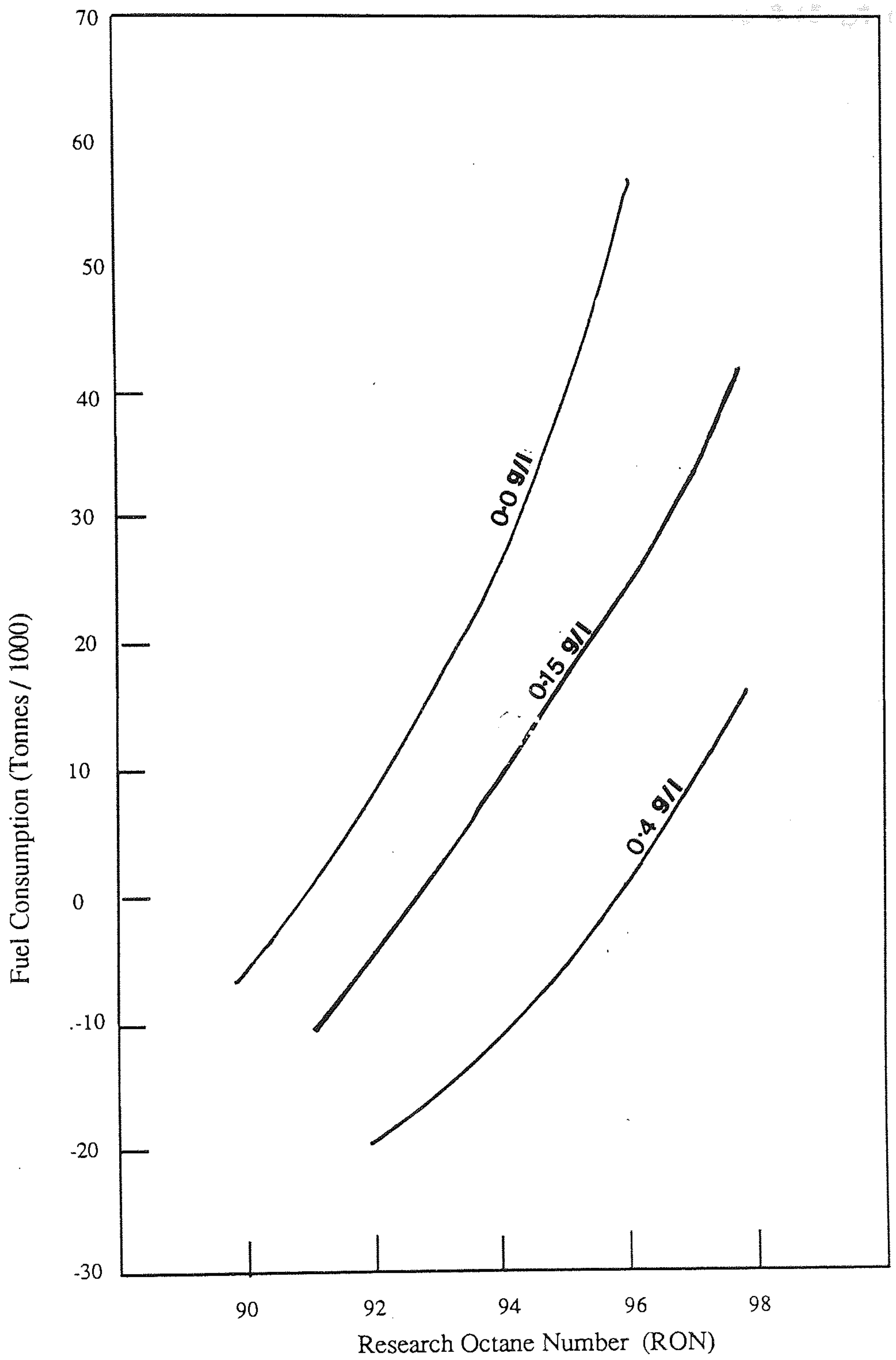


Table 3. Cost analyis of producing lead-free gasoline with RON of 92 as compared with gasoline of 98 RON containing 0.15 g/l of lead.

Year	Forecast of petrol consumption x 10^6 tonnes	Crude consumption x 10^6 tonnes	Less consumption if all petrol was lead free x10^6 barrels (6) (2) (1)	% of lead-free petrol sold of all petrol sold	Saving with annual increase of 2.2% $(3) x 10^6 (5)	Saving with annual increase of 4.0% $(3) x 10^6 (5)
1988	21.89	26.27	6.63	5	6.29	6.29
1989	22.35	26.82	6.71	10	13.03	13.26
1990	22.75	27.30	6.88	20	27.31	28.28
1991	23.17	27.80	6.96	30	42.35	44.63
1992	23.62	28.34	7.13	50	73.89	79.24
1993	24.02	28.82	7.21	70	106.92	116.67
1994	24.32	29.18	7.38	90	143.79	158.68
1995	24.65	29.58	7.46	95	156.81	177.19
1996	24.95	29.94	7.55	95	162.19	186.51
1997	25.17	30.20	7.63	95	167.52	196.02
1998	25.37	30.44	7.63	95	171.20	203.86
1999	25.62	30.74	7.72	95	177.03	214.52
2000	25.82	30.98	7.80	95	182.80	225.41
				TOTAL (4)	1431.13	1651.56
				≡	£808.55 x 10^6	£933.08 x 10^6

One other factor that entails an energy penalty that is significant and has been the source of great concern, for it is comprehendable that it can be eliminated. The octane requirement increase (ORI) due to the build up of deposits on piston heads, though relatively small in extent, affects the performance of the engine. In a paper by Duckworth (26) it is reported that the deposit is responsible for up to 12 octane numbers ORI. The variation of octane requirement increase is affected by the type of fuel used. Leaded fuel results in relatively larger amounts of combustion deposits than lead-free fuel, but these are friable and continually break away. Deposits derived from the use of lead-free fuel result in higher ORI than leaded deposits.

The economic penalty of both factors mentioned here would be significant for the individual consumer.

2.8 Costs to the Automobile Industry

So far all the costs considered have been estimated in forms of annual cash flow. However, in the case of the automobile industry there are two factors that make up the cost:

1) Unlike the oil industry where capital cost could be spread over a number of years, the automobile industry would have to put up front all initial capital costs incurred including manufacturing investment, design, development and certification of products to Government requirements.

2) Annual production costs related to the price of the vehicle.

As in the case of total petrol production costs, it is difficult to estimate the costs, given the particular methods of cost accounting in motor manufacturing, to assimilate totally into a single form. Again there is great difficulty in finding anything but the basic data. The WOPLIP Report (22) estimated that the investment and engineering cost for the whole UK market of phasing out lead (Option 5) would be of the order of £141 million at 1978 prices. At today's prices this would be in the region of £280 million. However it is not clear as to how much of this estimate is considered to be genuinely incremental expenditure, which the industry would be investing in any case, in updating and replacing current models over the period of 1988-2000.

As far as the annual production costs related to the price of the vehicle are concerned, Options 2 and 4 would be most significant. Option 2 employs the use of lead filters and is unique in that it entails no additional refinery requirements in manufacturing petrol, but of course the motor industry entails additional costs to cover manufacturing and fitting. Lead filters would be fitted as an integral part of the vehicles exhaust system and consist of a chamber filled with chemically impregnated alumina-coated steel thread through which the exhaust gases pass on their way out. In the course of this filtering a substantial proportion of the lead in the gases is deposited and retained. Trials have been made of filters with a catchment of 70% at the time of installation, but for the purpose of this analysis an average catchment of 60% is assumed.

Filters can be either of the axial or radial flow type, with the axial flow filters(85) showing the better results of the two, and a useful life of 50,000 miles or 5 years. It also seems reasonable in calculating costs to assume that the whole of the exhaust system would in practice be geared to this life.

In the case of the earlier lead filters developed, problems arose in certain conditions of purging of the lead trapped in the exhaust system. A further problem which is not yet entirely overcome is that of disposal of used lead filters. If the lead traps at the end of their useful life were simply thrown on rubbish tips or melted down, the pollution would be reintroduced into the environment.

The cost of the filters varies with size but should not be more than £50 additional cost, exclusive of initial capital cost to motor manufacturers.

Option 4 employs the use of a three-way catalyst. Nothing more will be discussed here concerning the three-way catalyst converter except its price of around £250 for a system that may be employed for 50,000 miles. See Chapter 3.

2.9 Costs to the Motorist

In very broad terms a penalty of 2.5 % would be incurred by a motorist switching from 98 RON with 0.15 g/l to 98 RON lead-free petrol. This in real terms means 0.4p/mile or £41 per annum, table 6 and 7. With the option of 92 RON lead-free petrol there is a saving of 3% at the refinery, but this is offset by a lower efficiency of approximately 6%, due to the reduction in compression ratio of the engine. The use of filters, as has been discussed, is unlikely to be a serious option for the future because, in practice, it is far more sensible to eliminate lead at source than to collect it by extraction. Here again the economic penalty would be of the order of £10 per annum at 1988 prices. table 5.

The effect of introduction of unleaded petrol on petrol prices is impossible to predict other than what has been presented, because of the complex pricing and marketing strategies of the oil industry and the difficulty of finding reliable data for capital investment. If we assume it is left to market forces to determine prices, here again the impact may be overshadowed because of intrinsic taxation policies (i.e. Japan). In Britain ESSO, since last year, have marketed the equivalent of four star petrol but lead free, and the price differential between the leaded and the lead-free petrol is 4.5p per gallon. Again this figure must be treated with caution because it may be a commercial stunt to keep the price lower than if it were to be marketed such that no leaded petrol was available.

It is also true that any increase in pump price directly attributable to the removal of lead could be vastly less than the increases regularly experienced as a result of fiscal changes, the vagaries of the world market or the external value of the sterling. But, however, this is not constructive practice and if not rationally approached could result in the misuse of resources.

There is information in the literature relating to saving in maintenance costs with the use of lead-free petrol. It is generally accepted that spark plugs and exhaust systems last longer with lead-free petrol than with leaded petrol, but this is not widely accepted. Even so, the saving is very small and presumed to be not more than £1 per annum maximum. However, in the analysis, this saving has been credited and included in the maintenance expense of the vehicle. The consequence of increased ORI arising due to combustion chamber deposits, is assumed to result in costs 2% higher with unleaded fuels than with leaded-fuel.

Table 4. Option 1 .Total Driving Cost for Individual Consumer 10,000 miles per year with 4 star petrol having a lead content of 0.15 g

Expenditure Item	£ / year	%
Car depreciation (1)	625	38.82
Insurance	250	15.53
Road Tax	95	5.90
Petrol (2)	567	35.22
Tyres	18	1.12
Maintenance	50	3.10
Oil	5	0.31
TOTAL	1610	100

(1) Average car price assumed is £7000 with a depreciation of 20% of the price year before, spread over ten years.

(2) Price of gallon at £1.70 with an average mileage of 30 per gallon (ref. Transport Statistics).

Table 5. Option 2 Total Driving Cost for Individual Consumer 10,000 miles per year with 4 star petrol having a lead filter

Expenditure Item	£ / year	%
Car depreciation	625	38.58
Insurance	250	15.43
Road Tax	95	5.86
Petrol	567	35.00
Tyres	18	1.11
Maintenance (3)	60	3.71
Oil	5	0.31
TOTAL	1620	100

(3) Higher maintenance due to nature of particulate filters

Table 6. Option 3 Total Driving Cost for Individual Consumer 10,000 miles per year lead-free petrol (RON 98)

Expenditure Item	£ / year	%
Car depreciation	625	37.86
Insurance	250	15.14
Road Tax	95	5.75
Petrol (4) (5)	609	36.89
Tyres	18	1.09
Maintenance (6)	49	2.97
Oil	5	0.30
TOTAL	1651	100

(4) 2% economy penalty arising from higher octane requirement increase, due to the nature of deposits

(5) 5.4% increased refining cost

(6) Lower maintenance cost due to saving on spark plugs

(7) Does not include any cost incurred due to capital investment

Table 7. Option 4 Total Driving Cost for Individual Consumer 10,000 miles per year lead-free petrol (RON 98) and the employment of a three-way catalytic converter

Expenditure Item	£ / year	%
Car depreciation	625	36.74
Insurance	250	14.70
Road Tax	95	5.59
Petrol	609	35.79
Tyres	18	1.06
Maintenance	49	2.89
Oil	5	0.29
Catalyst depreciation (8)	50	2.94
TOTAL	1701	100

(8) Catalyst life limited to 50,000 miles

Table 8. Option 5 Total Driving Cost for Individual Consumer 10,000 miles per year with lead-free petrol (RON 95)

Expenditure Item	£ / year	%
Car depreciation	625	38.16
Insurance	250	15.26
Road Tax	95	5.79
Petrol (9) (10)	596	36.39
Tyres	18	1.10
Maintenance	49	2.98
Oil	5	0.31
TOTAL	1638	100

(9) Loss of efficiency by 2% due to nature of combustion chamber deposits yielding higher ORI

(10) Loss of 3% efficiency due to lower compression ratio

Table 9 Option 6 Total Driving Cost for Individual Consumer

10,000 miles per year lead-free petrol (RON 92)

Expenditure Item	£ / year	%
Car depreciation	625	38.20
Insurance	250	15.28
Road Tax	95	5.81
Petrol (11) (12) (13)	594	36.31
Tyres	18	1.10
Maintenance	49	2.99
Oil	5	0.31
TOTAL	1636	100

(11) Saving of 3% at refinery

(12) 6% penalty in performance due to lower compression ratio

(13) 2% penalty due to nature of deposits

Figure 10 Future Trading in Leaded and Unleaded Gasoline at New York Merchantile Exchange (Trading date: 15th May 1986)

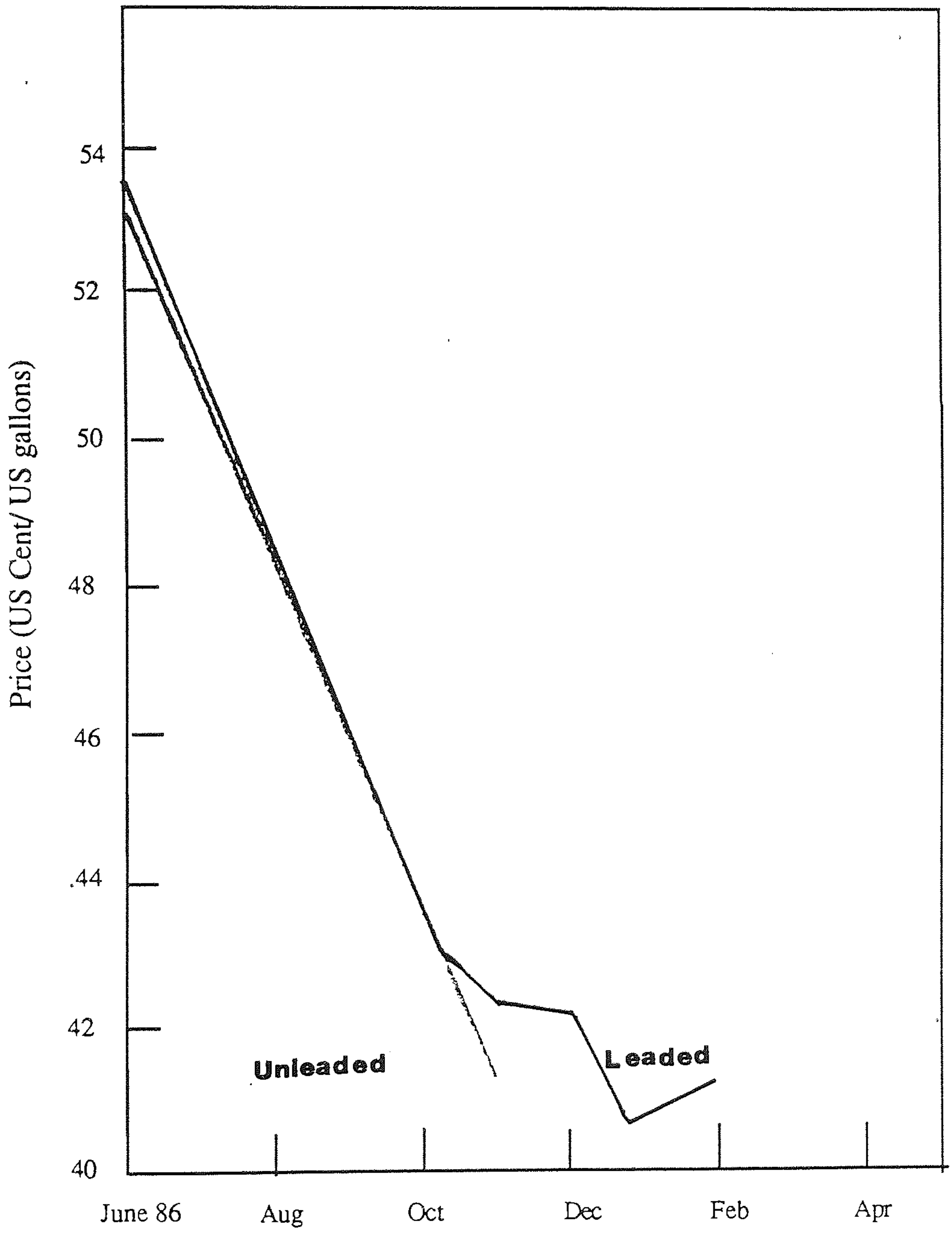


Figure 11 Private Car Ownership in Great Britain.

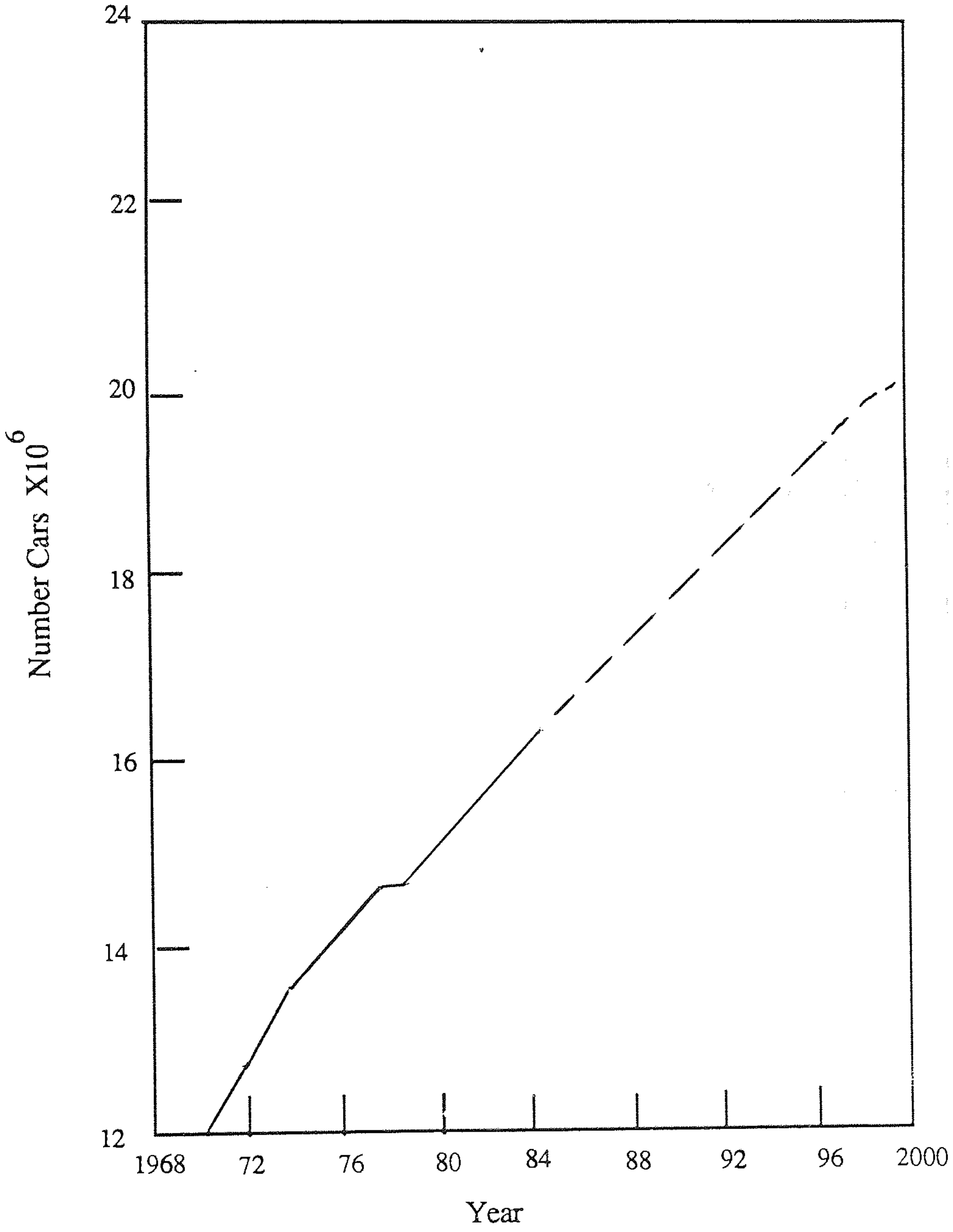


Table 10 Lead Emissions from Vehicle Exhausts for Alternative Options

Year	% of option implemented	No. of cars x 106	LEAD EMISSIONS (TONNES)					
			Option (1)	Option (2)	Option (3)	Option (4)	Option (5)	Option (6)
1988	5	17.32	2755	2687	2618			
1989	10	17.65	2755	2617	2480			
1990	20	17.95	2755	2480	2204			
1991	30	18.25	2755	2342	1929			
1992	50	18.52	2755	2066	1378			
1993	70	18.77	2755	1791	827			
1994	90	18.98	2755	1516	275	As	Option	3
1995	95	19.15	2755	1446	138			
1996	95	19.30	2755	1446	138			
1997	95	19.45	2755	1446	138			
1998	95	19.57	2755	1446	138			
1999	95	19.75	2755	1446	138			
2000	95	19.85	2755	1446	138			

2.10 National Considerations

Having determined financial penalties for future likely options, it must be emphasised that relative costing by themselves provide no final basis for choice. The question of relative degree of benefits must also be taken into account. Figure12 represents a diagrammatic indication of lead emissions for each option considered but includes no consideration of other pollutants, such as carbon monoxide, hydrocarbons and polynuclear aromatics (PNA's). So far as benefits are concerned, these can only be evaluated on the basis of medical advice, and all that can be done here is to assume for the purpose of comparison that the benefits of options bear an approximate proportionate relationship to their effect in reducing all emissions.

The options have been treated as alternatives to one another, but in theory a combination of options may be employed if decided. If that was to be the case then the aggregate costs would exceed by far the cost incurred with substantial capital investment.

Option 3 appears attractive in terms of financial costs, social acceptance and reduced lead emissions, but it is unlikely to be accepted, because reduction in lead in fuel results in increases in aromatic content to maintain octane quality. Increases in aromatics in fuel (86,78) have been associated, in some studies, with the increasing emission of carcinogenic PNA's in exhaust emissions and increased atmospheric photochemical reactivity, the latter being particularly undesirable in relation to smog. Although increase of aromatic content is not the only means of maintaining octane quality, it appears to be the only practical means of reaching this objective quickly.

The question of what the end solution might be cannot be considered independently of future policy on gaseous emissions, because further restrictions on gaseous emissions have a more particular implication for the future options for reducing lead emissions. This lies in the fact that if, say, by the first half of the 1990's restrictions on gaseous emissions are so severe that catalytic exhaust converters are necessary, and if by then it has not been found possible to produce converters which show a higher lead tolerance than those in use in Japan, Germany and USA today, then lead-free petrol will be needed for that reason alone.

It must also be noted that this study indicates a financial penalty of £41 - Option 3, £18 - Option 5 and £16 - Option 6. But recent sales in the New York market indicate no price differential figure 11; this can be due to any of the following reasons:

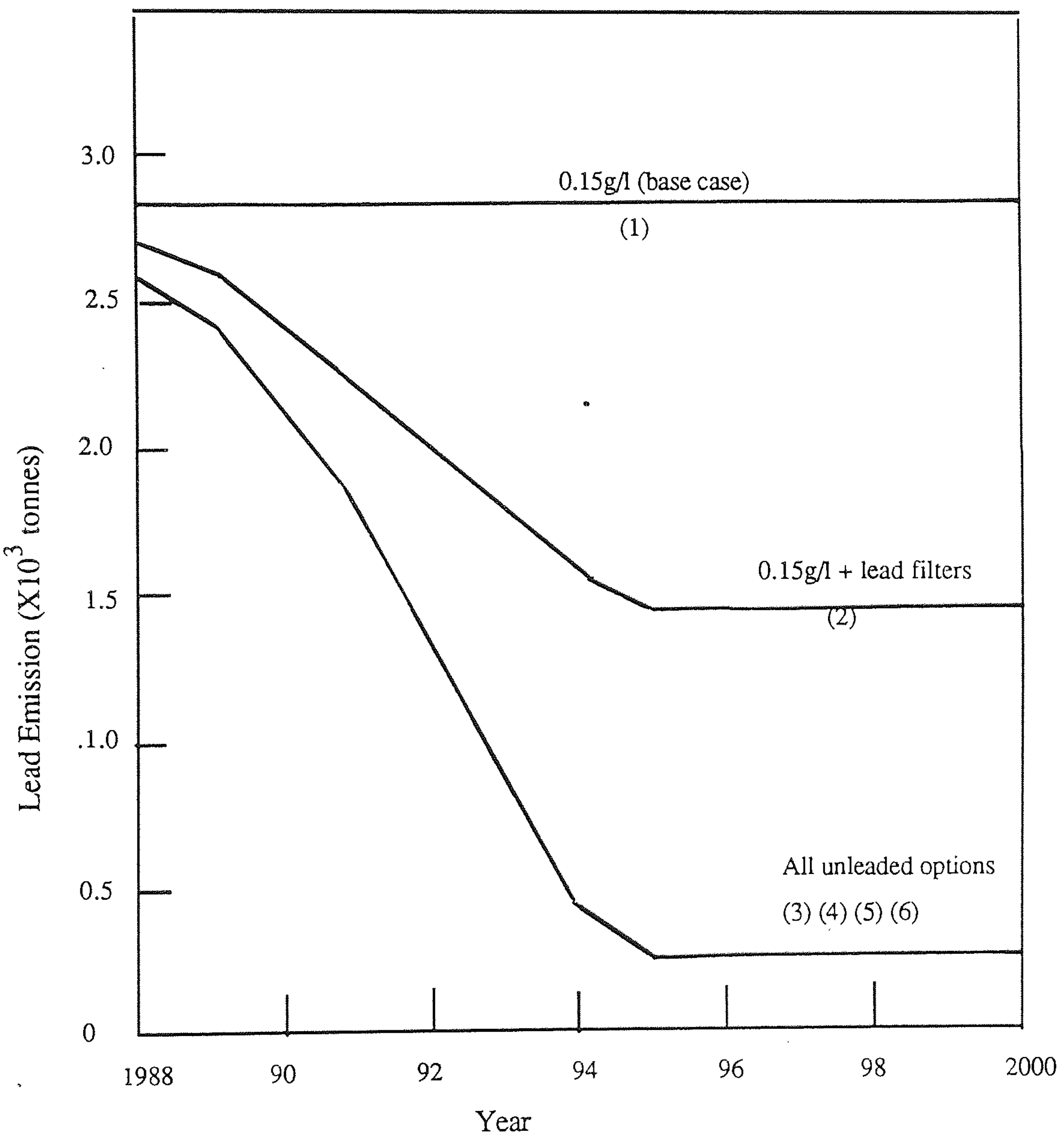
1. The RON and MON are lower for the lead-free gasoline than the leaded gasoline.
2. Tax incentive; loss or lower profits on unleaded gasoline is counter balanced by lower taxation.
3. Actual capital investment and refining costs to produce lead-free gasoline are no different than to produce leaded petrol.

It is therefore not surprising that the use of lead-free petrol is on the increase in the USA.

In this study the problem has been approached, and suggestions have been made, from a scientific point of view. The Government may decide its policy on a political issue altogether; Option 3 entails no burden on the motor industry, Option 2 entails no burden on the oil industry. The Government in deciding its policy may find it easier to burden one industry than the other.

The conclusion from this study is that whilst there is indeed an economic cost in the unleaded option, for the 92 RON, 95 RON and 98 RON, or with each other, the potential penalties must be considered in a wider aspect, because the cost in real terms would indeed be smaller than they appear, because of the indirect savings on health, trees and a cleaner environment in general. The difference is between long term and short term benefits.

Figure 12 Lead Emission Forcasts for Alternative Options



CHAPTER 3

EXPERIMENTAL WORK

EXPERIMENTAL WORK

3.1 Introduction

The experimental work in this research consisted, firstly, of a study of the physical properties of the unleaded deposits, and secondly, to extend previous work carried out in this department on emission control. Previous studies of engine fuels, carried out in this research group, consisted mainly of running the Fiat 127cc engine on blends of various alcohols and oxygenates with light key and heavy key component gasolines. The remaining work had been carried out on pure alcohols; their corrosive properties on various parts of the engine were examined (64.65). The engine was also run on pure alcohols with the aid of carburation changes, and performance comparisons were made. In this research programme a three-way catalyst was installed in the engine so as to determine emission results with the use of lead-free gasoline. It had also been hoped to carry out emission experiments using the same blends as in previous work but with the use of a three-way catalyst. However, due to lack of time, only the lead-free gasoline had been analysed thoroughly and it is recommended that the remaining work be completed by other researchers to come; as it represents an important section for understanding the viability of various compounds as prospective octane boosters of unleaded gasoline.

In order to quantify the effect of deposits on the octane requirement increase, a thermal conductivity experiment was designed to simulate in situ conditions. Previous work (65) carried out on thermal conductivity of deposits involved scraping of the deposit from the piston and crushing to fine powder followed by washing with a solvent so as to remove any oils. Although the experimental procedure had not been stated further it is nevertheless envisaged that it involved the covering of a metal wire with the powdered deposit through which an electric current is passed, thus raising the temperature of the metal wire and the deposit. It is obvious that results thus obtained have no bearing on the actual thermal conductivity, because in practice the deposit is not regular and very porous in nature photographs 47-- 57 and in situ condition would yield completely different results.

There has been yet another method employed to determine the thermal conductivity of deposits. This involved installing a very fine thermocouple on the surface of a clean piston, the piston is then re-assembled (11). As the engine is run, a deposit builds up on the piston and the temperature of the piston surface is monitored. It is clear that in situations of this nature, the thermocouple would act as a localised catalyst and yield misleading results.

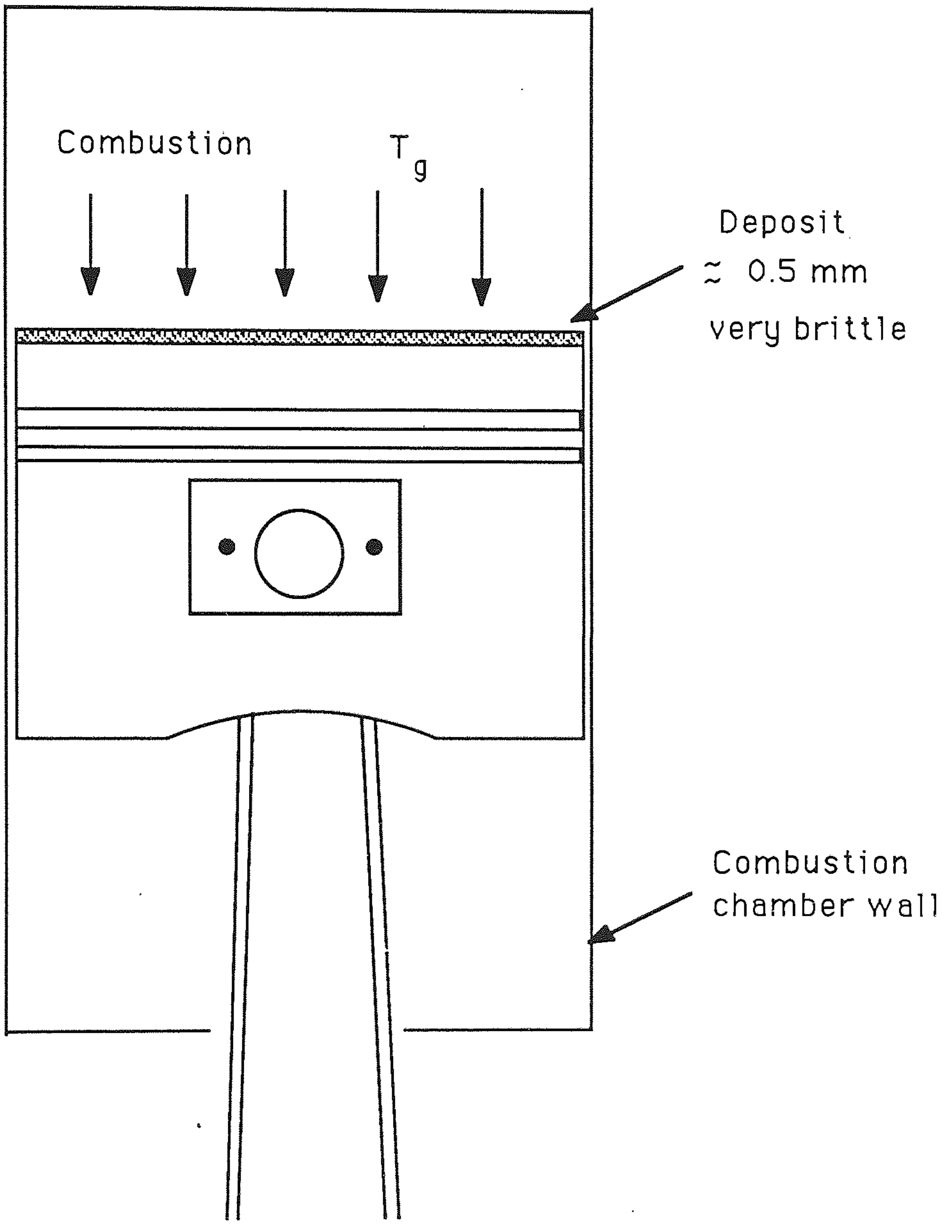
Bearing in mind the above attempts at measuring thermal conductivity in situ, the aim of this research was to design a technique that would be:

i) Fundamental in heat transfer concepts rather than empirical.
ii) Avoid creating localised catalyst conditions.
iii) Represent or be in situ conditions.

Figure 13, shows the in situ conditions that are prevalent and Figure 14, shows the apparatus employed in this research to determine the thermal conductivity of the deposits.

Further visual analysis of leaded and unleaded deposits was carried out using the University's scanning electron microscope. This analysis is presented in the form of

Figure 13 Heat Transfer in Situ Conditions



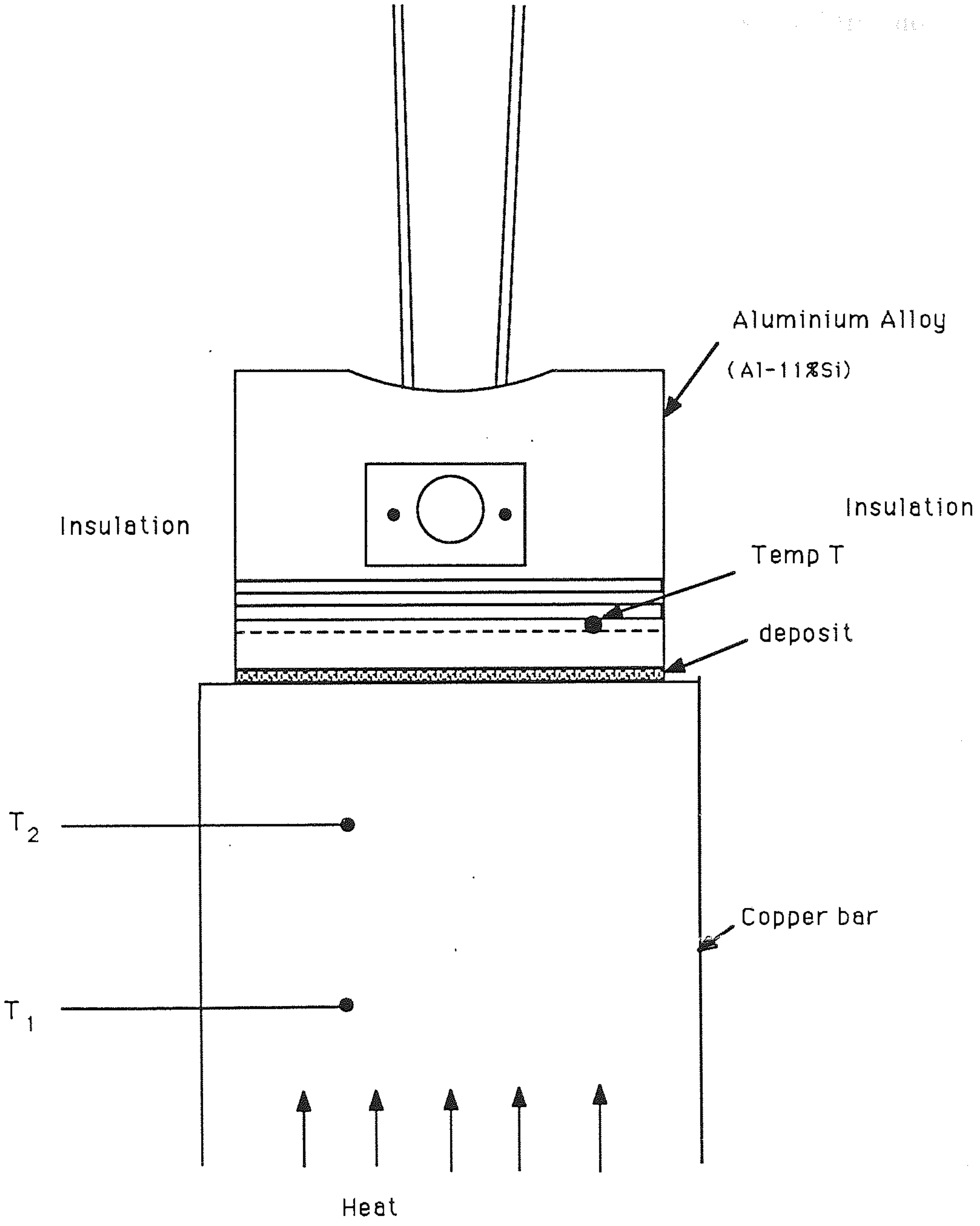


Figure 14 Measurement of Thermal Conductivity

photographs under various magnification. Due to the deposits having an irregular surface an attempt was also made to determine the average thickness of the whole of the deposit without physically removing it from the piston, using an x-ray diffraction technique, but unfortunately the efforts were fruitless due to the great irregularity of the deposit surface. However estimates of the thickness of the deposit from various parts of the piston were made, with the exception of the deposit from the central region of the piston, where flakes of the deposit could not be extracted without fragmentation.

An attempt was also made to measure the porosity of the deposit, but unfortunately, non of the standard techniques could be employed due to the limited quantity of the deposit. Nevertheless it is recognised that this is a crucial property and a technique should be sought to measure this quantity . However, the permeability of the deposit was measured using Lea and Nurse (71) apparatus, which had been employed in earlier work in the department and standardised using cement (Figure 3.3)(72-74).

3.2 Thermal Conductivity Equipment

As mentioned earlier the combustion chamber deposits increase the octane requirement of an engine, either because they accelerate the reactions which lead to knock, or they ignite the air-fuel mixture, thus leading to uncontrolled combustion. The deposit acts as a thermal insulator, and though these mechanisms or factors would no doubt be inter-related, it is postulated from literature that the insulating effect is by far the most significant factor leading to octane requirement increase.

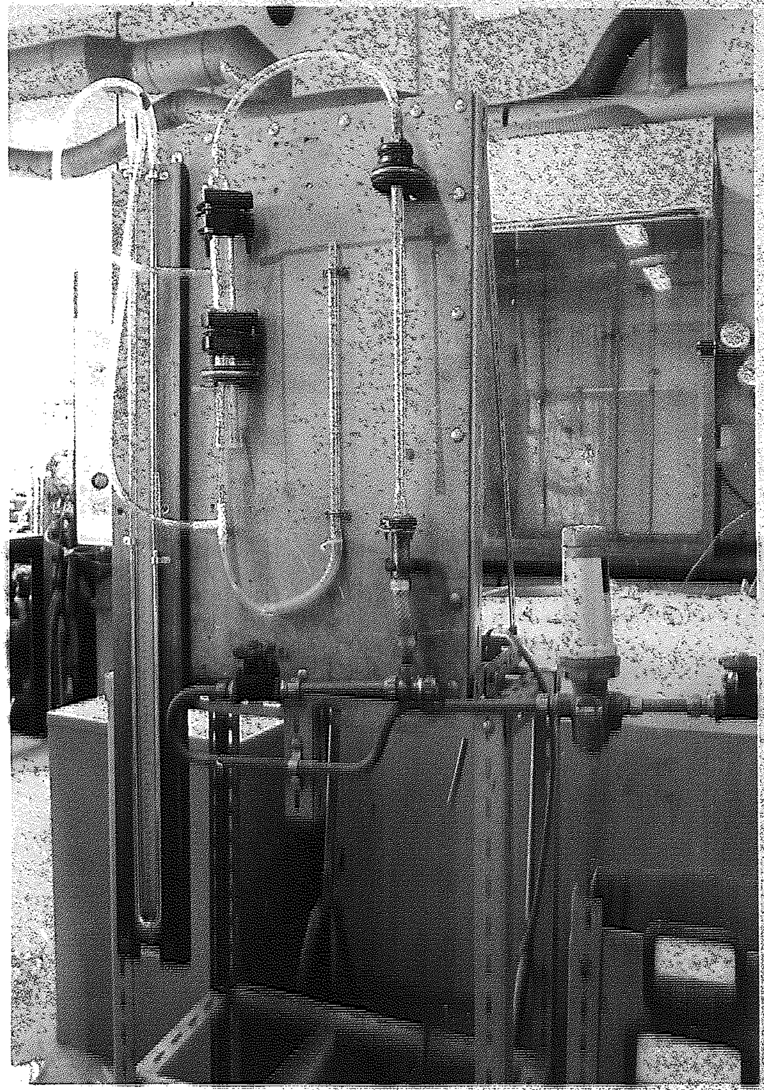


Figure 15: Photograph of Improvised Lea & Nurse's PermeabilityApparatus

3.2.1 Ancillary Equipment

The lower end of the copper piece was symmetrically drilled so as to house four cartridge heaters of 0.75kw power each. The power was supplied using a variable power source. The copper piece was used for providing the hot medium for uniformly raising the surface temperature of the deposit. Nickel/chromel thermal couples were used to measure all temperatures, these were connected to a comark selector switch and the voltage measured using a digital voltmeter.

The whole apparatus, with the test piece in position, is well lagged using fiber glass insulation, and enclosed in a safety cabinet. The power is switched on and kept at a minimum value, the apparatus is slowly allowed to heat up and reach steady state (i.e. until the point is such that there is no temperature change for two minutes on all the thermocouples). The power is then increased to a higher value and the apparatus again allowed to reach steady state at this higher temperature. The power is gradually increased and a table of temperatures is recorded.

The apparatus is calibrated using an aluminium disc and a Sindanyo plate. Figure 17 shows the diagram with the aluminium disc in place, and table 15, the various temperatures that were recorded. Similarly, table 16 shows the data obtained using the Sindanyo plate. Figure 18 represents conditions that are prevalent with our situation of a lower thermal conductivity medium or material attached to a high thermal conductivity metal. Table 17 shows the data obtained with this arrangement.

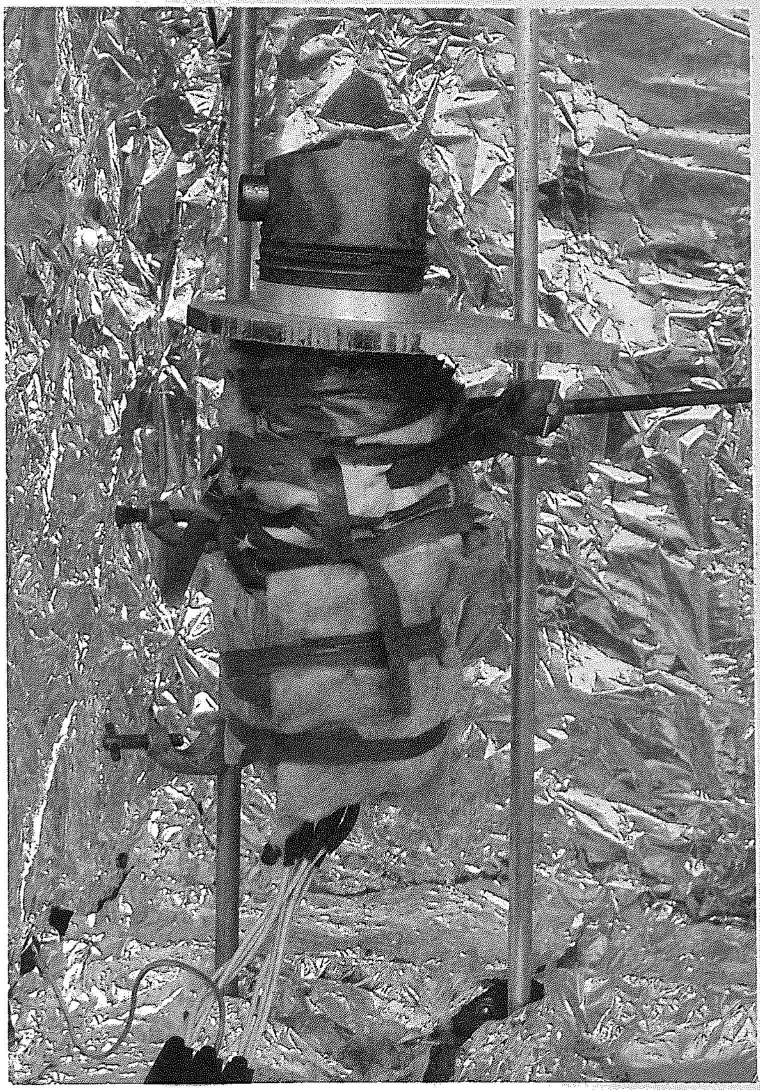


Figure 16: Photograph of Thermal Conductivity Apparatus

3.2.2 Calibration of Apparatus

Figure 17 shows the experimental set up for calibrating the apparatus, the following assumption are made:

i) No interface resistance between aluminium and copper

ii) Seventy minutes were thought sufficient between each set of readings for the apparatus to reach steady-state

iii) Unidirectional heat flow.

Heat flow between thermocouples (1) and (2) in copper

$$Q_1 = \frac{K_{cu} A}{x_2} (T_1 - T_2) \qquad \text{......(1)}$$

Heat flow between T_2 and T_{CA}

$$Q_2 = \frac{K_{cu} A}{x_1} (T_2 - T_{CA}) \qquad \text{......(2)}$$

Heat flow between T_{CA} and T_3 (temperature at the top surface of the aluminium disc)

$$Q_3 = \frac{K_{A1} A}{x_3} (T_{CA} - T_3) \qquad \text{......(3)}$$

At steady state $Q_1 = Q_2 = Q_3$

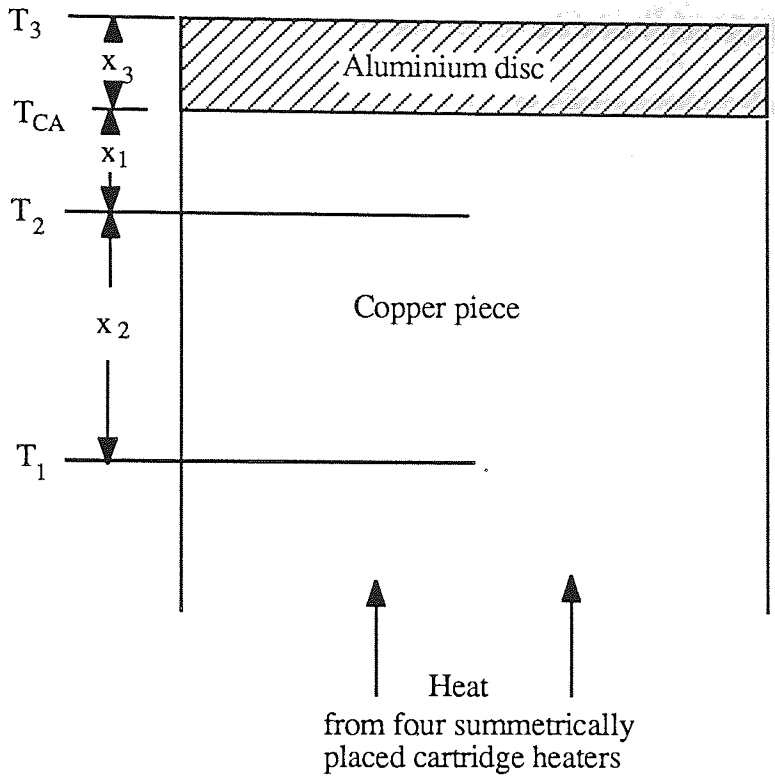
From equations (1) and (2)

$$T_{CA} = T_2 - \frac{x_1}{x_2} (T_1 - T_2)$$

From equation (3)

$$K_{A1} = \frac{Q_3 x_3}{A(T_{CA} - T_3)}$$

Figure 17 Calibration of Apparatus with Aluminium Disc



T_1

T_2 Thermocouples

T_3

T_{CA} Temperature at copper and aluminium interface

x_1 = Distance between thermocouple (2) and the copper/aluminium interface (10.32mm)

x_2 = Distance between thermocouple (1) and (2) (30.58mm)

x_3 = Thickness of aluminium disc (12.85mm)

Table 16 shows the data obtained using a Sandanyo plate in place of the aluminium disc. Figure 18 shows the third set of calibrations set up with both the aluminium disc and Sindanyo plate in place; Table 17 chapter 4 shows the corresponding data obtained, and the following analysis is employed:

Heat flow between T_1 and T_2

$$Q_1 = \frac{K_{CU} A}{x_2} (T_1 - T_2) \qquad \text{\_\_\_\_\_\_\_\_\_\_(1)}$$

Heat flow between T_2 and T_{CS}

$$Q_{CS} = \frac{K_{CU} A}{x_1} (T_2 - T_{CS}) \qquad \text{\_\_\_\_\_\_\_\_\_\_(2)}$$

Heat flow between T_{CS} and T_{AS}

$$Q_{AS} = \frac{K_{sind} A}{x_{sind}} (T_{CS} - T_{AS}) \qquad \text{\_\_\_\_\_\_\_\_\_\_(3)}$$

Heat flow between T_{AS} and T_3

$$Q_A = \frac{K_{A1} A}{x_{A1}} (T_{AS} - T_3) \qquad \text{\_\_\_\_\_\_\_\_\_\_(4)}$$

Assuming:

i) Perfect contacts at interfaces

ii) Steady state conditions

iii) Sindanyo is the material with unknown thermal properties

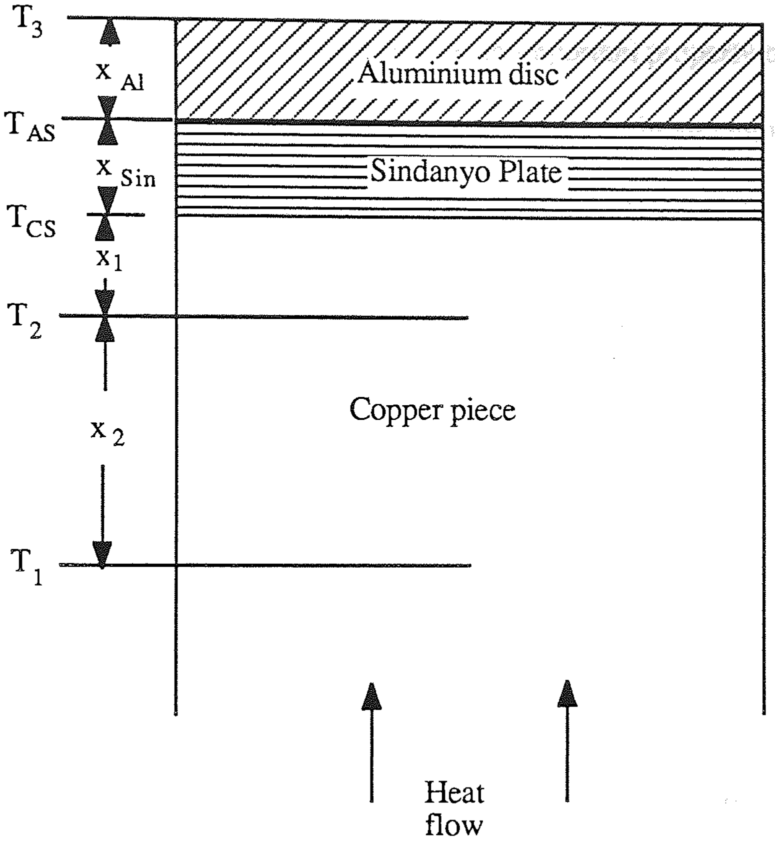
Ay steady state

$$Q_1 = Q_{CS} = Q_{AS} = Q_A$$

From equation 1 the heat flow is determined, thus allowing T_{CS} to be determined from equation 2.

Similarly from equation 4, T_{AS} is determined, and hence from equation 3 the corresponding value of K_{sind} at the particular temperature.

Figure 18 Calibration of Apparatus Using an Aluminium Disc and a Sindanyo Plate



x_{sind} = Thickness of Sindanyo plate (9.57mm)

x_{Al} = Thickness of aluminium disc (12.85mm)

T_{CS} = Temperature at copper/Sindanyo interface

T_{AS} = Temperature at aluminium/Sindanyo interface

3.3 Permeability and Porosity

The permeability and porosity of deposits are an important property of the deposit which influences the octane requirement increase of an engine. In an engine a porous deposit may initially trap some of the combustible mixture, thus preventing its immediate combustion, otherwise it could trap some of the exhaust gases produced under high pressure and temperature, and discharge the heat to the fresh incoming charge. Dumont(67) showed that with leaded deposit this accounted for a significant proportion of the total ORI.

Permeability represents pores or channels in the deposit that lead from one end of the surface to the other. These channels again would be a source for trapping gases and also facilitate in the transfer of heat from the combustion chamber to the walls, or vice versa. Thus a very permeable deposit would, in effect, show large differences in the transfer of heat in relation to a deposit that is not so permeable. Figures 49,50 and 51 show the cross-section of the deposit and a normal surface, they also show that it is virtually impossible, first of all to define the length of the channel, for it is likely that no channel in the real sense exists but rather crevices that have been built up by the deposit flaking and re-building. Similarly, pore or channel size cannot be estimated with confidence, thus limiting our estimation of the total flow area.

In this analysis the length of the channels has been assumed to be equal to the thickness of the deposit and it is further assumed that the molecular size of air used in the test would be close to the molecular size of combusting uses encountered in the engine.

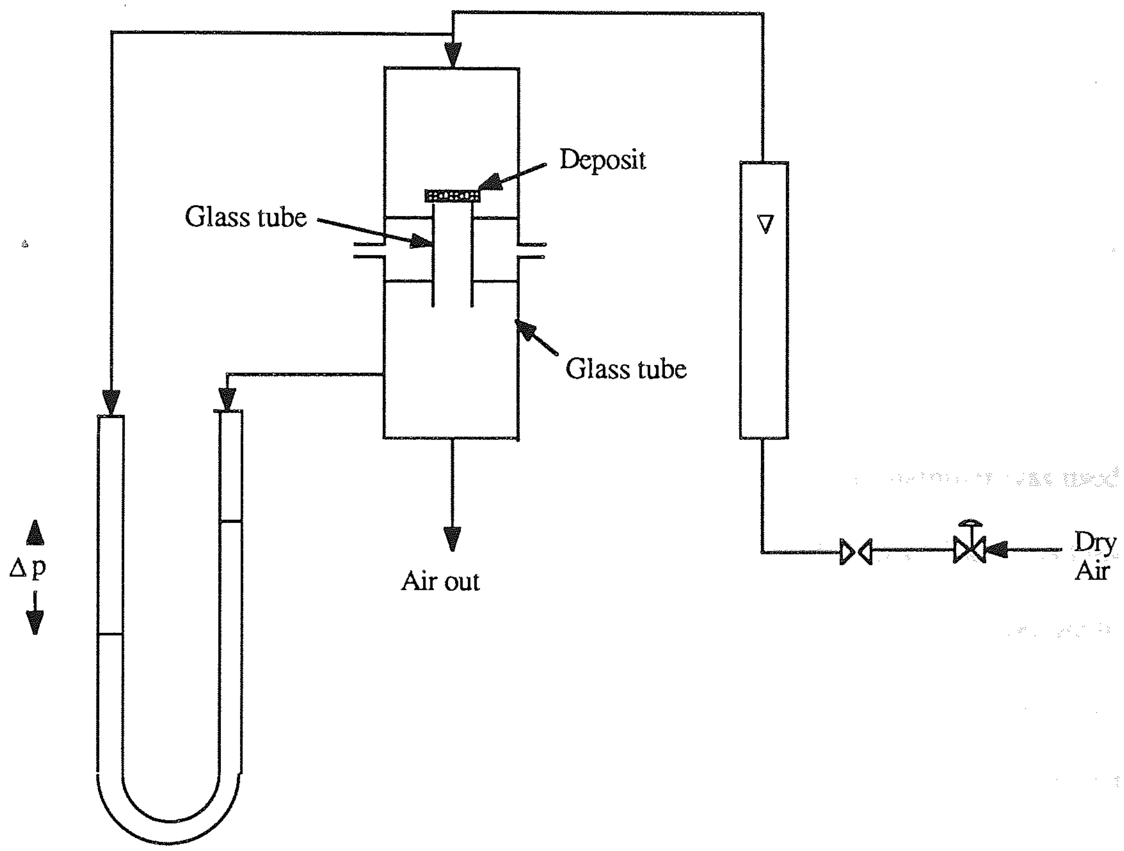
Apparatus for Pressure Drop Across the Deposit

Pressure drop across the deposit was determined using Lea and Nurse apparatus, as shown in Figure 19. The assembly consisted of two QVF tubes, two rotameters, a U-tube manometer and a deposit support.

The test section consisted of two QVF glass tubes of 33mm diameter and 150mm length, respectively, with side connections to the manometer. A deposit support was mounted between them.

Dry air was passed through a Saunders diaphragm valve and then reduced to atmospheric pressure by a 12.7mm spiral source pressure reducing valve type BRV. The flowrate of inlet and outlet air was measured by a rotameter and controlled with 12.7mm Saunders diaphragm valve. The pressure drop across the deposit was recorded by means of a U-tube manometer.

Figure 19 Diagrammatic Presentation of Permeability Apparatus



3.4 Analysis of Deposits

An attempt was made to visually analyse the deposits by photography at various magnifications and also to highlight the physical structure of the deposits. Photographs at high magnifications were greatly sought after, as it was thought that they would indicate the flakiness of the deposits and nature (mechanism) of accumulation.

3.4.1 Procedure

The deposit could not be scraped from the piston as scraping would jeopardise the porous nature of the deposit - this is an important factor as using this or any other method, specimens measuring 3mm by 3mm (approximately) could not be extracted. Scraping would destroy the porous nature of the deposit, thus a small hammer was used to create vibrations (simulating extreme knocking conditions) and pieces of deposits thus flaked off, were used for the analysis. The extracted deposit was glued with araldite to metallic studs, and when the araldite had set and the deposit firmly secured to the studs, the specimen was sprayed with a suspension of gold and palladium, which then formed a thin layer. This was carried out so as to hold the surface of the deposit at constant electric potential. The coating was less than 50 angstroms, thin enough not to obscure any fine details such as pores and cracks which might be present.

Each specimen was then introduced into the specimen chamber of the scanning electron microscope and photomicrographs were recorded with a 35mm film.

3.5 Emission Control Experiments

This section of the experimental work was carried out using a Fiat 127 903cc engine, with a variable load to simulate driving conditions. The same engine has been previously used for work carried out on oxygenates and alcohols, Figures 20, 24 and 21 show the engine, dynamometer and analytical instrumentation, etc. The engine was connected directly to the load controlling dynamometer with a prop-shaft.

The cooling of the engine was attained by using a small heat exchanger and cold water supply. At times this had been found insufficient and was also supplemented with a Fiat radiator and an electric fan. Fins had also been welded onto the engine sump, over which air from the radiator fan was blown. Initially thermocouples had been used to monitor the temperature of the cooling water and the engine oil in the sump together with the engine air intake and dynamometer cooling water outlet. Later it was thought necessary only to monitor the engine sump temperature.

An Alcock viscous air flowmeter, type H8006, connected to the inlet of the engine air filter box, was used to provide the inlet air. This involved an air stream-liner across which the pressure drop was monitored and correlation charts were available to determine volumetric air flow. Table 13 shows the data obtained and Figure 31, plots this data.

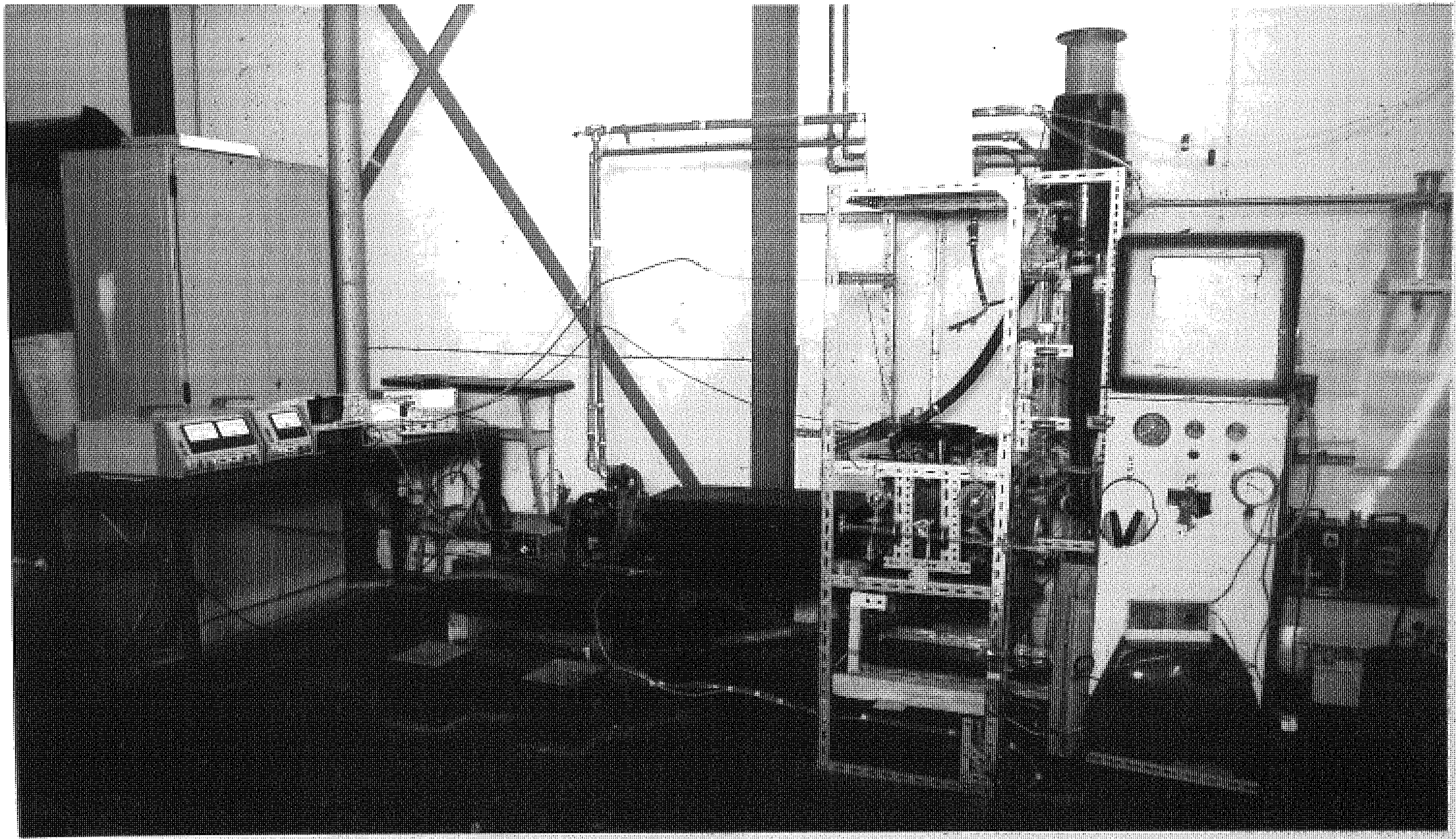


Figure 20: Overall Photograph of Fiat Engine and Rig

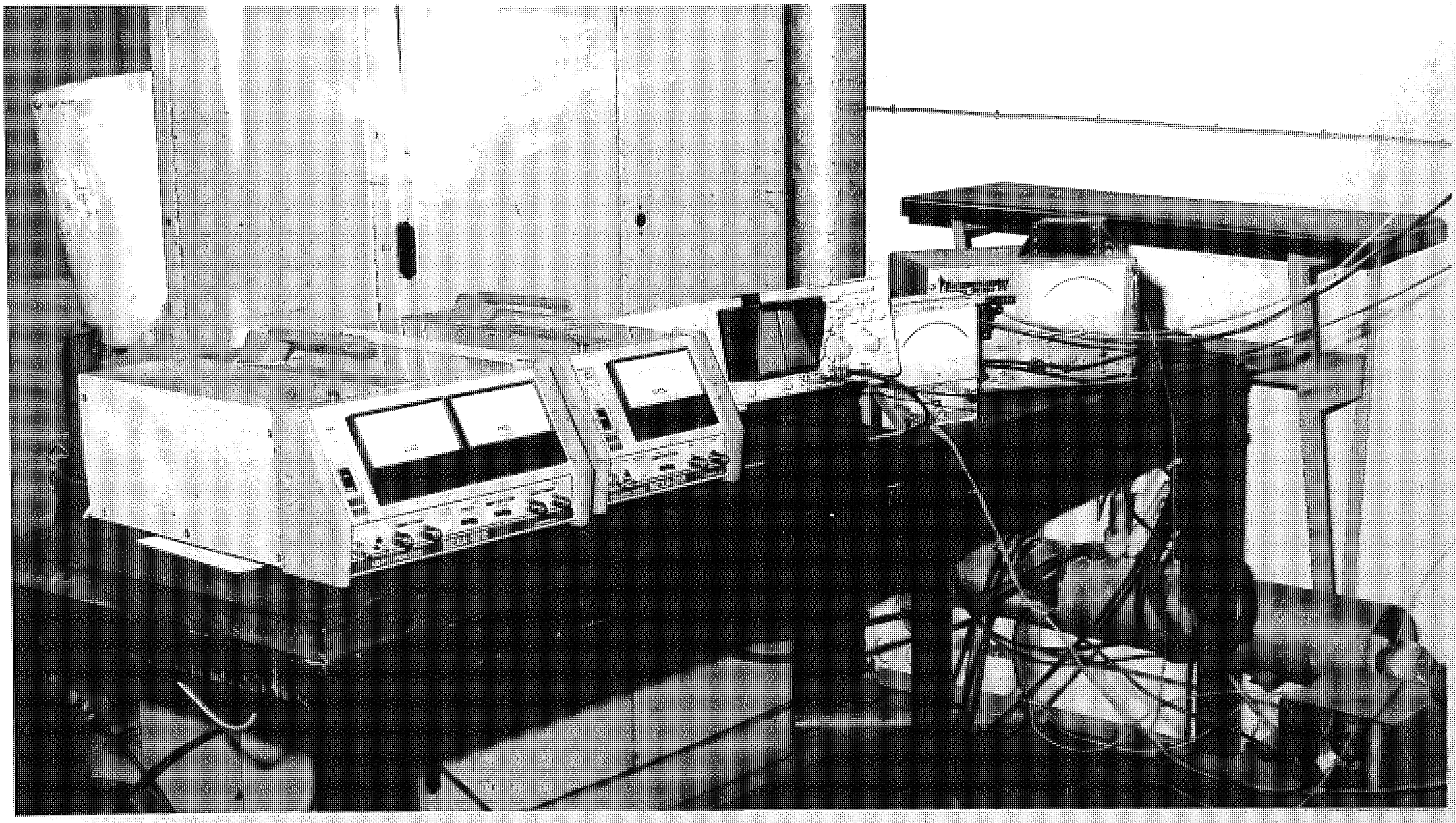


Figure 21: Photograph of Instrumentation

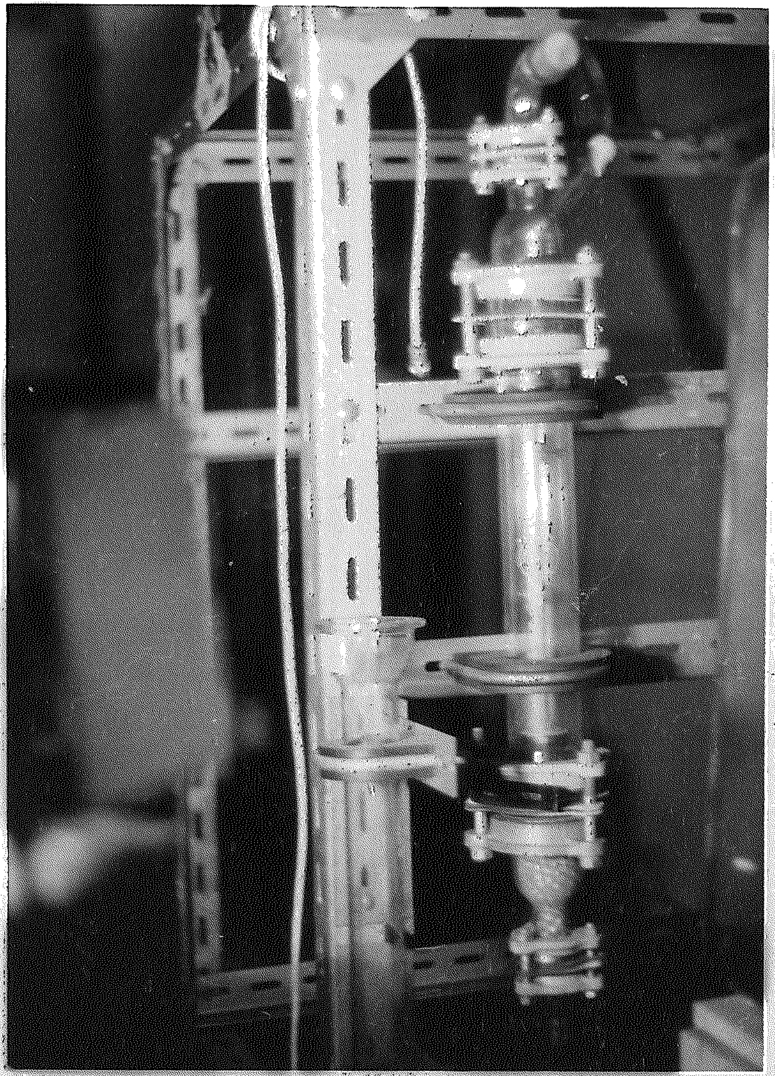
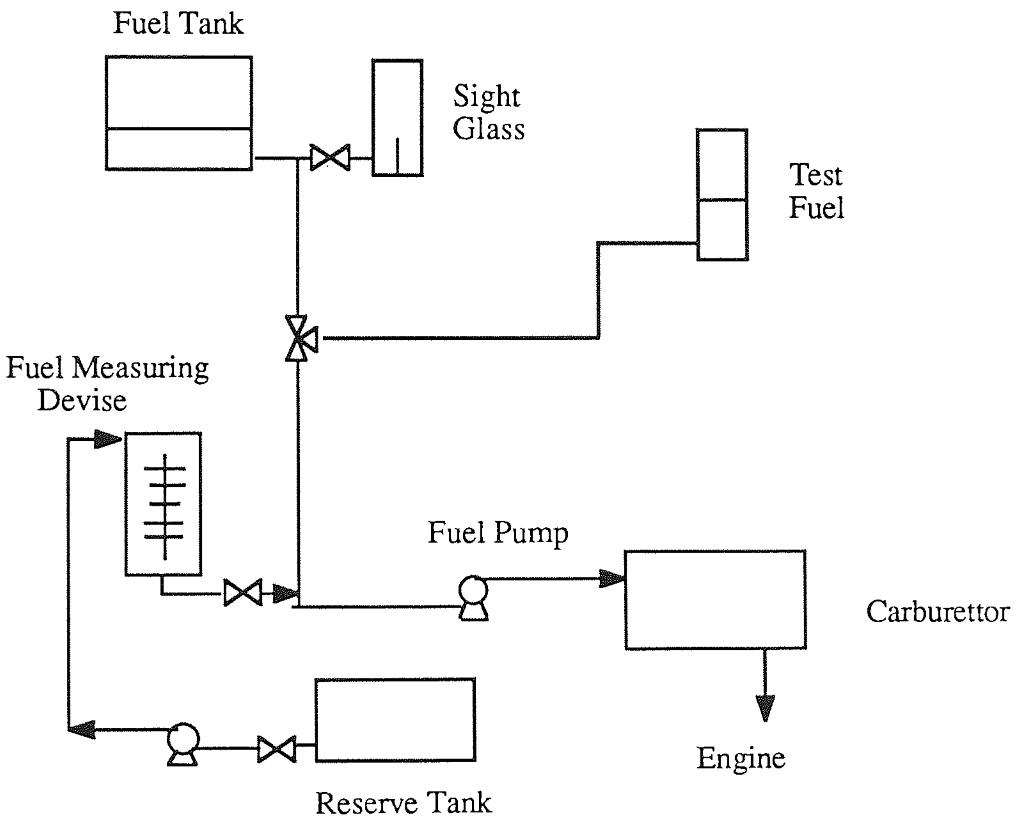


Figure 22: Photograph of the Fuel Measuring Device

Figure 23 Schematic Diagram Engine Fuel System



3.5.2 Distributor Timing Curve Check

Spark timing is an important factor that influences knock. The previous two researchers(64,65), whose work involved a great deal of knock monitoring, checked the distributor using the Sun 504 distributor tester at Abingdon ESSO. It is vital to maintain constant spark timing setting,because it is well known that advanced ignition leads to knock promotion because extra ignition delay allows the formation of large quantities of peroxide radicals which initiate the reactions leading to knock.

Dwell angle and its variations, contact breaker tension and cam accuracy were all checked (see Table 12). Ignition advance was observed a number of times with a stroboscopic timing light during the period of experimental work and was found to be satisfactory.

Table 11 Engine Distributor Evaluation

Engine :	Fiat 127 (45 PS) Type 100GLOOO 1971
Distributor type:	Marelli S156AX
Static timing:	10°
Dynamic timing	10° ≈ 850 rpm
	19-23° ≈ 1500 rpm
	28-32° ≈ 3200 rpm
	36-40° ≈ 4700 rpm
Contact breaker gap	0.4 mm
Dwell angle	52°-58° (58-64%)
Idle speed	740-800 rpm

Tests

Dwell angle found	54.5°	
Distributor cam accuracy	1.	0.0°
	2.	270.5°
	3.	89.5°
	4.	180.0°
Contact breaker spring tension		20 oz.

3.5.3 DP X 1 Heenan-Froude Dynamometer

The DPX1 dynamometer is also known as a water brake as it uses water to absorb the engine power. Load is exerted on the engine by directing the inlet water onto a rotor, using adjustable sluice gates. The power absorbed is converted to heat which is detected in the outlet water. The load applied by the dynamometer on the Fiat engine at wide open throttle can vary the engine speed from a minimum of 840 to a maximum of 4800rpm for maximum and minimum loads, respectively.

The rpm of the engine was measured using the M48 optical tachometer. This involved a piece of reflective tape stuck to the end of the dynamometer, which reflected the light emitted by the optical head back to the built in receiver. The engine rpm was then displayed digitally. The short sampling time of the instrument insured a fast response to change in engine speed, this also gave an indication of any irregular operation of the engine (see photographs Fig. 25 and 26).

3.5.4 Dynamometer and Load Measuring Device

To the dynamometer was attached a load measuring device that consisted of four strain gauges in a wheat stone bridge arrangement mounted on a cantilever, acted on by an arm attached to the dynamometer case. The strain gauges were mounted in the usual manner with two on the upper side and two on the lower side, resulting in two being under compression and two in tensile strain at any time figure 27. A variable resistor was placed across the bridge circuit to enable zeroing, and power was supplied from a Brandenburg STI stabilised D.C. supply.

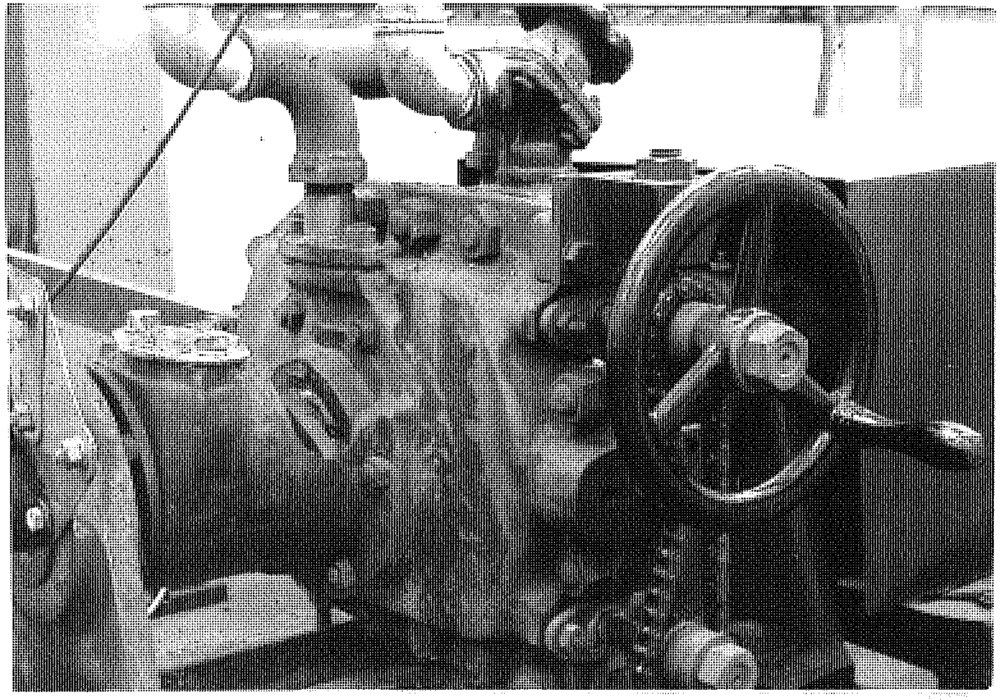


Figure 24: Photograph of DFX1 Heenan-Froude Dynamometer

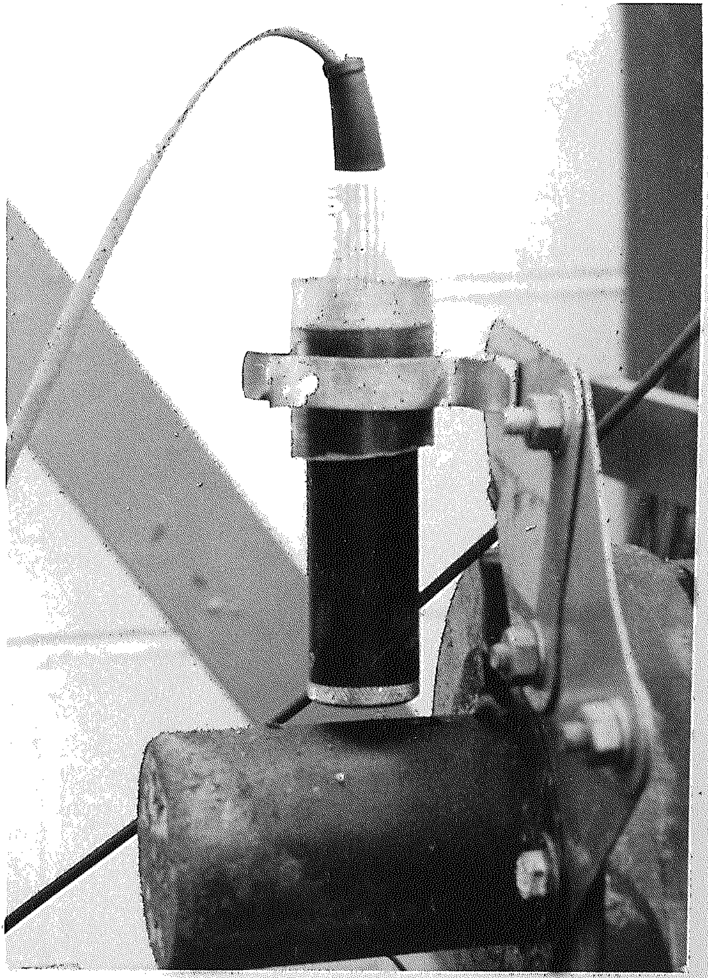


Figure 25: Photograph of M48 Optical Tachometer

The deflection of the beam, due to the load exerted on it, changes the resistance of strain gauges proportionally, and the change in voltage which results is measured using a digital voltmeter.

The beam attached to the dynamometer casing was designed to allow weights to be suspended freely for calibration and periodic checking of the bridge circuit. This is an important aspect as the readings were spread over a long time and the arm attached to the dynamometer could have attained a permanent bend. Tables 1 and 2 show the results of calibration, and Figures 26 and 28 plot this data, is can be seen, in a straight line relationship. The conversion factor from multivolts to torque was obtained from the graph and found to be 27.83 x mV.

Table 12 Calibration of Dynamometer and Load Measuring Device

Suspended wt. kg	Voltage output mV	Torque * produced Nm
0.0	0.00	0.00
1.0	0.15	5.35
2.0	0.31	10.69
3.0	0.56	16.04
4.0	0.76	21.39
5.0	0.95	26.73
6.0	1.12	32.08
7.0	1.35	37.43
8.0	1.55	42.77
9.0	1.73	48.12
10.0	1.95	53.46
11.0	2.11	58.81
12.0	2.31	64.16
13.0	2.39	69.50
14.0	2.69	74.85

Figure 26 Graph showing Relationship of Dynamometer Load and Voltage produced by Strain Gauge

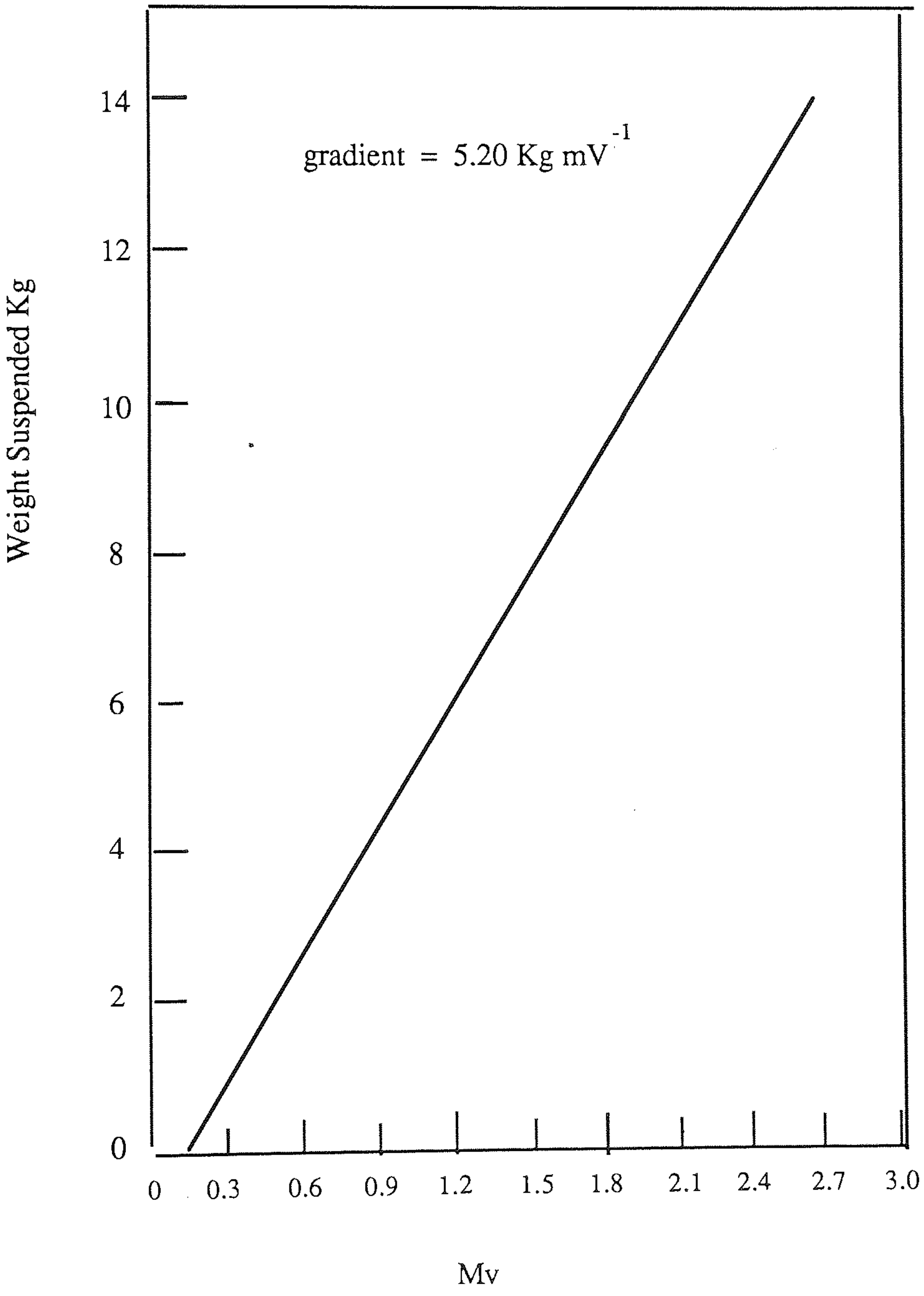


Figure 27 Bridge Circuit For Strain Gauges in Load Measuring Devise

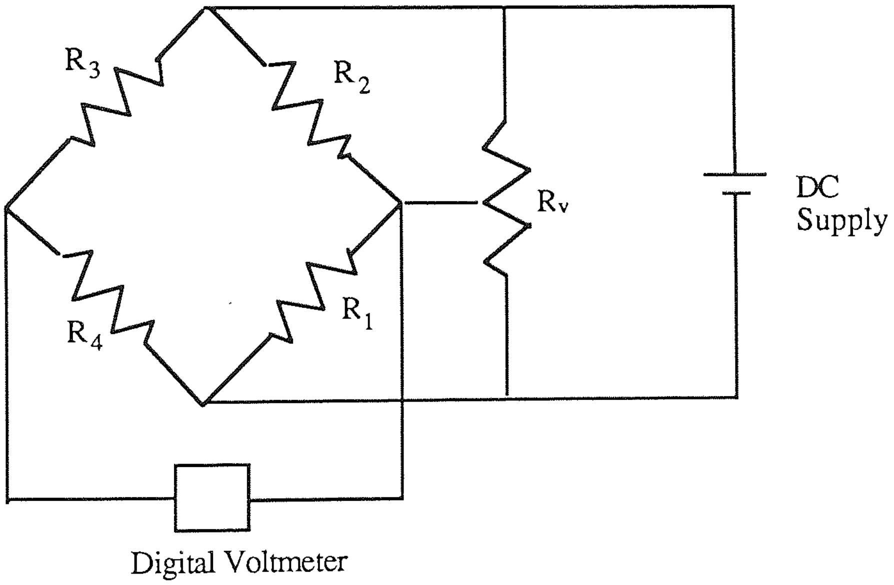
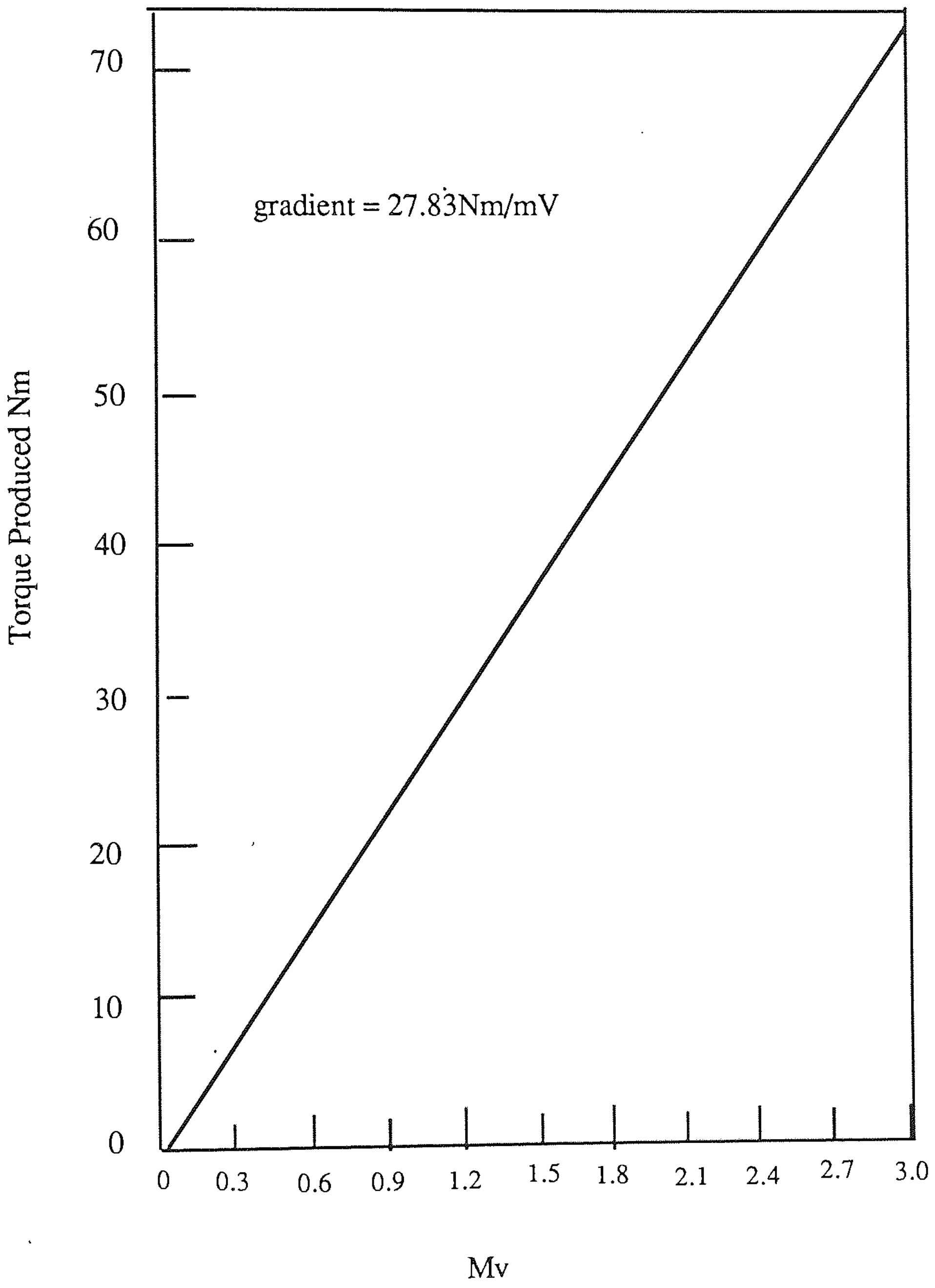


Figure 28 Calibration of Strain gauges and Load Cell



3.5.5 Engine Power Output

Power output from the engine was determined from its minimum value of 840 rpm to 4000 rpm at wide open throttle. The engine had been fitted with an electric fan by the previous researchers in an attempt to match handbook specifications. In a typical run, after an initial warm-up period of ten minutes, readings were taken and engine torque and power output were derived table 24, and plotted figure 60 and 61. Although in the present research there would be no direct information derived or concerned with power output from engine, it was thought it should be presented to make the report comprehensive.

3.5.6 Engine Compression Ratio

Compression ratio of each cylinder was measured by Sidue and Gribble(64,65), who after dismantling the engine found that there was variation amongst the cylinders, and measured the displacement and compression ratio of the cylinders 1 to 4 of 8.92, 9.13, 9.07 and 9.07, respectively, with the total engine capacity being 904cc. Two further methods were employed to determine the compression ratio, in each case the second cylinder was found to be appreciably higher than the others, indicating that it would be the one most likely to knock as the fuel quality is reduced or other deterioration occurs.

3.5.7 Knock Detection

At low engine speeds, knock can be easily detected by listening to the engine wearing ear defenders which muffle the background engine noise. However, at higher engine speeds the background noise increases in frequency and volume, thus making the mechanical tapping sound of the engine virtually impossible to distinguish by ear. Two different knock sensors were therefore employed, the first a Bruel and Kjaer type 4360 piezoelectric accelerometer, and the second a CEL type 7G11 piezoelectric pressure washer.

The Bruel and Kjaer accelerometer is quite adequate to withstand high temperatures and has a detection frequency of 5 to 15 kHz, which is in line with that of the knocking frequency. The accelerometer had been mounted by the previous researchers on one of the cylinder head bolts, following tests using a magnetic coupling to determine the optimum mounting position to emphasise pick-up from all four cylinders above the engine noise figure 29. The signal produced was fed into a dual beam oscilloscope via a Kistle type 566 charge amplifier. This produced a trace of four peaks representing the firing of the cylinders.

The pressure washer used is in the form of a ring, which replaces the compression washer on a spark plug and detects the pressure variation within that cylinder figure 30 and 33 As mentioned in the previous section the second cylinder was chosen because it was the most likely to knock. The signal from this pressure transducer was in the form of a typical pressure trace .

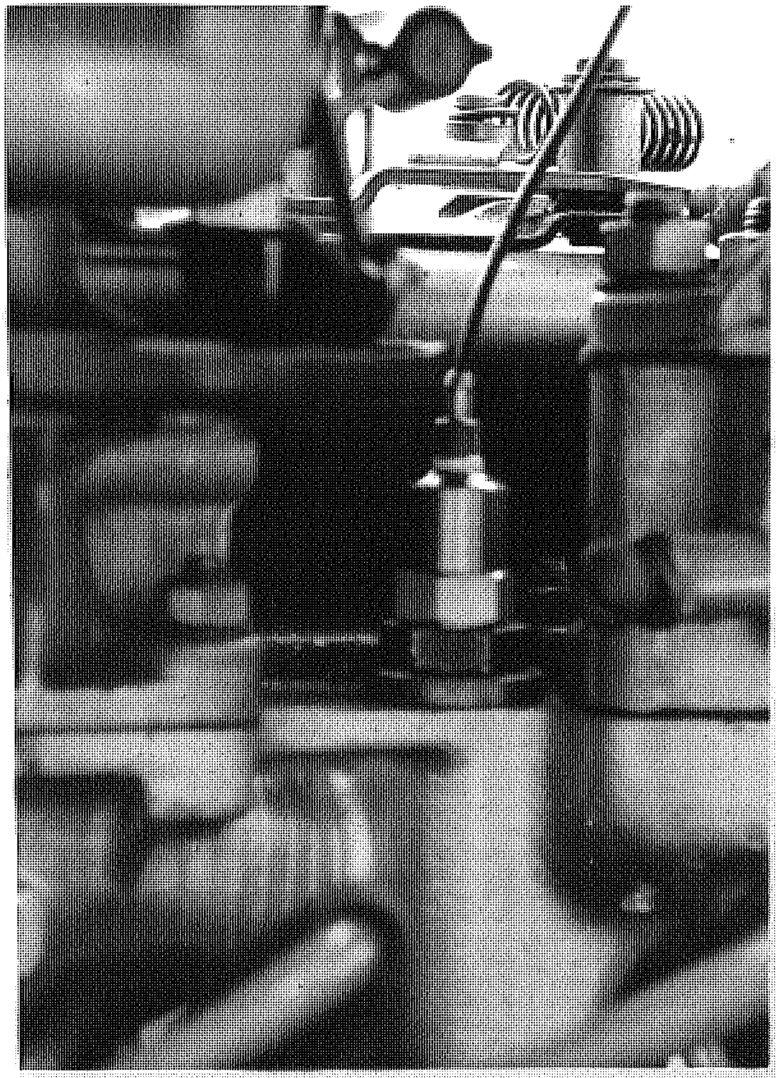


Figure 29: Bruel and Kjaer Type 4369 Piezoelectric Accelerometer

Figure 30: CEL Type YG11 Piezoelectric Pressure Washer

3.5.8 Procedure

The dynamometer is set to a minimum load with an adequate water supply, the oscilloscope and airflow meter and gas analysers are switched on about twenty to thirty minutes before the engine is started. The fuel is turned on and the choke set, the engine is started. After five to ten minutes the engine cooling water and the electric fan are turned on and the choke closed. Throttle opening is simultaneously carried out with increasing dynamometer load until the condition of wide open throttle is achieved. The engine speed can now be solely controlled by varying the load on the dynamometer.

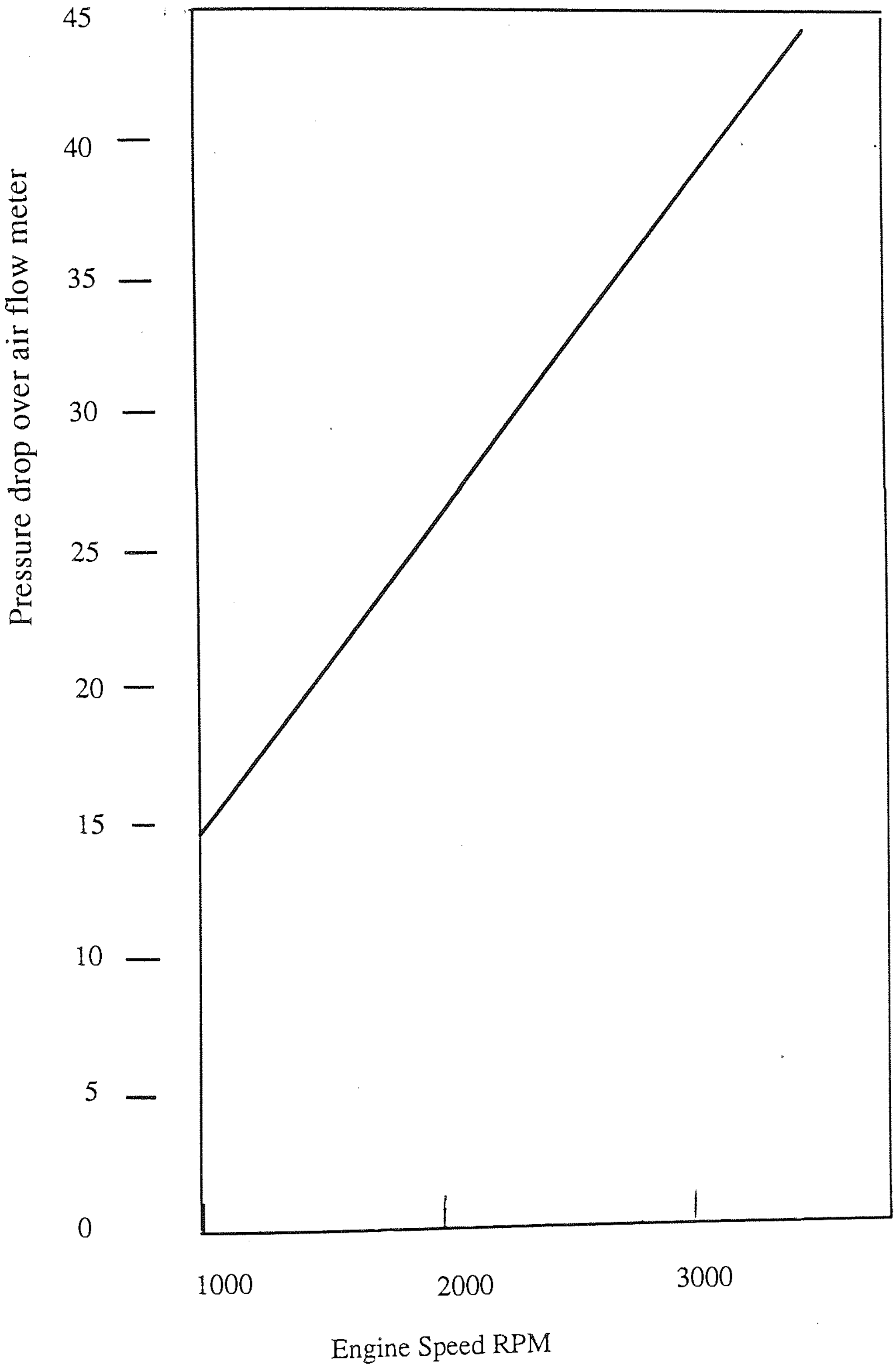
When the engine is running smoothly the test fuel is switched on and the engine further allowed to run for a few minutes on the test fuel before testing is allowed to take place, and readings on the analysers are subsequently recorded. The engine speed is slowly increased by varying the load and each reading is repeated a number of times by increasing and decreasing the load. Readings were again repeated a fortnight later so as to average out changes due to atmospheric conditions. No allowance for humidity or atmospheric temperature were taken into account because it was thought to assess variations that would prevail under ambient conditions.

For shut down, the throttle opening is slowly reduced, with subsequent decrease of the dynamometer load, until it is at a minimum load and the engine is running at idle speed. The engine is switched off together with the oscilloscope, gas analysers and the electric fan; the engine and dynamometer cooling water pump are also switched off after about ten minutes.

Table 13 Pressure Variation Across Alcock Viscous Air Flow Meter with respect to Engine Speed

Engine Speed (rpm)	Pressure Drop over air flow meter (mm H_2O)
1000	11.7
1100	13.0
1200	14.7
1300	15.8
1400	16.9
1500	18.5
1700	20.2
2000	24.2
2400	29.9
2600	32.3
3000	38.2
3500	44.3

Figure 31 Relationship between Engine Speed and Pressure-drop Across the Air Flow Meter



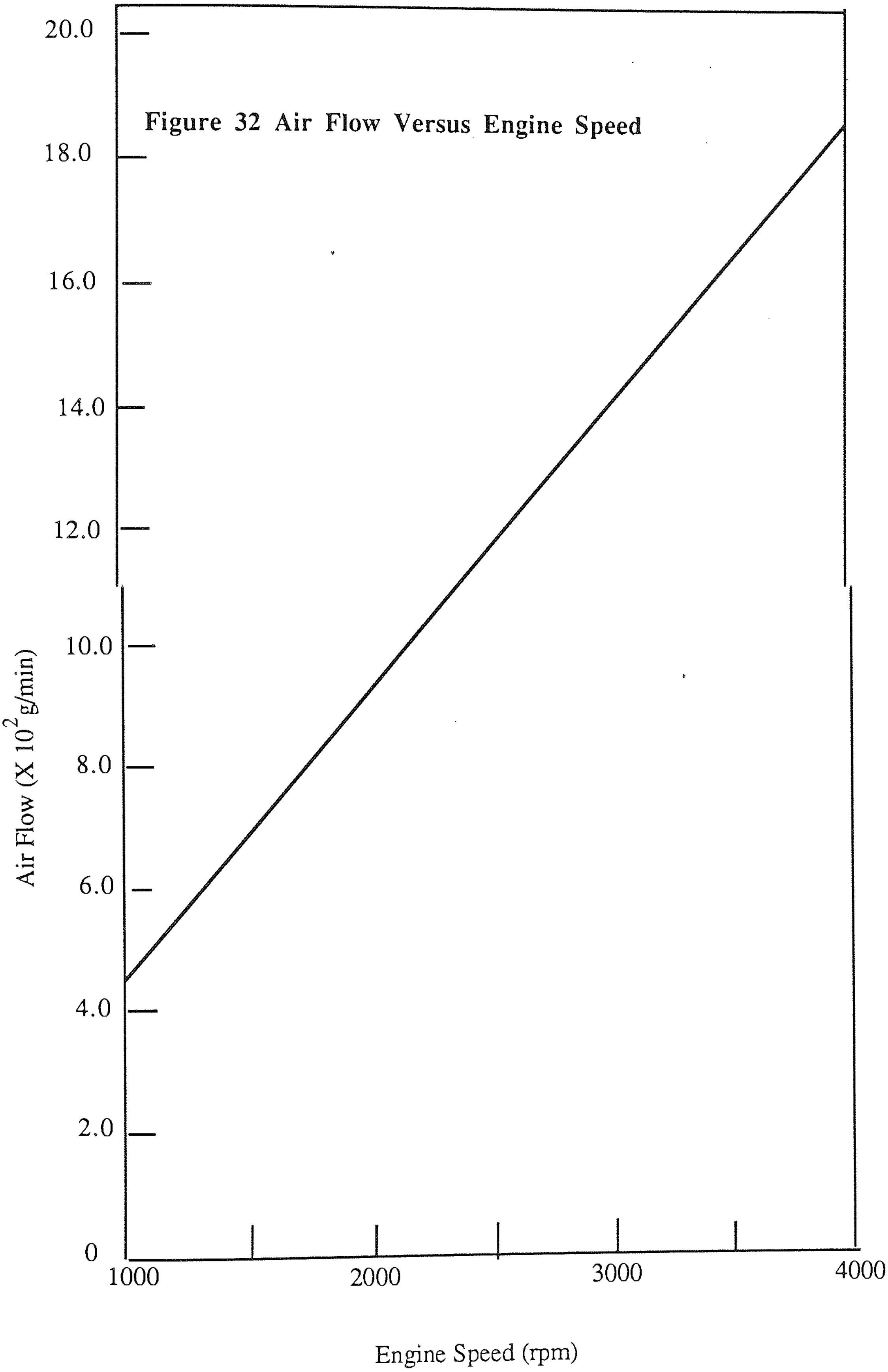


Figure 32 Air Flow Versus Engine Speed

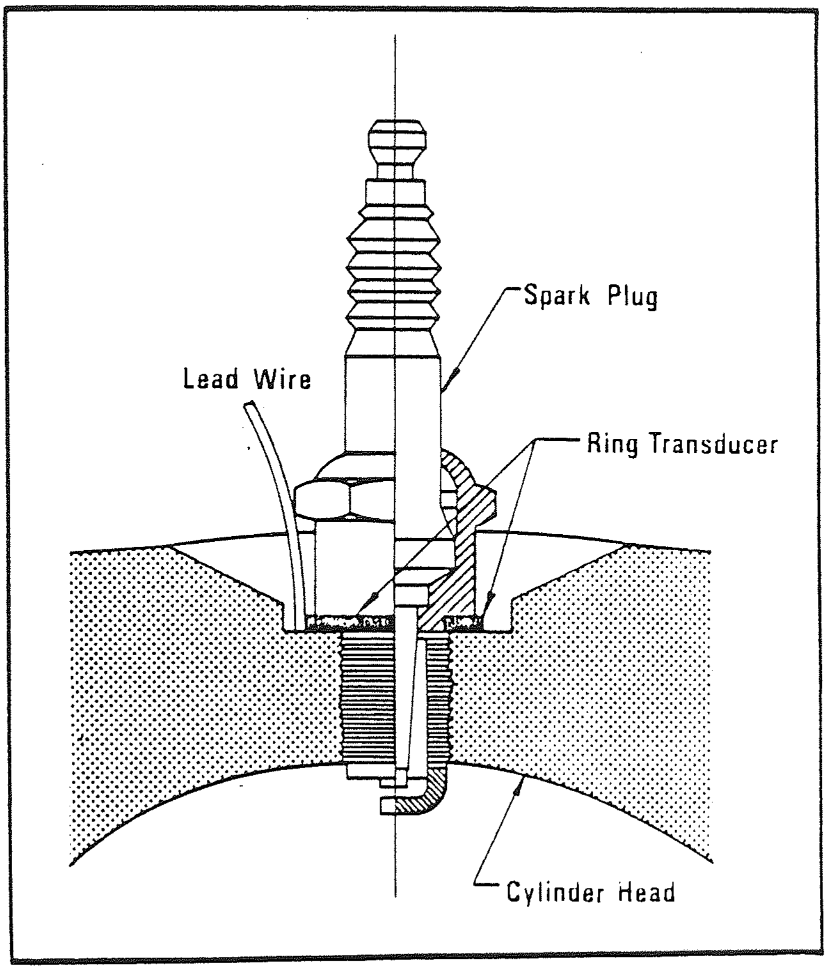


Figure 33: Method of Mounting YG11 Piezoelectric Pressure Washer

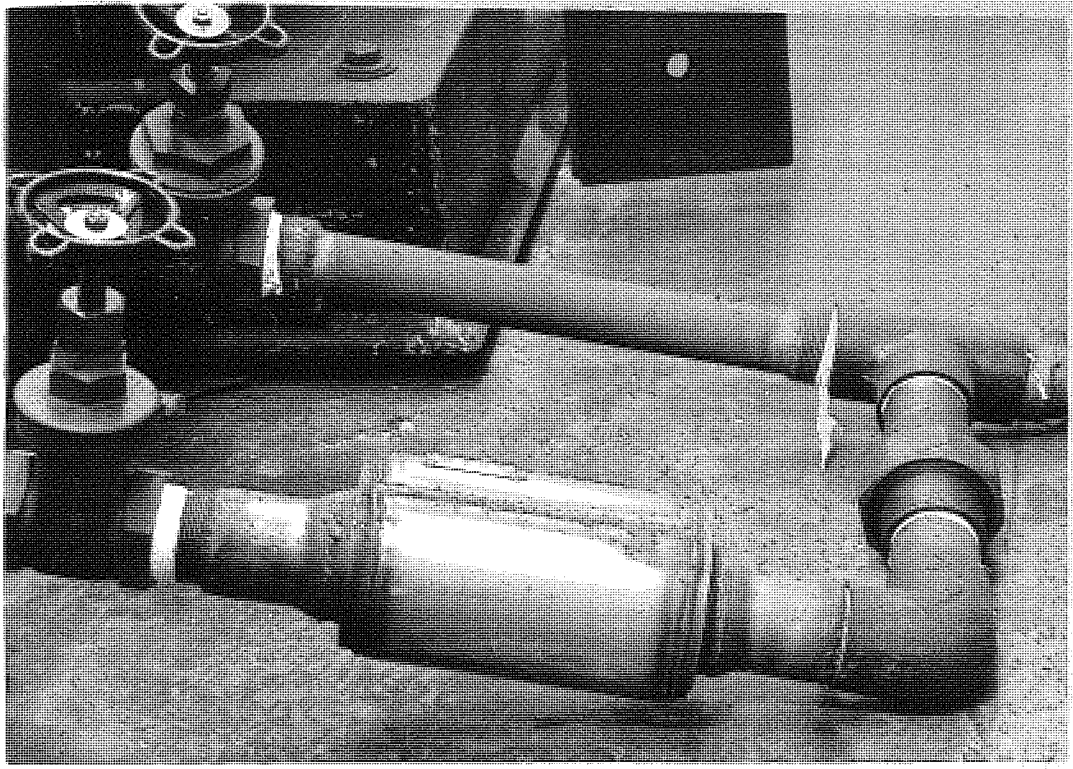


Figure 34: Photograph of Honeycomb Three-way Catalytic Converter

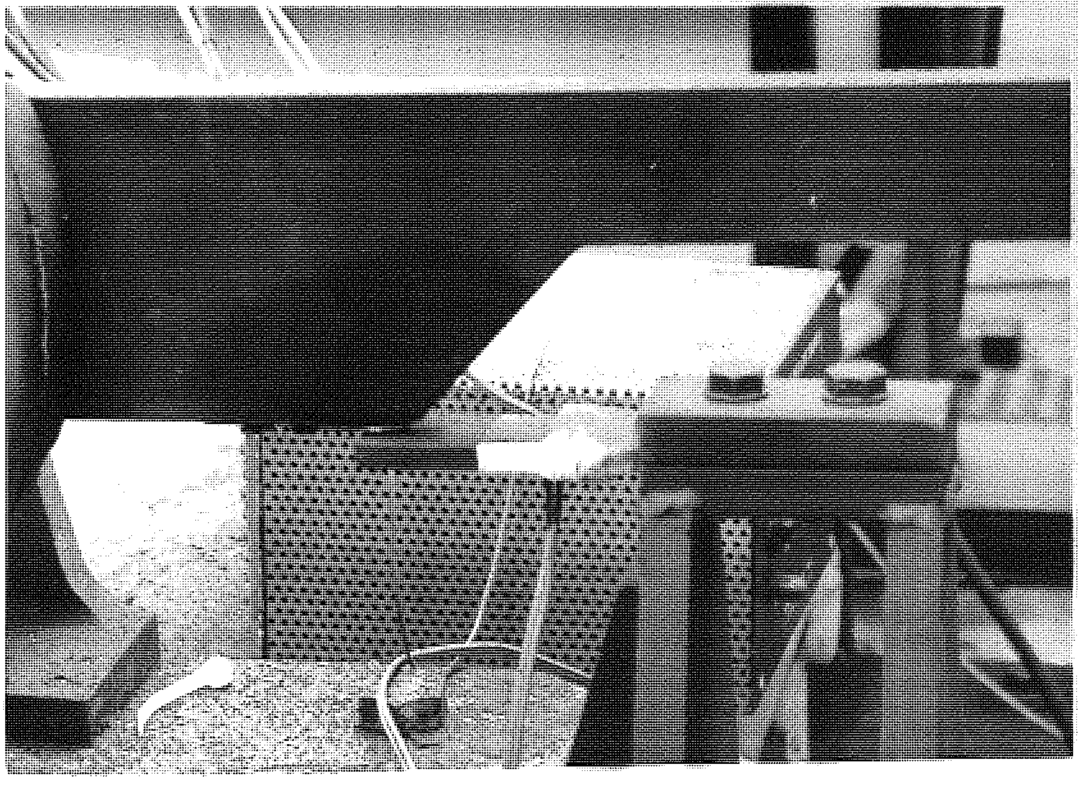


Figure 35: Photograph of Strain Gauges and Load Measuring Device

3.5.9 Gas Analysers

As the composition of the petrol used in the vehicle is changed the composition of the exhaust is also naturally expected to change, and the concentration of individual hydrocarbons is also affected by incomplete combustion. The total concentration of the hydrocarbons present can be obtained by summing the concentrations of each of the individual hydrocarbons. The concentration expressed as parts per million. Expressing the concentration in such a manner would provide a measure of the number of hydrocarbon molecules present in a given quantity of exhaust. However, the complexity associated with the above technique can be recognised, since a significant number of individual hydrocarbons of differing mol wt are present.

An alternative method for expressing the total hydrocarbon content in the exhaust consists of normalising the hydrocarbon concentration to n-hexane basis. This is done in effect by determining the concentration of carbon atoms represented by the hydrocarbons in the exhaust and dividing by six, to give the n-hexane equivalent. The concentration, as in this present research, is conveniently expressed as PPM C_6.

3.5.10 Catalytic Converter

After emission readings had been carried out using two star and four star leaded petrol, the engine is flushed. The exhaust pipe was then disconnected and thoroughly cleaned with a bristle brush so as to remove soot and leaded deposit that had collected in the exhaust prior to installing the catalytic converter, which is poisoned by lead and its compounds.

The catalyst is of a honeycomb structure with the first portion coated with rhodium to reduce nitrogen oxides, followed by a buffer zone. The latter part of the catalyst consists of platinum and palladium coating for oxidising unburnt hydrocarbons and carbon monoxide. The whole catalyst is enclosed as a unit in a steel casing with end connections of adequate sizing so as to be connected to the exhaust pipe as a bypass figure 37 and 34.

Table 14 Fuel Consumption Data

Engine speed (rpm)	Fuel consumption (ml/min)
1400	65.0
1800	84.5
2000	92.0
2500	114.0
3000	137.0
3500	159.0
4000	

Figure 36 Pressure Drop AGainst Fuel Consumption

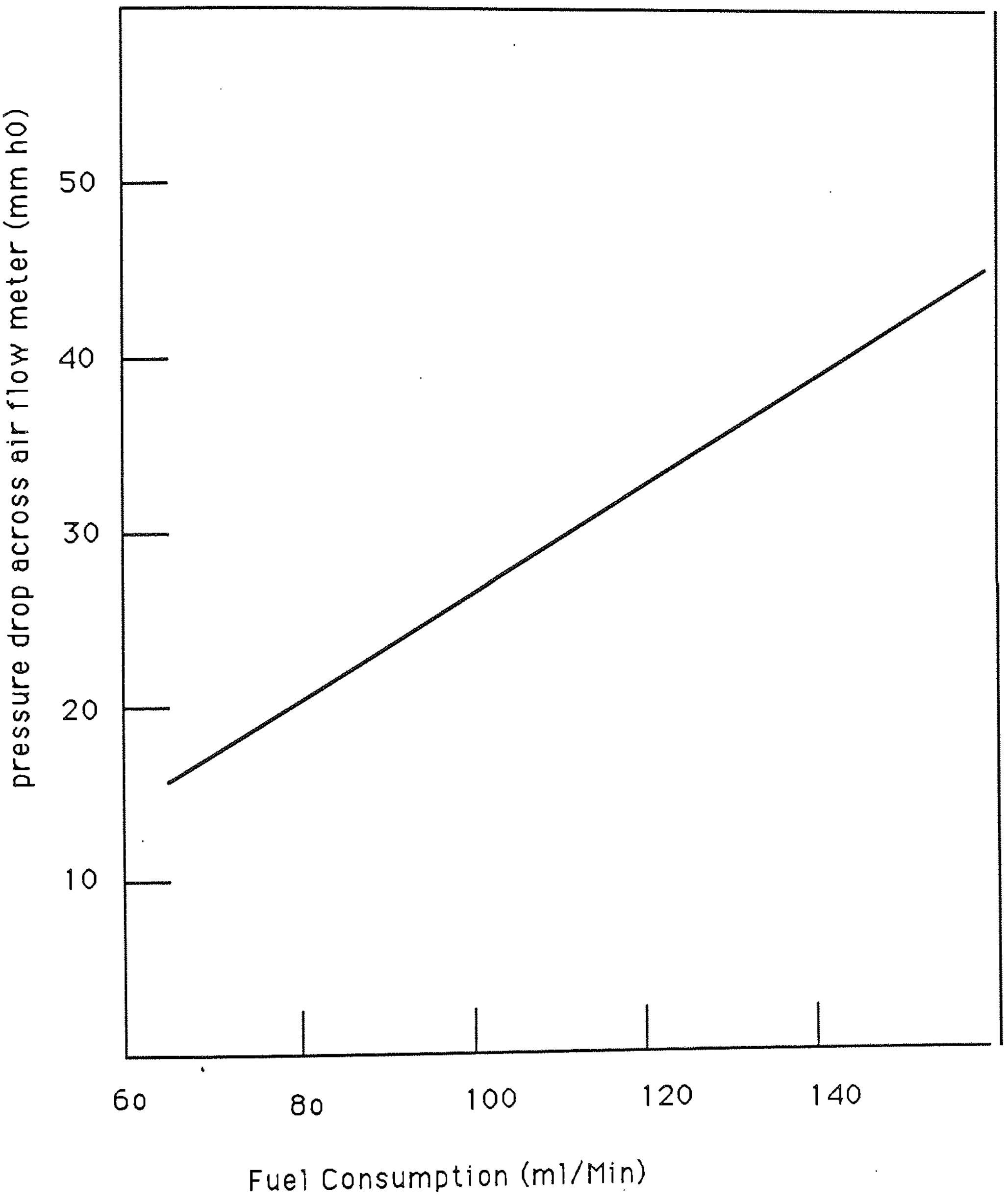


Figure 37 Honeycomb Three-way Catalytic Converter

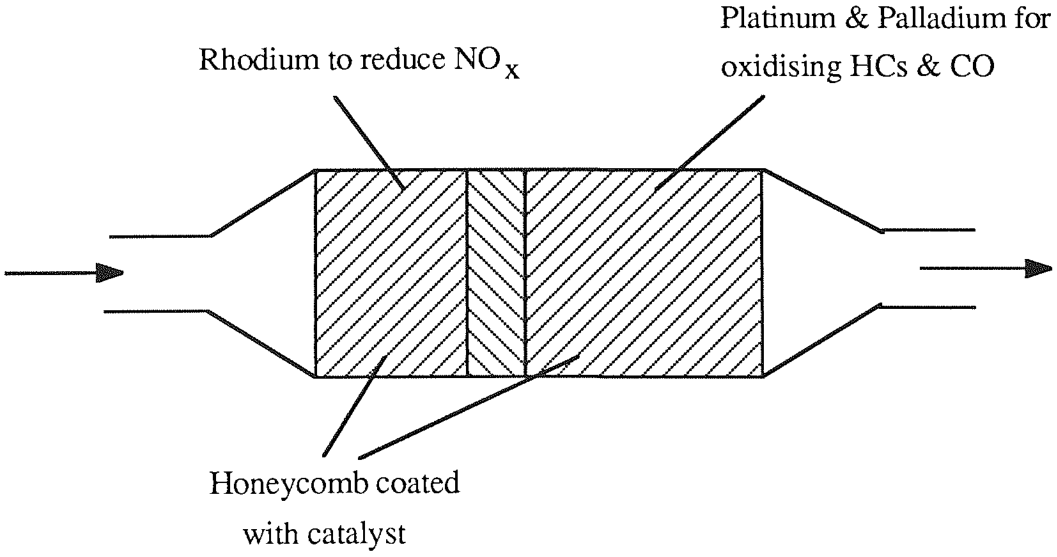
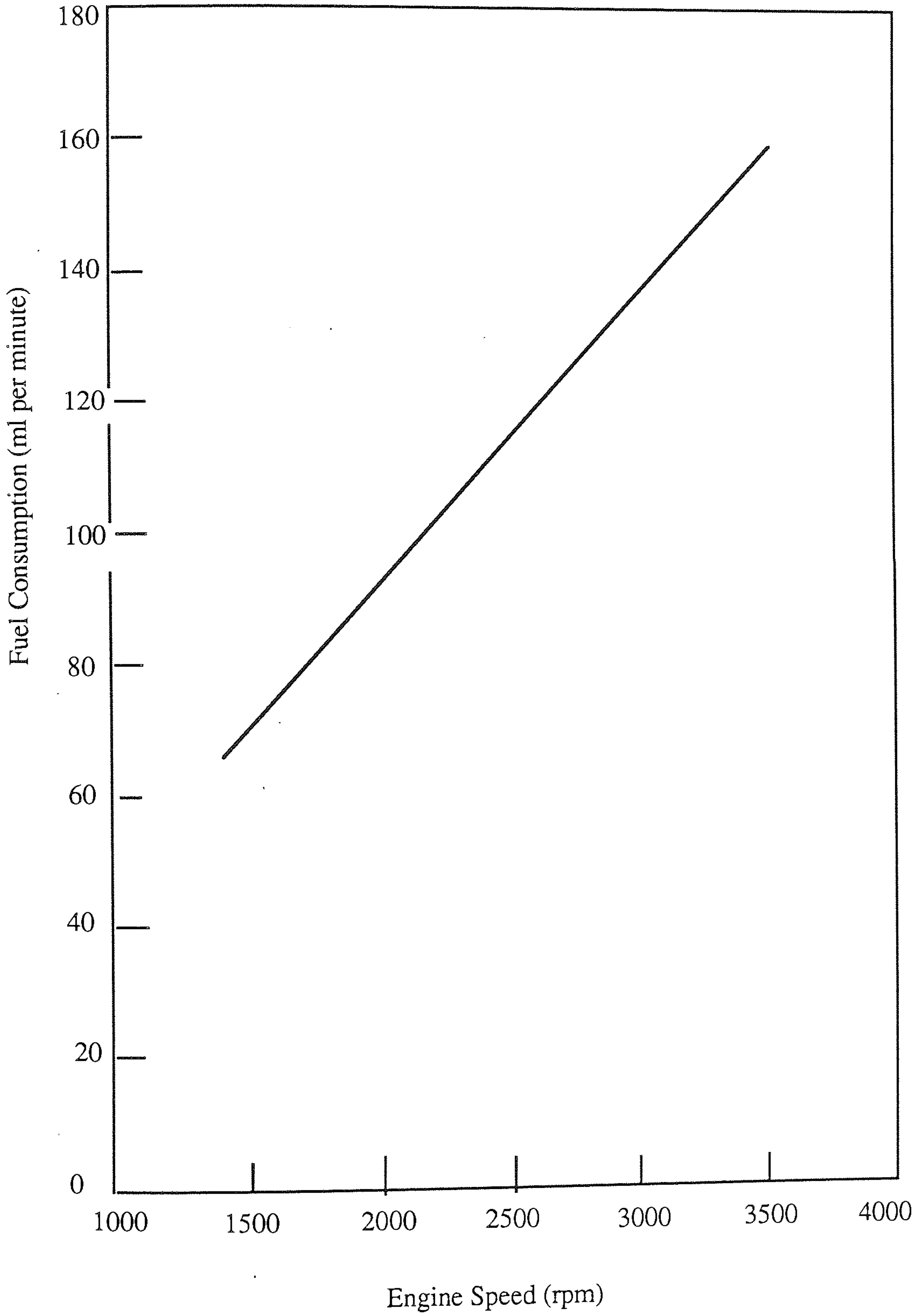


Figure 38 Fuel Consumption at Wide Open Throttle



CHAPTER 4
RESULTS

RESULTS

4.1 Thermal Conductivity Results

Thermal conductivity of a number of materials has been measured using the method described in Chapter 3.Thirty gauge Aluminal-Chromel thermal couples encased in mounting rods were used to measure the temperatures and the results obtained represent average data obtained on a number of different occasions. The thermal conductivity of aluminium,quoted in data manuals shows a uniform rise in thermal conductivity between 200 and 300^{o}K. This is followed by an equivalent decrease in the conductivity until 400^{o}K. After this point it remains between 240Wm^{-1}K^{-1} and 235Wm^{-1}K^{-1}, for the range of temperatures involved in this investigation.

However in the experimental measurements, shown in table 15 and figure 39,no sudden increase or decrease was found and the measured value is approximately 20% lower than the quoted values. The thermal conductivity for aluminium between temperatures of 80°C and 280°C is found to be around 195 Wm^{-1}K^{-1}. This compares well with the quoted values between 127°C and 280°C; Table 15, shows the data obtained for calculating the thermal conductivity of aluminium, and figure 39, plots this data. Figure 40 shows the thermal conductivity of copper.

After measuring the thermal conductivity of a material with a relatively high thermal conductivity, an attempt was next made to measure the thermal conductivity of a Sindanyo plate - normal to face. The quoted values by the manufacturers being 0.66

$wm^{-1}k^{-1}$. This is an average figure of actual tests carried out over a range of temperatures and cannot be taken as the exact value.The results of the measured thermal conductivity of sindanyo plate are shown in table 16. Table 17 shows the data obtained when using both the Aluminium disc and the Sindanyo plate. The system in the latter case representing a low thermal conductivity medium attached to a high thermal conductivity medium, as is the case with deposits on pistons.The results obtained in both set of arrangements are in agreement and of the correct order in comparison to the quoted values and consistently reproduced.

The lead free deposit used in this research had been attained on a Chevrolet in the U.S.A. and supplied by the courtesy of ESSO Research. The car had been operated for 1300Km under conditions representing operation of an average private passenger car. The leaded deposit used in this work came from a Fiat engine that had been operated on a private passenger car for 1480Km,over a period of one year. The similar mileage under which the deposits were accumulated made them a reasonable comparison. Tables 18 and 19 show the measured data and figure 41, plots this data and, as can be seen, the thermal conductivity of the leaded deposit lies in the region of 0.75 $Wm^{-1}K^{-1}$, whereas the thermal conductivity for lead-free deposit is in the region of approximately 0.5 $Wm^{-1}K^{-1}$, somewhat 50% lower than the leaded deposit. Figure 44 and 45, show the elemental analysis of the deposits. In comparing the thermal conductivities it is understandable why the deposits induce octane requirement increase, and that lead-free deposit with its lower thermal conductivity results in higher octane requirement increase, relative to the leaded deposit.

The maximum temperature was deliberately kept below 300°C, due to earlier experience with dummy runs using leaded deposits. At these high temperatures the deposits underwent some burning or coking effect.It is not possible at this stage to determine or postulate why such a large difference in the thermal conductivity exists except from the elemental analysis ,shown in figure 44 and figure 45,together with the occurrence of voidage. However in the elemental analysis some account must be taken because of the different fuels used in the U.S.A. and Britain.

Table 20 and figure 42, show octane requirement increase that arises from the volumetric effect of the deposit. This is the same as the results obtained by Dumont (62) who used a coating of teflon and attributed 10 to 40% of the ORI to the physical volume of the deposit. Figure 42 show a hypothetical analysis of the variation of the compression ratio with increasing deposit thickness. In the combustion chamber of a spark ignition engine, because of the continuous removal of the deposit, it would never be expected to exceed a thickness of 0.4mm. Even at this thickness the thermal stresses and higher temperatures in the combustion chamber would result in malfunction of the engine very quickly.

Table 15 Thermal Conductivity Calibration Data using Aluminium Disc

T_1°C	T_2°C	T_3°C	T_{CA}°C	$K_{Al} Wm^{-1}K^{-1}$
81.25	80.75	80.25	80.58	195.46
89.50	89.00	88.50	88.83	190.38
112.25	111.75	111.25	111.58	194.72
129.75	129.00	128.50	128.75	
141.00	140.25	139.50	139.99	195.96
157.00	156.25	155.50	155.99	195.58
179.25	178.50	177.75	178.25	191.67
219.75	218.75	217.75	218.41	192.24
241.25	240.25	239.25	239.91	191.87
281.50	280.50	279.50	280.16	190.88

See figure 17 and 18 for definition of temperatures

Figure 39 Variation of Thermal conductivity with Temperature for Aluminium disc

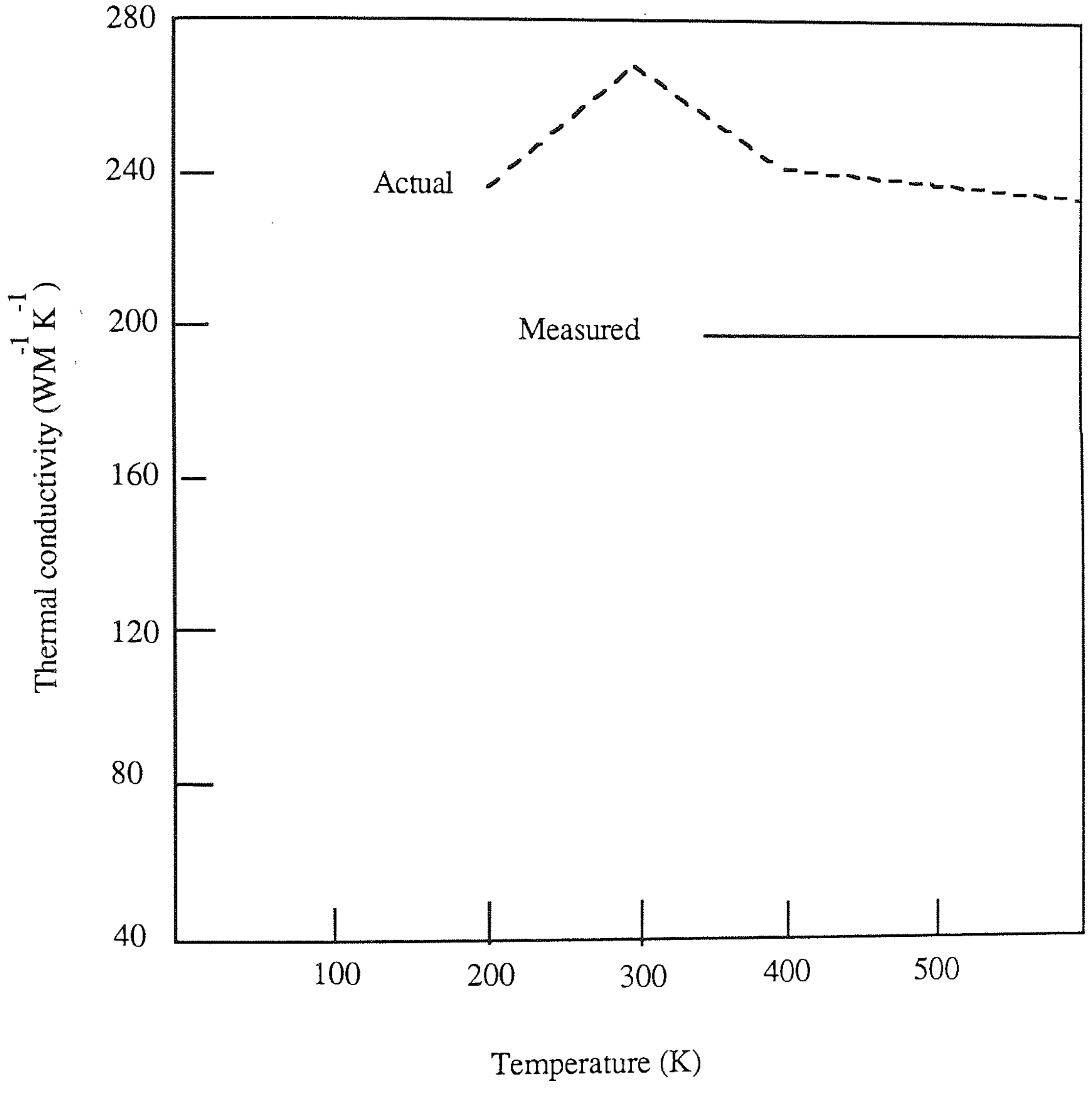


Figure 40 Variation of Thermal conductivity with Temperature for Copper

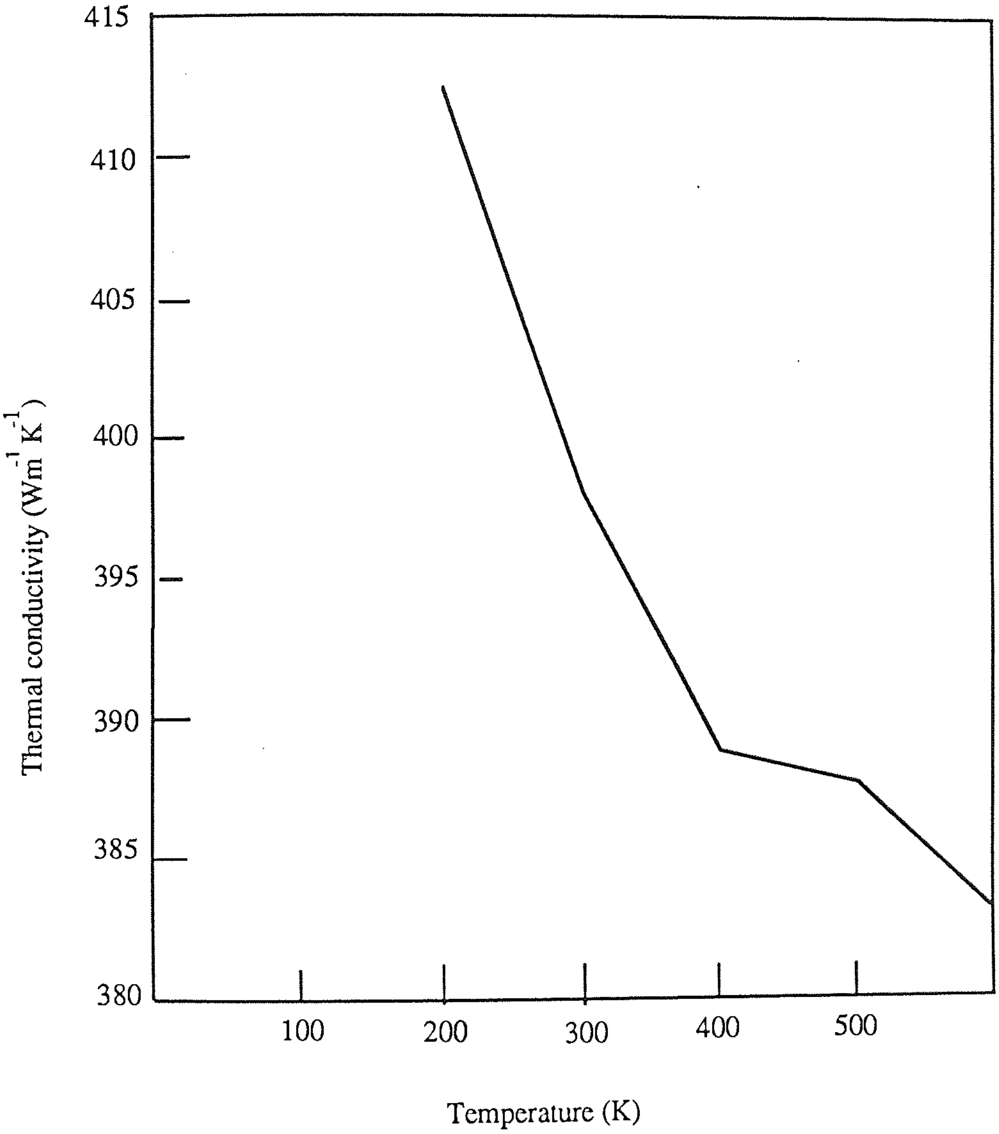


Table 16 Thermal Conductivity Calibration Data using Sindanyo Plate

T_1°C	T_2°C	T_3°C	T_{CS}°C	$K_{Sindanyo}$ ($Wm^{-1}K^{-1}$)
82.50	82.00	81.00	81.83	
91.75	91.25	29.50	91.08	1.00
104.25	103.75	42.75	103.58	1.01
117.75	117.25	55.50	117.08	0.99
150.50	149.75	75.25	149.49	0.83
187.00	186.25	84.25	185.99	0.90
270.25	269.25	137.25	268.91	0.92
310.75	309.75	172.00	309.41	0.87
360.50	359.50	219.75	359.16	0.86
393.50	392.50	246.50	392.07	0.82

Table 17 Thermal Conductivity Calibration Data using both the Aluminium Di and Sindanyo Plate

T_1°C	T_2°C	T_3°C	T_{AS}°C	T_{CS}°C	$K_{Sindanyo}$ ($Wm^{-1}K^{-1}$)
103.50	103.00	34.00	34.50	102.83	0.90
140.00	139.50	71.00	71.35	139.33	0.89
180.50	179.25	97.00	97.45	178.99	1.12
213.25	212.50	111.25	111.85	212.25	0.91
241.75	240.75	128.50	129.20	240.41	1.09
291.50	290.50	159.75	160.30	290.16	0.93
343.50	342.50	202.50	203.15	342.16	0.86
371.25	370.25	226.00	227.59	369.91	0.84
407.50	406.50	256.75	257.42	406.08	0.79

Table 18 Thermal Conductivity of Leaded Deposit

T_1°C	T_2°C	T_3°C	T_{CD}°C	$K_{leaded\ deposit}$ ($Wm^{-1}K^{-1}$)
137.25	136.75	134.25	136.58	0.77
145.75	145.25	142.50	145.08	0.69
153.25	152.75	150.00	152.75	0.69
170.00	169.50	167.00	169.50	0.76
192.25	191.75	189.00	191.75	0.69
211.50	210.75	207.25	210.75	0.82
219.75	219.25	216.50	219.25	0.69
230.25	229.50	226.00	229.50	0.8
239.50	239.00	236.50	239.00	0.76
244.50	243.75	240.50	243.75	0.76

Table 19 Thermal Conductivity of Lead-free Deposit

T_1°C	T_2°C	T_3°C	T_{CD}°C	$K_{lead\text{-}free}$ $Wm^{-1} K^{-1}$
87.25	86.75	83.75	86.58	0.52
96.50	96.00	92.50	95.83	0.44
110.25	109.75	106.50	109.58	0.48
119.00	118.50	114.75	118.33	0.41
129.75	129.25	125.75	129.08	0.44
143.75	143.25	140.00	143.08	0.48
167.25	166.75	163.75	166.58	0.52
183.50	183.00	180.00	182.83	0.52
195.25	194.50	190.50	194.25	0.58
210.00	209.50	206.00	209.33	0.44
225.25	224.50	220.25	224.25	0.55
242.50	241.75	237.25	241.49	0.51

Figure 41 Thermal Conductivity of Leaded and Unleaded Deposit

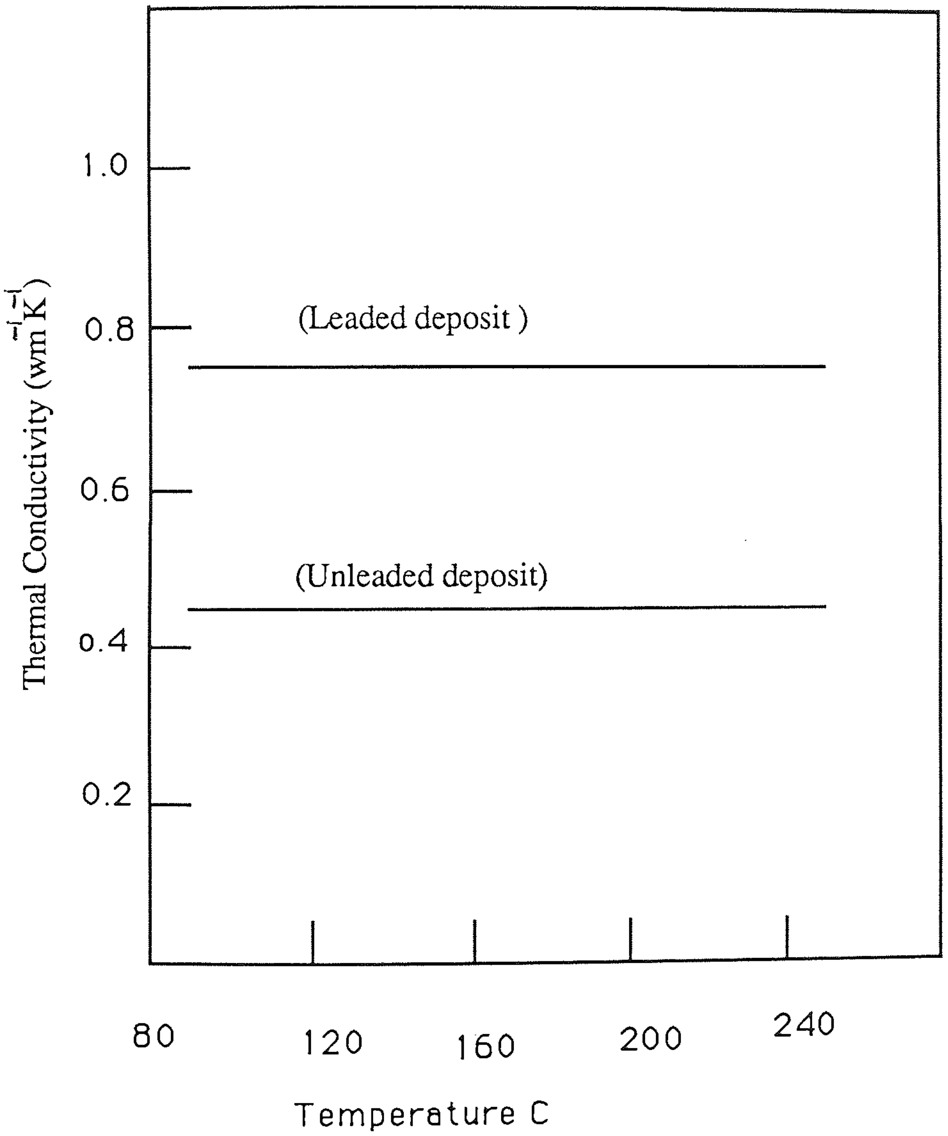


Figure 42 Relationship between Compression Ratio and Combustion Chamber Deposits

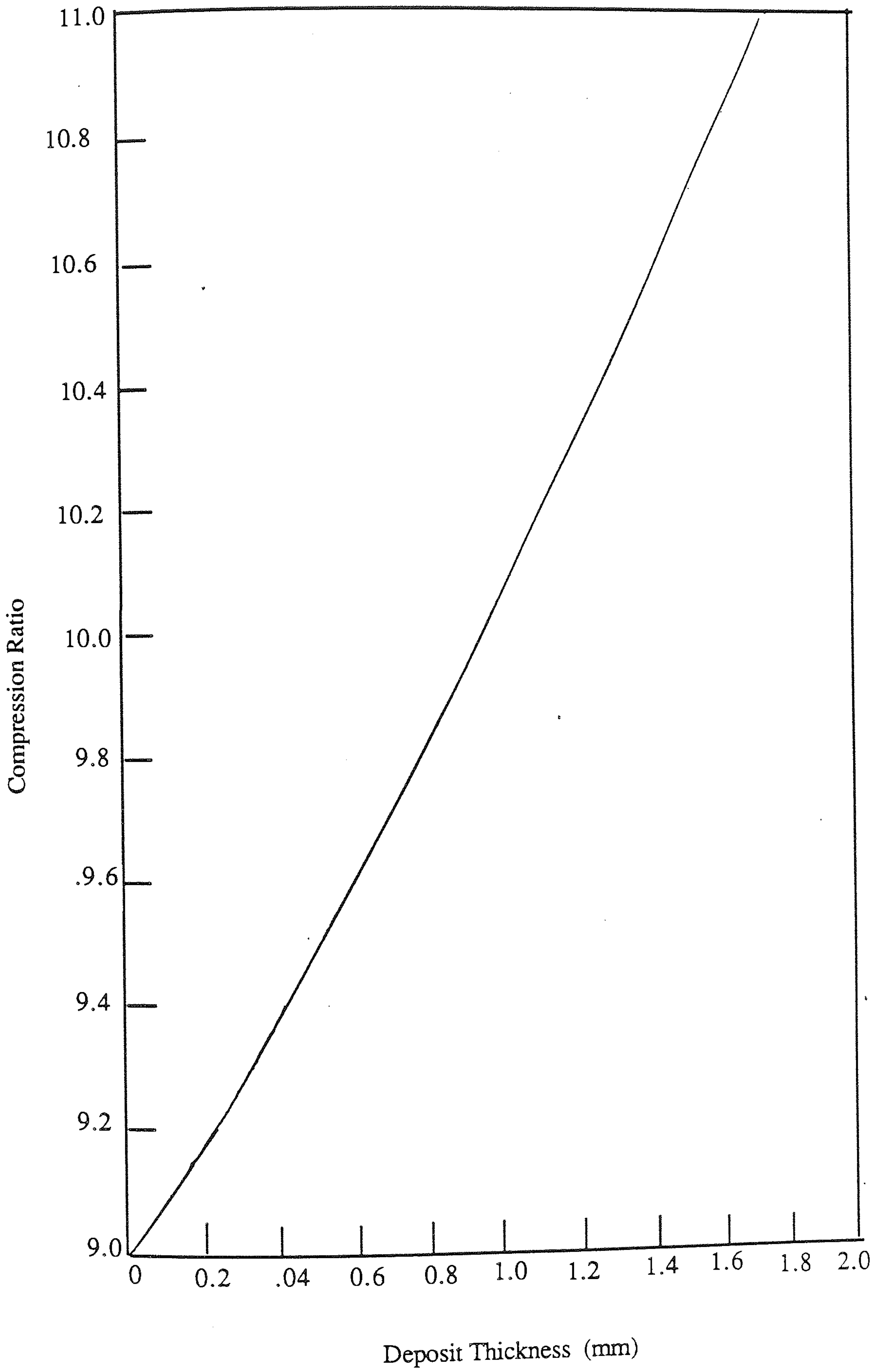


Table 23 **Relationship between Compression Ratio and Combustion Chamber Deposits**

(Fiat 127A Engine , Compression ratio 9. 0Displacement stroke 68mm

Deposit thickness (mm)	Compression ratio V_1/V_2
0.00	9.000
0.1	9.10
0.2	9.19
0.5	9.50
0.7	9.72
1.0	10.06
1.2	10.03
1.5	10.71
1.7	11.00
2.0	11.46

4.2 Permeability Results

The problem of simulating flow conditions in test specimens of porous masses centres almost entirely on the conditions of the pores and the shape of the specimen employed. In this investigation Lea and Nurse's apparatus is employed which had previously been standardised.

In order to ensure that the specimen is kept free of foreign matter; after being extracted from the piston it was placed in a clean glass container. However, any foreign matter that may have attached to the specimen is very difficult to remove but because of the safe handling and repetitive experiments it has been assumed that the specimen is free of any significant matter. Furthermore the specimen was heated up to 50°C in an oven for 2 hours so as to evaporate any moisture and oils that may be blocking the pores, before being placed in a dessicator for 24 hours.

The deposit specimen was mounted on one end of the glass capillary by covering uniformally the end edges with araldite. In order to average out variations introduced due to the thickness of the deposits the tests were carried out on three different specimens and the results presented are the average values. Table 21 shows the results obtained and graph 43 plots this data.

From Darcy's work for compressible flow under isothermal conditions

$$U \alpha \quad {}^{\Delta P}\!/_{L}$$

$$U = K \frac{(\Delta P)}{L}$$

$\frac{(\Delta P)}{L}$ = pressure gradient across the porous medium

U = Average velocity of flow of the fluid $\left(\frac{1}{A}\right)\left(\frac{dr}{dt}\right)$

$$\therefore\ U = K\frac{\Delta P}{L} = \frac{\beta\left(\Delta P\right)}{\mu L}$$

Qv = Volumetric flowrate of air

β = permeability of the bed or porous medium and depends only on the properties of the bed.

$$\therefore\ \frac{Qv}{A} = \frac{\beta\,\Delta P}{\mu L}$$

$$\rightarrow Qv = \Delta P\,\frac{\beta\,A}{L\mu}$$

A graph of volumetric flow against pressure drop yields the gradient $\frac{\beta A}{L\mu}$

Area presented by the deposit opposing air-flow where d = 4mm

$$= \pi\frac{d^2}{4}$$

$$= \pi \times 4/10^6$$

$\mu = 1.8 \times 10^{-5}\ \mathrm{Nsm^{-2}}$

$L = 2.3 \times 10^{-4}\ \mathrm{m}$

From figure 43, gradient = $1.471 \times 10^{-8}\ \mathrm{m^3\,s^{-1}N^{-1}m^2}$

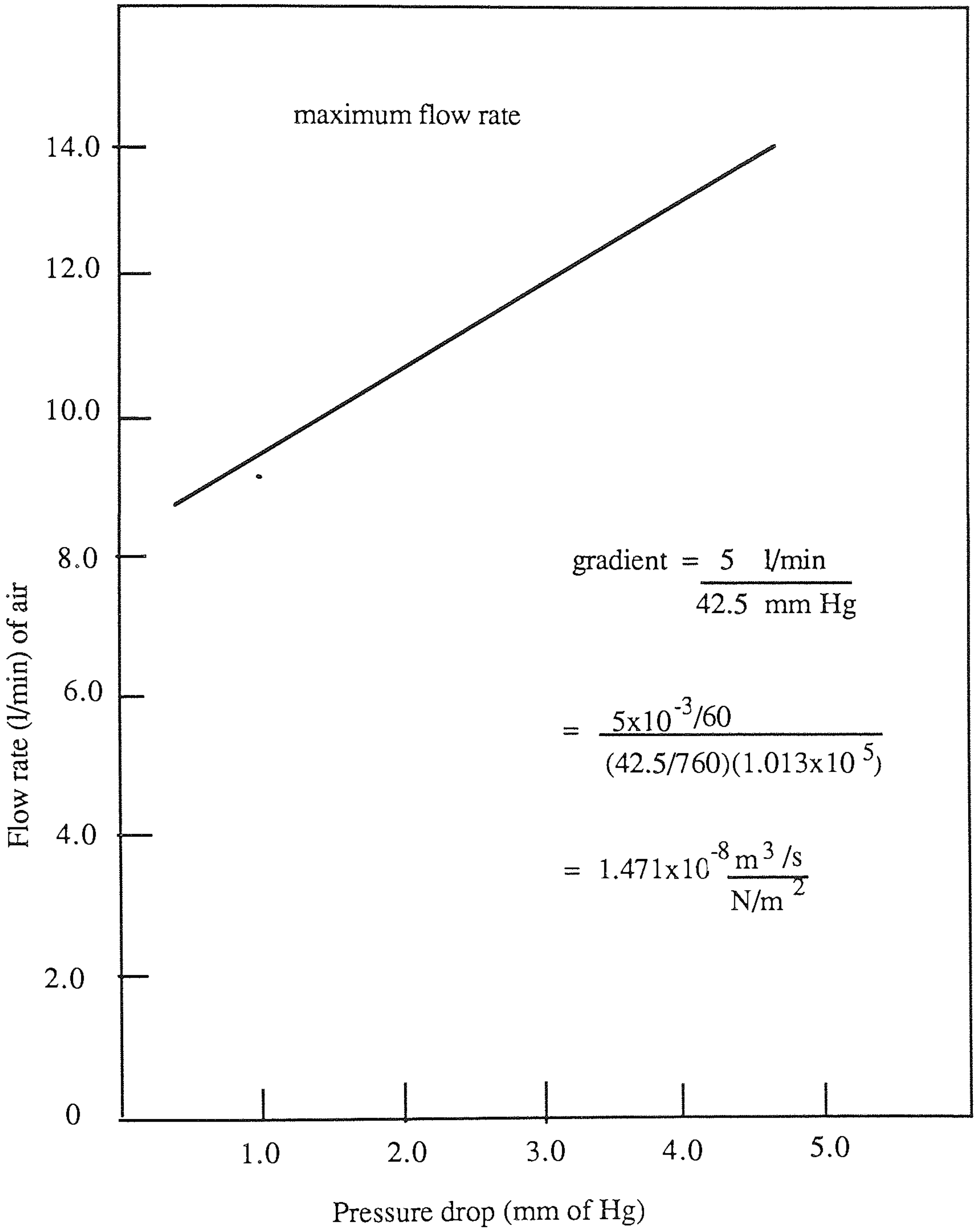
i.e. $\beta = 4.846\ \mathrm{m^2}$

Permeability coefficient for the unleaded deposit is $4.846 \times 10^{12}\ \mathrm{m^2}$

Table 21 Pressure Drop Across Combustion Chamber
Lead Free Deposit

Qv (L/min)	δP mm of H_g	Qv $m^3/s \times 10^{-4}$	δP N/m
8.0	7.0	1.33	1015.3
9.0	9.0	1.50	1305.4
10.0	12.5	1.66	1813.1
11.0	17.5	1.83	2538.3
12.0	22.5	2.00	3263.5
13.0	32.5	2.16	4713.9
14.0	48.0	2.33	6962.2

Figure 43 Pressure drop across lead free deposit



$$\text{gradient} = \frac{5 \ \text{l/min}}{42.5 \ \text{mm Hg}}$$

$$= \frac{5\text{x}10^{-3}/60}{(42.5/760)(1.013\text{x}10^{5})}$$

$$= 1.471\text{x}10^{-8} \frac{\text{m}^3/\text{s}}{\text{N/m}^2}$$

4.4 Deposit Analysis

The elemental analysis of the deposits was carried out on the electron microscope ,in conjunction with the micrographs shown in figures 54 - 57. The elemental analysis of the deposits shown in figure 44, for the leaded deposit and figure 45, for the unleaded deposit. The large difference in the two deposits was very surprising and a number of analysis were undertaken to ascertain the result. The analysers were not sufficiently adapted to record carbon, hydrogen and oxygen content but never the less,interesting results were obtained.The leaded deposit containing, lead, bromine, chlorine and to a small degree calcium.

The lead free deposit contained a relatively larger number of elements and these included ; magnesium,chlorine,aluminium,silicon,phosphorus,sulphur andor molybdenum,barium and zinc. Once again these results must be treated with caution, because as mentioned previously the lead free deposit was obtained from the U.S.A. and the leaded deposit from Britain.

Figure 47 - 50, show photographs of the lead free deposits taken with Practika model 5 camera. Figure 47 shows the build up of the deposit on the sides of the piston and showing how seizing of the piston rings occurs.The deposit on the side of the piston was generally thicker than on the piston head surface,shown in figures 49 and 50. The deposit on the side of the pistons arises largely due to the burning of the lubricant and is not significiantly affecting the out flow of heat .

From an examination of figure 49, different layers of the deposits with varying thickness can be seen. This supports the theories of localised flaking. Figures 51,52 and 53 are photographs taken under the microscope, enlarged between 200 and 400 times.

Figure 51 together with figure 53 show very fine cracks along the cross section of the deposit,indicating ideal situations were localised flaking may occur. Figure 52 and 53, show a layer stratum with large variations of porosity between the two layers. At this stage it is not possible to postulate why the large differences in the porosity of the two layers. Figures 54 and 55 show the lead free deposit and in comparison the leaded deposit (figures 56 and 57) is apparently composed of bulkier layers.

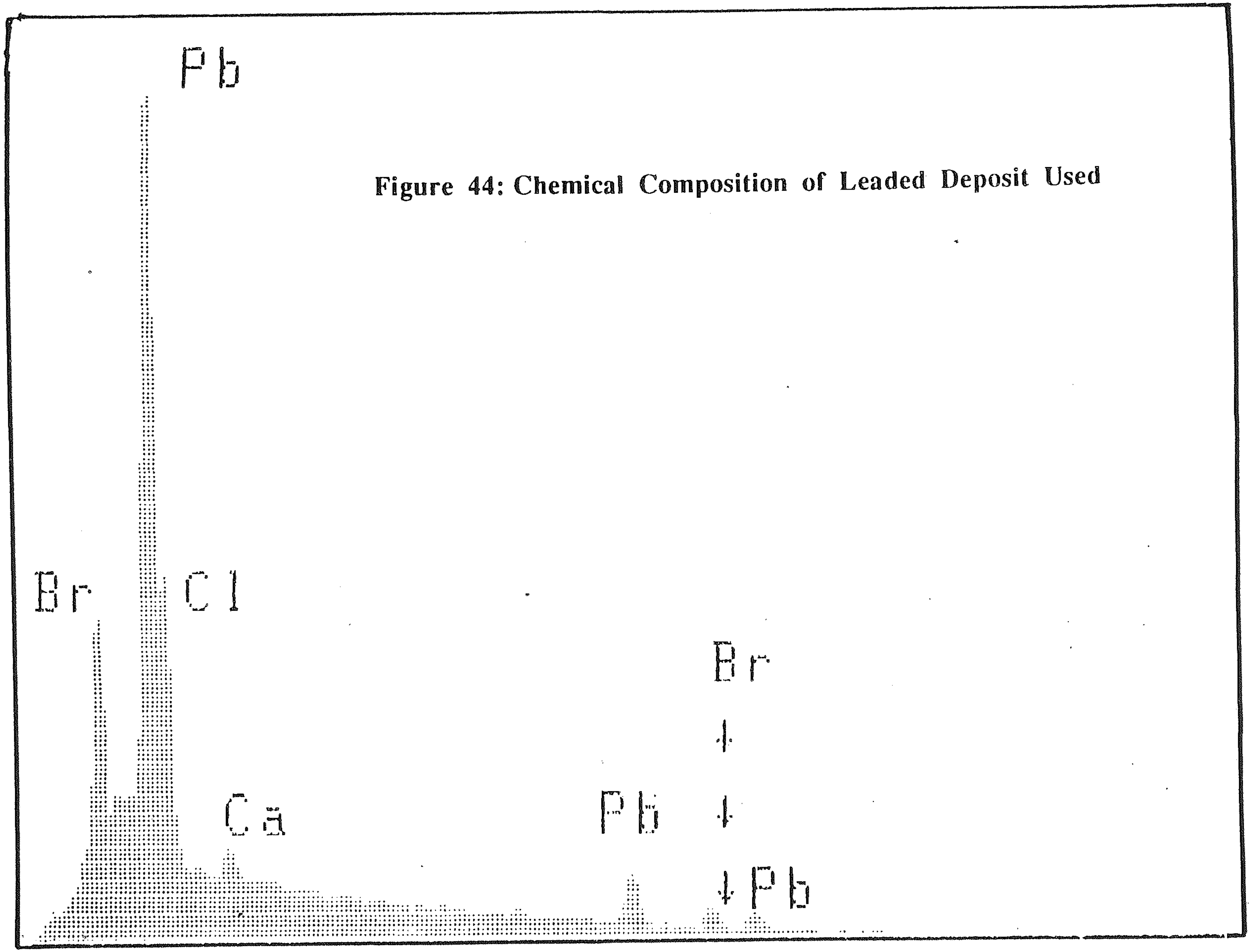
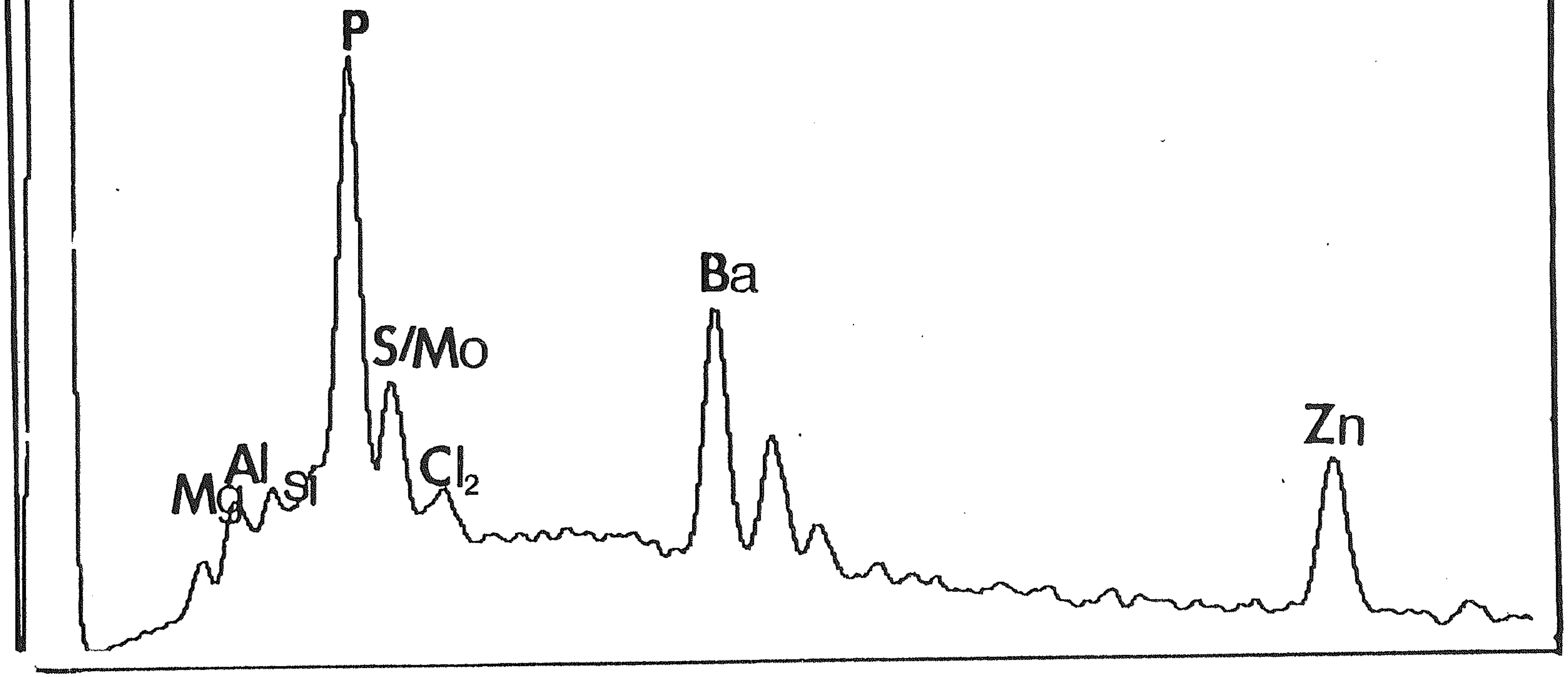


Figure 44: Chemical Composition of Leaded Deposit Used

Figure 45: Chemical Composition of Lead-free Deposit Used



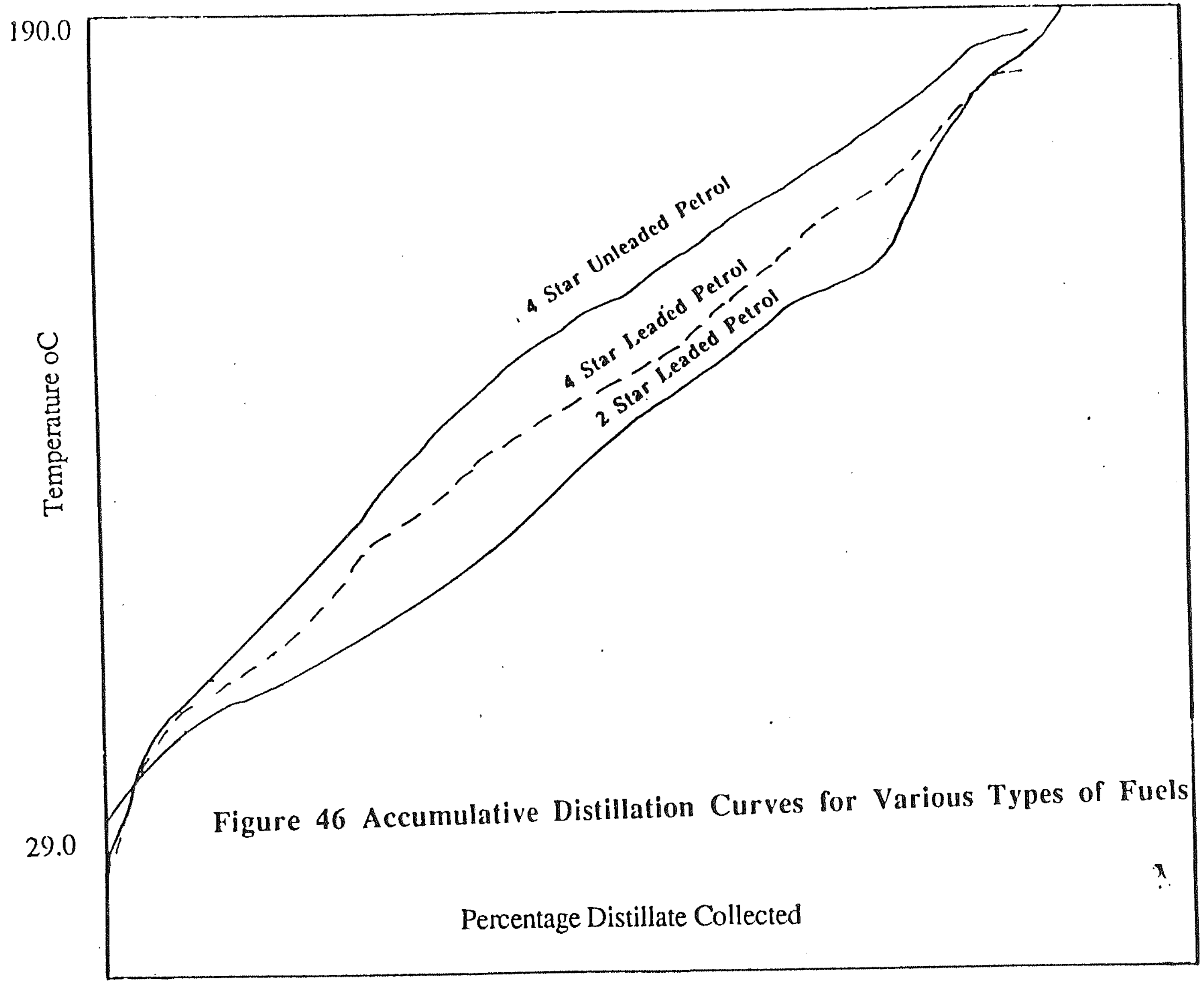


Figure 46 Accumulative Distillation Curves for Various Types of Fuels

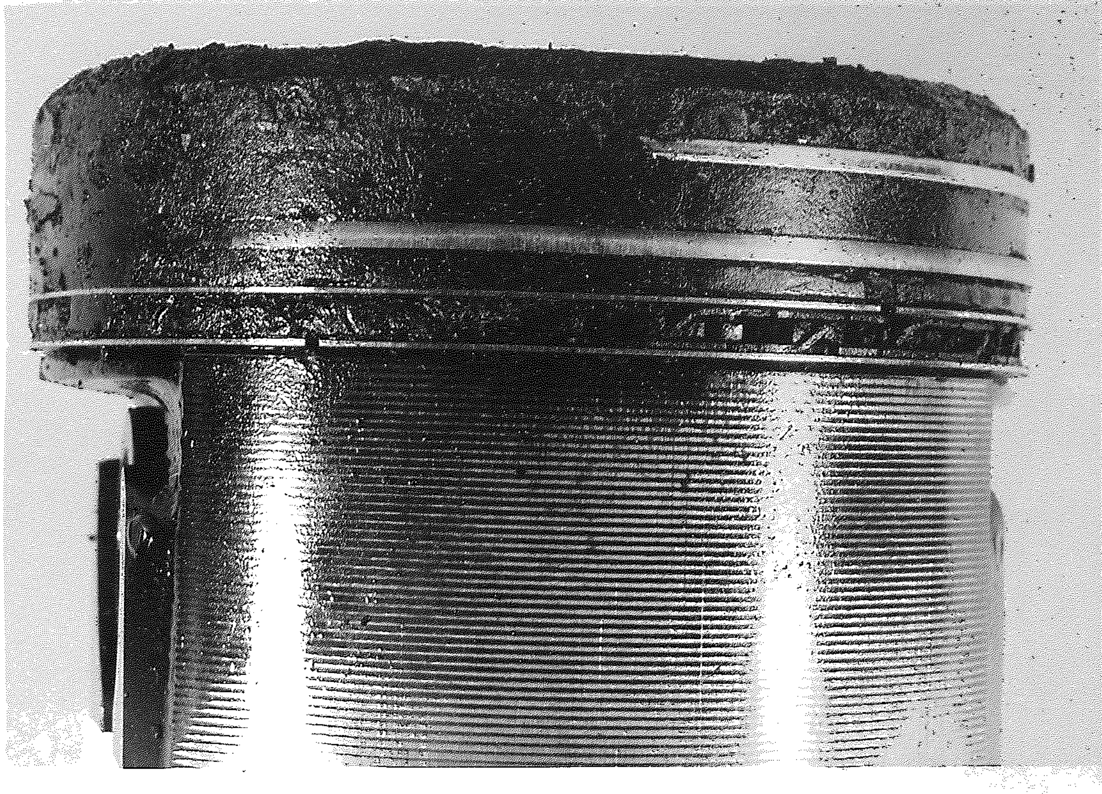


Figure 47: Build-up of Deposits and Gum on Piston Rings

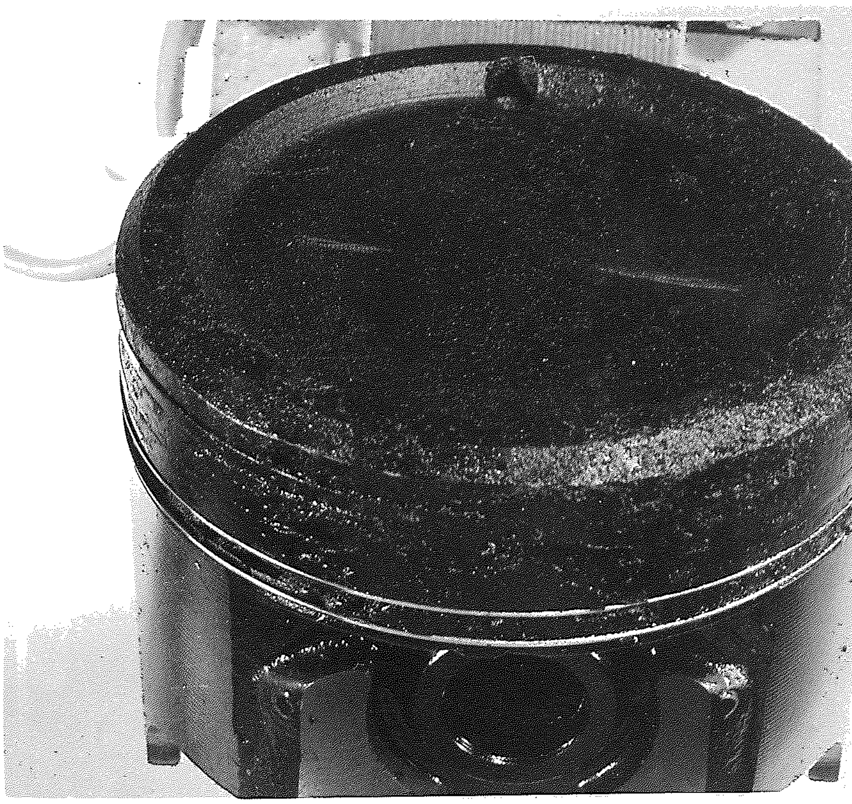


Figure 48: Overall View of Piston with Lead-free Deposit

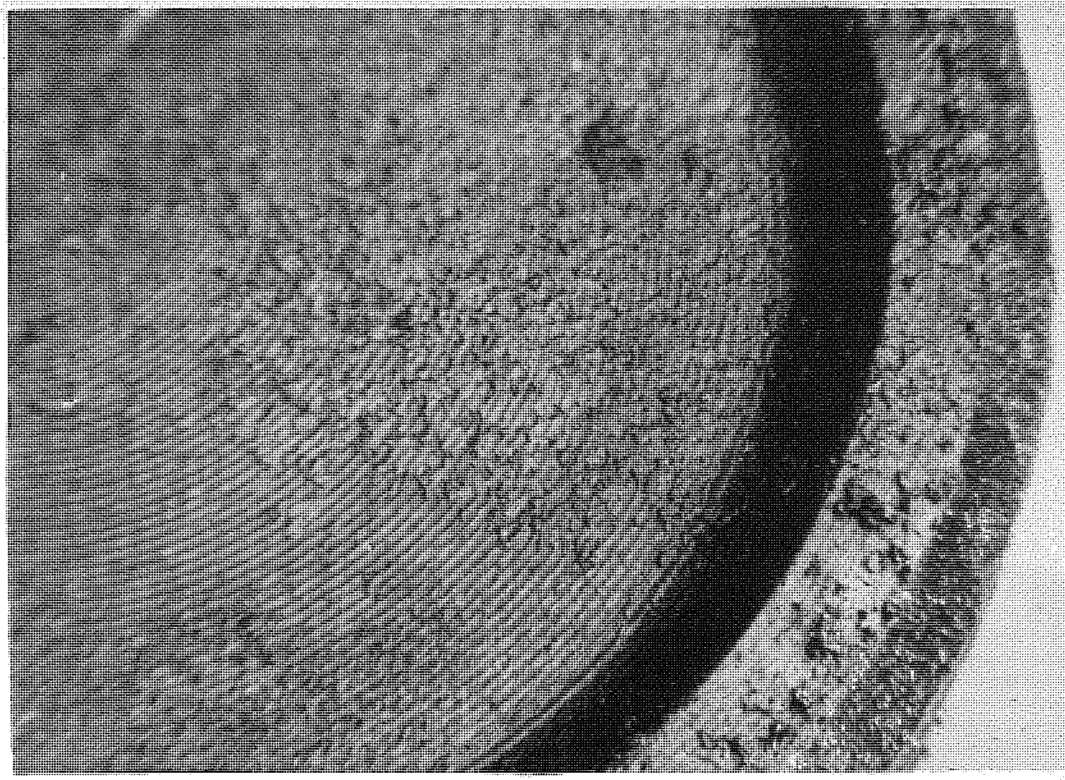


Figure 49: Lead-free Deposit

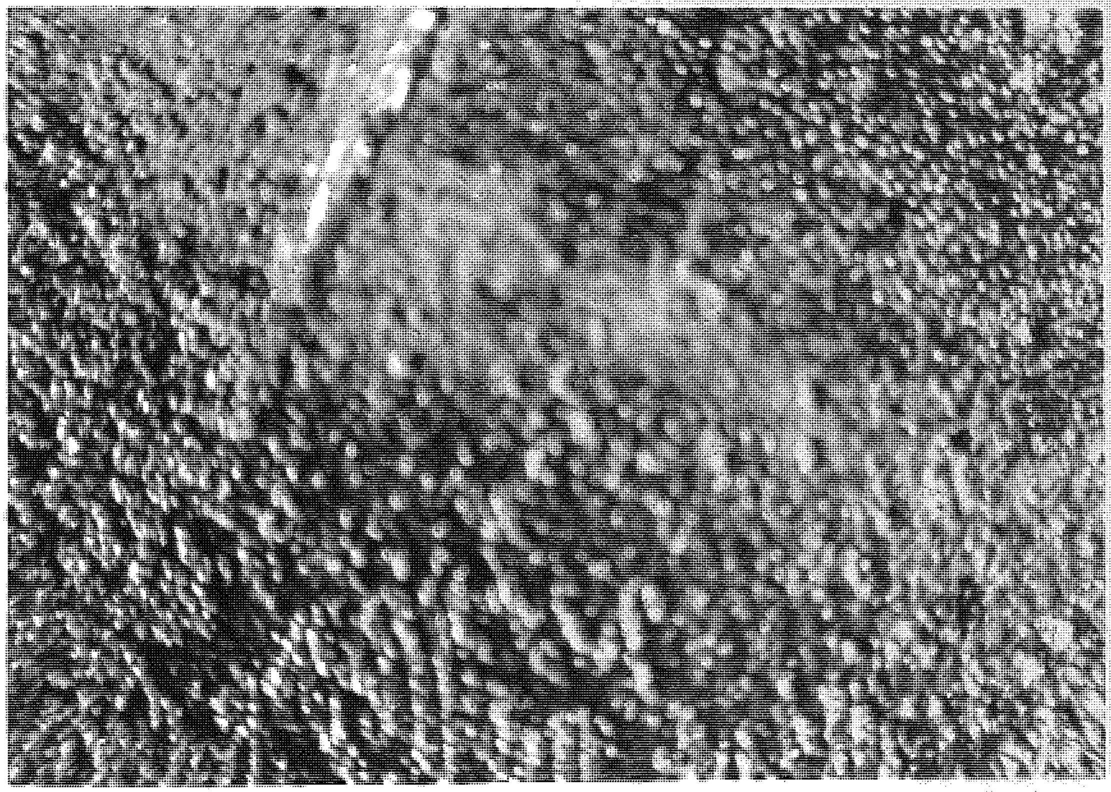


Figure 50: Lead-free Deposit

Figure 51: Cross-section of Lead-free Deposit showing High Degree of Porosity

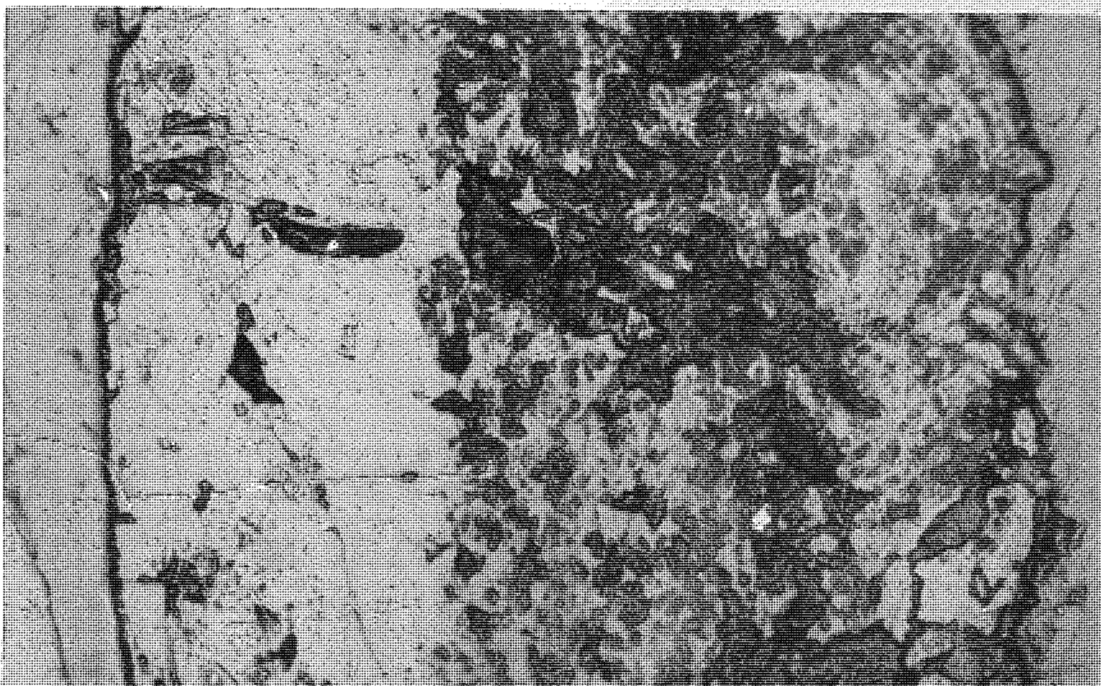


Figure 52: Cross-section of Lead-free Deposit showing Two-layer Stratum

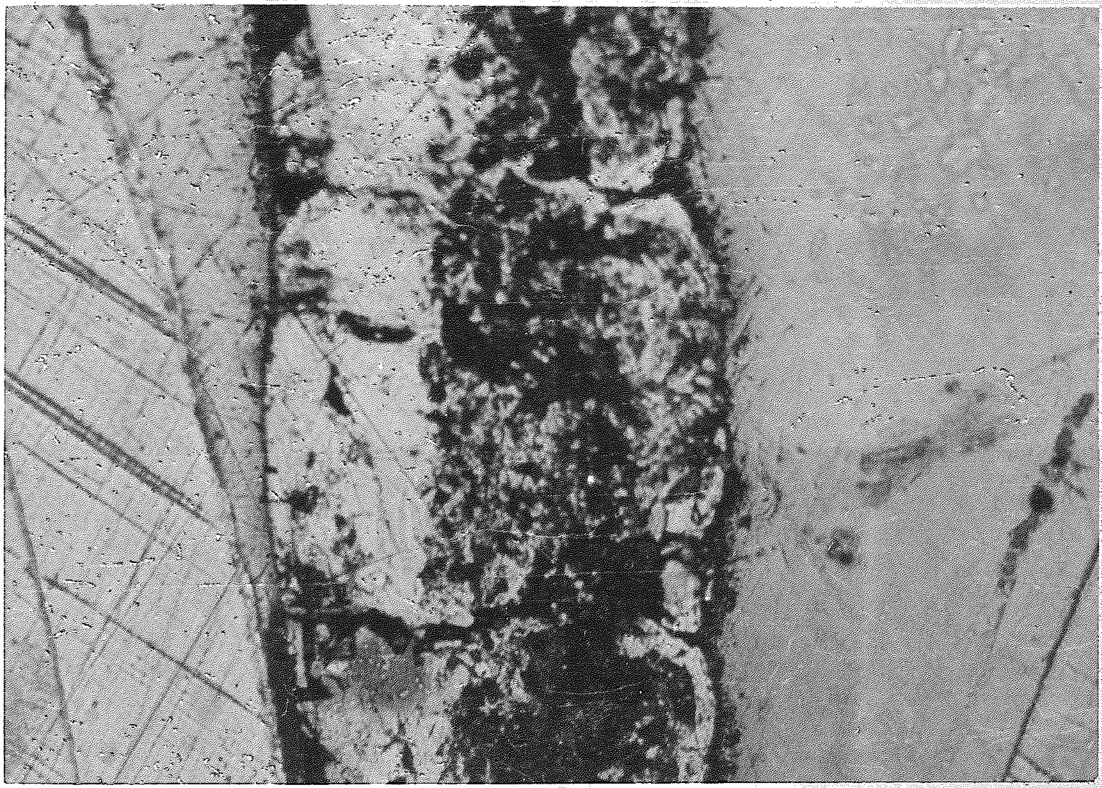


Figure 53: Cross-section of Lead-free Deposit showing Two-layer Stratum

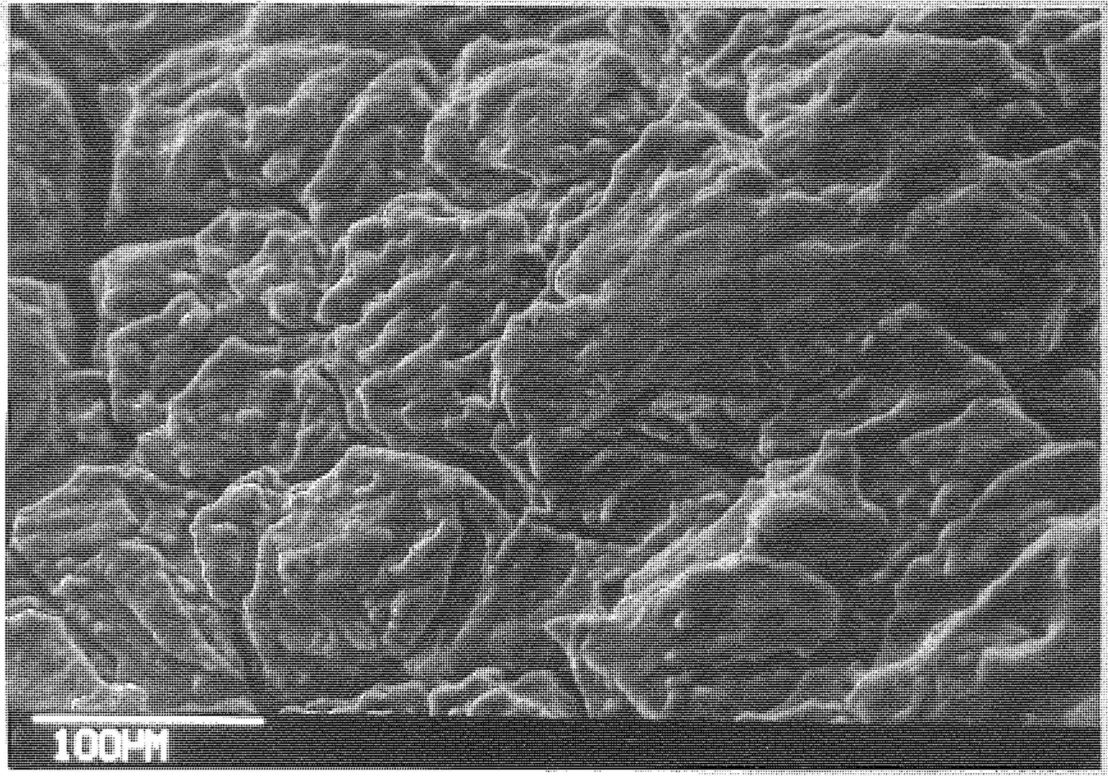


Figure 54: Photograph of Lead-free Deposit under Scanning Electron Microscope

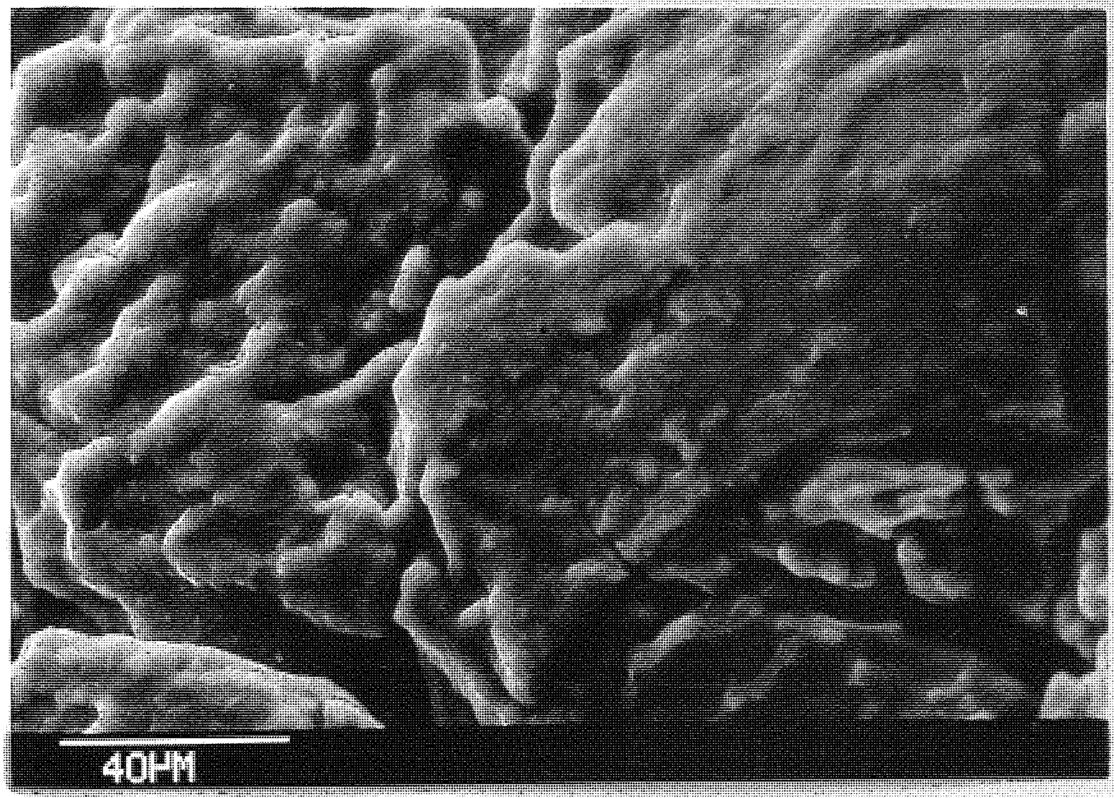


Figure 55: Photograph of Lead-free Deposit under Scanning Electron Microscope

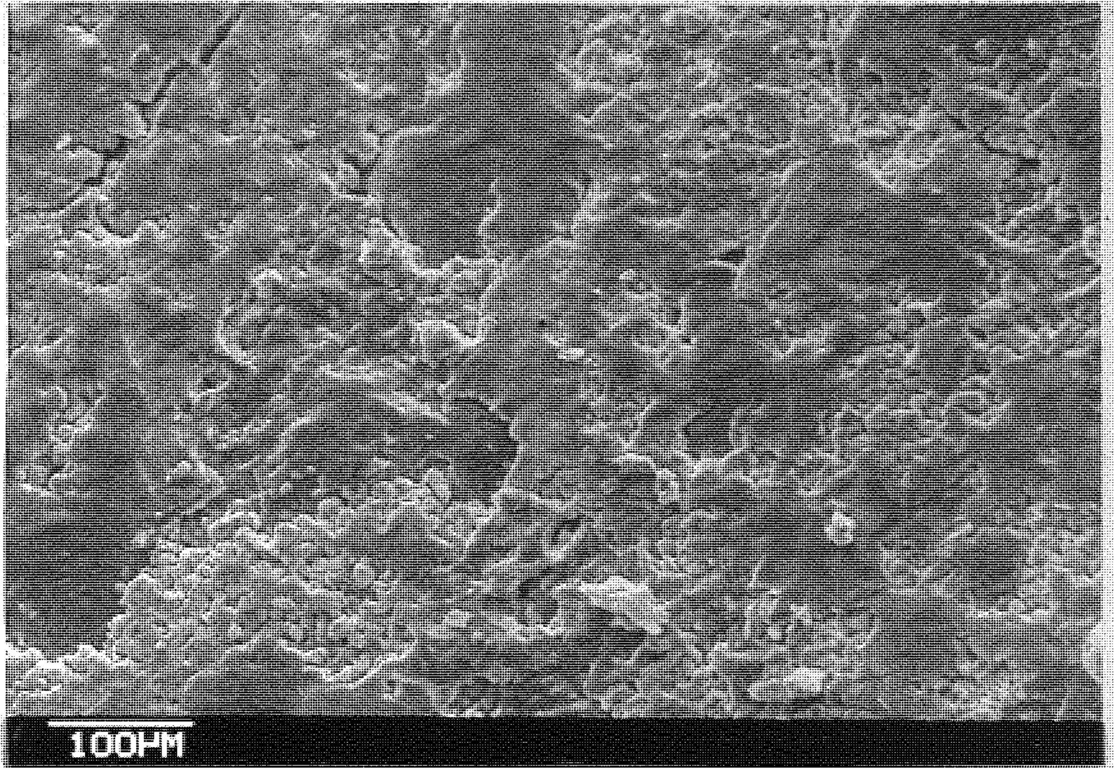


Figure 56: Photograph of Leaded Deposit under Scanning Electron Microscope

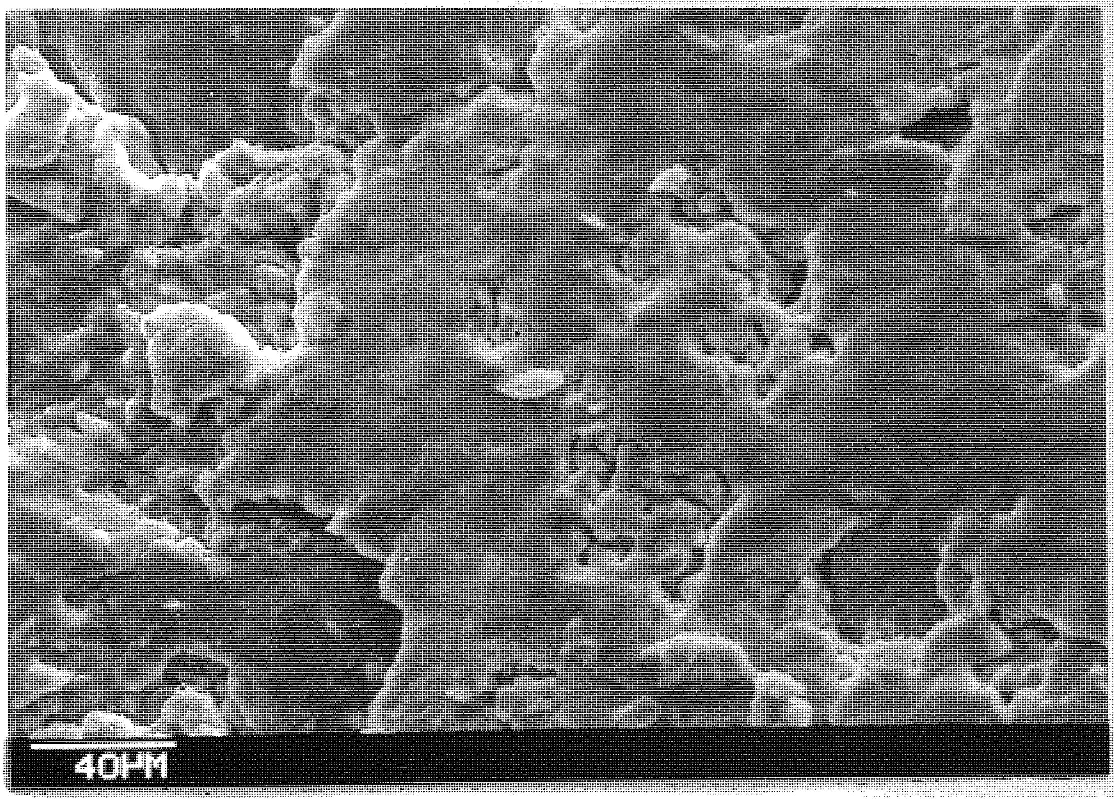


Figure 57: Photograph of Leaded Deposit under Scanning Electron Microscope

4.3 Exhaust Emission Results

As exhaust emissions are becoming one of the principle criteria in selecting a fuel, the Fiat 127 engine installed with a Froude dynamometer has been used to measure the exhaust emissions from various fuels.

Initially experimental work was carried out using four star leaded petrol, which is also taken as the reference fuel in this investigation. Alcock viscous air flowmeter table 22 and figure 58 was used to measure the air flow and hence air-fuel ratio using 4 star leaded petrol. Table 22 and 24 show the data obtained with increasing engine speed and figure 60 and 61 show the power and torque output of the engine.

The engine was run at a maximum speed of 4000 rpm. It was found that further increases in engine speed resulted in violent vibrations, and damage to instruments was envisaged due to continuous vibrations. It must however, be pointed out that the maximum speed attainable on the engine is above 5000 rpm. Power output of the engine was found to increase linearly with engine speed and a maximum torque of 67.1 Nm was obtained at around 3000 rpm.

Figure 46, shows the accumulative distillation graphs of the different fuels used in this research programme. The results attained show very clearly that due to the elimination of lead from petrol, the increased refining has introduced an increased proportion of higher boiling point components. This trend is also reflected between two star and four star petrol.

The emission control experimental programme was carried out as listed below and results are shown in tables 25-33 and figures 62-71.

1. Emissions with 2 star leaded petrol
2. Emissions with 4 star leaded petrol
3. Emissions with 2 star leaded petrol + 10% ethanol (by vol.)
4. Emissions with 4 star leaded petrol + 10% ethanol (by vol.)

After the experiments with leaded petrol had been carried out, and prior to the installation of the three-way catalytic converter, the engine was flushed using a commercial engine flush and the engine run on lead-free petrol erratically, so as to remove any leaded deposits in the engine. Following this the exhaust emissions from the use of fuels listed below were carried out:

5. Emissions with 4 star lead-free petrol
6. Emissions with 4 star lead-free petrol + employment of a three-way catalytic converter.
7. Emissions with 4 star lead-free petrol + 10% ethanol
8. Emissions with 4 star lead-free petrol + 10% ethanol with employment of a three-way catalytic converter.

4.3.1 Air/Fuel Ratio

Average air flowmeter readings were used to determine air/fuel ratio of the engine,which remains essentially constant from fuel to fuel, except for blends of ethanol where additional oxygen in the fuel raises this value.

Pressure drop across the Alcock viscous air flow meter was converted to air flow using calibration chart (mm water gauge times 36.54 gives grams per minute), table 22 and figure 58. Fuel consumption was measured against engine speed and the data used in air/fuel ratio calculations, with average fuel density assumed to be 0.802g per ml. the results obtained together with the derived data are shown in table 23 and figure 59.

Table 22 Relationship Between Air Flow and Pressure Drop Across Air Flow Meter

Pressure Drop Over Air Flow Meter (mm H_2O)	Air Flow (g/min)
10	365.4
20	730.8
30	1096.2
40	1461.6
50	1827.0

Figure 58 Relationship between Air Flow and Pressure Drop across Air Flow Meter

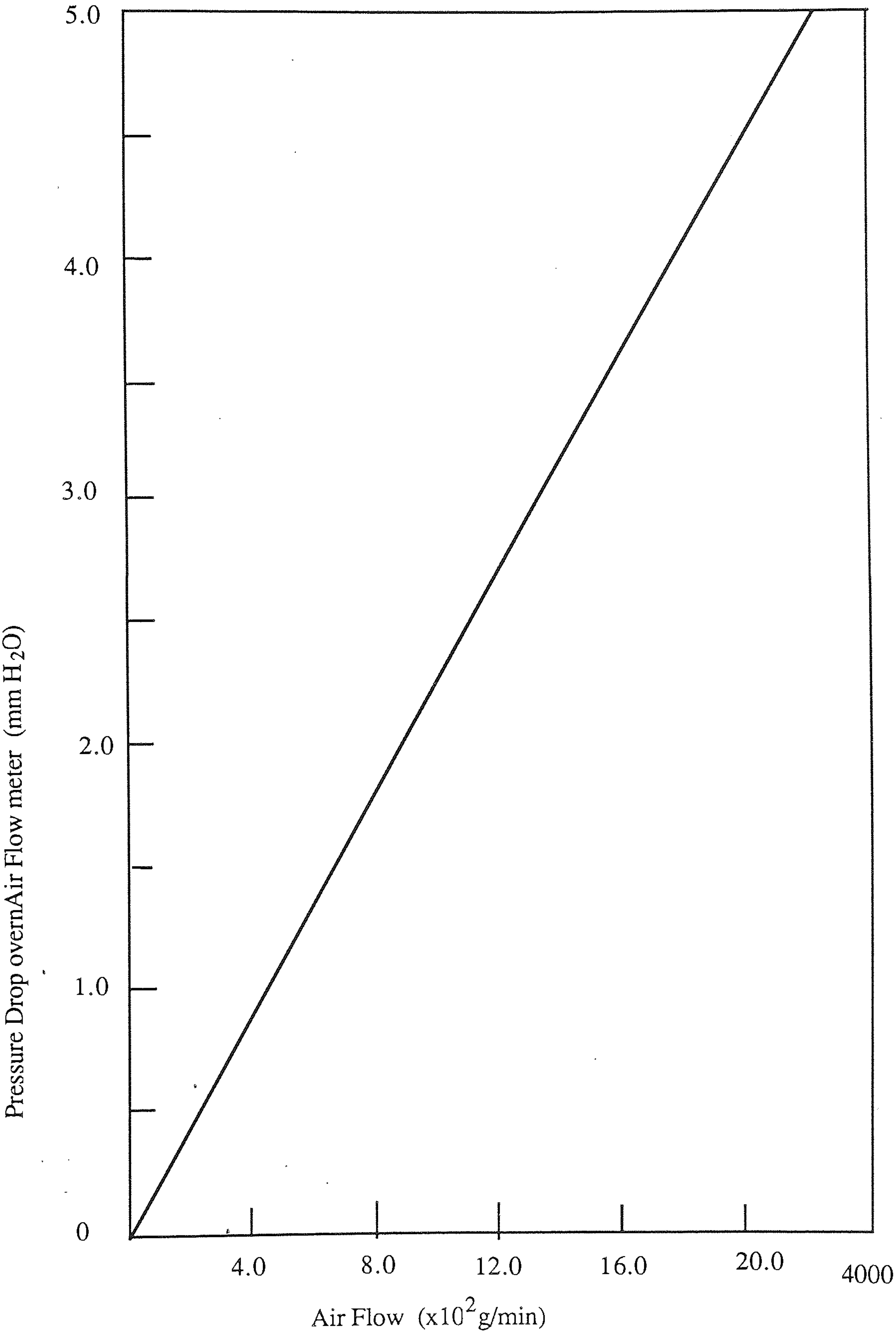
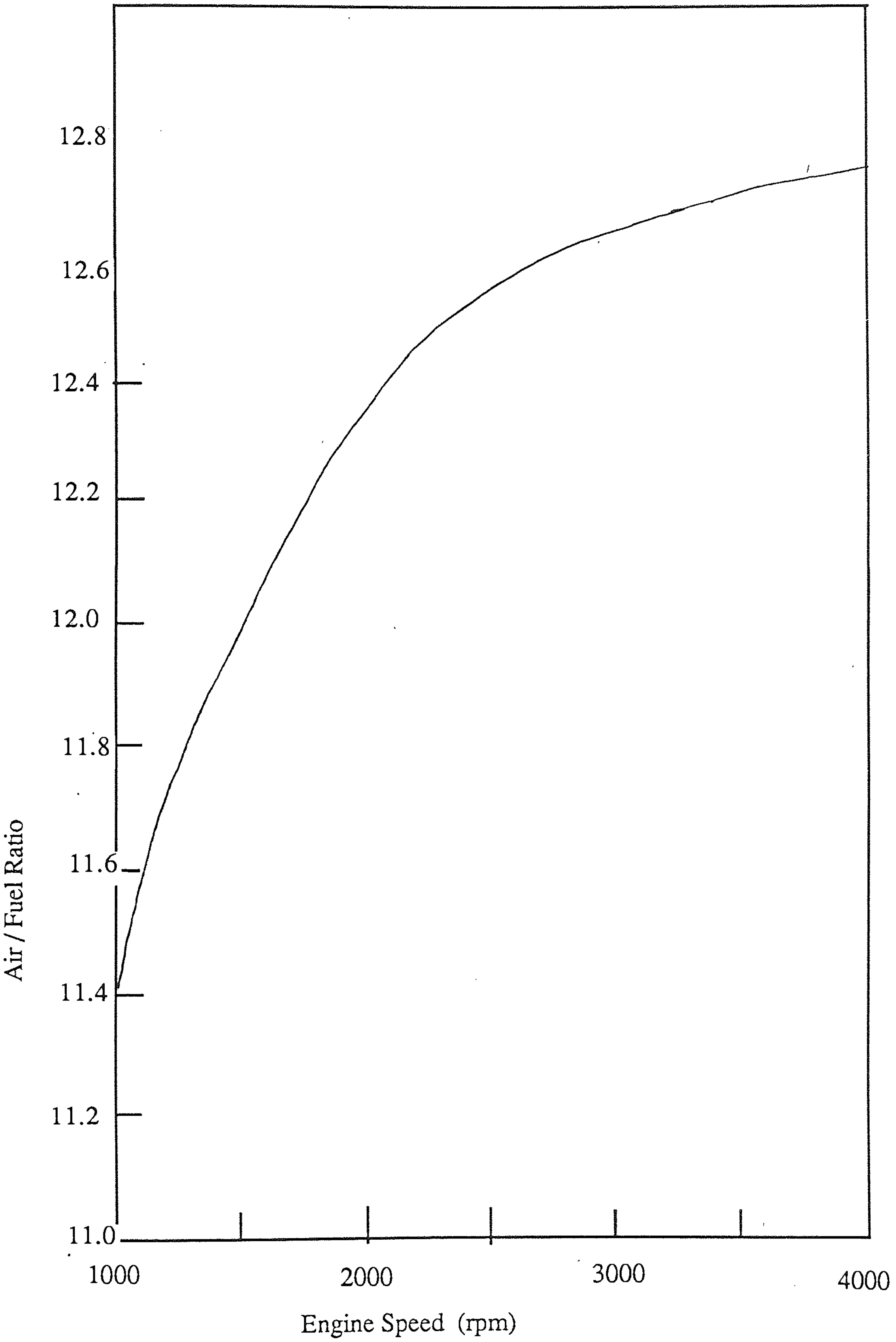


Table 23 Derived Data from Fuel Consumption and Air Flow

Engine speed (rpm)	Fuel (ml/min)	Air (g/min)	Fuel (g/min)	Air/Fuel ratio
1000	47.0	430	37.7	11.41
1200	56.0	525	44.9	11.69
1400	65.0	620	52.1	11.90
1600	73.5	715	58.9	12.14
1800	82.5	810	66.1	12.26
2000	92.0	905	73.7	12.28
2500	114.0	1145	91.3	12.54
3000	137.0	1385	109.8	12.61
3500	159.0	1619	127.4	12.71
4000	181.5	1850	145.4	12.72

Figure 59 Air / Fuel Ratio Against Engine Speed



4.3.2 Engine Power Output

The engine power output was measured using a load device on the dynamometer, with output being measured in millivolts. Engine torque equals 27.83 times mV reading;obtained from calibration of the device, table 12 and figure 28.

Average results obtained with four-star leaded are presented in table 24 and figure 61. The results are in agreement with those obtained by the previous two researchers. The engine power tests were repeated many times during the course of this research programme,to test the consistency of the engine.

Table 24 Power and Torque Tests

RPM	Voltage Output mV	Torque Nm	Power hp
1100	2.11	58.72	9.07
1300	2.15	59.83	10.92
1500	2.20	61.23	12.89
1700	2.24	62.34	14.89
1900	2.28	63.45	16.92
2100	2.31	64.29	18.95
2300	2.33	64.84	20.94
2500	2.35	64.40	21.11
2700	2.43	67.63	25.63
2900	2.44	67.91	27.65
3100	2.44	67.91	29.55
3300	2.39	66.51	30.81
3500	2.39	66.51	32.68
3700	2.38	66.23	34.39
4000	2.37	65.96	37.04

Figure 60 Engine Power produced against Engine Speed

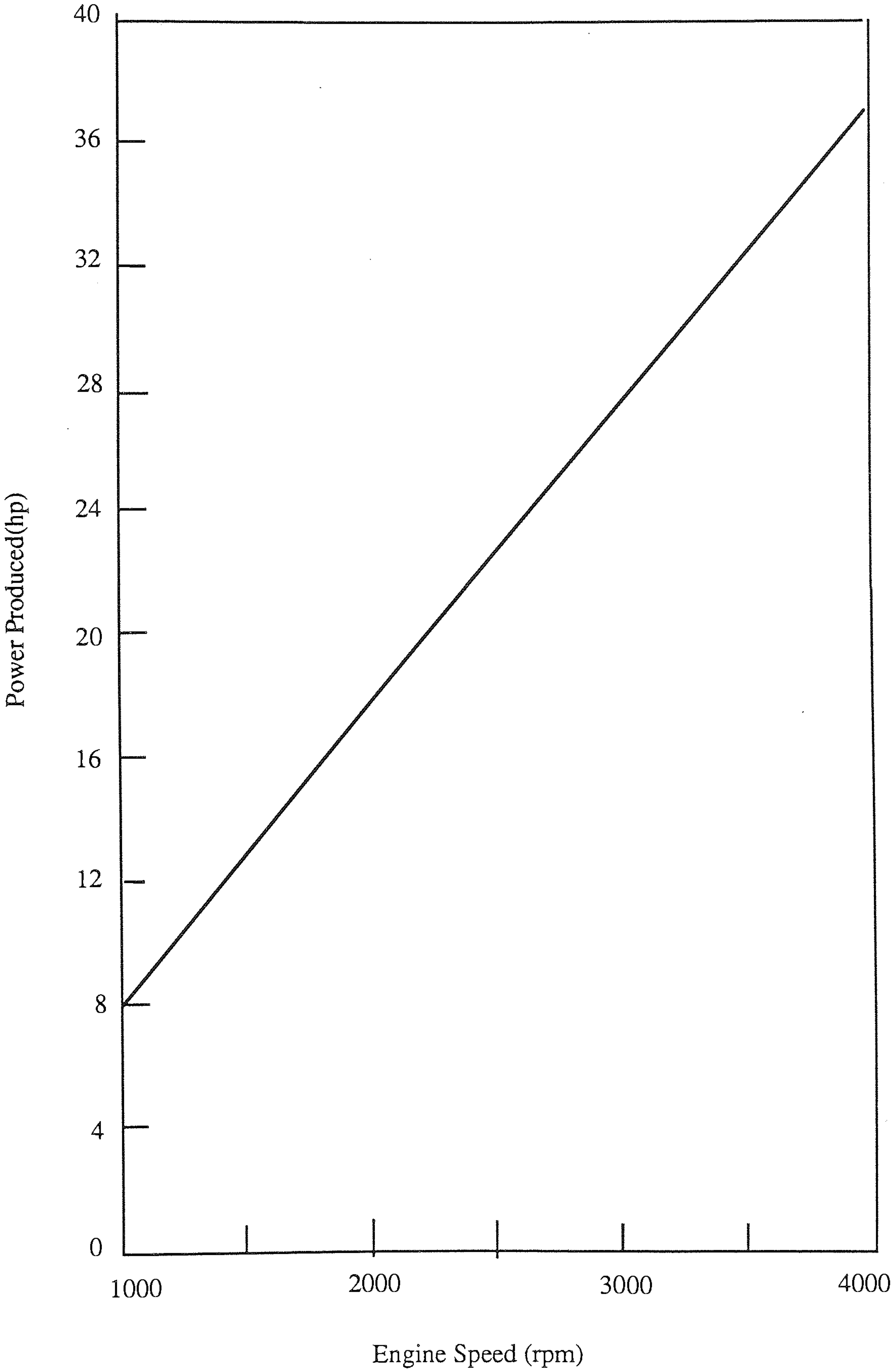


Figure 61 Torque produced against Engine Speed

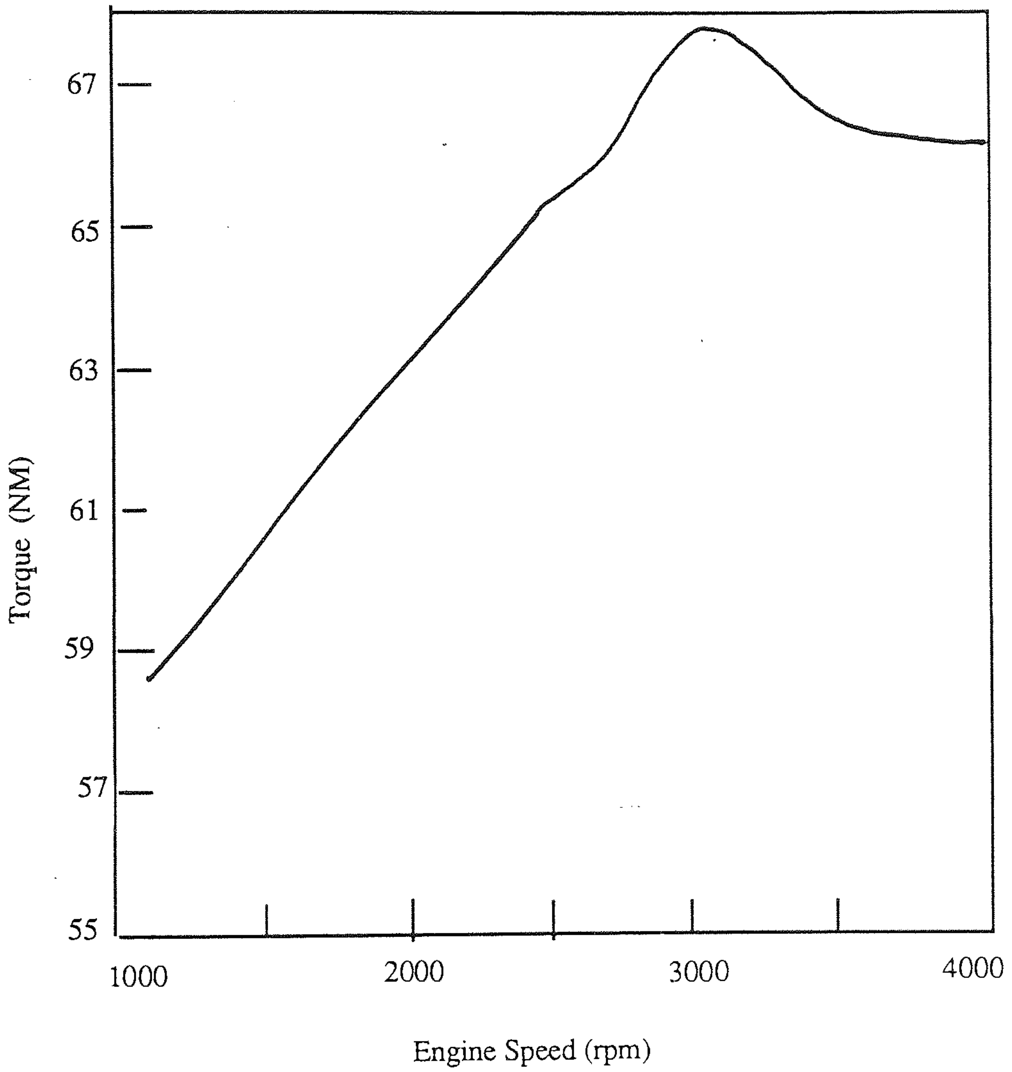


Table 25 Exhaust Emission Data with 2 Star Leaded Petrol

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.5	6.0	10.3
1400	4.3	5.8	10.4
1600	3.6	5.7	10.6
1800	3.4	5.6	10.7
2000	3.2	5.5	10.8
2400	2.8	5.2	11.1
2800	2.2	4.9	11.4
3000	2.3	4.7	11.6
3500	2.2	4.1	11.8

Figure 62 Exhaust Emissions with 2 Star Leaded Petrol

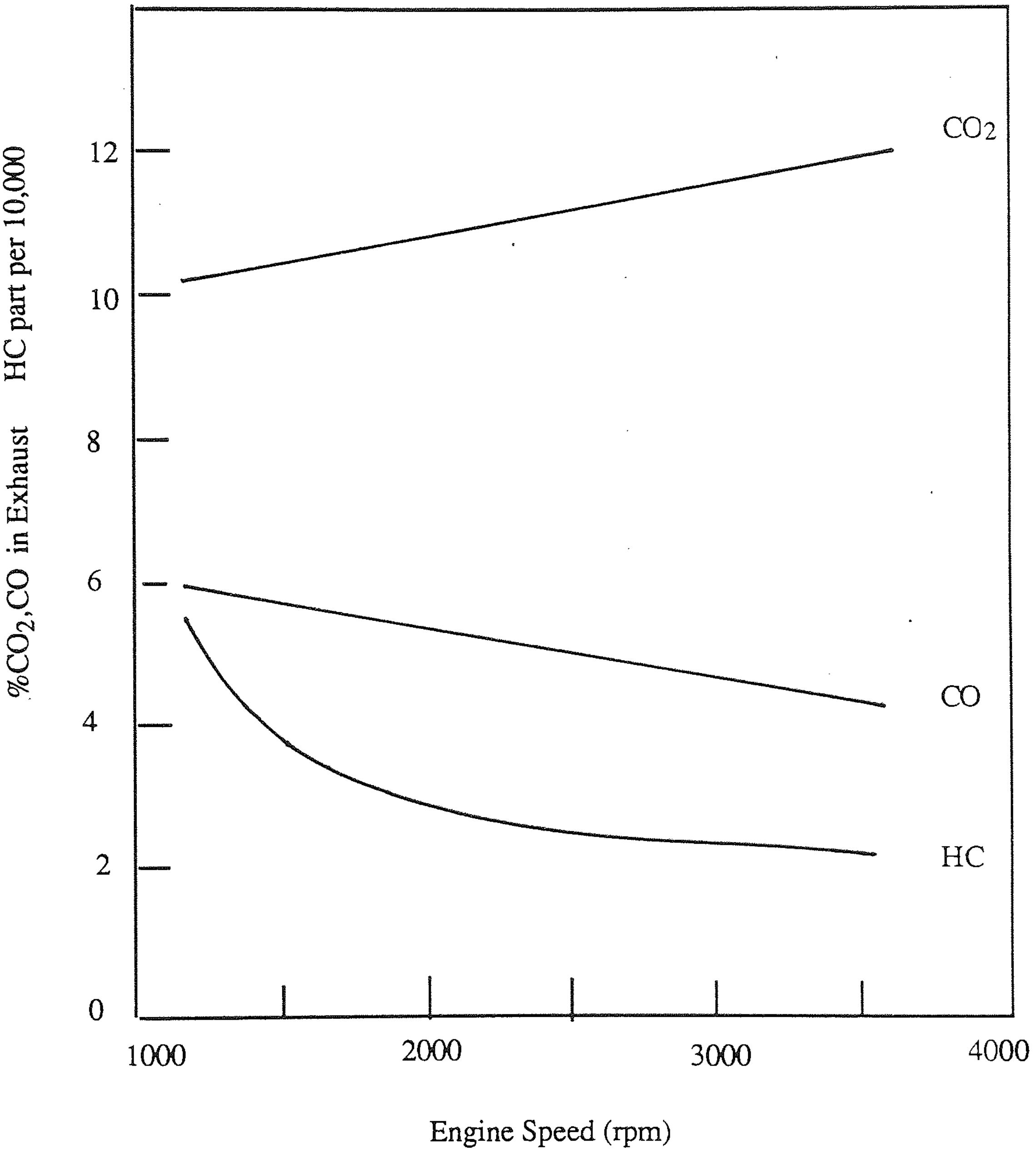


Table 26 Exhaust Emission Data for 4 Star Leaded Petrol

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.9	5.9	11.2
1400	4.7	5.5	11.4
1600	3.9	5.2	11.6
1800	3.7	4.9	11.8
2000	3.6	4.7	12.0
2400	2.8	4.5	12.1
2800	2.3	3.9	12.3
3000	2.3	3.4	12.6
3500	2.1	2.9	12.8

Figure 63 Exhaust Emissions with 4 Star Leaded Petrol

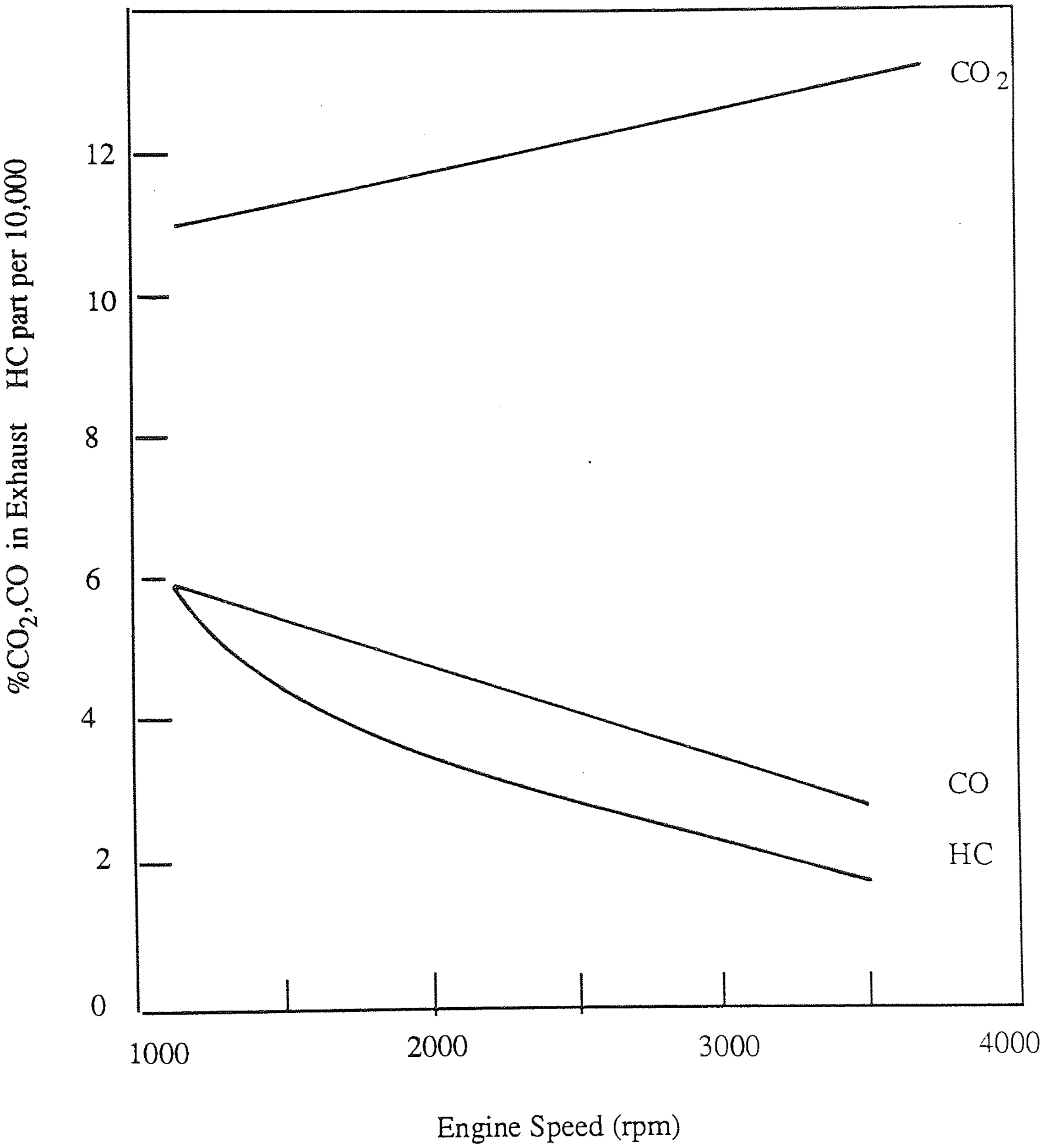


Table 27 Exhaust Emission Data with 2 Star Petrol + 10% Ethanol

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.1	5.3	11.1
1400	4.5	5.3	11.2
1600	3.9	5.1	11.4
1800	3.5	5.1	11.4
2000	3.3	4.9	11.5
2400	2.9	4.5	11.7
2800	2.5	4.3	11.9
3000	2.3	4.1	12.1
3500	2.1	3.9	12.2

Figure 64 Emissions Data with 2 Star Leaded Petrol + 10% Ethanol

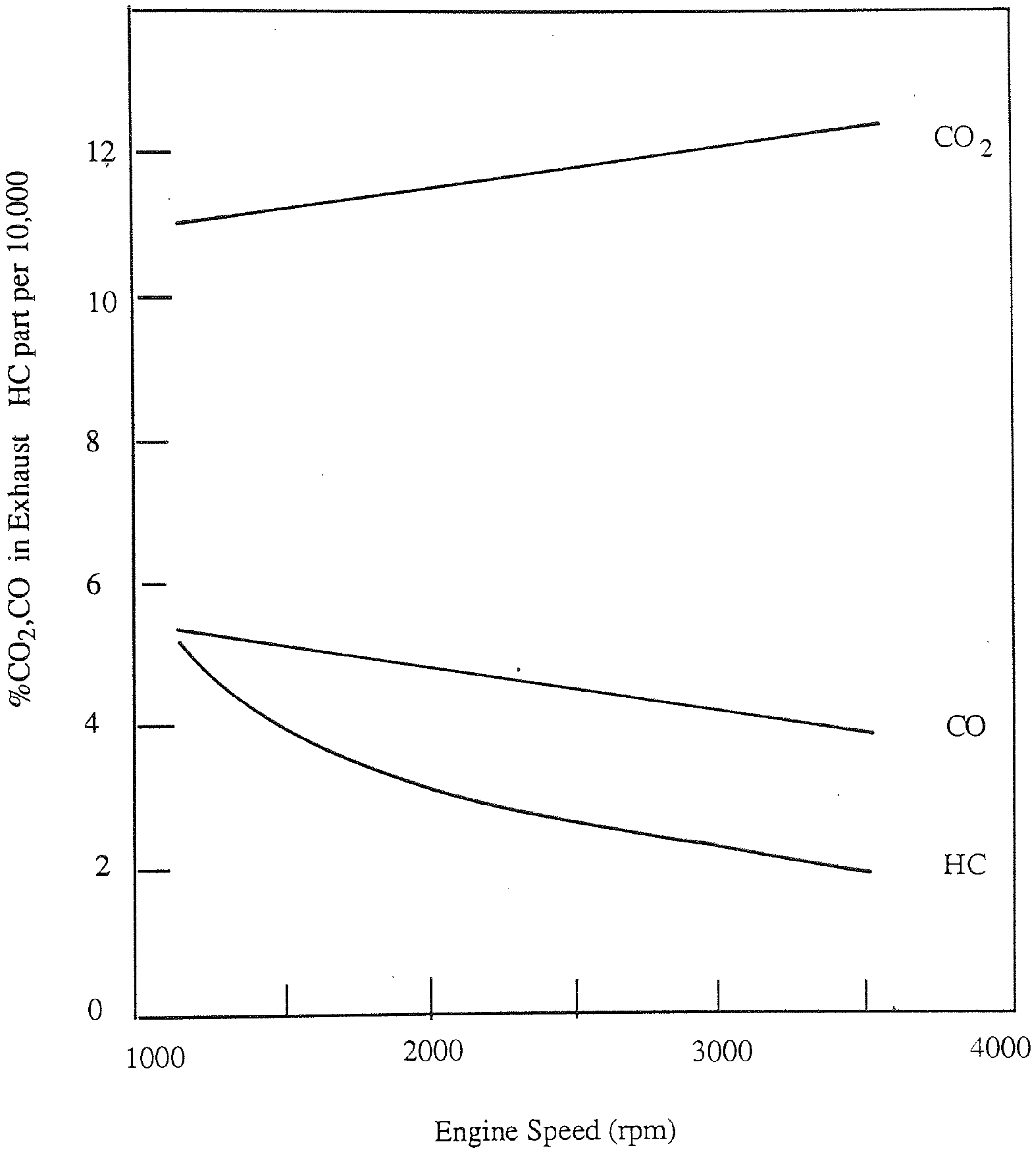


Table 28 Exhaust Emission Data with 4 Star Leaded Petrol + 10% Ethanol

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.3	5.3	11.3
1400	4.5	4.9	11.3
1600	3.9	4.5	11.7
1800	3.4	4.0	11.9
2000	3.0	3.7	12.2
2400	2.7	3.2	12.5
2800	2.3	2.9	12.7
3000	2.2	2.7	12.8
3500	2.1	2.6	12.9

Figure 65 Emissions Data with 4 Leaded Star Petrol + 10% Ethanol

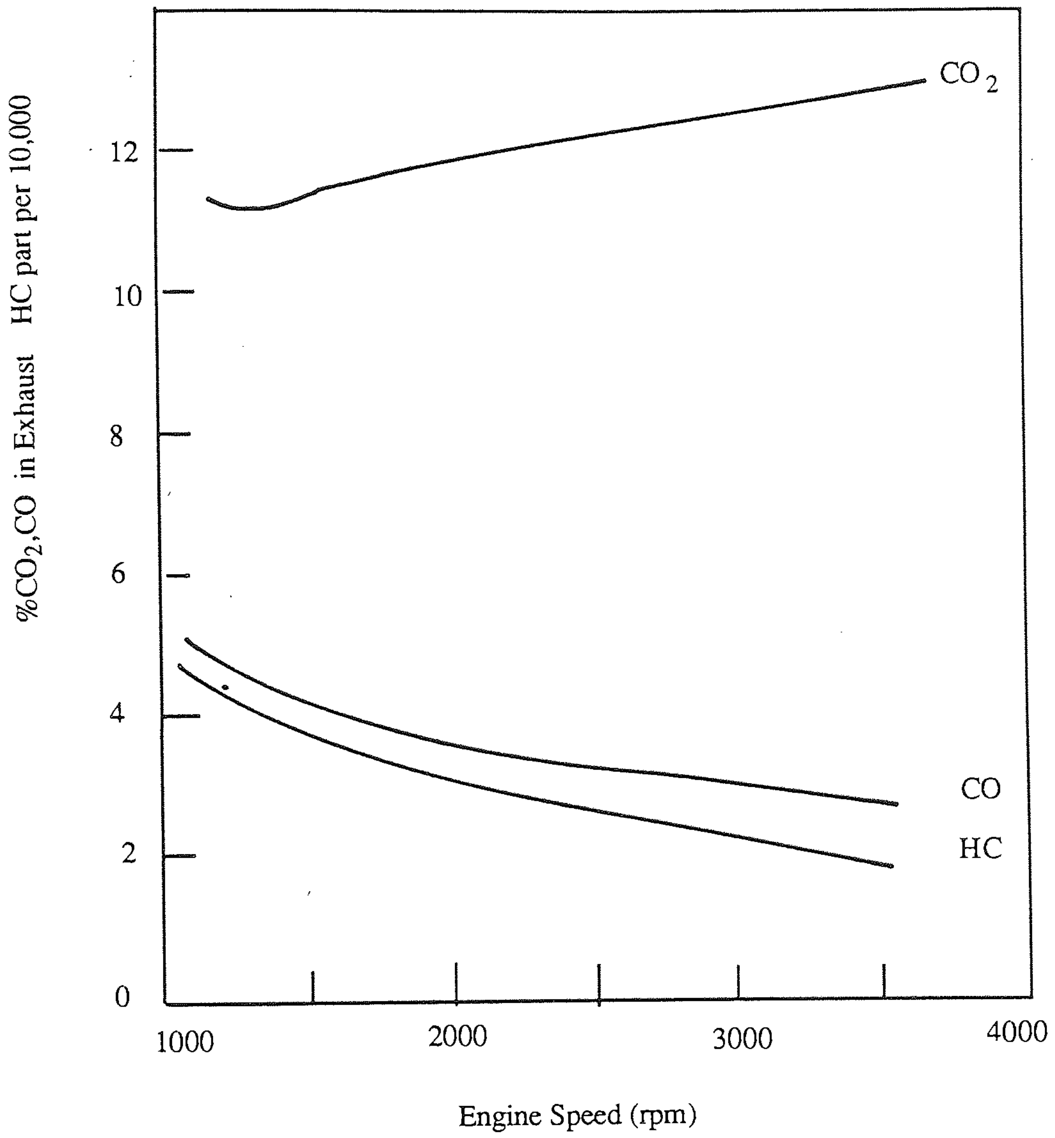


Table 29 Exhaust Emission Data with 4 Star Unleaded Petrol

RPM	HC PP 10,000	CO %	CO_2 %
1200	6.2	7.0	9.0
1400	5.1	6.5	9.3
1600	4.1	6.0	9.6
1800	3.9	5.7	9.9
2000	3.8	5.5	10.1
2400	3.2	5.1	10.2
2800	2.8	4.4	10.7
3000	2.7	4.2	11.1
3500	2.6	4.0	11.4

Figure 66 Exhaust Emission with 4 Star Unleaded Petrol

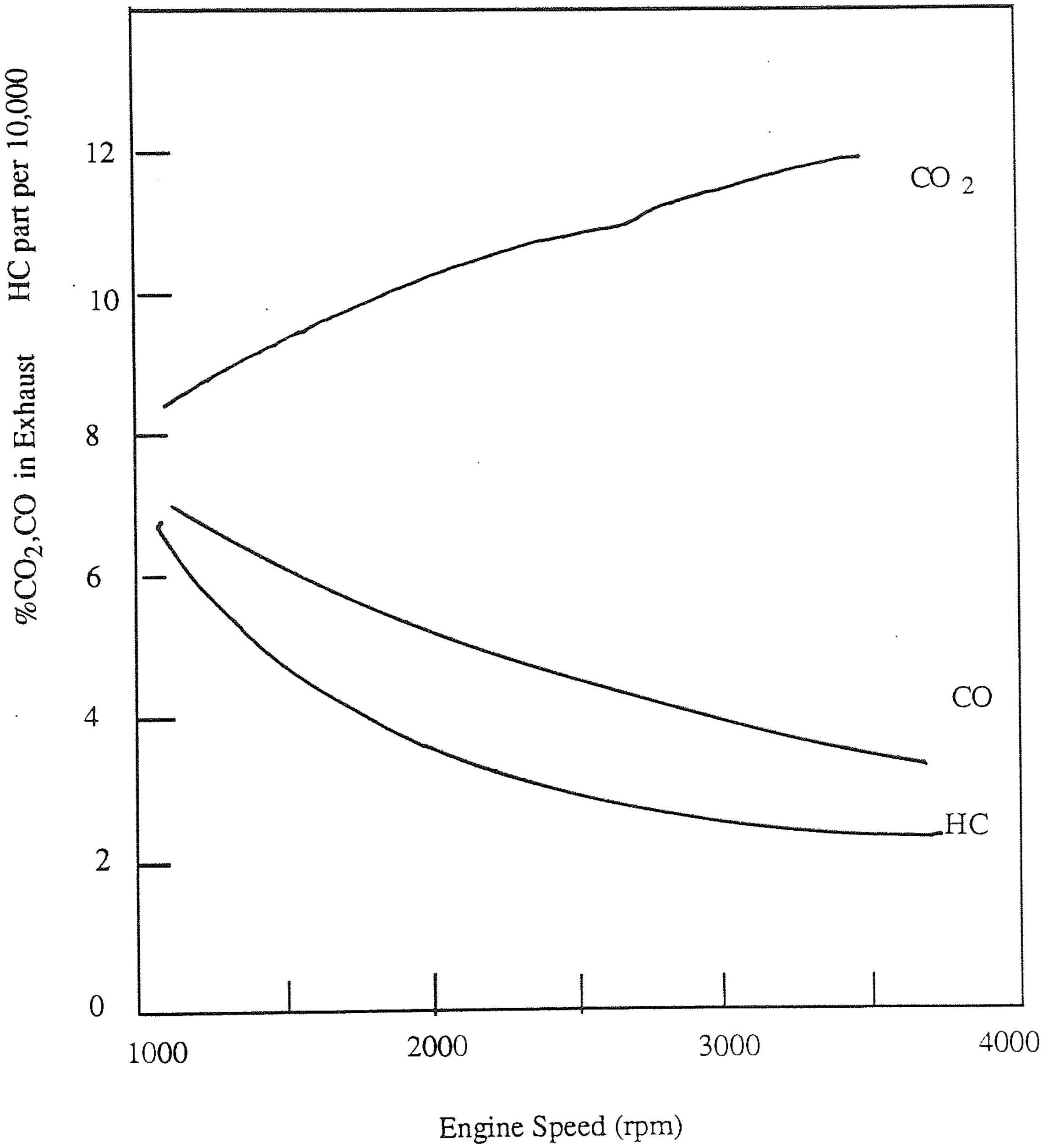


Table 30 Exhaust Emission with 4 Star Unleaded Petrol and with the Employment of a Three-Way Catalyst

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.7	6.7	9.3
1400	4.7	6.0	9.5
1600	3.7	5.5	10.0
1800	3.2	5.2	10.5
2000	2.8	5.0	10.6
2400	2.3	4.5	11.2
2800	2.0	3.7	12.5
3000	1.8	3.2	13.0
3500	1.3	2.4	14.8

Fig. 67 Exhaust Emission with 4 Star Unleaded Petrol and with the employment of Three-way catalyst.

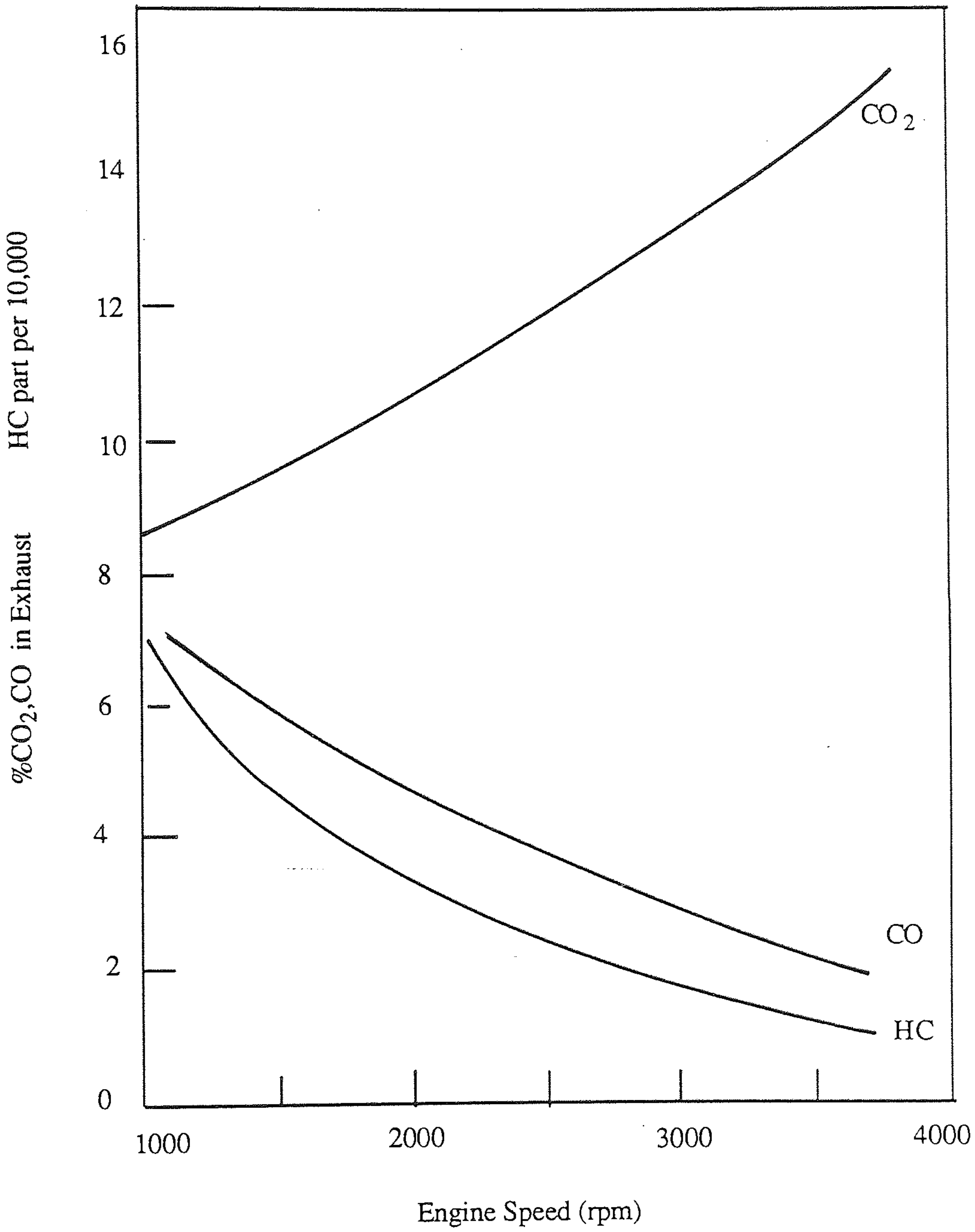


Table 31 Variation of Exhaust Emission Data with Air/Fuel Ratio

RPM	A/F	Without Catalyst HC	Without Catalyst CO	Without Catalyst CO_2	With Catalyst HC	With Catalyst CO	With Catalyst CO_2	Catalyst Eff. %
1000	14.41	7.3	7.6	8.4	6.8	7.5	8.8	4.8
1500	12.00	4.7	6.2	9.4	4.1	5.9	9.8	4.2
2000	12.34	3.5	5.5	10.0	2.8	4.9	10.7	7.0
2500	12.54	3.1	4.7	10.4	2.2	4.1	11.6	5.8
3000	12.61	2.7	4.2	11.1	1.6	3.4	13.0	17.1
3500	12.71	2.6	3.8	11.4	1.3	2.7	14.8	29.8

Fig.68 Variations of Exhaust Emission with Air / Fuel Ratio

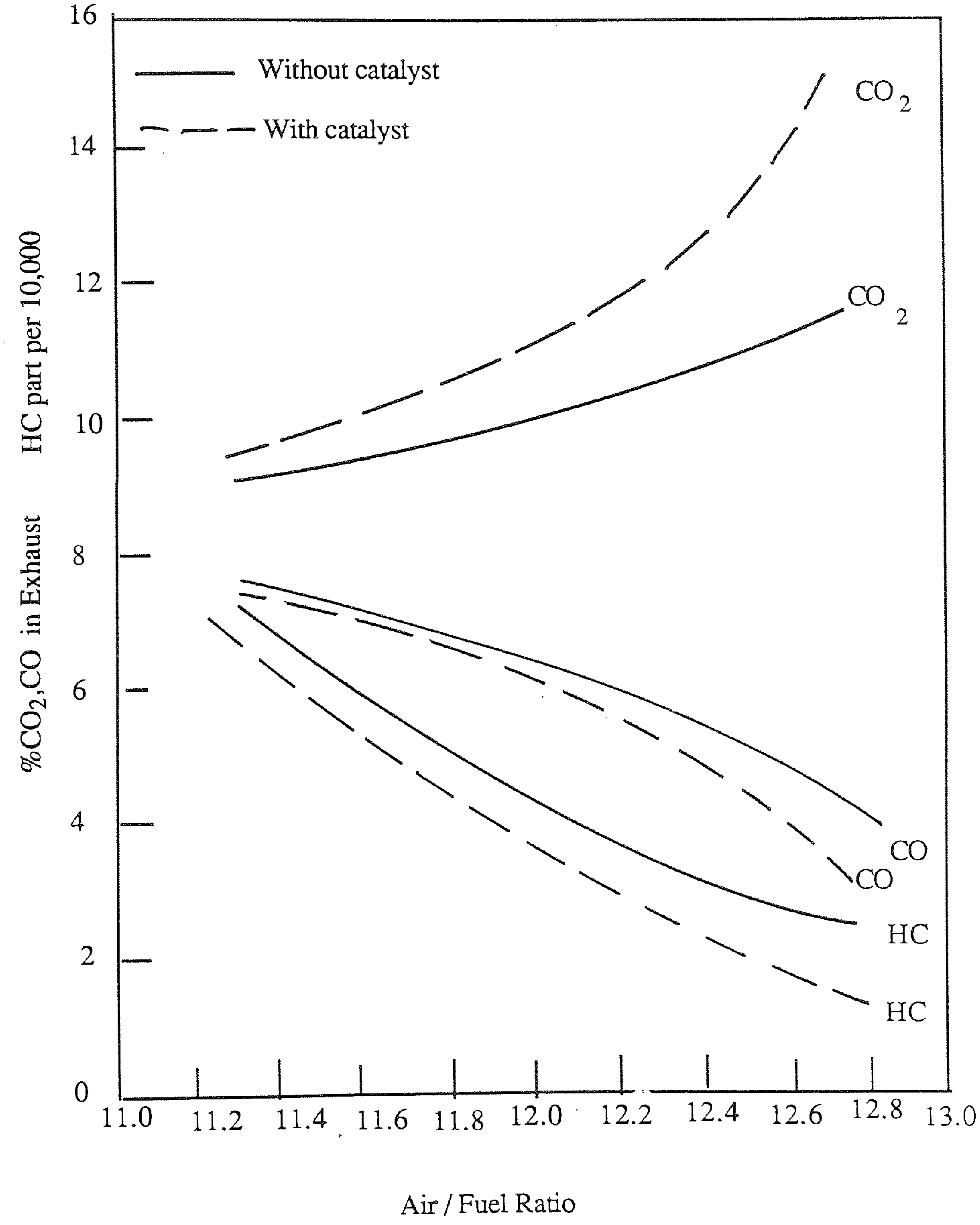


Figure 69 Catalyst Efficiency Relative to RPM

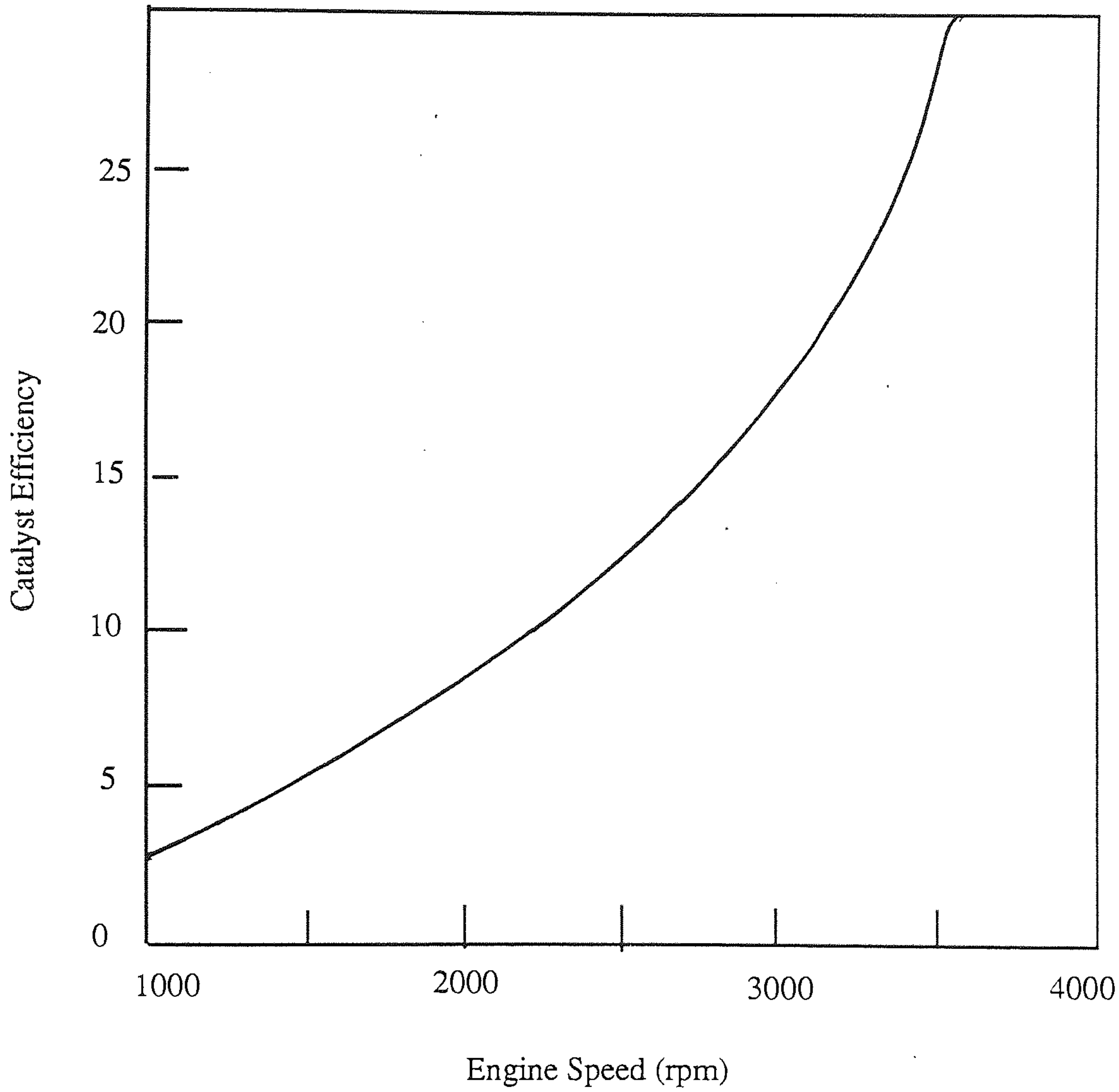


Table 32 Emission Data with 4 Star Unleaded Petrol + 10% Ethanol

RPM	HC PP 10,000	CO %	CO_2 %
1200	6.0	6.3	9.4
1400	5.6	5.7	9.7
1600	5.0	5.2	10.0
1800	4.4	4.7	11.1
2000	4.0	4.3	11.2
2400	3.4	4.1	11.4
2800	2.8	4.1	11.3
3000	2.6	4.0	11.5
3500	2.2	3.8	11.4

Figure 70 Exhaust Emissions with 4 Star Unleaded Petrol + 10% Ethanol

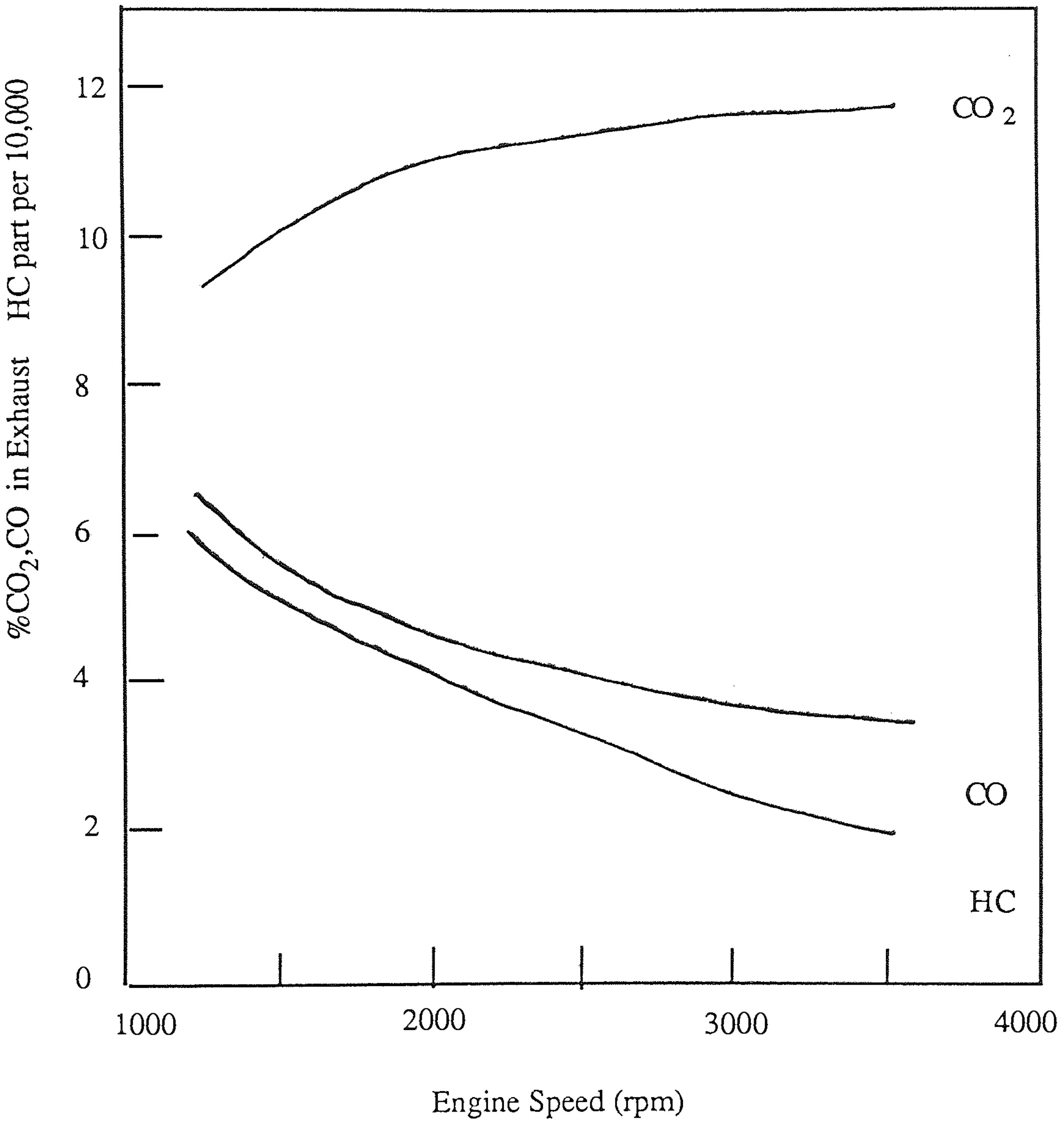
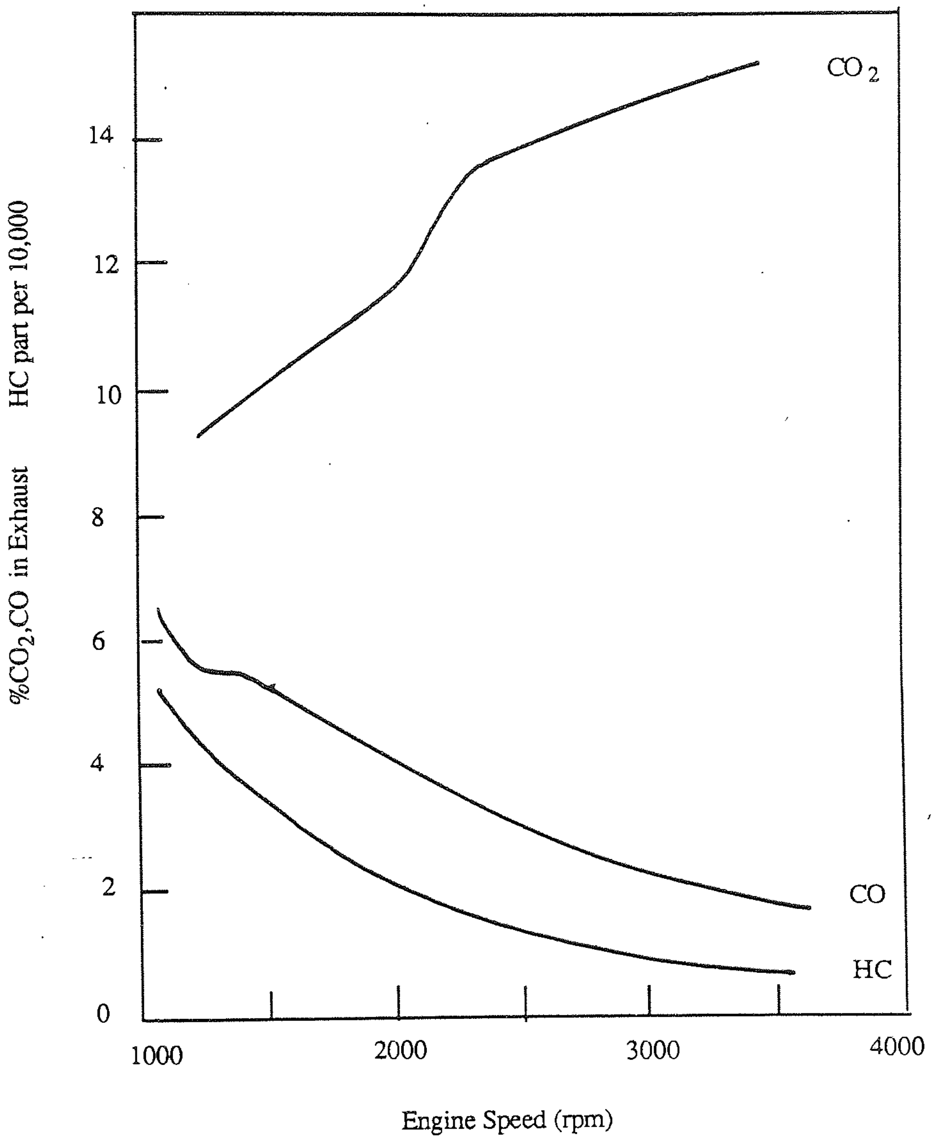


Table 33 Emission Data with Unleaded 4 Star Petrol + 10% Ethanol and with the Employment of a Three-Way Catalyst

RPM	HC PP 10,000	CO %	CO_2 %
1200	5.3	6.3	9.6
1400	4.4	5.8	10.2
1600	3.8	5.5	10.7
1800	3.1	4.9	11.2
2000	2.7	4.1	11.7
2400	2.1	3.2	13.7
2800	1.4	2.1	14.4
3000	1.0	2.5	14.6
3500	0.7	1.9	14.9

Fig. 71 Exhaust Emissions with 4 Star Unleaded Petrol
+ 10% Ethanol and with the employment of
a three-way catalyst



4.3.3 Analysis of Emission Results

In these experiments no change to the carburettor was made and as such the air/fuel ratio varies from fuels with no blending and fuels which were blended with ethanol.Therefore the emissions of carbon monoxide and hydrocarbons were expected to be lower in the blends due to the extra oxygen present. this is shown in the results of two-star petrol, table 25, 27 and figures 62,64. At lower speeds the reduction in carbon monoxide being approximately 11% and at speeds of 3500rpm,the reduction being 5%. Correspondingly the hydrocarbon emissions were reduced at lower speeds by 7% and at 3500rpm by 5%.Similarly with four-star leaded petrol, tables 26,28 and figures 63,65. Carbon monoxide and hydrocarbon emissions were reduced by 10%, at low speeds. However at a speed of 3500rpm there is no signficiant reductions in hydrocarbons but the carbon monoxide emissions are reduced by 10%.

In conclusion as a comparison of blends from exhaust emission results it is not possible to conclude if four-star or two-star petrol is better for blends with ethanol.

The most desired work in this analysis was to assess if ethanol blended with lead free petrol would result in reduced emissions. The initial work on lead free petrol showed an increase in the emission of carbon monoxide and hydrocarbons,both at low and high engine speeds. The increased emissions at low speeds being 32% for carbon monoxide and 17% for hydrocarbons. Similarly at high engine speeds the carbon monoxide emissions increased by 50% and hydrocarbon emission by 23%.

This is indeed a significient increase in the exhaust emissions of carbon monoxide and overall hydrocarbons. It would be interesting to know what proportion of the hydrocarbons are polynuclear aromatics in each of the tests. However if the results obtained on the Fiat 127A engine in the laboratory,are indicative of average national data ,then further changes in exhaust emission legalislation are immenant in the near future.

Blending the lead free petrol with 10% ethanol, showed a decrease in overall emissions, table 32 and figure 70.At low engine speeds the emissions of CO were reduced by 10% and HC'S by 3%. At speeds of 3500rpm the CO emissions were reduced by 15% and HC'S by 5%. With the use of the catalyst together with ethanol blending, results shown in table 33 and figure 71, show a reduction in emissions relative to the use of unleaded petrol without blending or use of exhaust catalyst. The reduction at low engine speeds being 10% for CO and 14% for HC'S. At speeds of 3500rpm, the reduction in CO being 53% and in hydrocarbons 73%.

In comparing results , of the effect of blending in the presence of an exhaust catalyst. There is a reduction of CO at low engine speeds by 6% and HC'S by 7%. At engine speeds of 3500rpm the subsequent decrease in CO emission is 20% and HC'S reduction by 46%.

In comparing results of blended and non blended fuels, it is noted ,that the engine is free of deposits and therefore emissions of unblended fuels are lower then would be expected in a private passenger car.

CHAPTER 5
MATHEMATICAL MODEL

CHAPTER 5

MATHEMATICAL MODEL

5.1 Introduction

As outlined in Chapter 1, deposits in spark ignition engines cause increased knock together with a decrease in efficiency and heat rejection. The understanding of this problem has become increasingly important as attempts are continuously being made to raise levels of performance and to compete in the economic markets of today, without incurring high costs.

It is quite clear from the present study and earlier work that the deposit is a thermal insulator and that, as such, it has adverse effects on engine heat transfer resulting in high octane requirements for smooth operation. This study attempts to determine the changes in heat transfer using the measured thermal conductivities. Many techniques have been developed over the years to study the problems associated with combustion deposits, and present knowledge of the circumstances surrounding the engine response has increased substantially. Nevertheless the complexity of the deposit itself and the difficulty of reproducing exact engine cycles, together with time and cost of making any meaningful measurements, has led to the initiation of this study. The wider objectives of such a model are that it may be employed by engine designers to simulate heat flow changes with various construction materials and thicknesses and the relative effects of different fuels. Past researchers(79) have carried out some work with heat transfer in the engine and have provided some useful information regarding steady-state or average heat transfer rates in an engine. However, caution must now be applied due to the variation of heat transfer coefficient in a wide range of conditions, leading to many unexpected results. Though the conditions of heavy knock are relatively rare, its detrimental effects are substantial and must form a prime concern of any such study.

The model attempts to stress the complexity of the problem of assessing how engine deposits accumulate and their effect on engine performance. Attacking the problem experimentally would result in problems of statistical cycle behaviour as well as that of expense and delicate instrumentation. Furthermore, engine surface temperatures can be measured and heat transfer rates can be estimated providing good heat transfer coefficient data is available in a changing medium. An attempt is made in this study to gain knowledge of heat transfer along every stage of the gas cycle and the effects different deposit thickness and thermal conductivity will have on it. Heat flow through the piston head, cylinder top and cylinder wall is considered. Each plane is assumed to be a one dimensional heat flow path. The engine can be treated both as clean with no deposits and for cases with deposits of various thicknesses of combustion deposits. It is also assumed that the cylinder walls and head are free of any deposits at all times, though in reality a small amount of deposit may accumulate in the latter case.

The following assumptions are also taken into consideration:

1. During all parts of the engine cycle the gas in the combustion chamber is assumed to be homogeneous.
2. Pressures and temperature at any one instant are assumed to be uniform throughout the chamber.
3. Air-fuel ratio is stoichiometric.

4. The species comprising the gas mixtures are assumed to be ideal gases. The unburnt gas is assumed to comprise of a non-reacting mixture of air, iso-octane fuel vapour and residual burned gas.
5. The combustion chamber walls, including piston head, are assumed to be of a uniform thickness. On the outside there is a uniform time independent temperature coolant. The coolant boundary layer is assumed to be described by a constant heat transfer coefficient figure 72.

The assumptions outlined above are fairly standard and have been used in previous studies(75,80,81).

Before beginning to attempt to define this model, the structural elements are listed below and each is analysed and considered separately to avoid complexity.

1. Gas temperatures and pressures in the gas cycle.
2. Heat transfer coefficient and its variations with conditions prevailing in the engine.
3. Instantaneous temperatures across the cylinder top, cylinder walls and deposit together with piston head.

Ultimately a computer program of the model would help in the ease of determining data.

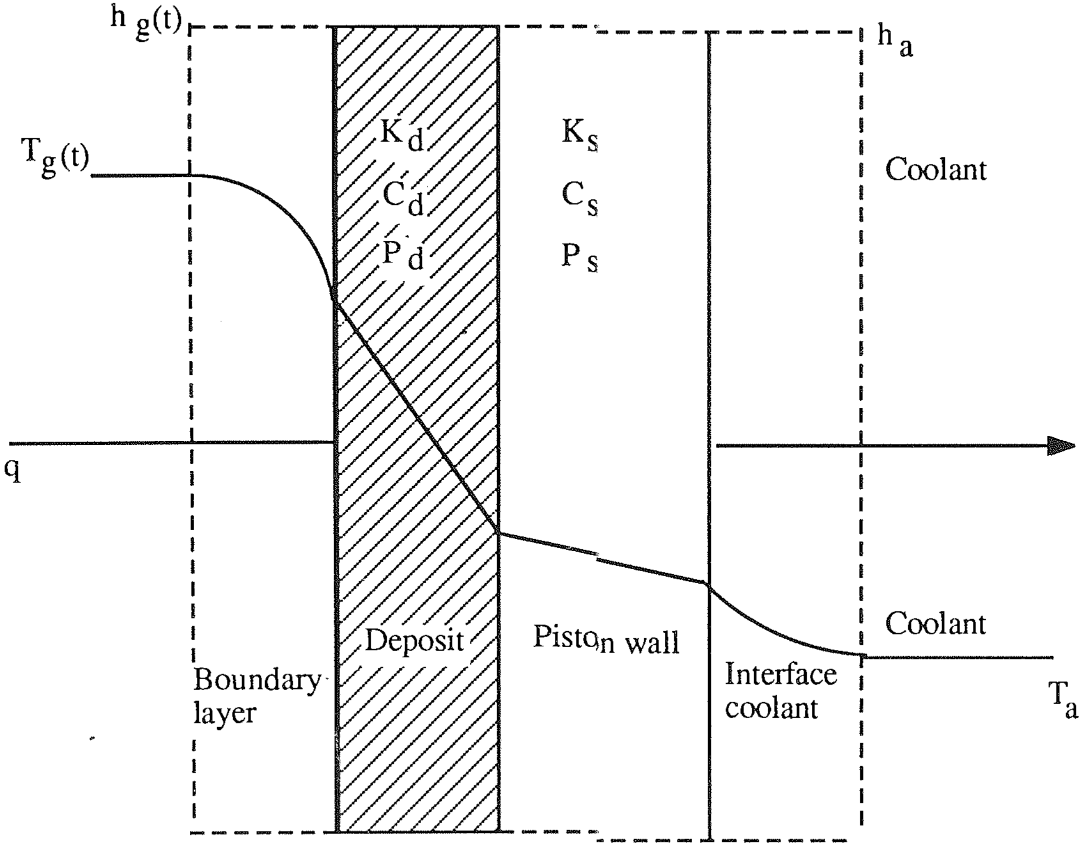


Figure 72 Schematic diagram of heat transfer through the deposit and piston head

5.2 Gas Temperatures and Pressures in a Gas Cycle

Many different approaches are possible when deciding on the form of the temperature cycle to be used for such a mathematical model, for example, the Otto cycle or any other cycle backed up by experimental data. Experimental data would normally be the first choice, as experimental values of thermal conductivity are being employed and thus the conclusions reached would indicate practical results. But due to the length of time and facilities available a theoretical solution is sought.

Since the study is to indicate the relative detrimental effects on the engine with different deposits (leaded and lead-free deposits), the precise cycle is perhaps not of paramount importance at this stage.

Due to the deposits enhancing detonation, data is determined using the Hottel charts as this procedure involves combustion at constant volume (as is the case in extreme knock conditions) resulting in very high temperatures and pressures being set up. Since the temperatures and pressures are sudden and indicative of extreme conditions, thus the resultant wall temperatures and heat flow rate changes will also indicate maximum values.

The engine characteristics are based on the engine used in this research, the Fiat 127A. The Hottel charts have been drawn for the case of one pound of air plus the fuel and represented in degrees Rankin. For simplicity it was decided to work in these units, since much of the literature remains in °R and lb wt., etc.

The data was assumed as given below and the following solution is obtained using Hottel charts, and following the method as shown by Obert (82).The following assumptions are also considered to be applicable to the model.

1. Stoichiometric mixture
2. Compression ratio 9 to 1
3. Manifold pressure 14.4 psi and temperature 80°F (540°R)
4. Exhaust pressure 15 psi and temperature 2500°R.

The exhaust temperature has been fixed at 2500°R, after a number of repeated attempts, so as to obtain agreement of exhaust residuals calculated at the beginning of the calculation, with the value determined as a check at the end of the calculations.

$$\text{Exhaust residual } E_R = \frac{T_m}{T_m + T_c\left[\left(\frac{P_m}{P_e}\right) r - \left(\frac{P_m}{P_e}\right)^b\right]}$$

$b = 0$ for wide open throttle and

$$E_R = \frac{540}{540 + 2500\left(\left(\frac{14.4}{15}\right) 9 - 1\right)} = 2.78 \times 10^{-2}$$

$$T_{\text{mixture}} = T_1 = E_R \, r \, T_c\left(\frac{P_m}{P_c}\right) = 600.48^\circ\text{R}$$

At these conditions using the perfect gas law, volume of mixture is given by:

$$V_1 = \frac{nRT_1}{P} = \frac{(1545 \text{ x } 600.48)\ n}{14.4 \text{ x } 144}$$

n = no of moles of charge $= 3.53 \text{ x } 10^{-2} + 2.0 \text{ x } 10^{-3}E_R = 3.535 \text{ x } 10^{-2}$

$$\therefore \quad V_1 = 15.82 \text{ ft}^3$$

At these conditions from Hottels energy charts for unburnt mixture

U_1 = sensible internal engergy = 10.2 BTU

H_1 = Enthalpy of mixture = 60.0 BTU

For isentropic compression to V_2 for unburnt mixture

$$V_2 = \frac{15.82}{9} = 1.757 \text{ ft}^3$$

From Hottel charts $T_2 = 1090°R$

and $$P_2 = \frac{nR_0T}{v} = \frac{3.535 \text{ x } 10^{-2} \text{ x } 1545 \text{ x } 1090}{1.757 \text{ x } 144} = 235.3 \text{ psi}$$

and $U_2 = 119$ BTU

After isentropic compression, combustion at constant volume takes place

$$V_3 = V_2 = 1.757 \text{ ft}^3$$

Internal energy is given by

$$U_3 = U_2 + U_c$$

$$U_c = 1281\,(1 - f)$$

and $U_3 = 1364.38$ BTU

From Hottels product charts for stoichiometric conditions

$$S_3 = \text{Entropy} = 0.498$$

and the resultant pressure $P_3 = 1175$ psi

and temperature $T_3 = 5050°R$

Combustion at constant volume is followed by isentropic expansion to

$$V_4 = V = 15.82 \text{ ft}^3$$

$$T_4 = 3250°R$$

$$P_4 = 85 \text{ psi}$$

$$U_4 = 688 \text{ BTU}$$

After the exhaust valve opens the combustion products in the cylinder are assumed to undergo an adiabatic reversible expansion to the exhaust pressure then

$$P_5 = P_4^{|} = 15 \text{ psi}$$

and $$V_4^{|} = 61 \text{ ft}^3$$

$$T_4^{|} = 2270°\text{R}$$

$$H_4^{|} = 545 \text{ BTU}$$

$$U_4^{|} = 410 \text{ BTU}$$

At the exhaust stroke

$$P_5 = P_4^{|} = 15 \text{ psi} \quad \text{and } V_5 = 15.82 \text{ ft}^3$$

$$U_5 = \frac{V_5}{V_4^{|}} \text{ x } U_4^{|} = \frac{15.82}{61} \text{ x } 410 = 106.3 \text{ BTU}$$

$$H_5 = \frac{15.82}{61} \text{ x } 545$$

$$T_5 = 2270$$

On the exhaust stroke the volume of gases left in the cylinder is 1.757 ft^3

The total volume of exhaust gases was $V_4 = 61 \text{ ft}^3$

Hence the fraction left as exhaust residual is

$$\frac{V_2}{V_4^{|}} = \frac{1.757}{61} = 2.88 \text{ x } 10^{-2}$$

This is reasonably close to 2.78 x 10^{-2}.

Enthalpy of mixture $h_m = E_R (h_e) + (1-E_R)\, h_a$

$$= 2.88 \text{ x } 10^{-2} (545) + (1 - 2.88 \text{ x } 10^{-2}) (43) = 57.43$$

and this checks with T_1 from energy charts.

The combustion cycle is plotted in figure 73 and table 34 shows the summary of the results

Table 34 Summary of the Pressure, Volume and Temperature of the Combustion Cycle

Point	Pressure psi	Relative Volume ft^3	Temperature °R
0	14.4	1.757	2270
1	14.4	15.82	600.48
2	235	1.757	1090
3	1175	1.757	5050
4	85	15.82	3250
5	15	15.82	2270
6	15	1.757	2270

From the Hottel charts and using the procedure provided by Obert, engine conditions at various key points in the engine cycle have been determined, in order to complete the cycle with values of pressure, temperature and volume at each degree of the crank angle.

Considering firstly the engine volume. The engine tranverses through 720° in one cycle. Comprising of the two part, 0-360°, intake and compression and 360°-720°, power and exhaust. The volume transversed can be represented by an equation of the form,

$$V_\theta = V_o + V\sin\theta \quad \_\_\_\_\_\_ \quad (1)$$

where:

θ = crank angle ÷ 2 and has a value from 0 to 180^o

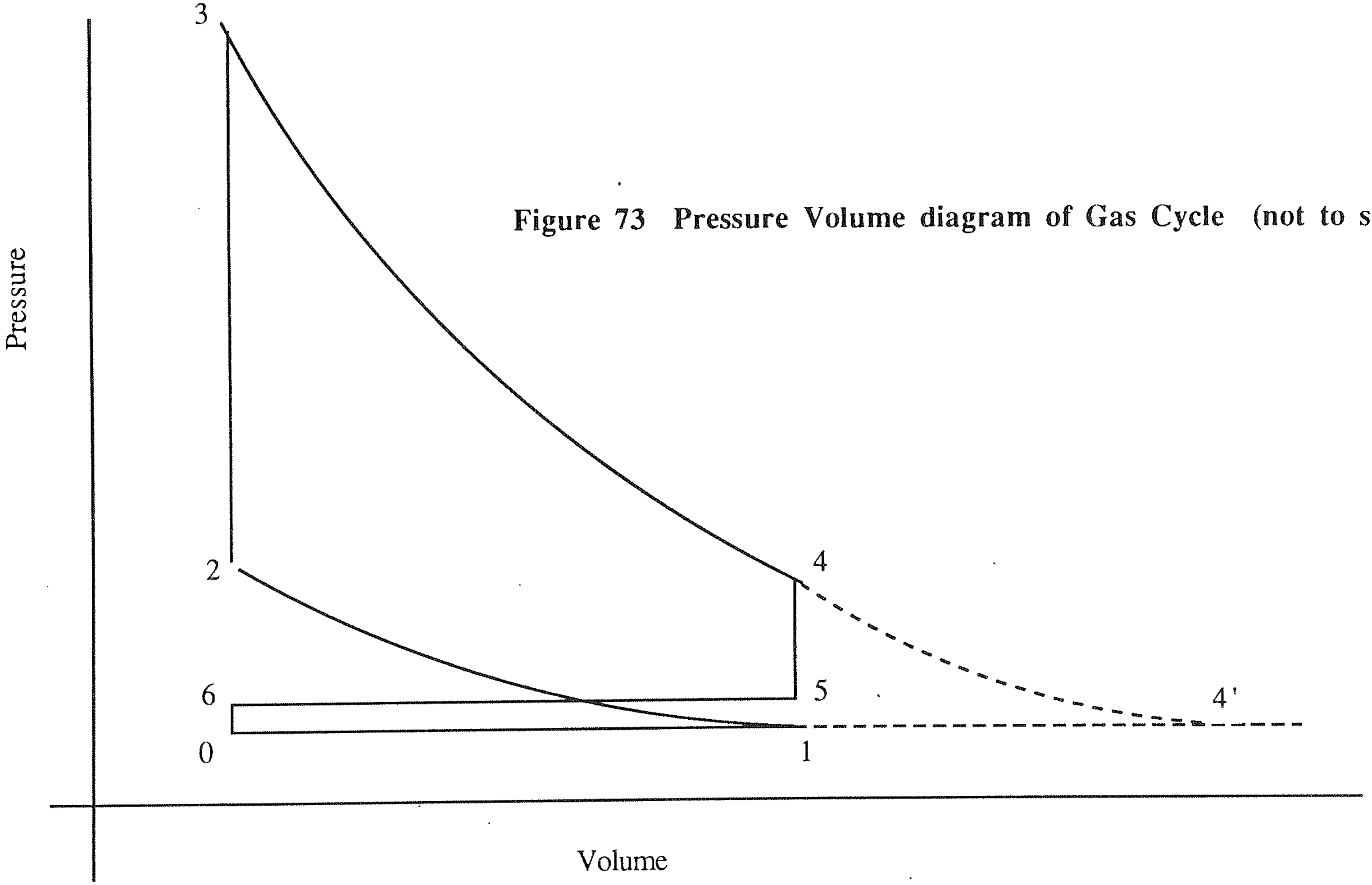


Figure 73 Pressure Volume diagram of Gas Cycle (not to scale)

V_θ = Volume displacement at $\theta°$

V_o = Fixed retained volume

V = Maximum displacement volume

$$V_\theta = V_o - V\sin\theta \qquad (2)$$

$$\theta = 180 \rightarrow 360°$$

represents power and exhaust stroke.

5.2.1 Intake Stroke

There is initially 2.88×10^{-2} fraction of exhaust residue left at a temperature of 2270°R. As the new charge is introduced the temperature of the mixture will fall.

The enthalpy of the intake charge at any point can be represented as:

$$H_m = A(h_s) + B(h_a) \qquad (3)$$

where

$$A = 1 \rightarrow 2.88 \times 10^{-2}$$

and $B = 0 \rightarrow (1 - (2.88 \times 10^{-2}))$

A and B can be further represented in terms of θ as:

$$A = 1 - \left(\frac{V_\theta - V_o}{V}\right) 0.972$$

and

$$B = \left(\frac{V_\theta - V_o}{V}\right) 0.972$$

Check: 1. when $\theta = 0$ $V_\theta = V_o$

$A = 1$ and $B = 0$

2. when $\theta = 180°$

$$V_\theta = V_o = V$$

$\therefore$ $A = 0.0288$ and $B = 0.972$

Thus, a plot can be made for temperature against θ, by determining volume of charge which is proportional to mass - hence enthalpy of mixture using equation 3 and from Hottel energy charts the corresponding temperature. The data obtained is shown in table 35, 36 and 37.

Table 35 Volume, Enthalpy and Temperature Data for the Intake Stroke

Crank Angle θ	Gas Volume V (ft3)	A	B	H_m(Btu)	T(°R)
0	1.757	1.000	0.000	545	2270
20	6.568	0.615	0.385	460	1910
30	8.79	0.514	0.486	351.7	1590
40	10.798	0.375	0.625	301.0	1430
50	12.532	0.255	0.745	171.0	1000
60	13.936	0.158	0.842	122.3	825
70	14.975	0.086	0.914	86.2	700
80	15.609	0.043	0.957	64.6	620
90	15.823	0.0288	0.971	57.5	600

5.2.2 Compression Stroke

During compression it is difficult to express a procedure that will suffice at the beginning as well as at the end. Nevertheless it was assumed that PV^{γ} = constant, to be reasonably accurate.

Using end point values already known, value of γ can be calculated.

$V_2 = 15.82$	P_2 14.4
$V_3 = 1.757$	P_3 235.3
$n = 1.271$	

Now using the perfect gas law $T = \dfrac{PV}{nR_o}$

where n = no. of moles = $0.0353 + 0.02\, E_R = 0.03535$

The coresponding data of pressure, volume and temperature for different values of θ is shown in table 36.

Table 36 Pressure, Volume and Temperature data for Compression Stroke

Pressure P(psia)	Volume V(ft3)	Crank Angle θ	Temp.°R T
14.4	15.82	90	600.48
20.0	12.217	131.94	644.33
30.0	8.879	149.5	702.3
40.0	7.08	157.8	746.7
50.0	5.941	162.7	783.2
70.0	4.559	168.5	841.4
90.0	3.741	171.9	887.7
130.0	2.801	175.7	960.0
180.0	2.169	177.9	1024.4
210.0	1.92	179.3	1063.0
235.0	1.757	180.0	1088.6

5.2.3 Power Stroke

As with the compression stroke using the end point data

$P_3V_3{}^{\gamma} = P_4V_4{}^{\gamma}$

$V_3 \quad 1.757\mathrm{ft}^3 \qquad P_1 = 1175$ psi

$V_4 \quad 15.82 \qquad P_2 = 85$ psi

$\therefore \gamma = 1.195$

Volume of gas: $V_\theta = V_o - V\sin\theta$

$\theta = 180 - 270°$

$$T = \frac{PV}{nR_o}$$

$$n = \frac{64}{1716} = 0.0373$$

The corresponding values of pressure, volume and temperature for θ from 180^o-270^o are shown in table (37).

Table37 Pressure, Volume and Temperature data for Power Stroke

Pressure P(psi)	Gas Volume V(ft^3)	Crank Angle θ	Temp. T(°R)
1175	1.757	180	5158
414.8	4.199	190	4352
243.1	6.567	200	3989
171.6	8.789	210	3768
134.2	10.796	220	3620
112.3	12.53	230	3516
98.9	13.936	240	3443
90.8	14.972	250	3396
86.4	15.606	260	3369
85.01	15.82	270	3360

Using the above data plots of pressure and temperature are shown in figure 74-76 with respect to crank angle.

Figure 74: Gas Cycle-Volume Dispersed versus Crank Angle

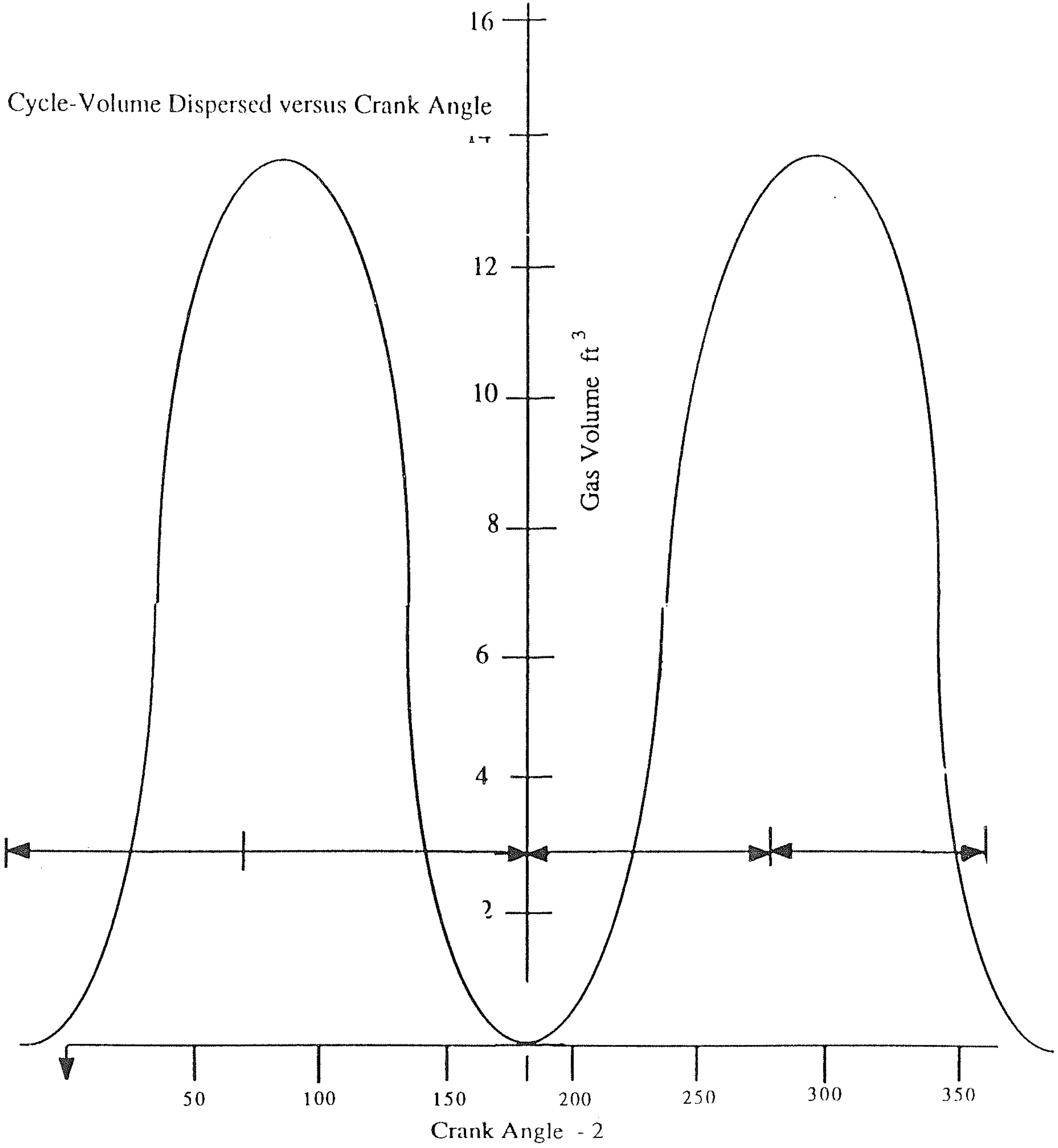


Figure 75 Gas Pressure Verses Crank Angle

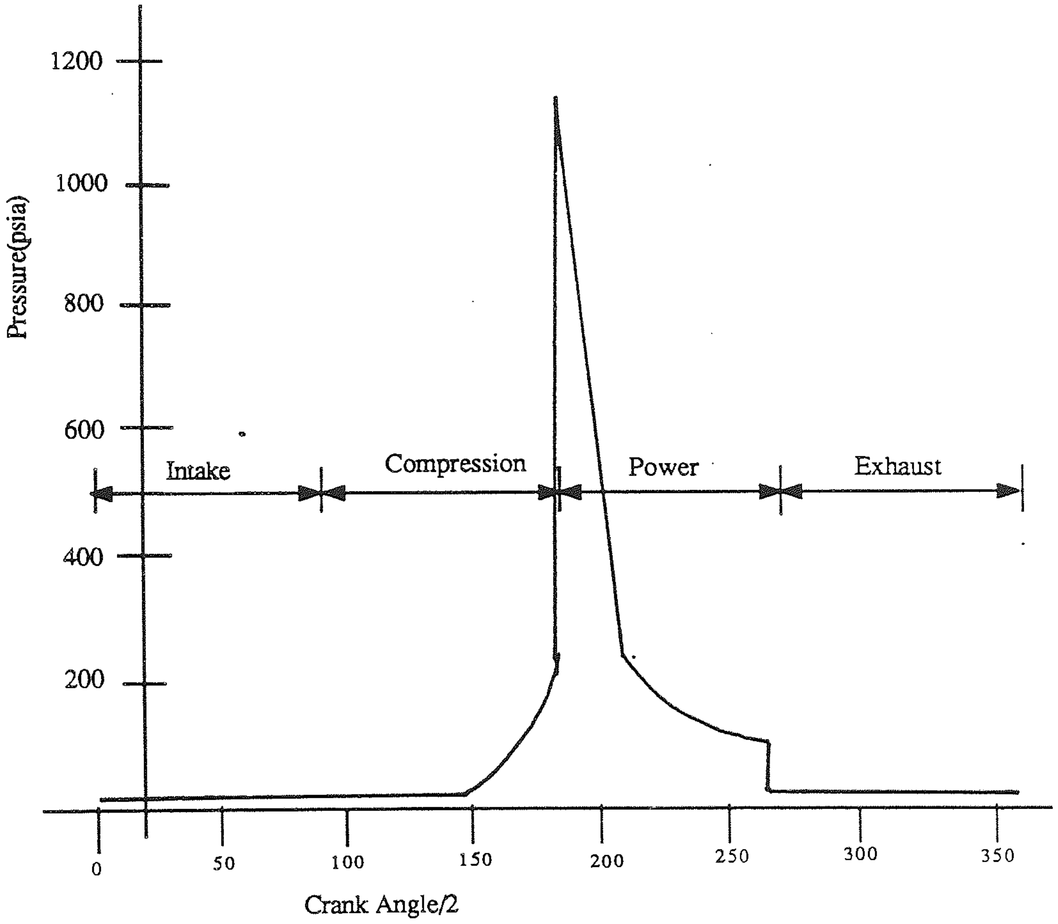
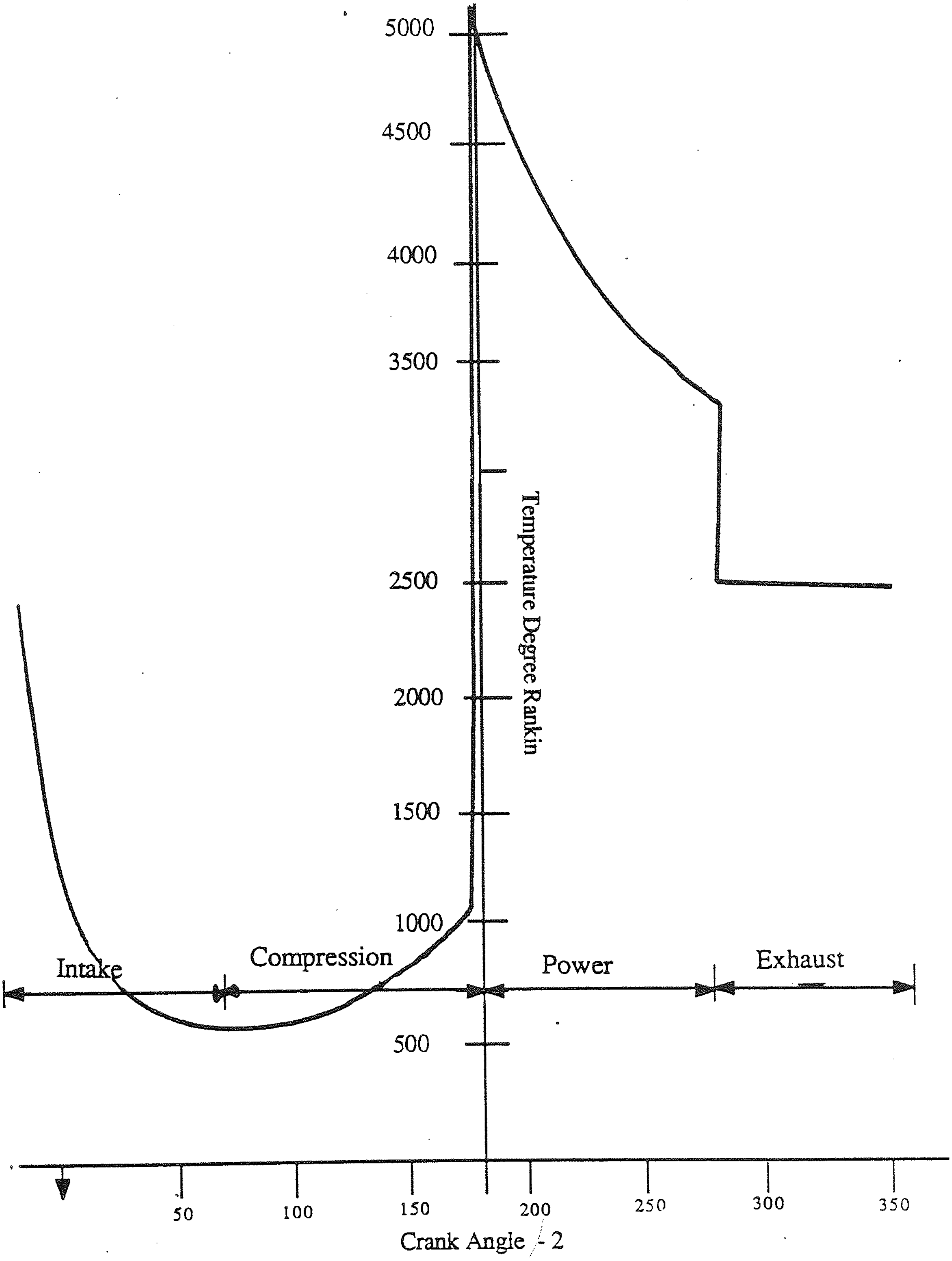


Figure 76 A Profile of Gas Temperature
Crank Angle



5.3 Heat TransferCoefficient

5.3.1 Introduction

Over the years there have been approximately ten empirical formulae for the estimation of instantaneous heat transfer coefficient (68). Yet each has been found to contain its share of shortcomings. The relationship of Eichelberg (69) was used by Professor Bradish and Professor Urethaya (70), in a mathematical model using estimated temperatures to determine heat flow through the piston head. Recently, DeGregoria (75) used a relationship developed by Woschni (76) in a detailed mathematical model, based on average measured temperatures. Both models produced large sets of data based on different principles and no comparison has yet been made of these results.

In order to retain conciseness three different relationships of heat transfer coefficient are very briefly discussed and general comparisons made. Eichelberg's and Woshni's relationships, together with Annard's, are the most popular and have therefore been chosen. It is an anomaly as to why three relationships quite different in nature find similar popularity in the same field.

Before beginning the comparisons, this is an appropriate point to mention the problem of phase lag. Phase lag exists between driving temperature difference and resulting flux at the surface, due partly to the thermal capacity of the system (69,77). Because of the complexity of introducing phase lag into the calculations and scarcity of available data, its effects are intentionally omitted.

Furthermore in a spark ignition engine the conditions are by no means steady but vary cyclically. In order that the idea of an instantaneous heat transfer coefficient can be conceived, the engine is considered in this subject to be in a quasi-steady state.

5.3.2 Empirical Heat Transfer Equations

1. $h_{Eichelberg} = 0.1627\,(PT)^{1/2}\,\left(\frac{RPM}{1000}\right)^{1/3}$ $\quad$ BTU $hr^{-1}\,ft^{-2}\,{}^{0}F^{-1}$

P = Gas pressure (psia)

T = Temperature (°F)

2. $h_{Woschin} = 110(PW)^{0.8}\,d^{-0.2}\,T^{-0.53}$ $\quad$ Kcal $m^{-1}hr^{-1}K^{-1}$

$W = W_n + W_c$

W_n = 2.28 CM during compression and expansion

and = 6.18 CM during intake and exhaust

CM = Mean piston speed M/S

$W_c = 3.24 \times 10^{-3}\,\frac{Vd}{Vs}\,\frac{(P-PM)}{Ps}$ during compression and expansion

= 0 otherwise

d = Bore diameter (m)

Vd = Displacement volume (m^3)

PM = Manifold pressure (atmos)

Ps, Ts = Pressure and temperature (K) at spark

Annard's equation is best written as rate of heat transfer, due to the importance attached to heat transfer by radiation (68).

$$\frac{q}{A} = \frac{aR}{d}(Re)^b\ (T-Tw) + C(T^4 - Tw^4)$$

$b = 0.7$

$a = 0.35 - 0.8$ increasing with RPM

$c = 0$ for compression

or $= 2.1 \times 10^{-13}$ during combustion / expansion

$d =$ bore diameter (ft)

$R =$ Thermal conductivity of gas

c.h.u. ft^{-1} sec^{-1} $(deg.\ C)^{-1}$

$T =$ Gas Temp. (K)

Annard arrived at the heat transfer equation from a purely theoretical and dimensionless point. It would be wrong in this instance to ignore the significant contribution due to radiation . However in order to keep the calculations in a simplified form and since the work is greatly concerned with thermal conductivity, it is therefore ignored here.

Eichelberg's formula has a wide acceptance in the USA and is derived from perhaps the first direct measurements obtained on a low-speed, two stroke diesel engine. The formula is intended to account for both convective and radiant transfer. The multiplying factor is not dimensionless. It is very difficult even to comprehend that it can be reduced to dimensional homogeneity; similarly with Woschni's expression.

The charge velocity is represented in each of three equations but compression ratio has been omitted. In Eichelberg's expression the cylinder diameter has also not been considered.

DeGregoria obtained a large set of results and it would be interesting to compare results of the present theoretical study with that of DeGregoria. The three correlations discussed in this report are amongst the most accepted in this very complex subject. Ideally they should be evaluated with much more scrutiny than presented here. However, in order to avoid diverging from the goal of calculating the effect of deposits on heat transfer, it is with regret that such an important and interesting section is laid to rest here.

In Conclusion:-

1. Eichelberg's relationship does not take into consideration the engine parameters, such as compression ratio, bore diameter and cylinder volume. The contribution by radiative transfer has not been highlighted either.

2. Woschni's relationship takes into consideration, unlike Eichelberg's, the engine parameters, but the heat transfer due to radiation is ignored.

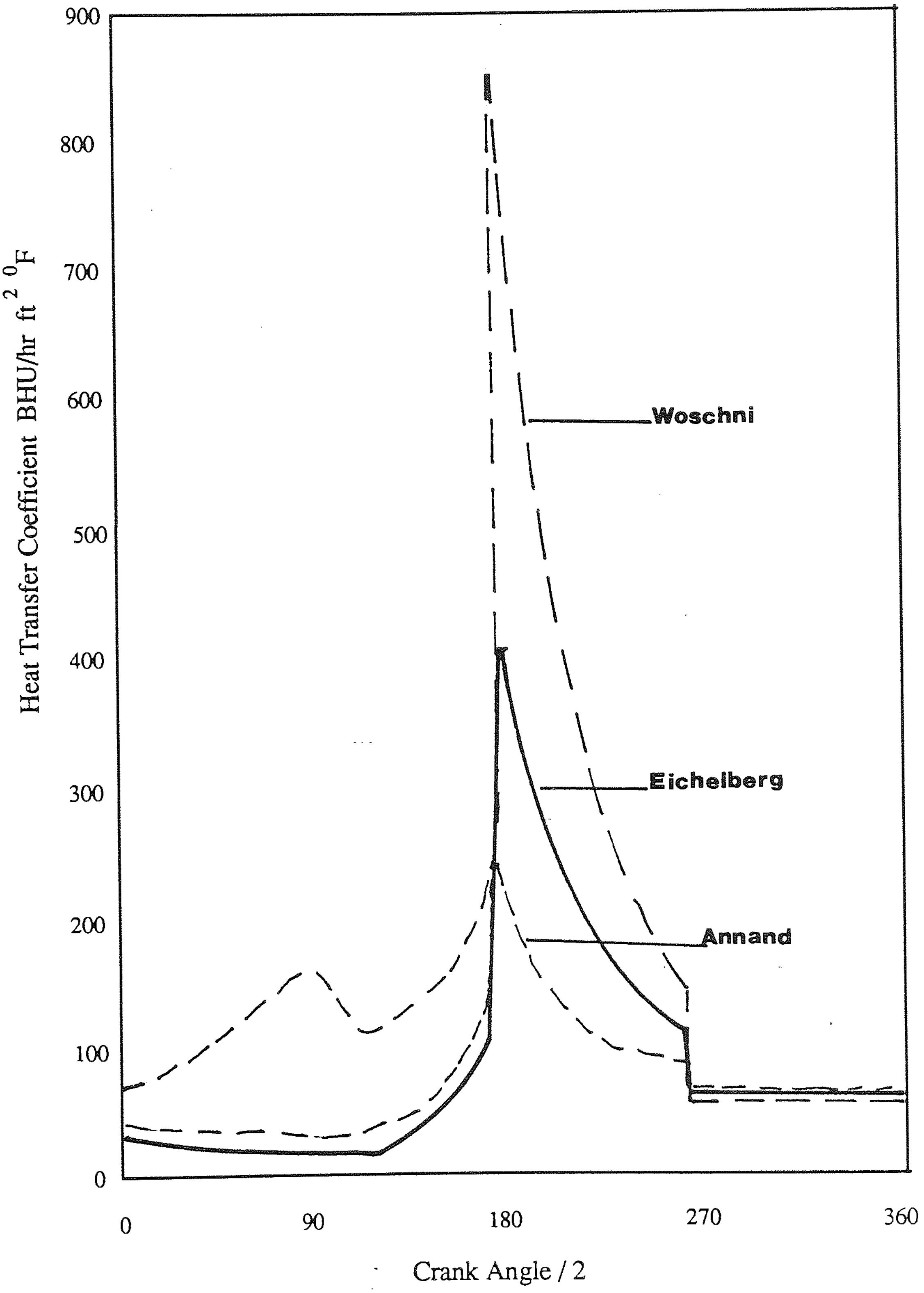
3. Annard's correlation considers both the engine parameters as well as attributing relative importance to radiation, contrary to popular belief.

See appendix 2 for calculations of heat transfer coefficients.

Table 38 Heat Transfer Coefficient Data

ø $h_{Eichelberg}$ Crank angle/2	$h_{Woschni}$ $Wm^{-2}K^{-1}$	h_{Annard} $Wm^{-2}K^{-1}$	$Wm^{-2}K^{-1}$
0	170.35	484.36	286.13
30	136.28	585.89	245.24
6o	76.66	811.99	204.36
90	45.43	981.2	188.06
120	56.78		204.36
150	90.85	731.48	147.58
180	408/2487	3015/4849	715/1368
210	948.27	1604.68	531.49
240	6o7.57	903.98	367.95
270	522/187	734/158	388/204
300	187.38	158.99	204.36
330	187.38	158.99	204.36
360	187.38	158.99	204.36

Figure 77 Comparison of Different Heat Transfer Coefficients



5.4 Instantaneous Temperatures Across Combustion Chamber Walls

Assuming the engine has reached a quasi-steady state with heat transferred in and out of the combustion chamber; a certain time later the cylinder walls will also reach a "steady" state when temperature and pressure are steady but periodically varying (see Section 5.1). Thus the temperature at any point in the wall will vary periodically, dependent on its position in the wall as well as the periodic stage.

In order to calculate the temperature profile across the combustion walls ,consider the energy equation at the gas deposit interface with the deposit divided into n segments and similarly the piston wall divided into m equal segments; then the energy equation at the gas deposit interface may be written as:

Rate of heat (in or out) of segment 1 from gas mixture	+	Rate of heat (in or out) to segment 1 from segment 2	=	Rate of energy stored in segment 1 in time $D\tau$ (Assuming the flow rates continue at this rate for a time $D\tau$.

This may be written in equation terms as:

$$h_{g(\tau)} A \left[T_{g(\tau)} - T_{(1,\tau)} \right] + \frac{Kd.A}{D\,x\,D} \left[T_{(2,\tau)} - T_{(1,\tau)} \right]$$

$$= \frac{(\rho c)_d}{D\tau} . A . \frac{D\,x\,D}{2} \left[T_{(1,\tau+D\tau)} - T_{(1,\tau)} \right]$$

$$\therefore \quad T_{(1,\tau+D\tau)} = \frac{2\alpha d.D\tau}{Kd.DxD} h_{g(\tau)} \left[T_{g(\tau)} - T_{(1,\tau)} \right]$$

$$+ \frac{2\alpha d.D\tau}{(DxD)^2} \left[T_{(2,\tau)} - T_{(1,\tau)} \right] + T_{(1,\tau)} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

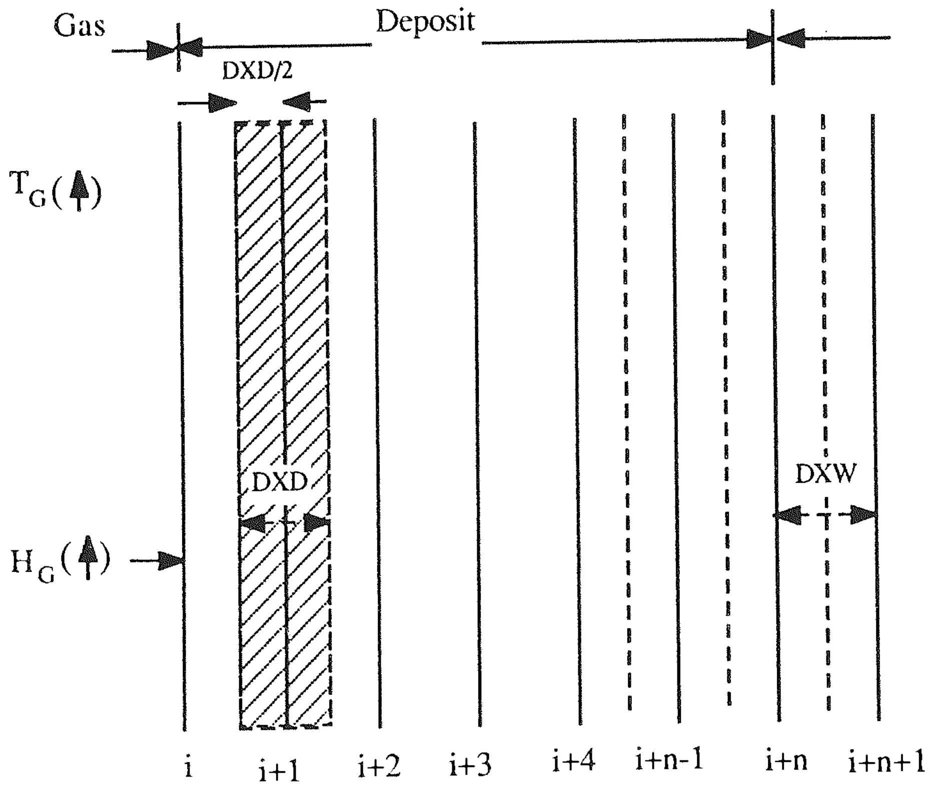


Figure 78 Schematic diagram of deposit and piston wall

In order to determine temperature of segment 1 at time (τ+Dτ) the following information is required

$$T_{g(\tau)}, \quad T_{(1,\tau)}, \quad T_{(2,\tau)}$$

At this stage only $T_{g(\tau)}$ is known (Section 5.1), therefore estimated initial values are given to $T_{(1,\tau)}$ and $T_{(2,\tau)}$. Following an iterative procedure as outlined by (5), will be explained later.

Now if a point at a plane inside the deposit layer is considered the energy equation may be written as:

Rate of heat (in or out) to segment 2 from segment 1	+	Rate of heat (in or out) to segment 2 from segment 3	=	Rate of energy stored or lost from segment 2 in time Dτ. (Again presuming that this rate of heat flow continues through a time interval of Dτ).

In equation form this may be written as

$$\frac{Kd.A}{DxD}\left[T_{(1,\tau)} - T_{(2,\tau)}\right] + \frac{Kw.A}{D\,x\,W}\left[T_{(3,\tau)} - T_{(2,\tau)}\right]$$

$$= \frac{(\rho c)_d}{D\tau} . A . \frac{D\,x\,D}{2} + \frac{(\rho c)_w}{D\tau} . A . \frac{D\,x\,W}{2}\left[T_{(i+n,\tau+D\tau)} - T_{(i+n,\tau)}\right]$$

$$\therefore \quad T_{(2,\tau+D\tau)} = \frac{\alpha d\, D\tau}{(DxD)^2}\left[T_{(1,\tau)} + T_{(3,\tau)} - 2T_{(2,\tau)}\right] + T_{(2,\tau)} \qquad ....(2)$$

NB. $T_{(3,\tau)} \equiv T_{(i+2,\tau)}$ $\quad T_{(2,\tau)} \equiv T_{(i+1,\tau)}$ $\quad T_{(1)} \equiv T_i$

Similarly for any other inner point in the deposit

The next point of interest is the interface of the deposit and the wall. Here heat conduction path differs on each side of the plane with one half of the deposit segment and one half of the wall segment being heated or cooled, Figure 78. The energy equation for a plane at the deposit wall interface is written as:

$$\frac{Kd.A}{DxD}\left[T_{(i+n-1,\tau)} - T_{(i+n,\tau)}\right] + \frac{Kw.A}{DxW}\left[T_{(i+n+1,\tau)} - T_{(i+n,\tau)}\right]$$

$$= \left[\frac{(\rho c)_d}{D\tau} . A . \frac{DxD}{2} + \frac{(\rho c)_w}{D\tau} . A . \frac{DxW}{2}\right]\left[T_{(i+n,\tau+D\tau)} - T_{(i+n,\tau)}\right]$$

$$\therefore \quad T_{(i+n),\tau+D\tau)} = \left[\frac{2D\tau . \alpha d . \alpha w}{(\alpha w . Kd . DxD) + (\alpha d . Kw . DxW)}\right] \frac{Kd}{DxD}\left(T_{(i+n-1,\tau)} - T_{(i+n,\tau)}\right)$$

$$+ \quad \frac{Kw}{DxW}\, T_{(i+1+n,\tau)} - T_{(i+n,\tau)} + T_{(i+n,\tau)} \qquad \ldots\ldots\ldots..(3)$$

The energy equation for a plane within the wall is similar to the one written for within the deposit equation (2) and is expressed as:

$$T_{(i+n+1,\tau+D\tau)} = \frac{\alpha w\, D\tau}{(DxW)^2}\left[T_{(i+n,\tau)} + T_{(i+n+2,\tau)} - 2T_{(i+n+1,\tau)}\right] + T_{(i+n+1,\tau)} \quad \ldots..(4)$$

Finally, the energy balance equation at the coolant wall interface:-

$$\frac{Kw.A}{DxW}\left[Tw_{(i+m-1,\tau)} + T_{(i+m,\tau)}\right] + hc.A\left[Tc - T_{(i+m,\tau)}\right]$$

$$= \quad \frac{(\rho c)_w}{D\tau} . A . \frac{DxW}{2}\left[T_{(i+m,\tau+D\tau)} - T_{(i+m,\tau)}\right]$$

$$\therefore \quad T_{(i+m,\tau+D\tau)} = \frac{2\alpha w\ D\tau}{(DxW)^2}\left[T_{(i+m-1,\tau)} - T_{(i+m,\tau)}\right]$$

$$+ \quad \frac{2\alpha w\ D\tau}{(DxW)} .hc\left[Tc - T_{(i+m,\tau)}\right] + T_{(i+m,\tau)} \qquad \text{............(5)}$$

We thus have a method of determining temperatures at any point in the plane of the deposit and piston head after time $D\tau$, which may be represented in degrees of crank angle. Similarly, the cylinder top and cylinder walls have to be considered. The variable area of the cylinder walls must also be taken into account.

The energy equation at the cylinder head may be written as:

$$n_2.A.\left[T_{g(\tau)} - T_{(j,\tau)}\right] + \frac{KwA}{DxW_{(2)}}\left[T_{(j+1,\tau)} - T_{(j,\tau)}\right]$$

$$= \quad \frac{(\rho c)}{D\tau}.A.\frac{DxW_{(2)}}{2}\left[T_{(j,\tau+D\tau)} - T_{(j,\tau)}\right] \qquad \text{..........(6)}$$

The energy equation through a plane inside the cylinder top is similar to equation (4) and is:

$$T_{(j+1,\tau+D\tau)} = \frac{\alpha w D\tau}{(DxW_2)^2}\left[T_{(j,\tau)} + T_{(j+1,\tau)} - 2T_{(j+1,\tau)}\right] + T_{(j+1,\tau)} \qquad \text{...........(7)}$$

Heat flow through the cylinder walls can be expressed by a similar expression as equation 7. In practice the thickness of piston head, cylinder wall and cylinder head may all be different, thus resulting in a different temperature profile in each of the three sections.

Next step in the development of the mathematical model is to test its applicability. This is shown for a case when $\theta = 180°$, i.e. at the point of combustion, just before the power stroke, (see Appendix).

The heat transfer has been calculated, using each of the three relationships of heat transfer discussed in Section 5.3. The deposit properties are listed in the appendix and the deposit surface temperatures together with outside wall temperature are listed below. Using Woschni's relationship this is further compared with the case of a clean engine.

Heat transfer correlation used	The deposit surface temperature T_D (°F)	Outside wall temp. T_{OW} (°F)
Eichelberg's	4108	2659
Woschni's	4376	2833
Annand's	3728	2417
Woschni's with a clean engine	4220	4161

If the conditions as used in the example were continuously prevalent for one minute, then the difference in heat transfer using Woschni's relationship is equivalent to 41.1 BTU for an engine with a piston diameter of 2.67 ins.

If the resulting ORI arising from such a deposit as used in the example were known then this would help in understanding the relationship between ORI and heat transfer through the combustion chamber walls.

In the long term, it is recommended that use is made of a computer, such that the properties of the wall materials can be varied. This would help in determining the best construction material and the thickness of the wall, together with values of heat transfer every two degrees of the combustion cycle.

CHAPTER 6

DISCUSSION AND CONCLUSION

There is a wide range of work covered in this investigation and comparisons made with past research, in addition to the new work described. The three main concerns relating to unleaded fuel use are economic effect, octane requirement increase and environmental impact.

Economic Effects

Different options for fuels of the future were reviewed and a lot of very vague past data was found (39),with assessments that are questionable and inconclusive.

In the economic analysis of the six different options considered, it was realised that the choice of option would not only depend on the economic factor but on whether it would be the automobile or the oil industry that would have to bear the strain of the inevitable investment costs. The options chosen have been treated as alternatives to one another, but in practice a combination of options may be employed and if that was to be the case, it would obviously be very uneconomic due to the capital investment associated with each option.

In the past the options adopted by other countries have been given undue credit. That is not to say the particular option is wrong, but an exact similarity made for the purposes of costing should not be made for the case of the UK.

Britain's choice of following Germany's initiative, firstly in reducing lead from 0.4 g/l to 0.15 g.l of petrol and now secondly, to lead free petrol while still retaining the present octane quality as been found in the analysis not to be a commendable one, from both an economic and environmental point of view.

In Germany the estimates in the former case were only one third of the actual costs incurred and similarly there is no unanimity between government and industry on the question. This is further complicated by the fact that Germany imports over 50% of the petrol consumed as a finished product, unlike Britain, where virtually all the refining is carried out in this country. Therefore, no straightforward analogy can be drawn to the case of the UK, and also there is no concrete evidence to suggest that these particular options are the most favourable.

The comparisons have been made with reference to the present four star forecourt grade with lead content of 0.15 g/l of petrol, yielding lead emissions of 2755 tonnes of exhaust lead pollutant. Figure 12 shows a diagrammatic presentation of lead emissions for each option considered. Emissions of other pollutants, such as carbon monoxide and hydrocarbonsare referred to later in the chapter on exhaust emission experiments.

So far as benefits are concerned, these can only be evaluated on the basis of medical advice, and all that can be done here is to assume for the purpose of comparisons that the benefits of options bear an approximate proportionate relationship to their effect in reducing all emissions.

The second option, employing the use of lead filter traps, with an annual penalty of ten pounds per motorist per annum, is concluded to be an interim solution, as disposal of the used traps is an obstacle that has hindered future progress, as it is easier to administer and control elimination at a point source than when it is widely dispersed.

In considering the options, account was taken of the increased refining costs of producing unleaded petrol at 98 RON and the increased, octane requirement increase (ORI) resulting from the use of unleaded petrol. Accordingly in the case of options five and six account was taken of the reduced efficiency that arises due to lower compression ratio that is associated with these options. Savings of 3% on refinery costs for option six were also considered. In the analysis the most astonishing results revealed are those of options three, five and six. The reduction in the research octane numbers in the case of options three and five. This results in the loss of efficiency by 3%, however this is largely overcome by the reduced refinery costs. Overall, option five shows an annual saving of £13 relative to Option three. This may not seem considerable when considered for the individual motorist, but nationally it would result in savings of over two hundred million pounds per annum.

Although lead-free petrol is being introduced with the intention of reducing obnoxious exhaust emission. However it will be realised that without lead additives to boost the final octane quality of the petrol the extra refining undertaken increases the percentage content of aromatics in the petrol, which results in the increase of polynuclear aromatics in the exhaust. The work concerning the increased emissions of polynuclear aromatics together with their carcinogenic property is well documented (86).

Although increase of aromatic content is not the only means of maintaining peresent octane quality, it appears to be the only practical means of reaching this objective quickly. With the PNA emissions taken into consideration then option 4 would be most attractive, resulting in reduced emission of all pollutants. This is the option adopted by Germany, and if the British Government's choice of Option three eventually proves to be an interim stage, then Option four will be the implemented option. Option four employs the use of a three-way catalytic converter which chemically reduces oxides of nitrogen, at the same time oxidising unburned hydrocarbons and carbon monoxide emissions.

In eliminating lead from petrol a scheme of gradual introduction of the new option is considered with 95% of all motor cars running on the new option after seven years. In these calculations exhaust emissions of lead were calculated, account being taken of the increased petrol consumption, but no technological improvement in the efficiency of the engine that may offset this increase. There is also an underlying assumption that in the event of the government choosing a particular option it would ultimately be enforced by legislation.

The economic penalty associated with each option for 100% implementation is shown in the table below, together with incurred cost to the individual motorist:

Option	Increased annual cost to individual motorist (Ref. Option 1) £	Increased cost on petrol, nationally (Ref Option 1) £ x 10^6
1	-	-
2	10	173
3	41	710
4	91	1576
5	28	485
6	26	450

The above table reflects the vast national differences between the various options. Of particular interest are the options four and five, which are the options recommended, because they result in the reduction of all emissions. The question of what the end solution might be cannot be considered independently of the future policy on gaseous emissions. Any further restriction on gaseous emissions of carbon monoxide, oxides of nitrogen and uburned hydrocarbons, would require the use of a three-way catalytic converter for this reason alone. Certainly the British Government's preference for Option three is both economically and environmentally disadvantageous; for with this option the removal of one hazardous compound is being replaced by another.

This study has been concerned with the problem and suggestions have been made from a scientific point of view. The Government may decide its policy on a political issue altogether; Option three entails no economic burden on the oil industry. The Government in deciding its policy may find it easier to burden one industry than another.

The final concluding point on this subject must be that whilst there is indeed an economic cost in the unleaded options, the potential penalties must be considered in a wider aspect, because the costs in real terms would indeed be smaller than they appear, because of the indirect savings on health, trees and a cleaner environment in general.

Octane Requirement Increase

Octane requirement increase of an engine is assumed to arise due to the volumetric and thermal insulating effect of the deposit. The volumetric effect has been calculated by considering the increased compression ratio that arises. The resulting octane level of fuel required for steady operation of the engine is read from a graph of octane requirement against compression ratio. The average value for the likely increase due to deposits in cars has been reported as approximately ten octane numbers. The increase in compression ratio of 0.25 units is equivalent to an increase of two octane numbers. With the Fiat engine in the laboratory an increase of 0.25 in compression ratio could easily arise with a deposit of thickness 0.23mm. However, deposits of relatively much greater thickness have been reported by other researchers, the average thickness of the unleaded deposit under investigation being 0.238mm. If the fuel quality does not incorporate the resulting ORI, the engine will knock.

Often the knocking inside an engine may itself dislodge some of the deposit. The random irregularity of the deposit, as seen under the scanning electron microscope, to some degree confirmed the continuous flaking and build up of deposit in very small localised layers.

Photographs of the deposit were taken under the scanning electron microscope and the optical microscope. Efforts were made under different magnification to identify a three layer strata that has been reported to exist (11). However no such precise strata type formation of the deposit could be found. The cross-sectional photographs highlighted the intensity of porosity of the deposit and inspired the technique for the measurement of the thermal conductivity.

Visual differences between the leaded and lead-free deposit are apparent from the photographs, together with deposit composition graphs. As mentioned earlier the photographs indicate the flaky nature of the deposit by the irregularity of its deposition.

Two previous studies made on the thermal conductivity of the deposit are of particular interest. In the first study (8) the deposit had been scraped, ground to a fine powder, washed and then coated uniformly onto a metal wire. This procedure destroys the porous nature of the original deposit and its treatment with a solvent could also affect its composition. In the second study (62) a thermocouple is embedded into the surface of the piston. As the deposit builds up the temperature recording from the thermocouple is continuously monitored. Although a great deal of useful data was obtained from this method, the fluctuating nature of the conditions inside the engine, made it difficult to determine thermal conductivity with precision. The thermocouple may also act as a localised catalyst and yield higher temperature values than would be reached without the thermocouple.

Because of the fundamental nature of the procedure followed in this research, in measuring thermal conductivity, the results have been obtained with confidence that they represent typical values of the right order and, because of the uneven surface, it is rather the effective thermal conductivity that has been measured. The values obtained for the Sindanyo plate are roughly 20% lower than the average quoted value, and similarly for the aluminium disc. Extra fibre glass insulation around the apparatus seemed to have little effect upon the measured values.

The thermal conductivity of the leaded deposit was measured between the range of 137°C and 244°C and averaged to a value of 0.75 $Wm^{-1}K^{-1}$. Similarly, the thermal conductivity of the lead free deposit stayed reasonably constant over a similar temperature range at 0.5 $Wm^{-1}K^{-1}$. These compare with the thermal conductivity of powdered graphite of 0.18 $Wm^{-1}K^{-1}$.

With the thermal conductivity of leaded deposit being somewhat 50% greater than that of the lead-free deposit, it is understandable why the engine run on lead-free petrol shows a greater ORI than when run on leaded fuel.

There is no previous data in the past relating to the porosity or the permeability of the combustion chamber deposits. Although standard equipment exists for the measurement of permeability for paper and boards (BS 6538), the size of the sample required made the apparatus impractical. However an improvised apparatus, that of Lea and Nurse, was used to determine the permeability of the deposit. In the past measurements made on this apparatus have been wrongfully used as one yielding data for porosity instead of permeability. Because of the nature of experimental technique, different samples had to be used for measuring permeability than those that are photographed.

In the past very little significance has been attributed to the porosity and permeability of the deposits, especially due to the earlier techniques used for determining thermal conductivity. In the present research,due to the availability of a single lead-free deposit with a fixed mileage of 13,000 km, the results obtained must be treated with caution due to their singularity. In determining both the thermal conductivity and permeability, the ideal set of experiments would have to be based on a number of deposits that are known to result in a known level of ORI. Only if such extensive data could be obtained, would it be possible for correlations of deposit properties to the induced ORI to be drawn with confidence. It is hoped that the present study will be an initiator in this field. Alternatively, a set of non-reactive artificial deposits could be formed on the piston head, with known thermal capacity, permeability, porosity and thermal conductivity, and precise correlations drawn in terms of ORI induced.

The measurement of permeability has been undertaken at atmospheric pressure and room temperature. The values therefore should be treated in a comparative manner, and values existing under turbulent conditions may be predicted.

Exhaust Emissions

There is a vast amount of general data available on the subject of exhaust emission. Previous work in this department (64) gave extensive data using petrol and blends containing oxygenates. A great deal of work was also carried out on alcohols. It was decided to analyse exhaust emissions arising from blends of fuels with ethanol using a three-way catalytic converter. This study complemented previous study in the department as a finishing touch to the subject.

Preliminary experiments were made with other fuels of various natures to gain experience with the engine and checks were made with various blends to ensure comparable results were obtainable. However only new experimental results are reported here, even though much other data was obtained.

Emission measurement produced relatively comparable results when plotted against engine speed. A greater variation of air/fuel ratio was hoped for but the range was found to be limited from 11.4 to 12.7. Thus, the performance of the catalyst could not be monitored using blends over a greater air/fuel ratio. In practice, in order to gain more efficient performance in a vehicle installed with a three-way catalytic converter, it should also be accompanied by a carbon monoxide sensing probe situated in the exhaust pipe. The sensing probe would electronically adjust carburettor inflow of fuel so as to retain the combustion mixture near stoichiometric value as much as possible. Experimental measurements during any knocking period were deliberately avoided as they represent unworkable conditions of the engine and resulted in greater emission of carbon monoxide and hydrocarbons.

The main programme of emission experiments involved initially the forecourt four star grade and the two star grade. Results indicated that greater emissions of CO and HC's resulted with the lead-free petrol than with the leaded grades, figure 63 and 66. However, as anticipated, the lead-free grade gave lower emissions with the use of the catalyst, determined at various engine speeds of the Fiat 127C engine,figure 67. The increased emissions of HC's and CO in the former case supporting work carried out by earlier researchers and assessments in the economic analysis.

Blends of alcohols with lead-free petrol gave reduced emission of carbon monoxide and hydrocarbons, both with and without the catalyst respectively, showing that blending with alcohol was another method of reducing emissions,figure 64,65,70 and 71. These tests were carried out without any changes to the carburettor or the engine, a general trend of reduction in carbon monoxide and hydrocarbons was obtained with increasing engine speed.

Mathematical Modelling

It is clear from measurements made in this study that the combustion chamber deposits act as thermal insulators and as such have adverse effects on the heat transfer through the engine, and from previous studies (69), the remaining portion of ORI (other than due to volumetric effect) is due to the insulating effect.

Many techniques have been developed over the years to study the problems associated with combustion deposits, and present knowledge of the circumstances surrounding the engine response has increased substantially. Nevertheless it was envisaged that the difficulty involved with reproducing exact engine cycles together with time and cost involved, led to the initiation of this particular theoretical approach to the problem. The work carried out in the past with heat transfer in the engine provided some useful information regarding steady-state or average heat transfer rates in an engine. However, the variation of heat transfer in a wide range of conditions would lead to some unexpected results, especially the relatively rare occasions when heavy knock arises with devastating effects. It therefore forms the basis of this study.

The mathematical model in Chapter 5 has been designed so as to yield results firstly when properties of the engine material can be varied together with the thickness of the construction material. Similarly, deposit build-up can be simulated by stepwise consideration of deposits of different thicknesses.

One of the uncertainties associated with any model is the value of the heat transfer coefficient. Though there are a large number of empirical formulae associated with this subject, only relationships of Annand, Wischoni and Eichelberg have been considered. All three of the relationships surprisingly show a similar degree of popularity, but show vast differences in numerical values of heat transfer coefficient, and also have been formulated from different basic fundamentals. However the pattern of heat transfer coefficient over the entire cycle is somewhat similar.

Heat flow through the piston head, cylinder top and cylinder walls has been considered. Each plane is assumed to be a one dimensional heat flow path. In simulating the deposit build up the engine is considered as:

i) clean with no deposits

ii) with deposit build-up.

The object of this model is to assess the heat flow at each degree of the engine cycle and to incorporate some form of feed back of heat into the incoming charge. This would affect the maximum temperature of the combustion process and in practice also indicate if premature ignition is to take place through hot spots that may occur. However, for the purpose of the mathematical model a temperature and pressure cycle was required to meet the needs of assessing the enthalpy and properties of the combustible mixture prior to burning. Similarly, properties of the burnt gases also need to be known. Experimental values of temperature and pressure would be ideal as experimental results of thermal conductivity are being employed and as such conclusions reached would indicate practical results. As this data was not available due to difficulties associated with it, a theoretical approach had to be adopted.

Due to the deposits enhancing detonation, data is determined using Hottel charts, as this procedure involves combustion at constant volume, as is the case in extreme knock conditions, resulting in very high temperatures and pressures being set up. Since the temperatures and pressures are sudden and indicative of extreme conditions, thus the resultant wall temperatures and heat flow changes also indicate maximum values. It however, does not incorporate the increase of compression ratio associated with the deposit volume and it is envisaged that further results can be obtained from this model presented in Chapter 5. Considerations of different wall materials and the effect of engine speed are incorporated and comparisons made using the three empirical heat transfer formulae discussed. Further work is recommended on the use of this model as it is envisaged that as an initial attempt only a small fragment of the results have been obtained and the possibility of other information being obtained is vast and varied.

It is recommended for future work that as a first step in improving the use of the mathematical model, that a computer program is written that will yield results at every 2° intervals of crank angle in the cycle, and incorporate in the model some criterion that will be directly related to the evidence of engine knock. In practice the outside heat transfer coefficient would be expected to be more variable in the air cooled engines, and it would be interesting to compare the results with the water-cooled engines. Further impending questions arose during the duration of this research on the equilibrium stage of deposition.

Resume' Of Conclusions

*Lead free petrol is being introduced with the intention of reducing obnoxious exhaust emissions.However without lead additives to boost the octane quality of the petrol, the extra refining undertaken increases the percentage content of aromatics.This is represented in an accumulative distillation graph,which shows relatively higher boiling constituents in lead free petrol.

*Due to different conditions, no straight forward analogy can be drawn between what option the British Government should follow,in regard to the options followed by other countries, on economic bases.

*From an economic analysis the present option adopted by the British Government for lead free petrol is both economically and environmentally disadvantageous,as demonstrated by the emission experiments.

*The option employing lead free petrol, RON 95,is concluded to be favourable in terms of being accepted socially due to no apparent increase in emissions and increased cost per gallonage.

*ORI effect due to the physical volume of the deposit is calculated by considering the increased compression ratio arising from that deposit.

*There is a vast difference between the elemental composition of leaded and unleaded deposits.

*Lead free deposit was found to consist of a two layer stratum, one much more porous than the other.

*The thermal conductivity of the lead free deposit is 0.5$Wm^{-1}K^{-1}$.The leaded deposit has a thermal conductivity about 50% greater.These compare with that of powdered graphite 0.18$Wm^{-1}K^{-1}$

*The permeability of the leaded deposit is 4.846 x $10^{-12}m^2$.

*Blends of alcohols with petrol gave reduced emissions of carbon monoxide and hydrocarbons. These were further reduced when the three way catalyst was employed, thus showing that blending with alcohol was another means of reducing exhaust emissions. A general trend of reduction in carbon monoxide and hydrocarbon emissions was obtained with increasing engine speed.

*Blending of petrol with ethanol has the adventage of boosting octane quality of the fuel together with reducing emissions of carbon monoxide and hydrocarbons. Ethanol also has the adventage of reducing or completely eliminating combustion chamber deposits,hence ORI.

*Higher exhaust pollulant emissions are obtained with lead free petrol than with leaded fuel.

*Using the mathematical model to simulate extreme knocking conditions it is shown that large differences in the heat transfer occur due to the presence of deposits in the combustion chamber.

NOMENCLATURE

A/F	Air / Fuel ratio
A and B	Crank angle related factors
b	Permeability of deposit (m-2)
b1	Constant in calculation of residual exhaust
	= 0 for wide open throttle
CORC	Co-operative Fuel Research Committee
Cp	Thermal capacity
D x D	Thickness of deposit segment in mathematical model
D x W	Thickness of wall segment in mathematical model
E	Thermal efficiency
E_{98}	Thermal efficiency attained with petrol of 98 RON
E_{86}	Thermal efficiency attained with petrol of 86 RON
ER	Exhaust residual (lb)
H	Enthalpy
ha	Enthalpy of fresh charge
h_{Annaud}	Annaud's heat transfer coefficient
He	Enthalpy of exhaust gases
$h_{Eichelberg}$	Eichelberg's heat transfer coefficient
hm	Enthalpy of combustion mixture
$h_{Woschin}$	Woschin's heat transfer coefficient
HC	Hydrocarbon
K	Constant
K_{Al}	Thermal conductivity of aluminium Wm-1 K-1
K_{Cu}	Thermal conductivity of copper Wm-1 K-1

K_d	Thermal conductivity of deposit Wm-1 K-1
K_{leaded}	Thermal conductivity of leaded deposit Wm-1 K-1
$K_{unleaded}$	Thermal conductivity of unleaded deposit Wm-1 K-1
$K_{Sindanyo}$	Thermal conductivity of Sindanyo plate Wm-1 K-1
MON	Motor Octane Number
n	Number of moles of gas
NO_x	Nitrogen oxides
ORI	Octane requirement increase
Pe	Exhaust pressure psia
PNA	Polynuclear Aromatics
$\frac{DP}{L}$	Pressure gradient across the deposit
Qv	Volumetric air flow through Alcock airflow meter l/min
R	Universal gas constant
r	Compression ratio
R1	Thermal conductivity of gas Cp μ / 0.7
Re	Reynolds number
RON	Research Octane Number
rpm	Revolutions per minute
T	Temperature (°C)
TEL	Tetra ethyl lead
Te	Exhaust temperature °R
Tm	Manifold temperature °R
TML	Tetra methyl lead

T(i,t)	Temperature of plane i at time t
U	Average velocity of gas through deposit
V1, V2, V3, V4, V5, V6	Volume, pressure and temperature at:
P1, P2, P3, P4, P5, P6	1.Unburnt mixture
T1, T2, T3, T4, T5, T6	2.After sentropic compression of unburnt mixture
	3.Conditions after combustion at constant volume
	4.After isentropic expansion after the combustion process
	5.Adiabatic expansion as the exhaust valves open
	6 .Exhaust gases left in the combustion chamber prior to mixing with fresh charge
W	Velocity factor = Wn + Wc
X	Distance between two indicated points H
αd	Thermal diffusivity of deposit $= \frac{(\rho c)_d}{Kd}$
αw	Thermal diffusivity of wall $= \frac{(\rho c)_w}{Kd}$
γ	Ratio of Cp / Cv
θ	Crank angle ÷ 2

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APPENDIX

APPENDIX

As an example to test the model, consider the deposit divided into two equal segments and the wall into two segments as well.

Consider a plane , that is surrounded by mass of material within the two dotted lines,figure 78, Equation 1 can therefore be written as

$$T_{(1,\tau D\tau)} = \frac{2\alpha d.D\tau}{Kd\ DxD} h_{g(\tau)}\left[T_{g(\tau)} - T_{(1,\tau)}\right] + \frac{2\alpha d.D\tau}{(DxD)^2}\left[T_{(2,\tau)} - T_{(1,\tau)}\right] + T_{(1,\tau)}$$

$h_{(g)}$= heat transfer on gas side

deposit density ρd= 17.33 lb/ft^3

Deposit thermal conductivity Kd = 0.3 Btu/hrftF

Volumetric specific heat Cd = 0.06 Btu/lbf

$D\tau$ = Time increment = = 9.26×10^{-8} hr

DxD = (deposit 0.5m) = 8.20×10^{-4} ft

Thermal diffusivity of deposit = 0.289

Putting the values in known terms, the equation for temperature at the gas, deposit interface becomes:

$$T_{(1,\tau+D\tau)} = 2 \times 1.088 \times 10^{-4} \times hg\left[Tg_{\tau} - T_{(1,\tau)}\right] + 2 \times 3.979 \times 10^{-2}\left[T_{(2,\tau)} - T_{(1,\tau)}\right] + T_{(1,\tau)}$$

........(11)

Similarly equation 2 reduces to:

$$T_{(2,\tau+D\tau)} = \frac{\alpha d\ D\tau}{(DxD)^2}\left[T_{(1,\tau)} + T_{(3,\tau)} - 2T_{(2,\tau)}\right] + T_{(2,\tau)}$$

$$T_{(2,\tau+D\tau)} = 2 \times 1.989 \times 10^{-2}\left[T_{(1,\tau)} + T_{(3,\tau)} - 2T_{(2,\tau)}\right] + T_{(2,\tau)} \qquad \text{............(12)}$$

Next the equation for the interface between deposit and wall can be written. Here the plane 3 is being heated or cooled by a different medium on each side.

$$T_{(3,\tau+D\tau)} = \left[\frac{\alpha d.\alpha w\ 2D\tau}{(\alpha w.Kd.DxW}\right]\left[\left[\frac{Kd}{DxD}(T_{(2,\tau)} - T_{(3,\tau)})\right] + \frac{Kw}{DxW}\left[T_{(4,\tau)} - T_{(3,\tau)}\right]\right] + T_{(3,\tau)}$$

Assuming the wall material to be aluminium.

Thermal conductivity of wall	Kw = 137 Btu/hrftF
Density of wall	$\rho w = 169$ lb/ft^3
Volumetric specific heat of wall	Cw = 0.248 Btu / ft^3 F
Thermal diffusivity of wall	$\alpha w = 3.269$
Wall thickness of segment	DxW = 9.84 x 10^{-3} ft

Putting the known values this reduces to

$$T_{(3,\tau+D\tau)} = 2x2.24x10^{-7}\left[\left[365.854\,(T_{(2,\tau)} - T_{(3,\tau)}) + 13922.764\left(T_{(4,\tau)} - T_{(3,\tau)}\right)\right]\right]$$

$$+ T_{(3,\tau)} \qquad \text{...........(13)}$$

The energy equation for a plane in the wall of the piston or cylinder wall is written by rewriting equation (4)

$$T_{(4,\tau+D\tau)} = \frac{\alpha w\, D\tau}{(DxW)^2}\left[T_{(3,\tau)} + T_{(5,\tau)} - 2T_{(4,\tau)}\right] + T_{(4,\tau)}$$

hence ∴

$$T_{(4,\tau+D\tau)} = 2 \text{ x } 1.563x10^{-3}\left[T_{(3,\tau)} + T_{(5,\tau)} - 2T_{(4,\tau)}\right] + T_{(4,\tau)} \qquad \text{.........(14)}$$

finally for the coolant and wall interface

$$T_{(5,\tau+D\tau)} = \frac{2\alpha w\, D\tau}{(DxW)^2}\left[T_{(4,\tau)} - T_{(5,\tau)}\right] + \frac{2\alpha w\, D\tau}{(Kw.DxW)}\, hc\left[T_{(c)} - T_{(5,\tau)}\right] + T_{(5,\tau)}$$

$$T_{(5,\tau+D\tau)} = 2x3.126x10^{-3}\left[T_{(4,\tau)} - T_{(5,\tau)}\right] + 2x1.820x10^{-5}\left[T_{(c)} - T_{(5,\tau)}\right] + T_{(5,\tau)}$$

$$\text{.........(15)}$$

heat transfer on coolant side hc = 100

when θ $=180^{o}$

Temperature of gas $= 4698^{o}F$

and pressure =

hg for Eichelberg = 438

Also assuming coolant temperature = 80^{o}F

Rewriting all the equations with initial temperatures listed

$$T_{(1,\tau+D\tau)} = 9.54\ \text{x}10^{-2}\left[T_{(g,\tau)} - T_{(1,\tau)})\right] + 7.96\ \text{x}10^{-2}\left[T_{(2,\tau)} - T_{(1,\tau)}\right] + T_{(1,\tau)}$$

$$T_{(2,\tau+D\tau)} = 3.98\ \text{x}10^{-2}\left[T_{(1,\tau)} + T_{(3,\tau)} - 2T_{(2,\tau)}\right] + T_{(2,\tau)}$$

$$T_{(3,\tau+D\tau)} = 4.48\ \text{x}10^{-7}\left[365.85\left(T_{(2,\tau)} - T_{(3,\tau)}\right) + 13922.76\left(T_{(4,\tau)} - T_{(3,\tau)}\right)\right] + T_{(3,\tau)}$$

$$T_{(4,\tau+D\tau)} = 3.13\ \text{x}10^{-3}\left[T_{(3,\tau)} + T_{(5,\tau)} - 2T_{(4,\tau)}\right] + T_{(4,\tau)}$$

$$T_{(5,\tau+D\tau)} = 6.25\ \text{x}10^{-3}\left[T_{(4,\tau)} - T_{(5,\tau)}\right] + 3.64\ \text{x}\ 10^{-5}\left[T_{c} - T_{(5,\tau)}\right] + T_{(5,\tau)}$$

let the initial temperatures be equal to

$T_1 = 1500^{\circ}$F

$T_2 = 1300^{\circ}$F

$T_3 = 1300^{\circ}$F

$T_4 = 1000^{\circ}$F

$T_5 = 400^{\circ}$F

$T`_c = 80^\circ F$

$T_g = 4698^\circ F$

$h_g = 438^\circ F$

1st Iteration	2nd Iteration
$T_1 = 11789.17$	T_1 2028.65
$T_2 = 1311.51$	T_2 1331.61
$T_3 = 1099.41$	T_3 1089.82
$T_4 = 998.43$	T_4 996.88
$T_5 = 403.73$	T_5 407.43

3rd Iteration	4th Iteration
$T_1 = 2227.82$	T_1 2394.24
$T_2 = 1358.01$	T_2 1391.04
$T_3 = 1098.23$	T_3 1097.63
$T_4 = 995.35$	T_4 993.84
$T_5 = 411.09$	T_5 414.72

The initial values were arbitrarily chosen but temperature swings are apparent with each iteration. From these iterations we can see that the initial temperatures chosen are far away from the true temperatures, therefore another estimate is made.

$T_1 = 4109$	T_1 4108.91
$T_2 = 3402$	T_2 3402.04

$T_3 = 12696$	T_3 2696.00
$T_4 = 2678$	T_4 2677.99
$T_5 = 2659$	T_5 2659.02

Now since the greatest difference in the new temperatures and the temperatures calculated in the previous iteration is less than 0.1°F, thetemperatures in and on the deposit and wall are as stated above and calculation terminated.

Similarly using Woschani relationship where hg = 354 Btu/ft^2 F.

The temperature profile using the above formulae has been calculated and shown below

$T_1 = 4376^{\circ}$F

$T_2 = 3624^{\circ}$F

$T_3 = 2873^{\circ}$F

$T_4 = 2851^{\circ}$F

$T_5 = 2833^{\circ}$F

Finally using Annands relationship hg = 241 Btu/ft^2 F

The temperature profile is obtained and listed below

$T_1 = 3728^{\circ}$F

$T_2 = 3089^{\circ}$F

$T_3 = 2451^{\circ}$F

$T_4 = 2434^{\circ}$F

$T_5 = 2417^{\circ}$F

Using the simplest model with deposit, surface temperatures have been calculated for each of the three relationships most common in use. The correct choice of transfer correlation is important, as temperatures can differ by up to 648°F depending on the correlation used.

Similar equations for the case of a clean engine have been written and for the case of Woschani correlations the temperatures are presented below

$Tc_1 = 4220^{\circ}F$

$Tc_2 = 4191^{\circ}F$

$Tc_3 = 4161^{\circ}F$

The above temperatures correspond to Tc_1 gas-wall interface; Tc_2 within the centre of the wall and Tc_3 at the coolant-wall interface.

The difference of heat flow between the two cases for an engine with a piston radius of 2.67in. is equivalent to 41.1 Btu in one minute if the conditions were continuously retained as when $\theta = 1800$.

The above calculations have been calculated for heat flow through an engine, with and without a deposit on the piston head. Similar equations can be written and evaluated for the case of cylinder top and cylinder walls.

Appendix 2

Woschni's heat transfer coefficient

$h = 110\,(PW)^{0.8}\ d^{-0.2}\ T^{-0.53}$ Kcal / M hr k

P = Gas pressure (psia)

T = Gas temperature (K)

d = Bore diameter (M)

W = Gas velocity $\equiv$ Wn + Wc

Wc = 2.28 CM during compression and expansion

or 618 CM during intake and exhaust

CM = Mean piston speed

Wc = $3.24 \times 10^{-3}\ \frac{Vd}{Vs}\ \frac{(P\ \ Pm)}{Ps}$ during compression and expansion

Pm = Manifold pressure

Ps, Vs, Ts = pressure, volume and temperature at spark

θ crank angle	P Gas press. (psia)	T Gas temp. °F	h Heat transfer coeff $BTU hr^{-1} ft^{-2} F^{-1}$
0	14.4	1810	85.3
30	14.4	1130	103.18
60	14.4	365	143.0
90	14.4	140	172.8
150	30.0	242	128.8
180	235/1175	628/4698	531.0/854.1
210	243	3308	282.6
240	112	2983	159.2
270	85/15.0	2900/2040	129.3/28.1
300	15.0	2040	28.1
330	15.0	2040	28.1
360	15.0	2040	28.1

Annards heat transfer

Approximate gas properties $h_{Annard} = \frac{a}{d} k (Re)^b$

$Cp = C_0 + C_1 T$

$C_0 = 0.263, \quad C_1 = 0.5288 \times 10^{-4}$

$\mu = \mu_0 T^m$

$m = 0.645, \quad \mu_0 = 3.07 \times 10^{-7}$

$a \cong 0.5$ for 4 stroke engines

$b = 0.7$

Bore diameter (d) = 65 mm = 0.213 ft

Velocity of gas ≡ velocity of piston = 3.4 m/s = 11.155 ft/sec

$R = Cp\,\mu / 0.7$, rpm = 1500, stroke = 68 mm

θ crank angle	T (K) gas temp.	$\mu \times 10^{-7}$ Gas Viscosity lb ft^{-1} sec^{-1}	Cp Gas heat capacity c.h.u. lb^{-1} $°C^{-1}$	Rt Reynold's number	$k \times 10^{-5}$ Thermal conductivity c.h.u. ft^{-1} sec^{-1} $°C^{-1}$	e gas density lb/ft^3 x 10^{-2}	h BTU hr^{-1} ft^{-1} F^{-1}
0	1261	306.97	0.3297	5465.39	1.446	7.05	50.39
30	883	243.94	0.3097	6877.56	1.079	7.05	43.19
60	476	163.75	0.2882	10245.57	0.674	7.05	35.99
90	333	130.05	0.2806	12900.51	0.521	7.05	33.12
120	349	134.85	0.2815	14344.08	0.539	8.08	35.99
150	390	144.00	0.2836	207773.08	0.408	12.57	25.99
180	604/ 2865	190.94/ 521	0.2949/ 0.4143	79129.18/ 28999.85	0.560/ 2.157	63.49	126/ 241
210	2093	425.63	0.3737	7027.99	2.272	12.57	93.6
240	1912	401.51	0.3641	4788.98	2.088	8.08	64.8
270	1866/ 1388	395/ 326.57	0.3617/ 0.3364	4247.37	2.041/ 1.096	7.05	68.4
300	1388	326.57	0.3364	5137.37	1.096	7.05	35.99
330	1388	326.57	0.3364	5137.37	1.096	7.05	35.99
360	1388	326.57	0.3364	5137.37	1.096	7.05	35.99

Eichelberg's heat transfer coefficient

$$h = 0.1627\ (PT)^{1/2}\ (RPM / 1000)^{1/3}\ \mathrm{BTU\ hr^{-1}\ ft^{-2}\ {}^{\circ}F^{-1}}$$

θ crank angle	P Gas press. psia	T Gas temp. °F	h Heat transfer coefficient BTU hr^{-1} ft^{-2} °F^{-1}
0	14.4	1810	30
30	14.4	1130	24
60	14.4	365	13.5
90	14.4	140	8
120	17.0	170	10
150	30.0	242	16
180	235/1175	628/4698	72/438
210	243	3308	167
240	112	2983	107
270	85/12.0	1900/2040	92/33
300	15.0	2040	33
330	15.0	2040	33
360	15.0	2040	33