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EFFECT OF ADDITIVES ON THE LEAN DETONATION LIMIT OF KEROSENE SPRAYS IN AIR

Final Report

by

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December 1980

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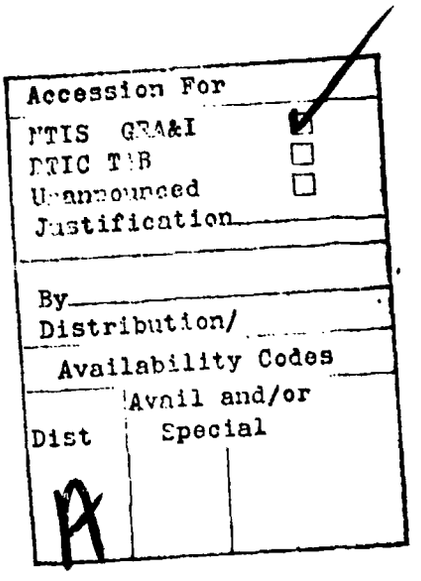
FOREWORD

This report summarizes the results on the research work performed under Army Research Office Grant No. DAAG 29-78-G-0074 which started in March 1978 and terminated in October 1979. During that period the University of Connecticut Research Foundation provided additional financial support through grant no. 0507-139.

The study covered by this report was under the direction of Professor E. K. Dabora, Department of Mechanical Engineering with Mr. James J. Murray of ARO as contract monitor and Dr. Norman Slagg of ARRADCOM as Scientific Liaison Representative.



ABSTRACT

A shock tube technique was used to determine the lean detonation limit of sprays of kerosene in air when the kerosene is sensitized by either propyl nitrate or butyl nitrite. The technique is described in detail and is used as a first step to determine the relationship between the detonation initiation energy and the initiation power for stoichiometric H_2^{Π}-air mixtures at .5 atmosphere. It is found that if the initiation energy, E is expressed in J/cm^2 and the power P, in Kw/cm^2, then $(E - 10)(P - 27) = 555$ J-Kw/cm^4. The method is also used to check on the lean limit of H_2^{Π}-air at atmospheric pressure. It was found that for an initiation energy of 50 J/cm^2 at P = 160 Kw/cm^2 (initiation M $\cong$ 3.5), the lean limit is between 10-14% H_2^{Π} in air. This value is somewhat lower than that found in the literature which is 18.2% H_2^{Π} in air.

Approximately the same energy and power were used to determine the lean limit of kerosene sprays. Monodisperse sprays having droplets diameter = 780 μm were used. Three equivalence ratios were tested: .59, .44, and .3. Kerosene was mixed with 10% and 20% of either propyl nitrate (PN) or butyl nitrite (BN). The results indicate that the addition of propyl nitrate reduces the limiting equivalence ratio, ϕ. Thus, for 10% PN the limiting ϕ is between .44 and .3; and for 20% PN, ϕ is below .3. Erratic behavior was detected when 10% BN was used. However, when 20% of BN was mixed in kerosene, the limiting ϕ was again below .3.

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I. INTRODUCTION

Two-phase detonations are currently of interest and the state of their understanding has been reported by Dabora and Weinberger (1) and Nettleton (2). One particular type of two phase detonations, namely spray detonations has been investigated in some depth within the last two decades. For example, the work of Dabora et al. (3) and Ragland et al. (4) dealt with the properties and structure of spray detonations as manifested in a constant area tube and that of Nicholls et al. (5) was concerned with cylindrical detonations. A more up to date work in the latter category is given by Bar Or et al.(6). Lu et al. (7) were concerned with the chemical and the physical processes effects on the detonation phenomenon and in particular found that certain additives to the fuel can affect the establishment of detonations.

More recently Dabora (8, 9) presented a theoretical model for spray detonations from which the critical energy and power required for initiation could be established. The model treats all three types of detonations: planar, cylindrical and spherical.

Despite the rather extensive work performed so far on spray detonations, the experimental difficulties involved have precluded the treatment of some aspects of the phenomenon in an exhaustive manner. For example, very few systematic studies have been conducted to determine the detonability limits. This situation is to be contrasted with the detonability limits of gaseous mixtures which are reasonably well-known for many different combinations.

Knowledge of detonability limits is of importance from at least two considerations: the fuel-air explosion (FAE) concept and hazards elimination.

In the former, one is interested in conditions that would insure the occurance of detonation and in the other, the conditions that would reduce the probability of detonations. So far the determination of limits seems to elude theoretical considerations alone, and therefore, almost all limits are based on either direct or indirect experiments.

The most important parameter in the determination of limits is the initiation energy. For detonable mixtures there is a minimum critical energy that is usually necessary to initiate a detonation, and for a given combination of fuel and oxidizer the minimum critical energy depends on the mixture ratio. Near-stoichiometric mixtures require the least critical energy but as the mixture becomes either fuel rich or fuel lean the critical energy increases. The composition limits are then reasoned to be those compositions that require inordinate amounts of energy before a detonation would occur. In principle, however, true limits are those that would not support detonation no matter how large the initiating energy is. Limits according to this definition would however be hard, if not impossible, to determine. A more practical approach is to define limits as those compositions that require an arbitrary order of magnitude higher energy than say the stoichiometric mixture would require for a detonation to take place.

Although the initiation energy seems to be the most important parameter, there is reason to believe that the rate of energy deposition to be of importance as well (10, 11). Thus, it can be argued, that there is a minimum initiation energy below which no detonation would occur no matter how high the power is, and that there is a minimum power below which no detonation would occur no matter how high the total energy is. This idea is explored somewhat in this report.

The main purpose of this report however, is to determine in a practical way the lean limit of kerosene spray in air, when two additives are mixed with kerosene: namely, propyl-nitrate and butyl-nitrate. Since one would expect that the limit is affected by drop size, the limit must be determined for each drop size. Unfortunately the scope of the work was limited because of time consideration, so that only sprays with drop size of the order of 800 μm were considered.

II. EXPERIMENTAL METHOD

1. Experimental Apparatus:

The shock tube technique was used to determine the lean limit. In this method a shock wave of finite strength is induced into the driven section of the shock tube which is prefilled by the desired mixture. The decay or the acceleration of the wave is observed. If no acceleration is observed, the mixture is deemed non-detonable. If however, acceleration is observed which is indicative of a detonation, the fuel air mixture is then leaned in subsequent runs until no detonation takes place and in this way the lean limit is identified.

The shock tube which was used in this study is described in detail in (12) and is shown schematically in Fig. 1. Briefly, the driven section of the tube is 9 ft. long with a 2" x 2" square cross-section. The tube is topped by a tee-section to accommodate a dump tank on the side. Another section on top of the tee accommodates a spray generator which is similar to the one described by Dabora (13). To insure a reasonable spray along the tube, the tube is oriented in the vertical direction. The driver section is circular in cross-section providing a driver to driven area ratio, $A_4/A_1 = 1.65$. The driver length is variable although in most of the tests a 6" driver length was used. The tube operates on the double diaphragm principle to insure diaphragm break up at a desired pressure ratio. The theoretically obtainable Mach numbers are shown in Fig. 2 when the driver gas is helium and the driven gas is air. Generally the actual Mach numbers obtained were closer to the $A_4/A_1 = 1$ curve.

The tube was provided with pressure switches at one foot intervals, starting at .5 ft. from the diaphragm. In addition, two piezoelectric pressure

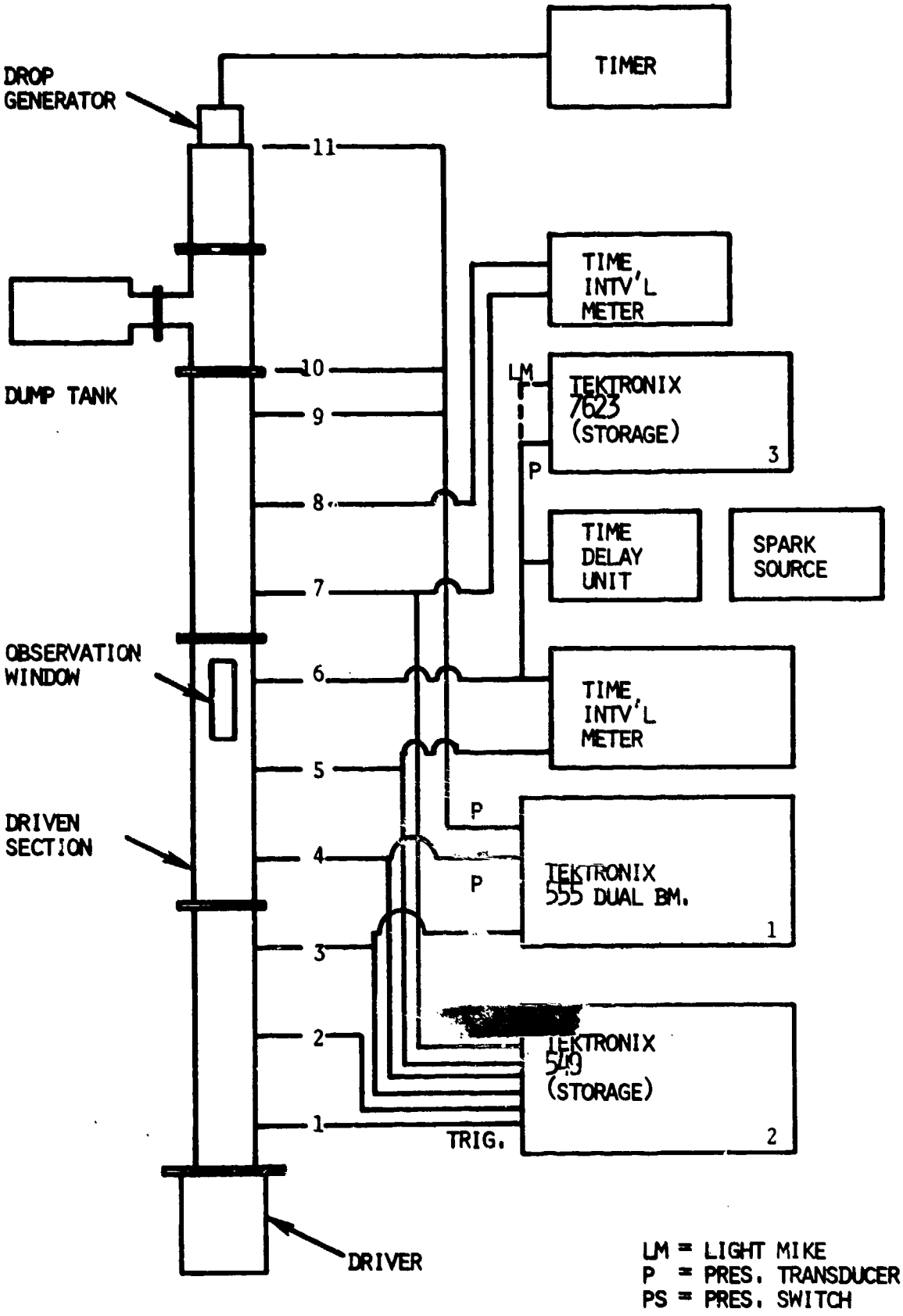


FIG. 1. SCHEMATIC OF TUBE AND INSTRUMENTATION

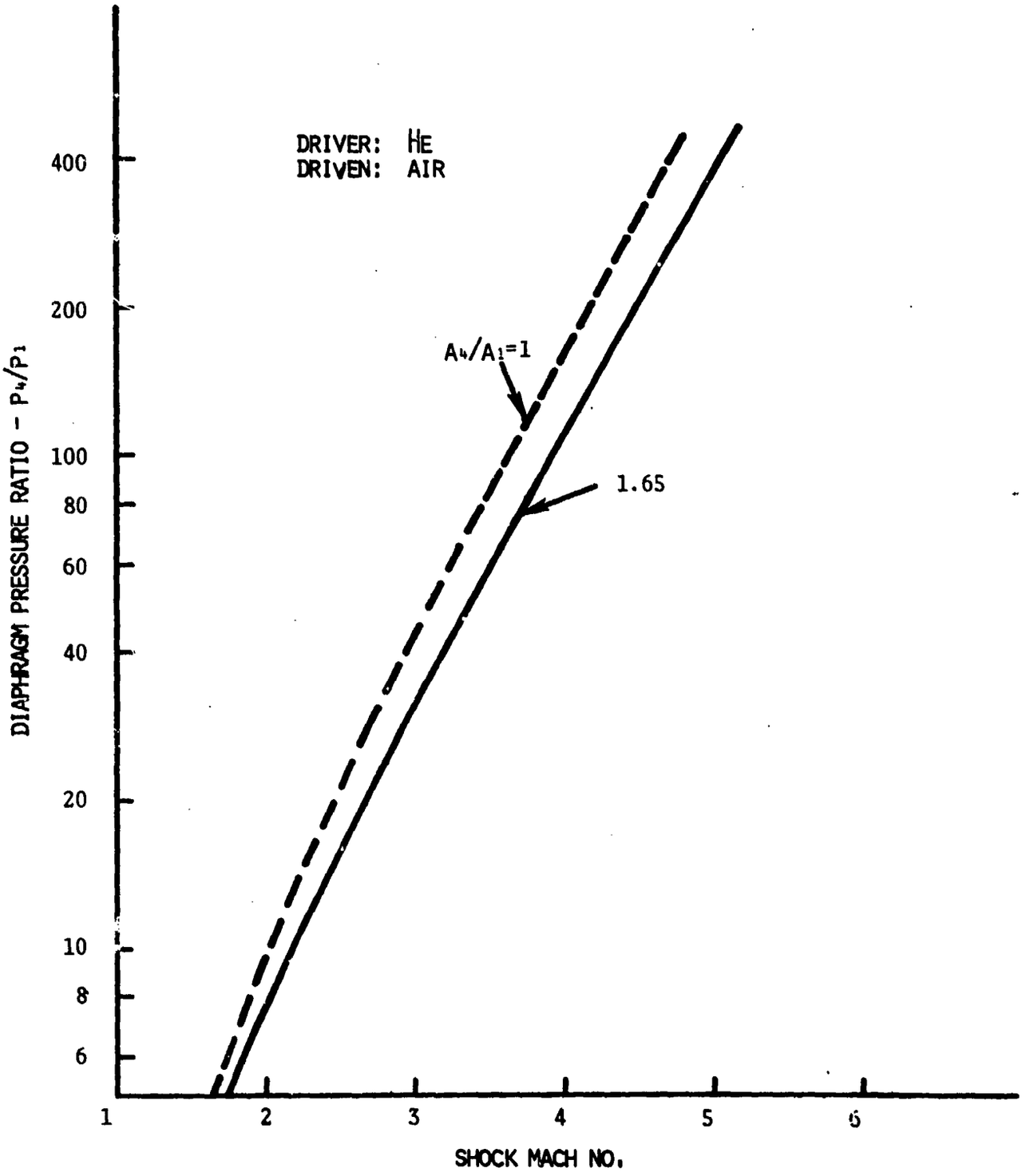


FIG. 2, THEORETICAL MACH NUMBER VS DIAPHRAGM PRESSURE RATIO

transducers are placed at selected locations. At location 6, in addition to the pressure measurement, optical radiation is monitored with an EGG Lite Mike. Photographic observation of the phenomenon is made near that location with a spark source schlieren system.

The wave velocity is measured from time intervals as recorded in a raster display of the pressure switches as well as from two electronic time interval units. Pressure measurements and radiation measurement are recorded with oscilloscopes as indicated in Fig. 1.

The spray runs are conducted as follows. The tube is purged with air, and fresh air is established in the tube. The driver and the diaphragm sections are filled to the desired pressure. Through a mechanical timer, the drop generator is started, and stopped and the diaphragm section is dumped to the atmosphere via a solenoid valve. The shock is thus initiated and the measurements are automatically recorded.

2. Theoretical Background: Shock Wave Decay:

For the usual use of a shock tube, the driver length is chosen long enough to insure a constant wave velocity throughout the driven section. However, since for our purpose we desired to observe whether a detonation occurs or not by noting the wave velocity, it was decided that a short driver would be useful. With a short driver, the rarefaction wave in the driver, after reflection catches up with the wave and reduces its velocity if the wave is non-reactive. If the wave is reactive as in a detonation, it is expected that the wave will continue to propagate unhampered by the rarefaction wave.

In order to get an approximate value of the decay of the wave, we note that the initiation Mach number of interest is between 3 and 4. For the gases used, helium in the driver and air in the driven section, the Mach number obtainable for a given pressure ratio is shown in Fig. 2. Fox (12) has calculated the location at which the rarefaction wave catches up with shock wave as a function of the driver length. The ratio of this critical location over the driver length, X_c/ℓ_4, is found to be 2.8-5.2 for $M = 3\text{-}4$ when the area ratio is 1.65. If after that location the wave is considered as a constant energy blast wave then its decay can be approximated (14) by

$$\frac{dM}{M} = \frac{\alpha+1}{2}\left(1-\frac{1}{M^2}\right)\frac{dR}{R} \qquad (1)$$

where R is the blast wave distance and α is a geometric factor = 0, 1, 2 for planar, cylindrical or spherical wave. For the shock tube, $\alpha = 0$ and therefore:

$$\frac{dR}{R} = \frac{M\,dM}{M^2-1} \qquad (2)$$

This equation can be integrated to give:

$$\frac{R}{R_o} = \frac{M_o^2-1}{M^2-1} \qquad (3)$$

For a 20% decay in M, $R/R_o \cong 1.65$ for $M_o = 3\text{-}5$ and for a 50% decay, R/R_o varies from 4.57 to 6.40 when M_o varies from 5 to 3. If R_o is assumed to be the location where the rarefaction overtakes the shock wave, the driver length can then be designed so that observable decay could be effected within a reasonable length of the driven section. Thus for the 6" driver at $M_o = 3.5$, for which $X_c/\ell_4 = R_o/\ell_4 = 4$, 20% decrement is expected at $.5 \times 4 \times 1.65 = 3.3$ ft. from the diaphragm.

Some tests were conducted to check the predicted velocity decrement. For a 6" long driver the velocity decrement of a shock wave in air at $M \cong 3.6$ resulted in a decrement of 17% at 6 ft. from the diaphragm. Thus it appears that the experimental decrement is about half the theoretically predictable decrement.

3. The Relation Between Energy and Power for Detonation Initiation:

It was indicated in the introduction that the relationship between power and energy for detonation initiations would be examined. In a shock tube experiment the power is effectively related to the initiation Mach number and the energy is related to the effective energy stored in the driver. Thus for a given set of driver and driven gases, the power is related to the pressure ratio p_4/p_1 and the energy to the length of the driver.

The rate of energy input to the driven section must equal the rate of work performed by the interface. Thus the rate per unit area is $= p_2\bar{u}_2$, or the power per unit area is:

$$P = p_2\bar{u}_2 \tag{4}$$

$$= p_1(p_2/p_1)(u_1-u_2)$$

$$= (p_2/p_1)(1 - u_2/u_1)p_1u_1$$

$$= (p_2/p_1)(1 - \rho_1/\rho_2)p_1M_1a_1 \tag{5}$$

Eq. 5 can be written in terms of the shock Mach numbers after using the shock relations. Thus:

$$P = \left[\frac{2\gamma}{\gamma+1}(M_1^2-1) + 1\right] \quad \left[\frac{2(M_1^2-1)}{(\gamma+1)M_1}\right] \quad p_1a_1 \tag{6}$$

The energy involved is equal to this rate multiplied by the time in which this rate is effective. This time is considered to be the time in which the wave propagates until the rarefaction wave reflected from the driver end wall

catches-up with the shock front. Thus if X_c is the distance from the diaphragm at which the rarefaction wave reaches the shock front, then the energy per unit area:

$$E = P\, X_c/u_1 \qquad (7)$$

or

$$E = P(X_c/\ell_4)\ell_4/M_1 a_1 \qquad (8)$$

where ℓ_4 is the driver length and X_c/ℓ_4 depends on M_1 for a given combination of gases.

Some tests on the initiation of H_2-air mixtures were performed. As background, the detonation velocity and Mach number have been calculated using the computer code of Gordon and McBride (15). These are shown in Fig. 3 and 4. The initiation of a stoichiometric mixture initially at a pressure of 0.5 atmosphere was checked with three drivers of different lengths (2", 4" and 8") with varied pressure ratios. The location at which the Chapman-Jouguet (CJ) Mach number is reached is noted and the results are shown in Fig. 5. It can be seen that the 8" and 4" results show reasonable variations whereas the 2" results show much scatter. At any rate, the pressure ratio below which detonation is expected to take place at extremely long distance from the diaphragm can be estimated. The corresponding initiation Mach number can be found from Fig. 2 and the corresponding X_c/ℓ_4 is found from (12). Equations (6) and (8) are then used to determine the power and energy for initiation. The results are presented in Table I, and plotted in Fig. 6. From this figure the asymptotes of energy and power can be estimated.

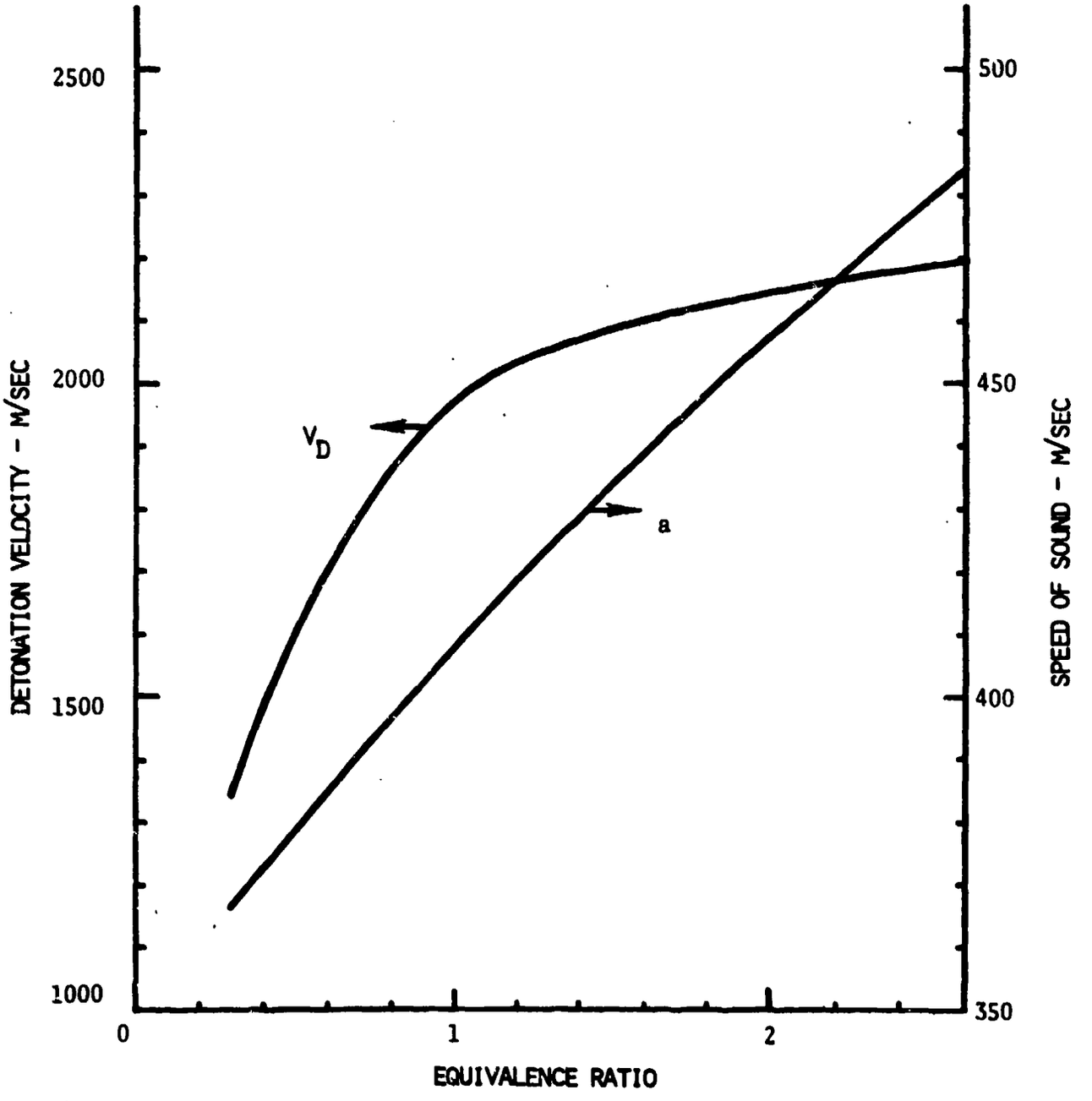


FIG. 3. DETONATION VELOCITY AND SPEED OF SOUND OF H_2-AIR MIXTURES

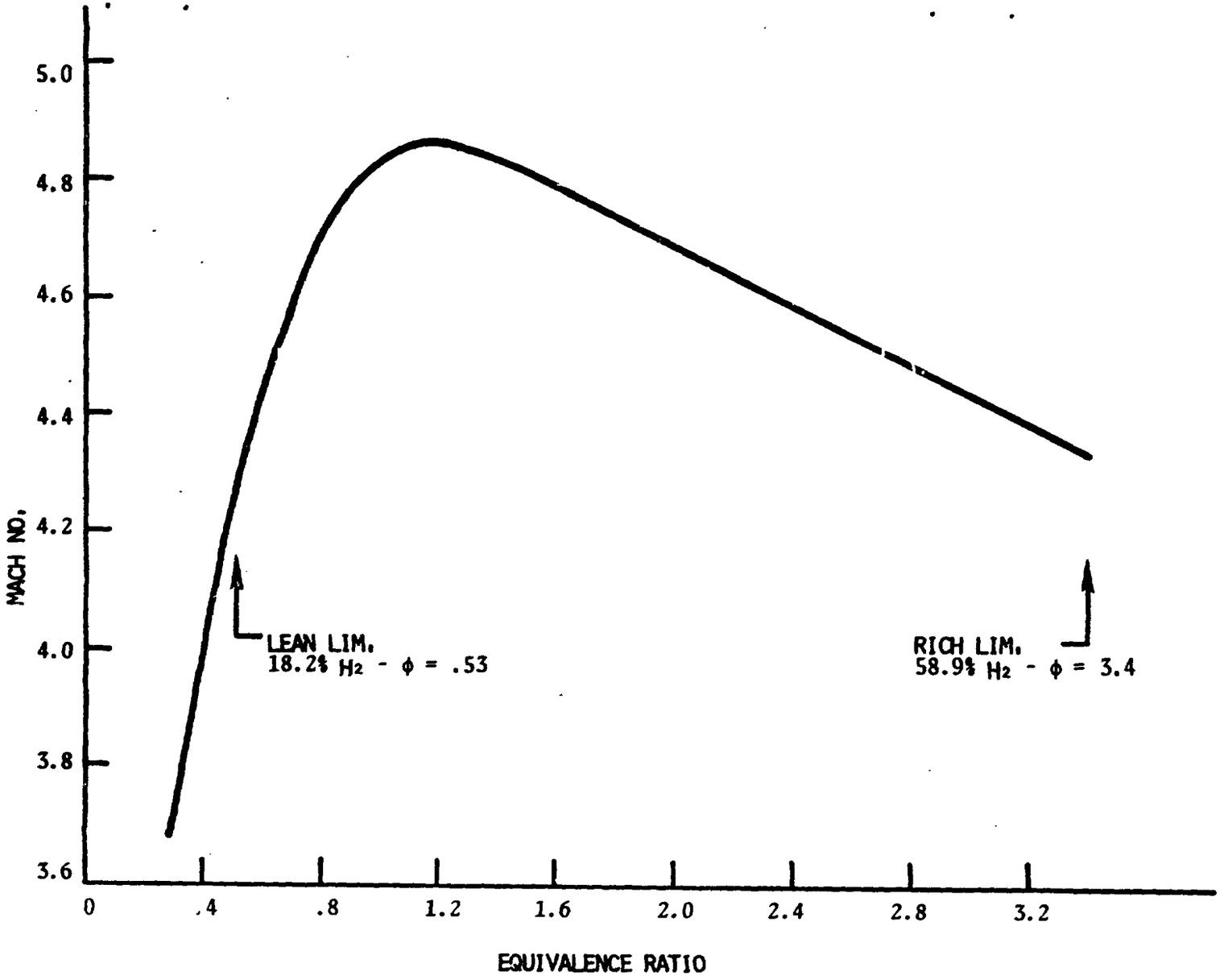


FIG. 4. CHAPMAN-JOUGUET MACH NUMBER OF H_2-AIR MIXTURES

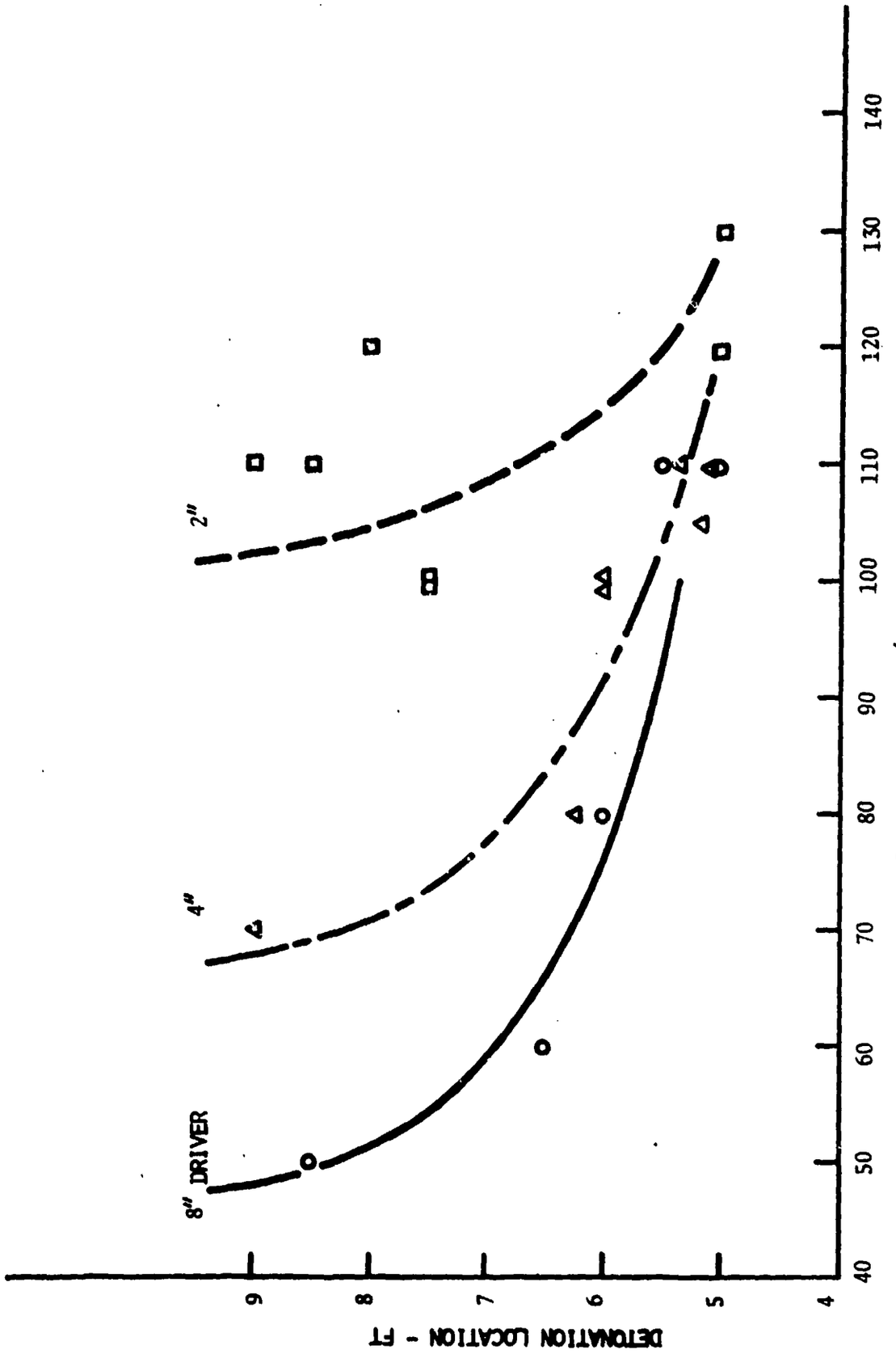


FIG. 5, DETONATION LOCATION VS. DIAPHRAGM PRESSURE RATIO

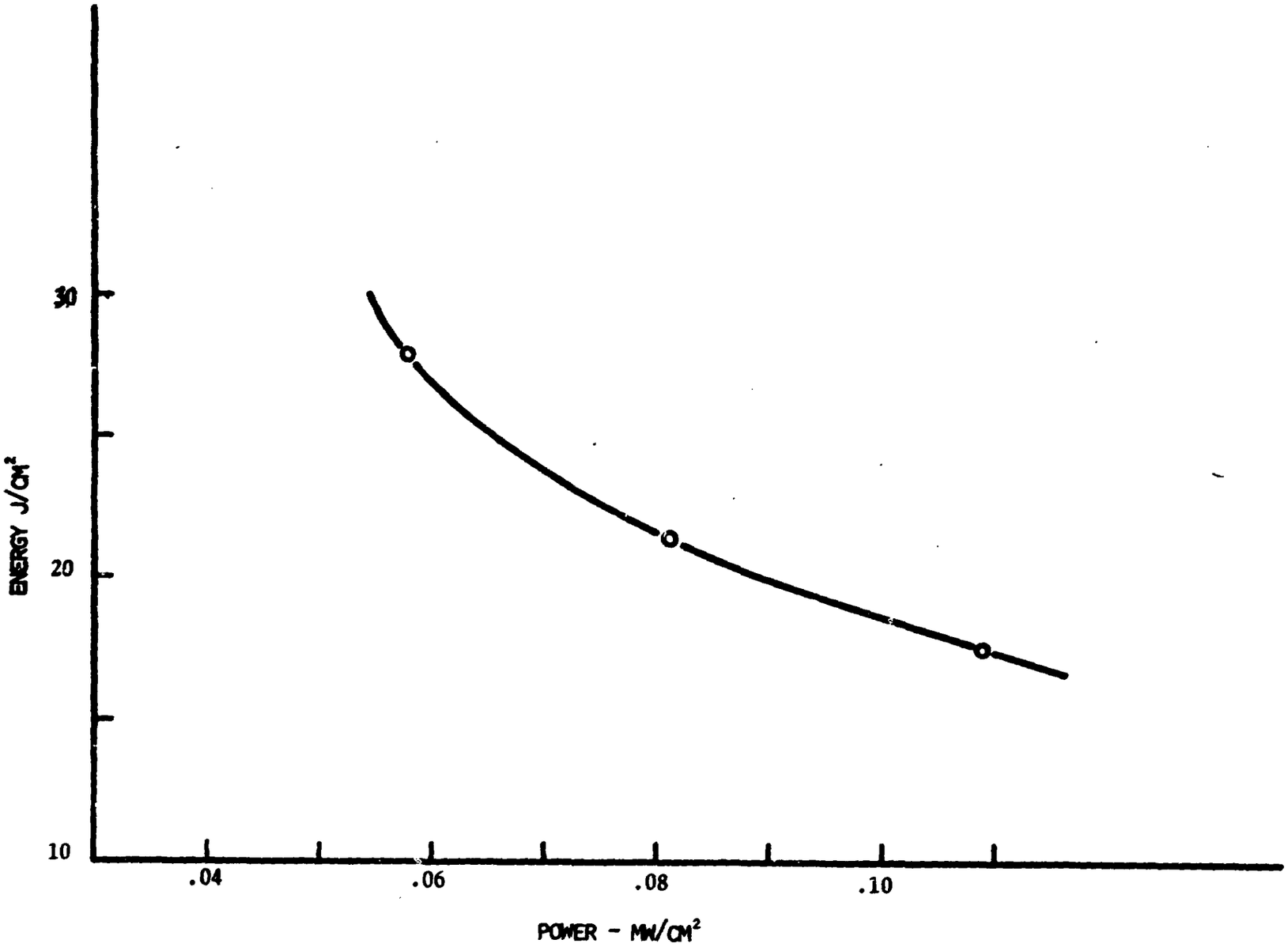


FIG. 6. ENERGY-POWER RELATION FOR STOICHIOMETRIC H_2-AIR AT P_1 = .5 ATM

Table I

ENERGY AND POWER RELATION FOR THE INITIATION OF STOICHIOMETRIC H_2-AIR AT p_1 = 0.5 atm.

Driver Length p_4(in)	p_4/p_1	M_1	X_c/ℓ_4	X_c cm	P watts/cm^2	E J/cm^2
2	100	3.90	4.8	24.4	10.89×10^4	16.69
4	65	3.55	3.8	38.6	8.08×10^4	21.50
8	40	3.2	3.1	63	5.78×10^4	27.89

These would correspond to the minimum initiation energy and power. The minimum energy can also be determined by plotting E vs. X_c, as is done in Fig. 7, and finding the interupt. This gives E_{min} = 10 J/cm^2 for a stoichiometric mixture of H_2-air at 0.5 atmos. If the induction distance is is inversely proportional to pressure (16), the minimum initiation energy at atmospheric pressure becomes 5 J/cm^2 since the energy for a planar wave can be considered proportional to the induction distance.

It can be shown from a plot of P vs. $1/X_c$ that $P_{min} = 2.7 \times 10^4$ watts/cm^2 which corresponds to an initiation Mach number of 2.55 The two asymptotic values of E_{min} and P_{min} can be combined to give the following relation between P and E:

$$(P - 2.7 \times 10^4)(E - 10) = 55.5 \times 10^4 \ \frac{\text{watts-Joules}}{\text{cm}^4} \qquad (9)$$

This equation is at variance with the relationship of energy and power found by Knystautas and Lee (11) for spark initiation of stoichiometric acetylene-oxygen detonations. In their case they found a double value of energy for a given power which appears to be physically unsatisfactory. For the question arises as to why, for a given initiating source operating at a certain rate of energy deposition, there should result a detonation at

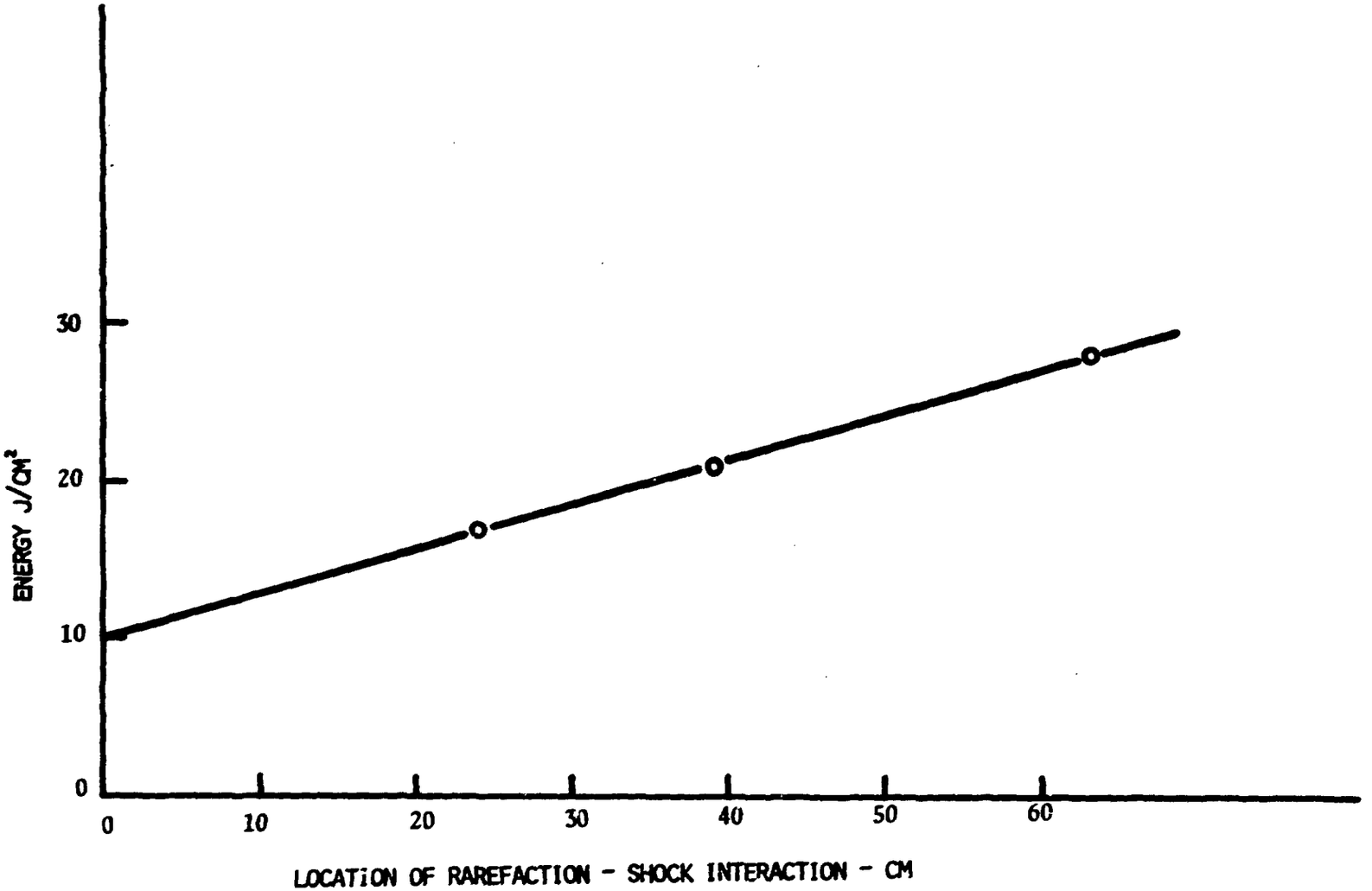


FIG. 7, ENERGY AS RELATED TO RAREFACTION - SHOCK LOCATION

two values of energy deposition, one high, one low. If the energy deposition could be stopped at the lower value, a detonation should still be possible, be initiated and the additional input energy would seem superfluous. It is hoped that future work would resolve this apparent anomaly.

At any rate, the values of E_{min} and P_{min} found here can be used as guidelines for the determination of limits. The lean limit of H_2-air will be checked first.

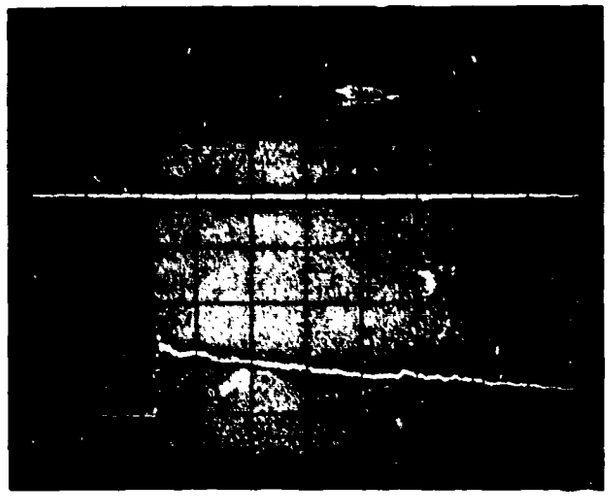
III. THE LEAN LIMIT OF H_2-AIR

It was thought that the method for determining the limits of kerosene-air should first be tried for a combination of fuel-oxidizer of known limits. Since the detonation limits of H_2-air are supposedly well known, this mixture was chosen for testing. The accepted value of the lean limit is 18.2% H_2 in air at $\phi = .53$ (17, 18).

Tests were made on H_2-air mixtures at 0, 10, 14, 16, 20 and 30% H_2 to determine the initiation behavior. The mixtures were at an initial pressure of 1 atmosphere and the initiation Mach number was about 3.5. The driver length was 6" providing an approximate energy input 50 J/cm^2 at a power of 16×10^4 watts/cm^2. The energy input is about an order of magnitude larger than what is needed to initiate the stoichiometric mixture.

For each run, the velocity was monitored throughout the tube and pressure measurements were made. In particular the pressure at location 6 (Fig. 1), 5 1/2 ft. from the diaphragm as well as light emission were recorded. Figure 8 shows representative oscilloscope records for the pure air case, the 10% H_2 and the 20% H_2 runs. The pressure records seem to be identical in shape. This reflects the fact that whether an adiabatic shock wave or a detonation wave is involved, the wave is followed by an expansion. In the detonation case this is an inherent phenomenon. In the shock case, this is due to the limited driver length and the resultant early interaction of the reflected expansion wave with the shock wave.

The lack of emission in the pure air is, of course, expected. The lack of emission for the 10% H_2 is taken as indication of the lack of reaction and therefore, absence of detonation. In the 20% H_2 case, emission is prominent and indicative of at least some reaction.



(a) Air

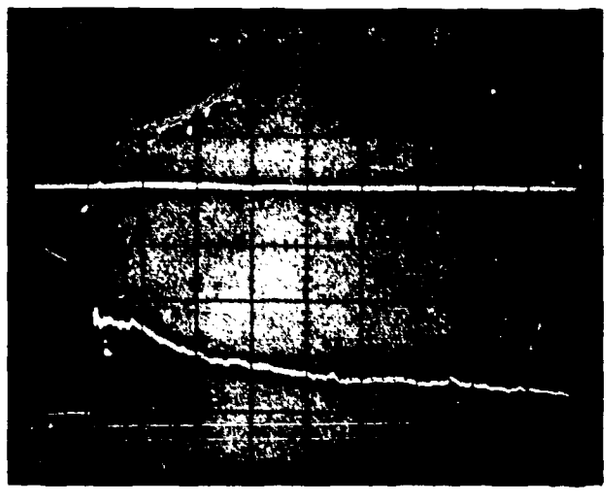
Run #54

Trig. delay from 3 = 600 μs.

Horz. = 100 μs/div

Vert. Top = 10 mV/div

Bot = 100 psi/div



(b) 10% H_2

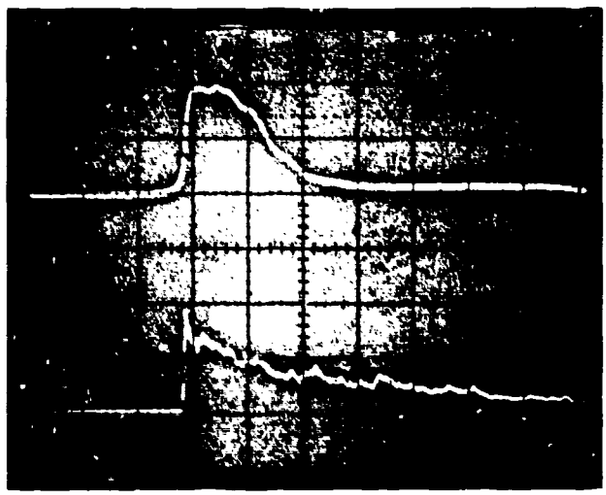
Run #63

Trig. delay from 3 = 500 μs.

Horz. = 200 μs/div

Vert. Top = 5 mV/div

Bot = 100 psi/div



(c) 20% H_2

Run #49

Trig. delay from 3 = 250 μs.

Horz. = 100 μs/div

Vert. Top = 20 mV/div

Bot = 200 psi/div

FIG. 8 EMISSION AND PRESSURE RECORDS AT LOCATION 6 FOR AIR, AIR + 10% H_2 and AIR + 20% H_2

Figure 9 shows the Mach number variation throughout the tube for the six cases. It is seen that for the pure air case and the 10% H_2 case the wave slows down generally. In the 14% H_2 case the Mach number can reach a value of 3.9 which is the corresponding CJ Mach number. In the 16%, 20% and 30% H_2 cases the Mach number exceeds the corresponding CJ Mach number of 4.12, 4.45 and 4.85 respectively. However, no steady detonation could be observed as the Mach number seems to decrease after a peak. It is felt that if the tube length could be increased a steady detonation would eventually develop. Unfortunately it was not possible to do this. However, some basis for determining the limit had to be made.

Two criteria were used; one, indication of emission and the other, the attainment at some point in the tube of a Mach number equal or exceeding the CJ Mach, especially when the initiating Mach number is lower than the CJ Mach number as in these runs. Based on these two criteria, it appears that the lean detonation limit for H_2-air as determined by our method is somewhere between 10% H_2 and 14% H_2 which is lower than the currently accepted value.

At this point, it is appropriate to mention that recent experiments(19) on shock initiation of H_2-O_2 mixtures with argon dilution indicate that conditions exist in which, instead of obtaining CJ detonations, "reaction enhanced" waves are observed. These waves are observed in weakly reactive mixtures (due to either low reactants' concentrations or high inert dilution) wherein only part of the possible heat release influences the wave velocity. The experiments were conducted with a long driver such that the adiabatic wave would propagate without decay. In contrast, our experiments are at high reactants' concentrations (high pressure) and in a tube with a short driver.

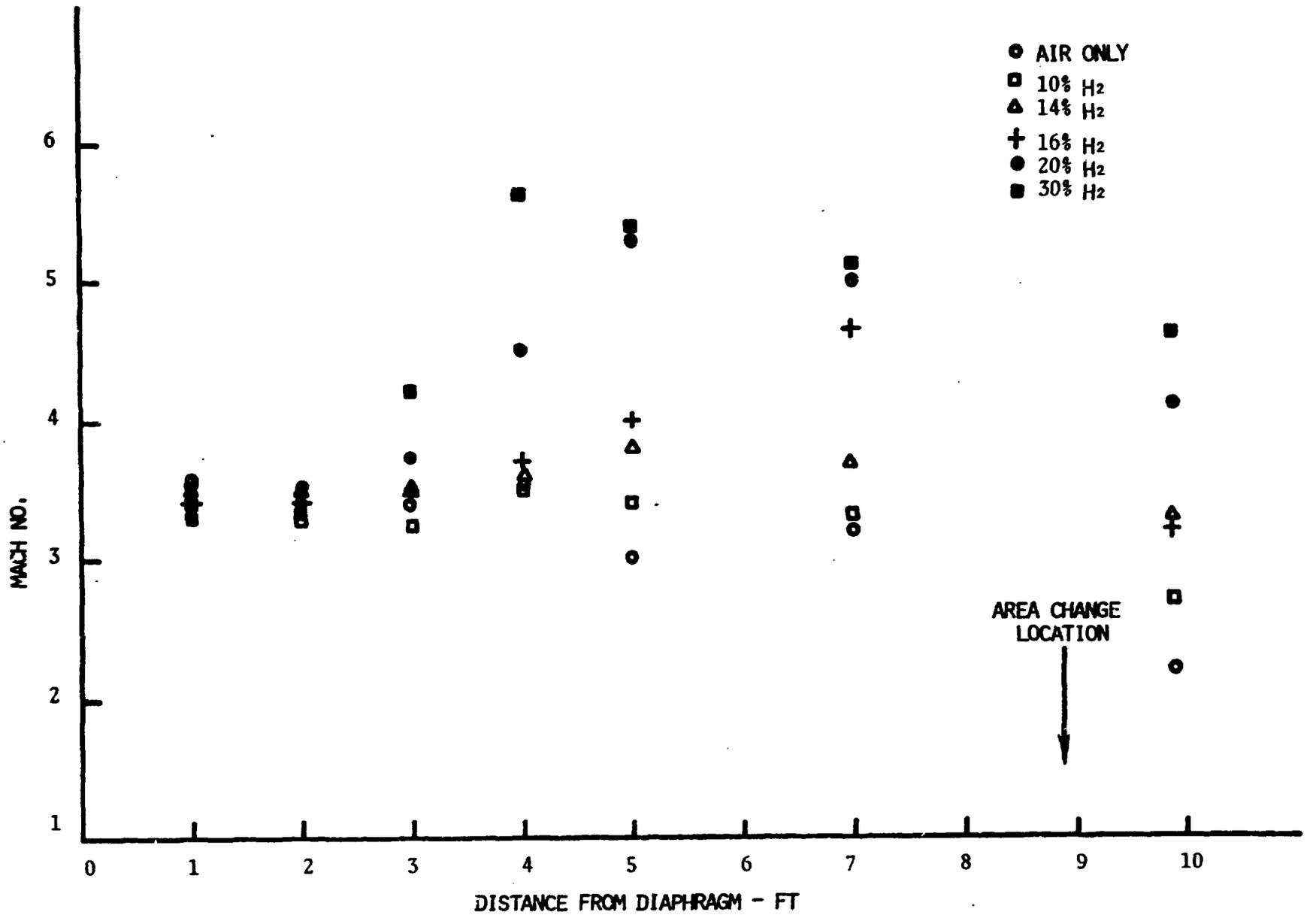


FIG. 9. PROPAGATION MACH NUMBER VARIATION WITH DISTANCE

In the experiments of (19) "the reaction enhanced" waves do not reach or exceed the CJ velocity when the initiation Mach number is below the CJ Mach number. However, in our experiments we detect regions in which the CJ velocity is exceeded. Thus, it is felt that our method which is based on a decaying adiabatic wave is a reasonable method for determining limits.

IV. KEROSENE-AIR EXPERIMENTS

1. Theoretical Calculations:

The Chapman Jouguet detonation properties of mixtures of kerosene-air and kerosene + additives-air were calculated using the computer code of Gordon and McBride (15). Kerosene was assumed to have an average formula of $C_{11.6}H_{23.2}$ with a heat of formation of -5.6 Kcal/mole. The additives used were n-propyl nitrate ($C_3H_7NO_3$) and n-butyl nitrate ($C_4H_9NO_2$). Their heats of formation were taken as -41.6 and -50.0 Kcal/mole. In the calculations, the fuel was assumed to be in the gaseous phase, an assumption which has practically no effect on the detonation velocity. However, the fact that the fuel is liquid does have an effect on the detonation Mach number and the pressure ratio. The effect depends on the loading factor or the mass ratio of the liquid component (20). For lean mixtures which are of interest in this work the effect is negligible.

The calculated properties, such as the detonation velocity, Mach number and pressure ratio are plotted in Figs. (10, 11, 12) respectively. These plots do not include any correction due to the loading factor.

2. Fuel-Air Mixture Ratio Determination:

The tests were to be made in monodisperse sprays. As was indicated before the spray is formed by a method similar to that of Dabora (13) where capillary jets are broken up into equal size droplets by inducing deliberate disturbances into the liquid jets at an appropriate frequency. The nominal size of the drops desired was 700 μm. The closest capillary needle that can produce this drop size is guage #22 with an internal diameter of .413 mm. The drop size produced is .413 x 1.89 = .780 mm or 780 μm.

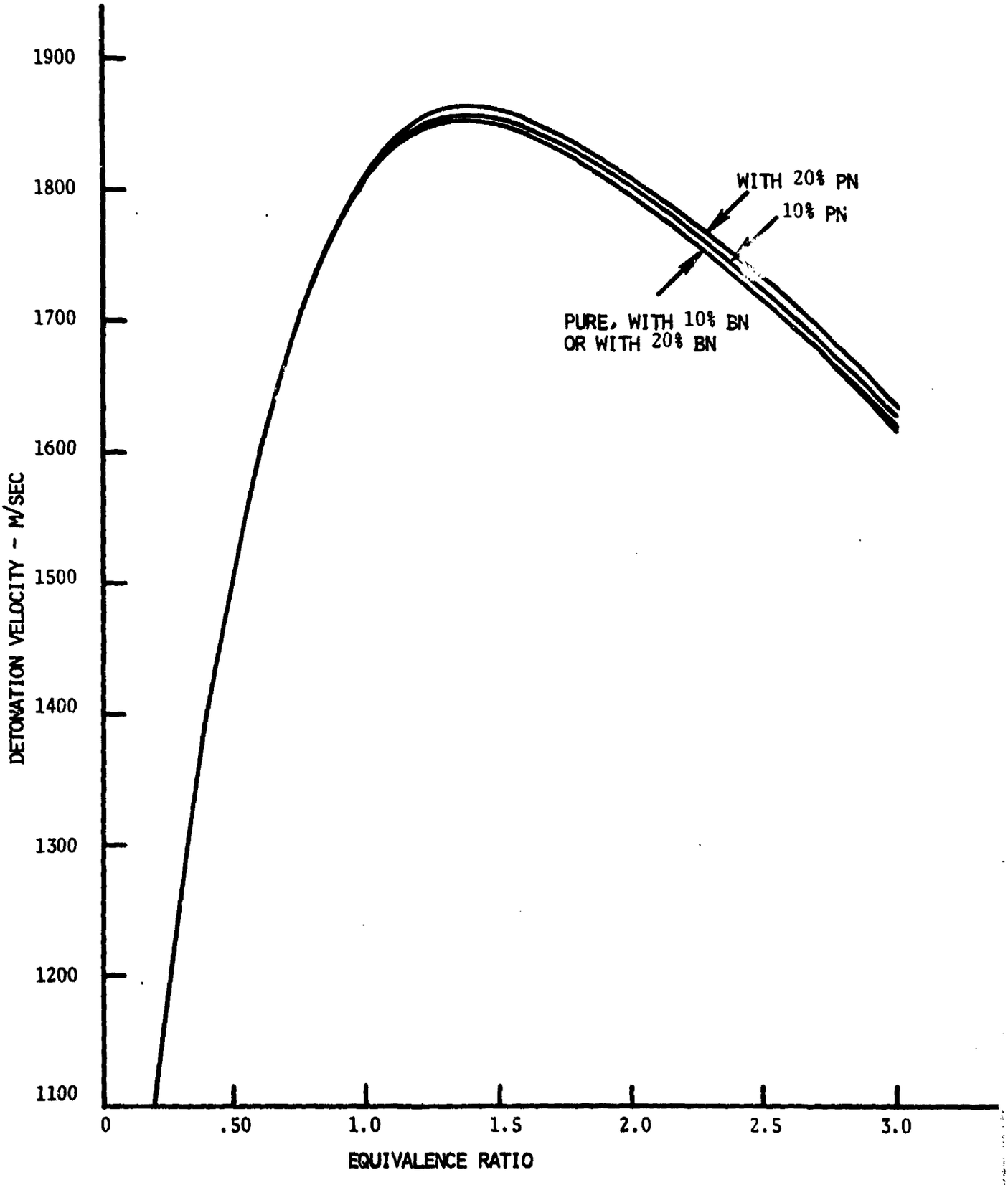


FIG. 10, CHAPMAN JOUGUET DETONATION VELOCITY OF KEROSENE, WITHOUT AND WITH ADDITIVES, AND AIR

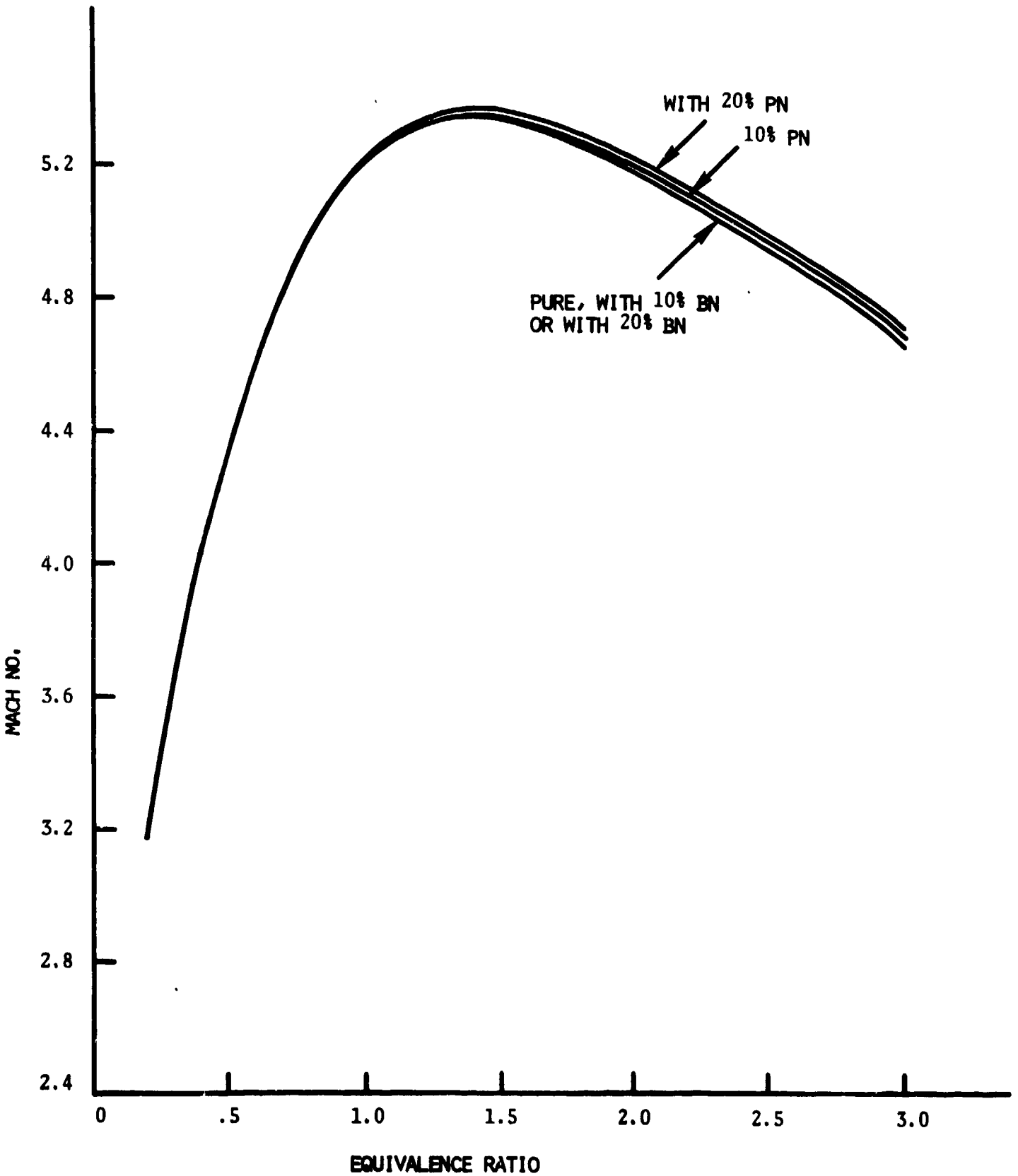


FIG. 11, DETONATION MACH NUMBER OF KEROSENE (+ ADDITIVES) AND AIR

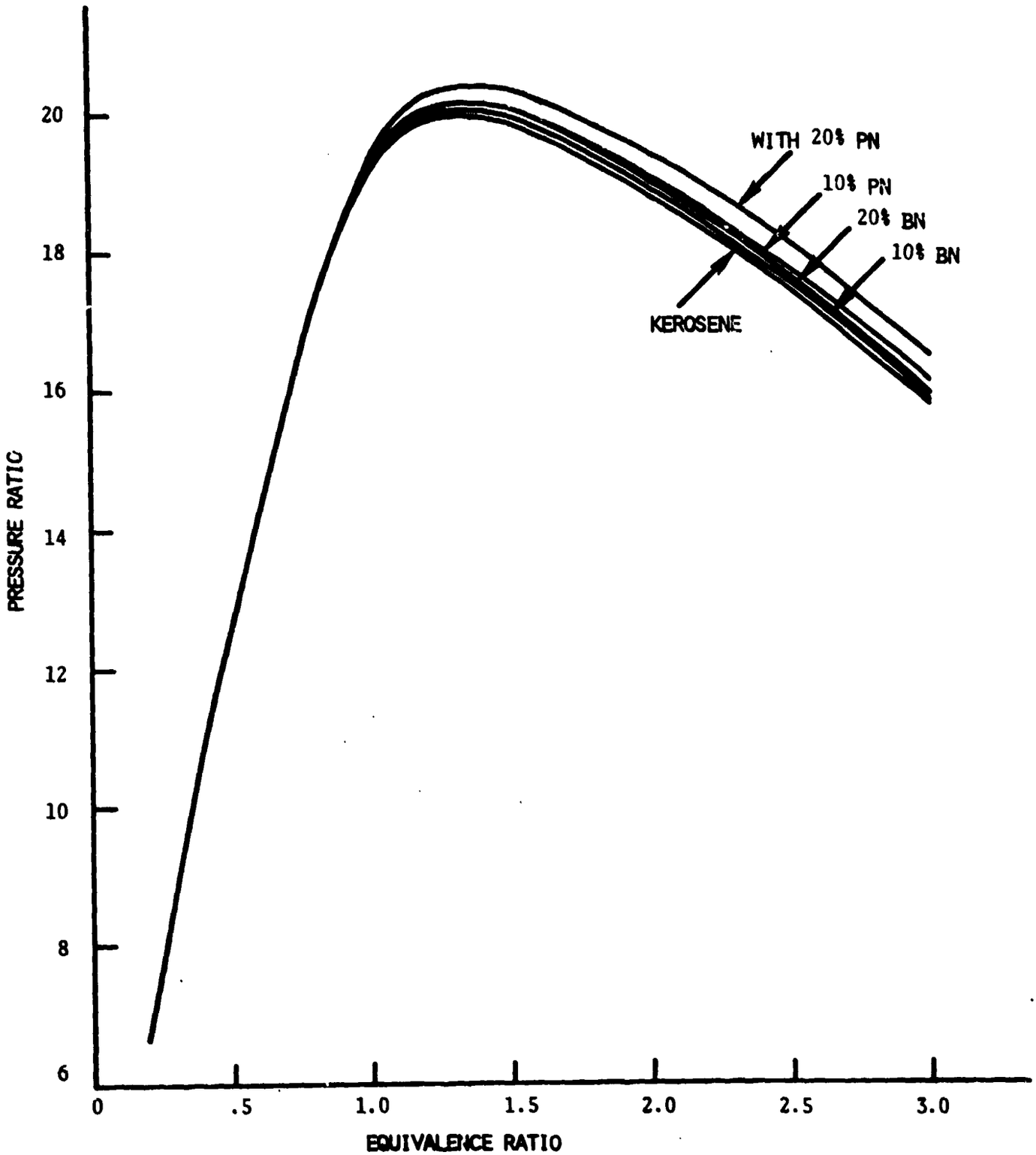


FIG. 12, DETONATION PRESSURE RATIO OF KEROSENE (+ ADDITIVES) AND AIR

According to (13) the appropriate frequency and the shedding velocity of a kerosene jet are 390 Hz and 74 cm/sec. The terminal velocity of the droplet is 250 cm/sec.

The air-fuel ratio per single column of fuel drops can be calculated from the following equation:

$$\frac{m_{air}}{m_{fuel}} = \frac{6\ A u_{\ell} \rho_{air}}{\pi d^3\ f\ \rho_{\ell}} \qquad (10)$$

where A is the area of the shock tube, u_{ℓ} the terminal velocity of the droplets, d, their diameter and f, the frequency. Using the appropriate values ($A = 25.8\ cm^2$), the air fuel ratio is found to be 99.6 per column of drops. The stoichiometric air-fuel ratio as determined from the stoichiometric equation is found to be 14.76. So that the equivalence ratio per column is 0.148. Because of the manner in which the spray is generated the equivalence ratio can be varied in a discrete manner only. Thus equivalence ratios of .3, .44, .59, etc. are obtainable.

It should be mentioned that because the shedding velocity is smaller than the terminal velocity,the fuel-air ratio is larger near the top of the tube than the bottom of the tube. It is possible to estimate the distance for the drops to travel before they reach a velocity within 95% of the terminal velocity (20). For our conditions this turns out to be about 3 ft.

In the calculations above the effect of propyl-nitrate and butyl-nitrite is assumed to be negligible. The reason is that the maximum amounts used are 20% by weight and their densities are close to that of kerosene. Furthermore, the carbon to hydrogen ratio is approximately the same as that of kerosene.

3. Energy Requirement for Initiation:

The minimum energy requirement for the initiation of detonations in sprays depends on many factors such as the drop size, the mixture ratio, the ignition delay and the energy deposition profile after ignition (9). The last two properties are not known for either kerosene or kerosene with additives, and it is therefore, necessary to make some assumptions before the minimum initiation energy could be estimated. If the ignition delay is assumed to be equal to one-half the drop breakup time and if the heat release from each drop is assumed to be instantaneous, then the method of (9) can provide an estimate of the minimum initiation energy. From Table 1 and Fig. 2 of (9), it is found that $E^*/d \cong 100$ J/cm^3 which, for $d = 780\ \mu$, gives $E^* = 7.8$ J/cm^2. As indicated in Section III, a 6" driver provides ~50 J/cm^2 when the initial Mach number is 3.5. It is also indicated in (9) that if the breakup time is controlling then the minimum initiation energy is minimally affected by the equivalence ratio. On the other hand, if the ignition delay is controlled by a chemical induction time the minimum ignition energy can be two orders of magnitude larger for $\phi = .5$ than that of $\phi = 1$. Thus the 50 J/cm^2 provided by the driver used in our experiments can be considered adequate for the determination of limits, only if the drop breakup time is controlling the ignition delay.

4. Experimental Results:

Previous work (21) has indicated that kerosene-air mixtures are non-detonable. Limited runs conducted here with pure kerosene at $\phi = .44$ produced no detonation either. Thus, our work concentrated on the effect of the two additives - propyl nitrate and butyl nitrite.

Specifically tests at ϕ = .59, .44 and .3 were conducted for 10% and 20% of the additives in the fuel. For each test a schlieren photograph was taken to insure that the spray is present and to give us a visual feel of the phenomenon. In addition, pressure data and emission records were taken. Also, the progress of the wave is monitored throughout the tube. Not all of the instrumentation worked perfectly every run, so that some runs had to be discarded because of incomplete data. As indicated before, the criteria for detonation were light emission and the attainment of a wave speed equal or higher than the CJ wave speed at some point in the detonation tube.

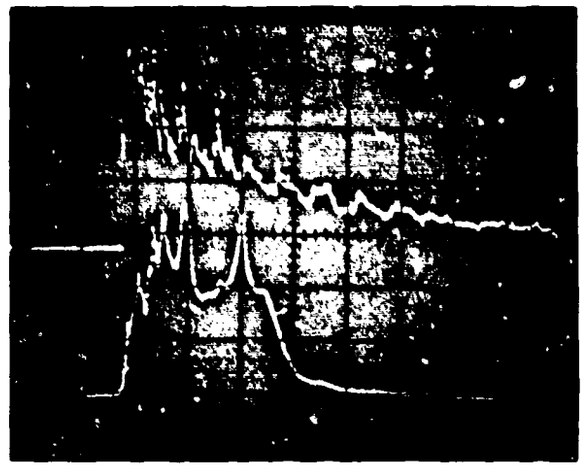
Representative data are reported here. For the 10% propyl nitrate, Figs. (13 & 14) show schlieren photographs, pressure and emission records at ϕ = .44 and .3. The schlieren photograph in Fig. 13 shows a typical detonation wave in which the front appears as a non-planar front because of some interactions from waves behind it. The pressure record shows some oscillations and pronounced peaks which could be due to blast waves from each drop although such blast waves do not seem to be detectable in the schlieren photograph. The emission record seems to indicate the presence of the peaks also. One interesting feature is the very short ignition delay.

The schlieren photograph in Fig. 14 shows a typical non-reactive front. Usually in such a situation the front remains planar. The pressure record shows no pronounced peaks and the emission trace shows no radiation.

The wave velocity variation is shown in Fig. 15. It can be seen that for ϕ = .59 and .44 the propagation velocity increases at some point in the tube and reaches a velocity comparable to the respective CJ velocity. On the other hand for ϕ = .3 the velocity does not veer too much from the initiation velocity

Run #130

Tube width = 5.08 cm.



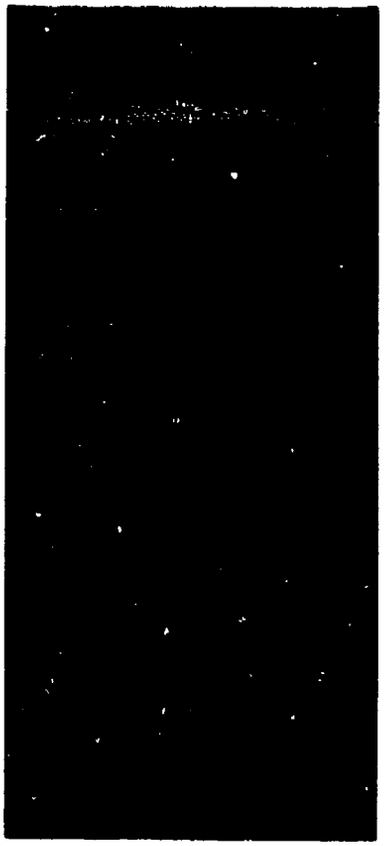
Trig. delay from 3 = 400 μsec

Horz. = 200 μs/div

Vert. Top = 100 psi/div

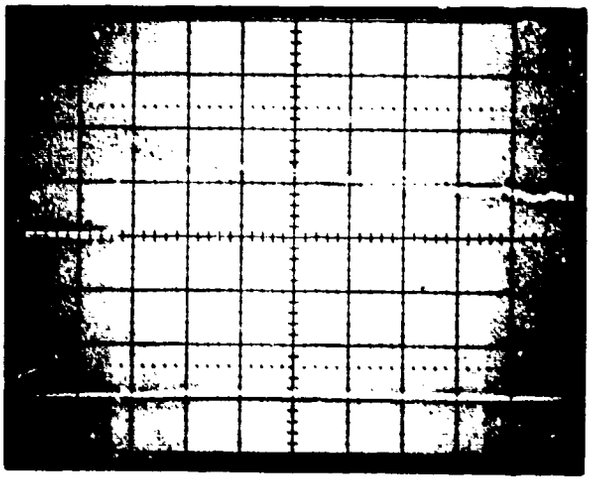
Bot = 5 mV/div

FIG. 13 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 10% PROPYL NITRATE AT LOCATION 6 (ϕ = .44)



Run #128

Tube width = 5.08 cm.



Trig. delay from 3 = 400 μs

Horz. = 200 μs/div

Vert. Top = 100 psi/div

Bot = 5 mV/div

FIG. 14 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 10% PROPYL NITRATE AT LOCATION 6 (ϕ = .3)

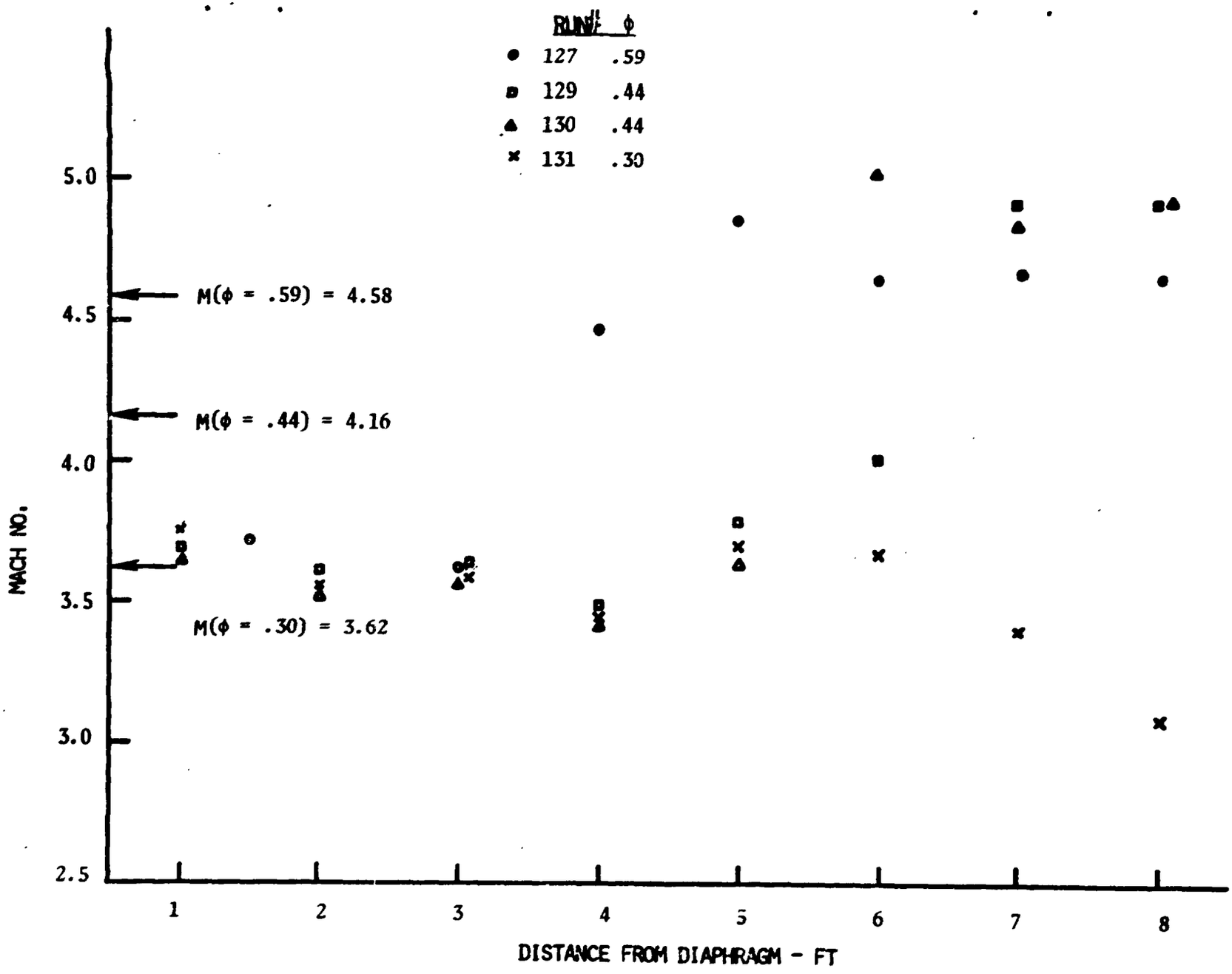


FIG. 15 VARIATION OF PROPAGATION MACH NUMBER WITH DISTANCE FOR KEROSENE + 10% PROPYL-NITRATE

and eventually drops down to below the CJ velocity. This situation together with the emission records is interpreted as absence of a detonation. Thus, the conclusion is that the lean limit for kerosene with 10% propyl-nitrate is somewhere between $\phi = .44$ and .3. As indicated before, because of our method of generating the spray, it is not possible to give a more precise limit.

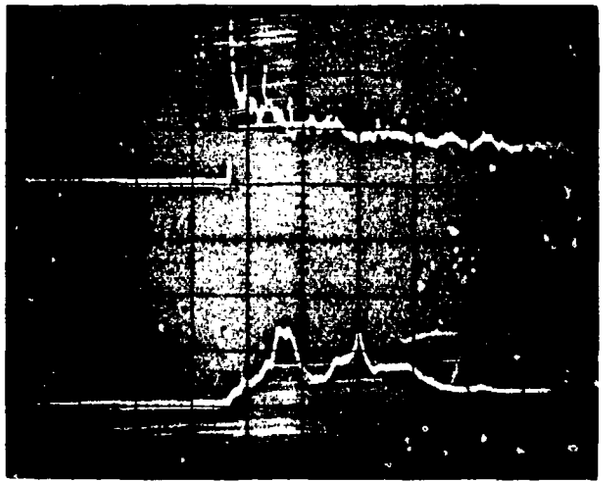
The results on runs with 20% propyl nitrate are exemplified by Figs. 16 and 17. For the $\phi = .44$ case, Fig. 16, similar comments to the 10% propyl nitrate case apply. For the $\phi = .3$ case, Fig. 17, the wave again is non planar and the pressure record shows peaks. The emission trace shows that a reaction has taken place, however the rise in emission takes longer time than for the $\phi = .44$. The velocity data of Fig. 18 show that a detonation is possible down to $\phi = .3$ and therefore, the detonation limit in this case is lower than $\phi = .3$. Thus it appears that propyl nitrate does affect the limit in a qualitative way: the higher its mass fraction in the fuel, the lower the lean limit.

The results with 10% butyl nitrate were rather erratic. There seemed to be cases of no detonation even at $\phi = .59$ whereas sometimes detonations at $\phi = .3$ could be observed. As a result of this situation the limit for this mixture could not be determined with any certainty.

For the 20% butyl nitrite mixture, the data seem to be comparable to the 20% propyl nitrate. Figure 19 shows typical results for $\phi = .44$ and Fig. 20 is indicative of the results for $\phi = .3$. Again detonation appears possible at $\phi = .3$ as cirribirated by the wave velocity data shown in Fig. 21. Thus the limit for this mixture is below $\phi = .3$.

Run #121

Tube width = 5.08 cm.



Trig. delay from 3 = 400 μsec

Horz. = 100 μs/div

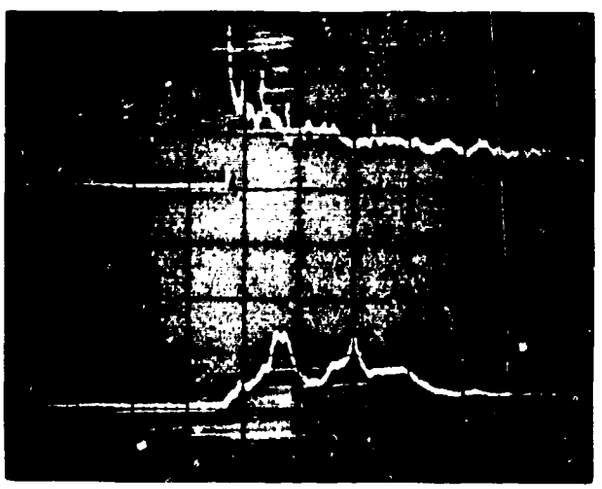
Vert. Top = 200 psi/div

Bot = 10 mV/div

FIG. 16 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 20% PROPYL NITRATE AT LOCATION 6 (ϕ = .44)

Run #121

Tube width = 5.08 cm.



Trig. delay from 3 = 400 μsec

Horz. = 100 μs/div

Vert. Top = 200 psi/div

Bot = 10 mV/div

FIG. 16 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 20% PROPYL NITRATE AT LOCATION 6 (ϕ = .44)

Run #125

Tube width = 5.08 cm.

Trig. delay from 6 = 400 μsec

Horz. = 100 μs/div

Vert. Top = 200 psi/div

Bot = 5 mV/div

FIG. 17 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 20% PROPYL NITRATE AT LOCATION 6 (ϕ = .3)

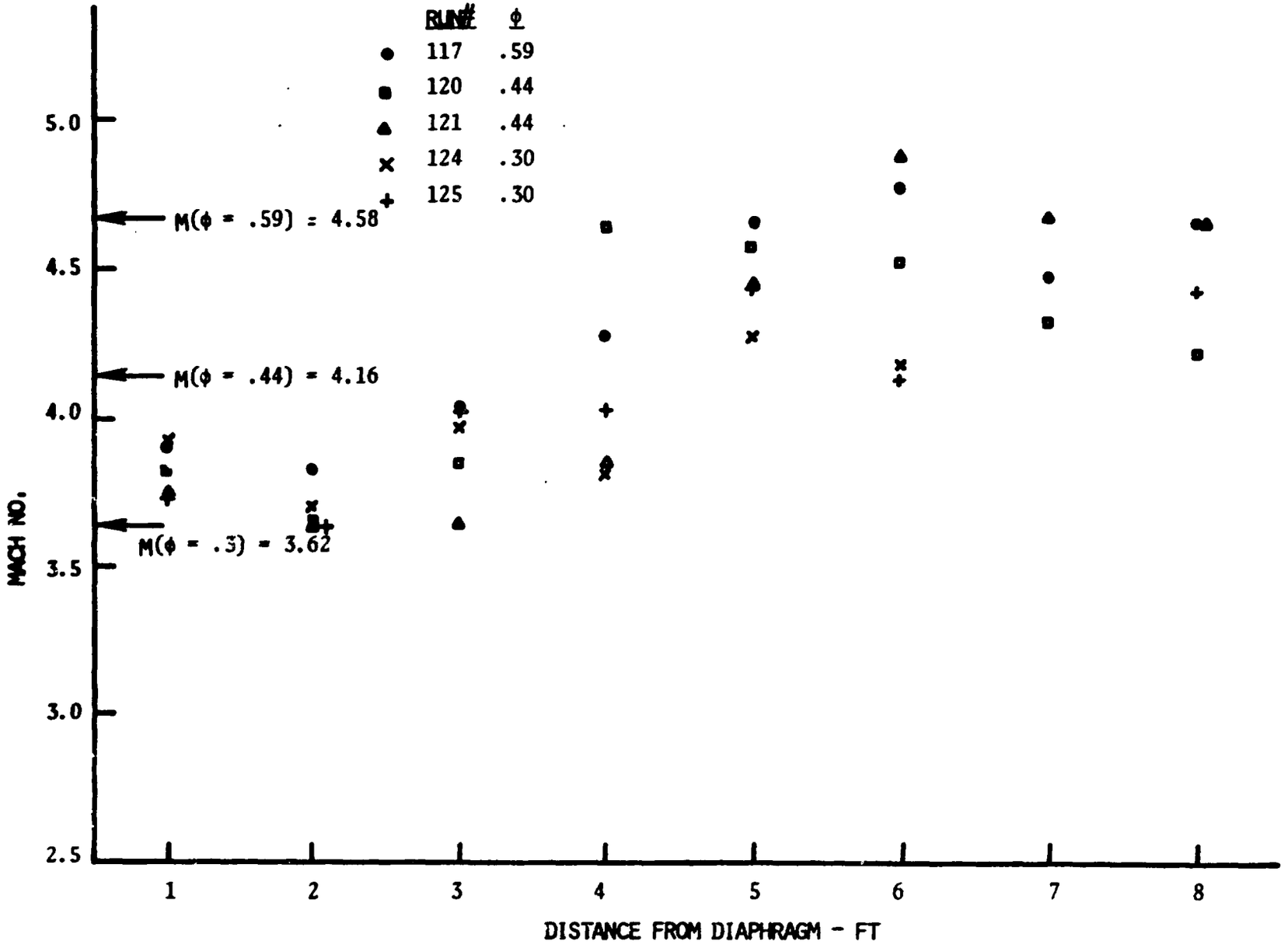
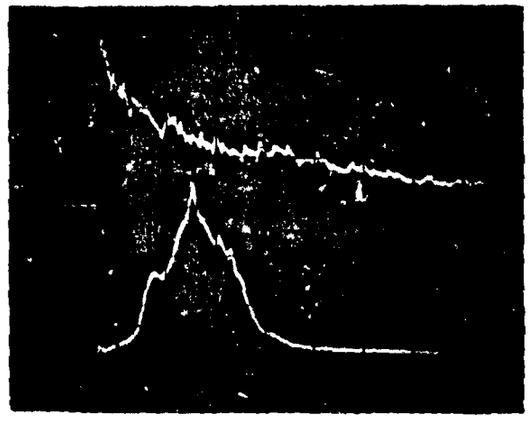


FIG. 18 VARIATION OF PROPAGATION MACH NUMBER WITH DISTANCE FOR KEROSENE + 20% PROPYL-NITRATE

Run #145

Tube width = 5.08 cm.



Trig. delay from 3 = 400 μs

Horz. = 200 μs/div

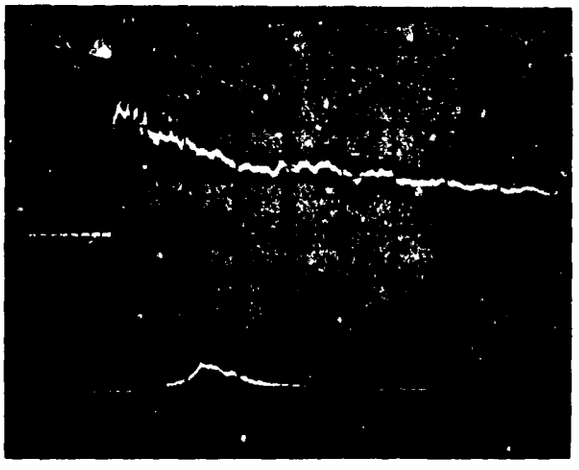
Vert. Top = 100 psi/div

Bot = 5 mV/div

FIG. 19 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 20% BUTYL NITRITE AT LOCATION 6 (ϕ = .44)

Run #148

Tube width = 5.08 cm.



Trig. delay from 3 = 400 μsec

Horz. = 200 μs/div

Vert. Top = 100 psi/div

Bot = 5 mV/div

FIG. 20 SCHLIEREN PHOTOGRAPH, EMISSION AND PRESSURE RECORD FOR KEROSENE + 20% BUTYL NITRITE AT LOCATION 6 (ϕ = .3)

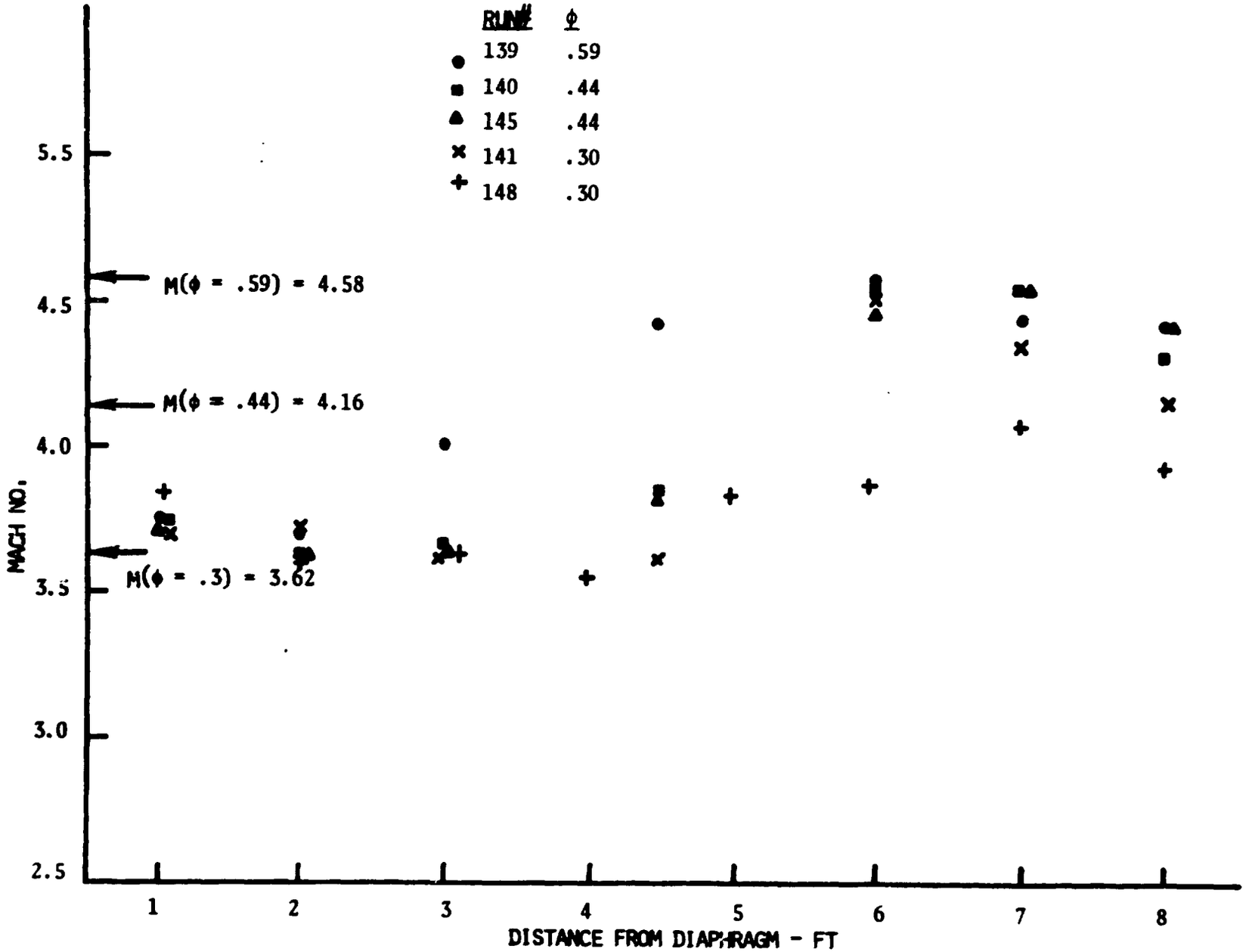


FIG. 21 VARIATION OF PROPAGATION MACH NUMBER WITH DISTANCE FOR KEROSENE + 20% BUTYL-NITRITE

In brief then, at an initiation energy of approximately 50 J/cm^2 the lean limit of kerosene with 10% propyl nitrate in air is between $\phi = .3$ and $\phi = .44$. For 20% of propyl nitrate or butyl nitrate the limit is below $\phi = .3$.

V. CONCLUSIONS AND RECOMMENDATIONS

The shock initiation technique is shown to be an adequate technique to determine the limits for direct initiation of detonation waves. The technique rests on the idea that if no reaction takes place, the wave would slow down, provided a proper length driver is chosen. On the other hand, if a detonation occurs the wave velocity would increase or at least the wave will be self-driven after the effect of the driver ceases.

The shock initiation technique can be used to determine the relationship between energy and power necessary to induce direct detonation. This was done for stoichiometric H_2-Air mixtures and it was found that in addition to a minimum energy requirement, there is a minimum power requirement as well. For values higher than these minima a monotonic relationship between power and energy exists.

The technique was used to check the lean limit of H_2-Air. The limiting equivalence ratio was found to be lower than that quoted in the literature. This suggests, as per current awareness in the literature, that the method of initiation can have a definite effect on the initiation energy and therefore, on the limiting equivalence ratio. The technique needs to be explored further for other combustible mixtures, and the results need to be compared with those of other initiation methods to ascertain the reasons for any differences.

Although the shock tube technique was used here for spray detonations, it should be realized that some fundamental data on the ignition of sprays is still necessary before the technique could be considered completely valid. In particular, data on ignition delays and comparison with drop breakup delays are needed. The ignition delay affects the minimum initiation energy which in

turn can be used as a guideline for what energy input should be used to determine the composition limit.

The composition limit for kerosene with propyl nitrate and butyl nitrite was determined here. However, the energy input was limited to 50 J/cm^2. and the drop size to 800 μm. Other drop sizes need to be investigated and the effect of larger energy input should be ascertained.

The technique used here is limited to planar geometry. The application of the results to other geometries in particular to the spherical geometry (unconfined detonations), need to be checked. Fundamental data such as ignition delay and energy deposition rates are deemed necessary to carry over the planar results to the spherical geometry. A relatively inexpensive manner to effect this is to use gaseous detonative mixtures which offer handling simplicity.

VI. NOMENCLATURE

A_1 = Driven section area

A_2 = Driver section area

a_1 = Speed of sound of gas in driven section

d = Drop diameter

E = Energy

E^* = Critical initiation energy

f = Droplet shedding frequency

ℓ_4 = Driver length

M = Mach number

M_o = Initial Mach number

m = Mass

P = Power

p_1 = Original pressure in driven section

p_2 = Pressure behind shock wave

p_4 = Driver pressure

R = Distance from initiation source

R = Gas constant

u_1 = Shock velocity

u_2 = Velocity downstream of shock

$\bar{u}_2$ = Convective velocity behind shock wave

u_ℓ = Terminal velocity of droplet

X_c = Distance from diaphragm at which the rarefaction wave interacts with shock front.

α = Geometric factor = 0, 1, 2 for planar, cylindrical or spherical wave respectively

ϕ = Equivalence ratio = fuel-air ratio/(fuel-air ratio) stoich.

ρ = Density

ρ_1 = Density ahead of wave

ρ_2 = Density behind wave

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A shock tube technique was used to determine the lean detonation limit of sprays of kerosene in air when the kerosene is sensitized by either propyl nitrate or butyl nitrite. The technique is described in detail and is used, as a first step, to determine the relationship between the detonation initiation energy and the initiation power for stoichiometric H_2-air mixtures at .5 atmosphere. It is found that if the initiation energy, E is expressed in J/cm^2 and the power P, in Kw/cm^2, then $(E - 10)(P - 27) = 555$ $J\text{-}Kw/cm^4$.

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Abstract Continued.

The method is also used to check on the lean limit of H_2-air at atmospheric pressure. It was found that for an initiation energy of 50 J/cm^2 at P = 160 Kw/cm^2 (initiation M $\cong$ 3.5), the lean limit is between 10-14% H_2 in air. This value is somewhat lower than that found in the literature which is 18.2% H_2 in air.

Approximately the same energy and power were used to determine the lean limit of kerosene sprays. Monodisperse sprays having droplets diameter = 780 μm were used. Three equivalence ratios were tested: .59, .44, .3. Kerosene was mixed with 10% and 20% of either propyl nitrate (PN) or butyl nitrite (BN). The results indicate that the addition of propyl nitrate reduces the limiting equivalence ratio, ϕ. Thus, for 10% PN the limiting ϕ is between .44 and .3 and for 20% PN, ϕ is below .3. Erratic behavior was detected when 10% BN was used. However, when 20% of BN was mixed in kerosene the limiting ϕ was again below .3.