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A THESIS

entitled

EFFECTS OF SULPHUR COMPOUNDS ON THE COMBUSTION OF LEADED FUELS.

by

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Submitted for the
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CONTENTS.

ABSTRACT.

Measurements of the reduction in the octane number of leaded fuels by various sulphur compounds were made using a Cooperative Fuel Research Engine. The effects of seven different sulphur compounds were studied and three fuel blends were used. Attempts were then made to correlate the gaseous oxidation characteristics of these sulphur compounds under laboratory conditions with their observed effects on combustion in an engine. Studies were also made of the spontaneous ignition of isooctane-oxygen mixtures in uncoated and lead oxide-coated vessels and of the effects of small additions of three sulphur compounds, namely sulphur dioxide, thiophene and thiophenol, on the ignition limits. Similar measurements were made with a leaded isooctane blend in an uncoated vessel. Finally lead oxide-coated vessels were pre-treated with these three gaseous sulphur compounds in turn and studies were then made of the ignition limits of isooctane-oxygen mixtures in these vessels. Electron diffraction and other related techniques were used to examine the lead oxide coatings before and after treatment with the sulphur compounds.

The Introduction (Section 1) outlines the problems associated with the presence of sulphur compounds in motor gasolines. "Knock" in internal combustion engines and means of suppressing it are also reviewed. The relation of "knock" to the preflame combustion reactions of hydrocarbons and the mode of action of lead-based additives in its suppress-

ion are also discussed.

The Experimental Section (Section 2) describes the Cooperative Fuel Research Engine and its use for the measurement of octane numbers. The vacuum apparatus constructed and used for laboratory studies of fuel combustion and the accessory equipment are also described. The procedure for coating the inner surface of the reaction vessels with lead oxide and the subsequent treatment of these vessels with sulphur compounds are outlined. A brief account is given too of the electron diffraction techniques used to study surface properties of the lead oxide coatings and the effects on them of exposure to gaseous sulphur compounds.

The Results Section (Section 3) gives detailed values of the increase in octane number caused by the addition to the fuel blends of tetraethyl and tetramethyl lead, and of the effects of 0.05 and 0.10 wt. % S when introduced in the form of various sulphur compounds, into the leaded fuels. Studies of the gaseous oxidation of four of the sulphur compounds, viz. thiophene, dipropyl sulphide, dimethyl disulphide and thiophenol, showed that the order of lead antagonism runs parallel with the rates of oxidation and the tendency to form sulphur dioxide. Lead oxide inhibited combustion of the hydrocarbon fuels and ignition studies showed that the sulphur compounds also inhibited isooctane combustion in an uncoated vessel, but promoted it in a lead oxide-coated vessel. Results obtained with leaded isooctane also showed the inhibiting effect of dissolved lead. After pre-treatment with sulphur compounds, the chain-terminating efficiency of the lead oxide appeared to be much reduced and was indeed even lower than that of an uncoated vessel. The order of effectiveness of the sulphur compounds in reducing the inhibiting influence of the lead oxide coating was: sulphur dioxide $<$ thiophene $<$ thiophenol. Electron diffraction studies of the lead oxide before and after treatment with the gaseous sulphur compounds revealed changes in its surface properties, the magnitude of which varied with the nature of the sulphur compound in the above order.

Finally in the Discussion (Section 4), an attempt is made to correlate the engine and laboratory results obtained in this work. It appears to be the chemical nature of the organic sulphur compounds and their initial decomposition and/or oxidation products rather than the sulphur dioxide formed from them, which affect the properties of the lead oxide particles generated during the combustion of the leaded hydrocarbon fuels.

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SECTION 1.

INTRODUCTION.

SECTION 1.

Introduction (cont'd)

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1.1. General Introduction.

Low-boiling petroleum fractions constitute the bulk of the world's motor fuels. Early gasoline engines were not exacting in their requirements and their design enabled the use of all petroleum distillates boiling up to 220°C. However, with the improvement of engine design, other qualities such as antiknock efficiency, chemical stability and controlled volatility, have become important.

Today's gasoline is usually a blend of hydrocarbons boiling within the range 40-200°C, which occur naturally in petroleum and natural gas, together with similar hydrocarbons made largely by the catalytic cracking of heavy oils. The composition of uncracked (straight run) and lightly cracked gasolines is influenced by the nature of the crude oil from which the gasolines are made. When the cracking temperature is raised or when catalytic and reforming processes are employed, the composition of the product is largely independent of the nature of the initial crude oil. Owing to the large number of possible hydrocarbons in each class, gasoline is a very complex mixture.

The most important property of a gasoline is its volatility under the conditions of its use. An explosive and completely combustible mixture of fuel and air must be produced in the combustion chamber. The carburettor aspirates gasoline in the form of a spray into the stream of air drawn into the engine by the pistons. In principle, the spray vaporises to give a mixture of air and fuel vapour. In practice however, the vaporisation process is incomplete and a substantial portion of the liquid is carried through the intake manifold and into the cylinder as droplets or as a thin film moving along the manifold wall. The degree of vaporisation can usually be improved by increasing the time of contact of the fuel with air, by raising the temperature of the mixture[1,2], or by using a more volatile fuel. The first consideration is limited by engine design and operation, the second by a decrease in volumetric efficiency and the third by economic considerations. The second most important factor affecting the quality of motor gasolines is the "knock" rating. One property of secondary importance but which nevertheless needs careful attention is the sulphur content.

Forty years ago, there were only two million motor vehicles on the roads of Great Britain[3]. Today there are over fifteen million. This rapid growth of motor traffic over a relatively short period of time has given rise to much concern about motor vehicle emissions. The pollutants from motor vehicles include unburnt hydrocarbons, carbon monoxide, oxides of nitrogen, smoke, lead and sulphur dioxide.

Lead, which is used as an additive in gasoline to improve resistance to "knock", is discharged into the atmosphere from vehicle exhausts. These emissions account for a significant proportion of the lead present in the atmosphere[4] and although research suggests that little of the lead present in the atmosphere is absorbed into the blood stream via the lungs[5,6], pressure to reduce atmospheric pollution has led to a reduction in the concentration of lead in gasolines. A programme of phased reductions in the lead content of motor gasolines was introduced in 1973 and by the end of 1975, the maximum level was $0.45 g.l^{-1}$ compared with the previous level of $0.84 g.l^{-1}$.

A second reason for the elimination of lead in motor gasolines is that it acts as a catalyst poison, and if catalytic reactors should have to be widely used to reduce carbon monoxide and hydrocarbon emissions, the elimination of lead might then become essential. In 1970, the President of General Motors proposed the elimination of lead compounds from motor fuels[7]. This was seen as the quickest and most effective way of eliminating the air pollution problems associated with gasoline powered vehicles. The motor industry supported this proposal by designing many of the 1971 cars to operate on unleaded fuels. This anticipated general use of unleaded gasoline in the U.S.A., together with the many changes in engine and emissions controls required by the various governmental standards for automotive emissions, led to a significant research programme by the auto, fuel and lubricant industries. In work carried out on the effect of unleaded gasolines on exhaust emissions and lubricant performance[8], the fuel gave more "varnish", less rust, slightly less sludge deposit, higher wear on certain engine parts, for example the exhaust valves, less oil thickening, higher octane requirements under full throttle conditions and decreased spark plug fouling.

The elimination or reduction of lead from gasolines is purely a question of economics, since lead is the most economical way of achieving high octane levels in commercial gasolines. Since high octane levels are needed, the cost of producing gasolines without lead will increase substantially. If lower octane levels are acceptable, then engines will result with lower compression ratios and consequently higher fuel consumption.

The reduction of the lead content of gasolines has led to another problem for crude oil refiners. Until recently the problem of sulphur compounds in crude oil was a comparatively minor one. With the heavy depletion of low-sulphur crudes during the last World War, the effect of sulphur compounds in gasolines has become increasingly important. There are three main reasons for this. First the presence of sulphur compounds gives the gasoline a bad odour; and second the oxidation products, sulphur dioxide and sulphur trioxide, lead to atmospheric pollution and to engine corrosion.

Sulphur dioxide occurs naturally in the atmosphere in low concentrations and is essential to the life cycle of much living matter. Natural processes occur which produce and remove this gas from the atmosphere. Sulphur dioxide "pollution" is thus not caused simply by the presence of the gas[9] but occurs only when concentrations are higher than those associated with the natural sulphur cycle. The combustion of fuels containing sulphur invariably releases sulphur dioxide into the atmosphere. This gas combines with water and particulate matter in the air and is subsequently oxidised to form dilute sulphuric acid which is corrosive and can damage many materials. In sufficiently high concentrations, sulphur dioxide is an irritant to the respiratory system of man and animals and can damage plants.

The third and most important reason why the presence of sulphur compounds is so undesirable is that motor fuels containing sulphur adversely affect the lead response of the gasolines. The new legislation on the lead content of gasolines therefore has a two-fold effect. It caused a fifty percent reduction in the amount of lead alkyl used, but owing to the antagonistic effect of sulphur compounds on the "anti-knock" action of the lead compounds, it called also for a reduction in the sulphur content of crude oils. In recent years, a number of desulphurisation processes have been developed in order to remove as much sulphur as possible from crude oils. The percentage of sulphur present in such oils varies considerably and is dependent on the source of the crude. Oils from some Mexican fields may contain as much as 5%S, compared with some Argentinian crudes which have as little as 0.1%S[10]. Low-sulphur crudes usually command a higher price on the world market.

The present project compares the effects of different sulphur compounds on leaded primary reference fuels, including particularly their ability to reduce the octane numbers. The work involved initially the measurement of the "knock" characteristics of the leaded fuels in the Co-operative Fuel Research Engine, in the absence and presence of the sulphur compounds. Studies were also undertaken of the oxidation characteristics of the sulphur compounds under laboratory conditions and of their effects on the ignition limits of isooctane in the absence and presence of lead. Sulphur compounds interact with the lead alkyls present in gasolines, rendering them less effective in reducing "knock". Attempts are made to postulate mechanisms for these lead-sulphur interactions.

1.2. Knock phenomena.

The phenomenon of "knock" in spark ignition engines was discovered as early as 1882[11], but its importance as a factor which limits the power output and the economy of engines was not realised until World War I, when these engines were developed for flying. In the twenty years following the war, a great deal of work was done to combat the occurrence of "knock", mainly by improvements in engine design and careful choice of fuels[12].

During the combustion of a fuel at constant volume, a considerable pressure rise occurs. This is partly due to the chemical interaction of the fuel and oxygen molecules to yield a larger number of smaller product molecules, such as carbon dioxide and steam. It is also partly attributable to the accompanying large heat release, which results in a sharp rise in temperature. This dramatic pressure rise accompanying explosion of the fuel-oxygen mixture is in a sense the basis of spark ignition engines.

In these engines a fuel air mixture is compressed by the movement of a piston in a cylinder. Towards the end of the compression stroke, a flame is initiated by a spark from one or more of the sparking plugs. This flame spreads rapidly through the compressed gas mixture and should theoretically produce a smooth rise in pressure. The high pressure developed then pushes down the piston and power is produced. In some cases, however the pressure rises suddenly rather than smoothly and, when this occurs, a noise like a series of hammer-like blows may be heard which is referred to as "knock". This "knocking" explosion can occasionally be violent enough to lead to mechanical damage. Even if no damage occurs, however, there is a considerable loss of heat to the cylinder walls which results in decreased efficiency.

Kinetic studies of hydrocarbon combustion [13-16] show that this reaction has all the characteristics of a free-radical chain reaction (Sect.1.3.1.). When such a chain starts to propagate, it will continue until termination occurs, generally as a result of the destruction of the chain-carriers at the walls. If chain-termination takes place as rapidly as chain-propagation, slow controlled combustion occurs. If however, destruction of the chain-carriers is not as efficient as their multiplication, a stage is reached when the number of chains starts to increase rapidly, so that the reaction eventually takes place almost infinitely rapidly and thus with sudden violence. Photographic and spectrographic studies[15, 16] have shown that, during normal combustion in a gasoline engine, a narrow ideally convex combustion wave travels from the sparking plugs across the combustion chamber at a fairly constant rate. Under "knocking" conditions, the flame front is altered only during the burning of the last part of the charge and travels much faster. "Knocking" therefore occurs only after most of the fuel has undergone controlled combustion.

The most commonly accepted theory of

"knock" assumes that the advancing flame front compresses the unburnt charge, raising its temperature and pressure. When certain critical temperature and pressure conditions are exceeded, an autocatalytic reaction takes place in the unburnt charge ahead of the flame front, eventually becoming so rapid that self-ignition occurs before combustion can be completed in an orderly manner. This results in a sudden pressure rise as shock waves are set up. These have a much higher velocity than in a normal flame, and the same frequency as the sound associated with "knock"[17].

The explosive combustion which gives rise to "knock" normally occurs in the last part of the fuel-air mixture to burn[12,18,19], referred to as the "end-gas". This is the part furthest away from the point of initiation of the spark, and whether or not "knock" occurs is determined by a race between the advancing flame front and the reactivity of the fuel-air mixture in the "end-gas". The velocity of the normal flame spreading from the sparking plugs and the development of the pressure in the cylinder prior to the inflammation of the "end-gas" give no indication as to whether "knock" will take place. Its occurrence thus depends on the pressure-time relationship in the "end-gas".

1.3. Theory of "knock" reactions.

1.3.1. Mechanism of hydrocarbon combustion.

The gaseous oxidation of hydrocarbons proceeds via a complicated free radical chain mechanism involving degenerate chain branching[20]. In reactions of this kind, four types of elementary steps are involved, viz. chain initiation, chain propagation, chain branching and chain termination. For the branching process to be degenerate, the reciprocal of ϕ, the net branching factor, must exceed the average lifetime of the chain carriers. In other words, chain branching must be slow. Hydrocarbon combustion is therefore characterised by a non-branching propagation reaction, leading to a moderately stable product, which then slowly breaks down to generate further reactive chain carriers. When conditions are such that $\phi > 0$, the concentration of chain carriers increases exponentially, although at low temperatures, the first non-isothermal event is cool flame reaction.

In the following sections the combustion of alkanes is considered:

1.3.1.1. Chain Initiation.

This probably involves the abstraction of a hydrogen atom from the alkane by molecular oxygen[21], to yield an alkyl radical and a hydroperoxy radical (reaction 1):

$$C_nH_{2n+2} + O_2 \longrightarrow C_nH_{2n+1} + HO_2^{\bullet} \qquad (1).$$

Since the activation energy of this reaction is ca. 167-230kJ. mole^{-1}, it takes place relatively slowly and selectively. The ease with which C-H bonds are broken decreases in the order tertiary $>$ secondary $>$ primary.

1.3.1.2. Chain Propagation.

During this stage, the alkyl radical formed during the initiation step may follow several paths. It may, at least in principle, decompose, disproportionate, isomerise or react with either fuel or oxygen. In presence of oxygen, at temperatures below ca. 300°C, the predominant path of alkyl radicals is addition to yield an alkylperoxy radical, a reaction which requires virtually no activation energy[22]:

$$C_nH_{2n+1}^{\cdot} + O_2 \rightleftharpoons C_nH_{2n+1}OO^{\cdot} \qquad (2)$$

These radicals may then react further:

$$C_nH_{2n+1}OO^{\cdot} \rightleftharpoons {}^{\cdot}C_nH_{2n}OOH \qquad (3)$$

$${}^{\cdot}C_nH_{2n}OOH \longrightarrow \text{products} + {}^{\cdot}OH \qquad (4)$$

$$C_nH_{2n+2} + {}^{\cdot}OH \longrightarrow C_nH_{2n+1}^{\cdot} + H_2O \qquad (5)$$

Reaction (3) represents the isomerisation of an alkylperoxy radical, and involves the internal abstraction of a hydrogen atom and the formation of an O-H bond incorporating the outer oxygen atom of the peroxy group. The alkyl hydroperoxy radical formed in reaction (3) may then decompose to give rise to ketones, aldehydes or O-heterocyclics (depending on the molecular structure of the radical) together with an OH radical.

$${}^{\cdot}C_nH_{2n}OOH + O_2 \longrightarrow OOC_nH_{2n}OOH \qquad (6)$$

Reaction (6), involving the addition of oxygen to the alkyl hydroperoxy radical, may then compete with reaction (4) and is more likely to occur with α alkyl hydroperoxy radicals[23].

The abstraction of a hydrogen atom from an alkane by an OH radical (reaction (5)), which competes with the primary chain, requires a low activation energy ($E = 4.2\text{-}8.4\,\mathrm{kJ.mole^{-1}}$)[24]. However at higher temperatures ($> 400^\circ C$) reaction (7)

$$C_nH_{2n+1} + O_2 \longrightarrow C_nH_{2n} + HO_2^{\cdot} \qquad (7)$$

$$E = 29.3 - 41.9\ \mathrm{kJ.mole^{-1}}.$$

competes with reaction (2), and the initial $C_nH_{2n+1}OO^{\cdot}$ complex breaks down almost immediately to yield an HO_2 radical and an alkene.

1.3.1.3. Degenerate Chain Branching.

These reactions involve the thermal decomposition of peroxides, and account for the autocatalytic nature of hydrocarbon combustion. Monohydroperoxides may in certain cases be formed by reaction (8)

$$C_nH_{2n+1}OO^{\cdot} + C_nH_{2n+2} \longrightarrow C_nH_{2n+1}OOH + C_nH_{2n+1}^{\cdot} \quad (8)$$

which competes with reaction (3), and these peroxides may then decompose by reaction (9)

$$C_nH_{2n+1}OOH \longrightarrow C_nH_{2n+1}O^{\cdot} + {}^{\cdot}OH\ (E > 146.5\mathrm{kJ.mole^{-1}}) \quad (9)$$

to give an alkoxy radical and a hydroxyl radical. When sufficiently labile hydrogen atoms are present (e.g. as in aldehydes), reaction (10)

$$C_nH_{2n+1}OO^{\cdot} + AH \longrightarrow C_nH_{2n+1}OOH + {}^{\cdot}A \quad (10)$$

may be more important than reaction (8).

Dihydroperoxyalkyl radicals may be formed by reaction (11)

$${}^{\cdot}OOC_nH_{2n}OOH + C_nH_{2n+2} \longrightarrow HOOC_nH_{2n}OOH + C_nH_{2n+1} \quad (11)$$

and these compounds may decompose according to reaction (12)

$$HOOC_nH_{2n}OOH \longrightarrow \text{carbonyl compounds} + 2{}^{\cdot}OH \quad (12)$$

to give carbonyl compounds and hydroxyl radicals.

1.3.1.4 Chain Termination.

Termination of chains may occur both by homogeneous radical-radical interactions (15 -17)

$$2C_nH_{2n+1}OO^{\cdot} \longrightarrow C_nH_{2n+1}OOH + C_nH_{2n} + O_2 \quad (15)$$

$$C_nH_{2n}OO^{\cdot} + {}^{\cdot}HO_2 \longrightarrow C_nH_{2n+1}OOH + O_2 \quad (16)$$

$$2HO_2{}^{\cdot} \longrightarrow H_2O_2 + O_2 \quad (17)$$

or by destruction of chain carriers at the walls.

1.3.2. Preflame Oxidation Reactions in Relation to "Knock".

The spontaneous combustion reactions occurring before spark ignition in the internal combustion engine are complex in nature and are usually accompanied by the release of a considerable proportion of the heat of combustion. A substantial part of the reactions occurs during the compression stroke and these continue until the spark-induced flame takes over. Variations in the extent of preflame reactions do not alter the total energy released in combustion, but they do affect the timing of its distribution throughout the cycle and thus influence engine performance.

Studies of these reactions have been carried out in open tubes and bombs[21,25,26], motored and rapid compression devices[27-30], by gas sampling from fired engines[31,32] and by flame photometry[33]. In a fired engine with a delayed spark, a heptane-isooctane fuel may lose 10-27% of its calorific value through precombustion reactions[27-34]. In a motored engine with a compression ratio of 10:1, approximately 52% of a 3:1 isooctane -heptane mixture was converted to other products during precombustion reactions[28,29].

The preflame region is therefore one of intense chemical activity. Cracking, dehydrogenation, polymerisation of oxidation products and formation of various acids, alcohols, aldehydes, ketones and peroxides may all occur[31]. As a result, investigation of precombustion reactions in the internal combustion engine is difficult, since these reactions occur in the fuel-air mixture ahead of the normal flame and prior to the occurrence of "knock". These reactions usually proceed in a step-wise manner and give rise to a variety of intermediate products. The precise chemical mechanism is not well defined, since the reactions occur very rapidly and many of the intermediates formed are unstable.

The chemical reactions preceding "knock" may be divided into two classes: (1) those called precombustion reactions which are characterised by the evolution of substantial heat and light and by a high pressure rise, but do not lead to complete combustion; and (2) those referred to as pre-cool flame combustion reactions which are not accompanied by any appreciable energy release, and are usually detected by absorption spectroscopy[35].

A motored and a fired engine were used to study precombustion reactions[35]. A fuel-air mixture was introduced into the motored engine via a conventional co-operative fuel research carburettor, and the exit gases from this engine, containing the products of the precombustion reactions, were then passed to the intake manifold of the fired engine. The results obtained suggested that, in the motored engine below a critical compression ratio (c.c.r.), the "antiknock" quality of the exit gases decreases and then, for some fuels, increases to a value exceeding that for mixtures where the compression ratio of the motored engine is below the limiting value.

Four types of behaviour were therefore distinguished in the motored engine. The first was characterised by no change in the "knocking" tendency of the exit gases, so that the engine was functioning merely as a pump to supply fuel to the fired engine, without any change in the chemical nature of the fuel-air mixture. In the second type, the exit gases from the first engine decreased in "anti-knock" quality as the compression ratio of the engine was increased; chemical reactions were now occurring which gave rise to "knock-inducing" products. In the third type of behaviour, as the compression ratio of the motored engine was further increased, there was an increase in "anti-knock" quality of the exit gases: it was suggested[35] that, since the fuel was undergoing partial oxidation in the first engine, the exit gases entering the second engine had a lower heat of combustion. An alternative possible explanation was that water vapour and other products tended to decrease "knock" in the fired engine. The fourth and final type was characterised by autoignition in the motored engine with the result that no "knock" rating could be measured in the fired engine.

The fuels used in this experimental work involved mixtures of isooctane and diisobutylene in heptane. With mixtures containing 0-100% isooctane the first, second and fourth types of behaviour were exhibited. With mixtures containing more than 90% isooctane, the third type became evident, since isooctane can tolerate high concentrations of proknock material without the occurrence of autoignition. The limiting compression ratio was therefore related to the concentrations of isooctane and heptane in the fuel blend. With the diisobutylene blend, the diisobutylene appeared to have a greater ability to suppress the higher reactivity of heptane.

In similar work carried out in a motored engine, a probe was used in the exhaust manifold to obtain samples of the exhaust gases[32]. These were analysed for peroxides, carbonyl compounds, unsaturated compounds and other stable intermediates. The engine conditions used in this investigation varied from those producing no observable reaction to those producing autoignition. Four fuels were used in this study, heptane, isooctane, diisobutylene and benzene. Heptane, which is very "knock-prone", formed large amounts of partial oxidation products, particularly higher aldehydes and ketones, unsaturated compounds, hydrogen peroxide and formaldehyde, prior to the onset of autoignition. Isooctane, which is very "knock" resistant, formed only limited amounts of these intermediates. With diisobutylene, an inhibiting action appeared to be present in the initial stages of the oxidation process and this is believed to be due to the activity of the double bond in deactivating the radicals necessary for the continued attack on unchanged diisobutylene. This inhibiting action probably explains the good blending characteristics of diisobutylene, in that it inhibits not only its own oxidation, but the oxidation of any hydrocarbon with which it is blended. Benzene did not form any detectable intermediate products prior to autoignition, and the high resistance of this fuel to oxidation was attributed to the resonance stabilisation of the benzene ring. However, once oxidation was initiated, the reaction proceeded very rapidly.

Fundamental studies of the precombustion characteristics of fuels in an engine have also been carried out using spectrometric[35,36] and photographic analysis[37,38], and by pressure and radiation measurements[39]. Analyses were difficult to make due to the small sample sizes and to the rapid completion of many of the constituent reactions before analysis. From absorption spectra studies, it was found that the chemical changes occurring during the preflame period are greater in "knocking" than in "non-knocking" combustion. Similar studies[40] of the end gas were made by passing a continuous light source through two quartz windows on opposite sides of the combustion chamber. Formaldehyde was always detected in the charge which was about to "knock", and the amount increased as the "knock" intensity increased. If it was not detected, "knock" did not occur.

1.3.3. Hydrocarbon Combustion Phenomena.

The non-isothermal oxidation of a hydrocarbon taking place in a closed vessel is usually accompanied by a transient pressure change, whose characteristics serve to classify the various types of combustion behaviour. These may be divided into four main classes:

(1) Slow combustion - an almost isothermal process which gives rise to a small and gradual pressure increase.

(2) Single or Multiple cool flames - pressure fluctuations superimposed on slow combustion.

(3) Two stage-ignition - a cool flame followed by a large pressure pulse which represents an explosive consumption of reactants.

(4) Single stage ignition - a large pressure pulse

representing explosive reactant consumption.

The variation with temperature and pressure of the several types of combustion behaviour leads to a complex ignition profile which exhibits distinct "high" and "low" temperature regions. Figure 1.1 shows a simplified ignition profile for hydrocarbon combustion.

1.3.3.1. The "low-temperature" region ($< 350^{\circ}$C)

In a static system, this region is associated with cool flames, and ignition is a two-stage process, the propagation of a cool flame being followed by that of a hot flame. At pressures too low for ignition, cool flames still propagate.

The "low-temperature" region may be divided into several regions. As the temperature is increased, the pressure required for ignition sometimes passes through several minimum and maximum values, and the region surrounding a particular minimum is referred to as a "lobe". The existence of several lobes shows that the cool flame region is a complex kinetic system and this complexity is also shown by the formation of periodic cool flames. In fuel oxidant mixtures of suitable pressure, temperature and composition, several cool flames may propagate, one following each other after a discrete time interval, during which little reaction occurs.

1.3.3.1.1. Factors affecting cool flame formation.

The precise nature and position of the temperature/pressure ignition profile for hydrocarbon oxidation depends on the experimental conditions. Factors such as the nature and amount of oxidant, the nature and extent of the containing vessel surface and the molecular structure of the fuel affect the ease and extent of cool flame reaction.

1.3.3.1.1.1. The oxidant.

During the combustion of hydrocarbons in air or oxygen, cool flames are found. The temperature range for these cool flames is slightly higher for the reaction of a given fuel with air, than for reaction with oxygen. The major difference between the two oxidants however, is the pressure range within which the limiting profiles of two-stage ignition and cool flames lie. In combustion with oxygen, the limits of "low-temperature" oxidation are lower than with air, although the phenomena are otherwise similar[21].

The amount of oxidant present affects the properties of the cool flames, the intensity of these flames increasing with the proportion of fuel present, since the intensity is related to the heat release. Although the quantitative properties of these flames are dependent on the nature of the oxidant and on mixture composition, the chemical processes involved are independent of these factors.

1.3.3.1.1.2. The nature of the reaction vessel.

The nature of the reaction vessel has a profound effect on the rates of hydrocarbon oxidation. At low pressures, the predominant chain termination steps in such reactions are heterogeneous, involving the removal at the wall of chain carriers and/or branching agents to give inactive products. The nature and amounts of the minor products can also depend on the nature of the reaction vessel surface[41].

In metal reaction vessels, the spontaneous ignition pressure of a heptane-air mixture at 505°C has been found to be considerably higher than those in glass vessels of corresponding size and shape[42]. The limiting ignition pressure of a hydrocarbon fuel was also found to be different for the same reaction vessel depending on whether the surface was rough or smooth[43]. The effects of coating glass vessels with alkali halides on the combustion of different hydrocarbon fuels have also been studied. Propane and heptane oxidation were unaffected by the presence of a KCl surface[43,44], whereas the cool flames of cyclohexane were inhibited[45]. Surface coatings of lead oxide also suppressed cool flame reactions[43,45,46]. Studies of the slow oxidation of methane in PbO-coated, heat-treated, HF-treated and aged silica vessels indicate that the various surfaces differentially destroyed the important HO_2 and H_2O_2[47-49].

1.3.3.1.1.3. The extent of the vessel surface.

The surface to volume ratio (S/V) of a reaction vessel is used to correlate the spontaneous ignition pressure of a particular compound with the size and shape of the vessel. Variations in the reported values of the spontaneous ignition temperatures of a given compound are due mainly to differences in the S/V ratios of the vessels employed by the various investigators.

Detailed studies of the combustion of ten hydrocarbons in a number of different quartz reaction vessels[22] have shown that the main effects of increasing the S/V ratio are as follows: (a) slow reaction is inhibited in the earlier stages but promoted in subsequent stages; (b) ignition is strongly inhibited. Inhibition in the early stages of reaction is due to chemisorption of OH and HO_2 radicals on the reaction vessel surface. This continues until all the active sites have been "hydroxylated" and promotion then occurs as a result of hydrogen bonding between surface hydroxyl groups and RO_2 radicals, leading to decomposition of the latter to yield more reactive $RO^{\cdot}$ radicals. Inhibition of ignition is believed to be due mainly to the heterogeneous destruction of hydrogen atoms.

1.3.3.1.2. Chemical products of cool flames.

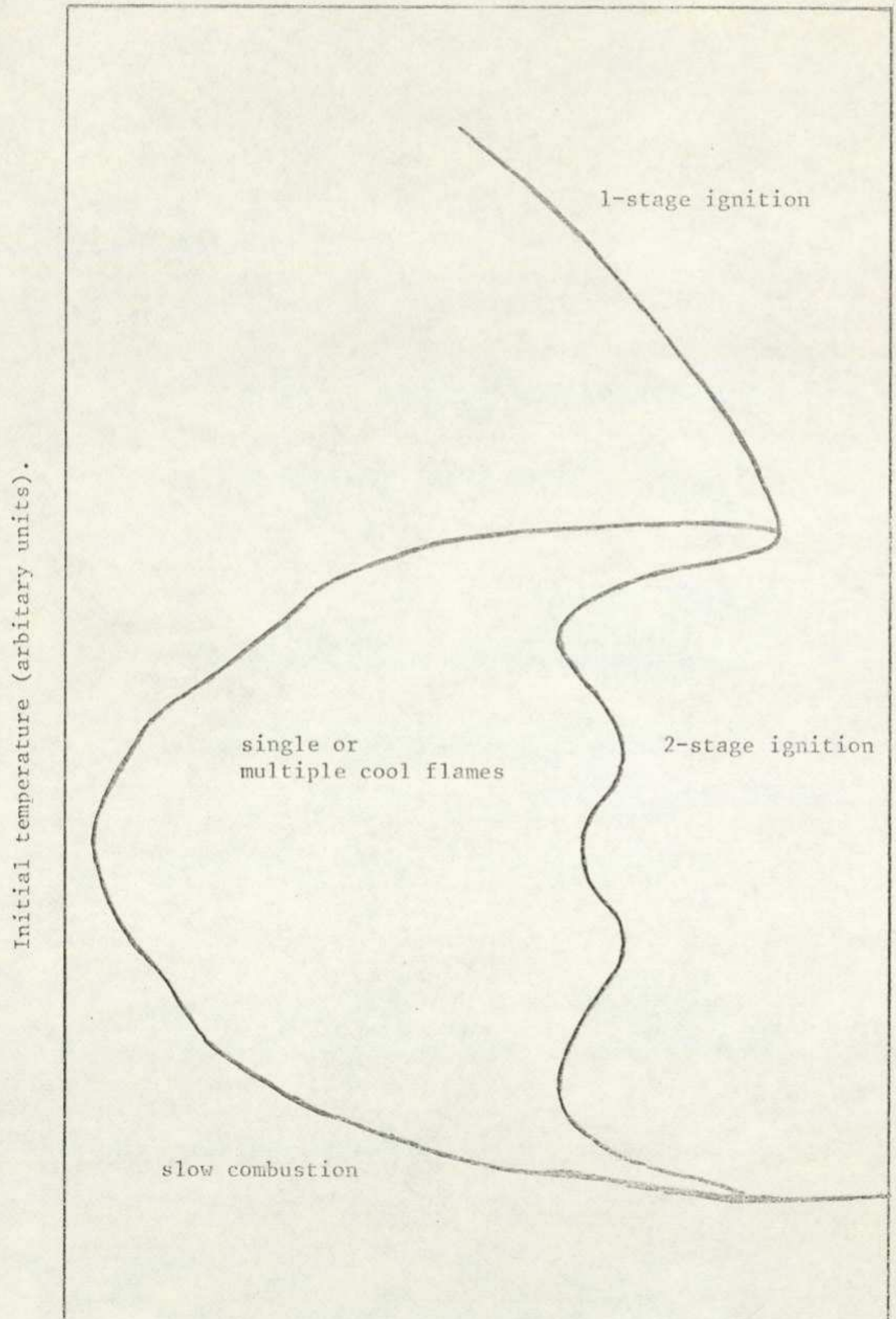
Oxidation of hydrocarbons in the cool flame region produces a wide variety of moderately stable or stable products such as alkenes, alcohols, saturated and unsaturated aldehydes and ketones, and O-heterocyclic compounds[23]. Organic peroxides are also important products of cool flame combustion and these may include unsaturated hydroperoxides and alkane dihydroperoxides. In addition to the many organic products, oxides of carbon and water are formed, the amounts increasing with the availability of oxygen. At temperatures above the maximum for cool flame formation, the yields of oxygenated organic products gradually decrease, while those of alkenes and hydrogen peroxide increase.

Several studies of hydrocarbon oxidation[50,51] describe the phenomena occurring during "low temperature" combustion, and these have been substantiated[52]. The formation of cool flames and ultimate ignition seem to depend on the prior formation of a critical concentration of aldehydes. The character of the pressure-time curve for oxidation in the cool flame region (Fig.1.1) and the variation with time of the products obtained, show that the cool flame is a temporary interruption of normal combustion. During the passage of a cool flame, the amounts of formaldehyde and higher aldehydes tend to increase, while the concentration of organic peroxides frequently drops but builds up between each successive flame. Whereas the concentration of organic peroxides increases up to the position of the cool flame and then drops to zero, hydrogen peroxide starts to be formed just before the flame and its concentration rises rapidly. Thus the total peroxide concentration continues to rise on passing through the cool flame region. After the passage of the cool flame, there is a relatively high proportion of aldehydes, especially formaldehyde, in the reaction mixture.

During the highly exothermic second stage of ignition, the wide variety of oxygenated products formed in the cool flame region is destroyed. In contrast, the concentrations of water, oxides of carbon and smaller hydrocarbons increase.

Figure 1.1

A typical ignition diagram for a hydrocarbon-oxygen mixture.



1.3.3.2. The "high-temperature" region (> 350°C)

In this region, ignition is a one-stage process and cool flames do not propagate at pressures too low for ignition. With certain fuels e.g. formaldehyde[53] and methane[54], preignition glows and pressure pulses have been observed.

1.3.3.2.1. Spontaneous ignition.

In a static system, the spontaneous ignition of a gas mixture is accompanied by the release of a large amount of heat and a sudden increase in the number of molecules present. When the temperature of the containing vessel is below the spontaneous ignition temperature of the gas mixture, slow combustion reactions take place accompanied by a slow release of heat, which is quickly dissipated through the gas and lost at the vessel walls. When the temperature of the reaction vessel is raised to the spontaneous ignition temperature of the gas mixture, the rate of heat release becomes greater than the rate of heat dissipation, causing self-heating of the gases and self-acceleration of the reaction, which results in autoignition.

The spontaneous ignition temperature is therefore the temperature to which a combustible gas mixture must be heated for the gas to ignite. Studies of the spontaneous ignition tendencies of such mixtures have shown that ignition occurs more rapidly in large spherical vessels than in vessels of any other size or shape[55]. Variations in the reported values of spontaneous ignition temperatures for hydrocarbons are often largely due to the different sizes and shapes of the containing vessels.

1.3.3.2.2. Products of spontaneous ignition reactions.

The products formed during autoignition are similar to those formed during two-stage ignition in the "low temperature" region, being mainly oxides of carbon and water. In the presence of excess fuel, some low-molecular-weight hydrocarbons are also formed.

1.3.4. Hydrocarbon oxidation in relation to "knock".

Most fuels "knock" by a "low-temperature" ignition mechanism[31] and are therefore associated with cool-flame and two-stage ignition reactions. At the pressure corresponding to the tip of the envelope of the "low-temperature" ignition peninsula, "knock" rating varies with fuel structure. The higher the pressure at the tip (in ignition profiles plotted under comparable conditions), the greater in general is the "knock" rating. Methane and benzene therefore have high "knock" ratings, since they do not show the presence of cool flames or two-stage ignitions.

The "knock" resistance of a fuel corresponds therefore to its ability to resist cool flame formation[56]. Cool flames arise when the net branching factor (ϕ) is sufficiently great. The less prone a hydrocarbon is to cool flame formation i.e. $\phi = 0$, the more "knock" resistant it is. The "antiknock" characteristics of hydrocarbons are therefore associated with their relative resistance to preflame oxidation and these are in turn determined by their differences in molecular structure[57].

1.4. Relation of hydrocarbon structure to "knock".

As early as 1920, marked variations were observed in the ease of combustion of different hydrocarbon fuels in the internal combustion engine. Ricardo[58] published results on the determination of the highest useful compression ratio of a number of hydrocarbons, and found wide variations in the values for different fuels. Data published on an extended series of pure alkanes and alkenes showed a number of consistent and regular relationships between the molecular structure and the tendency to "knock". Measurements were also made on blends of alkenes[59], cycloalkanes and aromatic hydrocarbons[60] and in 1934, extensive information was published on the behaviour of approximately one hundred hydrocarbons[61].

In the examination of any relationship between structure and the "knocking" tendency of hydrocarbons, it is convenient to divide the hydrocarbons into chemical classes and to consider each class separately. It is necessary to have a common basis for comparison or alternatively some set of engine conditions under which all measurements are made. Compounds of a particular chemical class behave similarly when conditions are changed, but when different classes are compared, attention should be paid to the engine operating conditions under which the comparison is made.

The most outstanding feature of the relationship between hydrocarbon structure and "knock" characteristics is the effect of isomerism within the same chemical class. Differences in the tendency to "knock" among isomers may be so great as to cover almost the whole known range of freedom from "knock" and may be equivalent to enormous variations in the power to be obtained from a fuel in a suitable engine. A review published by Lovell[62] tabulated results for the "knocking" characteristics of a large number of hydrocarbons of different classes.

Empirical relationships between structure and tendency to "knock" show that the compounds which are most prone to "knock" have long unbranched carbon chains. Branching of the chains produces "knock" resistance. Ring compounds "knock" less readily than compounds with unbranched carbon chain and unsaturation in a straight carbon chain also tends to prevent "knock", especially if the double bond is centralised in the molecule. The fuels which are least prone to "knock" are thus those with compact molecular structures. The fundamental relationship between structure and "knock" tendency depends of course on the rates of oxidation of these hydrocarbons under engine conditions.

A method of correlating the "knock" rating of hydrocarbons with their chemical structure was formulated by Livingston[63]. This correlation was based on the use of a standard retardation factor. The resistance of hydrocarbons to "knock" is a function of structural factors, which are dependent on electronic effects contributed by retarding groups such as the methyl group. This method of correlation met with a considerable measure of success and emphasised the importance of the initial oxidation reaction in the series of reactions which lead to "knock"[63].

1.4.1. "Knock" characteristics of alkanes.

The alkanes as a class have been studied very fully. The effect of isomerism is very marked within this class of compound, n-octane and isooctane being typical examples. The effect of branching in isooctane has the effect of increasing the value of the compound by more than the entire octane scale. The two most salient facts about the "knocking" tendencies of alkanes may therefore be summarised as follows: (1) the "knock" rating decreases as the unbroken carbon chain is lengthened, and (2) the tendency to "knock" decreases as the extent of branching increases.

There is a fairly consistent and regular decrease in the critical compression ratio of the alkanes from methane to n-heptane. This rule may presumably be applied to higher alkanes as inferred by measurements made with mixtures, since straight chain alkanes longer than n-heptane are so prone to "knock" that it is difficult to study them in the pure state.

1.4.1.1 Ring closure.

Cyclisation of the alkanes to yield cycloalkanes increases the critical compression ratio and so increases the "knock" rating. The cyclopentanes form a very interesting class. When a single unbranched side chain is added to the ring, the critical compression ratio decreases progressively with increasing length of the side chain. Branching of the side chain in an isomeric series increases the critical compression ratio considerably, the effect being similar to that observed with straight chain alkanes. The simple ring compound is more resistant to "knock" than the isomeric straight chain alkene or the corresponding alkane. Similar conclusions can be drawn for cyclohexane although this compound has less resistant to "knock" than cyclopentane, "knock" resistance decreasing with increased size of the ring.

1.4.2. <u>"Knock" characteristics of alkenes.</u>

Alkenes form a very interesting group of chemical compounds, mainly due to the fact that they include a number of isomers boiling within the gasoline range. These compounds are however difficult to prepare in a pure state and tend to be unstable during storage.

1.4.2.1 <u>Straight-chain alkenes.</u>

The simplest method of considering the straight-chain alkenes is to compare them with the corresponding alkanes. There is a progressive decrease in the critical compression ratio of alkenes as the number of carbon atoms in the chain increases. This decrease is not however as great as that for alkanes. As a result of this decrease, the alkenes lighter than butenes appear to have a lower critical compression ratio than the corresponding alkanes, while the reverse is true for alkenes heavier than butenes.

The introduction therefore of a double bond into a straight chain alkane of higher molecular weight than butane results in an increase in the critical compression ratio. The extent of this increase varies with the position of the double bond in a straight chain alkene, and is greater, the closer the double bond is to the centre of the molecule. Centralisation of the double bond in the straight chain alkenes therefore produces an increased "knock" rating.

1.4.2.2. Branched chain alkenes.

The introduction of a double bond into an alkane to form a branched-chain alkene might be expected, by analogy with the straight-chain alkenes, to increase the critical compression ratio, the extent of the increase depending upon the position of the double bond. Studies of the branched-chain alkenes generally confirm this. However, if the resistance to "knock" of the parent alkane is very high, the introduction of a double bond may decrease rather than increase this resistance.

1.4.3. "Knock" characteristics of aromatic hydrocarbons.

The aromatic hydrocarbons are an interesting class of compounds because, in addition to being very sensitive, almost all lie within the gasoline boiling range, have an octane number of over 100, and exhibit a considerable effect of position isomerism on "knock" characteristics. A survey was made of the "antiknock" effect of aromatic compounds in the internal combustion engine, and a correlation was established between the "antiknock" effect of aromatics and the influence of side chains on the electronic properties of the benzene ring.

The site of the "antiknock" property of aromatic compounds is the benzene ring, side groups merely increasing or decreasing the reactivity of the ring. The "antiknock" effect of benzene derivatives is therefore related to the electronic properties of the side chains, if allowance is made for the complicating effects of pyrolysis and oxidation of the compounds.

Work was carried out by several investigators [64-66] on aromatic compounds and their "knocking" tendencies. Some disagreement between the various sets of results is evident, but in view of the different engine operating conditions, mixture strengths, etc. this is perhaps to be expected. Spires[66] showed that the "antiknock" effect of aromatic hydrocarbons increases in the order: benzene $<$ toluene $<$ ethylbenzene, and Callendar[64] and Boyd[65] showed that: benzyl alcohol $<$ benzene $<$ phenol. From a comparison of the results, it was concluded that, if the benzene derivative bears a positive charge relative to benzene, then the aromatic compound is a less effective "antiknock" than benzene; this is the case for example with benzyl alcohol, benzaldehyde and bromobenzene. With the exception of the halogens, groups which are ortho-and para-directing when present in substituted benzene, are "antiknock", while the reverse is true for meta-directing groups. Similarly simple side chains which activate the benzene ring give better "antiknock" properties than benzene, while those which deactivate the ring have the opposite effect.

Since the "antiknock" effect of aromatics is determined by the binding power of the π electrons of the benzene ring, the effect is one in which the molecules are unchanged. Simple aromatic compounds have, in general, considerable stability to pyrolysis and oxidation, whereas many aliphatic compounds decompose and oxidise at relatively low temperatures i.e. ca.250°C.

In order to exert their "antiknock" effect, the lead alkyls have to decompose and/or be oxidised. In contrast, simple aromatics exert their antiknock effect as whole molecules. If decomposition does occur, then a reduced "antiknock" or even a "proknock" effect will result. This may result from fragmentation of the side chain which splits off, having profound effects on "knock" reactions. The correlation with the properties of the benzene ring can no longer hold in these cases. Therefore, as the length or complexity of the side chain is increased, its tendency to split or oxidise is increased, and deviations from the correlation of "knock" effect and ring properties occur.

1.5. Physical factors involved in "knock".

The occurrence of "knock" is dependent on several physical factors, viz. compression ratio of the engine, ignition timing, temperature, speed, load and mixture strength.

1.5.1. Compression ratio.

The compression ratio is the ratio of the volume of air and fuel when the piston is at the lower end of the cylinder (bottom dead centre) to that when the mixture is fully compressed and the piston is at the top end (top dead centre). This ratio affects the performance of the engine more than any other factor and an increase in it tends to make the fuel "knock". The higher the compression ratio, the higher is the thermal efficiency, that is the ratio of power obtained from the engine to the maximum power available from combustion of the fuel.

From thermodynamic considerations, the thermal efficiency of internal combustion engines is a function of the compression ratio, and it increases with increasing compression ratio, according to the relationship:

$$E = (1 - 1/r)^{y-1} \qquad (18)$$

where E = thermal efficiency

r = compression ratio

y = ratio of the specific heats of the working fluid at constant pressure and constant volume.

This theoretical equation assumes that air is the working fluid, that it behaves as a perfect gas and that there is no heat loss. In practice, if y is replaced by an experimentally determined figure, an acceptable relationship is obtained between thermal efficiency and compression ratio. The actual thermal efficiency and the influence of compression ratio vary from engine to engine.

Figure 1.2 Effect of compression ratio on brake thermal efficiency.

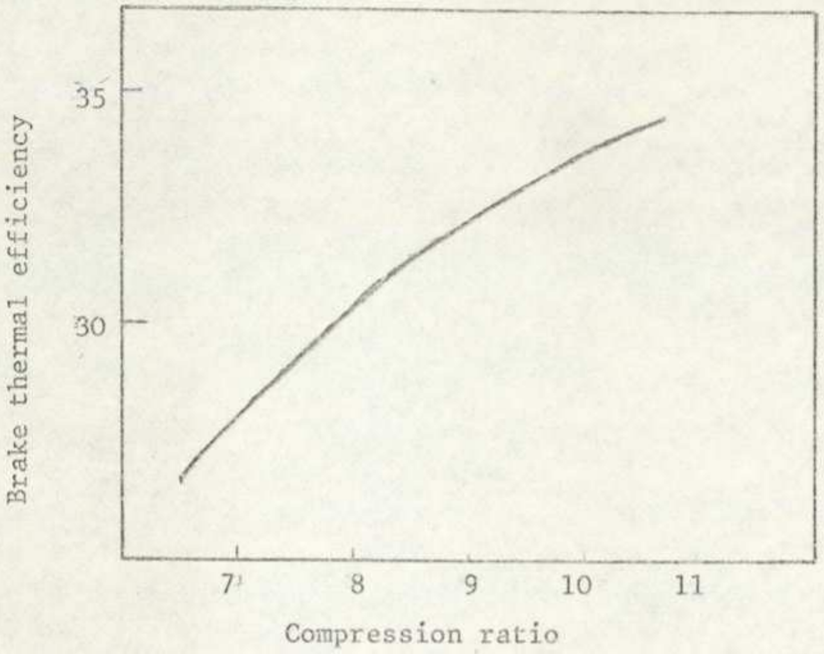


Figure 1.2 shows a typical curve obtained when compression ratios are changed in a conventional engine. An improvement in thermal efficiency gives rise to greater power output for the same size of engine or to an improved fuel economy at the same power output.

The limiting compression ratio which can be used in an engine is set by the "knock" characteristics of the fuel and is usually referred to as the highest useful compression ratio (h.u.c.r.). An increase in the compression ratio reduces the "knock" resistance of fuels. However an increase in the octane number of the fuel permits the use of higher compression ratios, giving more power, higher efficiency and lower fuel consumption. There is no advantage in increasing the octane number beyond that necessary to give "knock-free" performance.

1.5.2. Ignition timing.

The tendency of a fuel to "knock" increases as the spark advance is increased, since preflame reactions are likely to have proceeded further, so that the "end-gas" reactions reach explosive proportions before the spark can engulf it.

1.5.3. Temperature.

An increase in engine temperature increases the tendency to "knock". The Motor Octane Method used in the determination of octane numbers in the Co-operative Fuel Research Engine has a much higher charge temperature than the Research Octane Method and as a result, most fuels have lower motor octane numbers than research octane numbers. Fuels of low sensitivity to "knock" are influenced by temperature to a smaller extent than fuels of high sensitivity.

1.5.4. Engine speed.

An increase in engine speed normally reduces the "knocking" tendency of a fuel because less time is available for preflame reactions to occur and also because increased turbulence in the charge accelerates complete combustion. However, in modern cars the timing of the spark advances as the engine speed increases in order to ensure maximum power is obtained in all speed ranges, so that high-speed operation can sometimes be as critical as low-speed operation.

1.5.5. Load.

Increasing the load increases engine temperatures and end gas pressure and as a result "knock" increases.

1.5.6. Mixture strength.

The tendency of a fuel to "knock" varies with mixture strength and is greatest with a fuel to air ratio of 13.5:1. The mixture strength for maximum "knock" varies however from fuel to fuel.

1.6. "Knock" rating of motor fuels.

1.6.1. The octane scale.

Before the evolution of the octane scale, laboratories "knock-rated" fuels in terms of their chemical composition, giving the lowest rating to the normal alkanes. In 1926, Edgar[67] discovered the importance of branched chain alkanes with respect to "knock", and his work helped to clarify the importance of the effect of fuel structure on "knock". Further investigations were carried out of the use of fuel scales for the purpose of "knock-rating" fuels, and benzene and synthetic octane were originally chosen for the upper and lower limits respectively of an arbitrary fuel scale. However, when the high "antiknock" properties of isooctane were realised, this compound was used as the upper limit of the scale and heptane replaced octane at the lower limit of the scale, on account of the latter compound's similarity in properties to hydrocarbons present in gasolines. The results of this work led to the adoption of the octane scale by the Co-operative Fuel Research Council, and the development of the Co-operative Fuel Research Engine for the determination of octane numbers of gasolines.

The octane scale is used to express the "antiknock" quality of motor fuels and of gasoline stocks from which they are made. The scale below 100 is based upon the different "knocking" tendencies of two pure hydrocarbons of almost similar boiling points, isooctane and heptane. Heptane is assigned an octane number of zero and isooctane a value of 100. By definition, therefore, the percentage by volume of isooctane in a blend of heptane is the octane number of a motor fuel with an octane number of less than 100. With the design of modern high-compression engines, octane numbers greater than 100 are sometimes required. The scale above 100 is based on an isooctane-tetraethyl lead relationship, a table of which can be found in the A.S.T.M. Manual for the rating of motor fuels[68].

Heptane and isooctane are referred to as primary reference fuels, and are not allowed to vary in their "antiknock" quality, or the scale of reference will not be fixed. Both primary reference fuels are made synthetically and are therefore expensive. As a result, secondary reference fuels are sometimes used. These are blends of specially selected gasolines of adequate stability on storage. In the engine studies carried out as part of this investigation, only primary reference blends were used for octane number determinations.

1.6.2. Methods for the determination of octane numbers.

The Co-operative Fuel Research (C.F.R.) engine uses the octane scale for the determination of the "knocking" tendencies of motor fuels. A description of this engine and its mode of operation is given in Section 2.1. There are two methods for rating fuels, the Research Method and the Motor Method.

The Research Method was the first to be universally adopted. However, after it had been in use for some years, the discrepancy between laboratory test results and the behaviour of fuels in service on road vehicles led to a series of road tests in the United States of America. From these the Motor Method was evolved and this was designed to approach more closely actual service conditions. The engine, instrumentation and general techniques used are the same in both methods. However, the engine operating conditions are slightly different. Table 1.1 shows a comparison of the operating conditions used in the two methods

The Motor Method uses a much higher mixture temperature, and operating conditions are generally more severe than in the Research Method, despite the increased engine speed. The ignition timing is varied in a similar way to the modern practice of using automatic ignition controls.

The Motor and Research Methods of rating fuels may give different results for the same fuel, and the value quoted must therefore be qualified by the type of test from which it is obtained. The Research Octane Number is usually greater than the Motor Octane Number. The difference between the two is known as the research appreciation and indicates the sensitivity of the fuel to temperature. Some fuels have the same value when determined by both methods but aromatics and cracked fuels are temperature sensitive.

Table 1.1. Comparison of Research and Motor Methods.

Title of method	Research	Motor
Date of adoption	1930	1932
Engine Speed (r.p.m.)	600	900
Coolant temperature (^{o}C)	100	100
Air intake temperature (^{o}C)	37.8 or 51.7	23.9-51.7
Mixture temperature (^{o}C)	ca. 32.2 (mild)	149 (severe)
Ignition timing	13^{o}	$19-46^{o}$ (variable)

1.7. "Knock" suppression.

Engine "knock" can be suppressed or at least minimized by various mechanical adjustments. Some of them are however undesirable from the standpoint of engine operation and include decreasing the manifold pressure, increasing the engine speed, retarding the ignition timing and changing the fuel to air ratio. Alteration of engine design may also be effective. For example, decreasing the compression ratio, increasing the turbulence of the charge, altering the shape of the combustion chamber and relocating the spark plugs may all have an influence. Most of these adjustments affect the time-temperature history of the unburnt charge[69].

A more effective method has been discovered for suppressing engine "knock", and this involves the use of "antiknock" additives, such as tetraethyl lead.

1.8. "Antiknock" additives.

Over the past forty years more efficient and powerful internal combustion engines have been designed, and as a result the compression ratio and octane requirements of these engines have been increasing. In order to achieve economically the required octane levels in commercial gasolines, "antiknock" additives are used. "Antiknock" agents or anti-detonants are substances which, when added to gasoline in small quantities, increase the "knock" resistance of the fuels. The most common "antiknock" additives are the lead alkyls, tetraethyl and tetramethyl lead. There are also a whole range of other lead alkyls which are commercially available; these include triethylmethyl lead $(C_2H_5)_3CH_3Pb$, diethyldimethyl lead $(C_2H_5)_2(CH_3)_2Pb$ and ethyltrimethyl lead $C_2H_5(CH_3)_3Pb$. In most cases however, blends of tetraethyl and tetramethyl lead are used to give the correct octane levels.

1.8.1. Alternative "antiknocks".

Tetraethyl lead was discovered to be a very powerful "antiknock" additive as early as 1922, and to date no cheaper additive has been found for increasing the octane number of motor gasolines. Several alternative "antiknock" compounds have recently been discovered but they all suffer from serious disadvantages. Iron pentacarbonyl is a good "antiknock" additive and is fairly economical to produce, but it suffers from one important disadvantage in that it decomposes to form abrasive iron oxide which leads to engine wear and short-circuiting of the sparking plugs. Another disadvantage is that this "antiknock" decomposes rapidly when the gasoline is exposed to light.

Methylcyclopentadienyl manganese tricarbonyl is another "antiknock" which is commercially available, but its production is too expensive for it to be considered as a replacement for the lead alkyls. However, when combined with the lead alkyls, this compound has a synergistic effect, so that the total amount of lead alkyl necessary to achieve the required octane level is reduced. This compound has the added disadvantage that "scavenging" the deposits after combustion is difficult.

Ashless "antiknocks" are also known, but have to be used in higher concentrations. Monoethylamine is one such "antiknock". This compound acts as an "antiknock" agent in its undecomposed form. However, if decomposition occurs too early in the combustion cycle, it may have a "proknock" effect. This amine type of "antiknock" additive has the additional disadvantage of toxicity.

Table 1.2 gives a representative list of "antiknock" compounds. Their effectiveness is expressed as a reciprocal of the number of molecules giving the same effect as one molecule of aniline. This gives a measure of their relative "antiknock" effectiveness.

Table 1.2 Relative effectiveness of "antiknock" compounds.

"Antiknock" compound	Reciprocal of number of moles giving "antiknock" effectiveness equal to one mole of aniline.
Tetraethyl lead	118
Dimethyldiethyl lead	115
Tetraphenyl lead	70
Iron carbonyl	50
Tetraethyl tin	4.0
Diphenyl amine	1.5
Aniline	1.0

1.8.2. Effect of fuel composition on lead susceptibility.

As small amounts of tetraethyl lead are added to a gasoline, the effectiveness of each successive addition decreases and there is therefore no advantage in using high concentrations of this additive. The effectiveness of tetraethyl lead in a gasoline is a function of the chemical composition of the gasoline as well as the conditions under which the gasoline is burnt.

Gasoline and individual hydrocarbons are characterised by their octane numbers as well as by the magnitude of their response, in octane number, to the addition of tetraethyl lead. Similar differences probably exist in relation to other "antiknock" agents. Several investigators[62,70,71] have reviewed the effect of tetraethyl lead on individual hydrocarbons, and have shown that alkanes (with the exception of a few highly branched compounds) respond favourably, giving a consistent 10% increase in power output. The increases obtained appear constant whatever the engine conditions, mild or severe. The effect of tetraethyl lead on cycloalkanes was similar to that with alkanes; with the cycloalkanes, the smaller the ring size, the higher the lead susceptibility.

The presence of TEL in an alkenic fuel also results in an increase in "antiknock" properties. However, the increase is not a constant percentage as in the case of alkanes and cycloalkanes Alkenic fuels are normally less responsive to the addition of lead, although the effects observed with some of the low-octane alkenes, chiefly the straight chain compounds with terminal double bonds, approach those found with the alkanes. However with high-octane alkenes (chiefly highly branched compounds), the response may be only a fraction of that obtained with alkanes or cycloalkanes of equivalent octane number. This poor response of the alkenes has been attributed to the deactivating effect of the double bond.

With aromatic hydrocarbons, a large variation in response to tetraethyl lead exists even between isomers, ranging from a negative effect to a positive one, and is sometimes as high as that found with alkanes. TEL is a mild "proknock" in benzene. Branching of the alkyl side chain is accompanied by a considerably lower lead response. In general, the more resistant a hydrocarbon is to "knock", the smaller is the response to lead additives.

The response of gasolines to TEL is dependent on a number of factors, such as the source, the degree of cracking, volatility, type and amount of refining and the presence of dissolved sulphur compounds. Two gasolines of the same octane rating may therefore respond differently to a given amount of lead. Straight-run gasolines are useful in making high "antiknock" fuels due to their good response to TEL. While the gasoline itself may have a low octane number, the small addition of TEL, required to bring it up to a certain standard value, often renders it more suitable premium gasoline stock than a less susceptible cracked gasoline. More volatile straight-run gasolines have higher octane numbers as well as higher lead susceptibilites than less volatile ones.

1.8.3. Mode of action of lead alkyls in "knock" suppression.

Although the "antiknock" effect of tetraethyl lead was discovered as early as 1922, its mode of action was not at all understood until nearly thirty years later. "Knock" is caused by pressure oscillations in the combustion chamber of the engine and results from the rapid release of chemical energy, which may occur following the spontaneous ignition of that portion of the charge ("end-gas") which has not been consumed by the advancing flame front[72]. Tetraethyl lead must in some way interfere with this sequence of reactions in suppressing "knock".

Since the introduction of tetraethyl lead as an "antiknock" agent in the internal combustion engine, several theories[73] have been proposed to explain the "antiknock" properties of this compound. These may be subdivided into two classes, those which characterise tetraethyl lead as a promoter of combustion and those which consider it as an inhibitor.

1.8.3.1. Promoter mechanisms.

It has been suggested that the ethyl radicals released during the decomposition of tetraethyl lead induce an oxidation of the degenerate branching type which competes with the cool flame reactions of the hydrocarbons. This results in a decrease of cool flame intensity and a consequent increase in the induction period preceding spontaneous ignition. Arguments against this theory are numerous, and evidence[31] obtained from experiments involving addition of compounds such as azomethane suggest that these radicals have a "proknock" and not an "antiknock" effect.

King[112] suggested that lead is continuously deposited on the combustion chamber walls, catalysing the "flameless oxidation" of the fuel to steam and carbon dioxide. The steam then causes a reduction in the flammability of the fuel. Badin[74] however attributed the promoter action to a primary pre-oxidation product of tetraethyl lead. This product serves as a "feeder" of peroxides into the reaction mixture, giving a gradual controlled oxidation, eliminating the relatively long induction period and rapidly accelerating reactions observed in "knocking" fuels. These theories have now been superseded by more realistic ones based on experimental work carried out in glass vessels and engines.

1.8.3.2. Inhibitor mechanisms.

It is now generally accepted that the active species involved in reactions leading to "knock" in the internal combustion engine are OH and HO_2 radicals. These act as chain carriers in the propagation of hydrocarbon oxidation at high temperatures. Destruction of these chain carriers would therefore inhibit "knock". The dramatic reduction in the concentrations of hydroperoxides and formaldehyde was the most significant change brought about by the addition of tetraethyl lead. Since radicals from the decomposition of organic peroxides are believed to be the precursors of hydrogen peroxide and formaldehyde, the observed effects suggest that tetraethyl lead is destroying these radicals. This radical destruction is one explanation for the "antiknock" effect of tetraethyl lead.

Callendar[75] was the first to suggest that TEL had an inhibiting effect on hydrocarbon oxidation, caused by the deposition of lead in "nuclear drops"; these then consumed the peroxides. Egerton and Gates[69] extended this theory by proposing that the active ingredient was lead peroxide, which then undergoes mutual reduction with the fuel peroxides, which would otherwise lead to "knock". The resultant lead oxide is "reperoxidised" by the available oxygen and the catalyst is regenerated. Several other early inhibition theories have been put forward[13,36], but they are mostly based on the assumption that the active "antiknock" species is molecular in nature.

Most of the experimental evidence obtained support the inhibitor theory of the action of tetraethyl lead. Examples are the definite increase in the self-ignition temperature of the fuels[76-78] and the decrease in the overall reaction rates of oxidation systems[79] in the presence of tetraethyl lead. The most convincing evidence is that supplied by Rifkin and co-workers[34], who showed that, in an engine operated with a delayed spark, there is, when tetraethyl lead is added, a small but definite increase in the preflame heat of release of a fuel and a corresponding postponement of auto-ignition. These facts cannot easily be reconciled with a promoter mechanism.

1.8.3.3. Mechanism of tetraethyl lead action.

The action of tetraethyl lead has been studied by two methods. One group of investigators studied the phenomena in conventional apparatus. These studies were impeded by inconsistent and irreproducible surface effects, the low volatility of tetraethyl lead and limitations imposed by the flammability of the hydrocarbon-air mixtures and the consequent necessity of working at low pressures. On account of these difficulties, other investigators carried out studies in engines. These also involved difficulties related to the problem of maintaining the same conditions from cycle to cycle.

It is generally accepted that lead alkyls decompose in the presence of oxygen to form lead oxide, which acts as the active species for "knock" suppression[91]. Norrish[80], on the basis of flash photolysis experiments, concluded that the mechanism of the "antiknock" action of tetraethyl lead is a homogeneous reaction taking place through the medium of gaseous lead oxide and gaseous lead. Several investigators[73,81] observed that the vapour from an arc struck between lead electrodes has a definite "antiknock" effect, and that colloidal particles of lead suspended in the fuel do not have any "antiknock" action[31,81]. The vapour from the lead arc consists of particles of metallic lead and lead monoxide and, since lead on its own has no effect, the "antiknock" action was assumed to be due to the lead monoxide. Walsh and his co-workers[48] contended however, that a "fog" of solid lead monoxide particles is formed in the engine as a result of the decomposition and oxidation of tetraethyl lead.

Norrish[82] argued that in an engine cycle there would be insufficient time for the TEL to form a "fog" of lead oxide particles and that the high pressures present in the engine would greatly impede the growth of solid particles. Wright[83] in his experimental work showed however, that it was possible for growth of particles to occur in the time available. Norrish's essential observation was that TEL additions increase the delay period before the growth of the concentration of hydroxyl radicals, and do so under conditions where a "fog" of solid particles cannot be formed It was therefore suggested[84] that TEL acts as an "antiknock" by a homogeneous mechanism.

Initially Norrish[13] suggested that gaseous lead atoms are responsible for the inhibiting effect of TEL via the following reactions:

$$Pb + OH \longrightarrow PbOH \qquad (19)$$

$$PbOH + OH \longrightarrow PbO + H_2O \quad (20)$$

the lead monoxide then being reconverted to lead atoms by the reaction:

$$PbO + R \longrightarrow RO + Pb \qquad (21)$$

After further experimental work[73,81], this mechanism was revised to:

$$PbO + OH \longrightarrow PbO(OH) \qquad (22)$$

$$PbO(OH) + OH \longrightarrow PbO_2 + H_2O \ (23)$$

$$PbO_2 + R \longrightarrow PbO + RO \qquad (24)$$

According to these later suggestions[85], gaseous lead monoxide molecules are the species responsible for the inhibiting effect. These reactions are not particularly convincing, since lead monoxide is not an established vapour phase species. The flash photolysis experiments carried out were not correlated with engine studies.

Walsh and co-workers[31,79] maintain that a "fog" of lead oxide particles is formed when TEL decomposes, thereby providing a surface on which the active OH and HO_2 radicals are destroyed. "Low-temperature" oxidation studies on several organic fuels e.g. diisopropyl ether and methane[79,86], butane[87] and hexane[88], have shown that lead oxide surfaces inhibit combustion and raise the cool-flame and ignition limits to higher temperatures. The tendency of a fuel to "knock" is related to its "low-temperature" ignition profile[89,90] and experiments also show that two-stage ignition in an engine is similar to that observed at low pressures. All this evidence suggests that, if particles of lead oxide with adequate surfaces were formed in an engine, these surfaces could then inhibit the "end-gas" reactions and so inhibit "knock".

Downs[91] showed that, in a petrol engine, a "fog" of inorganic lead compounds is formed in the cylinder sufficiently early to influence the reactions leading to "knock". It is not known, however, if these particles did actually affect combustion[82,92]. Inorganic lead salt particles of varying size

(0.2-5 μ) have been collected from the exhaust of engines running on fuels containing tetraethyl lead and lead "scavengers". By direct sampling[93], it has been found that, in an engine running on a fuel containing tetraethyl lead, lead oxide particles are formed in the "end-gas" prior to the arrival of the flame front.

These experiments support Walsh's hypothesis that solid lead monoxide particles are formed in an engine running on fuel containing tetraethyl lead but, while the observations are consistent with a heterogeneous mechanism, they not prove conclusively that the particles inhibit the "knock" reaction heterogeneously. There was no evidence that the molecular lead oxide also present was not the active species. If the "antiknock" action of TEL were due to the production of a surface of lead oxide particles, then a direct introduction of surfaces coated with this compound should theoretically suppress "knock" reactions. However, when the cylinder walls and piston were coated with this compound[48], there was very little effect. It was suggested that this may have been due to the fact that the active chain carriers had to diffuse to the walls in order to be destroyed by lead oxide, and certainly in the high pressure environment of the engine cylinder, the diffusion times are very long compared with the times between gas phase collisions.

In an attempt to elucidate the mechanism of action of TEL in engines[94], powders of lead oxide, lead chloride, aluminium oxide and magnesium oxide were introduced into the combustion chamber. The results obtained proved conclusively that lead oxide in the solid phase does inhibit engine "knock", since the "antiknock" effectiveness of the lead oxide increases with increasing surface area. Such an increase would not be observed if the lead oxide were active only in the vapour phase.

Tetraethyl lead is an effective "antiknock" additive because:

1. It is soluble in gasoline.
2. It is not much less volatile than normal commercial grade gasolines.
3. It yields a "fog" of solid lead oxide particles in the "end-gas" of an engine.
4. The surfaces of these particles convert OH and HO_2 radicals to inert products.
5. The oxidation product of tetraethyl lead, lead oxide, is capable of being "scavenged" from the cylinder, so that deleterious solid deposits are not readily formed. These "scavengers" must act after the active "antiknock" species have exerted their inhibiting effect. The normal "scavengers" used are ethylene dibromide and dichloride; these bring about the formation of lead halides, which have a greater volatility at engine temperatures than lead oxide and so are renewed in the exhaust gases.

1.8.3.4. Tetramethyl lead.

The possibility of improving on tetraethyl lead by the formation of a "fog" of particles at a different time in the engine cycle has led to recent interest in tetramethyl lead as a commercial "antiknock". Although the "antiknock" effect of tetramethyl lead was known at about the same time as that of tetraethyl lead, with the type of fuel and engine then in use tetramethyl lead did not offer any advantage. Furthermore, the economic manufacture of tetramethyl lead was, and still is, a much more difficult problem than that of tetraethyl lead. A further factor which discouraged the use of tetramethyl lead was the assumption that its higher volatility would make it more toxic that the ethyl compound. Recent work has shown that this assumption is not valid and that in modern high compression engines, TML can be more effective than TEL due to its higher volatility and stability.

In a multicylinder engine, the comparatively low volatility of TEL may cause it to be badly distributed in the cylinders, so that it tends to follow the heavy "end" components of the fuel. Tetramethyl lead has, however, under certain conditions a small advantage even in single cylinder engines[95]. This advantage is attributable to the greater stability of TML. Lead oxide particles are therefore formed at a later stage in the engine cycle. If under certain conditions tetraethyl lead gives rise to lead oxide at an optimum stage in the engine cycle, then in engines of higher compression ratio, these particles will tend to be formed at an earlier stage, so that aggregation and loss of surface area occur. Tetramethyl lead would survive unchanged for a longer time, and this explains the advantage obtained with TML when higher compression ratios are used.

1.9. The occurrence of sulphur compounds in gasolines.

Until recently the problem of sulphur compounds in motor gasolines was a comparatively minor one. However, with the gradual depletion of crude oils which are low in sulphur, as well as the introduction of new governmental standards limiting the amount of lead present in gasolines, the sulphur content of crude oils has assumed major significance.

Most crude oils contain less than 0.5 wt. % sulphur, but analyses reveal that 1.0 wt. % is not infrequent. Refining processes alter the structure of these compounds and in some cases introduce new ones. Gasolines formed by simple distillation of the crude oils (straight-run gasolines) contain a very small proportion of the original sulphur due to the high boiling points of the sulphur compounds. Cracked gasolines contain, however, between two and ten times as much sulphur as the corresponding straight-run gasolines, since during cracking some of the heavier sulphur compounds decompose.

Free sulphur is generally absent from crude oils, but is occasionally found in gasolines containing hydrogen sulphide, due to the oxidation of the latter compound:

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

The hydrogen sulphide may be present in the original crude or it may be formed as a result of the decompostion of mercaptans during distillation. The sulphur present in crude oils is usually found as hydrogen sulphide, mercaptans, sulphides, disulphides, thiophanes and thiophenes. Alkyl polysulphides may also be formed during certain sweetening processes and in aromatic gasolines, CS_2 may also be present. Mercaptans are more prevalent in straight-run gasolines, while thiophenes predominate in cracked gasolines. This is because cracking conditions favour the formation of cyclic structures which are more stable at the higher temperatures. Straight-run gasolines contain a higher percentage of high molecular weight mercaptans than do cracked gasolines. Due to the cracking conditions, the latter do not contain many mercaptans above C_4.

1.10. The effects of sulphur compounds in motor gasolines.

There are two main objections to the presence of sulphur in motor gasolines:

1. Certain combustion products, particularly sulphur trioxide, are corrosive.
2. The octane number and lead response are adversely affected.

1.10.1 Sulphur compounds and engine wear.

Corrosion of automotive engine parts is predominantly a cold weather problem. Low engine temperatures promote corrosion by facilitating the condensation of water in the crankcase, which combines with other combustion products, such as carbon and sulphur oxides, which attack exposed metal surfaces. This problem of corrosion is partially solved by the use of higher engine temperatures, and ventilation of the crankcase, which prevents accumulation of corrosive products, so that engine wear is minimised. Under these conditions, fuels containing less than 0.1 wt. % of sulphur can be safely used.

1.10.2. Effect of sulphur compounds on octane number.

The effect of sulphur compounds in lowering the octane number of gasolines is in general a function of the quantity and types of such compounds present. Birch and Stanfield[96] investigated the effects of various sulphur compounds on the "knock" rating of a heptane-isooctane blend of octane number 65. It was found that elemental sulphur, mercaptans and ethyl trisulphide had the maximum adverse effect on octane number, while monosulphides, thiophenes and carbon disulphide were inactive. In general 0.1 wt. % of sulphur lowers the octane number by between 0 and 2 units depending on the form in which the sulphur is introduced. Mercaptans and disulphides exhibit similar effects and these may be correlated with results obtained by Holloway and Bonnell[97].

In a more detailed study, Ryan[98] determined the order in which sulphur compounds affect the octane number, using a cracked gasoline containing 0.0033 wt. % of sulphur as base fuel. When sulphides and thiophene were added in concentrations corresponding to 0.1 wt. % of sulphur, they had no effect. Mercaptan, disulphides, and polysulphides had, however, an increasingly large effect in the order given. This result differed from the findings of Holloway and Bonnell[97] and suggests that the effects of different sulphur compounds may depend on the nature of the hydrocarbons in the gasoline. It was also found[98] that the detrimental effect of sulphur compounds increased with increasing molecular weight, and that branched sulphur compounds had a greater adverse effect on octane number than did the straight-chain isomers.

1.10.3. Effect of sulphur compounds on lead susceptibility.

In addition to lowering the octane number of a gasoline, sulphur compounds also reduce the lead susceptibility i.e. the change in octane number resulting from a given addition of tetraethyl lead to the fuel. The presence of sulphur even in relatively low concentrations (0.01 - 0.1 wt. %), causes a significant reduction in octane numbers of leaded gasolines. This adverse effect of sulphur compounds on TEL was reported independently by three groups of investigators[96,99,100], and severely limits the maximum benefical results obtainable in the commercial use of tetraethyl lead.

This interaction between sulphur compounds present in gasolines and tetraethyl lead therefore causes a marked reduction in the effectiveness of the "antiknock" compound, and it appears that this interaction occurs before the fuel-air mixture is completely burnt in an engine cylinder for the following reasons:

1. Different sulphur compounds have different effects on tetraethyl lead[98,101,102].
2. On combustion, organic sulphur compounds yield water, carbon dioxide, carbon monoxide and sulphur oxides. Since all compounds should theoretically give the same combustion products, they should have the same effect, if the critical reaction involving tetraethyl lead occurs after the fuel-air mixture has undergone combustion.
3. Different sulphur compounds undergo markedly different reactions at the various temperatures attained by portions of the unburnt mixture in the engine cylinder. It has been suggested[103] that the reactivities of the organic sulphur compounds decrease in approximately the same order as their lead antagonism effect.

In work carried out with simple organic sulphur compounds[103], sulphur dioxide and hydrogen sulphide were more effective in reducing the octane numbers of leaded gasolines than carbonyl sulphide and sulphur hexafluoride. The small effect of the latter compounds on leaded gasolines is particularly significant when the oxidation characteristics of these compounds are considered. Carbonyl sulphide and sulphur hexafluoride are resistant to slow oxidation and preflame reactions at temperatures as high as 800°C[104,105]. Hydrogen sulphide and sulphur dioxide, on the other hand, undergo oxidation at temperatures as low as 320°C[100]. The temperature of the hottest portion of the unburnt fuel-air mixture in the engine cylinder has been calculated to be less than 700°C and , under these conditions, carbonyl sulphide and sulphur hexafluoride undergo little or no reaction. Hydrogen sulphide and sulphur dioxide , on the other hand, enter into reaction before all the fuel-air mixture has been burnt.

The findings therefore that (a) the sulphur compounds which resist preflame reactions have little or no effect on tetraethyl lead efficiency, and (b) the sulphur compounds which react readily have a large antagonistic effect, support the theory that preflame oxidation products or other products formed from sulphur compounds are the species which react with tetraethyl lead to reduce its "antiknock" effectiveness, and that the different effects of the sulphur compounds are due to their different reactivities.

Schulze and Buell[100] were first to describe quantitatively, the pronounced decrease in octane number produced by the addition of sulphur compounds to leaded gasolines. Their results were later verified by several other investigators [97,107-109]. It was found too that the order of reactivity of sulphur compounds in leaded gasolines may be defined as follows:

disulphides > sulphides > thiophene

Schulze and Buell[110], as well as Ryan[98], showed that disulphides and mercaptans have equivalent activity on leaded gasolines. Livingston[111] found, however, that the primary alkyl disulphides are less deleterious than the mercaptans from which they are formed. The following principal conclusions regarding the effects of sulphur compounds on leaded gasolines may therefore be drawn:

1. At equal sulphur concentrations, all thiols have approximately the same effect on octane number.
2. Sulphides and disulphides containing aromatic rings are less antagonistic towards tetraethyl lead than are aliphatic sulphides and disulphides.
3. Saturated heterocyclic sulphides are antagonistic to the same extent as acyclic sulphides.
4. An increase in the chain length of sulphur compounds in a homologous series does not alter their effect on octane number as long as all the compounds are compared at the same sulphur concentration. Sulphur antagonism is therefore dependent on the sulphur concentration and on the chemical environment of the sulphur atom.

In discussing the results of work done on the combined action of sulphur compounds and tetraethyl lead in gasoline, it must be remembered that different workers used different gasolines and the results obtained are not strictly comparable, although certain well-defined trends can be distinguished.

1.11. The present work.

It has been shown in Section 1.3.4. that "knock" in spark engines is caused by the preflame reactions of the gasoline in the "end-gas" region reaching explosive proportions before they are engulfed by the flame initiated by the spark. This autoignition of the "end-gas" depends on several factors such as fuel structure and composition, engine temperature, ignition timing etc (Sect.1.5). Tetraethyl lead is used as an additive to suppress these reaction and acts by the heterogeneous destruction of the radicals which propagate the hydrocarbon oxidation chains. Such destruction takes place on the surface of lead oxide particles formed by the oxidation of the additive (Sect. 1.8.3), which is normally present in a concentration of 3 ml. per U.S. gallon.

In the presence of sulphur compounds, the "antiknock" effect of the tetraethyl lead was severely reduced (Sect. 1.10.3). At equal sulphur concentrations, different sulphur compounds have different effects, and it therefore seems unlikely that the final combustion products of these compounds, namely water, carbon dioxide and sulphur oxides, are the species responsible. The present work reports a comparison of the effects of different sulphur compounds on leaded gasolines, and also elucidates the oxidation products of these sulphur compounds.

Studies were also undertaken of the effects of sulphur compounds on the combustion of a hydrocarbon, isooctane, and these were carried out in a static apparatus using both uncoated and lead-oxide coated vessels, in an attempt to elucidate the mechanism of the interaction of sulphur with lead. Some electron diffraction studies were made of the lead oxide coating saturated with the sulphur compounds, in order to determine any effects of the sulphur compounds on the surface of lead monoxide.

SECTION 2.

EXPERIMENTAL.

SECTION 2.

Section 2 (cont'd). Page No.

2.1 Engine Studies.

2.1.1. The Cooperative Fuel Research Engine.

The Cooperative Fuel Research Engine is the standard engine used all over the world for the determination of the octane numbers of gasolines. A pictorial representation of this engine is shown in Figure 2.1. This unit consists of a single-cylinder engine with a compression ratio which may be varied while the engine is operating by turning a handle, E, the side which raises or lowers the cylinder head. A locking device, J, may be used when the compression ratio has been adjusted to the required value. A link network situated on the cylinder head maintains the tappet clearances when the head is adjusted vertically. An evaporative cooling system, B, is employed with a water-cooled condenser coil above the coolant level, in order to maintain a constant jacket temperature.

A multi-bowl carburettor is fitted to accommodate a number of fuels ready for test. In the engine concerned, there were four bowls, a selector valve being used to feed the fuel from the required bowl. The mixture strength is controlled by raising or lowering each bowl above a jet. An ignition spark indicator is driven by the engine, and a calibrated brass scale is provided for measuring the spark advance. An air inlet heater, mixture heater and oil heater are all incorporated into the unit, together with an ice tower for controlling the humidity of the intake air. An electric dynamometer is provided together with a standard control panel.

Key to figure 2.1.

A = Intake surge tank.

B = Coolant condenser.

C = Exhaust surge tank.

D = Exhaust manifold.

E = Crank for adjustment of compression ratio.

F = Oil drain cap.

G = Waste fuel can closed for safety.

H = Oil filter.

I = Ignition breaker.

J = Cylinder clamp.

K = Intake air thermometer.

L = Ignition coil.

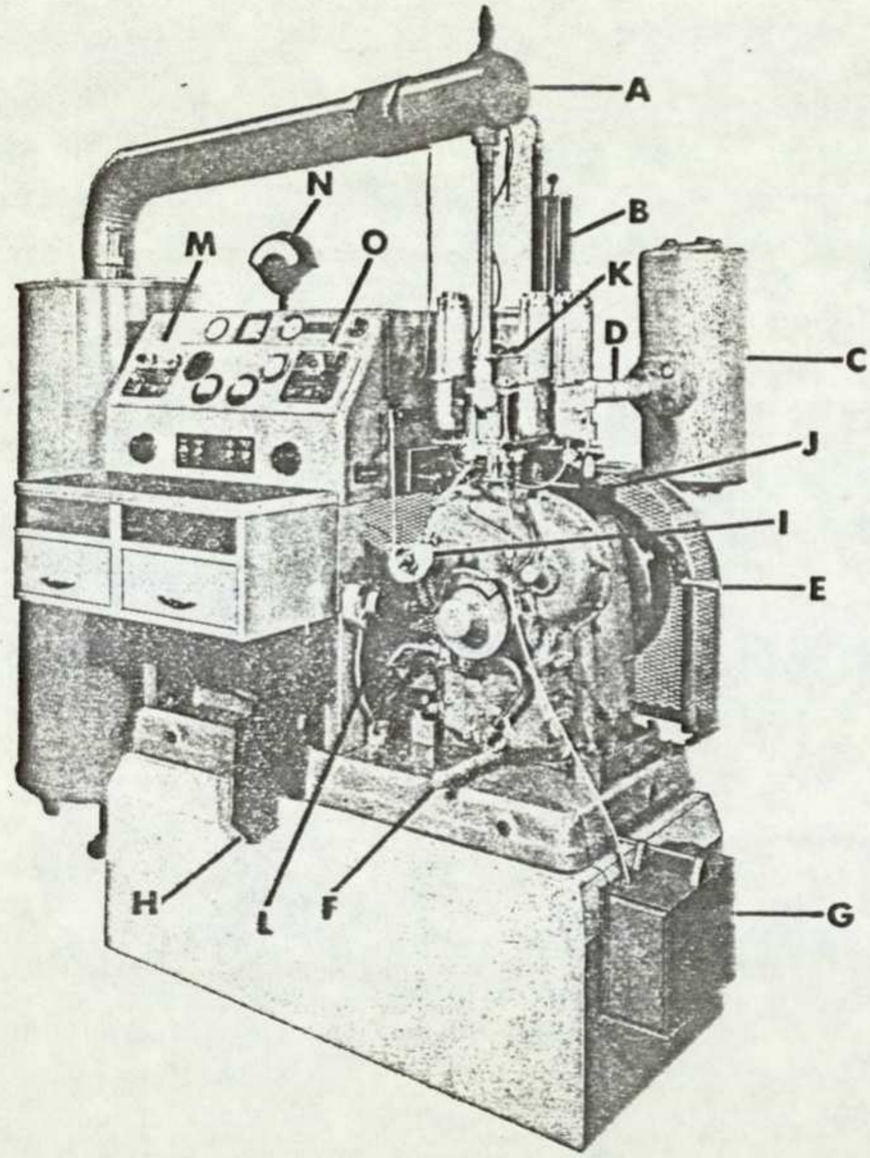
M = Detonation meter.

N = Knockmeter.

O = Temperature controller.

Figure 2.1

The Cooperative Fuel Research Engine.



An 18mm. spark plug is used and "knock", when it occurs, begins from the "end-gas" zone situated opposite to the plug position. In this region, a specified type of "knock-detecting" instrument is fitted. Although, in many engines, the intensity of "knock" may be measured audibly, the precision required in the rating of fuels necessitates the use of a more sensitive detecting instrument.

2.1.2. Materials used.

Isooctane, toluene, diisobutylene and heptane were the four fuels used in these studies. Isooctane, heptane and toluene were standard grade materials used for octane number determinations and were obtained from the Esso Research Centre, Abingdon. The diisobutylene was obtained from the Fawley Refinery and was 95% pure. Tetraethyl lead and tetramethyl lead were also obtained from the Esso Research Centre.

The sulphur compounds were thiophene, diphenyl disulphide, dipropyl sulphide, diphenyl sulphide, tertiary octyl mercaptan, dimethyl disulphide and thiophenol. These were obtained from the Esso Laboratories, their purities varying between 99.0 and 99.5%.

2.1.3. General procedure.

2.1.3.1. Fuel blending.

The fuel blends used always contained heptane as one component. 80% isooctane in heptane gave a primary reference blend of 80 octane number. Similar blends of toluene and diisobutylene in heptane were also prepared. 62% toluene in heptane also gave an octane number of approximately 80. Since the diisobutylene was impure and octane rating of a test sample revealed an octane number of 94.8, a calibration curve (Fig.2.2) was constructed of percentage diisobutylene in heptane versus Research Octane Number. A blend of 61.5% diisobutylene in heptane gave an octane rating of approximately 80.

Ten-gallon blends of isooctane and toluene in heptane were prepared. With the diisobutylene blend, only five gallons were made. To separate 5-gallon amounts of the various blends were added 0.4 grams per litre of tetraethyl lead and tetramethyl lead respectively. In the case of the diisobutylene blend, only tetramethyl lead was used. Calibration curves of Research Octane Number versus lead alkyl concentration were then obtained by dilution of the leaded blends with unleaded fuel.

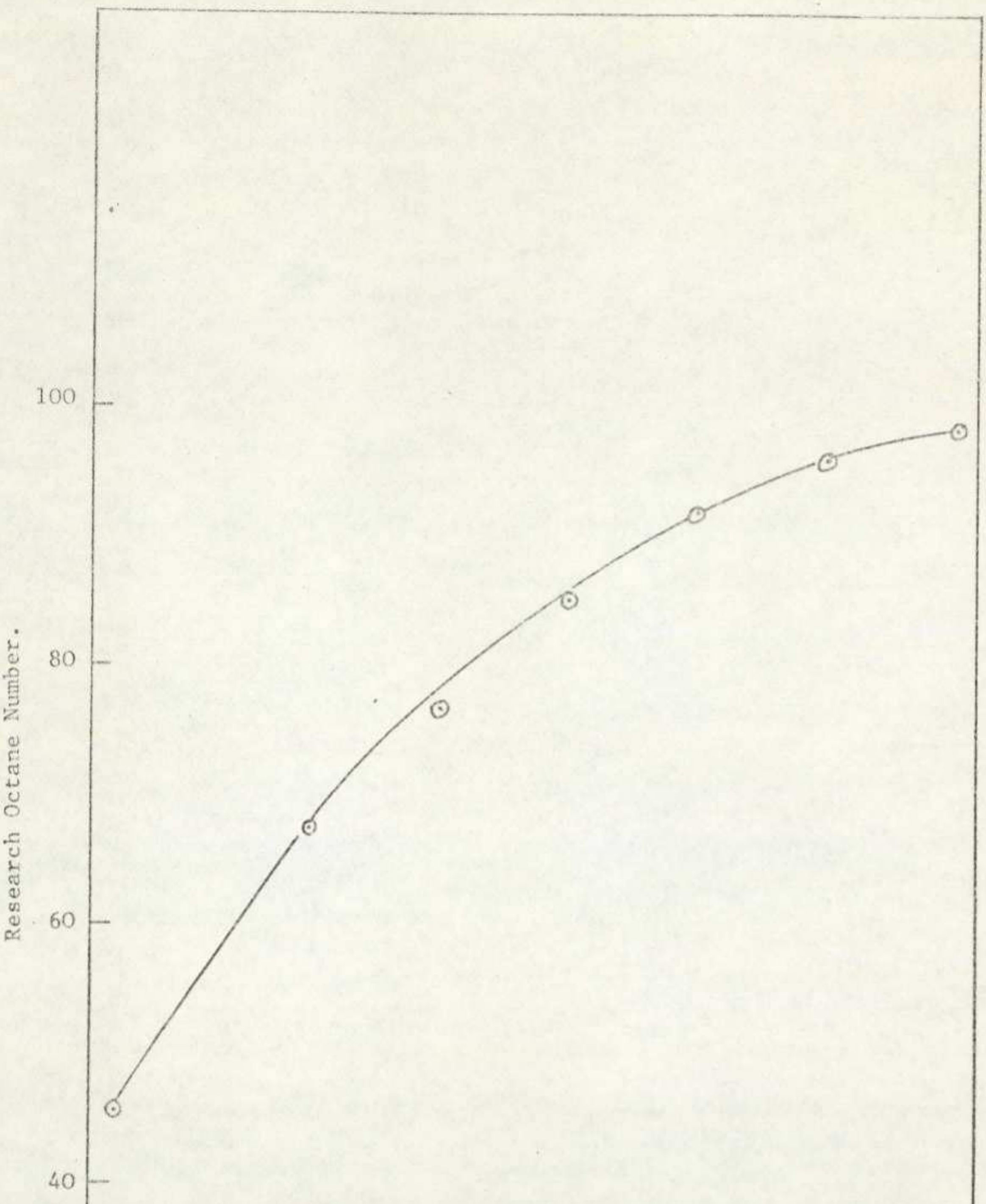
The sulphur compounds were added to separate samples of the leaded fuels in the proportion of 0.10% and 0.05% by weight.

2.1.3.2. Determination of octane numbers.

The first step in "knock-rating" a fuel blend is to set the knockmeter. The engine is run with a blend of reference fuels of octane number somewhere near the expected rating of the test fuel and the compression ratio is adjusted to the value for that particular blend. The knockmeter is then set

Figure 2.2.

The variation of Research Octane Number with the percentage of diisobutylene in heptane.



to read 55 divisions on the knockmeter dial. This number is arbitarily set as the point of standard "knock". Tables are available[68] showing the appropriate values of compression ratio needed to provide standard "knock" for various reference fuel blends, under different atmospheric conditions.

With the knockmeter set, the test fuel was placed in the first carburettor. The mixture strength for maximum "knock" intensity, that is in the region of 55±3, was then determined by variation of the fuel level above the carburettor jet. Using the correct mixture ratio, the compression ratio was increased until standard "knock" intensity was obtained. The micrometer reading of the compression ratio was noted and, using standard tables of micrometer setting versus Research Octane Number, an idea of the octane number of the test fuel was obtained. Reference blends prepared from the primary reference fuels, isooctane and heptane, were placed in carburettors 3 and 4. The second carburettor contained "dump" fuel which was burnt between test runs. The reference fuels "bracket" the test sample and their octane numbers varied by no more that 2. Under conditions similar to those used for the test sample, the higher octane blend gave a knockmeter reading of less than 55, while the lower reference blend gave a reading greater than this. Duplicate readings were taken for each fuel, care being taken each time that the test fuel continued to give a reading of 55±3 on the knockmeter dial. The readings were then averaged and the required octane number was obtained by interpolation between the averages. Determinations were carried out for all the leaded fuels and the effects of the sulphur compounds on the octane numbers of these blends were also obtained.

Since the rating capabilities of a given engine vary with time due to carbon formation, wear and loss of adjustment, special routine checks and maintenance procedures were necessary to ensure continued accuracy.

2.2 Laboratory studies.

In the light of the results obtained in the engine experiments, it was felt that a laboratory study of the gaseous oxidation of one sulphur compound in each principal class would help to elucidate their effects on the combustion of both non-leaded and leaded fuels. The compounds chosen, on the grounds of their relatively high volatility, were thiophene (b.p. 84°C), dimethyl disulphide (b.p. 110°C), dipropyl sulphide (b.p. 142°C) and thiophenol (b.p. 169.5°C). In these studies, determinations were made of the reactivity towards oxidation of the sulphur compounds and in particular of the amounts of sulphur dioxide formed from them.

Studies were also carried out of the gas-phase oxidation of isooctane in both a clean and a lead oxide-coated reaction vessel, and the effects were measured of small additions of sulphur dioxide, thiophene and thiophenol on the "low-temperature" ignition limits.

2.2.1. The apparatus.

This consisted mainly of a vacuum system, together with a furnace and other accessory electronic equipment.

2.2.1.1. The vacuum system.

The vacuum apparatus was constructed of pyrex glass and is shown diagrammatically in Figure 2.3.

The section of the line bounded by taps T1 to T10 was constructed from 8 mm. i.d. tubing. The section of the line bounded by TR4 and TR6 was constructed from 30 mm. i.d. tubing. Permanent gases were introduced into the apparatus via T1, dried by passage through a column of Linde 5A molecular sieve and silica gel and then condensed and fractionated between traps TR1 and TR2 which were cooled by liquid nitrogen. A mercury manometer, M1, was used for calibration purposes and as a pressure safety valve during fractionation of the gases.

The permanent gases were stored in vessels S1 (1 litre), S2 (5 litre) and S3 (3 litre). Round-bottomed flasks, F1 and F2 (50 cm^3), were used to store the liquid sulphur compounds and isooctane, and were attached to the vacuum line by cylindrical joints sealed with Viton rubber "O" rings. The heated premix vessels, PM1 and PM2 (3 and 5 litres respectively), were encased in metal boxes as a protection against explosion resulting from flashback from the reaction vessel. A flame trap, FT, filled with 2 mm. diam. glass beads was also incorporated into the line between the premix vessels and the

Key to figure 2.3.

CV = 500 cm^3 volume, calibration vessel.

DC = drying column containing Linde 5A molecular sieve.

DP = mercury pump.

F = vertical tube furnace.

F1 and F2 = 50 cm^3 volume, alkane storage vessels.

FT = flame trap packed with 2 mm. diameter glass beads.

M1 and M2 = mercury manometers.

PG = Pirani gauge.

PM1 and PM2 = heated premix vessels.

PT1 and PT2 = pressure transducers.

RP = rotary oil pump.

RV = 500 cm^3 volume reaction vessel.

S1, S2 and S3 = permanent gas storage vessels.

SL = sample loop.

SV = solenoid-operated valve.

T1 to T15 = taps. ⊤ = Rotaflo greaseless taps.
⇞ = ground-glass stopcocks.

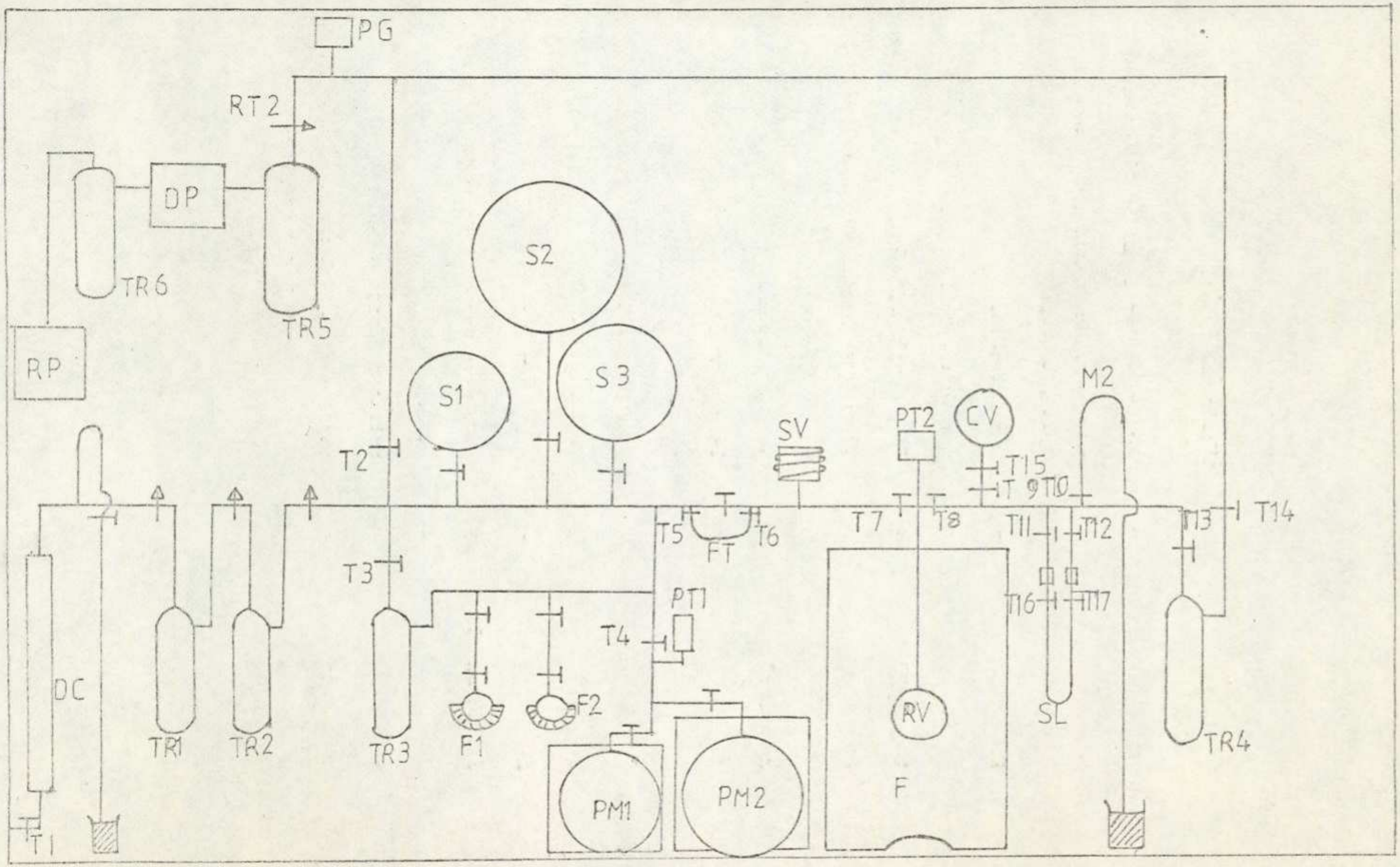


Figure 2.3.

A line diagram of the vacuum system.

reaction vessel, in order to reduce the risk of flash-back from the reaction vessel.

The introduction of the premixed reactants into the reaction vessel was controlled by a solenoid-operated valve. The valve was attached to an electronic timer which controlled the length of time for which the valve was open. Combustion was carried out in a 500 cm.^{3} spherical reaction vessel which was washed with fuming nitric acid, rinsed with distilled water and baked in air at 450°C for 24 hours prior to use. The neck of the reaction vessel was sealed by the pressure transducer PT2, and a constant volume was obtained with taps T7 and T8 closed. This transducer measured the pressure changes which occurred during the combustion reactions. A calibration vessel, CV, (500 cm.^{3}) and a mercury manometer, M2, were also attached to the line adjacent to the reaction section. The sample loop, SL, which consists of a U-tube made of 6 mm. i.d. glass tube, was attached to the line by cylindrical joints sealed with Viton "O" rings. Products of combustion were analysed on a Perkin Elmer 452 Gas Chromatograph fitted with a katharometer detector. A trap TR4, cooled by liquid nitrogen, prevented combustion products from condensing in the 30 mm. i.d. by-pass line bounded by T14 and RT1.

The pumping section, bounded by TR5 and the rotary pump, RP, was constructed of 8 mm. i.d. tubing. A vacuum of 10^{-4} torr was obtained by means of a single-stage mercury diffusion pump, DP, backed by an Edwards Speedivac rotary oil pump. A Pirani Gauge (Model 8/2) was used for measuring the pressure. Liquid nitrogen-cooled traps, TR5 and TR6, protected the diffusion pump from contamination by combustion products and prevented mercury from diffusing into the line or rotary pump. Rotaflo taps with PTFE keys were used in the heated parts of the line. Ground-glass stopcocks, lubricated with Apiezon high-vacuum grease, were used in the other parts of the system.

The apparatus, with the exception of the gas chromatography equipment, was constructed in a fume cupboard due to the very unpleasant smell of the sulphur compounds.

2.2.1.2. Furnace and line heating.

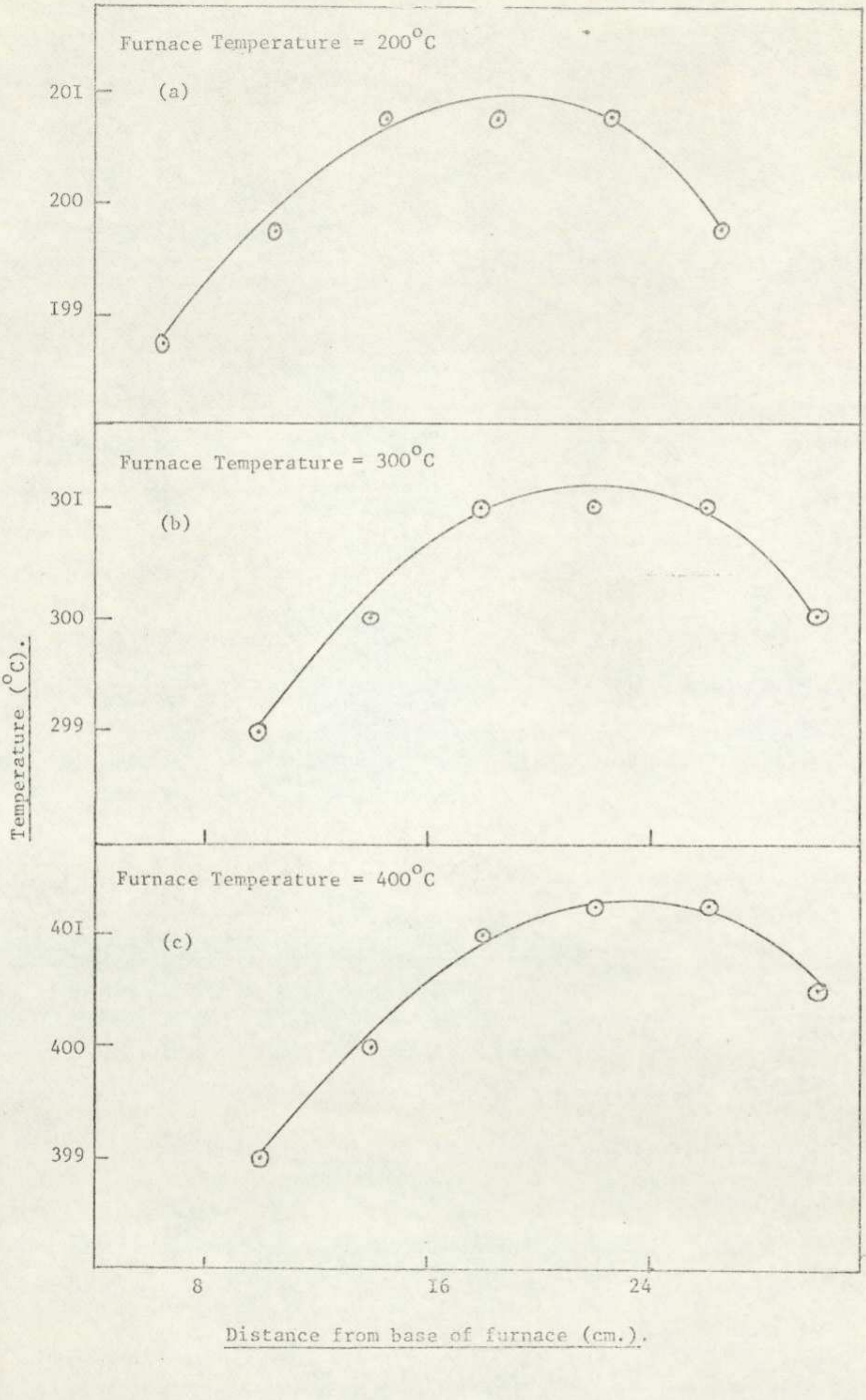
The temperature distribution of the vertical tube furnace was measured with a chromel-alumel thermocouple, which had been previously calibrated against a Pt-Pt/13% Rh thermocouple. Measurements were taken at three temperatures and the results obtained (Figures 2.4 a,b and c) show a stable temperature region ($\pm 1^{o}$C) over a 18 cm. length of the furnace. The reaction vessel was therefore placed in a reasonably uniform temperature region, 18 cm. from the base of the furnace.

The furnace temperature was controlled to within $\pm 0.5^{o}$C by an A.E.I. type RT3/RMk2 proportional temperature controller. This regulator was operated in conjunction with a platinum resistance thermometer temperature sensor, the nominal resistance of which is 10 ohms at 273K. This thermometer was placed as near as possible to the reaction vessel.

The vacuum line between T3 and T13 was

Figure 2.4.

Temperature distributions along the vertical tube furnace.



heated by 1-inch wide electrical heating tape. The temperature to which the line was heated was dependent on the boiling points of the sulphur compounds and the hydrocarbon fuel. Thermocouples were placed at several points along the surface of the line to ensure that the temperature was reasonably constant. The premix vessels were heated by means of 3-inch wide heating tapes; thermocouples were also placed alongside the surface of the vessels to ensure that there were no hotspots and that the temperature was uniform.

The storage vessels, F1 and F2, were heated by isomantles connected to Variac transformers.

2.2.I.3. Solenoid valve and timing circuit.

The solenoid valve is shown diagrammatically in Figure 2.5. This valve was made by compressing a Viton "O" ring attached to a metal rod into a glass cup. The top of the valve carried a spring which prevented the rod from breaking the glass top, when the valve was operated. When the solenoid coil was activated, a magnetic field was induced which lifted the metal rod from the glass cup and permitted gas to flow through the valve. When the coil was isolated from the voltage supply, the metal rod returned quickly under the force of gravity and the action of the spring, thus renewing the seal.

The length of time for which the solenoid coil was activated was controlled by an electronic timer, which was of special design and enabled the valve to be opened for periods between 0.1 and 9.9 sec. Figure 2.6 shows the circuit

Key to figure 2.5.

I = gas inlet.

M = iron rod.

O = gas outlet.

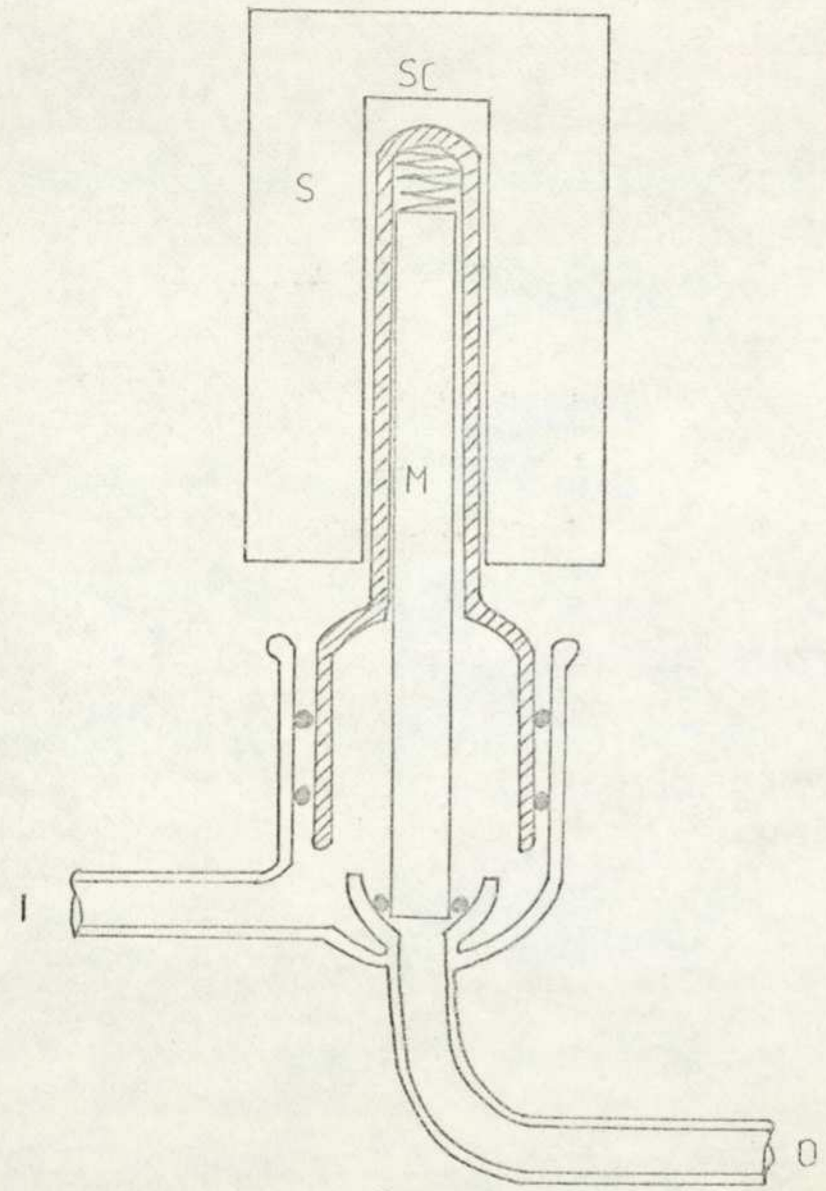
S = spring.

SC = 240V a.c. solenoid coil.

● = viton-rubber 'O' ring.

Figure 2.5.

The solenoid valve.



Key to figure 2.6.

ICI = SN 7490 = IC2 = IC3.

IC4 = SN 7442 = IC5.

IC6 = radio spares 305-377 5V regulator.

IC7 = SN 7400.

IC8 = SN 7402.

TR1 = BC I09 = TR2.

DI = B2 x 85 4.7V zener diode (or equivalent).

D2 = IN 914 (or equivalent).

D3 = D4 = radio spares 261-328 bridge rectifier.

D5 = IN 9 4.

CI = C2 = C3 = 0.1 μF.

C4 = 10,000 F, 40V.

C5 = 0.47 μF.

C6 = 0.22 μF.

R = 1k.

R2 = 3k9.

R3 =39k.

R4 = R5 = 1k.

R6 = 4k7.

S1 = 1 pole, 12 way break before male = S2.

S3 = Mains toggle switch.

S4 = radio spares 337-9 4 minature push button switch.

T1 = radio spares 196-381 minature transformer.

R1 = radio spares 349-125 relay 6V coil.

L1 = any 5V low current indicator lamp.

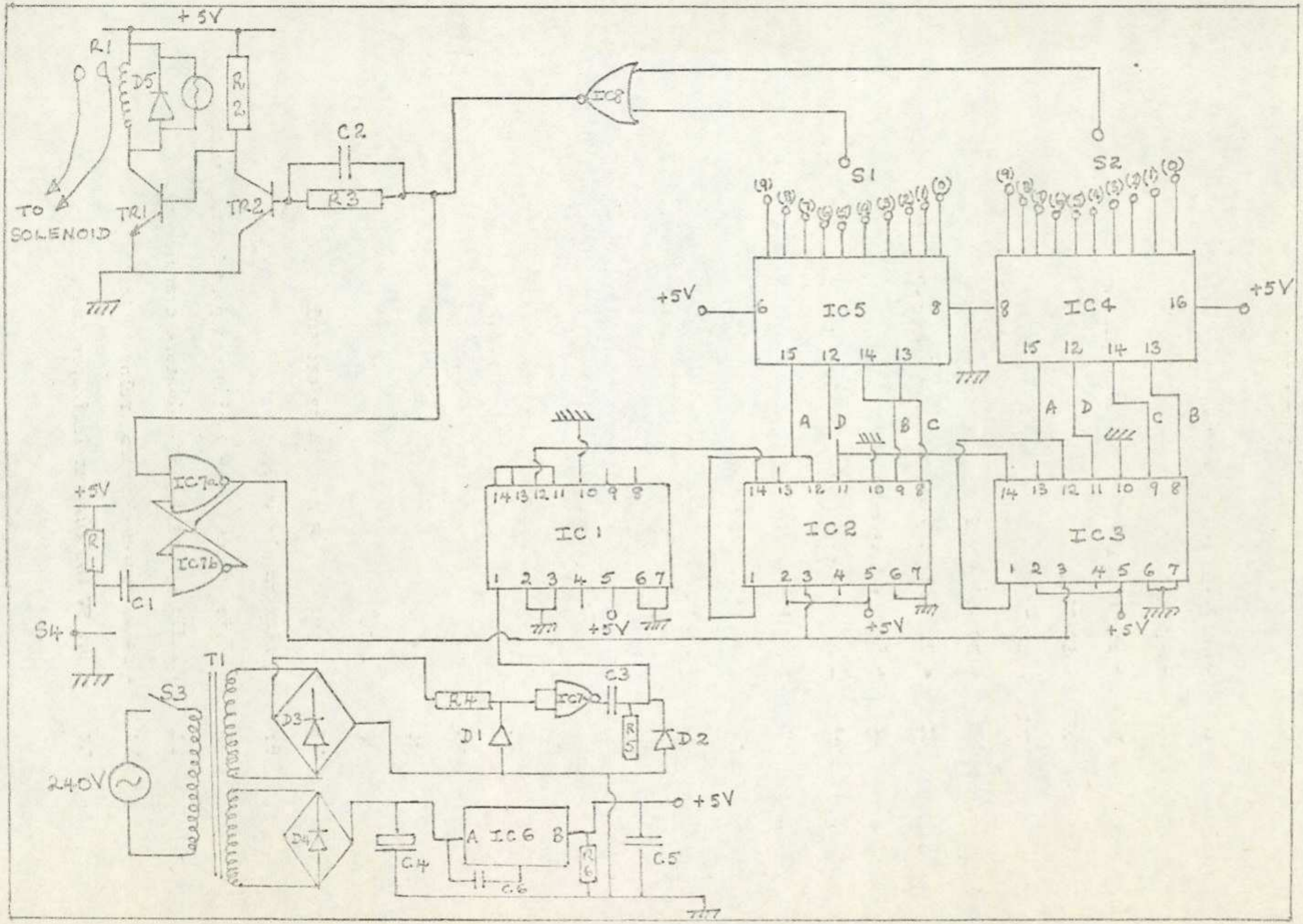


Figure 2.6.

Digital Timing Circuit.

diagram for this timer.

2.2.1.4. Calibration of pressure transducers.

Two pressure transducers were incorporated into the apparatus, the first for premixing the reactants and the second for following the pressure changes occurring during combustion. Both transducers were Bell and Howell 4-366 general purpose models and showed linear behaviour over a 0 - 50 p.s.i. and 0 - 40mV output. Since the pressures used were sub-atmospheric, the linearity of the response of the transducers was checked under these conditions.

2.2.1.4.1 Premix vessel pressure transducer.

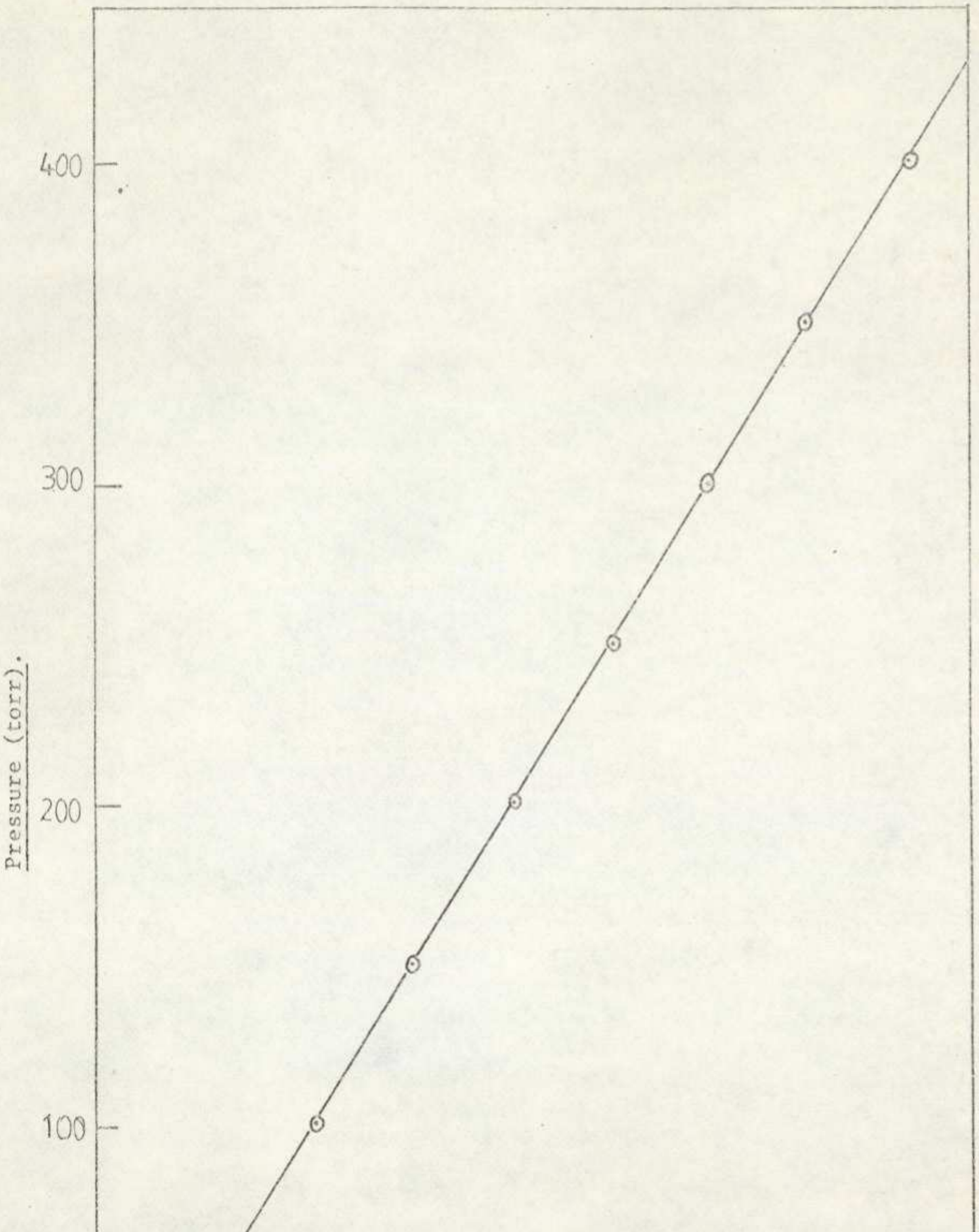
The apparatus was first evacuated to a pressure of 10^{-4} torr and, using the mercury manometer, M1, different amounts of nitrogen were admitted to the premix vessels. Readings of the millivolt output were obtained on a Doran potentiometer attached to a Scalamp galvanometer. The results of this calibration are shown in Figure 2.7. Calibrations were carried out using both increasing and decreasing amounts of nitrogen in order to ensure that no hysteresis occurred.

2.2.1.4.2. Reaction vessel pressure transducer.

Signals from this transducer were amplified on a Honeywell 1706 Visicorder. This instrument uses a mercury arc lamp to produce an intense ultraviolet light beam, which is then focussed onto a mirror galvanometer. The light reflected from the mirror strikes a strip of photographic paper as it is drawn through the recorder. The resulting image becomes visible

Figure 2.7.

Calibration of pressure transducer for premix vessel.



within seconds of the paper emerging from the instrument. The use of this Visicorder resulted in high sensitivity and good reproducibility.

Using manometer, M2, varying amounts of nitrogen were admitted to the reaction vessel, and the distance travelled by the light spot was recorded. This transducer was attached to an amplifier and the procedure was repeated for different amplifications using increasing and decreasing amounts of nitrogen to ensure that no hysteresis occurred. Figures 2.8 a,b,c and d show transducer calibrations at amplifications of 100, 200, 300, 560 and 1000 respectively.

2.2.1.5. Transducer power supply.

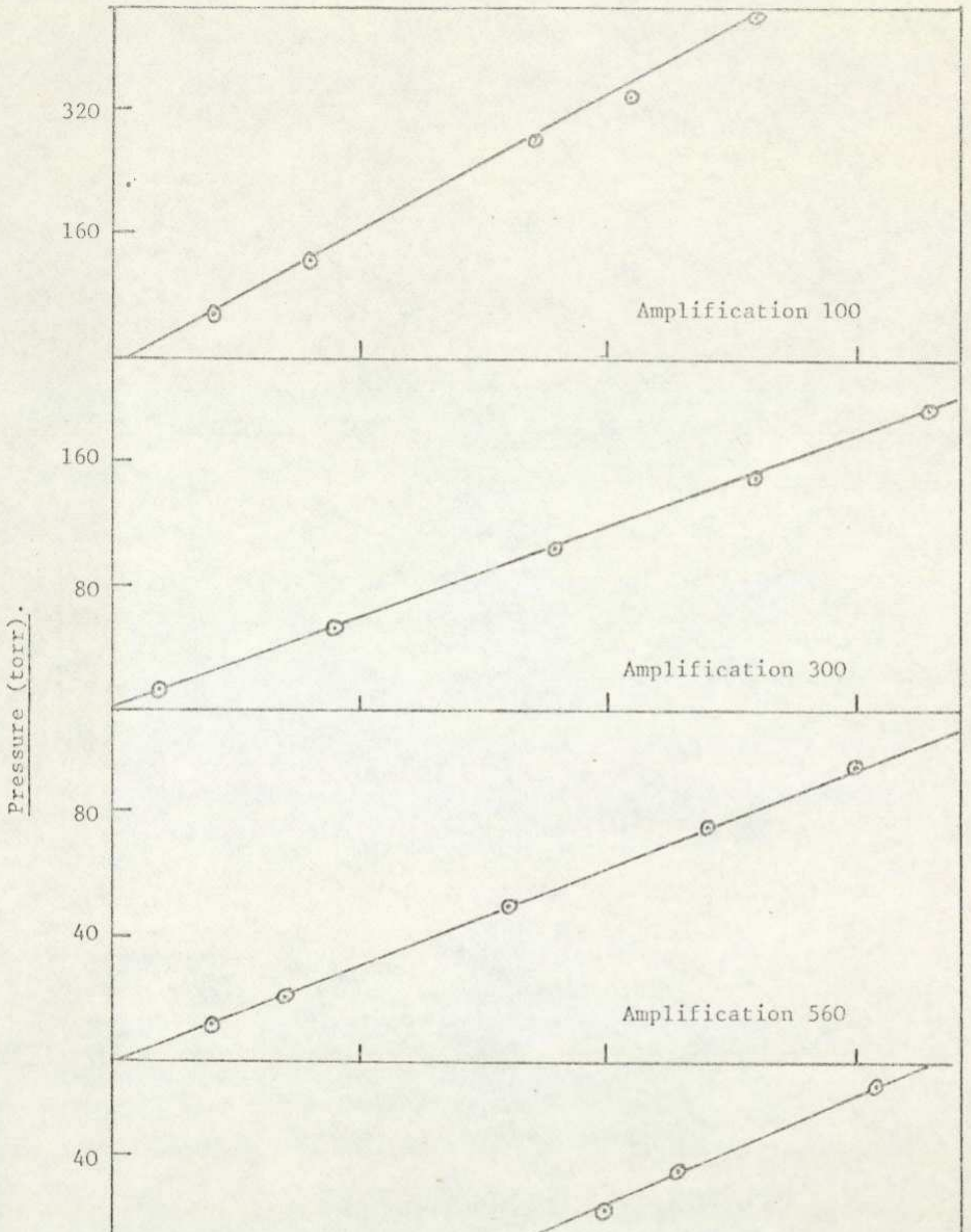
The circuit for the pressure transducer power supply is shown in Figure 2.9, and is of the conventional type. A high-gain operational amplifier was used in the feed-back loop, and this gave the output a high stability. Any variations in the input voltage or load current had therefore little effect on the output voltage. The latter was set by varying R1 and the input voltage was provided by the positive rectified voltage to the amplifier power supply. This prevented the pressure transducer power supply from overloading the amplifier power supply integrated circuit. This power supply unit was capable of operating both pressure transducers.

2.2.1.6. Pressure transducer and zero-balance circuit.

The pressure transducer circuit and the zero balancing network are shown in Figure 2.10. In the transducers

Figure 2.8

The calibration of the reaction vessel pressure transducer.



Key to figure 2.9.

C1 = 0.1 μF.

D1 = IN827.

IC1 = radio spares 741.

R1 = 2k2.

R2 = 560 Ω.

R3 = 3k3.

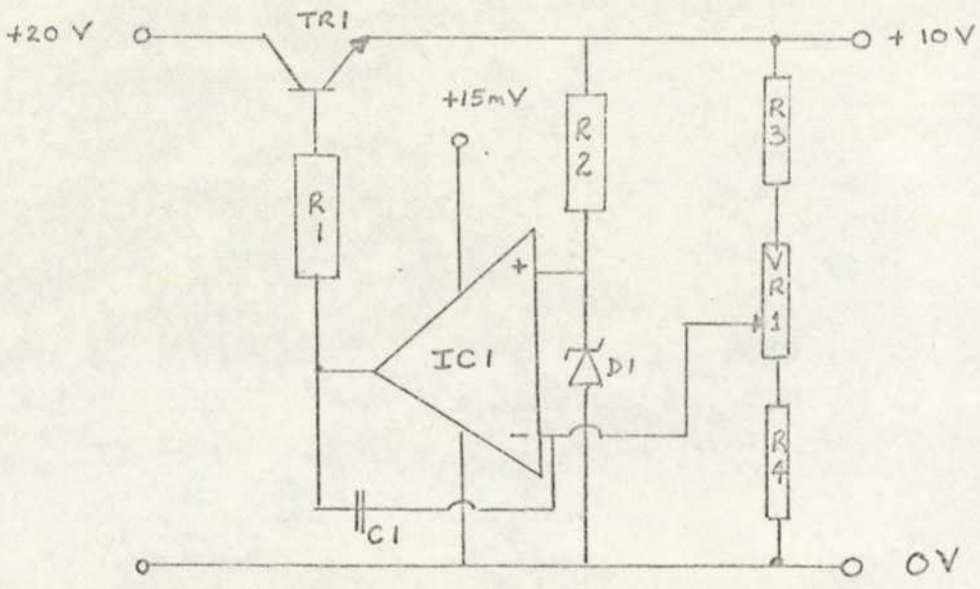
R4 = 5k6.

TR1 = 2N3053 + heat sink.

VR1 = 1k.

Figure 2.9.

Power supply for pressure transducer.



Key to figure 2.10.

R1 = 3k9.

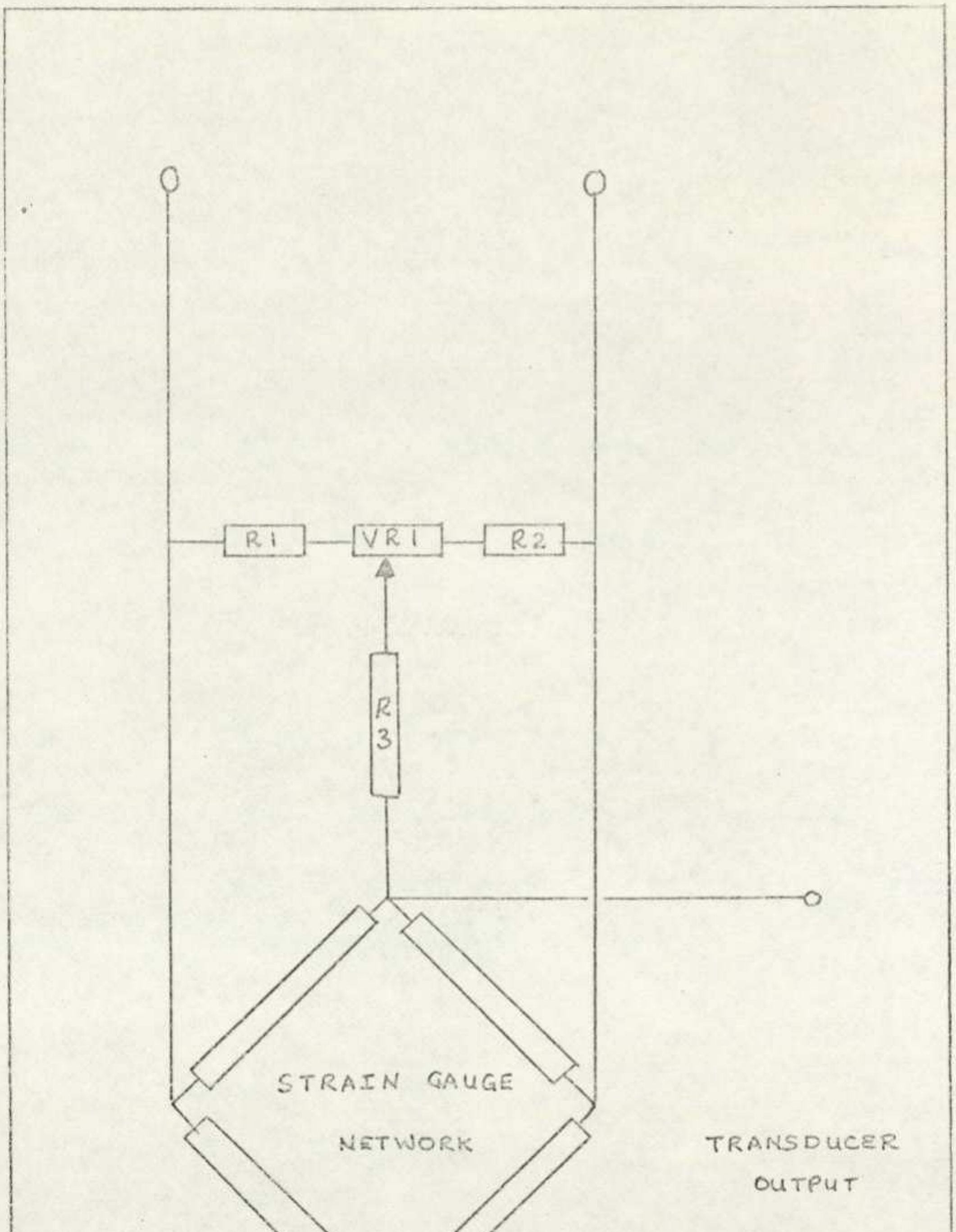
R2 = 3k9.

R3 = 68k.

VR1 = 5k, multi helical potentiometer.

Figure 2.10.

The pressure transducer and zero-balance circuit.



used, pressure changes unbalanced a control strain in a Wheatstone bridge of strain gauges, in which all four arms were activated. Resistors R1, R2 and R3, formed a zero-balance circuit, which with the aid of VR1 facilitated fine adjustment of the transducer output.

2.2.1.7. Amplifier for the reaction vessel transducer.

The circuit diagram for this amplifier is shown in Figure 2.11 and is basically a differential amplifier with a high input resistance, capable of amplifying signals in the millivolt region with little or no noise. The main reason for its choice was its ability to reject common mode noise.

The circuit formed by IC2 constituted the essential part of the amplifier. This is a variable gain system with a differential output. The gain of the circuit is given by R_f/R_n, where R_f is the selected feedback resistance and R_n is the input resistance. R_f is determined by selecting any one of the resistors R5-R10, whilst R_n was determined by R4. For good temperature stability, a network of resistors, equivalent to the feed-back resistors, was connected between the non-inverting input and ground. By changing the feed-back resistors, therefore, the gain of the circuit was altered. In some applications, the circuit formed by IC2 can be used by itself and is very satisfactory. A problem arises, however, when large gains are required, together with a high input resistance. This means that the resistance of R4 has to be very large and the resistance of the feedback resistor has also therefore to be large. As a

Key to figure 2.11.

IC1a = ½ 747 = IC1b

IC2 = 741

R1 = 1M

R2 = 8k2

R3 = 47k = R6

R4 = 10k = R5

R7 = 100k

R8 = 300k

R9 = 560k

R10 = 1M

R11 = 1k8

R12 = 30 Ω

R13 = 220 Ω

S1a = 1 POLE, 6-way.

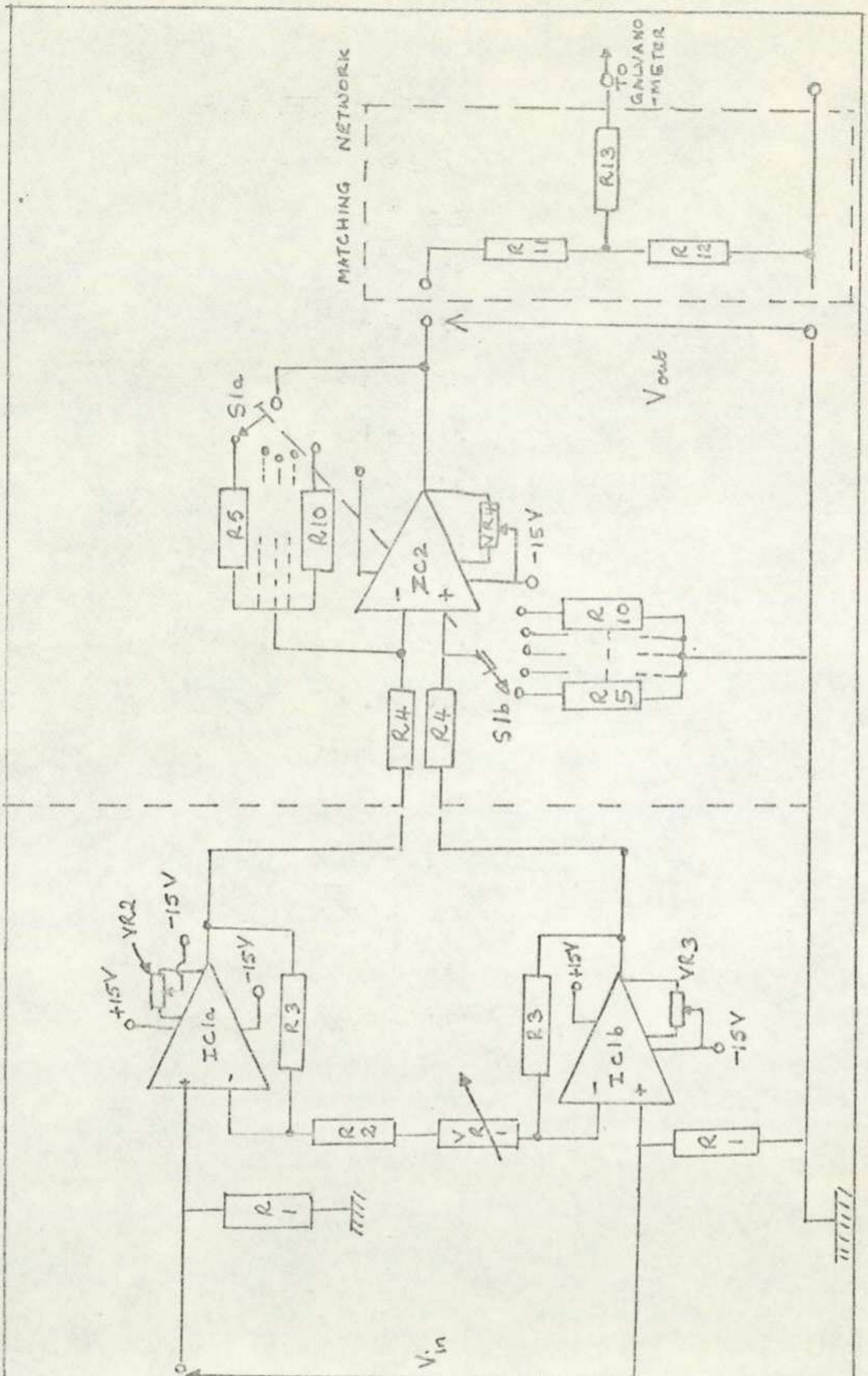
S1b = 1 POLE, 6-way.

VR1 = 4k7

VR2 = VR3 = VR4 = 10k.

Figure 2.11.

Amplifier and matching network for pressure transducer.



result, the performance of the amplifier tends to deteriorate.

This problem was solved by connecting two amplifiers in series. The front amplifier provided the high input impedance, together with a medium value of gain. This enabled the output stage amplifier to use a lower gain and also a lower input resistance. The front end amplifier comprised the circuit formed by IC1a and IC1b. This circuit consists of two voltage followers, giving non-inversion of the input signal, with gain. In order to define the input resistance precisely, resistor R1 was connected from the non-inverting input to ground. Hence R1 was the actual input resistance of the circuit. The gain of the input circuit is given by

$$G_1 = 1 + \frac{2R_3}{R_2 + VR1} \qquad \text{Equation 2.1}$$

By varying VR1 the gain of the circuit can be altered. Using the values given in the key to Figure 2.11, the gain of the input circuit was fixed at the value of 10. As a result, the gain of the differentail amplifier circuit IC2 was only a tenth of what it would be if the preamplification stage was omitted. This enabled resistors of lower resistance to be used. The gain of the overall circuit was given by;

$$G = G_1 G_2 = \frac{1 + 2R_3}{R_2 + VR1} \times \frac{R_5 \rightarrow R_{10}}{R_4} \qquad \text{Equation 2.2}$$

$$= G_1 \times \frac{R_5 \rightarrow R_{10}}{R_4} \qquad \text{Equation 2.3.}$$

With the values given in the key, the gain of the amplifier was 1, 4.7, 10, 30, 56 and 100 giving overall gains of 10, 47, 100, 300, 560 and 1000.

2.2.1.8. Matching network.

The matching network was connected to the output of the amplifier and consisted of resistors R_{11}, R_{12} and R_{13}. There were several reasons for using such a network. If a vibrating system is totally undamped, it would theoretically vibrate forever. If a fixed amount of damping is applied, the amplitude of each successive cycle would decrease in a geometric ratio. A system is "critically damped", if, when it is displaced and then released, no overshoot occurs past the rest position for a given amount of damping.

If a galvanometer was undamped, it would be extremely vibration-sensitive and would tend to vibrate excessively at its natural frequency. Damping is gnerally applied to obtain an acceptable compromise between two interdependent quantities:

(a) Maximum flat frequency response.

and (b) Minimum recovery time for a step function input.

There are several ways of damping galvanometers depending on their design. The type used, Honeywell 130A, merely required a simple matching network between the amplifier and galvanometer input. This network provided two functions:

1. The correct damping resistance for the galvanometer.

and 2. The correct load resistance for the driving source namely the amplifier. Figure 2.12 shows a typical network.

2.2.1.9. Amplifier power supply.

The circuit for the amplifier power supply is shown in Figure 2.13. This was a straight-forward circuit based on an integrated circuit from Radiospares, which was capable of delivering ±15 mV at 40mA per rail.

2.2.10. Calibration of reaction vessel volume.

The volume of the reaction vessel and of the line between taps T7 and T8 was found by weighing the amount of "Analar" acetone required to fill the space at 295K.

2.2.1.11. Sampling system for combustion products.

This system consisted of a heated glass loop attached to the line of the apparatus adjacent to the furnace. The loop consisted of a U-tube made of 6 mm. i.d. glass tube and was attached to the line by means of two "ball and socket" joints, together with clips. The seal was maintained by the use of Viton "O" rings attached to the ball joints. The volume of the loop was determined by weighing the amount of "Analar" acetone required to fill the space at 295K. The loop was removed when filled with the combustion products and attached to the gas chromatographic system via ball joints.

2.2.1.11.1. Method of sampling.

When combustion reactions were completed, and with taps T11, T12 and T13 closed, tap T8 was opened. The pressure was measured via the galvanometer and the mercury

Key to figure 2.12.

R_L = optimum load resistance for driving source.

R_s = output resistance of driving force.

R_D = required damping resistance.

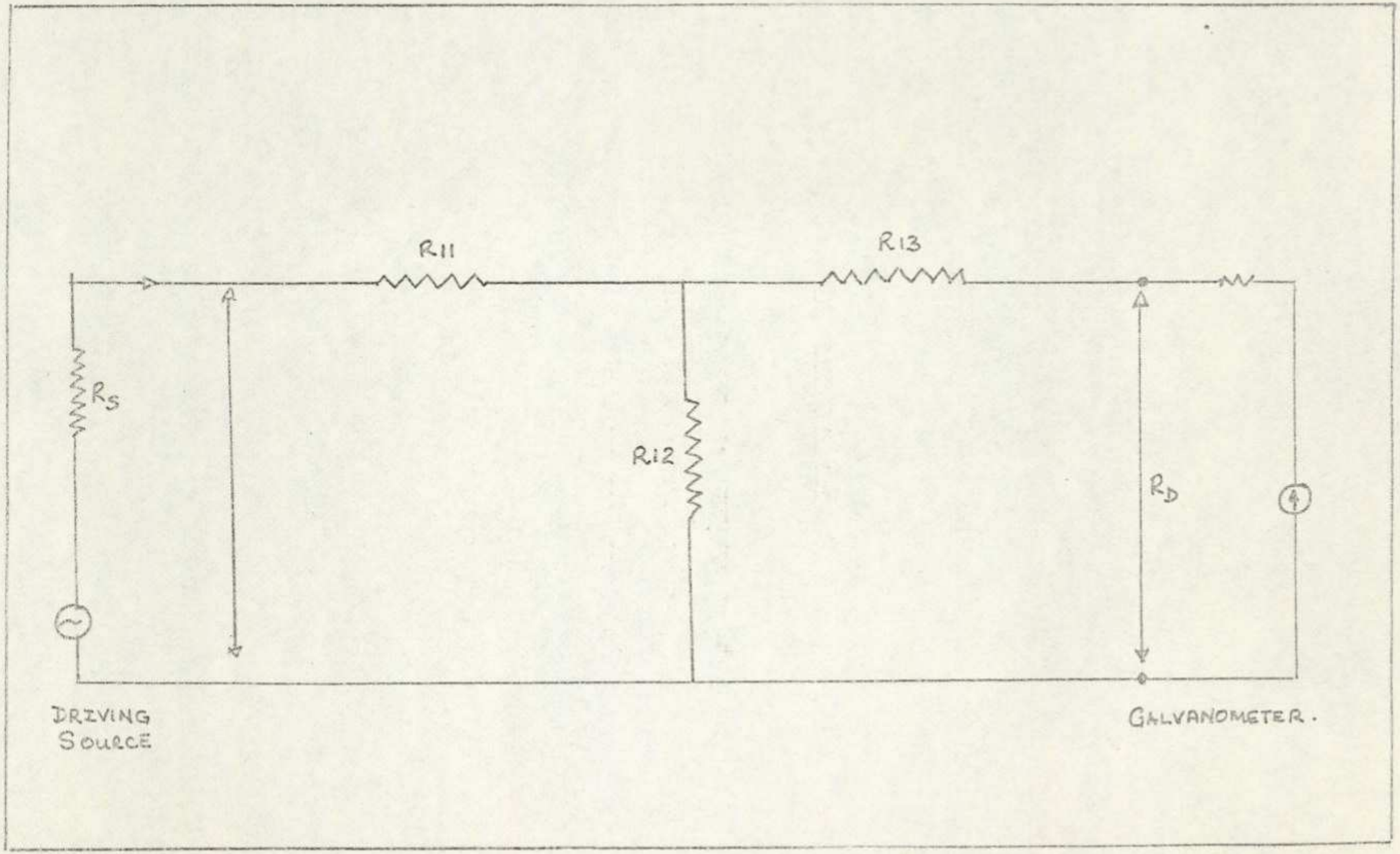


Figure 2.12.

Matching Network.

Key to figure 2.13.

C1 = C2 = 1000 µl, 25V.

C3 = C6 = 0.1 µF

C4 = C5 10 µF. 25V

D1 = radio spares 261-328

IC1 = radio spares 305-636

T1 = radio spares 207-217.

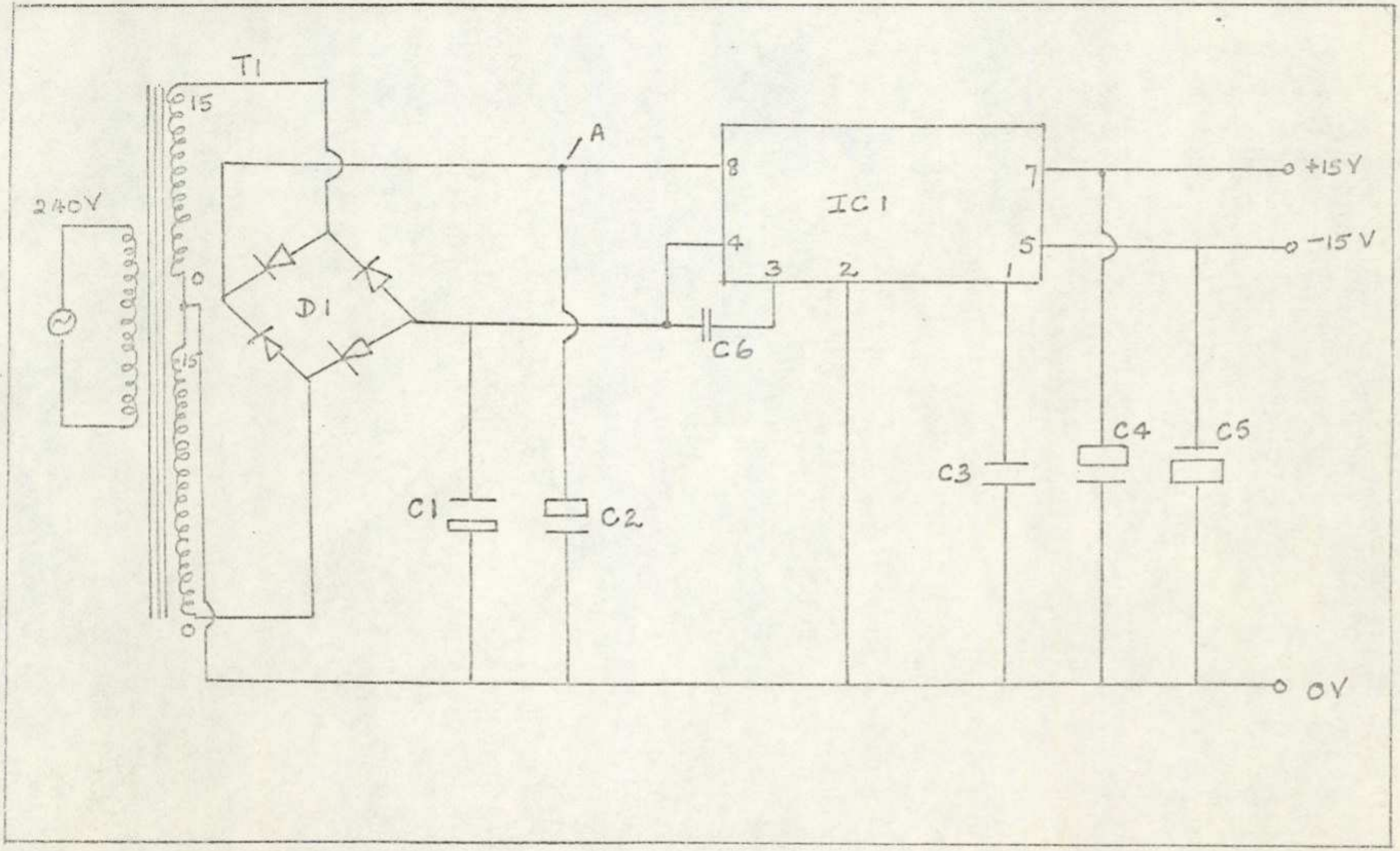


Figure 2.13.

Power supply for amplifier.

manometer, M2, and taps T11 and T12 were then opened. Taps T16, T17, T11 and T12 were then closed and the sample loop was removed from the line to the chromatographic system for analysis.

2.2.1.12. Gas chromatographic system.

The Perkin Elmer Model 452 chromatograph was used for the analysis of combustion products. The carrier gas used was helium, since the retention time for nitrogen was similar to that of sulphur dioxide on the column used. The sample to be analysed was introduced into the system via a special gas sampling valve. The combined carrier gas and sample mixture were then passed through a 6 ft, 0.25 in. o.d. stainless steel column, packed with Poropak Q. On leaving the column, the components were passed to the sensing chamber of the katharometer detector. Changes caused by the elution of the individual components of the gaseous mixture were recorded on a Vitatron two-pen chart recorder. The second pen was used for integration of the chromatogram.

2.2. Reactants.

Oxygen (99.6% pure) and nitorgen (99.9% pure) were supplied by the British Oxygen Company and were purified as described in Section 2.2.4.1. Liquefied sulphur dioxide was obtained from B.D.H. Chemicals ans was 99% pure. The sulphur compounds and isooctane used were the same as those described in Section 2.1.2. The powdered lead monoxide used was obtained from B.D.H. Chemicals and was 99% pure.

2.2.3. General procedure.

2.2.3.1. Introduction of reactants into the apparatus.

Oxygen from a cylinder was passed through the drying column, DC, and condensed in traps TR1 and TR2, which were cooled by liquid nitrogen. When sufficient oxygen had been collected, a middle fraction was vaporised into the storage vessel, S2, considerable head and tail fractions being rejected. Gaseous nitrogen was taken directly from a cylinder and allowed to flow into the storage vessel, S3, after passing through the drying column and the traps cooled with liquid nitrogen. Sulphur dioxide was stored in storage vessel, S1, after passage through the drying column.

The liquid sulphur compounds and hydrocarbon fuels were stored in bulbs F1 and F2. These compounds were transferred by syringes to the bulbs and degassed by successive freeze-thaw operations, which were carried out under vacuum until bubbles of gas ceased to leave the liquid. These compounds were then stored in an atmosphere of nitrogen to prevent oxidation.

2.2.3.2. Preparation of reaction mixtures.

Gaseous reactant mixtures were prepared on a partial pressure basis, the component with the lowest partial pressure being admitted first to the premix vessels, PM1 and PM2. During the preparation of the reactant mixtures, the pressure transducer, PT1, was used. The liquid hydrocarbon was vaporised into the evacuated premix vessels, oxygen was then added from the storage vessel S2, and the mixture was allowed to stand for 15 min. after which time it was believed to be homogeneous[113].

2.2.3.3. Conditioning of reaction vessel.

Reactant mixtures of total pressure 200 torr were prepared in the premix vessels. With tap T8 closed, the solenoid valve was opened for a specific length of time and a fraction of the premix was admitted to the reaction vessel. As soon as the solenoid valve was opened, tap T7 was shut. With the aid of the Visicorder and accessory equipment, cool flame and two-stage ignition reactions were observed, until a reproducible surface was obtained in the reaction vessel. The results were considered reproducible when the induction period preceding a cool flame varied by less than 5% for consecutive reactions carried out under the same initial conditions of pressure and temperature. Between these consecutive runs, the reaction vessel was evacuated for a standard period of 5 min.

2.2.3.4. Studies of oxidation of organic sulphur compounds.

Oxygen and the vapour of the organic sulphur compound were premixed as described in Section 2.2.3.2. Ratios of 1:1 and 1:3 (sulphur compound to oxygen) were used. The reactants were allowed to react for one hour and the products were then analysed for the unchanged organic sulphur compound and for any sulphur dioxide formed. These studies were carried out at three temperatures 250°C, 350°C and 450°C. A standard pressure of 200 torr was used. In all cases the amounts of oxygen present were substoichiometric.

2.2.3.4.1. Calculation of results.

The first step involved the calculation of the number of moles of product present in the sample. With a knowledge of the volume of the loop, its temperature and the pressure of the products, the number of moles present was calculated as follows:

22400 cm^3 of any gas at 760 torr and 273K is equivalent to one mole.

Therefore 14.2 cm^3 of any gas at a pressure of A torr and a temperature of BK contain

$$\frac{1 \times 14.2 \times A \times 273}{22400 \times 760 \times B} \qquad \text{Equation 2.4.}$$

where 14.2 cm^3 = sample loop volume.

Equation 2.4 gives the total number of moles present in the sample loop. With a knowledge of the S:O ratio, calculations were made of the number of moles of the sulphur compound which would have been present assuming no reaction. Several reactions were carried out using nitrogen instead of oxygen in order to calculate the actual amount of sulphur compound in the sample loop. The theoretical value was approximately 4% greater than the measured value.

From the chromatograms obtained the volume of unchanged sulphur compound was determined. From a knowledge of the density of the particular compound the number of moles of unchanged sulphur compound was calculated using the formula:

$$n = \frac{c.d}{MW} \qquad \text{Equation 2.5.}$$

where n = number of moles

c = volume of unchanged sulphur compound (cm^3)

d = density ($g.cm^{-3}$)

The amount of organic sulphur compound which had reacted was equal to the difference between the quantities given by equations 2.4 and 2.5. The amount of sulphur dioxide formed was also calculated.

2.2.3.5. Studies of the oxidation of isooctane.

Studies of the oxidation of isooctane at low temperatures were carried out in a clean reaction vessel and in a lead oxide-coated reaction vessel. Investigations were also made of the behaviour of isooctane containing 0.4 $g.l^{-1}$ of tetraethyl lead. The ratio of oxygen to isooctane used was 3:1. The effects of small additions of sulphur compounds on the ignition limits were determined and analysis of the products was carried out by gas chromatography. Approximately 6.25 volume% of sulphur dioxide, thiophene and thiophenol was used.

2.2.3.5.1. Coating of the reaction vessel with powdered lead oxide.

Powdered lead monoxide was mixed with a small volume of water to form a suspension, and then transferred to the reaction vessel. The vessel was heated to ca. 80°C by immersion in a water bath, and connected to an aspirator and continuously rotated in such a way that the suspension was in contact with all parts of the inner surface. As the water evaporated, a dry deposit was left clinging to the inside of the vessel wall. This method was similar to that used by Bardwell[87] in studies of the inhibition of combustion reactions by inorganic lead compounds. The density of the lead oxide deposits was about 1 mg. cm^{-2} in the present experiments.

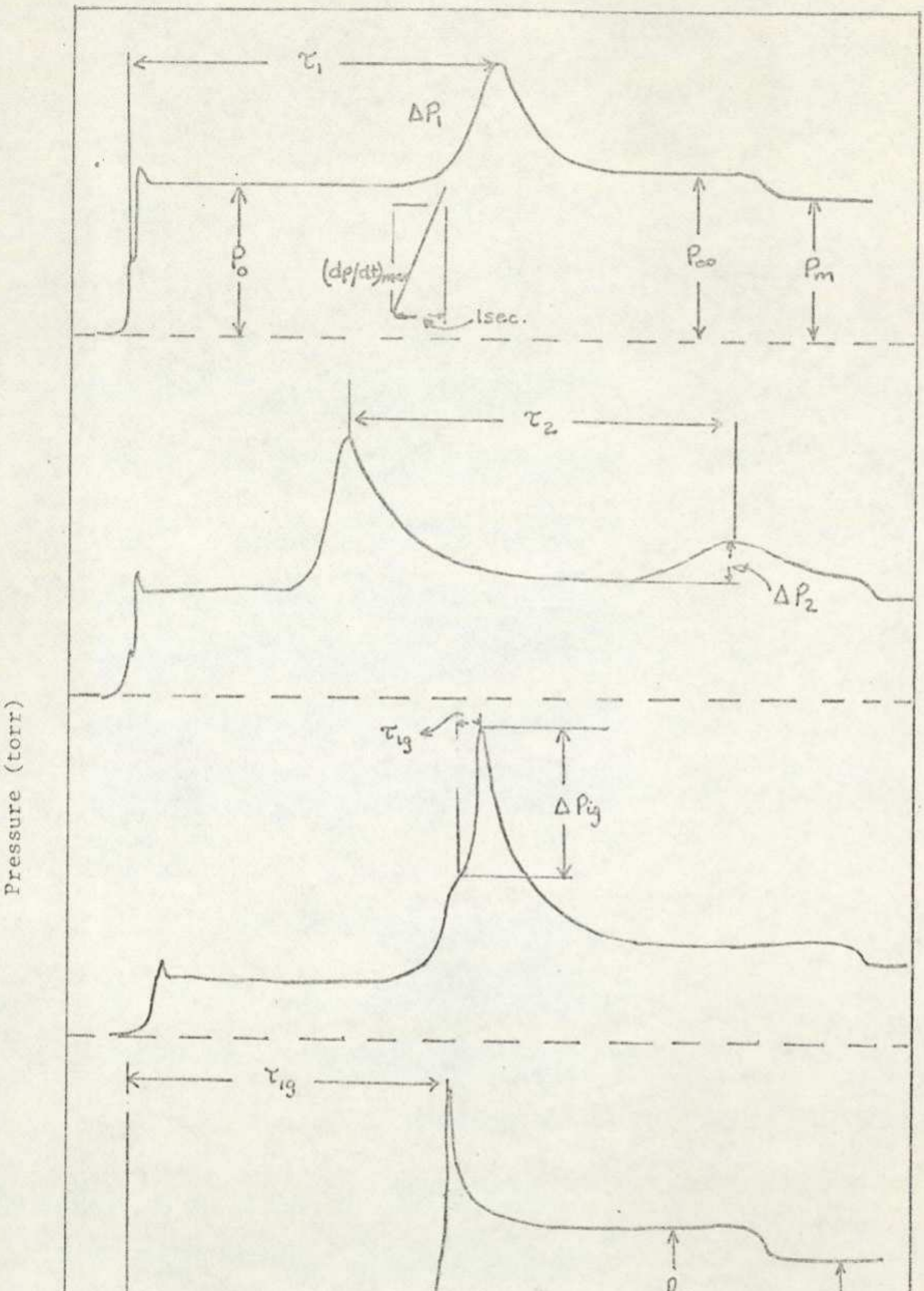
2.2.3.6. Calculation of kinetic parameters from pressure time records.

Since the output from the pressure transducer, PT2, was not always amplified at the same gain, it was necessary to make separate calibration checks for the transducer for each run. These calibrations were performed when the combustion reactions were completed, by opening tap T8, while taps T9, T11, T12 and T13 remained closed. The pressure was measured using manometer M2. The measured pressure corresponded to a deflection, P_m, on the pressure-time record shown in Figure 2.14a, from which a calibration of pressure per unit deflection was obtained.

The induction period preceding the first cool flame, τ_1, (Fig.2.14b) was taken as the time elapsing between the introduction of the reactants into the reaction vessel and the maximum value of the pressure rise of the cool flame, ΔP_1. The induction period of the ignition effect pulse, τ_{ig}, was taken as the time elapsing between τ_1 and ΔP_{ig}, (Fig. 2.14c). In the case of multiple cool flames, the induction periods of cool flames subsequent to the first cool flame were

Figure 2.14.

Kinetic measurements from pressure time records



taken as the time elapsing between τ_1 and the appropriate pressure pulse (Fig. 2.14b).

In Figure 2.14, P_o and P_m represent the initial and final pressures in the reaction vessel and ΔP_1 is the maximum pressure rise associated with the cool flame. These kinetic records were used in the construction of "low-temperature" ignition diagrams for isooctane-oxygen mixtures in clean and lead oxide-coated vessels and also for mixtures where tetraethyl lead was added to the fuel. The effects on these ignition limits of the three sulphur compounds were also determined.

2.2.3.7. Oxidation of isooctane in lead oxide- coated vessels treated with the vapour of the sulphur compounds.

Lead oxide was used to coat the reaction vessels as described in Section 2.2.3.5.1, and sulphur dioxide, thiophene or thiophenol, at a pressure of ca. 100 torr, was introduced into these vessels. These vessels were then heated to ca. 450°C and left for 24 hours. The sulphur compounds were pumped away and the vessels were then used to study the ignition limits of 3:1 oxygen-isooctane mixtures. The effects of 6.25 volume % of sulphur dioxide on the ignition limits of this hydrocarbon were also determined.

2.2.4. Analytical studies of lead oxide coating.

From the results of the combustion studies, it was decided that analysis of the lead oxide surface before and after treatment with the sulphur compounds would help to elucidate the mechanism of interaction of these sulphur compounds with tetraethyl lead. The technique used in these studies is known as E.D.A.X. (Energy Dispersive Analysis of X-rays).

2.2.4.1. E.D.A.X.

This method uses a scanning electron microscope (SEM) to examine directly the surface of rough specimens at high magnifications. Since the SEM operates by bombarding the specimen with a beam of electrons, characteristic X-rays are generated at the point of impact and these can be used to determine the composition. The SEM uses a fine electron beam to strike the specimen and at the point of impact, a variety of phenomena occur which can be used to obtain information about the specimen. By scanning the electron beam across the specimen surface in synchronization with a cathode ray tube, it is possible to map the specimen surface onto a display screen.

The Energy Dispersive spectrometer is used to measure the X-ray energy, producing a spectrum of counts versus energy in keV. As each ray enters the detector, it produces a shower of photoelectrons which strike the silicon atoms, and raise bound electrons to the conduction band. Each such event requires 3.8 electron volts of energy, so that the total number of electrons freed is linearly proportional to the energy of the impinging X-ray. The charge is collected from the detector, amplified and filtered to reduce noise, and the signal is integrated to produce a train of pulses. Each pulse has a height proportional to the energy of the X-rays which produced it, and a multi-channel pulse height analyser is used to measure and store these pulses in a spectrum. The resulting spectrum can then be displayed with a suitable scale for interpretation. The heights of the peaks are not a good direct measure of concentration, because the various elements are not all excited with the same efficiency and the X-rays generated in the sample are subject to absorption and secondary fluorescence effects before reaching the detector. Nevertheless a simple comparison of peak height often suffices for semi-quantitative purposes.

2.2.4.2. Preparation of samples for E.D.A.X. studies.

Four reaction vessels were coated with lead monoxide as described in Section 2.2.3.5.1. The vessels were then placed in a furnace at ca. 450°C and evacuated to a pressure of ca. 10^{-4} torr. Sulphur dioxide, thiophene and thiophenol were vaporised into three of the vessels to a pressure of 100 torr, and these vessels were then left for 24 hours. The fourth vessel was empty. The sulphur compounds were pumped off and the vessels were removed from the furnace. Samples of the lead oxide coating were obtained by scraping the surface wall and it was on these samples that the E.D.A.X. studies were carried out.

SECTION 3.

RESULTS.

SECTION 3

Results (cont'd)

Results (cont'd)

3.1. Results of engine studies.

3.1.1. The effect of lead alkyls on blended fuels.

The addition of sufficient quantities of lead alkyls to the fuel blends used invariably raised the octane number. The alkyls were more effective in increasing the octane number of the isooctane/heptane blend than that of toluene/heptane. Tetraethyl lead was a more effective "antiknock" than tetramethyl lead with both the fuel blends used. With the diisobutylene blend, tetramethyl lead had a slightly "pro-knock" effect at the lower concentrations and the eventual increase in octane number was small compared with that found with the alkane and aromatic blends. Table 3.1 and Figure 3.1 show the change in octane number obtained on addition of varying amounts of the lead alkyls. In all cases, except initially with tetramethyl lead in diisobutylene, the octane number increases with increasing concentration of lead alkyl. Table 3.2 and Figure 3.2 show the corresponding percentage increase in octane number on addition of the lead alkyls to the three blends.

3.1.2. The effect of sulphur compounds on the leaded fuels.

The presence in the leaded fuels of the seven different organic sulphur compounds used caused a reduction in octane number. Thiophene had the smallest influence in reducing the "antiknock" effect of the lead alkyls, whereas thiophenol was the most effective. The order of lead antagonism may

Table 3.1

Variation of Research Octane Number with lead alkyl concentration.

Lead alkyl concentration $g.l^{-1}$	Isooctane/heptane		Toluene/heptane		Diisobutylene/ heptane.
	Octane Number		Octane Number		Octane number
	TEL	TML	TEL	TML	TML
0.0	80.0	80.0	79.2	79.2	80.2
0.1	82.3	81.8	82.3	81.0	78.8
0.2	86.8	84.8	85.3	83.2	80.0
0.3	89.7	87.5	88.0	85.5	81.4
0.4	91.2	90.2	89.8	87.7	82.4

Table 3.2

Percentage change in Octane Number with lead alkyl concentration.

Lead alkyl concentration $g.l^{-1}$	Isooctane/heptane		Toluene/heptane		Diisobutylene/heptane
	% change in octane number		% change in octane number		% change in octane number.
	TEL	TML	TEL	TML	TML
0.1	2.9	2.25	3.9	2.27	-1.7
0.2	8.5	6.00	7.7	5.1	-0.25
0.3	12.1	9.4	11.1	8.0	1.5
0.4	14.0	12.75	13.4	10.7	2.7

Figure 3.1

Concentration of lead alkyl versus Research Octane Number.

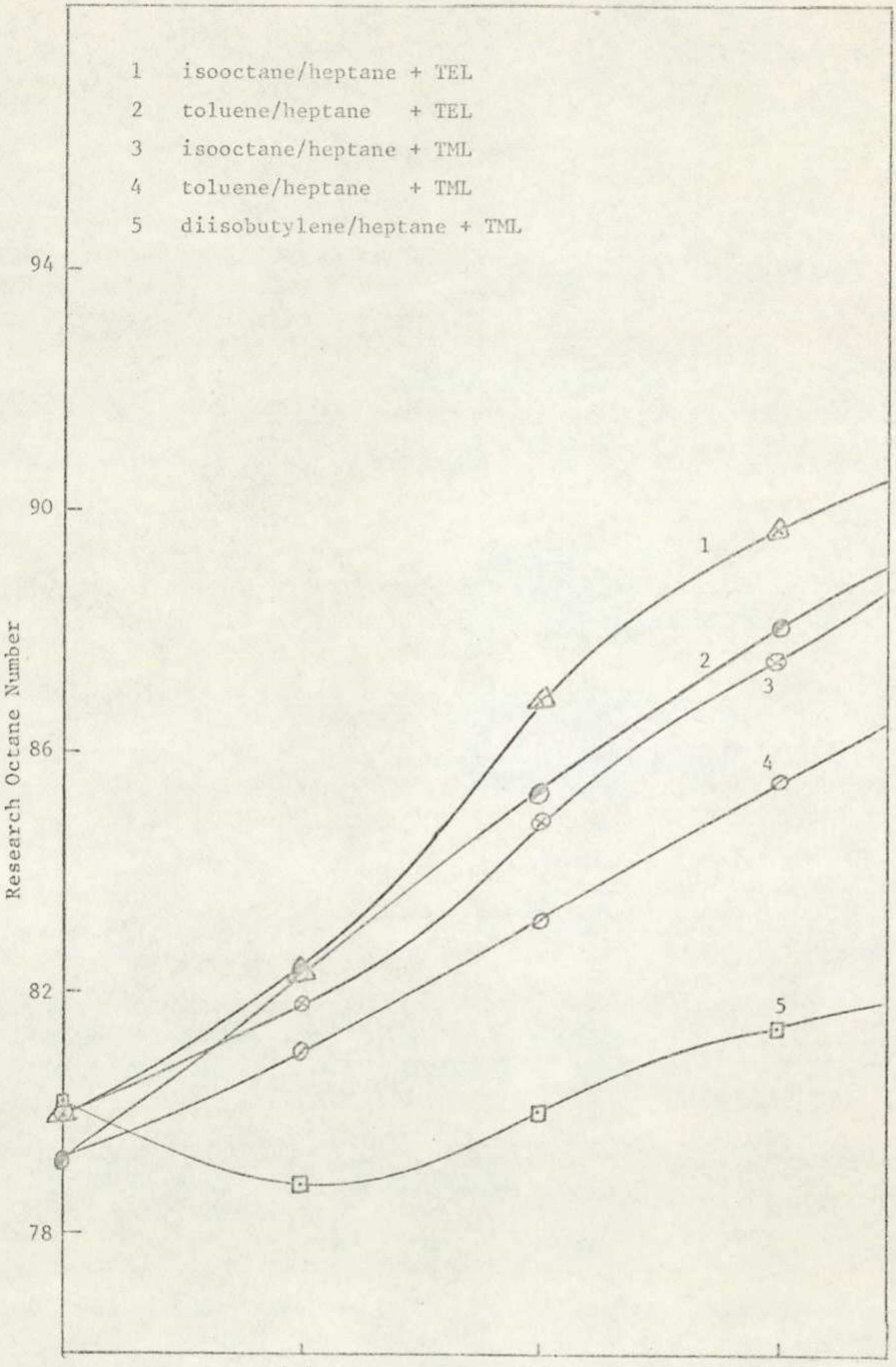
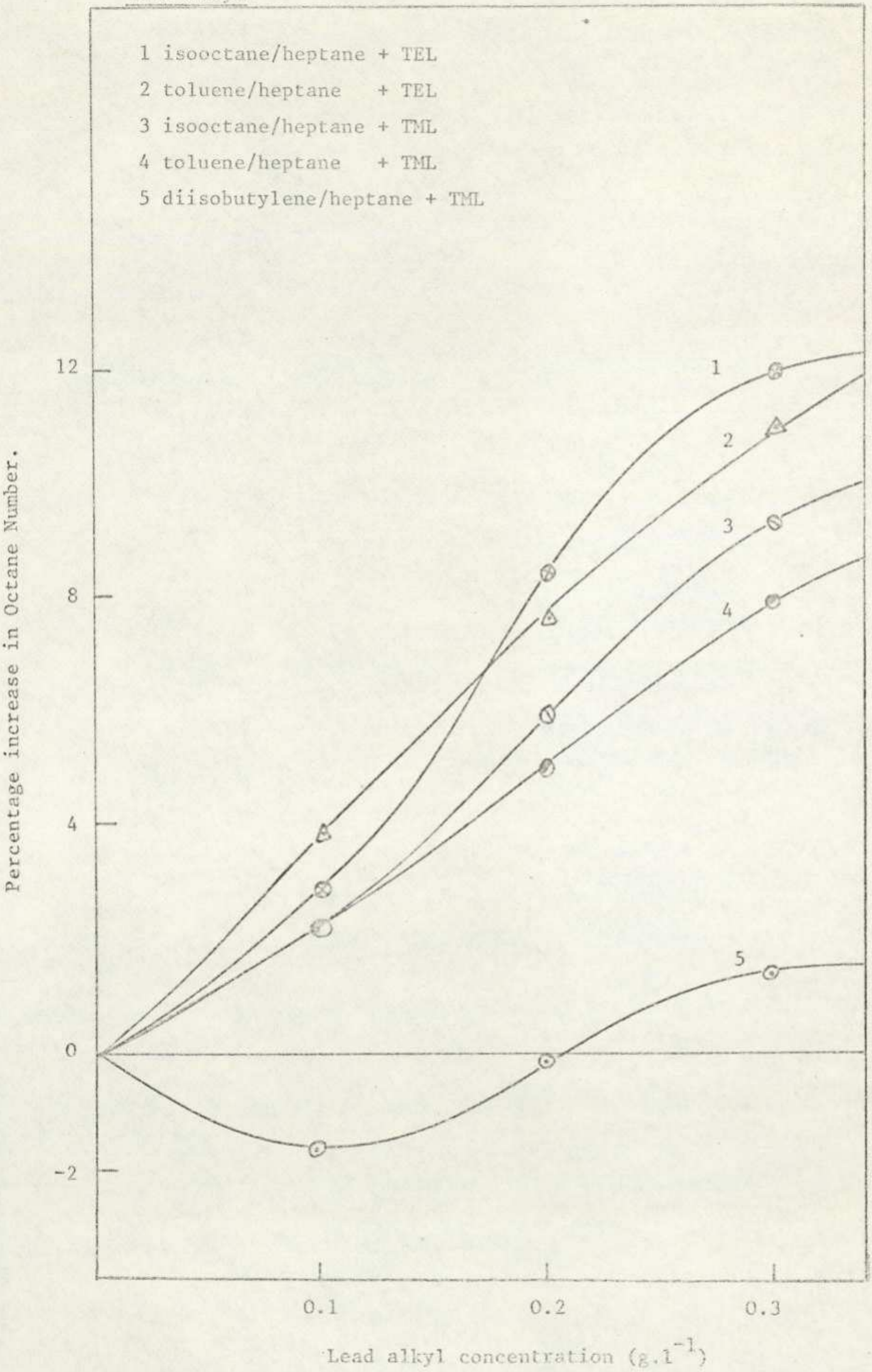


Figure 3.2

Percentage increase in octane number versus concentration of lead alkyl.



in fact be defined as follows: thiophene < diphenyl sulphide < diphenyl disulphide < dipropyl sulphide < tertiary octyl mercaptan < dimethyl disulphide < thiophenol. This same trend was observed with all three fuel blends. Results obtained with the isooctane/heptane blend are listed in Table 3.3 and are also shown in Figures 3.3 (a) and (b), from which the different effects of the various sulphur compounds can be seen. Results for sulphur antagonism with the toluene/heptane blend are shown in Table 3.4 and Figure 3.4 and those with the diisobutylene/heptane blend are shown in Figure 3.5 and Table 3.5. It can thus be seen that the sulphur compounds have a greater effect on the alkane fuel than they do on the aromatic blend.

It is also clear that the sulphur compounds are antagonistic towards the leaded fuel and, although this antagonism may be expressed in terms of the decrease in octane number, the decrease in lead efficiency is of greater significance in the comparison of the behaviour of different fuels.

3.1.2.1. Calculation of the lead antagonism of the sulphur compounds.

The percentage loss of lead efficiency, L, may be expressed by the equation

$$L = \frac{a_o - a}{a} \times 100 \qquad \text{Equation 3.1}$$

where a_o = actual concentration of lead alkyl.

a = concentration of lead alkyl in sulphur-free fuel corresponding to the observed octane number. This

Table 3.3

Variation with sulphur compound concentration of Octane Number of leaded isooctane/heptane blend.

Sulphur Compound Added	Octane Number			
	TEL (0.4g.1^{-1}) + 80.0 O.N. iso-octane + heptane = 91.2		TML (0.4g.1^{-1}) + 80.0 O.N. isooctane /heptane = 90.2	
	Sulphur by weight		Sulphur by weight	
	0.1%	0.05%	0.1%	0.05%
Thiophene	88.6	89.6	86.6	87.5
Diphenyl sulphide	87.5	88.8	85.1	86.9
Diphenyl disulphide	86.8	88.0	84.5	85.4
Dipropyl sulphide	86.7	87.9	84.7	85.8
Tert-octyl mercaptan	85.8	87.0	83.9	85.1
Dimethyl disulphide	85.5	86.7	83.7	84.8
Thiophenol	84.1	85.9	84.3	85.3

Key to figure 3.3.

1 = Thiophene.

2 = Diphenyl sulphide.

3 = Diphenyl disulphide.

4 = Dipropyl sulphide.

5 = Tert-octyl mercaptan.

6 = Dimethyl disulphide.

7 = Thiophenol.

Figure 3.3.

Variation of Research Octane Number with weight percent of sulphur in base fuel.

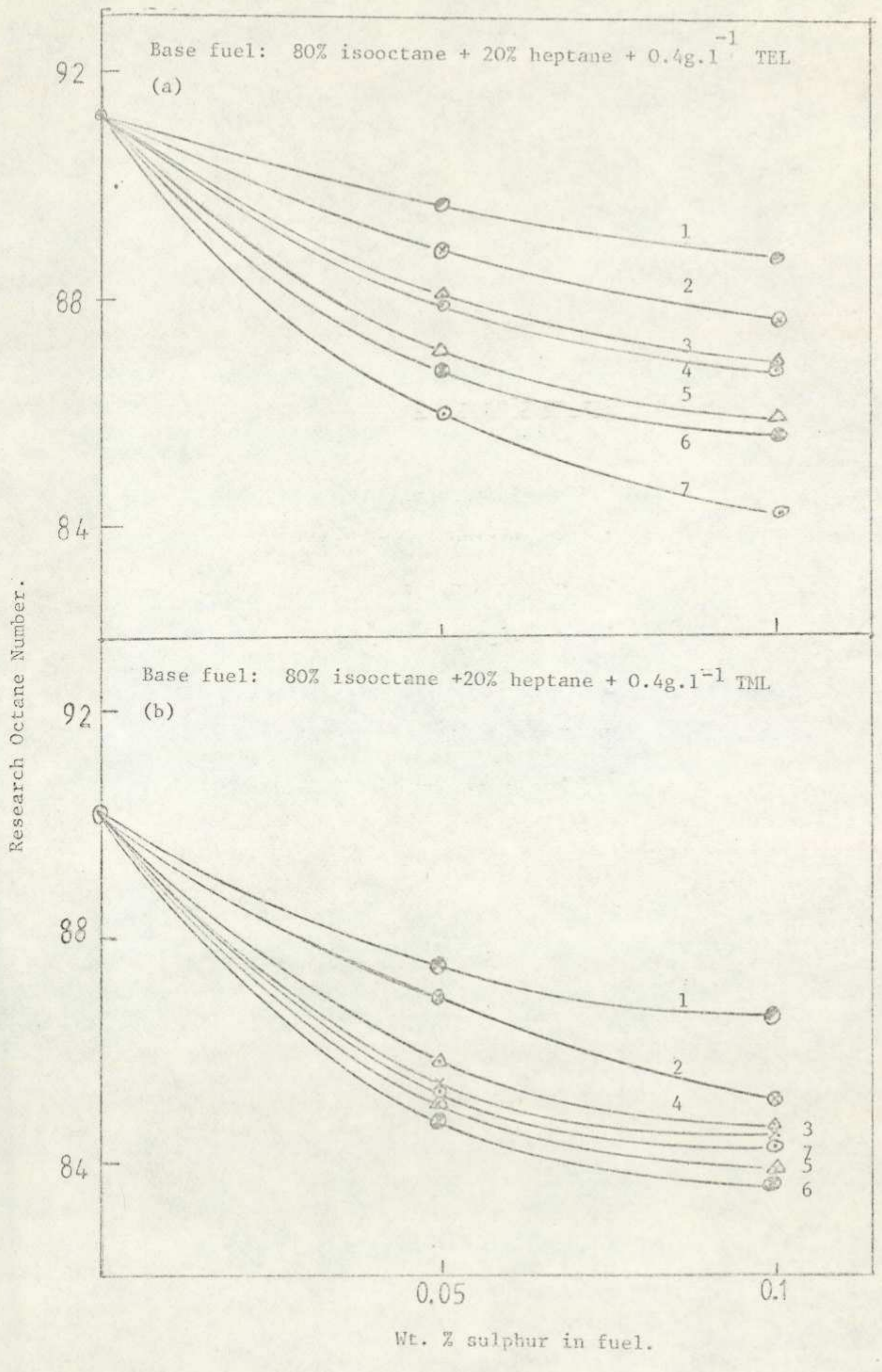


Table 3.4.

Variation with sulphur compound concentration of Octane Number of leaded toluene/heptane blend.

Sulphur Compound Added	Octane Number.			
	TEL ($0.4g.l^{-1}$) + 80 O.N. toluene/heptane = 89.8		TML ($0.4g.l^{-1}$) + 80 O.N. toluene /heptane = 87.7	
	Sulphur by weight		Sulphur by weight	
	0.1%	0.05%	0.1%	0.05%
Thiophene	89.0	89.8	86.8	87.3
Diphenyl sulphide	88.4	89.5	86.2	87.0
Diphenyl disulphide	87.1	88.2	85.4	86.2
Dipropyl sulphide	87.0	88.3	85.2	86.3
Tert-octyl mercaptan	86.4	87.8	84.5	85.8
Dimethyl disulphide	86.4	87.6	84.9	86.0
Thiophenol	84.4	85.9	84.9	85.8

Key to figure 3.4.

1 = Thiophene.

2 = Diphenyl sulphide.

3 = Diphenyl disulphide.

4 = Dipropyl sulphide.

5 = Tert-octyl mercaptan.

6 = Dimethyl disulhide.

7 = Thiophenol.

Figure 3.4.

Variation of Research Octane Number with weight percent of sulphur in base fuel.

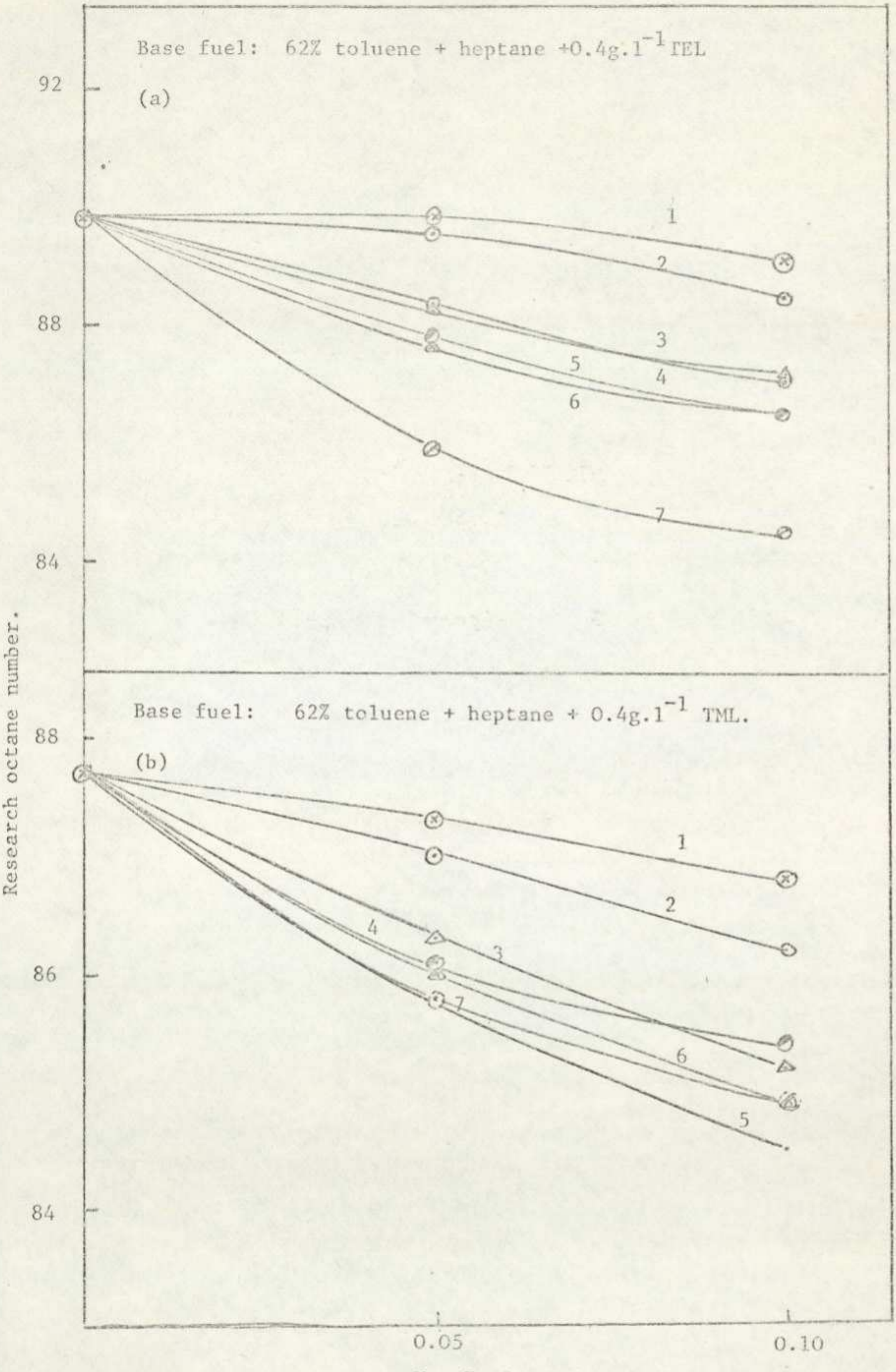


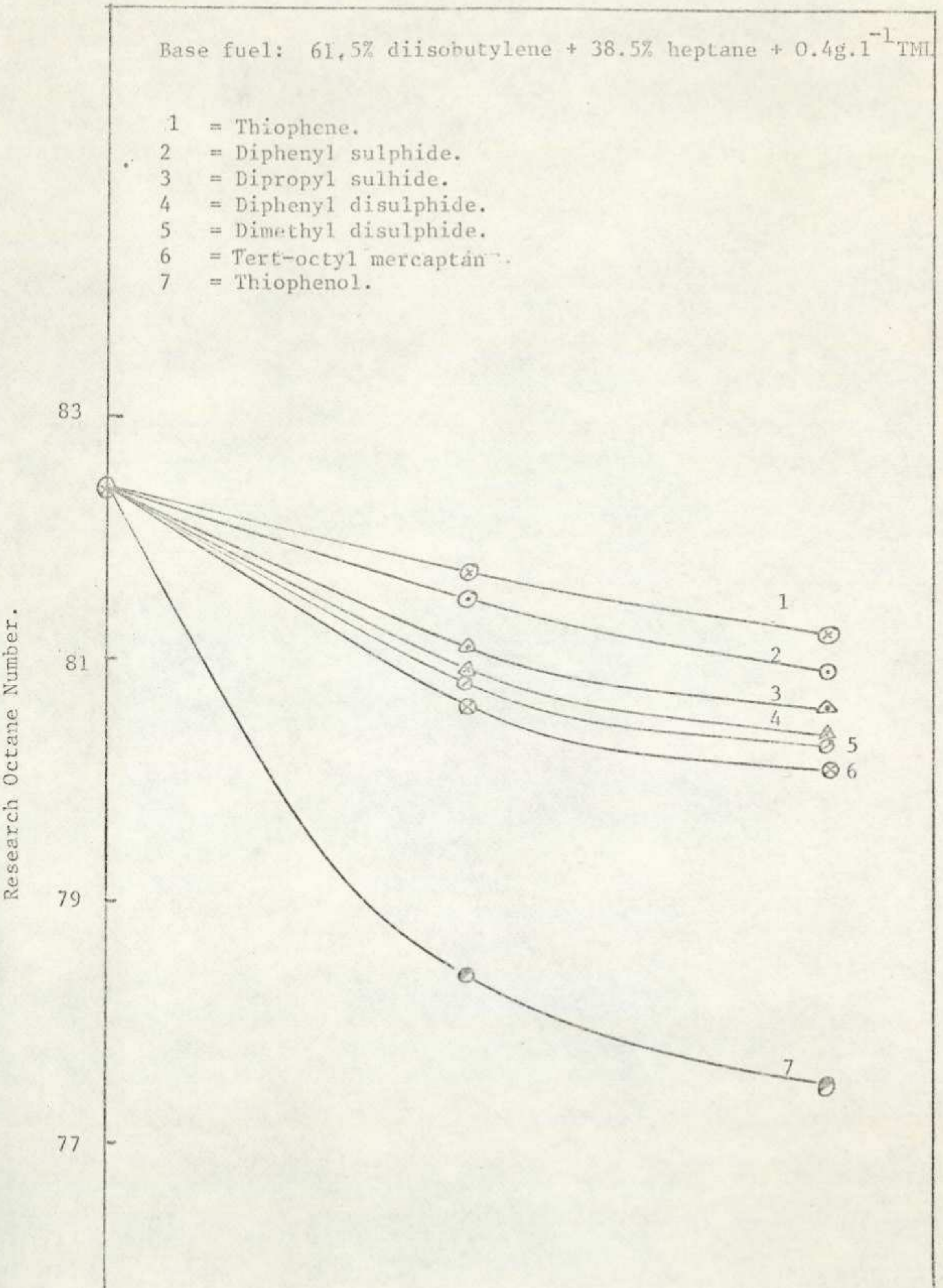
Table 3.5

Variation with sulphur compound concentration of octane number of leaded diisobutylene/heptane blend.

Sulphur Compound Added	Octane Number	
	Sulphur by weight	Sulphur by weight
	0.1%	0.05%
Thiophene	81.2	81.7
Diphenyl sulphide	80.9	81.5
Diphenyl disulphide	80.4	80.9
Dipropyl sulphide	80.6	81.1
Tert-octyl mercaptan	80.1	80.6
Dimethyl disulphide	80.3	80.8
Thiophenol	77.5	78.4

Figure 3.5.

Variation of Research Octane Number with weight percent of sulphur in base fuel.



was obtained from the calibration curves of Research Octane Number (R.O.N.) versus lead alkyl concentration (Figure 3.1).

Tables 3.6, 3.7 and 3.8 show the decrease in lead efficiency of the lead alkyls in the presence of the sulphur compounds for the isooctane, toluene and diisobutylene blends respectively. Figures 3.6, 3.7 and 3.8 show the relationship between the loss in lead efficiency and the percentage by weight of sulphur present.

Figure 3.9 shows the percentage loss in lead efficiency caused by the various sulphur compounds. This gives a better comparison of the effect of the sulphur compounds on the three leaded fuels used. With the blends containing tetraethyl lead, thiophenol had a very large deleterious effect on the lead efficiency and the order of effectiveness for these blends is as shown in Section 3.1.2.

With the tetramethyl lead-containing fuels, however, the effect of thiophenol was not exceptionally large except for the diisobutylene blend, where the normal increase in octane number was completely nullified. Although the order of lead antagonism of the different sulphur compounds was generally similar to that found with the fuels containing tetraethyl lead, dimethyl disulphide and tertiary octyl mercaptan were sometimes found to be more deleterious in their effect than thiophenol, in the tetramethyl blends.

In general the sulphur compounds were more

Table 3.6.

Variation with sulphur compound concentration of percentage loss of lead efficiency of iso-octane/heptane fuels.

Sulphur Compound Added	% Loss in Lead Efficiency			
	TEL fuel		TML fuel	
	0.1% S	0.05% S	0.1% S	0.05% S
Thiophene	37.5	25.0	35.0	26.9
Diphenyl sulphide	49.6	35.6	49.8	32.5
Diphenyl disulphide	50.0	42.5	52.5	49.5
Dipropyl sulphide	50.6	43.75	50.6	41.9
Tert-octyl mercaptan	55.0	50.0	56.9	49.8
Dimethyl disulphide	56.25	50.6	58.1	50.0
Thiophenol	63.1	54.4	53.75	49.6

Figure 3.6(a).

Variation with sulphur compound concentration of percentage loss of lead efficiency of isooctane/heptane fuels.

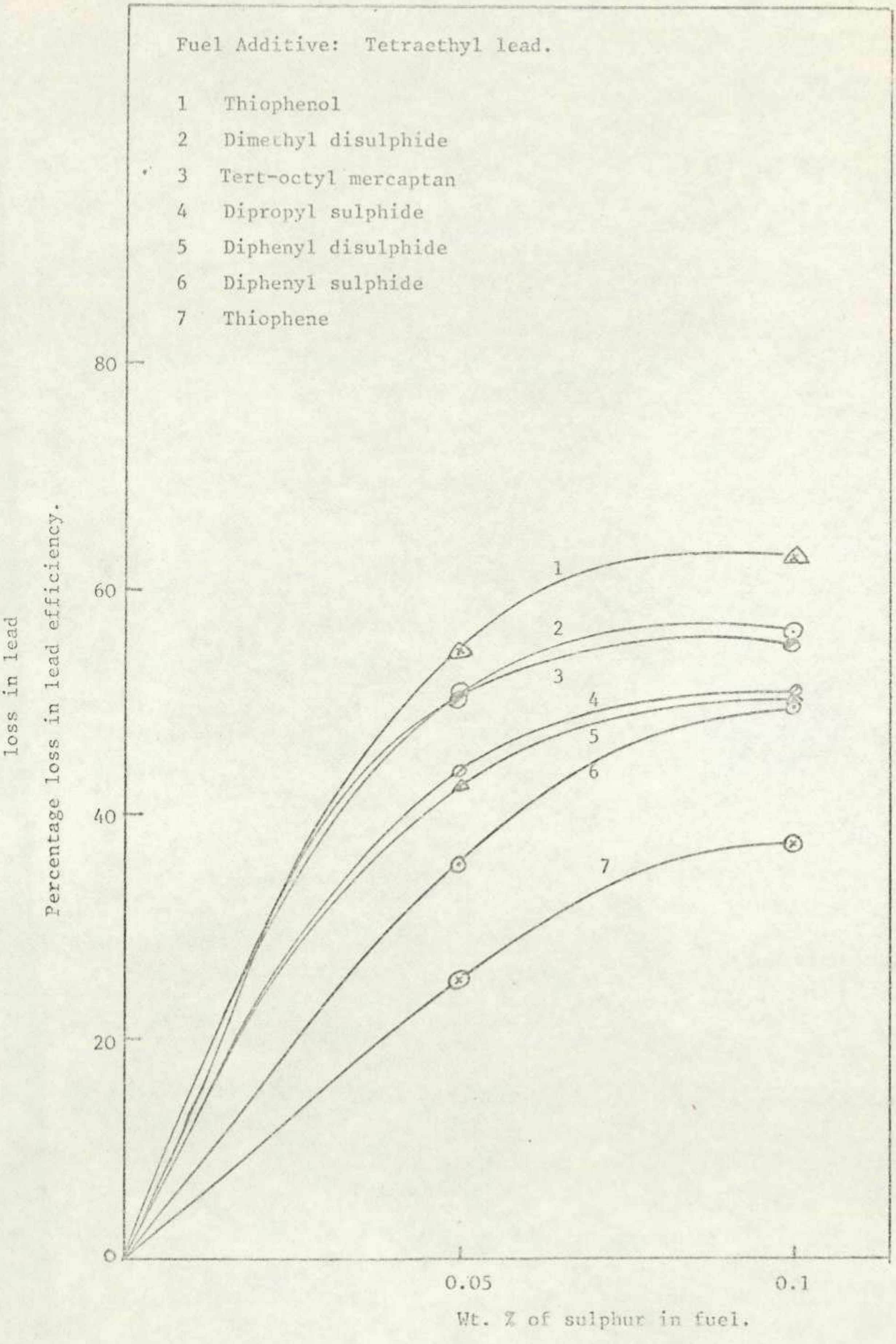


Figure 3.6(b).

Variation with sulphur compound concentration of percentage loss of lead efficiency of isooctane/heptane fuels.

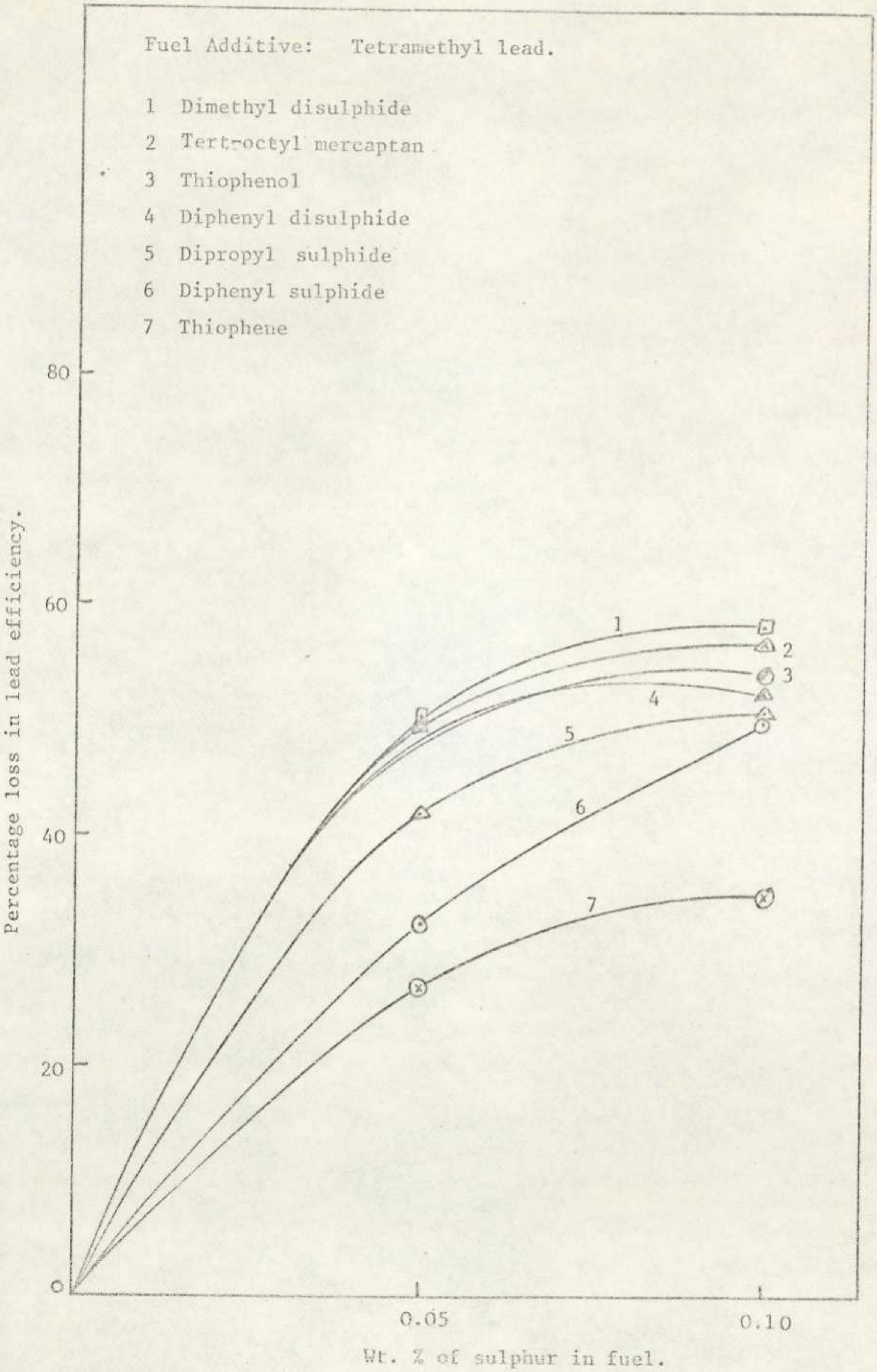


Table 3.7.

Variation with sulphur compound concentration of percentage loss of lead efficiency of toluene /heptane fuels.

Sulphur Compound Added	% Loss in Lead Efficiency			
	TEL fuel		TML fuel	
	0.1% S	0.05% S	0.1% S	0.05% S
Thiophene	13.1	NIL	10.6	5.0
Diphenyl sulphide	24.5	6.25	17.5	8.1
Diphenyl disulphide	33.75	24.75	25.6	17.5
Dipropyl sulphide	35.0	24.6	27.5	16.25
Tert-octyl mercaptan	40.6	26.3	36.25	24.75
Dimethyl disulphide	40.6	28.75	30.6	24.5
Thiophenol	57.5	49.5	30.6	24.75

Key to Figure 3.7

1 = Thiophenol.

2 = Dimethyl disulphide.

3 = Tert-octyl mercaptan

4 = Dipropyl sulphide.

5 = Diphenyl disulphide.

6 = Diphenyl sulphide

7 = Thiophene.

Figure 3.7

Variation with sulphur compound concentration of percentage loss of lead efficiency of toluene/heptane fuels.

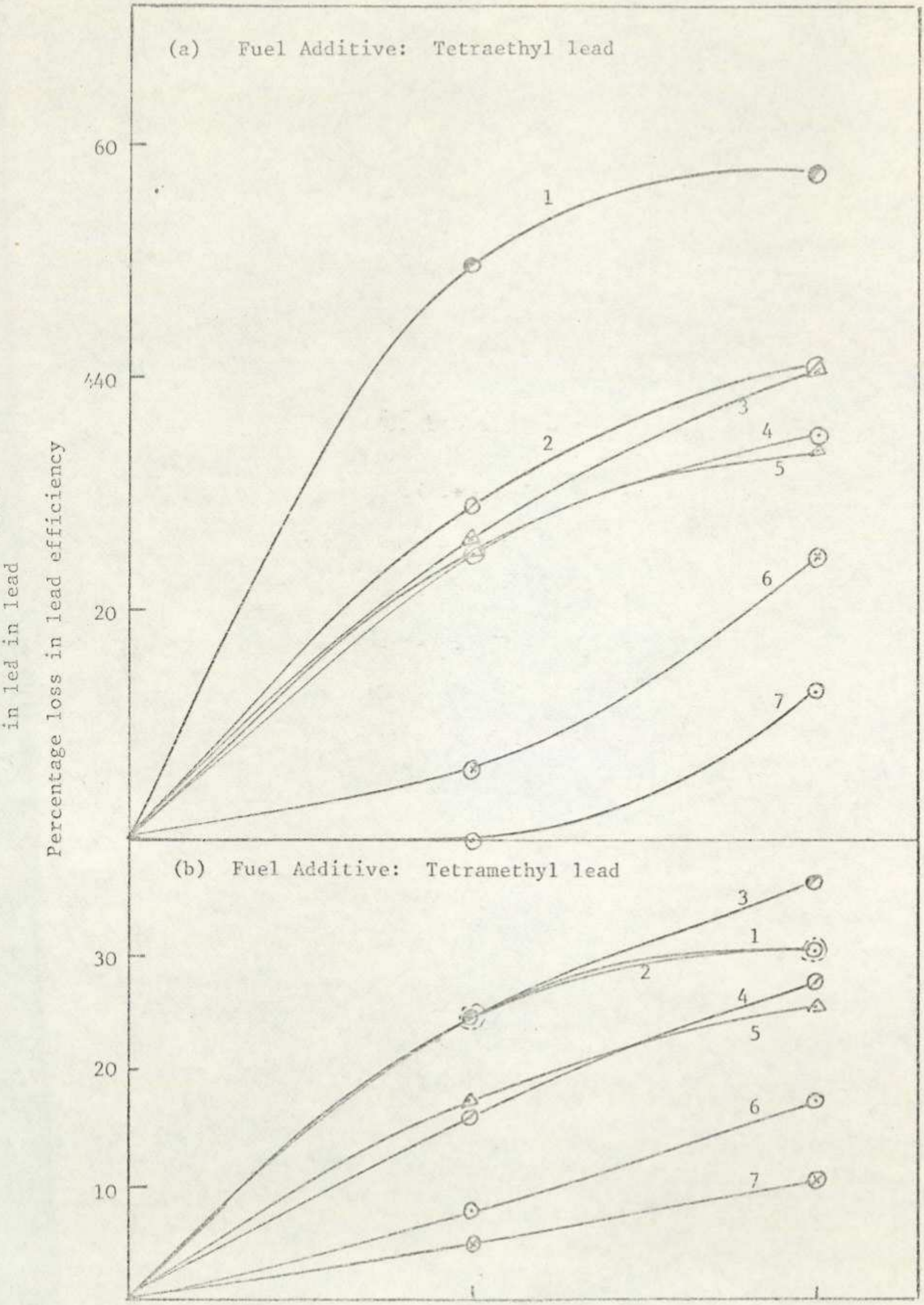


Table 3.8.

<u>Variation with sulphur compound concentration of percentage loss of lead efficiency of diisobutylene/heptane blend.</u>

Sulphur Compound Added	% Loss in Lead Efficiency	
	TML containing fuel	
	0.1% S	0.05% S
Thiophene	29.4	18.75
Diphenyl sulphide	35.0	24.75
Diphenyl disulphide	43.1	35.0
Dipropyl sulphide	40.0	31.25
Tert.-octyl mercaptan	49.75	40.0
Dimethyl disulphide	49.5	36.9
Thiophenol	100	100

Key to Figure 3.8.

1 = Thiophenol

2 = Tert-octyl mercaptan.

3 = Dimethyl disulphide.

4 = Diphenyl disulphide.

5 = Dipropyl sulphide.

6 = Diphenyl sulphide.

7 = Thiophene.

Figure 3.8

Variation with sulphur compound concentration of percentage loss of lead efficiency of diisobutylene/heptane fuels.

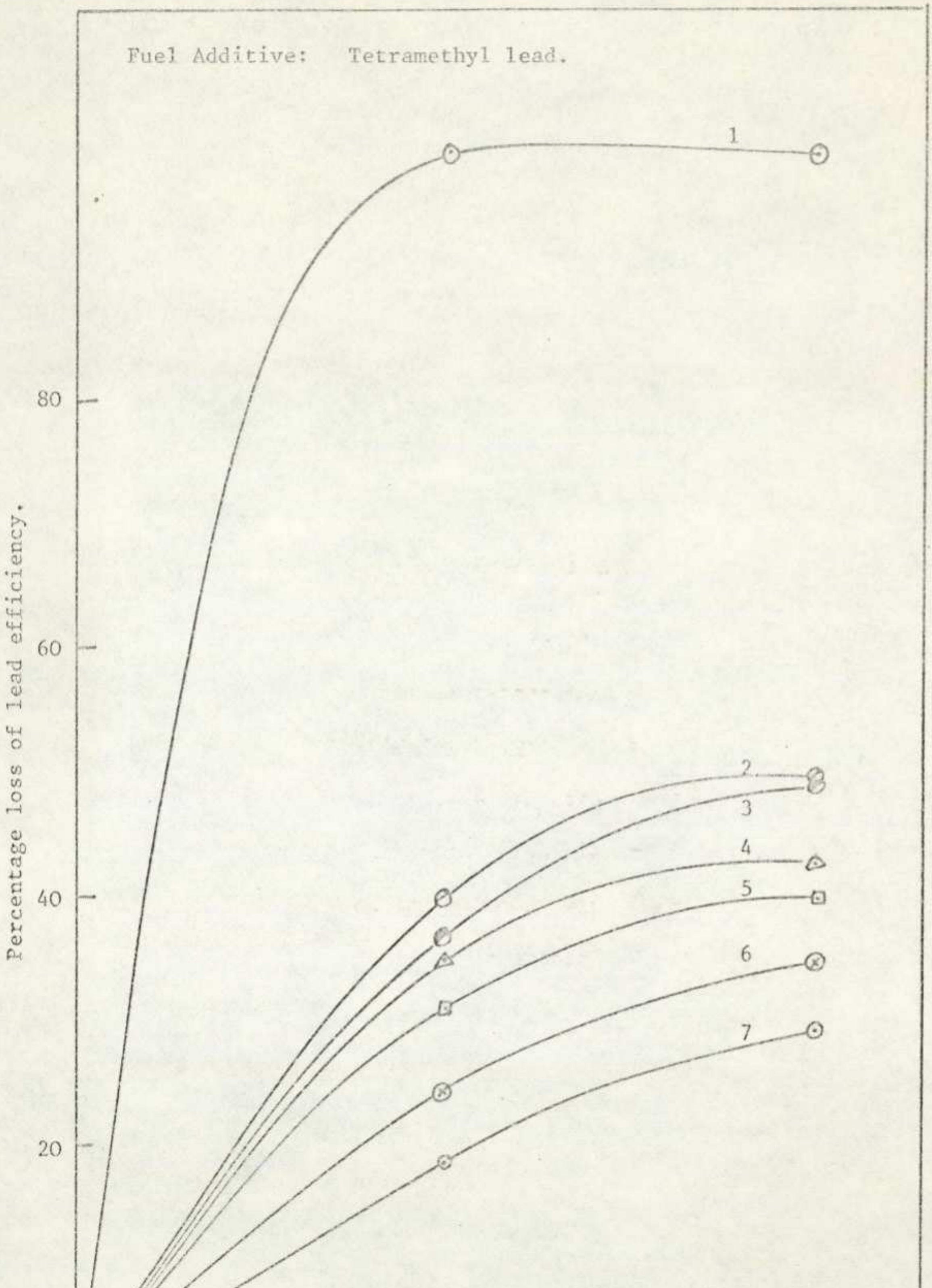
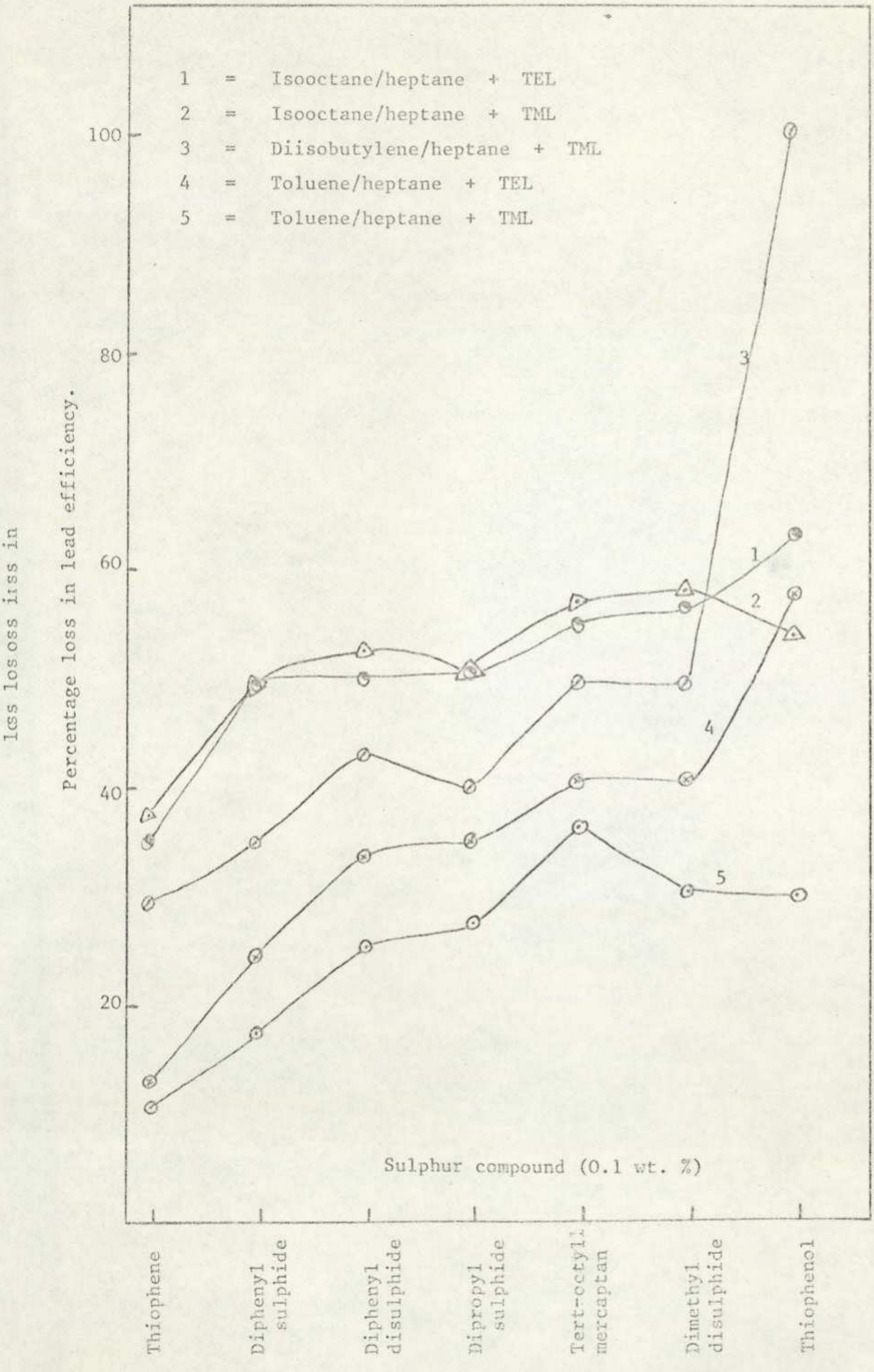


Figure 3.9

Variation with sulphur compound concentration of percentage loss of lead efficiency.



more effective in reducing the lead efficiency of the isooctane/heptane blends than that of the other fuels studied. The toluene/tetramethyl lead blend was least affected by the addition of sulphur compounds. Diisobutylene fuels exhibited effects which were smaller than those obtained with the isooctane/heptane blend, but greater than those found with the toluene/heptane blend. The order of resistance of the fuel blends to sulphur antagonism may therefore be written as toluene/heptane + TML > toluene/heptane + TEL > diisobutylene/heptane + TML > isooctane/heptane + TML > isooctane/heptane + TEL. This is shown graphically in Figure 3.9.

3.2. Laboratory studies of the gaseous oxidation of sulphur compounds.

3.2.1. Thiophene.

This compound had the smallest effect in reducing the octane numbers of the leaded fuels used in the engine studies and was also the most resistant to "low-temperature" oxidation. At 250°C, the amount of thiophene which had reacted was small, namely ca. 25% of the total quantity initially present, and no sulphur dioxide was formed. At the higher temperature of 350°C, considerably more of the thiophene reacted and some sulphur dioxide was formed. The reactions occurring at these two temperatures were slow combustion-type reactions. At 450°C, cool flame (1:1 thiophene to oxygen) and hot ignition (1:3 thiophene to oxygen) reactions were observed, and virtually all the initial sulphur compound was consumed. However the amount of sulphur dioxide formed per mole of thiophene consumed was smaller than that at 350°C. Figures 3.10 (a) and (b) show respectively the percentage oxidation of thiophene and the number of moles of sulphur dioxide formed per mole of thiophene used up as functions of temperature.

3.2.2. Dipropyl sulphide.

This compound was extremely reactive and cool flames were observed at pressures as low as 80 torr and at a temperature of 250°C. On account of the high reactivity and explosibility of this compound, studies of its oxidation were confined to the lower temperatures, 250°C and 350°C. Complete

Figure 3.10 (a).

The variation with temperature of the percentage of thiophene oxidised.

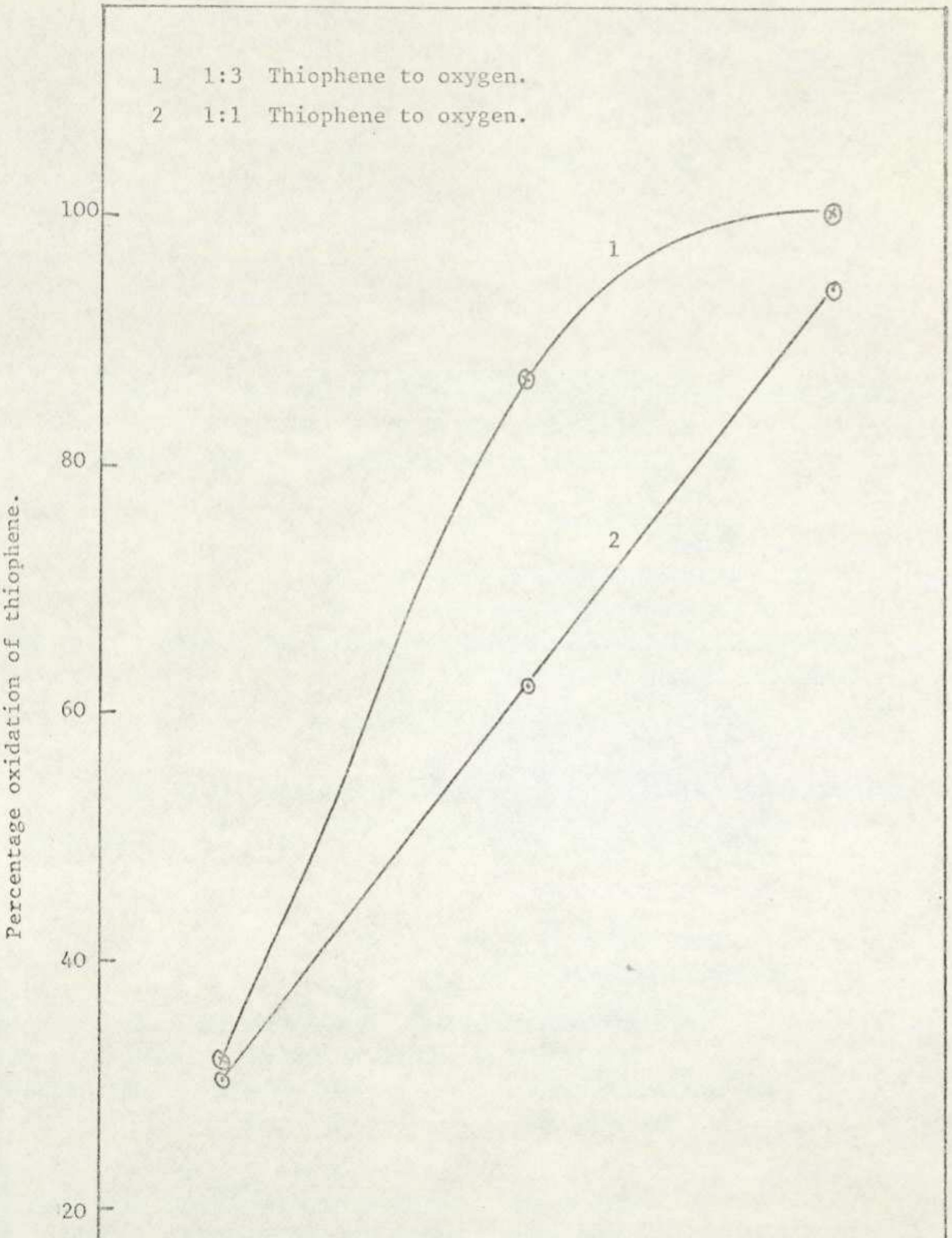
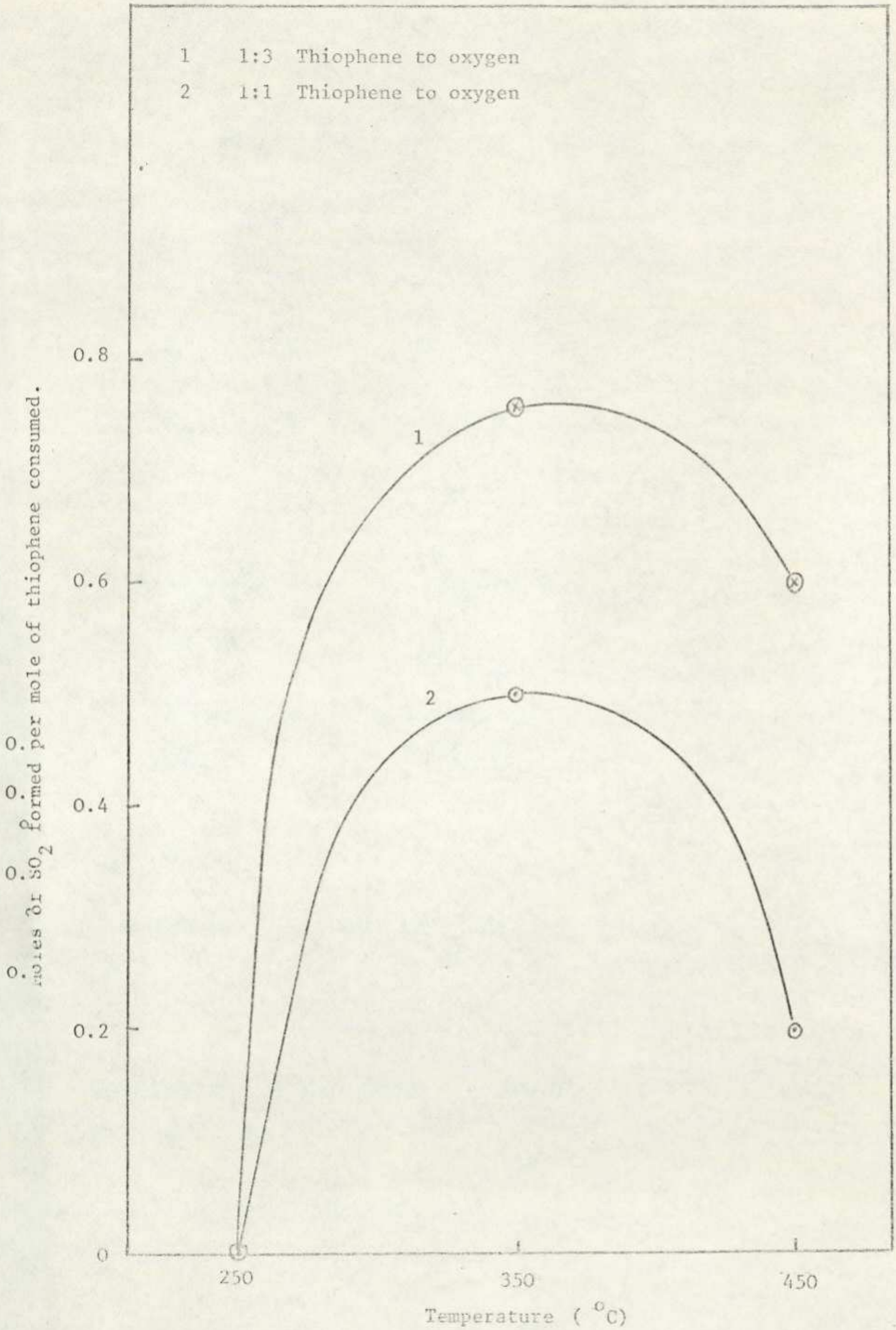


Figure 3.10 (b).

The variation with temperature of the amount of sulphur dioxide formed from thiophene.



consumption of the dipropyl sulphide occurred at both temperatures, though not all the sulphur in it was converted to sulphur dioxide.

3.2.3. Dimethyl disulphide.

The reactivity of this compound was found to lie between that of thiophene and dipropyl sulphide. At 250°C for example, dimethyl disulphide was only slightly more reactive than thiophene. However, whereas with thiophene no sulphur dioxide was formed, dimethyl disulphide did yield some sulphur dioxide though less than that derived from dipropyl sulphide. At 350°C, dimethyl disulphide reacted completely but again not all the sulphur was converted to sulphur dioxide. Figures 3.11 (a) and (b) show respectively the percentage oxidation, and the amount of sulphur dioxide formed per mole of initial sulphur compound used up, as functions of temperature.

3.2.4. Thiophenol.

This compound was similar to dipropyl sulphide in its reactivity, being almost completely consumed at all temperatures except in a 1:1 mixture with oxygen at 250°C. At all temperatures used, the reactions were of the slow combustion type and almost all the sulphur was converted to sulphur dioxide. Figures 3.12 (a) and (b) show respectively the percentage oxidation, and the amount of sulphur dioxide formed per mole of sulphur compound used up, plotted against temperature.

Figure 3.11 (a).

The variation with temperature of the percentage of dimethyl disulphide oxidised.

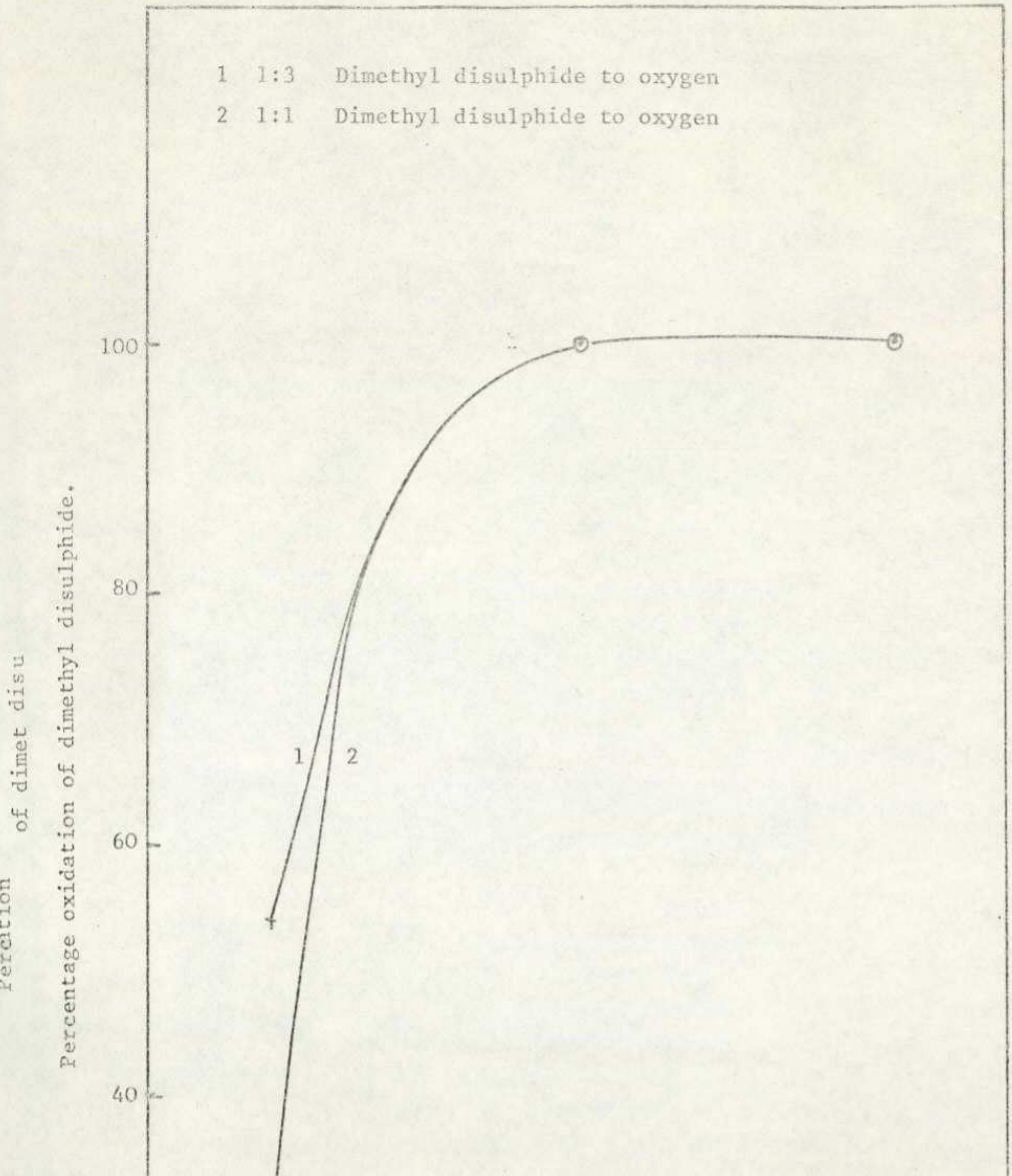


Figure 3.11 (b).

The variation with temperature of the amount of sulphur dioxide formed from dimethyl disulphide.

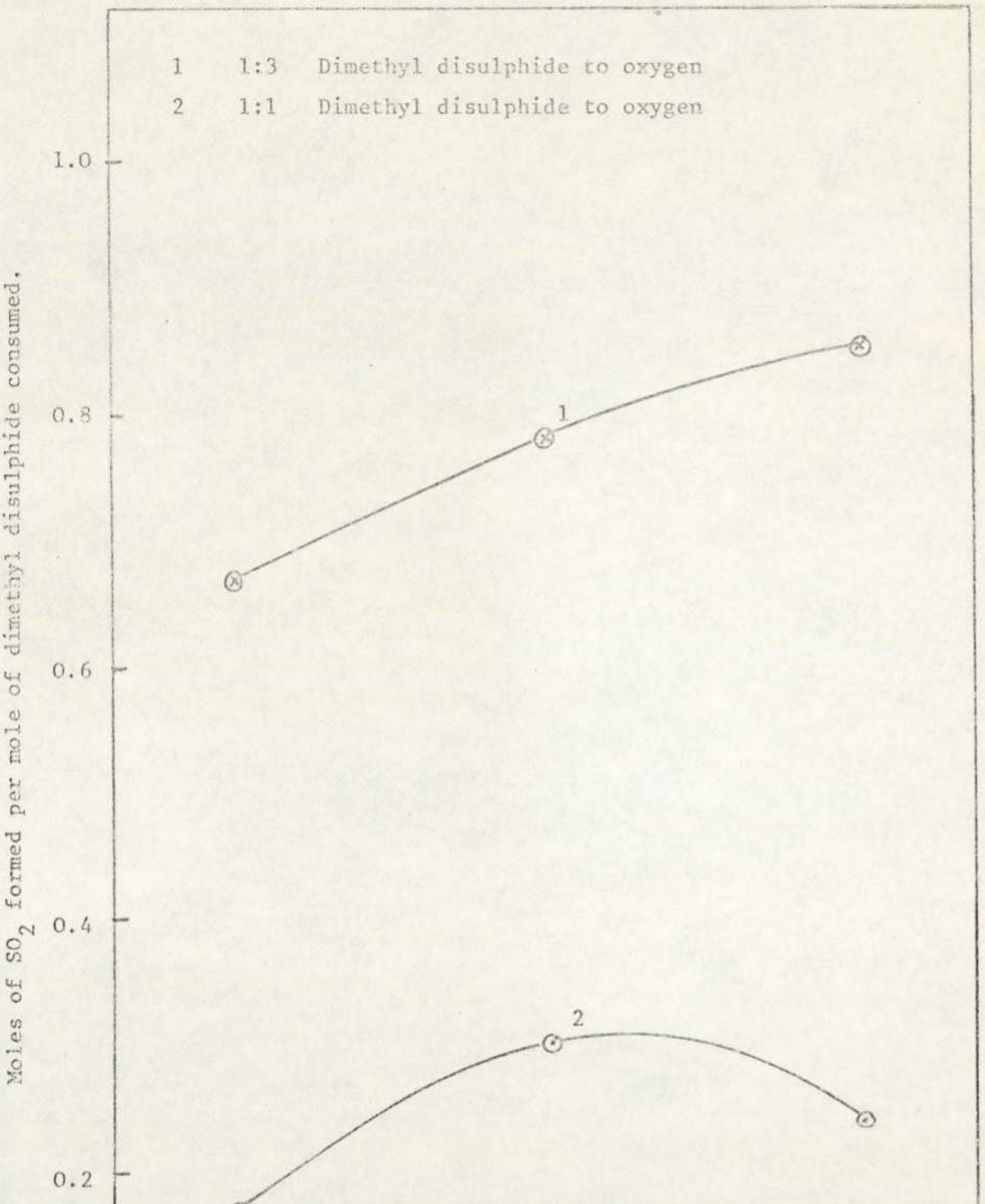


Figure 3.12 (a).

The variation with temperature of the percentage of thiophenol oxidised.

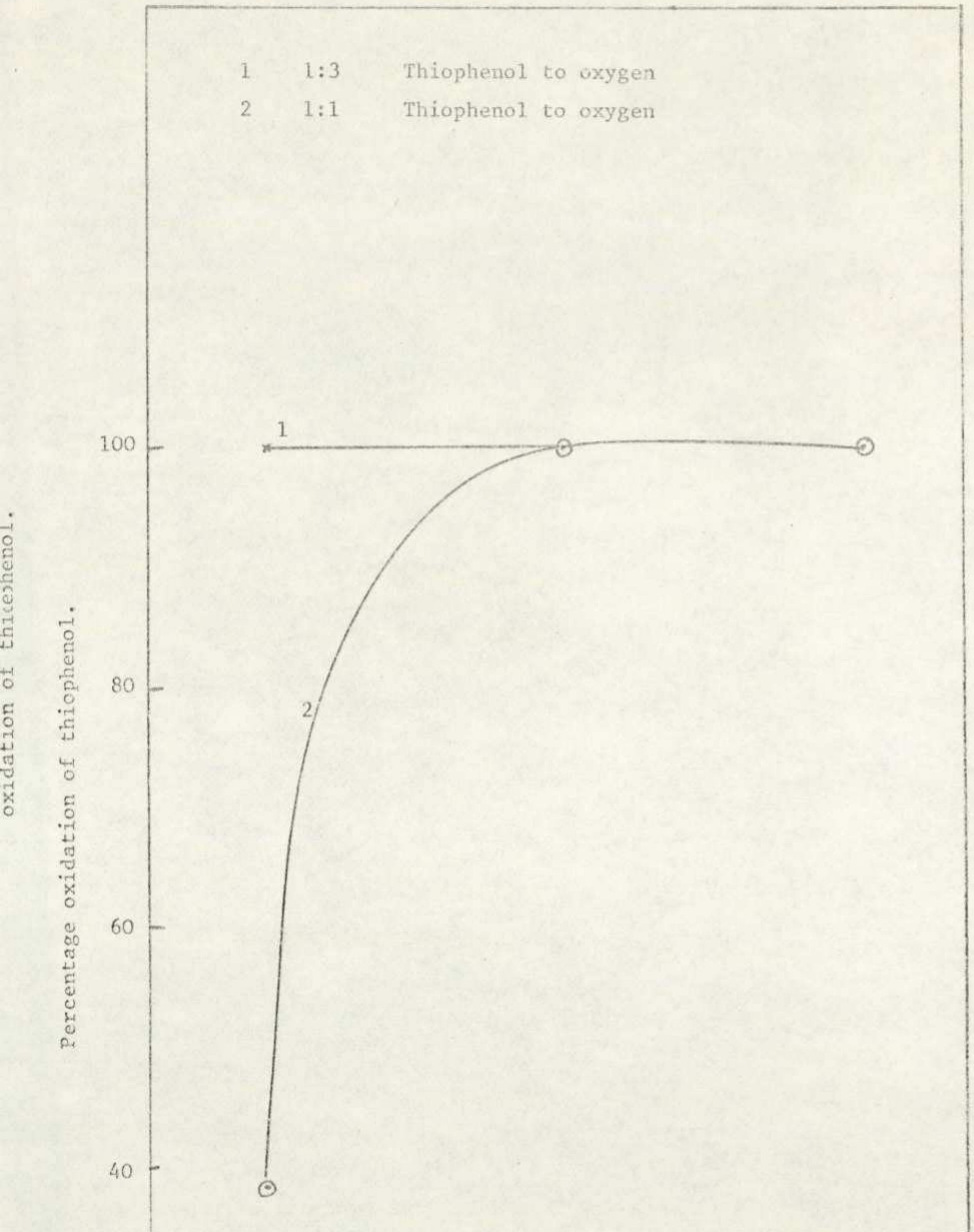
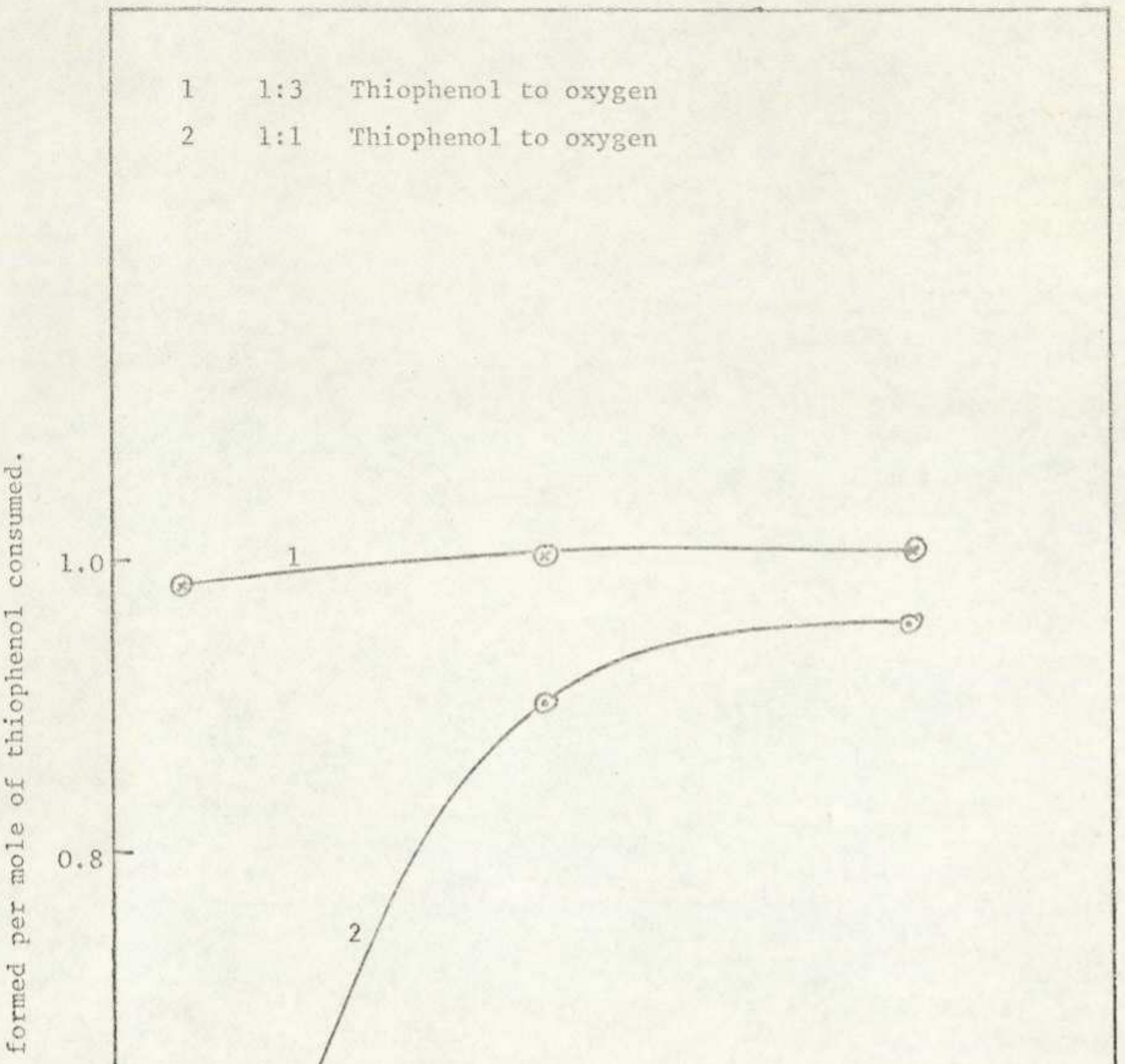


Figure 3.12 (b).

The variation with temperature of the amount of sulphur dioxide formed from thiophenol.



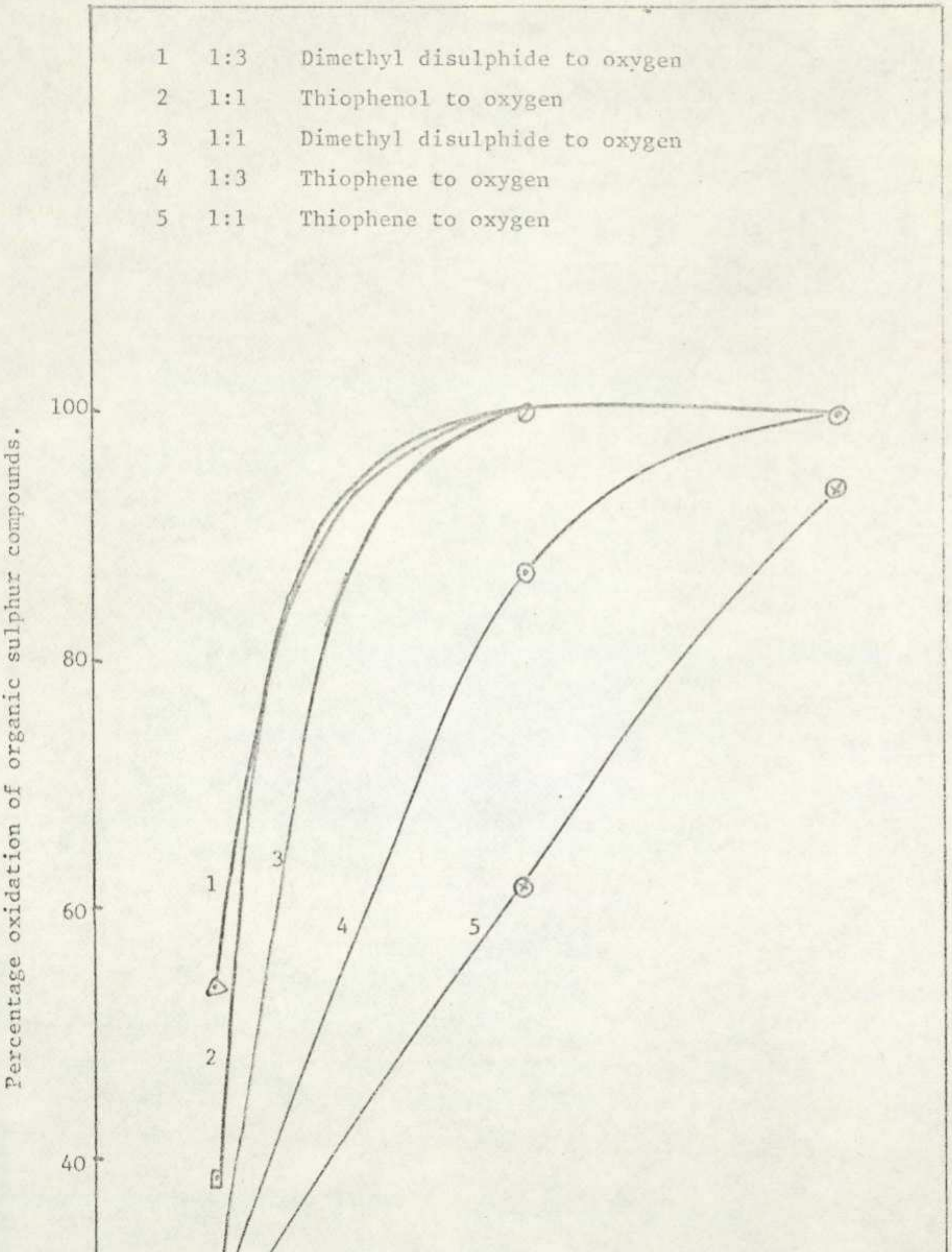
3.2.5 Comparison of results.

The order of susceptibility to oxidation of the above sulphur compounds can be written: thiophene $\angle$ dimethyl disulphide $\leq$ dipropyl sulphide $<$ thiophenol. The order of reactivity is more or less the same as that obtained from the engine results. Thiophene, which was the least susceptible to oxidation and which in general yielded least sulphur dioxide, had the least antagonistic effect on the leaded gasolines. Thiophenol which was the most susceptible to oxidation and yielded almost complete conversion of sulphur to sulphur dioxide, had the most deleterious effect on the leaded fuels.

With dipropyl sulphide and dimethyl disulphide, the results were the reverse of those obtained in the engine experiments. Dimethyl disulphide was less susceptible to oxidation and the yield of sulphur dioxide was marginally smaller than with dipropyl sulphide. Table 3.9 gives a comparison of the results obtained from these oxidation studies and Figures 3.13 (a) and (b) give comparisons of the percentage oxidation, and extent of sulphur dioxide formation, as functions of temperature.

Figure 3.13 (a).

The variation with temperature of the percentage oxidation of the organic sulphur compounds.



Key to Figure 3.13 (b).

1 = 1:3 Thiophenol to oxygen.

2 = 1:1 Thiophenol to oxygen.

3 = 1:3 Dipropyl sulphide to oxygen.

4 = 1:3 Dimethyl disulphide to oxygen.

5 = 1:3 Thiophene to oxygen.

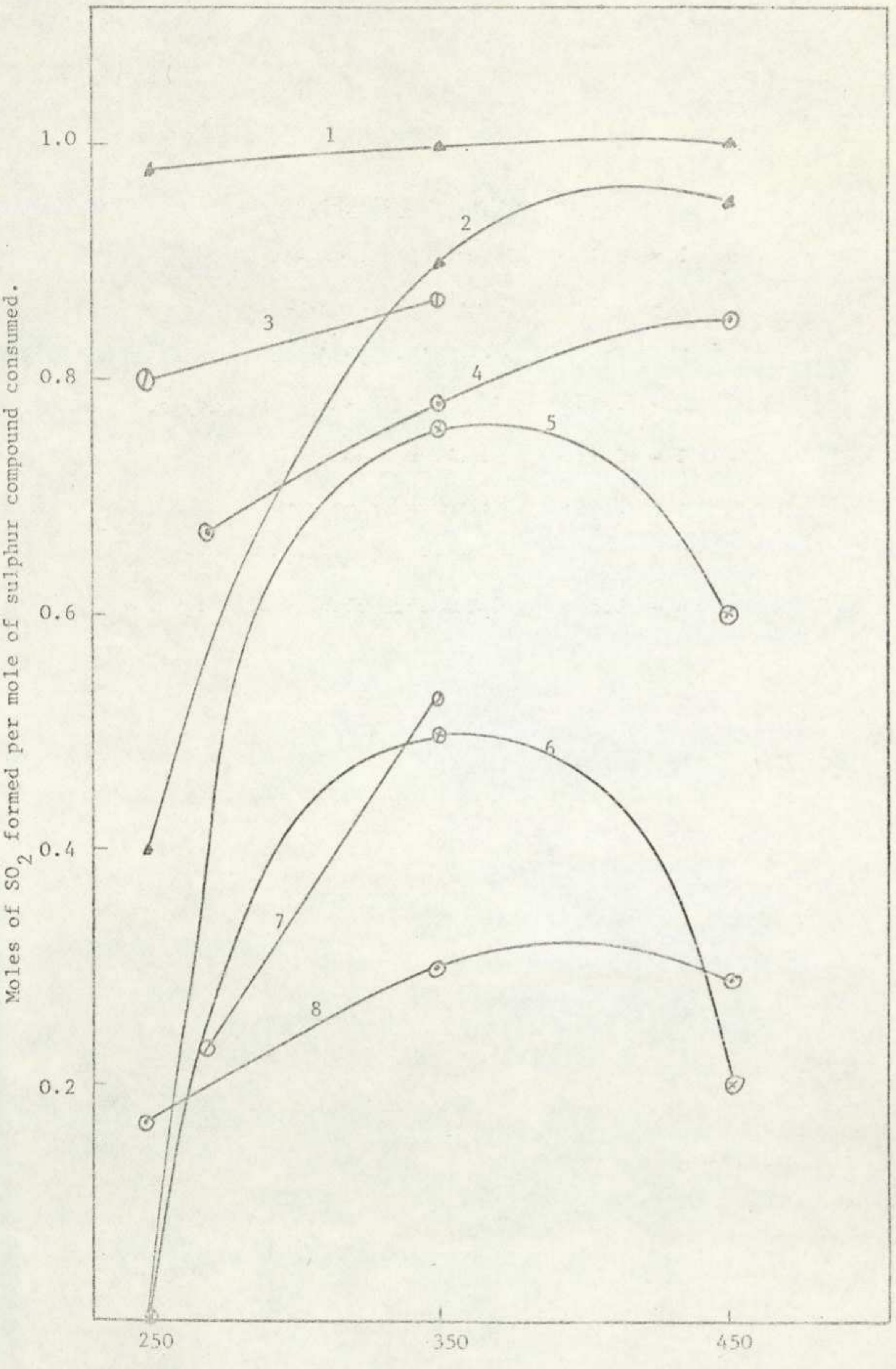
6 = 1:1 Thiophene to oxygen.

7 = 1:1 Dipropyl sulphide to oxygen.

8 = 1:1 Dimethyl disulphide to oxygen.

Figure 3.13 (b).

The variation with temperature of the extent of sulphur dioxide formation from the organic sulphur compounds.



Key to Table 3.9

+ = Slow combustion reactions.

x = Cool flame reactions.

* = Two-stage/hot ignition reactions.

Pressure used = 200 ± 10 torr.

Table 3.9.

Comparison of results obtained during oxidation studies of the sulphur compounds.

Sulphur compound to oxygen ratio.	Temperature (°C)					
	250		350		450	
	% oxidation	SO_2 formed per atom S consumed	% oxidation	SO_2 formed per mole S consumed	% oxidation	SO_2 formed per mole S consumed
Thiophene-O_2						
1 : 1	25.4^{+}	-	62^{+}	0.50	94^{x}	0.20
1 : 3	27.1^{+}	-	87^{+}	0.76	100^{*}	0.60
Dimethyl disulphide-O_2						
1 : 1	28.6^{+}	0.17	100^{x}	0.30	100^{*}	0.24
1 : 3	54^{+}	0.67	100^{*}	0.78	100^{*}	0.85
Dipropyl sulphide to O_2						
1 : 1	100^{x}	0.23	100^{X}	0.53	-	-
1 : 3	100^{x}	0.80	100^{*}	0.87	-	-
Thiophenol-O_2						
1 : 1	38.5^{+}	0.40	100^{+}	0.90	100^{+}	0.95
1 : 3	100^{+}	0.98	100^{+}	0.99	100^{+}	0.99

3.3. Spontaneous ignition studies.

3.3.1. Combustion of isooctane in an uncoated reaction vessel.

The initial conditions of temperature and pressure under which isooctane + $3O_2$ mixtures ignite in an uncoated reaction vessel are shown in Figure 3.14. For mixtures of initial pressure, P_o, greater than 180 torr, there is a large single cool flame region with a smooth boundary, which extends from 287 to 381°C. The passage of a cool flame is accompanied by a pressure rise as shown in Figure 2.14(a). This pressure rise increased to a maximum at 325°C and then gradually decreased up to ca. 381°C, when hot ignition (Fig.2.14(d)) started to occur. The induction period, τ_1, (Fig.2.14(a)) which was taken as the time from the introduction of the reaction mixture into the reaction vessel to the passage of the first cool flame, was found to decrease with increasing temperature.

Within the cool flame region, there is a region in which two or more cool flames may propagate consecutively. With the isooctane/oxygen mixture used, the centre of this region corresponded to a temperature of ca. 321°C. The second cool flame was usually accompanied by a smaller pressure rise. τ_2, the time between the first and second cool flames (Fig. 2.14(b)), also decreased with increasing temperature.

An indication of the maximum overall rate of oxidation occurring during cool flame propagation was given by the maximum rate of pressure rise of the cool flame, $(dP/dt)_{max}$.

Key to Figure 3.14.

1 = Isooctane + oxygen + sulphur dioxide.

2 = Isooctane + oxygen + thiophene.

3 = Isooctane + oxygen.

4 = Isooctane + oxygen + thiophenol.

Figure 3.14.

Comparison of ignition profiles of isooctane-oxygen mixtures in the absence and presence of sulphur containing additives.

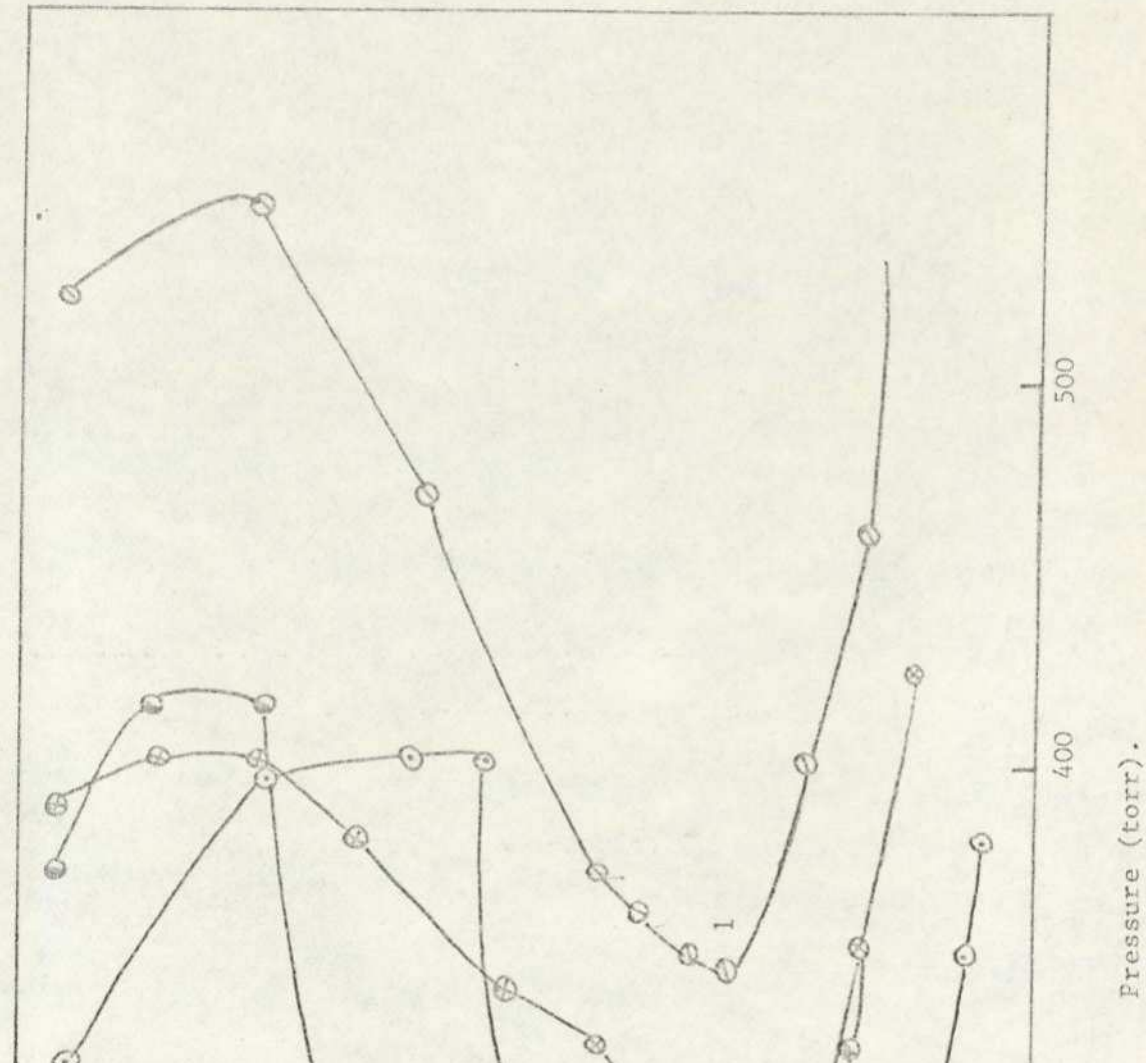
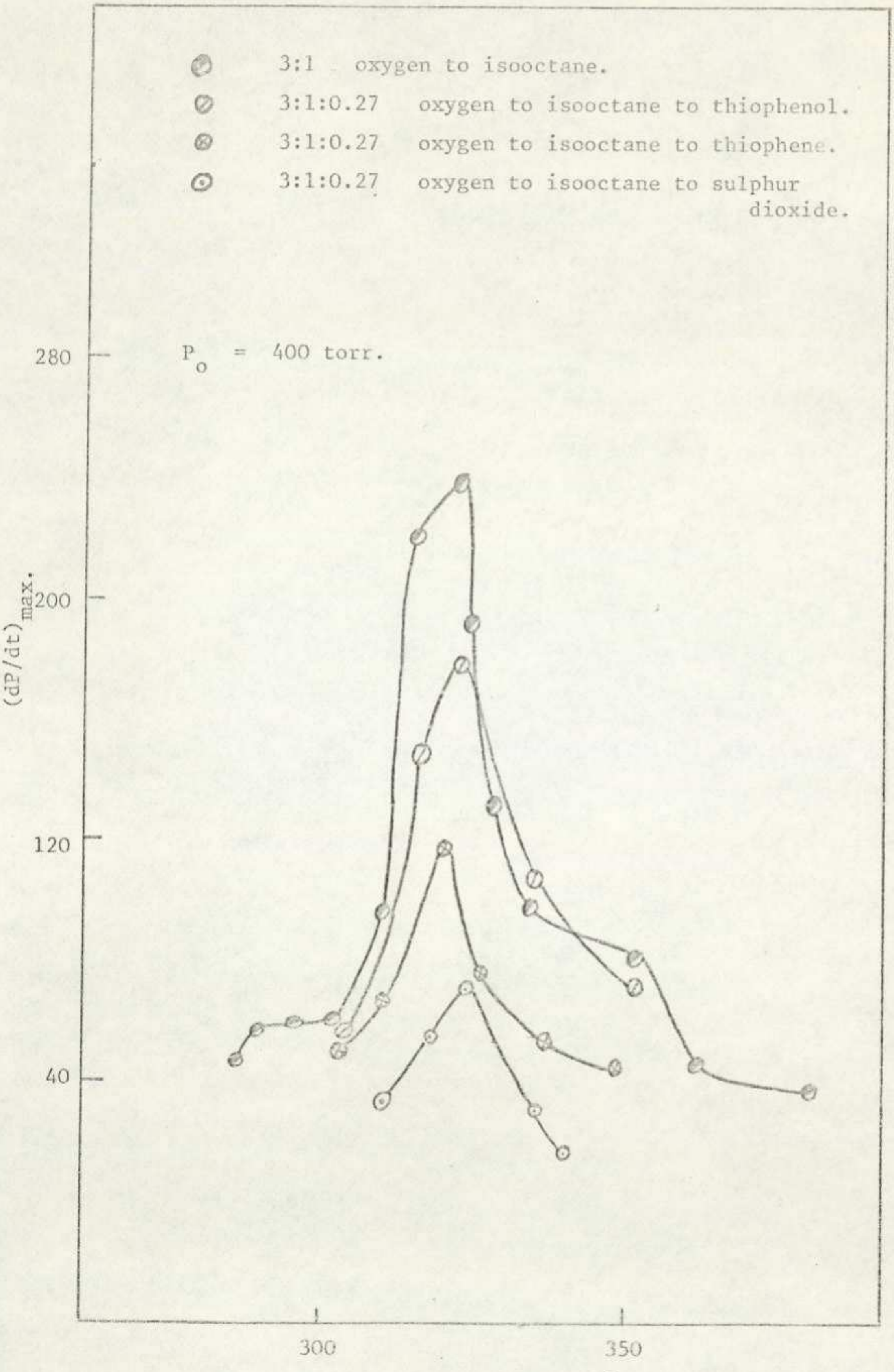


Figure 3.15 shows the maximum rate of reaction for an isooctane -oxygen mixture in the cool flame region. The reaction rate increased with temperature up to 325°C and then decreased as the temperature was further raised to 381°C, when hot ignition reactions were observed, leading to a sharp increase in reaction rate. This region of negative temperature coefficient of reaction rate is typical of the "low-temperature" oxidation of many hydrocarbons. At initial pressures greater than 400 torr, two-stage ignition was observed (Fig.2.14(c)). The two-stage ignition profile exhibited a series of "low-temperature" lobes, which were not clearly defined.

Analysis of the combustion products was undertaken in order to determine the amount of isooctane consumed. This revealed that, during hot ignition and two-stage ignition, 100% of the isooctane reacted, though complete oxidation did not occur, as shown by the number of intermediates formed. In the cool flame region, however, reaction of the isooctane was incomplete, only 90-95% of it being used up. In the slow combustion region, the extent of isooctane consumption fell to 80 ± 5%. This variation depended on the temperature of the reaction vessel as well as on the time for which the reaction mixture remained in the vessel before sampling.

Figure 3.15.

The variation of maximum rate of pressure change with temperature, under cool flame conditions.



3.3.1.1. Effect of sulphur additives on the combustion of isooctane in an uncoated vessel.

3.3.1.1.1. Sulphur dioxide.

Figure 3.14 shows the explosive limits of a 3:1:0.27 O_2-isooctane-SO_2 mixture. For initial pressures, P_o, greater than 325 torr, there is a large single cool flame region extending from 295 to 382°C. The behaviour observed with the isooctane + $3O_2$ mixture, e.g. the increase in reaction rate with temperature up to ca. 325°C and the subsequent decrease, was generally similar to that observed in the presence of sulphur dioxide. However, the induction period, τ_1, preceding the cool flame was greatly increased and the rate of oxidation was considerably decreased when sulphur dioxide was present. Figure 3.15 shows the variation with temperature of the rate of oxidation in the cool flame region.

The presence of sulphur dioxide in general inhibited isooctane combustion. In the high temperature region, i.e. at temperatures above 400°C, where hot ignition occurred, ca. 85% of the isooctane and 65% of the sulphur dioxide reacted. In the cool flame region the amount of isooctane reacting fell to 75%, but the consumption of sulphur dioxide increased to 80%. Similar inhibition of hydrocarbon oxidation in the "low-temperature" region has been reported[114,115], and the investigators attributed the effect to the interaction of the sulphur dioxide and oxygen to form sulphur trioxide, thus terminating chain reactions and reducing the oxidation rate.

3.3.1.1.2. Thiophene.

The ignition limits of a 3:1:0.27 O_2- isooctane-thiophene mixture are shown in Figure 3.14. At initial pressures, P_o, above 256 torr, there is a large single cool flame region, which extends from 292 to 381°C. The behaviour was much the same as in the O_2- isooctane-SO_2 mixture, except that the induction period, τ_1, was intermediate between those obtained in the absence and presence of sulphur dioxide. Fig. 3.15 shows the variation with temperature of the rate of oxidation in the cool flame region.

As with sulphur dioxide, the presence of thiophene inhibited isooctane oxidation. In the hot ignition and two-stage ignition regions, 95% of the isooctane reacted as did 92% of the thiophene. However, the amount of sulphur dioxide formed corresponded to only ca. 20% of the thiophene consumed. In the cool flame region, ca. 70% of the isooctane and 65% of the thiophene reacted, and the amount of sulphur dioxide formed correspond to ca. 55% of the thiophene used up. In the slow combustion region, 55% of the isooctane and 48% of the thiophene reacted, and the sulphur dioxide formed corresponded to 90% of the thiophene used up.

3.3.1.1.3. Thiophenol.

Figure 3.14 shows the initial conditions under which 3:1:0.27 O_2-isooctane- thiophenol mixtures ignite. With initial pressures above 190 torr, there is a large single cool flame region, which extends from 300 to 381°C. The behaviour observed was similar to that of the other mixtures described, but thiophenol did not inhibit isooctane oxidation as strongly as did thiophene and sulphur dioxide. In other words the oxidation rate in the presence of thiophenol was higher than that of the other mixtures (Fig. 3.15).

Analysis of the combustion products revealed that at all the temperatures used complete oxidation of the thiophenol occurred. However, at temperatures above 400°C, only 20% of the thiophenol was converted to sulphur dioxide. In this region, isooctane consumption was ca. 95%. In the cool flame region, the amount of sulphur dioxide in the final products increased to 80% of the thiophenol used up, but the percentage of isooctane oxidised fell to 60%. In the slow combustion region, the amount of sulphur dioxide produced increased to 90% of the thiophenol consumed and the proportion of isooctane reacting fell to 45%.

3.3.1.2. Comparison of the effects of added sulphur compounds on the combustion of isooctane in an uncoated reaction vessel.

The effects of added sulphur dioxide, thiophene and thiophenol on the ignition of isooctane can be readily compared by inspection of Figure 3.14. These additives all inhibited combustion of the hydrocarbon and, although the minimum reaction temperature was not affected, the pressures required for cool flame and two-stage ignition were raised. The order in which the additives inhibit combustion is as follows:

sulphur dioxide > thiophene > thiophenol.

This inhibition was also shown by comparison of the maximum overall rates of reaction, $(dP/dt)_{max}$, for the mixtures (Fig.3.15). The isooctane-O_2 mixtures had a very high overall maximum reaction rate. However, the presence of the sulphur compounds considerably reduced this rate. Sulphur dioxide was the most effective in this respect, followed by thiophene and thiophenol.

A comparison of the induction periods, τ_1, preceding cool flames (Fig.3.16) shows that the inhibition by sulphur dioxide was the most pronounced. Table 3.10 shows the results of the analysis of the oxidation products and Figure 3.17 compares the percentage oxidation of isooctane in the presence of the additives.

Key to Figure 3.16.

1 = Isooctane + oxygen + sulphur dioxide.

2 = Isooctane + oxygen + thiophene.

3 = Isooctane + oxygen + thiophenol.

4 = Isooctane + oxygen.

Figure 3.16.

Comparison of the variation of the induction period with pressure for isooctane-oxygen mixtures in the absence and presence of sulphur containing additives.

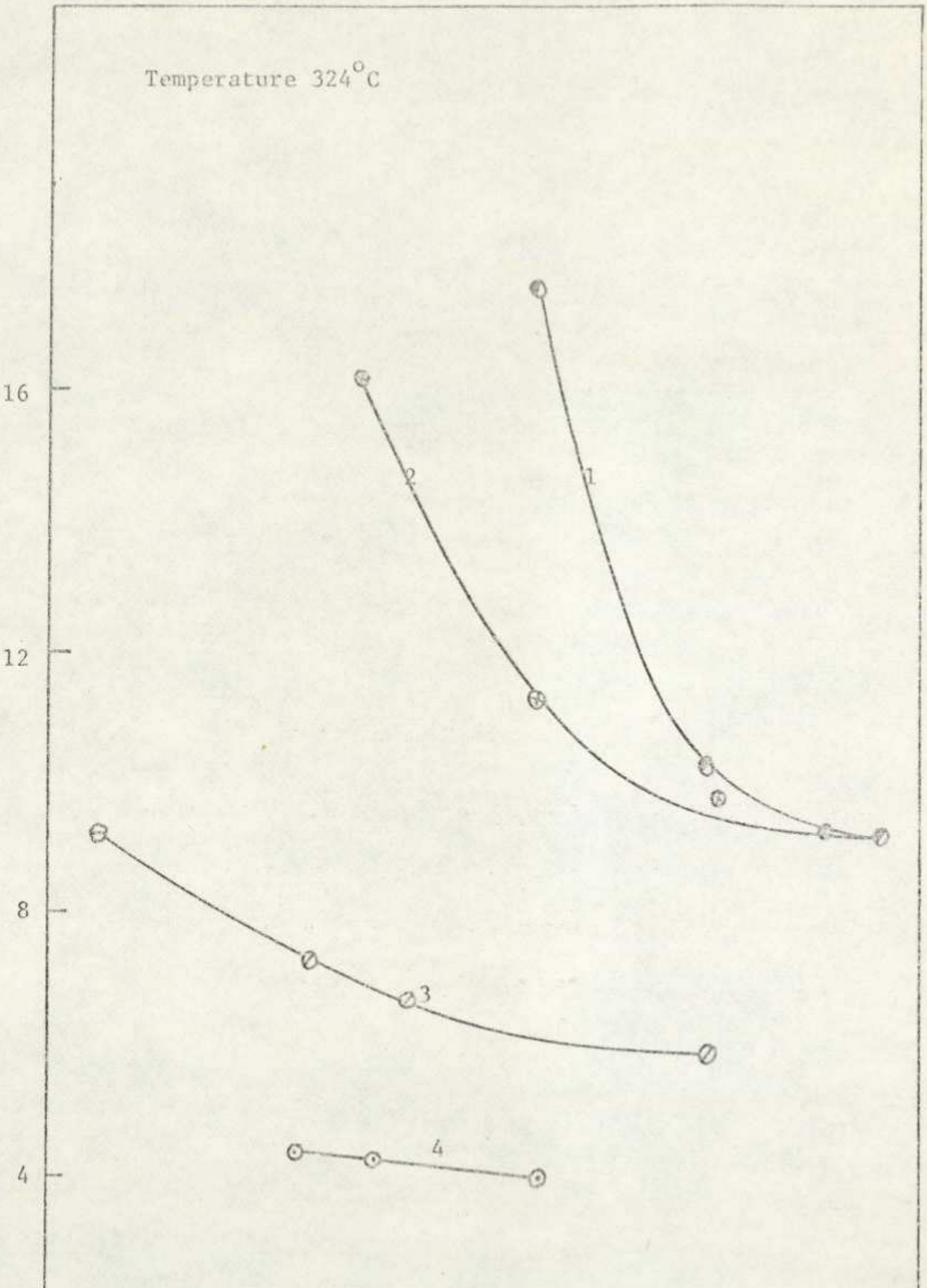


Figure 3.17.

Percentage oxidation of isooctane in the absence and presence of sulphur containing additives.

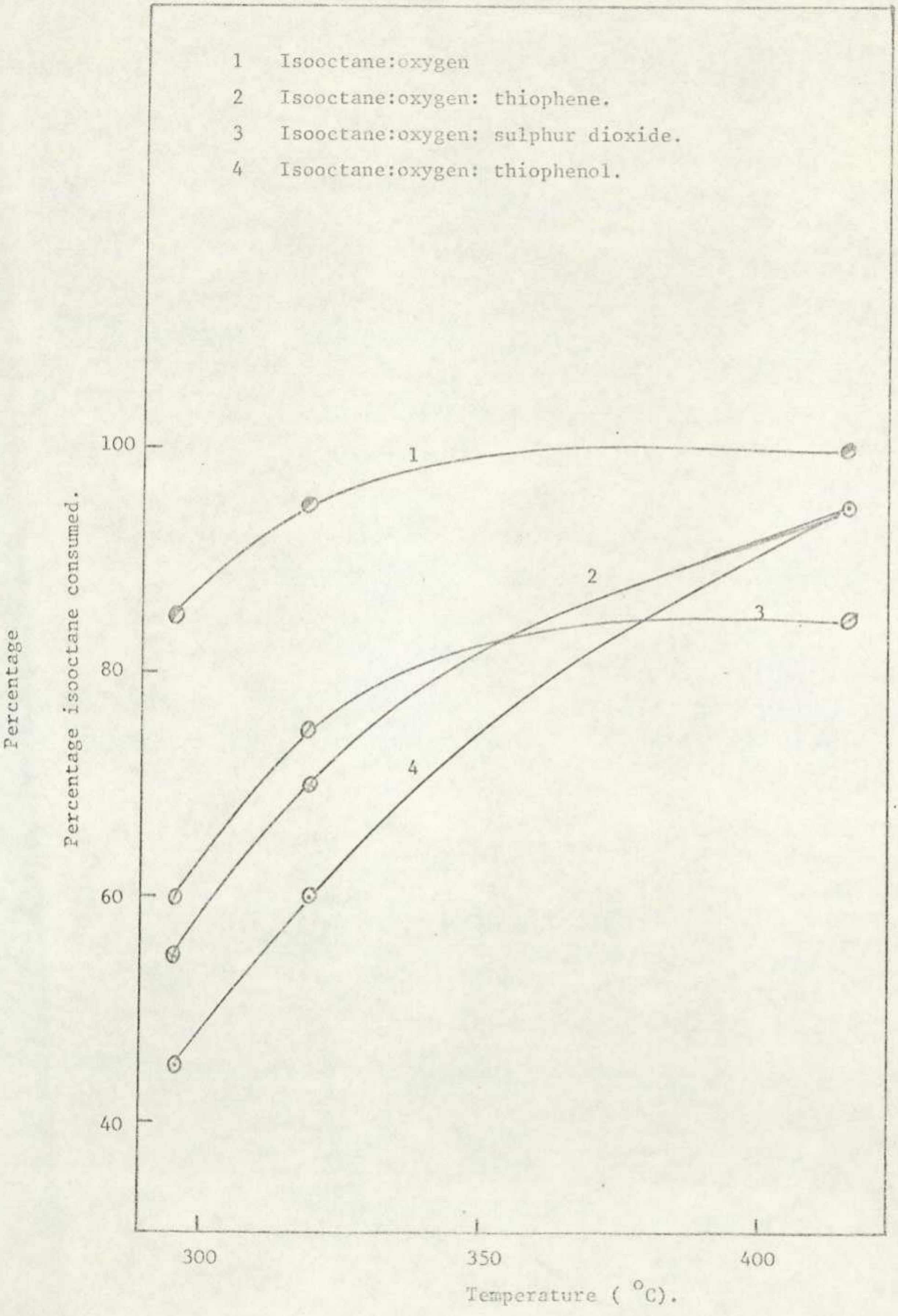


Table 3.10.

The consumption of isooctane in the presence and absence of added sulphur compounds.

Type of reaction	O_2-isooctane 3 : 1	O_2-isooctane-SO_2 3 : 1 : 0.27		O_2-isooctane-C_4H_4S 3 : 1 : 0.27			O_2-isooctane-C_6H_5SH 3 : 1 : 0.27		
	% isooctane consumed	% isooctane conumed	SO_2 consumed (%)	% isooctane consumed	% C_4H_4S consumed	SO_2 formed per mole C_4H_4S conumed	% isooctane consumed	% C_6H_5SH consumed	SO_2 formed per mole C_6H_5SH consumed.
Hot ignition	100	85	62	95	92	0.20	95	100	0.20
Cool Flame	95	75	80	70	65	0.56	60	100	0.80
Slow combustion	85	60	-	55	48	0.90	45	100	0.90

3.3.2. Combustion of isooctane in a lead oxide-coated vessel.

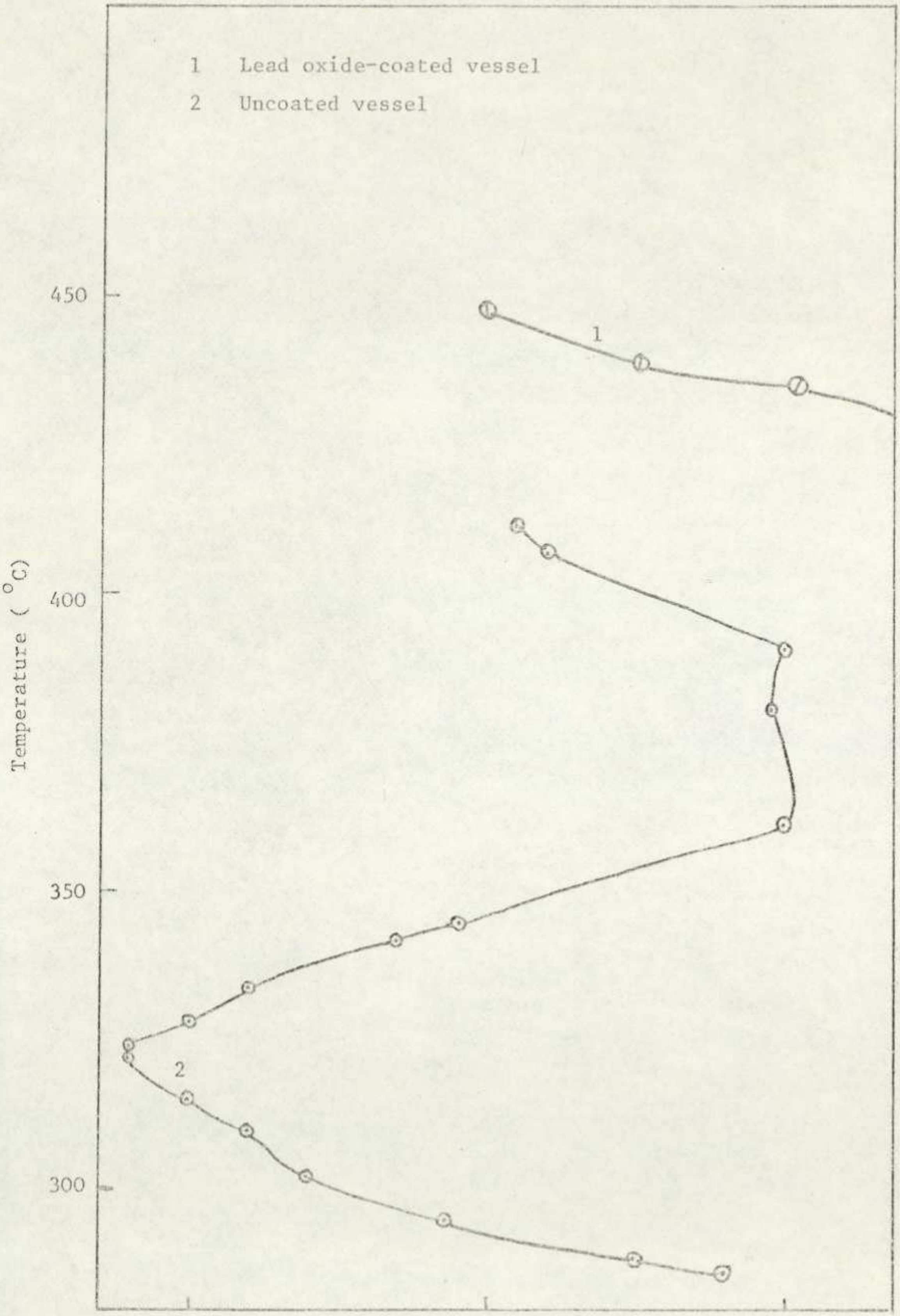
Powdered lead oxide was used to coat the reaction vessel as described in Section 2.2.3.5.1 and studies were made of the initial conditions under which an isooctane + $3O_2$ mixture ignited. No cool flames or two-stage ignitions were observed, the one-stage or hot ignition reactions occurring mainly in the "high-temperature" region ($>400^{\circ}C$). Figure 3.18 compares the ignition profiles obtained with an isooctane-oxygen mixture in an uncoated and a lead oxide-coated vessel.

In the coated vessel, combustion in the "low-temperature" region was eliminated and the ignition limits were considerably raised. The induction period was also increased from a few seconds to about one minute. Figure 3.19 compares the induction periods for this mixture in both vessels. The maximum overall rate of reaction increased rapidly with temperature.

Analysis of the combustion products showed that, during the hot ignition reactions, complete consumption of the isooctane occurred, although during slow combustion the amount used up varied between 85 and 90% depending on the temperature.

Figure 3.18.

Ignition profiles of isooctane-oxygen mixture in an uncoated and lead oxide-coated vessel.



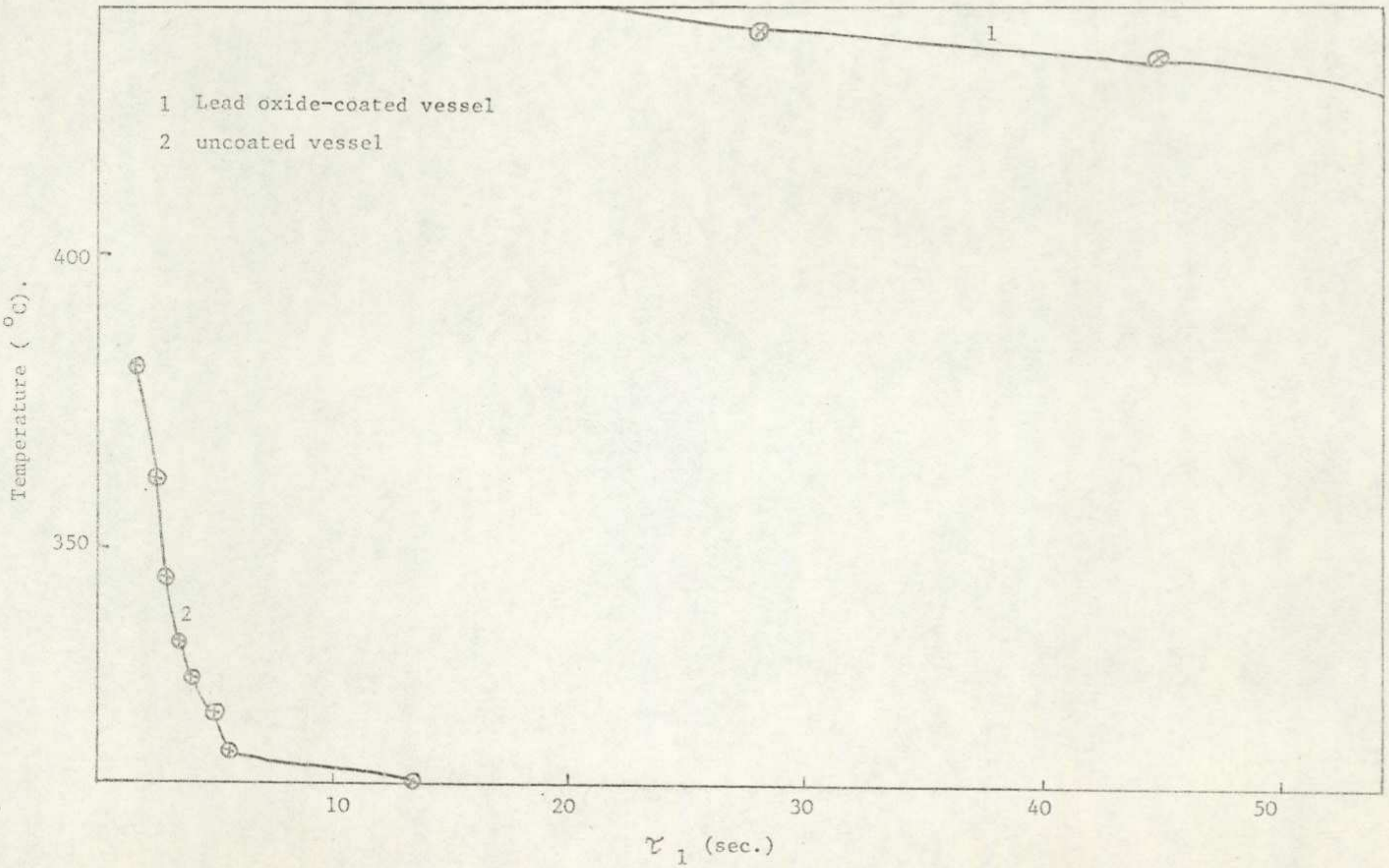


Figure 3.19.

Variation of induction period (τ) with temperature for an iso-octane-oxygen mixture in an uncoated and coated reaction vessel.

3.3.2.1. Effect of sulphur additives on the combustion of isooctane in a lead oxide-coated vessel.

3.3.2.1.1. Sulphur dioxide.

Figure 3.20 shows the effect of sulphur dioxide on the oxidation of isooctane in a lead oxide-coated vessel and compares this effect with the behaviour in an uncoated vessel. The effects were similar to those observed during isooctane combustion in the coated vessel, in that all reactions occurred in the "high-temperature" region and were one-stage ignitions. The induction periods were, however, much shorter and the maximum overall rate of reaction was higher in the presence of sulphur dioxide. Figure 3.21 compares the induction periods for a 3:1:0.27 O_2-isooctane-SO_2 mixture in coated and uncoated vessels. Sulphur dioxide lowered the ignition limits for isooctane combustion in the lead-coated vessel whereas in a clean reaction vessel it raised the limits.

Analysis of the combustion products showed that ca. 93% of the isooctane reacted, while 50% of the sulphur dioxide remained unchanged after ignition. In the "high-temperature" region ($> 400^{\circ}C$) however, lead oxide appeared to promote ignition of the O_2-isooctane-SO_2 mixture.

3.3.2.1.2. Thiophene.

Figure 3.22 compares the effect of a lead oxide-coated vessel on the combustion of a 3:1:0.27 O_2-isooctane-thiophene mixture with the behaviour in an uncoated vessel. No

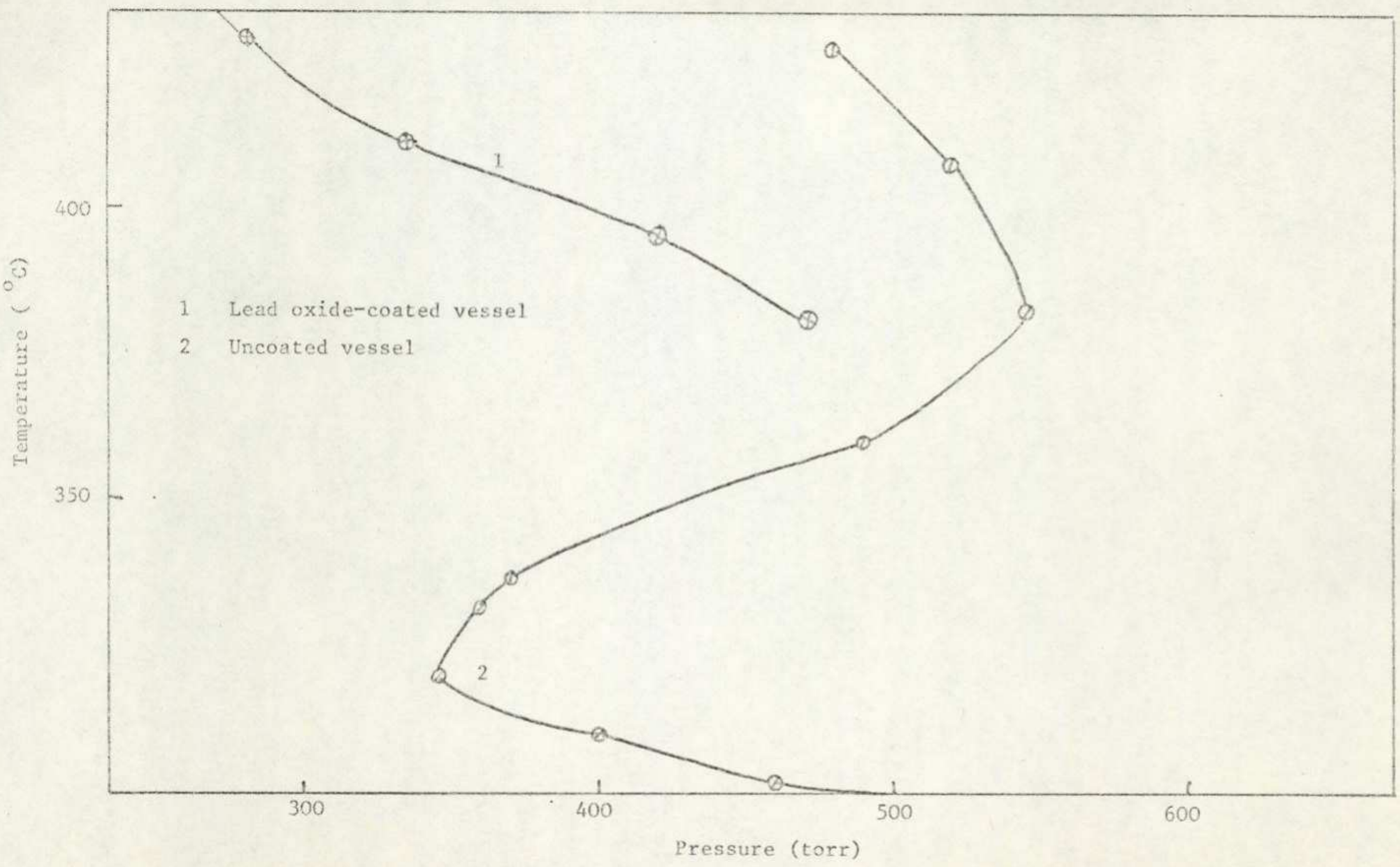


Figure 3.20.

Ignition profiles of a 3:1:0.27 oxygen-isooctane- sulphur dioxide mixture in a lead oxide-coated and uncoated vessel.

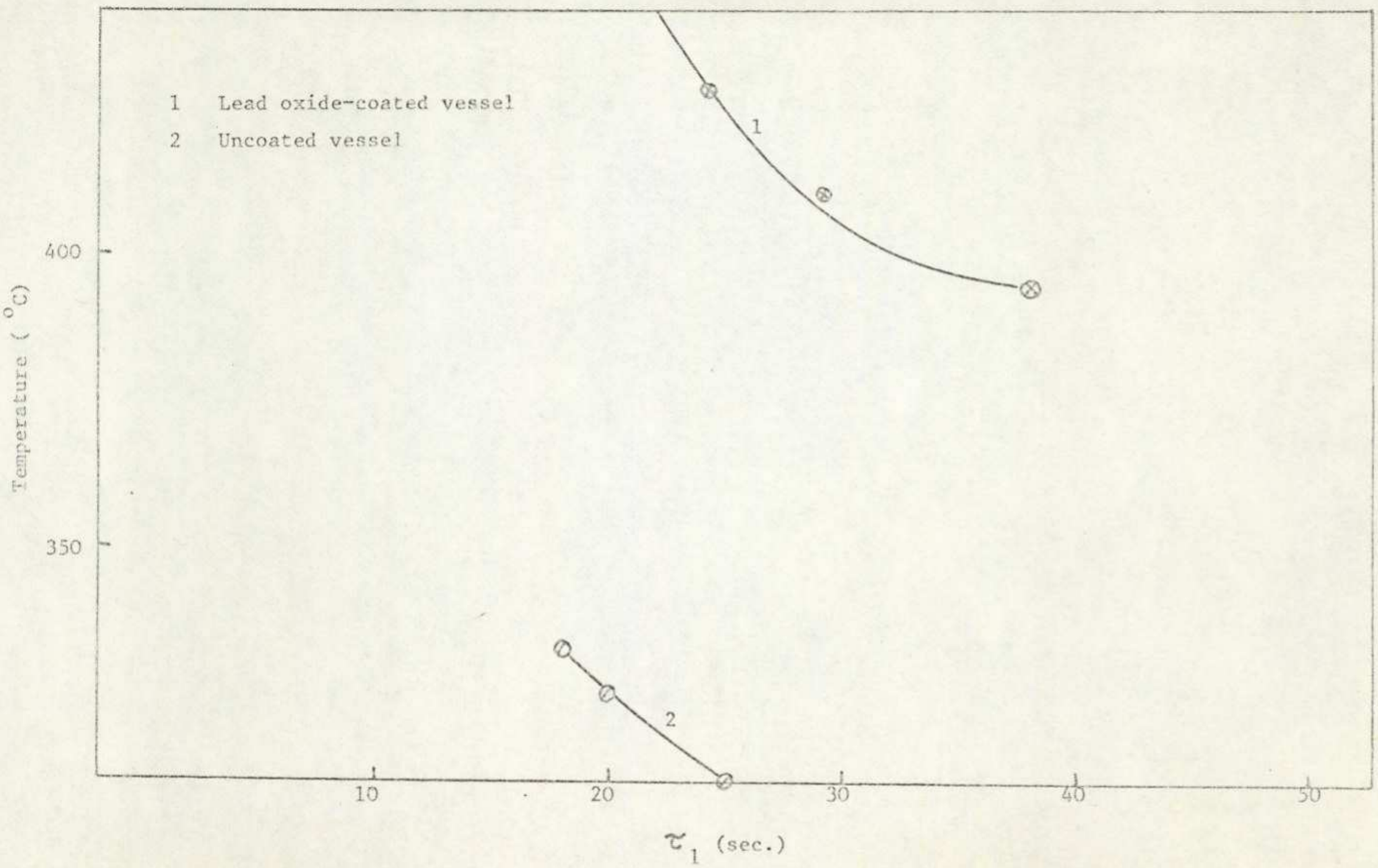
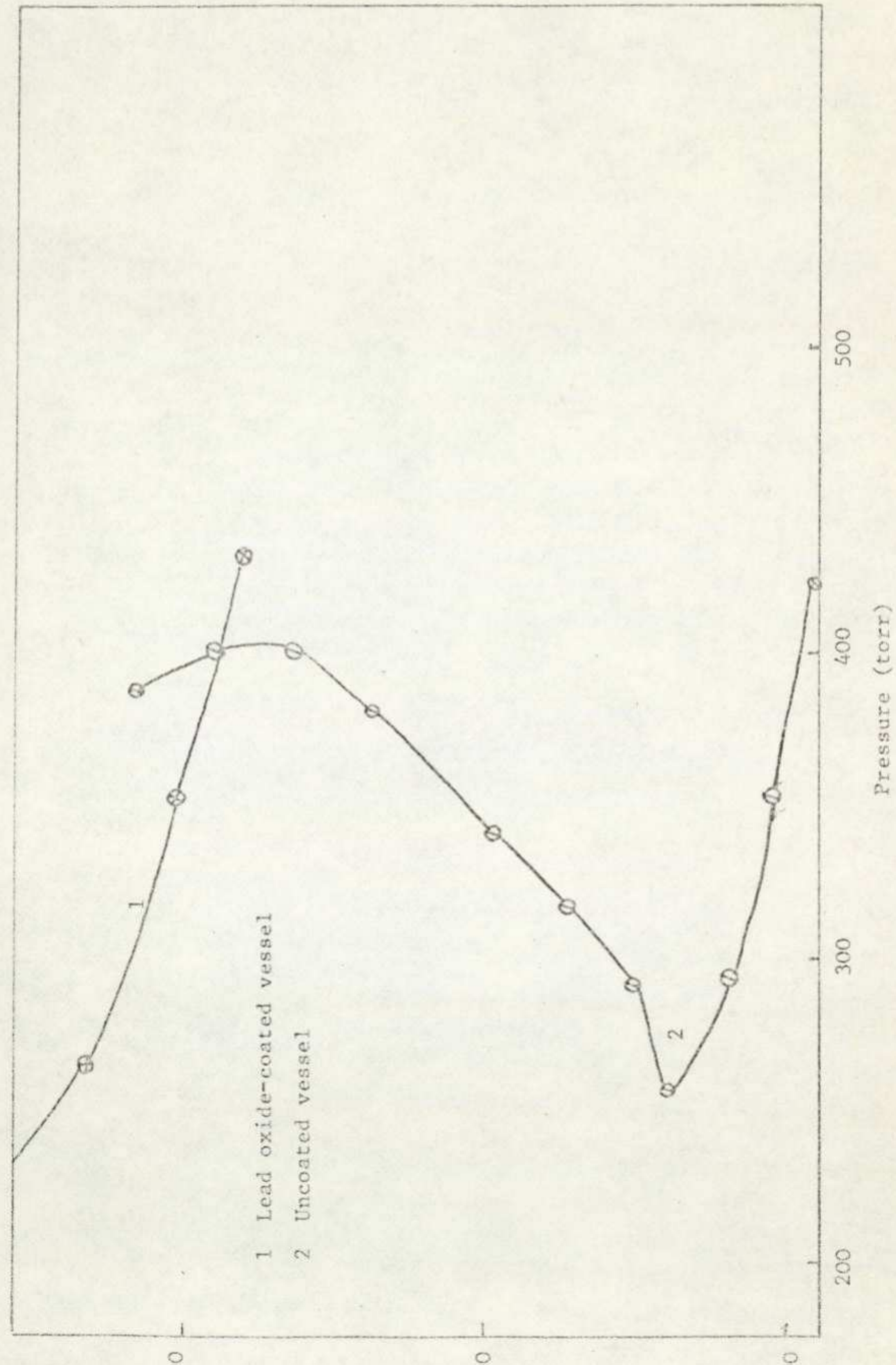


Figure 3.21.

Variation of induction period (τ) with temperature for a 3:1: 0.27 oxygen-isooctane-sulphur dioxide mixture.

Figure 3.22.

Ignition profiles of a 3:1:0.27 oxygen-isooctane-thiophene mixture in an uncoated and lead oxide coated vessel.



cool flames or two-stage ignitions were observed, all reactions being either slow combustion or one-stage ignitions. Thiophene was more effective than sulphur dioxide in lowering the ignition limits of an isooctane-oxygen mixture.

The induction periods preceding ignition were decreased by thiophene and were similar to those in an uncoated vessel (Figure 3.23). Analysis of the combustion products showed that 85% of the isooctane and 75% of the thiophene were oxidised. However only 50% of the thiophene oxidised was present as sulphur dioxide in the final products.

3.3.2.1.3. Thiophenol.

Figure 3.24 compares the ignition behaviour of a 3:1:0.27 O_2-isooctane-thiophenol mixture in a lead oxide-coated vessel with that found in an uncoated vessel. The lead oxide coating had an effect similar to that observed with the previous mixtures, but thiophenol reduced the ignition limits of the isooctane to an even greater extent than did sulphur dioxide and thiophene. The induction period preceding ignition was several seconds shorter than in an uncoated vessel (Fig. 3.25).

Analysis of the products revealed complete combustion of the thiophenol and 98% oxidation of isooctane. Only ca. 50% of the thiophenol reacting was converted to sulphur dioxide.

3.3.2.2. Comparison of the effects of added sulphur compounds on the combustion of isooctane in a lead oxide-coated vessel.

The presence of a 1 mg.cm^{-2} coating of lead

Figure 3.23.

Comparison of the induction period leading to ignition in a 3:1:0.27 oxygen-isooctane-thiophene mixture.

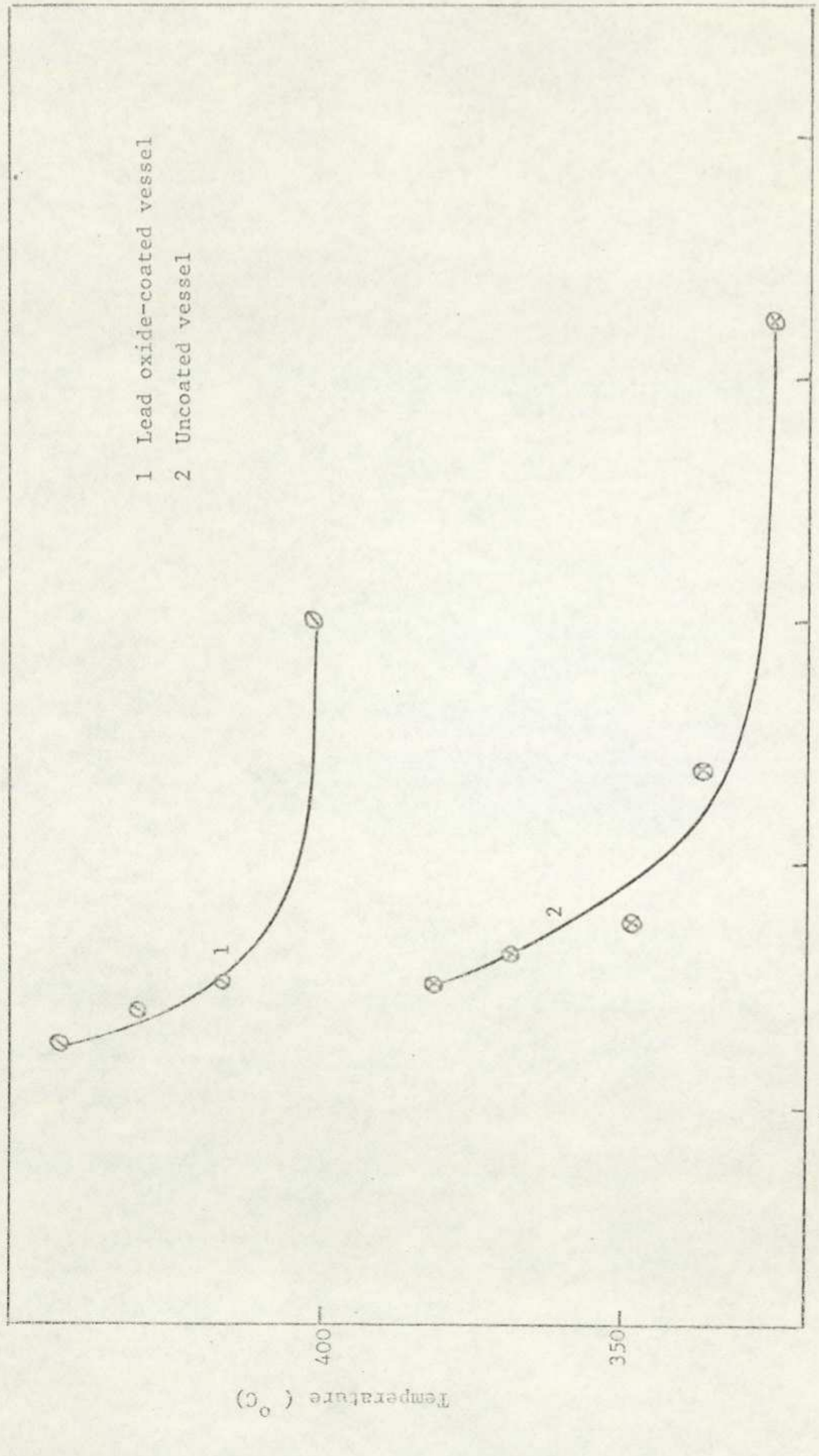


Figure 3.24.

Ignition profiles of a 3:1:0.27 oxygen-isooctane-thiophenol mixture in an uncoated and lead oxide-coated vessel.

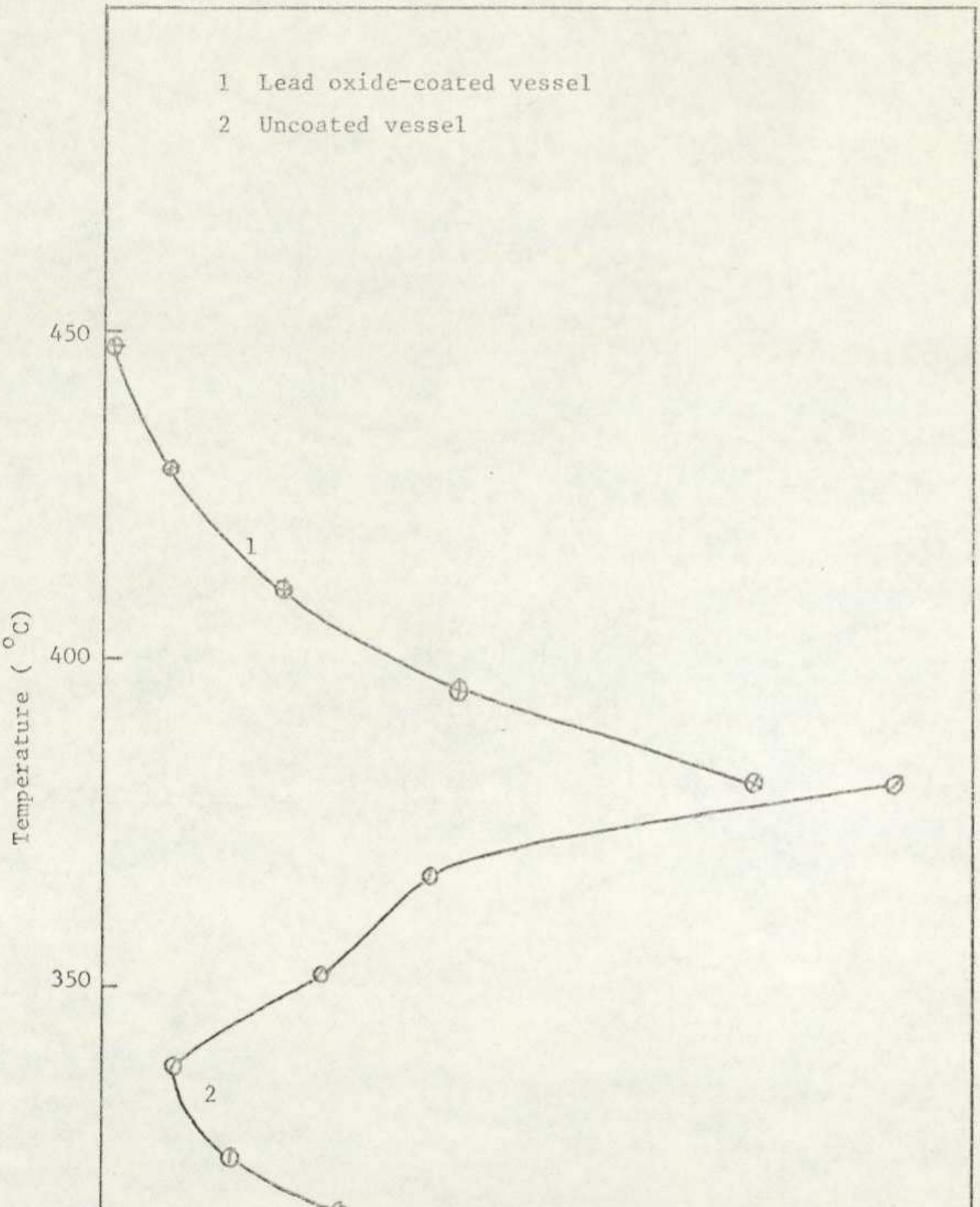
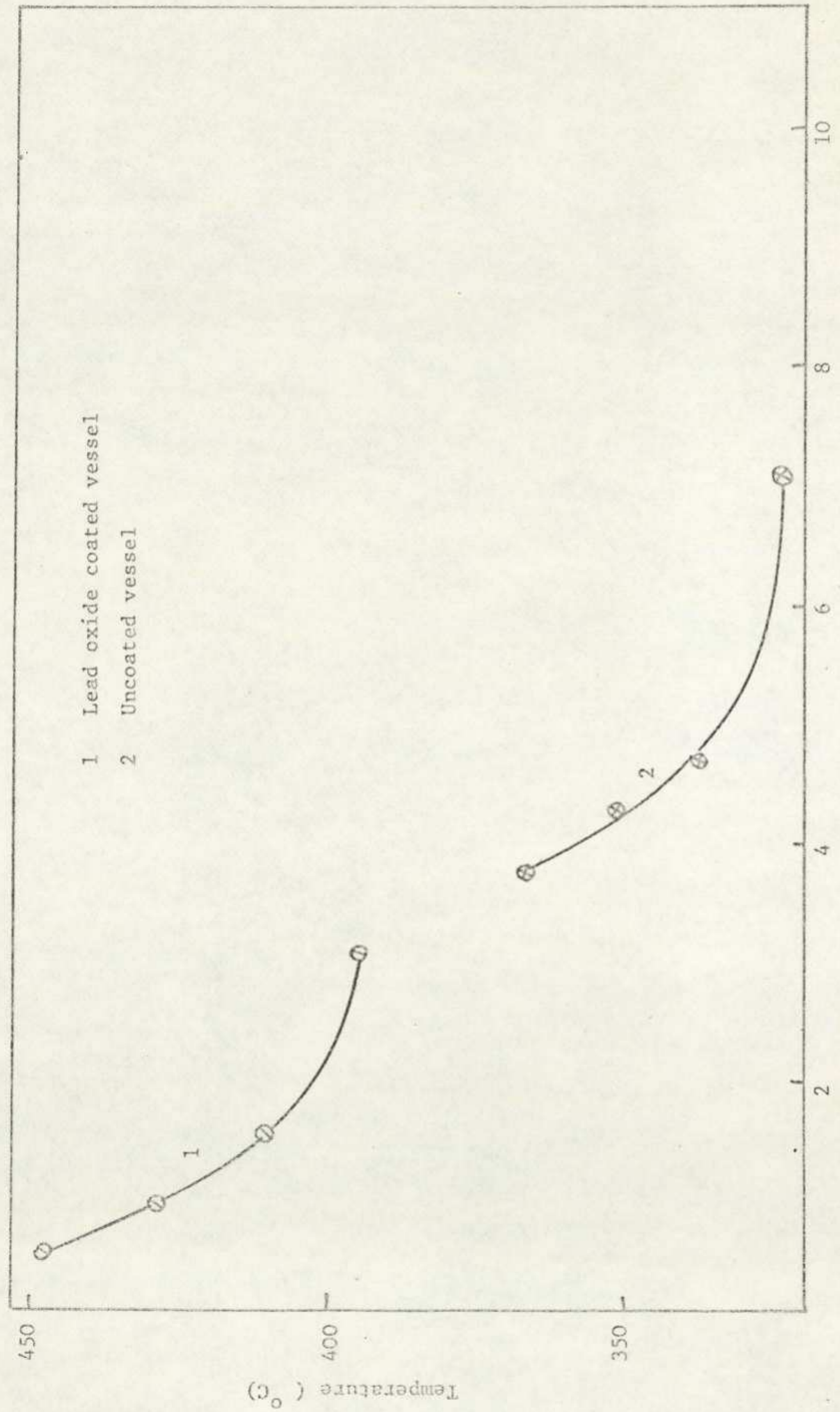


Figure 3.25.

Comparison of the induction period leading to ignition in a 3:1:0.27 oxygen- isooctane-thiophenol mixture.



oxide in the reaction vessel had a very marked effect on the ignition limits of an isooctane + $3O_2$ mixture. All reactions in the "low-temperature" region ($\lessdot$ 400°C) were of the slow combustion type and cool flames and two-stage ignitions were eliminated. In the "high-temperature" region ($\gtrdot$ 400°C), one-stage or hot ignitions were observed. The lead oxide coating thus raised the ignition limits and this effect was also observed in the presence of added sulphur compounds.

The additives had, however, the opposite effect when compared with the reactions previously carried out in an uncoated vessel, where the sulphur compounds inhibited the ignition of the isooctane. In a lead oxide-coated vessel all the sulphur compounds lowered the ignition limits of the hydrocarbon and Fig.3.26 compares these limits.

The effect of the sulphur compounds in the presence of lead oxide was also correlated by comparison of the induction periods (Fig. 3.27) and the maximum overall rates of oxidation (Fig. 3.28). The order of these rates in the coated vessel were:

O_2-isooctane-thiophenol $>$ O_2-isooctane-thiophene $>$ O_2-isooctane-SO_2 $>$ O_2-isooctane.

Table 3.11 compares the combustion products of isooctane in an uncoated and lead oxide-coated vessel.

Key to Figure 3.26.

1 = Isooctane + oxygen.

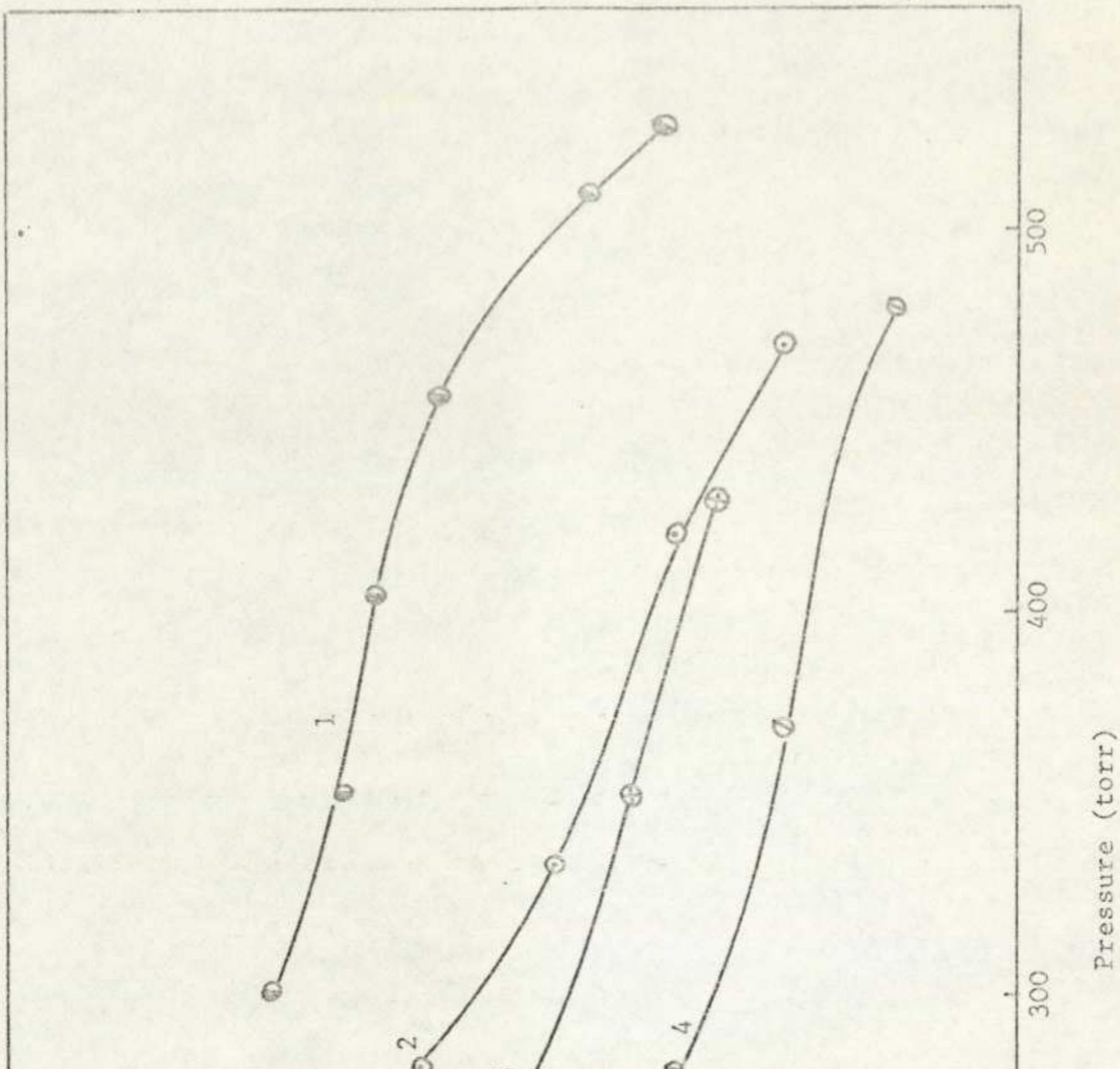
2 = Isooctane + oxygen + sulphur dioxide.

3 = Isooctane + oxygen + thiophene,

4 = Isooctane + oxygen + thiophenol.

Figure 3.26.

Comparison of the ignition limits of isooctane and oxygen in a lead oxide-coated vessel in the presence of sulphur additives.



Key to Figure 3.27.

1 = Isooctane + oxygen + sulphur dioxide.

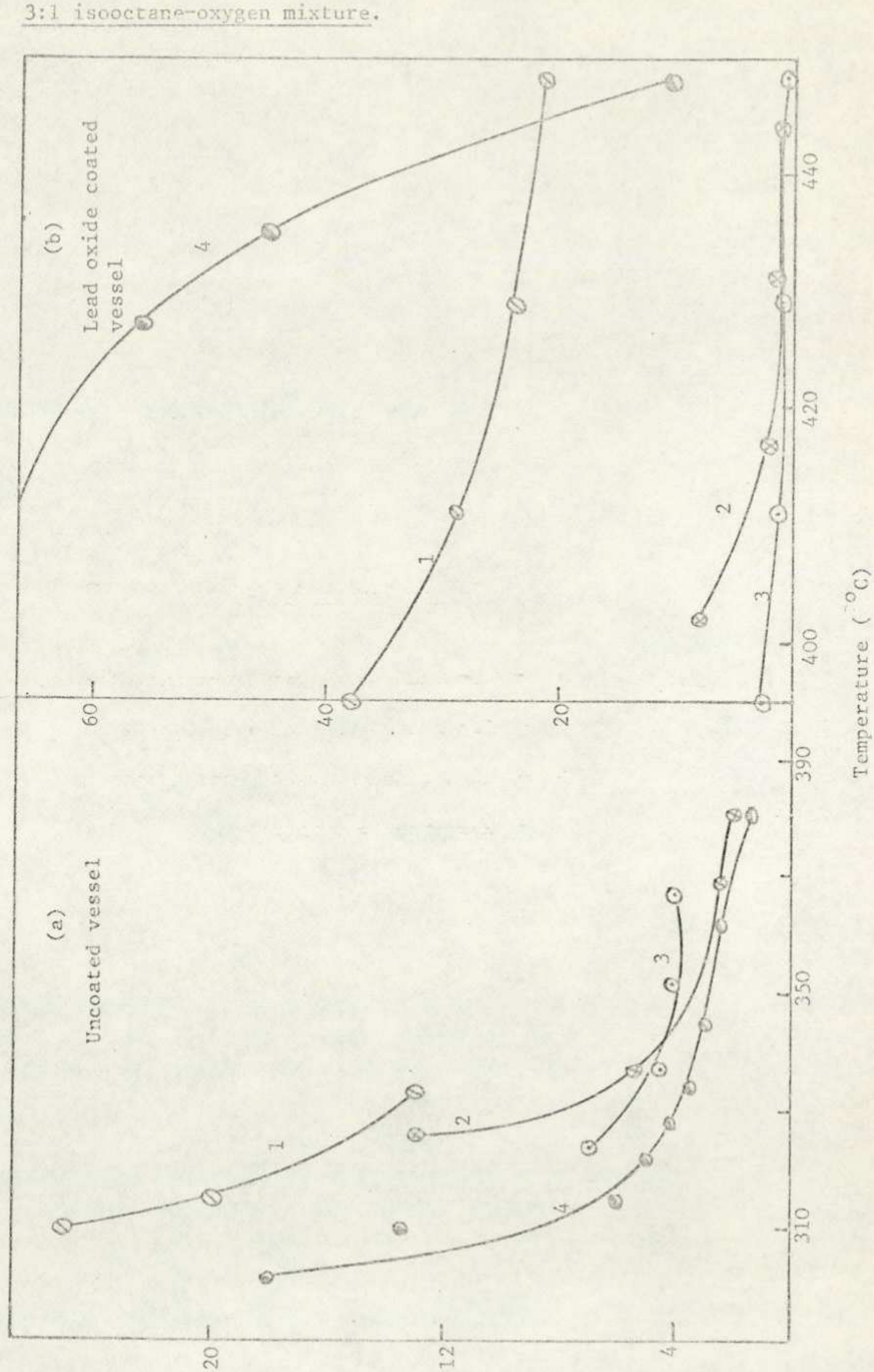
2 = Isooctane + oxygen + thiophene.

3 = Isooctane + oxygen + thiophenol

4 = Isooctane + oxygen.

Figure 3.27.

The effect of sulphur additives on the induction period of a 3:1 isooctane-oxygen mixture.



Key to Figure 3.28.

1 = Isooctane + oxygen + thiophenol.

2 = Isooctane + oxygen + thiophene.

3 = Isooctane + oxygen + sulphur dioxide.

4 = Isooctane + oxygen.

Figure 3.28.

The effect of sulphur additives on the overall reaction rate in a lead oxide-coated vessel.

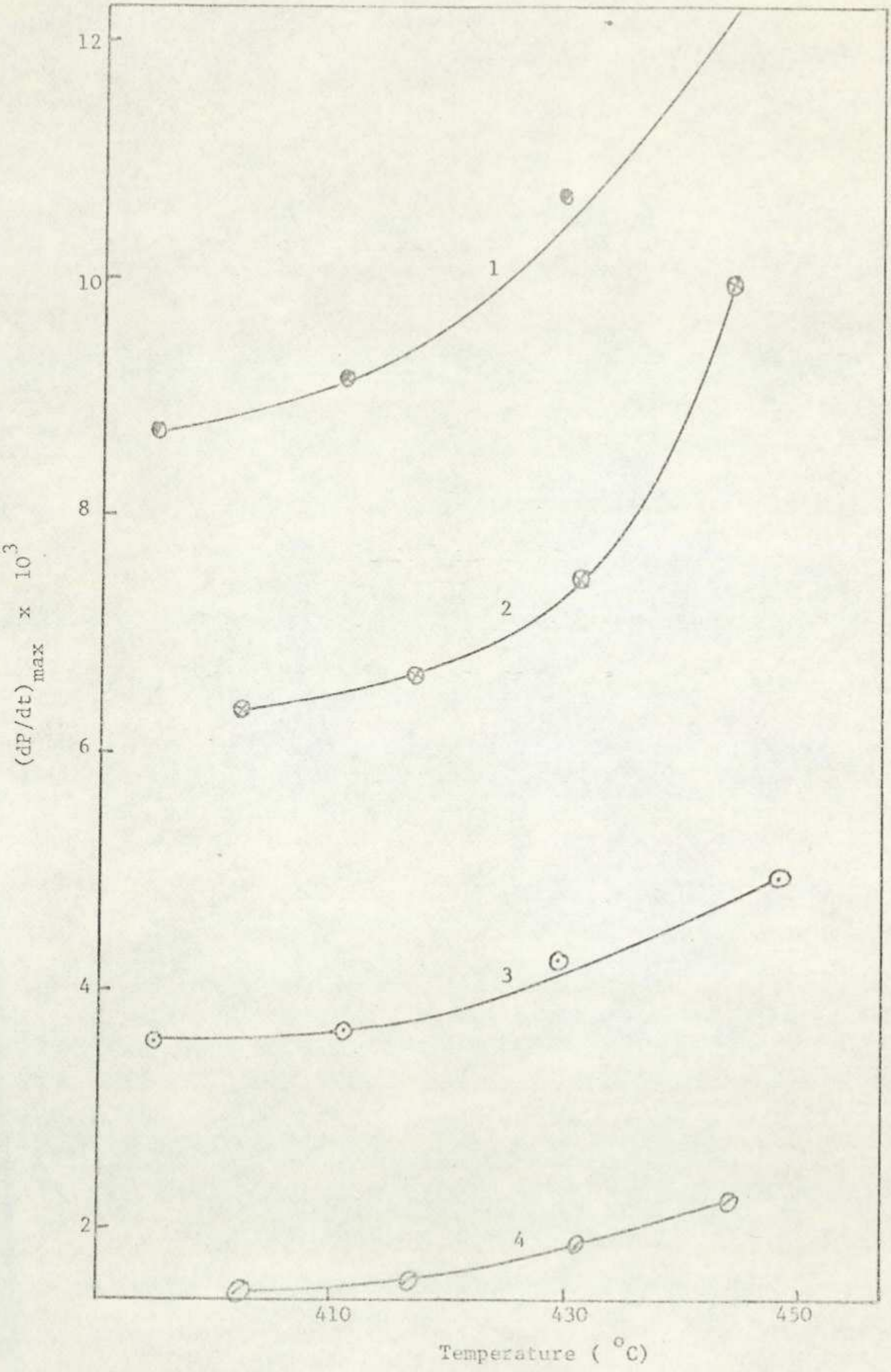


Table 3.11

Comparison of combustion products obtained from an isooctane-oxygen mixture in coated and uncoated reaction vessels and the effects of sulphur compounds on these products.

Fuel mixture 3 : 1 : 0.27	Uncoated vessel			Coated vessel		
	% isooctane consumed	% S consumed	moles SO_2 per mole S consumed	% isooctane consumed	% S consumed	moles SO_2 per mole S consumed
O_2 : isooctane	100	-	-	100	-	-
O_2: isooctane: SO_2	85	62	-	93	50	-
O_2: isooctane: thiophene	95	92	0.20	85	75	0.50
O_2:isooctane: thiophenol	95	100	0.20	98	100	0.50

3.3.3 Studies of the combustion of leaded isooctane.

Tetraethyl lead has an inhibiting effect on isooctane combustion similar to that observed when reaction takes place in a lead oxide-coated vessel. All reactions were of either the slow combustion or one-stage ignition type. Cool flames and two-stage ignitions were not observed. Tetraethyl lead is, however, generally less effective than a lead oxide coating in inhibiting isooctane combustion. Figure 3.29 compares an ignition profile for leaded isooctane with that obtained for clear isooctane in a lead oxide-coated vessel.

From the kinetic measurements made during the combustion of leaded isooctane, the induction period leading to ignition was found to be slightly longer than that for clear isooctane in an uncoated vessel, but considerably shorter than that in a lead oxide-coated vessel. Figure 3.30 shows the difference in the induction periods preceding ignition of an isooctane-oxygen mixture in a lead oxide-coated vessel, and when tetraethyl lead is present in the fuel. This same trend is also apparent in the overall reaction rates (Fig. 3.31). Analysis of the combustion products showed that during hot ignition the leaded isooctane was completely oxidised.

3.3.3.1 Effects of sulphur additives on the combustion of leaded isooctane.

3.3.3.1.1. Sulphur dioxide.

Figure 3.32 illustrates the effect of 6.25

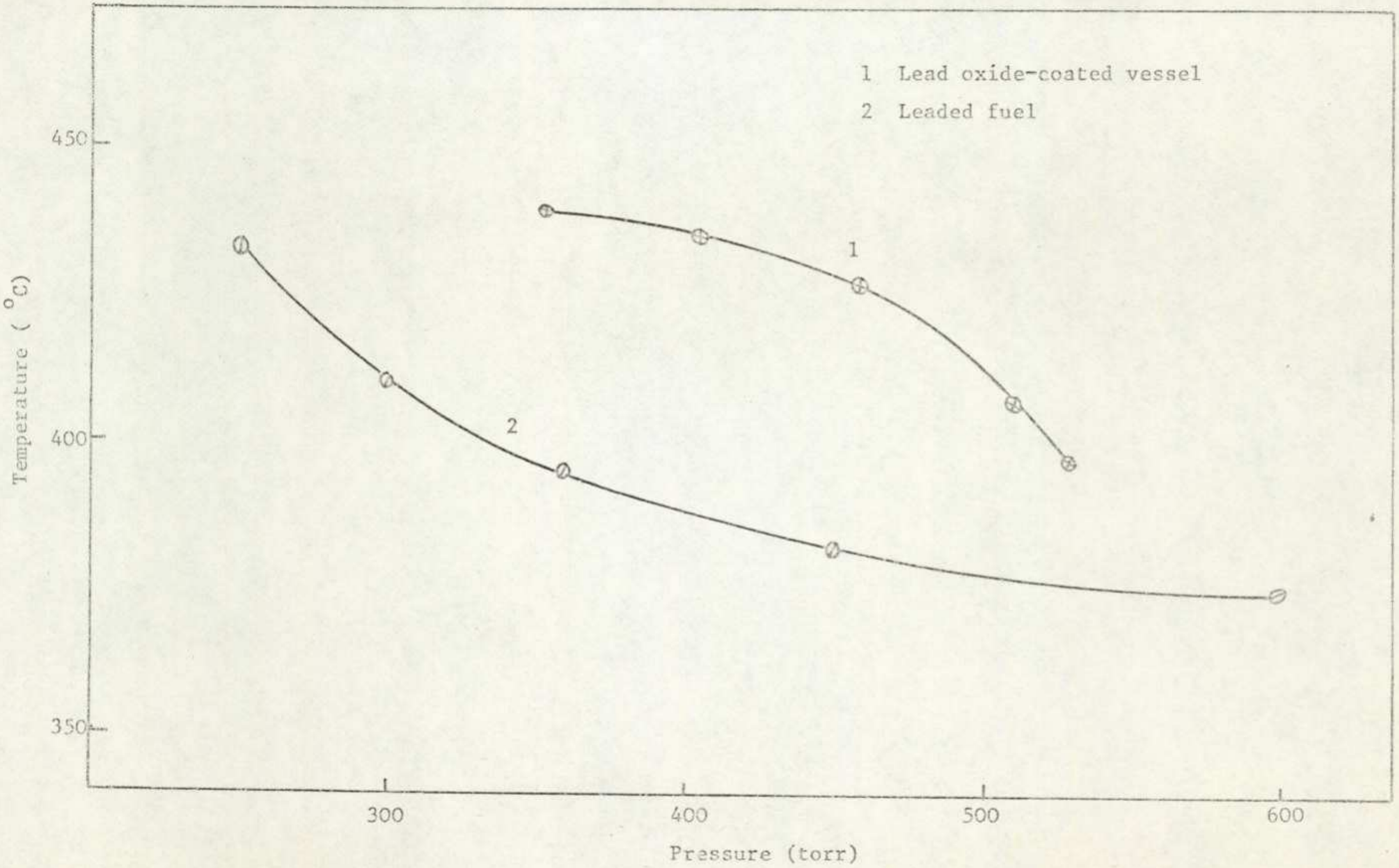


Figure 3.29.

Ignition diagrams for isooctane combustion.

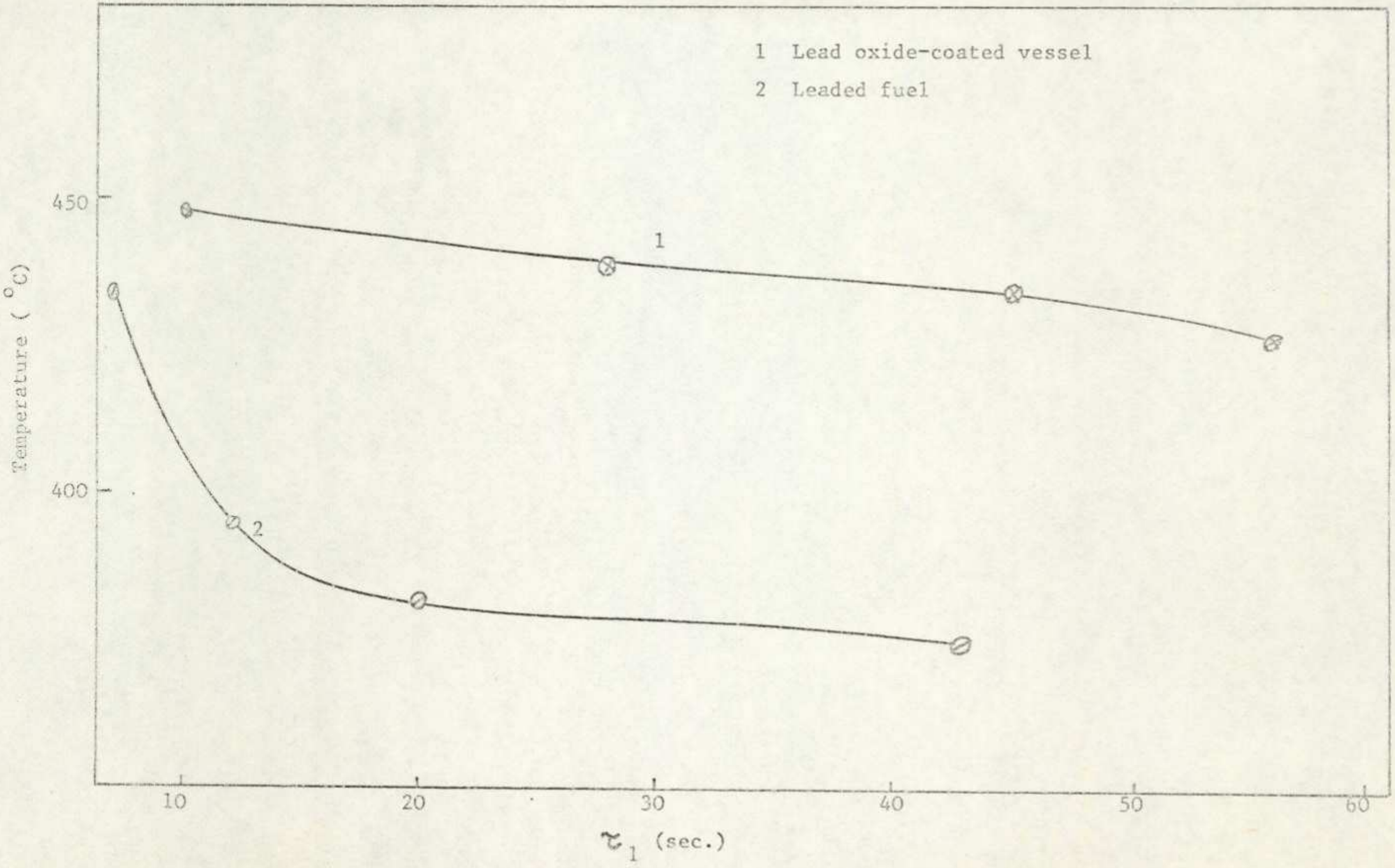
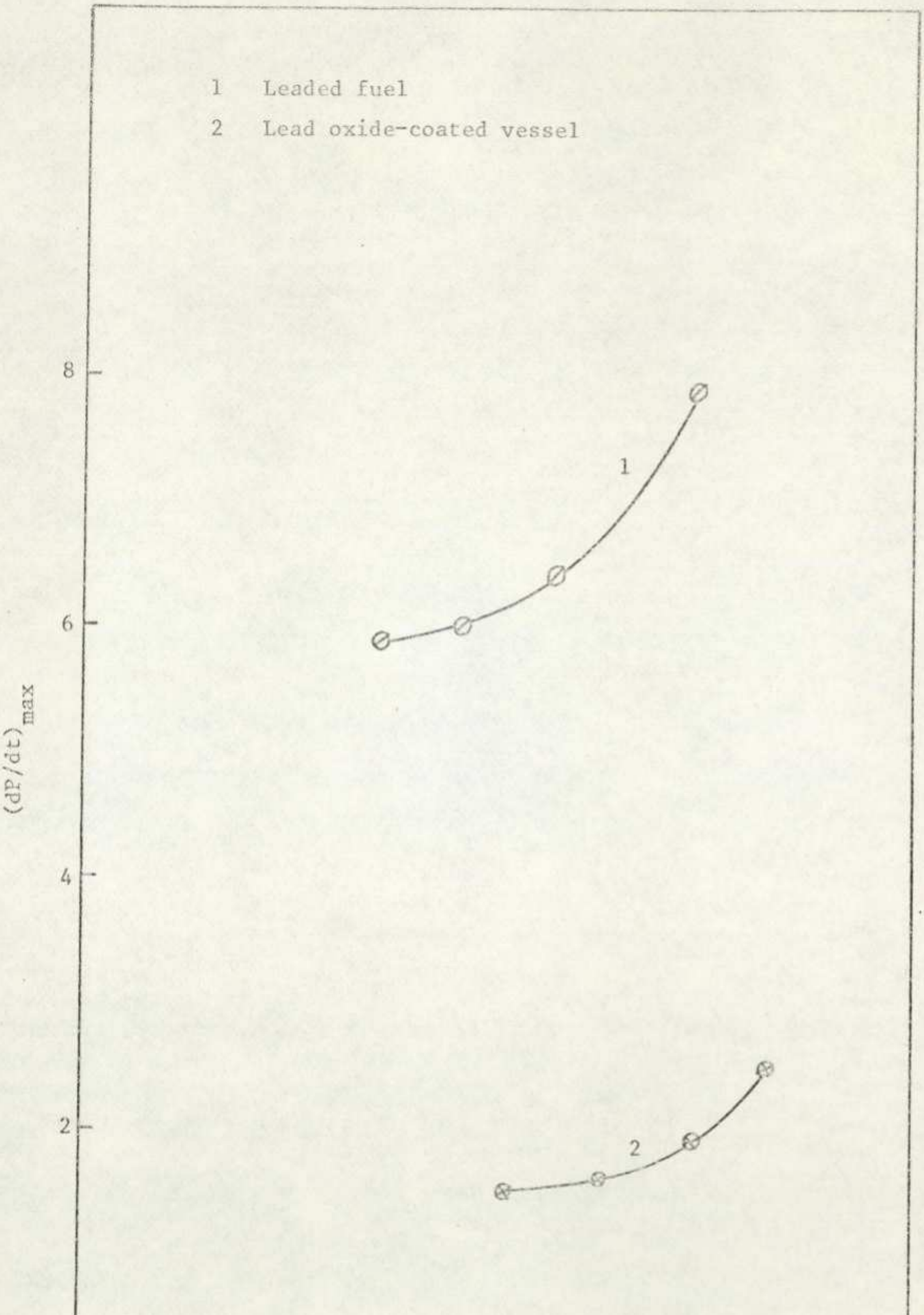


Figure 3.30.

Comparison of the induction periods preceding ignition of isooctane.

Figure 3.31.

Comparison of the variation with temperature of the maximum rate of isooctane combustion $(dP/dt)_{max}$.



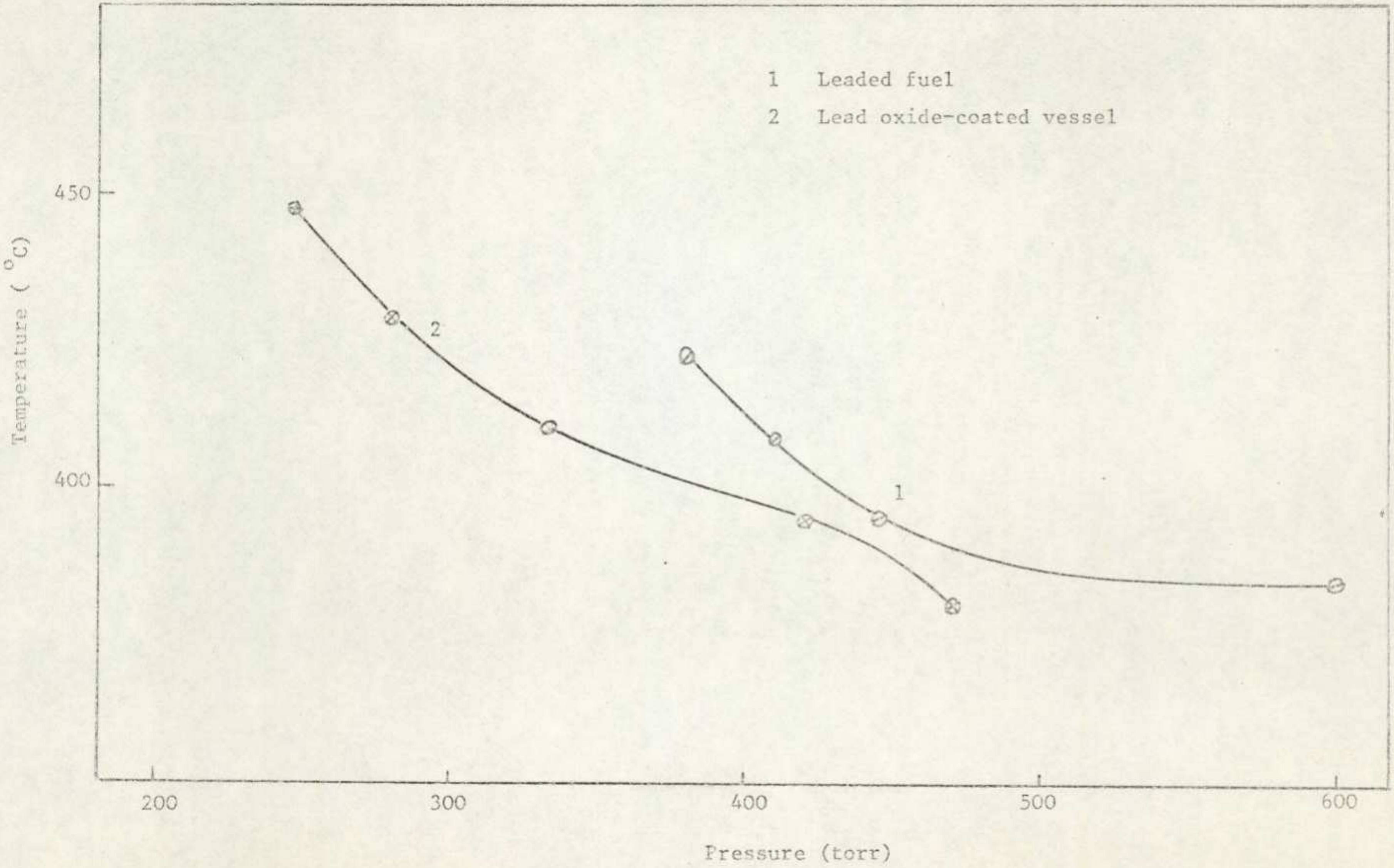


Figure 3.32. Ignition diagrams for isooctane-oxygen-sulphur dioxide mixtures.

vol. % of sulphur dioxide on the combustion of a 3:1 O_2-leaded isooctane mixture. The sulphur dioxide inhibited combustion of the leaded isooctane to a greater extent than that of clear isooctane in a lead oxide-coated vessel. The induction period preceding ignition was longer than that in a lead oxide-coated vessel (Fig. 3.33) and the maximum rate of reaction, $(dP/dt)_{max}$ was smaller.

Analysis of the combustion products revealed that complete oxidation of the isooctane occurred during ignition and that ca. 85% of the sulphur dioxide was used up.

3.3.3.1.2. Thiophene.

Thiophene has a slight inhibiting effect on the combustion of leaded isooctane. In Fig. 3.34, its effect is compared with that found in a lead oxide-coated vessel. Analysis showed that complete oxidation of the isooctane occurred and ca. 70% of the thiophene was consumed. Only 50% of the thiophene reacting was converted to sulphur dioxide.

3.3.3.1.3 Thiophenol.

The effect of thiophenol is similar to that observed with sulphur dioxide in the combustion of leaded isooctane. An oxygen-leaded isooctane-thiophenol mixture was less ignitable than a mixture of oxygen-clear isooctane-thiophenol in a lead oxide-coated vessel (Fig. 3.35). The induction period preceding ignition of leaded isooctane was increased in the presence of thiophenol (Fig. 3.36). The maximum rate of reaction $(dP/dt)_{max}$, was however greater than that of clear

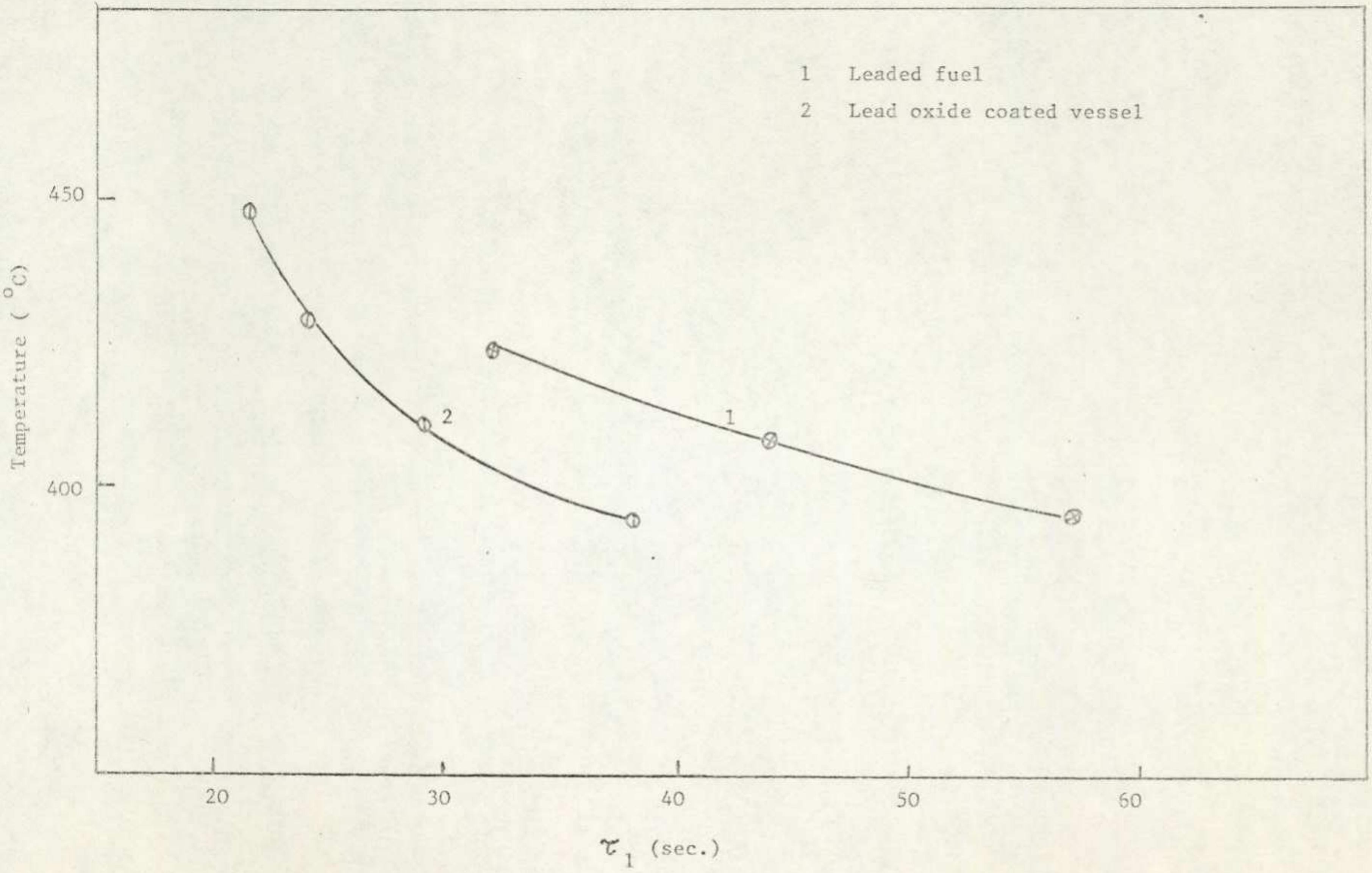


Figure 3.33.

Comparison of the induction period leading to ignition in an isooctane-oxygen-sulphur dioxide mixture.

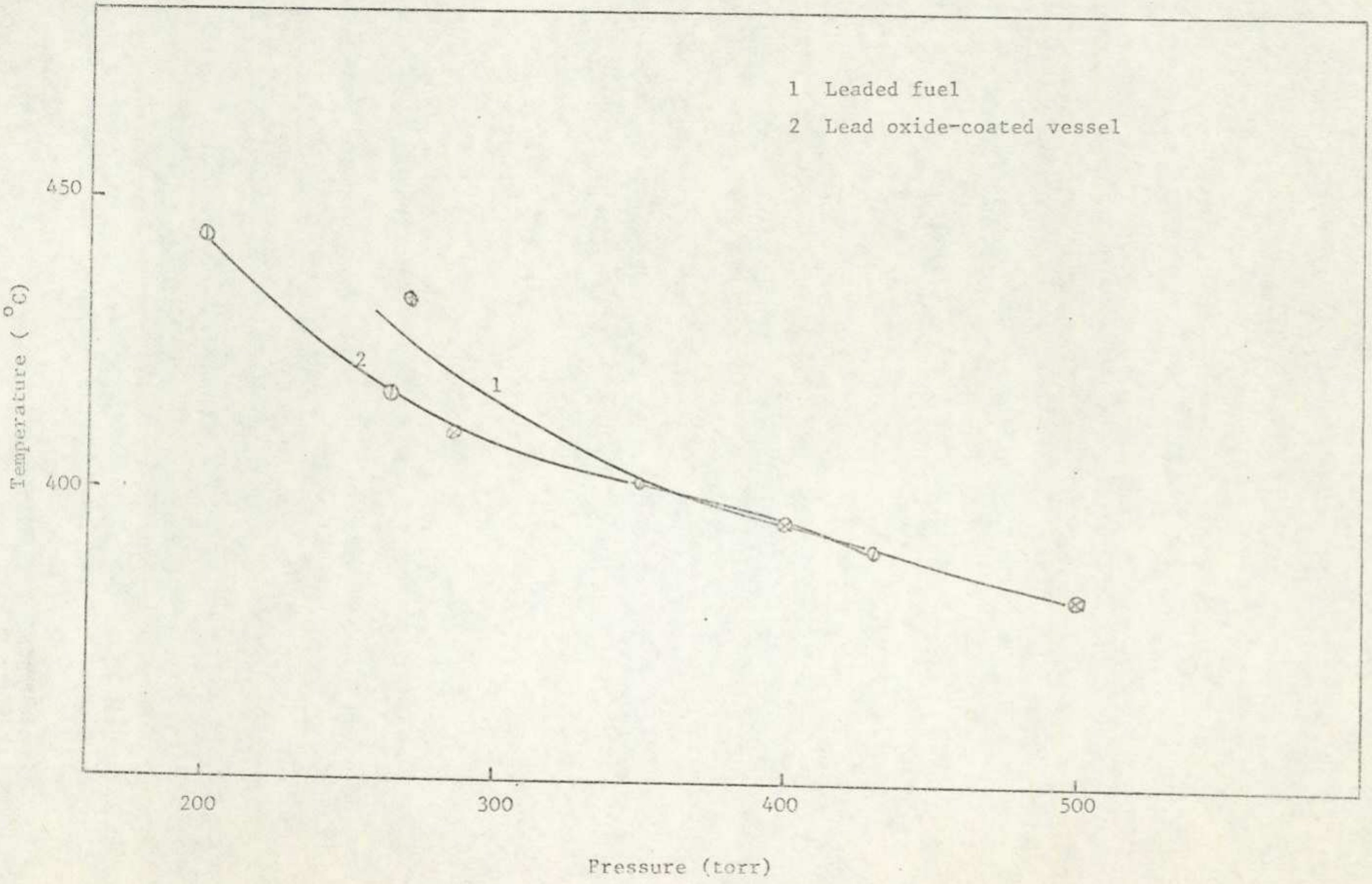


Figure 3.34. Ignition diagrams for isooctane combustion in the presence of thiophene.

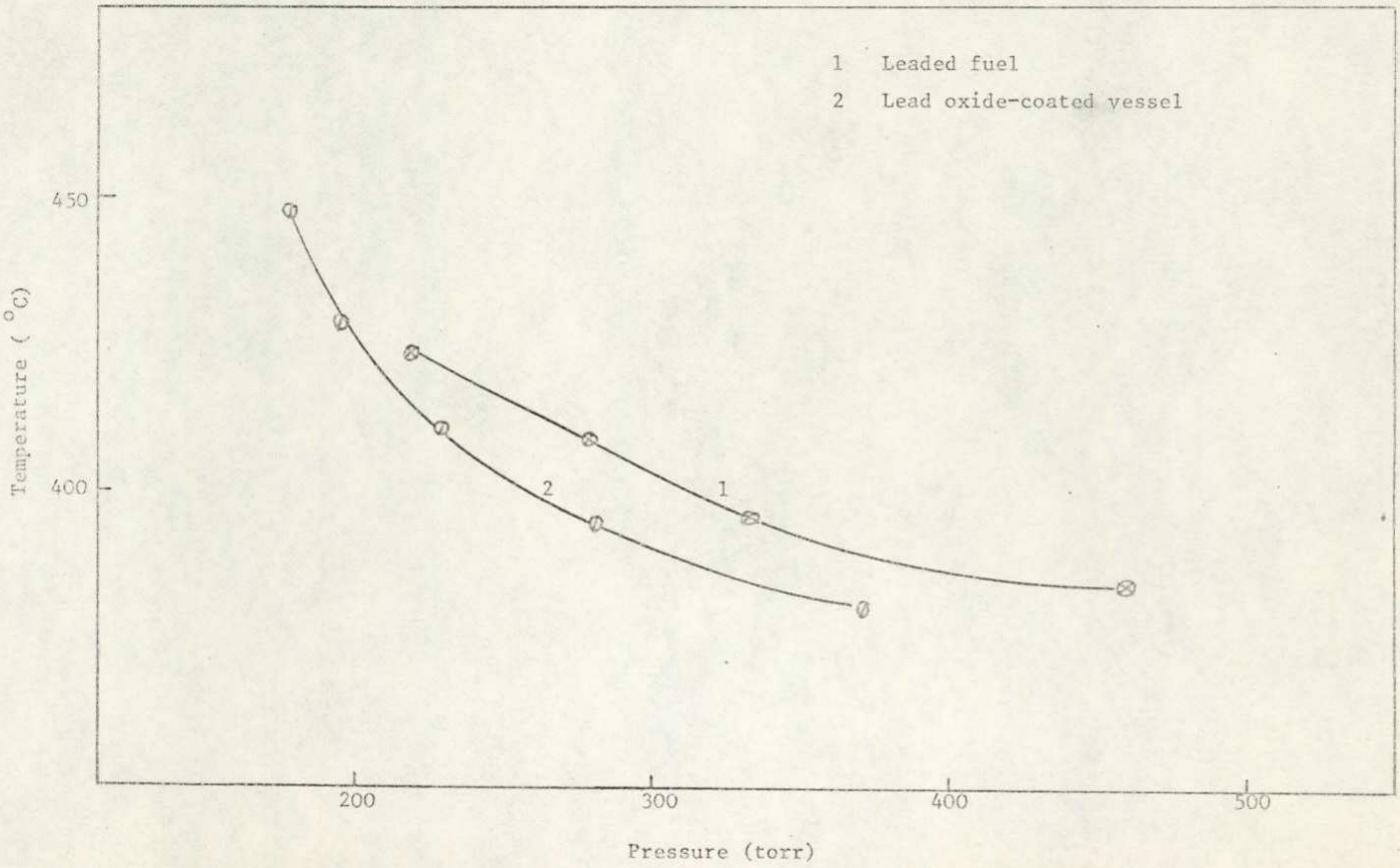


Figure 3.35.

Ignition diagrams for isooctane combustion in the presence of thiophenol.

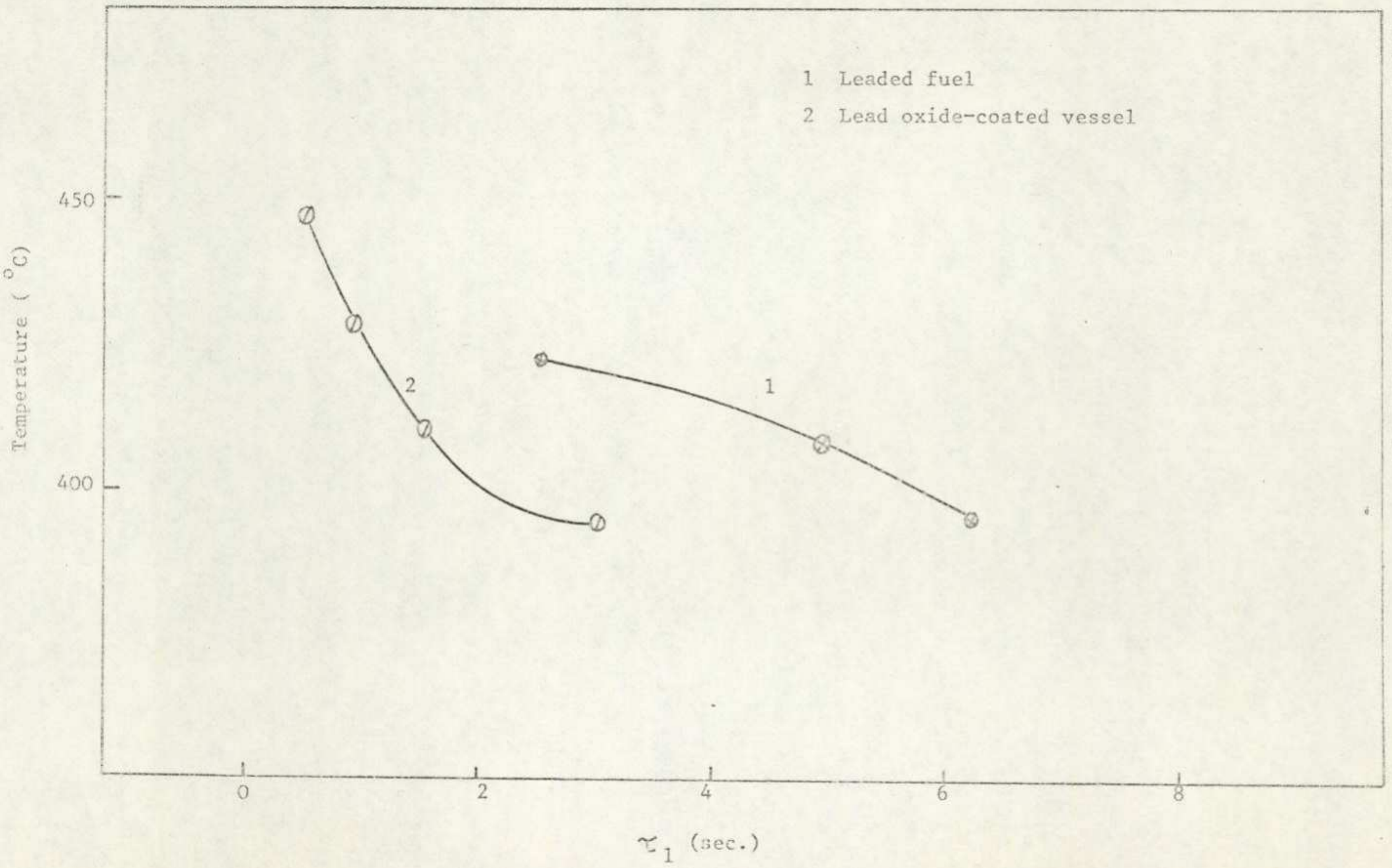


Figure 3.36.

Comparison of the induction period leading to ignition of an isooctane-oxygen-thiophenol mixture.

isooctane in a lead oxide-coated vessel.

Analysis of the combustion products revealed that all the isooctane reacted during ignition as did all the thiophenol. However, only ca. 30% of the thiophenol which reacted was present as sulphur dioxide in the final products.

3.3.3.2. Comparison of the effects of sulphur compounds on leaded isooctane combustion.

Figure 3.37 shows the effects of sulphur dioxide, thiophene and thiophenol on the combustion of leaded isooctane. The first two compounds inhibited the combustion of the leaded isooctane but thiophenol lowered the ignition limits. The effects of thiophene and sulphur dioxide were very similar to those observed during the combustion of clear isooctane. Table 3.12 compares the effects of the three sulphur compounds on the products of isooctane combustion in a lead oxide-coated vessel and in the presence of tetraethyl lead.

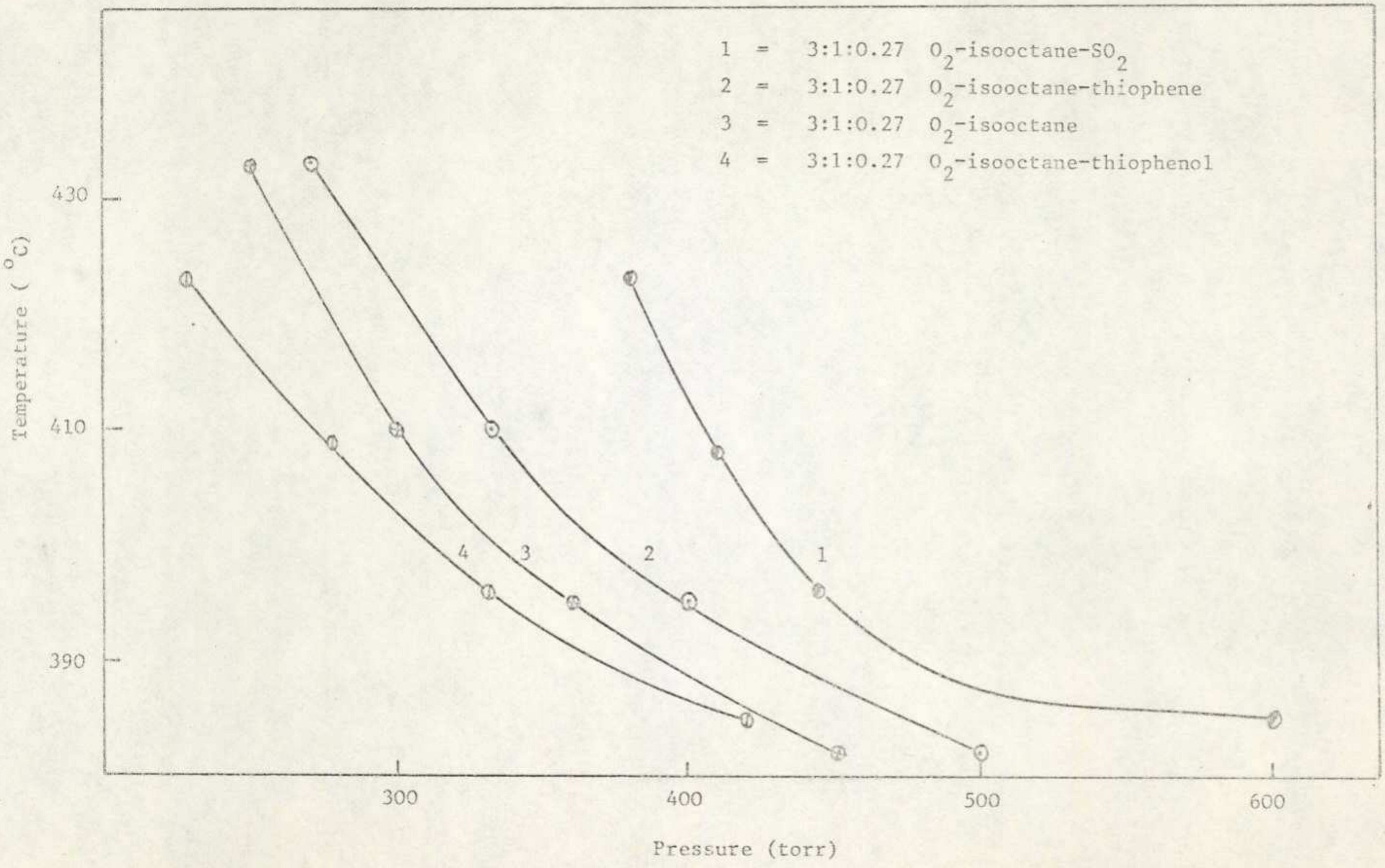


Figure 3.37.

Comparison of the ignition limits of leaded isooctane combustion in the presence of sulphur additives.

Table 3.12.

The effects of sulphur compounds on isooctane combustion in lead oxide-coated vessels and with the added tetraethyl lead.

Sulphur additive	Lead oxide-coated vessel			Leaded fuel.		
	% isooctane consumed	% S consumed	moles SO_2 formed per mole S consumed	% isooctane consumed	% S consumed	mole SO_2 formed per mole S consumed
None	100	-	-	100	-	-
Sulphur dioxide	93	50	-	100	85	-
Thiophene	85	75	0.50	100	70	0.50
Thiophenol	98	100	0.50	100	100	0.30

3.3.4. Combustion of isooctane in lead oxide-coated vessel treated with gaseous sulphur compounds.

3.3.4.1. Lead oxide coating treated with sulphur dioxide.

A lead oxide-coated vessel was treated with sulphur dioxide as described in Section 2.2.3.7, and studies were made of the initial conditions under which ignition of isooctane occurs. Figure 3.38 shows the resulting ignition limits and also the effect of 6.25 vol. % of sulphur dioxide on isooctane combustion. The type of combustion observed was similar to that in a vessel coated only with powdered lead oxide, and cool flames and two-stage ignitions were again eliminated.

The ignition limits of isooctane in this vessel were approximately the same as in a lead oxide-coated vessel and sulphur dioxide again had a similar effect in that it reduced the ignition limits of the isooctane (Fig. 3.38). However, in a lead oxide-coated vessel treated with sulphur dioxide, the induction period preceding ignition was much shorter than in a lead oxide-coated vessel but slightly longer than in an uncoated vessel (Fig.3.39). Furthermore, the overall rate of reaction was greater than in a coated vessel.

Analysis of the combustion products showed that complete reaction of the isooctane occurred during ignition and with the addition of the sulphur dioxide, 40% of this

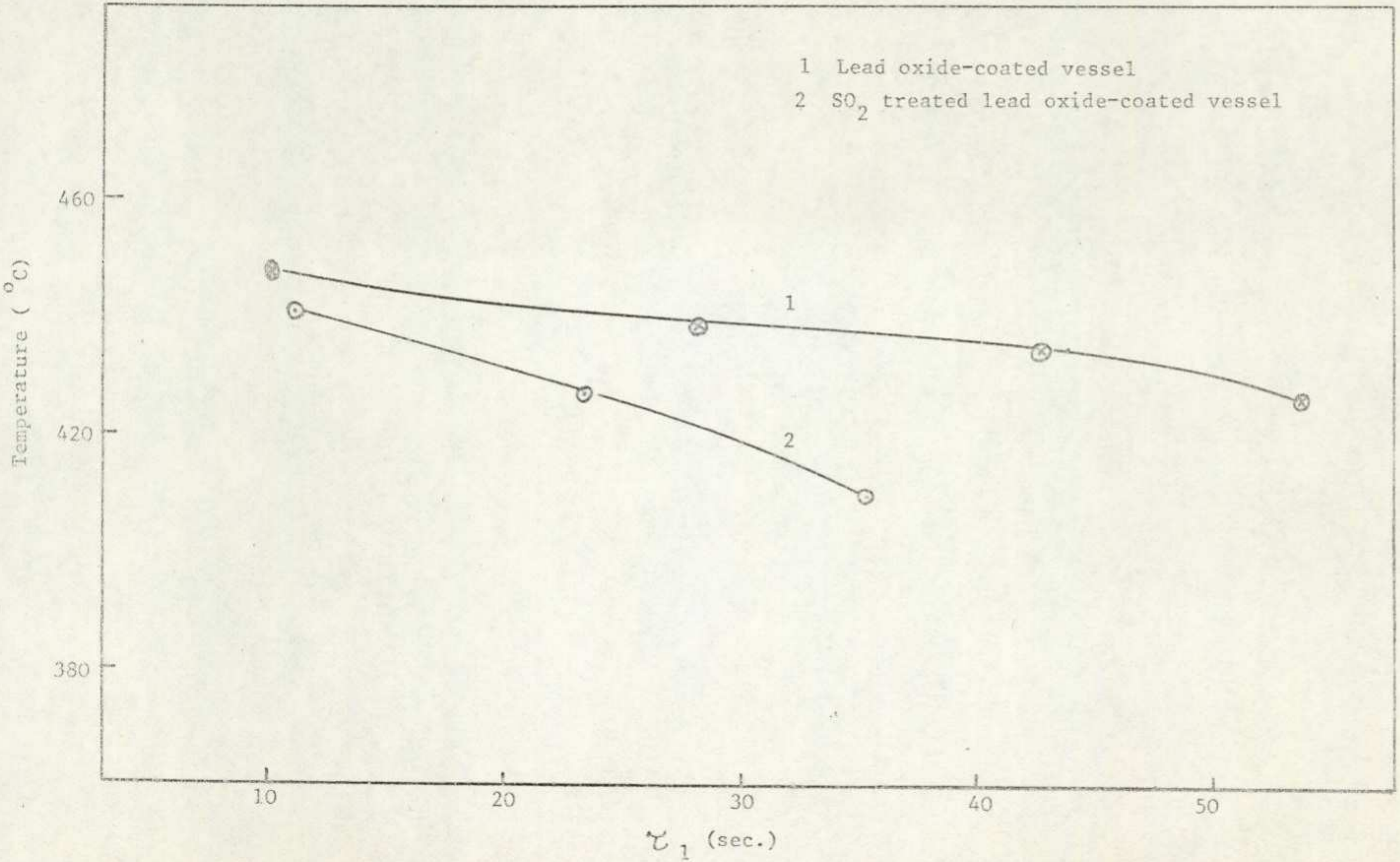


Figure 3.39.

Induction periods preceding isooctane ignition in an SO_2-treated lead oxide-coated vessel.

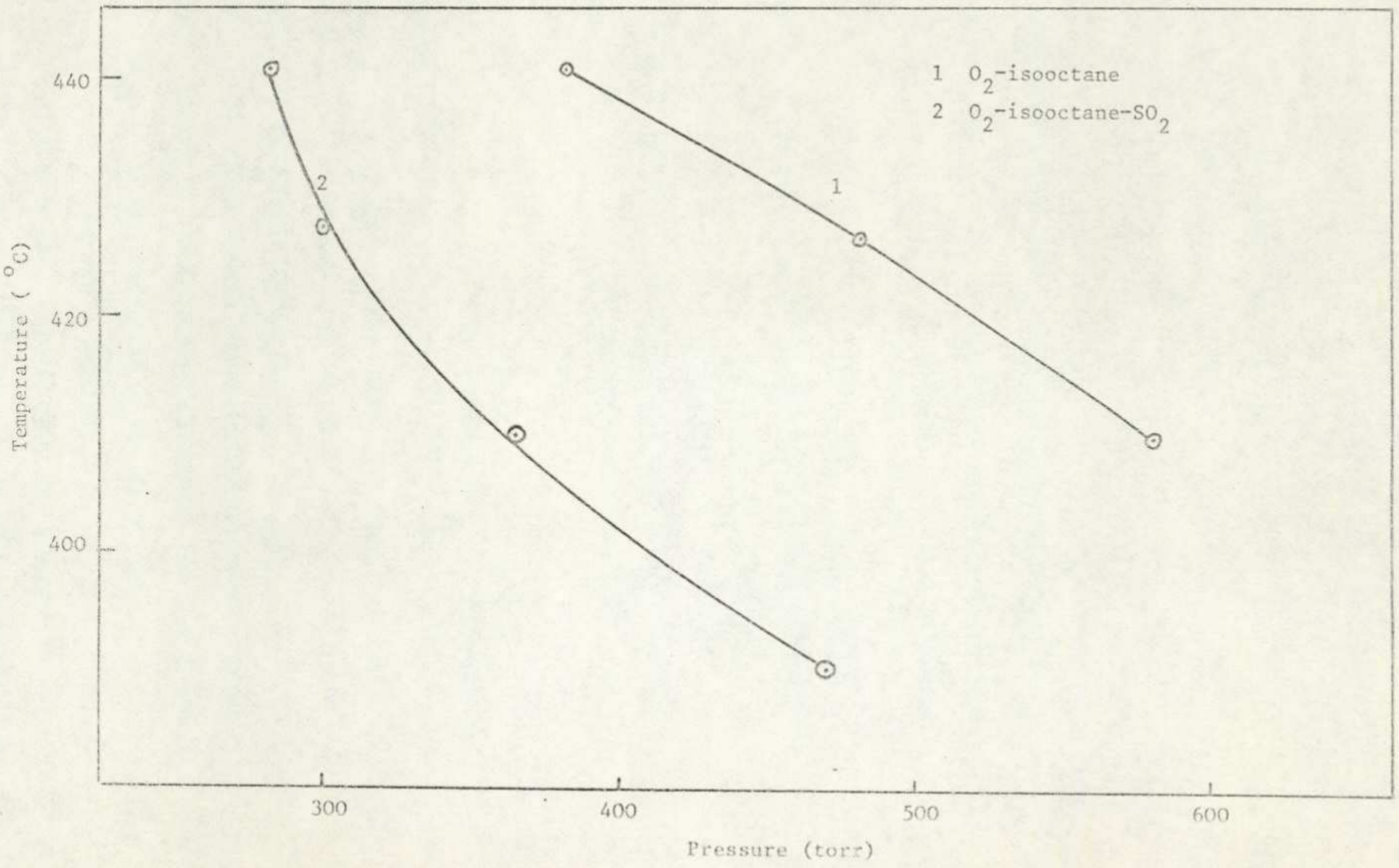


Figure 3.38.

Ignition profiles for isooctane combustion in an SO_2-treated lead oxide-coated vessel.

compound disappeared during combustion.

3.3.4.2. Lead oxide coating treated with thiophene.

Thiophene was used to treat a vessel coated with powdered lead oxide, and the ignition limits of isooctane were measured in this vessel (Fig. 3.40). The reactions were similar to those obtained in an uncoated vessel, cool flames and two-stage ignitions being observed at temperatures between 300 and 380°C. The maximum rate of reaction increased with temperature up to ca. 324°C and then decreased as the temperature was further increased to 381°C, when hot ignitions were observed, leading to a sharp increase in reaction rate.

The addition of 6.25 vol. % of sulphur dioxide raised the ignition limits (Fig. 3.40). This inhibiting effect was similar to that observed in an uncoated vessel. In general therefore the thiophene destroyed the chain terminating properties of the lead oxide coating and in doing so created a surface which was even less effective than the uncoated vessel in inhibiting reaction.

Analysis of the combustion products showed complete combustion of the isooctane and that ca. 40% of the added sulphur dioxide reacted.

3.3.4.3. Lead oxide coating treated with thiophenol.

The ignition limits of isooctane were also determined in a reaction vessel coated with lead oxide and treated with thiophenol. Figure 3.41 shows the ignition limits for isooctane combustion in this vessel and the effects on these

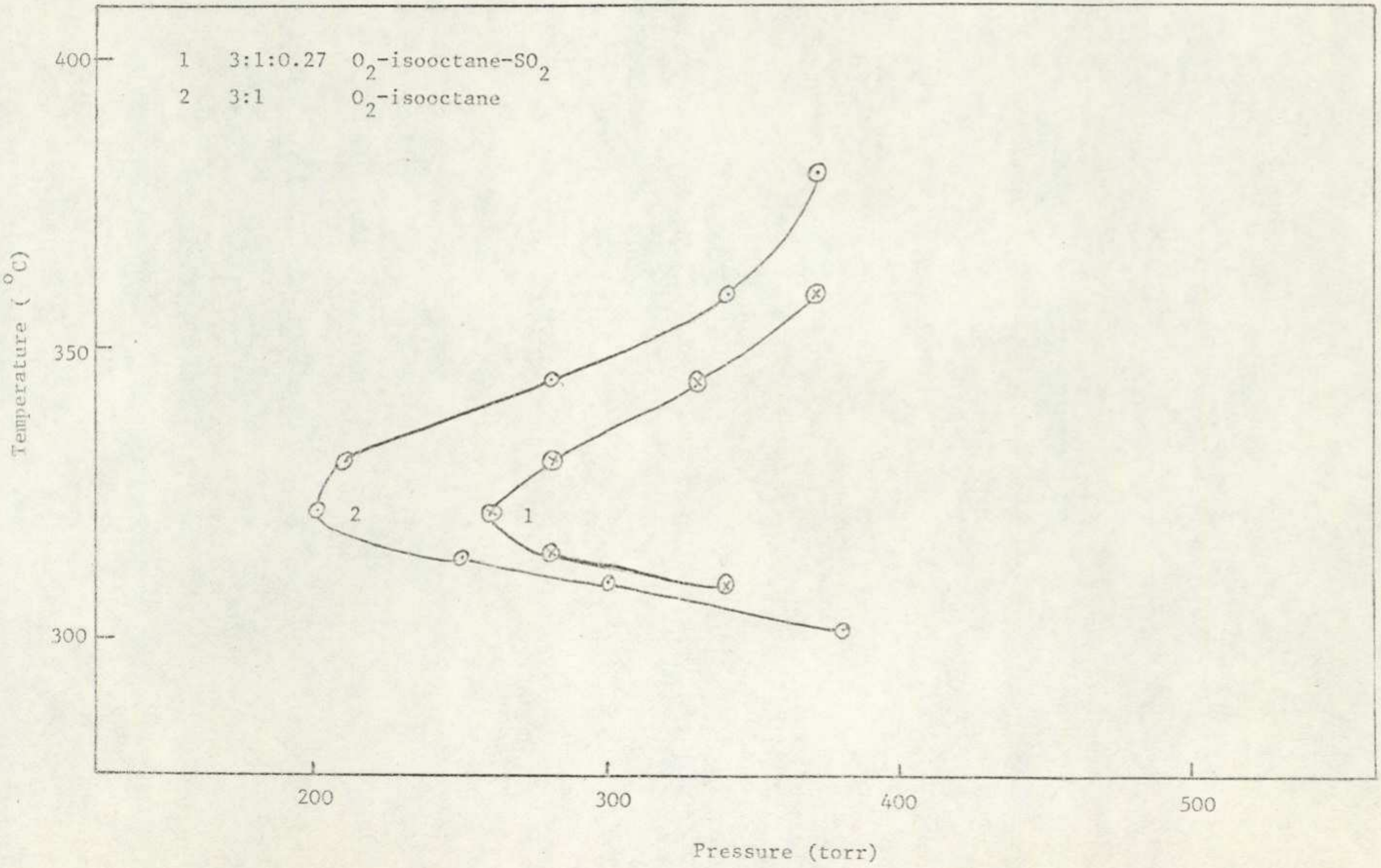


Figure 3.40.

Ignition profile of isooctane combustion in a thiophene-treated lead oxide coated vessel.

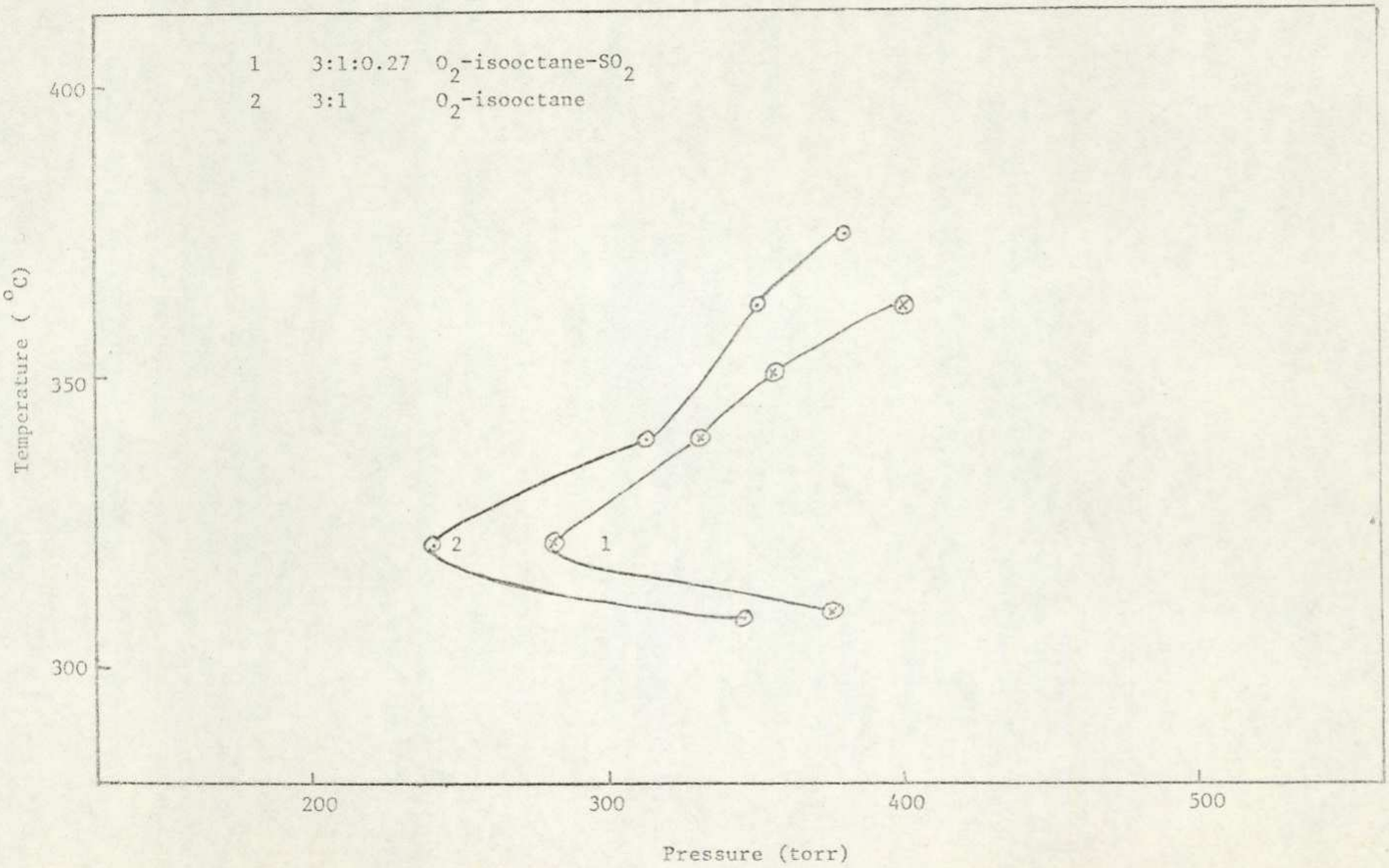


Figure 3.41.

Ignition profile of isooctane combustion in a thiophenol-treated lead oxide coated vessel.

limits of added sulphur dioxide. The results obtained were similar to those in an uncoated vessel, cool flames and two-stage ignitions being observed. The ignition limits decreased with increasing temperature to ca. 322°C and then increased as the temperature was further increased to 380°C, when hot ignitions were observed. The maximum rate of reaction was greater than that in an uncoated reaction vessel.

The addition of 6.25 vol. % of sulphur dioxide raised the ignition limits in this vessel, and its effect was similar to that in an uncoated vessel. Analysis of the combustion products showed complete oxidation of the isooctane in the ignition region and ca. 75% reaction of the isooctane in the cool flame region. In the presence of sulphur dioxide ca. 65% of this compound underwent combustion.

3.3.5. Comparison of the effects on isooctane combustion of lead oxide-coated vessels treated with sulphur compounds.

When sulphur dioxide was used to treat a lead oxide coating, there was no noticeable pressure drop in the vessel suggesting that the sulphur dioxide was not absorbed by the coating. The ignition limits of isooctane combustion were not markedly affected in this vessel, although there was a slight increase in the overall rate of reaction

Approximately 40 torr of thiophene and 80 torr of thiophenol were absorbed onto the lead oxide surfaces when the vessels were treated with these compounds. The presence of these organic sulphur compounds caused a marked change on isooctane combustion and lowered the ignition limits. Cool flames and two-stage ignitions were observed and reactions were similar to those in an uncoated vessel. This implies that the sulphur compounds destroyed the chain terminating properties of the lead oxide coating. The increase in $(dP/dt)_{max}$ being higher than in an uncoated vessel showed that the surface was deactivated to such an extent that it was even less effective in causing chain termination than the walls.

3.4 Results of the E.D.A.X. studies.

3.4.1 Surface scanning.

Samples of powdered lead oxide and lead oxide treated with the sulphur compounds were placed on a carbon support and the surfaces were scanned with a 40kV beam. The magnification used was 1000 and the particle size was found to be ca. 40 μm. Pictorial representations of these scanning results are shown in Figures 3.42-3.45. Figure 3.42 shows the lead oxide which was untreated, while Fig.3.43 shows the lead oxide surface after it had been treated with sulphur dioxide. There is little apparent difference in the surface except for a slight furriness on the lead oxide surface.

Figures 3.44 and 3.45 show the effects of thiophene and thiophenol respectively. The furriness on the surface increased considerably in both cases but was more pronounced in the case of thiophenol. This suggests some interaction of the sulphur compounds with the lead oxide, and this interaction was more severe with the organic sulphur compounds than with sulphur dioxide.

3.4.2. Analytical results.

Due to the limitations of the instrument, it was not possible to separate the sulphur and lead peaks and therefore a ratio of the combined lead peaks had to be used to detect the presence of sulphur in the samples (Fig. 3.46). The S_k and Pb_m line was given a standard height of 2000 units and for samples of pure lead oxide the ratio of the Pb_m line to the Pb_α line was fixed. The Pb_α line of pure lead oxide was cal-

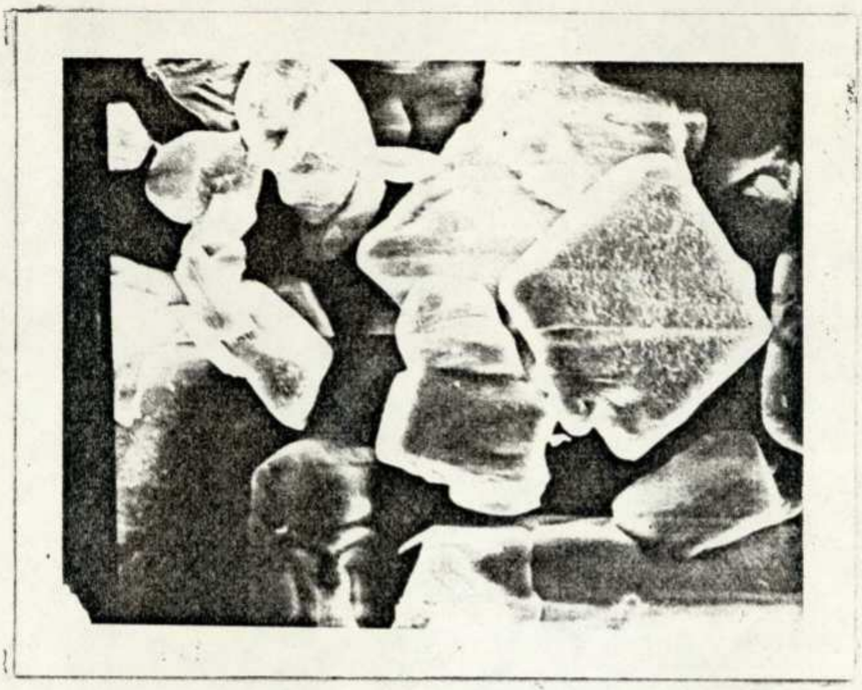


Figure 3.42. Pure lead oxide, magnification 1000.

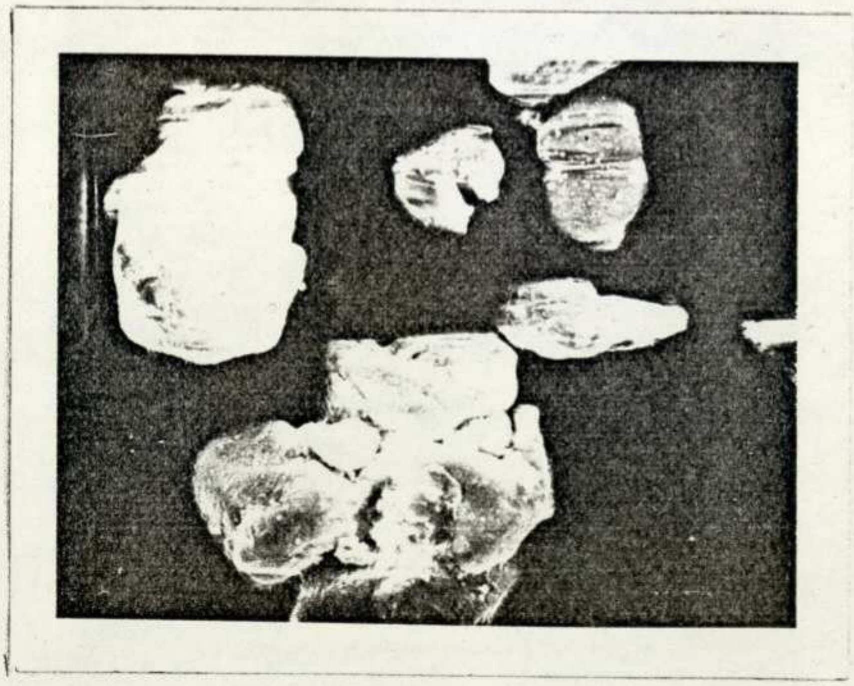


Figure 3.43. Lead oxide treated with SO_2, magnification 1000.

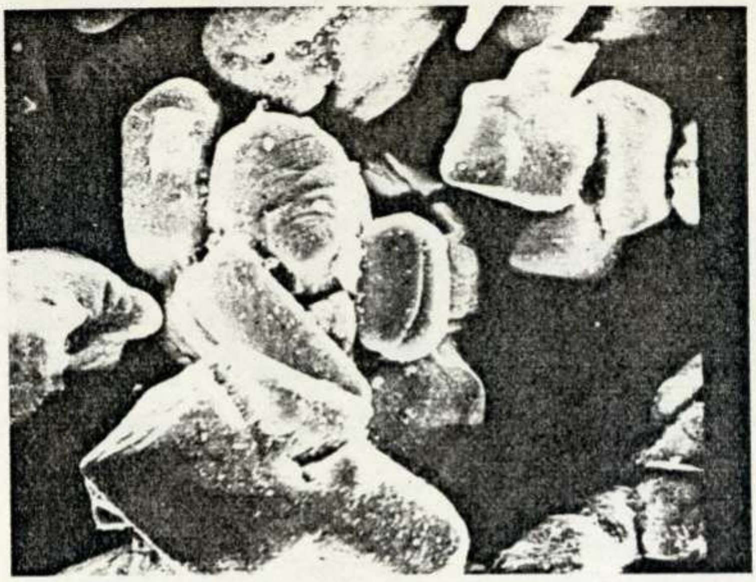


Figure 3.44. Lead oxide treated with thiophene, magnification 1000.

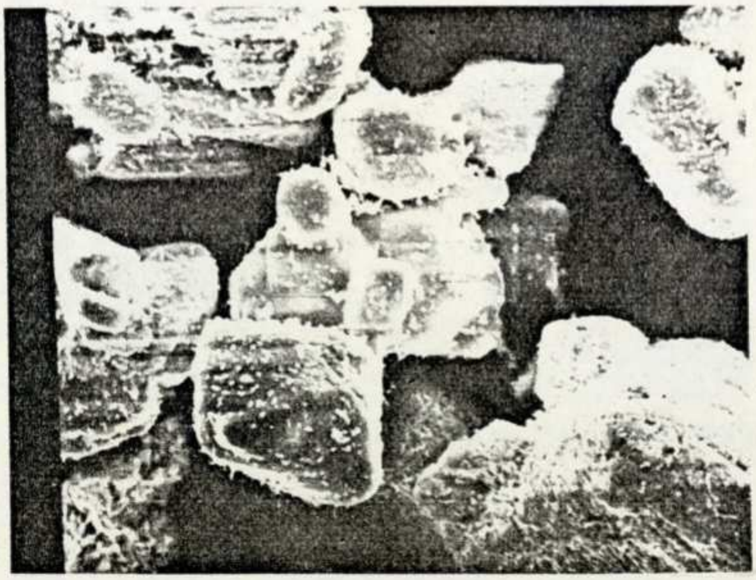
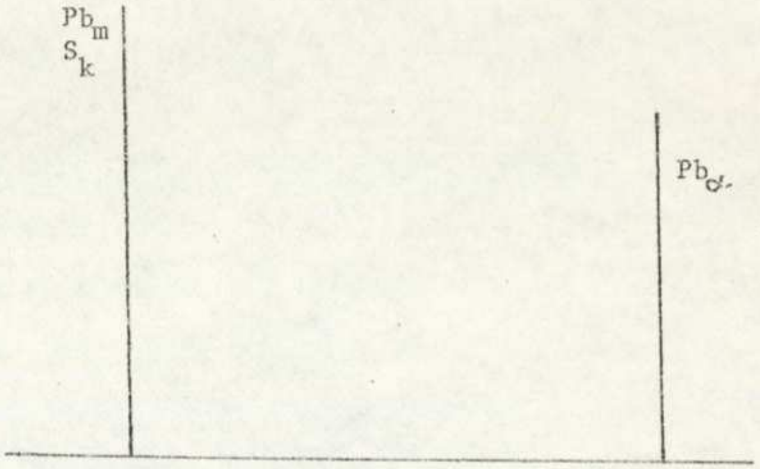


Figure 3.45. Lead oxide treated with thiophenol, magnification 1000.

culated to be 1600.

Figure 3.46.

Diagram showing the form of the S_k, Pb_m line and the Pb_α line.



$\therefore$ for pure lead oxide:

$$\frac{Pb_m}{Pb_\alpha} = \frac{2000}{1600} = 1.25$$

In the presence of sulphur, however, the Pb_m line will be enhanced, the Pb_m/Pb_α ratio becoming greater than in the absence of sulphur. The Pb_α values for the lead oxide treated with the sulphur compounds are given below. In each case five values of Pb_α were calculated to obtain an average value.

Pb_α for the SO_2 treated lead oxide = 1244.8

$$\therefore \quad \frac{Pb_m}{Pb_\alpha} = 1.60$$

Pb_α for the thiophene treated lead oxide = 1489.0

$$\therefore \quad \frac{Pb_m}{Pb_\alpha} = 1.34$$

Pb_{α} for the thiophenol treated lead oxide = 1366.4

$$\therefore \frac{Pb_m}{Pb_{\alpha}} = 1.46$$

Figures 3.47- 3.49 show the spectra obtained from the measurements of the lead oxide coatings treated with the three sulphur compounds. The dot seen at the top of the Pb_{α} line represents the Pb_{α} value for pure lead oxide.

The amounts of sulphur in the treated lead oxide coatings decreased in the order: $SO_2 >$ thiophenol $>$ thiophene. However, sulphur dioxide had the smallest influence on the lead oxide coating in so far as the ignition limits are concerned. This therefore suggests that, although a greater amount of sulphur was present in the SO_2-treated lead oxide-coated vessel, the organic sulphur compounds had the most marked effect in reducing the chain-terminating properties of the lead oxide.

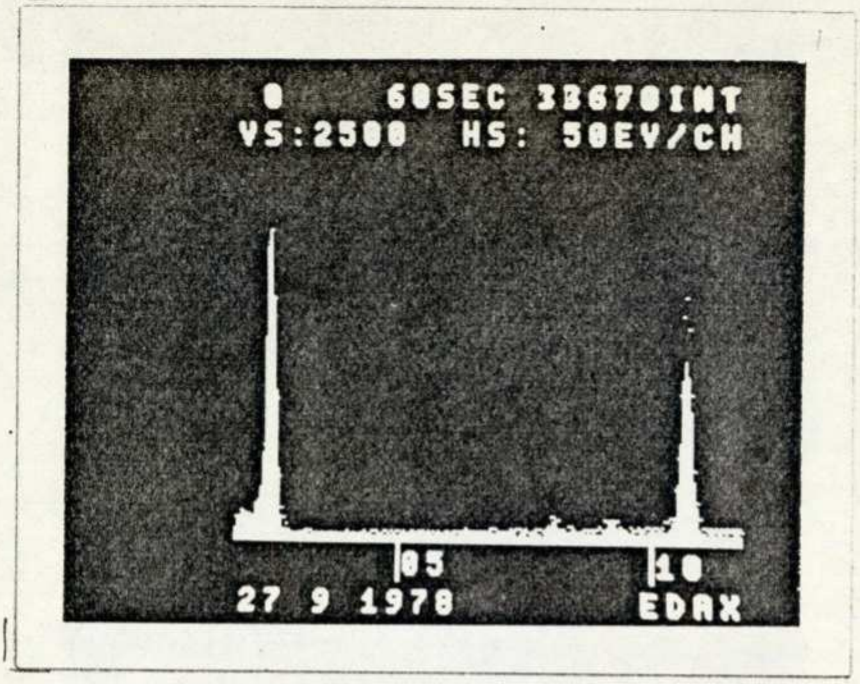


Figure 3.47. Spectrum obtained from X-ray analysis of lead oxide treated with sulphur dioxide.

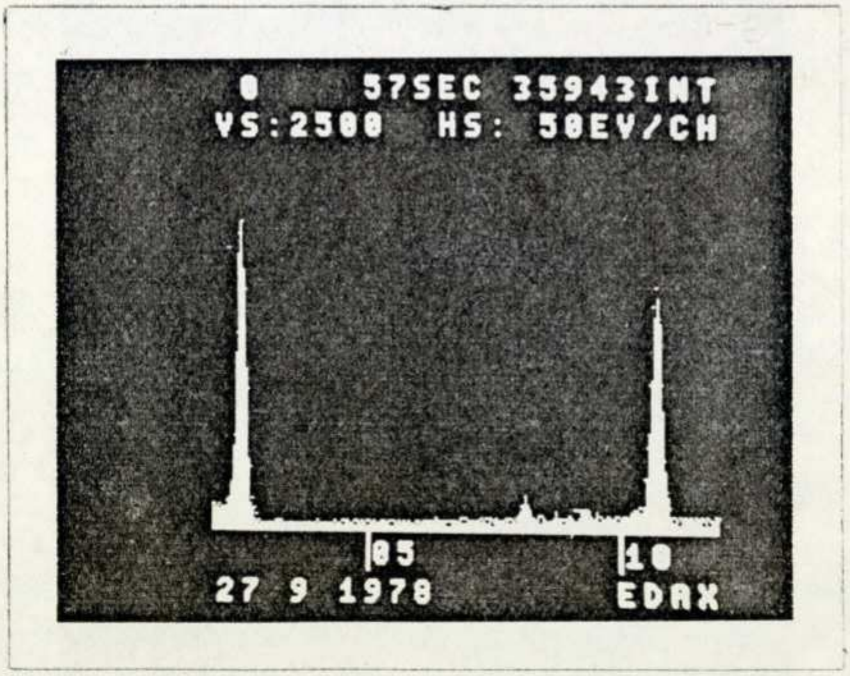


Figure 3.48. Spectrum obtained from X-ray analysis of lead oxide coated with thiophene.

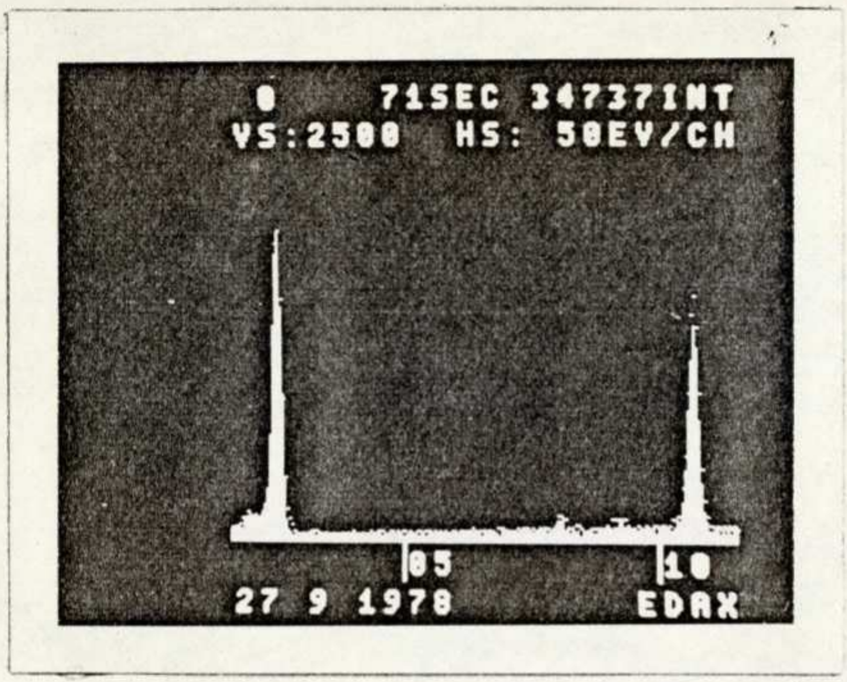


Figure 3.49. Spectrum obtained from lead oxide treated with thiophenol.

SECTION 4.

DISCUSSION.

SECTION 4.

4.1. Sulphur - lead interactions in the combustion of motor gasolines in engines.

It has long been known that the presence of small quantities of lead alkyls in motor gasolines decreases the "knocking" tendency. Engine studies undertaken during the present work show that tetraethyl lead is in general more effective than tetramethyl lead in increasing the octane number of the fuel blends. The lead alkyls were better "anti-knocks" in an isooctane-heptane blend than in a toluene-heptane blend. A diisobutylene-heptane fuel showed a very low lead response, giving an initial decrease in octane number for the first addition of tetramethyl lead and then only a rather small increase.

The seven sulphur compounds studied all had varying effects on the lead response of the fuels, thiophene having the smallest affect and thiophenol the greatest. The order of lead antagonism was: thiophene $<$ diphenyl sulphide diphenyl disulphide $<$ dipropyl sulphide $<$ tertiary octyl mercaptan $<$ dimethyl disulphide $<$ thiophenol. These results are in general agreement with those obtained by earlier investigators of sulphur-lead antagonism[96,102,111,116].

It has been postulated[103] that sulphur compounds exert their antagonistic action, when they are oxidised under engine conditions to sulphur dioxide. It is then suggested that this gas renders the surface of the active "antiknock" agent, lead oxide[73, 117], less efficient in terminating chains. However, if this theory was correct, then all sulphur compounds used in this work should have the same effect, since equal quantities of sulphur (0.10 wt. % and 0.05 wt. %) were used and all the sulphur is oxidised to sulphur dioxide under engine conditions. Since the compounds all had different effects, it appears that it is not the final oxidation products of these compounds, but the intermediate products of their decomposition and oxidation, which render the lead oxide less effective in reducing engine "knock".

Although the isooctane-heptane blend had a better lead response, it was more susceptible to sulphur antagonism. Livingston[118] suggested that the nature of the fuel is of little importance when sulphur-lead interaction is considered, and that equivalent amounts of a particular sulphur compound will give the same reduction in lead effeciency, regardless of the fuel. Figures 4.1-4.7 show that this is not true, and illustrate that a particular sulphur compound has different effects on lead response depending on the fuel.

The main conclusions which can be drawn from these studies are thus:

1. Sulphur compounds have a more antagonistic effect in leaded isooctane-heptane blends than in leaded toluene-heptane blends.
2. The effect of sulphur on leaded diisobutylene-heptane fuel is in general greater than with leaded toluene-heptane fuel but smaller than with leaded isooctane-heptane fuel. However thiophenol has a very powerful

Key to Figures 4.1 - 4.7.

1 = Isooctane + heptane + TEL.

2 = Isooctane + heptane + TML.

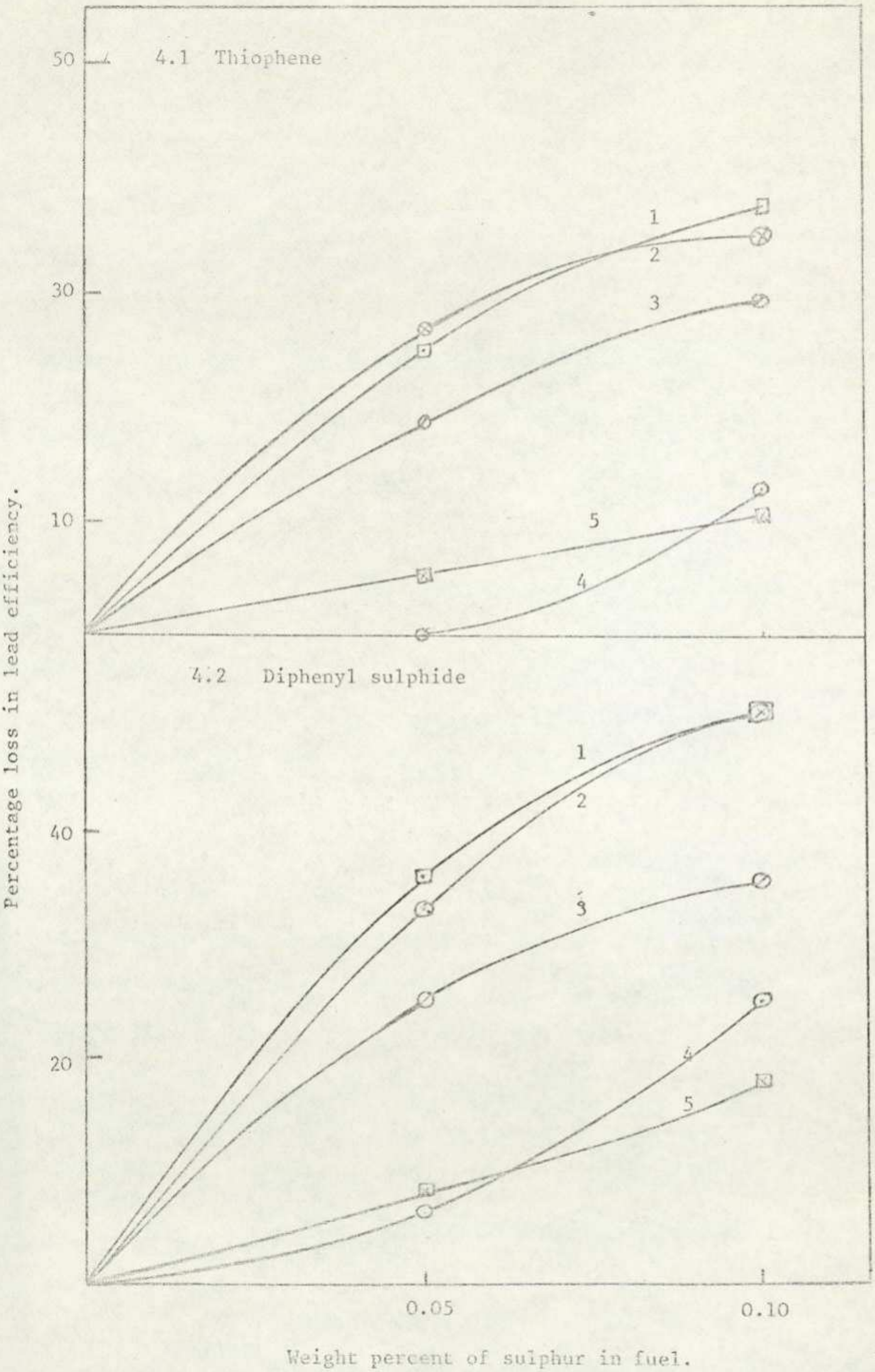
3 = Diisobutylene + heptane + TML.

4 = Toluene + heptane + TEL.

5 = Toluene + heptane + TML.

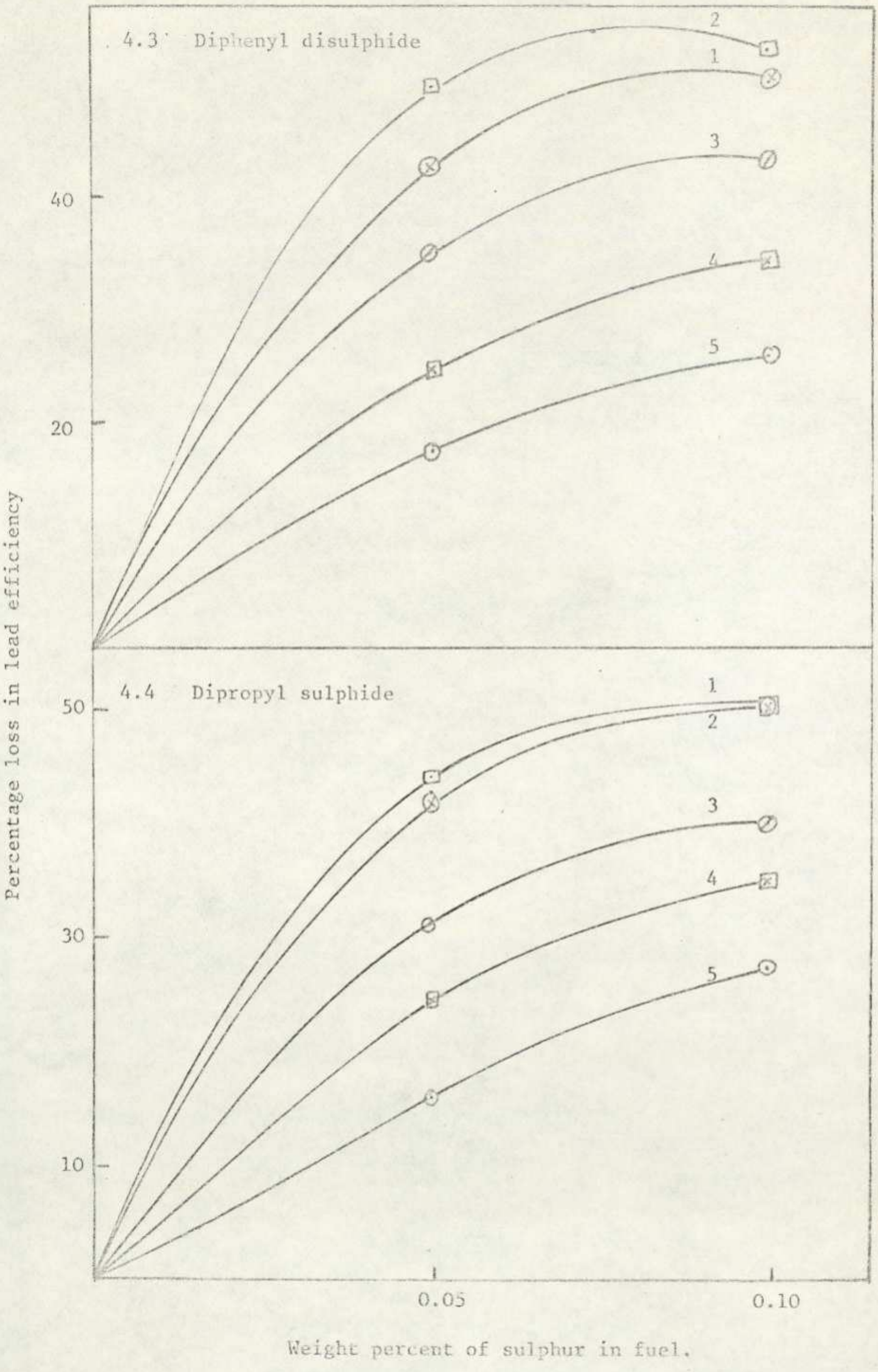
Figures 4.1 and 4.2.

The effect of sulphur compounds on the leaded fuel blends.



Figures 4.3 and 4.4.

The effect of sulphur compounds on the leaded fuel blends.



Figures 4.5 and 4.6.

The effect of sulphur compounds on the leaded fuel blends.

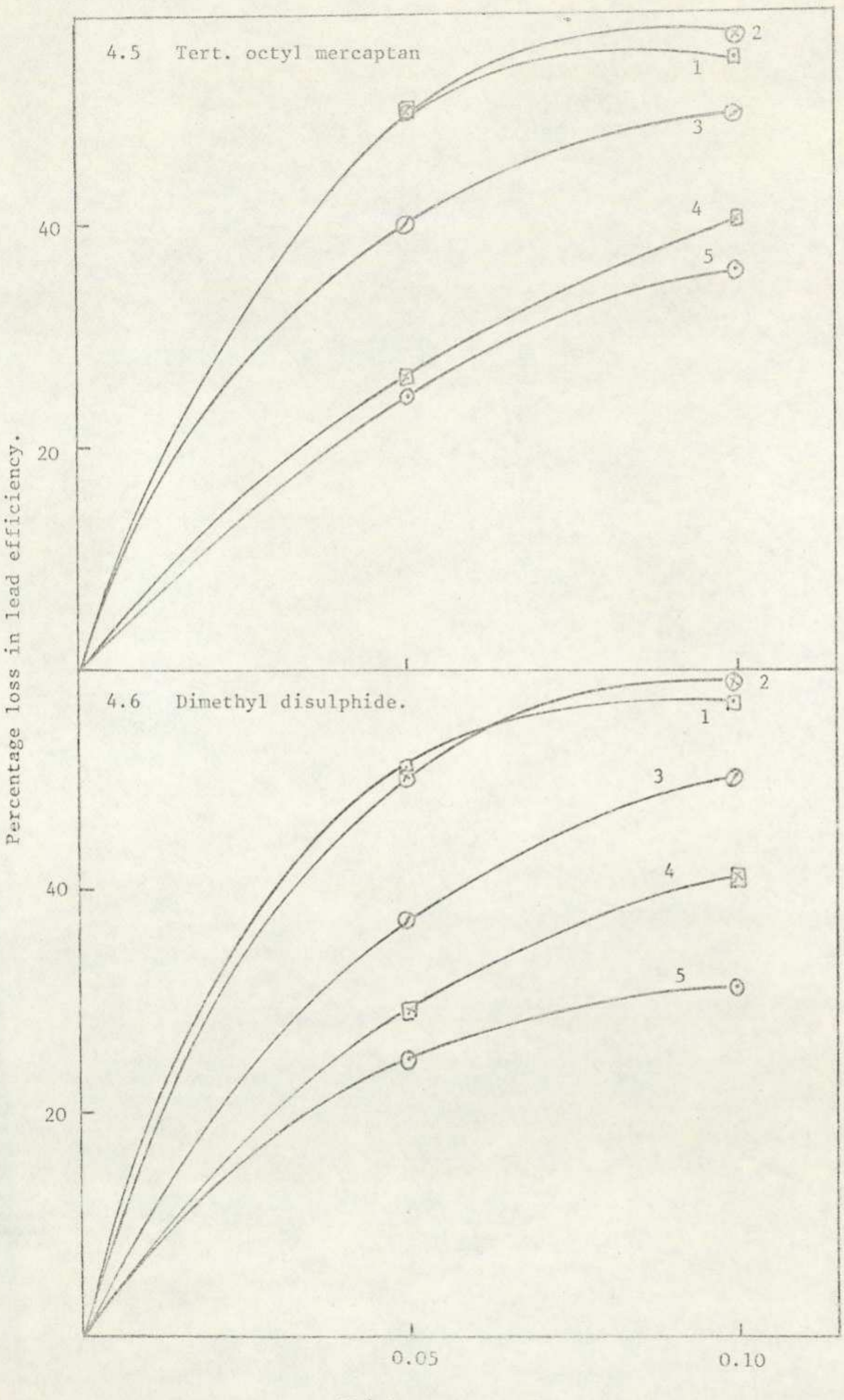
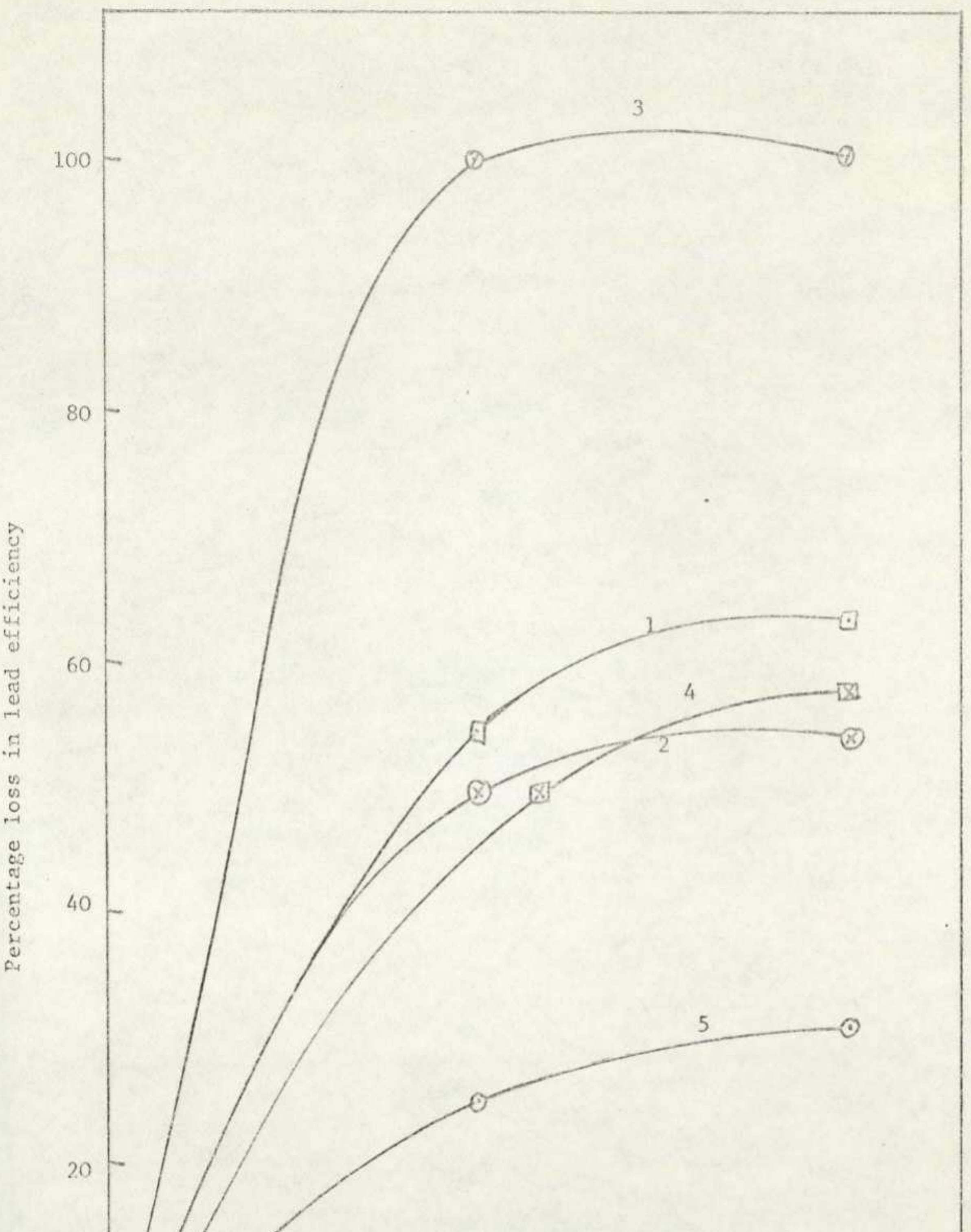


Figure 4.7.

The effect of thiophenol on the leaded fuel blends.



antagonistic effect when added to the leaded diisobutylene blend, the loss in lead efficiency being virtually 100%.

3. Aromatic sulphides and disulphides are less antagonistic towards the lead alkyls than are aliphatic sulphides and disulphides.
4. With a given fuel, the antagonistic effects of the sulphur compounds lie in the order:
   thiophene $<$ monosulphides $<$ disulphides $<$ thiol.
5. The antagonism of the sulphur compounds seems to be related to the rate and products of oxidation of these compounds and also to the ease of breakdown of the lead alkyls.

4.2 Combustion of organic sulphur compounds.

From the results of the engine experiments, laboratory studies were undertaken of the gaseous oxidation of four of the seven sulphur compounds and an attempt was made to correlate their combustion characteristics with their lead antagonistic effects. The four compounds, thiophene dipropyl sulphide, dimethyl disulphide and thiophenol, were chosen on account of their comparatively high volatility and as representatives of the different chemical classes. Thiophene showed the smallest tendency to react, yielding considerably less sulphur dioxide than the other three sulphur compounds. This may account for the smaller effect of thiophene in reducing octane number. Thiophenol however, reacted completely even at temperatures as low as 250°C and yielded larger amounts of sulphur dioxide. Dimethyl disulphide and dipropyl sulphide were intermediate both in their lead antagonistic effect and in their ease of oxidation. Dipropyl sulphide was more reactive than dimethyl disulphide and yielded slightly more sulphur dioxide on an " equal number of sulphur atoms consumed" basis. The differences between the amounts of sulphur dioxide formed from these two organic sulphur compounds were quite small, but they did not correlate with the engine results (Table 3.9).

4.3. Spontaneous ignition studies.

4.3.1. The effects of sulphur compounds on isooctane combustion.

The effects of sulphur dioxide, thiophene, and thiophenol on isooctane combustion were studied in the laboratory under different reaction conditions. In an uncoated reaction vessel, these additives inhibited the combustion of the hydrocarbon, raising the temperatures and pressures required for cool flames and two-stage ignition (Fig.3.14). These results sre similar to those obtained by previous investigators [115,119], who found that the strong retarding effect of sulphur dioxide on combustion could be ascribed to its interaction with oxygen atoms. This reaction gives sulphur trioxide, thereby causing chain-termination, and reduction of the oxidation rate. Of the three sulphur compounds studied, sulphur dioxide was more inhibitory than thiophene and thiophenol, the order of inhibition being thiophenol $<$ thiophene $<$ sulphur dioxide.

In a lead oxide-coated vessel, cool flame and two-stage ignition reactions were completely eliminated during hydrocarbon oxidation. The lead oxide was very efficient in causing chain termination, and the temperatures and pressures required for ignition were therefore greatly increased. The addition of the sulphur compounds, however, lowered the ignition limits for isooctane combustion (Fig.3.26), in the lead oxide-coated vessel. The lead oxide coating was therefore less efficient, in the presence of the sulphur compounds, causing chain termination. The order of effectiveness of the sulphur compounds in decreasing the ignition limits is as follows: thiophenol > thiophene > sulphur dioxide.

This result shows that the final oxidation product, sulphur dioxide, is by no means as effective as thiophene and thiophenol in reducing the chain terminating efficiency of the lead oxide. The organic sulphur compounds therefore probably give rise to an intermediate oxidation product which plays a more important role in reducing the effectiveness of the lead oxide coating. The ease of oxidation or decompostion of the sulphur compound thus controls the extent to which the surface is affected, thiophenol being more antagonistic than thiophene.

When isooctane containing tetraethyl lead underwent combustion, the lead present also raised the ignition limits, just as when the lead was present as a surface coating of lead oxide. The presence of sulphur dioxide and thiophene increased the ignition limits of the isooctane, whereas thiophenol decreased them. The interpretation of these results is difficult due to several complicating factors:

1. The leaded isooctane was a mixture of clear isooctane containing $0.4g.l^{-1}$ of tetraethyl lead. Since TEL has a very low vapour pressure, it was difficult to determine the quantity of lead actually entering into the premix gases and therefore reacting.
2. The lead present has to be oxidised before it can exert its antagonistic effect.
3. By competing with the isooctane and sulphur additive for oxygen atoms, the tetraethyl lead inhibits combustion reactions. The inhibition is not therefore solely due to the presence of the lead oxide particles.

4.4. Isooctane combustion in lead oxide-coated vessels treated with sulphur compounds.

Three vessels were coated with lead oxide and treated with sulphur dioxide, thiophene and thiophenol respectively as described in Section 2.2.3.7. The effects of these surfaces on isooctane combustion were determined. The chain terminating properties of the lead oxide surface were completely destroyed in the presence of the thiophene and thiophenol treated vessels. Cool flame and two-stage ignition reactions were observed once more, and in general these surfaces were even less efficient than uncoated surfaces in causing chain termination. With the sulphur dioxide-treated vessel there was a slight lowering of the ignition limits required for combustion. However, the surface was still very effective in causing chain termination and cool flames and two-stage ignitions were not observed.

4.5. E.D.A.X. studies of lead oxide coatings.

These studies revealed changes in the surface of the lead oxide after it had been treated with the sulphur compounds (Figs. 3.42-3.45). The change was most marked in the case of thiophenol followed by thiophene and then sulphur dioxide.

E.D.A.X. examination of the sulphur-treated coatings showed that the lead oxide exposed to sulphur dioxide contained more sulphur than the other two coatings. However, the amount of sulphur incorporated, seems not to be the main factor in the reduction of the lead oxide efficiency. What appears to be more important is the chemical form in which the sulphur is present. In general it seems to be the initial nature of the organic sulphur compound as well as its ease of decomposition or oxidation, which is the principle factor affecting sulphur-lead interaction during the combustion of motor fuels.

REFERENCES.

1. Mock, F.C. and Chandler, M.E.; J. Soc. Auto. Engrs., 11: 474, (1922).

2. Mock, F.C. and Chandler, M.E.; J. Soc. Auto. Engrs., 39: 257, (1936).

3. "Clean Air Today" Published by the Dept. of the Environment (1974).

4. Bloom, N., Ayling, G.M., O'Brien, T.R. and Todd, J.J.; International Clean Air Conference (Brisbane 1978) p. 565, Publ. Ann Arbor Science (1978).

5. "Air Pollution and Health" Summary and Report on Air Pollution by the Royal College of Physicians (London), Publ. Pitman Medical and Scientific Publ. Co. Ltd. (1970).

6. Lawther, P.J.; Taiki Osen Kenkyu., 4 (3); 223-230 (1970).

7. Cole, E.N.; Address to Soc. Auto. Engrs Congress, Detroit, Michigan Jan 14th. (1970).

8. Coleman, L.E.; J. Inst. Petroleum, 59:568:154-163 (1973).

9. "Development of Air Quality Standards" Edited by A. Atkinson and R.S. Gaines, Publ. C.E. Merill Publ. Co. Columbus, Ohio (1970).

10. Fookson, A. and Buell, A.D.; Petroleum Refiner, 27:459 (1948).

11. Clerk, D.; Trans. Faraday Soc., 22:338. (1926).

12. Ricardo, H.R.; "The High Speed Internal Combustion Engine." Published Blackie, London (1941).

13. Norrish, R.G.W.; Proc. Roy. Soc. (London) A 150 : 36 (1935).

14. George, P. and Robertson,A.; Proc.Roy.Soc.(London) A 185 288-309 (1946).

15. Von Elbe, G. and Lewis, B.; Ind. Eng. Chem. 29:551 (1937).

16. George, P. and Robertson, A.; J. Inst. Petroleum, 32:382 (1946).

17. Grimstead, L.; J. Aeronautical Sci. 6:412 (1939).

18. Miller, C.D.; Quart. Trans. Soc. Auto. Engrs. 1:98 (1947)

19. Male, T.; Third Symposium on Combustion (Baltimore 1949) p. 721, Publ. Williams and Wilkins.

20. Semenov, N.N.; "Chemical Kinetics and Chain Reactions"., Oxford University Press (1935).

21. Johnson, J.E., Crellin, J.W. and Carhart, H.W.; Ind. Eng. Chem. 46:1512 (1954).

22. Fish, A.; Angewandte Chemie (International Edition), 7(1), 45 (1968).

23. Fish, A.; Proc. Roy. Soc., A298, 204 (1967).

24. Berces, T. and Trotman-Dickenson, A.F.; J. Chem. Soc. 1481 (1961).

25. Walsh, A.D.; Trans. Faraday Soc., 43:297 (1947).

26. Johnson, J.E., Williams, K.G. and Carhart, H.W.; Ind. Eng. Chem. 47:2528 (1955).

27. Walcutt, E.B. and Rifkin, C.; Ind. Eng. Chem. 43: 2844: (1951).

28. Retailliau, E.R., Richards, H.A. and Jones, M.C.K.; Quart. Trans. Soc. Auto. Engrs., 4:438 (1950).

29. Retailliau. E.R., Richards, H.A. and Jones, M.C.K.; American Scientist, 39:656 (1951).

30. Livengood, J.C. and Leary, W.A.; Ind. Eng. Chem., 43: 2797 (1951).

31. Downs, D., Walsh, A.D. and Wheeler, R.W.; Phil. Trans. Roy. Soc. (London), A243 : 463 (1951).

32. Pahnke, A.J., Cohen, P.M. and Sturgis, B.M.; Ind. Eng. Chem. 46:1024 (1954).

33. Withrow, L. and Rassweiler, G.M.; Ind. Eng. Chem. 23:769 (1931) ; 28:627 (1936).

34. Rifkin, C. and Walcutt, E.B.; Quart. Trans. Soc. Auto. Engrs., 6:472 (1952).

35. Withrow, L. and Rassweiler, G.M.; Ind. Eng. Chem. 25: 923-931 (1933).

36. Withrow, L. and Rassweiler, G.M.; Ind. Eng. Chem. 22:945-951 (1930) ; 27:872-879 (1935).

37. Withrow, L. and Boyd, T.A.; Ind. Eng. Chem. 23:839 (1931).

38. Withrow, L. and Rassweiler, G.M. Ind. Eng. Chem. 33: 185 (1938).

39. Cornelius, W. and Caplan, J.D.; Quart. Trans. Soc. Auto. Engrs. 6:483 (1952).

40. Withrow, L. and Rassweiler, G.M.; Ind. Eng. Chem. 26: 1256, (1934) ; J. Appl. Phys. 9:362 (1938).

41. Hay, J., Knox, J.H. and Turner, J.M.C.; Tenth International Symposium on Combustion, Pittsburgh (1965) p. 331, Publ. The Combustion Institute.

42. Cullis, C.F., Fish, A. and Gibson, J.F.; Proc. Roy. Soc. A284, 108 (1965).

43. Bonner, B.H. and Tipper, C.F.H.; Combustion and Flame, 9, 387, (1965).

44. Day, R.A. and Pease, R.N.; J. Amer. Chem. Soc. 62:2234 (1940).

45. Bonner, B.H. and Tipper, C.F.H.; Combustion and Flame, 9, 317 (1965).

46. Cherneskey, M. and Bardwell, J.; Canad. J. Chem., 38:482 (1960).

47. Hoare, D.E. and Walsh, A.D.; Fifth Symposium on Combustion (Pittsburgh 1954) p. 467, Publ. Academic Press (1955).

48. Cheaney, D.E., Davies, D.A., Davis, A., Hoare, D.E., Protheroe, J. and Walsh, A.D.; Seventh Symposium on Combustion (Oxford 1958), p. 183, Butterworths 1959.

49. Peacock, D.F. and Ruxton, G.R.D.; Trans. Faraday Soc. 63: 2498 (1967).

50. Chamberlain, G.H.N. and Townend , D.T.A.; Proc. Roy. Soc. A160, 436 (1937).

51. Kane, G.P. and Townend , D.T.A.; Proc. Roy. Soc. A160, 174 (1937).

52. Maccormac, M. and Townsend, D.T.A.; J. Chem. Soc. 238 (1938).

53. Vanpée, M.; C.R. Acad. Sci. Paris 241, 951 (1955).

54. Gaydon, A.G., Moore, N.P.W. and Simonson, J.R.; Proc. Roy. Soc. A230, 1 (1955).

55. Setchkin, N.P.; J. Research Natl. Bur. Standards, 53: 49 (1954).

56. Barusch, M.R. and Payne, J.Q.; Ind. Eng. Chem. 43: 2329 (1951).

57. Jost, W. and Croft, G. "Explosion and Combustion Processes in Gases". Chpts 11 and 12. Publ. McGraw-Hill (1946) N.Y.

58. Ricardo, H.R.; Automobile Engrs, 11:51:92 (1921).

59. Garner, F.H., Wilkinson, R. and Nash, A.w.; J. Soc. Chem. 51:265 (1932).

60. Garner, F.H. and Evans, E.B.; J. Inst. Petroleum Technol. 18:751 (1932).

61. Lovell, W.G., Campbell, J.M. and Boyd, T.A.; Ind. Eng. Chem. 26:1105 (1934).

62. Lovell, W.G.; Ind. Eng. Chem. 40:12:2388-2412 (1948).

63. Livingston, H.K.; Ind. Eng. Chem. 43:12:2834-2840 (1951).

64 Callendar, H.L.; Aer. Res. Common Report. No. 1018 (1925).

65. Boyd, T.A.; Ind. Eng. Chem. 16:893 (1924).

66. Spires, H.M. Tech. Data on Fuel., Natl. Com. World Power Conf. (1935).

67. Edgar, G. and Hinegarder, W.S.; Org. Syntheses 1V: 15-17 (1925).

68. A.S.T.M. Manual for rating Motor, Diesel and Aviation Fuels. (1971).

69. Young, G.A. and Holloway, J.H.; J. Soc. Auto. Engrs., 14: 315 (1924).

70. Lovell, W.G. and Zang, W.I.; Ind. Eng Chem. 43:2826 (1951).

71. Derfer, J.M. et al.; "Knocking Characteristics of Pure Hydrocarbons." A.S.T.M. Spec. Tech. Publication No. 225, Philadelphia 1958.

72. Ball, G.A.; Soc. Auto. Engrs. Natl. Fuels and Lubricants Meeting, Tulsa, Oklahoma Nov. 5th. (1954)

73. Ross, A. and Rifkin, E.B.; Ind. Eng. Chem. 48:9:1528 (1956).

74. Badin, E.J.; Third Symposium on Combustion (Baltimore 1949) p. 386, Publ. Williams and Wilkins.

75. Callendar, H.L., King, R.O. and Sims, C.J.; Aero. Res. Comm. Reports and Memoranda 1013,1052 (1925).

76. Egerton, A. C and Gates, S.F.; J. Inst. Petroleum Technol. 13:250 (1927).

77. Frank, C.E. and Blackham, A.U.; Ind. Eng. Chem. 44:862 (1954).

78. Sortman, C.W., Beatty, H.A. and Heron, S.D.; Ind. Eng. Chem. 33, 357 (1941).

79. Walsh, A.D. and Chamberlain, G.H.N.; Proc. Roy. Soc. (Lond.) A215, 175 (1952).

80. Norrish, R.G.W.; Plenary Lecture. Tenth Syposium on Combustion (Pittsburgh 1965) p. 11-15 Publ. The Combustion Institute.

81. Downs, D., Griffith, S.T. and Wheeler, R.W.; J. Inst. Petroleum 49:8 (1963).

82. Norrish, R.G.W.; Seventh Symposium on Combustion London (1958) p. 203 Publ. Butterworths.

83. Wright, P.G.; Combustion and Flame 5, 205 (1961).

84. Erhard, K.H.L. and Norrish, R.G.W; Proc. Roy. Soc. (Lond.) A234 : 178 (1956).

85. Erhard, K.H.L. and Norrish, R.G.W.; Proc. Roy. Soc.(Lond.) A259:297 (1960).

86. Hoare, D.E. and Walsh, A.D.; Proc. Roy. Soc. A215:454 (1952)

87. Bardwell, J.; Combustion and Flame 5,71 (1961).

88. Salooja, K.C.; Combustion and Flame 9:211 (1965) : 11:511 (1967).

89. Walsh, A.D.; Ninth Symposium on Combustion p. 1046 (1963).

90. Fish, A., Read, I.A., Affleck, W.S. and Haskell, W.W. Combustion and Flame 13,39 (1969).

91. Downs, D., Griffith,S.T. and Wheeler, R.W.; J. Inst. Petroleum 47:1 (1961).

92. Minkoff, G.J. and Tipper, C.F.H.; "Chemistry of Combustion Reactions" Publ. Butterworths, London (1962).

93. Zimpel, C.F. and Graiff, L.B.; 11th. Symposium on Combustion 1015 (1967).

94. Kuppu-Rao, V. and Prasad, C.R.; Combustion and Flame 18: 167-172 (1972).

95. Richardson, W.L., Barusch, M.R. and Stewart, W.T.; Ind. Eng. Chem. 53:306 (1961).

96. Birch, S.F. and Stanfield, R.; Ind. Eng. Chem. 28:668 (1936)

97. Holloway, C., and Bonnell, W.S.; Ind. Eng. Chem. 37: 1089 (1945).

98. Ryan, J.G.; Ind. Eng. Chem. 34:7:824 (1942).

99. Endo, E.; Chem. Abst. 28:4581 (1934) from J. Fuel Soc. Japan 13:292 (1934).

100. Schulze, W.A. and Buell, A.E.; Natl. Petroleum News. 27: 41:25 (1935).

101. Friedmann, W.; Refiner and Natl. Gasoline Manufacturer, 20,10, 395 (1941).

102. Livingston, H.K.; Ind. Eng. Chem. 41:888 (1949).

103. Livingston, H.K., Hyde, J.L. and Campbell, M.H. Ind. Eng. Chem. 41:12:2722 (1949).

104. Griffith, R.H. and Hill, S.G.; J. Chem. Soc. p. 2037 (1938).

105. Thompson, H.W., Houde, F.L. and Cairns, A.C.H. J. Chem. Soc. p. 208 (1933).

106. Cullis, C.F. and Mulcahy, M.F.R.; Combustion and Flame 18: 225 (1972).

107. Bottomley, H.; Oil and Gas Journal 40:24:37 (1941).

108. Cloud, G.H. J. Soc. Auto. Engrs. 51:408 (1943).

109. Hanson, T.K. and Coles, K.F.; J. Inst. Petroleum 33:589 (1947).

110. Schulze, W.A. and Buell, A.E.; Nalt. Petroleum News., 29: 23:54 (1937).

111. Livingston, H.K.; Oil and Gas Journal 46:45:80 (1948).

112. King, R.O.; Canada. J. Research 24:125 (1948).

113. Barat, P.; Ph.D Thesis The City University London 1969.

114. Tipper, C.F.H. and Williams, R.K.; Trans Faraday Soc., 55: 1805 (1960).

115. Webster, P. and Walsh, A.D.; 10th. Symposium on Combustion p. 463-472 (1965).

116. Schulze, W.A. and Buell, A.E.; Oil and Gas Journal, 34:21: 22-24 (1935).

117. Walsh, A.D.; J. Roy. Inst. Chem. 75: 323-6 (1951).

118. Livingston, H.K.; Oil and Gas Journal, 47:67 (1949).