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EXPLOSION HAZARDS ASSOCIATED WITH SPILLS OF
LARGE QUANTITIES OF HAZARDOUS MATERIALS
PHASE II

C. D. LIND
J. C. WHITSON



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Technical Report Documentation Page

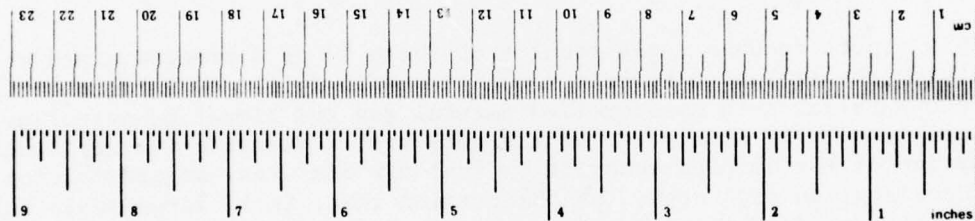
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12. Abstract <p>→ This report documents the results of Phase II of a program aimed at quantifying the explosion hazards associated with spills of large quantities of hazardous material such as liquefied natural gas and liquefied petroleum gas. The principal results of this phase of the work are: a quantitative empirical description of the burning behavior in fuel-air mixtures, an examination of flame acceleration processes, the observation that, in 17 large scale burn tests, no transition to detonation occurred, and that methane-air mixtures cannot be detonated with moderate size solid explosive boosters. ←</p>		13. Type of Report and Period Covered Final Report
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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
in ²	square inches	6.5	square centimeters	cm ²
ft ²	square feet	0.09	square meters	m ²
yd ²	square yards	0.8	square meters	m ²
mi ²	square miles	2.6	square kilometers	km ²
	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
VOLUME				
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft ³	cubic feet	0.03	cubic meters	m ³
yd ³	cubic yards	0.76	cubic meters	m ³
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm ²	square centimeters	0.16	square inches	in ²
m ²	square meters	1.2	square yards	yd ²
km ²	square kilometers	0.4	square miles	mi ²
ha	hectares (10,000 m ²)	2.5	acres	
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m ³	cubic meters	35	cubic feet	ft ³
m ³	cubic meters	1.3	cubic yards	yd ³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



*1 in = 2.54 exactly. For other exact conversions and more detailed tables, see NBS Monograph 286, Units of Weights and Measures, Price \$2.25, SD Catalog No. C1310-286.

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INTRODUCTION

The nation's navigable waters provide an efficient means for transporting large quantities of bulk materials. Among bulk items commonly shipped in large quantities are liquefied flammable gases such as ethylene, butadiene and petroleum products. Since the transport of such materials generally becomes more economical as the quantity shipped at one time is increased, there has been a trend to ever larger shipping containers. As a result of the recent advent of large tankers for shipping liquefied natural gas (LNG), there now exists the potential for accidental formation of extremely large vapor clouds. The need to know and understand the burning characteristics of such vapor clouds led to the investigation reported herein. Specifically, this study was aimed at determining the possibility and conditions under which a transition from burning to detonation of such a vapor cloud might occur.

Phase I of this investigation was reported on previously (Ref. 1). The Phase I effort resulted in (1) a phenomenological description of an accidental spill, (2) an examination of the detonation properties of fuel-air mixtures, (3) a qualitative theory of nonideal explosions, and (4) a plan for Phase II of the program.

This report provides a limited discussion of the Phase I results and details of the Phase II effort which endeavored to quantify the explosion hazards associated with large spills of hazardous materials such as LNG and liquefied petroleum gas (LPG).

PHASE I RESULTS

The description of an accidental spill was studied to determine the magnitude of the vapor cloud formed and the conditions that might affect the burning behavior. The primary fuel of interest was methane since it is anticipated that large quantities of LNG will be imported into the U.S. The detonation properties of methane were investigated both theoretically and experimentally to determine the properties for damage predictions as well as to devise instrumentation for later experiments to detect a detonation.

The theory of deflagrations in fuel-air clouds was examined by Professor F. A. Williams of the University of California, San Diego. The conclusions reached by this study were

1. A damaging pressure wave could be produced by a deflagration, but damage would be restricted to approximately the area covered by the cloud.
2. The development of a detonation from a deflagration does not appear likely.

Ideal detonation properties of fuel-air mixtures have been calculated using a computer code. This code assumes chemical equilibrium in the detonation wave and calculates detonation pressure, temperature, and velocity as a function of initial composition. The calculations do not determine if the mixture will detonate; they do predict the properties of the detonation if it should occur.

Some results of these detonation calculations are shown in Table 1. The detonation limits are generally narrower than the flammability limits and are dependent

TABLE 1. Calculated Detonation Properties.

Fuel	Composition, ^a %	Temperature, ^b K	Pressure, ^b bars	Velocity, ^b m/s	LFL, ^c volume %	UFL, ^c volume %
Ammonia	21.8	2820	17.0	1880	15.0	28.0
Butadiene	3.67	3100	19.0	1840	2.0	12.0
Ethylene	6.53	3100	17.8	1840	2.7	36.0
Ethylene oxide	7.73	2950	18.4	1830	3.6	100.0
Methane	9.48	2780	16.3	1810	5.0	15.0
Propane	4.02	2820	17.5	1800	2.1	9.5
Vinyl chloride	12.2	2820	19.2	1810	3.6	33.0

^a Stoichiometric composition assuming H₂O, CO₂ products, percent by volume.

^b Calculated temperature, pressure and velocity at the stoichiometric composition.

^c Experimentally determined lower and upper flammability limits from "Flammability Characteristics of Combustible Gases and Vapors," by G. Zabetakis, Bureau of Mines, Bulletin 627, 1965.

on the strength of initiation. The detonation properties at stoichiometric composition are not widely different for the different fuels considered. However, differences are apparent when the curves for one of the properties, such as pressure versus concentration as shown in Figure 1, are examined. Note that fuels such as propane and methane have relatively sharp peaks; fuels such as ethylene oxide and vinyl chloride have rather broad peaks. This suggests that methane and propane might have narrow detonation limits, should they detonate, and ethylene oxide and vinyl chloride might detonate over a wider concentration range. The vertical lines on Figure 1 are the flammability limits.

The detonation tube facility consisted of an 0.6-meter diameter steel tube with the following attachments: a gas introducing system, piezoelectric gauges for measuring pressure and velocity, and thermocouples for measuring temperature. The arrangement is shown in Figure 2. This facility was used for two types of experiments: detonation and burning. For the detonation experiments the tube was 1.8 meters long, for the burn experiments 3.6 meters long.

In the detonation experiments, an explosive booster was placed at one end of the tube, both ends were covered with polyethylene film, and a known amount of fuel was introduced. After mixing, the explosive booster was detonated and the results were sensed by transducers in the side of the tube.

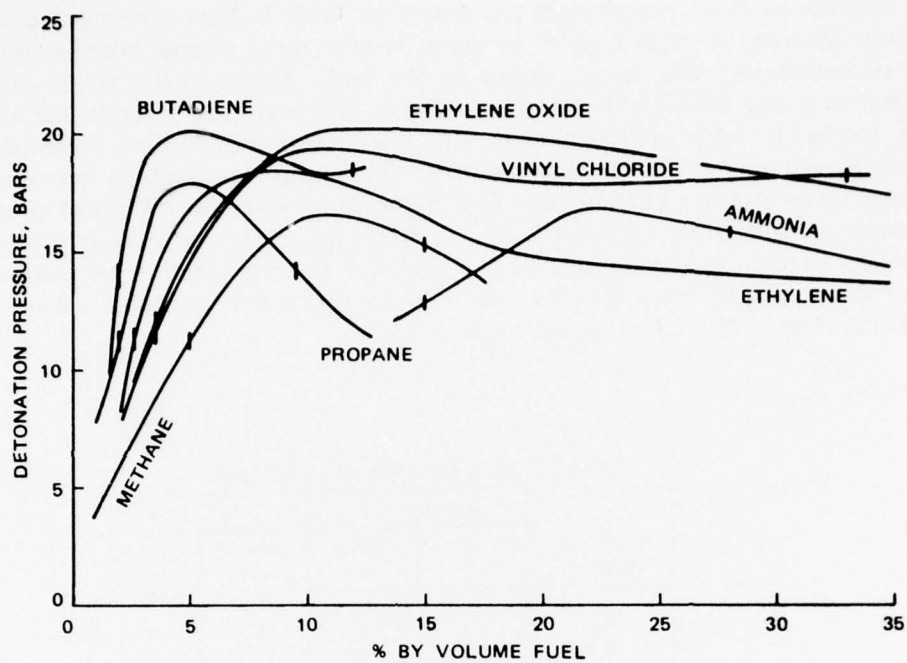


FIGURE 1. Calculated Detonation Pressure.

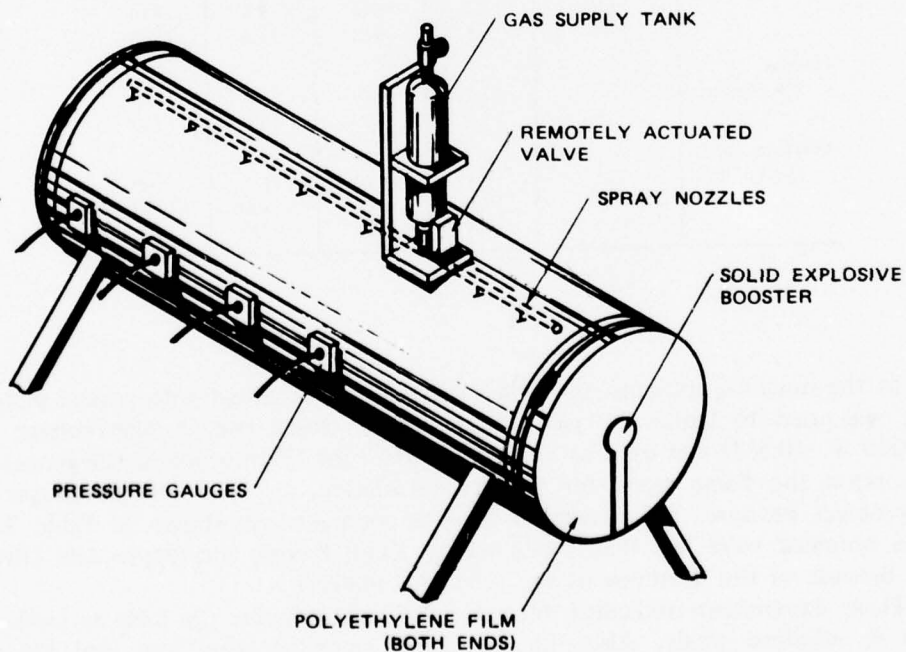


FIGURE 2. Detonation Tube Facility.

Results of these experiments are shown in Table 2. With methane, no reaction was observed using a small booster (5 grams tetryl); using a large booster (90 grams sheet explosive) gave the results shown in the table. Notice that the pressures and velocities were far below the calculated values. The detonation limits for methane appear to be 6-12.5%; although, with the low extent of reaction observed, it is difficult to determine the limits accurately. The results for methane are somewhat surprising since Kogarko (Ref. 2) obtained detonations with the calculated properties. The propane results were obtained with the 90-gram booster; with the ethylene oxide the 5-gram booster was sufficient. The purpose of these detonation experiments was not to obtain precise measurements but only to verify the calculated values and to demonstrate that a detonation could occur.

TABLE 2. Measured Detonation Properties.

Fuel	Concentration, volume %	Experimental		Calculated	
		Pressure, bar	Velocity, m/s	Pressure, bar	Velocity, m/s
Methane (90 g booster)	5.0	5.4	950	11.2	1490
	6.0	5.6	950	12.6	1590
	7.0	6.5	1010	14.0	1675
	8.0	5.4	1030	15.2	1730
	9.0	7.0	1030	16.0	1780
	10.0	7.8	1050	16.5	1820
	11.0	7.1	950	16.6	1830
	12.0	6.6	910	16.4	1820
Propane (90 g booster)	3.0	13.7	1710	15.2	1675
	3.6	15.2	1800	16.6	1750
Ethylene oxide (5 g booster)	5.4	15.5	1770	15.5	1700
	9.7	17.0	1840	19.6	1880
	19.9	19.5	1810	19.9	1900

In the burn experiments, one end of the tube was closed with a steel plate and a spark was used to ignite the gas mixture at the closed end. A high voltage firing unit (3000 V, 10.5 J) was used as a spark source. Fine thermocouples (28-gauge) were used to sense the flame front for velocity calculation, and piezoelectric gauges were used to detect pressure. The results of these experiments are shown in Table 3. The pressures obtained were less than predicted by Kuhl, Kamel, and Oppenheim (Ref. 3), perhaps because of the shortness of the tube (3.6 meters).

These experiments indicated the order of reactivity for the fuels as methane < propane < ethylene oxide. Also, the pressures generated were low, and the spark source, which would be used in later experiments, did not cause immediate detonation.

TABLE 3. Measured Flame Velocities and Pressures.

(3000 V, 10.5 J, spark ignition source).

Fuel	Concentration, volume, %	Velocity, m/s	Pressure, bar
Methane	8.0	45	0.014
	9.0	63	0.019
	9.5	58	0.019
	10.0	55	0.026
Propane	4.0	128	0.034
	5.0	91	0.033
Ethylene oxide	6.0	116	0.061
	7.0	233	0.110
	7.5	270	0.120
	8.0	130	0.076

HEMISPHERE BURN TESTS

Detonation properties and early ignition behavior can be studied with small scale experiments. However, the evolution of combustion in a fuel-air cloud, including flame acceleration and transition to detonation if they occur, can only be studied with larger scale tests. It would be desirable to study the burning behavior in completely unconfined clouds; however, it is difficult to control the position and concentration of the mixture when unconfined. Therefore, plastic film hemispheres were used to contain the mixture. The calculated internal pressure necessary to burst the film is very low (1.4×10^{-3} bars) and its thinness and low density should produce weak pressure wave reflections, so the presence of the film was predicted not to affect the burning properties, and no effect was detected in the tests. The hemispherical shape maximizes the flame travel distance before a boundary is reached for a given gas volume and film cost.

EXPERIMENTAL EQUIPMENT

The experimental arrangement for the 5-meter-radius hemisphere tests is shown in Figure 3. The arrangement for the 10-meter-radius hemisphere tests was similar, except a larger fuel line was used. The air was introduced into the hemisphere by a centrifugal blower via part of the instrumentation channel. It was found that the blower inflates the 5-meter-radius hemisphere in about 1 hour. Additional fans were used during the first part of the inflation of the 10-meter-radius hemispheres to decrease inflation time. The inlet to the hemisphere was covered by a "flapper" valve which directed the incoming air tangentially into the hemisphere, producing turbulent mixing. When the blower was turned off, the "flapper" valve closed, preventing escape

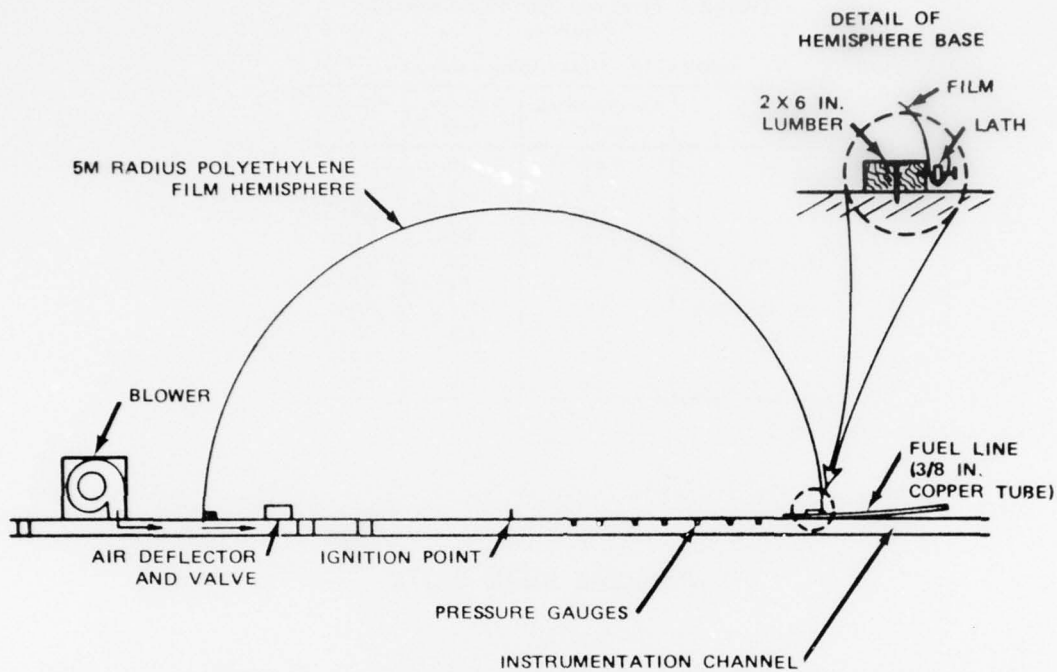


FIGURE 3. Hemispherical Burn Test, Experimental Arrangement.

of the gas mixture. The partially inflated 5- and 10-meter-radius hemispheres can be seen in Figures 4 and 5.

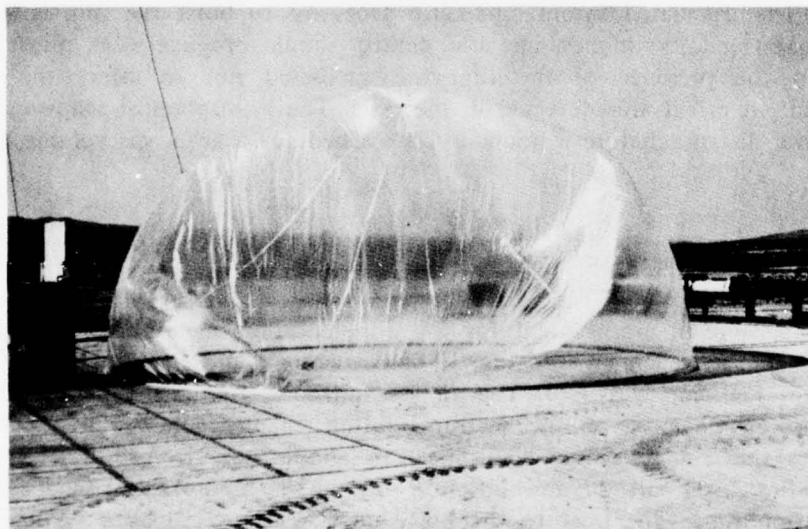


FIGURE 4. 5 m Radius Hemisphere.

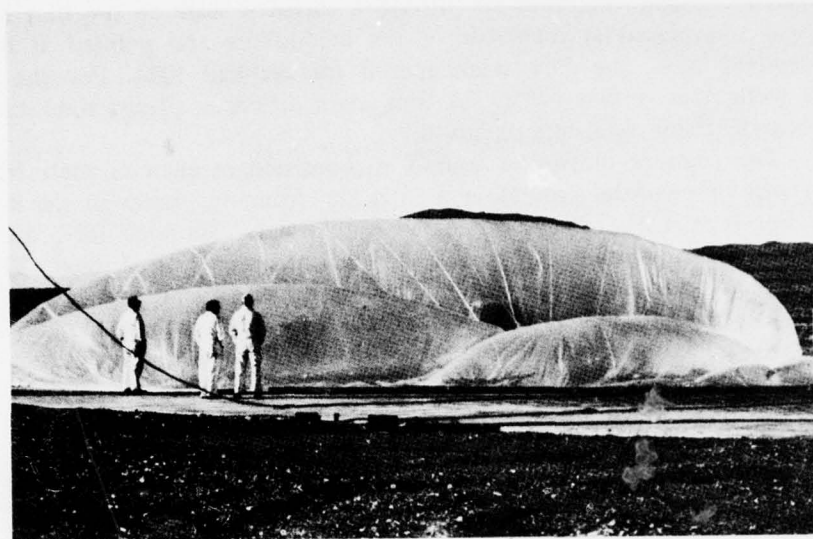


FIGURE 5. 10 m Radius Hemisphere.

The fuel to be investigated was introduced into the hemisphere through a 30-meter-long tube (two tubes for the 10-meter-radius hemisphere) from storage tanks containing the proper amount of fuel to give the desired concentration. For the fuels stored as liquids (propane, butadiene, and ethylene oxide), a hot water heat exchanger was used to vaporize the fuel.

The fuel-air mixture was ignited by a spark. The equipment used was an exploding bridgewire detonator firing unit which consisted of a $3\text{-}\mu\text{f}$ capacitor charged to 3 kV (13.5 joules stored energy) which discharged through 27.6 meters of coaxial cable to a 1.65-mm gap. This unit was used because it was already available at the test site, and because it gave a sufficiently bright spark to be seen on the photographs, thus marking the time of ignition.

Recent work by J. H. Lee (Ref. 4) indicates that detonations can be directly initiated in some gas mixtures by a spark. Because of this possibility, the characteristics of the spark used were accurately determined. Details of these measurements can be found in Appendix A. The results indicate that the energy dissipated in the spark up to the first quarter cycle was 2.79 J/cm and the power level was 0.861 MW/cm. According to Lee a spark with these characteristics would be sufficient to initiate a detonation in an acetylene-oxygen mixture. Since the mixtures used in the hemisphere burn tests are much less sensitive than acetylene-oxygen, they would not be expected to detonate directly from the spark.

Photographic coverage for the tests was provided by 1000-2000 frame-per-second and 400 frame-per-second cameras positioned at ground level. In addition, for tests 4 through 19, a 1000 frame-per-second camera was suspended 40 meters overhead. Because of the difficulty of precisely aiming the overhead camera, a short focal length lens was used giving a wide field of view. Tests 4 through 19 were

conducted at night. In order to provide a distance scale on the film for these tests, a flashlight was placed at each side of the hemisphere and pointed at the cameras. For the daylight tests, the film was exposed for ambient light. For the night tests, the lenses were opened two f-stops. A time mark generator placed time marks on the film for accurate frame rate determination.

The pressure measuring equipment consisted of eight piezoelectric gauges placed flush with or near the ground, and in a line from the center of the hemisphere to its edge. For tests 1 to 10, odd-numbered gauges were calibrated for a maximum pressure of 20 bars, even-numbered gauges for a maximum of 2 bars. The gauges were calibrated in this manner to ensure a recording of pressure whether or not detonation occurred. The odd-numbered gauges would provide a record of detonation; low level pressures would be recorded by the even-numbered gauges if there were no detonation. Since pressures were not detected in tests 1 to 7 and only a very slight indication of pressure was recorded in tests 8 to 10, all gauges were subsequently calibrated for a maximum pressure of 0.8 bar for tests 11 to 18.

It was found that electrical noise in the system limited the lowest pressure that could be recorded to 0.1 bar. The output of the charge amplifiers was recorded on a high speed instrumentation tape recorder. One channel of the tape also recorded time signals so a time base was available. A signal from the ignition source (spark gap) was recorded and, since the flash from the spark was visible on the photographic coverage, both the electronic and photographic recording systems had the same zero time.

In an attempt to determine the effect of perturbations on the flame front, three types of obstacles were placed in the hemisphere in test 6: (1) a steel grid 0.5 m \times 1.5 m placed flat on the concrete pad to increase surface roughness; (2) a steel grid 0.3 m \times 0.3 m (25-mm-square grid holes) placed vertical to the ground and facing the ignition point to increase turbulence of the flame as it passed through the grid; and (3) a structure built of 50 \times 150 \times 150-mm steel blocks which presented a 0.3 \times 0.6-m reflecting surface to the flame, and included a 0.5-m long tunnel with a 150-mm-square cross section for the flame to travel through. The open tubes of test 11 were placed on the concrete test pad radiating from the ignition point. The fan was placed on the opposite side of the ignition point facing the tubes to ensure the mixture entered the tubes. The wire screen cylinder of test 12 was 500 mm in diameter and 240 mm high, made of 0.7-mm diameter wire with 5.5-mm spacing.

EXPERIMENTAL PROCEDURE

The general procedure for the tests was as follows:

1. Measure and connect fuel supply.
2. Check pressure measuring system.
3. Load film and check photographic system.
4. Attach plastic film hemisphere to frame on ground.
5. Start blower.
6. When hemisphere is about half full, turn on flashlights, open fuel valve, and clear area.

7. When hemisphere is full, turn off blower and wait 10 minutes for turbulence to subside.
8. Start firing sequence. This sequence automatically starts cameras and tape recorder, discharges capacitor (10 J, 3000 V) to spark gap to ignite gas, and stops tape recorder and cameras.

The test sequence and conditions are shown in Table 4.

TABLE 4. Test Sequence and Conditions.

Hemisphere Burn Tests				
Test no.	Fuel	Concentration, volume %	Ambient temperature, °C	Remarks
1	Propane	4,0	30	Daylight test; flame barely visible.
2	↓	5,0	30	Concentration increased to enhance visibility. Mixture pre-ignited by static discharge. No data.
3		5,0	30	Flame barely visible; all subsequent tests done at night.
4		5,0	20	
5	Methane	10,0	20	
6	Propane	5,0	20	Obstacles placed in hemisphere to increase turbulence.
7	Methane	10,0	20	
10 Meter Radius Hemisphere				
8	Ethylene oxide	7,7	8	Instrumentation failure. No data.
9	↓	7,7	8	
10		7,7	8	
11	Propane	5,0	27	Open tubes 2 meters long and 50-, 100-, and 150-mm diameter, placed in hemisphere. Fan used in this and all subsequent tests to insure uniform mixture and that mixture was in tubes.
12	↓	4,0	27	Wire screen cylinder placed over ignition source to increase turbulence.
13	Methane	10,0	15	
5 Meter Radius Hemisphere				
14	Ethylene	6,5	15	Acetylene cylinders did not completely empty, giving low concentration.
15	Acetylene	3,5	8	
16	Methane	10,0	8	Detonation test.
17	Butadiene	3,5	10	
18	Acetylene	7,7	10	
19	Methane	10,0	30	Detonation test.

The films from the tests were assessed using frame-by-frame analysis on a projection comparator. The frame rate was determined from the timing marks, and the magnification by measuring the image of an object of known dimensions. Time measurement was accurate to better than ± 2 ms and distance measurement accuracy was ± 20 mm to ± 100 mm (depending on image sharpness).

The pressure record on the instrumentation tape was assessed by playing the tape back through an oscilloscope and photographing the trace. The oscilloscope trace could then be compared to calibration curves for each pressure gauge to obtain pressure measurements.

RESULTS

Detailed observations from each hemisphere test are provided in Appendix B. Qualitatively, all tests appeared similar. The photo record showed the ignition spark followed by about a 100-ms period when the flame was difficult to detect. The flame then appeared as a blue, expanding hemisphere. As the flame expanded, it became rough with a "pebbled" appearance. This structure increased in size to about 0.4-1.0 meter with a finer structure superimposed. The plastic film tore at the base between 300 and 400 ms (for the 5-meter tests) and the entire hemisphere rose vertically.

Many tests differed somewhat from this generalized picture. The plastic film always tore at its base where it was attached to the wooden ring; however, in some tests, the film tore unsymmetrically and lifted off, due to expansion during the combustion process, by tilting or rotating around the region where it remained attached. Depending on how strongly the film was held, the flame shape was distorted away from the held region. This was not a serious problem, but it did represent a deviation from the ideal symmetrical combustion.

Another difference in some of the tests was multiple ignition of the charge by flame getting into the instrument channel and accelerating because of confinement. This flame traveled ahead of the main flame and then broke out of the channel, igniting the main combustion mixture at a number of points inside the hemisphere. In some tests this behavior caused a series of spherical flames of different sizes to appear. These eventually coalesced without noticeable accelerations. It should be emphasized that, even though this behavior destroyed symmetry and produced a variety of odd shaped flames, the very complex flame propagation patterns that occurred did not produce noticeable accelerations of the flame or any other important unusual effects. In fact, it was surprising that, even when there was very unusual flame propagation, the final flame volume always retained a relatively hemispherical shape; this simply indicates that expansion of the products behind the flame tends to push the surrounding gas uniformly in all directions so that roughly spherical symmetry is maintained in the final flame volume.

In none of the 5-meter tests was a pressure wave recorded. This result agrees with the subjective impression of personnel at the test site that little sound was produced. This result is perhaps not surprising since Kuhl et al. (see Ref. 3) have predicted that a flame speed of 10 m/s should produce a pressure wave of 0.1 bar and the lower limit of detection of the equipment used was 0.1 bar. Pressures were recorded during ethylene oxide tests; however the signals were barely detectable and difficult to distinguish from the signal caused by the heating of the gauges by the flame.

An example of the measurements made from burn tests photo records can be found in Figures 6 and 7. Complete results are given in Appendix C. The horizontal radius of the flame is measured from the ignition point to the flame boundary at a distance of about 0.2 meter up from the concrete pad so that distortion due to the surface would not affect the measurement. The horizontal radius versus time curves were straight lines in all cases indicating a constant velocity. It is apparent (especially in Figure 6) that the curves do not pass through the origin. It is possible that some time is required to build up to constant flame velocity due, perhaps, to the

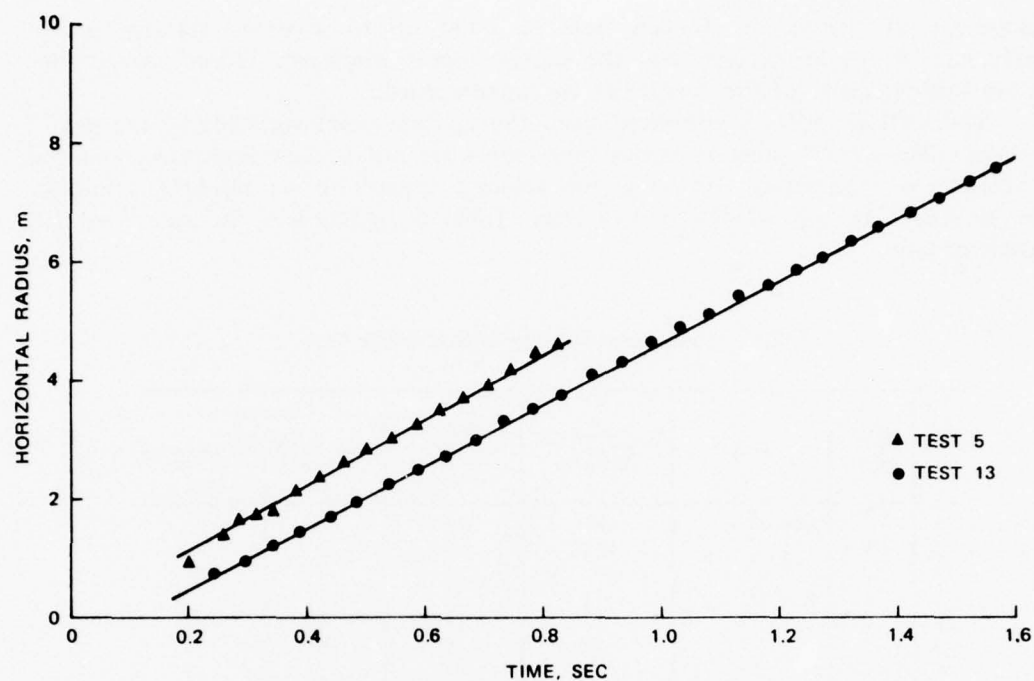


FIGURE 6. Horizontal Flame Position 10% Methane.

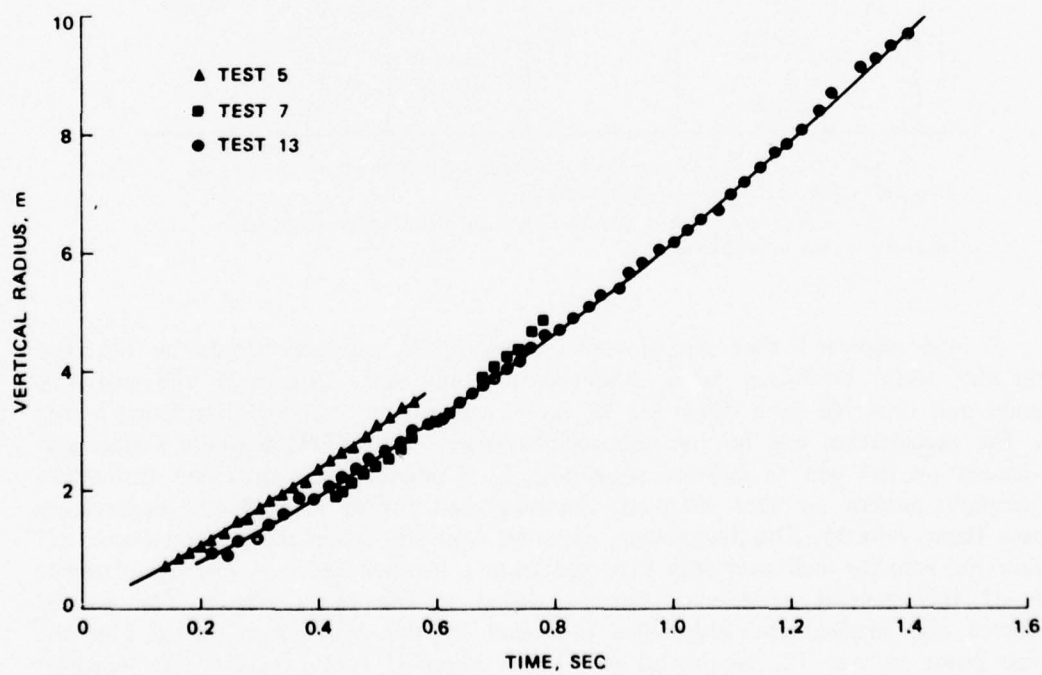


FIGURE 7. Vertical Flame Position 10% Methane.

development of turbulence. If this time to build up to constant velocity is not reproducible, it would explain why the curves appear displaced. Indeed, if the time axes are shifted, many of the curves can be superimposed.

The vertical radius is measured from the ignition point vertically to the top of the flame. The vertical position versus time curves are not straight lines but show that the velocity is accelerating. However, the velocity appears to be reaching a limiting value especially in the 10-meter-radius tests. Table 5 summarizes the results of the hemisphere tests.

TABLE 5. Summary of Results of Hemisphere Tests.

Test no.	Size, meters	Fuel	Concentration, volume %	Horizontal velocity, m/s	Vertical velocity	
					at 3 m, m/s	at 8 m, m/s
5	5	Methane	10.0	5.8	7.3	...
7	5	↓	10.0	... ^a	7.3	...
13	10	↓	10.0	5.2	6.5	8.9
1	5	Propane	4.0	... ^b	6.3	...
12	10	↓	4.0	6.1	7.8	10.6
3	5	↓	5.0	... ^a	7.4	...
6	5	↓	5.0	6.9	9.5	...
4	5	↓	5.0	8.3	10.2	...
11	10	↓	5.0	9.6	9.9	12.6
10	10	Ethylene oxide	7.7	13.4	15.2	22.5
8	10	↓	7.7	14.7	16.0	22.4
14	5	Ethylene	6.5	8.8	17.3	...
15	5	Acetylene	3.5	3.6	4.6	...
18	5	↓	7.7	23.7	35.4	...
17	5	Butadiene	3.5	3.9	5.5	...

^a Burning fuel in the instrumentation channel distorted the shape of the flame and no horizontal velocity could be obtained.

^b Test performed in daylight and flame base was insufficiently visible for horizontal velocity to be obtained.

It was expected that several flame acceleration processes would be observed during the tests. Boundary layer acceleration along the surface of the pad was expected and observed as a distortion of the hemispherical shape of the flame at the base. The acceleration was not pronounced, however, even in test 6 where a steel grid was placed on the pad to increase roughness. It is possible that sufficient turbulence was already present so that boundary layer-induced turbulence did not appreciably increase flame velocity. This turbulence, apparent over the entire flame hemisphere, did increase the velocity well over that expected from a laminar flame. A discussion of the cause of this general turbulence can be found in the next section. The general turbulence also masked the turbulence produced by the wire screen placed over the ignition point in test 12. Wagner (Ref. 5) has observed that a screen grid increases flame velocity greatly.

The buoyancy of the hot combustion products is probably the cause of the difference between the horizontal and vertical flame velocities. A rough calculation based on Scorer (Ref. 6) yields approximately the velocity difference observed.

The obstacles placed in test 6 and the open tubes in test 11 did not appreciably influence the flame; however when the flame reached the 2- by 6-inch (5- by 15-centimeter) wooden ring to which the film had been attached there was a noticeable acceleration.

AUGMENTATION OF FLAME VELOCITY BY TURBULENCE

When a volume of a fuel-air mixture is centrally ignited, the flame moves radially outward from the ignition point. One effect of the flame is to raise the temperature and, thus, for a constant pressure process, expand the gases within the flame envelope. This expansion causes the flame to have a higher velocity than it would have if no expansion occurred. Thus, the measured velocity is made up of an expansion component and the basic flame speed (S). This flame speed may be calculated by multiplying the observed flame velocity by the density ratio across the flame. The density ratio can be calculated from the temperatures and average molecular weights before and after burning. The results of such calculations for the gases tested are shown in Table 6. The flame speed so calculated is labeled S' . The literature value for the laminar flame speed is given as S . The ratio of calculated speed to laminar speed S'/S is labeled ψ . It is proposed that this ψ is the augmentation of the flame due to turbulence and, as can be seen, varies from 1.6 to 2.1 for all of the fuels except butadiene. As noted in the description of the individual tests, Appendix B, the concentration of butadiene may have been low due to incomplete vaporization of the fuel.

TABLE 6. Augmentation of Flame Velocity by Turbulence.

Fuel	Concentration, volume %	Flame temp., °C ^a	Density ratio across flame	Horizontal flame velocity, m/s	S' , m/s	S , ^a m/s	ψ
Methane	10.0	1960	0.131	5.8	0.76	0.37	2.1
Ethylene	6.5	2100	0.137	8.8	1.21	0.75	1.6
Acetylene	7.7	2325	0.112	23.7	2.65	1.56	1.7
Propane	4.0	1980	0.128	6.1	0.78	0.43	1.8
Butadiene	3.5	2100	0.117	3.9	0.46	0.60	0.8
Ethylene oxide	7.7	2140	0.113	14.0	1.58	1.01	1.6

^a Ed Barnett, H. C. and Hibbard, "Basic Considerations in the Combustion of Hydrocarbon Fuels with Air", R. R., National Advisory Committee for Aeronautics, Report No. 1300, 1959. Pp. 256-8.

The turbulence noticed in the flames could be caused by a mechanism proposed by Landau (Ref. 7). According to this mechanism, an initial incipient wrinkling of the flame front caused by concentration or temperature inhomogeneities (or in the case of the present experiments by the ignition spark) is amplified because combustion products moving normal to the flame front converge behind any bulges and diverge behind depressions. Therefore, the pressure of the combustion products increases behind bulges and decreases behind the depressions. This pressure difference causes an increase in the wrinkling of the flame front, thus an increase of the burning surface area and an acceleration of the flame velocity. A description of this process is given by Shchelkin and Troshin (Ref. 8). They cite experimental evidence that this turbulence becomes significant when the Reynolds number becomes greater than 10^4 . The Reynolds number (R_e) is defined as follows:

$$R_e = \frac{\rho SR}{\mu}$$

where ρ is the density, S the laminar flame velocity, R the radius of the flame and μ the viscosity. For the fuels tested, the Reynolds number is above 10^4 for radii over 0.1 to 0.5 meter, depending on the fuel. Thus, the turbulence described would be significant in these experiments. It is interesting also that the calculated radii are the radii when the flames first become visible.

Based on small burner experiments, Bollinger and Williams (Ref. 9) have reported augmentation ratios (ψ) for Reynolds numbers equal to those in the hemisphere tests between 1.5 and 2.0. Thus, the augmentation observed is in agreement with past experiments.

HEMISPHERE DETONATION TESTS

Two attempts were made (tests 16 and 19) to detonate a stoichiometric (10% by volume) methane-air mixture in 5-meter-radius hemispheres. The experimental arrangement was the same as for the hemisphere burn tests except solid explosive boosters were used and the cameras were run at 8000 frames per second. In test 16 a 1.35-kg and in test 19 a 2.05-kg hemispherical Composition B booster was used. The photo record from both tests appeared similar. On initiation of the booster, an intense light appeared from the detonation products. These products expanded rapidly to about 3 meters, then a blue flame front became visible. The flame front expanded much more slowly than the initial detonation product expansion. Figure 8 is one

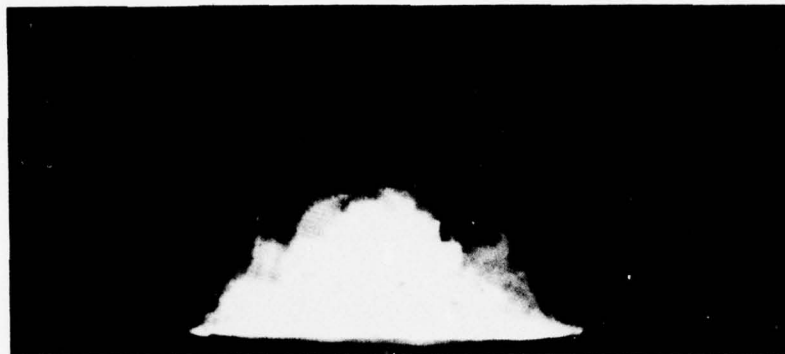


FIGURE 8. Attempted Detonation 10% Methane.

frame from the high speed photo record of test 19. The position of the flame front in tests 16 and 19 are shown in Figures 9 and 10, respectively.

The flame reaches 3 meters in 3 ms, then expands at a velocity of 34 m/s. This is a higher velocity than previously observed, perhaps because it is moving into shock heated and accelerated mixture. Figure 10 also shows the position of the shock

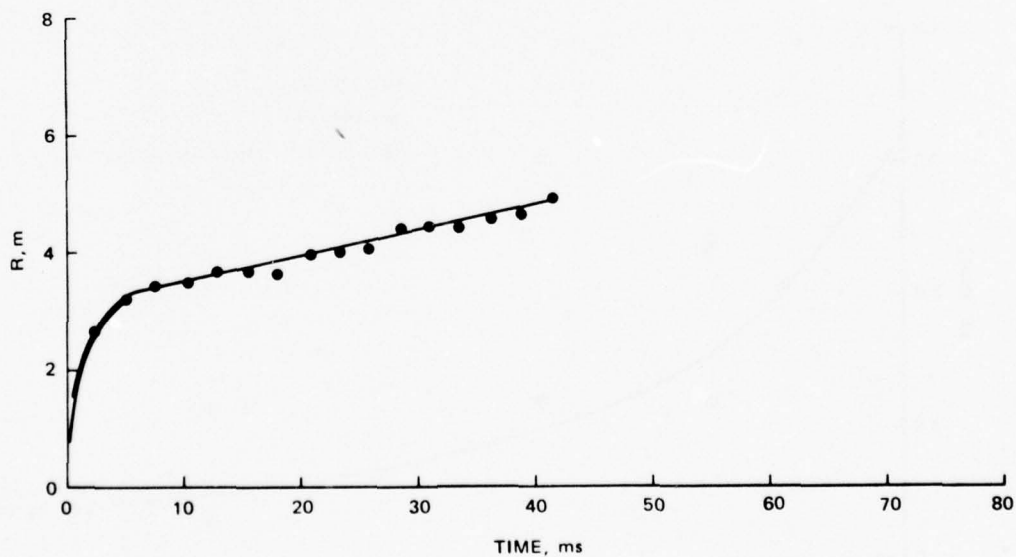


FIGURE 9. Flame Position, Detonation Test #16.

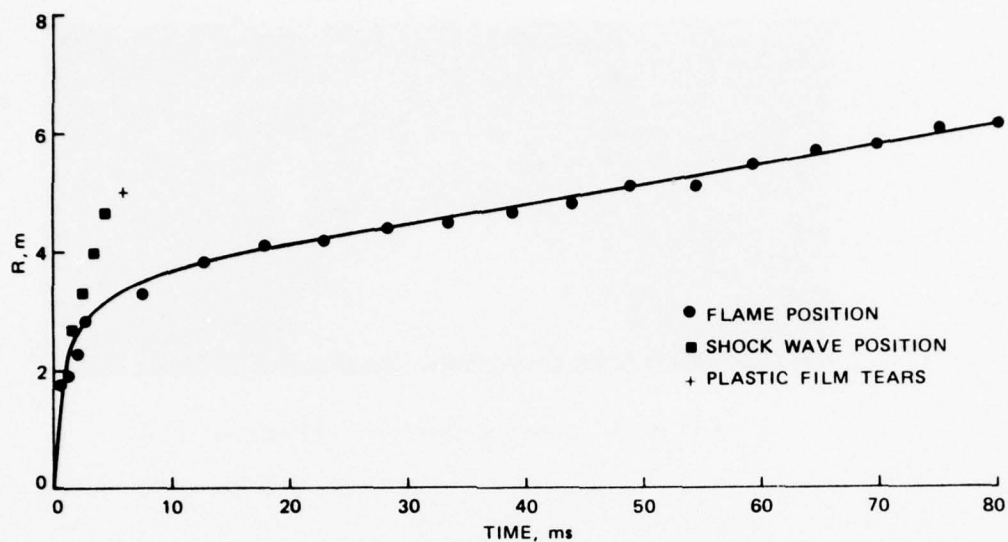


FIGURE 10. Flame Position, Detonation Test #19.

wave as recorded by the pressure gauges, and the time the plastic film tears. Figure 11 shows the predicted pressure from a 2.05-kg solid explosive (Ref. 11), actual measurements from a booster only, and the measurements from test 19.

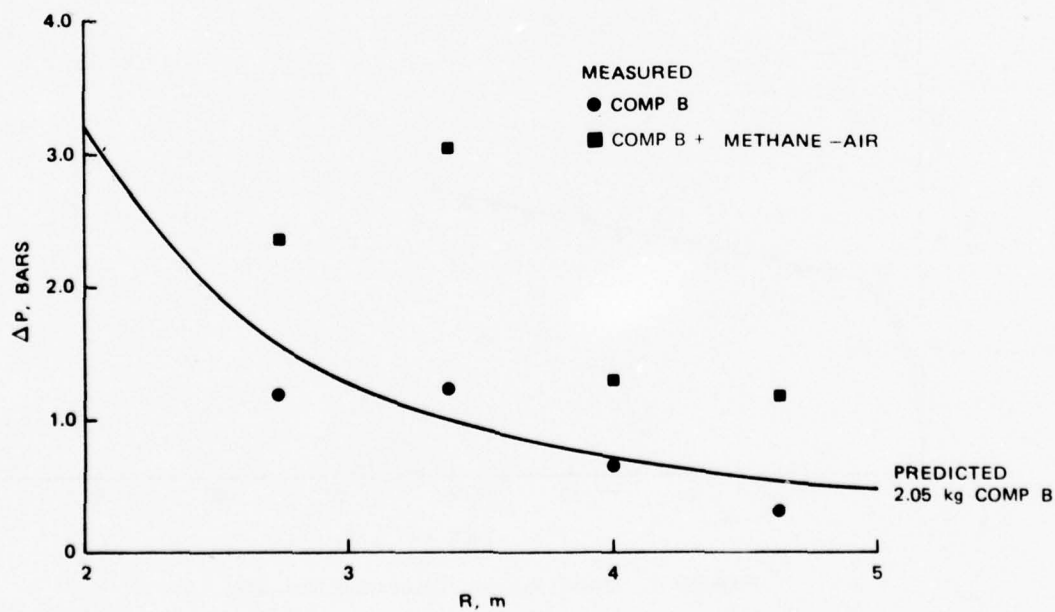


FIGURE 11. Pressure Measurement, Detonation Test.

Because the shock wave moves away from the flame, and the flame reaches a constant velocity far less than the detonation velocity (1810 m/s), and the shock wave decays to far less than the detonation pressure (16.3 bars), the evidence indicates a sustained detonation did not occur. The pressures measured for the methane-air mixture were greater than either predicted or measured for the booster alone. This could have been caused by partial reaction of methane in the shock wave. The failure to obtain a detonation is in disagreement with the work of Kogarko (Ref. 2) but is consistent with that of Bull et al. (Ref. 10).

The latter researches determined the amount of solid explosive required to detonate mixtures of methane and oxygen diluted with nitrogen. An extrapolation of their data indicates that a charge of 22 kg of solid explosive would be required to detonate a methane-air mixture.

Consider a hypothetical experiment with a 2.3-meter-diameter vertical tube open at the top. The tube and a region above the tube contain a methane-air mixture. By some means a detonation is produced in the tube and moves upward and out of the tube. The pressure in the wave as it enters the region above the tube is the detonation pressure (16.2 bars). This is also the calculated pressure of the shock wave from the 2.05-kg solid explosive charge when it has expanded to this diameter (2.3 meters). In the experiment, even though the pressure was higher due to some contribution of the methane, no sustained detonation was produced. This implies that a detonation in an enclosed space (possible because of confinement) would have to exit the space through an opening larger than 2.3 meters to produce a sustained detonation in an unconfined methane-air cloud. It was not determined how much larger the opening would have to be, if indeed an unconfined detonation is possible, but only that openings smaller than 2.3 meters do not produce a detonation.

In the above paragraph it was stated that the shock wave at 2.3-m-diameter radius had the same characteristics as a detonation wave in methane-air. This is not strictly correct since the detonation wave has a shock front of twice the detonation pressure. This so called spike pressure is usually not considered in detonation effects because it is of short duration. However, if the "spike" pressure is effective in producing a sustained detonation the above argument is still valid but with a limiting diameter of 1.5 meters.

CONCLUSIONS

The unconfined burning characteristics have been investigated for premixed fuel-air mixtures using methane, propane, ethylene, butadiene, ethylene oxide and acetylene fuels. Although attempts were made to optimize conditions for transition from burning to detonation in unconfined mixtures, no transition occurred. Flame accelerations did occur; however, the flames appeared to reach a constant velocity after an initial acceleration, and accelerations which would be expected to lead to a transition to detonation in larger clouds were not observed.

A sustained detonation in unconfined methane-air mixtures is not produced with solid explosive boosters of up to 2 kg. This implies that, if a detonation occurred in a confined space due to confinement, the exit of the detonation wave from the confinement would have to be through an opening over 2.3 meters in diameter, or the detonation would not be sustained. How much larger the opening would have to be was not determined.

FUTURE PLANS

Several areas of work originally planned for Phase II will be reported separately. These include the following experiments and studies:

1. Long Tube Experiments. It is known that ignition of a flammable mixture at the closed end of a long tube will lead to a detonation. These experiments will determine the effect of venting on the transition to detonation.

2. Ignition Source Survey. A survey will be made of possible ignition sources that could be present in the vicinity of an accidental LNG spill. The strengths of these sources will be compared, and the likelihood that these sources could produce direct initiation of detonation will be determined.

3. Large Spill Feasibility Study. A study will be made of the feasibility of conducting very large spill tests of LNG and the benefits of conducting such spills.

4. Methane-Propane Detonation Tests. A determination will be made as to what percentage of propane in methane is required to produce a detonable mixture.

Phase III of the Vapor Cloud Explosion Study will consist of a study of the burning characteristics of LNG spilled on water. A facility has been constructed with the capability for rapidly spilling up to 6 m³ of LNG onto a 50- by 50-meter pond. Measurements will be made of the LNG pool size, the heat transfer from the water to the LNG pool, the vapor composition, the flame size and shape, the radiation from the flame, and the spectral distribution of the radiation from the flame. There will be two series of tests. The first series will involve spilling the LNG and immediately igniting the vapor. The second series will consist of spilling the LNG, permitting it to vaporize, and igniting the vapor downwind. Six of the first series of tests have already been carried out; however data have not been fully analyzed.

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Appendix A

SPARK INITIATION SOURCE USED IN THE HEMISPHERE TESTS

The source of ignition for the hemisphere tests consisted of a spark produced between the electrodes shown in Figure A-1 by an exploding bridgewire detonator firing unit. The essential features of the firing unit, manufactured by Reynolds Industries* are shown in Figure A-2. The electrical characteristics of the discharge circuit are: voltage 3.08 KV, capacitance 3.05 μf , inductance 6.40 μh , and resistance 1.10 Ω (with spark gap shorted). Most of the inductance and resistance are in the 27.6 m of coaxial cable.

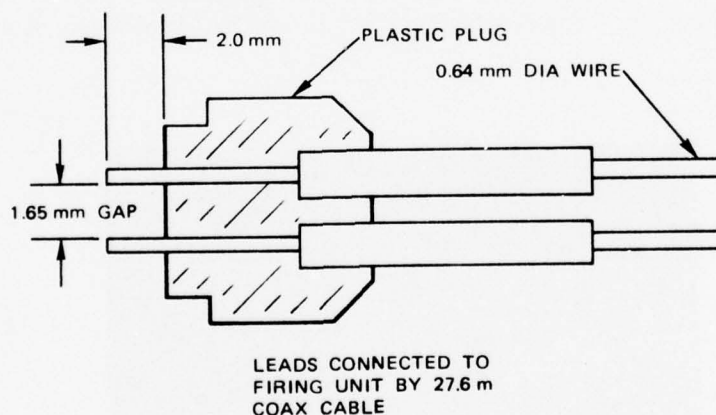


FIGURE A-1. Spark Gap.

* Reynolds Industries, Inc., P. O. Box 1170, Marina del Rey, CA. 90291.

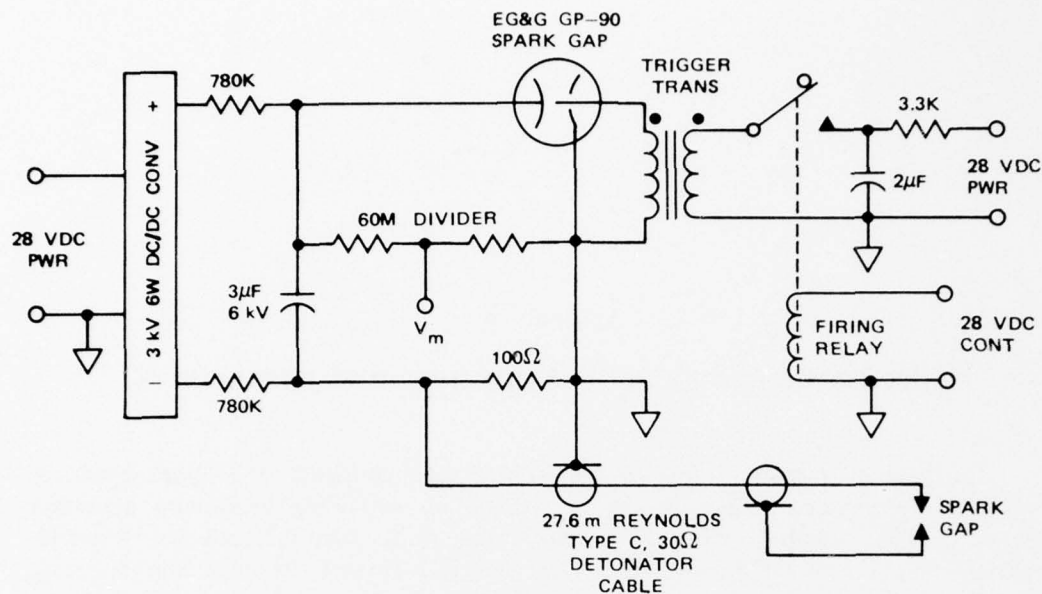


FIGURE A-2. Firing Unit.

In order to measure the characteristics of the spark a 500 MHz bandwidth coaxial current and voltage viewing network was inserted between the spark gap and the 27.6 m of coaxial cable. The current through the gap, the voltage across the gap and the output of a photodetector measuring the light output of the spark were recorded on oscilloscopes. Typical recordings are shown in Figures A-3, A-4 and A-5.

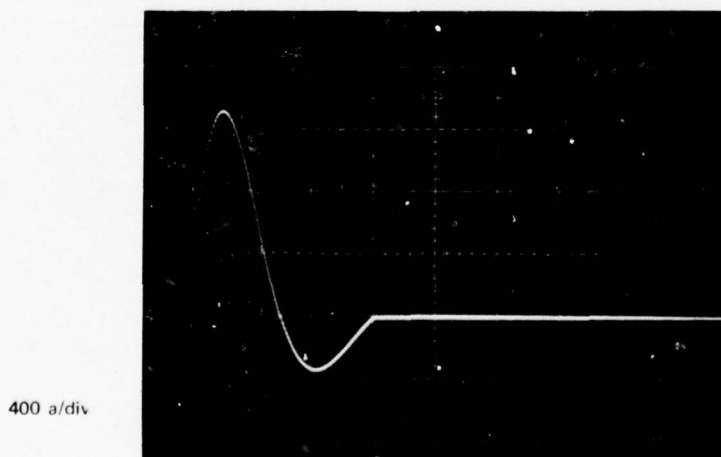
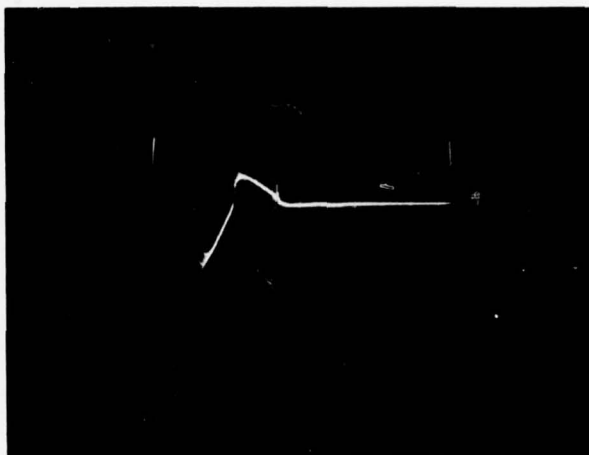


FIGURE A-3. Spark Current.

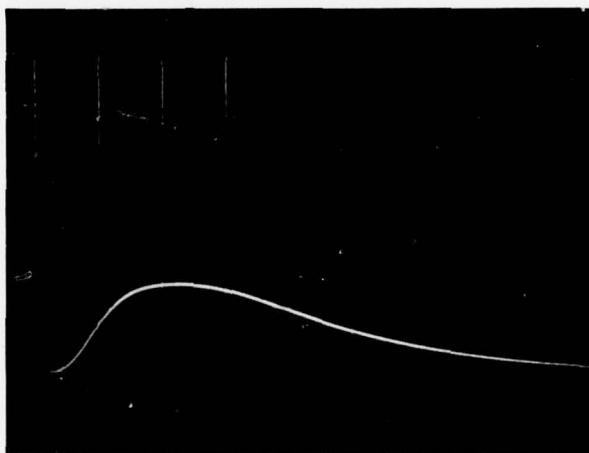
50 V/div



10 μ s/div

FIGURE A-4. Spark Voltage.

0.5 V/div



10 μ s/div

FIGURE A-5. Spark Light.

A calculation of the current through the gap (neglecting gap resistance) by the equations:

$$i = -\frac{E}{\omega L} \exp[-\alpha t \sin \omega t]$$

$$\alpha = \frac{R}{2L}$$

$$\omega = \frac{1}{LC} - \alpha^2$$

where:

i = current (amps)

t = time (sec)

E = voltage (3.08 KV)

L = inductance (6.4×10^{-6} henrys)

R = resistance (1.1 Ω)

C = capacitance (3.05×10^{-6} farads)

gave results in good agreement with the measured current. The gap resistance ($r = e/i$), spark energy ($E = \sum_0^t e \cdot i \cdot \Delta t$), and spark power ($P = e \cdot i$) were calculated from the current and voltage measurements. The results of these calculations are shown in Figures A-6, A-7 and A-8.

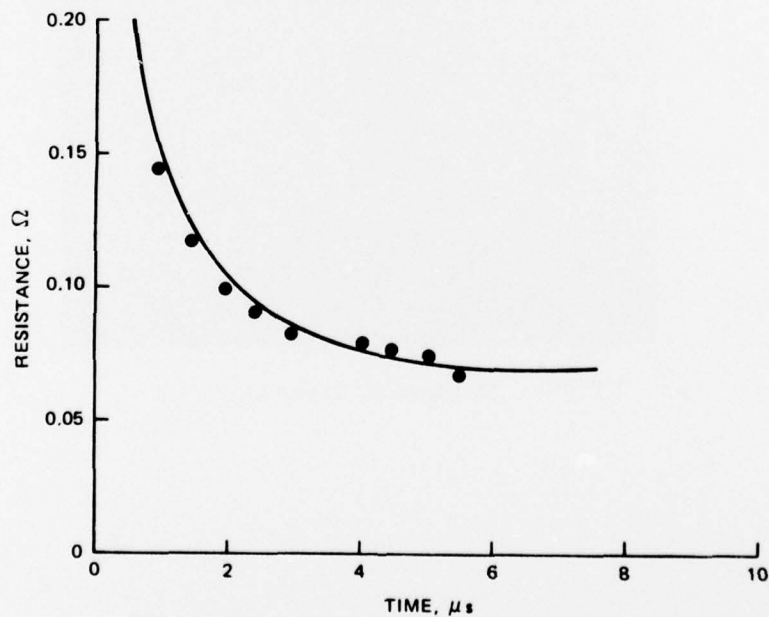


FIGURE A-6. Spark Resistance.

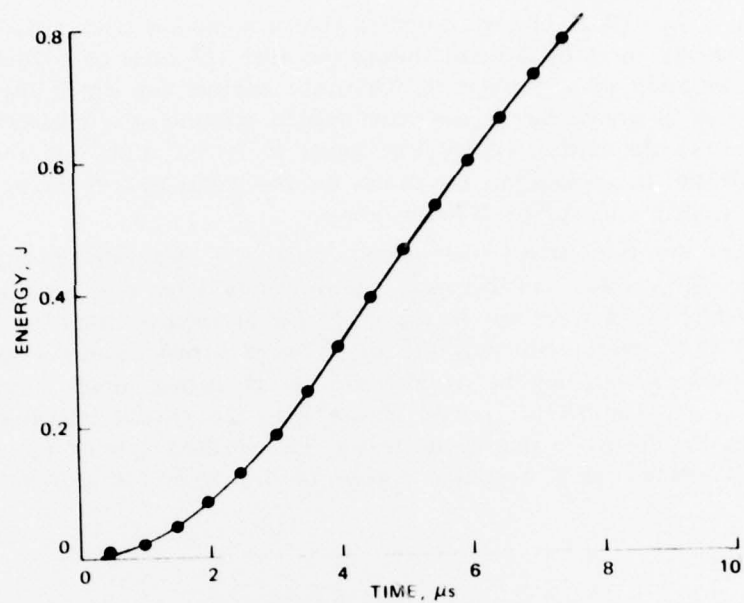


FIGURE A-7. Spark Energy.

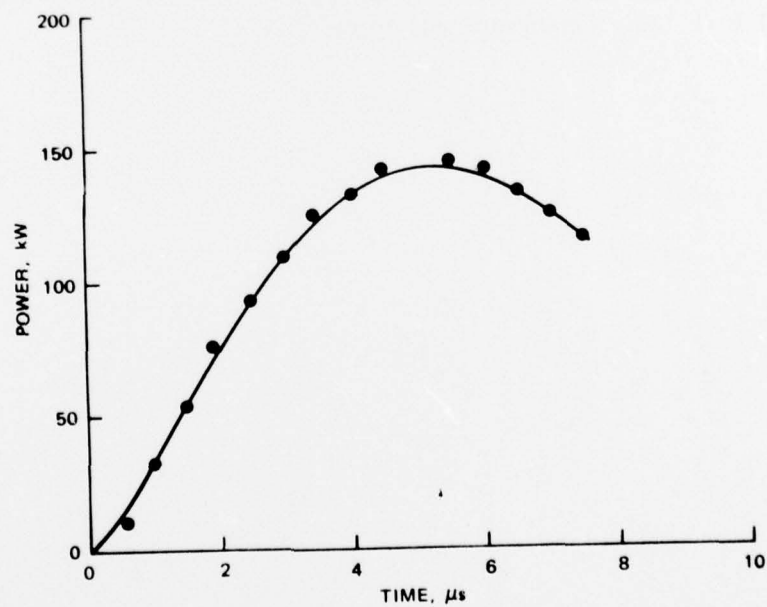


FIGURE A-8. Spark Power.

Knystantas & Lee (Ref. 1) have proposed that a minimum critical power and a minimum critical energy must be reached during the first 1/4 cycle of a discharge for the direct spark initiation of a detonation. The only mixture for which these values were determined was a stoichiometric acetylene-oxygen mixture at a pressure of 100 torr. For this mixture the critical energy was found to be 0.1 J/cm and the critical power was 0.1 MW/cm. In these terms the values for the spark used in the hemisphere tests are 2.79 J/cm energy and 0.861 MW/cm power.

These values are not strictly comparable since the electrode spacing of the spark gap used by Knystantas and Lee was comparatively large (37 mm) so that a cylindrically expanding shock wave was produced. In the hemisphere tests the electrode spacing was small (1.65 mm), and thus the shock wave would assume a spherically expanding shape and would not be as effective in producing direct initiation of detonation. Matsui and Lee (Ref. 2) have shown that the critical initiation energy (J/cm) increases as the electrode spacing decreases. The smallest spacing reported was 2.5 mm, and this spacing gave a critical energy of 1.5 J/cm for acetylene-oxygen mixtures.

REFERENCES

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Appendix B

DESCRIPTION OF INDIVIDUAL TESTS

TEST #1, 4% PROPANE

This was the first test and was a trial to check out instrumentation and photographic coverage. The burn was made in daylight. Because of ambient light the flame was barely visible, only the top of the flame hemisphere was visible and only a vertical velocity could be determined. There was some yellow incandescence at the base of the flame but because of the faint image it could not be determined if this incandescence affected the shape of the flame.

TEST 2, 5% PROPANE

In an attempt to increase the visibility of the flame, the fuel concentration was increased to 5% (4% is stoichiometric). Before the mixture could be ignited with the spark ignition source it preignited. It is possible that the propane flowing through the inlet tube generated a static charge, that arced to the metal of the instrumentation channel, igniting the mixture. To prevent this occurring the inlet tube was grounded to the instrumentation channel. It is also possible that the film hemisphere became electrically charged. A coating for the film was investigated to make it conductive; however, the coating decreased the transparency of the film and was not used.

TEST 3, 5% PROPANE

Test appeared similar to test one. The increased propane concentration did not cause increased visibility of the flame. Only vertical velocity could be obtained. All subsequent tests were done at night.

TEST 4, 5% PROPANE

This was the first night test. The blue flame was clearly visible. Yellow incandescence appeared at the base of the hemisphere. This incandescence appeared to be of two types; a diffuse incandescence radiating from the ignition point outward at ground level, and an intense jetting from the instrumentation channel. The first type,

which did not cause distortion of the hemispherical blue flame or secondary ignition ahead of the flame, could have been caused by dust swept up by the expanding gases. The second type, which did cause ignition ahead of the flame and subsequent distortion of the hemispherical flame, could have been caused by fuel burning in the instrumentation channel. It is difficult to determine the velocity of propagation in the channel because the time and location of ignition in the channel are not known. Another phenomenon was apparent on the film from the overhead camera. When the flame reached the 5-m-radius wooden ring used to fasten the plastic hemisphere, there was an acceleration from 8.3 m/s to a higher velocity of 13.8 m/s. The higher velocity then remained constant to a radius of 6.5 m then slowly decreased.

TEST 5, 10% METHANE

This was the first test with methane. The flame did not appear as bright as with propane. As with test 4, there was yellow incandescence, which caused multiple ignition and distorted the flame at later stages.

TEST 6, 5% PROPANE

As with tests 4 and 5, yellow incandescence caused secondary ignition and distortion of the flame. Because of the distortion it was not possible to measure the increase of flame velocity as the flame passed over the obstacles. However, the obstacles did not produce a pronounced effect on the flame.

TEST 7, 10% METHANE

This test appeared similar to test 5.

TEST 8, 7.7% ETHYLENE OXIDE

This was the first of the tests in 10-m-radius hemispheres; all previous tests were 5-m-radius. There was much less incandescence present in this test, and it did not cause secondary ignition. The flame started hemispherical in shape; then because of apparent boundary layer acceleration the hemisphere developed a conical base. The velocity of the flame at the surface was constant at 16.8 m/s as opposed to 14.7 m/s above the surface. During later stages the flame became distorted because of the plastic hemisphere tearing at one edge.

TEST 9, 7.7% ETHYLENE OXIDE

This test appeared subjectively, to the personnel at the test site, to be similar to test 8. However, because instrumentation malfunctioned, no data were obtained.

TEST 10, 7.7% ETHYLENE OXIDE

This test was similar to test 8 except the plastic hemisphere separated uniformly, and there was no distortion of the flame shape even at late times. The boundary layer acceleration caused a constant flame speed at the surface of 19.8 m/s as opposed to 13.4 m/s above the surface.

TEST 11, 5% PROPANE

Yellow incandescence was again apparent in this test with secondary ignition over the instrumentation channel. The tubes placed in the hemisphere had no apparent effect.

TEST 12, 4% PROPANE

This test appeared similar to test 11, although the yellow incandescence did not cause much distortion of the flame. The only apparent effect of the wire screen placed over the ignition source was to make the flame visible at a slightly earlier time. Decreasing the fuel concentration from 5 to 4% did not noticeably decrease the luminosity.

TEST 13, 10% METHANE

This test was a near perfect burn. There was almost no yellow incandescence. The flame was a hemisphere that evolved in later stages into a sphere on a conical pedestal. Because the flame velocity was so low, the buoyancy force caused the flame to rise and produce the shape of a sphere on a pedestal. The boundary layer velocity was only slightly higher than the velocity above the surface (5.4 m/s vs 5.2 m/s).

TEST 14, 6.5% ETHYLENE

Much incandescence and many secondary ignition points made this test difficult to assess.

TEST 15, 3.5% ACETYLENE

The acetylene supply tanks did not completely empty in this test, producing a low fuel concentration. The long burn time caused by the low flame velocity (3.6 m/s) permitted the buoyancy forces to raise the flame envelope off the surface. The complex flow pattern caused the measured horizontal velocity to accelerate and the vertical velocity to be constant; the reverse of that usually observed.

TEST 16, 10% METHANE

This was a detonation test and is discussed in a separate section.

TEST 17, 3.5% BUTADIENE

This test appeared similar to test 15. The low velocity permitted the buoyancy forces to lift the flame envelope off the surface. There was some afterburning from the end of the fuel line, so it is possible all of the fuel was not in the hemisphere at the start of the test and the 3.5% concentration was not achieved.

TEST 18, 7.7% ACETYLENE

The flame in this test was much brighter than the other tests. Secondary ignition occurred from burning in the instrumentation channel.

TEST 19, 10% METHANE

This, like test 16, was a detonation test and is discussed in a separate section.

Appendix C
FLAME, POSITION, BURN TESTS

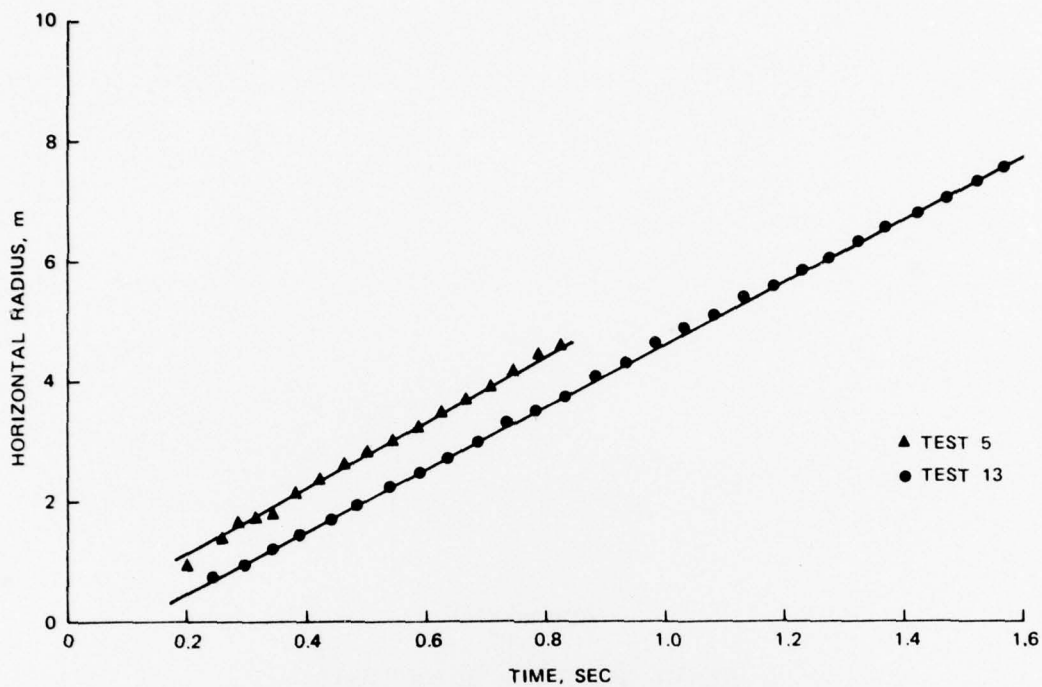


FIGURE C-1. Horizontal Flame Position 10% Methane.

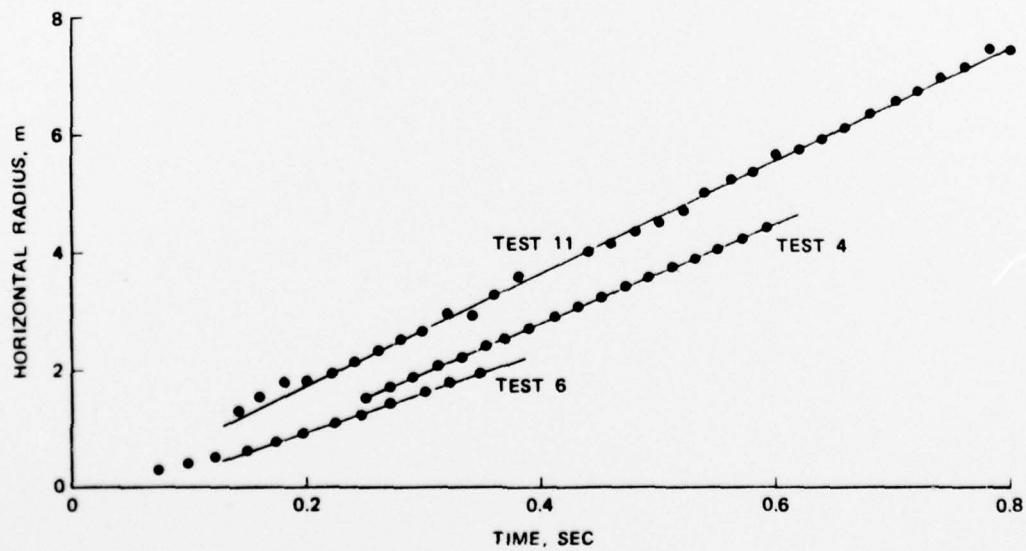


FIGURE C-2. Horizontal Flame Position 5% Propane.

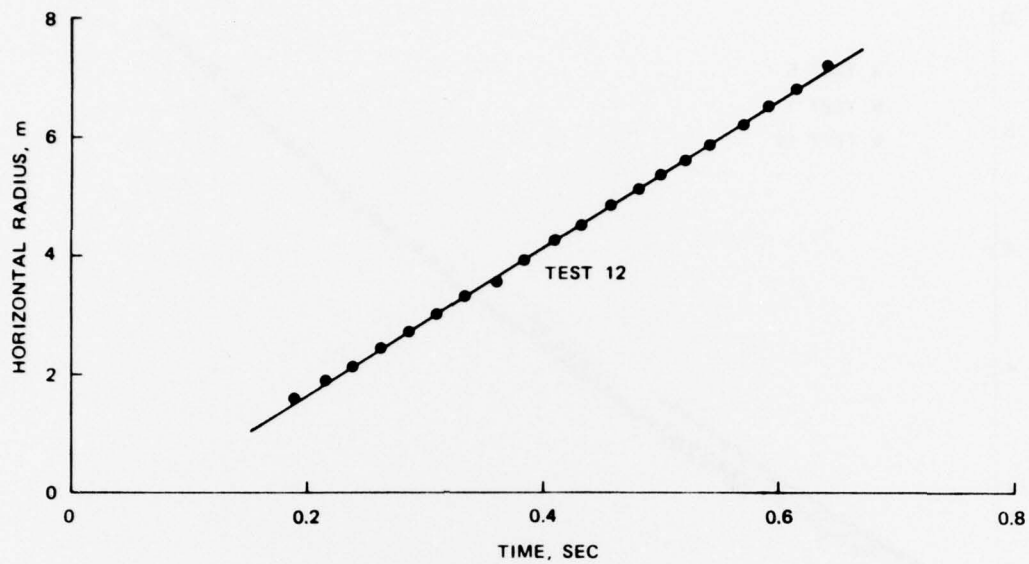


FIGURE C-3. Horizontal Flame Position 4% Propane.

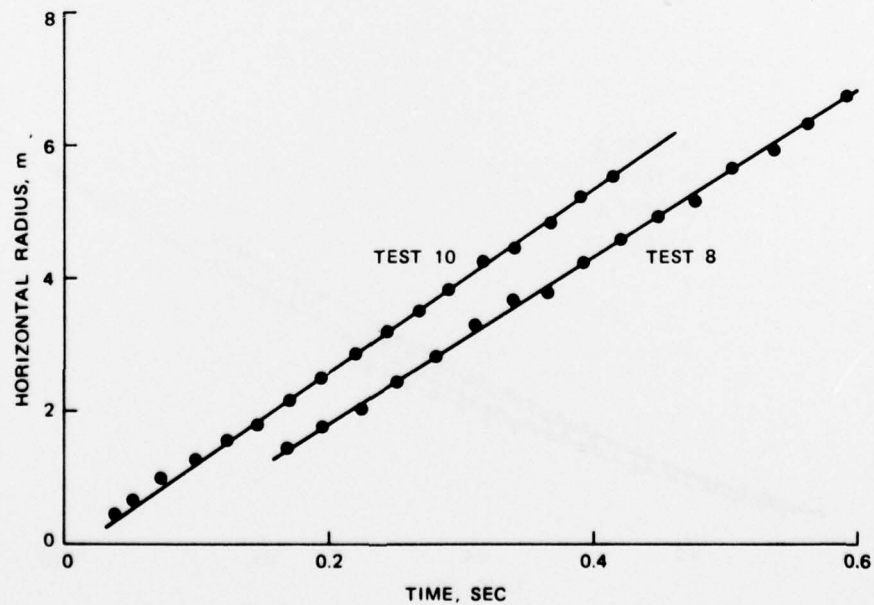


FIGURE C-4. Horizontal Flame Position 7.7% Ethylene Oxide.

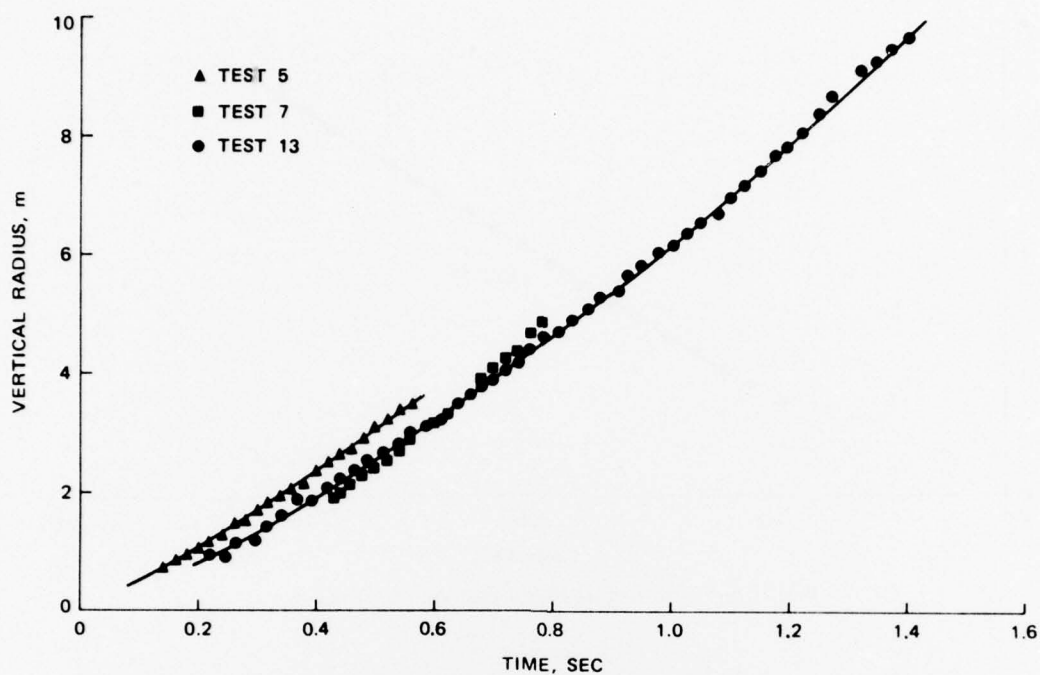


FIGURE C-5. Vertical Flame Position 10% Methane.

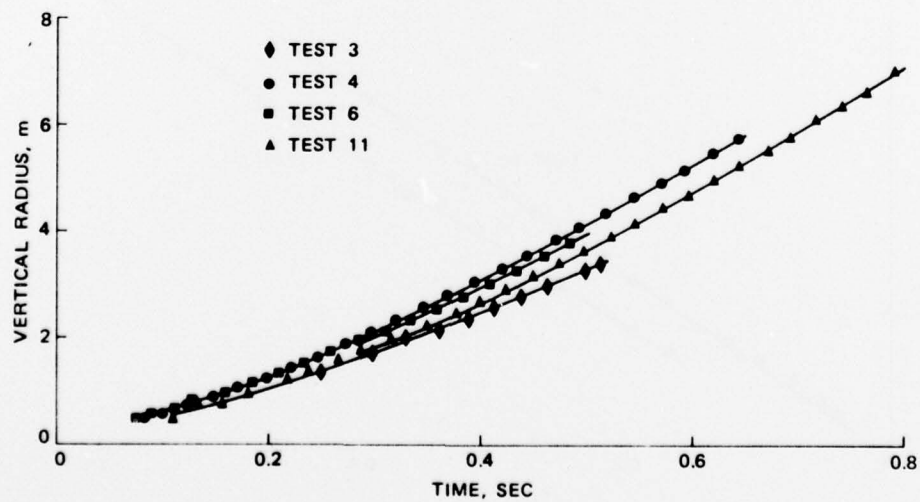


FIGURE C-6. Vertical Flame Position 5% Propane.

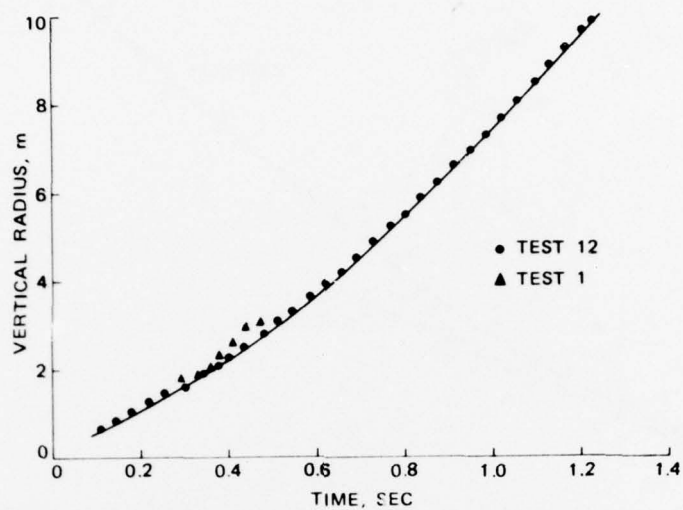


FIGURE C-7. Vertical Flame Position 4% Propane.

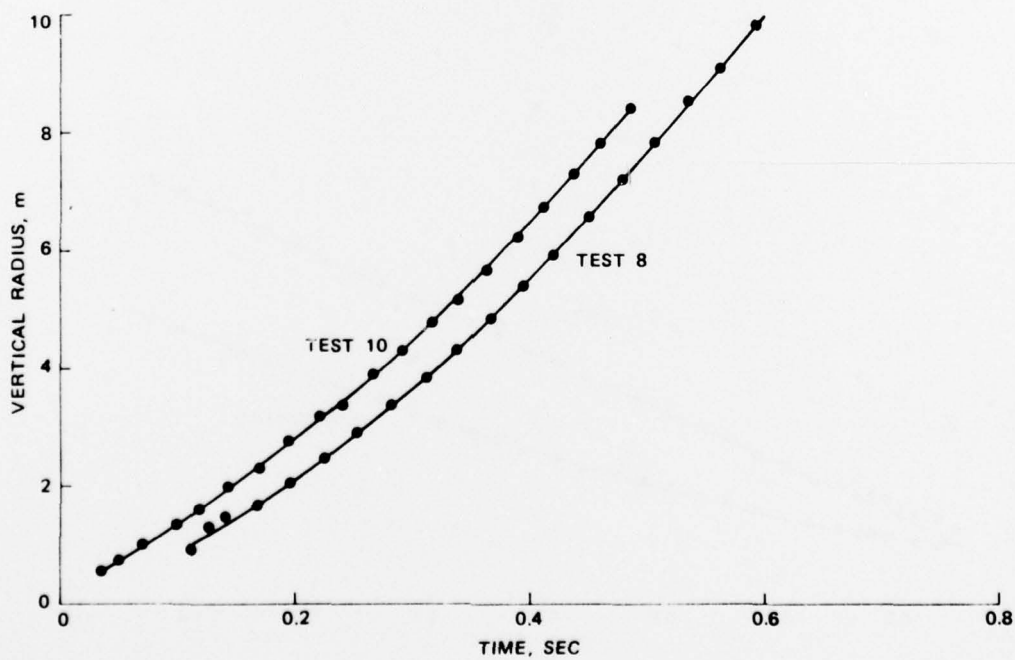


FIGURE C-8. Vertical Flame Position 7.7% Ethylene Oxide.

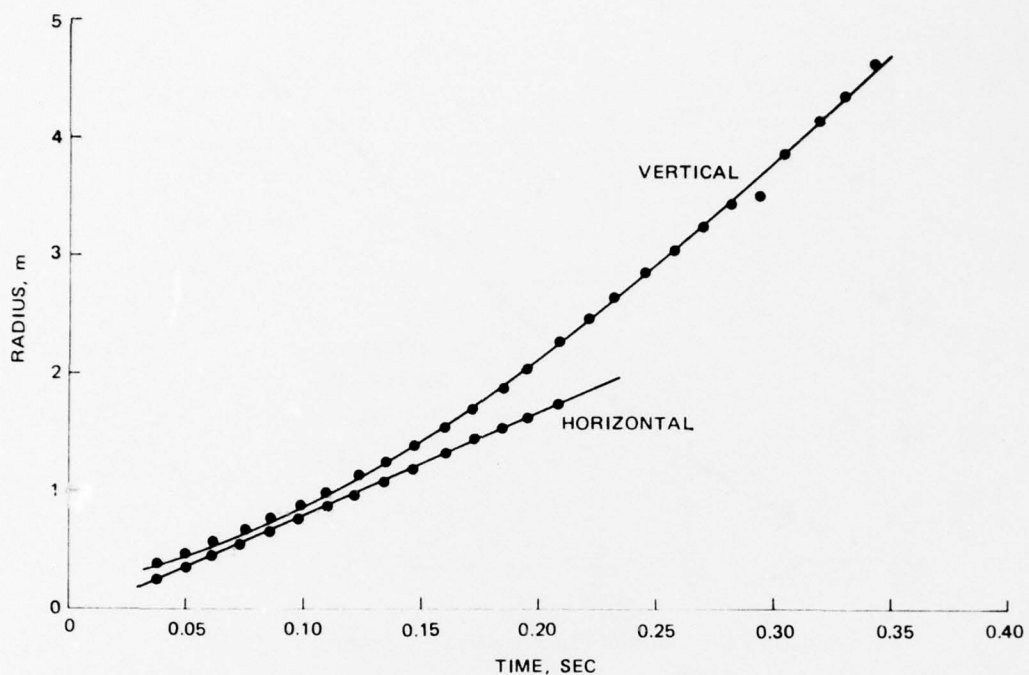


FIGURE C-9. Flame Position 6.5% Ethylene Test 14.

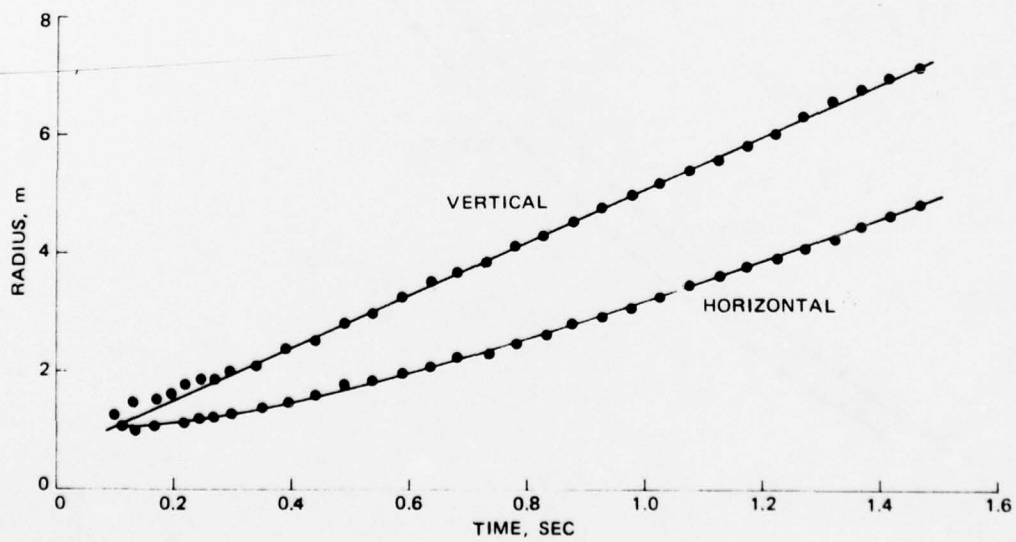


FIGURE C-10. Flame Position 3.5% Acetylene Test 15.

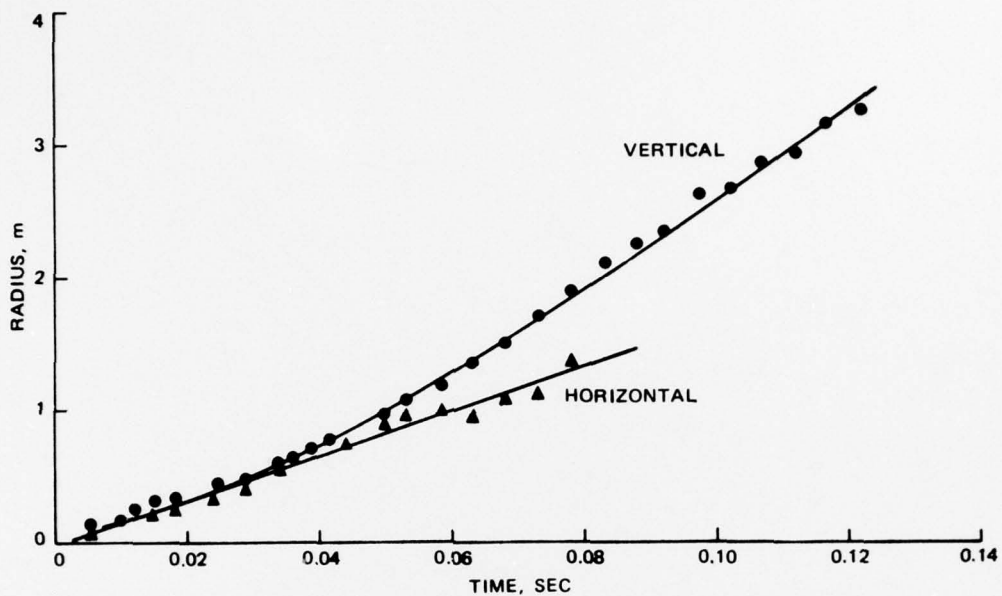


FIGURE C-11. Flame Position 7.7% Acetylene Test 18.

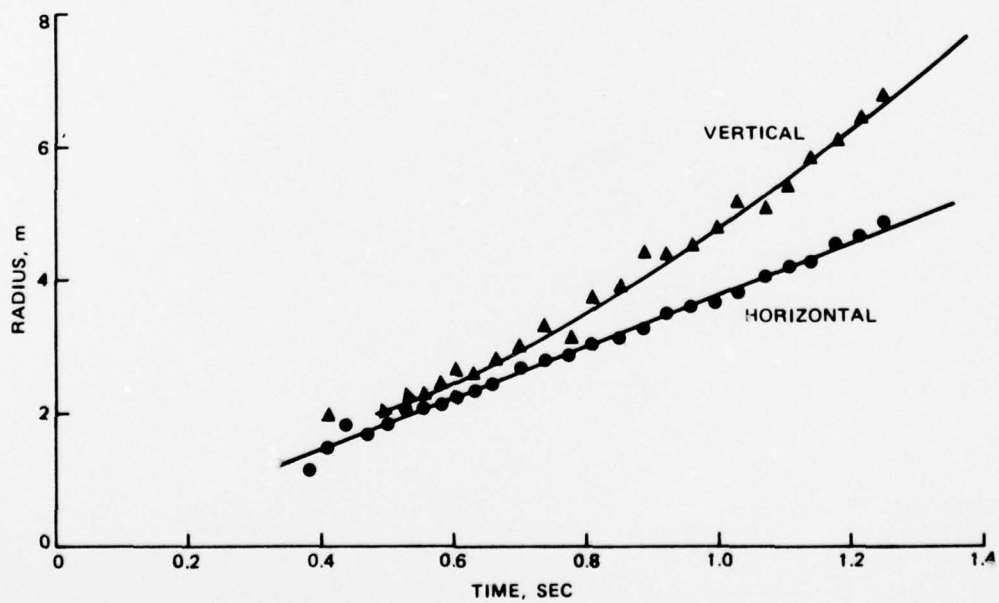


FIGURE C-12. Flame Position 3.5% Butadiene Test 17.