ALCOHOLS AND OTHER OXYGENATES IN AUTOMOTIVE FUELS

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Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

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The aim of this research was to assess the effect of oxygenated hydrocarbons on the knocking characteristics of an engine when blended with low-leaded gasoline.

Alcohols, ethers, esters and ketones were tested individually and in various combinations up to an oxygen content of 4 % wt/wt in a blend with Series F-7 gasoline of 90, 92, 94 and 96 RON. Tests were carried out at wide open throttle, constant speed and standard timing setting. Engine speed was varied using a dynamometer and knock was detected by two piezoelectric transducers, one on the cylinder head monitoring all four cylinders and one monitoring the cylinder most prone to knock. The engine speeds associated with trace and light knock of a continuous nature were noted.

Curves were produced for each oxygenate blend of base RON used against engine speed for the two knock conditions which were compared with those produced using pure Series F-7 fuels. From this a suggested RON of the blend was derived. RON increase was less when using a higher RON base fuel in the blend.

Most individual oxygenates showed similar effects in similar concentrations when their oxygen content was comparable. Blends containing more than one oxygenate showed some variation with methanol/MTBE/3 methyl butan-2-one and methanol/MTBE/4 methyl pentan-2-one knocking less than expected and methanol/MTBE/TBA also showing good knock resistance. Further tests to optimise initial findings suggested a blend of methanol and MTBE to be superior although partial replacement of MTBE by 4 methyl pentan-2-one resulted in a fuel of comparable performance.

Exhaust emissions were tested for a number of oxygenated blends in 2-star gasoline. 2-star and 4-star fuels were also tested for reference. All oxygenate blends reduced carbon monoxide emissions as expected and hydrocarbon emissions were also reduced. The largest reduction in carbon monoxide occurred using a 14.5 % (1 : 1 : 1) methanol/MTBE/4 methyl pentan-2-one blend. Hydrocarbon emissions were most markedly reduced by a blend containing 25.5 % 4 methyl pentan-2-one.

Power output was tested for the blends and indicated a maximum increase of about 5 % at low engine speeds. The most advantageous blends were methanol/ 4 methyl pentan-2-one (6 : 5) 11 % in 2-star and methanol/MTBE/4 methyl pentan-2-one (6 : 3 : 2) 11 % in 2-star.

In conclusion methanol/MTBE (6 : 5) and (5 : 5), and various combinations of methanol/MTBE/4 methyl pentan-2-one, notably (6 : 3 : 2) gave good results in all tests conducted. CFR testing of these blends showed them to increase both RON and MON substantially.

Key Words: *Alcohols* *Gasoline* *Knock* *Octane Number* *Oxygenate*

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INTRODUCTION

INTRODUCTION

Research during the last hundred years has shown that oxygenated hydrocarbons are very suitable fuels for the internal combustion engine. From its early beginnings Otto and others recommended ethanol as a fuel and this has gained and lost favour during changes in the availability of gasoline and variations in its relative price. Until the recent dramatic fall in oil prices oxygenates of many types were being seriously considered as blending agents at up to 20 % replacement of gasoline; however the present climate has reduced the economic attractiveness of such schemes. Brazil has a government policy to reduce oil imports by using home produced alcohol and this has not changed. The United States of America also supports ethanol blending in substantial quantities by subsidies to farmers and other countries are encouraging oxygenate blending. In many countries the production of ethanol from agricultural crops is not feasible due to the limited availability of land and this is the case in Europe. Methanol is favoured in many of these areas and in some methyl tertiary butyl ether (MTBE) is also used in small quantities.

Much research has been carried out using individual oxygenates including performance of the fuel blend, emissions, materials compatability and others. Very little information is available on ketones and esters and, apart from mixtures of tertiary butanol (TBA) with methanol, almost no information exists for combinations of oxygenates and any useful synergistic effects which may exist when blended with gasoline.

Oxygenated hydrocarbons which are relatively small and branched in structure have been found to be high quality fuels exhibiting higher octane numbers than gasoline in many cases. This property is the main reason for the current interest in their use especially in the cases of low and unleaded gasoline. Many oxygenates have shown better octane enhancement properties in unleaded fuels. The quality of a fuel is the determining factor for maximum compression ratio and hence power output that can be achieved for a given combustion volume without spontaneous combustion ahead of the steadily burning flame front which is known as "knock", "pinking" or "detonation". Engine knock is an annoyance to drivers but under certain conditions, usually high engine speed, can be destructive towards the engine.

In this research oxygenates have been tested in a low-leaded gasoline individually and in various combinations to determine their knocking characteristics as well as possible useful synergistic effects. The oxygenates chosen include many of the well known and extensively tested ones for comparison as well as virtually untested chemicals. Combinations of chemical type were tested to determine whether this played a significant roll in the overall effect or if it was purely component dependent. The oxygen content of the fuel blends was kept down to below 4 % wt/wt to avoid the need to change carburettor settings found in a normal automobile.

The test engine was operated as near to ordinary road conditions as possible and promising blends were retested using a standard CFR octane rating engine to determine actual blend octane numbers. Exhaust emissions and power output of the test engine used were also monitored for comparison with ordinary gasoline and each other.

CHAPTER 1

LITERATURE SURVEY

LITERATURE SURVEY

1.1 Spark Ignition Engine Knock

Knock is a major factor in determining the output of an engine as it limits the compression ratio (CR) which can be used. Excessive knocking is known to cause engine damage and in some cases complete structural failure (10, 11). Much work has been carried out on the subject since its discovery in the last part of the nineteenth century, the most intensive periods being in the 1950's and 1960's when higher performance cars were increasingly in demand. Tetra ethyl lead was discovered as a very effective anti-knock compound and has been used since the 1920's. However, due to concern over emissions its use is slowly being phased out. There is, therefore, renewed interest in knock, its causes and prevention.

It is generally accepted that knock is caused by the spontaneous combustion of the last fraction of the unburned charge in the cylinder leading to a rapid increase in pressure (Figure 1) producing a pressure wave which rebounds from side to side in the cylinder causing the knocking sound.

The velocity of the pressure wave is in the order of 500 m/s (29, 37) compared to the flame front speed of 25 m/s. Autoignition of the last part of the charge usually occurs between 2° and 15° after top dead centre (ATDC) (8, 29, 38), and the predominant frequency of knock has been reported by several authors as for example 5 to 7 kHz (28), 8.5 kHz at 2000 rpm and 9.3 kHz at 5000 rpm (39) and using holographic vibration analysis 8 to 12 kHz by Felski and Hoppe (40). As well as the sharp rise in pressure associated with knock measurements have shown (38) that there is an increase in actual peak cylinder pressure. Knock intensity appears to be a function of unburned charge mass remaining at the time of knocking combustion (28).

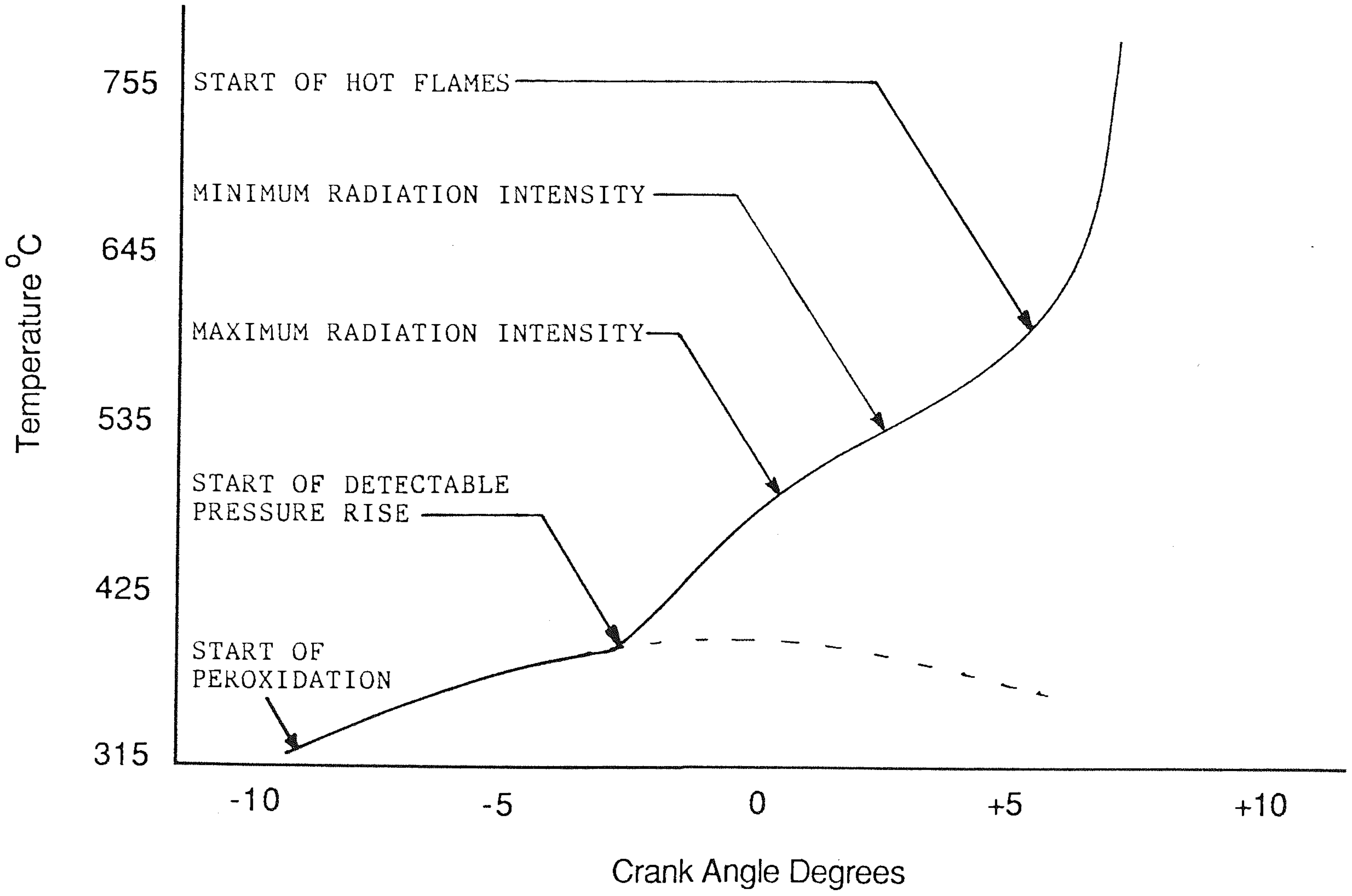

Figure 1 Temperature-Time Curve for N-hexane Auto-ignition Conditions

This is reasonable as a larger mass exploding is likely to produce greater shock waves.

Knocking combustion is a multistage oxidation involving the production of hydro-peroxides which decompose to free radicals at higher temperature and pressure. The reaction proceeds via a degenerate branched-chain mechanism resulting in a run-away reaction. The mechanisms involved are initiation, propagation, chain branching and termination.

1.2 Initiation

Initation occurs by the abstraction of a hydrogen atom from an alkane by an oxygen molecule to form an alkyl radical and a hydro-peroxy radical (1, 2, 3, 4). The reaction is slow and selective, C-H bonds being broken in the order 3^y, 2^y, 1^y.

$$R \quad + \quad O_2 \quad \text{------>} \quad R^* \quad + \quad HO_2^* \qquad \text{—— } 1$$

1.3 Propagation

The alkyl radical may do one of four things, decompose, disproportionate, isomerise or react with fuel or oxygen. Below 300°C in the presence of oxygen the predominant path is reaction with oxygen (3, 4, 5).

$$R^* \quad + \quad O_2 \quad \text{------>} \quad \underset{\text{peroxide radical}}{ROO^*} \qquad \text{—— } 2$$

The peroxide radical formed may isomerise to ${}^*C_nH_{2n}OOH$ and then decompose to aldehydes, ketones or o-heterocyclics plus a hydroxy radical. Many workers (3, 6, 7, 8, 16) have noted the occurence of aldehydes, ketones etc in partially combusted mixtures supporting this idea. The hydroxy radical may then react with another alkane, abstracting a hydrogen atom so that :-

$$OH^* \quad + \quad R \quad \text{------>} \quad R^* \quad + \quad H_2O \qquad \text{—} \quad 3$$

At higher temperatures the following is possible,

$$R^* \quad + \quad O_2 \quad \text{------>} \quad \underset{\text{alkene}}{R} \quad + \quad HO_2^* \qquad \text{—} \quad 4$$

1.4 Degenerate Chain Branching

Thermal decomposition of peroxide radicals may produce hydro-peroxides and complex intermediates,

$$ROO^* \quad + \quad R \quad \text{------>} \quad \underset{\text{hydro-peroxide}}{ROOH} \quad + \quad R^* \qquad \text{—} \quad 5$$

followed by

$$ROOH \quad \text{------>} \quad \underset{\text{alkoxy radical}}{RO^*} \quad + \quad OH^* \qquad \text{—} \quad 6$$

1.5 Termination

Termination of these reactions may occur by radical-radical interaction or destruction at the cylinder walls,

$$2ROO^{*} \text{ ------> } ROOH + \underset{\text{alkene}}{R} + O_2 \quad \text{—} \quad 7$$

$$ROO^{*} + HO_2^{*} \text{ ------> } ROOH + O_2 \quad \text{—} \quad 8$$

$$2HO_2^{*} \text{ ------> } H_2O_2 + O_2 \quad \text{—} \quad 9$$

Low engine speed knock is usually audible to the driver but is not damaging to the engine. High engine speed knock, however, is often inaudible above the engine, road and wind noise. The most severe knock, which can be very damaging, often occurs at motorway cruising speeds, 4000 to 5000 rpm (10) and modern high compression engines increase the tendency to knock. Engine design and previous abnormal operation are also important (11). Many engines will fail in less than 50 hours under conditions of heavy knock and the damaging effect of knock is cumulative.

The most common damage sustained by an engine is pitting of the piston and cylinder head, gasket failure and piston lands failure, the type of damage being dependent on the engine design. Some cars are now fitted with knock sensors which although useful to some degree may allow an engine to operate in light knock for long periods. This is because if set too light engine noise can be confused with knock leading to an automatic retarding of the ignition and hence worse performance. This results in manufacturers setting them to trigger under medium knocking conditions.

1.6 Hydrocarbon Combustion

Non-isothermal oxidation of hydrocarbons in a closed vessel is usually associated with a transient pressure change. The characteristics of which classify the combustion behaviour. Of the four basic types observed:-

i. Slow combustion - almost isothermal, gradual pressure rise.
ii. Single or multiple cool flame - fluctuations in slow combustion pressure rise.
iii. Two stage ignition - cool flame and large pressure pulse.
iv. Single stage - large pressure pulse.

Knocking combustion appears to be of the third type. The occurrence of cool and hot flames have been noted by many workers (12, 13, 14) and high speed photography up to 500,000 frames per second (15) indicates spontaneous ignition of the end gases in more than one place.

1.7 Low Temperature Combustion

A two stage ignition mechanism is one where as temperature increases the pressure required for ignition sometimes passes through several maximum and minimum values. The region surrounding a minimum is known as a "lobe" and from work by Walsh (9) it appears that the more lobes present, the more likely knock will occur. The nature and amount of oxidant, the nature and extent of the containing vessel surface and the structure of the fuel all affect the formation of cool flames. Among the products of these cool flames are alkenes, alcohols, aldehydes, ketones and organic peroxides. In a study using a CSTR to investigate knock, ie combustion in a steady state vessel, Lignola (12) observed cool flame oscillation which could be either damped or periodic in nature depending upon the temperature of the system. The damped cool flames were associated with a negative temperature coefficient of rate of reaction. He supports work by Fish (13) that the cool flame combustion is controlling but as yet which cool flame products control subsequent ignition are not known.

From Figure 2, a simplified ignition diagram for all hydrocarbons, the area in which cool flames occur can be seen. To the right of the curve ignition is possible. Following the line from A to B ignition becomes easier. From B to C it is more difficult and after C the higher temperature mode of combustion takes over. C to E extrapolates the high temperature mode and C to F the low. Between ABC and AGC is the cool flame region where B the point of minimum pressure is a lobe, and is also the point of minimum ignition delay. The value of pressure in the diagram is greater as the carbon chain length decreases and branching increases.

To the left of DCGA, slow no flame oxidation occurs where there is less chain branching. The autocatalytic action here eventually leads to hot and cool flames. The low temperature mode is sensitive to fuel structure and the association of structure to knock implies low temperature ignition is important.

Cool flames appear as a blue glow throughout the chamber over 30° or 40° crank angle at about 380°C (3).

1.8 Higher Temperature Combustion

As the temperature increases a deeper blue flame is apparent accompanied by a large energy release, and a motored engine will drive itself at this point. There is also an increase in hydro-peroxide and formaldehyde concentration. Greater

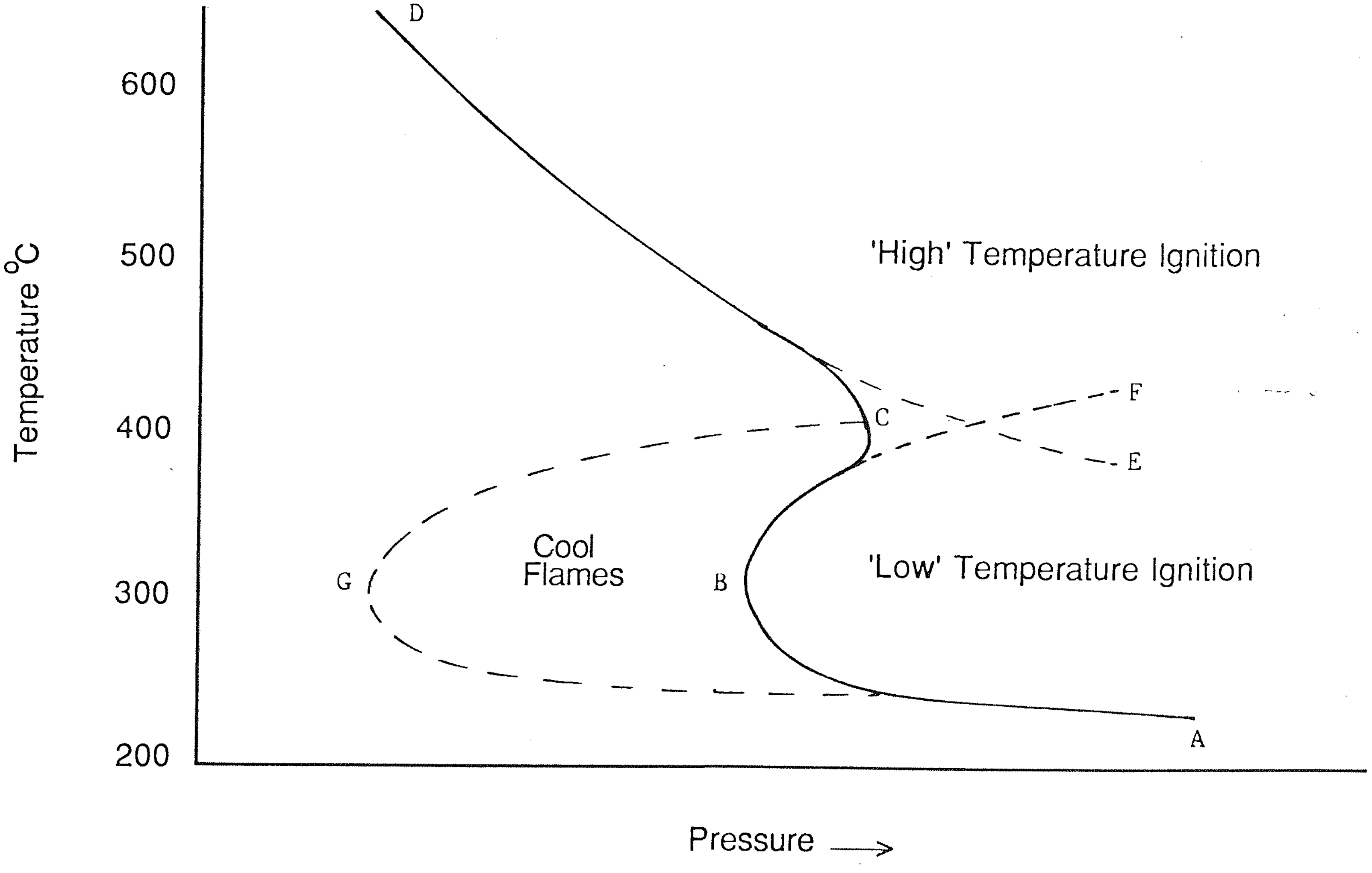

Figure 2 Simplified Ignition Diagram for Hydrcarbons

temperature still results in auto-ignition. This often occurs when the fuel air mixture [illegible] of higher [illegible]

1.9 Factors Affecting Knock

Many things influence the combustion behaviour of gasoline in a spark ignition engine. They can be broadly classed as external influences and fuel properties and it is the latter which are of the most interest in this study.

1.10 External Influences on Knock

As previously mentioned knock limits the compression ratio that can be used in an engine. This is because the increased pressure associated with a greater compression ratio promotes increased temperature before the spark which can cause spontaneous ignition. A higher inlet temperature promotes knock (35) as do higher mixture temperature and increase in cooling water temperature.

Knock is most likely in most cars at wide open throttle. This is because the charge is greater and so then is the pressure. Ignition advance is very important as is engine speed, higher speeds allowing less time for peroxide formation.

Air humidity (absolute) has a small effect as the vapourisation of water droplets reduces the charge temperature increase during compression, and air/fuel ratio has some effect although it varies among engine types as to whether a rich or lean mixture is worst. One of the most important factors is engine design where the shape of the cylinder head and its effect on turbulence, heat removal and flame path length can be crucial.

Fuel segregation during wide open throttle acceleration sometimes results in what is termed transient knock (17, 28). This often occurs when the fuel air mixture entering the inlet manifold contains a large number of droplets of higher boiling material. These droplets are commonly aromatic components which are highly resistant to knock. The vapourised portion of the fuel may thus be less resistant and depending upon the distribution of the droplets one or more cylinders may receive poor quality fuel and so knock.

Combustion chamber deposits are also important, and there is an octane requirement increase (ORI) as deposits increase (28). However, with leaded gasoline these deposits build up and fall away in a cyclic manner. Unleaded gasoline has a different type of deposit which does not break down and appears to be less thermally conductive which may lead to a large ORI with time.

1.11 Fuel Properties in Relation to Knock

Investigations into which hydrocarbons have the best resistance to knock soon identified trends. In the 1920s Ricardo showed toluene to be highly knock resistant and Edgar in 1931 found that branched chain hydrocarbons, such as iso-octane, have a high anti-knock rating. 1931 also saw the development of the standard tests for anti-knock quality using Ricardo's variable compression engine. Rating n-heptane as 0 and iso-octane as 100 the octane rating scale was developed. Hydrocarbons were then rated against a mixture of these two and given an octane number equal to the percentage of iso-octane in a comparable blend.

The main results of many researchers work have shown that the highest octane numbers are obtained with aromatics eg benzene, toluene followed by highly branched iso-paraffins. Paraffins and olefines decrease in octane number as the chain length increases but larger branched isomers are usually better than shorter straight chains. Naphthenes are also high octane compounds. Side chain addition to aromatics and naphthenes reduces the octane number, however, branching of the side chain reduces the deterioration.

Owen (17) states that fuels with a large amount of preflame oxidation are the most susceptible to knock, as would be expected from the earlier description of knock and the rate of formation of peroxides. Hawthorn and Scott (18) elaborate by suggesting that molecular structure influences the chain process by determining the amount and availability of internal energy required for bond fission and the relative attack of hydrogen-carbon bonds and also influences the stability and ease of oxidation of the radical fragments from fission and of the molecules of these radicals.

1.12 The Co-operative Fuel Research Committee (CORC) Octane Number Test Methods

As already mentioned the octane number of a fuel is the percentage by volume of iso-octane in an iso-octane/n-heptane mixture with the same knocking tendency as the fuel. The two CORC test methods for rating a fuel use the same variable compression CFR engine at different operating conditions. These are known as the Research and Motor methods and the conditions are shown below.

	Research Method	Motor Method
Engine speed rpm	600	900
Air intake temperature ˚C	room	38
Mixture temperature ˚C	not controlled	149
Ignition advance	13°	variable
Coolant temperature ˚C	100	100

Primary reference fuels (PRF) which are mixtures of iso-octane and n-heptane give the same results for each test. Gasoline blends, however, do not. The motor number is usually less than the research number by about nine octane numbers and this difference is known as the sensitivity of the fuel, s. For modern high compression engines the control of both of these numbers is important as at lower engine speeds the fuel is best represented by the research octane number (RON), whereas at higher speeds under more severe operating conditions the motor octane number (MON) of the fuel is more important, although for some engines MON appears to be more important throughout the speed range (10). That is to say that two fuels having a RON of 97 (typical premium gasoline) but MONs of 88 and 83 may be indistinguishable at low engine speeds but the one with the lower MON may knock severely at high engine speeds.

As previously stated fuel segregation may occur during wide open throttle (WOT) accelerations with some fuels and so a knowledge of the boiling characteristics related to octane numbers of a gasoline is important. The R_{100} number is a measure of research octane number of the lighter components which boil off up to 100°C, the front end octane number (FEON). The difference between this and the whole fuel research octane number is known as the ΔR_{100} which is preferably small.

1.13 The Anti-knock Quality of Oxygenates

Most of the work carried out in the past has concerned methanol and ethanol and more recently tert-butanol (TBA) and methyl tert butyl ether (MTBE). When Otto listed fuels suitable for his engine he included ethanol and its high anti-knock quality has been noted by many researchers. It was also used during the second world war mixed with kerosene when gasoline supplies were low. Methanol became of interest as a fuel for very high compression racing car engines and is still used today. Blending with forecourt gasoline was a later development.

Oxygenates burn in the same way as hydrocarbons (9, 20) with cool and hot flames, although the formation of knock-promoting formaldehyde has been detected as an intermediate with methanol and ethanol. Townsend and MacCormac noted the combustion of acetone in air produced one cool flame with one lobe and later work by Bradwel and Hinshelwood (20) noted cool flame periodicity with higher ketones but again only one lobe. This supports Walsh's suggestion (9) that one prominant lobe is a sign of high knock resistance when one considers the octane numbers of these ketones, eg 4 methyl pentan-2-one (4MP2 also known as methyl iso-butyl ketone, MIBK). Referring back to Figure 2, the temperature of the point B on the diagram, ie the lobe, for all hydrocarbons is around 300°C and D is well over 400°C. This is also the case for most oxygenates, however, ethers have lower ignition temperatures point B being of the order of 200°C (9, 21) and D is below 400°C (9). This low temperature ignition behaviour may in part account for the very high octane number of many of the ethers. Hinshelwood and Eastwood (21) observed two stage ignition with one lobe for dimethyl ether and two lobes with higher ethers which goes against a very high octane number, however, the low temperature ignition factor may offset this. Oxygenates are all high octane components which may in part be due to their fast flame spread speed compared with hydrocarbons (36).

One problem concerning the oxygenates is their sensitivity to more severe engine operating conditions, ie they have a relatively low MON. A large variation exists in reported RON and MON data especially for methanol and ethanol, eg 105 to 115 RON and 88 to 95 MON for methanol; however, these figures are for pure methanol and it has been observed that when blended with gasoline the effect observed is greater than these numbers suggest. A low octane number gasoline is very much more enhanced than a high one (23, 26, 30, 33) which has led to the use of research and motor blending octane numbers, RBN and MBN. Values for methanol and ethanol vary more greatly than others as before but part of this is now due to the base gasolines used in researchers work. Small temperature variations in RON and MON tests could also account for some of this (33). However, typically both methanol and ethanol have blending sensitivities of up to 30, compared to gasoline of 9 or 10. This worsening of sensitivity may result in a reduction in blend MON (24, 25, 27) leading to high speed knock or RON give-away which is expensive (33, 34). The low MON of methanol has been associated with pre-ignition tendencies (22), however, in blends up to 20 % this is not a problem.

There is a large variation in the range of RON, MON, RBN and MBN of oxygenates reported in the literature depending on the base fuel used. In this work and those given in Table 17, the RBN and MBN average for four gasoline bases reported by Cahn (23), are used. As can be seen these oxygenates are all high octane number components and they are also all very volatile. This has the effect that the FEON of a blend contains most of the oxygenate and thus the FEON is much improved (25, 26, 31) leading to a reduction in the occurrence of transient knock.

Work by Cahn (23) has shown that as with hydrocarbons branchiness of oxygenates increases the octane number. He agrees with other workers that a lower base gasoline gives the best octane improvement, as was found in this work. The results from his work helped to determine which oxygenates were worth pursuing especially the ketones. Correlations between functionality type, position and shape of hydrocarbon backbone were studied to enable extrapolation to predict other useful oxygenates. The general conclusions drawn were that the position of the functional group verses the hydrocarbon backbone showed no correlation, although secondary and tertiary positions were better than primary. The effect of the position is independent of the hydrocarbon backbone structure but is a function of the primary base octane number. There does, however, appear to be a correlation between functionality and backbone structure and a weak correlation between the position of functionality and functionality.

1.14 The Effect of the Olefinic Content of the Base Gasoline

From research by Russell (31), Marhold and Tranie (41), Mrstik (42) and others (24, 25, 26, 43) it has become accepted that the hydrocarbon types in a gasoline blended with oxygenates can affect the octane improving effect of the oxygenate. The most notable effect is of that due to the olefinic content of the base gasoline. Two conditions in which knock is usually studied are acceleration and constant speed. Critical knock speed is also determined. Critical knock speed has been found to be much higher with olefinic fuels, 3500 - 3900 rpm compared with 1300 - 1400 rpm for non-olefinic (31, 42) and Marhold and Tranie (41) determined the maximum octane requirement of non-olefinic fuels as 2500 rpm and 20 % olefinic fuels as 4500 rpm. Marhold (24) suggests that MTBE increases fuel quality no matter what the base fuel but that methanol and especially ethanol are detrimental in olefinic fuels.

Russell's treatment of data obtained by Associated Octel and ARCO (33) using RON depreciation [ie RON - Road ON where Road ON (RdON) = (RON + MON) / 2] attempts to eliminate any effect due to slight changes in RON of the blends. However, using the same data a different interpretation of these results may be found in a paper by Mrstik (42) who relates the oxygenate blends to change in RdON. This shows a reduction in lowering of RdON for olefinic fuels compared to non-olefinic fuels at constant speed which is the opposite of Russel's interpretation of these results. Otherwise they agree that all oxygenates improve the quality of a non-olefinic gasoline under accelerating conditions, and that at constant speed methanol and ethanol are detrimental whereas MTBE and TBA may be beneficial. Also fuel containing 15 % olefines was depreciated under accelerating conditions especially when ethanol was used.

Russell's interpretation of the constant speed olefine fuel results is supported by the fact that MON improvement especially for methanol and ethanol in such cases may be zero or even negative (34) and at constant RON high speed knock is more likely. To avert this RON give-away may be necessary. Benefits observed for MTBE and TBA in olefinic fuels appear to reduce with speed (26) although these two oxygenates still appear to be good blending components for olefinic bases.

1.15 Alkyl Lead Anti-knock Additives

Tetra ethyl lead (TEL) was discovered as a highly efficient anti-knock compound in 1921 and tetra methyl lead somewhat later (44). Straight run gasoline without lead additives would be too poor quality for present high compression engines and extra reforming, isomerising and cracking to boost gasoline octane is very expensive compared to the use of small quantities of lead anti-knocks. TML is quite volatile and has a major use in highly aromatic, ie low FEON, gasoline helping to avoid segregation and transient knock (17, 44). The octane improvement of hydrocarbons varies depending upon type. Paraffins have the best lead response followed by naphthenes, olefines and aromatics. Low octane fuels respond better than high ones (17).

The mechanism by which lead anti-knocks work is not fully understood, however, it appears that lead oxide formed in the combustion chamber deactivates free radicals by providing quenching sites (44). The active species, OH^* and HO_2^* acting as chain carriers leading to knock are mopped up thus reducing the hydro-peroxides and formaldehydes which promote knock. The reactions may be as follows (1):-

$$2Pb + O_2 \text{ ------> } 2PbO \quad \text{—} \quad 10$$

$$PbO + OH^* \text{ ------> } PbO(OH)^* \quad \text{—} \quad 11$$

$$PbO(OH)^* + OH^* \text{ ------> } PbO_2 + H_2O \quad \text{—} \quad 12$$

$$PbO_2 + R \text{ ------> } PbO + RO \quad \text{—} \quad 13$$

Lead oxides are prevented from depositing on the combustion chamber walls by dibromoethene included in the TEL fluid which converts them to more volatile halides.

Lead is also of great value as a lubricant for the valve stems and guides (45). Below 0.15 grams per litre lead in gasoline, problems of lubrication may arise which many have postulated will require a new engine design and vast capital investment therein, (50, 56, 57). Fear is expressed in the readiness of Japanese technology to fill the gap in Europe although West Germany is moving rapidly towards unleaded gasoline.

1.16 The Reasons for the Cutback in Lead Usage

There are two main reasons for the move towards unleaded gasoline. Firstly concern has been growing over possible health hazards of lead emissions and secondly the most widely used method of reducing nitrous oxide and carbon monoxide exhaust emissions involves the use of platinum/rhodium catalysts which are deactivated by lead. The controversy of lead and health has been raging for many years but no conclusive proof exists to link exhaust emissions to health. The most usual association is to brain damage in children and research (46) has shown lead to be very effective at cleaving RNA, the building blocks of protein and hence organs eg the brain. However, a much publicized report into IQ in children near Spaghetti Junction, Birmingham (47) found that social factors swamped any possible effects due to lead from exhaust emissions, water pipes and paint.

Lead exhaust emissions, however, constitute about 90 % of atmospheric lead (45) and studies using an isotope of lead in Turin and Belgium concluded that a substantial portion of the blood level of lead was attributable to exhaust emissions, some 24 to 60 % (48). A British Ministry of Agriculture, Fisheries and Food report also accepts that lead fall-out from cars is a significant factor in food lead content (50). Previous information based on the Lawther report 1981 sited inhalation as the only major source of exposure.

As previously stated no firm evidence exists to support claims concerning emissions and health, however, governments aware of public opinion have moved to reduce lead in gasoline, aiming eventually to eliminate it completely (50, 51). The new lead level in the EEC is 0.15 grams per litre, although there are concessions for some countries, and West Germany has taken the lead towards unleaded gasoline. All new German cars must be able to run on unleaded fuel. This decision stems from fear over acid rain pollution suspected in part to be caused by emissions of nitrogen oxides (NO_x) from cars. Again the link is not conclusive and Eastern bloc coal fired power stations are a much more likely cause. Reduction of NO_x emissions can be carried out using lean burn engines or the USA developed 3-way catalyst, poisoned by lead, which West Germany favours (52). Additional costs per car will be in the order of £250, and the need to maintain high octane quality of gasoline has led to the widespread use of oxygenates in German fuel.

1.17 High Octane Unleaded Gasoline

The RUFIT study (53) examining the prospects of unleaded gasoline concluded that the quality required to satisfy present high compression engines would involve an 8 to 10 % energy penalty compared to the 0.4 g/l leaded case. This is due to vehicle and refinery consumptions varying with clear pool RON. The optimum octane number for the unleaded case (ie minimum total crude oil consumption in refining and motoring) was found to be 92 RON and the minimum driving cost at 91 RON, much too low for most European cars and octane boosting by refining is expensive. In the case of hydroskimmer refineries octane boosting is limited without new investment (53, 54, 55). The extra costs of unleaded, high octane gasoline associated with refining have been reported widely (55, 56, 57, 58) but this appears to be the most cost effective method at present (55, 68). The options open to refiners to improve octane quality include stricter reforming, alkylation and isomerisation, propane polymerisation (59) new catalysts (62) and processes such as residue cracking (63), the Dimersol process (60, 61, 65) and the total isomerisation process (64). One problem associated with increased reforming is that the increased aromatic content of the gasoline may give rise to low volatility and poor engine cold start (32). The alternative, wholly or partly, to extra refining with the associated crude and product losses is the use of oxygenates which as previously stated are very high octane blending components.

1.18 The Present Use of Oxygenates

Many oxygenates are already in use around the world, those most commonly to be found are methanol, ethanol, TBA and MTBE. The use of iospropanol and secondary butanol as co-solvents with methanol is also carried out in some countries. The most widely used oxygenate is ethanol which is used in large quantities in Brazil and the USA. Gasohol (10 % ethanol) accounts for about 50 % of US gasoline sales and a 20 % blend is in use in Brazil although many vehicles run on pure ethanol. The primary sources of ethanol are the hydration of ethene and the fermentation of biomass both of which are very expensive. In order to reduce crude usage the fermentation method is preferred but is only viable with large government subsidies in countries which have vast tracts of land available for cultivation of fuel crops. The land required to support Brazil's alcohol program is in direct competition with food production (66) and estimates of requirements of land vary from 1 % (67) to 7 % (68) and even over 20 % (66) of all agricultural land in Brazil. Because of this excessive land usage ethanol is impractical as an alternative in Europe (69).

Methanol can be produced from any material which can be thermally decomposed to give a mixture of hydrogen and oxides of carbon which are converted to methanol using a catalyst. Natural gas is a major source and Middle East production will add greatly to that of Europe and the USSR. West Germany has shown a great interest in methanol as has New Zealand. Studies in Germany by Volkswagen have concentrated on a 15 % blend which requires modification of vehicle fuel system components and a modified carburettor but appears to work very well.

TBA, obtained as a by-product from the production of propene oxide, has been used as a co-solvent with methanol in the USA and West Germany. It is used to reduce some of the more detrimental effects of methanol such as its high volatility and phase separation tendency.

MTBE is produced from reacting iso-butene and methanol. The iso-butene can be selectively removed from the C_4 stream from a thermal or catalytic cracker or via a route from butane, involving isomerization and dehydrogenation (70).

MTBE is used at present in Italy, Switzerland, West Germany and Japan and many other countries are showing interest in it.

1.19 The Advantages and Disadvantages of Oxygenates

There has been a considerable amount of work carried out to test the suitability of various oxygenates as blending agents for octane improvement. This has tended to concentrate on material compatability, phase separation in the presence of water, volatility, exhaust emissions, octane quality of the blend and power output. In most cases where problems are thought to arise the most detrimental properties are exhibited by methanol followed by ethanol; however, these can be tempered by the use of co-solvents such as the butanols which have more gasoline-like qualities.

Some oxygenates are derived from non-crude oil sources and so reduce crude usage (58, 68, 75), and more efficient burning of the fuels in the engine (95) reduces total energy consumption further. Volumetric fuel consumption in automobiles is often higher because of the lower heating values of oxygenates especially methanol, however a 20 % blend of MTBE has been found to be little or no worse than gasoline (43, 75, 76). The power output of engines has been noted to increase when using oxygenate blends and efficiency also increases (30, 71, 72, 75, 76).

Storage of oxygenates has not been found to cause any extra problems and MTBE is especially stable showing no peroxide formation (43, 74, 92).

1.20 Materials Compatability

All materials which would come into contact with the oxygenated blend must be resitant to deterioration excessively greater than that produced by pure gasoline. This involves the distribution system to the gasoline filling station as well as the pumps themselves and the vehicle fuel system, because blending in the refinery is the most likely method of incorporating oxygenates (33, 53). In this way good control of product specification is possible. It appears thus far that no materials problems have been encountered up to the gasoline delivery pump; however, increased wear of the pump mechanism has been noted when gasohol was in the system and has been attributed to the solvent properties of ethanol removing lubricants which would otherwise prevent wear.

Most work has naturally concentrated on the fuel handling system of automobiles and attempts have been made to suggest suitable materials to avoid problems. Certain paint finishes, notably "touch-up" paints may be affected by methanol (73) and may fade. This could be a minor problem for older, repaired cars but is unlikely to affect the majority of the population. It has been observed that fuel tanks are stripped of their lead/tin (terne) plating by fuels containing substantial amounts of methanol or ethanol (36, 77, 78, 80); however, this can be overcome by the use of pure tin to plate the steel (79). Other metals are also subject to attack especially by methanol eg magnesium, aluminium, zinc and copper although cadmium plate can replace zinc in fuel pumps, carburettors can be nickel plated and more use made of brass to alleviate these problems (80). Also stainless steel has applications in the fuel system. MTBE and Oxinol (a blend of methanol and tert butanol - ARCO USA) do not appear to have any problems with metals (75, 76, 78, 92, 93).

The main problem associated with materials is the deterioration of fuel lines and gasket materials. Increased swelling caused by oxygenates may lead to constriction or blockage of fuel lines, leakage at joints and eventual break up of the system. There is conflicting evidence as to the degree of damage caused to rubbers and plastics and as this work considers multiple combinations of oxygenates rather than individual blends future materials must be resistant to many different oxygenates.

The polar nature of methanol makes it the most detrimental blending component followed by ethanol and the other less polar molecules. Graham and Judd (73) rule out almost all synthetic materials including vitons (fluorocarbons), pvc, nylon etc and suggest the use of rubber to be preferable. The use of nitrile rubbers is supported by Pinto (79) and Piazza et al (81) who noted slight but acceptable swelling with methanol and ethanol. MTBE was found to be similar to gasoline in effect. No significient problem has been associated between MTBE and elastomers by several workers (74, 75, 76, 82, 83), and Levinin (82) recommended the use of neoprene or neoprene-nitrile rubber blends for MTBE. Fayolle and Langlade (83) favour a pvc-nitrile blend.

Fluorocarbons appear to be very resistant to attack by oxygenates and may prove to be the most useful (36, 77, 84, 85). Although Graham and Judd (73) suggest vitons are unsuitable for methanol and Ismat (86) that MTBE attacks them, the majority of workers in this field consider them to be the most promising. Nersasian (89) lists Viton GH, B, VT-R-4590 and A-Hv as the most resistant to swelling for methanol and ethanol and VT-R-4590 and VT-R-5362 for MTBE due to their high fluorine content. Williams (36), however, suggests Viton VTX is suitable for all oxygenates.

It appears that a solution to the problem of materials compatability is available but existing vehicle fuel systems may have problems associated with attack by oxygenates. The widespread use of oxygenates in West Germany, does not as yet appear to have caused major problems with the existing vehicle population and it may be a number of years before fuel line failures become a common problem.

1.21 Phase Separation

From data available it would appear that phase separation due to the presence of water is a major problem with oxygenated gasoline blends. It would be difficult to eliminate water from the transport and storage system of gasoline although quantities of water present could be reduced to tolerable levels (79), and the use of co-solvents for methanol, which is most affected by the presence of water, such as iso-propanol, iso-butanol and others (30, 78, 80, 87) should solve the problem. No problems have been associated with MTBE (92, 93) and in fact this has been suggested as a co-solvent for methanol (87).

Phase separation appears to be worse at lower temperatures and higher aromatic content (30, 89).

1.22 Volatility

The high vapour pressures of ethanol and especially methanol have led to fears of vapour lock in fuel lines and poor cold starting. The high vapour pressure of methanol/gasoline blends (Figure 3) is associated with the azeotropy in the distillation curve (Figure 4) (80, 89). This is not such a problem with less polar molecules such as the ethers, Figure 5, and the high vapour pressure of methanol blends can be reduced by removing some butane from the blend (30, 68) or by using multiple oxygenate blends rather than pure methanol. Removal of butane incurs cost penalties as butane is very cheap. Vapour lock does not appear to be a problem in mild climates with up to 10 % methanol (73). Most authors agree that there is only a small butane loss with MTBE (34, 54, 78, 90) and depending upon the volatility of the base gasoline butane may be added to the blend to increase the cost effectiveness of MTBE (58, 74).

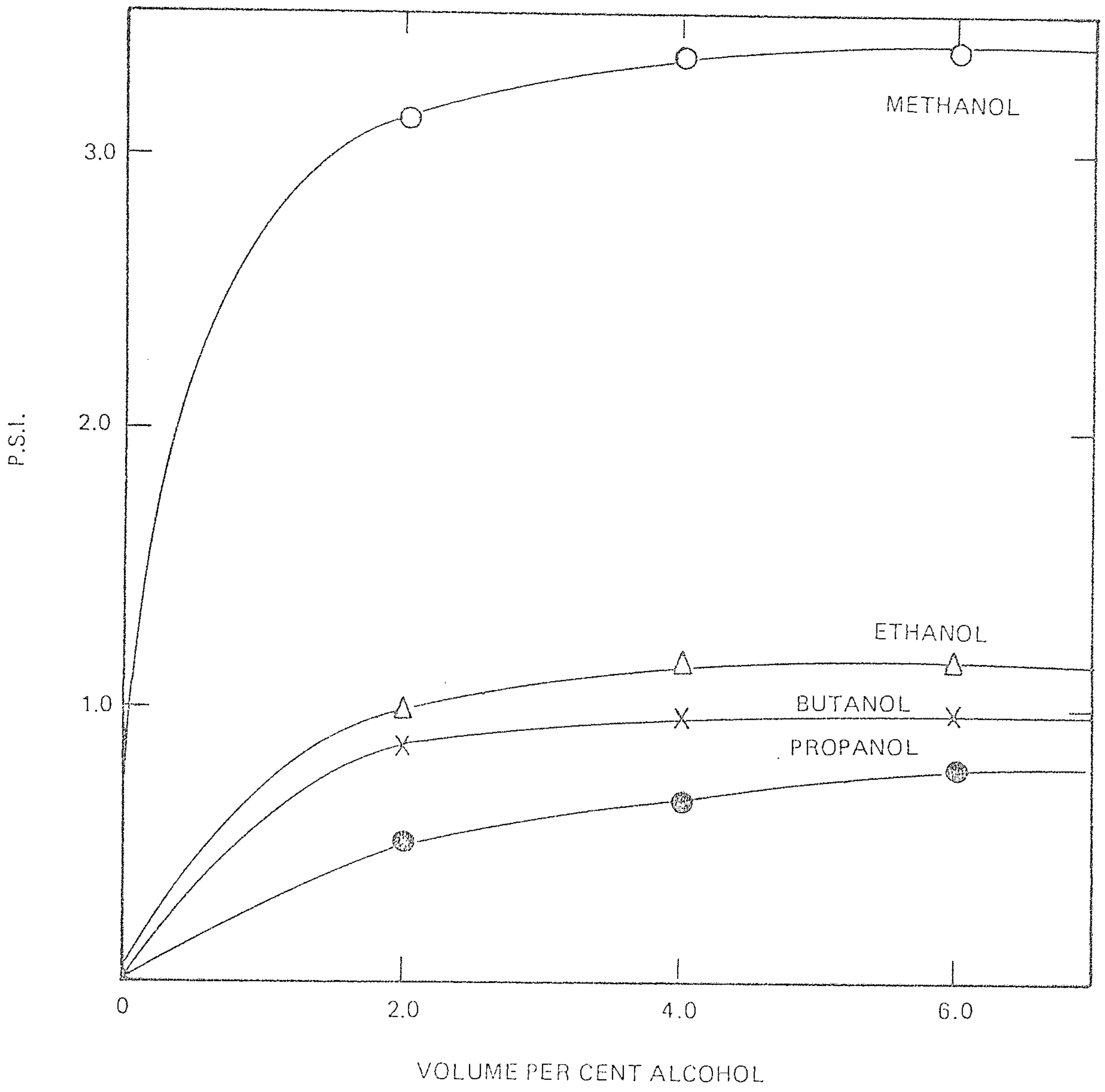

Figure 3 The Effect of Alcohol Addition on Reid Vapour Pressure

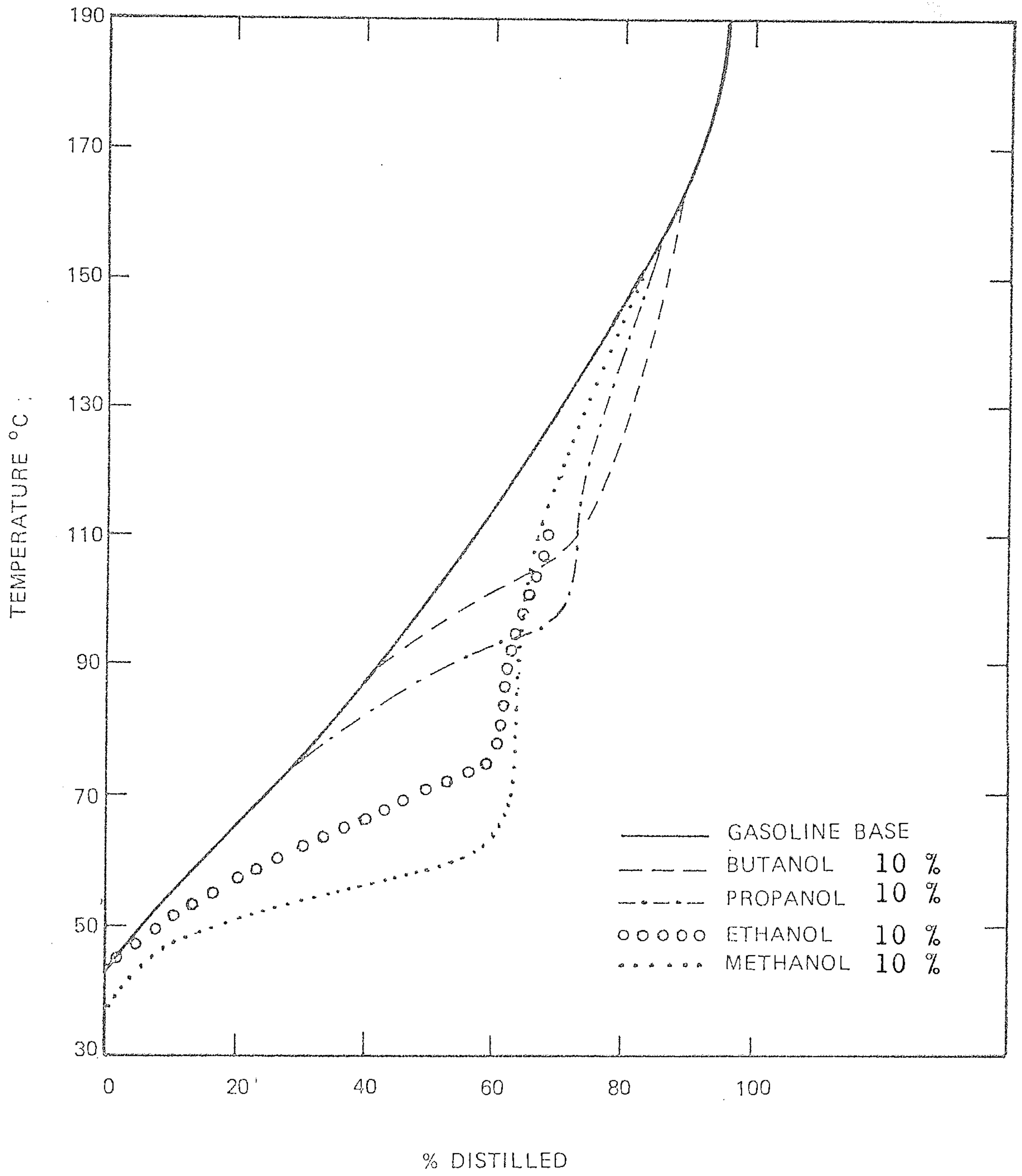

Figure 4 The Effect of Alcohols on Gasoline Distillation Characteristics

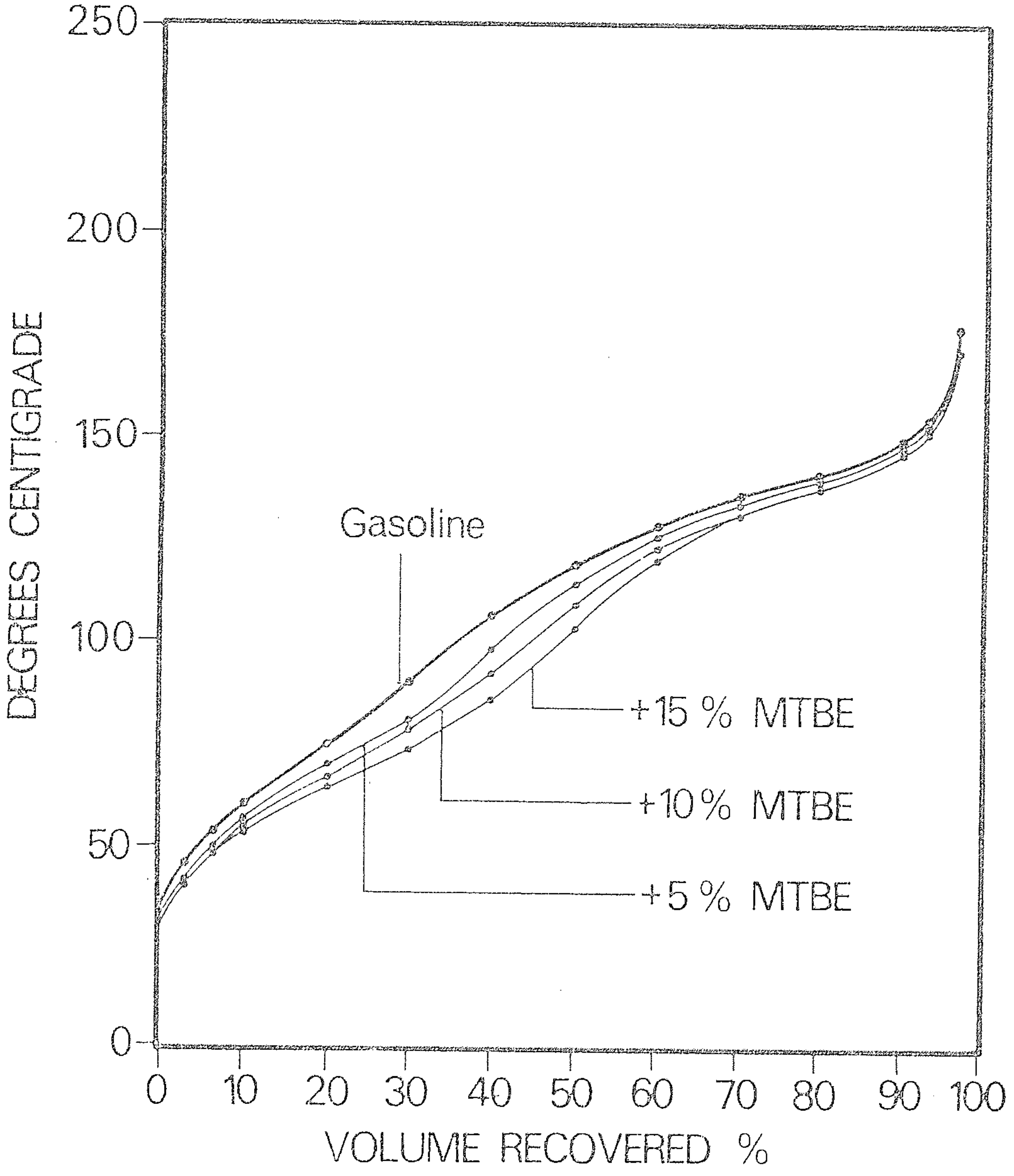

Figure 5 The Effect of MTBE on Gasoline Distillation Characteristics

1.23 Exhaust Emissions

Due to the oxygen contained within an oxygenated fuel blend, unless the carburettor is adjusted to the same equivalence ratio as for pure gasoline, the engine will run lean. This results in lower nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbon (HC) emissions. Even when the equivalence ratio is the same, some results have shown lower emissions (80). Harmful poly-nuclear aromatics are also reduced (43), however, there has been an increase in aldelyde emissions observed. These aldehydes are partly responsible for photo-chemical smogs and can be reduced by increasing the engine compression ratio (80) or by the use of a catalytic converter where they are destroyed.

1.24 Availability and Cost

Limits on the amount of oxygen allowed in blends, presently 2.5 % in Europe, result in a shortfall of RON if oxygenates are to be the only octane improvement method for unleaded gasoline (51). The present availability of oxygenates is limited and is only sufficient to cover the reduction in lead from 0.4 to 0.15 g/l (54, 55, 96). Extra use of aromatics, such as toluene, would be required to fill the gap (32, 94) although this could lead to RON give-away due to their high sensitivity and a low volatility fuel could have poor cold start characteristics. MTBE is limited by the availability of iso-butene although routes to it via isomerization and dehydrogenation of butanes are now possible (88, 91). It has been noted that oxygenates range from between 5 and 9 times as expensive as using TEL although methanol, MTBE and TBA appear to be close in cost to their value in gasoline (54). Ethanol is not a viable blending component in Europe due to its very high price and the limited agricultural land which could be spared for its production.

CHAPTER 2

EXPERIMENTAL EQUIPMENT

EXPERIMENTAL EQUIPMENT

2.1 Rig Construction

The experimental programme was carried out on a small car engine with an applied variable load to simulate driving conditions. The engine, a Fiat 127, 903 cc, was supplied by Esso Petroleum Limited for a previous project but had had only light use. This was stripped down to check for wear and damage on the bearings, valves, pistons , etc. Slight damage was noted on one of the pistons and on the corresponding cylinder head combustion chamber. The roughened surfaces were smoothed and as no other problems were apparent the engine was reassembled. Before repositioning the cylinder head, however, the combustion volume of each cylinder was measured using paraffin to determine the compression ratios, this will be discussed later. The engine was run for about 40 hours to build up deposits etc after the clean up operation. (Figures 6 - 9 show views of the experimental equipment).

2.2 Fuel System

A small petrol tank (Austin Mini) was used to store the ordinary gasoline on which the engine was warmed up and run on in between the test fuels. This was fitted with a sightglass and connected to the fuel pump via a three way valve, used to change over to the test fuels. A fuel measuring device fed from another reservoir was also connected to the main fuel line before the pump, as was the carburettor return line, Figure 10.

The fuel measuring device consisted of a glass tube held vertically with a threaded rod down the middle onto which were fixed a number of discs slightly smaller than the bore of the tube. The rate of change of height of gasoline across

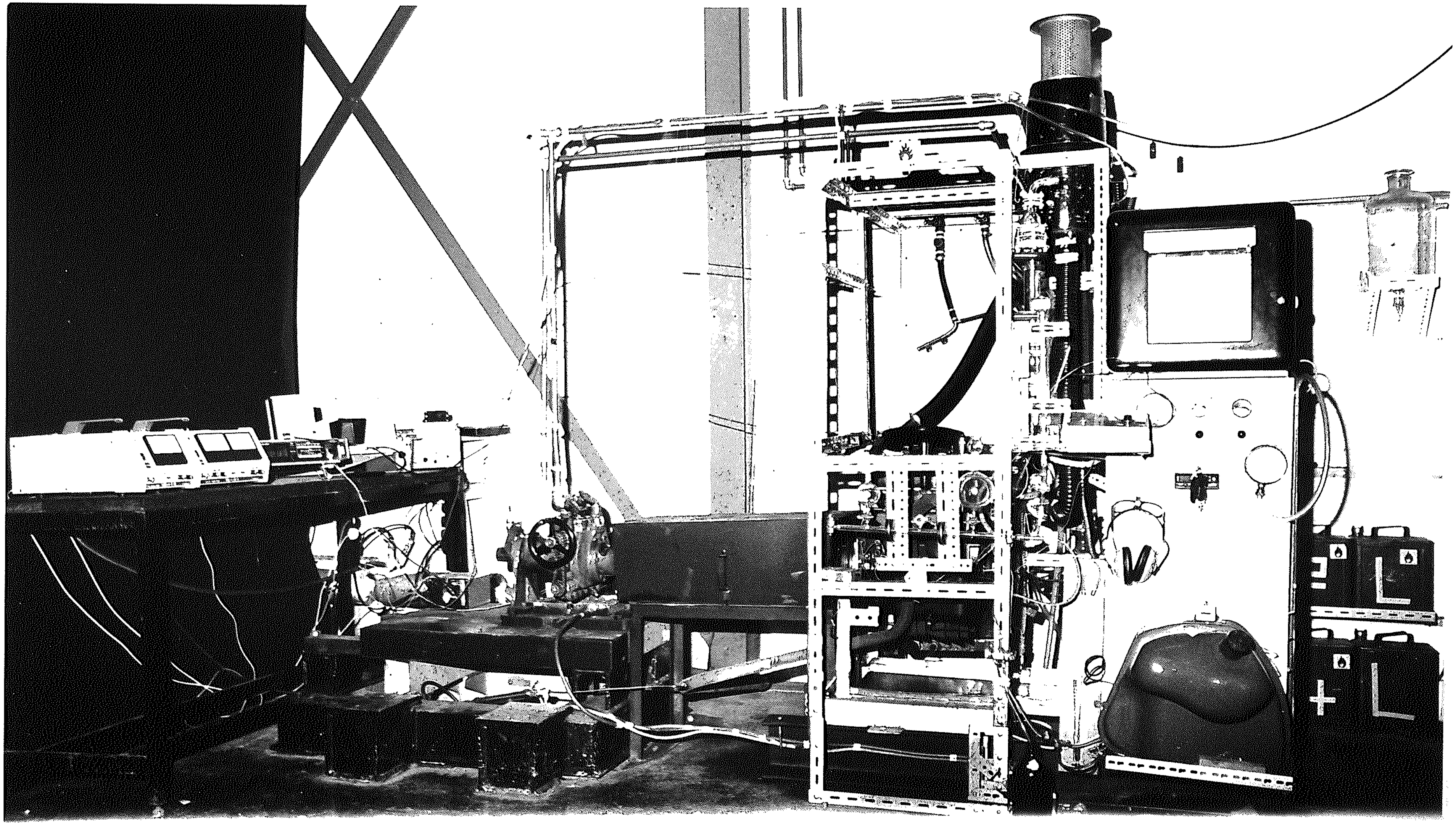

Figure 6 Overall View of Experimental Rig

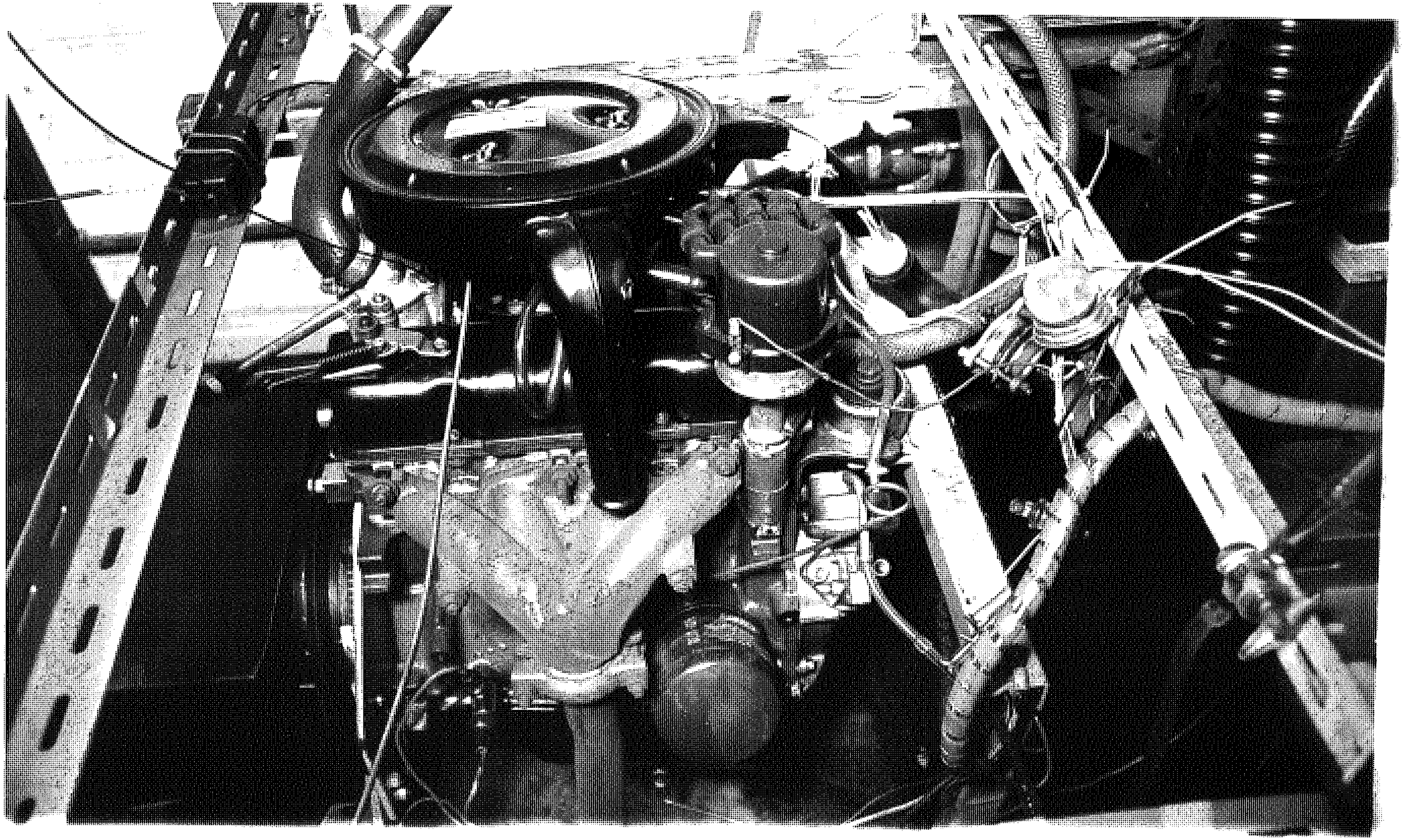

Figure 7 Fiat 903 cc Engine

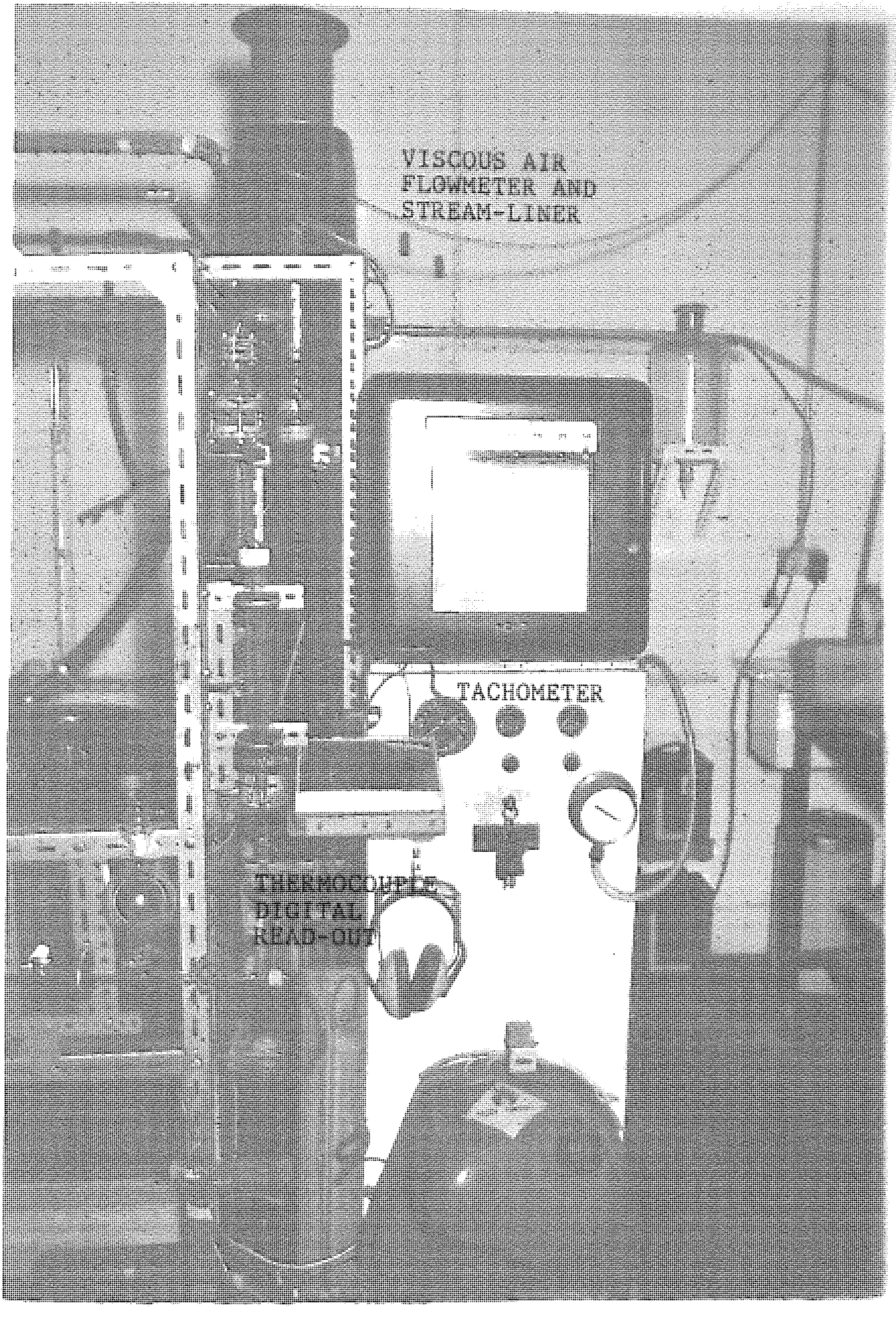

Figure 8 Instrumentation

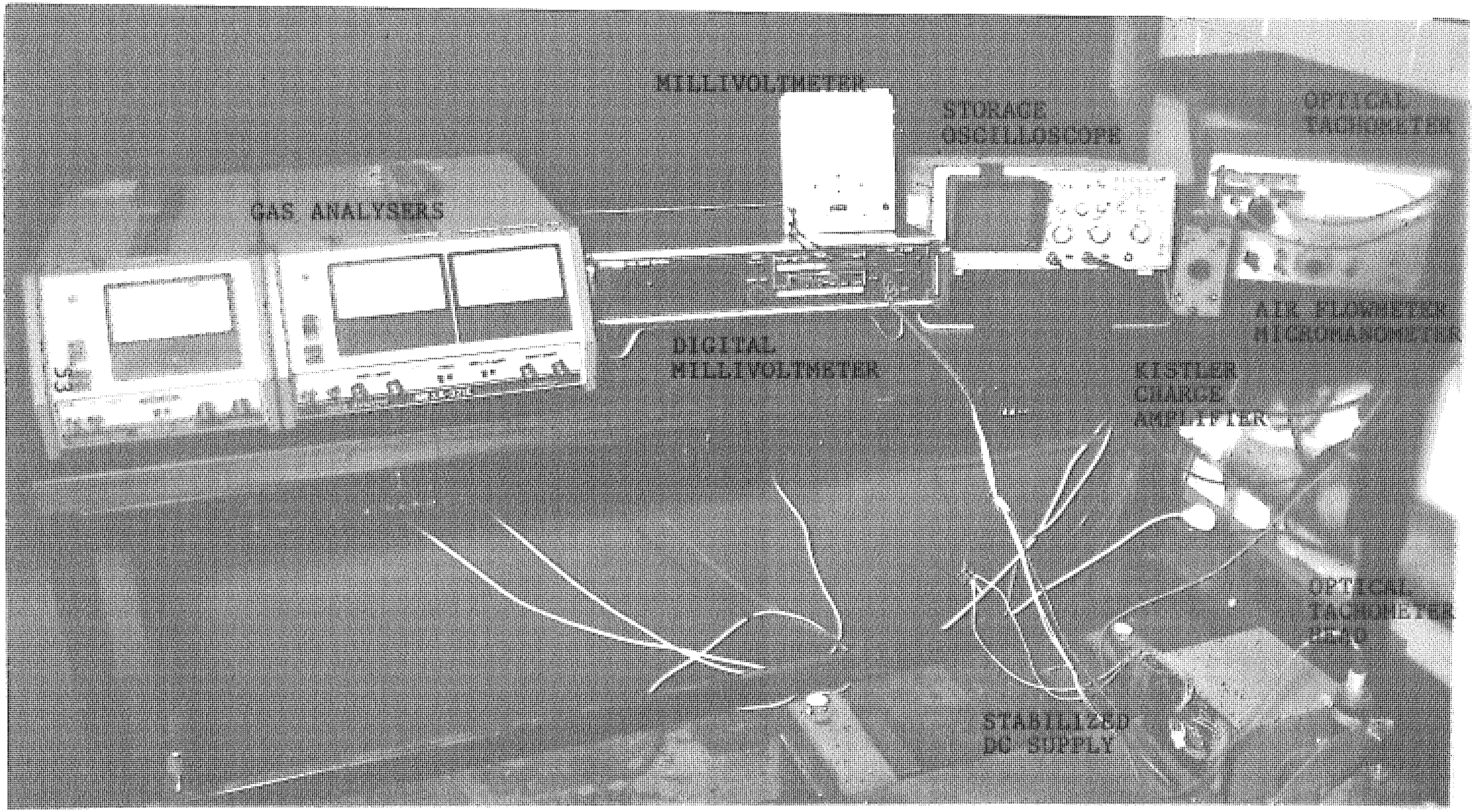

Figure 9 Instrumentation

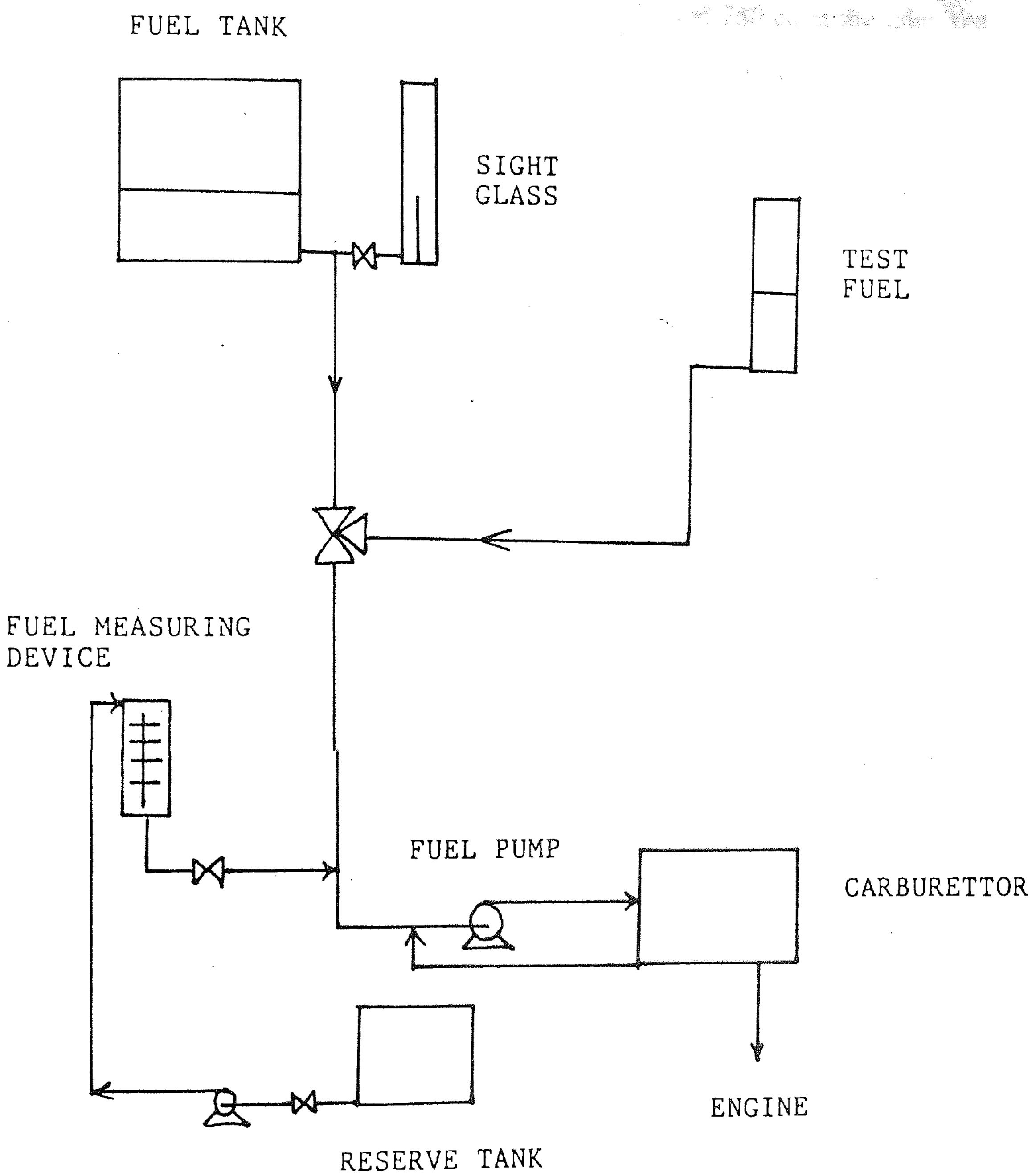

Figure 10   Test Engine Fuel System

these discs was much faster than in the rest of the tube and so these positions were easily discernable. Discs were positioned at 50, 150 and 250 cc in the tube, see Figure 11, and a stop-watch was used to determine fuel consumption.

2.3 Other Alterations to the Engine

Whilst the cylinder head was removed, top dead centre on pistons 1 and 4 was located in order to mark up a timing plate. The engine had no gear box but was connected directly to the load controlling dynamometer with a prop-shaft via a large aluminium alloy disc. This was painted matt black and marked with degrees of advance up to 30°.

Thermocouples were inserted into the coooling water in the cylinder head and the oil in the engine sump. These, along with thermocouples in the engine air intake and dynamometer cooling water outlet, were connected to a multi-channel digital display.

The cooling of the engine was achieved using a small heat exchanger and cold water supply. This proved insufficient and was amended to include a Fiat radiator with electric fan in series with the heat exchanger and fins were also welded on to the engine sump over which the air from the radiator fan was blown.

An Alcock viscous air flowmeter type H800 was connected to the inlet of the engine air filter box. This included an air stream-liner the pressure across which was monitored and recorded and a conversion chart was used to determine volumetric air flow, Figure 12 and 13.

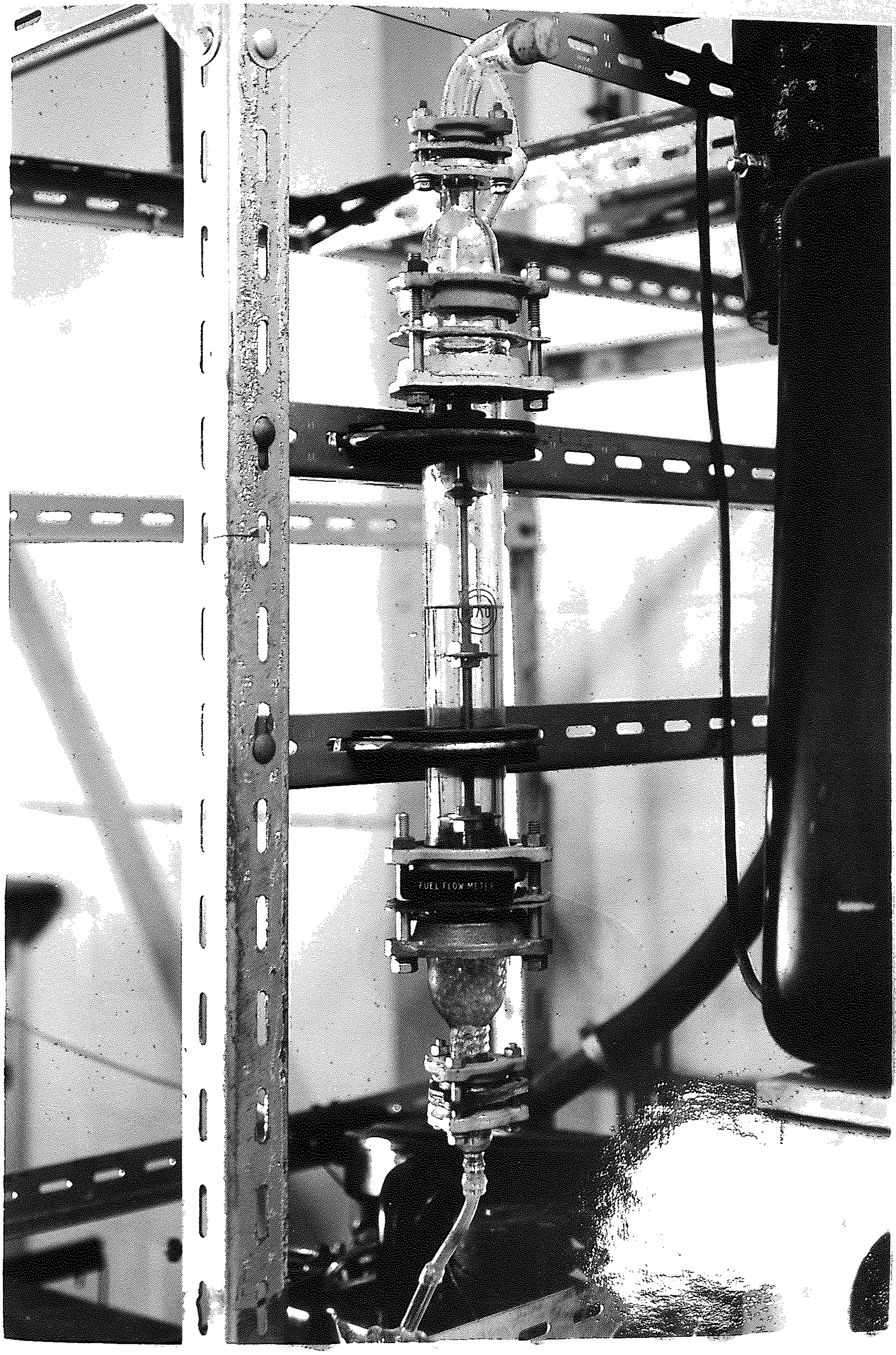

Figure 11 Fuel Measuring Device

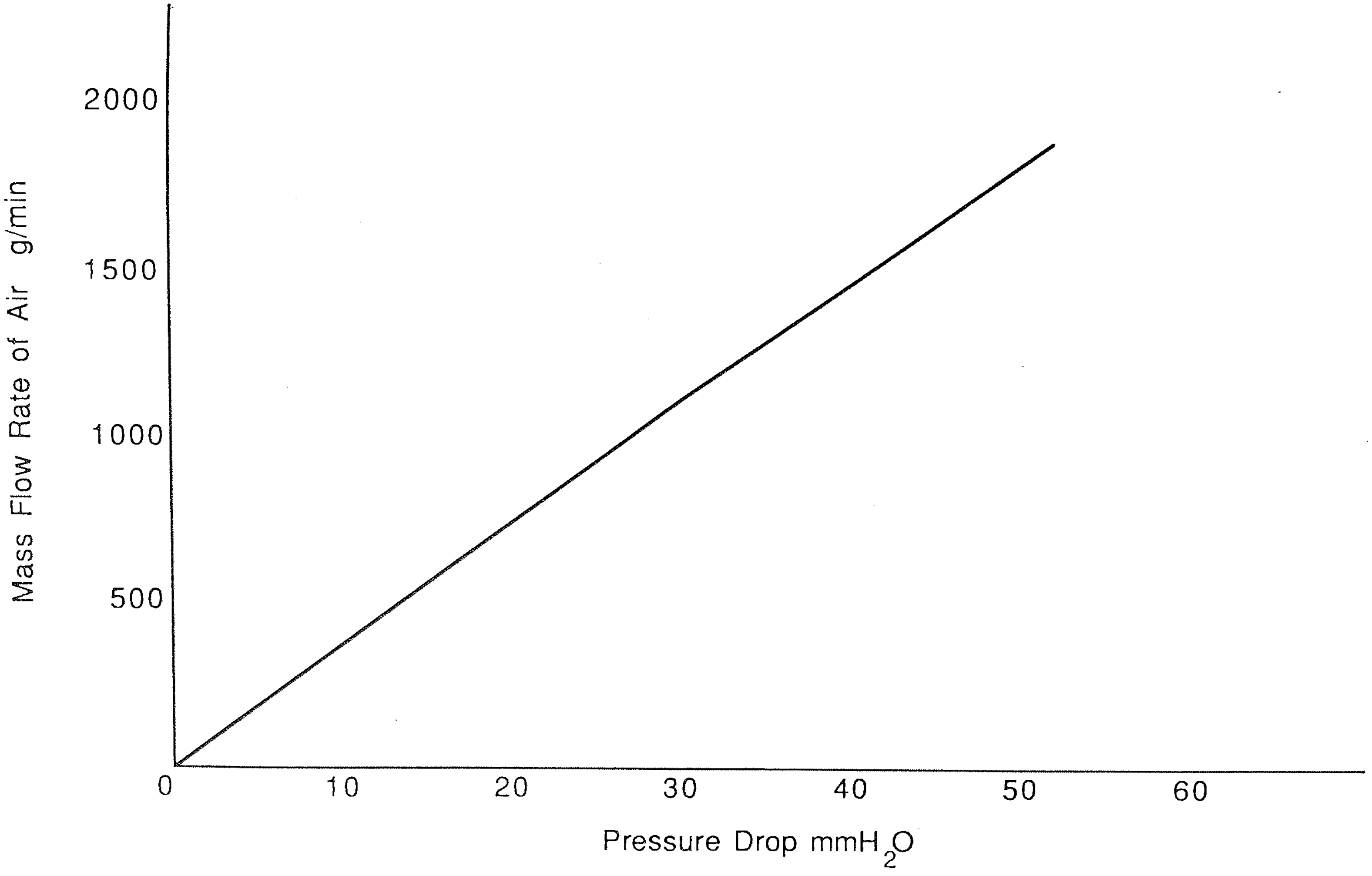

Figure 12 Mass Flow Rate of Air through Viscous Air Flowmeter

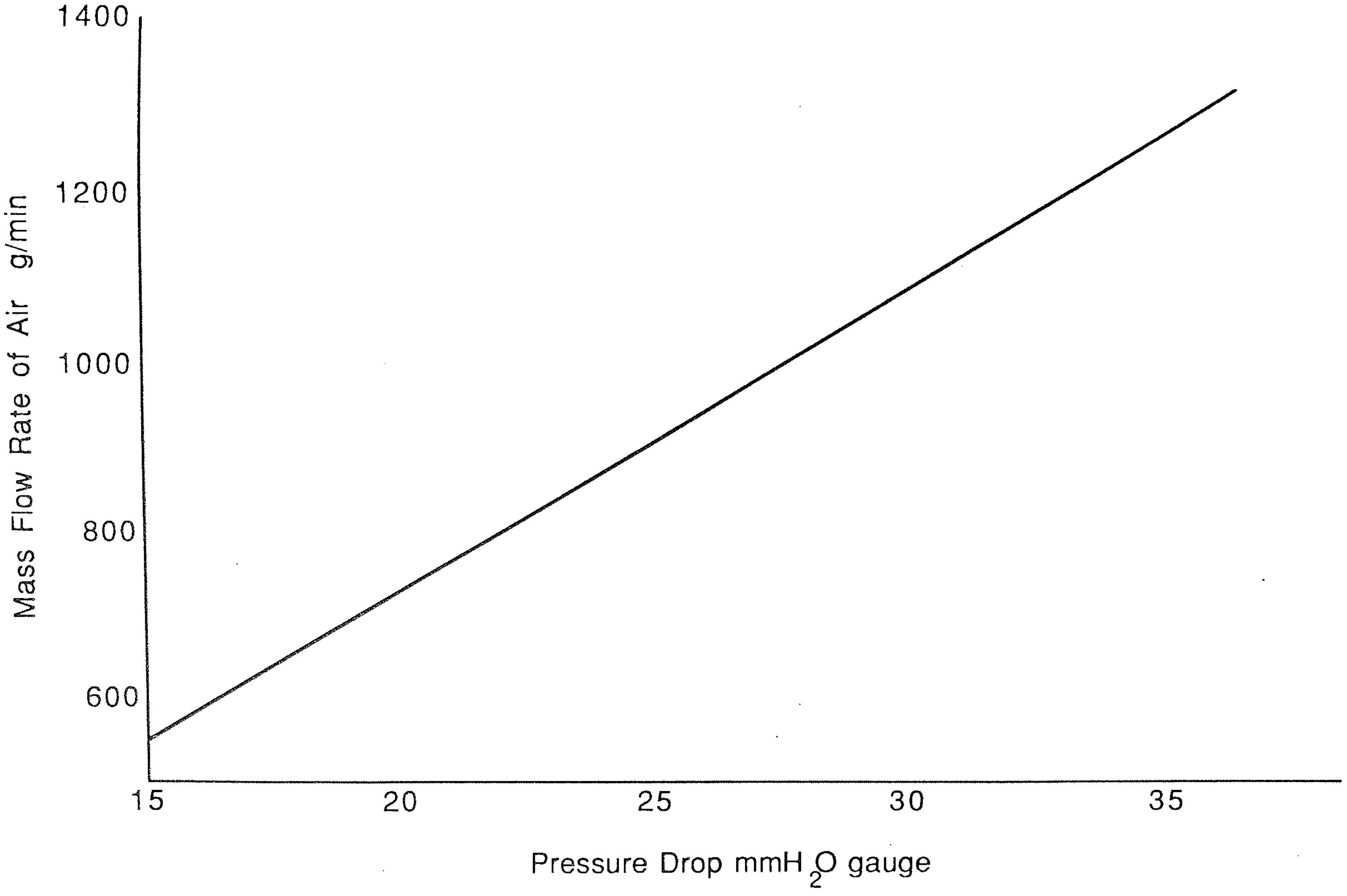

Figure 13 Mass Flow Rate of Air through Viscous Air Flowmeter

A forced air wet and dry bulb thermometer was made in order to measure air humidity in the laboratory as absolute humidity can affect the knocking intensity of an engine. High humidity reduces knock as some of the heat of combustion is used to vapourise the particulate moisture in the air. The equipment consisted of a small electric blower, two thermometers, a cruciform of QVF glassware and a wick. The cruciform QVF was mounted vertically and the thermometers were positioned such that the air from the blower blew across their bulbs, one of which was covered by the wick which dipped into a water reservoir, see Figure 14. A psychrometric chart, Figure 15 was used to obtain the humidity and the wet and dry bulb temperatures and air pressure were recorded for each days' experiments. Error due to air pressure variations was small and so neglected.

2.4 Distributor Timing Curve Check

As spark timing is very important when studying engine knock the distributor was checked using a Sun 504 distributor tester to ensure correct operation. Advanced ignition leads to knock promotion as the extra delay allows the formation of large quantities of hydro-peroxides, which initiate the chain-branching reactions leading to knock.

Dwell angle and its variation, contact breaker spring tension, cam accuracy and timing advance were all measured and found to be satisfactory (see Appendix 3). The ignition advance was also observed with a stroboscopic timing light on a number of occasions during fuel tests to ensure that it remained essentially constant and within the manufacturers limits, see Figure 101.

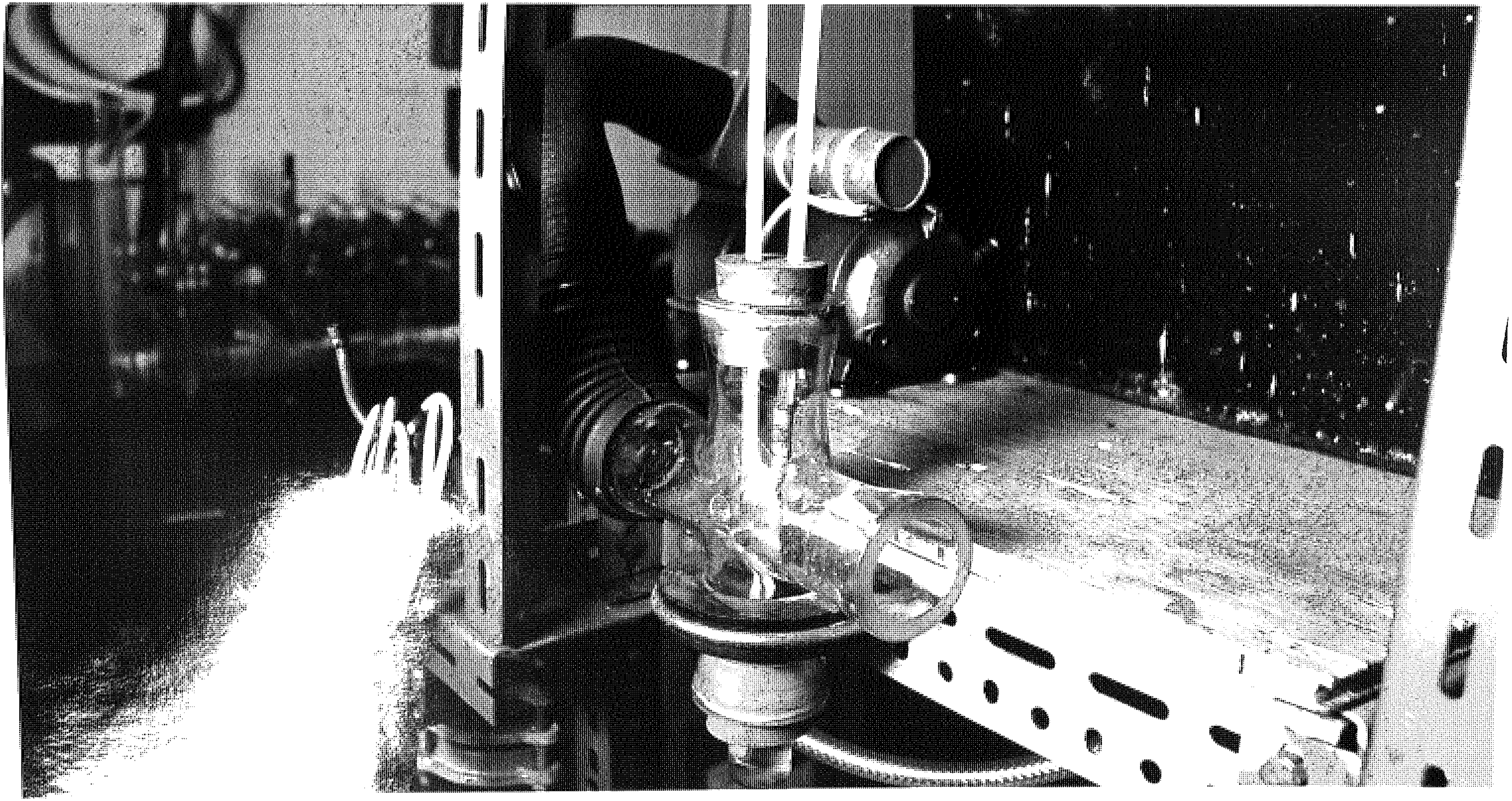

Figure 14 Wet and Dry Bulb Thermometer

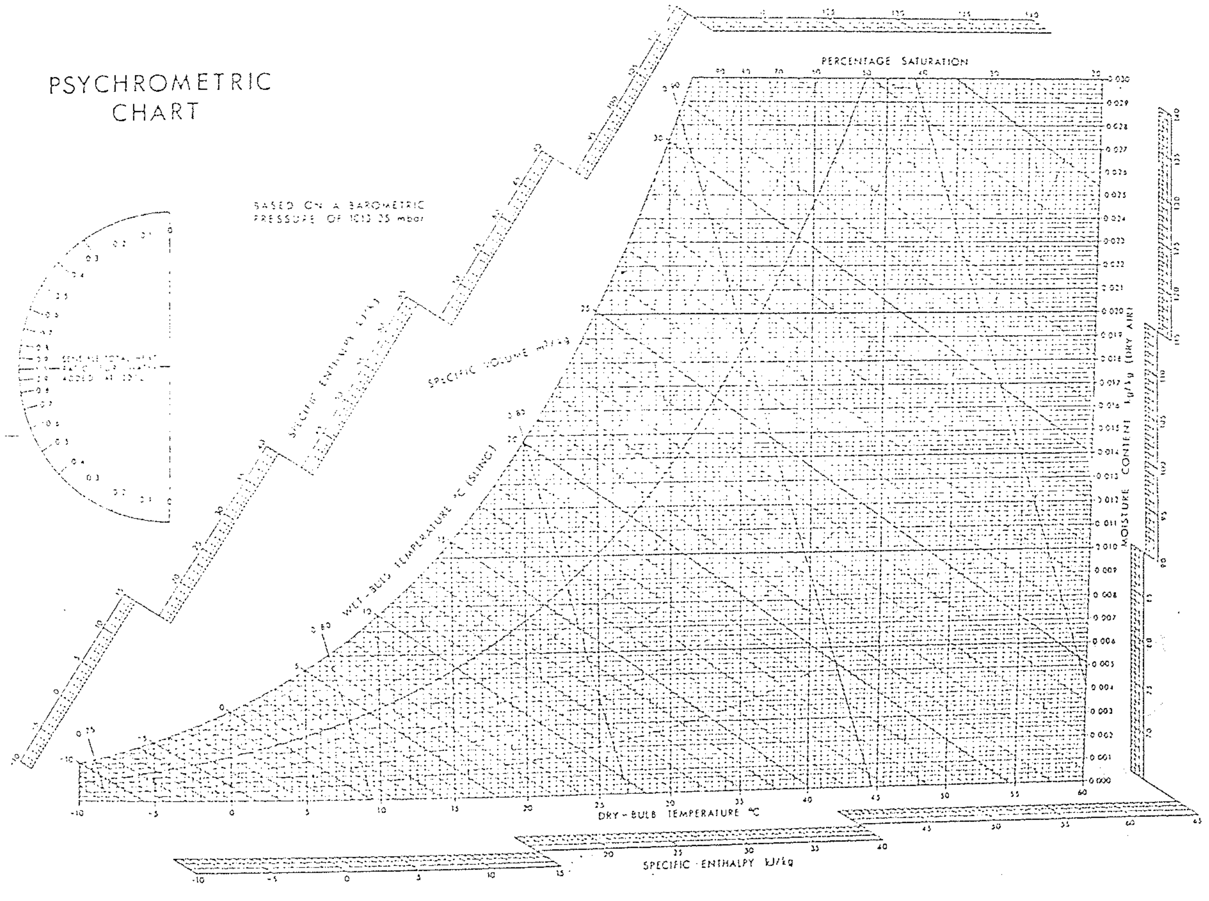

Figure 15 Psychrometric Chart

2.5 DPX1 Heenan-Froude Dynamometer

In order that the engine could operate under load an hydraulic dynamometer was purchased to replace exisiting non functional equipment. Connection to the engine was made by a propshaft of Hardy-Spicer design. The universal joints at both ends of the shaft reduce the need for perfect alignment as small amounts of shaft flexing can be absorbed without damage to the bearings.

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 sluice gates operated by turning a handle. The power absorbed is converted to heat which is detected in the outlet water. The load which the DPX1 could apply to the Fiat engine was sufficient to reduce the engine speed to about 1000 rpm at wide open throttle and the minimum load allowed operation well in excess of 6000 rpm.

Various methods of rpm measurment were tried, the most reliable and accurate of which proved to be a Compact type M48 optical tachometer. A piece of reflective tape was applied to the end of the dynamometer shaft (Figure 16) which refected 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 ensured a fast response to change in engine speed, and allowed any irregular engine operation to be observed.

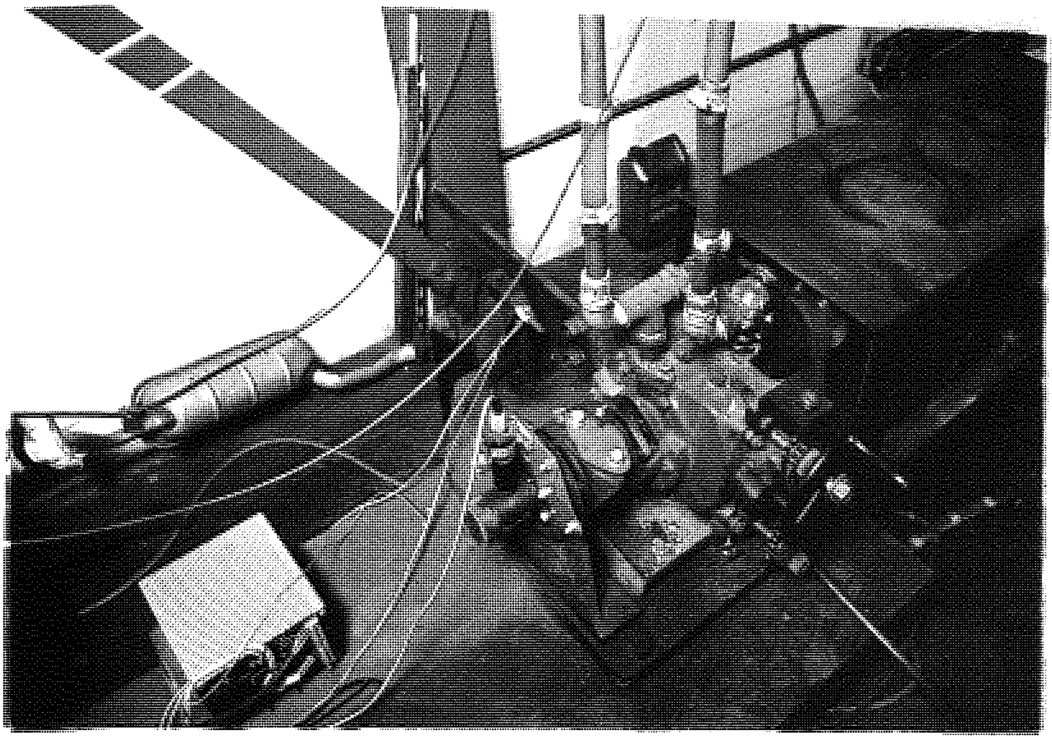

Figure 16 Heenan-Froude Dynamometer

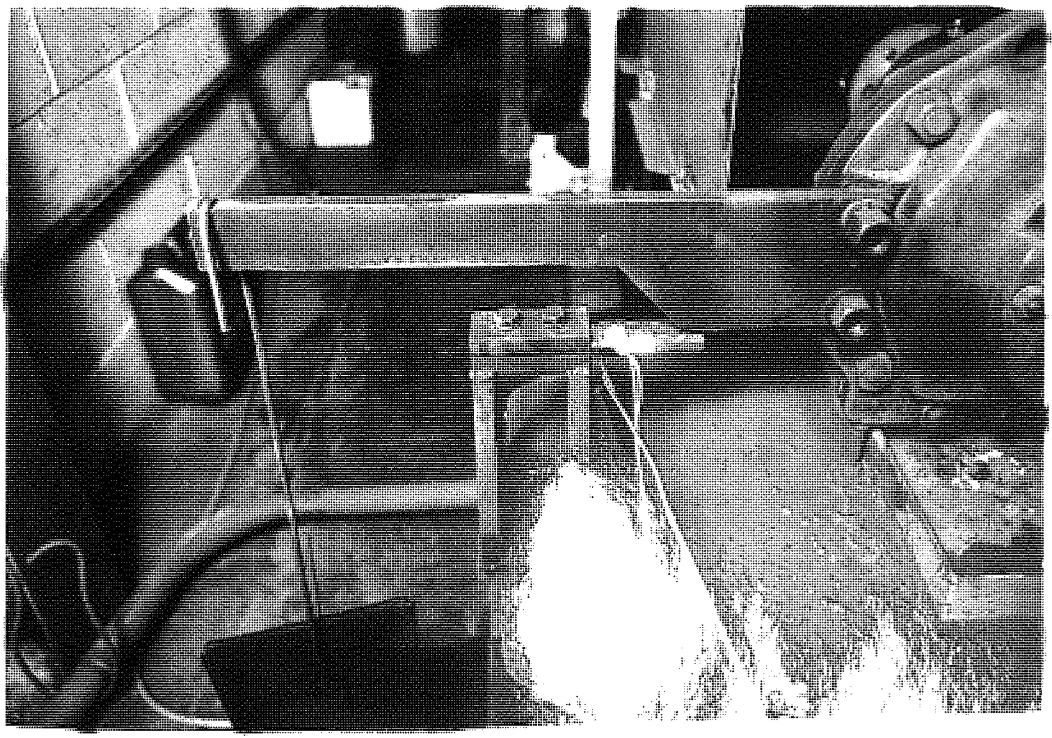

Figure 17 Load Measuring Device

2.6 Dynamometer Load Measuring Device

The dynamometer was obtained without a load cell and thus a load measuring device was designed using four strain gauges in a wheatstone bridge arrangement mounted on a cantilever acted on by an arm attached to the dynamometer casing, Figure 17. Two strain gauges were mounted on the upper side of the beam and two on the lower, thus two were subject to compressive strain and two to tensile strain, Figure 18. A variable resistor was placed across the bridge circuit to enable zeroing and power was supplied from a Brandenburg ST1 stabilized DC supply set to 5 V. The deflection of the beam due to the load exerted on it changed the resistance of the strain gauges proportionally and the change in voltage which resulted was measured using a Fluke 8300 A digital millivoltmeter, with 10 microvolt resolution. Using all four strain gauges in the bridge actively, the maximum signal was produced. The beam design is discussed in Appendix 4.

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. Tables 1 and 2 shows the results of calibration and Figures 19 and 20 plot this data which as can be seen is a straight line. The conversion factor from millivolts to torque was obtained from the gradient of the line and found to be 27.525.

2.7 Engine Power Output Testing

Engine power output was determined at all engine speeds at wide open throttle. The engine matched as close as possible one found in a car with electric fan etc thus power losses were assumed to be normal and power output expected to match handbook specifications.

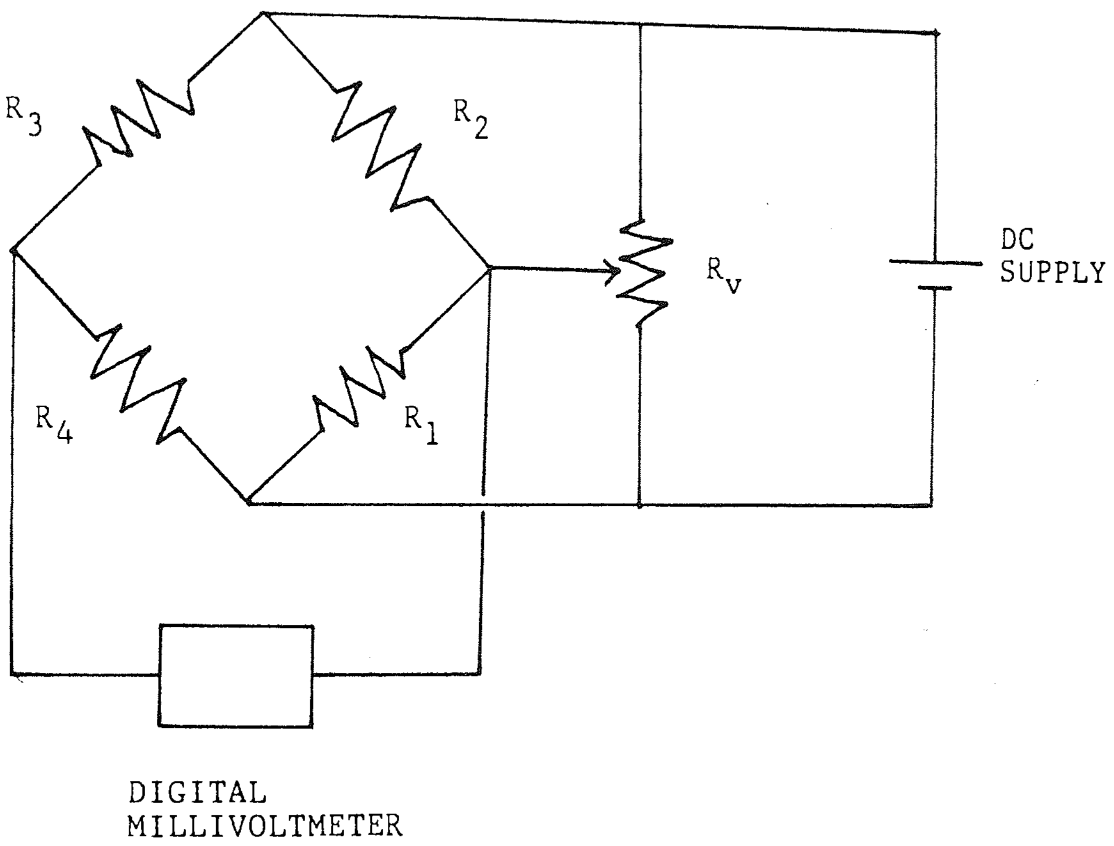

Figure 18 Bridge Circuit for Strain Gauges in the Load Measuring Device

Table 1 Calibration of Dynamometer Load Measuring Device

kg	Load (N)	Torque	Output (mV) Load Increasing	Output (mV) Load Decreasing
0.0	0.00	0.00	0.00	0.01
1.0	9.81	5.34	0.19	0.21
2.0	19.62	10.69	0.39	0.41
3.0	29.43	16.04	0.58	0.61
4.0	39.24	21.38	0.77	0.80
5.0	49.05	26.72	0.97	0.97
5.2	50.99	27.79	1.01	1.06
6.2	60.80	33.14	1.20	1.26
7.2	70.61	38.48	1.40	1.45
8.2	80.41	43.83	1.59	1.62
9.2	90.22	49.17	1.79	1.79
10.0	98.07	53.45	1.92	2.02
11.0	107.87	58.79	2.15	2.21
12.0	117.68	64.14	2.32	2.41
13.0	127.49	69.48	2.51	2.59
14.0	137.29	74.83	2.72	2.75
15.0	147.70	80.17	2.19	2.19

Table 2 Calibration Check During Testing Programme

kg	Increasing Load mV Output
1.00	0.18
2.00	0.39
3.00	0.57
4.00	0.77
5.00	0.97
6.00	1.17
7.00	1.37
8.00	1.57
9.00	1.75
10.00	1.95
5.83	1.13
6.83	1.33
7.83	1.75
8.83	1.73
9.83	1.93
10.83	2.14
11.83	2.34
12.83	2.54
13.83	2.73
14.84	2.93
15.83	3.13

Table 3 Power and Torque Tests

NB Cooling fan for radiator on

WOT 13.11.84

rpm	mV	Torque	hp
1100	2.15	59.18	9.14
1250	2.15	59.18	10.39
1500	2.21	60.83	12.81
2000	2.26	62.21	17.50
2500	2.36	64.96	22.80
3000	2.44	67.16	28.30
3500	2.40	66.06	32.50
4000	2.39	65.78	37.00
4500	2.35	64.68	40.90
5000	2.26	62.21	43.70
5400	2.15	59.18	44.87
5500	2.13	58.63	45.30
5670	2.04	58.63	44.70
6000	1.96	53.95	45.50
6440	1.81	49.82	45.10

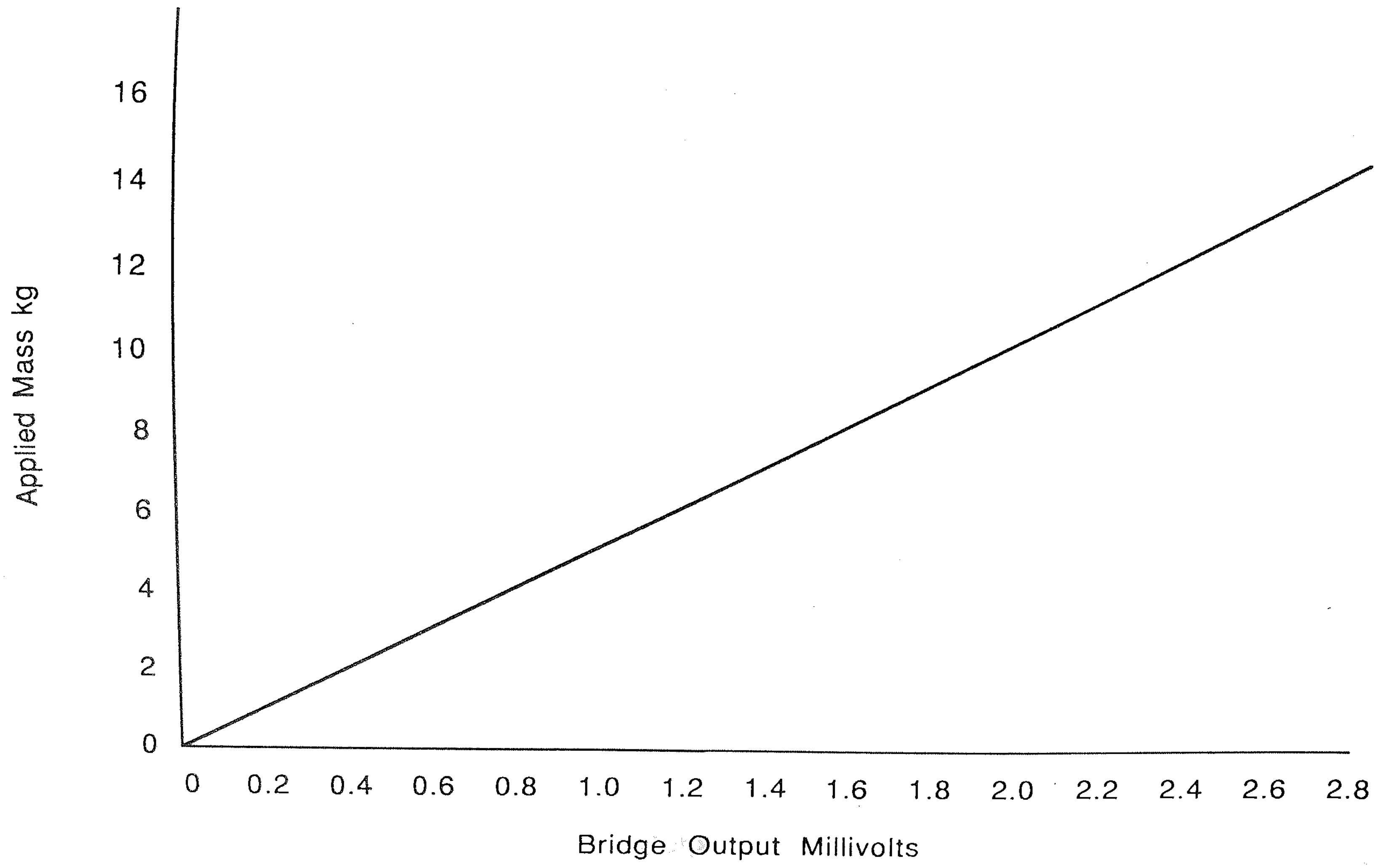

Figure 19 Calibration Curve for Load Measuring Device

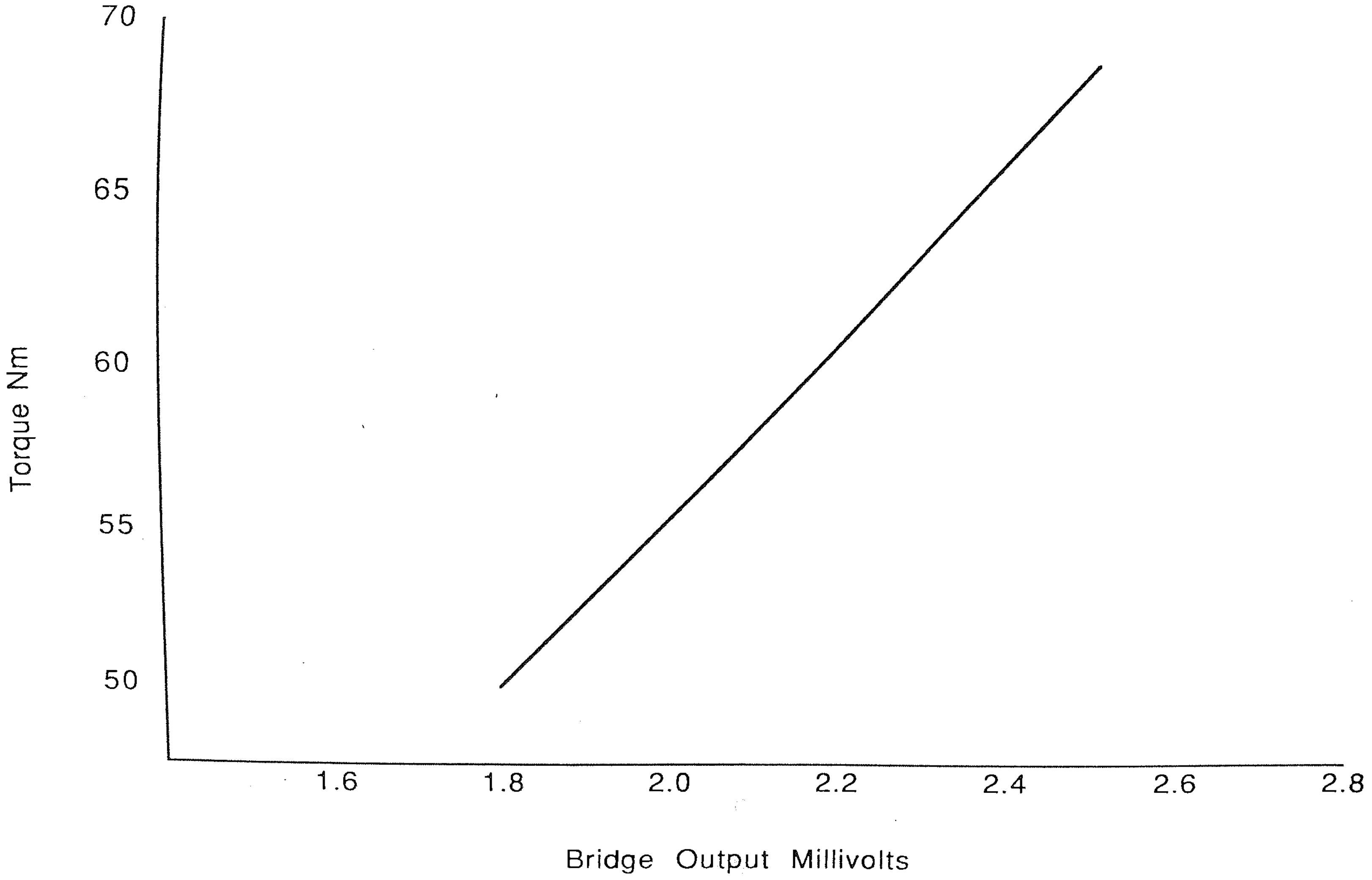

Figure 20 Torque Produced Versus mV for Load Measuring Device

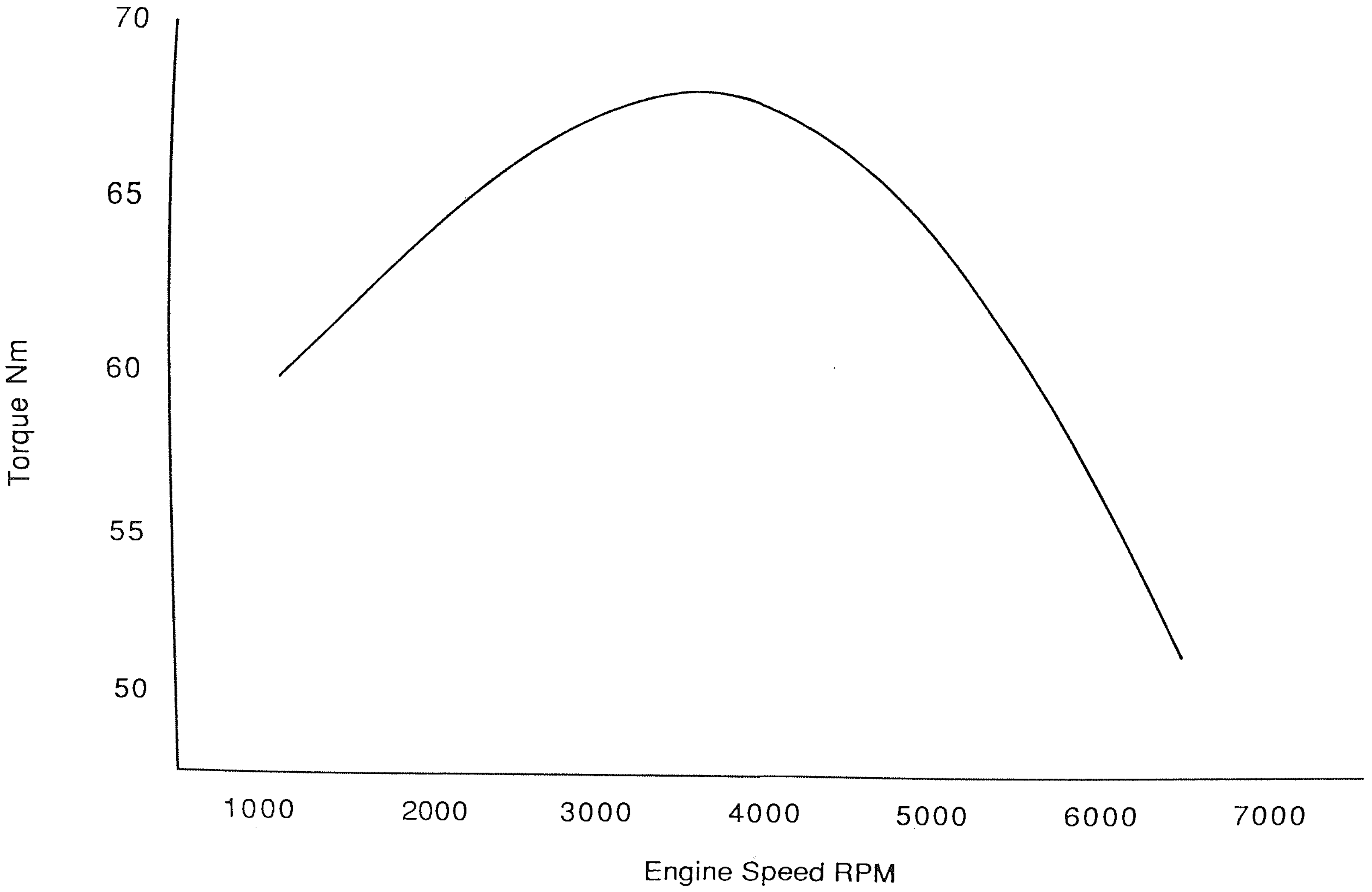

Figure 21 Torque Produced Versus Engine Speed

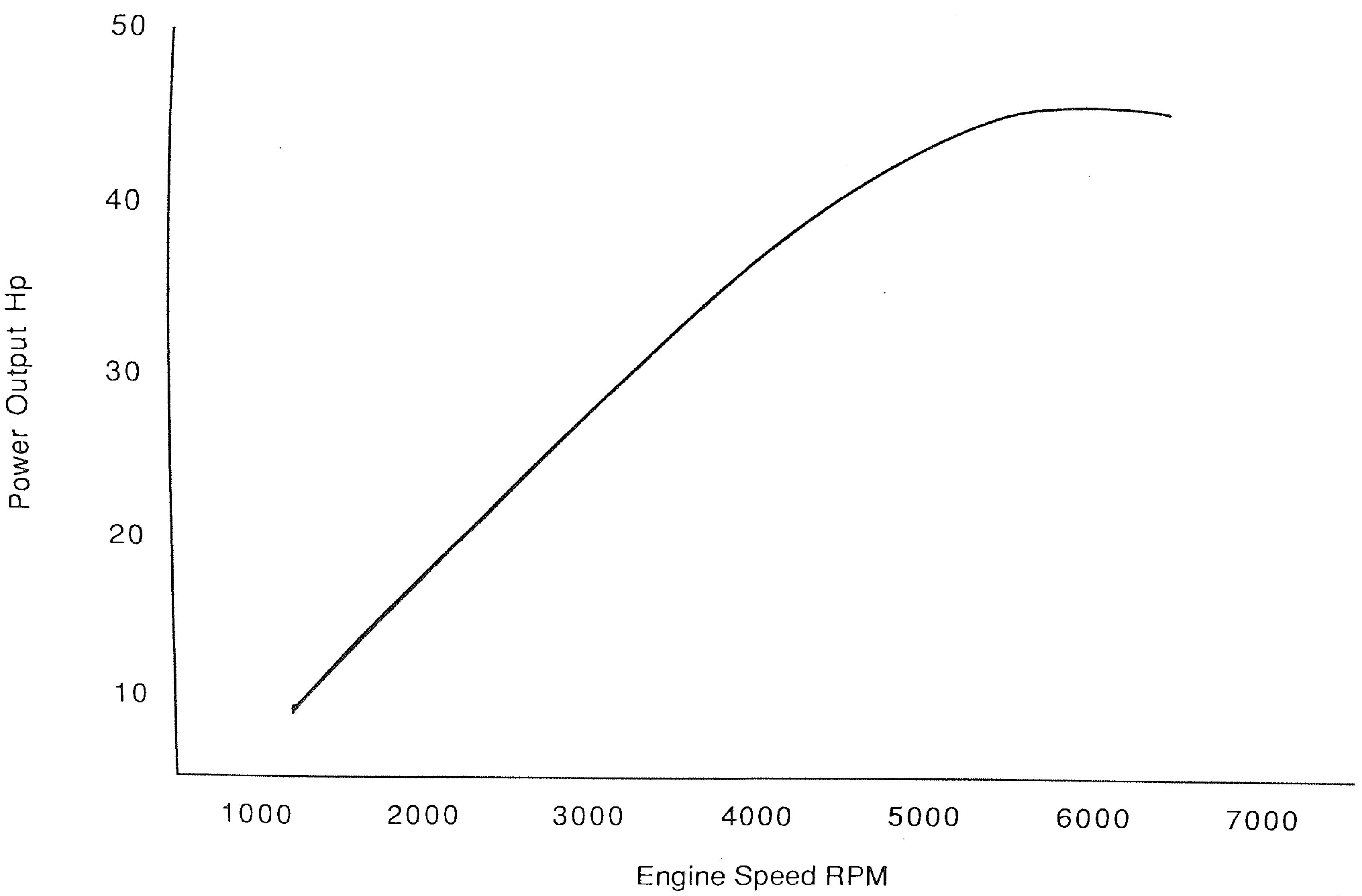

Figure 22 Engine Power Output Versus Engine Speed

After warming up of the engine various loads were applied randomly to ensure that a specific speed gave one millivolt reading. Engine speed was then reduced to a minimum and subsequently increased in steps up to 6500 rpm. Millivolt readings were taken and engine torque and power output were derived (Table 3) and plotted, Figures 21 and 22. Maximum torque was produced at 3000 rpm and maximum power at about 6000 rpm as expected. Values were slightly higher that the engine manual stated.

2.8 Engine Compression Ratio

Displacement and compression volumes measured when the engine was dismantled, using kerosene, suggested that there was a variation amonst the cylinders which needed to be checked. These measurements are given in Table 4 and produced compression ratios for cylinders 1 to 4 of 8.92, 9.13, 9.07 and 9.07 respectively. Total engine capacity was measured as 904 cc. Two further methods of measurement were made the first being the use of a compression tester. Results are given in Table 5, these show for cylinders 1 to 4 8.93, 9.52, 9.09 and 9.07 as the compression ratios. Cylinder 2 is noticeably higher and this may be due to tighter piston rings and/or better valve seating than the others. The other method tested, known as the Morse method involves power output measurement for the engine running on all four cylinders and on each combination of three to determine the cylinder with the least power loss. Results of two tests are given in Table 6, 7 and 8 which show that cylinder two has the least power loss associated with it when the spark plug is disconnected. Cylinder 2, therefore, had the highest compression ratio and/or the lowest leakage of gases from the chamber.

Later testing with knock detecting equipment found cylinder 2 to be the most likely to knock as the fuel quality was reduced.

Table 4 Displacement and Compression Volume

Cylinder	Head + Gasket (cm^3)	TDC Cylinder Volume (cm^3)	Total (cm^3)
1	24.3	4.2	28.5
2	23.8	4.0	27.8
3	24.0	4.0	28.0
4	24.0	4.0	28.0

Cylinder	BDC Cylinder Volume (cm^3)	Total Pre-compression Volume (cm^3)
1	230.0	254.3
2	230.0	253.8
3	230.0	254.0
4	230.0	254.0

Total Capacity = 904 cc (All measurements made by filling with kerosene)

Copression Ratio = Total Pre-compression Volume / Total Compression Volume

Cylinder	Compression Ratio
1	8.92
2	9.13
3	9.07
4	9.07

Table 5 Compression Test

Cylinder	Pressure (Psi)				Average Pressure (Psi)
1	131.5	126.0	130.0	131.5	131.33
2	139.0	140.0	140.5	140.0	139.88
3	135.0	132.5	134.0	133.0	133.63
4	132.5	133.0	134.0	134.0	133.38

Compression Ratios determined by this method were :-

(Atmospheric Pressure = 760 mm Hg = 1013.25 mbar = 14.696 Psi)

Cylinder	Compression Ratio
1	8.93
2	9.52
3	9.09
4	9.07

2.8.1 Morse Method Power Test

Wide Open Throttle

Constant Speed 4 Cylinder Operation)
) Morse Method
Reset to the Same Speed Running Only on 3 Cylinders)

Table 6 Morse Method at 1500 rpm

Plug Removed	Millivolts	Power (Hp)	Power Loss (Hp)	
0	2.55	14.79		
4	1.86 (1.85)	10.78	4.06	
0	2.56	14.84		
3	1.91(1.90)	11.07	3.77	
0	2.56	14.84		
2	1.95 (1.94)	11.31	3.53	
0	2.57	14.90		
1	1.88 (1.88)	10.90	3.94	
0	2.56	14.84		
			15.30	Total

Repeated experiments in brackets

Table 7 Morse Method at 2000 rpm

Plug Removed	Millivolts	Power (Hp)	Power Loss (Hp)
0	2.65	20.49	
4	1.90	14.67	5.82
0	2.65	20.49	
3	1.94	15.00	5.49
0	2.65	20.49	
2	1.96	15.15	5.34
0	2.66	20.49	
1	1.92	14.84	5.62
0	2.65	20.49	
			22.27 Total

Table 8 Summary of Morse Method Test Results

% of Total Losses	Cylinder	rpm	Order of Lowest Loss
26.53	4	1500	4
24.64	3	1500	2
23.07	2	1500	1
25.75	1	1500	3
26.13	4	2000	4
24.65	3	2000	2
23.98	2	2000	1
25.24	1	2000	3

Power loss on cylinder 2 is least.

CR on cylinder 2 is greatest; partly due to smaller combustion volume.

Pressure in cylinder 2 is greatest which could possibily be due to tighter piston rings and/or better seating of valves. The cylinder may act like a compressor having lower losses due to blow-by gases etc

Knock is greatest in cylinder 2.

2.9 Air Fuel Ratio

The fuel consumption of the engine was measured at a number of engine speeds at wide open throttle and air flow measurements were derived from graphs produced by the pressure variation across the air flowmeter. Figures 46 and 47 provided data for a plot of air fuel ratio against engine speed, shown as Figure 48 (see Results, Chapter 3). This was used with the emissions data gathered in later experiments, and also to determine quantities of oxygenates required in the test programme.

2.10 Knock Detection Equipment

Engine knock was detected by several methods the simplest of which was by listening to the engine when wearing ear defenders which muffled the ordinary engine noises. The knocking was easily detectable at low engine speeds as a mechanical tapping sound. A stethoscope arrangement was used at higher speeds with reasonable success, however, remote sensing was required to enable all instrumentation to be monitored simultaneously and because of the difficulty of detecting the onset of knock at high engine speeds. Two different knock sensors were obtained. One a Bruel and Kjaer type 4369 piezoelectric accelerometer and the other a CEL type 7G11 piezoelectric pressure washer.

The Bruel and Kjaer accelerometer was chosen by its frequency detection range which adequately covered that of knocking, 5 to 15 kHz, and on its ability to withstand quite high temperatures. It was mounted on one of the cylinder head bolts, which was tapped, by a stud following tests using a magnetic coupling to determine the optimum mounting position to emphasise pick-up from all four cylinders above other engine noise. The optimum place was found to be as shown in Figure 23. The signal produced was fed into a dual beam storage oscilloscope via an amplifier. Originally a small amplifier was built but this was not very satisfactory and a Kistle type 566 charge amplifier was later used. Two types of oscilloscope triggering mechanism were considered to allow identification of the accelerometer signals.

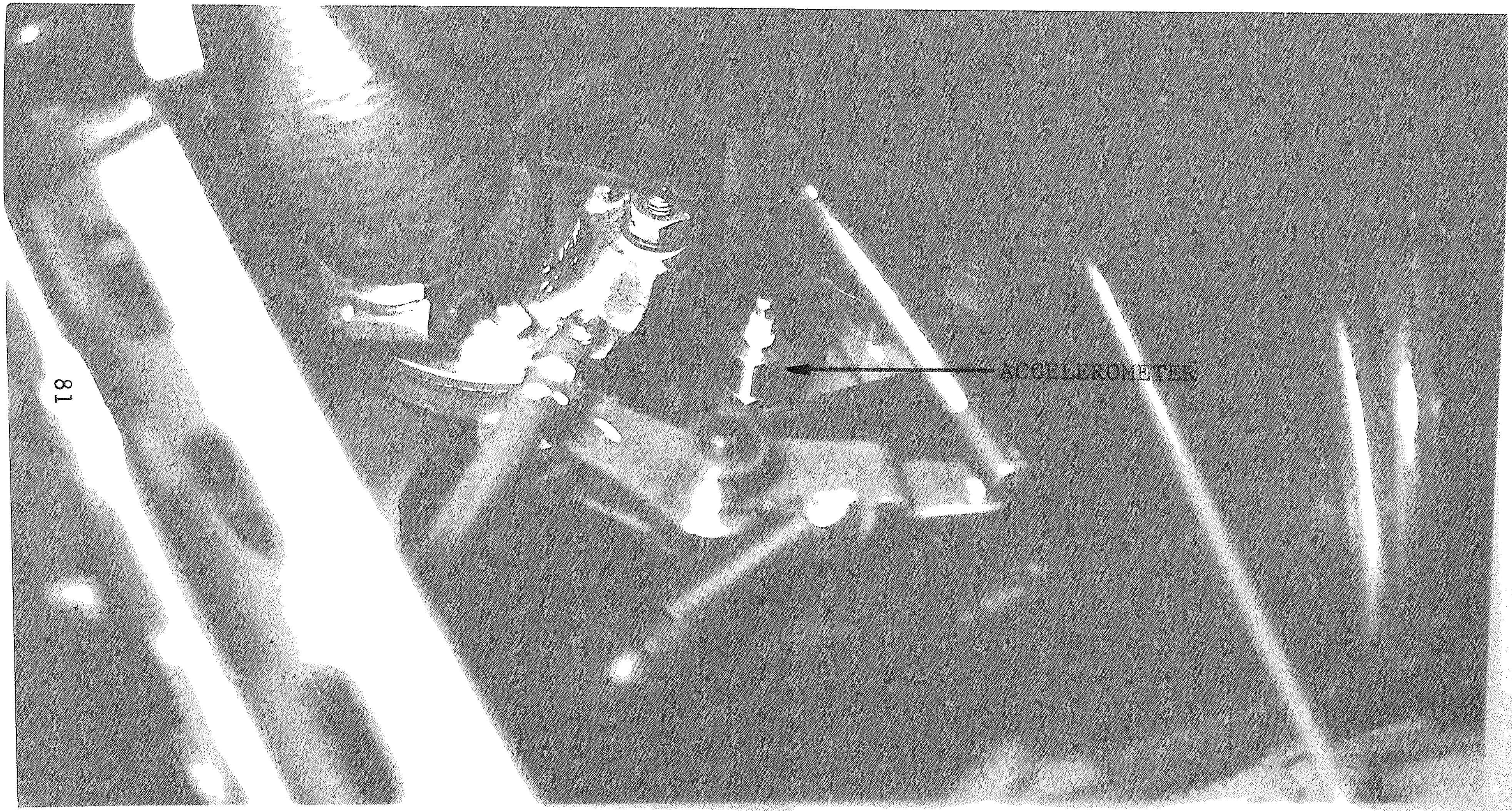

Figure 23 Bruel and Kjaer Accelerometer Shown Mounted in Position

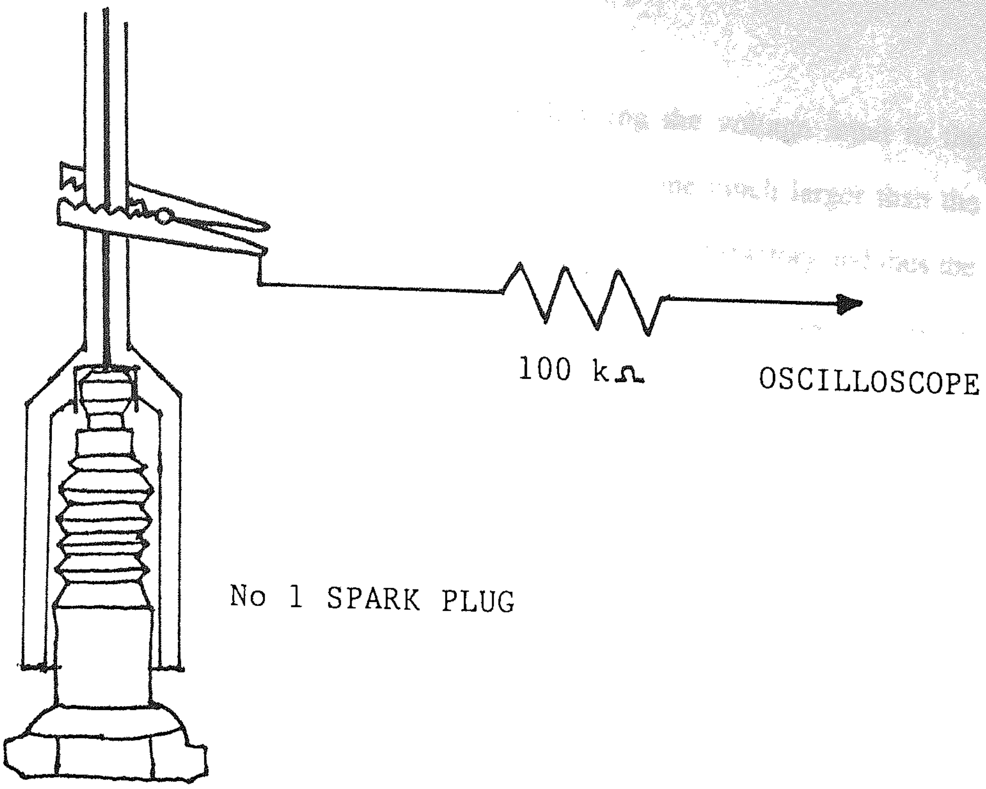

Figure 24 Simple Oscilloscope Triggering System

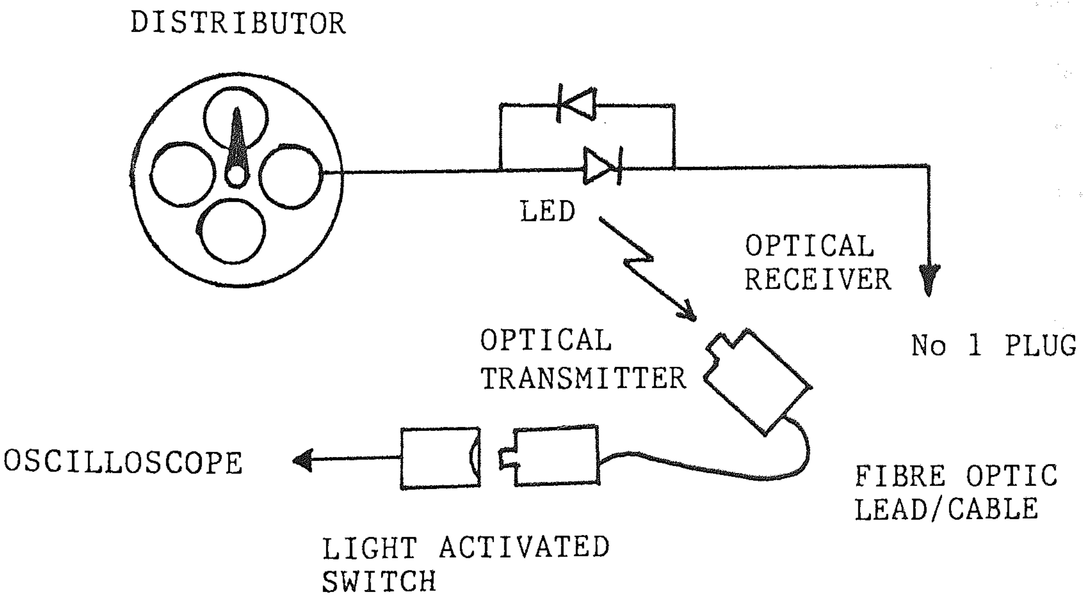

Figure 25 Light Activated Oscilloscope Triggering System

Connecting direct to plug number 1 lead and limiting the voltage input to the oscilloscope, Figure 24, produced a trace of four peaks, one much larger than the others which triggered the oscilloscope. This method proved satisfactory and thus the more complex method using a light emitting diode and a light activated switch was not explored, although it is used in industry, Figure 25.

The signal trace obtained by the accelerometer consisted of four bands of noise representing the firing of the cylinders in order, ie 1 3 4 2. A typical trace is shown as Figure 26. Using the storage mode on the oscilloscope the occurrence of knock is easily detectable due to the large spikes observed within the noise pattern associated with normal combustion.

The second piezoelectric knock detector used was in the form of a ring, often called a knock washer, which replaces the compression washer on a spark plug and detects the pressure variation within that one cylinder, Figure 27. For reasons previously given cylinder two was chosen for this detector, Figure 28. The signal from this pressure transducer was in the form of a typical pressure trace, Figure 29, and was powerful enough not to require amplification. The trace was also strong enough to be used to trigger the oscilloscope and thus marking the position of number 2 cylinder on the accelerometer trace, making the other trigger mechanism redundant.

Photographs of oscilloscope traces showing varying degress of knock, detected by the transducers are shown as Figures 30 - 36.

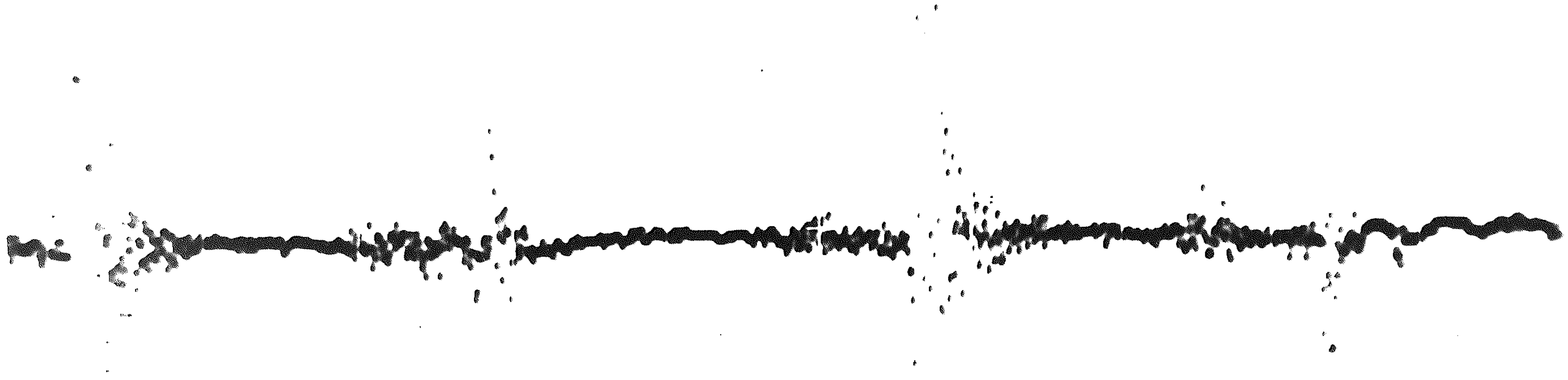

Figure 26 A Typical Trace Produced by the Bruel and Kjaer Accelerometer

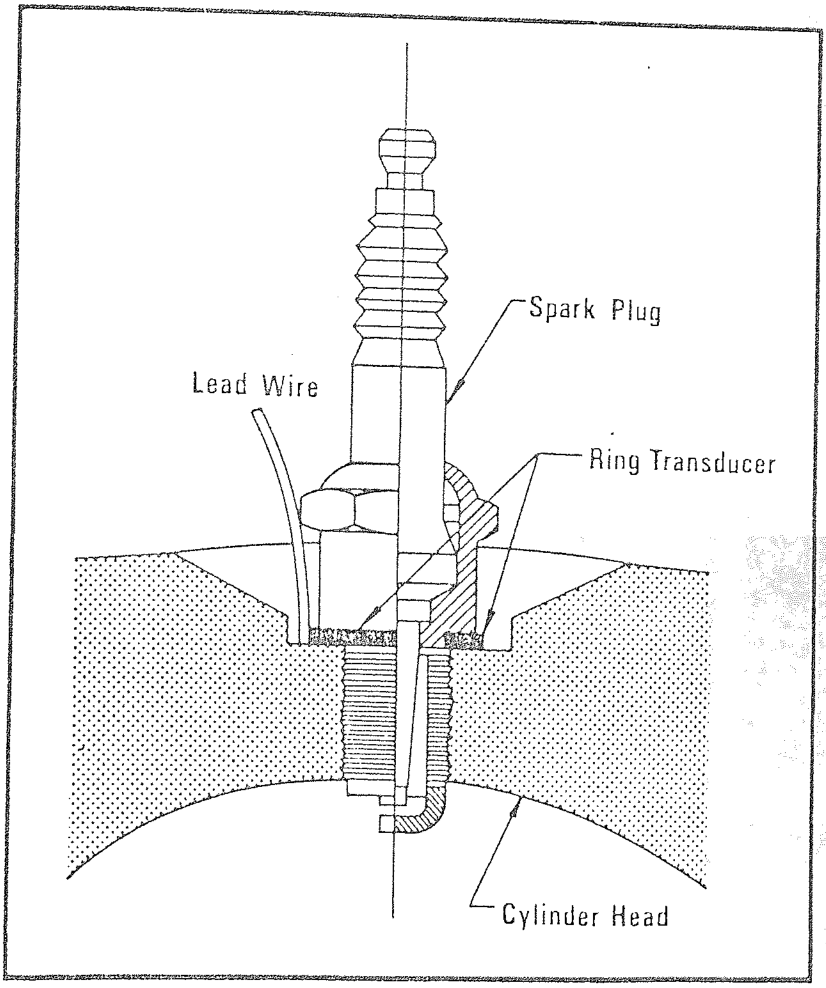

Figure 27 Method of Mounting YG11 Piezoelectric Transducer

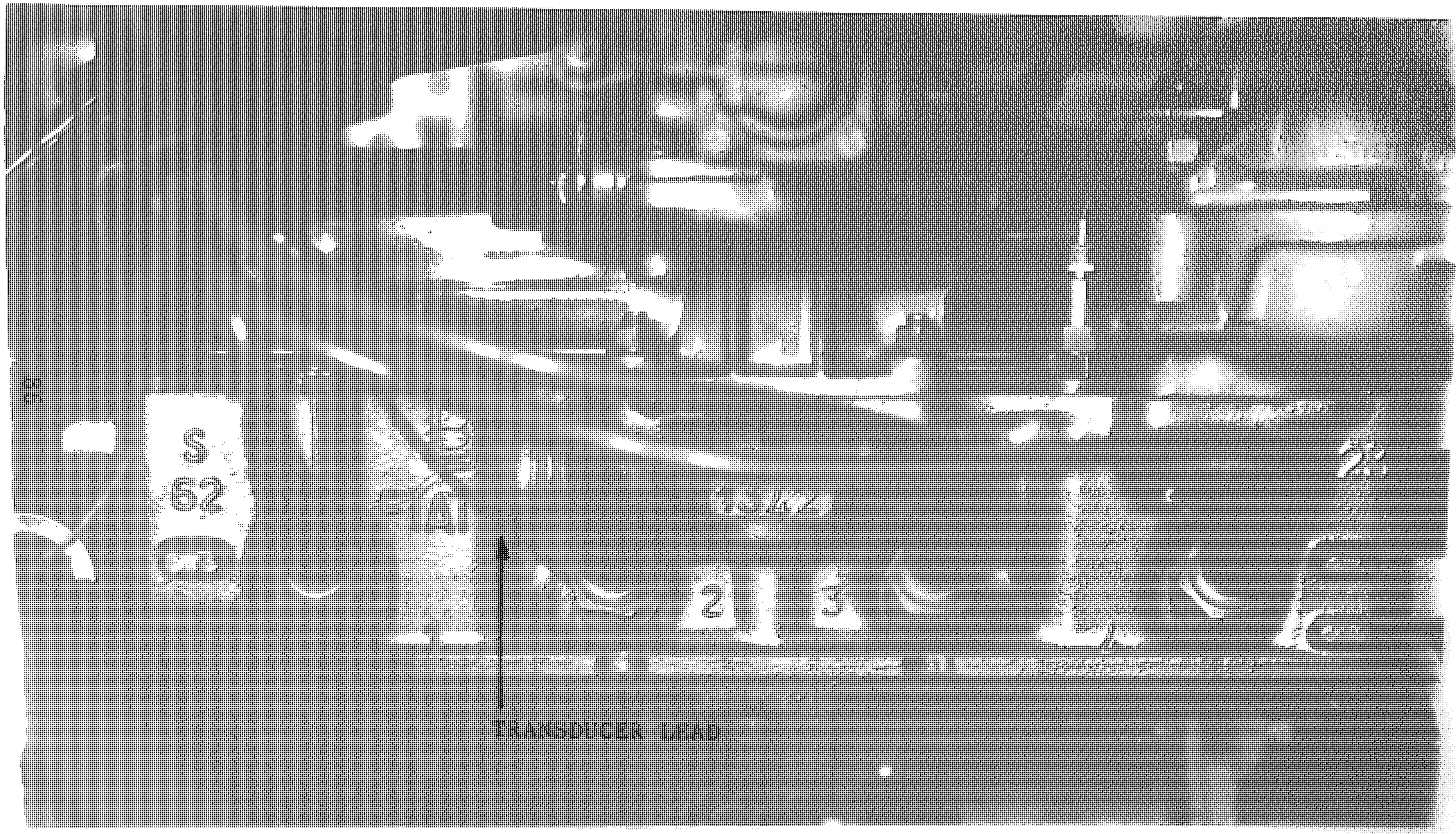

Figure 28 Positioning of YG11 Piezoelectric Transducer

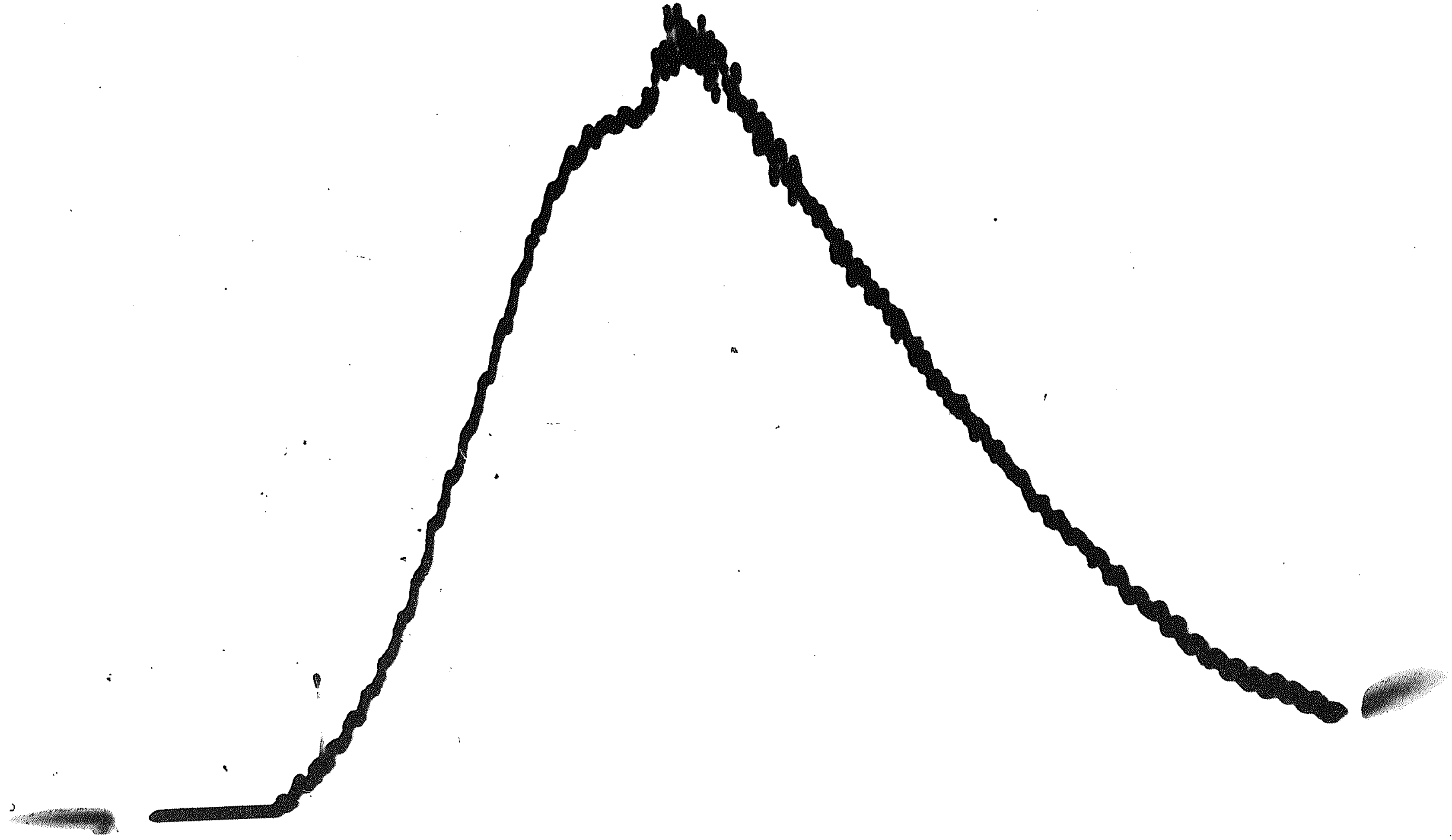

Figure 29 A Typical Trace Produced by the YG11 Transducer

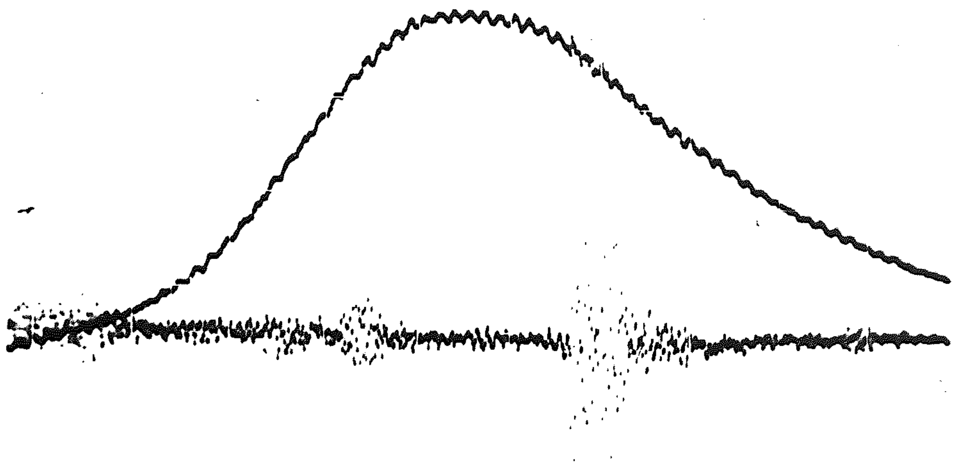

Figure 30

Figures 30 to 32 show the onset of trace knock from normal combustion

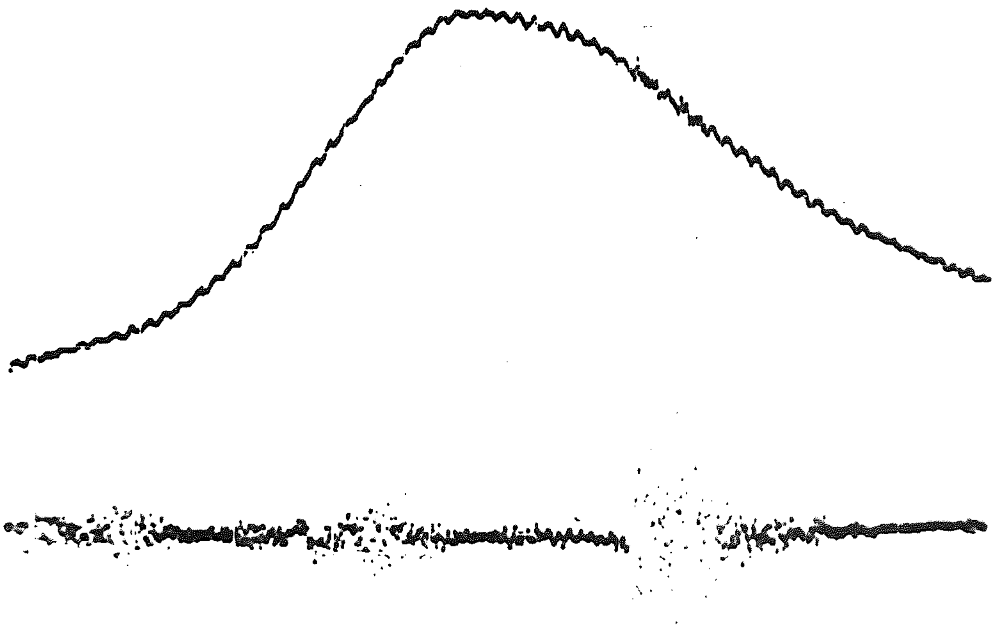

Figure 31

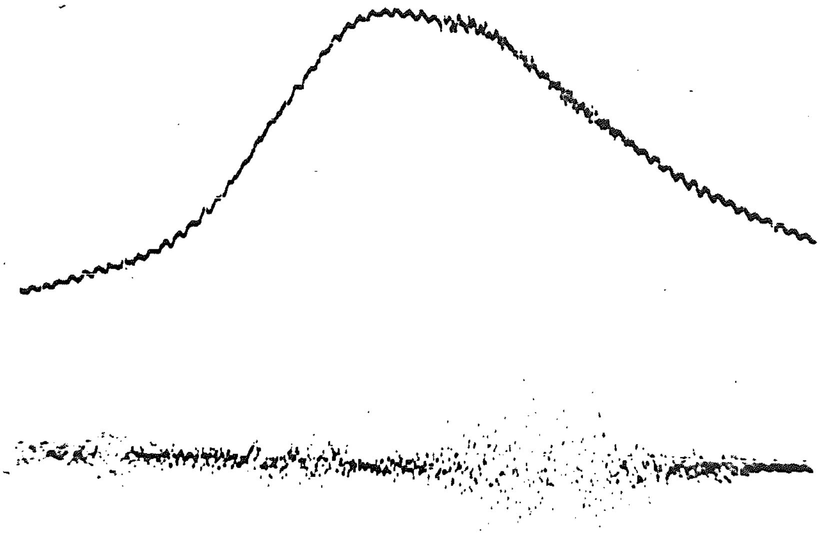

Figure 32

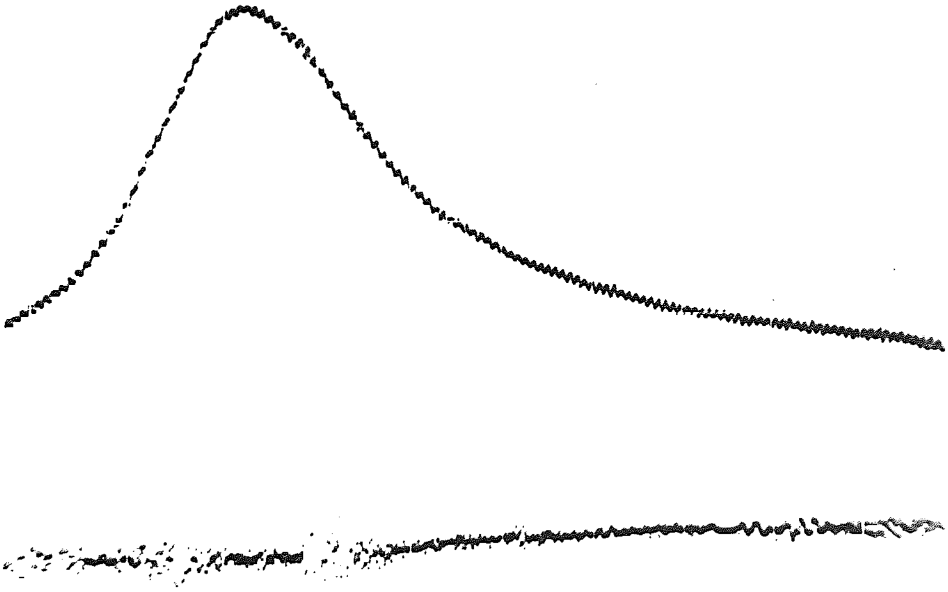

Figure 33 Normal Combustion

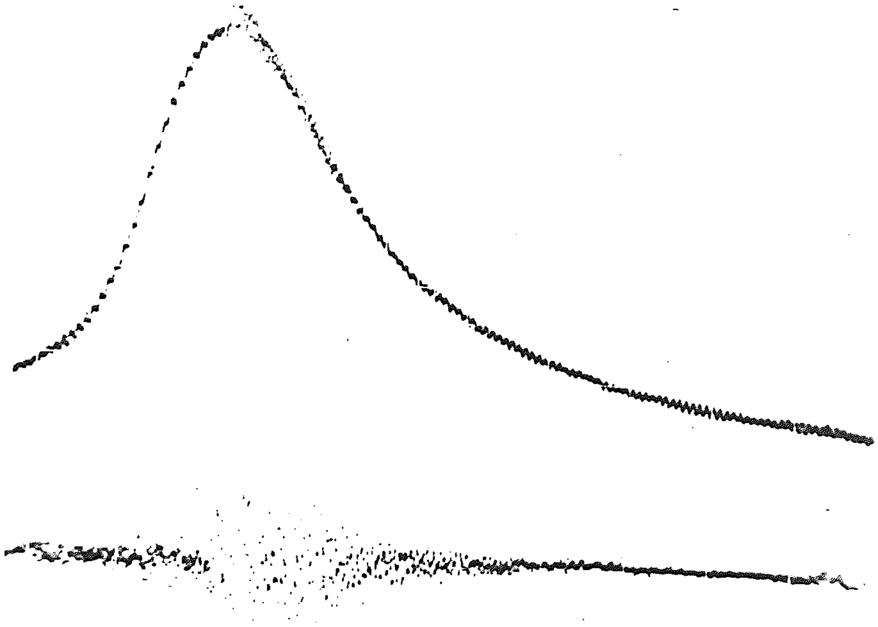

Figure 34 Light Knock

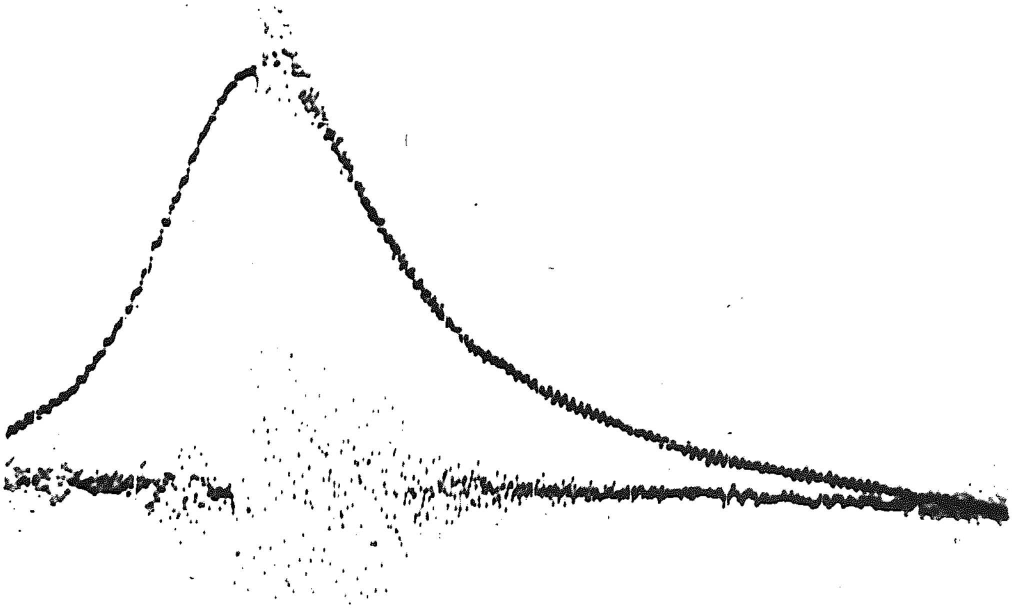

Figure 35 Heavy Knock

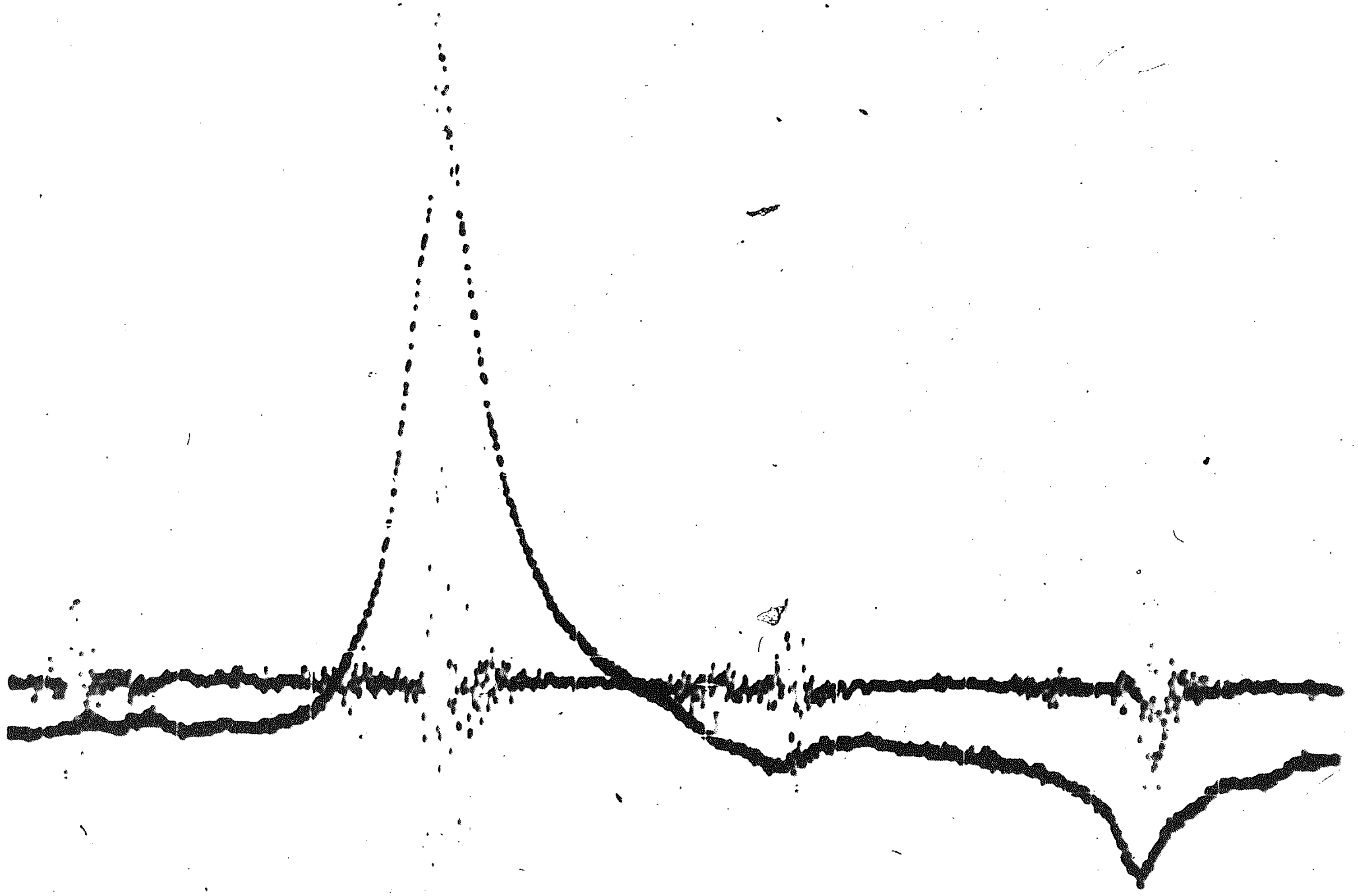

Figure 36 Full Engine Cycle Under Heavy Knocking Conditions

2.11 Operating Procedure for Test Engine Equipment

Having described the equipment used in the test programme a brief description of its operation is given here. At least 30 minutes is required for warm-up of the oscilloscope, air flowmeter, micromanometer and infra-red gas analyzers. Having ensured that the dynamometer is set to minimum load and that there is adequate water pressure, the dynamometer cooling water and engine cooling water can be switched on. The fuel may then be turned on, the choke set and the engine started. The electric radiator fan is next switched on and the engine warmed up for fifteen to twenty minutes or until the sump oil temperature is of the order of 80°C. Simultaneous engine throttle opening and load increase are carried out until wide open throttle (WOT) is achieved. Engine speed is now controlled solely by dynamometer load variation which for the Fiat engine ranges from 1050 rpm upwards. The change-over to the test fuel is made when it is felt that the engine is running smoothly under load. After about three to five minutes or 300 cc fuel used, testing can be undertaken. Starting at a low engine speed, which is slowly increased, the occurrence and disappearance of both light and trace knock are sought. Engine speed is then decreased and increased several times to check these values. Aural detection as well as oscilloscope trace analysis are used to determine the levels of knock. Light knock is defined as continuous, audible and easily distinquishable on the oscilloscope trace, (see Figure 34), which reduces dramatically with a slight increase in engine speed. Trace knock is the first detectable continuous knock which usually occurs at about 150 to 200 rpm above light knock.

Shut-down of the equipment is the reverse of start-up.

2.12 Test Fuels for Experimentation

The base gasoline used in the experiments to determine the effects of different oxygenates was chosen so that a comparison of these results could be made by companies associated with CORC, ["The Co-operative Octane Requirement Committee"]. The fuels used were blended from a high and a low key* and produced a series known as F-7. This series is a low leaded one averaging at 0.14 g/l, low in olefines and having a medium ΔR_{100} (8.5 to 10.5 octane numbers) and sensitivity (7.5 to 11.5 octane numbers). A detailed blending chart is given as Table 9 and blending curves as Figure 37. This series has now been superseded by G-7, a fuel with similar properties currently used in co-operative test programmes by the oil companies. Blending information is given as Table 10 and Figure 37.

Figure 38 shows the F-7 series plotted on ΔR_{100} vs sensitivity of the fuel. ΔR_{100} is the RON of a fuel less the RON of that part which distills off at 100°C. Sensitivity is the RON of a fuel less the MON, and for a given RON indicates the probability of engine knock at higher engine speeds, where MON appears to be more important. When compared to a 1979 Survey of European Gasolines (data from 24), Figure 39, it can be seen that F-7 is representative of the middle area of the bulk of those tested. Supplies of F-7 key components were obtained from Esso Petroleum and blended in the laboratory in single RON increments.

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* Key denotes a blend of components having a specific octane number.

Table 9 Blending Information for Series F-7 Gasoline

RON	% High Key	MON	R_{100}	s	ΔR_{100}	TEL	TML	Aromatics	Olefines
90.0	1.0	82.2	79.8	7.8	10.2	0.09	0.02	36.0	4.0
91.0	8.0	82.2	80.7	8.2	10.3	0.09	0.02	37.0	4.0
92.0	15.0	83.5	81.6	8.5	10.4	0.10	0.02	37.0	5.0
93.0	22.0	84.2	82.6	8.8	10.4	0.10	0.02	38.0	5.0
94.0	29.5	84.8	83.7	9.2	10.3	0.10	0.03	39.0	5.0
95.0	37.5	85.5	84.8	9.5	10.2	0.10	0.03	39.0	6.0
96.0	45.5	86.2	86.0	9.8	10.0	0.11	0.03	40.0	6.0
97.0	54.5	86.9	87.2	10.1	9.8	0.11	0.03	41.0	6.0
98.0	64.5	87.7	88.5	10.3	9.5	0.12	0.03	42.0	7.0
99.0	74.0	88.4	89.7	10.6	9.3	0.12	0.03	43.0	7.0
100.0	85.0	89.1	91.0	10.9	9.0	0.12	0.04	44.0	7.0
101.0	96.0	89.7	92.3	11.3	8.7	0.13	0.04	45.0	8.0

Table 10 Blending Information for Series G-7 Gasoline

RON	% High Key	MON	R_{100}	s	ΔR_{100}	TEL	TML	Aromatics	Olefines
89	5.2	81.3	81.6	7.7	7.4	0.13	0.01	30.9	10.9
90	12.3	81.9	82.2	8.1	7.8	0.13	0.01	31.8	10.9
91	19.6	82.9	82.9	8.5	8.1	0.13	0.01	32.7	10.8
92	27.2	83.2	83.6	8.8	8.4	0.13	0.01	33.7	10.8
93	34.9	83.9	84.4	9.1	8.6	0.13	0.01	34.6	10.8
94	42.9	84.5	85.2	9.5	8.8	0.13	0.01	35.6	10.7
95	51.2	85.2	86.1	9.8	8.9	0.14	0.01	36.6	10.7
96	59.8	85.9	87.0	10.1	9.0	0.14	0.01	37.7	10.7
97	68.7	86.6	87.9	10.4	9.1	0.14	0.01	38.8	10.6
98	78.0	87.3	89.0	10.7	9.0	0.14	0.01	40.0	10.6
99	87.8	88.0	90.1	11.0	8.9	0.14	0.01	41.2	10.5
100	98.0	88.8	91.3	11.2	8.7	0.14	0.01	42.5	10.5

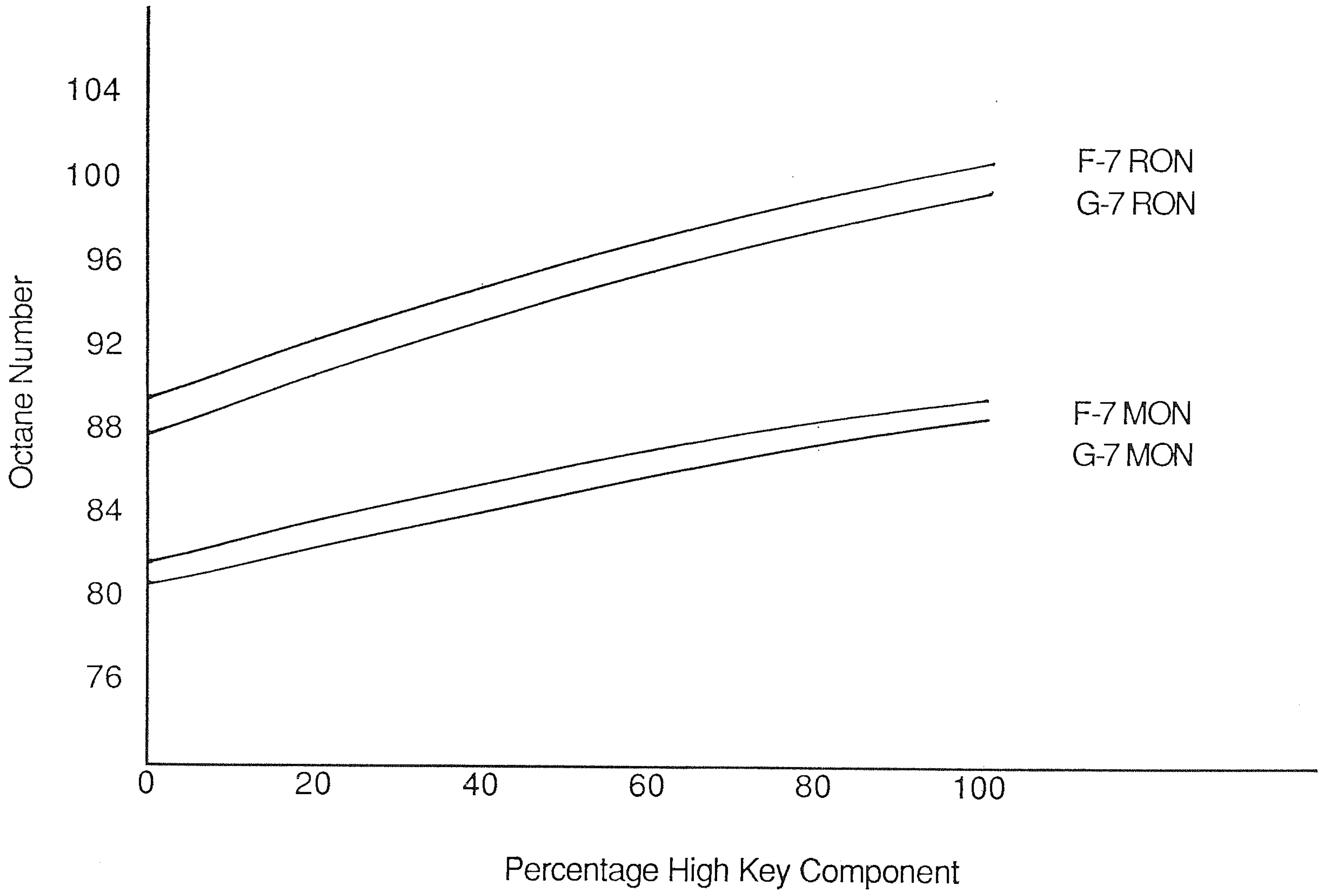

Figure 37 Series F-7 and G-7 Gasoline Blending Curves

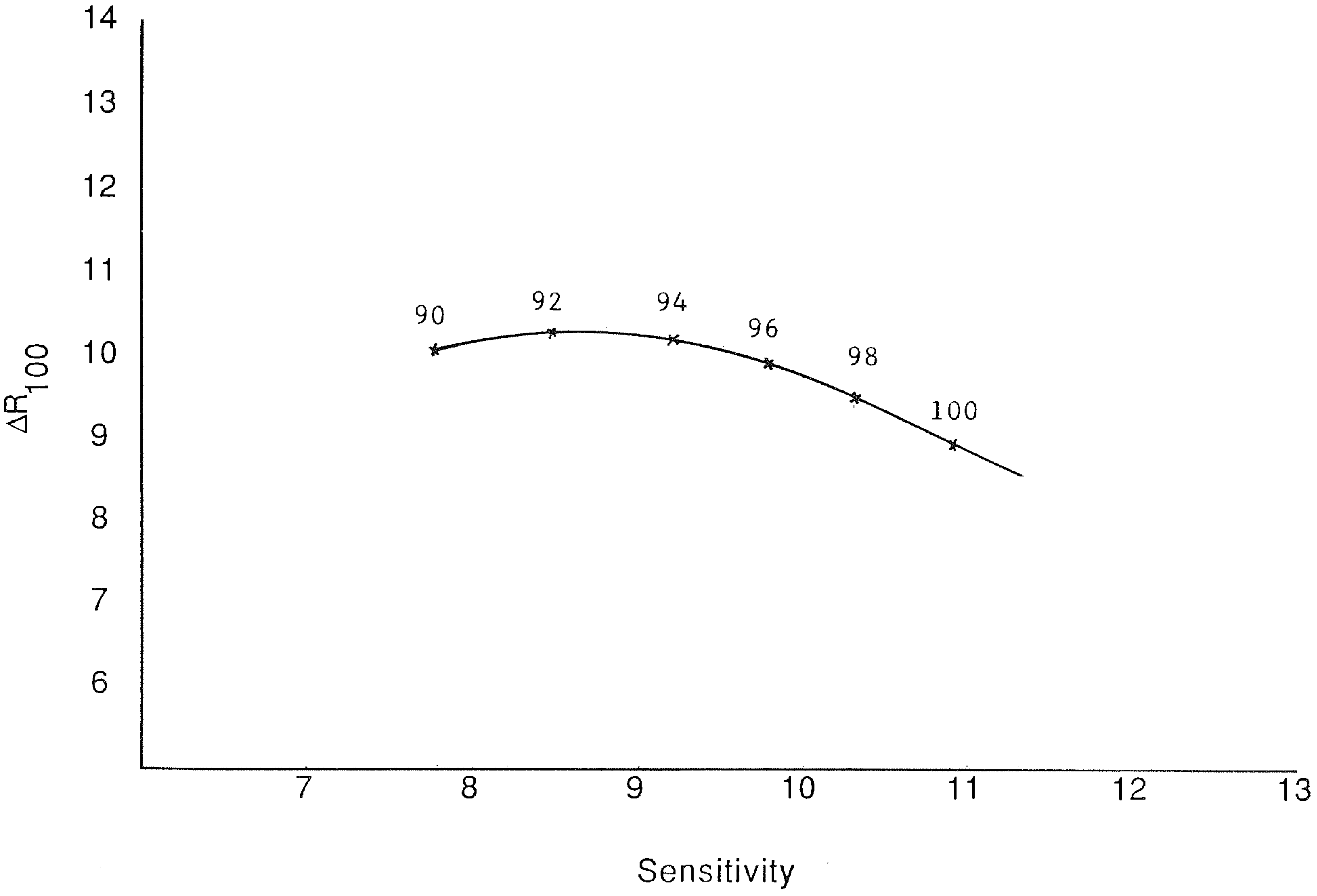

Figure 38 ΔR100 Verses Sensitivity for Series F-7 Gasoline

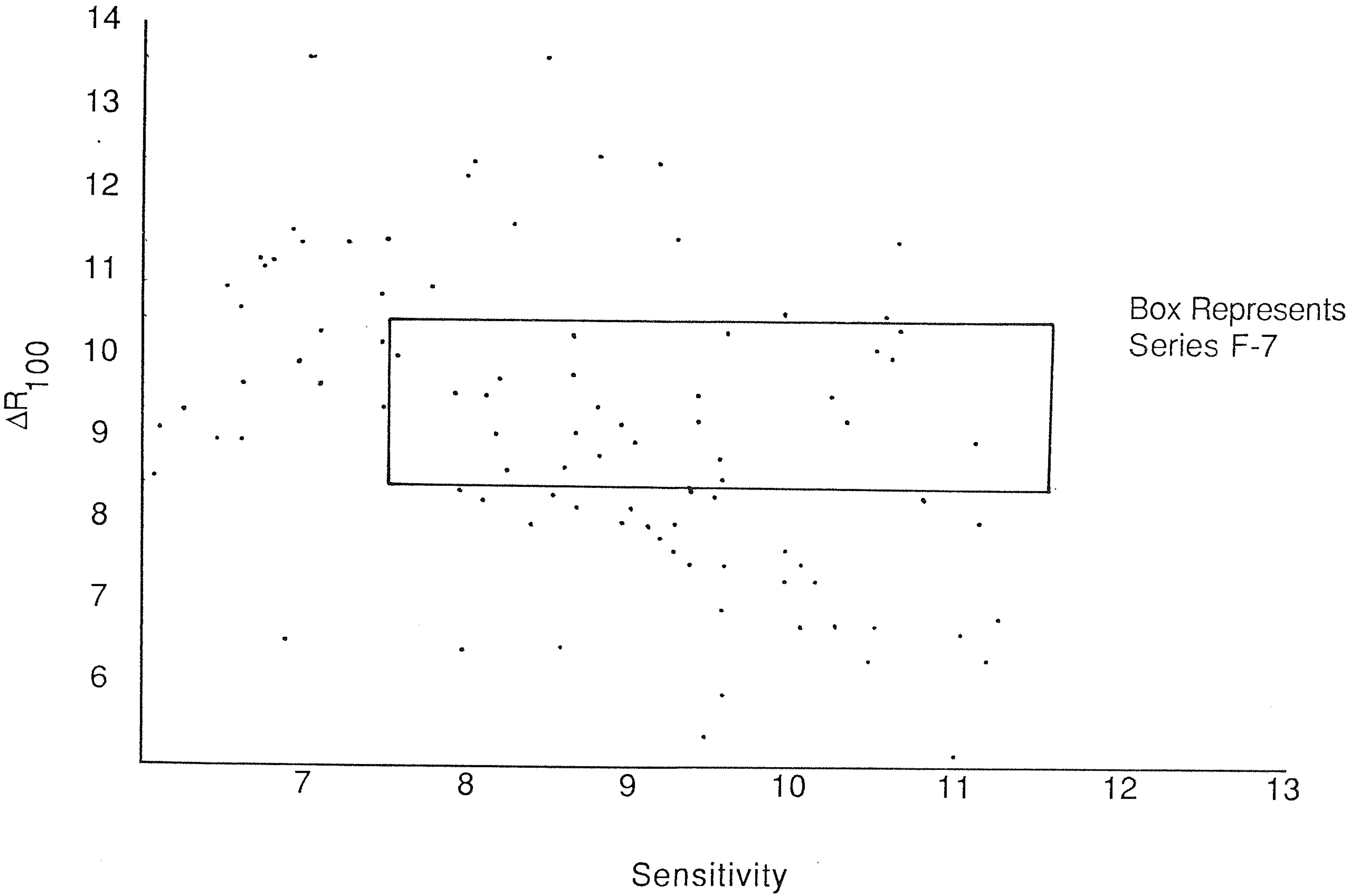

Figure 39 Series F-7 Gasoline Relative to Typical European Premium Gasolines from a Market Survey 1979 (Mahold and Tranie (41))

2.13 Oxygenates Used In Experiments

Four types of oxygenates were tested, namely alcohols, ethers, esters and ketones. There were several reasons for choosing those used which will be outlined here. The list of oxygenates and their concentrations is given in Table 11.

Table 11 Oxygenates Tested and the Volume Percent Blends Used

Alcohols		
	Methanol	5, 10, 15
	Ethanol	5, 10
	Tert Butanol	5, 10, 15, 20
Ethers		
	Methyl tert butyl ether	5, 10, 15, 20
	Diisopropyl ether	5, 10, 20
	Anisole	5, 10, 20
Esters		
	Dimethyl carbonate	5, 10
	Methyl Acetate	5, 10
Ketones		
	3 methyl butan-2-one	5, 10, 15, 20
	4 methyl pentan-2-one	5, 10, 15, 20
	Acetone	5, 10, 20
	Methyl ethyl ketone	10, 20

Working down the list, the alcohols and methyl tert butyl ether (MTBE) were included as a substantial amount of work has been done in the past using them, much of which is encouraging to those advocating the use of oxygenate/gasoline blends. This formed a solid base from which to start the research and ensure equipment and test procedures were adequate. The use of these first four in the list by others has been due to their low production cost, availability, effectiveness, materials compatability and for some their historical use over the past sixty years.

The majority of the other oxygenates in the table were chosen because of their branched structure small molecular size and in some cases prior knowledge of their RON and MON. Present cost was also important although bulk production of a presently expensive chemical and new processes could make other oxygenates not tested here viable.

It should be noted that unlike CORC group tests the oxygenates were lead-free causing a slight lead depletion in the fuel blend which will have resulted in a slightly lower RON than would otherwise be obtained. This effect was considered relatively small and coupled with the undesirability of handling TEL and TML led to it being neglected.

Concentrations used in experiments varied depending upon the oxygen content, weight percent, of each chemical. This was in order to limit total blend oxygen content to a maximum of about 4 % wt/wt, this is above EPA and European maximums at present but still within the limits of good drivability, ie no observed problems caused by the leaning effect due to the extra oxygen in the combustion process.

Initial tests were carried out using 2-star gasoline, followed by a limited set of tests using F-7. The bulk of the tests were carried out later including combinations of 2 and 3 oxygenates again using F-7 fuels after the new and better analysis equipment had been obtained.

CHAPTER 3

RESULTS

RESULTS

3.1 Preliminary Testing of Engine Using Oxygenates in 2-star

After stripping, cleaning and inspection the engine was run for 40 hours on forecourt four star to build up deposits in the cylinders prior to testing. This was done to ensure that the combustion charateristics varied little during the tests due to a "clean" or "dirty" engine. For each experiment the engine was warmed up using four star and then changed over to the test fuel. Two minutes were allowed for the carburettor to clear, followed by a further three minutes for the engine to settle down with the new fuel. 2-star gasoline was run through periodically to compare the audible and visual (oscilloscope trace) knock with the test fuels. During a test the level of knock was assessed, the fuel changed to four star and then back to the test fuel and reassessed to confirm initial results.

Results

1.

Engine speed	1600 rpm
Load	2.32 mV
Air pressure drop	21 mmH_2O
2-star	knocked severely
2-star + 10 % methanol	no detectable knock
2-star + 20 % ethanol	no detectable knock

2.

Engine speed	1500 rpm
Load	2.30 mV

	Air pressure drop	18 mmH_2O
	2-star	knocked severely
	2-star + 5 % methanol	no detectable knock
	2-star + 2 % methanol	knock detected, audible and visual
	2-star + 10 % ethanol	no detectable knock
	2-star + 5 % ethanol	slight knocking observed, audible and visual
3.	Engine speed	1580 rpm
	Load	2.32 mV
	Air pressure drop	21 mmH_2O
	2-star + 10 % MTBE	no detectable knock
4.	Engine speed	1640 rpm
	Load	2.33 mV
	Air pressure drop	21 mmH_2O
	2-star + 5 % MTBE	no detectable knock
5.	Engine speed	1575 rpm
	Load	2.31 mV
	Air pressure drop	20 mmH_2O
	2-star + 2 % MTBE	knock detectable, audible and visual

These tests gave an idea as to the requirements of the three oxygenates tested when blended with 2-star which has a RON of about 93. They proved the equipment to be working satisfactorily and helped to establish the testing procedure for the main experiments.

3.2 Preliminary F-7 Tests

These tests were carried out using methanol, TBA, Oxinol 50 (50 % v/v methanol and 50 % v/v TBA)and MTBE in varying concentrations blended with F-7 fuels. Tests for trace knock only were carried out which put the effect of each oxygenate into perspective. The results are shown in Figure 40 - 43 and show the large effect of MTBE even in small concentrations, as it can be seen that the maximum engine speed associated with knock is greatly reduced. These tests formed a basis for the main programme and analysis of results. The extension of the tests to include light knock and better equipment reduced their significance however.

Graphs 40 - 43 and 50 - 87 have the experimentally determined knock limited conditions connected by straight lines to allow each blend to be distinguishable from the others especially were overlapping occurs and does not intend to imply that the condition between the points is linear.

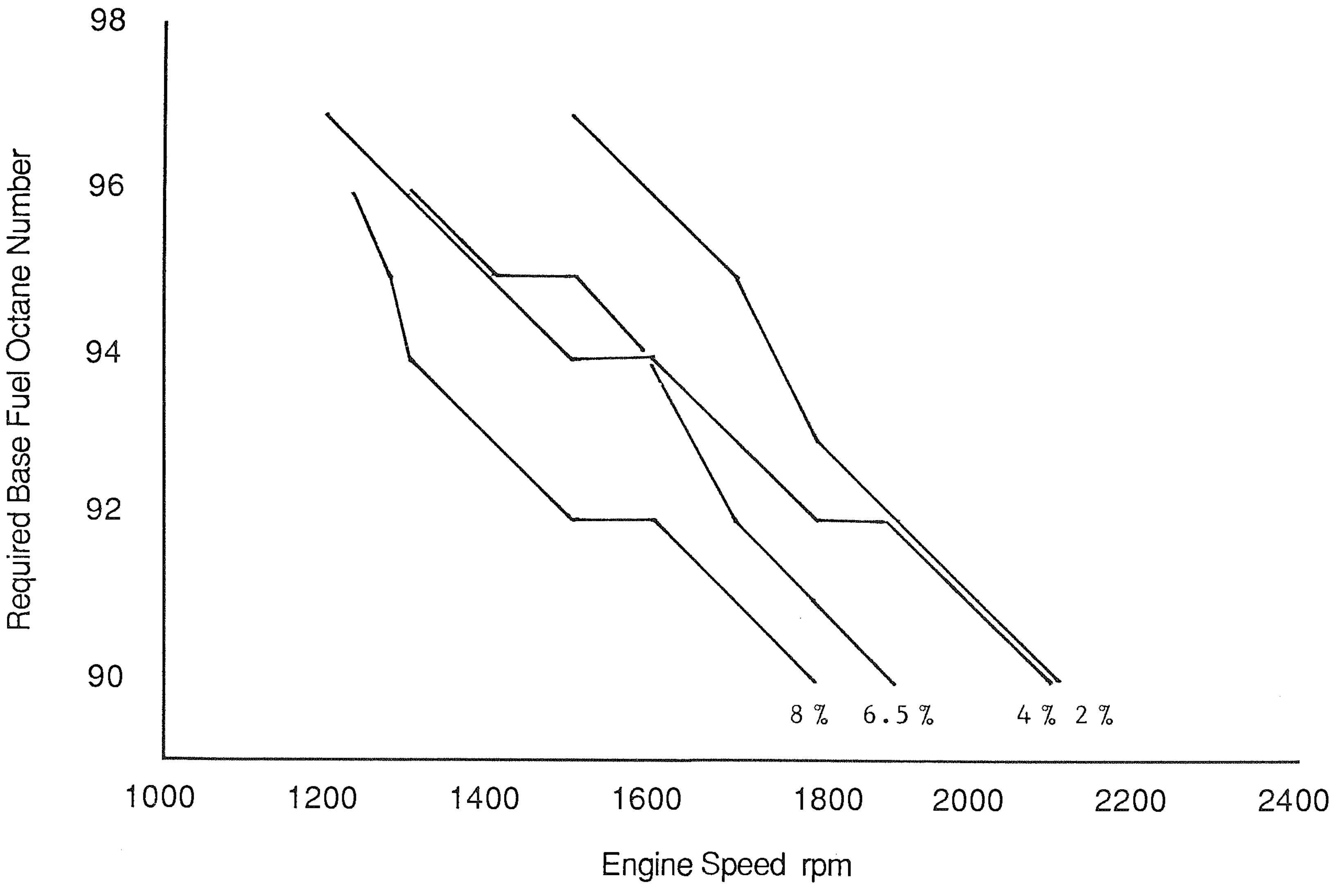

Figure 40 Preliminary Engine Test Results for Series F-7 Plus Methanol

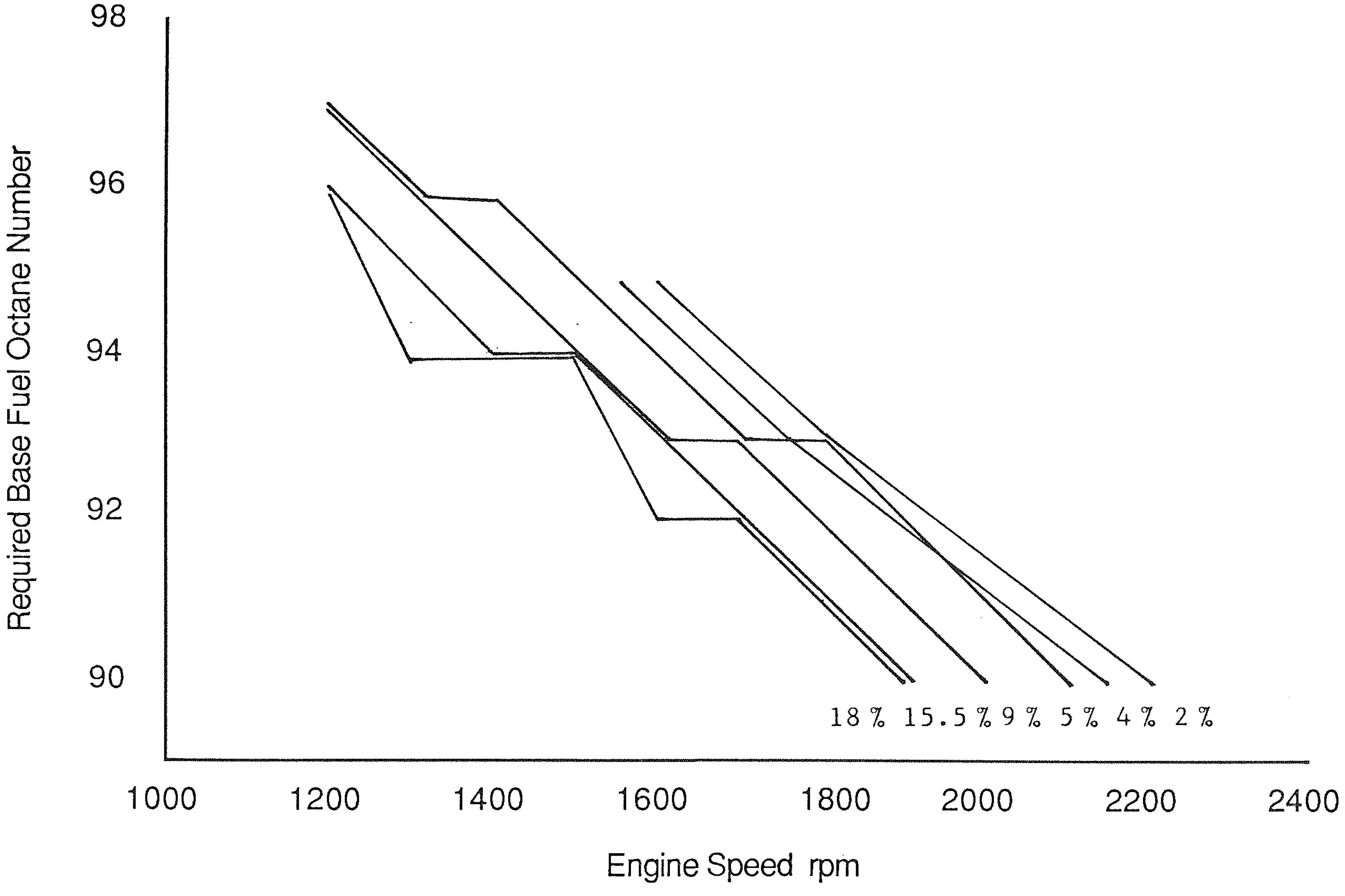

Figure 41 Preliminary Engine Test Results for Series F-7 Plus TBA

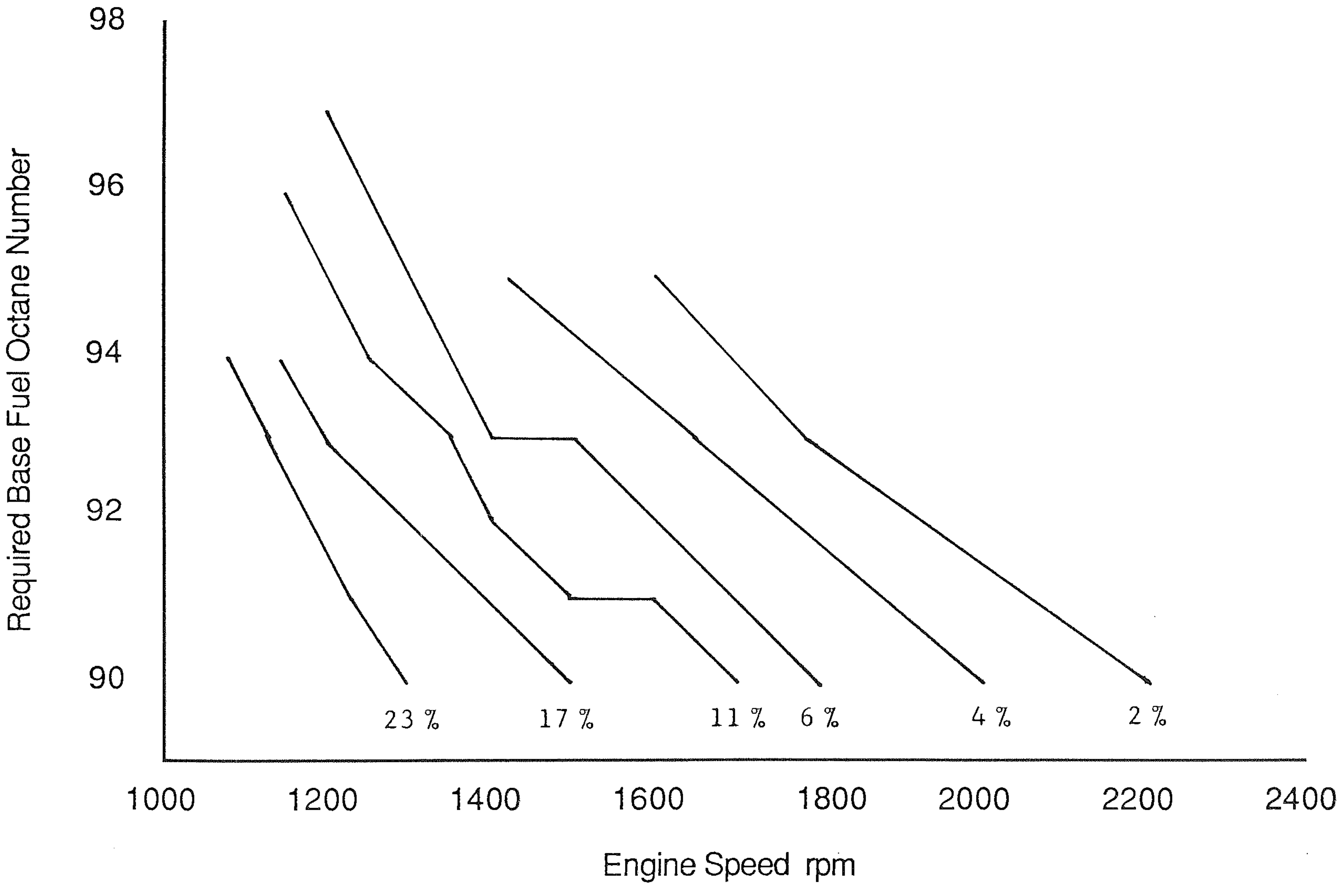

Figure 42 Preliminary Engine Test Results for Series F-7 Plus MTBE

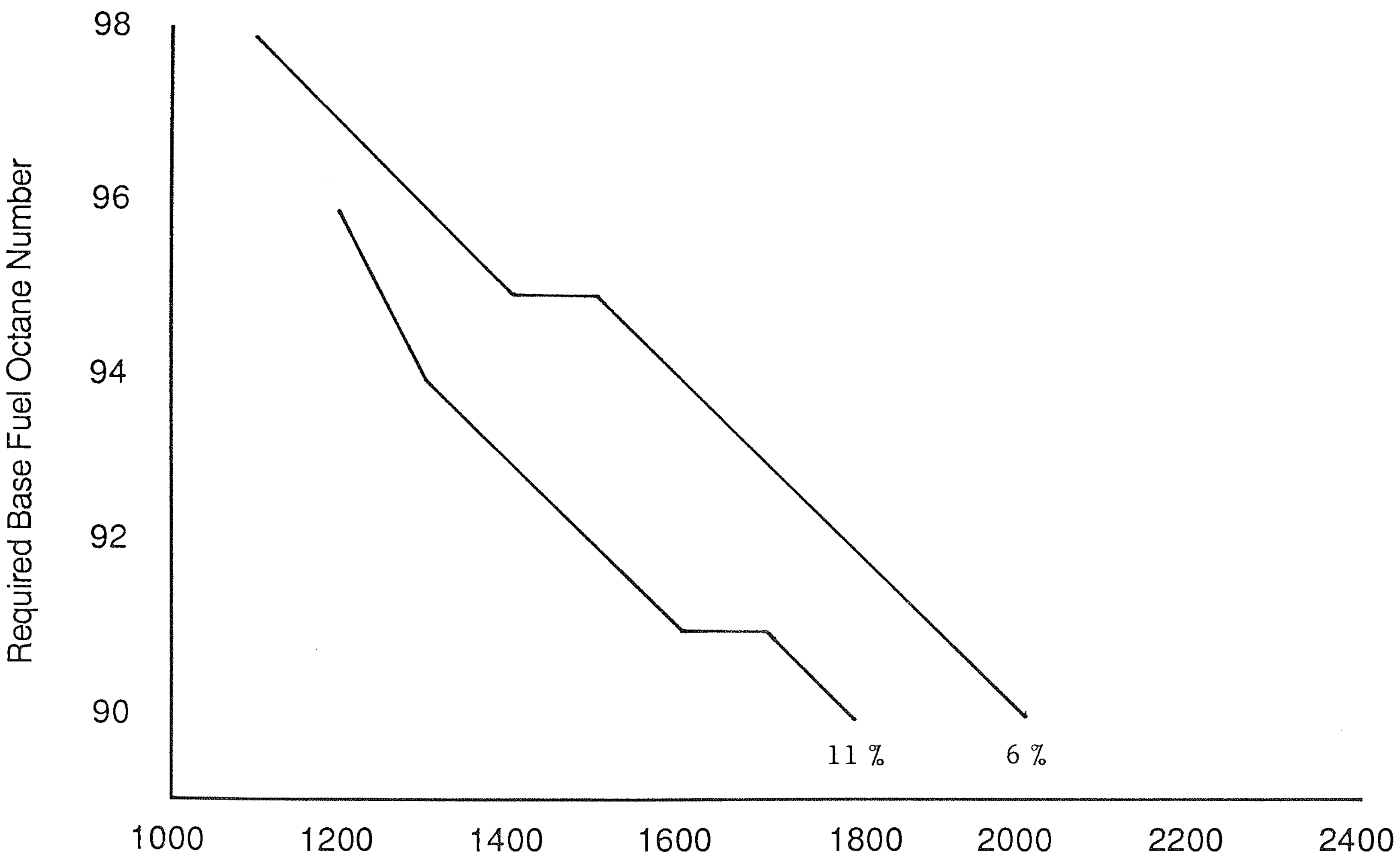

Figure 43 Preliminary Engine Test Results for Series F-7 Plus Oxinol 50

3.3 Main Experiments Involving Oxygenates

The aim of these experiments was (i) to test a number of oxygenates at different concentrations to detemine their effect on fuel antiknock quality and (ii) to combine two or more chemical types and change the individual chemicals in order to assess whether a synergistic effect is exhibited.

The oxygenates tested are listed in Table 11. The maximum concentration in a gasoline blend was set such that about 4 % wt/wt oxygen was contained in the blend. This limit should ensure that there were no adverse effects due to a too lean mixture. The concentrations chosen for the experiments are also listed in Table 11. The oxygenates fall into four categories : alcohols, ethers, esters and ketones.

The base fuels used for the experiment were the CORC Series F-7 90, 92, 94 and 96 RON gasolines. The oxygenates were blended with each base fuel and tested at wide open throttle and constant speed. Load was varied using a dynamometer and knock was detected by ear and also by a piezoelectric transducer connected to an oscilloscope. Two knocking conditions were examined, firstly trace continuous knock detectable only by instruments and, secondly, light knock audible, continuous and in most cases easily recognizable on the oscilloscope. Engine speeds at these two points were noted for each blend and limiting curves of engine speed against required octane number were drawn.

Comparison of the knock curves with one for pure base gasoline indicated the amount of appreciation due to the oxygenate. For example 10 % v/v MTBE in a 92 RON base knocks lightly at 1510 rpm. A pure base fuel of 94.4 RON would knock similarly suggesting an appreciation of 2.4 RON due to the MTBE. The appreciation was found to decrease with increasing base fuel RON.

Table 11 Oxygenates Tested and the Volume Percent Blends Used

Alcohols		
	Methanol (M)	5, 10, 15
	Ethanol (E)	5, 10
	Tert Butanol (TBA)	5, 10, 15, 20
Ethers		
	Methyl tert butyl ether (MTBE)	5, 10, 15, 20
	Diisopropyl ether (DIPE)	5, 10, 20
	Anisole	5, 10, 20
Esters		
	Dimethyl carbonate (DMC)	5, 10
	Methyl Acetate (MA)	5, 10
Ketones		
	3 methyl butan-2-one (3MB2)	5, 10, 15, 20
	4 methyl pentan-2-one (4MP2)	5, 10, 15, 20
	Acetone	5, 10, 20
	Methyl ethyl ketone (MEK)	10, 20

Combinations of oxygenates were expected to have an effect of an additive or less than additive nature when compared to their components. Anomalous fuel blend results of possible importance would be picked up during testing as less knock than average would be exhibited.

The results are shown as Figures 50 - 87 and in Tables 40 and 41 (Appendix 1). These show the maximum engine speed at which the knock occurred. Most results were obtained at the same absolute humidity although air pressure did vary slightly. Base fuels were checked regularly and many blends were retested to check for repeatability of results.

The results obtained for single oxygenates showed several chemicals to have similar effects in similar concentrations, when their oxygen content was comparable. Dual combinations were all tested as 10 % v/v blends which produced a range of 2 to 4 % wt/wt oxygen in the blends, with most at about 3.5 % wt/wt. Methanol/MTBE and methanol/ethanol blends appeared to have better than average effects in this concentration,most of the others having similar results. Treble combinations were blended at 15 % v/v. These showed some variation with methanol/MTBE/3methyl butan-2-one and methanol/MTBE/4methyl pentan-2-one being superior and methanol/MTBE/tert butanol also exhibiting quite good knock protection but not better than predicted for it from blending numbers.

Table 12 Weight Percent of Oxygen in the Oxygenates

M	50.0
E	34.8
TBA	21.6
MTBE	18.2
DIPE	15.7
Anisole	14.8
DMC	53.3
MA	43.2
3MB2	18.6
4MP2	16.0
Acetone	27.6
MEK	22.2

Table 13 Weight Percent of Oxygen in Blends of Oxygenates

	All oxygenates in equal % v/v (ie 1 : 1)
M/TBA	35.8
MTBE/TBA	19.9
M/MTBE/TBA	29.9
M/MTBE	34.1
M/DIPE	32.9
M/Anisole	32.4
M/4MP2	33.0
M/3MB2	34.3
M/E	42.4
M/DMC	51.6
M/MA	46.6
MTBE/4MP2	17.1
DIPE/4MP2	15.9
DMC/4MP2	34.7
MA/4MP2	29.6
MA/Anisole	29.0
MTBE/DMC	35.8
M/MTBE/DMC	40.5
M/MTBE/4MP2	28.1
M/DMC/4MP2	39.8

Table 14 Weight Percent of Oxygen in the Gasoline Blends Containing Oxygenates

	Blend	% Oxygen		Blend	% Oxygen
MEK	10	2.29	M/DIPE	10	3.30
MEK	20	4.56	M/Anisole	10	3.46
DIPE	5	0.74	M/4MP2	10	3.41
	10	1.48	M/3MB2	10	3.52
	20	2.98	DIPE/MTBE	10	1.61
4MP2	5	0.83	MTBE/4MP2	10	1.69
	10	1.65	MA	5	2.68
	15	2.47		10	5.29
	20	3.28	DMC	5	3.61
3MB2	5	0.97		10	7.09
	10	1.93	M/MA	10	5.20
	15	2.89	MA/Anisole	10	3.57
	20	3.85	MTBE/DMC	10	4.47
Anisole	5	0.94	MA/4MP2	10	3.49
	10	1.86	M/E	10	4.32
	20	3.62	M/DMC	10	6.16
Acetone	5	1.41	DMC/4MP2	10	4.42
	10	2.81	M/MTBE/DMC	15	6.98
Methanol	5	2.56	M/DMC/4MP2	15	6.91
	10	5.10	M/MTBE/TBA	15	4.52

	Blend	% Oxygen		Blend	% Oxygen
Methanol	15	7.65	M/MTBE/3MB2	15	4.39
Ethanol	5	1.77	E/MTBE/4MP2	15	3.46
	10	3.53	M/MTBE/4MP2	15	4.24
MTBE	5	0.87	M/DIPE/4MP2	15	4.12
	10	1.74	M/MTBE/4MP2	5:3:3=11	3.57
	15	2.61	M/MTBE/4MP2	6:3:1=10	3.75
	20	3.49	TBA	5	1.10
Oxinol	10	3.65		10	2.19
MTBE/TBA	10	1.97		15	3.29
M/MTBE	10	3.43		20	4.38

Tables 12 and 13 show the oxygen % wt/wt of each of the oxygenates and the various combinations tested. As can be seen this ranges from about 16 to 52 % wt/wt. Table 14 lists the blends used and the oxygen % wt/wt in the fuel.

Various methods of interpreting the results were investigated to determine the effect of blending multi-component blends. Firstly the addition of the effects due to each component was compared to the actual results of a multi-blend, eg a 10 % blend of a 50/50 mixture of A and B in gasoline was compared by adding the effects of 5 % A to 5 % B. This was not satisfactory as the effect due to 5 % of an oxygenate was not always very obvious. Also it was thought that the multi-blend might be represented better by one half of the sum of the RON appreciations due to 10 % of the components for dual-blends and a third of the sum due to 15 % for triple component blends as the quantity of gasoline would be the same in each separate blend as with the multi-component system. Results showed a fairly close agreement at the low RON base fuel end but this method could not be tested using 94 and 96 RON base fuel plus oxygenates. This was because trace knock was not detectable for a fuel above 98 RON or light knock for one above 97 RON.

Tables 15 and 16 show a worked example for each method. From Table 16 it can be seen that the results of the mixture are on a par with 15 % MTBE, lower than 15 % methanol and much greater than 15 % 4MP2.

Comparing the results by the % wt/wt oxygen in the blend was also examined. 15 % v/v M/MTBE/4MP2 ≈ 4.3 % wt/wt oxygen; this is equivalent to 8.5 % M, 25 % MTBE or 26 % 4MP2. The effect of the blend is greater than 10 % M, less than 20 % MTBE and much greater than 20 % 4MP2 by. 26 % 4MP2 was not tested. These results showed no correlation. Calculation of predicted effects using blending numbers of the oxygenates was then tried to compare predictions with actual experiments.

The blending octane numbers cited in the literature vary dramatically especially for methanol and ethanol ranging from 110 to 134. Values used in this analysis (Table 17) are taken from an internal report from PRD EXXON (23). They are based on a 10 % blend of each oxygenate on four different base gasolines and show a constant value for each oxygenate. MEK has no value given and an estimate has been made, partly based on work by Barronet et al (72). 3MB2 is also not given but experimentation has shown that the increase in fuel quality is very similar to 4MP2.

Table 15   Multi-component Blend Octane Number Prediction; Summation Method

Attempt to predict multi-component blend results, 5 % sum method. Numbers quoted are RON appreciation.

	90		92		94		96	
	T*	L*	T	L	T	L	T	L
4MP2	1.7	1.5	1.2	0.7	0.0	0.7	-	-
MTBE	1.4	0.0	0.8	0.0	0.0	0.0	-	-
M	3.1	3.1	2.5	1.5	2.1	2.2	-	-
Total predicted	6.2	4.5	4.3	2.2	2.1	2.9	-	-
Actual multi-component results	5.0	4.15	4.3	4.0	4.0	2.7	-	-

*   (L = Light knock, T = Trace knock)

Table 16 Multi-component Blend Octane Number Prediction; Averaging Method

Attempt to predict multi-component blend results by averaging the sum of 15 % oxygenate blends.

	90		92		94		96	
	T	L	T	L	T	L	T	L
4MP2	2.75	3.0	2.0	2.1	1.8	0.7	0.8	0.5
MTBE	5.2	5.5	4.9	4.5	4.5	3.5	?	?
M	6.6	6.1	6.0	5.1	?	?	?	?
Total	14.56	14.6	12.9	11.7	-	-	-	-
divide by 3	4.85	4.85	4.3	3.9	-	-	-	-
Actual multi-component blends	5.0	4.15	4.3	4.0	4.0	2.7	-	-

Table 17 Research and Motor Blending Numbers for Oxygenates {R P Cahn (23)}

Blending Numbers

10 % v/v blends used

	RBN	MBN
M	124	94
E	125	96
TBA	107	98
MTBE	117	99
DIPE	110	100
Anisole	115	98
DMC	111	97
MA	110	100
3MB2	108	103
4MP2	108	103
Acetone	109	98
MEK	119*	–

* Barronet (72)

An average overall fuel octane is achieved by adding the blending RONs and base RON in appropriate fractions. RON for the blend was determined from the RBN information given for M, MTBE and 4MP2 (Table 17), and using

$$\text{RON}_{\text{blend}} = 0.1\ \{\text{RBN}_{\text{oxygenate}} + (9.0 \times \text{RON}_{\text{pool}})\}$$

$$\text{RON increase} = \text{RON}_{\text{blend}} - \text{RON}_{\text{pool}}$$

the RON increase dependent on the RON_{pool} (the base gasoline) was found (Table 18). These were plotted as Figure 44. Co-ordinates for each oxygenate lay on a straight line. The lines were all parallel with a gradient of -0.1. The expected increase for the fuels under test, namely 90, 92, 94 and 96 RON were found and tabulated (Table19).

No account was taken for variation of RBN with blending concentration but from Figure 45, and according to Nichols (73), it can be seen that for methanol the relationship is not far from directly proportional; therefore, the error was assumed small.

Table 18 RON Increase Dependent Upon Pool RON

	RON increase	Pool RON
Methanol		
RBN = 124		
	3.05	93.5
	2.94	94.6
	2.74	96.6
	2.54	98.6
MTBE		
RBN = 117		
	2.35	93.5
	2.24	94.6
	2.04	96.6
	1.84	98.6
4MP2		
RBN = 108		
	1.45	93.5
	1.34	94.6
	1.14	96.6
	0.94	98.6

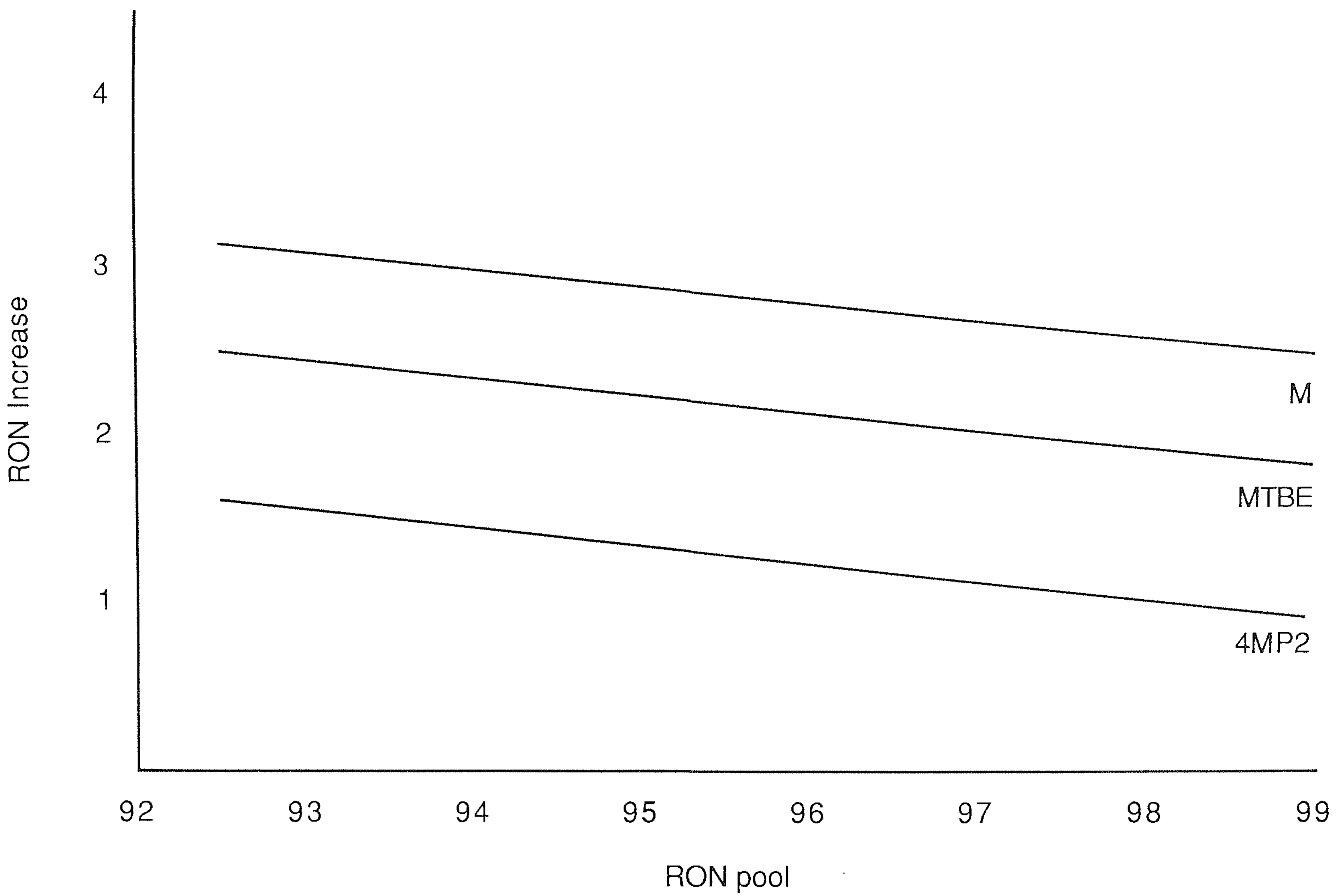

Figure 44 RON Increase Versus RON pool for Blends Containing Methanol, MTBE and 4MP2

from Data by Cahn(23)

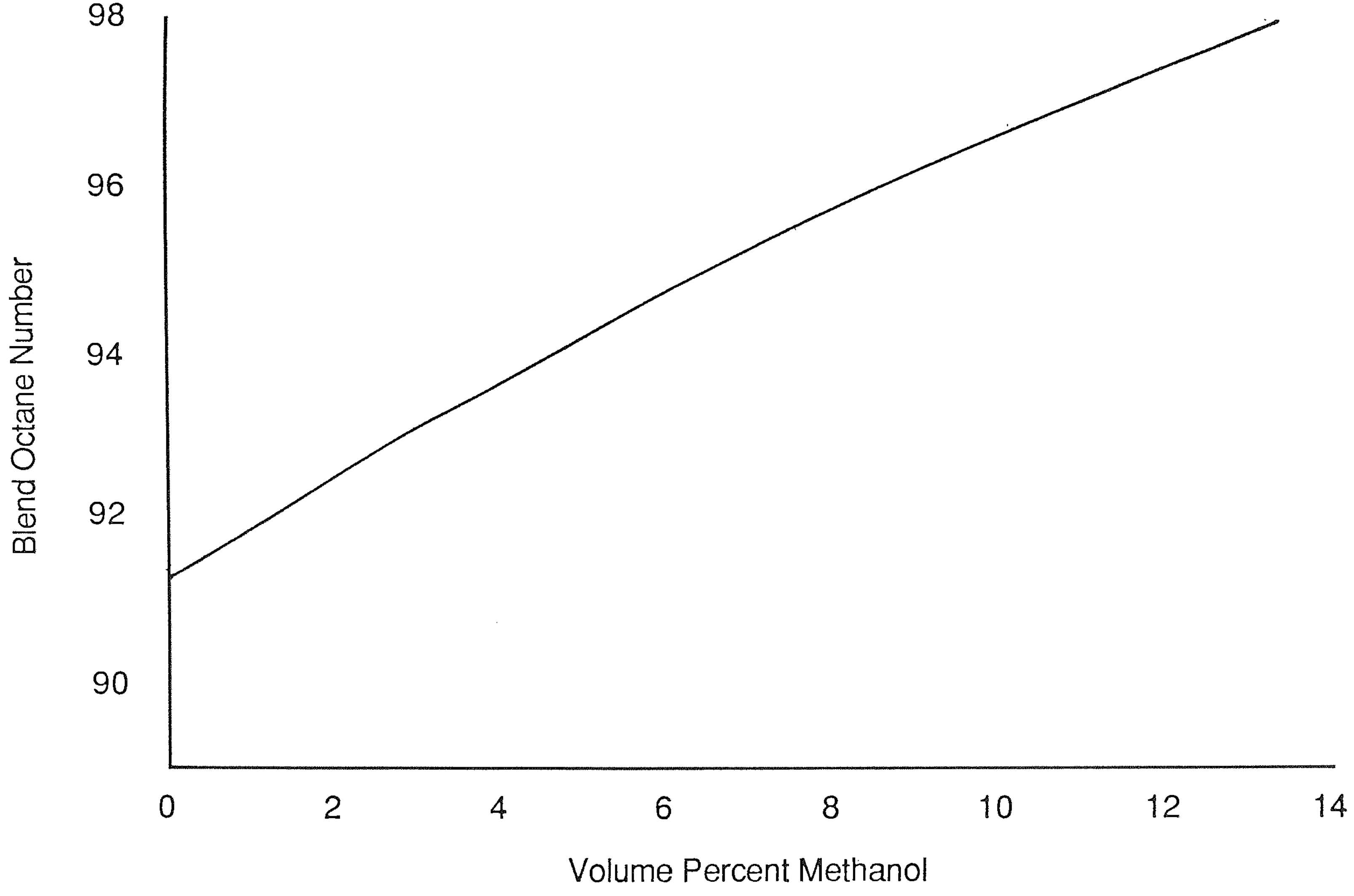

Figure 45 RON Appreciation due to Methanol in a 91 RON Base

Table 19 Expected RON Increase for Test Fuels at 10 % Blend, From Figure 44

Base RON	M	MTBE	4MP2
90	3.4	2.7	1.8
92	3.2	2.5	1.6
94	3.0	2.3	1.4
96	2.8	2.1	1.2

If we assume the effect of 5 % of an oxygenate is half that of 10 % and the increases for a combination of them is additive we find that the effect of oxygenates for a 15 % multi-blend is :-

Base RON	RON Increase
90	3.95
92	3.65
94	3.35
96	3.05

Similarly when working from the blending numbers :-

	RBN
M	124
MTBE	117
4MP2	108

Taking 5 % of these and adding them

5 % 124 = 6.20
5 % 117 = 5.85
5 % 108 = 5.40

Σ = 17.45

85 % of the RON of each base fuel is :-

85 % 90 = 76.5
85 % 92 = 78.2
85 % 94 = 79.9
85 % 96 = 81.6

Thus, assuming that the effect of the oxygenates is independent of base fuel RON, adding 17.45 to each 85 % base fuel value gives the RON_{blend}.

Base RON	RON_{blend}	RON increase
90	93.95	3.95
92	95.65	3.65
94	97.35	3.35
96	99.05	3.05

Experimental compared with predicted values of RON increase for 10 % M, MTBE and 4MP2 are reasonably in agreement for both trace and light knock, MTBE values are slightly low.

Combined as a 15 % blend the octane increases from these experiments are higher than predicted.

CFR testing of some blends has been carried out and methanol results compare favourably with those of Nichols. The actual RON increases due to the oxygenates are listed as Table 21. These can be compared with those in Table 22. (See Table 23.)

Table 20 Experimentally Derived Multi-blend Octane Increase

Data taken from graphs of engine speed vs the octane number of base fuel plus oxygenate (Figures 51 - 87) were compared with that of the pure base fuels (Figure 50) to find blend RON, from which the RON increase was calculated.

		90		92		94		96	
	% v/v	L*	T*	L	T	L	T	L	T
M	5	3.0	3.1	1.5	2.5	2.2	2.1	0.7	2.0
	10	3.3	3.9	2.7	3.2	3.3	3.8	-	-
MTBE	5	0.0	1.4	0.0	0.8	0.0	0.0	0.0	0.0
	10	1.7	2.5	2.2	1.8	1.6	2.5	1.5	1.3
4MP2	5	1.5	1.7	0.7	1.2	0.0	0.7	0.3	0.4
	10	2.3	1.9	1.3	1.7	0.4	1.2	0.3	0.6
M/MTBE /4MP2	15	4.15	5.0	4.0	4.3	2.7	4.0	-	-

* (L = Light knock, T = Trace knock)

Table 21 CFR Tests to Gauge RON Increase due to Oxygenate Addition to Series F-7 Base Fuels

Base RON	Oxygenate	% v/v	RON increase	Linear extrapolation to 10 % blend
96	M	2.0	0.7	3.5
97	M	2.0	0.5	2.5
94	M	4.0	1.8	4.5
94	M	6.5	3.0	4.6
91	TBA	5.0	0.1	0.2
94	TBA	5.0	0.8	1.6
91	MTBE	6.0	1.4	2.3
91	MTBE	11.0	2.4	2.2
91	Oxinol	6.0	1.6	2.7
91	Oxinol	11.0	3.0	2.7
96	-	-	0.0	-
97	-	-	0.2	-

For 98.6 RON_{pool}, RON increase for 10 % oxygenates blends were calculated.

M	2.54	DMC	1.24
E	2.64	MA	1.14

TBA	0.84	3MB2	0.94
MTBE	1.84	4MP2	0.94
DIPE	1.14	Acetone	1.04
Anisole	1.64		

Table 22 Expected RON Increase for 10% Blends in Series F-7 Base Fuel

	90	92	94	96
M	3.4	3.2	3.0	2.8
E	3.5	3.3	3.1	2.9
TBA	1.7	1.5	1.3	1.1
MTBE	2.7	2.5	2.3	2.1
DIPE	2.0	1.8	1.6	1.4
Anisole	2.5	2.3	2.1	1.9
DMC	2.0	1.9	1.7	1.5
MA	2.0	1.8	1.6	1.4
3MB2	1.8	1.6	1.4	1.2
4MP2	1.8	1.6	1.4	1.2
Acetone	1.9	1.7	1.3	1.1
MEK	2.7	2.5	2.3	2.1

Table 23 Comparison Between CFR and RBN Octane Increases for 10 % Blends

Blend	91	94	96	97
M_{RBN}	3.3	3.0	2.8	2.7
M_{CFR}	-	4.5	3.5	2.5
TBA_{RBN}	1.6	1.3	1.1	1.0
TBA_{CFR}	0.2	1.6	-	-
$MTBE_{RBN}$	2.6	2.3	2.1	2.0
$MTBE_{CFR}$	2.3	-	-	-
$Oxinol_{RBN}$	2.5	-	-	-
$Oxinol_{CFR}$	2.7	-	-	-

Table 23 shows that results for Oxinol, MTBE and TBA are in good agreement when considering the accuracy of CFR tests ie ± 0.3 RON. The CFR results for methanol are rather high. However, as can be seen below, 10 % blends in Series F-7 gasoline, tested in the test bed engine, give results similar to the RBN predicted values.

	90	91	92	93	94
10 % M Test bed	3.3	3.2	2.7	3.3	3.2
10 % M_{RBN}	3.4	3.3	3.2	3.1	3.0

From the results shown in Tables (22, 24, 25 and 26) it can be seen that in general the actual RON increases found under 4-cylinder conditions are in agreement with predicted values. Results for ethanol, anisole, DMC and MA are, however, lower than expected, and when combinations were compared some showed lower than expected results in higher RON bases. Better than expected results were obtained for M/MTBE, M/MTBE/3MB2 and M/MTBE/4MP2. A summary of the results can be seen in Table 27.

In order to compare multi-component blend results with RBN predictions appropriate fractions of the RBN values given in Table 22 were added to 90 % of the base fuel RON.

e.g 10 % M/MTBE

		90	92	94	96
RBN values		3.05	2.85	2.65	2.45
Test Bed Results	Trace	3.75	3.50	3.50	2.20
	Light	3.10	3.60	2.60	1.00

Table 24 Experimental results (RON appreciation Single Components)

		90		92		94		96	
		T	L	T	L	T	L	T	L
M	5	3.1	3.0	2.5	1.5	2.1	2.2	2.0	0.7
	10	3.9	3.3	3.2	2.7	3.8	3.3	-	-
	15	6.1	6.1	4.25	5.1	3.1	-	-	-
E	5	0.95	0.8	1.2	0.9	0.0	0.6	0.1	0.45
	10	2.85	2.45	1.9	2.5	2.4	2.2	1.7	1.4
TBA	5	1.5	1.1	1.25	0.5	0.0	0.0	0.0	0.55
	10	1.65	1.4	1.30	0.3	1.0	0.0	0.4	0.8
	15	2.05	2.1	1.5	0.85	0.8	0.0	0.65	1.0
	20	3.25	2.5	1.7	1.4	1.65	1.2	1.2	1.3
MTBE	5	1.4	0.0	0.8	0.0	0.0	0.0	0.0	0.0
	10	2.5	1.7	1.8	2.2	2.5	1.6	1.3	1.5
	15	5.2	5.6	4.8	4.5	4.5	3.5	-	-
	20	6.7	6.0	5.8	4.7	-	-	-	-
DIPE	5	2.2	2.5	1.5	1.0	0.0	0.4	0.8	0.8
	10	2.2	2.15	1.75	1.4	0.6	0.4	1.0	0.8
	20	4.0	3.55	3.5	3.0	2.3	2.0	1.9	-

		90		92		94		96	
		T	L	T	L	T	L	T	L
Anisole	5	1.45	2.25	1.6	1.0	0.0	0.35	0.7	0.6
	10	1.85	2.7	1.8	1.55	1.5	0.9	0.85	1.1
	20	4.0	3.9	3.25	3.6	2.8	4.0	-	-
DMC	5	0.9	0.0	0.0	0.75	0.0	0.0	0.1	0.0
	10	1.2	1.5	1.6	1.3	0.7	0.15	0.6	0.4
MA	5	0.9	0.4	1.0	0.0	0.0	0.0	0.0	0.0
	10	1.3	0.8	1.2	0.5	0.0	0.0	0.0	0.0
3MB2	5	1.55	1.5	1.15	0.6	0.0	0.15	0.1	0.0
	10	2.35	2.1	1.55	1.25	1.3	1.0	0.2	0.1
	20	3.4	3.5	2.75	2.4	2.1	2.1	1.8	-
4MP2	5	1.65	1.5	1.25	0.7	0.5	0.0	0.35	0.3
	10	1.9	2.3	1.7	1.3	1.1	0.4	0.55	0.3
	20	3.3	3.8	2.35	2.4	2.2	1.4	1.0	0.6
Acetone	5	1.7	0.9	1.25	0.7	0.3	0.0	0.6	0.15
	10	2.4	2.7	1.85	1.55	1.1	0.8	0.9	0.3
MEK	10	1.9	2.25	1.15	1.10	1.15	0.9	2.0	0.85
	20	3.9	3.8	2.5	2.7	3.0	2.55	2.2	-

Table 25 Expected Results for Oxygenated Blends from RBN Data

	90	92	94	96
Oxinol	2.55	2.35	2.15	1.95
MTBE/TBA	2.20	2.00	1.80	1.60
M/MTBE	3.05	2.85	2.65	2.45
M/DIPE	2.70	2.50	2.30	2.10
M/Anisole	2.95	2.75	2.55	2.35
M/4MP2	2.60	2.40	2.20	2.00
M/3MB2	2.60	2.40	2.20	2.00
DIPE/MTBE	2.35	2.15	1.95	1.75
MTBE/4MP2	2.25	2.05	1.85	1.65
M/MA	2.70	2.50	2.30	2.10
MA/Anisole	2.25	2.05	1.85	1.65
MTBE/DMC	2.40	2.20	2.00	1.80
MA/4MP2	1.90	1.70	1.50	1.30
M/E	3.45	3.25	3.05	2.85
M/DMC	2.75	2.55	2.35	2.15
DMC/4MP2	1.95	1.75	1.55	1.35

	90	92	94	96
M/MTBE/DMC	4.10	3.90	3.70	3.50
M/DMC/4MP2	3.65	3.45	3.25	3.05
M/MTBE/TBA	3.90	3.70	3.50	3.30
M/MTBE/3MB2	3.95	3.75	3.55	3.35
M/MTBE/4MP2	3.95	3.75	3.55	3.35
E/MTBE/4MP2	4.00	3.80	3.60	3.40
M/DIPE/4MP2	3.60	3.40	3.20	3.00
M/MTBE/4MP2 (5 : 3 : 3 11 %)	3.05	2.85	2.65	2.45
M/MTBE/4MP2 (6 : 3 : 1 10 %)	3.03	2.83	2.63	2.43

Table 26 Experimental Results for Oxygenated Blends

	90		92		94		96	
	T	L	T	L	T	L	T	L
Oxinol	3.5	2.8	2.3	2.25	2.7	2.65	-	-
MTBE/TBA	3.1	2.4	1.8	1.25	2.15	1.6	0.8 5	0.45
M/MTBE	3.75	3.1	3.5	3.6	3.5	2.6	2.2	1.0
M/DIPE	2.9	2.55	1.95	1.55	1.0	1.7	1.9	1.8
M/Anisole	3.05	2.7	1.85	1.55	1.25	1.0	1.55	1.1
M/4MP2	3.1	2.4	1.85	1.4	0.7	1.0	1.7	0.9
M/3MB2	2.5	2.1	1.35	0.9	0.9	0.75	1.2	0.7
DIPE/MTBE	2.45	1.2	1.1	0.25	0.0	0.0	0.8	0.4
MTBE/4MP2	2.7	1.55	1.4	0.75	0.5	0.35	0.9	0.7
M/MA	3.1	2.4	1.75	1.4	1.25	1.7	-	-
MA/Anisole	2.5	1.0	1.3	0.6	0.0	0.0	1.7	1.15
MTBE/DMC	2.5	1.0	1.3	0.9	1.2	1.6	-	-
MA/4MP2	1.75	0.3	1.2	0.35	1.2	0.5	-	-
M/E	3.8	3.25	3.1	2.75	3.1	2.6	-	-
M/DMC	3.35	2.7	2.0	1.35	2.0	2.0	-	-
DMC/4MP2	2.5	1.1	1.5	0.75	0.7	0.65	1.4	0.6

	90		92		94		96	
	T	L	T	L	T	L	T	L
M/MTBE/DMC	3.6	2.7	3.7	2.9	3.8	2.3	-	-
M/DCM/4MP2	3.65	2.8	1.9	2.6	3.7	2.7	-	-
M/MTBE/TBA	3.9	3.5	3.6	2.65	3.8	3.65	-	-
M/MTBE/3MB2	4.5	4.5-4.7	4.3-4.9	4.0-4.2	3.8-4.5	2.9	-	-
M/MTBE/4MP2	5.0	4.15	4.3	4.0	4.0	2.7	-	-
E/MTBE/4MP2	3.2	2.8	4.1	3.0	2.5	2.2	2.3	-
M/DIPE/4MP2	3.2	2.9	4.2	3.0	2.8	2.2	-	-
M/MTBE/4MP2 (5 : 3 : 3 11 %)	3.7	3.0	3.0	2.6	3.0	2.4	-	-
M/MTBE/4MP2 (6 : 3 : 1 10 %)	3.7	2.9	3.0	2.8	2.7	2.15	-	-

Table 27 Summary of the Effects of Oygenates Compared to those Predicted Using RBN Data

M	Equivalent to, or possibly higher octane increase than predicted
E	Lower octane increase than predicted
TBA	In reasonable agreement with predicted values
MTBE	In reasonable agreement with predicted values
DIPE	In reasonable agreement with predicted values
Anisole	Lower octane increase than predicted
DMC	Lower octane increase than predicted
MA	Lower octane increase than predicted
3MB2	Higher octane increase than predicted for low octane base fuels, lower octane increase for high ones
4MP2	Higher octane increase than predicted for low octane base fuels, lower octane increase for high ones
Acetone	In reasonable agreement with predicted values
MEK	In reasonable agreement with predicted values
Oxinol	Slightly higher octane increase than predicted
MTBE/TBA	In reasonable agreement with predicted values
M/MTBE	Higher octane increase than predicted
M/DIPE	Lower octane increase than predicted for high octane base fuels

M/Anisole	Lower octane increase than predicted for high octane base fuels
M/4MP2	Lower octane increase than predicted for high octane base fuels
M/3MB2	Lower octane increase than predicted for high octane base fuels
DIPE/MTBE	Lower octane increase than predicted for high octane base fuels
MTBE/4MP2	Lower octane increase than predicted for high octane base fuels
M/MA	Lower octane increase than predicted for high octane base fuels
MA/Anisole	In reasonable agreement with predicted values
MTBE/DMC	Lower octane increase than predicted for high octane base fuels
MA/4MP2	Lower octane increase than predicted
M/E	In reasonable agreement with predicted values
M/DMC	In reasonable agreement with predicted values
DMC/4MP2	Lower octane increase than predicted for high octane base fuels

M/MTBE/DMC	In reasonable agreement with predicted values
M/DMC/4MP2	In reasonable agreement with predicted values
M/MTBE/TBA	In reasonable agreement with predicted values
M/MTBE/3MB2	Higher octane increase than predicted
M/MTBE/4MP2	Higher octane increase than predicted
E/MTBE/4MP2	Lower octane increase than predicted
M/DIPE/4MP2	In reasonable agreement with predicted values

M/MTBE/4MP2 (5 : 3 : 3 11 %)	Higher octane increase than predicted for low octane base fuels, lower octane increase for high ones
M/MTBE/4MP2 (6 : 3 : 1 10 %)	Higher octane increase than predicted for low octane base fuels, lower octane increase for high ones

3.4 2-star Tests on Combinations of Methanol/Methyl Tert Butyl Ether/4 Methyl Pentan-2-one

As the main experimental programme suggested that a combination of M/MTBE/4MP2 could be useful in fuel blending, a series of tests was carried out using 2-star forecourt gasoline to determine the optimum combination. The results in Table 28 show that in fact the least knock was detected when no 4MP2 was present. As can be seen replacement of MTBE with 4MP2 had a small effect which, considering the limited availability of MTBE, makes the use of 4MP2 highly desirable. Tests using 3MB2 instead of 4MP2 gave almost identical results. However, due to its high cost 3MB2 is not an economic alternative at present.

Test Conditions

Inlet Air Temperature	25°C
Cooling Water Temperature	65°C
Engine Oil Temperature	80°C
Dynamometer Outlet Temperature	22°C
Atmospheric Pressure	759 mmHg
T_{dry}	23°C
T_{wet}	17°C
Absolute Humidity	0.0096 kg H_2O/kg dry air

Table 28 Results Obtained for Different Combinations of 4MP2 and 3MB2 with Methanol and MTBE in 2-star Gasoline

4MP2 Results :

MTBE	4MP2 (% v/v used)	M	Trace knock (max rpm)	Light knock (max rpm)
10	0	5	1610	1310
			1590	1270
5	5	5	1600	1330
			1620	1320
			1640	1360
			1620	1320
4	4	6	1590	1400
			1630	1380
3	3	6	1630	1550
			1620	1540
			1680	1550
0	10	5	1690	1600
			1660	1590
3	1	6	1660	1580
			1680	1590
4	0	6	1660	1600

MTBE	4MP2 (% v/v used)	M	Trace knock (max rpm)	Light knock (max rpm)
5	0	5	1700	1600
			1700	1600
			1700	1580
2	2	6	1680	1600
4	1	5	1680	1610
0	4	6	1690	1620
			1680	1590
2	3	5	1680	1600
			1700	1620
3.3	3.3	3.3	1730	1630
			1690	1610
0	5	5	1720	1630
5	5	0	1850	1690
0	0	0	2100	1800

3MB2 Results :

MTBE	3MB2 (% v/v used)	M	Trace knock (max rpm)	Light knock (max rpm)
5	5	5	1630	1300
			1620	1330
			1640	1320
5	5	0	1850	1680

4MP2 and 3MB2 produced similar results, as expected from earlier work.

3.5 Air/Fuel Ratio for Emission Tests

Average air flowmeter readings were used to determine the air/fuel ratio of the engine which remains essentially constant from blend to blend. Pressure drop across the meter was converted to air flow using a calibration chart (mm water gauge times 36.54 gives grams per minute). Fuel consumption was measured against engine speed and data from the resulting graph was used in air/fuel ratio calculations. The density of the blends was assumed constant at 0.774 g per ml. Accurate densities are given in Appendix 5.

Table 29 Data to Plot Air Flowmeter Pressure Drop Vs Engine Speed

Engine Speed (rpm)	Pressure Drop over Air Flowmeter (mmH_2O)
1100	13.5
1300	15.3
1500	17.7
1700	20.2
1900	22.6
2100	25.5
2300	28.2
2500	31.4
3000	38.2
3500	44.6
4000	51.1

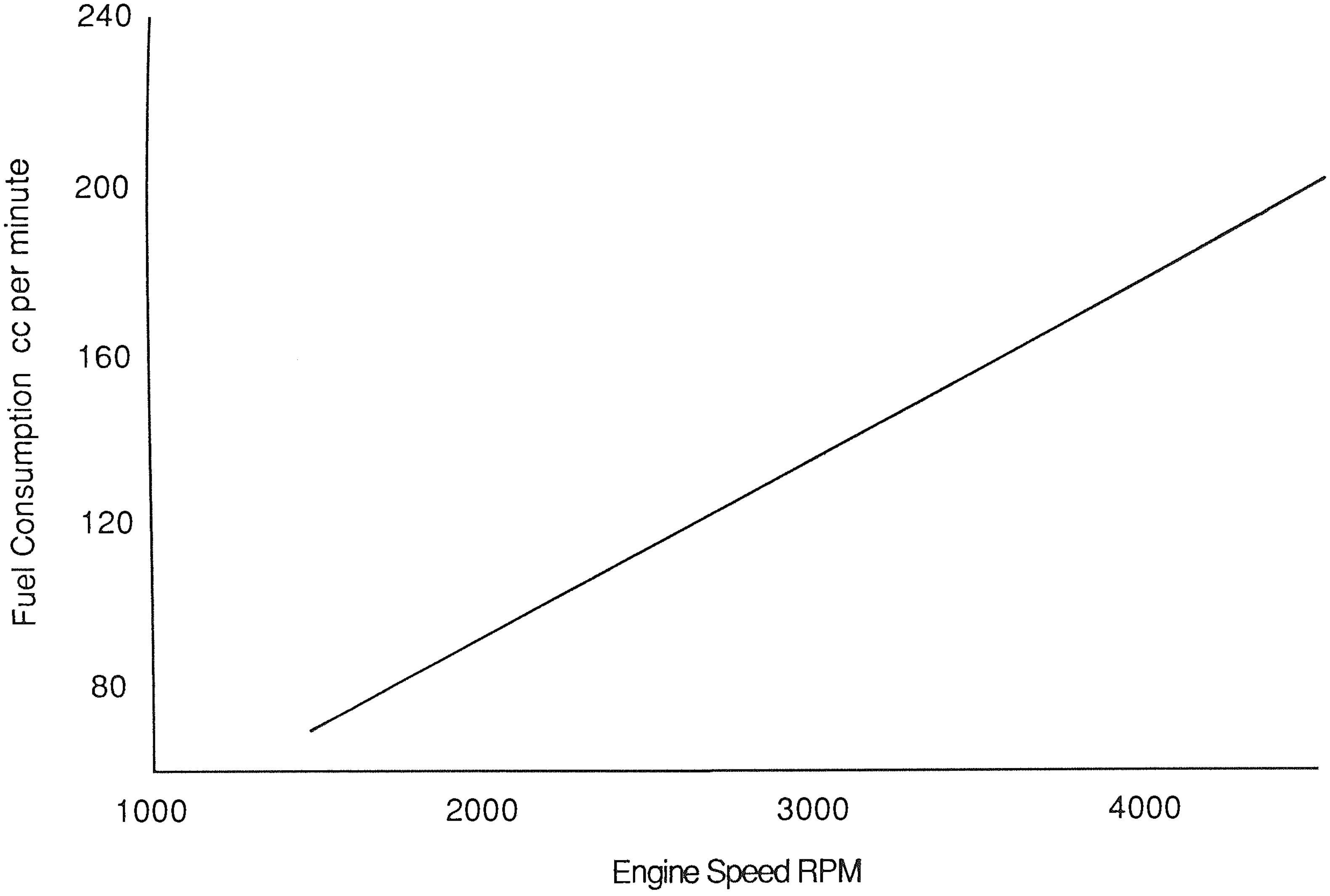

Figure 46 Fuel consumption Against Engine Speed (WOT)

Table 30 Fuel Consumption Data

At wide open throttle

Engine Speed (rpm)	Time for 100 ml fuel to be used (seconds)	Fuel consumption (ml per minute)
1500	86	70.0
2000	66	91.0
2500	53	113.0
3000	44	136.0
4650	28	214.0

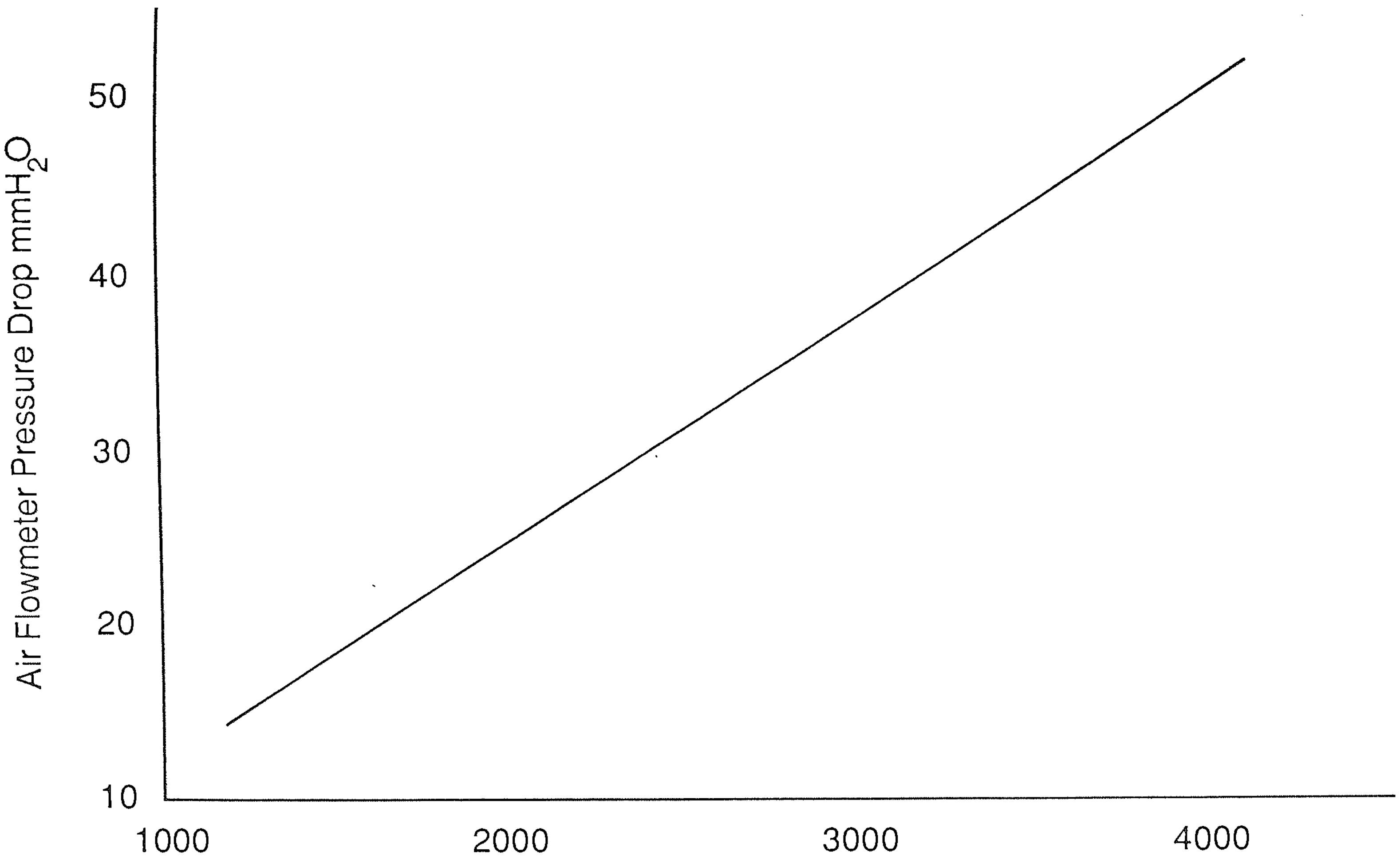

Figure 47 Pressure Drop Across Viscous Air Flowmeter Against Engine speed

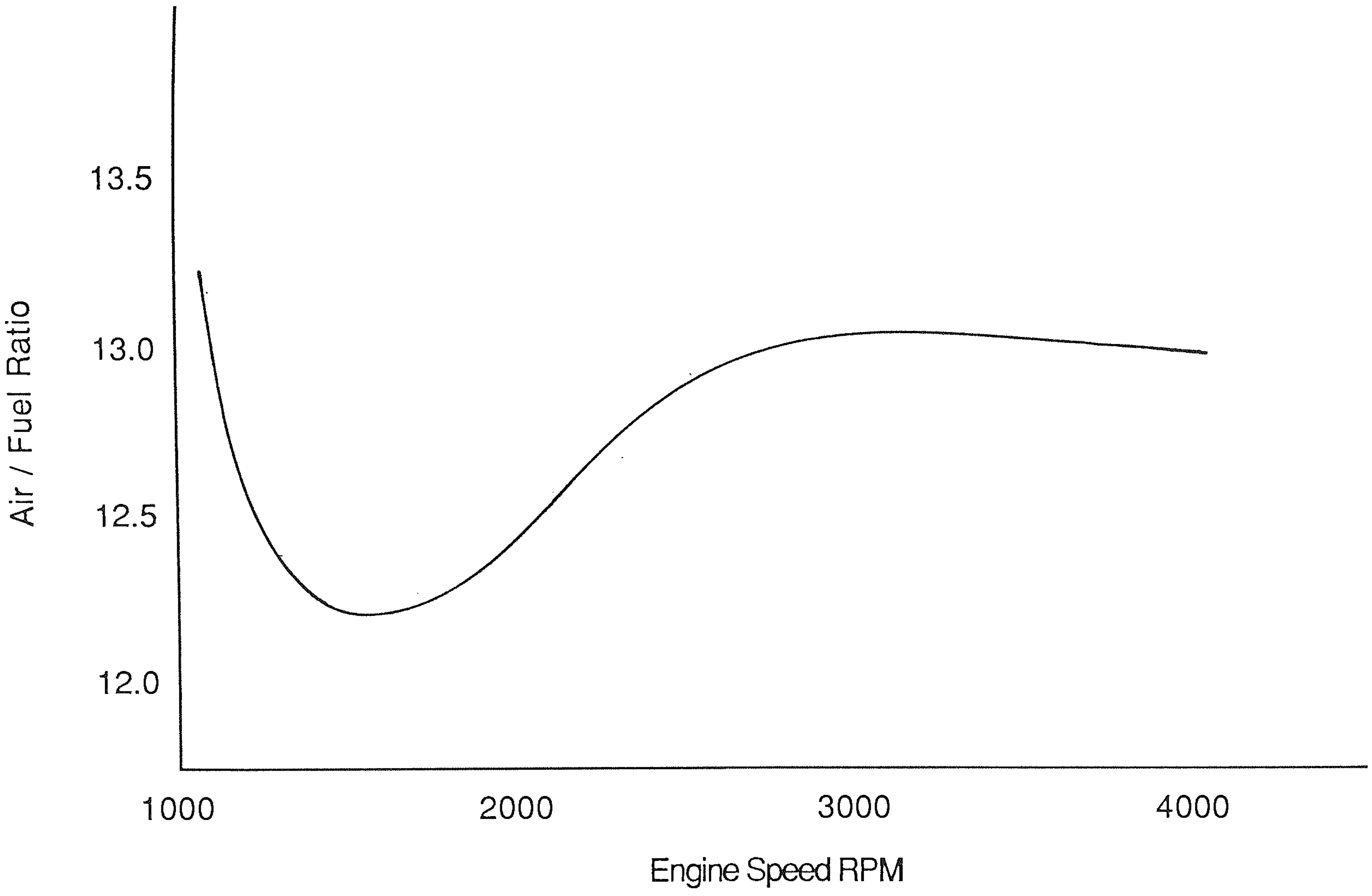

Figure 48 Air/Fuel Ratio Against Engine Speed

Table 31 Data Derived from Fuel Consumption and Air Flowmeter Readings

rpm	Fuel (ml/min)	Air (g/min)	Fuel (g/min)	Air/Fuel ratio
1100	48.0	493	37.4	13.18
1300	58.0	560	45.2	12.39
1500	68.0	647	53.0	12.21
1700	77.0	738	60.1	12.28
1900	86.0	826	67.1	12.31
2100	95.0	932	74.1	12.58
2300	104.5	1030	81.5	12.64
2500	113.5	1147	88.5	12.96
3000	137.0	1395	106.9	13.06
3500	160.0	1635	124.8	13.06
4000	184.0	1865	143.5	13.00

3.6 Engine Power Output

The engine power was monitored using a load device on the dynamometer, output being measured in millivolts. Engine torque equals 27.525 times mV from calibration of the device. After many runs average values for oxygenated blends were obtained and plotted, as Figure 49. 4-star fuel was used as a reference intermittently during the oxygenate/2-star blend experiments.

The plot shows a maximum power increase of about 5 % at 1100 rpm compared with 2-star when using M/4MP2 (6 : 5) 11 % in 2-star and M/MTBE/4MP2 (6 : 3 : 2) 14.5 % in 2-star. This reduces to 2 % at 2500 rpm. Maximum output is only about 1.5 % higher. Almost all oxygenate blends showed a slight increase in power.

Table 32 Data used to plot Power Output Curve

rpm	M/MTBE/4MP2 1 : 1 : 1 (mV)	M/MTBE 6 : 5 (mV)	MTBE 22 (mV)	4MP2 25.5 (mV)	Oxinol 11.5 (mV)	E 11.5 (mV)
1100	2.23	2.26	2.29	2.26	2.27	2.29
1300	2.28	2.28	2.31	2.29	2.30	2.31
1500	2.34	2.32	2.32	2.30	2.31	2.32
1700	2.37	2.35	2.37	2.36	2.36	2.35
1900	2.40	2.38	2.40	2.37	2.38	2.39
2100	2.45	2.42	2.46	2.43	2.44	2.45
2300	2.50	2.48	2.51	2.48	2.48	2.49
2500	2.53	2.52	2.54	2.52	2.52	2.53
3000	2.56	2.56	2.56	2.55	2.56	2.56
3500	2.55	2.56	2.55	2.52	2.55	2.54
4000	2.55	2.55	2.54	2.51	2.54	2.54

rpm	4-star (mV)	M/MTBE/4MP2 6 : 3 : 2 (mV)	M/4MP2 6 : 5 (mV)	2-star (mV)	M 8 (mV)
1100	2.24	2.31	2.31	2.20	2.29
1300	2.27	2.32	2.32	2.25	2.31
1500	2.31	2.35	2.34	2.27	2.31
1700	2.34	2.39	2.38	2.32	2.36
1900	2.37	2.42	2.41	2.36	2.40
2100	2.41	2.47	2.47	2.40	2.46
2300	2.48	2.51	2.52	2.47	2.51
2500	2.51	2.55	2.55	2.50	2.53
2700	2.53	2.55	-	-	-
2900	2.56	2.56	-	-	-
3000	2.56	2.57	2.56	2.55	2.56
3100	2.56	2.57	-	-	-
3300	2.55	2.57	-	-	-
3500	2.54	2.57	2.54	2.53	2.54
3700	2.53	2.56	-	-	-
3900	2.53	2.56	-	-	-
4000	2.52	2.56	2.56	2.52	2.53
4100	2.51	2.55	-	-	-

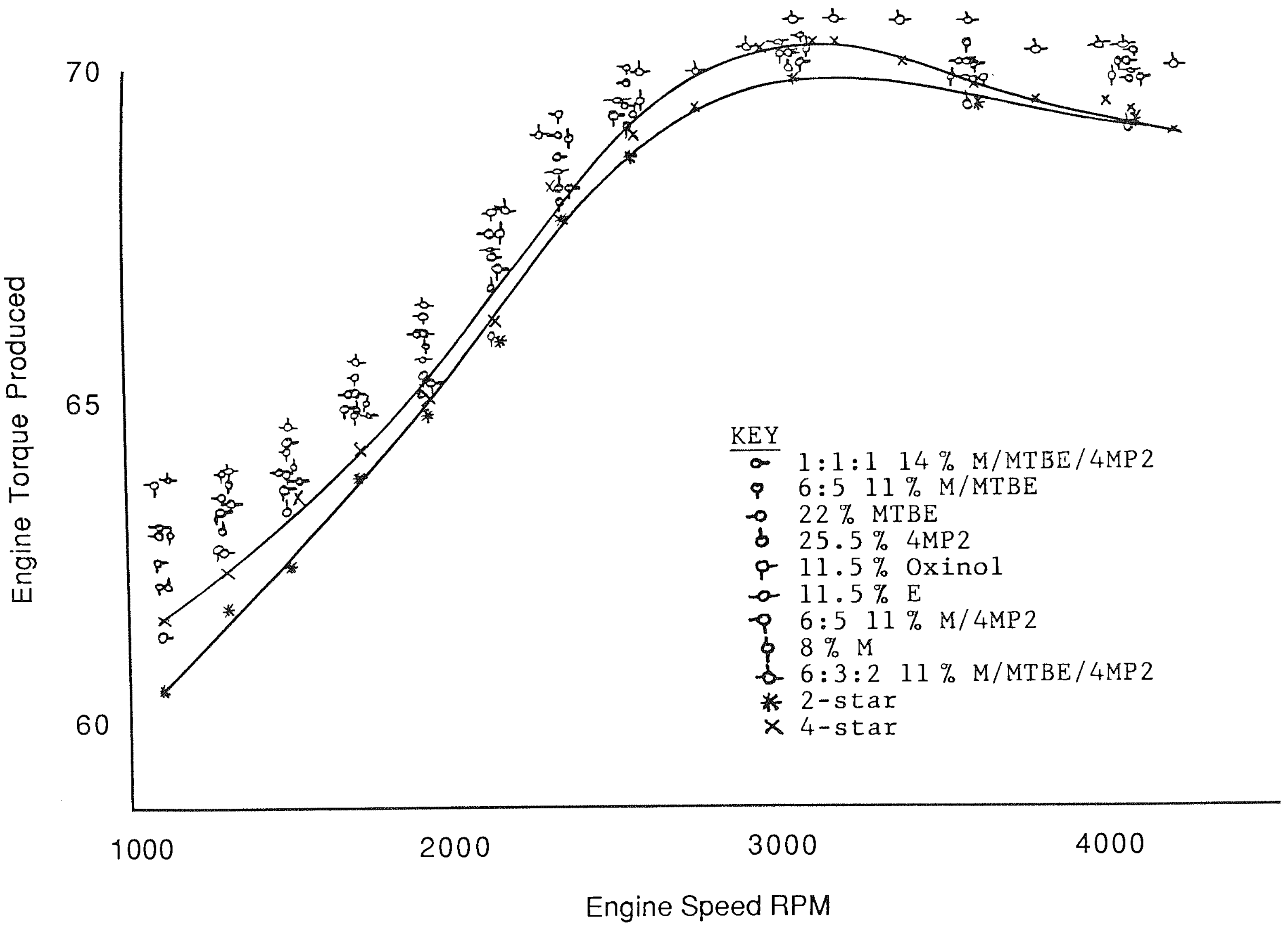

Figure 49 Engine Power Output Verses Engine Speed for Oxygenated Blends in 2-star Forecourt Gasoline

3.7 Comparison of the Emissions of Oxygenated Blends with 2-star and 4-star Gasoline

In these experiments no change to the carburettor was made so that actual air/fuel ratios vary from fuel to fuel and emissions of carbon monoxide and hydrocarbons for oygenated blends would be expected to be lower than ordinary gasoline due to the extra oxygen present. Oxygenates were blended into 2-star forecourt gasoline for these experiments. Graphs showing the concentrations of exhaust emissions for the tests are shown as Figures 88 - 98 in Appendix 1.

3.7.1 Comparing 2-star with 4-star

CO at less than 2000 rpm there was up to 1.5 % more CO produced.

Between 2000 and 3000 rpm the amount was similar to 4-star. Over 3000 rpm there was an increase in CO again by about 1 %.

CO peak occurs at about 1700 rpm for 2-star, 1750 for 4-star.

CO_2 CO_2 % with 2-star gasoline is lower than with 4-star by 1 %.

HC Similar HC curve initially lower, higher final figures.

3.7.2 Comparing Oxygenated Blends in 2-star with 2-star and 4-star

3.7.2.1 M/MTBE/4MP2 (1 : 1 : 1) 14.5 %

	2-star	4-star
CO	Lower by about 2 %	Less by 1 to 1.5 %
	Maximum peak about 0.5 that of 2-star	Peak lower by 1 %
	Similar shape	
	Peak occurs at 1950 rpm	
CO_2	Greater by 1 %	Greater up to 2500 rpm
HC	Slightly less at all speeds	Slightly less at all speeds

3.7.2.2 M/MTBE (6 : 5) 11 %

	2-star	4-star
CO	Similar shaped curve	1% lower until 3500 rpm
	Lower by 1 to 2 %	
	Peak 2 % lower	
	Peak at 1850 rpm	
CO_2	About 1 % higher	About 0.5 % higher
HC	Slightly less	Initially slightly less

3.7.2.3 M/4MP2 (6 : 5) 11 %

	2-star	4-star
CO	Curve 1.5 to 2 % lower Peak at 1700 rpm	Curve 1 to 1.5 % lower after 1600 rpm
CO_2	Greater by 1 to 1.5 %	Slightly higher
HC	Similar curve	Similar curve

3.7.2.4 M/MTBE/4MP2 (6:3:2) 11 %

	2-star	4-star
CO	Similar curve 1.5 % lower Peak 1700 rpm	1 % lower average
CO_2	About 1 % higher	Almost the same
HC	Similar curve	Very similar curve

3.7.2.5 M 8 %

	2-star	4-star
CO	Similar curve 1.5 to 2 % lower Peak at 1800 rpm	1 to 1.5 % lower Similar curve

CO_2	1 % higher after 1800 rpm	About 0.5 % higher
HC	Starts higher ends lower	Similar curve

3.7.2.6 E 11.5 %

	2-star	4-star
CO	Similar curve 0.5 to 1 % lower Peak at 1700 rpm	Greater CO up to 2000 rpm lower after 2000 rpm
CO_2	About 1 % higher	Lower at low speeds
HC	Lower (by 50 ppm)	Lower

3.7.2.7 Oxinol 11.5 %

	2-star	4-star
CO	About 1.5 % lower Peak at 1700 rpm	Lower by 1 % after 1800 rpm
CO_2	1 % higher similar curve	0.5 % higher above 1800 rpm
HC	Lower (by 50 ppm)	Lower

3.7.2.8 MTBE 22 %

	2-star	4-star
CO	1 % lower to peak 0.5 % thereafter Peak at 1800 rpm	Lower from 2000 to 4000 rpm by up to 1 %
CO_2	1 % higher similar curve	Similar curve
HC	Lower (by 50 ppm)	Lower at start, coincides at 4000 rpm

3.7.2.9 4MP2 25.5 %

	2-star	4-star
CO	Curves similar 1 % lower Peak at 1500 rpm	0.5 % lower
CO_2	1 to 1.5 % higher	Greater below 1500 and above 3500 rpm
HC	Lower (by 70 ppm)	Lower (starts 200 ppm lower)

3.7.3 Summary of Results of Emission Tests

Comparing the emissions of the oxygenated blends in 2-star gasoline with both 2-star and 4-star gasoline:

	Blend	2-star		4-star	
		CO	HC	CO	HC
1 : 1 : 1	M/MTBE/4MP2	«	<	«	<
6 : 5	M/MTBE	«	<	<	<
6 : 5	M/4MP2	«	=	<	=
6 : 3 : 2	M/MTBE/4MP2	«	=	<	=
8	M	«	=	<	=
11.5	E	<	<	<	<
11.5	Oxinol	«	<	<	<
22	MTBE	<	<	<	<
25.5	4MP2	<	<	<	<

Key : - < slight reduction
« large reduction
= little or no difference

3.7.4 Conclusions Regarding Emissions

3.7.4.1 2-star verses 4-star Gasoline

At low engine speeds CO emissions are higher with 2-star than with 4-star and again at over 3000 rpm. The peak CO output is slightly higher (1 %) using 2-star.

CO_2 output is lower for all engine speeds and HC output is similar throughout the speed range.

From the summary of results obtained by comparing the exhaust gas concentration curves (Figures 88 to 98) it can be seen that : -

i. in all circumstances CO is less when using a blend containing oxygenates.

ii. HC concentration is lower in almost all cases compared with pure 2-star and usually lower than pure 4-star.

iii. The engine speed at which the peak value of CO and the minimum CO_2 value occur is shifted for some blends compared to pure 2-star. The speed at which it occurs is increased for : -

6 : 5 M/MTBE
8 M
22 MTBE
25.5 4MP2
1 : 1 : 1 (14.5 %) M/MTBE/4MP2

The peak shift is usually in the order of 100 or 200 rpm and is always in an increasing rpm direction. Compared to 2-star the shift in almost all cases results in the peak coinciding with that of pure 4-star. The exceptions are 6 : 5 M/MTBE which is slighly more than the 4-star peak after shift and 1 : 1 : 1 M/MTBE/4MP2 which is greater than the 4-star peak.

It should be noted that the 1 : 1 : 1 M/MTBE/4MP2 peak is lower than the 4-star peak to a much greater degree than other blends. This blend contains more oxygen than most of the others tested and the emissions would be expected to be lower with no adjustment to the air/fuel ratio.

3 .8 CFR Testing

A blend is tested to produce a knock intensity of a value which is bracketed by a 2 octane number difference of primary reference fuels. From this the RON or MON of the test blend can be determined.

RON testing is done at lower inlet air and mixture temperatures than MON and also at lower engine speed. The RON results obtained reflect a modern car engine's requirements at low engine speeds whereas MON is more important at high engine speeds. Thus two gasolines may have the same RON eg 97 (4-star) and yet different MON, eg 88 and 85. The one with the lower MON may cause engine knock at higher engine speeds which can be annoying to the driver, if audible, and may be damaging to the engine. The difference between RON and MON is the sensitivity, s, and with forecourt gasoline it is usually about 9. Fuels with a greater sensitivity may require a higher RON than 97 for 4-star in order to have a sufficient MON to satisfy the mass car population. Olefinic fuels have a higher sensitivity than paraffinic fuels. Mixing of gasoline or of a gasoline with oxygenates can also affect the sensitivity other than as might be expected. Octane mixing is not linear as the knock promoting species in a low MON fuel are still present in the mixture and continue to act as such. (For example the F-7 blending curve (Figure 37) shows that a 50 % blend of the high and low key components has a sensitivity of 10.0, the low key has one of 7.9, the high key one of 11.4. Linear blending would predict a 50 % blend sensitivity of 9.6. Therefore the sensitivity of 10 is worse than would be predicted. Also 50 % blend RON = 96.6 but linearly this would be 95.6. Actual MON = 86.6, compared to linear blending predicting 86.0.)

3.9 CFR Tests on Blends Containing Oxygenates

Two sets of tests were carried out, one for blends containing single oxygenates to check initial findings suggested by preliminary engine tests, and the second set was done with promising multiple blends derived from the main experiments.

Both RON and MON were determined for the fuels using a standard single cylinder variable compression ratio engine under the usual test conditions.

Error in single sample determinations was ± 0.3 95 % confidence for RON and ± 0.5 95 % confidence for MON.

The first set of tests produced the following results :-

Table 33 Initial CFR RON and MON Determinations

Blend base F-7 octane number + x % v/v of y oxygenate	RON	MON
96 + 2 % Methanol	96.7	86.0
97 + 2 % Methanol	97.5	86.6
94 + 4 % Methanol	95.8	85.2
94 + 6.5 % Methanol	97.0	85.8
91 + 5 % TBA	91.1	83.3
94 + 5 % TBA	94.8	85.0
91 + 6 % MTBE	92.4	84.3
91 + 11 % MTBE	93.4	85.1
91 + 6 % Oxinol	92.6	84.0
91 + 11 % Oxinol	94.0	84.9
96 base fuel	96.0	86.3
97 base fuel	97.2	86.7

Comparison with base fuel values for RON and MON gave the following RON and MON increases : -

Table 34 Octane Increase Due to the Presence of Oxygenates

Blend	RON increase	MON increase
96 + 2 % M	0.7	- 0.2
97 + 2 % M	0.5	- 0.3
94 + 4 % M	1.8	0.4
94 + 6.5 % M	3.0	1.0
91 + 5 % TBA	0.1	0.5
94 + 5 % TBA	0.8	0.2
91 + 6 % MTBE	1.4	1.5
91 + 11 % MTBE	2.4	2.3
91 + 6 % Oxinol	1.6	1.2
91 + 11 % Oxinol	3.0	2.1
96 base	0.0	0.1
97 base	0.2	- 0.2

However, it must be remembered that RON is ± 0.3 and MON is ± 0.5. Comparing these results with those derived from a comparision of the blend curves with the base fuel curve (Figures 51 - 87 with Figure 50) shows that some CFR results support derived results whereas others do not. The absolute humidity of the air is an important factor which may account for some mis-match. For example early data were collected for MTBE blends on a very humid day which tends to suppress knock and hence infer better than actual knock protection.

3.10 CFR Experiments of Oxygenates with G-7, Compared to F-7 Tests

RON and MON determinations have previously been carried out by a number of companies to find the effect of adding MTBE, Oxinol, ethanol and TBA to the CORC Series G-7 gasoline, a similar series gasoline to F-7 used in these experiments. Quantities of oxygenates used were; MTBE 10 %, Oxinol 6 %, ethanol 5 %, TBA 5 %. All oxygenates were leaded to 0.15 g/l. Increase in Reid vapour pressure (Rvp) was greatest with Oxinol and least with TBA. MTBE also had a small effect.

The results showed MON, RON and s increases as follows : -

Table 35 Published RON and MON in Series G-7 Gasoline

Base fuel	RON	MON	s
1	88.3	80.8	7.5
2	91.0	82.5	8.5
3	94.0	84.5	9.5
4	97.0	86.6	10.4
5	100.1	88.9	11.2

	Base Fuel	Δ RON	Δ MON	Δ s
MTBE 10 %	1	3.1	2.5	0.6
	2	2.7	2.1	0.6
	3	2.2	1.6	0.6
	4	1.9	1.3	0.6
	5	1.3	1.0	0.3
Oxinol 6 %	1	2.0	1.4	0.6
	2	1.8	1.0	0.8
	3	1.5	0.6	0.9
	4	1.0	0.2	0.8
	5	0.5	0.2	0.3
TBA 5 %	1	0.6	0.7	- 0.1
	2	0.6	0.3	0.3
	3	0.6	0.2	0.4
	4	0.4	0.3	0.1
	5	0.1	0.6	- 0.5
Ethanol 5 %	1	2.2	1.4	0.8
	2	1.9	1.1	0.8
	3	1.9	0.9	1.0
	4	1.6	0.6	1.0
	5	0.9	0.1	0.8

From these results it can be seen that the RON increase is less the higher the base blending stock. The MON increase is variable but usually follows the RON trend. However, due to the high sensitivity of the oxygenates the MON increase is usually less than that of RON, leading to an increase in sensitivity of the gasoline blend. Comparing these results with those obtained on the Fiat engine : -

Table 36 Derived RON and MON Increases from Experimental CFR Work

	Base RON F-7	Δ RON	Δ MON	Δ s
MTBE 11 %	91	2.4	2.3	0.1
TBA 5 %	91	0.1	0.5	- 0.4
	94	0.8	0.2	0.6
Oxinol 6 %	91	1.6	1.2	0.4

Table 37 Comparative Series G-7 Published Data

	G-7 RON	Δ RON	Δ MON	Δ s
MTBE 10 %	91	2.7	2.1	0.6
TBA 5 %	91	0.6	0.3	0.3
	94	0.6	0.2	0.4
Oxinol 6 %	91	1.8	1.0	0.8

The F-7 results are single experiments and so are subject to the maximum error of RON ± 0.3 and MON ± 0.5 and so are in reasonable agreement with these other findings confirming the CFR test results used in this work. Small differences are expected as the G-7 series is not identical to the F-7 series.

The ΔR_{100} values are also of interest in the G-7 tests as they show a decrease. This is important as this indicates that the front end volatility of the fuel is closer to the RON in fuels containing the oxygenates. The higher front end RON is important when fuel segregation in a car inlet manifold occurs which can lead to RON starvation in some of the cylinders. The addition of oxygenates is therefore advantageous in these cases.

3.11 Multiple Blend CFR Test Result

Four different blends were produced each in two gasolines (90 and 94 RON F-7). The blends were 6 : 3 : 2 methanol/MTBE/4MP2 11 %, 6 : 5 methanol/MTBE 11 %, 1 : 1 : 1 methanol/MTBE/4MP2 15 % and 10 % 4MP2. The results are shown as Table 38. As can be seen the difference between 6 : 3 : 2 and 6 : 5 (ie replacement of some MTBE by 4-methyl pentan-2-one (4MP2) is very small although the blend with no 4MP2 is slightly better as found when testing them on the Fiat engine. Also as expected from 2-star experiments the greatest improvement was obtained when using the 1 : 1 : 1 blend. Oxygen content of the first three blends is around the 4 % wt/wt level, at present above the European and EPA maximum. RON improvement for these blends is about 4 and MON for 6 : 3 : 2 and 6 : 5 is about 2.6+. The 1 : 1 : 1 blend in 90 RON base fuel shows a Δ MON of 3.8 and Δ RON of 4.2. This is a much better result than expected probably due to the effect of the 4MP2. The 10 % 4MP2 blend reults show a greater Δ MON than Δ RON suggesting that the sensitivity of 4MP2 is less than gasoline and this counters the high sensitivity of methanol leading to the result obtained for the 1 : 1 : 1 M/MTBE/4MP2 blend.

Table 38 Multi-Component CFR Test Results

Blend	Base RON	RON	MON	ΔRON	ΔMON
-	90	90.0	82.2	-	-
-	94	94.0	84.8	-	-
M/MTBE/4MP2	90	94.0	84.8	4.0	2.6
(6 : 3 : 2) 11 %	94	97.7	87.4	3.7	2.6
M/MTBE	90	94.0	85.1	4.0	2.9
(6 : 5) 11 %	94	97.7	87.5	3.7	2.7
M/MTBE/4MP2	90	94.2	86.0	4.2	3.8
(1 : 1 : 1) 15 %	94	98.2	87.8	4.2	3.0
4MP2	90	90.9	84.4	0.9	2.2
10 %	94	95.2	86.7	1.2	1.9

Using the formula : -

$$BN = \frac{BN_{blend} - (1 - x)\,BN_{base}}{x}$$

where x is the volumetric fraction of oxygenate, the blending Research and Motor numbers for the oxygenate combinations were calculated.

Table 39 Multi-Component Blending Numbers Derived from CFR Results

Blend	Base RON	RBN	MBN	s
M/MTBE/4MP2	90	126.4	105.8	20.6
(6 : 3 : 2) 11 %	94	127.6	108.4	19.2
M/MTBE	90	126.4	108.6	17.8
(6 : 5) 11 %	94	127.6	109.3	18.3
M/MTBE/4MP2	90	118.0	107.5	10.5
(1 : 1 : 1) 15 %	94	122.0	104.8	17.2
4MP2	90	99.0	104.2	- 5.2
10 %	94	106.0	103.8	2.2

These show that the blending sensitivity of 4MP2 is very low and may be negative in certain circumstances. This compares with average results obtained by Cahn (23) of RBN 108 MBN 103 and Baronnet (72) RBN 110.3 for 4MP2. However, the sensitivity of M/MTBE is worsened when replacing some of the MTBE by 4MP2. Sensitivity is reduced in the 1 : 1 : 1 blend in the base fuel of 90 RON where the MTBE and 4MP2 fractions are higher. Interpretation of these results must be cautious due to the possible experimental error of ± 0.3 ON and the fact that the tests were only carried out once, but they do back up the 4 cylinder experimental work in that 6 : 3 : 2 and 6 : 5 results are similar.

CHAPTER 4

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

The abundance of work reported by other researchers concerning methanol, ethanol and MTBE indicated the sort of results which were to be expected in the experiments to be carried out in this work. There is general agreement on almost everything published in this field with only a slight variation in degree of antiknock quality etc.

The preliminary experiments were performed using these oxygenates to test the engine, dynamometer and instrumentation because of this available information. Reducing quantities of these were blended with 2-star gasoline and tested. They showed, as expected, an increase in knocking tendency with reduction of oxygenate quantity in the blend. Using the CORC Series F-7, which was blended up in increments of one RON, experiments were carried out to assess the antiknock quality of methanol, TBA, Oxinol 50 and MTBE. Their quantities were limited to a maximum of about 4 % wt/wt oxygen to avoid any driveability problems which could occur with too weak a mixture. The results shown as graphs of required base fuel octane number against engine speed (Figures 40 - 43) were produced by observing the point at which trace knock is no longer present. The actual RON of each blend was not known and their determination was not immediately possible as it had to be performed at Esso Abingdon. However, the graphs did suggest how those tested compared with each other and how increasing oxygenate quantities reduced the required base fuel RON to eliminate knock.

The first CFR tests concerned these blends and showed as expected a greater RON than MON increase. This is due to the higher sensitivity of the oxygenates than the gasoline that they were blended into, although the results for MTBE were close to each other. These CFR results were one-offs due to the limited availability of test equipment thus making error a maximum. However, as the base gasoline tests show they are reasonably reliable.

The Fiat engine tests showed the best improvement with MTBE up to 4 % wt/wt oxygen, ie the required octane number of the base fuel was lower than for the other oxygenates. This again was predicted as, at 4 % wt/wt oxygen in the blend, 23 % MTBE of RON 117 was present compared to, for example, only 8 % methanol of RON 124 to 134. On a volume basis methanol produced the greatest improvement.

Comparing the 6 and 11 % curves for Oxinol and MTBE it can be seen that they are somewhat similar in slope but that the MTBE curves require the same base fuel octane numbers at lower engine speeds than the Oxinol curves. The difference is small and suggests that in equal quantities MTBE gives better protection against knock than Oxinol. The CFR results for 91 ON base fuel show a slightly better RON improvement with Oxinol but worse MON improvement suggesting that MON is a more important factor for the Fiat engine. This is supported by comparing the 5 % TBA and 4 % methanol curves which are similar as would be suggested in the CFR results, ie similar MON but different RON.

These tests were useful in determining the methods by which to proceed in the main experiments and indicated agreement with the published work by other authors. They were, however, limited in their use because the condition of trace knock had been the only point of determination of the fuel quality required, and day to day variations in conditions did have a small but noticeable effect making it necessary to run several reference fuels to determine whether experiments could be performed to produce repeatable results with confidence.

For the main experimental programme two conditions of fuel rating were decided upon. These were trace continuous knock and light continuous knock. The light knock was easily distinguishable and disappeared over a very small increase in engine speed for each fuel. The range of oxygenates was extended to include other types, ie esters and ketones, some of which had previously been tested by others and some chosen purely because of their branched structure. To determine the apparent increase in quality of a base fuel by the addition of an oxygenate several engine tests were performed using the F-7 series to determine the required octane number at all engine speeds. Blends containing oxygenates were then tested and compared with this curve to indicate the new blend octane number.

The most important part of these experiments was the combining of oxygenates to produce multiple blends which might exhibit a synergistic effect which could not be predicted. The results were obtained on days of reasonably similar atmospheric conditions and reproduceability was very good. Many results were similar for single oxygenate blends as would be expected from their RBN and MBN data and in general trace knock occurred up to between 100 and 200 rpm after the cessation of light knock although the shape of the two curves was not always the same.

The aim of the dual and treble combinations was to combine chemical types as well as promising individual components so that if a mixture containing, for example, an alcohol, an ether and an ester gave excellent results other experiments containing these three chemical types would suggest whether it was the types in combination or the individual components that was responsible for the improvement in quality, so directing further research.

The results initially suggested methanol plus MTBE with a ketone was a better than average blend and also that methanol plus MTBE and TBA was good.

Dual blends suggest methanol plus MTBE and methanol plus ethanol were better than expected, and later experiments showed that in fact the best combination appeared to be methanol and MTBE, and that the TBA or ketones in the treble blends were useful in replacing some of the MTBE but did not improve the blend antiknock quality. CFR tests on combinations of these did, however, show the importance of the ketone, 4 methyl pentan-2-one, in reducing the sensitivity of the blend due to its own very low sensitivity. The replacement of a small amount of MTBE by 4MP2 showed no change in RON but a very small decrease in MON which supports the Fiat engine tests which suggested that the best results were achieved with no 4MP2, both in Series F-7 and in 2-star gasoline.

Comparing the apparent RON appreciation in the Fiat engine with actual CFR data shows some agreement but because of the limited CFR data available no definite correlation can be made between light or trace knock on the Fiat and ΔRON or ΔMON on the CFR although trends are very apparent, ie a large increase ΔRON and ΔMON is reflected by a large shift in the Fiat engine test curves.

Attempts to predict the effect of combinations of oxygenates resulted in the use of blending numbers rather than experimental results which were extrapolated. Blending numbers were useful in most cases, but were not able to predict the larger than expected and potentially valuable increases in quality for some blends.

The engine power output measured for a number of blends was seen to increase slightly when oxygenates were present and the largest increase was at low speeds, maximum output being almost unaffected. This may result in better acceleration for the blends especially over the first part of acceleration, but this should be tested to be confirmed.

Exhaust emissions were tested with no adjustment to the carburettor. Thus oxygenated fuels burnt in a leaner mixture because of the oxygen in the molecules which would be expected to reduce carbon monoxide and hydrocarbon emissions. A reduction in emissions was noted for all oxygenates which were blended at approximately 4 % wt/wt oxygen. The greatest reduction was noted for the 1 : 1 : 1 M/MTBE/4MP2 blend at 14.5 % which gave much lower emissions than the others even though the oxygen content was not the highest. Most blends showed a reduction in CO from a maximum of 7 % to 5 or 5.5 %, and a lower output at all speeds. Hydrocarbon emissions were reduced by the greatest amount in the 11.5 % ethanol, 11.5 % Oxinol, 22 % MTBE and 25.5 % 4MP2. The lower emissions may be due to more efficient combustion of the fuel although some blends did contain slightly more oxygen than others. The peak value of CO was observed to shift when some oxygenates were included. The peak always moved to a higher engine speed usually corresponding to that of 4-star gasoline ie greater than 2-star by about 150 to 200 rpm. However, that of the 1 : 1 : 1 M/MTBE/4MP2 blend shifted by a greater amount. This shift in peak may again be due to more efficient combustion, other possible causes such as lower bond energies and ease of oxidation were examined but no correlation could be found. If more efficient combustion is occurring, requiring less time for the same degree of combustion, emissions at a lower speed than that which may be critical will be lower so shifting the peak to a higher speed.

4.1 Ketones as Blending Components

Acetone, MEK and 4MP2 are among the hundred largest volume organic chemicals. The majority of work on oxygenates in the past has concentrated on the alcohols and a few ethers and little research into the use of ketones and esters has been carried out. At present the esters which appear to be useful are very expensive as noted by Beuther and Kobylinski (89) and are unlikely to figure highly in the near future as alternative fuels unless bulk production reduces their cost substantially. Some of the ketones, on the other hand, are close in price to other more accepted blending components and their very high octane numbers make them attractive. Little precise information is available but this research has shown acetone, MEK and especially 4MP2 to be worth considering further.

4MP2 is produced from acetone and is used mostly as a solvent in coatings and extractive distillation. It is also a powerful degreasant. One major use is as a paint solvent for automobiles. In the US the EPA is attempting to reduce evaporative emissions caused as the paint is dried and moves towards solvent-less coatings will liberate vast quantities of 4MP2 which is already over produced. Water based solvents, developed during the oil crisis, are already in use as primers and undercoats (100). They are produced by ICI and Herberts (who supply Opel cars) and they reduce emissions by 70 to 80 % although they do cost more than ordinary paints. There is also a move towards the use of powder coatings, resins and pigments, which are baked to form a type of enamelled coating. The move towards solvent-less coatings and the very low sensitivity and high RON of 4MP2 make it a likely candidate for blending in the future.

CHAPTER 5

CONCLUSION

CONCLUSION

Previous research by many workers in this field has shown the benefits and drawbacks of using certain oxygenates as blending components in gasoline. Oxygenated hydrocarbons burn in the same way, forming the same products, as the usual constistuents of gasoline. They also have the ability to form cool flames and peroxides which, as has been discussed, may lead on to spontaneous combustion. However many oxygenates have been found to be more resistant than gasoline to this problem under standard test conditions and this has generated the great interest shown in them as blending agents.

Small branched molecules are well known to exhibit a high resistance to knock and this criterion was used when selecting suitable candidates for testing. The base fuel for tests undertaken was a low-leaded, middle sensitive fuel, CORC Series F-7, well known to those engaged in gasoline testing in industry. Four types of oxygenate were tested: alcohols, ethers, esters and ketones, some of which are already in use as blending agents such as methanol, ethanol and MTBE. Many of the others are virtually untested. Little information is available concerning multiple blends of oxygenates with gasoline. Most work that is reported involves the use of the butanols as co-solvents with methanol to reduce its disadvantages such as its low vapour pressure, and tendency to separate from the blend in the presence of water.

This work has focussed on combinations of oxygenates in gasoline blended up to a maximum of 4 % wt/wt oxygen in the blend. This is greater than presently allowed by all countries and represents the maximum amount that would be acceptable in automobiles in present use without modifications to the carburettor.

No obvious chemical interaction was observed for multi-blends based on chemical type, ie such as an alcohol plus an ester plus a ketone always gave results better than expected, although methanol plus MTBE and a ketone appears promising. In fact most combinations of oxygenates appeared to give worse knock protection than might be expected from their blending numbers as individual components. This may be because detrimental properties of one of them reduced the enhancement properties of the others. It is also known that the blending octane number of a component reduces with increasing base fuel RON. Individual blending numbers might then be expected to be lower when in combination with other high octane components, such as the other oxygenates in the blend. From the various methods investigated to predict octane improvement due to a combination of oxygenates, the use of proportional fractions of each components blending number was used. This, as already discussed, may have predicted over optimistic results but was considered to be the best approach after examination of other methods. It should be noted that some multi-blends, notably M/MTBE, M/MTBE/4MP2, M/MTBE/3MB2 and M/MTBE/TBA, enhanced the base gasoline by the amount predicted, and in some cases by more, possibly showing a synergistic effect.

Tests involving 2-star gasoline suggested that although a blend of M/MTBE was shown to be the most beneficial one, replacement of two fifths of the MTBE by the lower RON, but higher MON, 4MP2 resulted in very little deterioration in fuel quality. CFR testing of these combinations supported this finding. This small difference in the results obtained may be due to the higher MBN of 4MP2 (103 cf 99) which reduced the overall blend sensitivity. However, CFR testing did not confirm this for the 6 : 3 : 2 M/MTBE/4MP2 blend compared to the 6 : 5 M/MTBE blend. Alternatively a chemical interaction between the oxygenates may be occurring, or the effect of replacing 2 % of a component with a RBN of 117 by one of 108 is negligible compared to the effect of the 6 % methanol and remaining MTBE in the blend.

Throughout the experimental programme many blends were regularly retested and the pure base fuels were used each day to ensure that the results would be comparable. Very little variation was noted between these characterisation tests; thus it was assumed that all oxygenated blend tests were conducted under reasonably similar conditions.

RON appreciation, determined by comparing the knock limited speed curve for blends (Figure 51 - 87) with that of the base fuel (Figure 50), was in reasonable agreement with CFR results and so proved to be a reliable method of rating fuels in an engine on a dynamometer.

It has been reported (42) that RON depreciation may occur with some oxygenates in olefinic fuels, such as methanol and ethanol. An olefinic fuel is one in which the olefine content is of the order of 15 %. Due to their high sensitivities the effect of methanol and ethanol is to increase the RON by substantially more than the MON in all blends. The critical knock range of olefinic fuels is greater than non-olefinic ones (3500 - 4000 rpm compared to 1300 - 1400 rpm) and this leads to a higher octane requirement at greater engine speeds. Under normal circumstances non-knocking high speed operation is often dependent on the MON of a fuel which may be insufficient in alcohol blends and with olefinic fuels having such a high critical knock speed the problem is compounded. MTBE and TBA are less of a problem (31) as their sensitivities are lower. Series F-7 fuel, as used in these experiments is low in olefines, 4 to 8 % , and represents the middle ground in the gasolines of Europe. No RON depreciation was expected, although results for ethanol on its own were disappointing. It is recommended that acceleration testing of the most promising blends is carried out in order to establish whether performance is affected but it is thought unlikely that it will be from the results obtained here.

When choosing the chemical to be tested in this work it was known that small, highly branched structures possessed the highest knock resistance. Some oxygenates used here, however, appeared to have greater anti-knock quality than others of a similar size, branchiness and position of functional group. No correlation between RON or MON and bond strength, Raman spectra, nuclear magnetic resonance, or any other internal property could be determined and it may be that the intermediates of combustion vary, so affecting their ability to promote knock.

Engine power output, tested using blends containing 2-star gasoline, showed an increase for all oxygenates with the largest increase, up to 5 %, being at the lowest engine speeds. The 6 : 3 : 2 M/MTBE/4MP2 blend gave some of the best results. Greater power at low speeds with wide open throttle may result in better acceleration and as previously stated, acceleration testing of the most promising blends should be undertaken.

Exhaust emissions were tested for the same blends as in the power output tests with no adjustment being made to the carburettor to offset the leaning of the fuel caused by the presence of extra oxygen. Lower exhaust emissions were expected for the oxygenated fuels and this was found to be the case for all of them. The greatest carbon monoxide reduction occurred when using 1 : 1 : 1 M/MTBE/4MP2 at 14.5 % which although high in oxygen content was not the highest. Most of the other blends gave similar reductions to each other. One of the criteria for the whole experimental programme was that a standard automobile engine with no alterations to it was used. The emissions results give the impression of being better than they are due to the leaning effect and if "real" effects are required the equivalence ratio during testing should be kept constant. However, this would involve changing carburettor jets and was not in the scope of this work. Also if jets were to be changed on road vehicles a national standard blend would be required to avoid driveability problems arising in the event of buying fuel from different oil companies. For this reason the oxygen limit for blends tested was set at 4 % wt/wt, which is considered the maximum that can be included without driveability problems being encountered by unmodified vehicles.

The peak value of carbon monoxide was noticed to shift to a higher engine speed when oxygenates were added to 2-star. This effect appears to have no real importance but may indicate more efficient combustion of the blends than of pure 2-star, that is less time is required to achieve the same degree of combustion so shifting the peak to a higher engine speed. The peak of the 1 : 1 : 1 M/MTBE/4MP2 blend was shifted by the greatest amount and this being the same blend with the lowest emissions supports a more efficient combustion scenario.

CFR testing of the most promising blends showed, as previously mentioned, that little difference could be detected between the 6 : 5 M/MTBE and 6 : 3 : 2 M/MTBE/4MP2 blends as the Fiat engine tests had shown. CFR results also showed the 1 : 1 : 1 M/MTBE/4MP2 15 % blend to give the best RON and MON improvement, as would be expected because of the greater percentage of high octane components included. It was interesting, however, that the MON improvement of this blend was almost as high as the RON improvement due to the higher percentage of 4MP2 in the blend. The large increase in MON is an important result as high speed engine operation is often dependent upon the MON rather than the RON of a fuel. Most oxygenates are highly sensitive compared to gasoline which in some circumstances leads to RON give-away being necessary in order to provide a fuel with sufficient MON to avoid knock at all speeds. CORC test results on 9 similar Fiat 903 cc engines show the importance of high MON at high engine speeds. The required octane number of PRF fuels, which have the same MON and RON, ie not sensitive, at high engine speeds is much lower than the Series F-7 fuels which have an average sensitivity of 9 octane numbers. Experimental results for blends with similar MON but different RON showed that MON was important for the test engine. An oxygenate which can enhance the MON of a base fuel by more than RON is a very valuable blending agent and may save substantial amounts of money by avoiding RON give-away. The CFR results for a 10 % 4MP2 blend showed the very low sensitivity of this component.

From the results obtained in this work it appears that a combination of oxygenates involving methanol, MTBE and 4 methyl pentan-2-one could be useful as a blending agent in gasoline to raise the octane level by 3 or 4 with no modifications to the fuel system of an automobile being required. The benefits of lower exhaust emissions and slightly improved power output are in addition to the octane improvement achieved. Methanol and MTBE are currently used individually by many countries and some, notably Switzerland, do include them together in some gasoline blends, although whether by design or coincidence it is not known. However, 4MP2 appears not to be used at present, perhaps because of its high cost. Present and future legislation concerning evaporative emissions of solvents from coatings etc to the atmosphere, and the current move towards water-based coatings as car paints will release large quantities of 4MP2, which is one of the 100 most produced solvents. Increased production, as would be required, would also reduce its price, which at present is slightly greater than MTBE, and this could be a decisive factor in its use as a blending component to supplement the restricted availability of MTBE. Oxygenates are most likely to be used when the incremental octane barrel cost is high, such as with hydroskimmer refineries. Unlike catalytic and steam cracker refineries, hydroskimmers are limited in their octane boosting capacity without substantial new investment and could not produce 97 RON unleaded gasoline in thieir present condition. Based on present estimates methanol, MTBE and TBA are close to viability and this research has proved that they, along with 4MP2, have the most significant effect on fuel quality.

NOMENCLATURE

NOMENCLATURE

Acetone	Dimetyl ketone
Anisole	Methoxybenzene (methyl phenyl benzene)
ATDC	After top dead centre
BTDC	Before top dead centre
CO	Carbon monoixde
CO_2	Carbon dioxide
CORC	Co-operative Fuel Research Committee
CR	Compression ratio
CSTR	Continuous stirred tank reactor
DIPE	Diisopropyl ether (isopropyl ether)
DMC	Dimethyl carbonate
E	Ethanol
FEON	Front end octane number
HC	Hydrocarbon
M	Methanol
MA	Methyl acetate (acetic acid, methyl ester)
MBN	Motor blending number
MEK	Methyl ethyl ketone
MON	Motor octane number
MTBE	Methyl tertiary butyl ether (tertiary butyl methyl ether)
NO_x	Nitrogen oxides
ORI	Octane requirement increase
PRF	Primary reference fuel
R_{100}	Research octane number of components which boil off up to 100°C
RBN	Research blending number

RdON	Road octane number ((RON + MON)/2)
RON	Research octane number
s	Sensitivity
TBA	Tertiary butanol
TEL	Tetra ethyl lead
TML	Tetra methyl lead
WOT	Wide open throttle
3MB2	3 methyl butan-2-one (3 methyl 2 butanone, methyl isopropyl ketone, MIPK)
4MP2	4 methyl pentan-2-one (4 methyl 2 pentanone, methyl isobutyl ketone, MIBK)
ΔR_{100}	RON - R_{100}

APPENDICES

APPENDIX 1

Experimental Results

The following tables and graphs relate to the experiments concerning engine knock and exhaust emissions. The knock limited rpms for both trace and light knock are given against the base fuel octane number into which the oxygenates have been blended. The first table, Table 40, indicates results for the pure base fuels, an average plot of these is shown as Figure 50. In the case of 4MP2 a 95 RON base fuel was used and these results are shown mid-way between 94 and 96 in Table 41. A cross (x) denotes "not tested" and a dash (-) that no knock could be detected at any speed down to 1050 rpm. Dates of tests can be cross referenced to humidity data in Appendix 6 if required. Plots of the knock limited rpm data for oxygenated blends are shown as Figures 51 to 87. The RON data given are that of the base fuel and not the final blend. Blend RONs, and hence octane improvement, were found by comparing the knock limited speed of a blend in a certain base fuel with those of the pure base fuels in Figure 50 at the same engine speed.

Exhaust emissions results are plotted as Figures 88 to 98 and show ppm hydrocarbons and volume percent carbon monoxide and dioxide emissions against engine speed, all on the same axis. The air/fuel ratios shown in Table 31 appear low but this may be due to equipment error as the carbon monoxide emissions for gasoline at normal idle speed (Figure 88) were within specification of between 2 and 3 %. Crosses (x) on these graphs indicate emissions at idle speed.

Table 40 Experimental Results for Series F-7 Gasoline

Date	Trace/	Rpm Knock Limit								
	Light	90	91	92	93	94	95	96	97	98
26. 9.84	T	3000	3000	2400	2000	1900	1650	1400	1300	1300
	L	x	x	x	x	x	x	x	x	x
10.10.84	T	3000	2500	2200	1950	1730	1600	1450	1330	1270
	L	x	x	x	x	x	x	x	x	x
29. 3.85	T	3200	2150	1940	1860	1660	1590	1540	1310	1250
	L	1930	1800	1720	1620	1550	1340	1290	1140	-
17. 4.85	T	3200	2150	1940	1860	x	1650	x	x	x
	L	1930	1800	1720	1620	x	1340	x	x	x
24. 4.85	T	3150	2550	2200	2030	1840	1720	1640	1530	1400
	L	2150	1950	1730	1680	1650	1610	1300	1270	1000
11. 7.85	T	x	1910	x	1670	x	1530	x	x	x
	L	1890	x	1730	x	1550	x	1280	x	x
17. 7.85	T	x	x	x	1790	x	1610	x	x	x
	L	x	x	x	1620	x	1290	x	x	x
23. 7.85	T	x	x	x	1930	x	1620	x	x	x
	L	x	x	x	1670	x	1330	x	x	x
25. 7.85	T	x	x	x	1880	x	1630	x	x	x
	L	x	x	x	1630	x	1300	x	x	x

Date	Trace/ Light	Rpm Knock Limit 90	91	92	93	94	95	96	97	98
26. 7.85	T	x	x	x	1870	x	1630	x	x	x
	L	x	x	x	1620	x	1320	x	x	x
13. 8.85	T	3100	2170	2020	1850	1780	1640	1630	1390	x
	L	1980	1910	1810	1670	1620	1600	1280	1160	x
13. 8.85	T	x	2150	1950	x	1670	1600	x	x	x
	L	x	1900	1740	x	1590	1370	x	x	x

Table 41 Experimental Results for Blends Containing Oxygenates

Date	Oxygenate	Blends	Trace/	Rpm Knock Limit			
	Type	% v/v	Light	90	92	94	96
11.7.85	MEK	10	T	1950	1830	1600	1240
			L	1700	1620	1350	1150
11.7.85	MEK	20	T	1620	1520	1300	1220
			L	1570	1380	1200	-
11.7.85	DIPE	5	T	1870	1760	1670	1350
			L	1690	1640	1470	1150
17.7.85	DIPE	5	T	1970	x	x	1340
			L	1850	x	x	1170
18.4.85	DIPE	10	T	1930	1750	1640	1330
			L	1720	1610	1470	1180
17.7.85	DIPE	10	T	1930	1700	x	1240
			L	1690	1590	x	1130
18.4.85	DIPE	20	T	1650	1570	1480	1250
			L	1580	1330	1270	-
11.7.85	4MP2	5	T	2000	1820	1630	1440
			L	1760	1660	1560	1230
17.7.85	4MP2	5	T	x	x	x	1540* x
			L	x	x	x	1370* x

Date	Oxygenate Type	Blends % v/v	Trace/ Light	Rpm Knock Limit 90	92	94	96
18.4.85	4MP2	10	T	1950	1720	1600	1400
			L	1700	1610	1480	1260
17.7.85	4MP2	10	T	x	x	x 1570*	x
			L	x	x	x 1300*	x
18.4.85	4MP2	20	T	1800	1640	1480	1290
			L	1550	1460	1300	1180
11.7.85	3MB2	5	T	2020	1840	1660	1520
			L	1760	1670	1520	1300
18.4.85	3MB2	10	T	1910	1800	1580	1500
			L	1720	1610	1330	1280
18.4.85	3MB2	20	T	1780	1610	1510	1250
			L	1590	1460	1260	-
11.7.85	Anisole	5	T	2040	1750	1660	1360
			L	1700	1640	1480	1190
19.4.85	Anisole	10	T	1960	1700	1580	1330
			L	1660	1580	1340	1100
19.4.85	Anisole	20	T	1660	1580	1350	-
			L	1560	1300	1050	-
17.7.85	Acetone	5	T	1980	1800	1640	1390
			L	1810	1660	1540	1260

Date	Oxygenate Type	Blends % v/v	Trace/ Light	Rpm Knock Limit 90	 92	 94	 96
17.7.85	Acetone	10	T	1900	1680	1590	1320
			L	1660	1580	1380	1240
17.7.85	M	5	T	1850	1640	1530	1250
			L	1680	1590	1270	1180
17.7.85	M	10	T	1680	1600	1250	1100
			L	1610	1380	1080	-
19.8.85	M	15	T	1400	1240	1120	-
			L	1270	1120	-	-
23.7.85	E	5	T	2200	1820	1660	1520
			L	1820	1640	1420	1220
23.7.85	E	10	T	1860	1680	1450	1260
			L	1680	1430	1250	1050
23.7.85	MTBE	5	T	2050	1880	1660	1530
			L	1900	1710	1580	1280
23.7.85	MTBE	10	T	1900	1700	1430	1290
			L	1740	1510	1300	1050
19.8.85	MTBE	15	T	1600	1320	1200	1060
			L	1300	1210	1050	-
23.7.85	MTBE	20	T	1370	1250	1140	-
			L	1280	1170	-	-

Date	Oxygenate	Blends	Trace/	Rpm Knock Limit			
	Type	% v/v	Light	90	92	94	96
23.7.85	Oxinol	10	T	1750	1640	1370	1170
			L	1650	1500	1180	1050
28.8.85	TBA	5	T	2030	1820	1660	1530
			L	1790	1680	1590	1200
28.8.85	TBA	10	T	2000	1810	1620	1450
			L	1770	1700	1560	1160
28.8.85	TBA	15	T	1930	1760	1630	1380
			L	1720	1650	1550	1140
28.885	TBA	20	T	1820	1720	1560	1290
			L	1680	1600	1320	1080
23.7.85	MTBE/TBA	10	T	1850	1700	1500	1330
			L	1690	1610	1290	1210
23.7.85	M/MTBE	10	T	1710	1570	1280	1220
			L	1620	1300	1190	1120
25.7.85	M/DIPE	10	T	1870	1660	1610	1240
			L	1670	1580	1290	1060
25.7.85	M/Anisole	10	T	1850	1680	1590	1260
			L	1660	1580	1310	1100
25.7.85	M/4MP2	10	T	1850	1680	1620	1250
			L	1690	1590	1320	1130

Date	Oxygenate	Blends	Trace/	Rpm Knock Limit			
	Type	% v/v	Light	90	92	94	96
25.7.85	M/3MB2	10	T	1900	1690	1620	1290
			L	1720	1640	1380	1180
26.7.85	MTBE/DIPE	10	T	1900	1840	1660	1350
			L	1780	1700	1560	1220
26.7.85	MTBE/4MP2	10	T	1880	1770	1630	1310
			L	1750	1650	1480	1170
19.4.85	Methyl Acetate	5	T	2220	1860	1730	1650
			L	1860	1720	1630	1340
19.4.85	Methyl Acetate	10	T	2080	1840	1670	1560
			L	1820	1680	1590	1290
19.4.85	DMC	5	T	2200	1940	1650	1500
			L	1900	1650	1590	1320
19.4.85	DMC	10	T	2100	1740	1620	1390
			L	1750	1610	1520	1220
26.7.85	M/MA	10	T	1840	1710	1590	1150
			L	1690	1600	1300	-
26.7.85	MA/Anisole	10	T	1910	1800	1670	1260
			L	1800	1670	1590	1100
26.7.85	MTBE/DMC	10	T	1900	1800	1600	1160
			L	1790	1630	1300	-

Date	Oxygenate Type	Blends % v/v	Trace/ Light	Rpm Knock Limit			
				90	92	94	96
26.7.85	MA/4MP2	10	T	1980	1820	1600	1130
			L	1870	1690	1440	-
26.7.85	M/E	10	T	1700	1600	1290	1050
			L	1610	1390	1180	-
26.7.85	M/DMC	10	T	1780	1660	1520	1060
			L	1670	1600	1280	-
26.7.85	DMC/4MP2	10	T	1900	1760	1620	1290
			L	1790	1650	1400	1180
26.7.85	M/MTBE/DMC	15	T	1740	1630	1290	1120
			L	1660	1340	1220	-
26.7.85	M/DMC/4MP2	15	T	1730	1660	1270	1100
			L	1650	1420	1180	-
25.7.85	M/MTBE/TBA	15	T	1670	1560	1240	1130
			L	1590	1290	1100	-
26.7.85	M/MTBE/3MB2	15	T	1630	1320	1160	1050
			L	1380	1250	-	-
13.8.85	M/MTBE/3MB2	15	T	1610	1420	1250	1110
			L	1430	1260	1140	-
13.8.85	E/MTBE/4MP2	15	T	1830	1500	1400	1200
			L	1640	1320	1250	-

Date	Oxygenate Type	Blends % v/v	Trace/ Light	Rpm Knock Limit 90	92	94	96
13.8.85	M/MTBE/4MP2	15	T	1610	1430	1250	1120
			L	1520	1270	1180	-
13.8.85	M/DIPE/4MP2	15	T	1820	1580	1340	1160
			L	1640	1320	1250	-
13.8.85	M/MTBE/4MP2	11	T	1720	1610	1310	1130
	(5 : 3 : 3)		L	1640	1420	1220	-
13.8.85	M/MTBE/4MP2	10	T	1720	1610	1380	1170
	(6 : 3 : 1)		L	1650	1360	1260	-

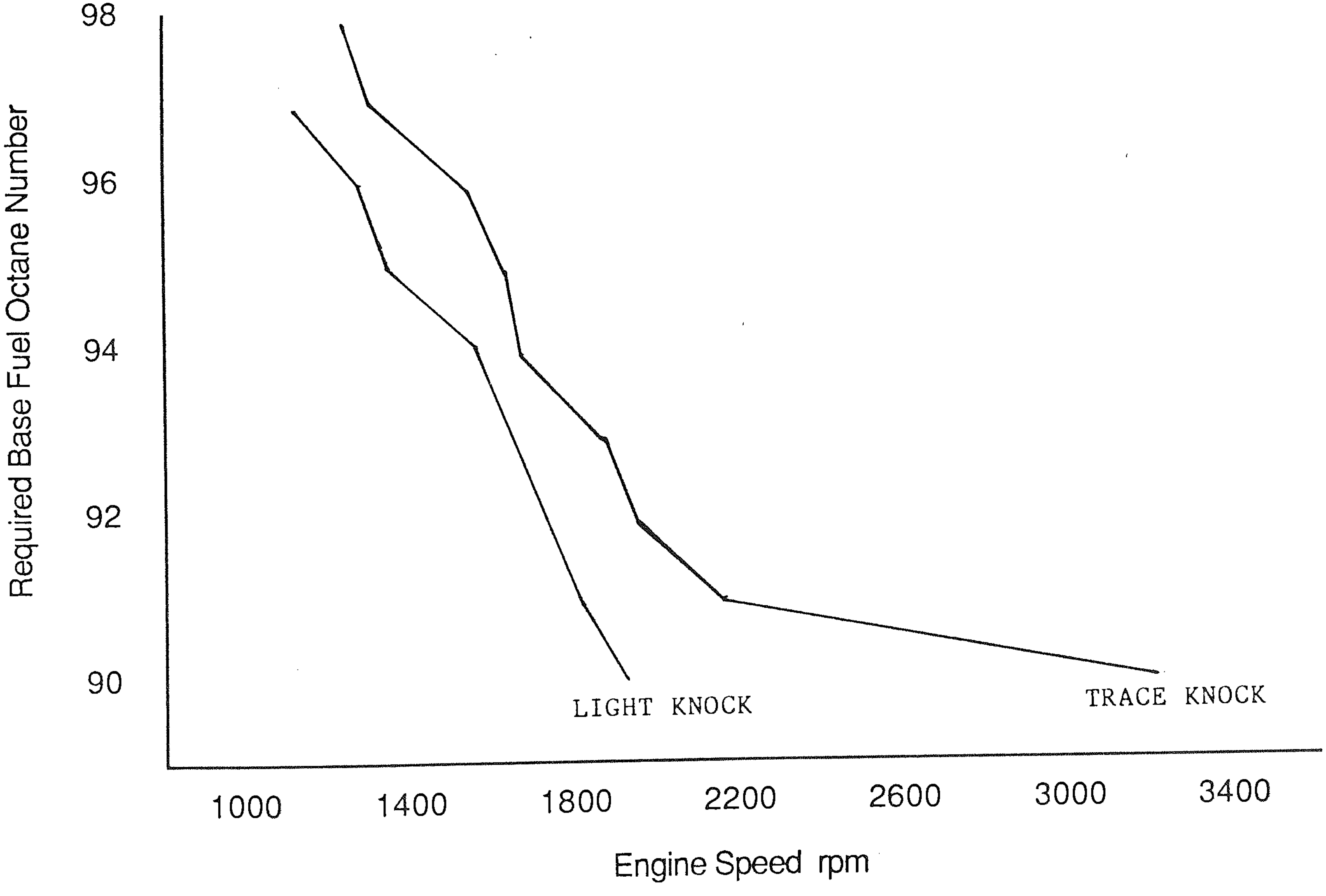

Figure 50 Base Fuel

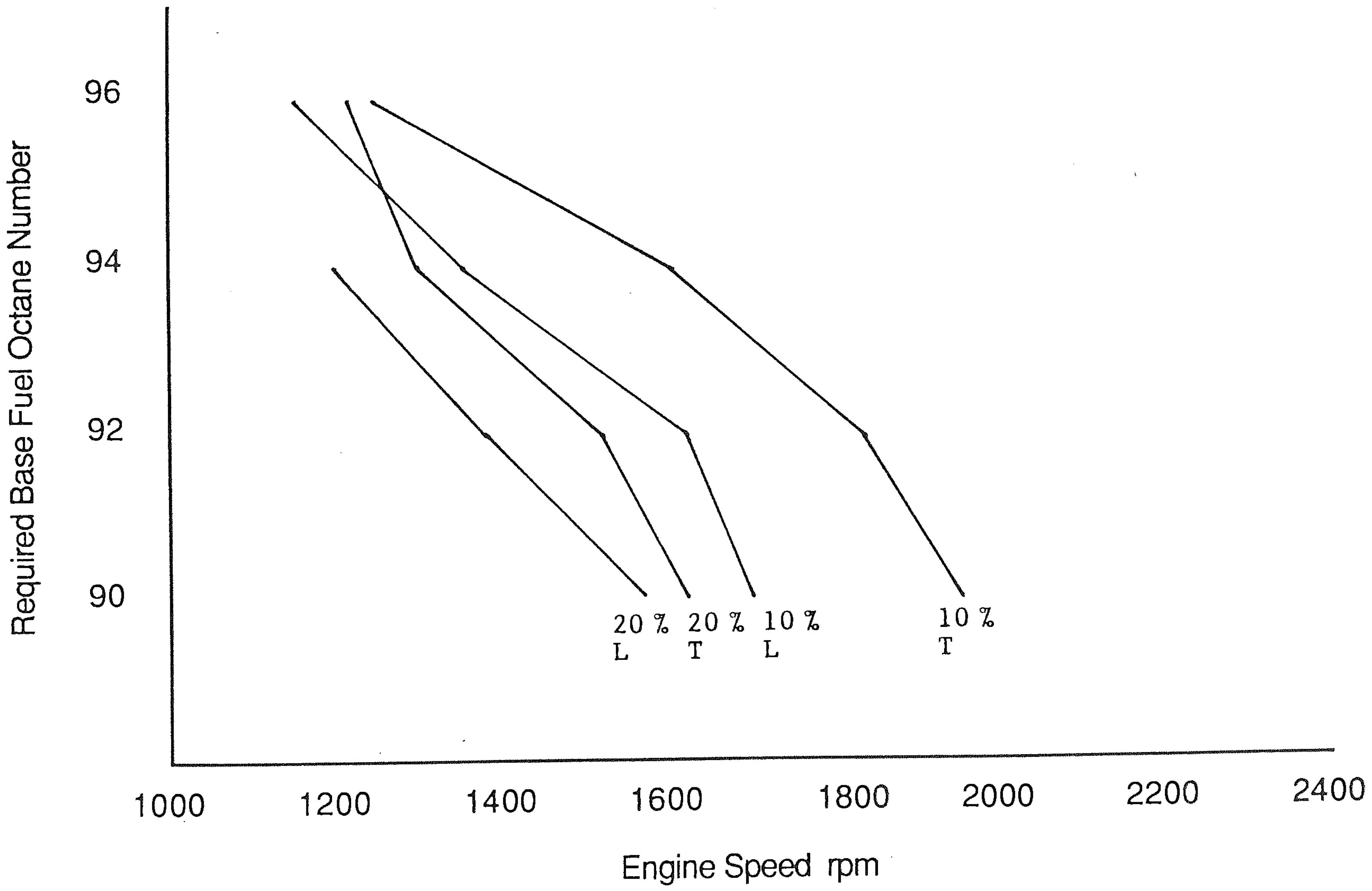

Figure 51 Methyl Ethyl Ketone

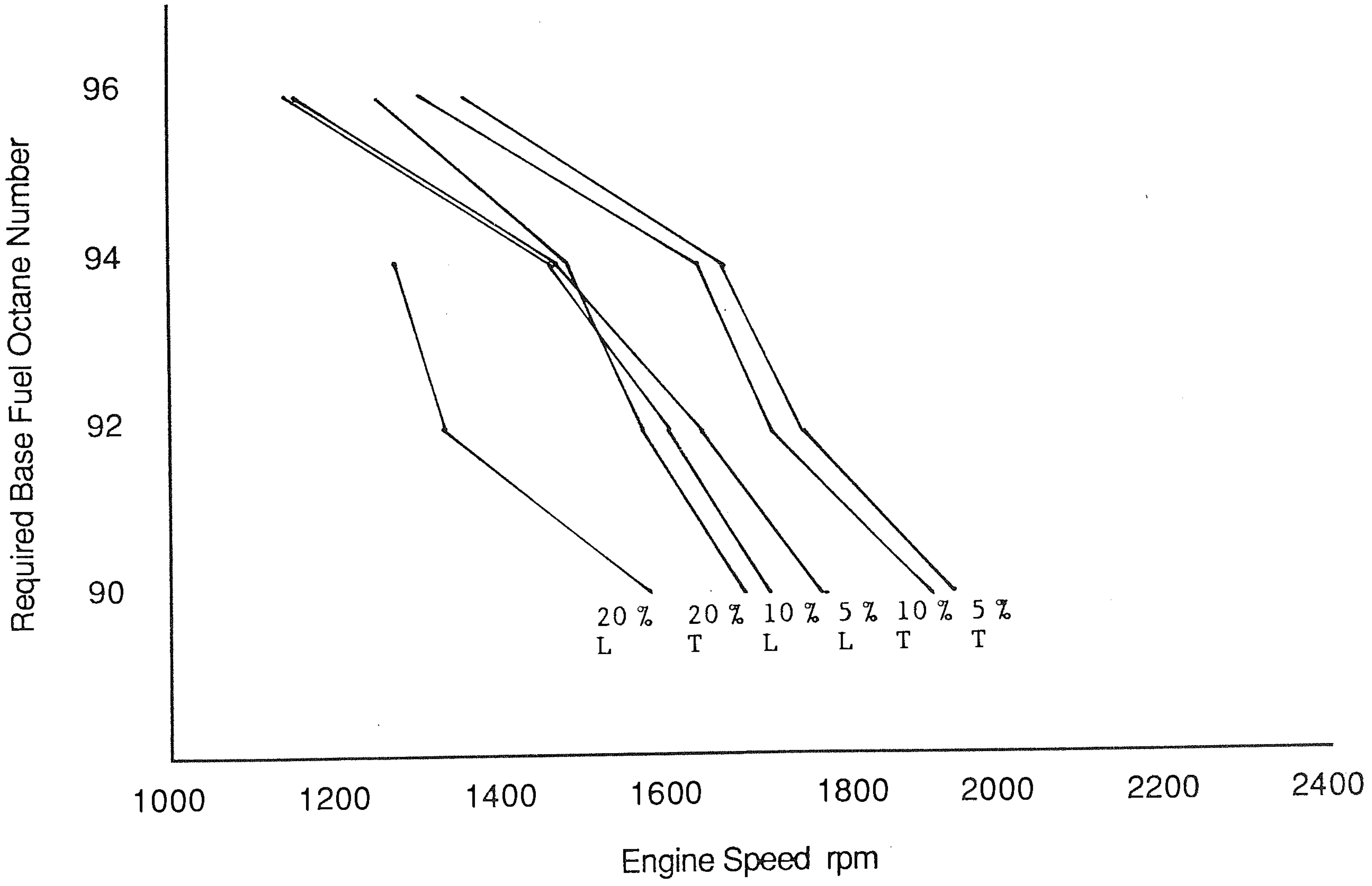

Figure 52 Di-iso-Propyl Ether

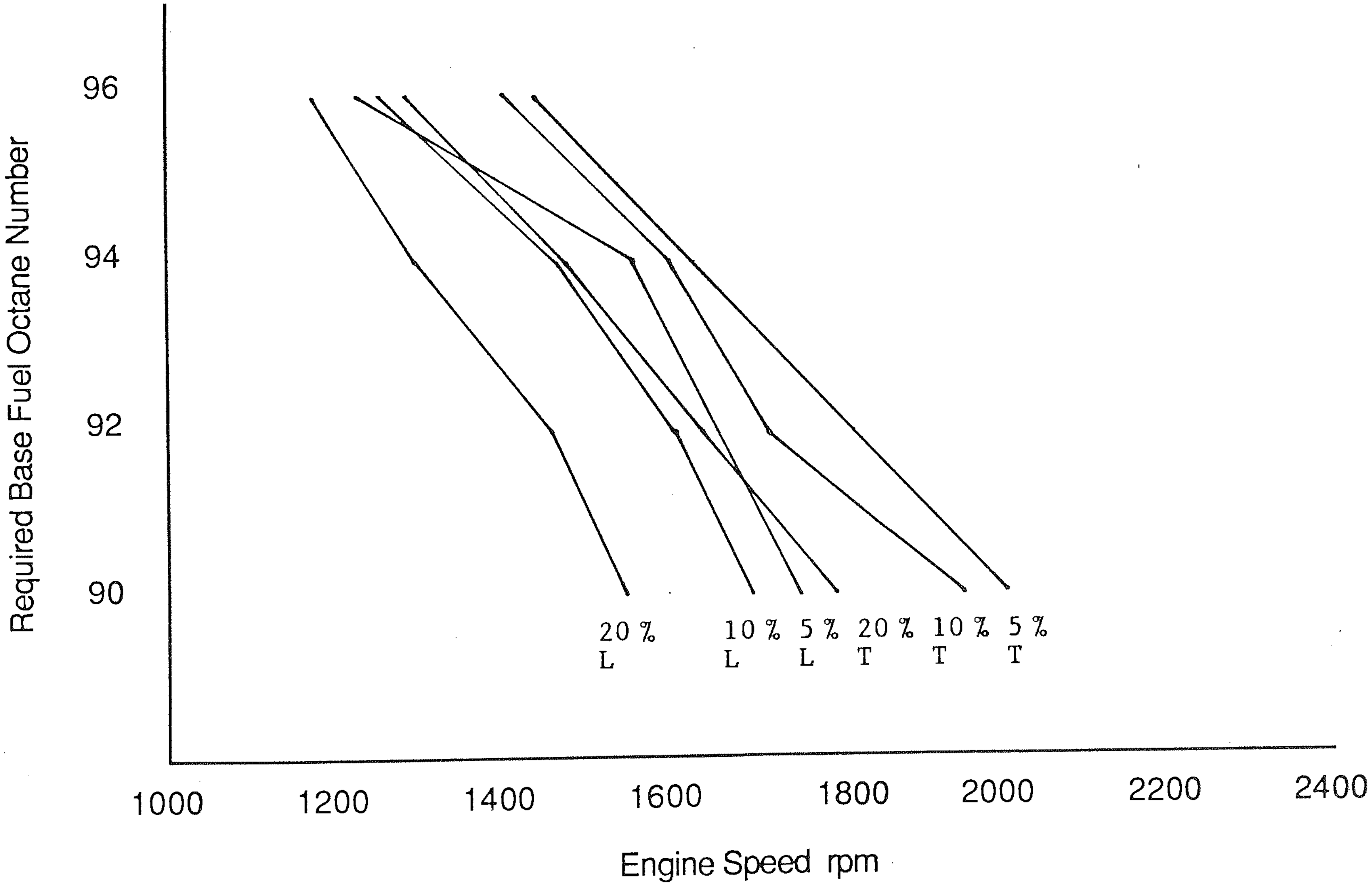

Figure 53 4 Methyl Pentan-2-one

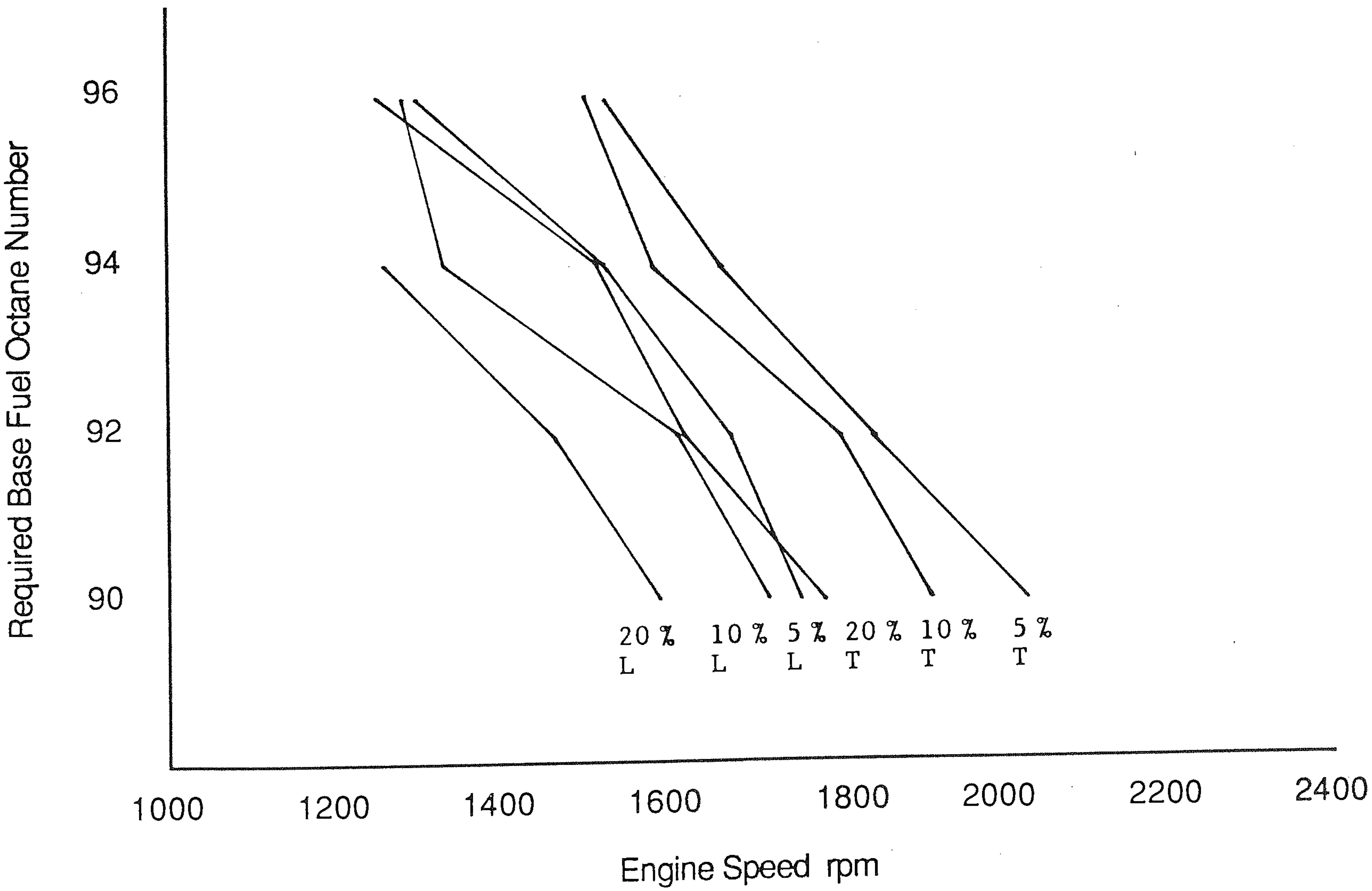

Figure 54   3 Methyl Butan-2-one

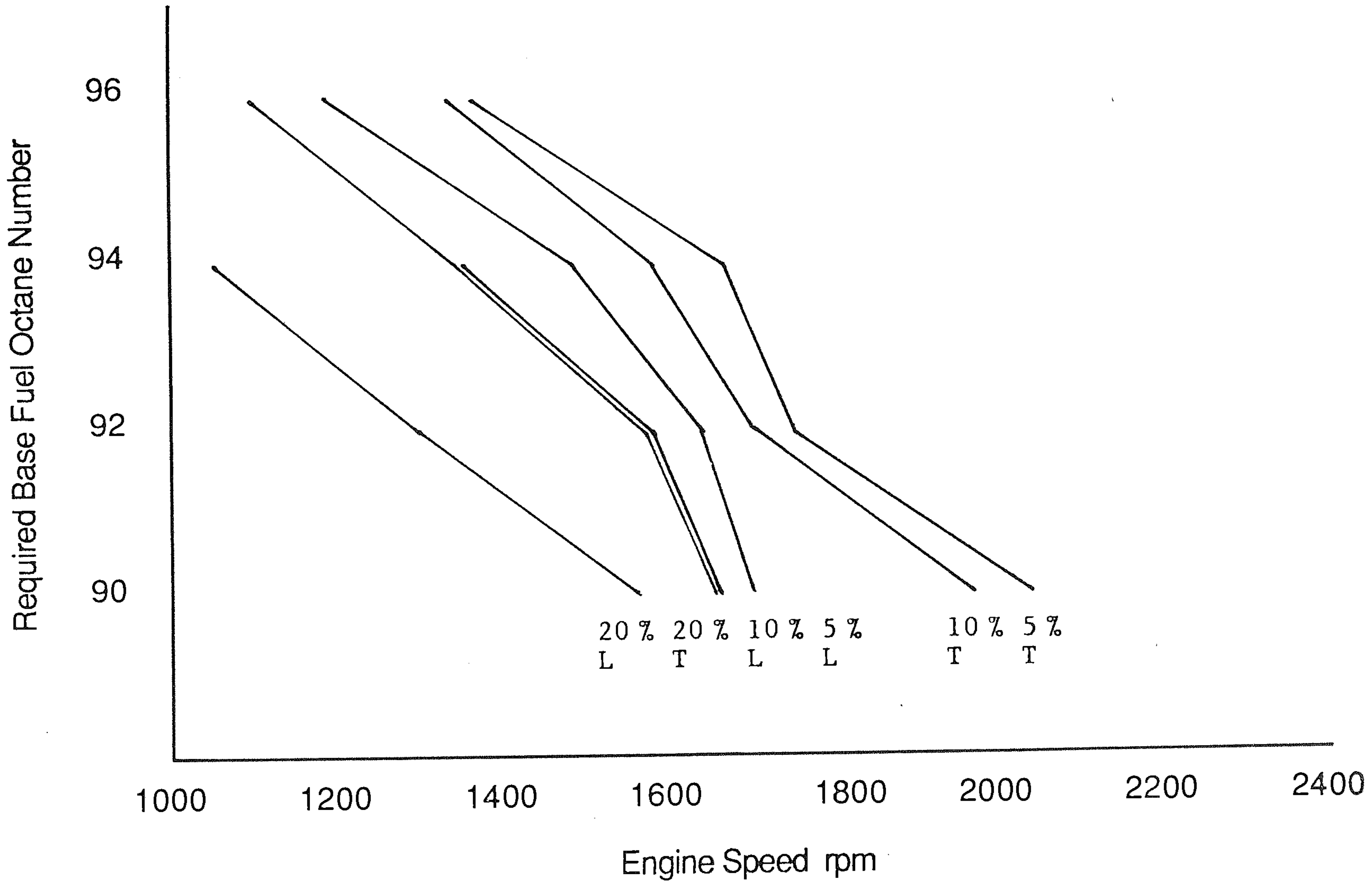

Figure 55 Anisole

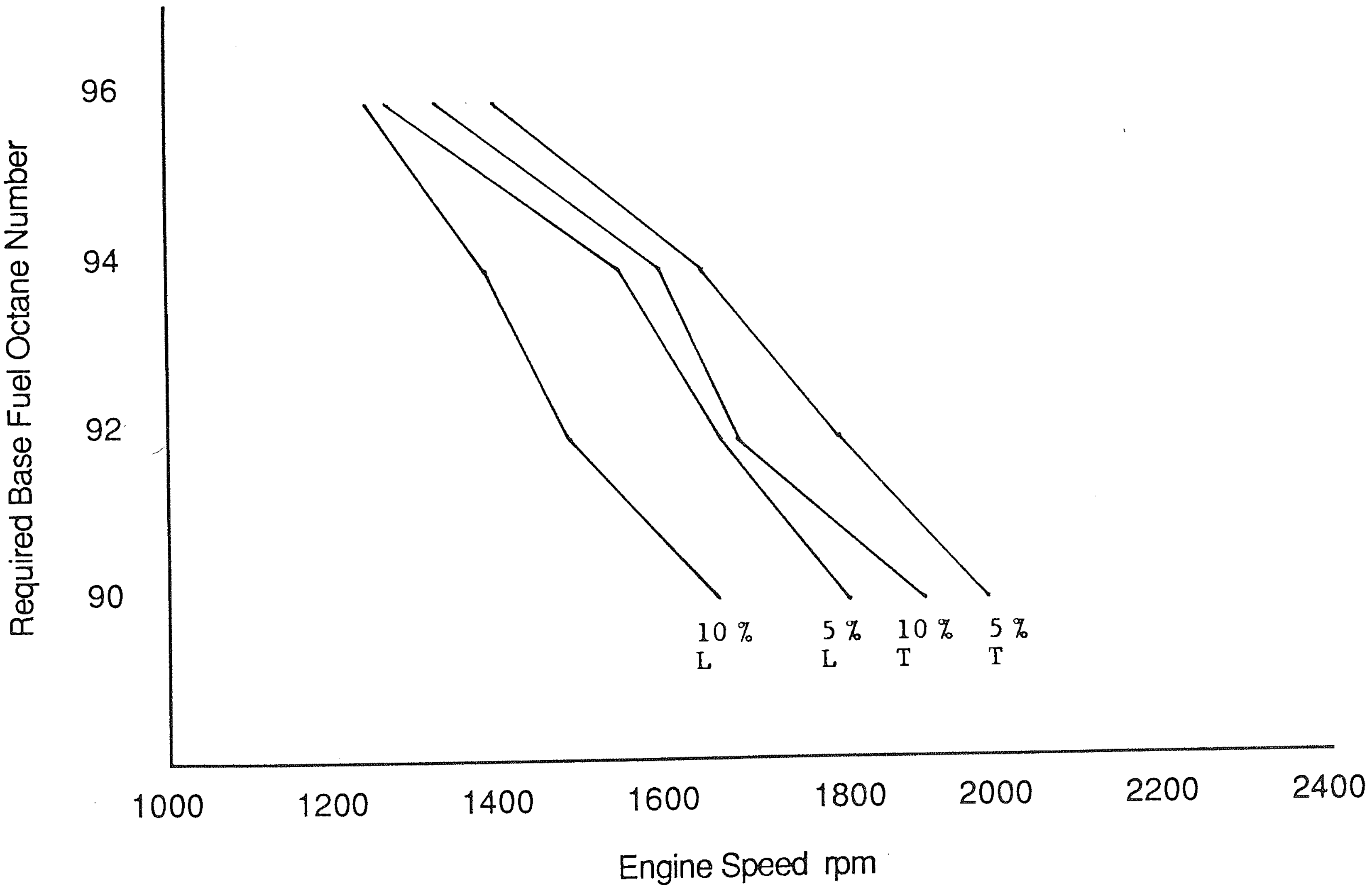

Figure 56 Acetone

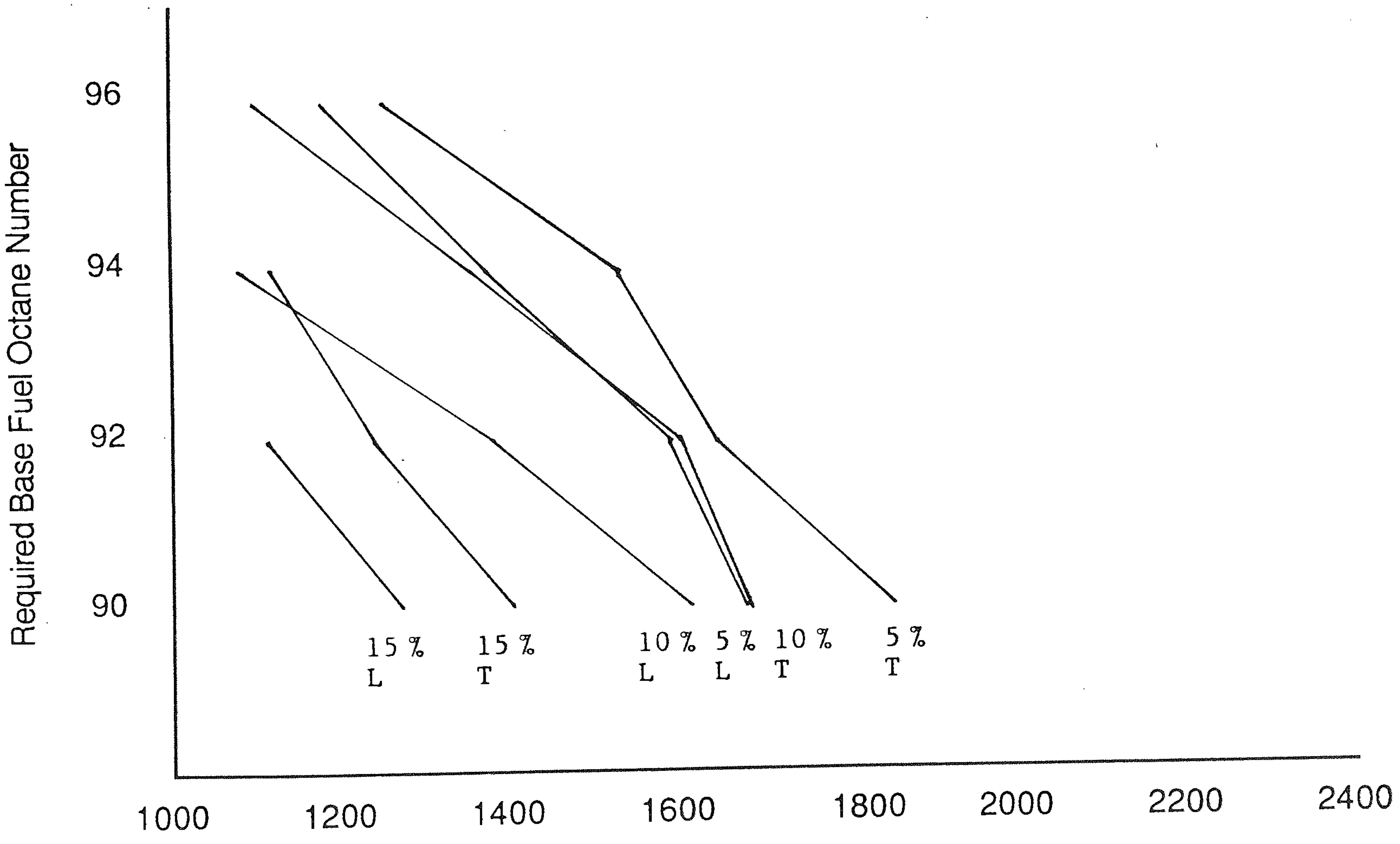

Figure 57 Methanol

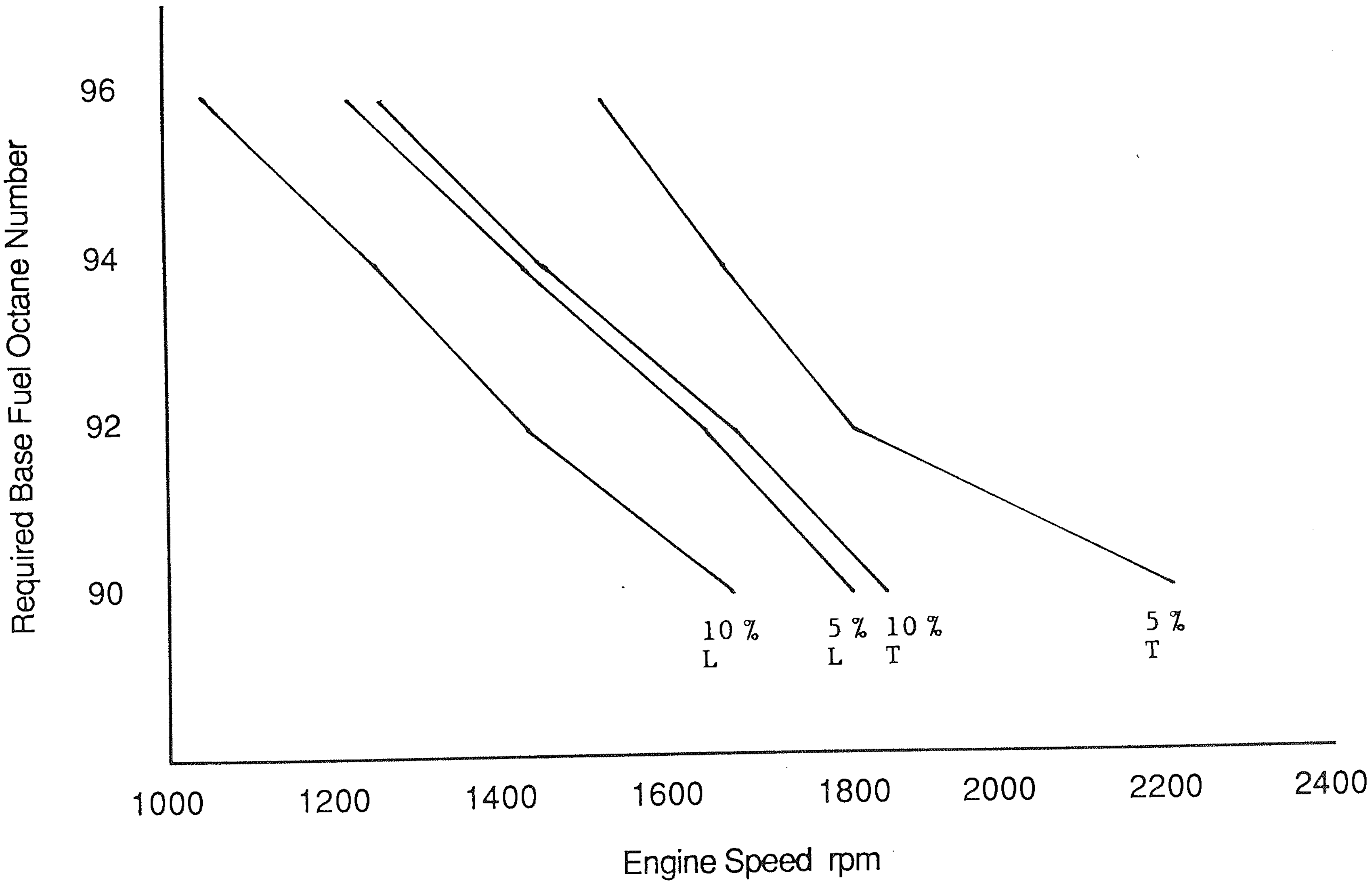

Figure 58 Ethanol

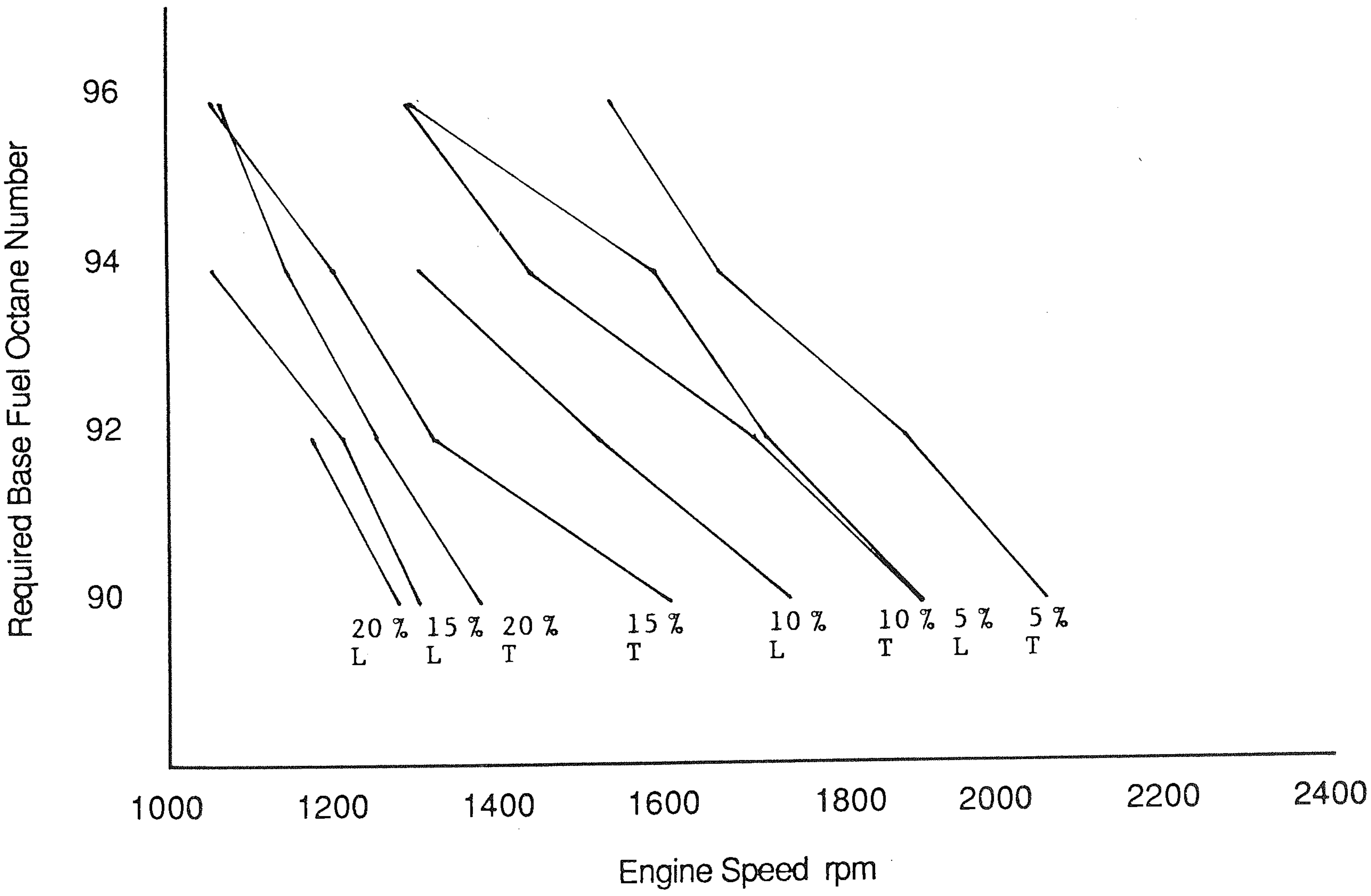

Figure 59 Methyl Tertiary Butyl Ether

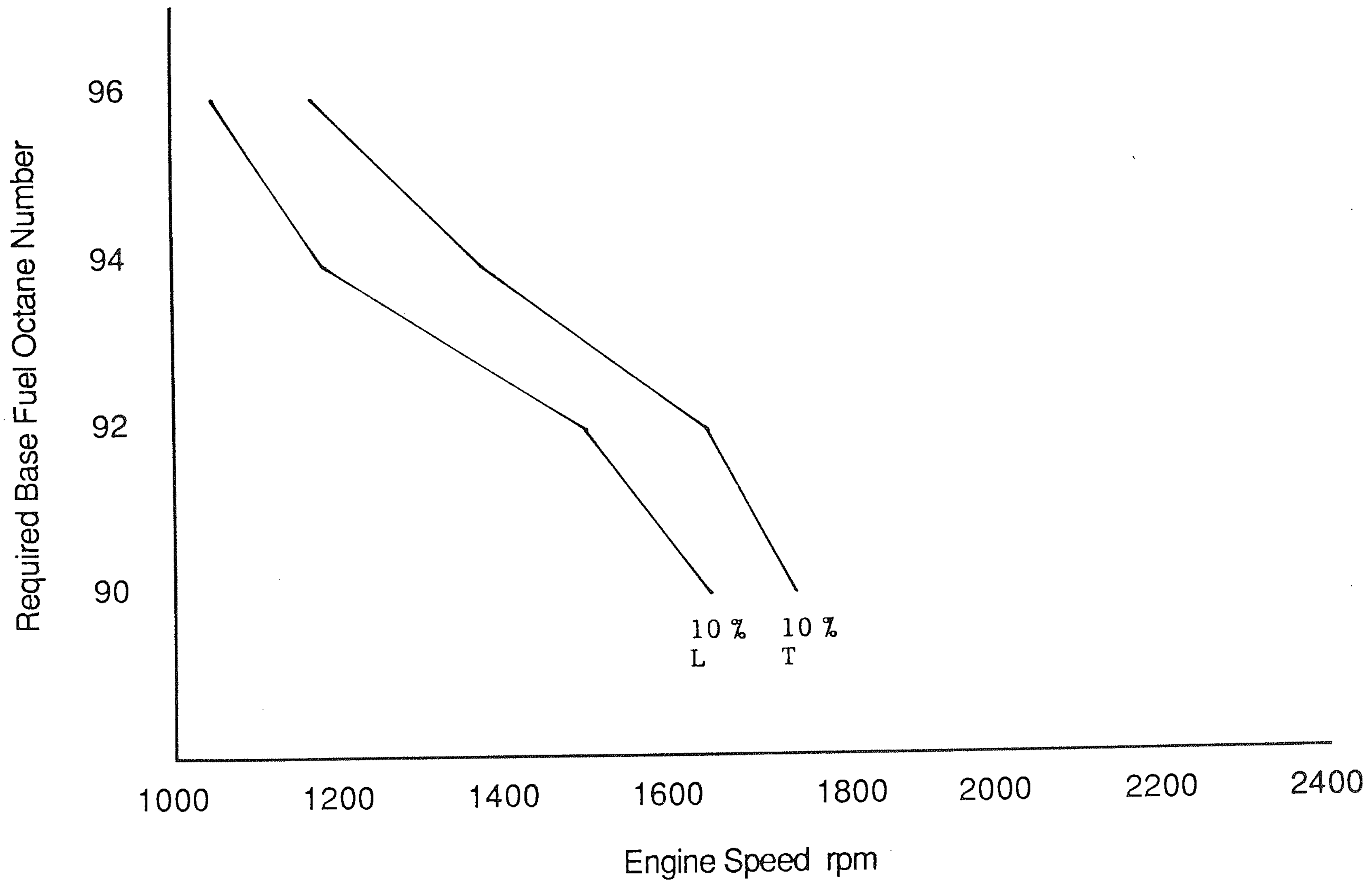

Figure 60 Oxinol

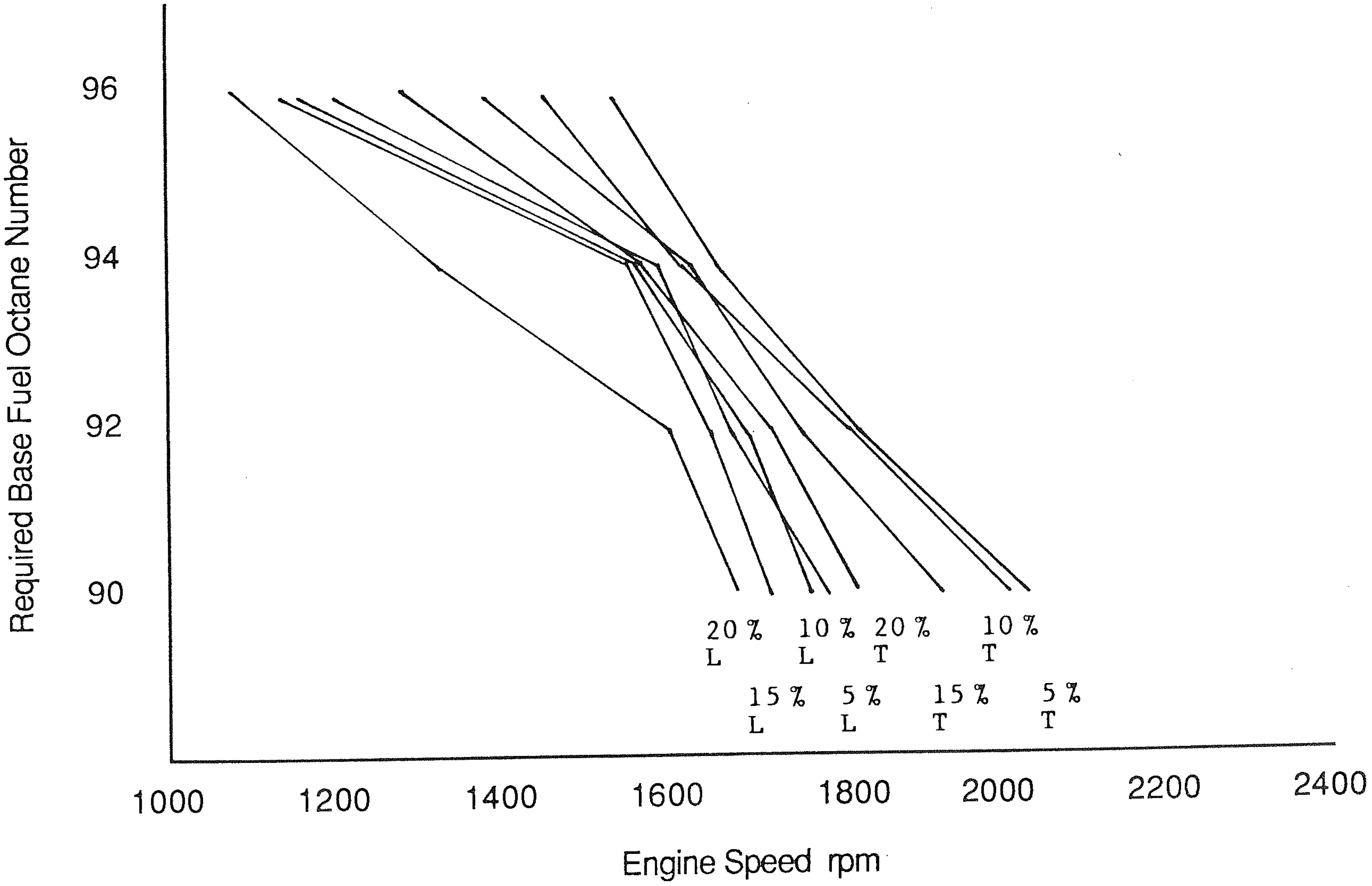

Figure 61 Tertiary Butanol

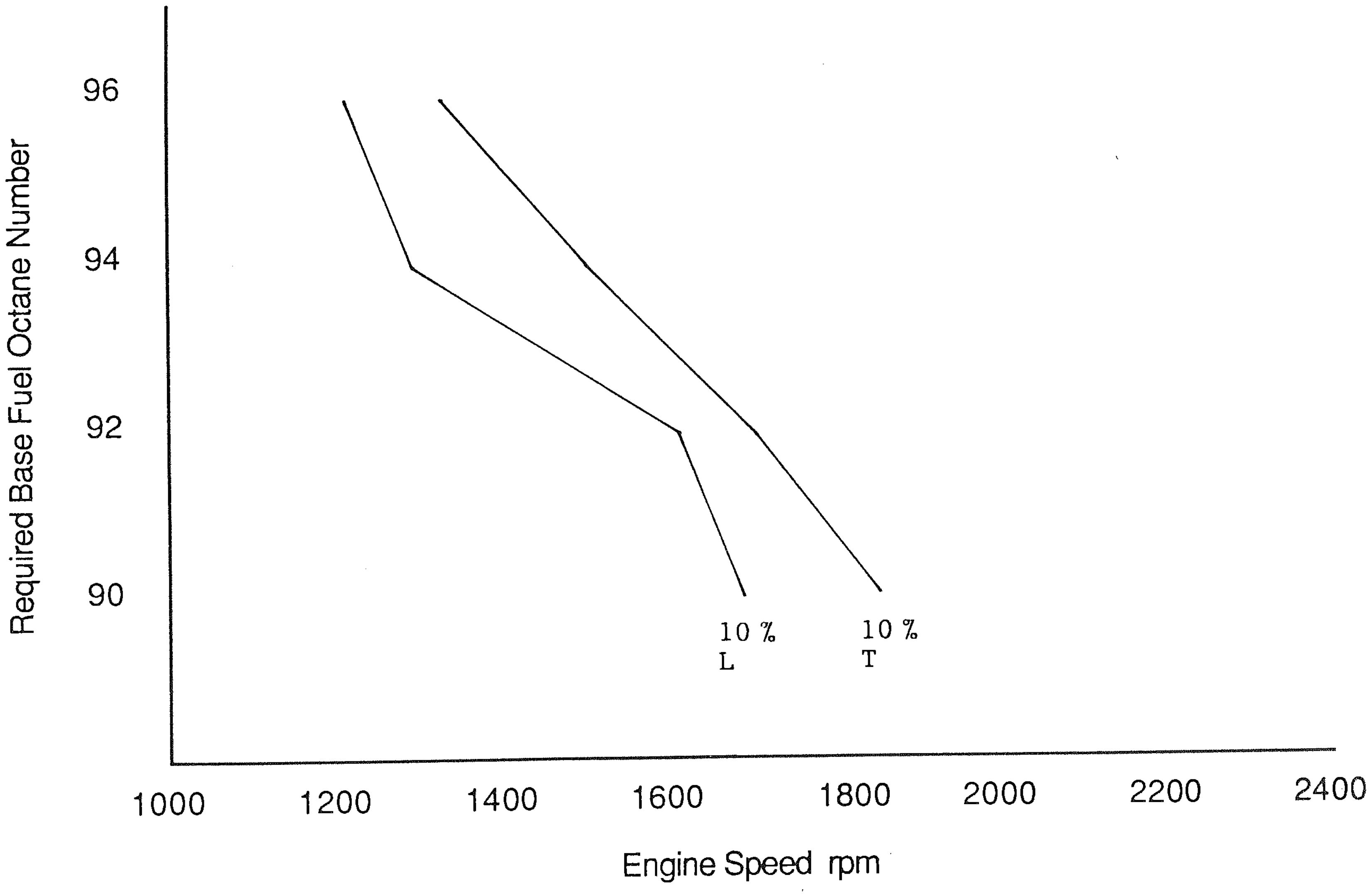

Figure 62 1 : 1 MTBE : TBA

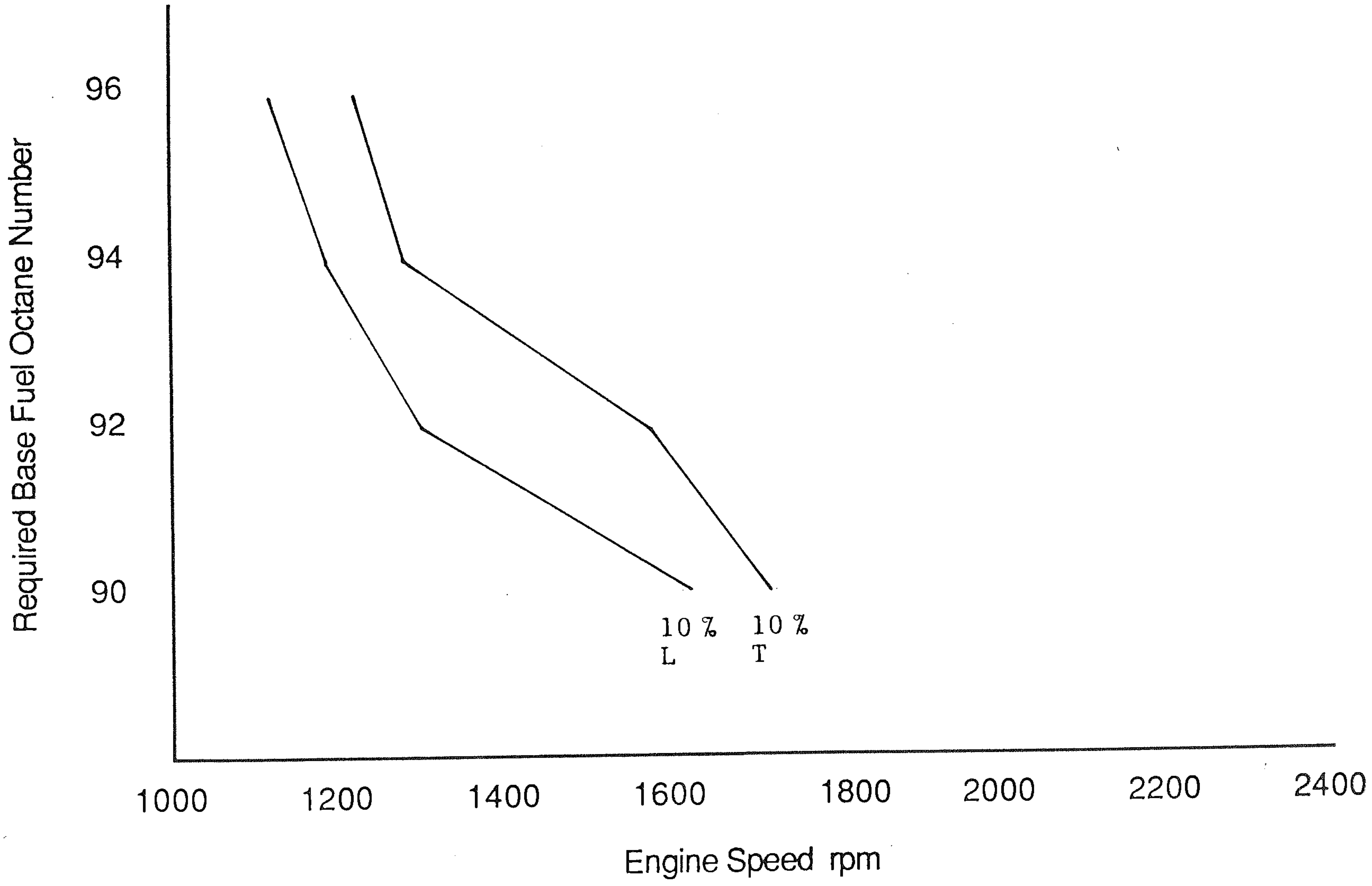

Figure 63 1 : 1 Methanol : MTBE

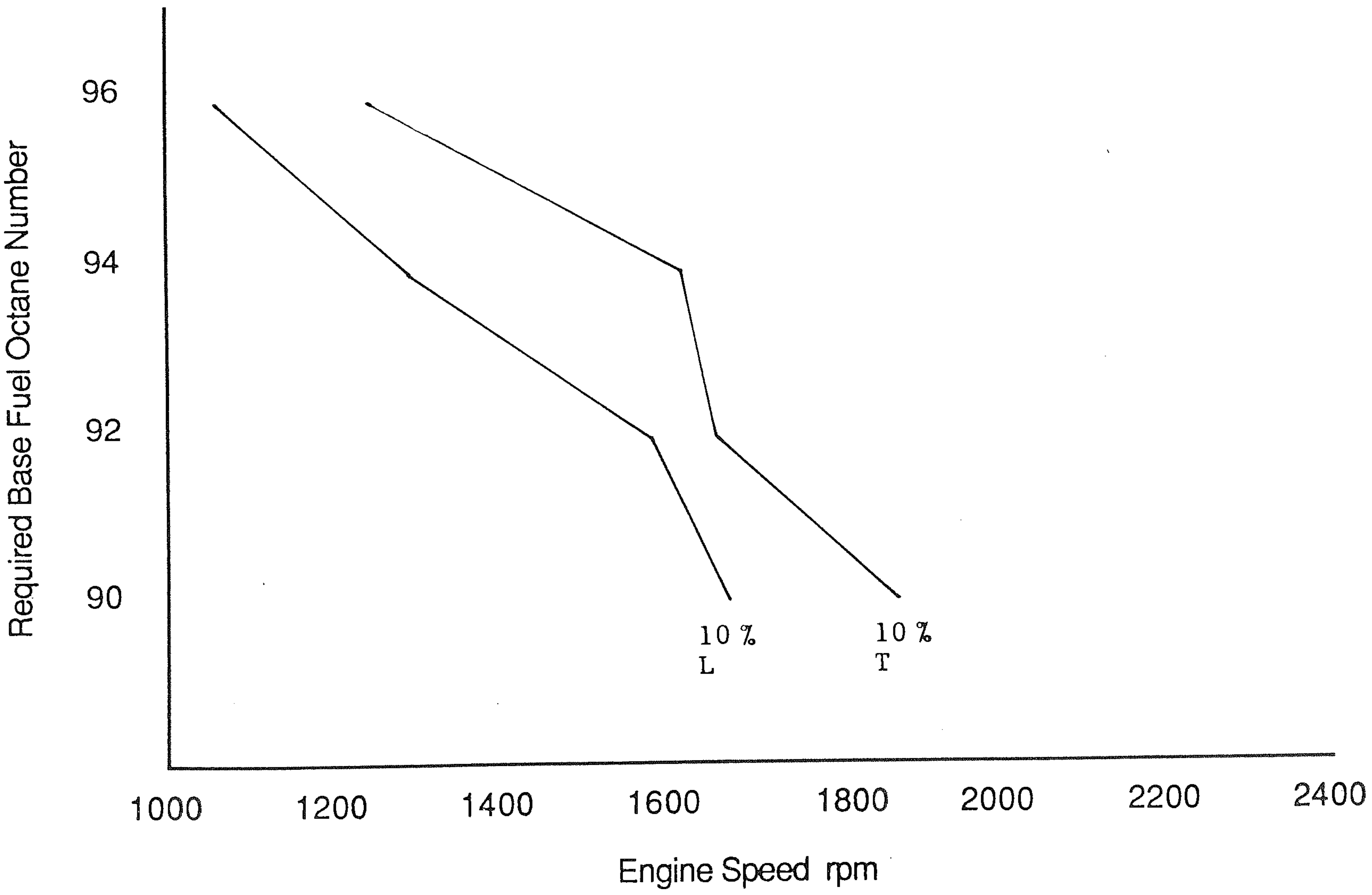

Figure 64 1 : 1 Methanol : DIPE

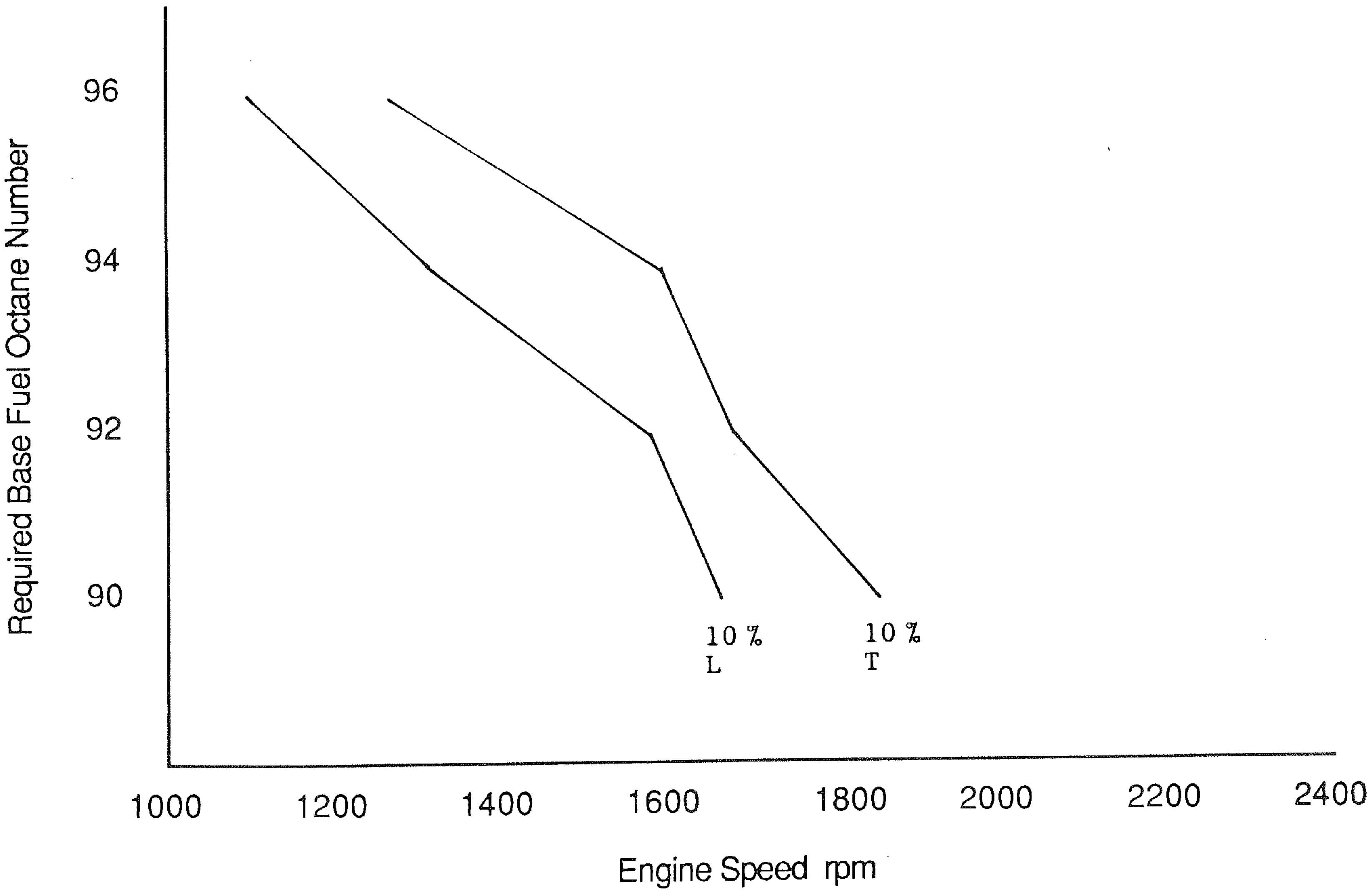

Figure 65 1 : 1 Methanol : Anisole

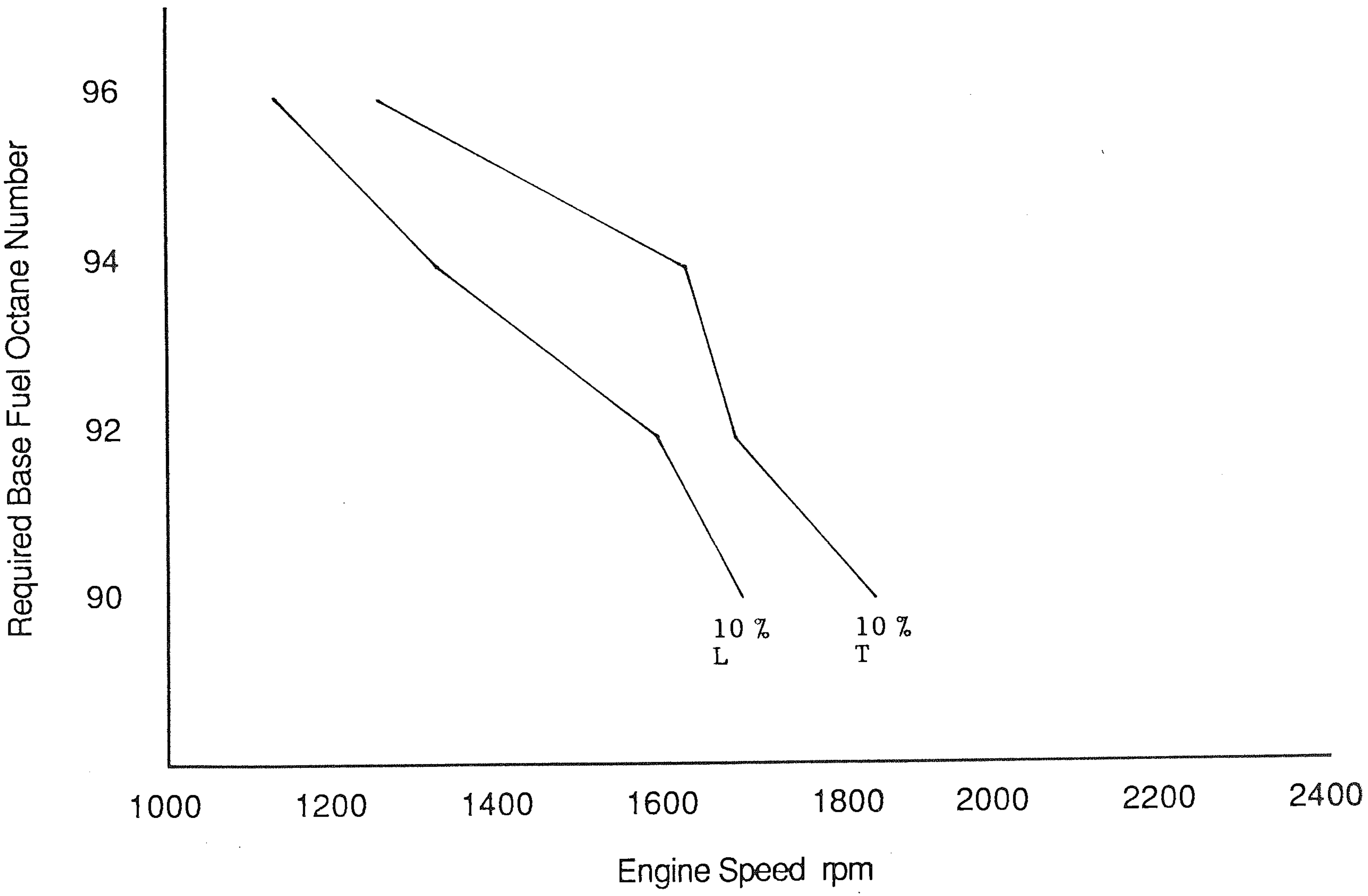

Figure 66 1 : 1 Methanol : 4MP2

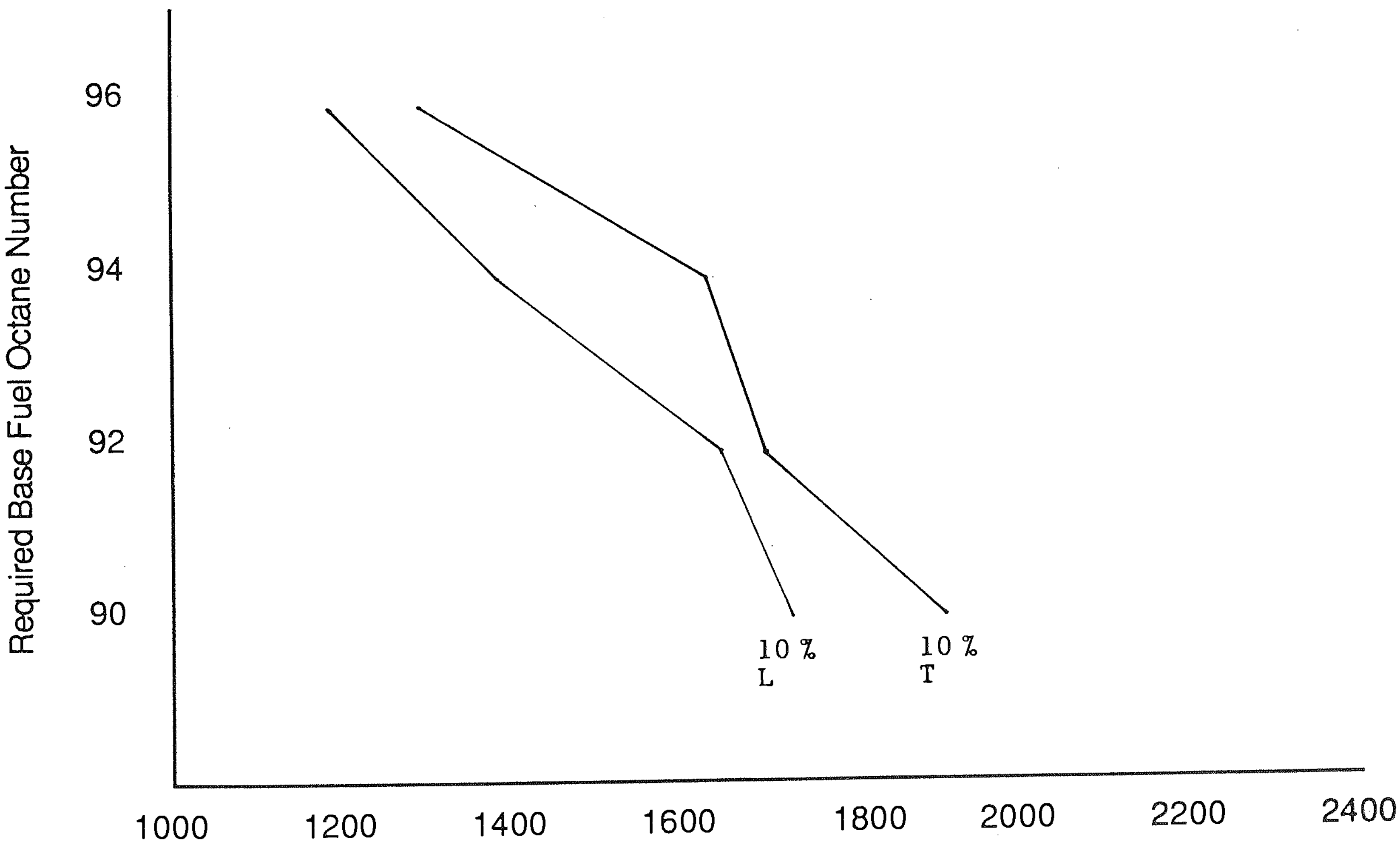

Figure 67 1 : 1 Methanol : 3MB2

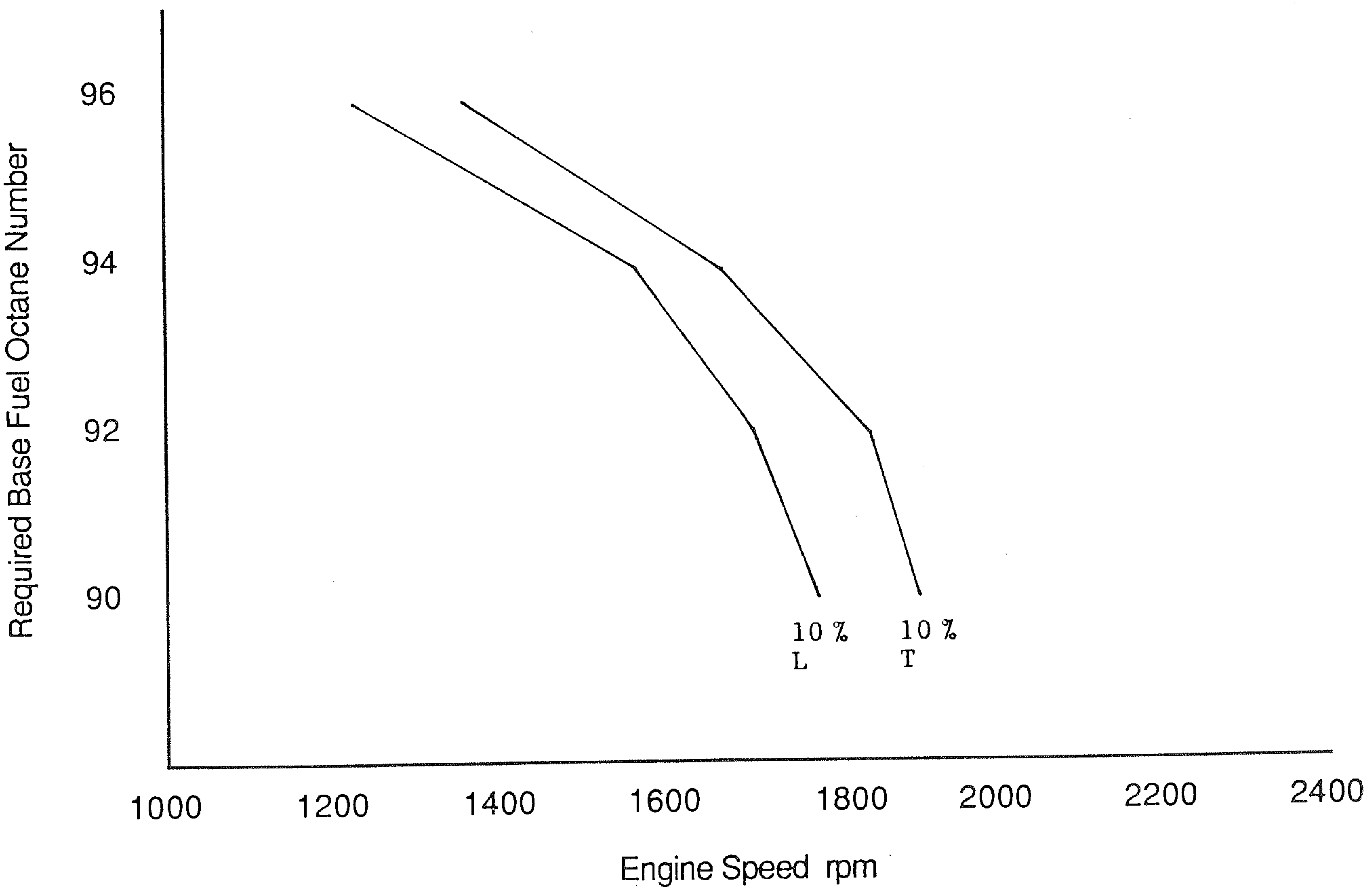

Figure 68 1 : 1 MTBE : DIPE

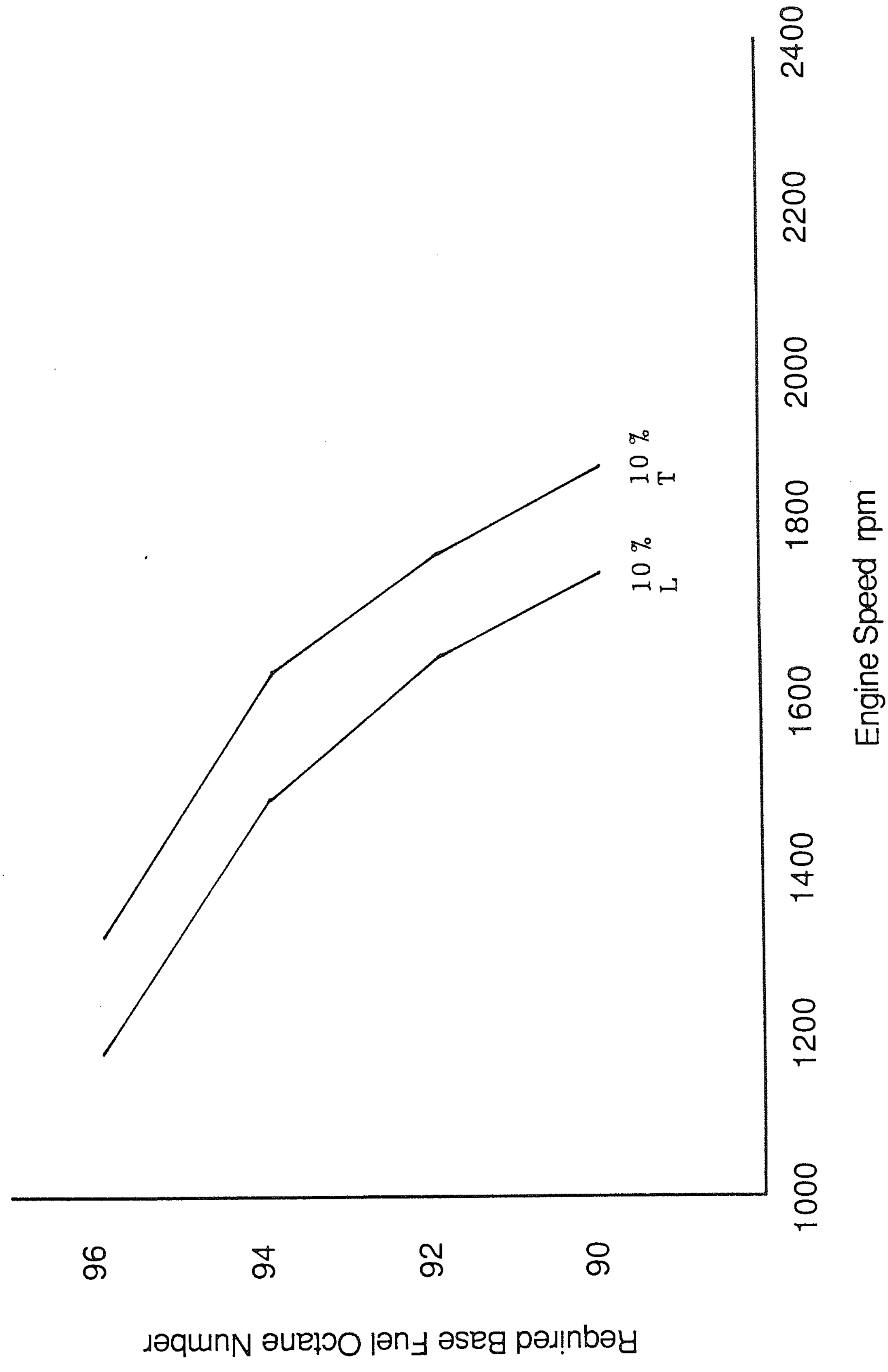

Figure 69 1 : 1 MTBE : 4MP2

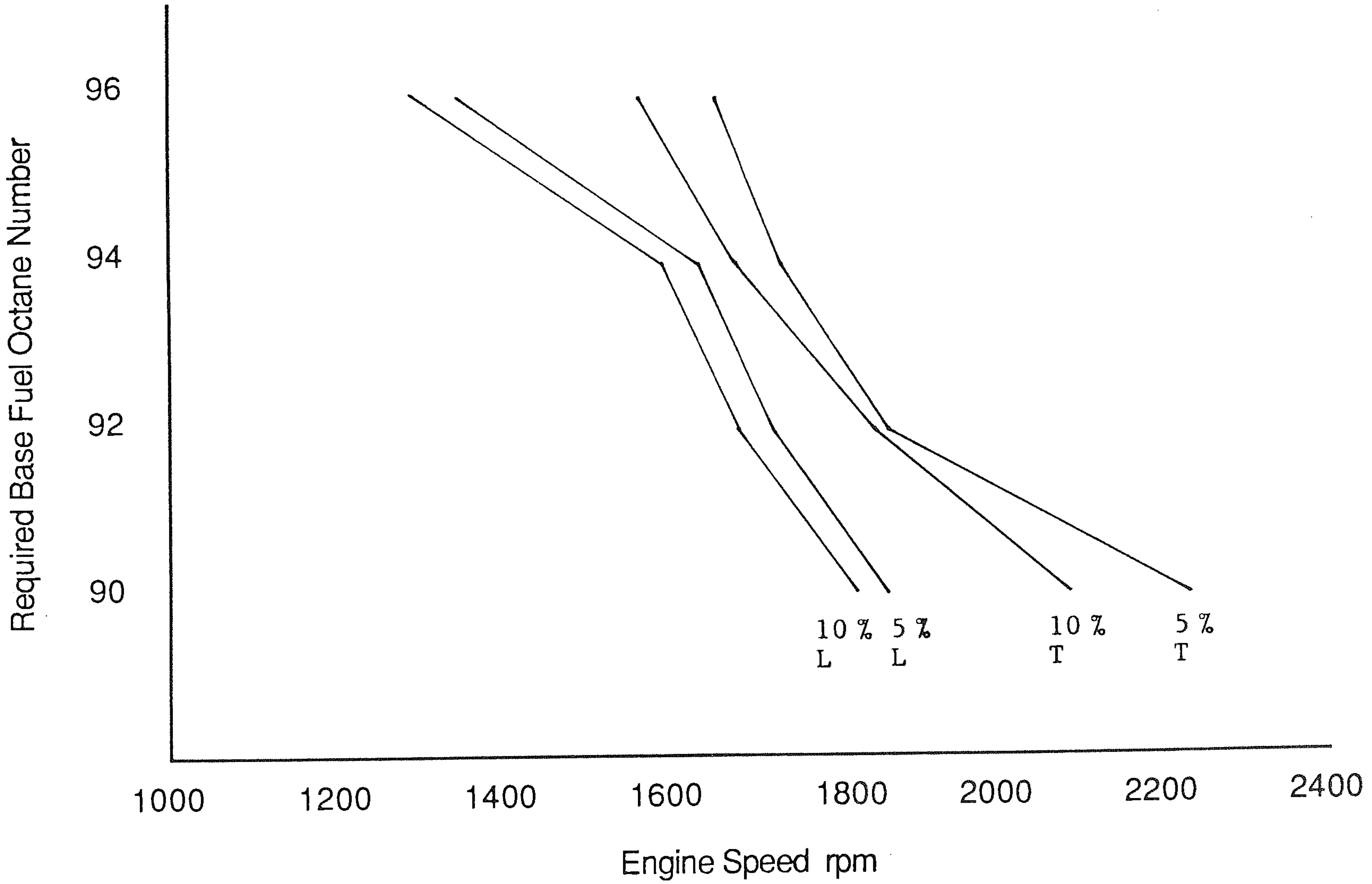

Figure 70 Methyl Acetate

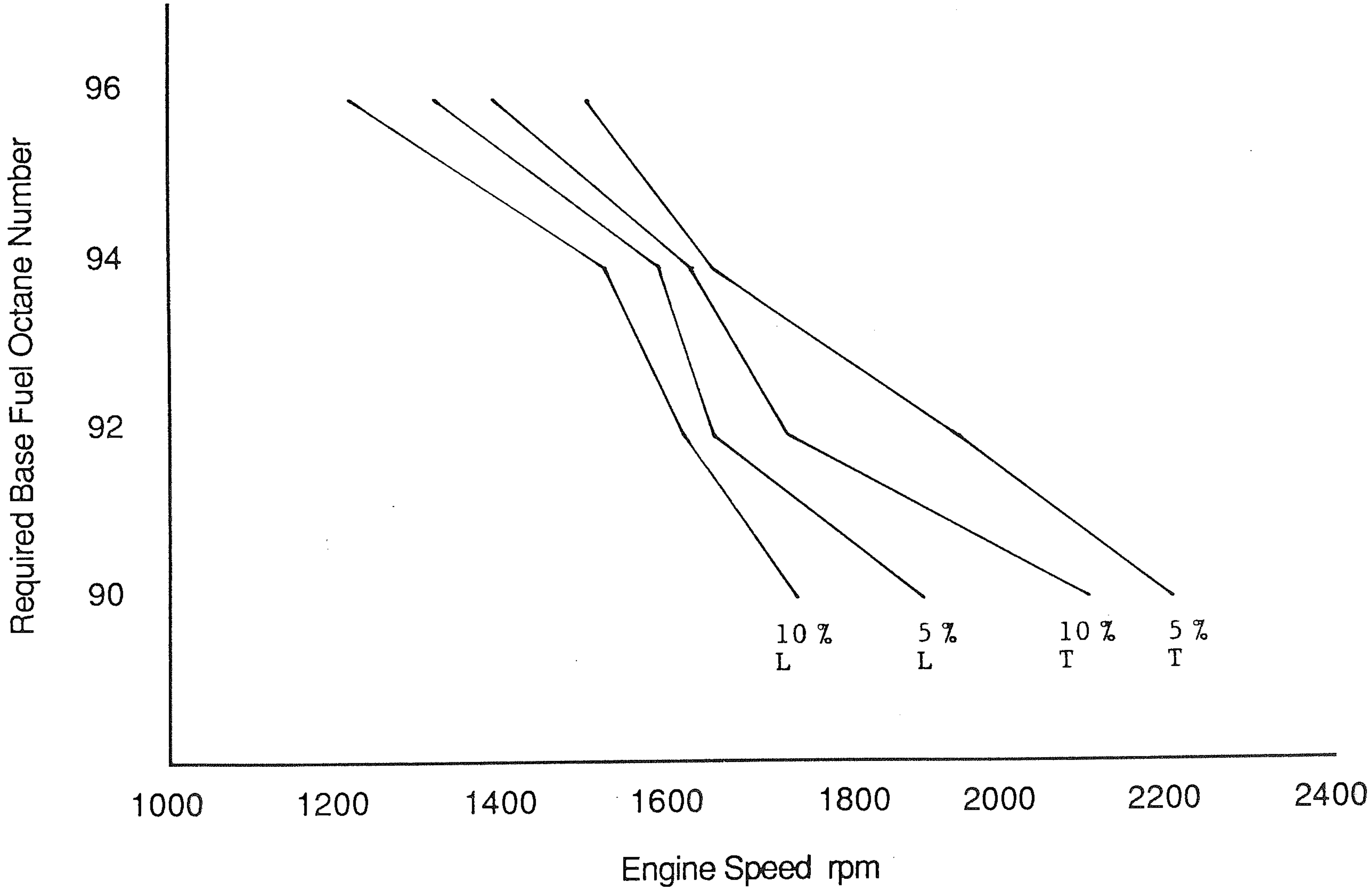

Figure 71 Di-Methyl Carbonate

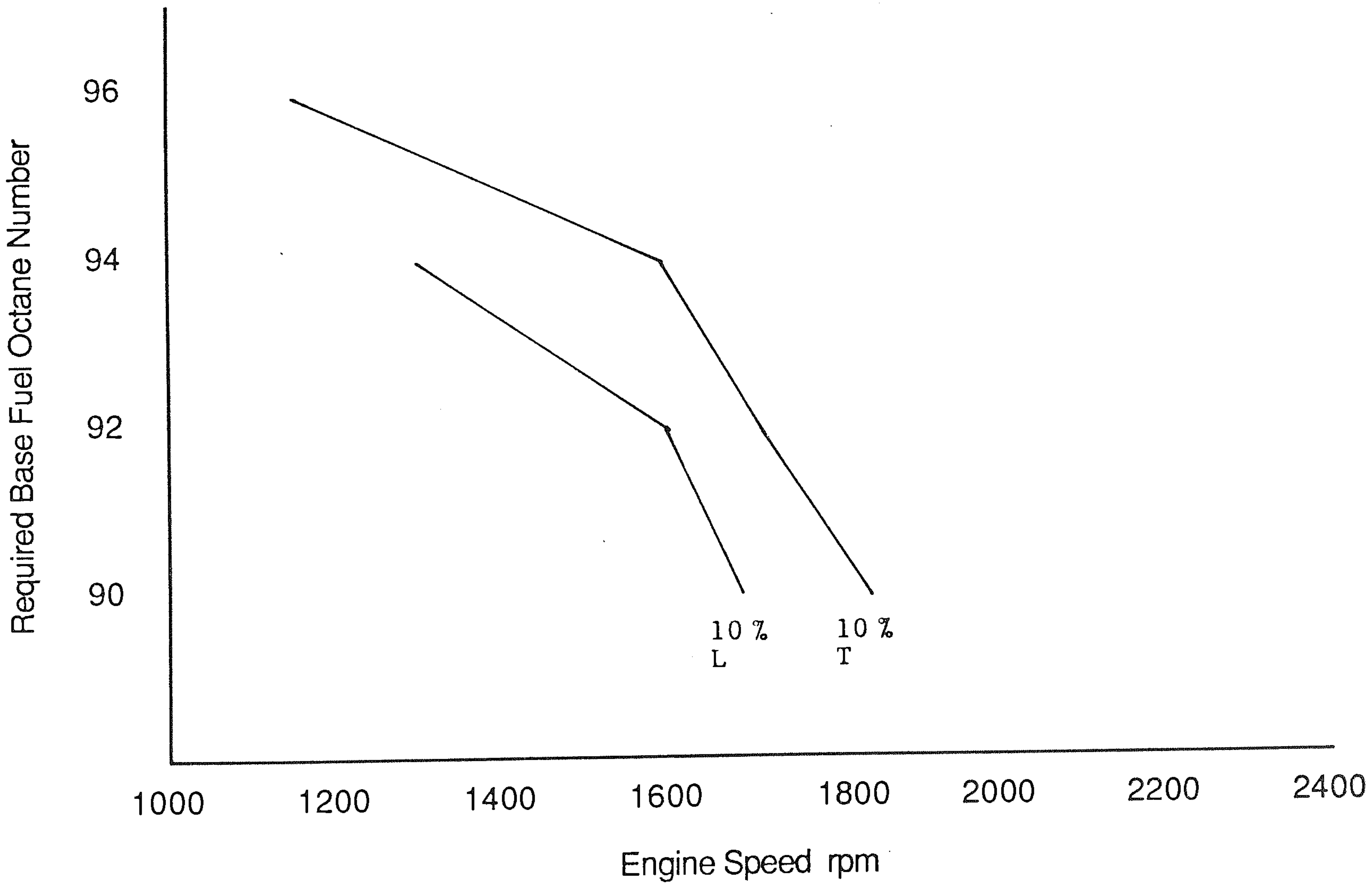

Figure 72 1 : 1 Methanol : Methyl Acetate

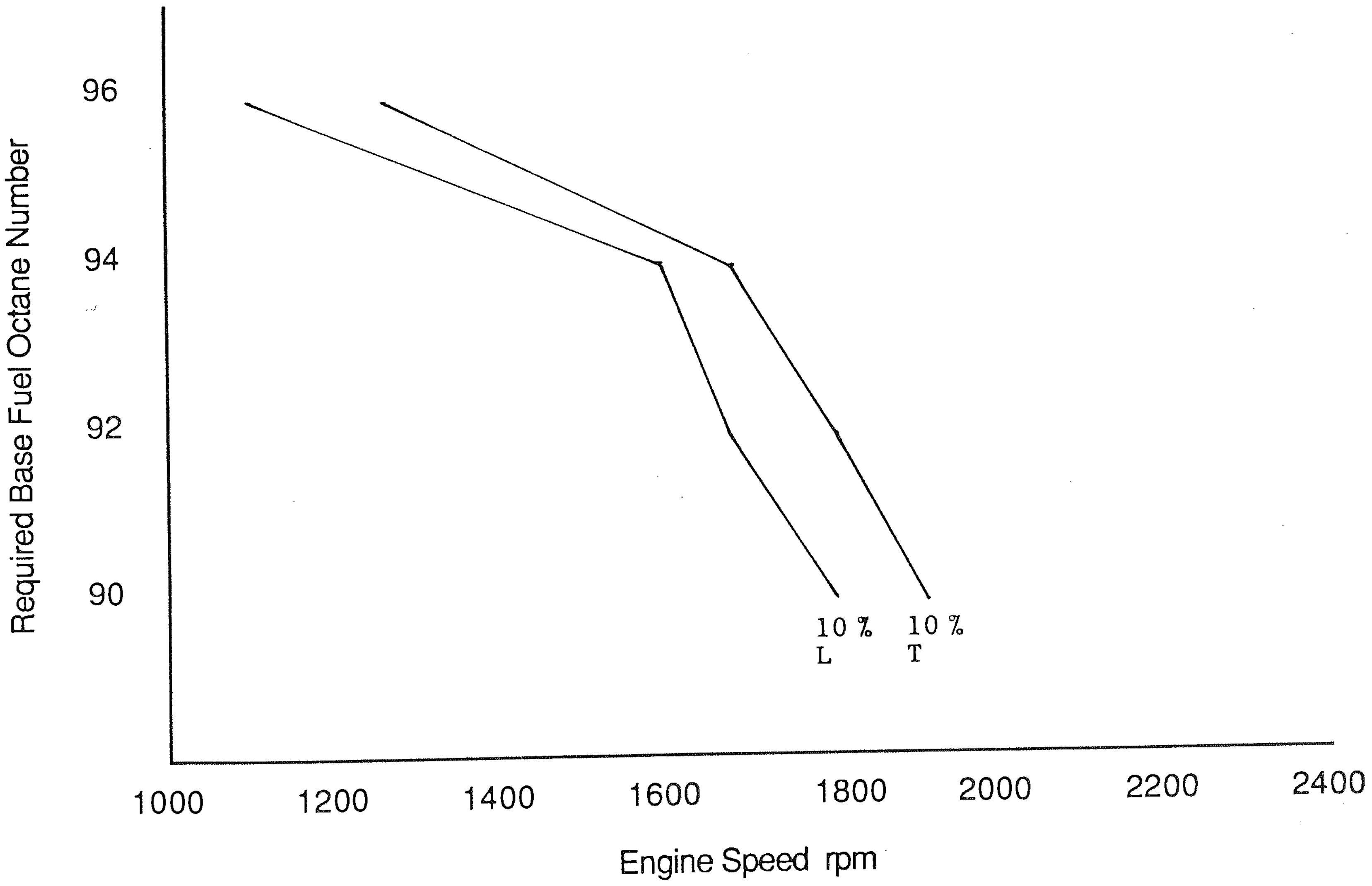

Figure 73 1 : 1 Methyl Acetate : Anisole

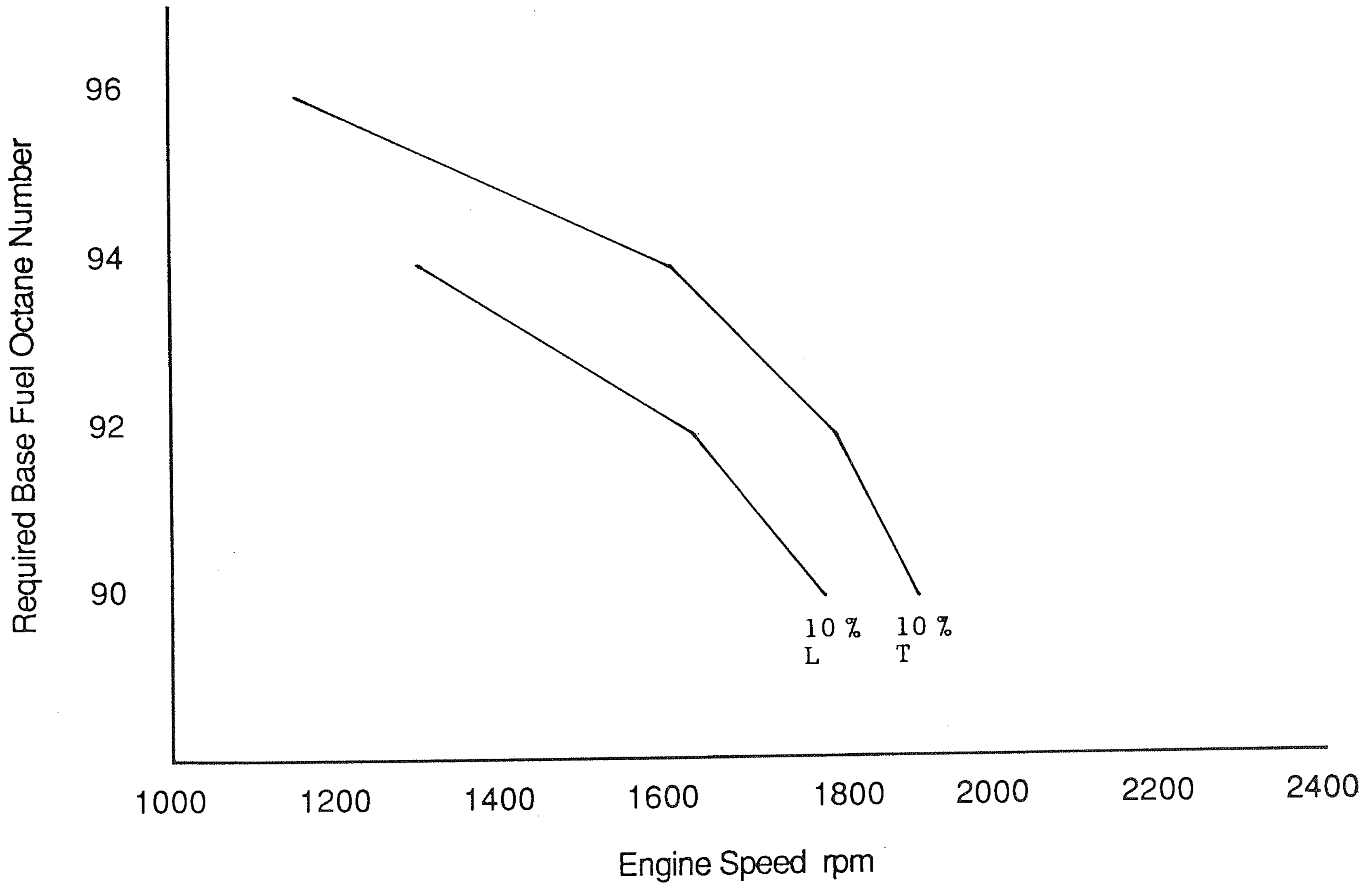

Figure 74 1 : 1 MTBE : DMC

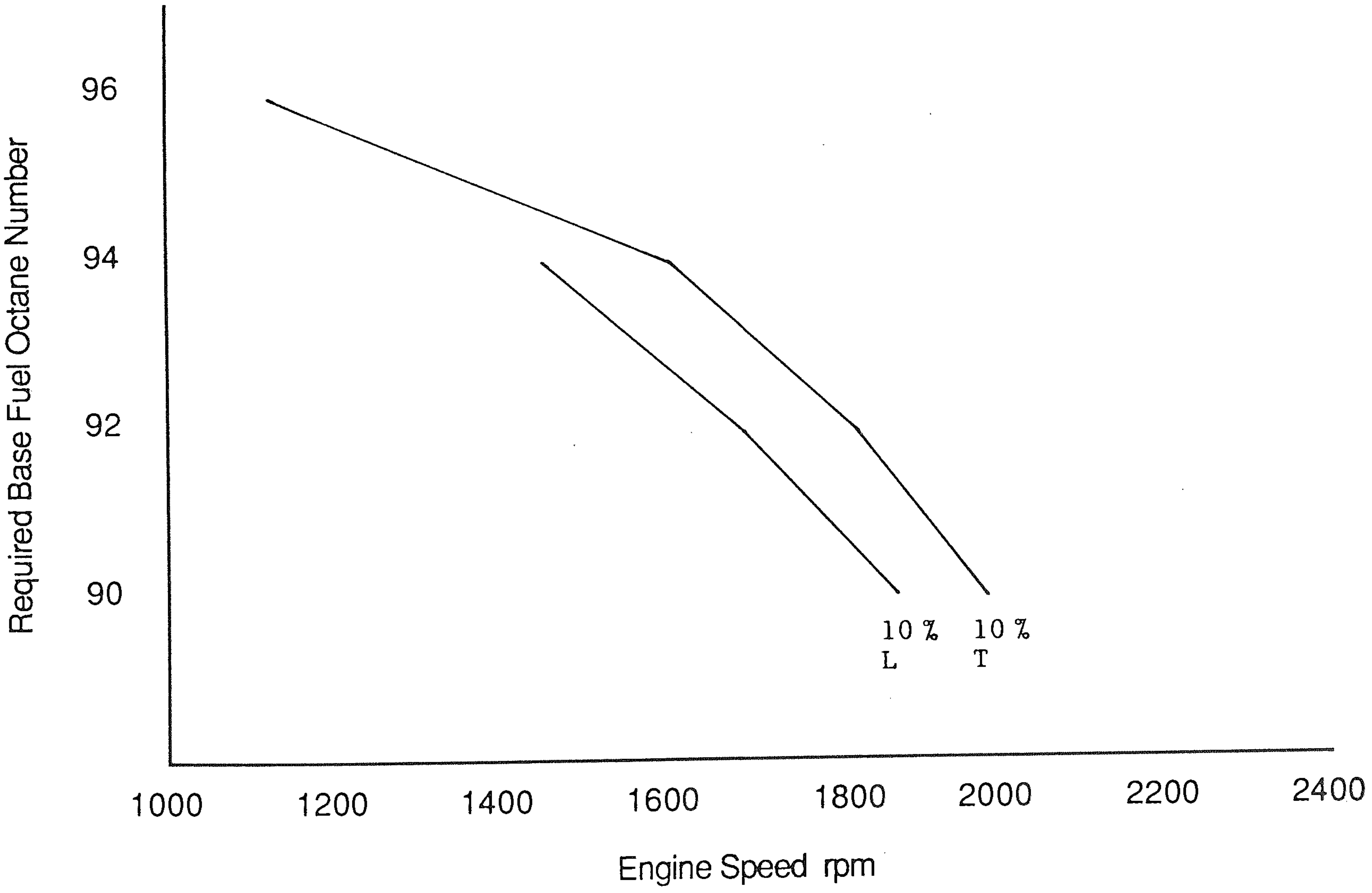

Figure 75 1 : 1 Methyl Acetate : 4MP2

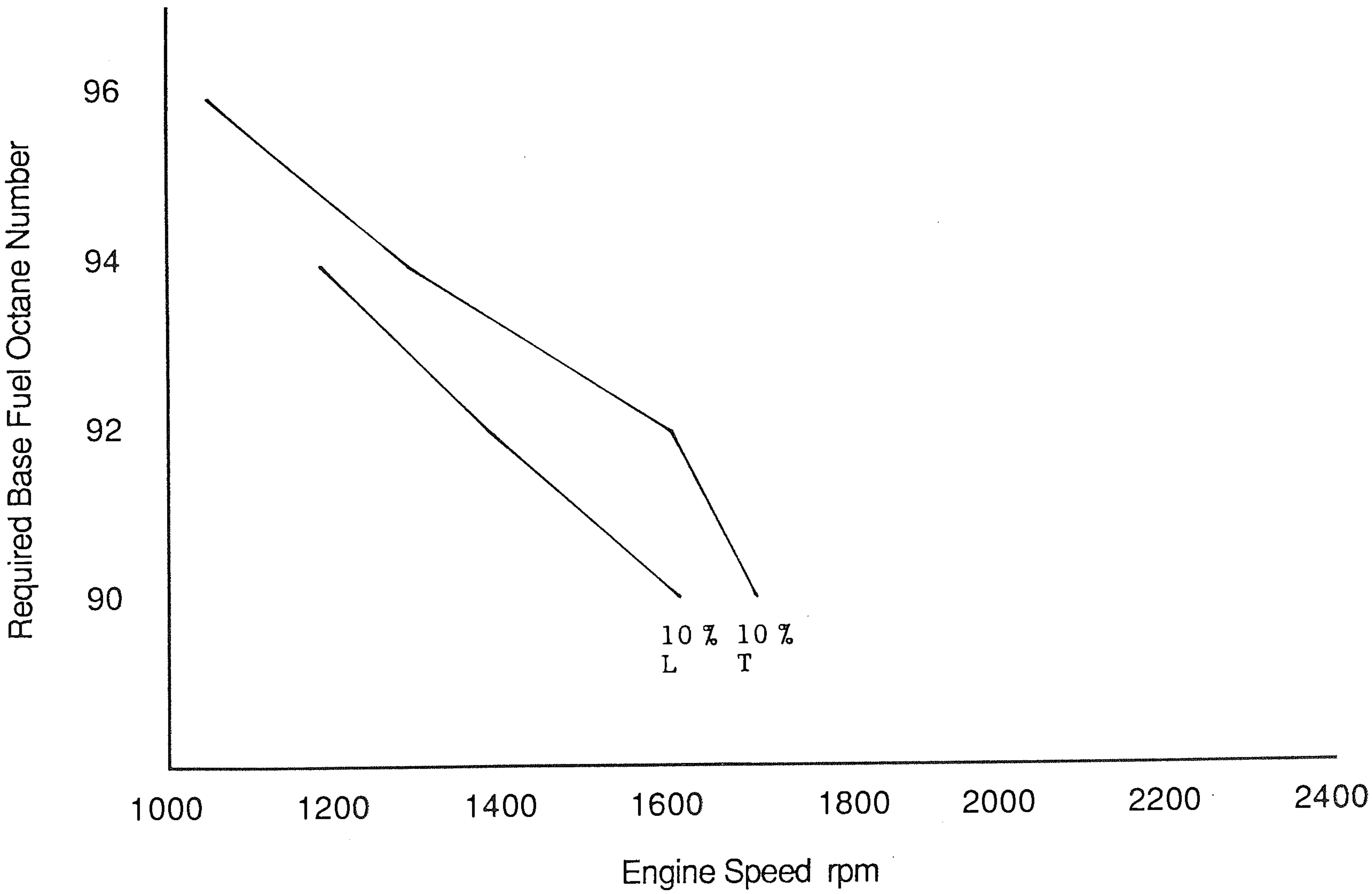

Figure 76 1 : 1 Methanol : Ethanol

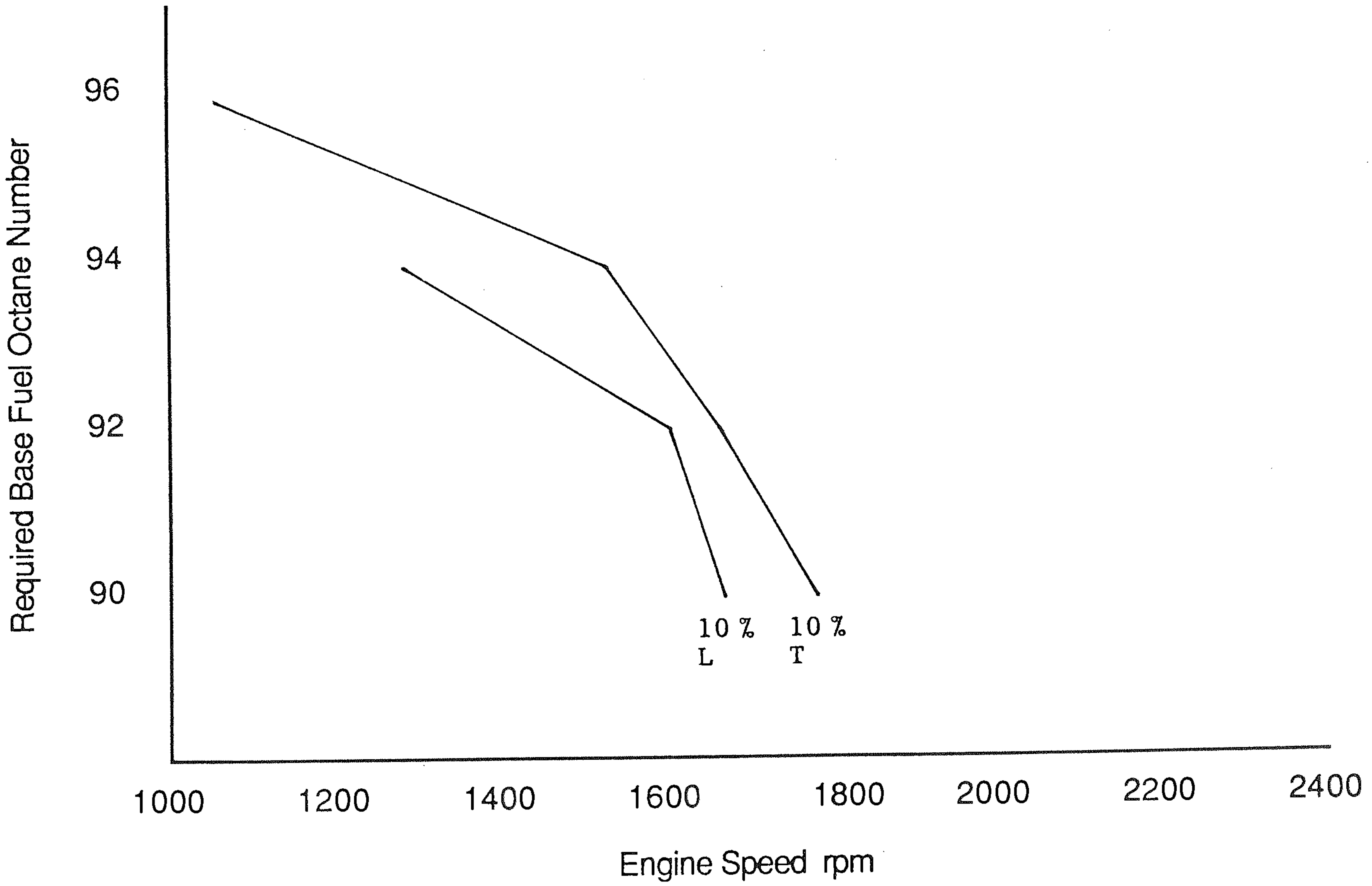

Figure 77 1 : 1 Methanol : DMC

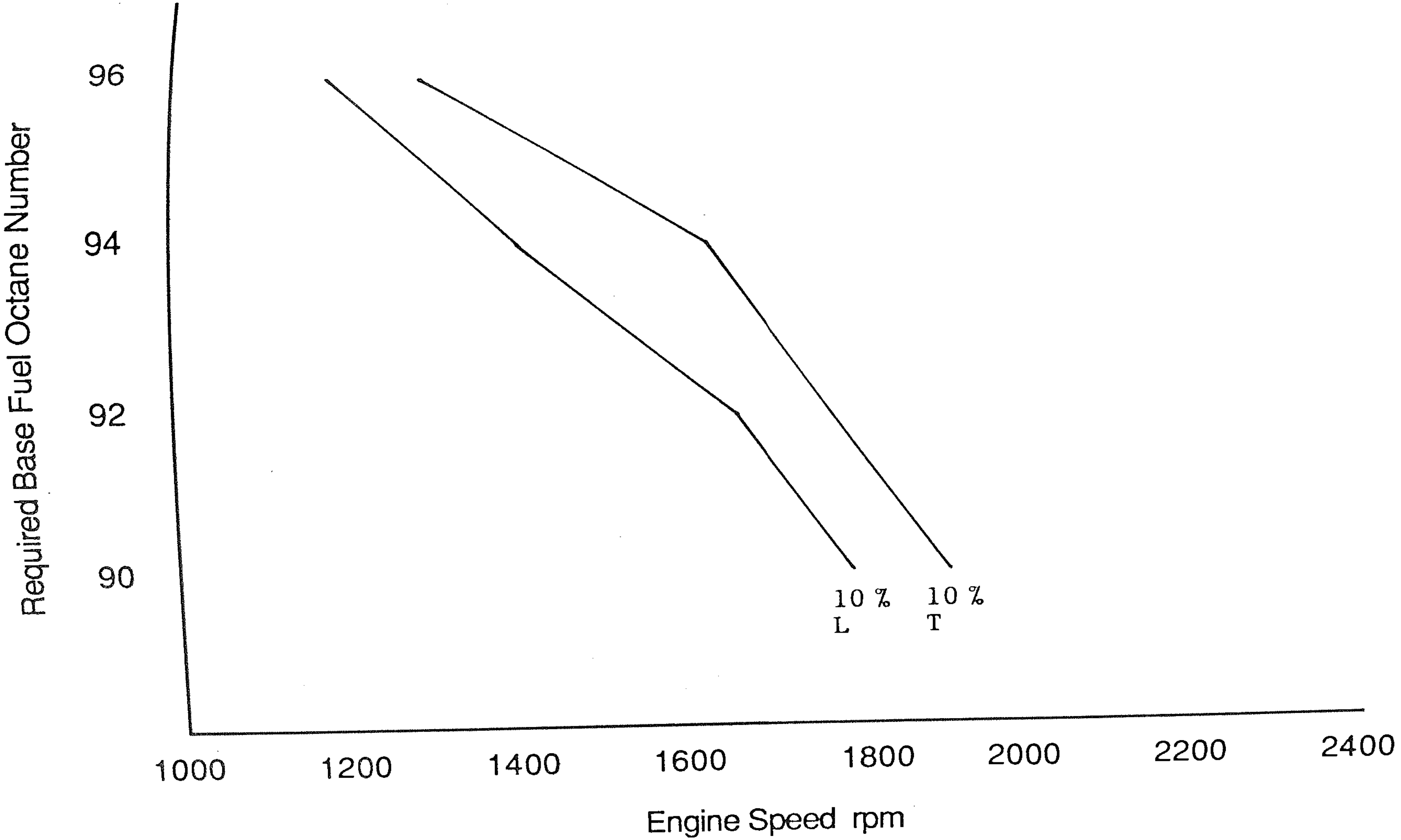

Figure 78 1 : 1 DMC : 4MP2

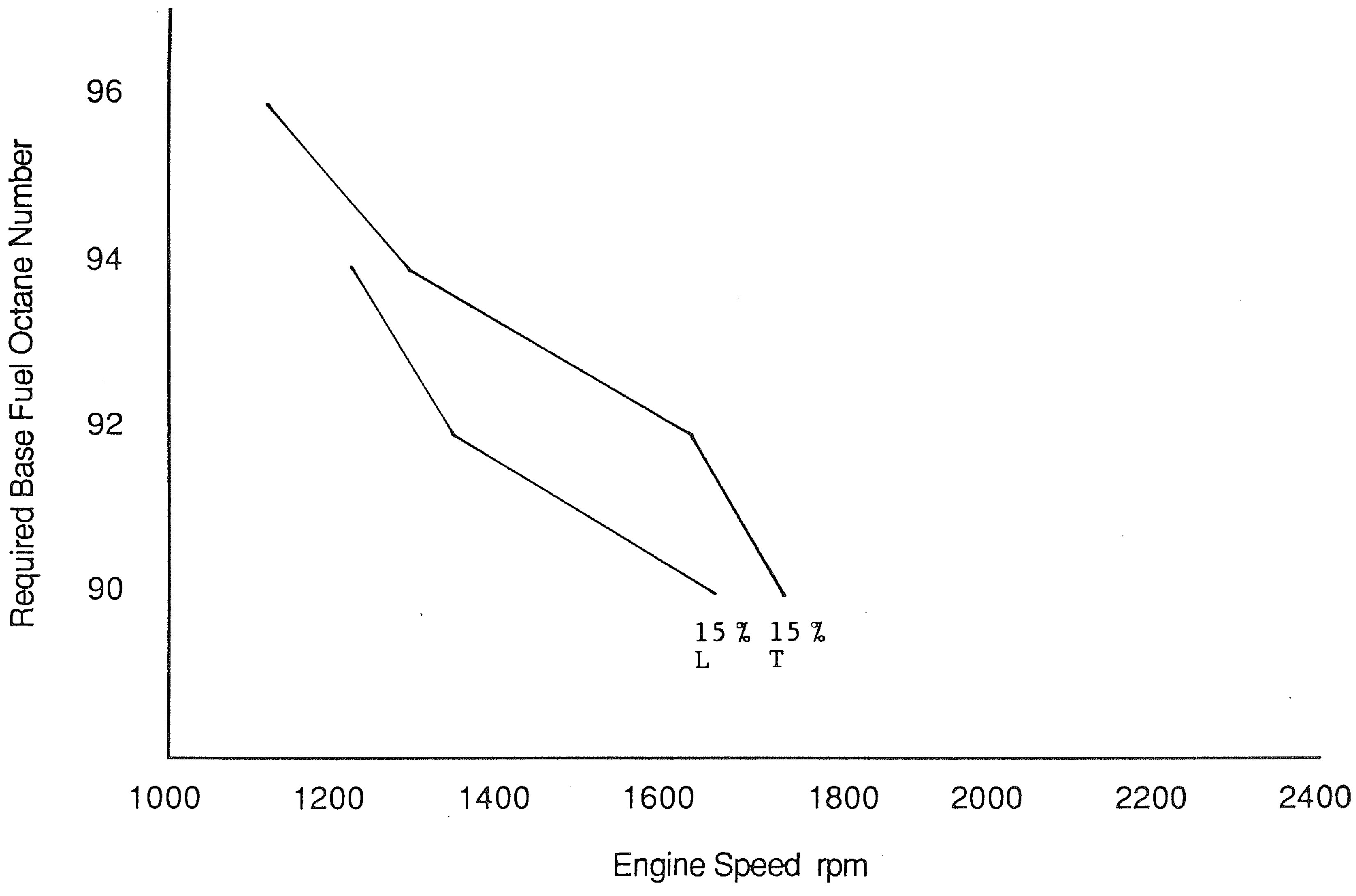

Figure 79 1 : 1 : 1 Methanol : MTBE : DMC

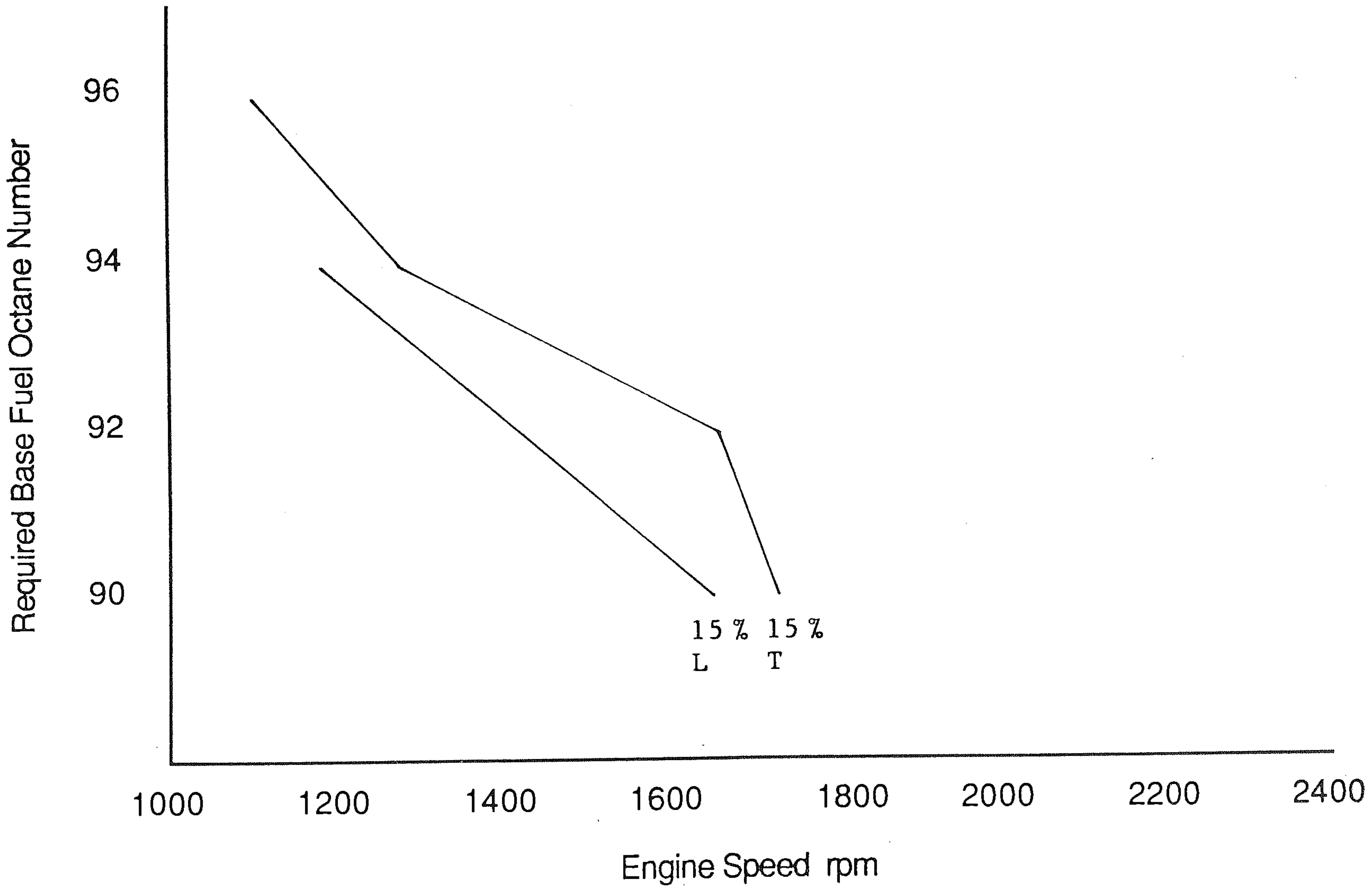

Figure 80 1 : 1 : 1 Methanol : 4MP2 : DMC

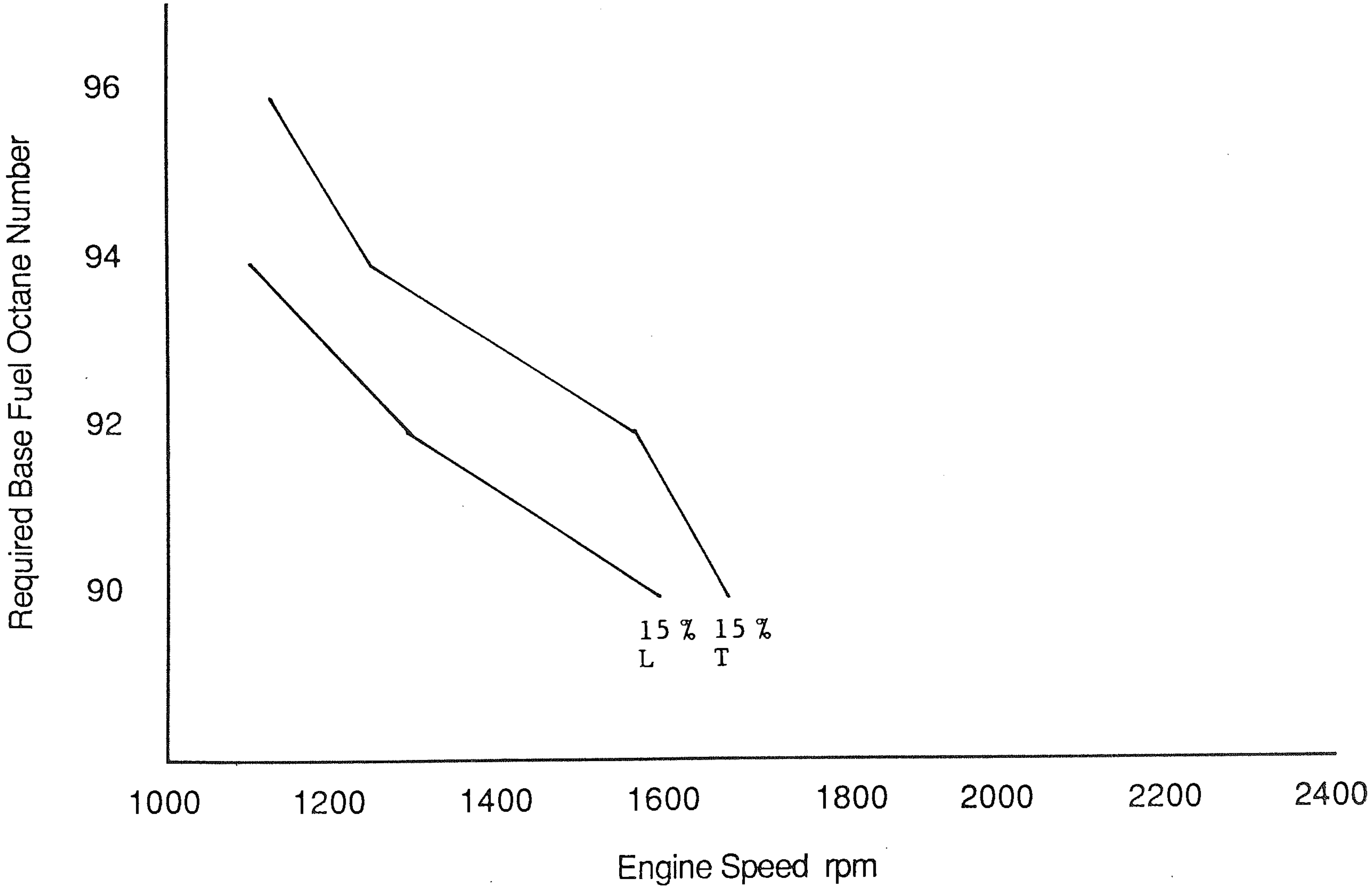

Figure 81 1 : 1 : 1 Methanol : MTBE : TBA

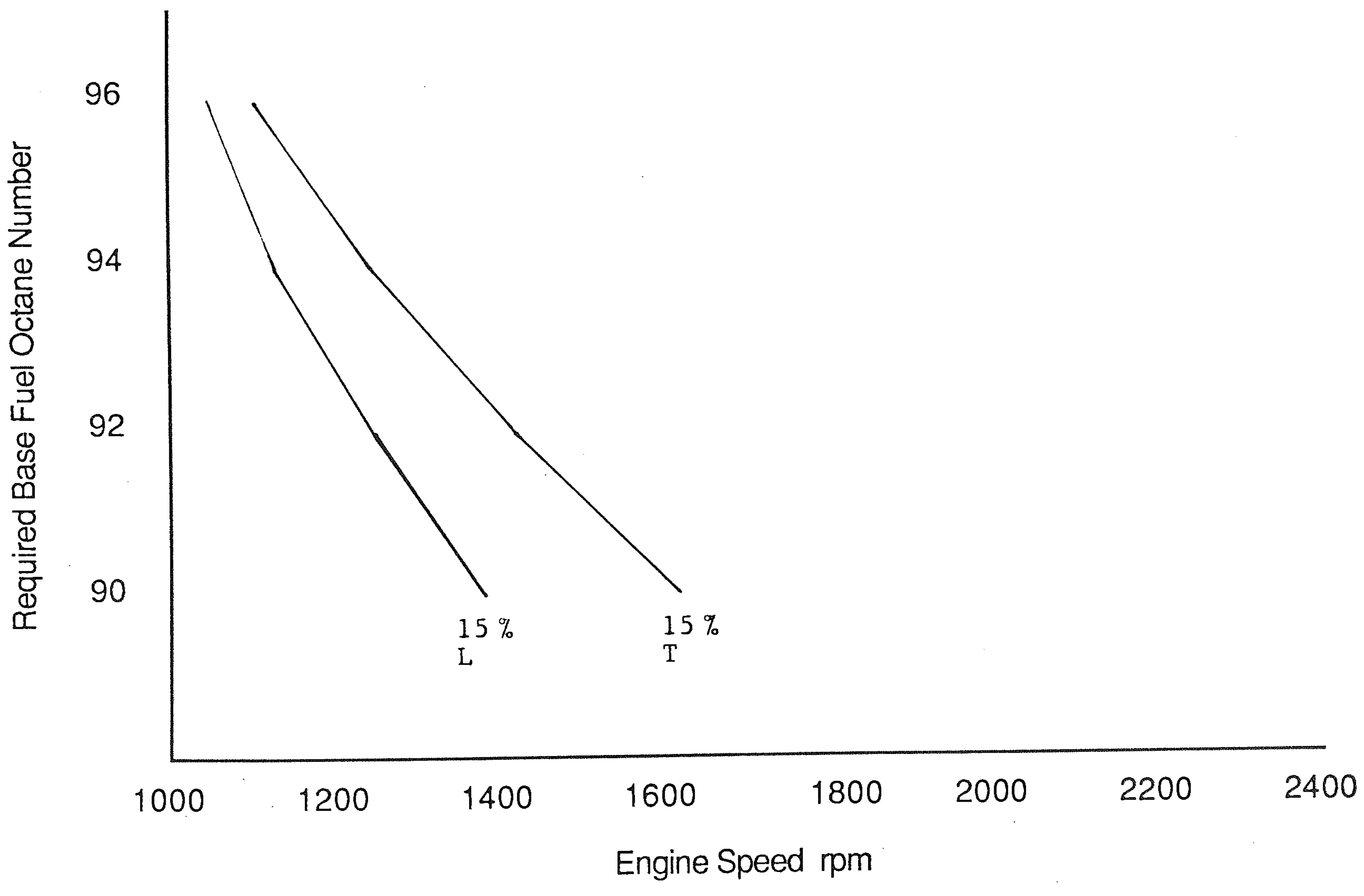

Figure 82 1 : 1 : 1 Methanol : MTBE : 3MB2

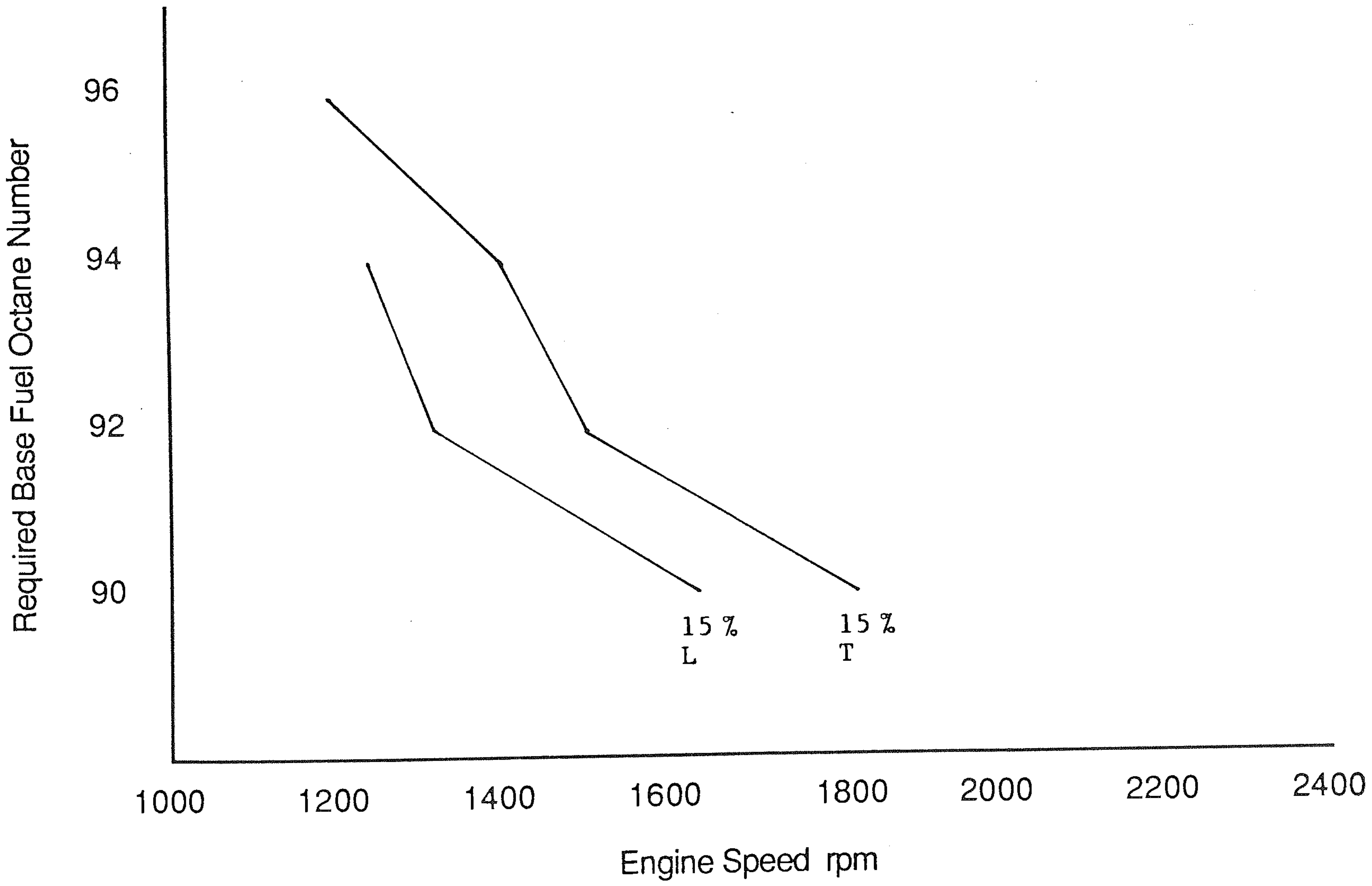

Figure 83 1 : 1 : 1 Ethanol : MTBE : 4MP2

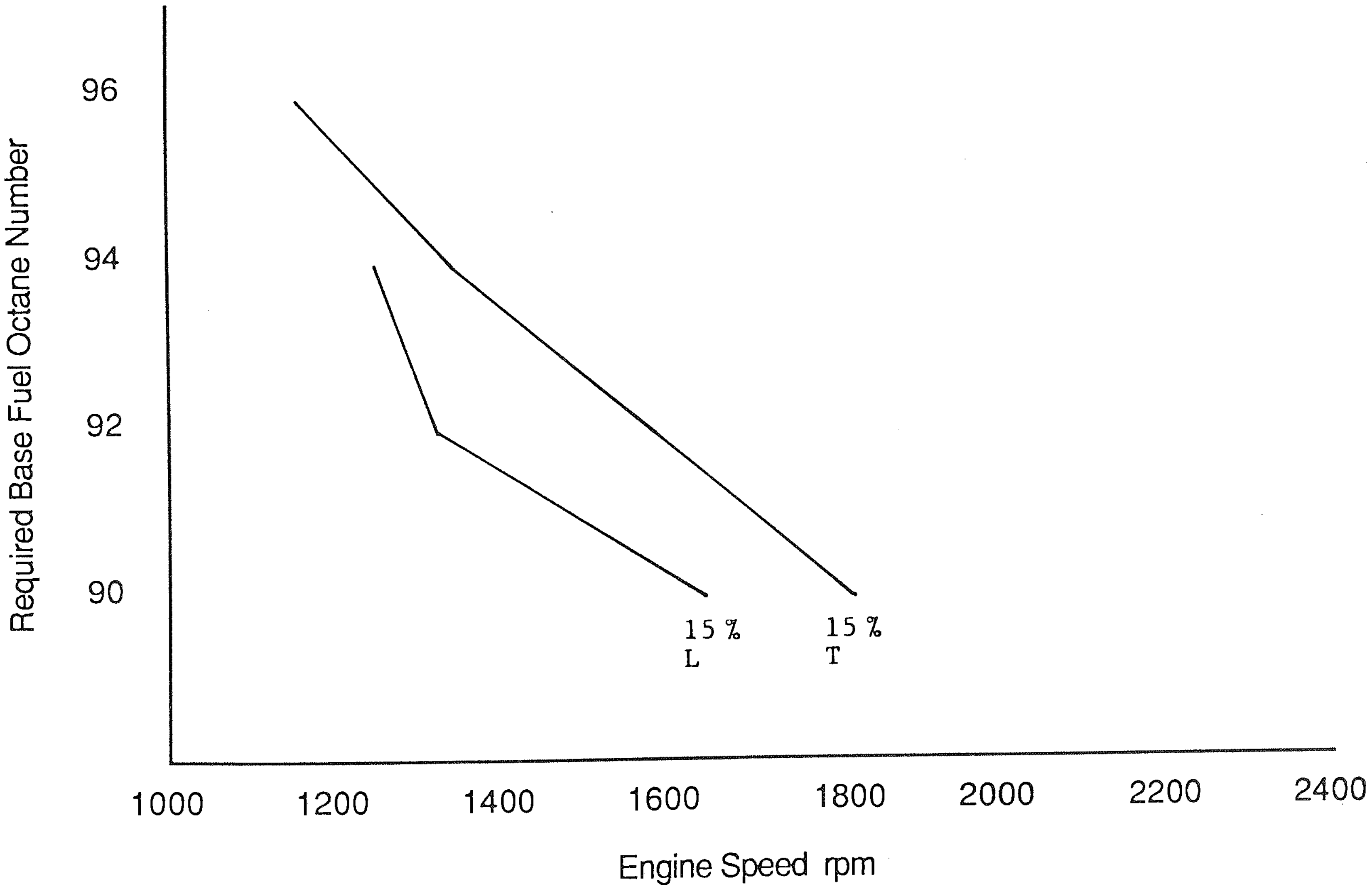

Figure 85 1 : 1 : 1 Methanol : DIPE : 4MP2

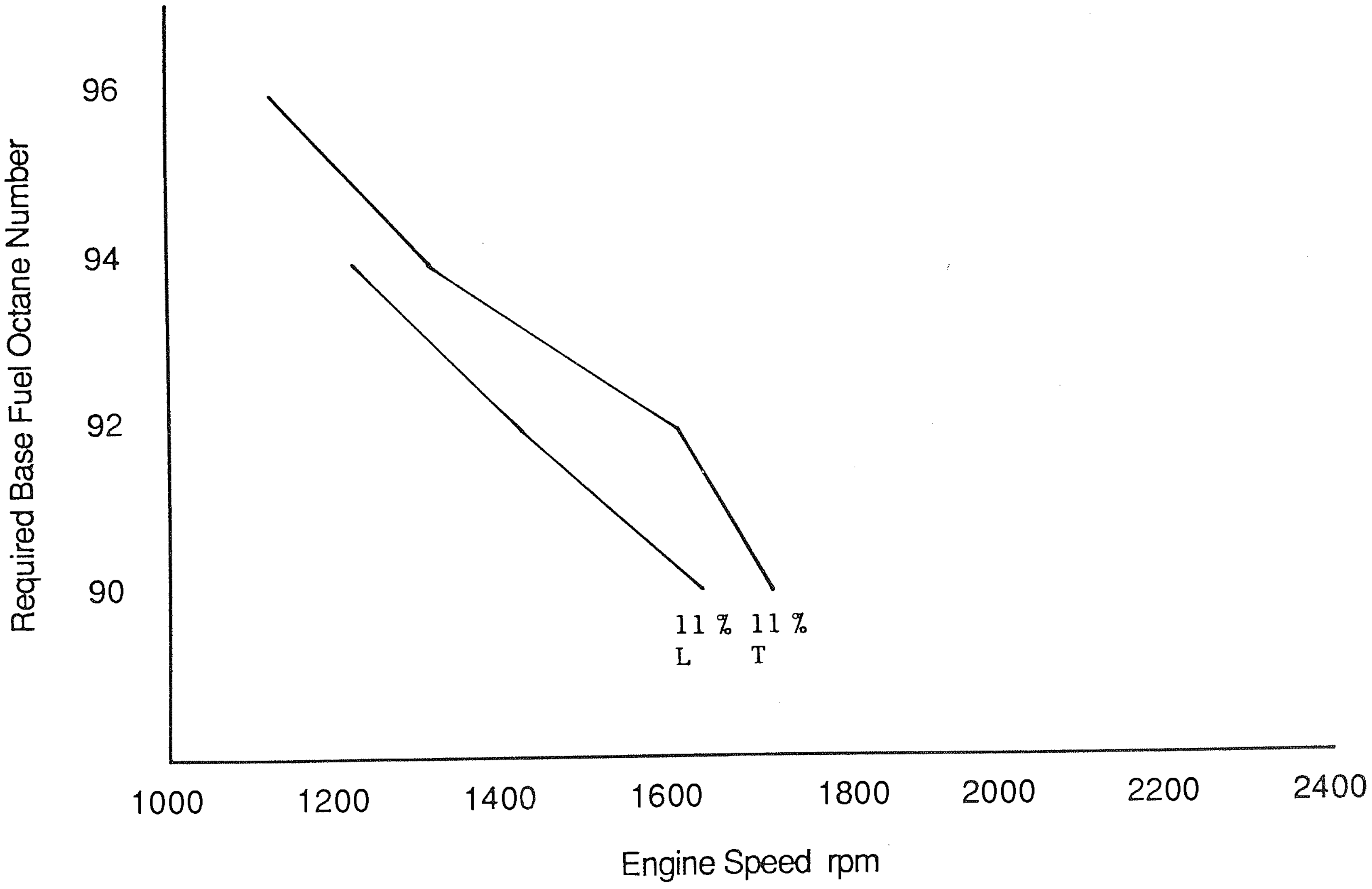

Figure 86 5 : 3 : 3 Methanol : MTBE : 4MP2

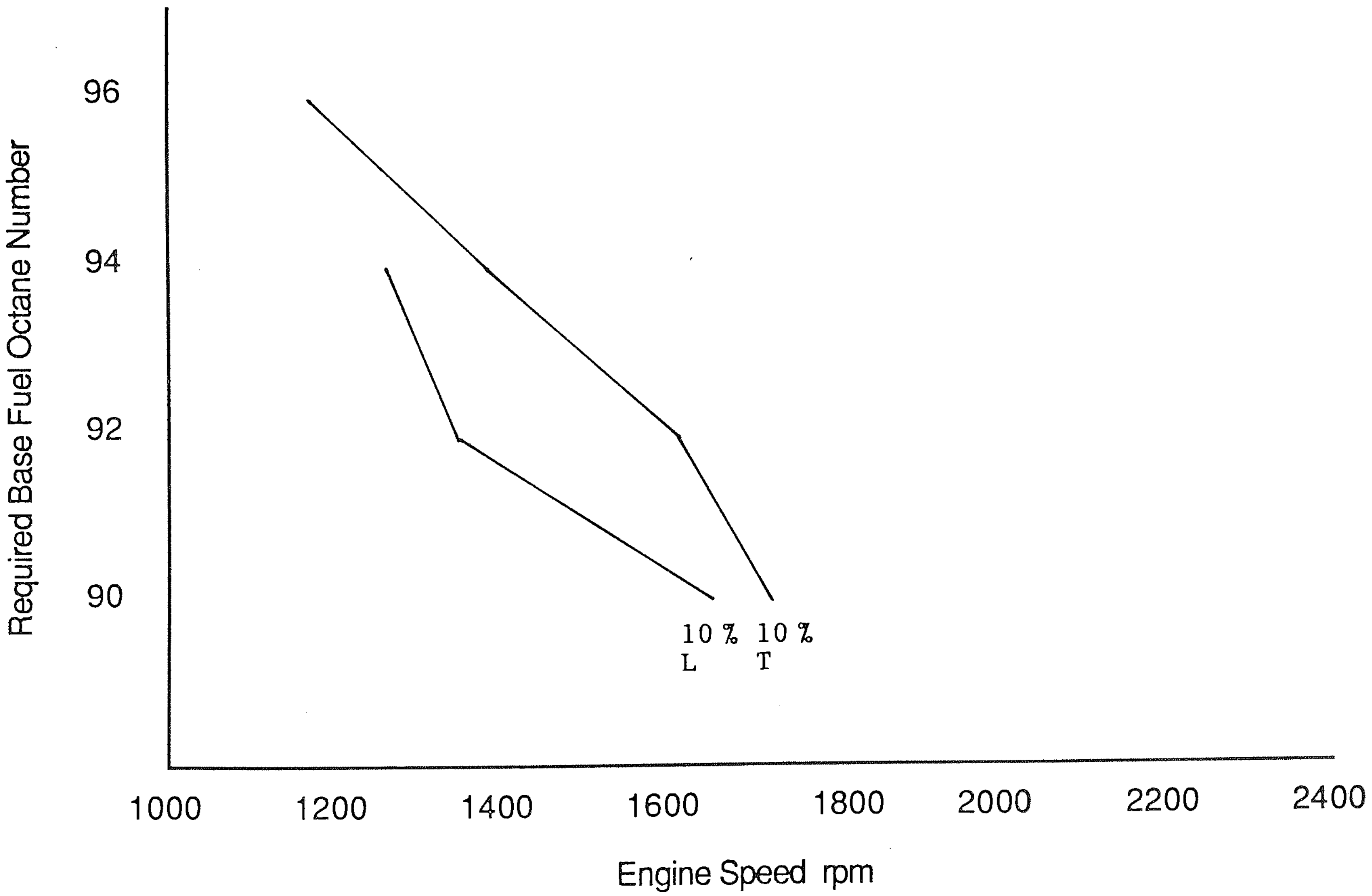

Figure 87 6 : 3 : 1 Methanol : MTBE : 4MP2

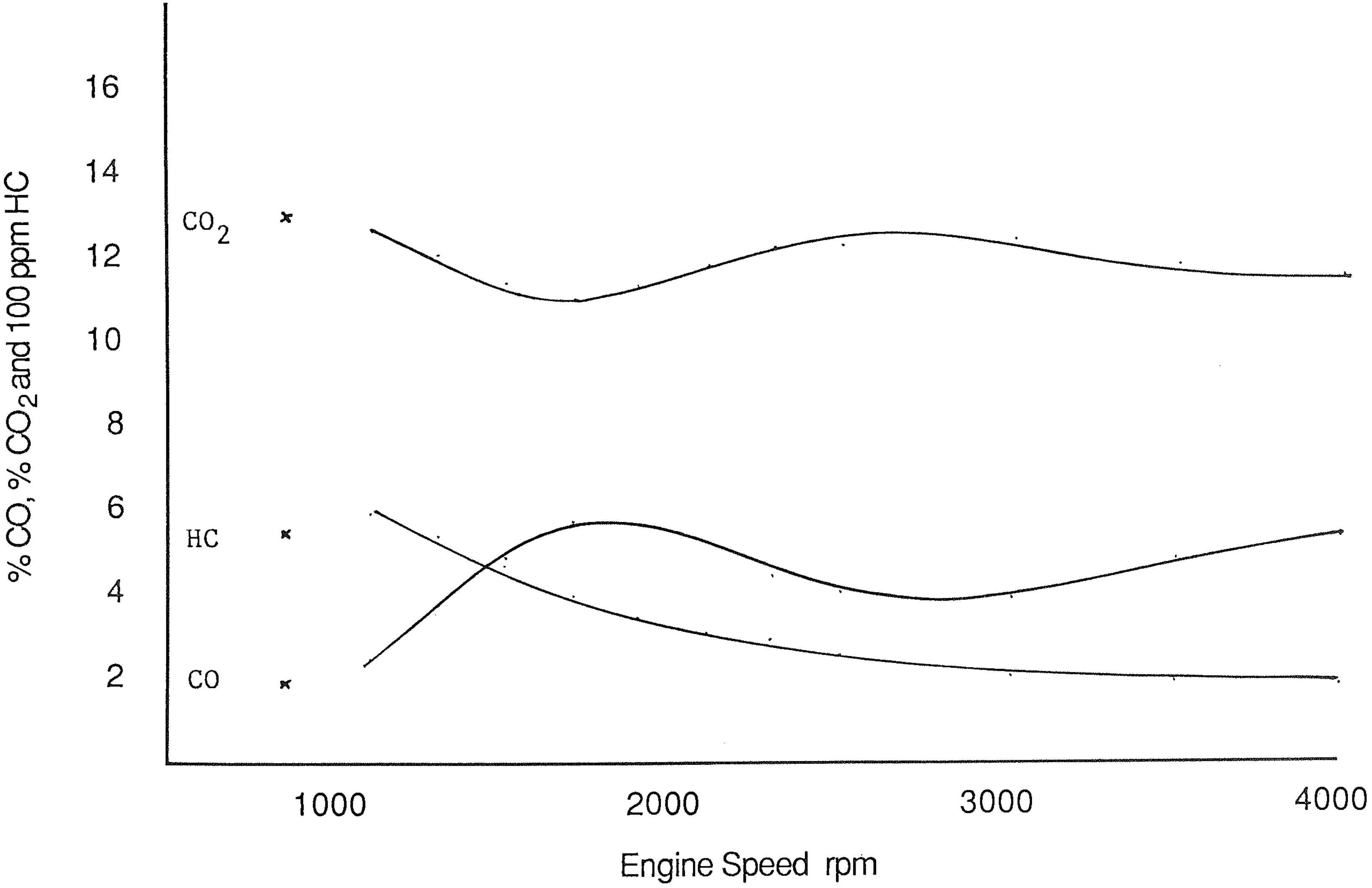

Figure 88 ESSO 4-Star

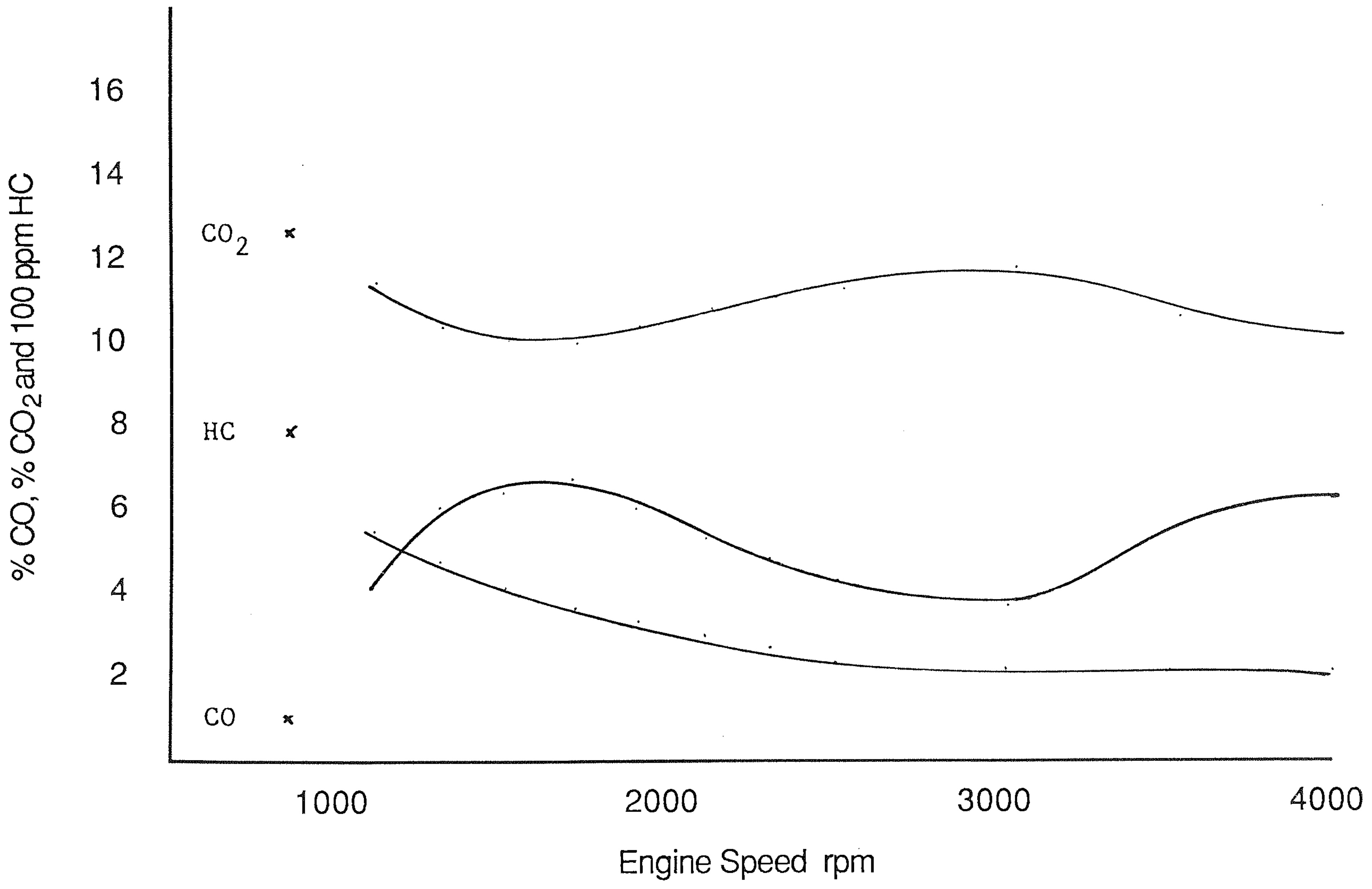

Figure 89 ESSO 2-Star

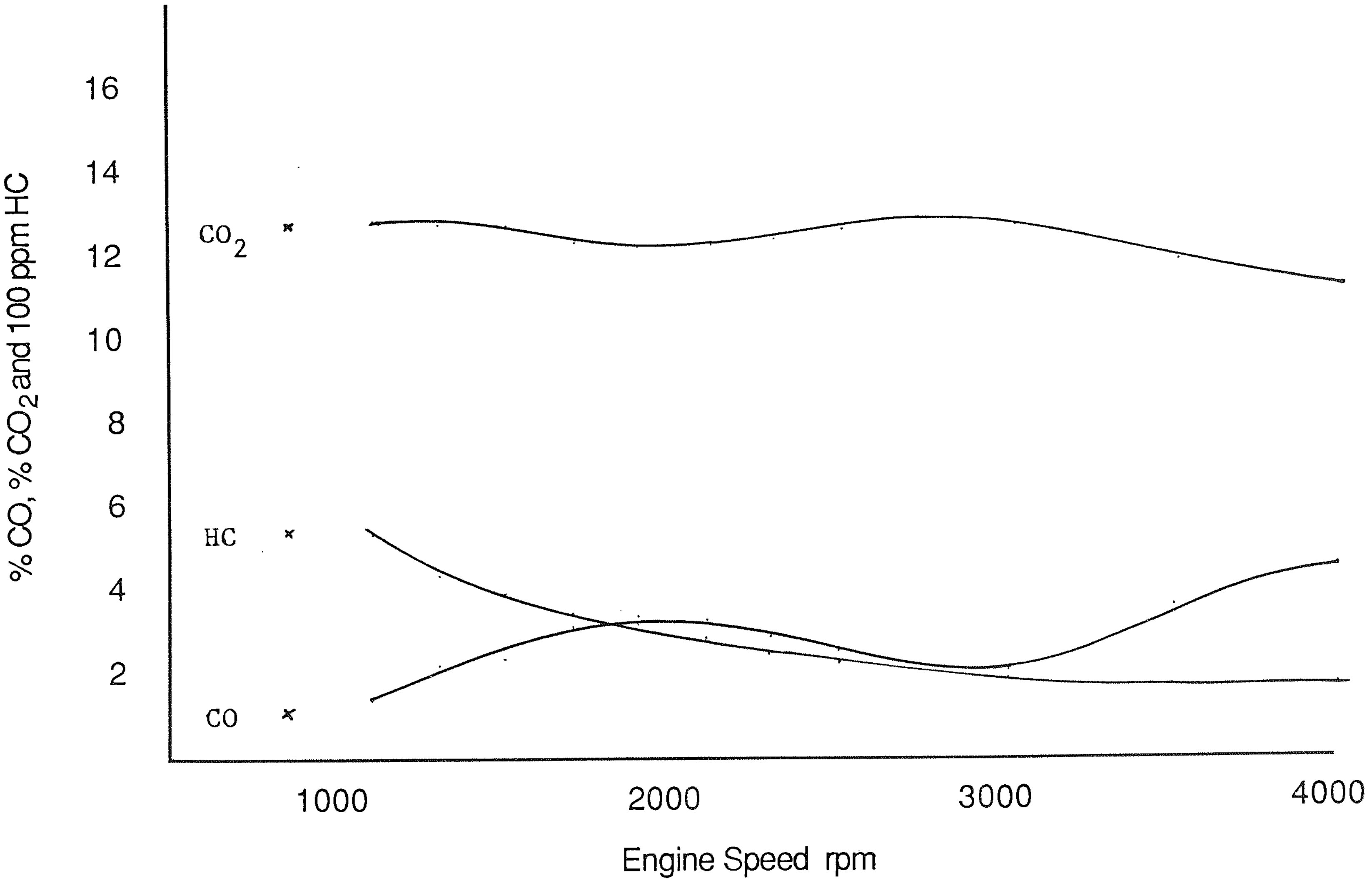

Figure 90 1 : 1 : 1 Methanol : MTBE : 4MP2 14.5% in 2-Star

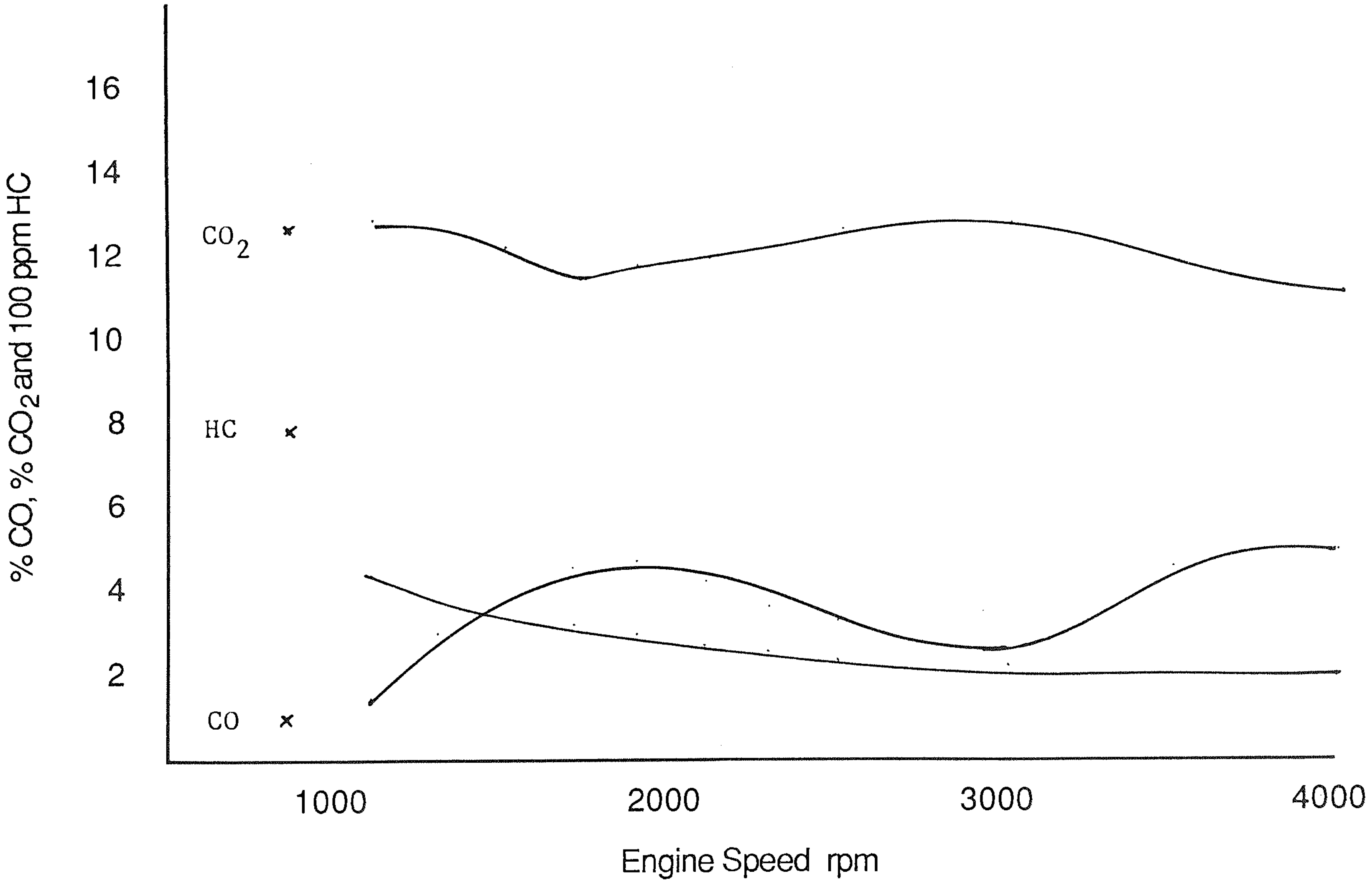

Figure 91 6 : 5 Methanol : MTBE 11.5% in 2-Star

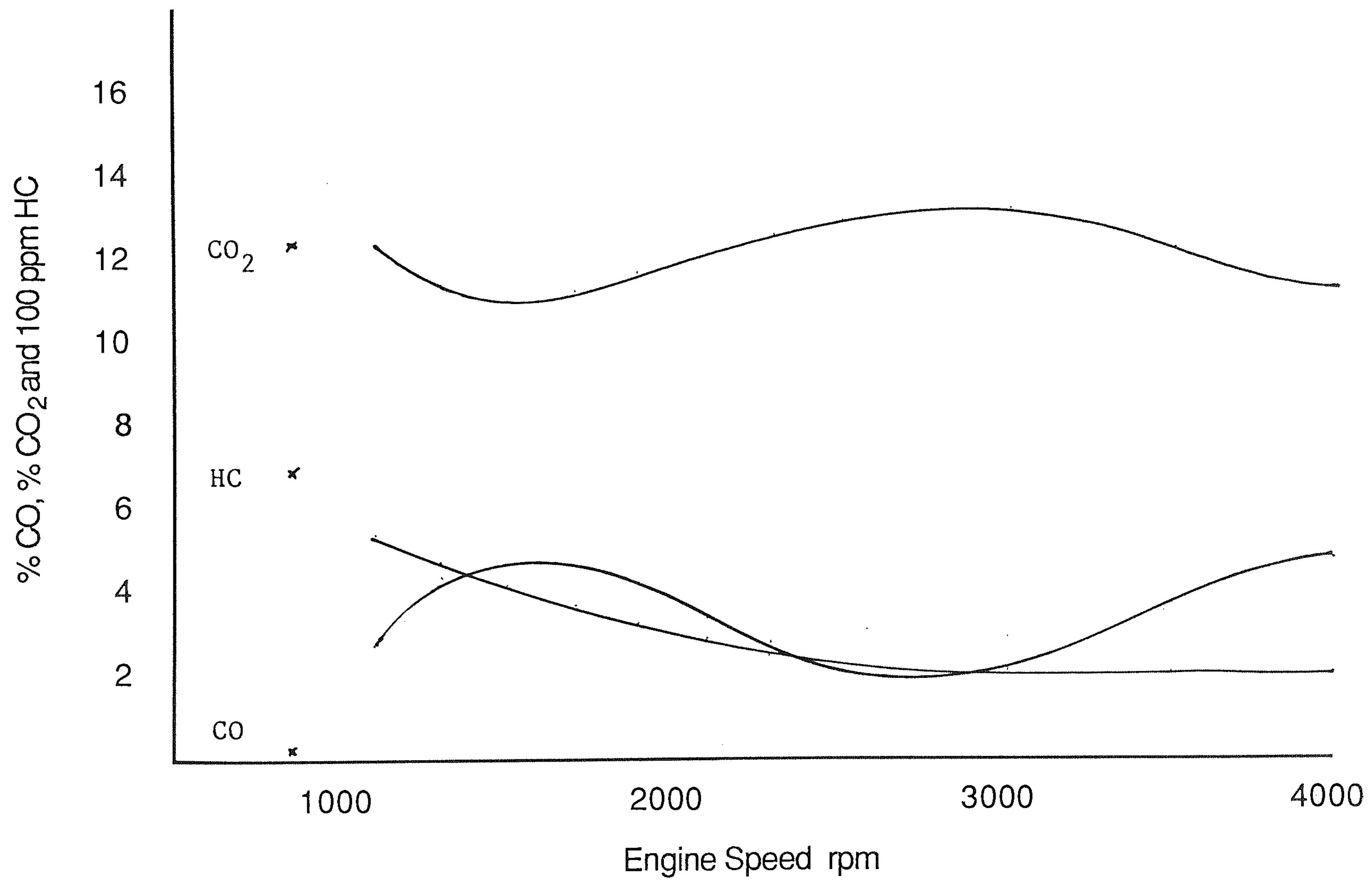

Figure 92 6 : 5 Methanol : 4MP2 11.5% in 2-Star

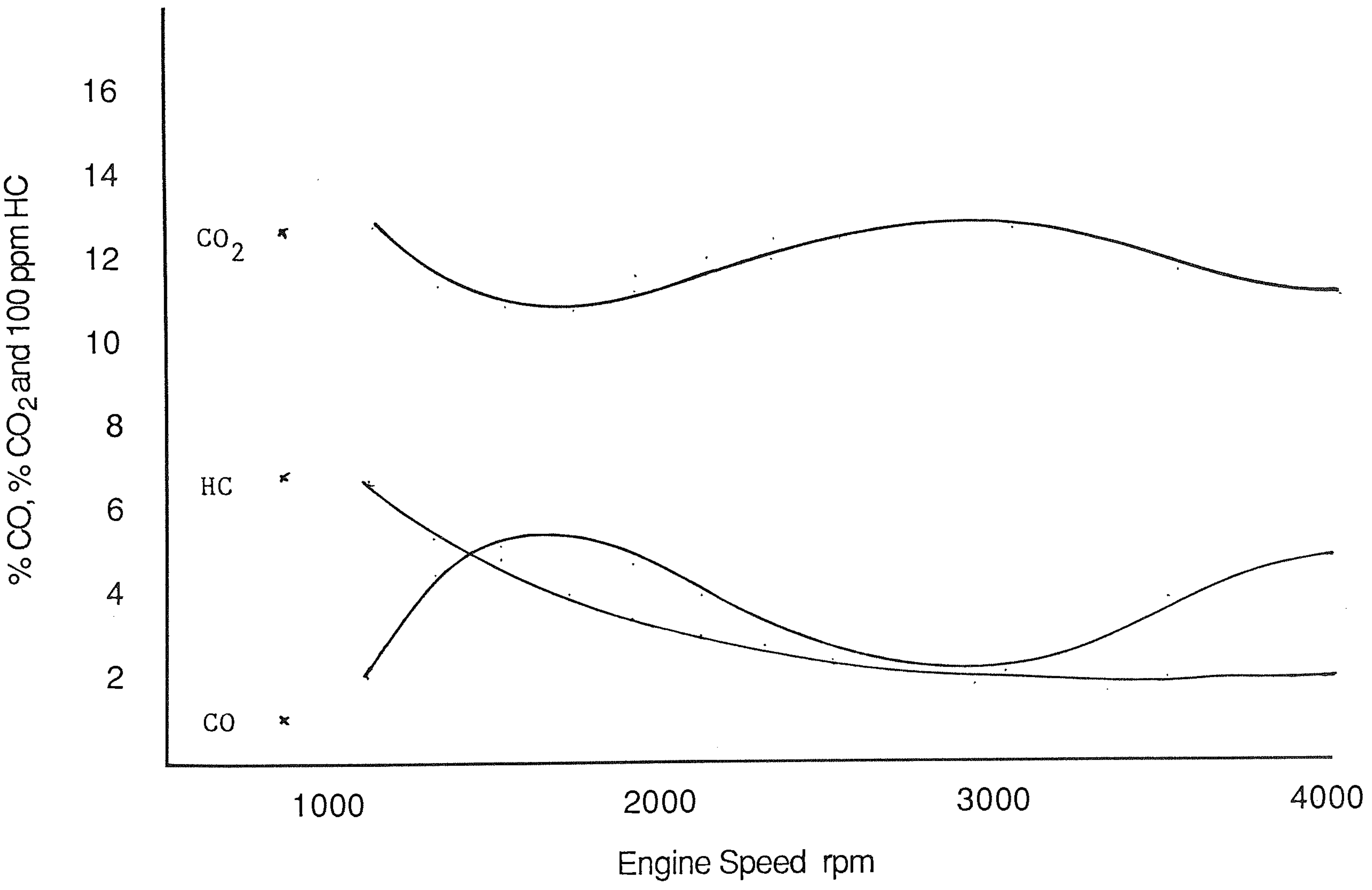

Figure 93 6 : 3 : 2 Methanol : MTBE : 4MP2 11.5% in 2-Star

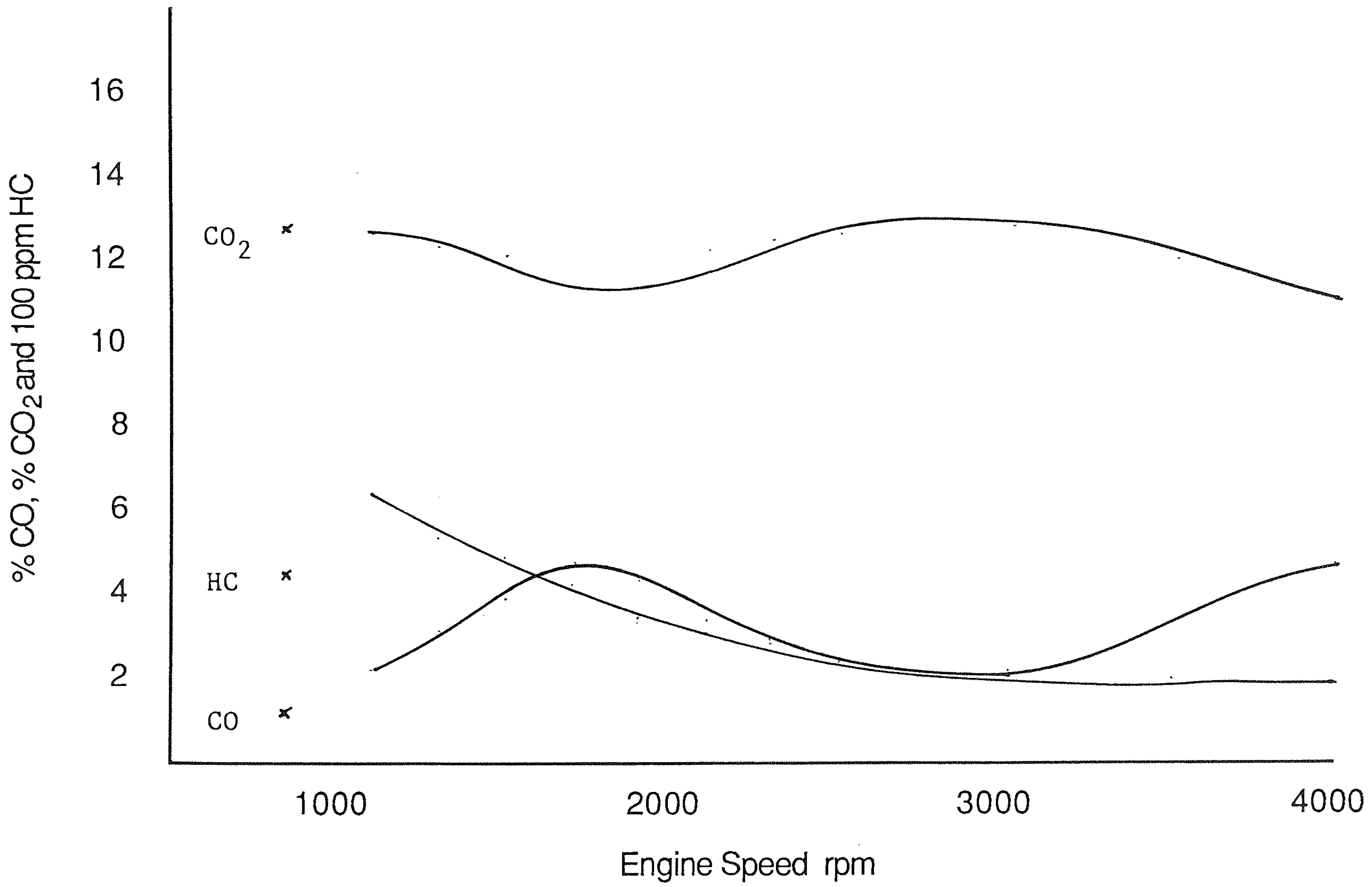

Figure 94 Methanol 8.0% in 2-Star

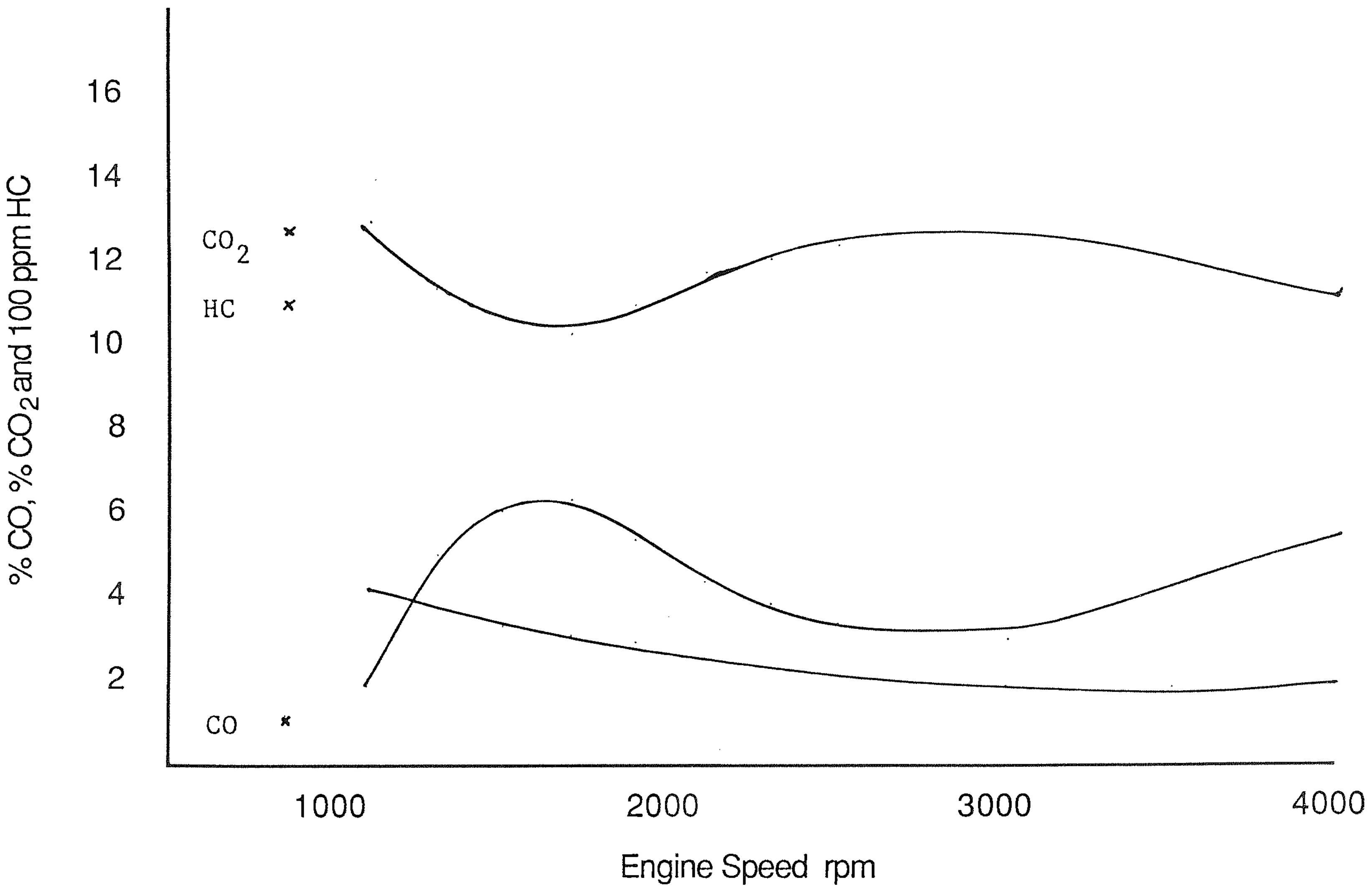

Figure 95 Ethanol 11.5% in 2-Star

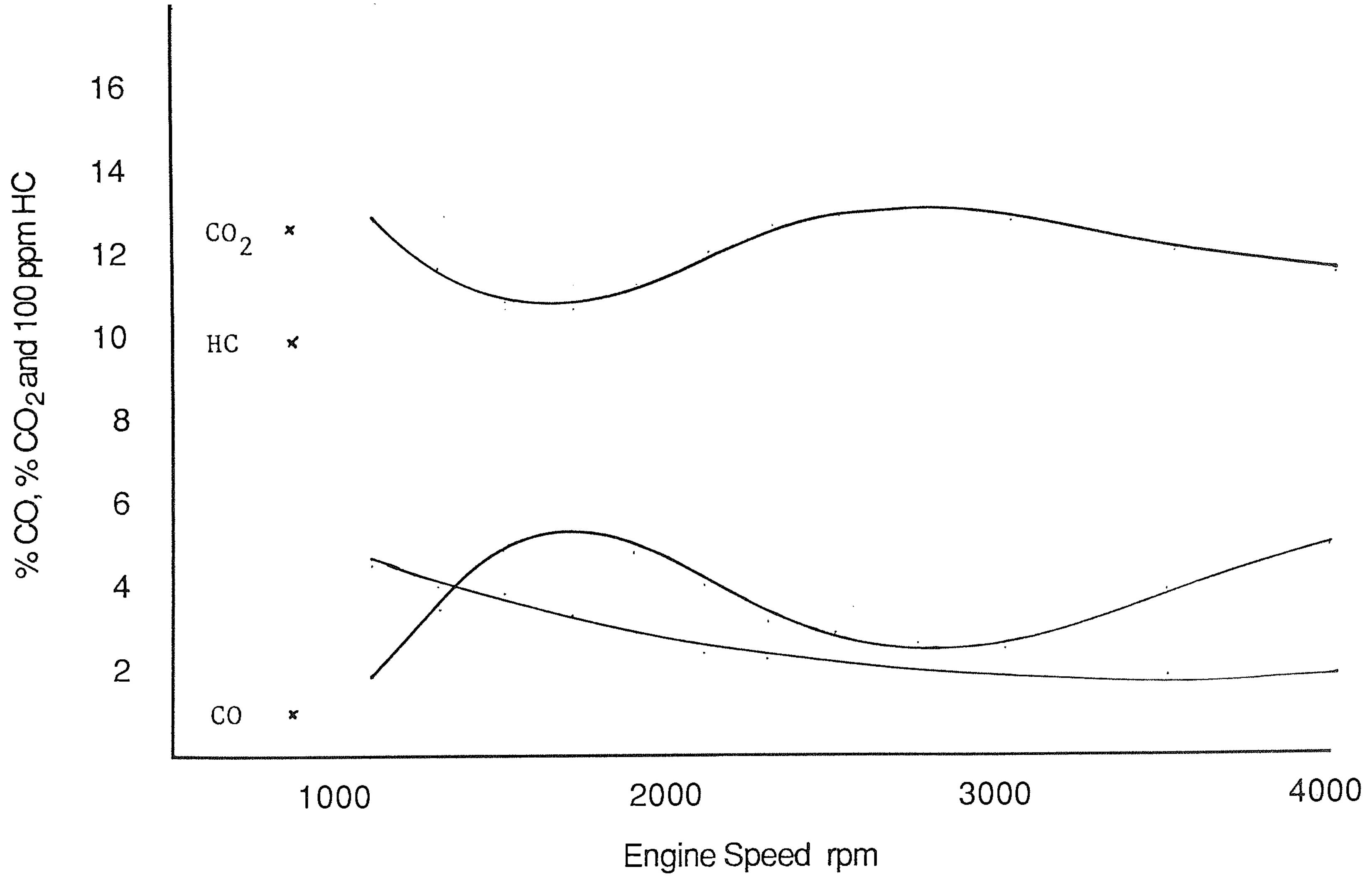

Figure 96 Oxinol 11.5% in 2-Star

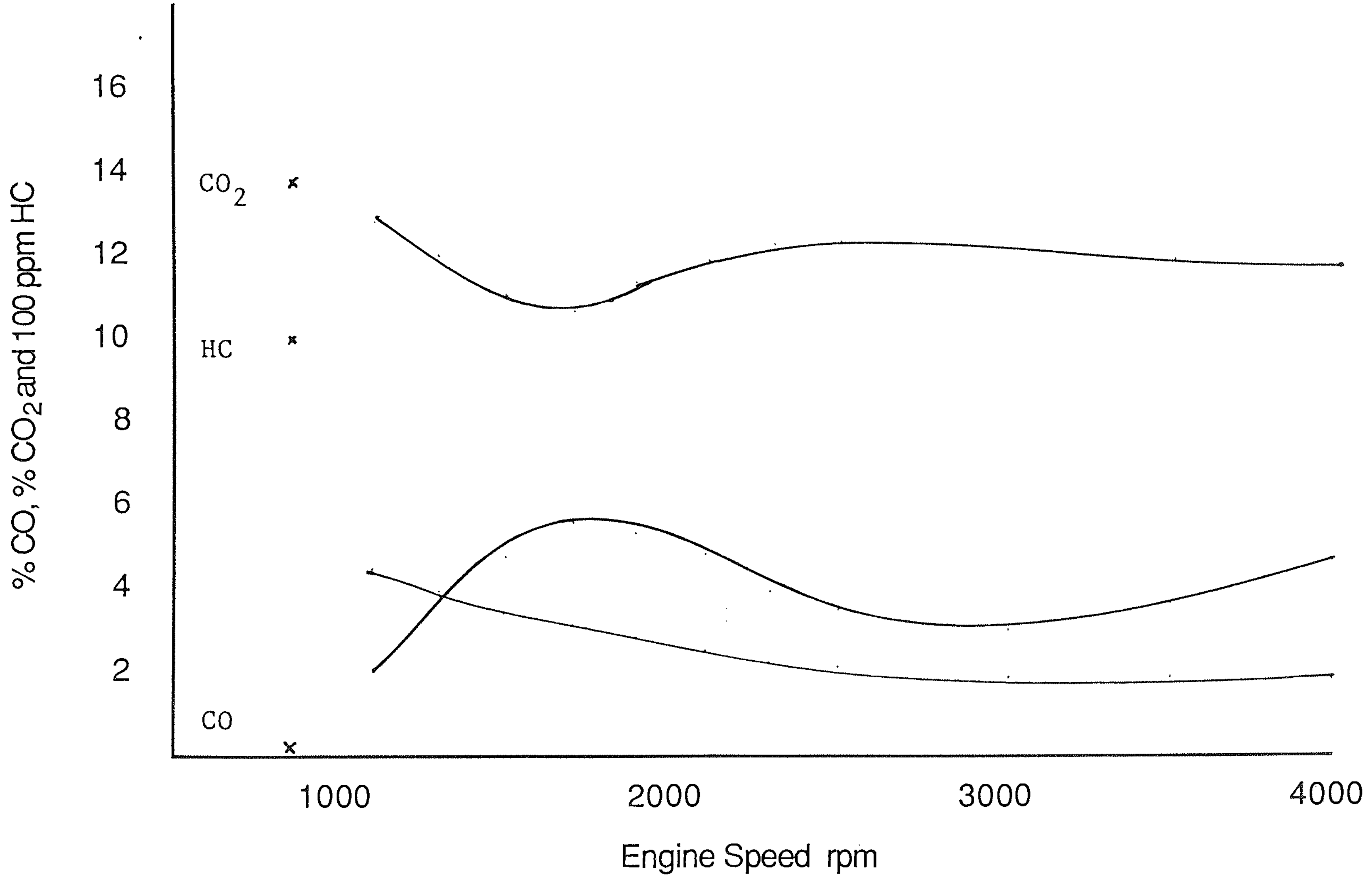

Figure 97 MTBE 22.0% in 2-Star

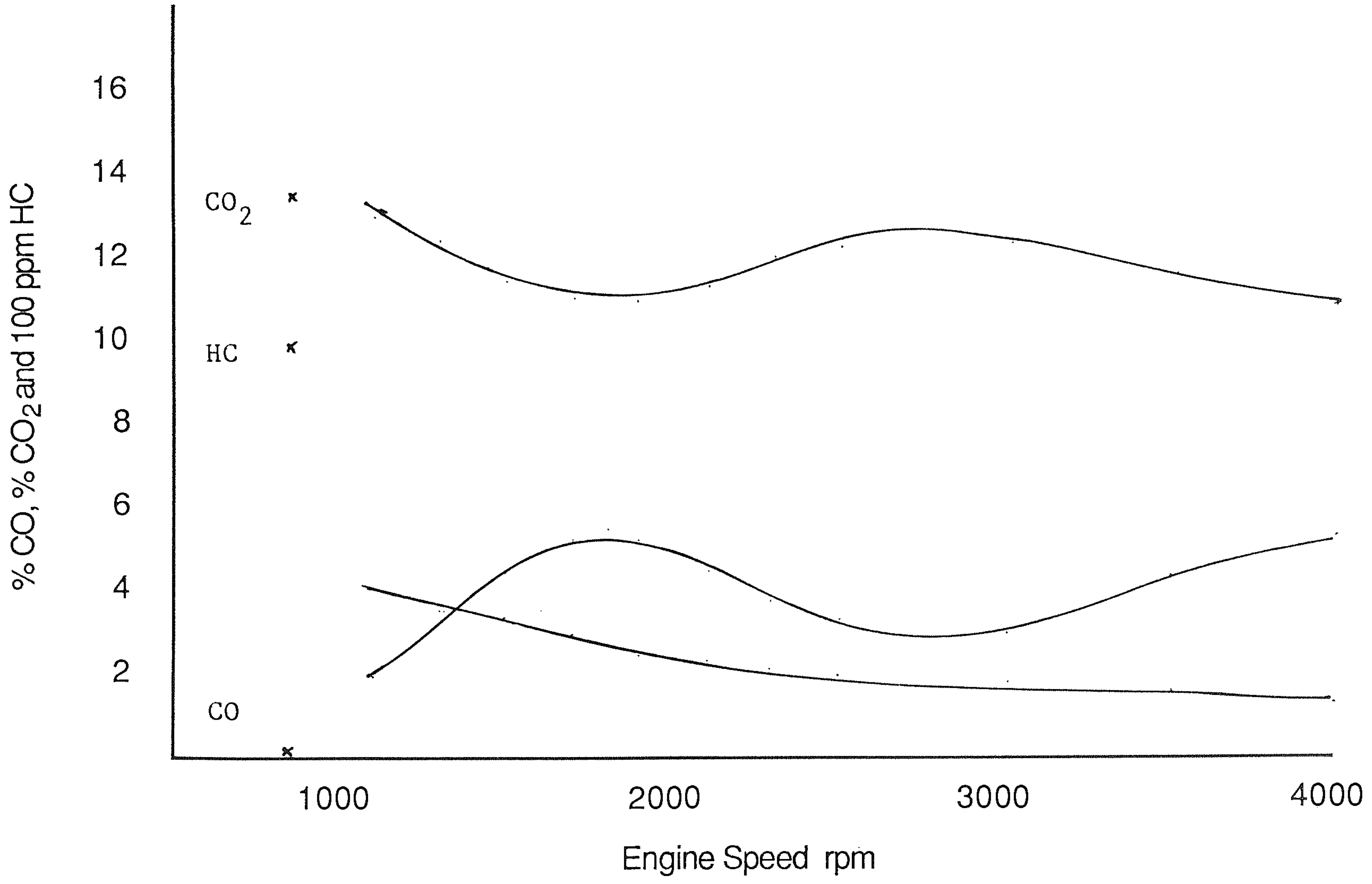

Figure 98 4MP2 25.5% in 2-Star

APPENDIX 2

Octane Requirement of Similar 903 cc Engines

Octane requirement against speed for nine Fiat 903 cc engines in cars on dynamometers shows a large variation, see Figures 99 and 100. The tests were carried out using primary reference fuels (PRF) and F-7 FBRRF (full boiling range reference fuel) by the major oil companies under the CORC programme. 1500 rpm and 80 kph acceleration tests were also carried out and indicated an average critical knock range of 1500 to 1800 rpm starting at 1500 rpm and one of 3000 to 3500 starting from 80 kph using F-7. Similar tests gave 1600 to 2500 starting from 1500 rpm and 3000 to 3500 rpm from 80 kph for the PRF. The constant speed tests were carried out at wide open throttle and all data obtained refers to trace knock.

1981 Co-operative Road Octane Requirement Data determined under accelerating and constant speed conditions of test, nearest 0.5 ON quoted.

Specification for F-7 (Full boiling range reference fuel - FBRRF)

RON	88 - 101	
s	8 - 11 (ON)	
ΔR_{100}	8 - 10	
Olefines	10 - 20 %	
Lead	0.1 g/l @ 88 to 0.15 g/l @ 101 RON	
ASTM Distillation	10 % Vol evap	40 - 60 °C
	50	85 - 115 °C
	90	140 - 180 °C

RVP	0.45 kg/cm^2 min	0.65 kg/cm^2 max
Induction Period	600 minutes	
Existent Gum	4 mg/100 ml max	
Benzene Content	7.5 % vol max	

CORC Car No 1231

Recommended ON 98	Timing 5° BTDC
Bore 65 mm	Stroke 68 mm
Final Drive ratio 446	

All results are trace knock, Dyna means tested on a dynamometer. Figures in brackets refer to PRF test data.

Table 42 Required ON for 9 Fiat 903 cc Engines Accelerating at WOT with Series F-7 Gasoline and PRF

Starting at 1500 rpm

Car No	Max ON	Critical Knock Range	Deposit km/1000	Test Location	Ignition as Tested
1	94 (93)	16 - 18 (16 - 20)	12	Dyna	5B
2	97 (95)	15 - 17 (24 - 26)	7	Dyna	5B
3	93 (92)	16 - 20 (18 - 20)	14	Road	5B8
4	96 (91)	15 - 17 (15 - 20)	6	Dyna	5B
5	95 (92)	15 - 16 (20 - 22)	6	Dyna	5B

Car No	Max ON	Critical Knock Range		Deposit km/1000	Test Location	Ignition as Tested
		1	2			
6	94 (94)	15 - 17	23 - 28	17	Dyna	5B8
		(23 - 25)				
7	94 (93)	16 - 20		18	Dyna	5B8
		(16 - 28)				
8	96 (94)	18 - 24*		15	Dyna	5B8
		(18 - 22)+				
9	93 (91)	24 - 26		15	Road	10B
		(16 - 17)	(20 - 22)			
10	96 (96)	18 - 20	26 - 28	18	Dyna	10B
		(20 - 22)				

* 7/10 WOT

\+ Max OR at WOT = Max OR at part throttle

Starting at 80 km/h

Car No	Max ON	Critical Knock Range	Deposit km/1000	Test Location	Ignition as Tested
1	90 (88)	30 - 32 (30 - 33)	12	Dyna	5B
2	96 (94)	29 - 31 (29 - 31)	7	Dyna	5B
3	91 (91)	31 - 36 (31 - 33)	14	Road	5B8
4	94 (90)	34 - 35 (34 - 36)	6	Dyna	5B
5	93 (90)	34 - 35 (38 - 40)	6	Dyna	5B

Car No	Max ON	Critical Knock Range 1	2	Deposit km/1000	Test Location	Ignition as Tested
6	93 (92)	35 - 37 (35 - 36)		17	Dyna	5B8
7	92 (91)	30 - 34 (30 - 34)		18	Dyna	5B8
8	93 (91)	36 - 38 (37 - 40)		15	Dyna	5B8
9	94 (89)	34 - 36 (32 - 34)	40 - 42 (38 - 40)	15	Road	10B
10	94 (91)	31 - 33 (30 -34)		18	Dyna	10B

Table 43 Required ON for 9 Fiat 903 cc Engines Tested at Constant Speed with Series F-7 Gasoline and PRF

Dynamometer tests at WOT

Car No	2500	3000	3500	4000	4500	5000
1	97 (95)	96 (93)	93 (91)	91 (87)	< 90 (85)	< 90 (84)
2	97 (95)	97 (94)	96 (94)	95 (91)	94 (88)	92 (84)
3	92 (91)	92 (90)	91 (88)	91 (87)	< 90 (85)	< 90 (80)
4	92 (91)	92 (90)	93 (90)	92 (90)	92 (89)	92 (89)
5	93 (93)	93 (92)	92 (93)	91 (90)	91 (89)	91 (88)
6	95 (93)	95 (92)	94 (91)	93 (88)	93 (88)	91 (86)
7	93 (91)	94 (91)	92 (89)	91 (87)	< 89 (85)	< 90 (81)
8	- -	- -	- -	- -	- -	- -
9	94 (93)	94 (92)	94 (91)	95 (89)	93 (87)	92 (86)
10	97 (96)	96 (94)	94 (93)	91 (91)	90 (86)	< 90 (80)

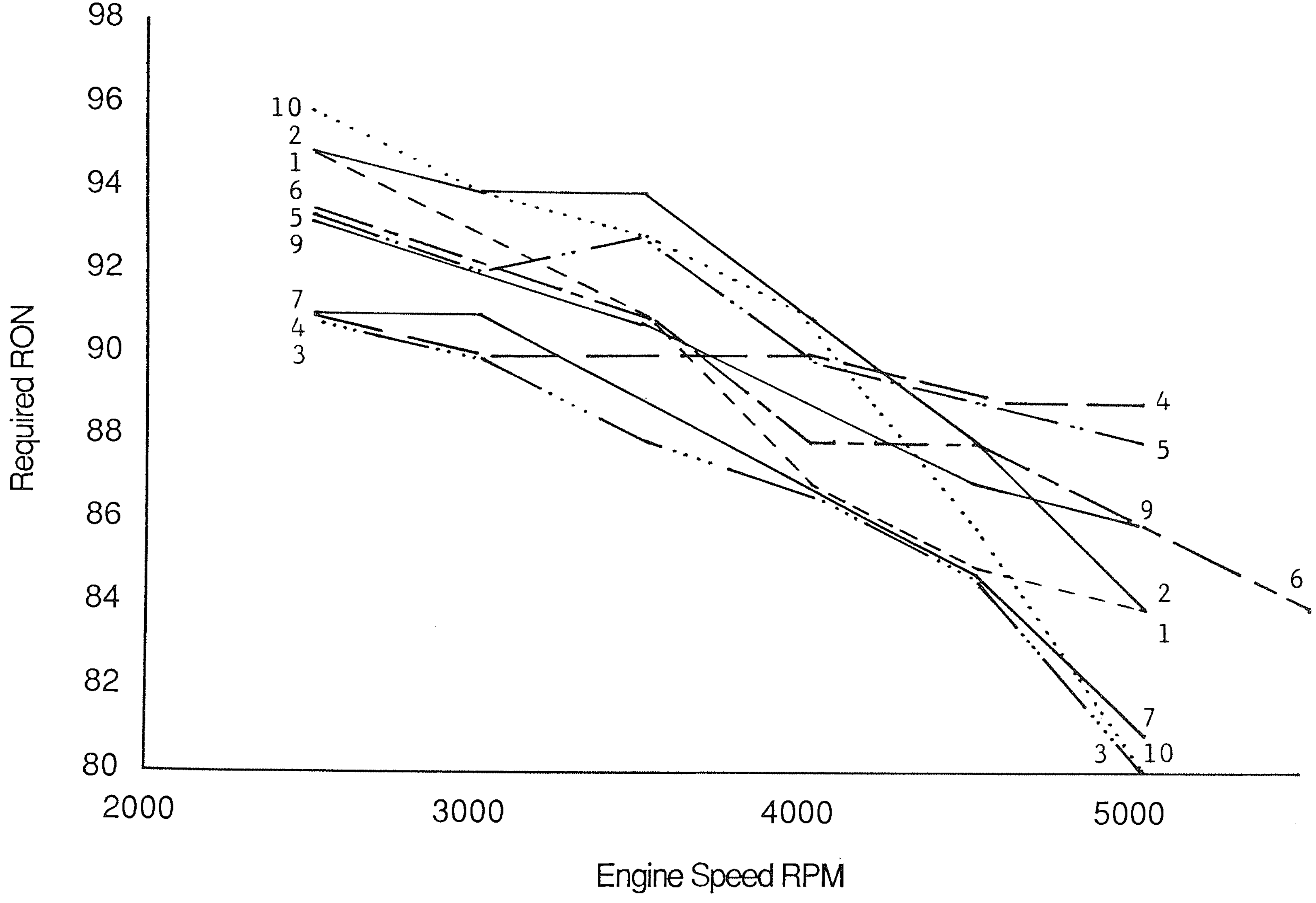

Figure 99 Octane Requirement of Nine Fiat 903 cc Engines in Cars on Dynamometers Tested Using Primary Reference Fuel at Constant Speed

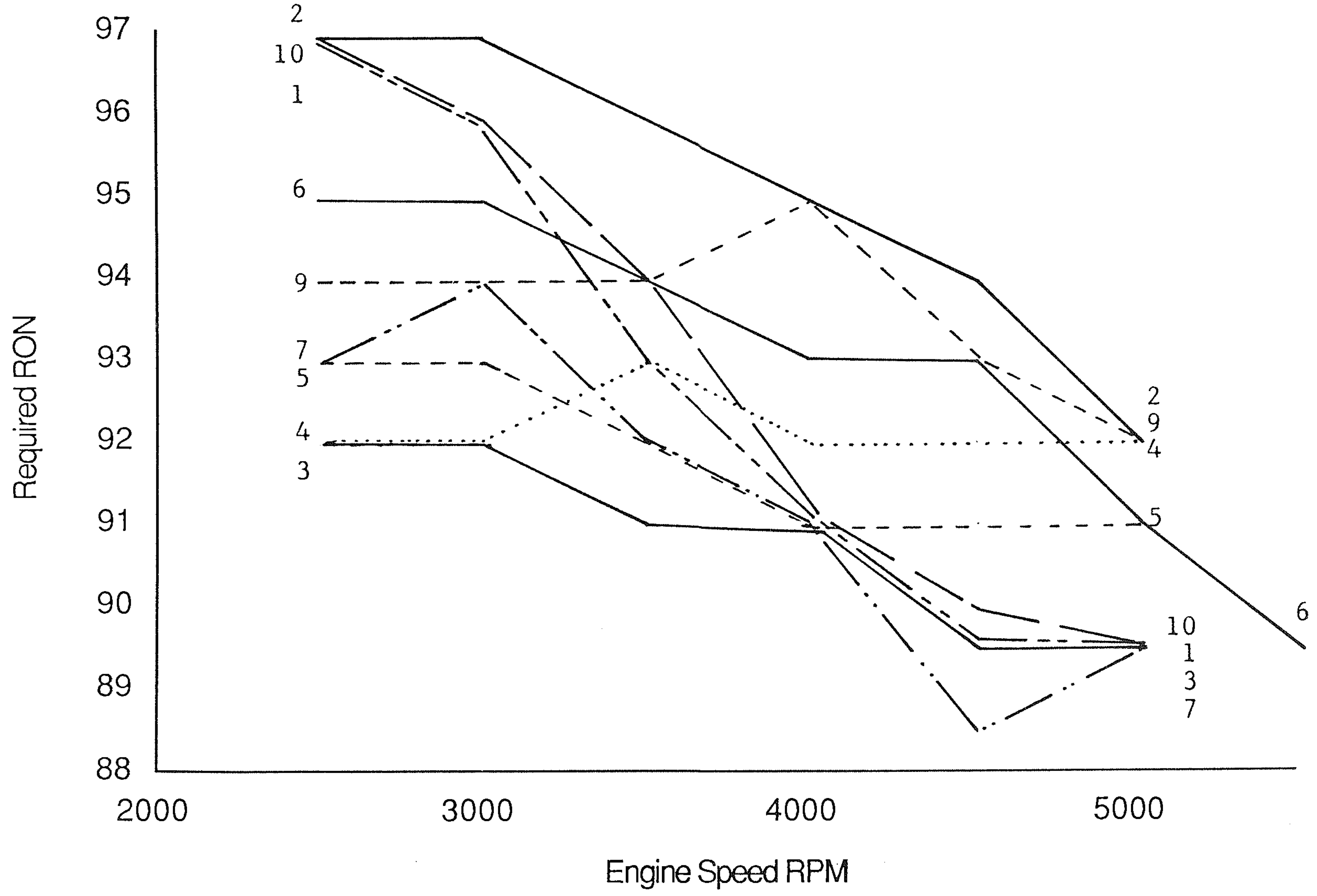

Figure 100 Octane Requirement of Nine Fiat 903 cc Engines in Cars on Dynamometers Tested Using Series F-7 Gasoline at Constant Speed

APPENDIX 3

Test Engine Distributor Evaluation

Engine Fiat 127 (45 PS) Type 100 G L 000 1971 - to date

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 (0.016")

Dwell Angle 52° - 58° (58 - 64 %)

Idle Speed 700 - 800 rpm

Tests

Dwell angle 54.5°

Dwell variation + 0.5 °
200 - 2000 Distributor rpm

Distributor cam accuracy
1. 0.0°
2. 270.5°
3. 89.5°
4. 179.5°

Contact breaker spring tension 20 oz

Table 44 Distributor Advance for 2 Marelli S156AX Distributors

Distributor rpm	Ascending		Descending	
	No 1	No 2	No 1	No 2
0	0.0	0.0	0.0	0.0
200	0.0	0.0	0.0	0.0
400	1.5	0.0	1.5	0.0
500	-	0.5	-	0.5
600	4.0	2.0	4.5	2.0
800	6.0	6.0	6.0	6.0
1000	6.5	7.0	6.5	7.5
1200	7.5	8.0	7.5	8.0
1400	8.0	9.0	8.0	9.0
1600	8.5	10.0	8.5	10.0
1800	9.5	11.5	9.5	11.5
2000	10.5	12.25	10.5	12.5
2200	12.0	13.0	12.0	13.5
2400	13.0	13.5	13.0	13.5
2600	13.5	14.0	13.5	14.0
2800	13.5	14.0	13.5	14.0
3000	13.5	14.0	13.5	14.0

Table 45 Stroboscopic Timing of Test Engine

Engine rpm	Ignition Advance No 1 Test 1	No 1 Test 2	No 1 Test 3	No 2
900	-	15.0	-	12.5
1050	-	-	16.0	-
1200	-	18.5	-	13.5
1500	-	23.5	21.0	18.0
1600	-	-	24.0	-
1750	-	25.0	-	23.0
2000	-	26.0	25.5	25.5
2250	-	27.0	-	27.0
2300	-	-	26.5	-
2450	-	27.5	-	28.0
2700	-	28.5	-	29.0
3000	-	-	30.0	-
3050	31.0	30.0	-	30.0
3400	32.0	31.0	-	31.5
3800	-	-	33.0	-
3850	33.0	32.5	-	32.5
4200	-	-	34.0	-
4500	36.0	36.0	-	35.0

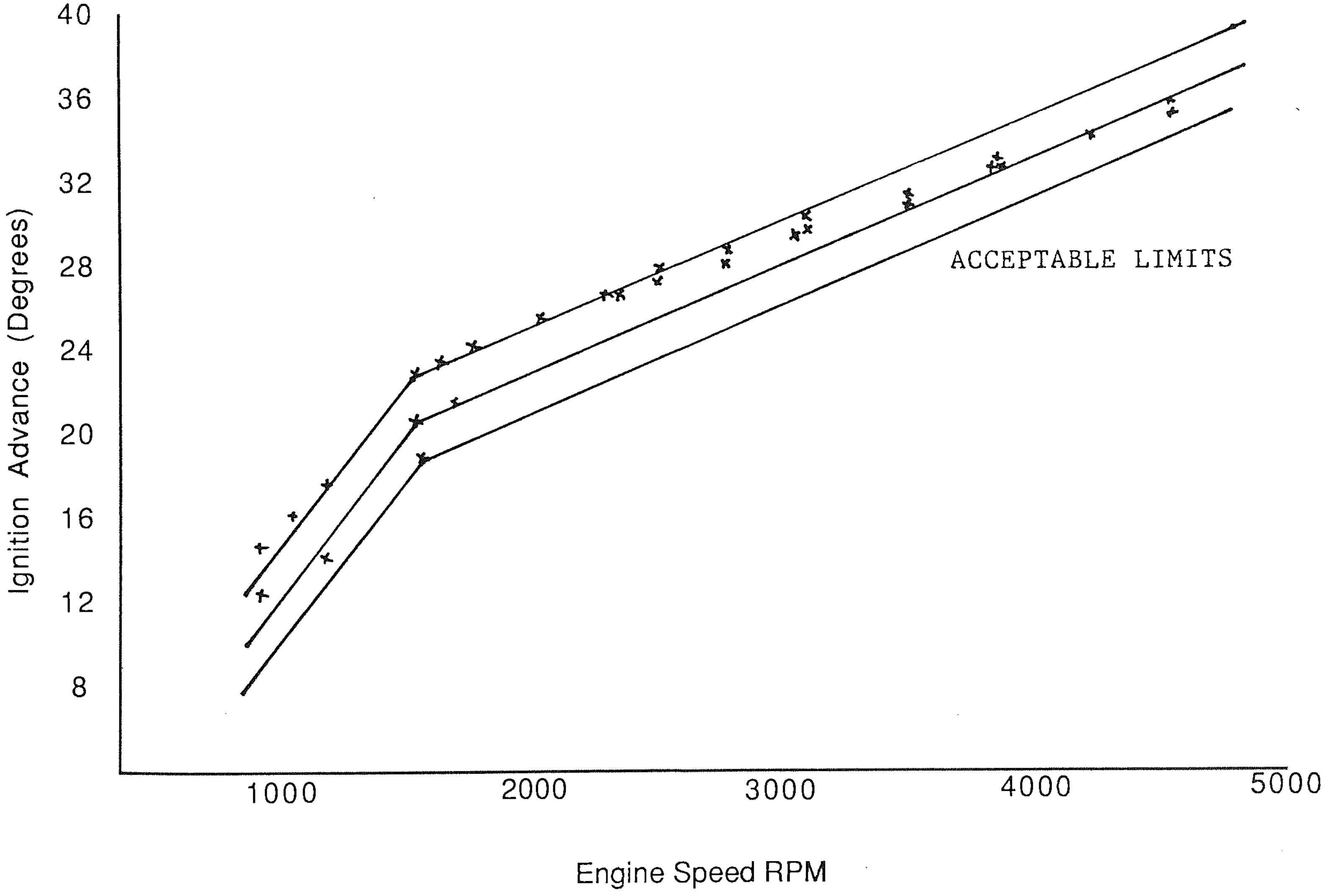

Figure 101 Distributor Timing Curve

APPENDIX 4

Design of Load Cell

The beam on to which the strain gauges were attached was designed to allow good deflection and yet not distort. The maximum engine power was 45 hp at 5600 rpm, however, the dynamometer maximum was 100 hp and as a second larger engine might have been available the higher value was taken. Engine torque at this speed and the assumed power was found from :-

$$\text{Torque} = \frac{\text{Power}}{\text{Speed}} = \frac{100 \times 0.746}{5600} \times 60 \times 10^3 \times \frac{1}{2\pi}$$

$$\text{Torque} = \underline{127.2 \text{ Nm}}$$

The arm attached to the dynamometer casing had a ball bearing mounted on it which acted on the cantilever at a distance of 26 cm from the axis of the dynamometer shaft. This was the maximum convenient distance. The force exerted was thus :-

$$\text{Force} = \frac{\text{Torque}}{\text{radius}} = \frac{127.2}{0.26}$$

$$\text{Force, } F = \underline{490 \text{ N}}$$

This value was increased to 800 N to allow for abnormal operation, surges etc during set-up, and as a safety factor.

The beam breadth was chosen as 2.5 cm to accommodate the strain gauges and the other beam dimensions were calculated from :-

$$E\,I\,\frac{d^2y}{dx^2} \quad = \quad M \quad = \quad -\,F\,x \qquad \text{——} \quad 1$$

where E is Youngs modulus

I is moment of inertia $= bh^3 / 12$

y is deflection

x is length of beam (0 to l)

M is bending moment

b is breadth of beam

h is height of beam

Integrating twice :-

$$E\,I\,\frac{dy}{dx} \quad = \quad -\,\frac{F\,x^2}{2} \quad + \quad A \qquad \text{——} \quad 2$$

and

$$E\,I\,y \quad = \quad -\,\frac{F\,x^3}{6} \quad + \quad A\,x \quad + \quad B \qquad \text{——} \quad 3$$

at $x = l$

$\frac{dy}{dx} = 0$ and $y = 0$

from 2 $\quad A = \frac{F\,l^2}{2}$

from 3 $\quad B = -\,\frac{F\,l^3}{3}$

at $x = 0$

$$B = E I y$$

Therefore $$E I y = \frac{F l^3}{3}$$

Thus beam height (thickness) $$h = \left(\frac{F l^3}{3} \times \frac{1}{E y} \times \frac{12}{b} \right)^{1/3}$$

and at $F = 800$ N

$l = 7.5$ cm (convenient beam length)

$E = 2.07 \times 10^{11}$ N/m^2 (mild steel)

$b = 2.5$ cm

$y = 2.5$ mm (maximum deflection)

$$h = 4.7 \times 10^{-3} \text{ m}$$

$$h = \underline{5 \text{ mm}}$$

Actual beam dimensions after manufacture were :-

length = 7.3 cm, 6.8 cm from load application point

bredth = 2.54 cm

height = 0.67 cm

This is thicker than designed but an adequate signal was obtained when the beam was tested, this was thus accepted and used in subsequent experiments. The strain gauges were mounted centred at 5.1 cm from the point of load application.

APPENDIX 5

Density of Series F-7 Gasoline Key Components

In a 50 ml density flask at 21.5 °C weighing 32.3662 g

Low key = 38.2629 g

High key = 40.1555 g

Therefore density of :-

Low key = 0.7653 g/ ml

High key = 0.8031 g/ ml

Table 46 Density of Series F-7 Blends

Blend RON	% Key Component		Density (g/ ml)
	Low	High	
90	99.0	1.0	0.7656
92	85.0	15.0	0.7710
94	70.5	29.5	0.7765
96	54.5	45.5	0.7825

An average density of 0.774 g/ml to be used for gasoline blends.

APPENDIX 6

Humidity Measurements Taken During Experiments

Table 47

Date	Dry Bulb Temperature °C	Wet Bulb Temperature °C	Air Pressure (corrected) mm Hg	Absolute Humidity kg H_2O/kg dry air x 10^{-3}
21. 5.84	16.9	11.4	755	6.4
22. 5.84	14.2	11.9	748	7.9
23. 5.84	18.3	13.3	759	7.6
24. 5.84	16.4	12.7	760	8.0
29. 5.84	13.0	10.0	764	6.4
6. 6.84	14.2	11.1	760	7.0
7. 6.84	15.8	13.3	763	8.6
12. 6.84	22.2	15.6	771	8.6
18. 6.84	18.9	15.0	773	9.0
19. 6.84	21.1	16.9	774	10.4
20. 6.84	21.7	18.0	768	11.7
21. 6.84	21.7	13.9	765	6.9
22. 6.84	22.5	15.8	761	8.7
25. 6.84	18.9	15.0	761	9.3

Date	Dry Bulb Temperature °C	Wet Bulb Temperature °C	Air Pressure (corrected) mm Hg	Absolute Humidity kg H_2O/kg dry air x 10^{-3}
27. 6.84	18.9	13.3	769	7.4
28. 6.84	18.0	12.5	768	6.9
10. 7.84	22.8	15.6	761	8.0
19. 9.84	18.3	12.8	760	7.1
20. 9.84	14.4	11.9	755	5.7
21. 9.84	14.0	9.7	758	5.8
26. 9.84	14.0	9.7	761	6.1
3.10.84	15.6	10.8	747	6.9
10.10.84	18.9	12.8	771	7.1
11.11.84	18.6	12.8	771	10.3
29.11.84	20.3	16.4	768	11.1
30.11.84	19.2	15.3	768	6.9
21. 2.85	21.9	13.9	782	5.1
25. 2.85	19.4	10.8	769	7.4
28. 2.85	23.9	15.3	771	6.3
6. 3.85	24.4	14.4	771	6.3
19. 3.85	17.2	8.9	761	3.7
25. 3.85	20.3	12.2	750	5.4
28. 3.85	20.6	11.9	766	5.4
29. 3.85	18.0	11.1	764	5.4

Date	Dry Bulb Temperature °C	Wet Bulb Temperature °C	Air Pressure (corrected) mm Hg	Absolute Humidity kg H_2O/kg dry air x 10^{-3}
1. 4.85	20.8	15.0	755	8.3
18. 4.85	23.6	16.1	774	8.3
19. 4.85	17.5	11.4	769	6.3
24. 4.85	13.9	7.8	774	4.0
11. 7.85	65.3	17.2	769	9.0
17. 7.85	18.1	13.9	766	8.3
23. 7.85	17.5	12.8	768	7.6
25. 7.85	22.2	16.7	766	9.9
26. 7.85	20.8	16.9	755	10.4
9. 8.85	16.1	13.3	755	8.6
13. 8.85	16.1	13.0	762	8.3
14. 8.85	17.8	13.6	762	8.3
19. 8.85	19.4	15.8	758	9.7
28. 8.85	19.7	16.4	769	10.3
4. 9.85	16.4	13.1	766	7.4
5. 9.85	15.6	12.5	764	7.9
10. 9.85	18.6	15.3	772	9.7
12. 9.85	18.3	14.2	767	8.4
29. 1.86	15.3	8.9	744	4.4
30. 1.86	10.8	6.9	755	4.7

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