Detonation of Fuel Molecules of Increasing Complexity

with Oxygen

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by

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ABSTRACT

In order to evaluate the influence of fuel molecule complexity on gaseous detonation, detonation velocities and limits were determined for the following hydrocarbon fuels in oxygen at I atm initial pressure in a I" diameter tube :-

n butane, n decane, n hexadecane, cyclohexane, decalin, adamantane, benzene, xylene, hexamethyl-benzene, naphthalene, methanol, acetone.

(Limits had not been determined before for the fuels underlined)

A technique was developed for the easy calculation of theoretical CJ detonation velocities for comparison with those experimentally determined. For fuel lean mixtures, velocities agreed to within 3% of those predicted. For fuel rich mixtures, beyond the stoichiometric composition for CO and H_2 agreement could be obtained within 3% between measured and theoretical velocities if acetylene was assumed to be formed at the CJ plane, rather than solid carbon as predicted by equilibrium calculations.

This conclusion was supported by extensive study of the solid carbonaceous product of many fuel rich detonations.

It is suggested that detonation limits are best compared on the basis of the "theoretical energy release". Fuel lean limit energies varied between about 9 and 17 kcals/mole of reactants and fuel rich limit energies between 15 and 30 kcals/mole. A trend of decreasing limit energy with increasing molecular size was observed at both fuel lean and fuel rich limits. Fuel molecules with a very condensed structure detonated less readily.

Heteroatoms in the molecule did not alter limit energies outside the spread observed for other hydrocarbons, provided hydrogen was still present in the fuel.

From the results of previous workers it was concluded that hetero-geneous detonations in oxygen are feasible provided sufficient energy is available to allow rapid gas phase reaction. This was found not to be the case for aerosols of solid carbon in oxygen, which could not be brought to detonate in the present work.

ACKNOWLEDGEMENTS

CONTENTS

Introduction

TABLES AND FIGURES

INDEX OF SYMBOLS

a   No. of carbon atoms in typical hydrocarbon molecule, C_aH_b

b   "   " hydrogen   "   "   "   "   "   "

c   Reduced specific heat, $2(H_2 - H_1)/R(T_2 - T_1)$

D^2 Slope of Rayleigh Line, $(p - 1)/(1 - v)$

H   Enthalpy per mole

m   Ratio of gaseous moles of reactants to gaseous moles of products

M   Detonation wave Mach Number

M_1 Average molecular weight of reactants

p   Reduced pressure, P_2/P_1

P   Pressure

q   Reduced chemical energy release, $2Q/RT_1$

Q   Chemical energy (heat) release per mole of reactants

Qth   Chemical energy release per mole of reactants based on simple equation for chemical reaction

R   Gas constant

s   Subscript to denote conditions after shock wave

T   Absolute temperature

U   Velocity

v   Reduced specific volume, V_2/V_1

V   Specific volume

x   Mole fraction of fuel in mixture

γ Ratio of specific heats

γM^2 Mach Product, $M_1U_1^2/RT_1$ (In this work the base temperature T_1 is taken as $298°K$ in all cases to enable comparison at different initial temperatures.)

θ Reduced temperature, T_2/T_1

1   Subscript to denote conditions in front of detonation wave

2   Subscript to denote conditions behind detonation wave (at the C J Plane).

ΔH_f Heat of formation (from elements in standard state at $298°K$)

INTRODUCTION

Chapter I   -   Theory of Detonation

A detonation consists of a shock wave sustained by an exothermic chemical reaction propagating in a combustible medium. The shock wave initiates the chemical reaction in the unreacted medium immediately ahead and is itself driven forward by the release of chemical energy.

A stable detonation travels at a steady velocity determined only by the thermodynamic properties of the reaction products and the heat release. This is shown inter alia by the very close agreement found between observed velocities and those calculated by the simple hydrodynamic theory (see e.g ref. I).

As a consequence the hydrodynamic theory must play a large part in any discussion of detonation and will now be considered.

a)   Hydrodynamic Theory of Detonation

The hydrodynamic (Chapman, Jouget) theory of detonation is based on the following analysis.

Considering a plane stationary detonation wave let I mole of reactants flow into the wave at pressure P_1, temperature T_1, specific volume V_1 and with a velocity U_1 and assume the products leave the wave at conditions P_2, T_2, V_2 and with a velocity U_2. The following conservation equations are valid assuming no mechanical or heat losses in the wave.

$$\text{Continuity} \qquad \frac{U_1}{V_1} = \frac{U_2}{V_2} \qquad\qquad (1)$$

$$\text{Momentum} \qquad P_1 + \frac{U_1^2}{V_1} = P_2 + \frac{U_2^2}{V_2} \qquad (2)$$

$$\text{Energy} \qquad H_1 + \tfrac{1}{2}U_1^2 = H_2 + \tfrac{1}{2}U_2^2 - Q \quad (3)$$

Where H_1 and H_2 are the initial and final enthalpies and Q the chemical energy release per mole of reaction mixture.

In order to simplify the equations the following reduced variables can be defined.

$$p = P_2 / P_1 \qquad v = V_2 / V_1 \qquad \theta = T_2 / T_1$$

$$c = \frac{2 (H_2 - H_1)}{R (T_2 - T_1)} \qquad q = \frac{2 Q}{R T_1}$$

R is the gas constant chosen to make c and q dimensionless.

Eliminating U_1 and U_2 from the conservation equations the Rankine - Hugoniot equation is derived.

$$c (\theta - 1) = (v + 1) (p - 1) + q \qquad\qquad (4)$$

Seeing that H_2 and T_2, and thus c and θ, are specified for any chosen values of p and v by the thermodynamic properties of the products, equation (4) gives a unique relationship between P_2 and V_2 for the products of a detonation. However from a consideration of only the conservation equations an infinite number of solutions to the problem are possible. The following further consideration is necessary.

Eliminating U_2 between equations (1) and (2)

$$U_1^2 = \frac{V_1^2 (P_2 - P_1)}{V_1 - V_2}$$

$$\therefore \quad \frac{U_1^2}{P_1 V_1} = \frac{p - 1}{1 - v} = D^2 \qquad\qquad (5)$$

For a stable detonation wave the velocity (U_1) has been shown to be the minimum possible. The other requirement for a solution therefore is that

$$\frac{p - 1}{1 - v} \qquad \text{should be a minimum.}$$

Equations (4) and (5) are shown schematically in fig I as plots of p versus v. The solution exists when equation (5), the Rayleigh Line is tangential to the curve of equation (4).

Invoking the ideal gas law, θ can be replaced by $p.v.m$, where m is the ratio of gaseous moles of reactants to gaseous moles of products.

Further eliminating v between equations (4) and (5), it is possible to express D^2 as a function of p only. The solution required is that D should be a minimum and real.

Two solutions fulfil this condition as can be seen from fig I.

Figure 1

Schematic Plot of Hugoniot and Rayleigh Lines

p

Shock Conditions

Rayleigh Line of Minimum Slope
which still yields a solution

C.J. Plane Conditions

Hugoniot for
    Equilibrium Products

1

    Initial
    Conditions

Solution with $P_2 < P_1$
    (not a Detonation)

        Hugoniot
        for Reactants
        (Q = 0)

1

v
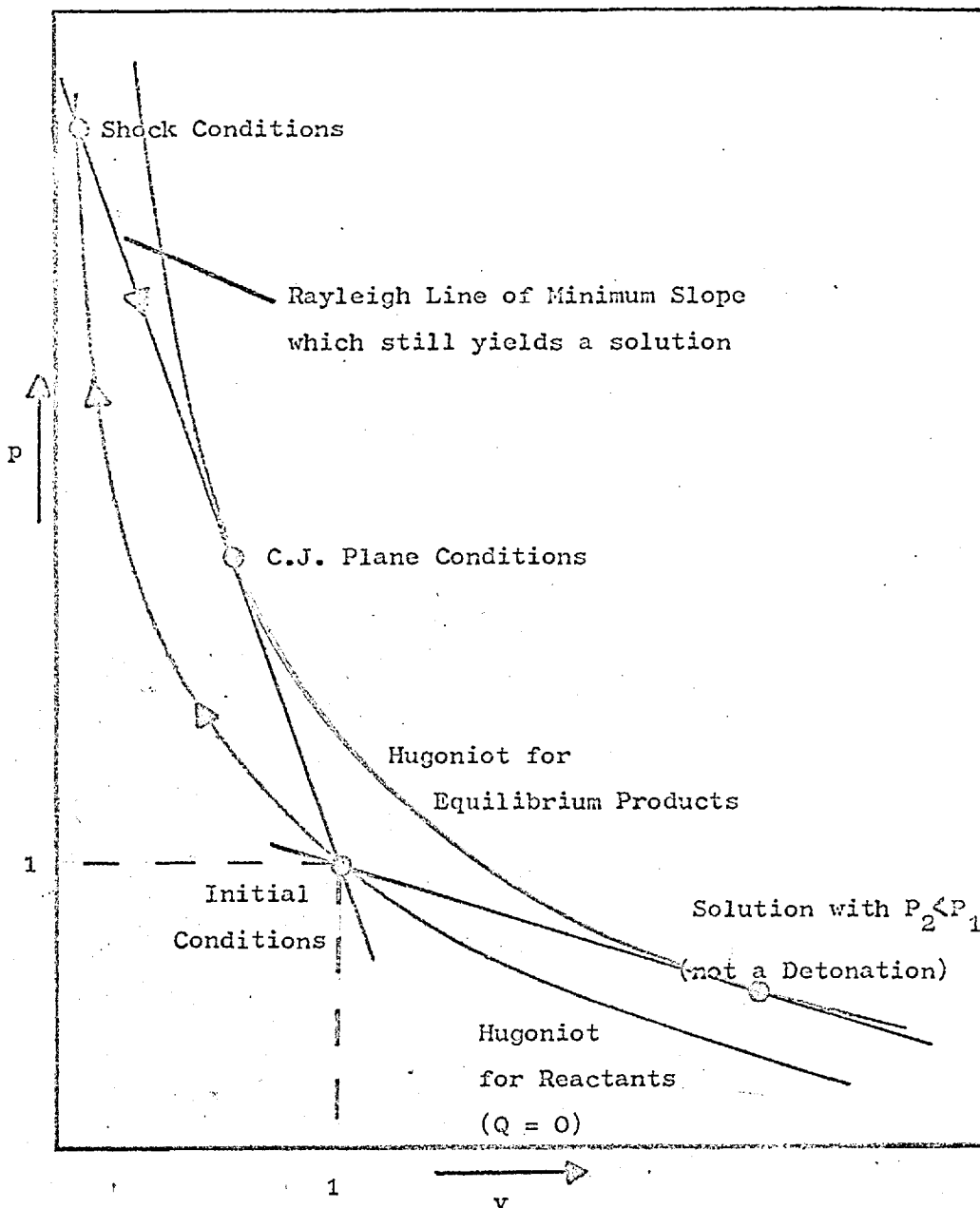
For a detonation there is a positive increase in pressure across the wave so the Rayleigh line of greater slope is required. The final solution for D^2 is

$$D^2 = X + (X^2 - Y)^{\frac{1}{2}} \quad \text{(positive square root required)} \quad (6)$$

where

$$X = \frac{2(cm - 1)(q + c) - c^2 m^2}{(cm - 2)^2}$$

$$Y = \frac{c^2 m^2}{(cm - 2)^2}$$

The other parameters are given by :-

$$v = cm(D + 1) / 2D(cm - 1) \qquad\qquad (7)$$

$$p = D(1 - v) + 1 \qquad\qquad (8)$$

$$\theta = pvm \qquad\qquad (9)$$

b)   Approximate Solutions

Considering again equation (6) some simplifications are possible for hydrocarbon/oxygen detonations where,

$$cm \sim 7 - 10$$

and $q > 24$ always.

then $X^2 \gg Y$

so $D^2 \doteq 2X$

Also as $2(cm - 1)(q + c) \gg c^2 m^2$

and $q \gg c$

Then $D^2 \propto q$

Considering equation (5)

$$D^2 = \frac{U_1^2}{P_1 V_1} = \frac{U_1^2 M_1}{RT_1}$$

Where M_1 = average molecular weight of reactants.

But the speed of sound in the unburnt gas.

$$= \sqrt{\gamma RT_1 / M_1}$$

$$\therefore D^2 = \gamma M^2 \quad \text{where } M = \text{detonation Mach Number.}$$

For detonations the factor "D^2" is usually referred to as "γM^2" or the "Mach product".

The simplification of equation (6) leads to

$$D^2 = \gamma M^2 \doteq \frac{2(cm - 1)\, q}{(cm - 2)^2}$$

Where $c = \dfrac{2M_1 \overline{Cp}}{R}$. $\overline{Cp}$ / gram of reactants

$\therefore\quad cm = \dfrac{2\overline{Cp}}{R}$ $\overline{Cp}$ / mole of products

$\therefore\quad \dfrac{\overline{Cp}/R}{\overline{Cp}/R - 1} = \dfrac{cm}{cm - 2} = \gamma$ average sp.ht. ratio for products

and $q = \dfrac{2Q}{M_1 RT_1}$

$\therefore\quad \dfrac{\gamma M^2}{Q} \doteq \dfrac{2(\gamma^2 - 1)}{RT_1}$ (10)

Therefore, for detonations yielding the same products at approximately the same final temperature and pressure,

$$\frac{\gamma M^2}{Q} \doteq \text{const.}$$

Also, from equation (10)

$$\frac{M_1 U_1^2}{RT_1} \doteq \frac{2(\gamma^2 - 1)}{RT_1} \cdot Q$$

$$\therefore\quad U_1 \doteq \sqrt{\frac{2(\gamma^2 - 1)\, Q}{M_1}}$$

Therefore, the detonation velocity is approximately independent of the initial temp and pressure.

c)   Zeldovich, von Neumann, Döering (Z.N.D.) Model

It was assumed in the original C J theory that the chemical reaction in a detonation wave occurred instantaneously. Zeldovich, von Neumann and Döering (ref 2) suggested that a detonation wave could

be considered as involving two separate processes. First the
reactant gas is shock heated and, after thermal equilibrium has
been attained behind the shock wave, the chemical reaction occurs.
The shock front and the C J plane, the plane at which chemical
equilibrium is attained, are separated by a finite distance. In
reality some chemical reaction will occur before thermal equilibrium
is attained, however, this simplification does allow the calculation
of the parameters behind the shock wave which may be critical for
the initiation of the chemical reaction.

Shock temperatures and pressures can be calculated from a similar
set of conservation equations to those for detonations (see e g
ref 3). For detonations near the limits shock temperatures are
usually sufficiently low for dissociation of the shocked gas to
be negligible. Under these conditions, therefore, the equations
can be simplified to :-

$$\frac{H_s - H_I}{RT_I} = \tfrac{1}{2}\gamma M^2 \ (1 - v_s^2) \qquad\qquad (11)$$

$$\text{and } \theta_s = v_s \left\{1 + \gamma M^2 \ (1 - v_s)\right\} \qquad\qquad (12)$$

Where $v_s = \dfrac{V_s}{V_I}$ and $\theta = \dfrac{T_s}{T_I}$ and the subscript s refers to

conditions after the shock.

From these two equations T_s can be found for any set of initial
conditions and γM^2 for the detonation. The value of γM^2 can be
found theoretically from a complete solution of the C J detonation
equations but where an experimental value of γM^2 is available its
use in the calculation of T_s is considered preferable.

Some reactant molecules, such as oxygen, have vibrational modes
with relaxation times much longer than typical detonation reaction
times. In these cases T_s is calculated assuming the vibrational
mode is not excited (see ref 4).

d) Incomplete Reaction

If for a detonation with a finite reaction rate, the speed of sound
in the burnt gas is calculated for different degrees of completion
of the reaction, a point, or points, of inflexion should be
found where there is no nett change in speed of sound with extent
of reaction through the wave. It has been suggested (refs 5, 6)
that the true C J plane for such a detonation occurs at this extent
of reaction and the detonation parameters should be calculated
accordingly. This speed of sound in the partially burnt gas is
the so called "frozen" speed of sound.

Unfortunately, as the kinetic data are generally incompletely
known and the variation in speeds of sound is only slight, a
complete calculation for a detonation is not usually possible.

In the case where a detonation reaction consists of a fast step
followed by a relatively slow step, a point of inflexion may
occur at the end of fast step and this intermediate composition
should be used for calculation of the theoretical detonation
velocity, rather than the final equilibruim composition.

e) Marginal Detonation

The C J and Z N D theories give no information as to whether
detonation is possible in a particular mixture. For chemical
reaction with both a negative enthalpy and free energy change
it is possible to calculate a set of realistic detonation parameters.

However, any mixture of fuel and oxidant is found experimentally
only to detonate over a certain range of compositions. In more
dilute mixtures, the chemical energy release per mole of reactants
is less which means that the initial shock is weaker. The
chemical reaction occurs more slowly and the assumptions implied
in the C J and Z N D theories begin to break down. Detonations
near these conditions are known as "marginal detonations".

f)   Mechanical and Thermal Losses

Under conditions of marginal detonation, the slower chemical
reaction increases the separation between the shock front and the
C J plane. Appreciable energy loss to the walls of the detonation
tube by conduction and friction may occur over the reaction zone;
losses by radiation may also need consideration. There is then
less energy available to propagate the shock wave so the detonation
travels more slowly than the C J theory would predict. (ref 7, 8)

The observed detonation limits are narrower, and the deficit in
velocity below theoretical is greater, in smaller tubes. This
supports the view that these losses to the walls do play some
significant part. It also raises the question as to what would be
the composition detonation limits in an infinitely large tube
where an infinite time for reaction was available without losses
occuring. (ref 9)

g)   Structure

For marginal detonations, as the thickness of the wave becomes
comparable to the tube size, experiment shows that the shock front
ceases to be planar and is made up of regions corresponding
to different shock strengths. (ref 10)

The C J theory can presumably still be applied to this more complex
wave with the provisos already mentioned, however, as the initial
shock is no longer simple the Z N D model cannot be used for the
complete wave.

At initial pressures around 1 atm, where all the experimental work
in this thesis was performed, evidence for this "structure" of
the detonation wave is only found over a proportion of the total
detonable composition range near both limits. The observed
velocities are found to agree to within 3% with those theoretically
calculated over the whole composition range right up to the
limits (see 5, a) i). This suggests that calculation of C J
detonation parameters is meaningful even for mixtures with a
pronounced "structure".

Chapter 2 — Aims of the Present Work

The aim of this work was the study of detonation of fuel molecules with widely differing chemical bond structures.

Previous work has been confined to relatively small and simple molecules, such as paraffins up to C_5 (ref·4). In order to investigate satisfactorily the effect of bond structure, larger, more complex fuel molecules were required. Detonation of such larger fuels was studied in the following ways.

a) Fuel Lean Mixtures

Detonation velocities were measured for fuel lean mixtures of a series of hydrocarbons with oxygen. A comparison was made between the measured and the calculated (C J) velocity for each mixture and the fuel lean detonation limit for each hydrocarbon was determined. From these results effects of molecular complexity on detonation were evaluated.

b) Fuel Rich Mixtures

Detonation velocities of fuel rich mixtures were also measured and limits determined. It was not possible to use such large molecules as in fuel lean mixtures because higher fuel concentrations were restricted by the volatilities of the hydrocarbons. Comparison between measured and theoretical velocities was also complicated by uncertainty as to the C J product composition of each mixture.

c) Solid Products

Properties of the solid carbonaceous products formed in many fuel rich mixtures were investigated as a further factor which might be influenced by the complexity of the fuel molecule detonated. A particularly detailed investigation of the solids formed in ethylene rich mixtures was carried out in an attempt to determine the true C J product composition in fuel rich mixtures.

d)   Aerosol Detonations

As a limiting asymptote to the series of hydrocarbons of increasing complexity, the detonation of an aerosol of solid "carbon" in oxygen was attempted. Results were compared with those of previous workers for other heterogeneous systems.

DETONATION VELOCITIES AND LIMITS OF GASEOUS MIXTURES

Chapter 3 - Experimental

a) General Considerations

Stabilised detonation waves are usually studied in long tubes.
Detonation is initiated at one end of the tube and propagation of
the detonation wave along the tube is observed. Limiting detonations
require a length of many tube diameters in which to stabilise after
initiation so the tube should have as large a length to diameter
ratio as possible. However in order to reduce the wall effect on
the detonation, the tube diameter should be as large as possible,
though this has the disadvantage of requiring larger quantities of
gas. The best compromise size for survey investigations such as
the present work is around 1" diameter with the maximum length feasible
in the laboratory (in this case 20'). The previous work on hydro-
carbons of small molecular weight (ref 4) was done in a tube of this
size.

The means of initiation of the detonation can influence the
observed limits. To reduce this effect a standard initiation can
be achieved by firing an already stabilised detonation wave into
the tube from a priming section. Previous work (ref 4) in 1" tubes
has shown this method to be reliable for limit determinations with
a 4' priming section filled with a mixture of stoichiometric
hydrogen/oxygen. To reduce the effect on the detonation wave on
moving from one mixture to another, the tube is made in two sections
which can be filled separately with the priming gas and the test
mixture. The two sections are separated by a ball valve, or a
similar valve which does not restrict the tube when completely open.
If the priming mixture is ignited within a few seconds after
opening no appreciable interdiffusion will have occurred at the
interface.

Due to the low volatility of the high molecular weight hydrocarbons
used in the present work, a heated detonation tube was required.
A major problem was to supply hot gas mixture to the tube. This
might have been tackled in various ways.

(i) Oxygen gas and the solid or liquid hydrocarbon could be added directly to the evacuated tube in measured proportions. The major difficulty would be to insure adequate mixing of the gases. Simple diffusion would not be sufficiently rapid. Sample calculations showed that several days would be required. Risks of some slow oxidation of the fuel during the mixing period might not be negligible. Any means of stirring a long tube would be extremely difficult. A technique has however been used to stir gases added directly to the priming section of a shock tube (ref II) using a magnetic trolley running inside the tube coupled to a moving electromagnet outside. The mixing achieved was not very satisfactory and the tube was considerably shorter than the detonation tube. These difficulties made the system relatively impracticable for the present researches.

(ii) The oxygen passing in the tube could be saturated with the hydrocarbon vapour, thus ensuring the gases were adequately mixed. This carburetion method had the objection that it was difficult to determine the mixture composition and hold it constant while the tube was filled. Risks of slow oxidation of the fuel also need some thought. Also the method could not be used to fill the tube with hydro-carbons which were gaseous at room temperature, when this was required for purposes of comparison.

(iii) The system was therefore finally adopted of mixing the oxygen and the hydrocarbon in a hot vessel which could be easily stirred. The hot, homogeneous mixture could then be added straight to the tube.

The maximum time ever required for the evaporation and mixing of the hydrocarbon was about 30 minutes. After this period all detonable mixtures gave reproducible velocities which, at compositions away from the limits, agreed with those theoretically calculated. In order to check on the possibility of slow oxidation occuring during these periods, in some cases the mixture, after stirring, was pumped out

of the tube and the hydrocarbon condensed in a vapour trap
operating at room temperature.   In all cases the mass of
hydrocarbon recovered agreed within 3% with that initially
added to the vessel.   Any slow oxidation would normally yield
some non condensing products, so the mass of hydrocarbon
collected would have been reduced.

b)   The Detonation Tube

The tube was made in three sections of 1" dia 0·128" wall thickness
seamless stainless steel tube.   The priming section was 4' long and
was separated from the test section by a 'Klinger' 1" stainless steel
ball valve.   The test section consisted of a 5' length connected
to the ball valve and a further 9' length in which the time
measuring probes were fixed.   These sections were jointed together
as shown in fig 2 and were sealed by "viton" o-rings.   This limited
the maximum temperature of operation to 200°C.

Timing probe holes, designed to take either ionisation probes or
light detectors, were positioned at 50 cm intervals along the
9' section.

Detailed Design of Joints of 1" I.D. Detonation Tube

(Drawn to Scale)

O-Ring

Tube Section
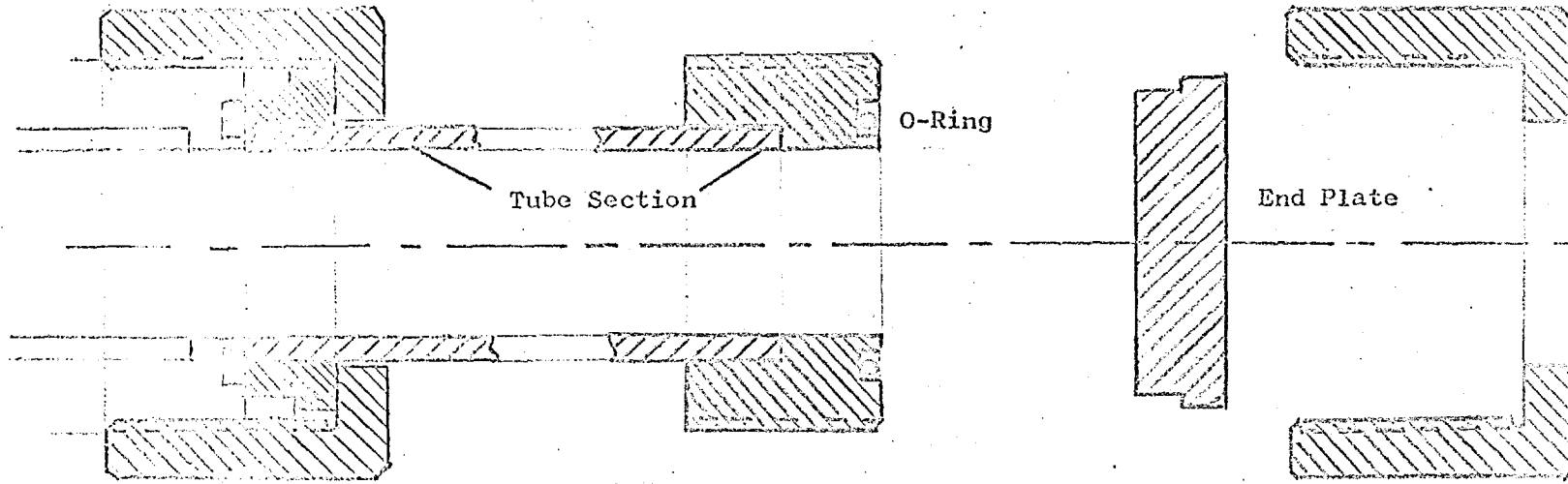
End Plate

Figure 2

c)   The Mixing Vessel

The mixing vessel (see fig 3) consisted of a 1' long 6" dia "Q V F" pyrex pipe section with two $\frac{1}{2}$" thick stainless steel end plates. The glass to metal seals were made with viton o-rings.

The shaft for the magnetic stirrer was a $\frac{1}{4}$" O D stainless steel tube with P T F E bearings and blades. The stirrer magnet was coated with "Araldite" epoxy resin glue to make it inert and baked to $200^{o}C$. A stainless steel tray was fitted vertically below the hole through which solid and liquid hydrocarbons were admitted. This provided a suitable surface from which they could readily evaporate. If the liquids were allowed to run straight down to the bottom of the vessel they attacked, in some cases, the viton o-rings at the glass metal seal.

The temperature of the gas in the vessel was measured with a chromel alumel thermocouple. Other thermocouples were placed at points outside the vessel to check for uniformity of temperature. The maximum variation was about $2^{o}C$.

For adding liquids to the vessel a small sheet of $\frac{1}{8}$" thick viton rubber was clamped over the $\frac{1}{4}$" hole in one end plate. This is illustrated in figure 4a. A measured volume of liquid was then injected into the vessel from a hypodermic syringe whose needle passed through the rubber sheet. The rubber withstood many injections with the needle before needing replacement. The maximum amount of liquid ever required to make up fuel rich mixtures was about 10 ml and the tray was designed to hold this quantity.

For adding solids to the vessel a more complex procedure was needed. The solid was first compressed into small pellets $^{3}/16"$ in diameter and about $\frac{1}{2}$" to 1" long. After filling the vessel with oxygen to 1 atm pressure at the required temperature, the P T F E plug sealing the $\frac{1}{4}$" hole in the end place (see fig 4b) was removed. A weighed amount of pellets were then placed in the channel and pushed into the tube and the plug was immediately replaced over the hole.

Mixing Vessel

Fixing Bolt (One of Six round
                        Perifery)

Fixing Ring

Asbestos Ring Gasket

Stainless
Steel
End Plate

PTFE Stirrer Blade

Motor-
Driven
Magnet

Magnet

$\frac{1}{4}''$ Stainless Steel
                    Tube   PTFE

PTFE Bearing

Trapezium Groove
and O-Ring

"Q.V.F." 6" Dia. 1' Long
Pyrex Pipe Section

1 Inch
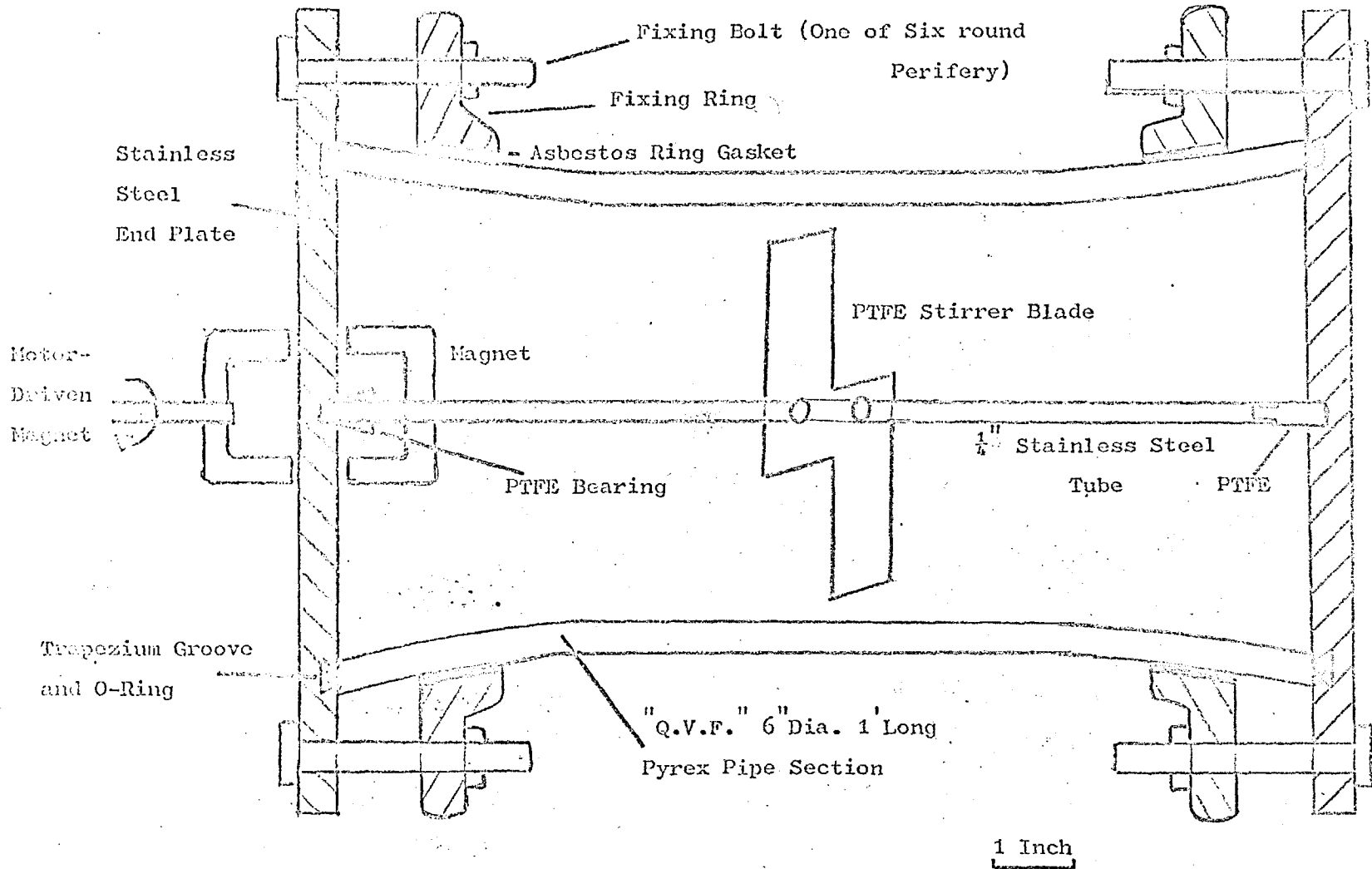
Figure 3

A small amount of air diffused into the mixing vessel during this process. Calculations showed however that it could be neglected in proportion to the large volume of oxygen in the vessel.

Figure 4

a) Apparatus for Liquid Injection

End Plate

Pyrex Pipe
Section

MIXING VESSEL

$\frac{1}{8}$" "Viton" Rubber
Sheet

Hole for Syringe Needle

Stainless
Steel Tray

$1\frac{1}{2}$" Dia. Brass Disc
Screwed to End Plate
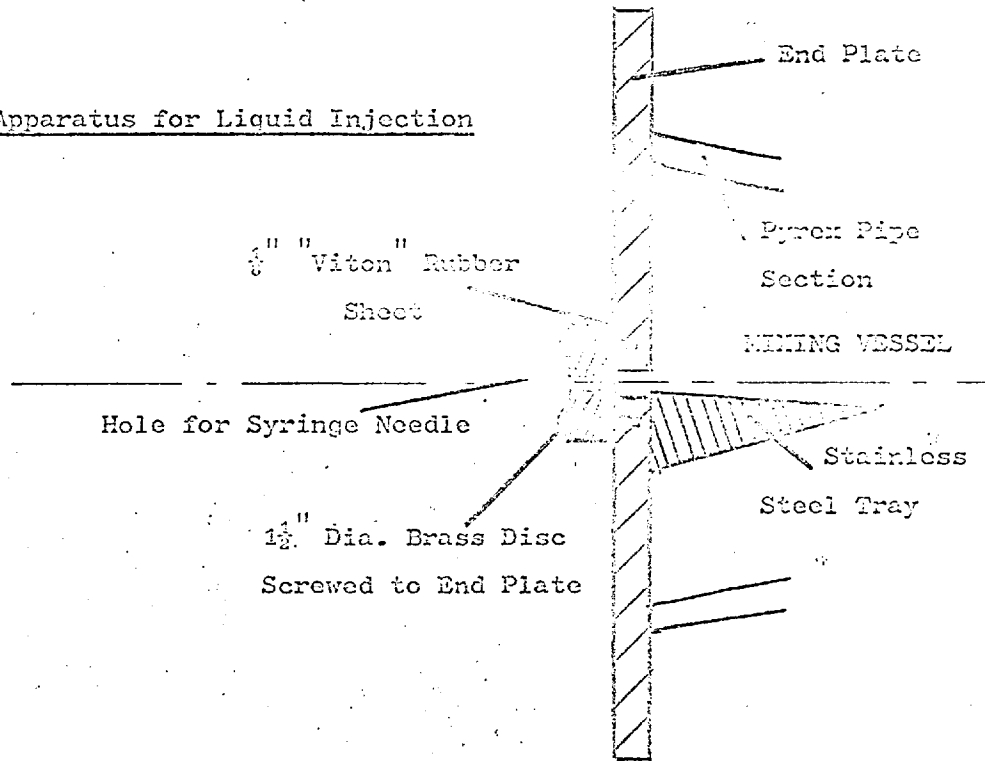
b) Apparatus for Solid Injection

Cylindrical Pellet of
Solid Hydrocarbon

MIXING VESSEL

$\frac{1}{4}$" Dia. Rod to Push
Pellet into Vessel

$\frac{1}{2}$" Dia. Brass Rod
Screwed into Disc
Drilled out with
$\frac{1}{4}$" Hole

($\frac{1}{2}$" Dia. Solid PTFE Rod
Screwed in to Seal Vessel)
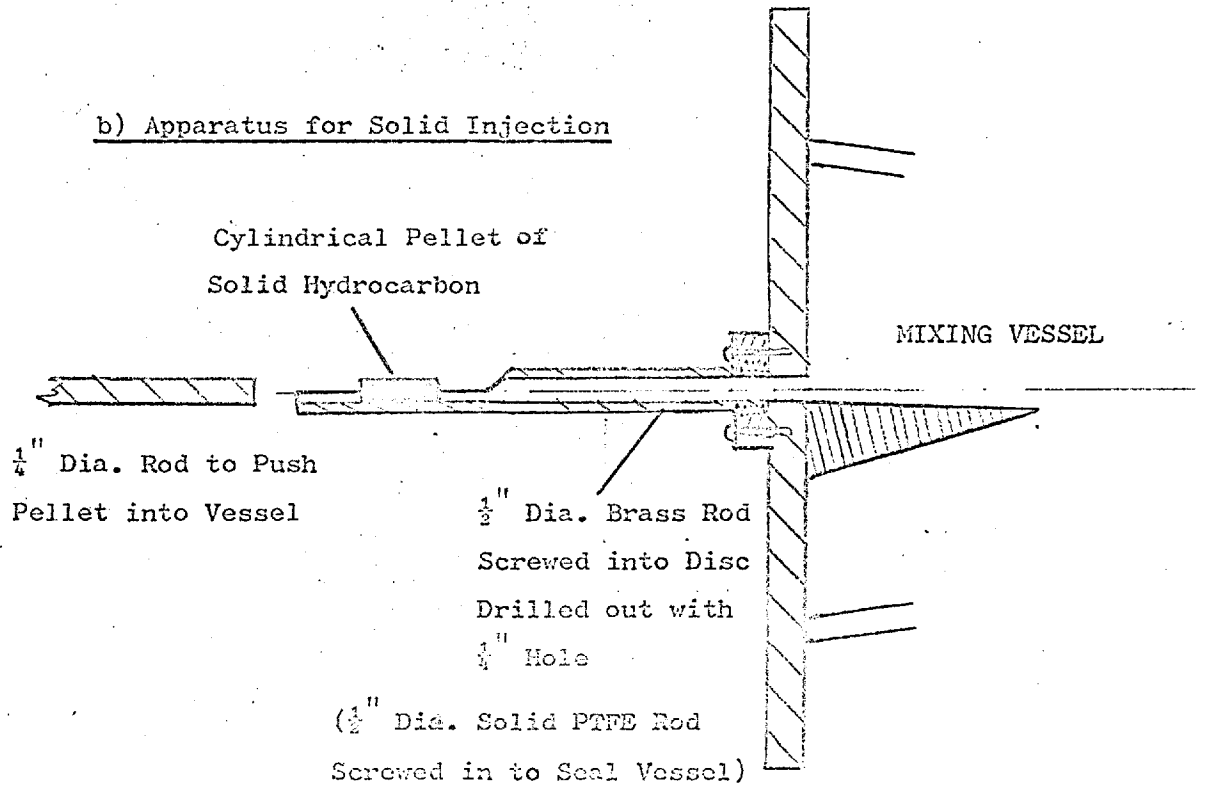
d)   Other Apparatus

The gas lines connecting the mixing vessel to the detonation tube
and the gas supplies are shown in fig 5.   A $^3/16$" I D stainless steel
tube, heated to 200°C to prevent condensation, joined the mixing
vessel to the test section of the detonation tube.   This heated
line was also connected to the vapour trap, which prevented
condensible vapours reaching the inlet gas lines, the vacuum pump
or the mercury manometer.   All these connecting lines were also
of $^3/16$" I D which was quite adequate for evacuating and filling
the vessel in less than five minutes.

In order to measure pressures in the vessel, the connecting lines
were evacuated and refilled with oxygen to approximately the
pressure in the vessel.   This prevented any condensible vapours
flowing through the trap into the cold section when the mixing
vessel was connected to the manometer and giving an incorrect
pressure reading.

The mixing vessel, tube and connecting line were heated electrically
by separate coils of nichrome wire.   Temperatures were measured by
ten chromel-alumel thermocouples spaced over the apparatus.
By controlling the heating current it was possible to set a uniform
temperature for the detonation tube to $\pm 1^\circ$C.

Schematic Drawing of Apparatus and Connections

Primer Section

Test Section

1" I.D. Detonation Tube

Ball Valves

Connections to 6 way Valve on Stoichiometric Filling System (see fig. 6)

3/16" I.D. Stainless Steel Tube

Fuel Gas Cylinder

Oxygen Cylinder

Mixing Vessel

Mercury Manometer

Vapour Trap

Air Bleed

Sections of Apparatus Outlined— — ,Heated

Vacuum Pump

⊗ Needle Valve
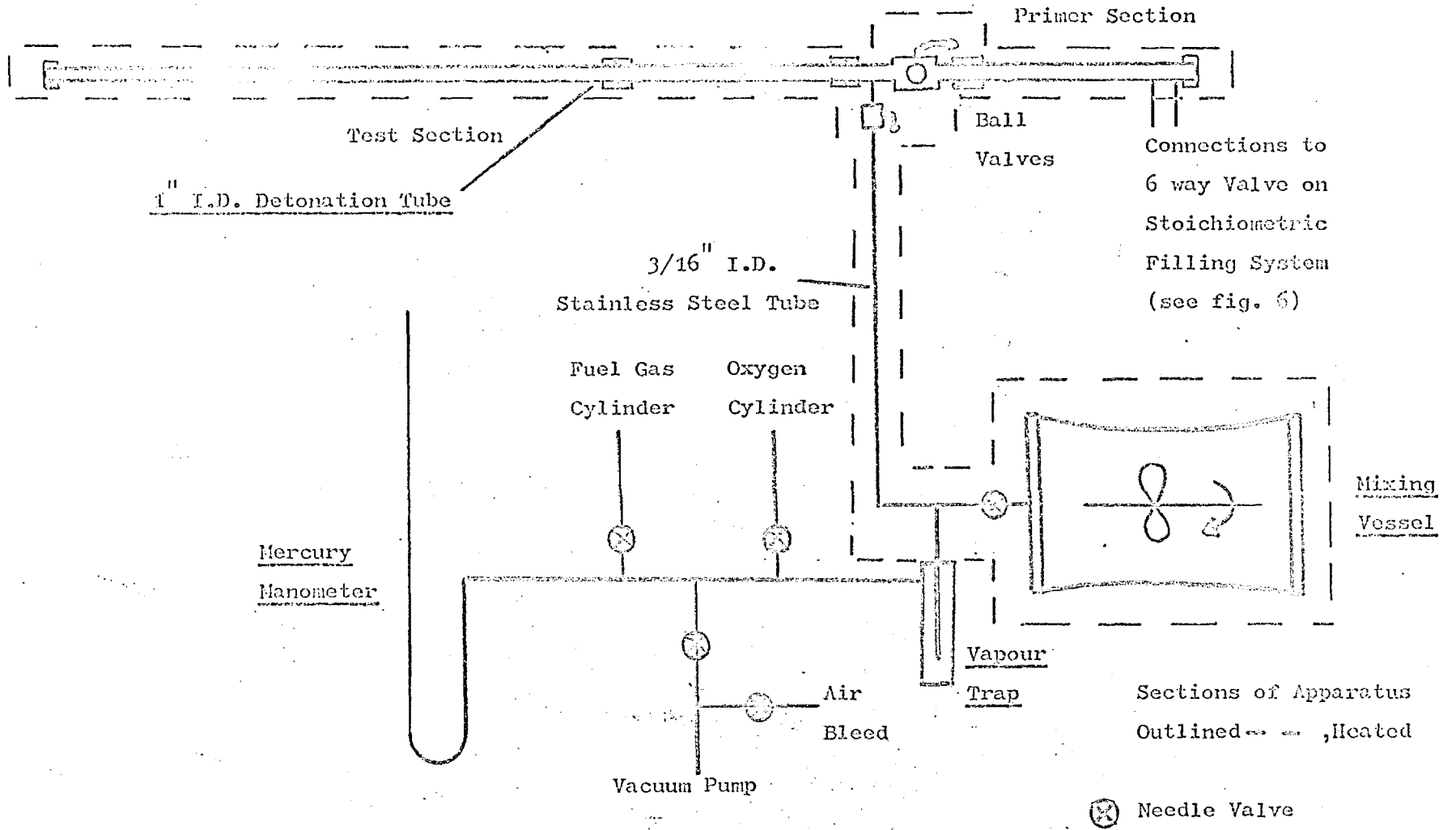
Figure 5

e) Priming Mixture

The apparatus developed to provide stoichiometric hydrogen /oxygen
priming mixtures on a semi continuous basis is shown schematically
in fig 6.

A hydrogen and an oxygen cylinder were each connected by a
"Drallim" 2 bank, 3 way switch valve to 2 glass vessels of 2 l.
and 1 l. capacity. A small quantity of vacuum oil was added to the
1 l. vessel to make the volume ratios exactly 2:1. (The vessels
were calibrated by filling with water and measuring the quantities
required). The other 2 outlets on the 3 way valve were connected
via "Circle Seal" one way check valves to a common needle valve,
which was joined via a 6 way switch valve to the detonation tube
priming section.

In order to fill the priming section, the 3 way valve was turned
to position 1, and both vessels were filled to 15 psi from
their respective cylinders. Next the valve was turned to position
3 and the 6 way valve to position 2. (the tube and connecting
lines having been previously evacuated). The needle valve was then
opened and the gas pressure in the priming section, as measured
by the manometer, was allowed to rise slowly (over about 1 minute)
to 1 atm.

As the needle valve offered by far the greatest restriction to
gas flow, the pressure on its downstreem side was practically
that in the priming section, while that on its upstream side
was that in the vessels. Therefore, as the two vessels were
always at equal pressures, the volumetric flowrates out of the
vessels were in the ratio 2:1. As a result, the priming section
was filled with homogeneous stoichiometric hydrogen/oxygen mixture.
/The composition was checked by filling the whole tube with
hydrogen/oxygen mixture and measuring the detonation velocity.
This showed that the mixture was between 66 and 67.5 mole %
hydrogen, which was adequate for a priming mixture7

Rotating the 6 way valve always in a clockwise direction ensured
that the correct sequence for filling the tube was followed.

Figure 6

Schematic Diagram of Stoichiometric Mixture System

Hydrogen from cylinder
regulated to 15 psig.

Oxygen from cylinder
regulated to 15 psig.

2 litre
vessel
(hydrogen)

1 litre
vessel
(oxygen)

C   F

A   D

B   E

Check Valves

2 bank switch valve

positions:-

1) A - C   D - F
2) All off
3) A - B   D - E

Needle Valve

Mercury
Manometer

Tube Priming
Section

Vacuum Pump

2   3

1   4

6   5

6 way switch valve

Vacuum Pump

Blank

Tube Priming
Section
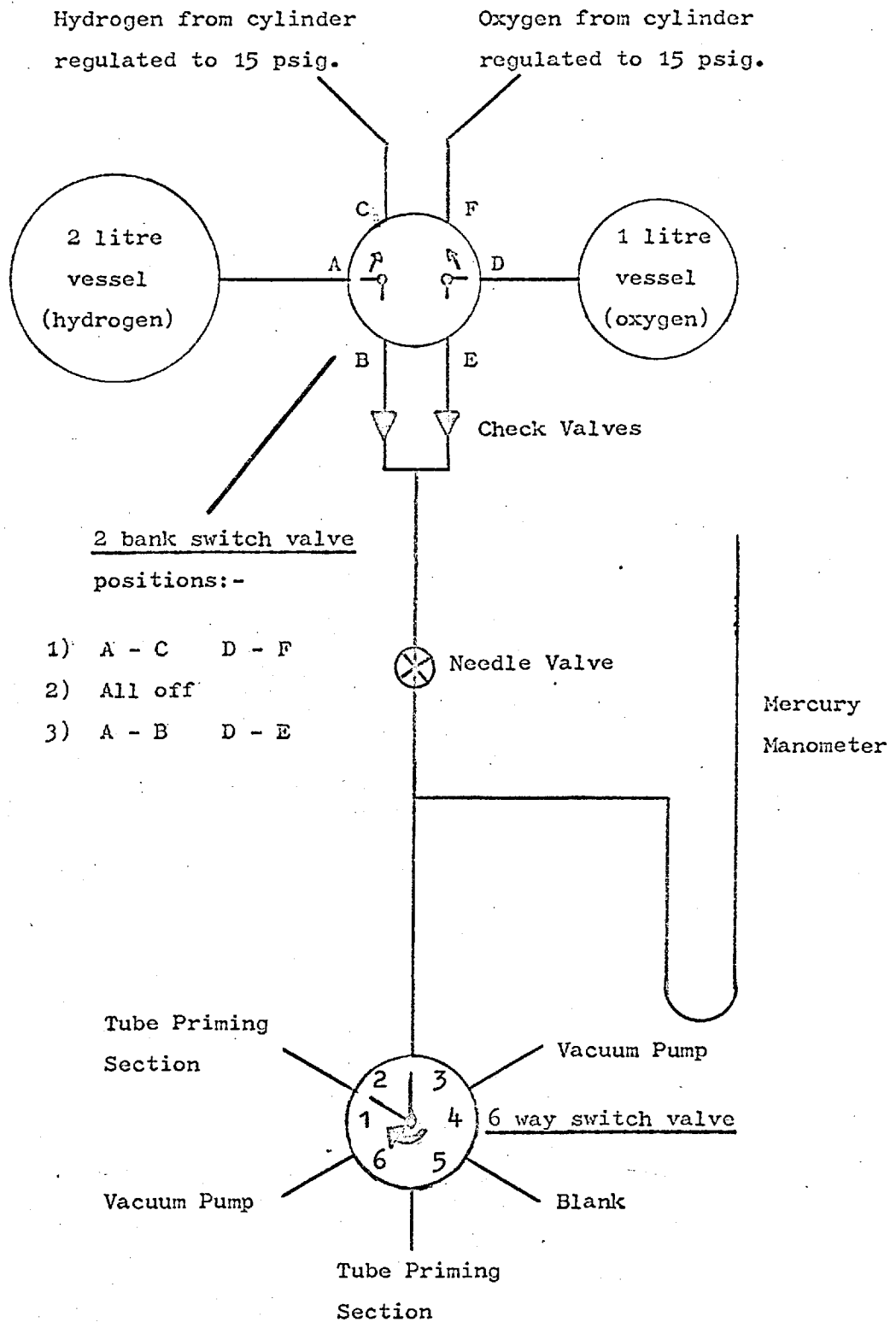
As a safety precaution to prevent any explosion travelling back down the gas filling line, an electric switch was incorporated in the 6 way valve such that the mixture could only be ignited in position (3).

A small electrically heated coil of nichrome wire was used to ignite the priming mixture. This method was found superior to a spark plug as it did not generate electrical interference for the timing equipment.

f) Timing Probes

The velocity of the detonation was measured by timing the arrival of the wave at several positions along the test section. Three types of probe were used for detecting the presence of the detonation wave.

(i) Ionisation Probes

These consisted of a conducting rod in the wall of the detonation tube but insulated from it (see fig 7). The ionisation behind the detonation wave was sufficient to make an electrical conducting path between the tube wall and the probe. A condenser connected between them was therefore discharged and the resulting pulse was amplified and then used to start or stop a counter.

The main disadvantage of this type of probe was that, because of the relatively high resistance of the conducting gas in the detonation wave, only very small amounts of water or other conducting contaminants need to be deposited on the probes to provide paths of even lower resistance and thus to effectively short them out. To be completely reliable the probes had to be cleaned after each detonation. This was not a very easy task with a heated tube so this type of probe was only used as a check on the other types used.

(ii) Light Probes

These were designed specifically for the present work and consisted of small photodiodes ("BENN 352") placed behind small glass windows in the side of the tube (see fig 7).

Figure 7

Timing Probes

Loose Collar

Screw-in Ionisation Probe

Detonation
Tube
1"

Conducting
Rod

Insulating
Cement

Design for <u>Glass Probe</u>
identical, except glass
sheath round conducting
rod

<u>Screw-in Light Probe</u>

Glass Rod (cemented
to probe)

Photodiode

Asbestos Compound Tube
(to protect photodiode from heat)

<u>Probe Signal Amplifier</u>

22.5V

Input.

Double Coax
Cable

68 MΩ   1 MΩ

1 pF

+18V supply Z_{out}
~300Ω

10KΩ

gain=600

Monostable
Trigger (-8V pul

<u>Ancillary Circuit for</u>
<u>Light Probes</u>

"Driven
Screen"

They detected the light emitted from the reaction zone behind
the detonation front which caused a change in their resistance.
This was converted by an amplifier into a suitable pulse for
a counter.

These probes were found to operate very satisfactorily with
very little attention. As the previous work on hydrocarbons
(ref 4) had used ionisation probes, the light probes were
carefully checked to see if they gave the same detonation
limits. No detectable difference was found compared with the
accuracy with which limits could be determined (see Table 14)
so the probes were used for most of the results in this work.

The photodiodes had a rise time of $1\,\mu$sec. This is not as
fast as a well designed ionisation probe, but was considered
quite adequate for this work.

(iii) Glass Probes

These were constructed in an attempt to produce an ionisation
probe which was not subject to the effects of contamination
referred to above. They consisted of a 1 mm dia. tungsten
rod coated with pyrex glass. This was then inserted into a
probe holder in the same manner as an ionisation probe.
The glass on the tip of the probe was ground down till its
thickness was about $1/100$". When a detonation passed the
probe the ionisation behind the wave caused a change in the
probe's capacity to earth. This was detected by a specially
designed amplifier, which triggered the counters.

The glass probes did not need to be cleaned after every
detonation but were however very sensitive to electrical
noise because of their high impedance. They were not as
reliable as the light probes or freshly cleaned ionisation
probes and had a relatively slow rise time on marginal
detonations (up to $50\,\mu$sec). This could very possibly have
been due to the effect of spin of the detonation front changing
the self capacity of the probe only gradually, but

it made it difficult to define an actual time at which the
wave passed.

These probes were only used therefore for some measurements
of velocities of mixtures away from the limits, where the
rise times of the signals were less than $1\,\mu$sec.

g)   Probe Amplifiers

Probe amplifiers with a response time better than $1\,\mu$sec for
driving the counters were designed specially for use with ionisation,
glass and light probes.   Ionisation and glass probes could be
connected directly to the amplifier input.   A simple preliminary
circuit was required for the light probes.

The glass probes had only a very small change in self capacity
when a detonation passed (~ 0.1pF) so in order to give an adequate
response in $1\,\mu$sec an input impedance of greater than $10M\Omega$
was required for the amplifier.

The amplifier was designed with an input impedance of $68M\Omega$ and a
variable bias of upto $+18$ volts for the glass probes.   The input·
stage of the amplifier is shown in fig 7.

With such a high input impedance extra care was required in screening
the input from noise.   An extra "driven" screen was required on
the coaxial cable from the probe to the amplifier in order to
reduce noise to a satisfactory level.

Following the final stage of the amplifiers was a trigger circuit
which produced -8V. pulses in order to drive the counters.

Chapter 4 - Accuracy of Results

a) Overall Accuracy

The aim of this work was to investigate possible trends in the effects of molecular size on detonation limits. It was considered that this could best be achieved by surveying detonation velocities and limits for a large number of fuel molecules with an accuracy that was acceptable for comparative purposes. More repeat experiments could have been used to refine the results even more, but the gain in information would not have warranted this.

b) Accuracy of Mixture Compositions

The method of making up mixtures has been described (3,c)). Important measurement errors are

(i)   mass of solid or liquid fuel, m ($\pm$ 1%)

(ii)   final mixture pressure, P ($\pm$ 0.2%)

(iii) temperature of gas mixture, T_m ($\pm$ 0.5% on absolute temperature)

The mole composition of fuel is given by

$$x = \frac{m/M}{PV/RT_m}$$

where V = vessel volume (5.58 l.)   R = gas constant
and   M = mol. wt. of fuel.

This would give an error in x of about $\pm$ 1.7%, assuming the gas mixture to be ideal. At the temperatures and pressures used all the gas mixtures could be considered ideal to better than $\pm$ 1%, except at temperatures just above their boiling points. Gas mixtures were therefore always made up at a temperature at least 30°C above the boiling point of the fuel at its partial pressure in the mixture. For single compositions the total mixture error is accordingly estimated to be around $\pm$ 2.5% on the calculated fuel composition. Since detonation limits were established using several different compositions, the final values estimated are known with considerably closer accuracy (see Table 14).

c) Accuracy of Velocity Measurements

The velocity of the detonations was determined in order to estimate
the limits and to be able to compare the measured velocity with
the theoretical, C J value. An accuracy of $\pm$ 0.5% was considered
sufficient for both these purposes.

The timing was done by μsec counters with the probes 2 m apart.
The time between probes of a typical wave would be 1msec, so
the accuracy of the measured velocity was to $\pm$ 0.1%.
(Any error in probe spacing being less than $\pm$ 0.005% could be
neglected).

In mixtures with compositions near the limits the timings   over
two separate 2 m spacings did not always exactly agree;   however
the fluctuations were certainly much less than those recorded by
ionisation probes over short measuring distances (ref 4).
Measuring over 2 ms with light probes as in the present work
probably tended to average out the fluctuations observable with
ionisation probes.   In most cases the velocity could be estimated
to the required $\pm$ 0.5% desired accuracy.

d) Accuracy of Limits

The accuracy to which limits could be determined was a function
of the number of different compositions investigated in the
limit region and the reproducibility of the results obtained.
These limits were estimated from the plots of velocity v composition
and by considering the composition at which detonation could be
said to be just no longer possible.   The accuracy of the limits
was expressed as the range of compositions over which this
could occur (see Table 14).

e) Purity of Hydrocarbons and Oxygen

The purity of the hydrocarbons used was in all cases stated to
be better than 99%, the main impurities being other hydrocarbons,
with similar detonating characteristics.   Thus the effect on the
results was probably far less than even a 1% error.

The oxygen used was of a stated purity of 99.5%, with the main impurities being nitrogen, argon, neon and water vapour. Control experiments (ref 12) have shown that detonation limits of hydrocarbon/oxygen systems are not appreciably affected by such traces of nitrogen and water vapour. The effect of inert gas impurities would be expected to be even less.

Considering the accuracy to which limits could be determined, the effect of impurities in the hydrocarbons and the oxygen was not regarded as significant.

f)   Effect of Initial Temperature on Detonation Limits

In order to able to compare detonation limits of different hydrocarbon mixtures the effect of the different necessary initial temperatures had to be considered.

Very little experimental work has been done on the effect of temperature on detonation limits. Sokolik and Rivin (ref 13) have measured the fuel lean detonation limits of hydrogen/air mixtures over the range of 20 - 490°C in a 20 mm. diameter tube at I atm initial pressure. Their results are shown in Table I. The observed effect of initial temperature was only of the order of the accuracy to which the limits could be determined as was also confirmed in the present work for other fuel lean limits (butane/oxygen and decane/oxygen) over the range 20 - 160°C (see Tables 2, 3).

This lack of influence of initial temperature on detonation limits is also confirmed by the insensitivity of calculated C J velocities and temperature to initial temperature. This result was derived approximately above (I b)). Table I shows accurately calculated C J velocities and temperatures for stoichiometric hydrogen/air mixtures at I atm and initial temperatures indicated (ref 14).

A small variation of fuel rich limits with temperature was observed in the present work (see 5 b) iv)). These limits were therefore compared at a standard initial temperature of 120°C.

Table 1

Effect of Initial Temperature on Detonation

Experimental Limits (ref. 13)

for hydrogen/air mixtures at 1 atm. pressure

in 20 mm. dia. tube

Initial Temp. °C	20	100	150	200	490
Fuel Lean Limit mole%	21	21-22	19-22	17-21	20

Calculated C.J. Conditions (ref. 14)

for stoichiometric hydrogen/air mixtures at 1 atm.

Initial Temp. °C	-49	60	171	283	505
Detonation Vel. m/sec	2137	2115	2094	2078	2042
Final Temp. °C	2677	2676	2681	2690	2715

Chapter 5 — Results and Discussion

a) Experimental Detonation Velocities and Limits for Hydrocarbon Oxygen Systems

Experimental detonation velocities are listed for mixtures of oxygen with n butane, n decane, n hexadecane, cyclohexane, decalin, benzene, xylene, hexamethyl-benzene, naphthalene, methanol and acetone. Estimated fuel lean detonation limits are tabulated and fuel rich limits in cases where a gaseous mixture could be made up at temperatures less than 200°C.

The velocity v composition results are also shown graphically, together with results of previous workers.

The measurements were all made in a 1" diameter tube at 1 atm initial pressure.

b) Discussion

.Tabulated results of the measured detonation velocities and composition limits for the different hydrocarbons cannot be compared directly. The possible influence of the molecular complexity of the hydrocarbon can only be seen if the results are reduced to some common form. A technique of comparison was developed in the courseof this work which could be applied to the marginal detonation region close to both the fuel lean and fuel rich limits. With slight modification the technique was extendedto compare velocities over the whole detonable composition range.

(i) Fuel Lean Mixtures

It has already been shown (1 b)) that

$$\frac{\gamma M^2}{Q} = \frac{2(\gamma^2 - 1)}{RT_1} \qquad (10)$$

γM^2 is simply a function of the detonation velocity of the mixture.

The measured detonation velocities agree approximately with those theoretically calculated right upto the limits (see e g fig 8). The energy release per mole of mixture (Q) is

Table 2

Detonation Velocity of n.Butane/Oxygen

Mole% fuel at 120°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
1.9	failed		12.1
2.0	1400	25.8	12.7
3.0	1595	33.6	19.1
10.0	2180	66.5	63.5
17.1	2470	89.6	70.5
20.0	2580	100.0	61.2
22.6	2580	102.0	54.2
30.0	2450	96.5	34.3
33.5	2180	78.1	24.8
34.8	2070	71.2	21.7
35.4	failed		20.2

at 160°C

1.88	1480	28.8	11.9
2.44	1600	33.8	15.5
2.90	1700	38.3	18.4

Table 3

Detonation Velocity of n.Decane/Oxygen

Mole% fuel	Velocity m/sec	γM^2	Q_{th} kcals/mole
at 100°C			
0.67	failed		10.2
0.67	1250	20.7	10.2
0.73	1350	24.1	11.1
0.94	1430	27.4	14.2
1.31	1610	35.1	19.9
1.90	1755	43.4	29.0
7.0	2310	85.6	73.3
7.6	2320	87.7	72.9
13.6	2450	114.0	49.4
at 160°C			
0.70	failed		10.6
0.70	1370	24.9	10.6
0.76	1400	26.0	11.6
0.89	1500	30.0	13.5
1.27	1660	37.1	19.3
8.74	2480	103.7	72.8
11.3	2490	108.7	60.4
17.3	2210	101.0	31.2
20.0	1850	74.5	18.4
20.8	1700	64.0	14.2
21.4	failed		11.0

Table 4

Detonation Velocity of n.Hexadecane/Oxygen

Mole% fuel at 160°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
0.40	failed		9.6
0.46	1390	25.7	11.1
0.60	1500	30.2	14.4
0.65	1610	34.8	15.7
0.79	1650	36.8	19.0
0.86	1700	39.4	20.7
1.04	1710	40.2	25.0
1.34	1740	42.3	32.2

Table 5

Detonation Velocity of Cyclohexane/Oxygen

Mole% fuel at 100°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
1.42	failed		12.5
1.44	1460	28.3	12.7
1.70	1520	30.7	15.0
2.06	1670	37.3	18.2
2.56	1720	39.8	22.6
3.14	1810	44.5	27.7
4.30	1930	51.5	38.0
9.8	2300	79.4	86.5
12.8	2440	93.1	80.0
15.2	2525	103.1	74.7
16.8	2560	107.8	67.3
20.4	2410	100.0	50.8
23.0	2330	96.4	38.8
27.8	1850	64.0	23.3
30.0	failed		16.4

Table 6

Detonation Velocity of Decalin/Oxygen

Mole% fuel at $100^\circ C$	Velocity m/sec	γM^2	Q_{th} kcals/mole
0.70	failed		9.9
0.75	1440	27.4	10.6
0.89	1430	27.2	12.6
0.91	1480	29.2	12.9
1.15	1580	33.4	16.3
1.48	1710	39.7	21.0
1.90	1800	44.5	26.9

Table 7

Detonation Velocity of Adamantane/Oxygen

Mole% fuel at $160^\circ C$	Velocity m/sec	γM^2	Q_{th} kcals/mole
0.81	failed		11.4
1.09	1490	29.5	15.4

Table 8

Detonation Velocity of Benzene/Oxygen

Mole% fuel at $100^{\circ}C$	Velocity m/sec	γM^2	Q_{th} kcals/mole
1.55	failed		11.7
1.60	1395	25.6	12.1
1.70	1425	26.9	12.9
1.80	1472	28.8	13.6
1.97	1540	31.6	15.0
2.0	1560	32.4	15.2
2.02	1530	31.1	15.4
2.30	1595	34.0	17.4
2.95	1680	38.0	22.4
4.1	1790	43.8	31.0
5.0	1910	50.5	37.8
35.5	1850	66.8	18.3
36.0	failed		17.0

Table 9

Detonation Velocity of Xylene*/Oxygen

Mole% fuel at 160°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
0.96	1320±	23.0	10.0
1.01	failed		10.6
1.07	1415	26.5	11.2
1.20[+]	1510	30.3	12.6
1.31	1500	30.0	13.7
1.40[+]	1520	30.8	14.7
1.63	1630	35.6	17.0
1.89	1660	37.2	19.8
7.2	2160	70.2	75.5
11.4	2340	90.3	77.0
16.0	2560	116.0	57.6
16.5	2510	112.7	55.7
19.1	2470	113.8	45.7
23.4	2135	90.5	32.2
25.6	2060	87.4	25.2
26.5	2035	86.2	22.3
28.0	failed		17.5

* Commercial Xylene   23% ortho, 43% meta, 19% para, 15% ethylbz.

[+] Average of velocities from 10 mixtures, standard deviation less than 5 m/sec.

Table 10

Detonation Velocity of Hexamethyl-Benzene/Oxygen

Mole% fuel at 180°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
0.41	failed		7.2
0.54	1330	23.4	9.5
0.64	1445	27.7	11.2
0.83	1390	25.9	14.5
0.91	1490	30.0	15.9
0.96	failed		16.8
1.08	failed		18.9
1.26	1260	21.6	22.1
1.40	1320	23.8	24.5
1.76	1690	38.0	30.8

Table 11

Detonation Velocity of Naphthalene/Oxygen

Mole% fuel at 160°C	Velocity m/sec	ym^2	Q_{th} kcals/mole
1.47	failed		16.7
1.49	1590	34.2	16.9
1.52	failed		17.3
1.57	1595	33.3	17.8
1.95	1700	39.5	22.1
2.36	1750	42.4	26.8
2.46	1830	46.5	28.0
2.56	1810	45.7	29.0
2.73	1840	47.5	31.0
3.32	1900	51.3	37.7

Table 12

Detonation Velocity of Methanol/Oxygen

Mole% fuel at 100°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
8.55	failed		13.8
9.20	1520	29.7	14.9
9.80	1510	29.5	15.8
10.1	1620	33.8	16.3
12.1	1670	36.0	19.5
20.2	1890	46.2	32.6
26.5	2015	52.4	42.8
35.0	2160	60.2	56.5
36.8	2220	63.6	59.5
46.2	2320	69.5	53.7
49.9	2360	72.0	47.0
61.0	2325	70.0	31.4
64.0	2200	62.5	27.7
66.7	failed		24.1

Table 13

Detonation Velocity of Acetone/Oxygen

Mole% fuel at 100°C	Velocity m/sec	γM^2	Q_{th} kcals/mole
3.16	failed		13.0
3.30	1450	28.0	13.6
4.03	1640	35.8	16.6
4.56	1680	37.8	18.8
6.38	1800	44.0	26.2
10.0	1930	52.1	41.2
13.6	2055	60.5	56.1
17.9	2190	71.1	73.7
22.5	2300	80.9	73.5
30.2	2415	94.0	59.2
31.5	2410	94.2	55.7
34.8	2400	95.5	47.0
39.8	2200	82.6	33.8
41.3	failed		29.9

Table 14

Measured Detonation Limits

Fuel	Fuel Lean Limit mole%	Fuel Rich Limit mole%	Initial Temp. °C
n.Butane, C_4H_{10}	1.95 - 2.05	35 - 36	120
n.Decane, $C_{10}H_{22}$	0.65 - 0.75	20.5 - 21.5	160
n.Hexadecane, $C_{16}H_{34}$	0.45 - 0.50	*	160
Cyclohexane, C_6H_{12}	1.35 - 1.45	28.5 - 29.5	100
Decalin, $C_{10}H_{18}$	0.65 - 0.75	*	100
Adamantane, $C_{10}H_{16}$	0.8 - 1.0	*	160
Benzene, C_6H_6	1.55 - 1.60	35 - 36	100
Xylene, C_8H_{10}	1.0 - 1.1	26 - 27	160
Hexamethyl-Benzene, $C_{12}H_{18}$	0.5 - 0.6	*	180
Naphthalene, $C_{10}H_8$	1.45 - 1.55	*	160
Methanol, CH_3OH	9.3 - 9.8	63.5 - 64.5	100
Acetone, CH_3COCH_3	3.1 - 3.4	39.5 - 40.5	100

* Temperature necessary for fuel rich mixture
too high for apparatus.

Limits determined in 1" i.d. tube at 1 atm.
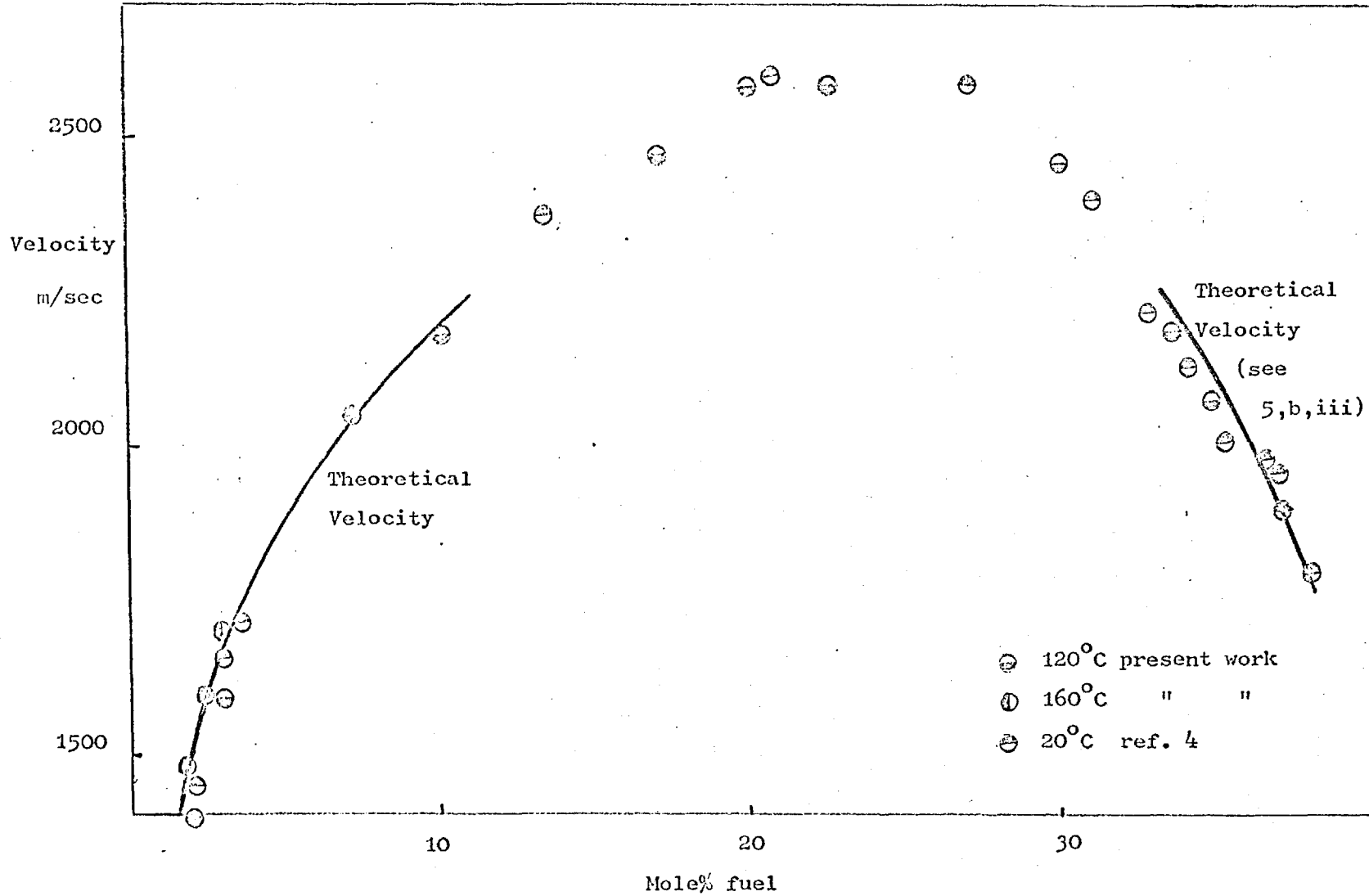initial pressure.
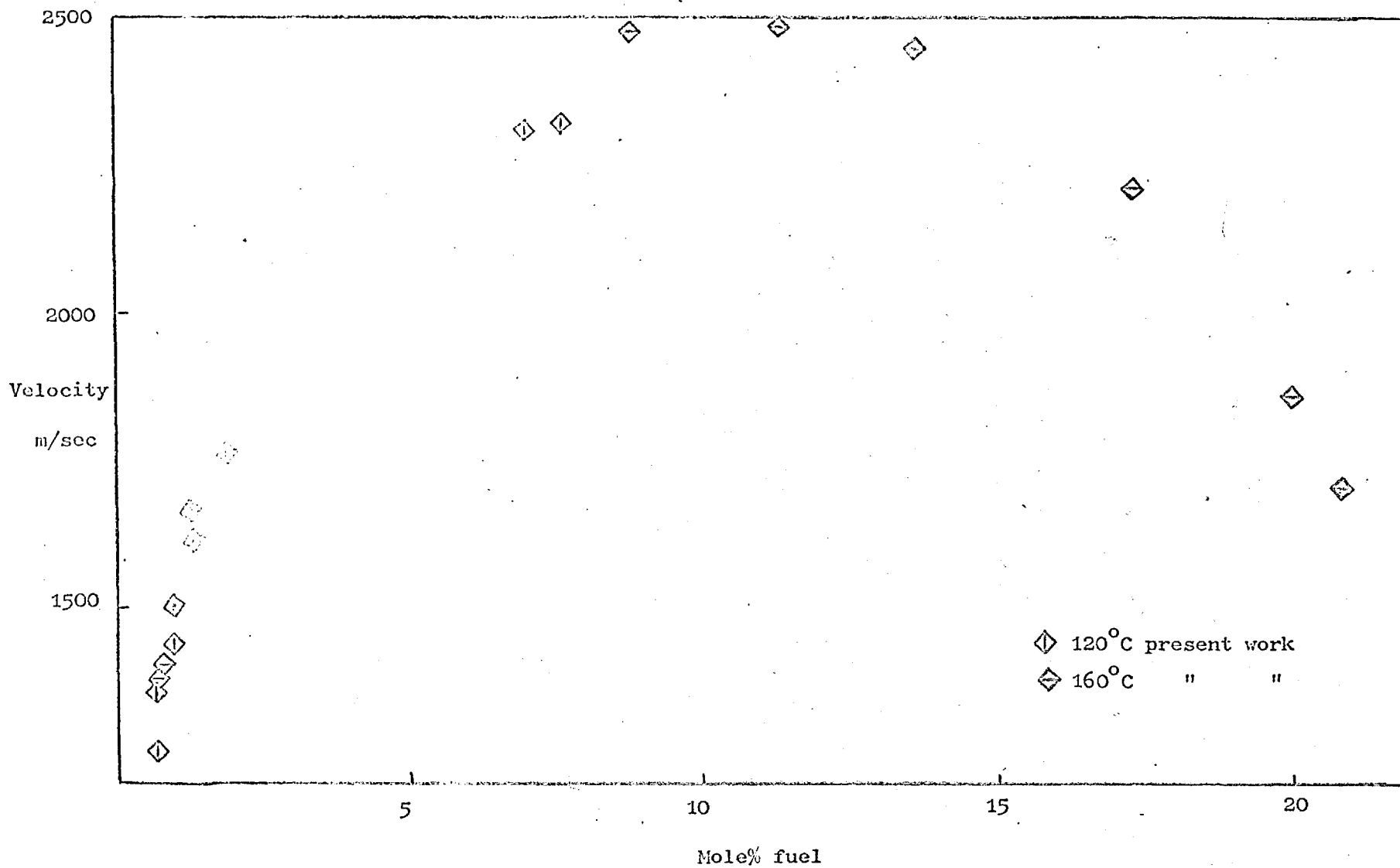
Detonation Velocity of n.Butane/Oxygen

Figure 8

Detonation Velocity of n.Decane/Oxygen

Figure 9

Velocity m/sec

Mole% fuel
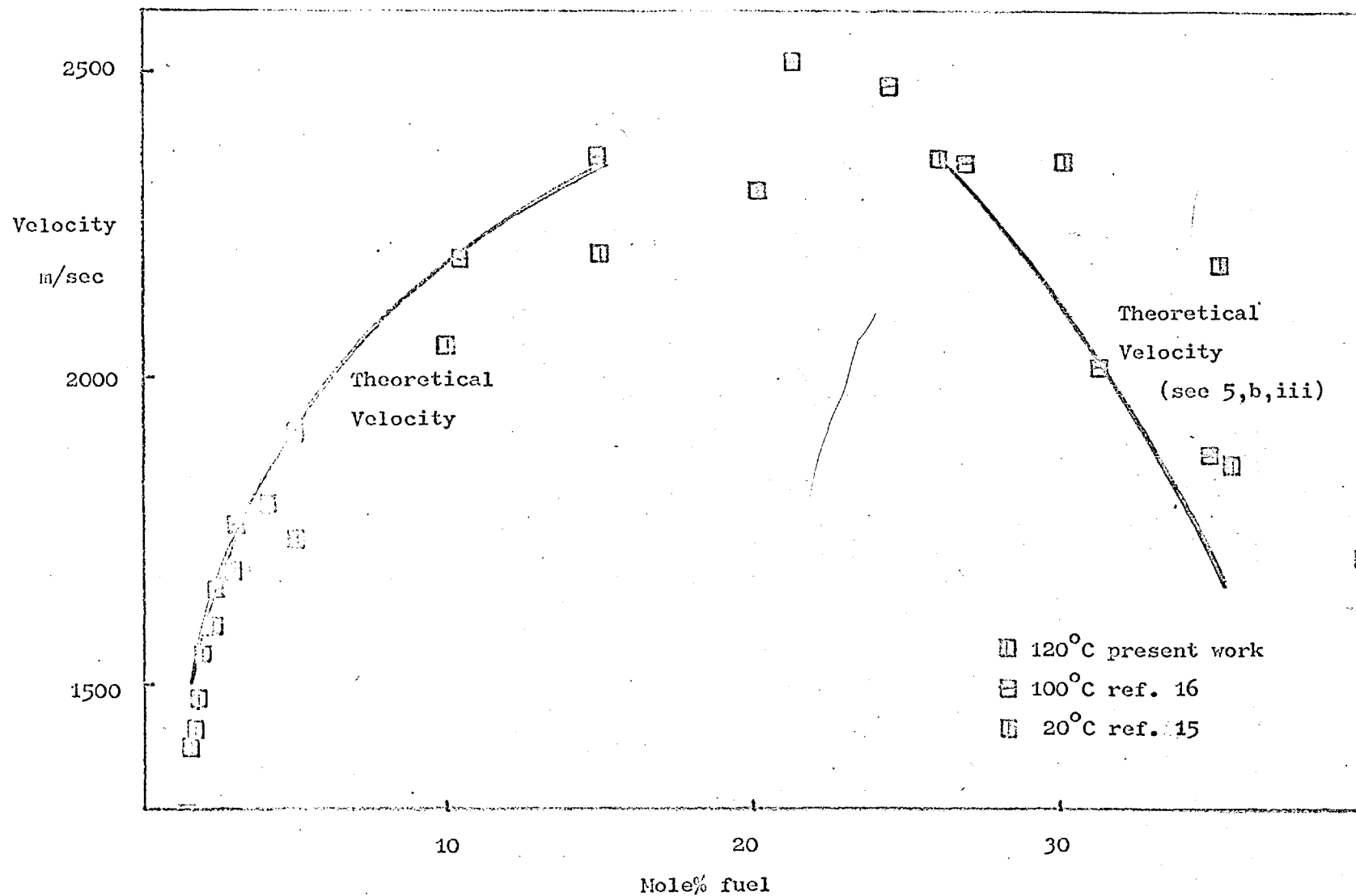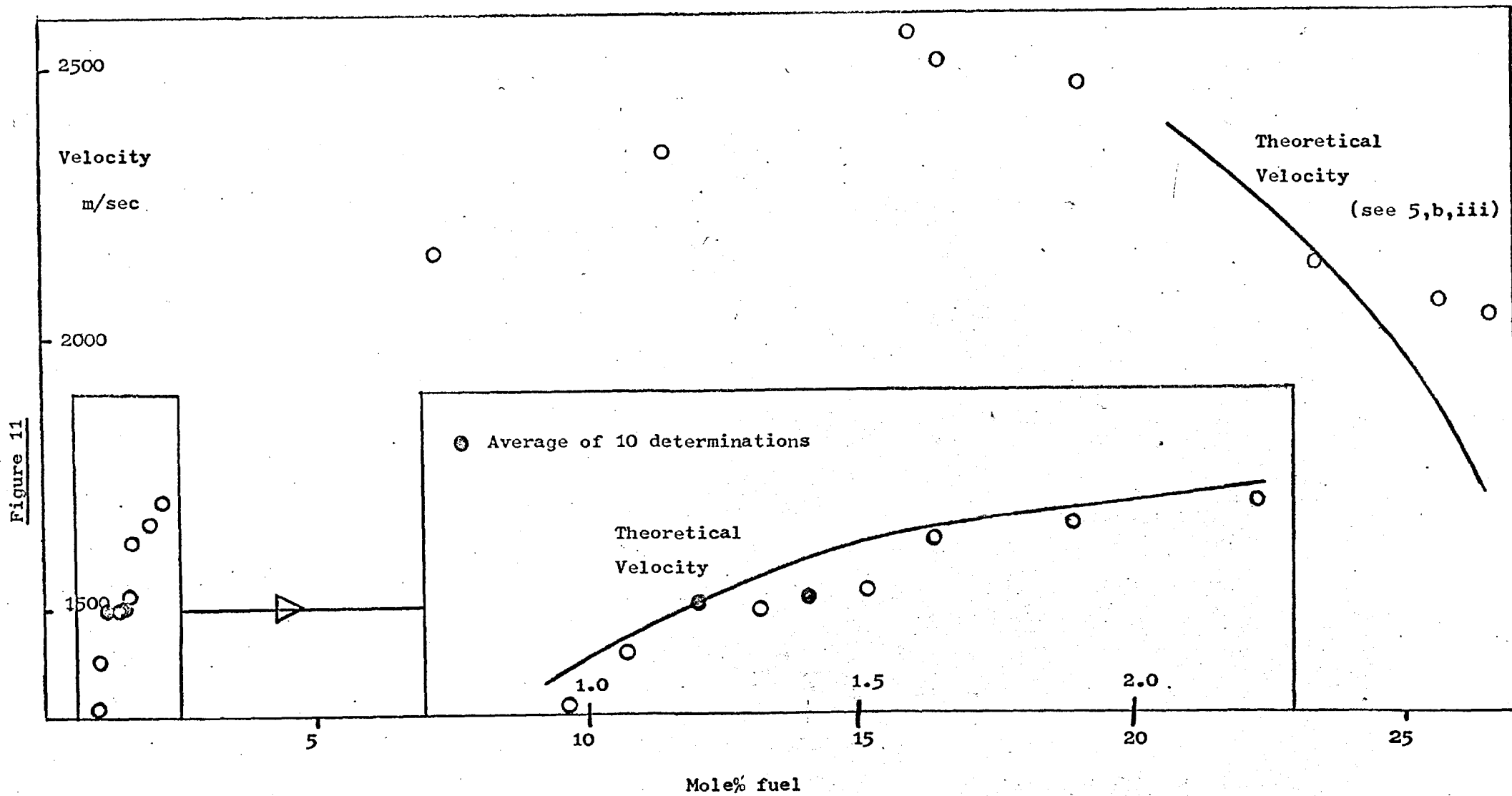
◇ 120°C present work
◈ 160°C   "   "

Figure 10

Detonation Velocity of Xylene/Oxygen

Figure 11

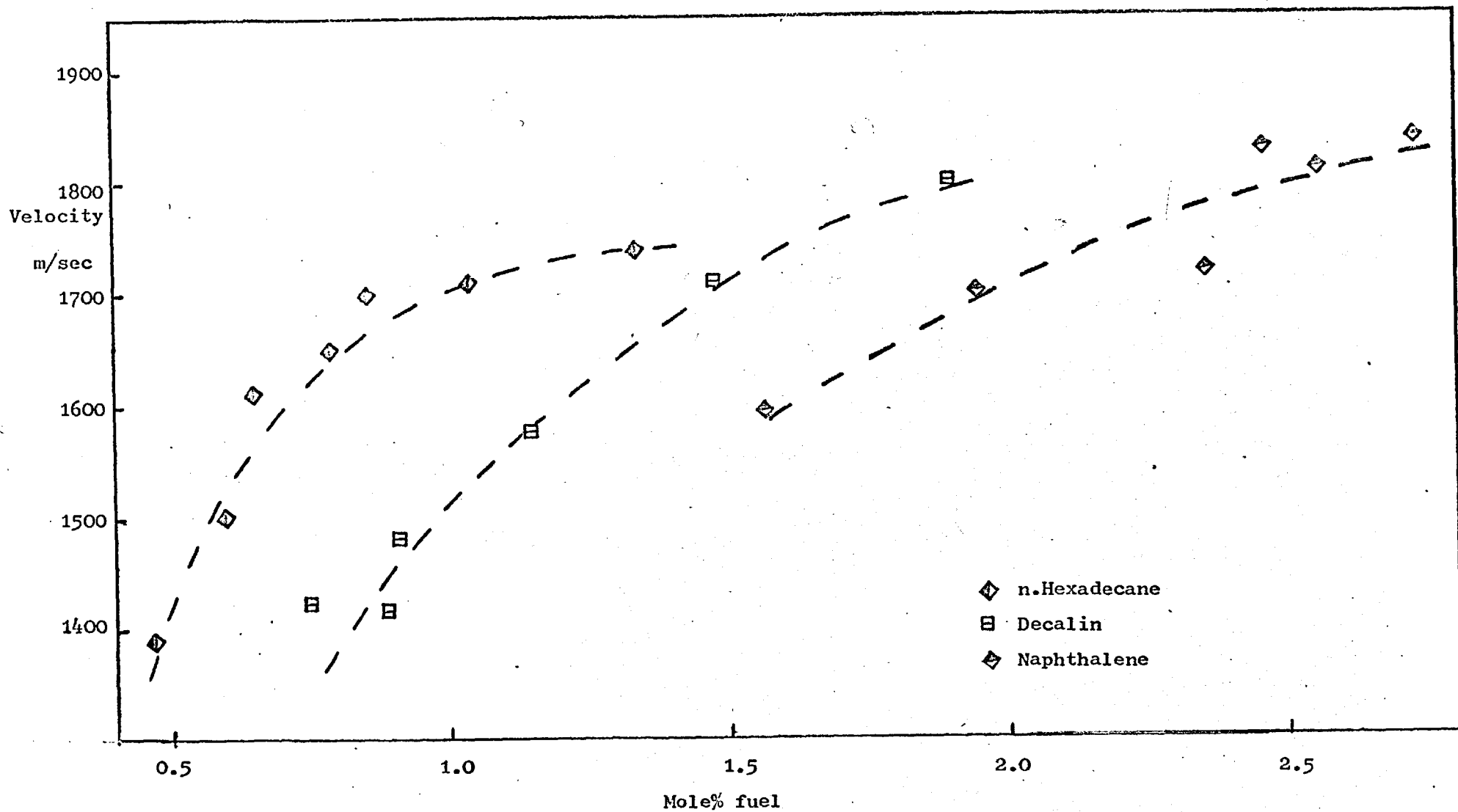Detonation Velocity of n.Hexadecane/Oxygen, Decalin/Oxygen and Naphthalene/Oxygen

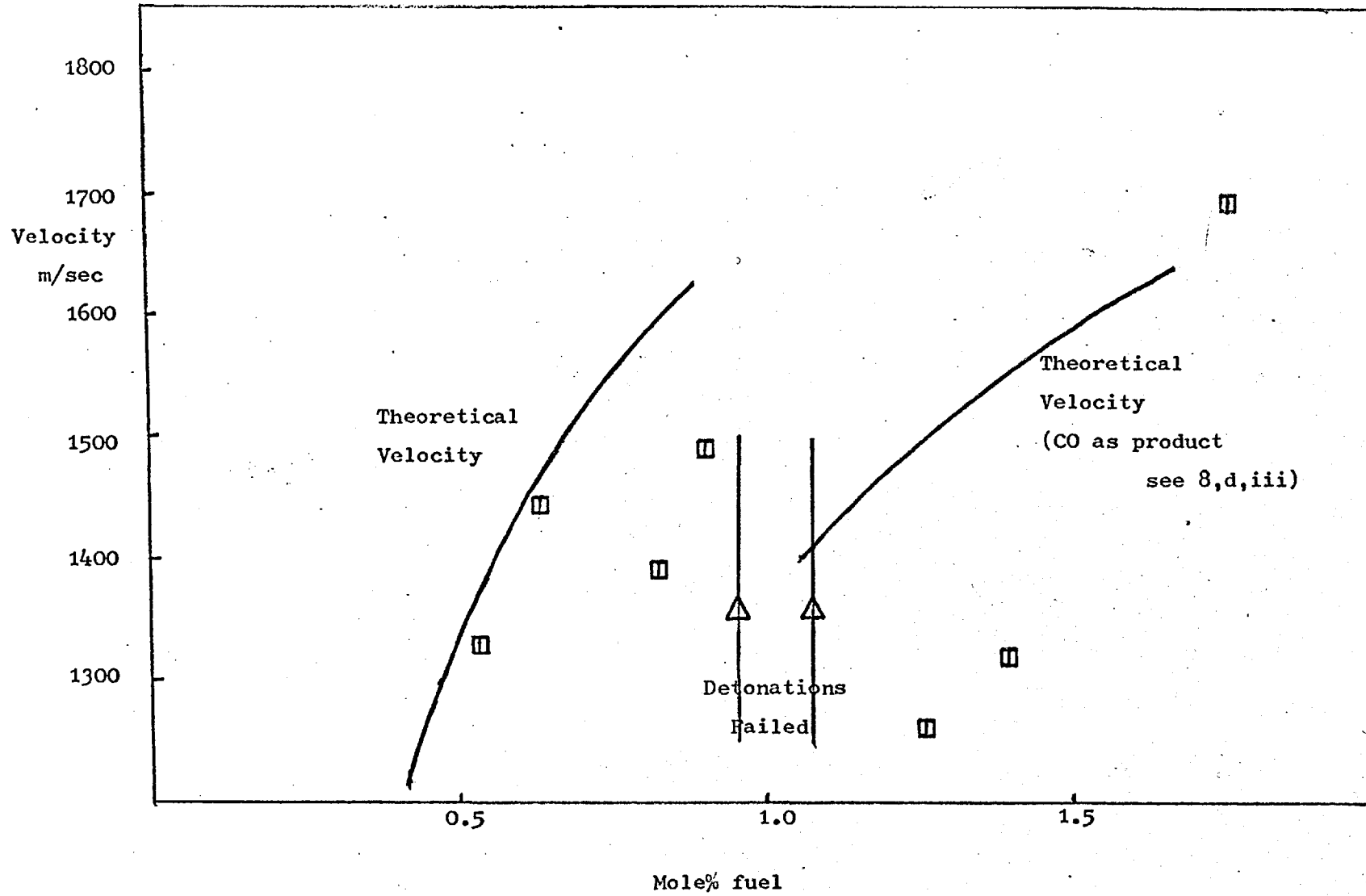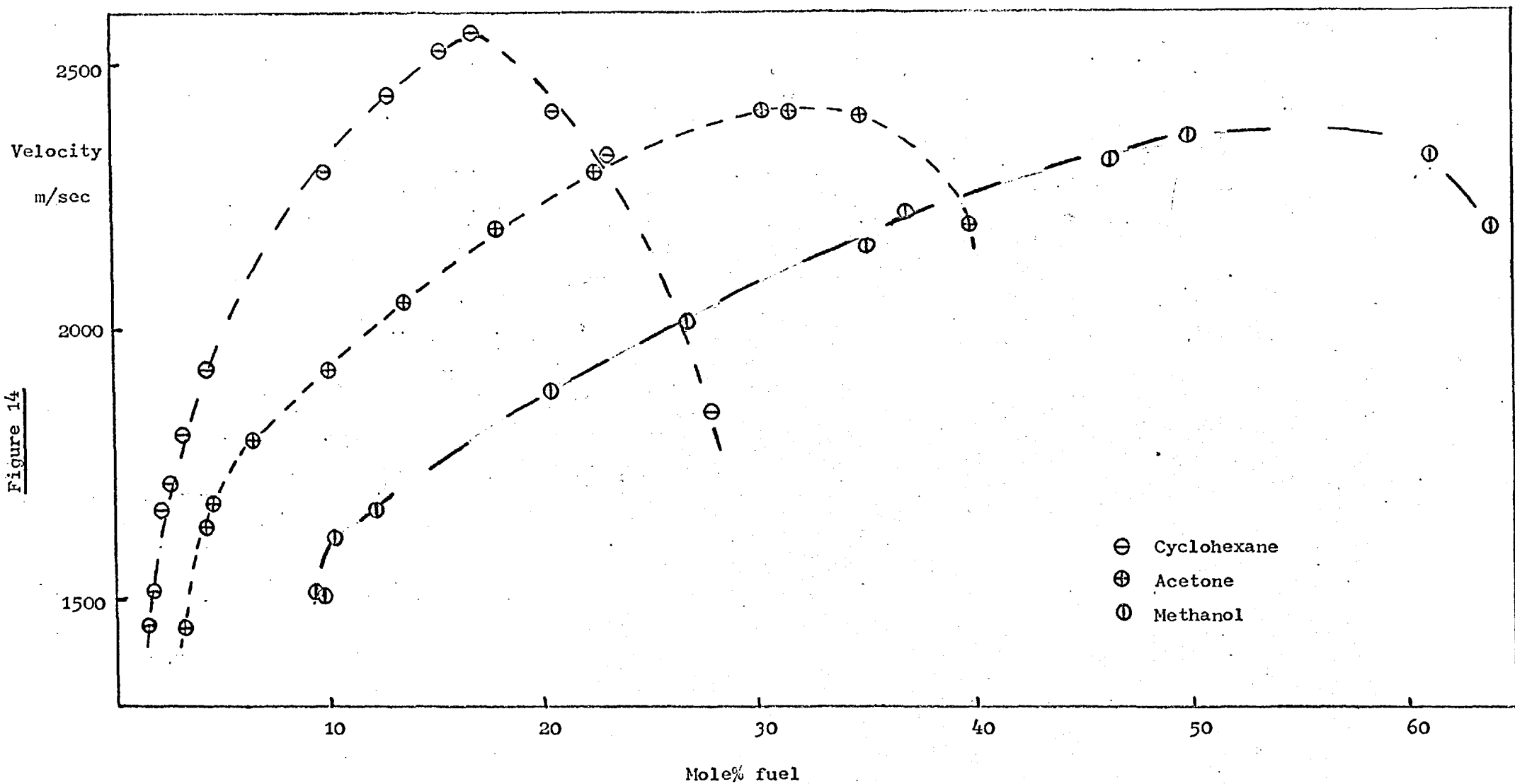Figure 12

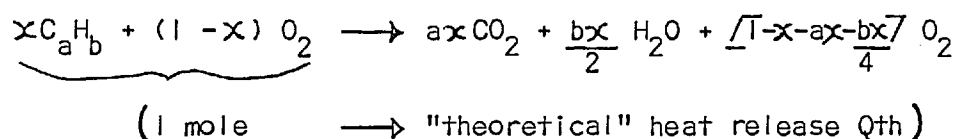Detonation Velocity of Hexamethyl-Benzene/Oxygen

Detonation Velocity of Cyclohexane/Oxygen, Acetone/Oxygen and Methanol/Oxygen

Figure 14

therefore approximately the heat of combustion of the
hydrocarbon to CO_2 and H_2O. (In all lower limit mixtures
the oxygen composition was always greatly in excess over
that required for stoichiometric combustion to CO_2 and H_2O).
A theoretical value of Q (Qth) for the mixture can
therefore be simply calculated from the equation

$$\underbrace{xC_aH_b + (1-x)O_2} \longrightarrow ax\,CO_2 + \frac{bx}{2}H_2O + \left[1-x-ax-\frac{bx}{4}\right]O_2$$

$$\left(1\ mole \longrightarrow \text{"theoretical" heat release Qth}\right)$$

and the heats of formation of the molecules involved.

γM^2 and Qth were found to be superior to the conventional
velocity and composition parameters for comparing results
from different mixtures. A plot of γM^2 (calculated from the
measured velocities and reduced to a common initial temperature
of $298^{\circ}K$) against Qth is shown for various fuel lean mixtures
in fig 15. For the sake of clarity not all hydrocarbon
mixtures are shown, but they all do fall on approximately the
same curve.

Towards the lower limit, the proportion of oxygen in both
the reactant and product mixtures becomes large and no
dissociation of the products occurs. The specific heats
of the various mixtures and therefore the L H S of eqn 10,
all become approximately the same. All the hydrocarbon
mixtures then lie much more closely on the same curve (see
fig 16).

Theoretically calculated values of γM^2 (from the C J theory)
are found to only vary by about 2% for any particular value
of Qth below 15 kcals, considering the whole range of
hydrocarbon mixtures which have the same heat release. Upto
about 15 kcals, therefore, the theoretical values of γM^2
can all be plotted on one curve, as is shown in figs 15, 16.

As can be seen from fig 16, the measured values of γM^2 are
consistently about 6% below those theoretically calculated.
As $\gamma M^2 \propto U_1^2$, this corresponds to a 3% deficit in velocity
possibly due to mechanical and thermal losses to the tube wall.

Figure 15

Mach Product v. Theoretical Energy Release for Fuel Lean Mixtures

Q_{th} kcals/mole

Legend:
- ⊙ Acetone, present work
- ◇ Acetylene, ref. 17
- ▣ Benzene, present work
- ⊙ n.Butane, "   "
- ⊖ Cyclohexane, "   "
- ⬦ n.Decane, "   "
- ◇ Ethylene, ref. 4
- ◈ n.Hexadecane, present work
- ▣ Methane, ref. 4
- ⊙ Methanol, present work
- ⬦ Naphthalene, "   "
- ◯ Xylene, "   "

Theoretical Curve

Figure 16
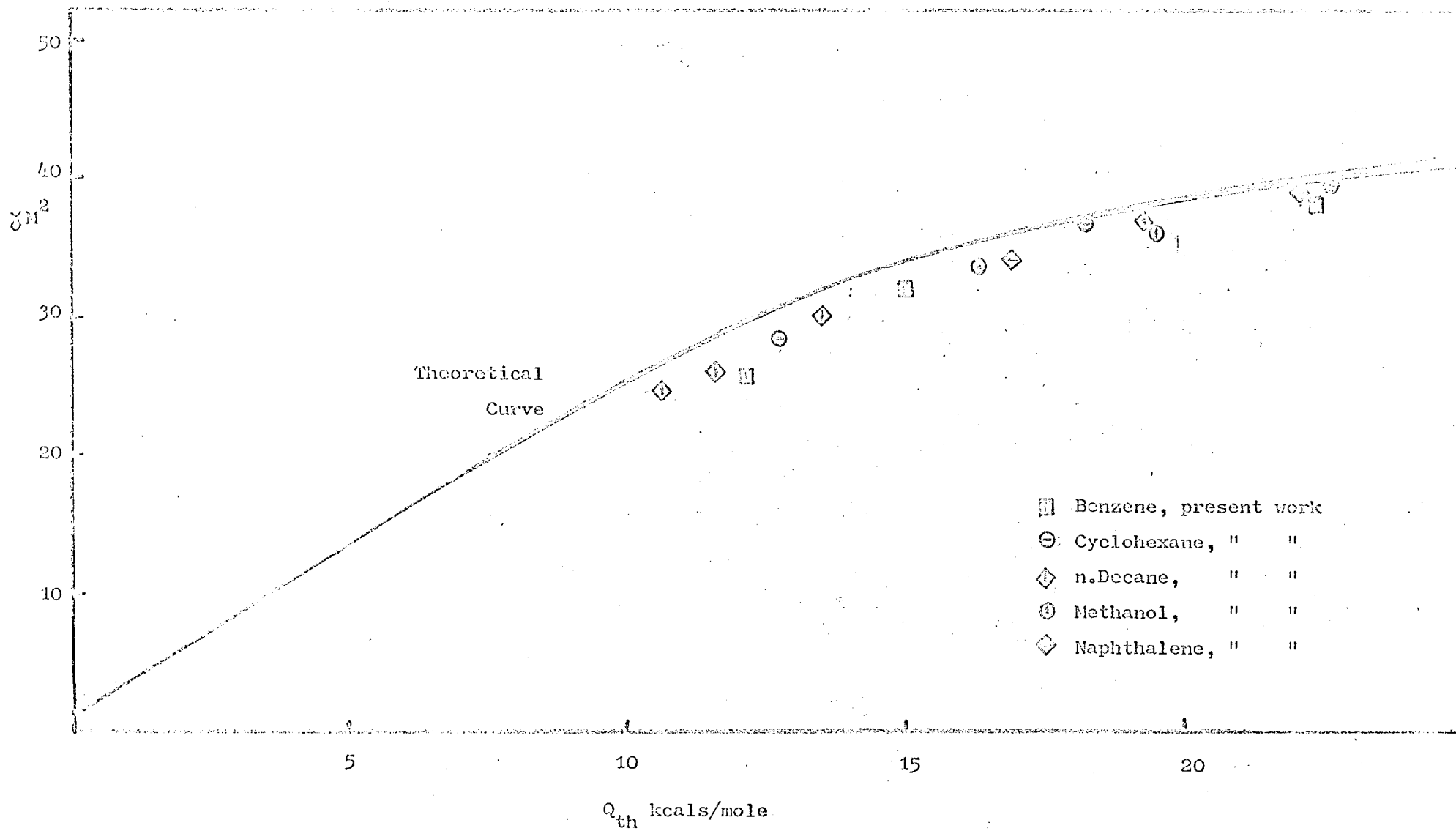
The agreement between measured and theoretical velocities
is therefore remarkably good for the majority of hydrocarbon
mixtures.

Notwithstanding this regularity a slight inflection is
however found in the curve for xylene and a marked deviation
from the theoretical curve is shown by hexamethyl benzene
(see figs 11, 13). For clarity the deviations are shown
on the velocity v composition curves. The various hydrocarbons
are considered separately in chapter 8.

(ii) Fuel Lean Detonation Limits

For the comparison of the fuel lean limits of different fuels,
the basic question is whether fuel molecules behave with
respect to detonation limits predominantly as an "atom soup"
with appropriate adjustment for energy terms, or whether
some "memory" of specific bond structure affects detonation
limits, as it undoubtedly does affect explosion limits.

The theoretical energy release, Qth, was also found to
be the most convenient parameter for comparing fuel lean
limits. Michels (ref 4) compared limits for small molecules
(paraffins upto C_5) on a "homology element" basis and by
considering shock temperatures. Neither of these techniques
was found to be as suitable for the wide range of data
obtained in the present work.

Theoretical Energy Release

For lower limit mixtures calculation showed that each value
for Qth corresponded to only one value of both γM^2 and T_2
(final temperature) within 2% over all the hydrocarbon fuels
used. Mixtures with the same values of Qth were therefore
similar in these important respects and the limits for
different fuels could be directly compared on the basis of
this simply calculated parameter. Table 15 gives the values
of Qth for lower limits of different fuels.

Homology Elements

Michels (4) was able to compare the limits for paraffins upto C_5 by expressing the compositions in "homology elements". That is considering the hydrocarbon as made up of $nCH_2 + H_2$. With the assumption that the H_2 is equivalent to one CH_2 it is possible to express each composition as the percentage of CH_2's in a mixture of CH_2's and O_2. This technique can, however, only be applied to the paraffins and hydrocarbons with a C/H ratio of 1/2. As each CH_2 burning to CO_2 and H_2O liberates approximately the same amount of energy, each homology composition is equivalent to a particular value of Qth. Comparison on this basis, where it is applicable, is therefore roughly equivalent to that on the basis of Qth. However Qth is the preferable parameter to use as it also takes account of the heat of formation of the hydrocarbon molecule (the differences in bond energies of the CH_2's) which the homology element treatment ignores. Calculated values of the homology element compositions are also given in table 15.

Shock Temperatures

Limit energies have also been compared on the basis of shock temperatures (ref 4), (calculated from the Z N D model). Temperatures are calculated from the measured values of γM^2 and the specific heat of the reactant mixture. Some uncertainty does arise as to whether vibrational modes with long relaxation times, compared with detonation reactions, should be included in the specific heat term. For hydrocarbon / oxygen mixtures the vibrational mode of the oxygen molecules is usually assumed to be unexited. (Including the vibrational mode reduces calculated shock temperatures uniformly by about $100°K$)

Shock temperatures for different mixtures are shown in Table 15. Again, because of the similarities between the mixtures, a correlation exists between shock temperatures and values of Qth. Comparison on a shock temperature basis therefore offers no advantage over values of Qth and, where a large number of results are involved, is much more time consuming.

Table 15

Fuel Lean Detonation Limit Parameters

Ref.	Fuel	Limit mole%	Th. Energy kcals/mole	Shock Temp. $^\circ$K*	Homology Comp^n. %
4	Methane, CH_4	8.25	15.8	1405	15.2
p	Methanol, CH_3OH	9.5	16.0		16.0
4	Ethane, C_2H_6	3.6	12.3	1335	10.1
4	Propane, C_3H_8	2.5	12.2	1300	9.30
p	n.Butane, C_4H_{10}	2.0	12.7	1325	9.26
4	Neopentane, C_5H_{12}	1.5	11.7	1245	8.37
p	n.Decane, $C_{10}H_{22}$	0.7	10.6	1220	7.19
p	n.Hexadecane, $C_{16}H_{34}$	0.46	11.1		7.26
4	Ethylene, C_2H_4	4.1	13.0		7.90
4	Propylene, C_3H_6	2.5	11.5	1190	7.01
p	Acetone, CH_3COCH_3	3.3	13.3		7.02
p	Cyclohexane, C_6H_{12}	1.4	12.5		7.84
p	Decalin, $C_{10}H_{18}$	0.7	9.9		
p	Adamantane, $C_{10}H_{16}$	0.9	12.7		
p	Hexamethyl-Bz., $C_{12}H_{18}$	0.55	9.6		
p	Xylene, C_8H_{10}	1.05	11.0		
17	Acetylene, C_2H_2	2.9	8.8		
12	Furan, C_4H_4O	2.6	12.4		
p	Benzene, C_6H_6	1.55	11.7	1190	
p	Naphthalene, $C_{10}H_8$	1.5	17.0		

Table 15 (cont.)

Ref.	Fuel	Limit mole%	Theoretical Energy Release,kcals/mole
18	Tetramethylsilane, $Si(CH_3)_4$	1.8	12.0
19	Monochloromethane, CH_3Cl	10.1	15.4
19	Dichloromethane, CH_2Cl_2	11.0	13.0
19	Trichloromethane, $CHCl_3$	18.0	16.5
19	Trichloroethylene, C_2HCl_3	6.6	13.6
19	Tetrachloroethylene, C_2Cl_4	12.5	22.0
1	Carbonmonoxide, CO	40.0	27.0
20	Cyanogen, C_2N_2	36.7	36.7
4	Hydrogen, H_2	15.5	9.5
1	Ammonia, NH_3	25.0	19.0
21	Ozone, O_3	9.0	3.1

Fuel lean detonation limits with oxygen for $1''$ dia. tube at 1 atm. initial pressure. Results of refs. 17 and 19 modified by method of Pusch and Wagner (ref. 22) to convert data for $1''$ tube.

* Temperature calculated assuming relaxation of all degrees of freedom except vibrational mode of oxygen.

Ref. p   Present Work

Influence of Molecular Size

The total variation of values of Q_{th} for lower limit mixtures corresponds to only about $^1/30$th of the total detonable composition range (see fig 15). To a first approximation therefore the lower limits occur at the same detonation conditions. A trend of Q_{th} with molecular size is nevertheless apparent.

Fig 17 is a plot of Q_{th} (for lower limit mixtures) v the number of carbon atoms in the hydrocarbon molecule. The range of experimental error in the value of Q_{th} is indicated in some typical cases. The results show that the larger molecules have smaller limit energies and therefore detonate more readily. There is no obvious trend with other parameters such as C/H ratio. (The limit for acetylene was measured in a different diameter tube (ref 17) and is included here merely to show that it is of the same order as the other results).

The most obvious exception to the trend is naphthalene. This was the hydrocarbon with the most condensed planar structure that was detonated in the present work. Particular hydrocarbons will be considered in detail in chapter 8.

(iii) Fuel Rich Mixtures

For the majority of hydrocarbons near the fuel rich limits the products consist mainly of CO and H_2. As these products both have similar specific heats, all mixtures near the fuel rich limit should fall on approximately the same plot of γM^2 v Q_{th}, as was found in this work fuel with fuel lean limits. In order to calculate the value of Q_{th} however the complete product composition must be known.

If thermodynamic equilibrium is attained at the C J plane only one possible product composition exists. For mixtures with fuel compositions in excess of that required to form stoichiometric CO and H_2, the major equilibrium products are CO, H_2, $H^\bullet$, graphite and acetylene. Using data on equilibrium constants of formation from N A S A, SP 3001 (1963) compositions of all other possible products are found to be

less than 10^{-4} mole fraction for all hydrocarbon fuels,
except acetylene, over the range of C J temperatures and
pressures. On approaching the fuel rich limit the proportions
of H• and acetylene also become negligible.

In order to estimate the value for Qth, the equation close
to the fuel rich limit can therefore be written as

$$x C_a H_b + (1-x) O_2 \longrightarrow 2 (1-x) CO + \underline{/a}x -2(1-x\underline{)/} C + \frac{bx}{2} H_2$$
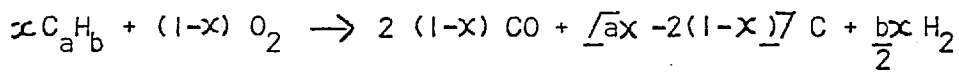
where C is all the carbon in the products not forming CO.

As the heat of formation of H_2 is zero, the quantity produced
does not effect the value of Qth. The value of Qth is
however greatly altered by the proportions of carbon at
the C J plane existing as graphite, acetylene and other
possible species, if the final thermal equilibrium state is
not attained. This carbon in the products above that
required to convert all the oxygen to CO will be termed
"excess carbon".

Fig 18 shows a plot of γM^2 v. Qth for fuel rich mixtures of
three hydrocarbons with widely different C/H ratios. The
values of Qth are calculated on the assumption that the
equilibrium products are formed at the C J plane; in this
case all the excess carbon should form graphite. Also shown
are the theoretical plots of γM^2 v. Qth for the mixtures. As
a solid product (graphite) is assumed formed, the theoretical
lines do not lie closely together, as would be the case for
fully gaseous products.

In each case, the experimental points lie below the theoretical
curves, the divergence being greater the greater the proportion
of "excess carbon" in the products. This suggests that the
"excess carbon" is unable to condense sufficiently rapidly to
form graphite at the C J plane but exists as some less stable,
more energetic intermediate product or alternatively an
equally stable product with a higher specific heat (see eqn 10)

Mach Product v. Theoretical Energy Release for Fuel Rich Mixtures

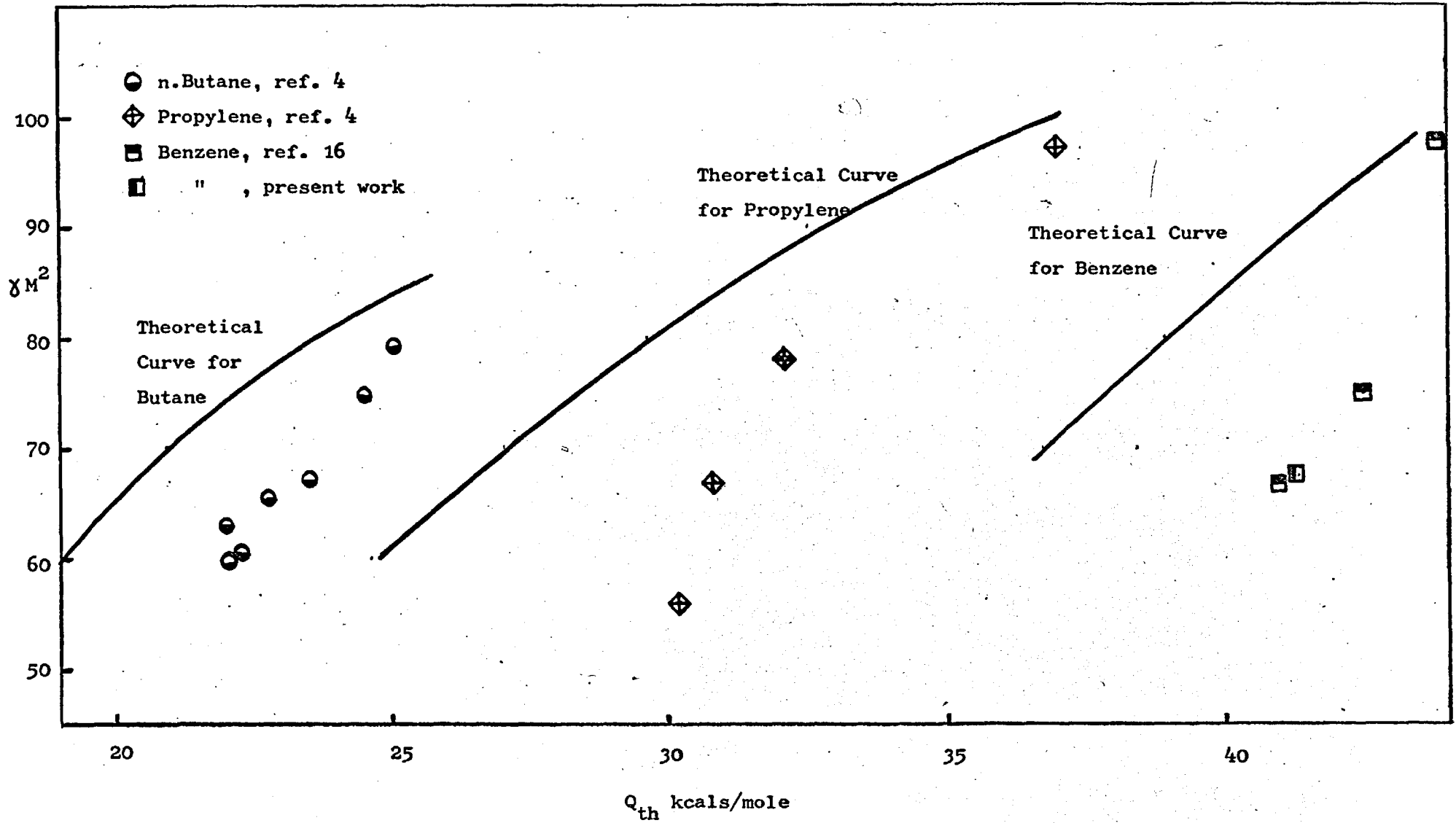(assuming excess carbon as solid carbon at the C.J. plane)

Figure 18

For four particular fuel rich mixtures of four different hydrocarbons detailed C J calculations were made. Fig 19 shows the loci of assumed values of specific heat and heat of formation of the "excess carbon" product which are necessary for agreement within 3% (see 5 b) i)) between the theoretical and measured detonation velocities. These plots suggest that if the "excess carbon" is assumed to exist as a compound with a heat of formation of about +25 to +30 kcals/ g atom of carbon and a specific heat in the range of 4 - 8 Kcals / g atom of carbon / $^\circ$K (no carbon compound has a specific heat less than 4) then the observed detonation velocities will agree with those theoretically calculated for each hydrocarbon.

Plots of γM^2 v Qth for fuel rich hydrocarbon mixtures should therefore lie approximately on the same curve if a value of about +25 to +30 kcals / g atom of excess carbon is included in the calculation of Qth. This is verified by Fig 20 in which an intermediate value of +27.5 kcals /g atom of excess carbon was used. This general agreement between hydrocarbons also strongly suggests that the "excess carbon" exists as a gaseous product at the C J plane. The plots for different C/H ratios would be displaced much more from each other (as in fig 18) if a solid product is formed. The possible nature of this gaseous C J product is fully discussed in 6 c).

(iv) <u>Fuel Rich Detonation Limits</u>

The techniques of comparison used for fuel lean limit mixtures can also be used at fuel rich limits. Because of the difficulty of estimating the limiting value of γM^2, shock temperatures can only be found approximately and homology compositions are very insensitive to changes in mole composition. Therefore, despite the correlation between γM^2 and Qth being not so good at fuel rich as fuel lean limits (c f. figs 16, 20), Qth is still the most satisfactory parameter for comparing limits. Table 16 shows Qth (calculated with a heat of formation of 27.5 kcals / g atom of excess carbon), homology compositions and representative shock temperatures for fuel rich limits.

Figure 19

Loci of Values Assumed for Specific Heat and Heat of Formation
of Excess Carbon Required to Reach Agreement between Measured
and Calculated Detonation Velocities

Heat of Formation of Excess Carbon at $298°K$
kcals/g.atom of carbon
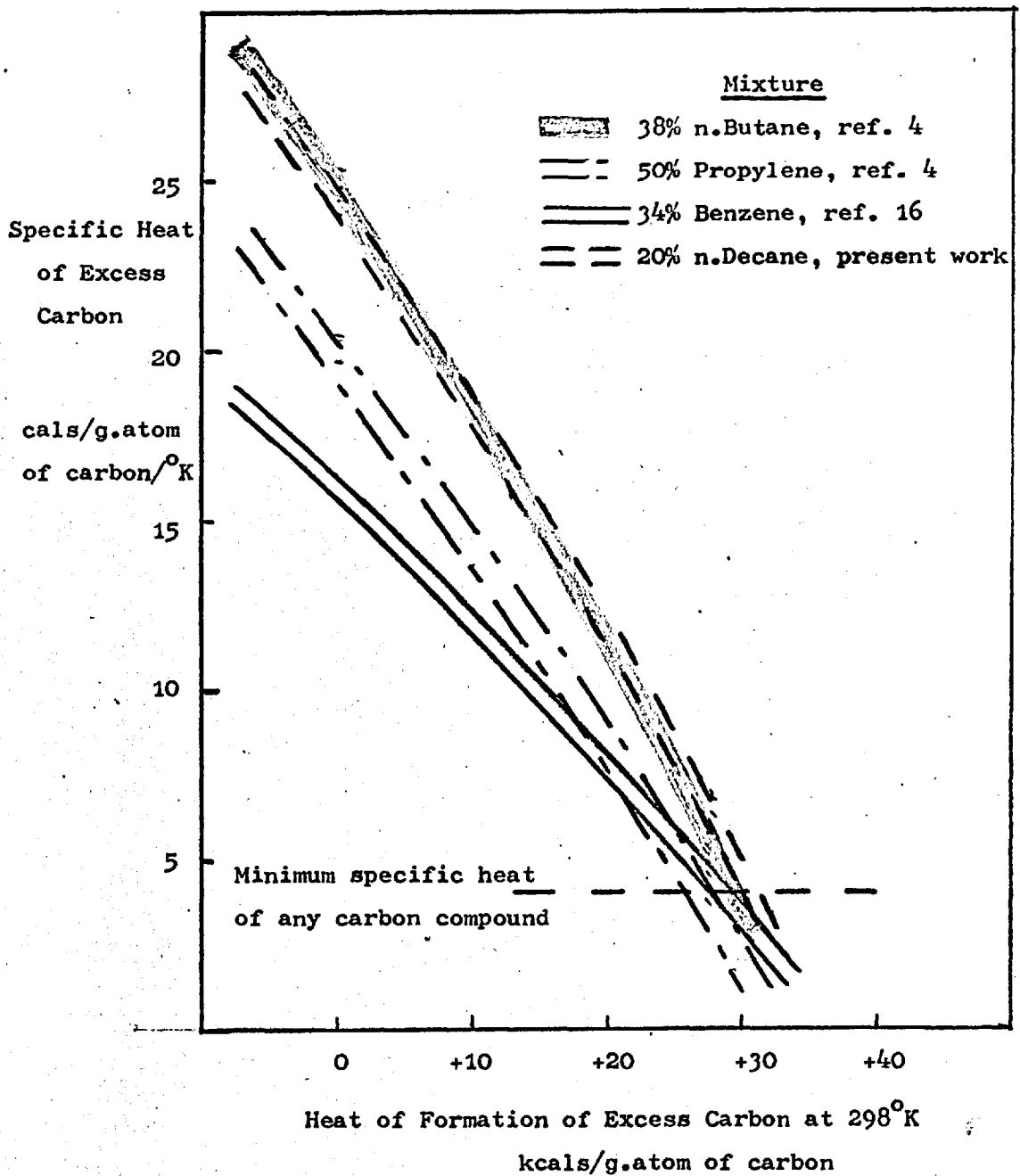
Width of curves indicates range of solutions for agreement
to within 3% between measured and calculated velocities.

Mach Product v. Theoretical Energy Release for Fuel Rich Mixtures

(assuming heat of formation of excess carbon = 27.5 kcals/g.atom)
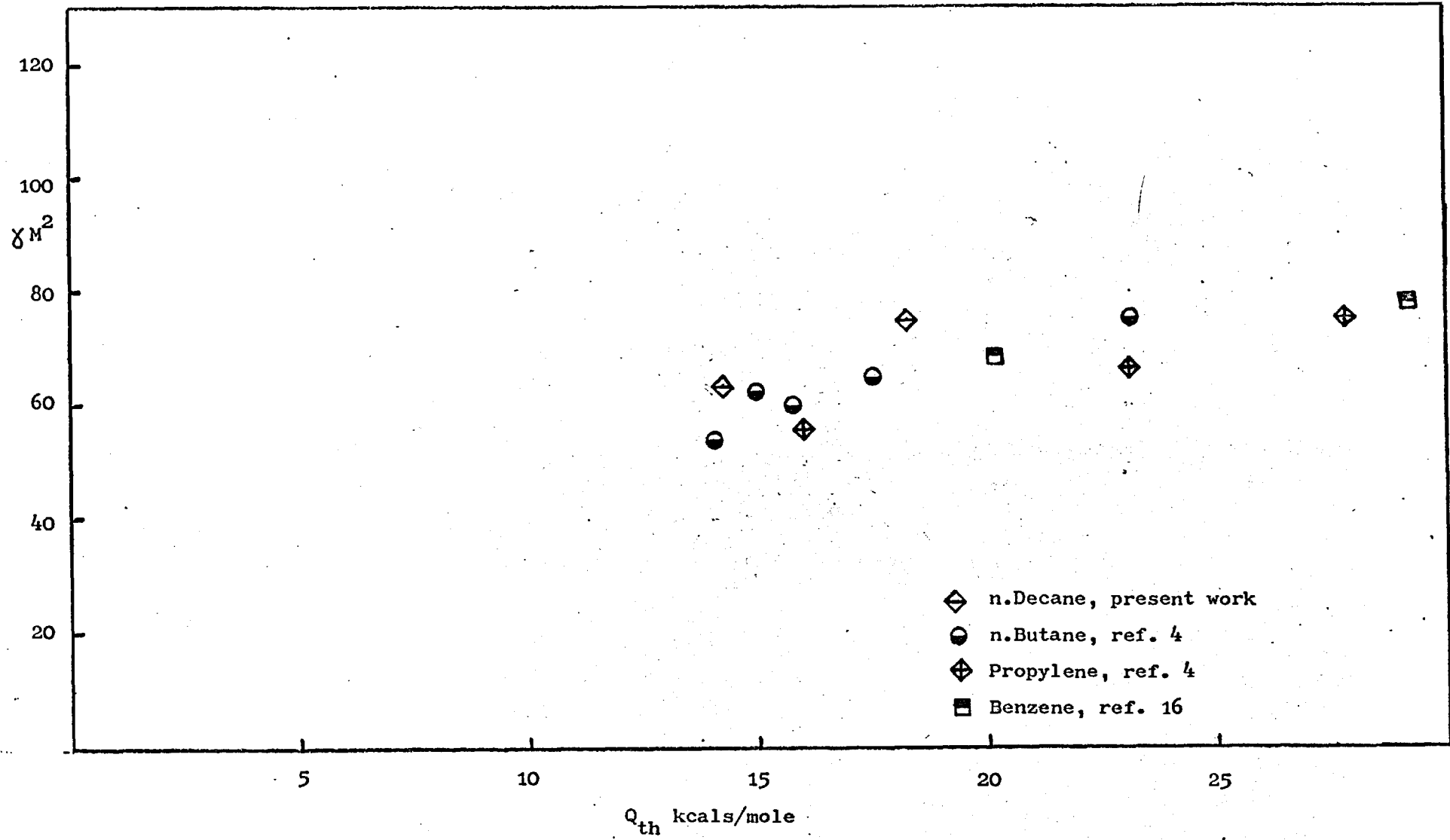
Figure 20

Table 16

Fuel Rich Detonation Limit Parameters

Ref.	Fuel and Initial Temp. °C	Limit mole%	Th. Energy kcals/mole	Shock Temp.°K*	Homology Comp^n. %
4	Propane,(20)	42.5	16.5	1220	74.7
4	n.Butane,(20)	38	13.8	1170	75.4
p	n.Butane,(120)	35	21.1	1375	72.9
4	Neopentane,(20)	33	13.8	1180	74.7
p	n.Decane,(160)	21	15.7	1080	74.4
4	Ethylene,(20)	60	17.6		75.0
4	Propylene,(20)	50	15.0	1205	75.0
p	Cyclohexane,(100)	29	20.4		71.0
p	Xylene,(160)	26.5	21.8		
17	Acetylene,(20)	92	7.8		
12	Furan,(30)	55.5	11.2		
p	Benzene,(120)	36	16.7	1320	

(Fuels with no excess carbon in limit mixture)

Ref.	Fuel and Initial Temp. °C	Limit mole%	Th. Energy kcals/mole	Shock Temp.°K*	Homology Comp^n. %
4	Methane,(20)	56	23.5	1680	71.6
p	Methanol,(100)	64.5	27.7		56.2
4	Ethane,(20)	46.5	24.0	1575	72.2
p	Acetone,(100)	40	33.2		54.5
18	Tetramethylsilane,(20)	50	15.2		

* Temperature calculated assuming relaxation of all degrees
of freedom except vibrational mode of oxygen.

Ref. p   Present Work

The fuel rich limit of butane/oxygen mixtures was found to
vary slightly with temperature (see Table 16). This
corresponded to an increase in limit energy of about 7 kcals /
mole per $100^{\circ}C$ above room temperature ($20^{\circ}C$).

In order to compare all the values of Qth calculated for
mixtures at different initial temperatures a correction was
made in proportion to the observed variation for butane,
reducing the values to a common temperature of $120^{\circ}C$. For
this reason, some uncertainty is introduced in comparing the
limit energies for the mixtures at high temperatures used in
this work with the room temperature results of previous
workers on small molecules.

Influence of Molecular Size

As was found with fuel lean limits, the total variation in
values of Qth was only small compared with the total
detonable composition range.

Fig 21 is a plot of the limit values of Qth, reduced to an
initial temperature of $120^{\circ}C$, against the number of carbon
atoms in the hydrocarbon (c f. fig 17). The same trend of
lower Qth's at greater molecular sizes is apparent as at
fuel lean limits, again bearing in mind the relatively large
errors in Qth as indicated by the typical error ranges
shown.

As was stated for fuel lean limits, the value of Qth for
acetylene is only approximate. Possible reasons for the
deviation of xylene and acetone from the trend will be dis-
cussed later (chapter 8).

(v) <u>Extended Comparison between Measured and Theoretical Velocities</u>

For compositions near the fuel lean and fuel rich detonation
limits the measured and theoretical velocities could be
adequately compared from plots of γM^2 v. Qth (see figs 16,
20). A technique was developed which enabled the comparison
of velocities over the whole detonable mixture composition
range.

For a detonation the calculated C J velocity is a function of the initial pressure, temperature and composition only. Variations in the initial pressure and temperature over the ranges used in this work do not significantly alter the calculated velocity (see I b)).

Each hydrocarbon/oxygen mixture is on this basis completely characterised by its C, H and O proportions and the heat of combustion, Q.
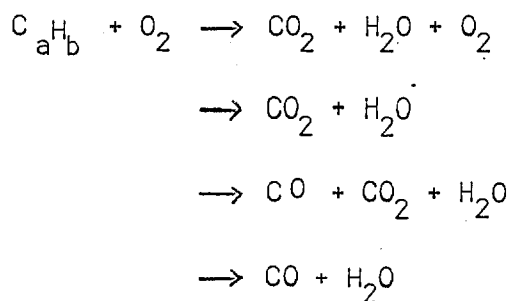
$$\text{But} \quad \frac{\gamma M^2}{Q} \doteq \frac{2(\gamma^2 - 1)}{RT_1} \tag{10}$$

$$\therefore \quad \frac{\gamma M^2}{Q} = \text{fn. (C/H/O) only}$$

For hydrocarbons with equal C/H ratios, plots of $\gamma M^2/Q$ v. $C/(C + O)$, where C and O are the proportions of carbon and oxygen atoms in the initial mixture, should be the same.

Near the limits, where dissociation of the products can be neglected, Q can be calculated directly. For other mixtures, the calculated value of Q (for undissociated products) will need readjustment. However for mixtures with corresponding C/H/O ratios, the energy releases will be sufficiently close to produce approximately equal detonation temperatures. The degree of dissociation and therefore the actual Q's will be approximately the same. The correlation between hydrocarbons should therefore still work with the "undissociated" value for Q.

Plots of $\gamma M^2/Q$ v. $C/C + O$ are shown in figs 22 - 25 for different C/H ratios. The values of Q have been calculated from the simplified reactions (at different hydrocarbon/oxygen proportions).

$$C_aH_b + O_2 \longrightarrow CO_2 + H_2O + O_2$$

$$\longrightarrow CO_2 + H_2O$$

$$\longrightarrow CO + CO_2 + H_2O$$

$$\longrightarrow CO + H_2O$$
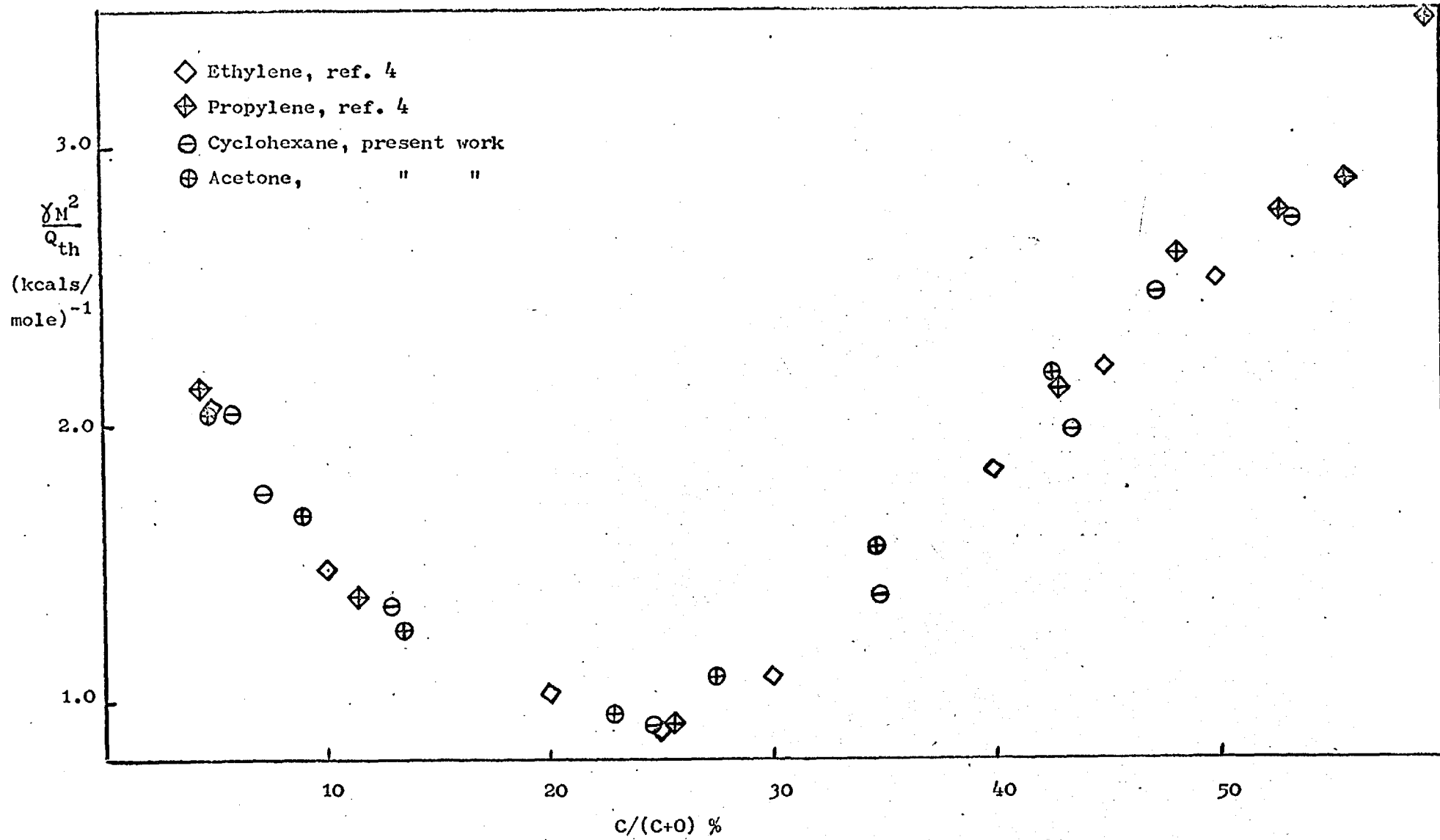
Figure 23

Figure 24

Figure 25

$$CO + H_2O + H_2$$

$$\cdot \; CO + H_2$$

$$CO + H_2 + C \;\; \text{(excess)}$$
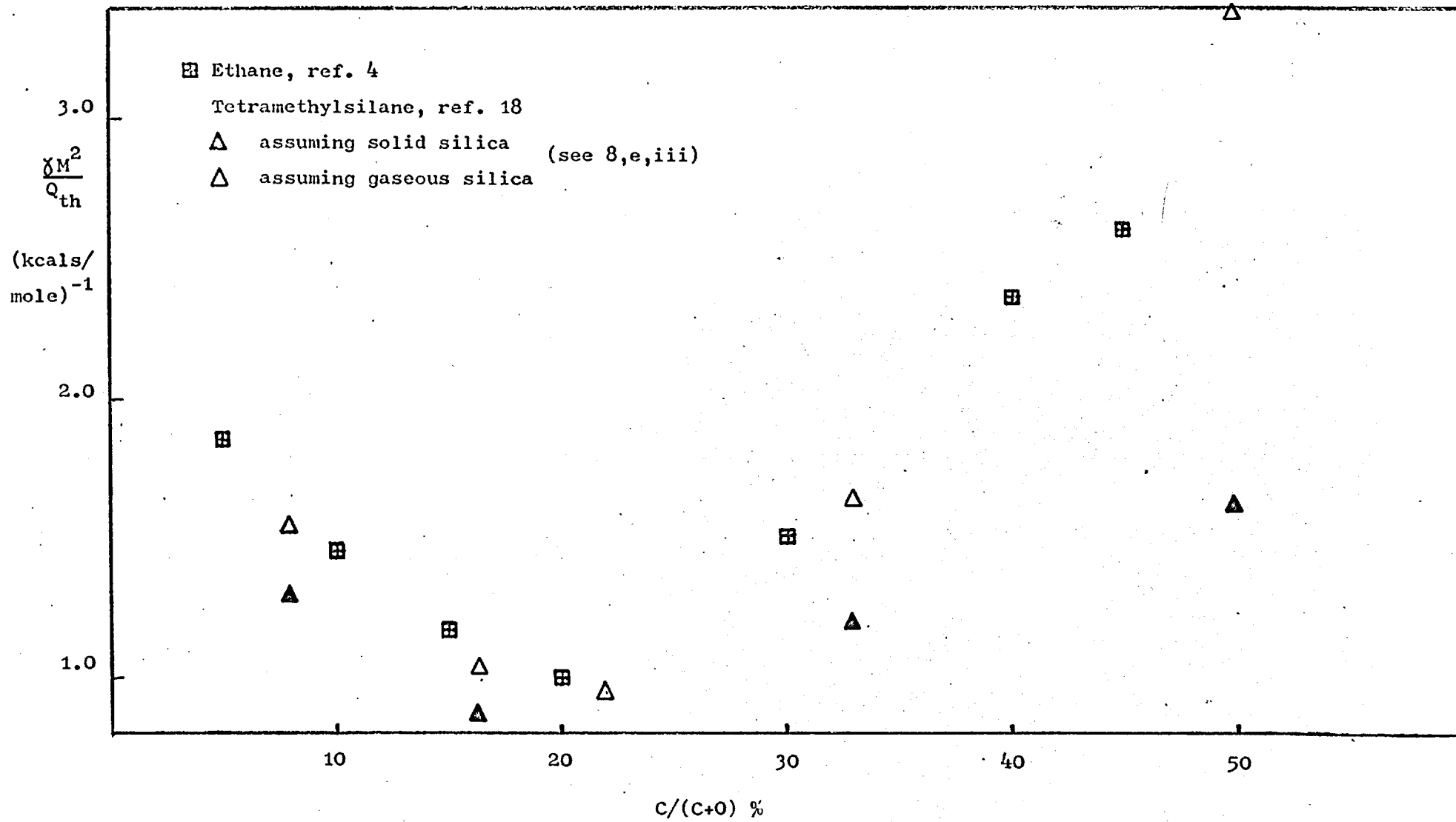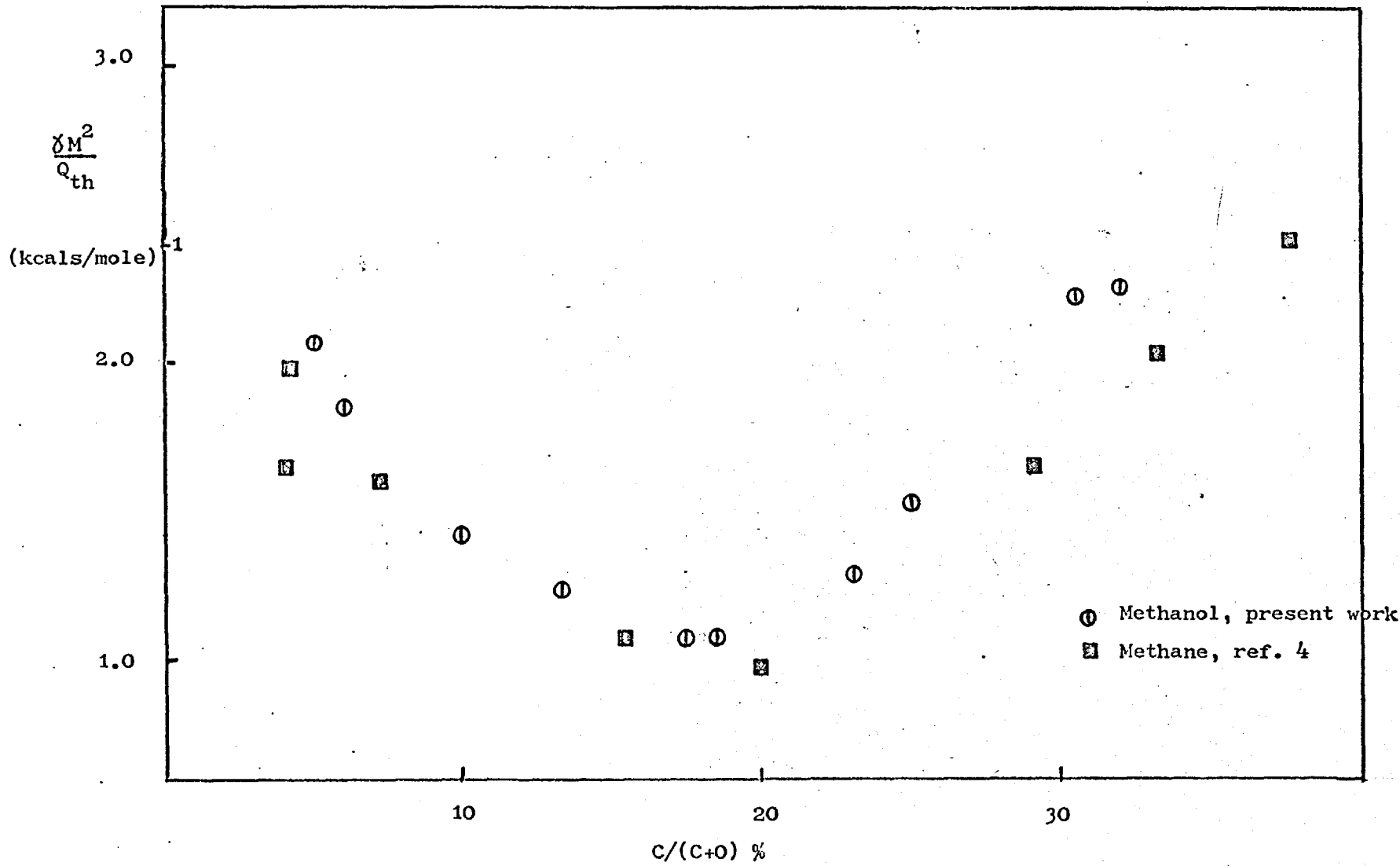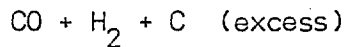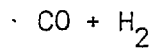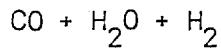
The heat of formation of the excess carbon has been taken as 27.5 k cals/g atom.

Hydrocarbons with the same C/H ratio all fall well on the same curve (less well for fuel rich mixtures). This agreement is especially striking as this method of plotting is more sensitive than plots of γM^2 v. Qth.

Fig 26 is a plot of γM^2/Qth v. H/C ratio for a fixed ^{C}/C + O ratio of 55% for various hydrocarbons. As a ^{C}/C + O ratio of 50% corresponds to the stoichiometric composition for the formation of CO + H_2, "excess carbon" is produced in all these mixtures. For each mixture the value of γM^2/Qth has been derived for heats of formation of 0, + 25 and +30 kcals/g atom of excess carbon. The spread of theoretical values of γM^2/Qth is also shown. This plot also shows that for agreement between the theoretical and practical results a heat of formation of about +25 to +30 kcals/g atom of excess carbon must be assumed.
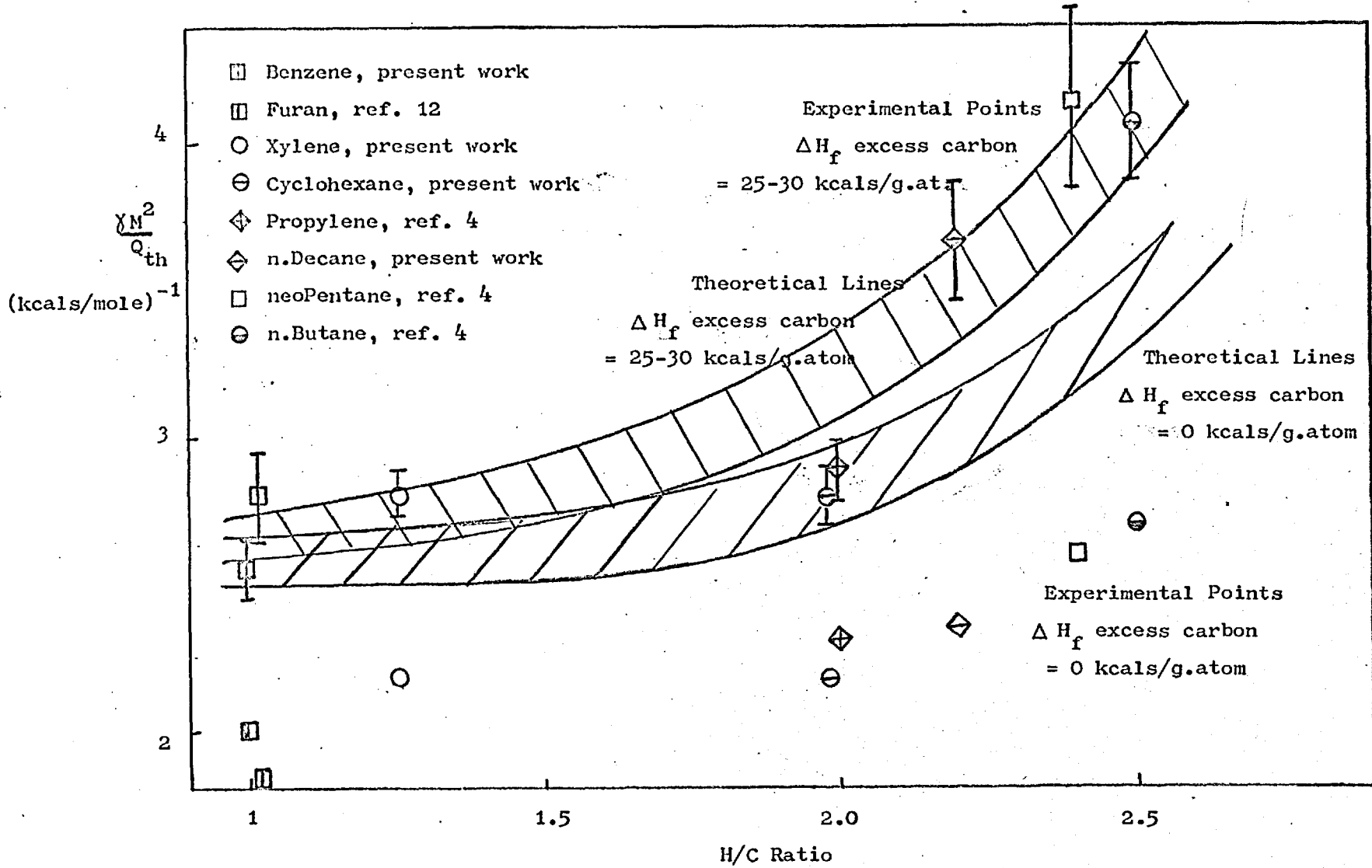
Figure 26

INVESTIGATION OF CARBONACEOUS SOLID PRODUCTS

Chapter 6 — Results and Discussion

Solid products formed in mixtures near the fuel rich detonation
limit of most hydrocarbons were investigated in various ways.

It was thought that the properties of the solids produced might
show some correlation with the molecular structure of the initial
hydrocarbon. A study of the quantity of solid produced was also
important as a result of the influence of the product composition
on the calculated energy release (see 5 b) iii)).

In view of the enormous range of data obtained in the course of this
work only a general survey of the solids produced could be carried
out.

a)   General Survey of Properties

i)   Composition

The chemical composition of a number of the solids was
determined by the Micro Analytical Laboratory. The results
are listed in Table 17. The solids consisted of over
90 wt% carbon in the majority of cases which is as much as
most carbon blacks.

The "carbons" were analysed for carbon and hydrogen, and as
no other elements were present in the initial mixtures, the
residue was assumed to be oxygen. No nitrogen was found
present so none could have been absorbed from the air after
the carbons were removed from the detonation tube. The
fact that the atomic proportions of oxygen were in most cases
many times less than hydrogen (see Table 17) in the "carbons"
seemed to preclude the later possible absorption of a large
quantity of water vapour.

ii)   C/H atom ratios

The C/H atom ratios found varied from nil hydrogen to about
3:1. There was no obvious correlation between C/H ratio and
the C/H ratio in the initial hydrocarbon, as might be expected
if some 'memory' of the initial molecular structure was
retained.

Table 17

Chemical Composition of Detonation Carbons

Fuel Mixture	Weight %			Atom Ratios	
	C	H	O[§]	C/H	C/O
35.5% Benzene	89.48	1.92	8.60	3.88	13.9
25.6% Xylene	87.31	1.70	10.99	4.28	10.6
– Furan (ref. 31)	–	–	–	11.2	45.0
– Ethylene	99.18	0.79	0.03	10.5	∞
31% Ethylene 31% Methane	97.05	1.68	1.37	4.82	94.5
33% Ethylene 33% Methane	96.55	2.47	0.98	3.26	132
58.3% Ethylene 8.5% Ammonia[+]	98.14	1.74	0.12	4.70	1080
45.7% Propylene	72.76*	0.629	(26.6)	9.83	–
49.0% Propylene	95.08	nil	4.92	∞	25.8
50.0% Propylene	94.39	2.25	3.36	3.53	37.4
– Neopentane	95.99	1.56	2.45	5.10	52.2
20.8% n.Decane	94.09	1.98	1.98	3.96	32.0

for comparison
Coronene $C_{24}H_{12}$ 96.0   4.0   –   2.0   –
(large polynuclear hydrocarbon)

[§] Found by subtraction from 100%

* Large solid residue also found

[+] No nitrogen found present

The total quantity of carbon produced in the 1" detonation
tube described varied upto about 0.6 grams. (see Table 18)
Apart from "carbons" produced in quantities less than 0.15
grams, the C/H ratios only varied from about 5:1 to 4:1.
This indicates that for these larger quantities produced the
C/H ratio is approximately independent of the initial hydro-
carbon mixture.

iii) <u>C/O atom ratios</u>

Carbon/oxygen ratios showed more variation between "carbons".
In flame carbon blacks it is known that the oxygen is all
contained as surface groups such as -COOH and -C = O on the
basic particles (ref 28). The "carbons" in the present work
were found by electronmicroscopy to consist of small spherical
particles of around 300Å diameter joined together in a loose
floc structure (see 6 b) ii)). If a carbon particle of
such a size has one oxygen atom per free surface valency the
C/O ratio would be of the order of 25:1. All the oxygen
could therefore be combined to the surface of the particles
in the majority of "carbons"(see Table 17). If this were
the case, the oxygen has combined with the particles after
they had been formed.

A possible correlating trend between the hydrocarbon molecule
structure and the C/O ratio was observable. "Carbons" from
the simpler molecules such as C_2H_4 contained least oxygen
and more complex molecules such as $nC_{10}H_{22}$ and neo C_5H_{12} an
increasing quantity. The highest proportion of oxygen was
found in the "carbons" from aromatic ring molecules such as
benzene and xylene. This suggests that the surface activity
of the "carbons" may have retained some 'memory' of the
initial hydrocarbons.

iv) <u>Quantity Produced</u>

The C J detonation products for mixtures forming solid "carbon"
close to the upper limits are CO, H_2, H˙ and some other
carbon containing compounds (5 b)iii). Equilibrium calcula-
tions indicate that all the carbon not existing as CO
should exist as graphite with a small proportion as acetylene.

Table 18

Mass Produced per Run (0.092 Moles of Mixture)
and Bulk Density of Detonation Carbons

Fuel Mixture	Mass grams.	Yield on total carbon in fuel, %	Density g/cc
35.5% Benzene	0.51[+]	21.6	0.0070
43.0% Furan	0.016		0.0033
55.0% Furan	0.44	18.2	0.0070
56.2% Ethylene	0.037*		0.043
62.4% Ethylene	0.40*		0.0090
67.3% Ethylene	0.43*	29.0	0.011
58.3% Ethylene 8.5% Ammonia	0.26*		0.0131
59.4% Ethylene 7.7% Ammonia	0.20*		0.012
62.1% Ethylene 4.2% Ammonia	0.33*		0.0094
64.5% Ethylene 2.4% Methane	0.36*		0.0147
57.2% Ethylene 7.7% Methane	0.34*		0.0081
53.3% Ethylene 11.2% Methane	0.25*		0.0092
41.1% Ethylene 21.8% Methane	0.16*		0.015
34.9% Ethylene 31.1% Methane	0.088*		0.028
20.8% n.Decane	0.22[+]	9.6	0.021
36.5% n.Butane	0.16		0.022
37.5% n.Butane	0.20	12.1	0.018
25.6% Xylene	0.035[+]		0.013
26.5% Xylene	0.10[+]	4.3	0.036

[+] Mass corrected for elevated initial temperature (lower gas. density).

* Carbon formed in 2" dia. detonation tube. Mass corrected for different initial gas mixture volume.

Figure 27

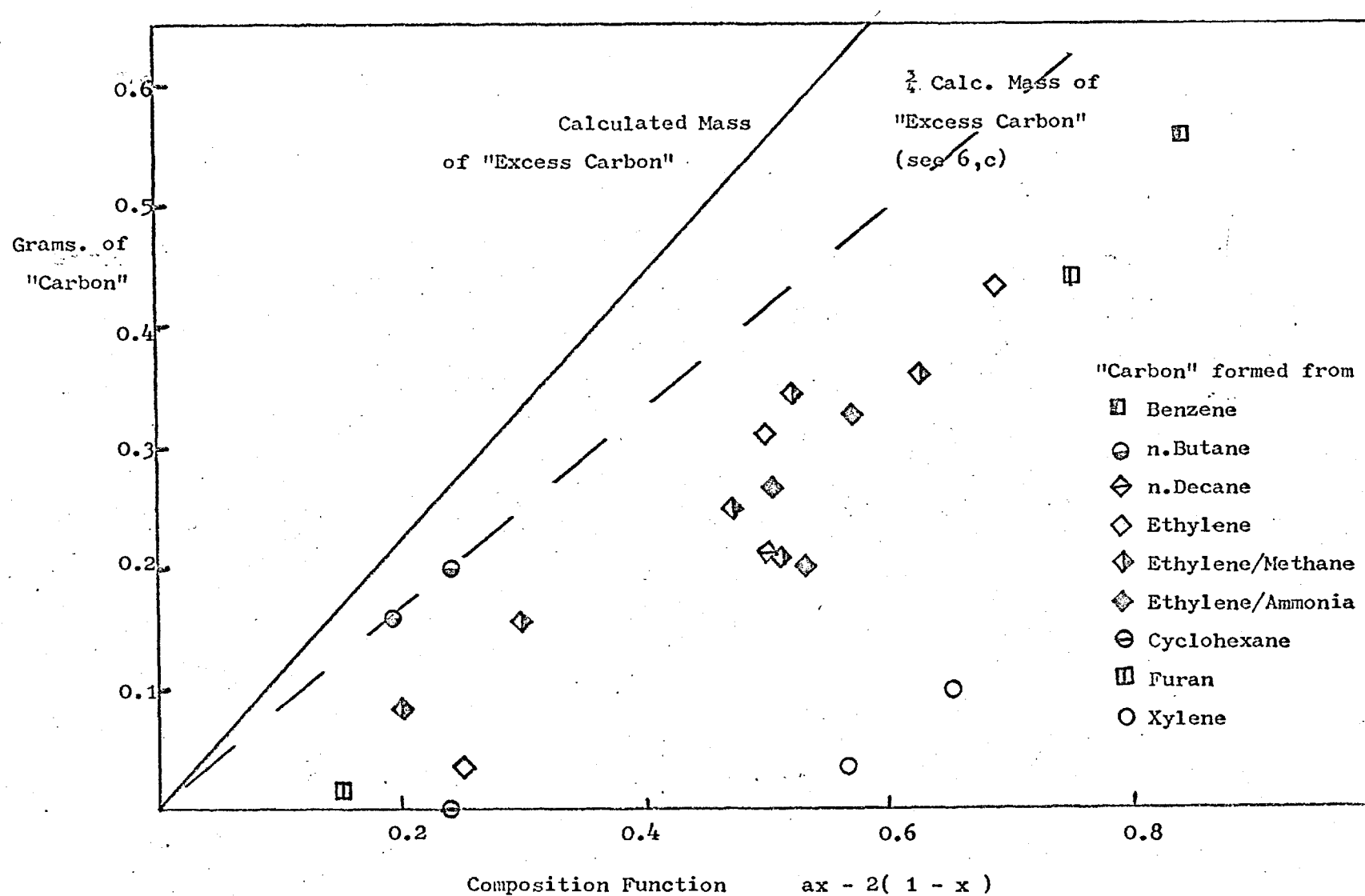Mass of "Carbon" Produced per Mixture in Detonation Tube (0.092 Moles)

(The amount of carbon as acetylene should never exceed about $^1/10$th of that as graphite). It is therefore instructive to compare the quantity of solid produced in a detonation with the calculated amount of "excess carbon" in the mixture.

The amount of excess carbon is given by the equation (see 5 b) iii).

$$xC_aH_b + (1-x)O_2 \longrightarrow 2(1-x)CO + \underline{/a}x - 2(1-x)\underline{7}C + \frac{bx}{2} H_2$$
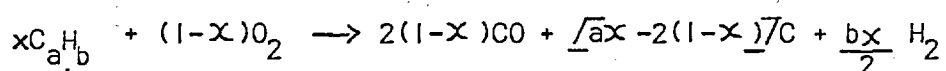
I mole mixture $\longrightarrow \underline{/a}x - 2(1-x)\underline{7}$ moles of "excess carbon".

When filled to 1 atm at room temperature $(20^\circ C)$ the test section of the detonation tube holds 0.092 moles of reactant mixture. The weight of excess carbon in the mixture is therefore given by $0.092 \times 12 \times \underline{/a}x - 2(1-x)\underline{7}$ grams.

Fig 27 shows the actual weights of solid collected from a series of mixtures plotted against the factor $\underline{/a}x - 2(1-x)\underline{7}$. A simple straight line of slope 0.092×12 grams gives the calculated weight of "excess carbon" for each mixture and is the same for all hydrocarbons. (In the case of furan the factor 'a' must be replaced by "a - 1" in the expression to account for the oxygen in the molecule). For those mixtures which were detonated at elevated initial temperatures the weight of solid collected has been corrected to allow for the reduced number of moles in the reactant mixture. (The weights of solid produced are also listed in Table 18).

In most cases the weight of carbon in the solid collected was about 60% of the weight of "excess carbon" (assuming the solids contain about 90 - 95 wt% carbon). Losses from the collection procedure would be less than 5%.

The remainder of the "excess carbon" probably existed as methane and other volatile hydrocarbons. In one case a full final product analysis (ref 4) of an upper limit butane/ oxygen mixture has verified that a significant quantity of methane was formed, but this operation was too laborious to be applicable generally in the present work.

The degree of general agreement in Fig 27, indicates that
the quantity of "carbon" produced is mainly a function of
the total quantity of carbon in the initial mixture and is
not greatly affected by the nature of the hydrocarbon fuel
molecule. As was found with C/H ratios, the agreement is
better at greater quantities produced (above about 0.15 grams).

Xylene was the main exception to this trend, as it also was
when limit energies were compared (see fig 21). This was
again possibly a consequence of its "condensed" molecular
structure.

Yields of "carbon" expressed as a fraction of the total
carbon in the mixture are also shown in Table 18 for the
fuel rich limit compositions of different fuels. (For
each fuel this should be the composition with the maximum
yield, as the "excess carbon" will be greatest).

v) <u>Bulk Density</u>

Measured bulk densities of the "carbons" are listed in
Table 18.

Electronmicroscope pictures show that the small particles
of about 300$\overset{\circ}{A}$ diameter of which the "carbons" are made up
are strongly bound together in a loose floc structure.
The density of the flocs is a function of their size. The
more rapidly the basic particles come together after
formation, the larger and lighter the flocs that are built
up. (ref 23).

An important factor determining the rate of collision of the
particles is their number concentration. Fig 28 is a plot
of the bulk density of the "carbons" v the mass of "carbon"
produced (per 0.092 moles of mixture), which is proportional
to the number concentration.

An approximate correlation exists between the density and
mass of "carbon" produced. The larger masses of "carbon"
are formed with lower densities, as would be expected from

Bulk Density v. Mass Produced per Mixture for Detonation Carbons
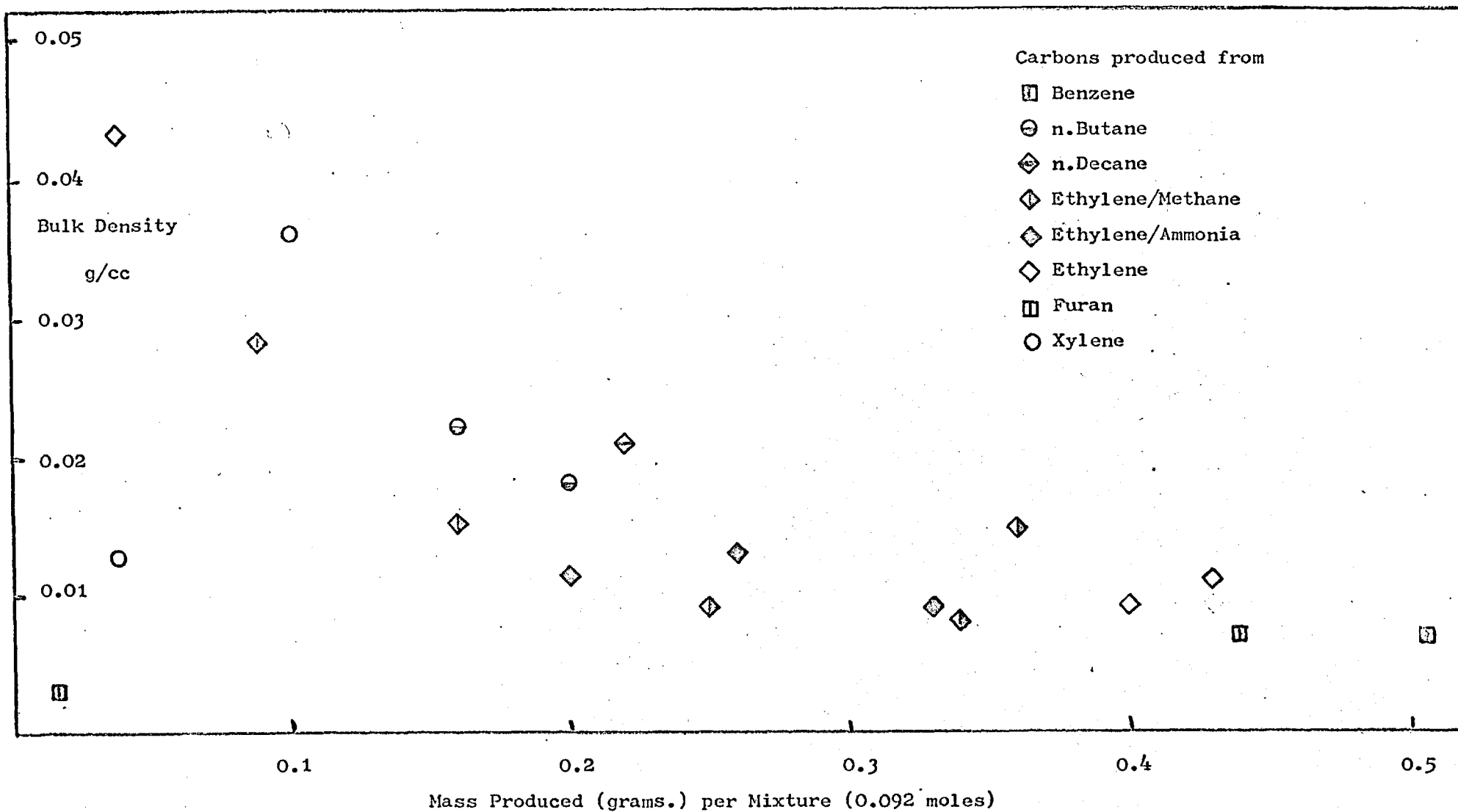
theories discussed in ref 23. As was found with other parameters, the correlation does not apply for smaller masses (below about 0.15 grams/0.092 moles of mixture)

In general, the density of the "carbon" produced seems not strongly dependent on the initial hydrocarbon molecule.

b) Detailed Investigation of Solid Products from Ethylene Rich Detonations

"Carbons" formed in detonations were sufficiently unusual, having such abnormally low bulk densities, to warrant a further detailed investigation of their properties. The results yielded significant information as regards the structure and possible mode of formation of the "carbon" and have been reported in detail in ref 23. Those aspects are reported and discussed here that are particularly relevant from the standpoint of the present work on detonation.

This investigation was restricted to "carbons" from ethylene rich detonations since it was not feasible to gain further information as to effect of the fuel molecule on the "carbon" produced. However though it had proved impossible to pin down the C J composition in fuel rich detonations from equilibrium calculations (see 5 b) iii)), comparisons between the properties of detonation carbon and other carbon blacks gave strong evidence as to the possible intermediate C J products in its formation.

i) X Ray Diffraction

X ray diffraction studies of detonation carbon showed a "graphitic" structure of intermediate crystallinity between carbon blacks and graphite* but similar to acetylene carbons.(ref 24) *(see fig 30). Crystallite sizes ($L_c \sim 25\text{Å}$) were of the same order as acetylene carbons and graphitised carbon blacks but larger than in carbon blacks ($L_c \sim 14\text{Å}$)

ii) Texture and Microstructure

Electronmicrographs of the "carbon" showed basic particles of around 300Å diameter joined in very large aggregates (see fig 29) at least 10 times larger than any found for carbon blacks (ref 25). Acetylene black has the largest aggregates of any

Figure 29

Photomicrographs of Detonation Carbon

Electron Microscope   Optical Microscope

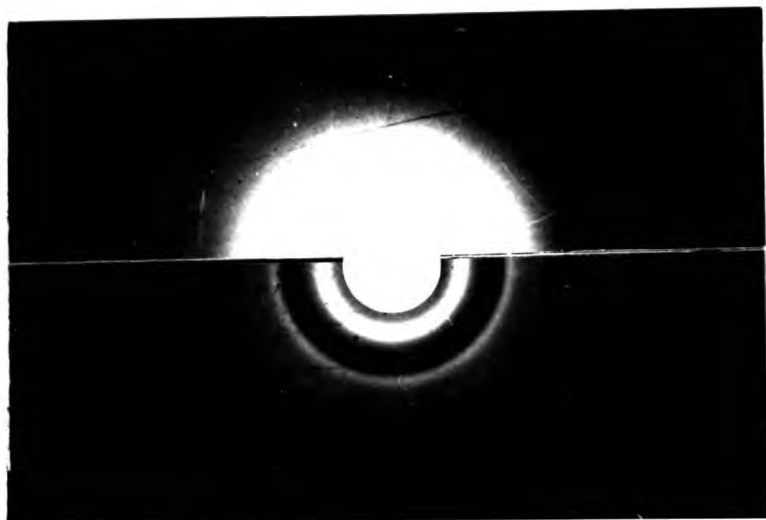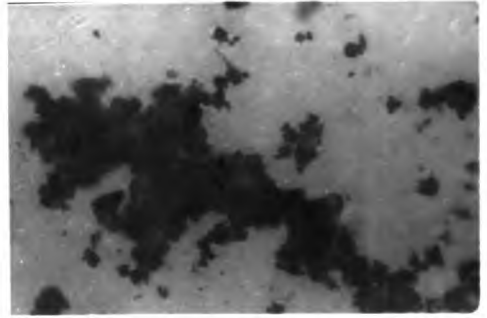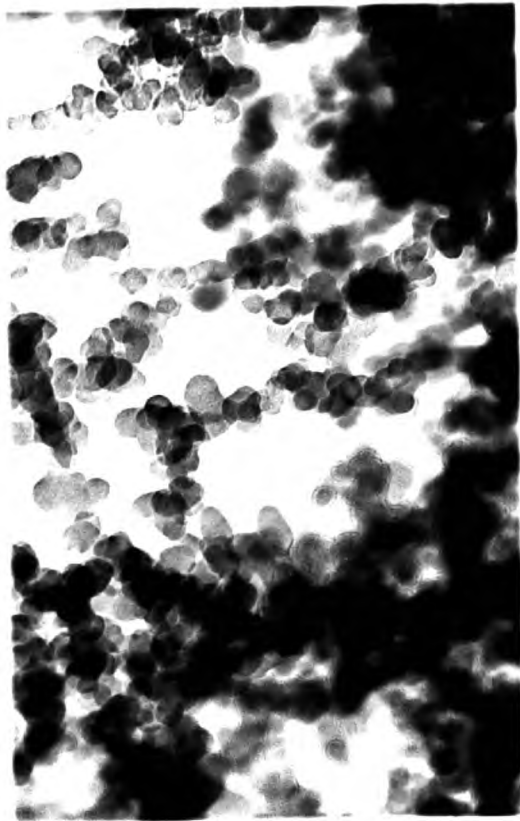|———————|

1 mm.

|———————|

0.1 μ

|——|

10 μ

(For these micrographs the detonation carbon used was in fact
that produced from n butane rich mixtures.)

Figure 30

X-Ray Powder Diffraction Photographs

Detonation Carbon from Fuel Rich Ethylene Mixture

Multicrystalline Pyrolytic Graphite for Comparison

carbon blacks and is again the most similar in properties to detonation carbon.

iii) Basic Particle Density

Detonation carbon just sank in a bromoform/chloroform mixture of density 2.2 g./c.c. This can be taken as a measure of the basic particle density (ref 26). It can be compared with a value of about 1.4 g./c.c. for most carbon blacks; again the properties of acetylene black are nearest ($\sim$1.8 g./c.c.)

iv) Chemical Tests

Intercalation :

A sample of detonation carbon was suspended in a stream of concentrated nitric acid vapour. The weight uptake of vapour by the "carbon" was measured for increasing partial pressures of acid vapour. Intercalation proceded to about one quarter of the total required for complete conversion to first stage compound. (ref 23). Similar tests on flame carbon blacks have shown no intercalation at all. This indicated a more graphitic structure and larger crystallite size for detonation carbon than carbon blacks, more in line with acetylene carbon.

Dissolution in Nitric Acid :

Detonation carbon did not completely dissolve in concentrated nitric acid on boiling for five hours. Using the same test, Norowitz and Galan (ref 27) found that carbon blacks completely dissolved whereas acetylene black did not.

Wetting :

Detonation carbon was not wet by water, like acetylene black, but unlike carbon blacks (ref 28). From general information about the surface chemistry of carbon blacks, this would suggest that oxygen atoms, linked e g, as hydroxyl, carbonyl or peroxide groups, are not present in the surface of the particles. Even carbons containing large proportions of oxygen (such as those from benzene and xylene) were found not to be wet by water. The tentative conclusion drawn in 6 a) iii) may therefore be in error and the oxygen present may be sorbed or combined throughout the particles, not just at the surface.

v)   Compressibility and Resistivity

An extensive study was made of the compressibility and
resistivity of detonation carbon. Although this revealed
other information about the nature of detonation carbon, as
regards comparisons with other carbon blacks, the results
particularly indicated its large aggregate size.

vi)   Electron Spin Resonance

Electron spin measurements were made on a sample of detonation
carbon by Dr J A Orr at the University of Dundee. No unpaired
spin could be detected. This is in contrast to results on
carbon blacks (ref 29) where the presence of free radicals
gives rise to unpaired spins.

c)   Acetylene as a Possible Detonation Intermediate

It was apparent from these studies that "carbons" from ethylene
rich detonations had many properties in common with acetylene
carbon. This suggests that some detonation carbons may also be
formed from acetylene, the acetylene being an intermediate in the
degradation of some of the initial hydrocarbon fuel molecules.

Converging evidence for this is provided by the conclusion reached
in 5 b) iii) that the "excess carbon" in fuel rich detonations
exists as a C J product with a heat of formation between +25 and
+30 k cals /g atom of carbon. Possible C J products which could
contain the "excess carbon" are listed in Table 19 together with
their heats of formation. No product is within 15 kcals of the
required range except acetylene and methyl radicals, $CH_3 \cdot$

The formation of methyl radicals as a C J product in fuel rich
detonations seems unlikely on two grounds
a)   It was also concluded in 5 b) iii) that the "excess carbon"
      product must have a specific heat in the range 4 - 8 cals/
      $^{\circ}K/$ g atom of carbon for agreement between calculated C J
      and measured detonation velocities (fig 19). On this basis
      the methyl radical has a specific heat of approximately 14,
      well outside the required range, while acetylene has a
      specific heat of approximately 8.

Table 19

Heats of Formation per Carbon Atom

    (from elements in standard state at $298^{\circ}K$)

	C	171.3	kcals/g.atom of carbon in molecule or radical
	C_2	100.0	
Gaseous	C_3	63.2	
Radicals	CH	142.4	
	CH_2	68.9	
	CH_3	33.5	
(Acetylene)	C_2H_2	27.1	
	C_2H_4	6.2	
	C_6H_6	3.3	
(Anthracene)	$C_{14}H_{10}$	$\simeq 1$	
(Coronene)	$C_{24}H_{12}$	0 - 5 (estimated)	
	C_2H_6	- 10.1	
	CH_4	- 17.8	

Data taken from NASA SP 3001 (1963)

b) Detonation reaction times are generally of the order of 10^{-6} sec (ref 30). Whereas any methyl radicals formed would be expected to have recombined in less than 10^{-9} sec even at $150^{o}C$ (ref 31). The existence of methyl radicals as an intermediate product at the C J plane seems unlikely.

It therefore seems a plausible hypothesis that the "excess carbon" in the hydrocarbon fuel rich detonations studied in the present work exists as acetylene. Behind the detonation wave an explosion wave may be supposed to occur in which the "carbon" is formed from the acetylene (such a second wave has been reported by Cher and Kistiakowsky (ref 15) in benzene and acetylene rich detonations with oxygen). On this hypothesis, for the different fuels used, the "carbons" are all produced via the same intermediate, the similarity found in such properties as C/H ratio and bulk density is therefore to be expected.

It is evident from fig 27 (6 a) iv)) that only around 60% of the "excess carbon" finally forms the solid product. Johnson and Anderson (ref 32) suggest that at high temperatures ($>1000^{o}C$) acetylene forms solid carbon by the reaction,

$$2C_2H_2 \longrightarrow 3C + CH_4$$
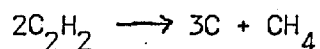
On this basis only 75% of the "excess carbon" would be expected as solid. Such a line is plotted in fig 27 and certainly gives closer agreement with the experimental results. Exact agreement from such simple stoichiometry considerations can hardly be expected. That methane is likely to be the other major final product besides solid "carbon".has already been indicated by a final product analysis of a butane rich mixture (6 a) iv)).

It should also be noted that where "carbon" is formed by pyrolysis from methane and other hydrocarbons by processes such as shock heating (ref 33), argon plasma arc heating (ref 34) and flash photolysis (ref 35) acetylene is reported as an intermediate. Similar to detonation, these processes also involve high temperatures with rapid heating and quenching, compared with the conditions of formation of flame carbon blacks.

There are however some objections to the hypothesis of acetylene formation at the C J plane which must be considered.

i)   It is a necessary assumption that the equilibrium product, solid carbon, is not formed at the C J plane. The rate of the condensation reaction producing solid carbon must be so slow that it becomes separated from the detonation reaction. Detonations have been reported however in which condensation of a solid product must have occurred before the C J plane for agreement between measured and calculated velocities to be obtained. Examples include the detonation of pure acetylene in which solid "carbon" is formed (ref 36), tetramethyl silane/oxygen mixtures forming silica (ref 18) (see also 8 e) iii)), diborane/air mixtures forming boric oxide (ref 37) aerosols of aluminium powder and oxygen forming alumina (ref 38).

Results of Kistiakowsky et al (ref 39) on the detonation of acetylene/oxygen mixtures showed that agreement between calculated and measured velocities could be obtained assuming no condensation of solid carbon at the C J plane for compositions upto about 70% acetylene (excess carbon first occurs at 50% acetylene). At compositions greater than 70% acetylene the energy contribution from the formation of an increasing proportion of solid carbon must be included for agreement between theoretical and measured velocities.

For a 70% acetylene, 30% oxygen mixture the proportion of "excess carbon" is about 43% of the total carbon in the initial hydrocarbon. The maximum proportion for any mixture detonated in the present work was about 41%, for fuel rich limit mixtures of benzene.

These results are consistent therefore with the hypothesis that, for detonations where the proportion of "excess carbon" is less than around 40%, the solid carbon is not formed sufficiently rapidly to contribute to the detonation, but for proportions of "excess carbon" greater than this an increasing proportion of the solid carbon is formed before the C J plane.

(For the detonation of pure acetylene considered above the proportion of "excess carbon" is 100%). Indeed for benzene/ oxygen detonations at compositions just before the fuel rich limit, the measured velocity is about 10% greater than that calculated assuming acetylene is a C J product (see fig 10) which suggests that some solid carbon is formed at the C J plane in this case.

The assumption that solid carbon is not formed at the C J plane of the majority of hydrocarbon fuel rich detonations studied in this work is consistent with results of previous workers.

ii) Much of the evidence for the formation of the acetylene is based on agreement between calculated C J and measured detonation velocities. It is possible however that solid carbon is indeed formed at the C J plane but, as a result of some form of energy loss, by the detonation, the velocity is below that calculated theoretically. The energy loss might result from processes connected with the condensation of the solid phase, radiation from the "carbon" particles is a possibility, and therefore not be apparent in fuel lean detonations.

It is evident that further experimental work is required before the C J product composition in fuel rich detonations can be definitely established (see chapter 9).

ATTEMPTED DETONATION OF SOLID CARBON

Chapter 7 - Experimental and Results

As a series limit to the detonation of hydrocarbons of increasing molecular complexity, attempts were made to detonate an aerosol of solid carbon.

The "carbon" produced in fuel rich limit hydrocarbon deonations was used. It had a small particle size ($\sim 300\overset{\circ}{A}$), giving it an equivalent molecular weight of only about 10^7, and was readily available.

a) Carbons Aerosols

One of the major difficulties in attempting to detonate a carbon/oxygen mixture was to disperse the carbon in the oxygen. In order to achieve a uniform dispersion the carbon flocs should be broken up into the basic $300\overset{\circ}{A}$ diameter particles.

The particles were very strongly held together. This made the flocs very large and light (ref 23). And even if the particles were once dispersed they would recombine very rapidly. No stable aerosol of $300\overset{\circ}{A}$ particles (at the number concentration required for stoichiometric combustion with oxygen) could be achieved. Indeed, complete dispersion of any powder with particle diameter less than $10,000\overset{\circ}{A}$ has not yet been achieved (ref 40).

Attempts to generate a satisfactory aerosol of the carbon flocs by stirring or allowing them to fall down a vertical tube were completely unsuccessful. This was apparent from the sedimentation velocity and from the extinction of light by the aerosol both of which indicated a floc diameter of the order already determined.

b) Formation of Carbon Aerosols by Shock Wave

The only satisfactory method found for breaking up and dispersing the flocs was by a shock wave, generated in the detonation tube prior to the attempted initiation of detonation.

A detonation tube similar to that described in 3 b) was used with the 9' and 5' lengths of the test section reversed and separated

by a thin aluminium foil diaphragm (fig 31) which burst at about
1.5 atm pressure difference. 0.3 g of "carbon", the stoichiometric
quantity (to form CO_2) for the 9' section, was spread in the 5'
section near the diaphragm and the whole test section was evacuated.

A ball valve connecting the 5' section to a reservoir of oxygen
was opened and the subsequent pressure rise burst the diaphragm
and generated a shock wave sufficient to break up and disperse the
carbon along the 9' section at a final oxygen pressure of 1 atm.

As a preliminary experiment in order to test the adequacy of the
aerosol dispersion the "carbon" was allowed to settle and its
distribution along the tube was measured. After about 5 minutes the
aerosol had settled and the "carbon" was swept out of successive
25 cm sections of the tube. For this purpose, a thin plastic disc
of the same cross-section as the tube (1" diameter) with a segment
of about 120° removed and attached to a long rod was used. The
disc was pushed the required distance into the tube with the cut
out segment facing downwards and rotated through 180°. All the
"carbon" in that portion of the tube was then removed when the disc
was withdrawn. Results for a typical aerosol are shown in fig 32
as the mole % of "carbon" in oxygen along the tube calculated from
the mass found in each 25 cm section of the tube. Despite the
large variation in mole % of carbon, the theoretical combustion
energy was greater than 12 k cals/mole (a typical figure for the
limits of hydrocarbon/oxygen detonations) for all aerosol
concentrations over the first 150 cms of the test section. Over
this length, the aerosol dispersion was therefore considered
adequate for attempted detonation.

c) Attempted Detonation of Aerosol

Aerosols were generated as described and explosion was initiated
from a detonating primer section, as was used with fully gaseous
mixtures (see 3 e)). Light (photomultipliers and photodiodes)
and ionisation probes were used to follow the explosion. Outputs
from the probes were amplified and fed to a Textronix 555 oscillo-
scope.

Sharp pulses (relative to the time scale involved) were recorded
by the ionisation probes which indicated a shock wave travelling

Figure 31

Aluminium Foil

Diaphragm

Dispersed Carbon Section

Primer Section

Ball Valve

Probes

Ball

Valve

Vacuum Line

Resevoir

Needle Valve

Oxygen

Cylinder

Distribution of Carbon in Aerosol

Figure 32

40
Mole%
Carbon
in Aerosol

30

20

10

Composition corresponding to

12 kcals/mole theoretical

energy release

Aluminium   200   150   100   50   Ball
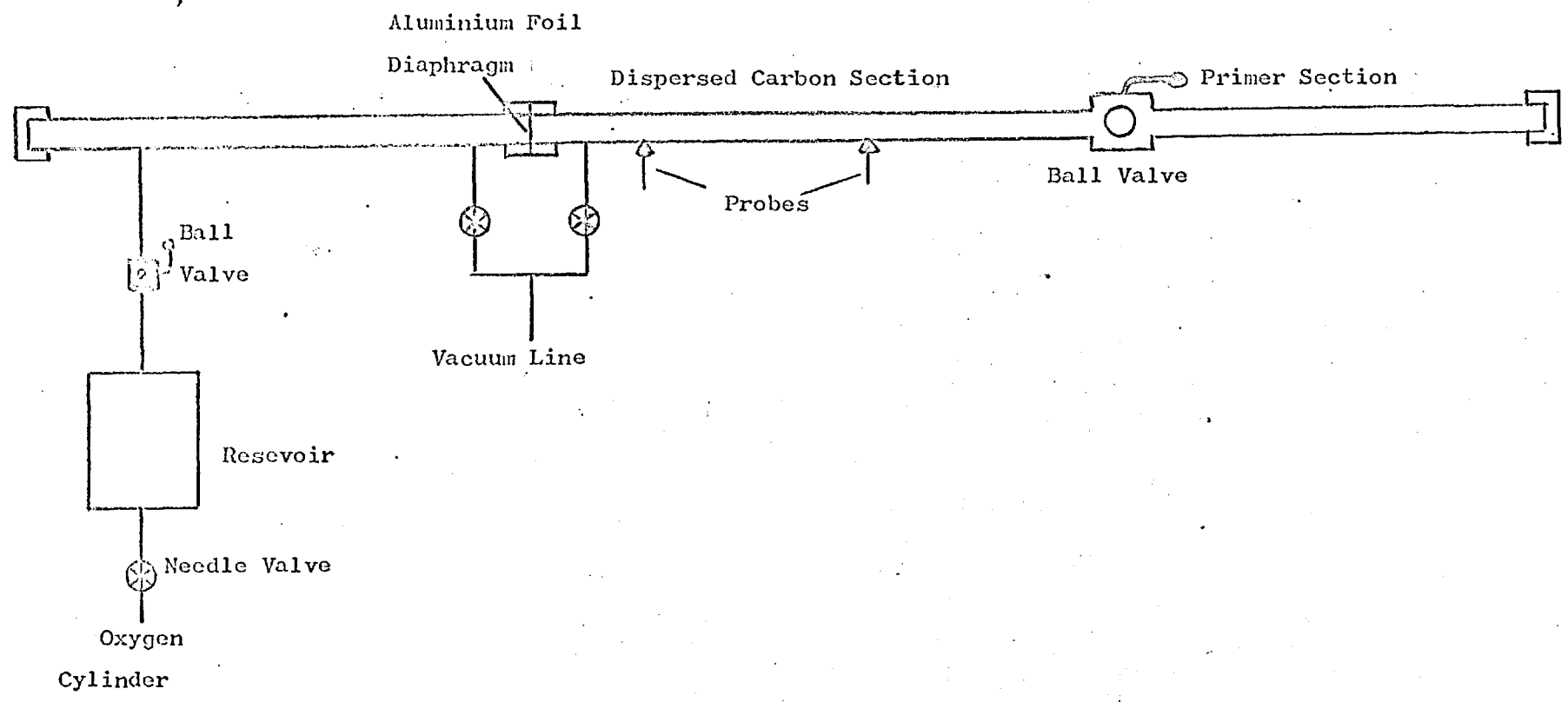Diaphragm   Valve

Distance along Tube   cm.
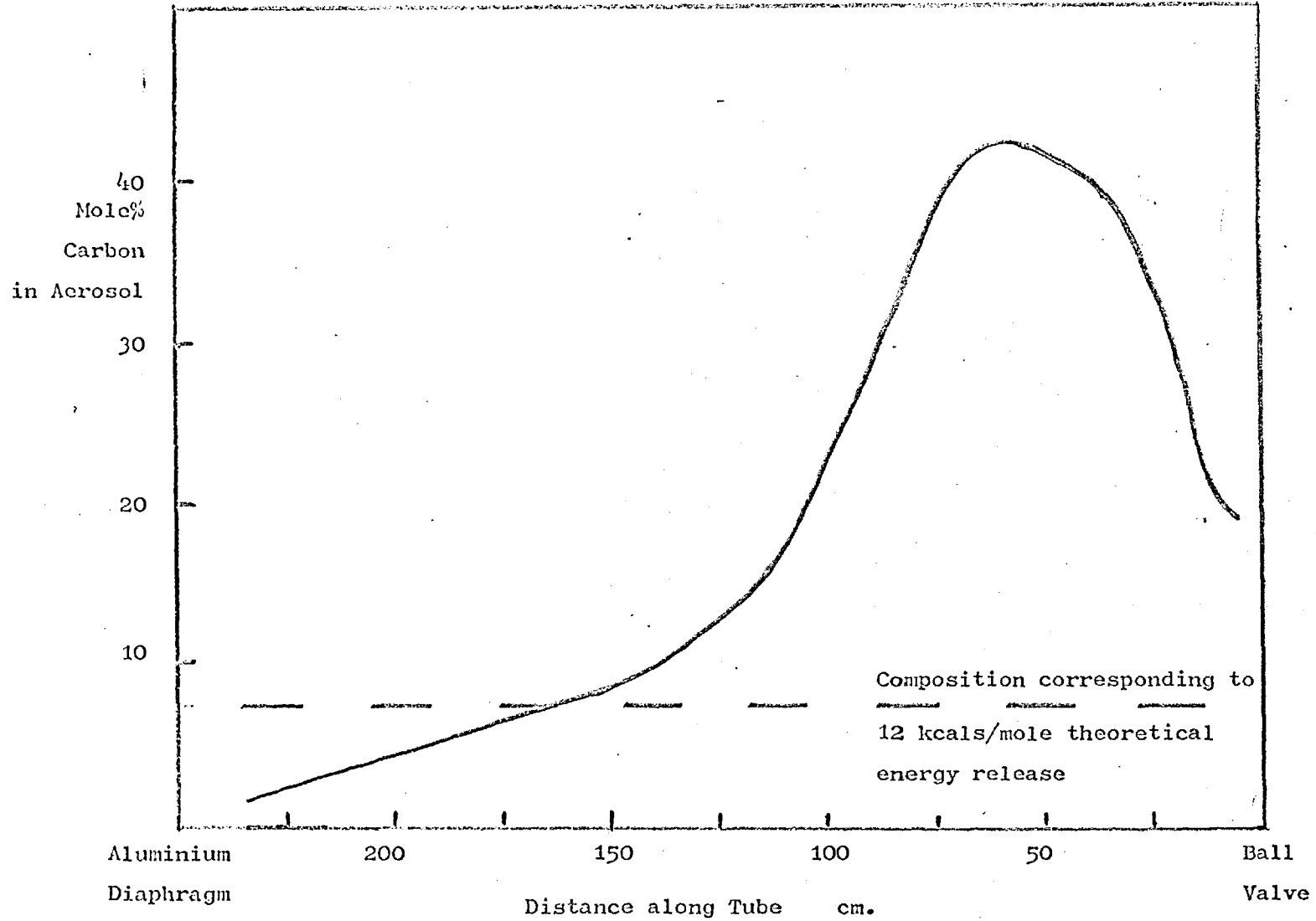
at about 1200 m/sec (fig 33).

/On firing primer mixture into pure oxygen, similar pulses were recorded for a shock wave travelling at about 800 m/sec7 Longer pulses (see fig 33) were recorded by the photomultipliers and photodiodes, indicating a combustion wave travelling at about 500 m/sec through the aerosol.

When the experiment was repeated with only a trace of "carbon" used to generate the aerosol, a combustion wave was still recorded at about 500 m/sec, and was therefore independent of the quantity present.

Discussion

From these results it is evident that the propagation of the shock wave was assisted by the combustion of the "carbon". Also, detonation waves have frequently been recorded with velocities as low as 1200 m/sec. However, for a detonation wave to propagate, the combustion wave (or reaction zone) must travel at the same average velocity as the shock wave, otherwise they will become detached. In this case, therefore, stable detonation of the "carbon" aerosol was not achieved. The "carbon" could not burn sufficiently rapidly to release more than a small proportion of its combustion energy for acceleration of the shock wave.

A rough estimate can be made of the energy required to drive the shock wave at 1200 m/sec instead of the speed of 800 m/sec to which it would naturally have attenuated.

Considering the shock wave equation (11)

$$\frac{H_s - H_l}{RT_l} = \tfrac{1}{2}\gamma M^2 (1 - \sigma_s^2)$$

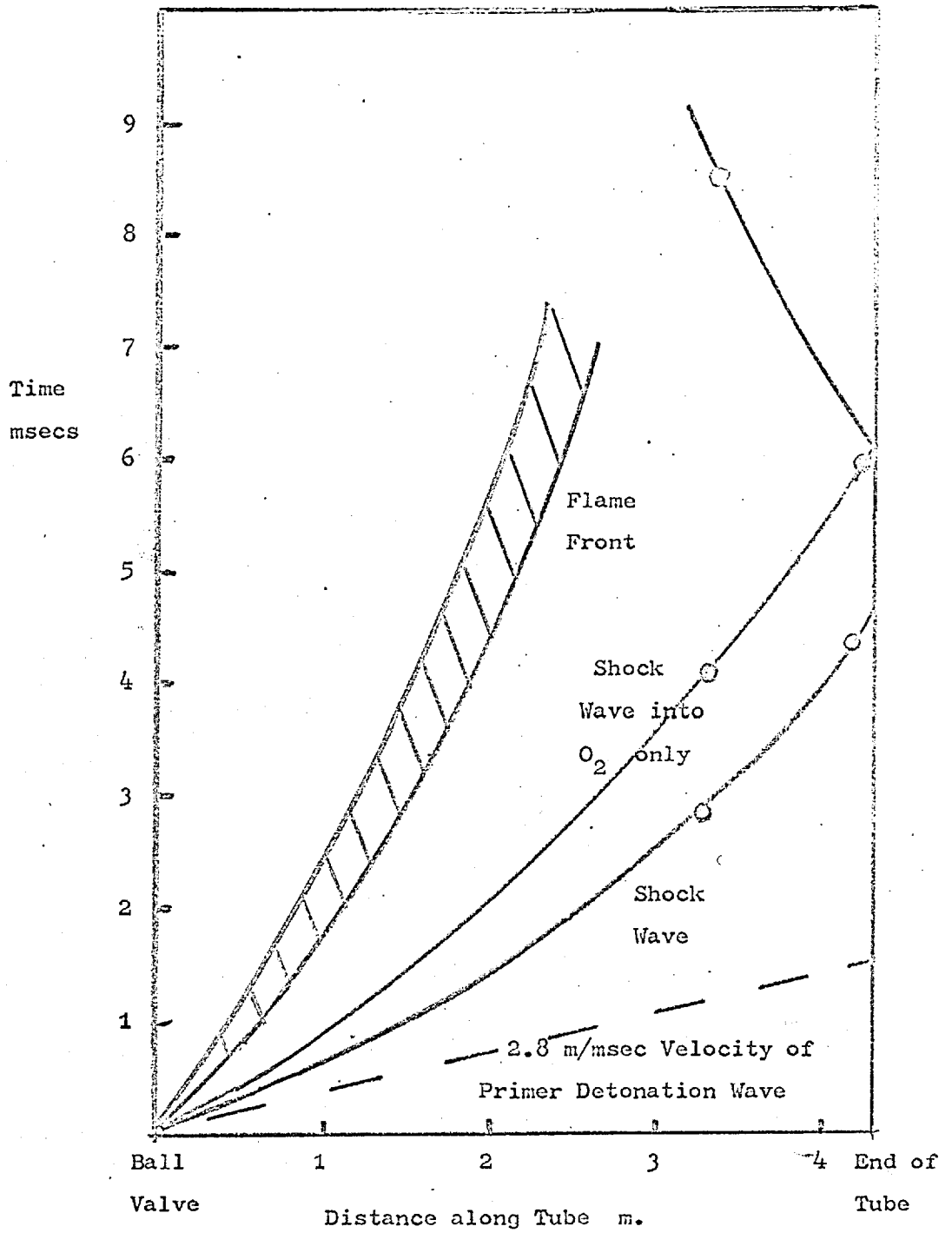then $\quad H_s - H_l = \tfrac{1}{2} U_l^2 (1 - \sigma_s^2)$

if the enthalpy is measured in mechanical energy units.

σ_s is generally small of the order of 0.25

$$\therefore \quad H_s - H_l \sim \tfrac{1}{2} U_l^2$$

Figure 33

Shock and Combustion Waves in Carbon/Oxygen Aerosols

Therefore any change in kinetic energy of the wave would require an approximately equal change in enthalpy difference across the wave. For a wave in an oxygen/carbon aerosol to change in speed from 800 to 1200 m/sec would require an extra energy release of approximately 2.6 kcals/mole.

Taking an average mixture of 30 mole % carbon, the energy of combustion to CO_2 would be 0.30 x 94 = 28 kcals/mole.

Therefore as a rough estimate one tenth of the total available combustion energy was fed forward to augment the shock wave. The figure of 2.6 kcals/mole can be compared with the typical minimum energy release for hydrocarbon/oxygen lower limit detonations of 12 kcals/mole.

d)   Attempted Detonation of Carbon in Hydrogen/Oxygen Mixtures

One possible reason for the long induction period of the carbon (i e the separation between the shock front and the combustion wave) which possibly prevented stable detonation, was that the initiating shock was not sufficiently strong.

The shock in the previous experiments was produced by a stoichiometric hydrogen/oxygen mixture detonation in the priming section. The shock wave from a detonation driver is closely followed by a rarefaction wave which interfers with the shock as it slows down on leaving the priming section. This further rapidly attenuates the shock.

For this type of detonating driver with a velocity of 2800 m/sec, the initial Mach number is 4.9. From the results in figure 33, after 1.5 m secs, the shock Mach number has fallen to less than 3.

A non attenuating shock wave can be generated by a bursting diaphragm. However, to obtain a shock strength of 4.9, a pressure ratio of over 100 across the diaphragm is required. The low pressure must be at least 1 atm to sustain a detonation, which means a driving pressure of over 100 atm. This was not feasible with the apparatus available.

As an alternative means of producing a non-attenuating shock, it was decided to attempt to burn the carbon in an oxygen rich, hydrogen/oxygen mixture. If the carbon was capable of burning sufficiently rapidly to sustain a detonation, the energy from the reaction should accelerate the hydrogen/oxygen detonation. A 40% hydrogen mixture was used which has a detonation Mach number of about 5.1.

The system of dispersing the carbon initially by a shock could not be used as the shock also ignited the hydrogen/oxygen mixture. A rarefaction wave was tried as a means of dispersing the carbon without igniting the mixture, however the carbon was very poorly distributed and the flocs were not broken up. However calculations suggested that a detonation wave should pick up and disperse "carbon" particles in about 10^{-9} sec, so the "carbon" was spread mechanically along the tube and a 40% hydrogen/oxygen mixture was detonated over it.

The velocity of the wave was measured to within $\pm 0.2\%$ with ionisation probes and photomultipliers by means of the oscilloscope delay. There was only about a 4% increase in velocity when carbon was present. However the photomultiplier signals were recorded about 5 μsec sooner than the corresponding ionisation probe signals and also were about 50% larger when carbon was present.

This increased and advanced light signal is probably due to glowing carbon particles in the detonation wave. They would increase the luminosity of the wave and, by scattering light forward, cause the signal to be observed earlier than expected.

An SLM type PZ6 pressure transducer was fixed in the side of the tube to follow the pressure history of the detonation. The transducer had a rise time of 2 μsec. The sharp pressure rise at the shock front caused it to ring excessively. The pressure time profile for the wave was approximately the same in each case. This suggests that the "carbon" was not appreciably altering the thermodynamic properties of the wave itself.

All these results indicate, that though the carbon was increasing the luminosity of the detonation wave, it was burning too slowly to effect the thermodynamics of the detonation and cause it to travel significantly faster.

A 4% increase in detonation velocity would mean approximately an 8% increase in γ_M^2. As $\gamma_M^2 \propto Q$ then this would correspond to approximately an 8% increase in energy release by the detonation. A 40% hydrogen/oxygen mixture would have an energy release of approximately 17 kcals/mole. The increase in energy release in the wave from the carbon combustion must be therefore approximately 1.4 kcals/mole of mixture, which again corresponds to roughly one tenth of the available energy from carbon combustion.

This result illustrates that only an insignificant proportion of the energy of combustion of the carbon was accelerating the detonation wave. No account has been taken of the small energy loss to the detonation of accelerating the carbon particles upto its particle velocity ($\sim$0.2 kcals/mole).

e) Possible Factors Inhibiting Detonation

From all these experiments it seems there is some limiting factor causing the long induction period and preventing a carbon/oxygen detonation. Possible limiting factors are considered.

i)   There is insufficient energy in the chemical reaction to sustain a detonation:- For a 50/50 mole % carbon/oxygen mixture (stoichiometric for forming CO_2) the detonation velocity is calculated as 2.0×10^5 cm/sec. The C J pressure is 30 atm and the C J temperature is $3000^\circ K$. By comparison for a 40% hydrogen/oxygen mixture, the detonation velocity is 2.1×10^5 cms/sec, the C J pressure is 17.5 atm and the C J temperature is $3250^\circ K$.

These figures are fairly comparable. The 40% hydrogen/oxygen mixture is well inside the detonation limits which suggests that there is no thermodynamic reason why the carbon/oxygen system cannot support a detonation.

ii) The flocs are not broken up sufficiently rapidly (if at all) by the shock wave.

If the flocs are not broken up by the initiating shock wave, the chemical reaction rate will be too slow to support a detonation.

No data exists on the breaking up of flocs in shock waves, however there are some papers on the breaking up of oil drops in shock waves. (e g refs 41, 42).

The first paper quotes some drop break up times for drops upto 2900μ diameter. For drops of this size the break up time is of the order of 300 μsec. The carbon flocs had diameters of around 40μ.

In the second paper the approximate relation is found,

$$U_c^2 D \sim 10^6$$

where $U_c \doteq$ shock velocity in ft/sec

D = the minimum drop diameter for drop to be broken up(μ)

At the detonation velocity (2 x 10^5 cms/sec), the critical diameter works out at 3 x 10^{-6} cms or 300Å, which by coincidence is the smallest particle diameter.

If it is assumed that a liquid drop is held together more firmly than a floc of solid particles of the same diameter, both these results suggest that the flocs should break up in a time much less than the measured induction period ($\sim$ 2 msecs)

iii) The heat and momentum transfer rates to the particles in the shock wave are not sufficiently rapid.

First the smallest interparticle distance must be compared to the mean free path in the gas, to see whether bulk transport properties apply. At 3000°K and 30 atm the mean free path is 3.2 x 10^{-7} cms. The interparticle distance for 300Å

particles in stoichiometric oxygen is approximately 3×10^{-5} cms. Therefore the inter particle distance is much greater than the mean free path and property gradients can be set up. The bulk transfer properties apply.

The relaxation distance, or the distance behind the shock wave before the particles reach equilibrium with the gas was estimated from the calculations performed in two papers.

relaxation distance $\sim 10^{-4}$ cms   (ref 43)

relaxation time $\sim 4 \times 10^{-10}$ secs

relaxation distance $\sim 2 \times 10^{-4}$ cms   (ref 44)

relaxation time $\sim 10^{-9}$ secs

These figures are only estimates and only strictly apply to shock waves, not detonation waves. However these times are so much less than the measured induction periods that they cannot be a limiting factor.

iv)   The chemical reaction rate of even the 300Å carbon particles with oxygen is not sufficiently rapid.

The rate controlling step for very small carbon particles ($<1\mu$) at high temperatures ($> 1000°C$) is the absorption of oxygen on the surface (ref 45). Figures in this reference give an estimated burning time,

$$t_b = 8.3 \times 10^{-4} \text{ secs}$$

also $t_b = 2 \times 10^{-4} \text{ secs}$ (ref 45)

$t_b = 10^{-5} \text{ secs}$ (ref 47)

All these estimates give much greater times than the relaxation time and also the first estimate is of the same order as the measured induction period ($\sim 10^{-3}$ secs).

It seems likely therefore that the limiting factor preventing detonation of carbon/oxygen aerosols is the chemical reaction rate. Detonation has been reported, however, for other heterogeneous fuel/ oxidant mixtures and these will now be briefly considered.

f)   Other Reported Heterogeneous Detonations

i)   Aluminium Powder

Since these experiments on carbon were performed, Strauss (ref 37)
has succeeded in detonating mixtures of aluminium powder in
oxygen.   The detonation tube had a diameter of 1" , was 9' long
and was mounted vertically.

Detonations were observed in mixtures of Al powder and flake
in oxygen from 52 to 68 mole % Al at initial conditions of 1 atm
and room temperature.   (The upper limit of 68% was dictated
by the apparatus).   The detonation velocities and pressures
were measured.   They were only a few percent lower than the
theoretically calculated values for equilibrium at the C J plane.

The equilibrium mixture contained a large proportion of Al_2O_3
(it is the stoichiometric product at 57.2% Al).   As this does
not exist as a vapour, in order to provide sufficient energy
for the detonation it must have condensed before the C J plane.
The observed reaction zone thickness was less than 20 μsec
so the reaction from solid Al to liquid Al_2O_3 must have been
very rapid.

The Al particles were much larger than the basic carbon
particles used in the present work.   The powder had an
average size of 5 μ and the flake of 40 μ.

Calculations from experimental data (ref 48) suggests that
the burning rate of such particles would be even slower than
the carbon flocs.

However the energy liberated in the reaction of Al to Al_2O_3
is approximately 110 kcals/mole of stoichiometric mixture
compared with only 47 kcals for C to CO_2.   Also Al vapourises
at around 2600°K requiring 50 kcals/mole of mixture while
carbon does not until 4000°K requiring 100 kcals/mole of
mixture, which is greater than the maximum possible energy
release.   Therefore it is possible that the Al powder is
able to vapourise sufficiently rapidly to permit detonation
with chemical reaction in the vapour phase, while "carbon"
is not.

ii)   Liquid Hydrocarbons

Detonation has been reported for liquid hydrocarbons in oxygen
dispersed both as aerosols (refs 49, 50) and a thin film on
the tube wall (refs 51, 52). In both cases it is thought that
the chemical reaction occurs almost exclusively in the vapour
phase. The shock rapidly evaporates a sufficient quantity of
hydrocarbon to propagate a detonation wave. Only a very small
proportion ($\sim 1\%$) of the total energy release is required to
evaporate the liquid.

iii)   Coal Dust Explosions

Much experimental work has been done on explosions of coal dust
suspensions in air in experimental galleries. In some cases
explosion waves have been recorded with speeds as great as
2000 m/sec (ref 53). Some doubt does exist as to whether these
are truely stabilised detonation waves or merely the decaying
shock wave caused by the initiator of the explosion (usually
a large explosive charge). Coal dust also contains a large
proportion of volatiles which could burn rapidly behind the initial
shock wave in the vapour phase.

DETAILED SUMMARY FOR PARTICULAR FUELS

Chapter 8 - Effect of Molecular Complexity on Detonation

The various fuels detonated will now be considered separately.
Results of previous workers are also discussed, using the methods
of analysis developed in this work.

a) Paraffins

A trend of theoretical energy release with molecular size is apparent
at both the fuel rich and fuel lean detonation limits (see figs 17,
21). The same trend is also observable with the corresponding parameters
of homology composition and shock temperature (Tables 15, 16). The
lower energy releases (and shock temperatures) required for the
detonation of larger paraffin molecules may be due to the greater
ease of radical formation.

No significant difference in fuel lean limit energies is observable
between straight chain paraffins and the cyclic paraffins, cyclohexane
and decalin. The fuel rich limit energy of cyclohexane was, however,
about 20% higher than might be expected from the trend in fig 21.

The fuel lean limit of adamantane, a paraffin with a very condensed
structure (see fig 34) could not be determined with the same precision
as other hydrocarbons as mixtures with oxygen spontaneously exploded at
the high temperatures required for vaporisation.

For adamantane the lower limit energy lies in the range of 11.0 to
13.7 kcals/mole of mixture. This is only slightly greater than the
value for paraffins of a similar size (see fig 17) and does not
indicate a very great effect due to its condensed ring structure.
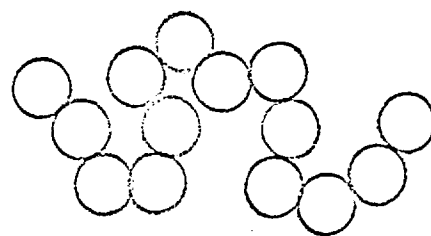
b) Olefins

Limit energies of the simple olefins, ethylene and propylene
(calculated from quoted limits (ref 4)) follow the molecular size
trend. Their detonation characteristics are not significantly
different from those of the corresponding paraffins.

Figure 34
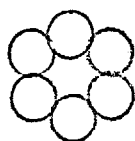
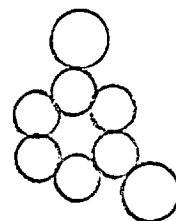## Schematic Carbon Skeletons of More Complex Hydrocarbon
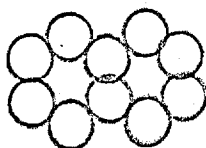
Molecules Detonated
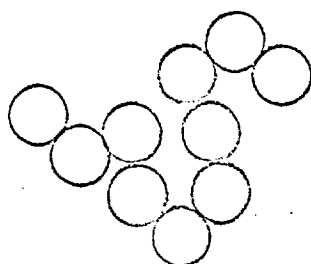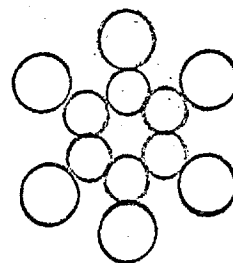
n decane

n hexadecane
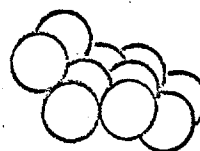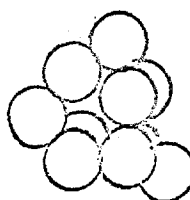
benzene

xylene (meta)

naphthalene

hexamethyl-benzene

cyclohexane

decalin (cis)

adamantane

c)   Acetylene

Detonation limit energies for acetylene can only be compared approximately with those of corresponding hydrocarbons because of differences in experimental set up (ref 17). Limit energies are certainly of the same order but somewhat less than those found for other hydrocarbons of similar molecular size. Acetylene has a significantly greater heat of formation per carbon atom than other hydrocarbons (see Table 19) which may account for the limit energies being somewhat less.

d)   Aromatics

i)   Benzene C_6H_6

The detonation limits of benzene compare with those for paraffins of similar molecular size (see figs 17, 21). However, some points of interest do arise from a general consideration of previous results of other workers.

The detonation velocities of benzene/oxygen mixtures have been determined by Cher and Kistiakowsky (ref 15) and of mixtures with oxygen and air by Fraser (ref 16).

Fraser's results for benzene/oxygen mixtures agree well with those of the present work (the experiments were also carried out in a 1" dia tube at 1 atm but at $100^{o}C$) and both agree with the theoretical C J velocities (see fig 10). However, Cher and Kistiakowsky's results (from a 2" dia tube at room temp and pressures upto 0.75 atm) for mixtures containing upto about 20 mole % benzene give velocities about 7% below theoretical.

In the present work, no significant change in velocity could be detected when initial pressures of 0.75 atm were used. As Cher and Kistiakowsky also initiated their detonations from an overdriven priming section, the different experimental conditions can hardly account for these discrepancies between results.

Cher and Kistiakowsky observed a secondary wave following the detonation wave in certain mixtures. The wave was characterised by light emission and occured about 10 μsecs behind the first

wave. They suggest that the deficit in velocity is due to incomplete reaction at the C J plane and that the second wave is that of the final stage of the reaction going to completion.

A second wave has also been reported in some propylene/oxygen mixtures (ref 4) however, no corresponding deficit in velocity is observed (see fig 23).

The fuel rich limit found by Cher and Kistiakowsky was around 40 mole % benzene (at room temperature). This difference in fuel rich limit with temperature (35 - 36% at $120^{\circ}C$ in the present work) is about the same as observed for butane/oxygen mixtures. (see 5 b) iv)). It corresponds to a difference in limit energy of about 9 kcals/mole/$100^{\circ}C$.

Fraser's results for benzene/air detonations are in agreement with the theoretically calculated velocities. He reported that over a certain range of compositions (4.0 - 5.2 mole % benzene) however he was unable to initiate detonation. Apart from this region, mixtures could be detonated between 1.6 and 5.55%. These limits correspond to theoretical energy releases of 12.1 and 15.6 kcals/mole (corrected to $120^{\circ}C$) and agree well with these for benzene/oxygen mixtures. No such gap in the detonating composition range was found for benzene/oxygen mixtures. In the present work a similar gap was found for hexamethyl-benzene/oxygen mixtures, see 8 d) iii).

The effect of the complexity of the benzene molecule on detonation is therefore apparent under the slightly different conditions used by previous workers.

ii)   Xylene (commercial) C_8H_{10}

The fuel lean detonation limit of xylene was in agreement with that for hydrocarbons of similar molecular size (see fig 17). The curve of velocity v composition, however, showed a slight deviation (upto 5%) from the theoretical near the fuel lean limit. (The relevant portion of the curve is shown on an expanded scale in fig 11). This inflection in the curve indicates that perhaps incomplete reaction occured in detonations

over a certain range of compositions. As the drop in velocity corresponded roughly to that found by Cher and Kistiakowsky with benzene, it may have been due to the same effect.

Xylene was the largest hydrocarbon molecule with a condensed structure for which fuel rich limits could be determined in the present work. Some effects of molecular complexity were apparent in fuel rich mixtures.

The fuel rich limit occured at an energy release about 20% higher than might be expected from the trend with molecular size (see fig 21) and the measured velocity in fuel rich mixtures was upto 10% greater than that theoretically predicted assuming acetylene was a C J product (see fig 11). Also, the mass of solid carbon produced was less than $^1/$5th of that from corresponding mixtures of other hydrocarbons (see fig 27).

The presence of 15% of ethylbenzene in the commercial xylene mixture was not considered important for a survey investigation such as the present work. Both hydrocarbons are similar in molecular structure and other properties.

iii)   Hexamethyl-benzene $C_{12}H_{18}$

The fuel lean detonation limit of this hydrocarbon also followed the trend with molecular size (fig 17). A similar inflexion in the velocity composition curve occured as in the case of xylene (fig 13). However the drop in velocity was so great as to cause a narrow failure region beyond which detonation was again possible upto the "true" fuel lean limit. (c.f. benzene/air mixtures, 8 d) i)).

Theoretical detonation velocities have been calculated assuming that the reaction goes to completion at the C J plane, forming CO_2 and H_2O and also assuming incomplete reaction, forming CO and H_2O (fig 13). Previous workers have suggested that CO rather than CO_2 may be the intermediate C J product in

certain hydrocarbon detonations (see e g ref 15). While
measured velocities at the "true" limit agree closely with the
theoretical values for complete reaction, those close to the
intermediate region of detonation failure do agree more
closely with theoretical values assuming CO is formed at the
C J plane.

iv) Naphthalene $C_{10}H_8$

This hydrocarbon required a higher fuel lean limit energy
release than any other investigated (see fig 17). Naphthalene has
a rigid planar molecular structure, as opposed to the other
C_{10} compounds investigated, which may account for the greater
energy release required for stable detonation. Despite this
deviation in limit energy from the trend for other hydrocarbons,
the measured detonation velocities agreed well with those
theoretically predicted (fig 16).

e) Hydrocarbon Molecules with Heteroatoms

i) Oxygen Containing Compounds

These compounds (acetone and methanol) approximately followed
the trend in limit energies (figs 17, 21). The results obtained
for furan (ref 12) are also in close agreement.

As a result of its relatively large heat of formation, compared
with other hydrocarbons, acetone reaches a fuel rich detonation
limit at a composition far richer in oxygen than that which is
stoichiometric for CO + H_2. Significant quantities of H_2O are
therefore also present in the C J products (c.f. 5 b) iii)).
This increases the specific heat of the mixture above that for a
mixture of diatomic CO and H_2 and probably accounts for the
limit energy release being somewhat above that indicated by the
trend with molecular size.

It may be added that this general agreement in limit energies
between hydrocarbons and compounds such as acetone suggests
that the critical step in detonation propagation cannot be
just simple pyrolysis of the fuel molecule by the initial shock.
Oxygen containing molecules such as acetone pyrolyse much more
readily than pure hydrocarbons yet the detonation limits are
not significantly wider.

ii) Chlorinated Hydrocarbons

Detonation of mixtures of simple chlorinated hydrocarbons with oxygen has been reported (ref 19). Theoretical fuel lean limit energies computed from the results are listed in Table 15. As the work was performed in a 20 mm diameter tube the limits have been adjusted by the method of Pusch and Wagner (ref 22) in order to make comparison with limits found in 1" (25.4 mm) diameter tubes. The correction required was only slight, the limit energies being increased by 4%. For fuel rich limit mixtures, the temperature was too high ($\sim 3000^{\circ}$K) for a simple product composition to be worked out. Theoretical limit energies could not therefore be easily computed.

Fuel lean limit energies are of the same order as those for corresponding hydrocarbons, except for C_2Cl_4. This also applies to CCl_4 which did not detonate at any composition, though a maximum theoretical energy of 34 kcals/mole is available. A tentative conclusion can therefore be drawn that the fuel lean detonation limit of hydrocarbons is not greatly effected by the substitution of chlorine atoms in the molecule, provided some hydrogen atoms are still present.

iii) Tetramethylsilane

Detonation of tetramethylsilane/oxygen mixtures has been investigated (ref 18).

Interpretation of the results is complicated by uncertainty as to whether the product SiO_2 exists as gas or a condensed solid at the C J plane. In fig 24 the results have been plotted on the basis $\gamma M^2/Q$ v $C/C+O$ assuming both possible states of the product. The results for a hydrocarbon with the same C/H ratio, ethane (ref 4) have also been plotted for comparison. In fuel lean mixtures it would appear that the SiO_2 exists in gaseous form at the C J plane, while in fuel rich mixtures it is necessary to include the condensation energy of SiO_2 to achieve reasonable agreement between theoretical and practical velocities.

The fuel rich and fuel lean limit energies have been calculated assuming these different states of the product, SiO_2. At both

limits the agreement with hydrocarbons of similar size is good. This indicates that the existence of a silicon hetero-atom does not alter the detonating characteristics of the molecule.

Unpublished results on the quantity of solid products in fuel rich mixtures indicate that, if it is assumed that all the Si in the fuel forms solid SiO_2 then the amount of solid "carbon" formed is about 60% of the calculated "excess carbon". This is again in agreement with the results found for pure hydro-carbons (see 6 a) iv)).

iv) Thiophene and Trimethylamine

Fuel rich mixtures of ethylene and both these compounds have been detonated in oxygen (ref 54).

A mixture of 53.2% C_2H_4 6.1% C_4H_4S and 40.7% O_2 yielded 0.267 grams of "carbon" (per 0.092 moles of mixture) on detonation. The corresponding quantity of "excess carbon" for the mixture was 0.494 moles. A mixture of 48.5% C_2H_4, 10.4% $N(CH_3)_3$ and 41% O_2 yielded 0.256 grams of carbon (per 0.092 moles of mixture) and the corresponding quantity of excess carbon was 0.462 moles.

Both these quantities agree with those measured for pure hydrocarbons (c.f fig 27). The amount of "carbon" produced is not seriously affected by the existence of heteroatoms in the organic fuel molecule.

f) Heterogeneous Systems

Detonation of heterogeneous fuel/oxidant systems is possible where rapid evapouration of the condensed phase can occur (see 7 f)).

For carbon/oxygen aerosols the possibility of such rapid evaporation seems unlikely and calculation showed that the heterogeneous reaction rate was probably insufficient to support detonation. The results of this work confirmed that detonation of such an aerosol was not possible.

Chapter 9 – Conclusions and Suggestions for Further Work

a) Conclusions

The main result of a practical nature of the present work is that fuel lean and fuel rich limit energies of all hydrocarbons over the wide range studied show little variation. The width of the detonable composition range varies by less than 10%, measured on an energy basis, between all hydrocarbons investigated.

This correlation between limit energies, together with the observed trend with molecular size, enables the detonation limits for many hydrocarbon molecules to be predicted quite accurately on a composition basis. A typical example might be to predict the detonation limits of any isomer of hexane. If the fuel lean limit energy is assumed to be in the range 11 – 13 kcals/mole (see fig 17) then the corresponding composition range is 1.06 – 1.26 mole % fuel. Taking the fuel rich limit energy to be in the relatively broad range of 15 – 25 kcals/mole (see fig 21), the limit composition is restricted to the range of 29.7 – 26.5 mole % fuel. Caution must be exercised, however, in applying such predictions to complex molecules, such as naphthalene, and those with relatively large heats of formation per carbon atom (see 8 c) and 8 e) i)).

This general agreement in limit energies between hydrocarbons is also indicative of agreement between other parameters of detonation such as final temperature and shock temperature (see 5 b) ii)). It is not possible therefore to draw any specific conclusions as to why a particular value of theoretical energy should correspond to a detonation limit. The variation of limit energies with molecular size, larger molecules requiring generally smaller energies, does, however, yield information about the possible mechanism of detonation.

Michels (ref 4) from his results on smaller molecules, suggested that the controlling factor in detonation might be the breaking of the weakest bond in the fuel molecule, thus initiating radical formation. Indeed a correlation between such bond energies and homology limit compositions was apparent for paraffins upto C_5.

However the results of Steiner et al. (ref 55) suggest that the weakest bond energies for normal paraffins reach a minimum for C_4 (3.80 eV for $C_2H_5 - C_2H_5$) and that the weakest bond energy for C_8 (4.66 eV for $C_4H_9 - C_4H_9$) is greater than that for C_1 (4.56 eV for $CH_3 - H$). An alternative explanation must be sought for the greater ease of detonation for larger molecules.

At the relatively high pressures existing in detonation reaction zones, it has been suggested that oxidation is initiated by a bimolecular process rather than pyrolysis of the fuel molecule (ref 30). For a bimolecular process the collision frequency is proportional to the square of the molecular collision radii and is only weakly dependent on the molecular masses. Thus the rate of collisions per fuel molecule is more than twice as great for n decane than for methane with oxygen for mixtures with the same energy release. If such a bimolecular mechanism does occur, the observed trend of smaller limit energies with increasing molecular size is to be expected.

This simple mechanism does not account entirely for the behaviour of larger aromatic molecules. Possibly the higher than expected fuel lean limit energy required for naphthalene is a function of the molecule being two dimensional and, therefore, having a relatively much smaller collision diameter than the equivalent paraffin. Non aromatic ring compounds, such as decalin, have a three dimensional structure (see fig 34).

As for the intermediate failure region found between approximately 20 and 16 kcals/mole for hexamethyl-benzene, it may be a result of the methyl groups and the aromatic ring being oxidised by different mechanisms which become sufficiently out of phase as to inhibit the stability of the detonation wave. With the assumption that the aromatic ring is able to oxidise completely before the C J plans and yet the methyl radicals merely recombine to form ethane as an intermediate, the theoretical energy release for a composition of 1.3 mole % fuel (see fig 13) becomes about 9 kcals/mole in approximate agreement with the energy release at 0.55 mole %, the fuel lean limit.

This theory would also explain the inflexion in the velocity composition curve of xylene. Assuming in this case that the methyl radicals are not oxidised before the C J plane, the theoretical energy release at

the inflexion (1.6 mole % fuel, see fig 11) becomes 11.2 kcals/mole which, if it is assumed that the inflexion occurs at conditions which correspond to a limit, can be compared with the fuel lean limit energy release of 11.0 kcals/mole. Such a mechanism could not however explain the intermediate failure region found by Fraser in benzene/air mixtures.

By comparing detonation of different fuels on the basis of limit energy releases, as developed in the present work, it is also apparent that substitution of heteroatoms into hydrocarbon molecules has no great effect provided some hydrogen is still present in the fuel molecule. Whereas limit energies of C_2Cl_4, C_2N_2, CO (and CCl_4) are all significantly greater than those for corresponding hydrocarbons (see Table 15 and 8 e) ii)). This result also cannot be explained on the basis of weakest bond energies. All these compounds, except CO, contain bonds at least 20% weaker than the C – H bond in methane, yet detonate less readily.

Previous workers (refs 56, 57) have suggested that the radical chain branching reaction,

$$H^. + O_2 \longrightarrow OH^. + O^.$$

is critical for the initiation of detonation.

Though the present work does not seem to support this conclusion in the case of hydrocarbons (no correlation between limit energies and the proportion of hydrogen in the fuel is apparent), it may be that when hydrogen is absent from the fuel molecule other, slower chain branching mechanisms are necessary and these become the critical step to detonation.

For heterogeneous mixtures, the critical step for detonation becomes rapid evaporation of the condensed phase to permit gas phase reaction. Though in the case of liquid hydrocarbons sufficiently rapid evaporation can occur, it cannot with carbon/oxygen aerosols and thus detonation is not feasible.

b)   Suggestions for Further Work

Various possibilities for further investigations are suggested by
the results of the present work.

Larger Molecules

Effects of molecular complexity on detonation observed in this work
were relatively small. To further investigate the phenomenon, detonation
of larger molecules than those which could be used in the present work
is necessary. This would complete the range of molecular sizes studied
between hydrocarbons around C_{16} and the solid carbon.

Larger molecules could not be investigated in the present work because
of limitations set by the maximum operating temperature of the
apparatus ($200^{o}C$). A detonation tube operating at higher temperatures
is practicable (indeed Sokolik (ref 13) operated at temperatures upto
$490^{o}C$, but on a mixture which was gaseous at room temperature).
Construction of satisfactory vacuum tight mixing vessel for over $200^{o}C$
would certainly present serious difficulties and the possibility of
pre-oxidation of the fuel, as indeed occured in the present work with
adamantane, must certainly be considered.

An interesting possibility would be to compare detonation of larger
molecules in heterogeneous systems. Komov and Troshin (ref 52) have
detonated, with oxygen, thin films of fuels such as hexadecane, on
a tube wall. For such a system the corresponding parameter to
mixture composition is thickness of the fuel layer and plots of
detonation velocity versus thickness give a definite fuel lean limit
at about twice the theoretical energy release found in fully gaseous
mixtures.

Using molecules such as hexadecane which have also been detonated in
gaseous mixtures, as a basis, it should be possible to extend the
study of detonation upto the largest hydrocarbon molecules that have
been isolated, such as coronene, $C_{24}H_{12}$, by measurement of this
detonation limit. By some such technique as operating the tube at a
constant temperature below the boiling point of the fuel it should,
be possible to isolate the influence of the evaporation rate on the
stability of the detonation wave.

Such an investigation would be worthwhile as it would show the degree of fuel molecular complexity at which the stability of detonation was substantially effected. Interesting products might also be formed from the partial oxidation of such large molecules, perhaps similar to the "detonation carbons" in fuel rich mixtures, which would yield information on the mechanism of the detonation reaction.

Other Fuels

A study of detonation limits of other, non hydrocarbon, fuels would be of interest. Measured limit energies of some such fuels show a wide variation (see Table 15). Information about the radical chain branching mechanisms and the influence of bond strengths in the fuel molecule on detonation might be obtained. Possible fuels which could be investigated in the present apparatus include CS_2, HCN, B_2H_6 and PH_3. Detonation of the halogens with hydrogen could also be studied, though a nickel-steel apparatus would be required. It should be possible to compare the fuel lean limit energies of all such fuels directly.

Two Stage Energy Release

The intermediate failure region observed in the case of hexamethyl-benzene was considered to be a result of oxidation of different parts of the molecule occuring at different rates. Thus in mixtures detonating near the failure region a two wave structure might be expected as has been observed in other mixtures (e g ref 15).

Conditions of detonation stability could perhaps be investigated in such mixtures. If a small but significant quantity of a second fuel were added to mixtures of hexamethyl-benzene and oxygen it would be of great interest to see whether the fuel contributed to detonation propagation, as would be revealed by comparing measured and theoretical velocities, or even moved the position of the intermediate failure region to occur within a different range of energy releases.

A more refined technique for studying detonation than simply measuring velocities would probably be required in order to elucidate the complex wave structure. Optical techniques could be used or perhaps ionisation measurements as developed by Cavenor (ref 58) which not only show up the oblique shocks behind the wave as they intersect the tube wall but also provided information on another parameter besides

velocity which can be compared with its calculated C J value. It might be possible to correlate the structure and stability of the detonation wave with the chemical reactions occuring.

Such studies could also be carried out of the two wave structure of "carbon" forming fuel rich detonations. The presence of acetylene could be confirmed by observation of light absorption at a wave number of 3287 cm^{-1}. (Such a technique has been used to follow acetylene concentrations in shock waves (ref 59)). A detailed study of detonations producing around 40% excess carbon would be of interest as it appears that the energy release from condensation may start contributing to detonation propagation at proportions of excess carbon greater than this (see 6 c)).

Current investigations of gaseous detonation seem to be mainly of a physical nature, concerned with the detailed structure of detonation waves in a particular system, or of a chemical nature, such as the present work. For further investigations both physical and chemical effects might better be studied in conjunction.

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