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IGNITION CHARACTERISTICS OF FUELS AND LUBRICANTS

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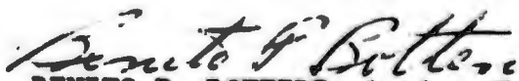
FOREWORD

This report was prepared by the Explosives Research Center of the U. S. Bureau of Mines under USAF Contract No. DO(33-657)-63-376. The contract was initiated under Project No. 3048 "Aviation Fuels", Task No. 304801 "Hydrocarbon Fuels". It was administered under the direction of the Air Force Aero Propulsion Laboratory, Research and Technology Division, with Messrs. B. Botteri and H. R. Lander acting as project engineers.

This report is a summary of the work that was conducted during the period 1 January 1963 to 31 December 1965.

Dr. Robert W. Van Dolah was the administrator for the U. S. Bureau of Mines and Dr. M. G. Zabetakis, Messrs. J. M. Kuchta, R. J. Cato, G. H. Martindill, W. H. Gilbert and Miss A. C. Imhof actively participated in this work at the U. S. Bureau of Mines Explosives Research Center, Bruceton, Pennsylvania.

This report has been reviewed and is approved.



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ABSTRACT

A summary is presented of the work which was conducted under a 3-year investigation of the ignition, flammability, and oxidation characteristics of hydrocarbon type combustibles in various oxygen-nitrogen atmospheres. The combustibles included n-hexane, n-octane, n-decane, JP-6 jet fuel, aircraft engine oil MIL-L-7808, and other hydrocarbon materials. Expressions based on thermal ignition theory are given which correlate minimum autoignition and wire ignition temperatures of the combustible vapor-oxidant mixtures as a function of the heat source dimensions, oxygen concentration, ignition delay, and initial mixture temperature (in wire ignitions). The ignition temperatures increased consistently with decreasing heat source diameter or surface area. Hot gas ignition temperatures determined for the combustibles with various size jets of hot air also varied with heat source diameter; they tended to approximate the hot surface ignition temperatures when the size of the heat source and ignition criterion were the same. Jet temperatures required to produce "hot" flames and luminous or "cool" flame reactions were also compared. In oxidation rate studies at reduced pressures with JP-6 and n-octane vapor-oxygen-nitrogen mixtures, the critical pressures for "cool" flame reactions increased with decreasing vessel size, temperature, oxygen concentration, and fuel concentration. Rate expressions are given for the octane oxidation experiments in which the temperature dependency of the rates is similar to that obtained in vessel ignition temperature experiments. In flammability studies with hydrocarbon fuel vapor-air mixtures, the upper limits of flammability are shown to increase markedly with increasing temperature, particularly in the the case of the high molecular weight paraffins which display a greater tendency to form "cool" flames.

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

ILLUSTRATIONS (Cont'd.)

ILLUSTRATIONS (Cont'd.)

TABLES

TABLES (Cont'd.)

INTRODUCTION

The present program was initiated in 1963 to define the ignition temperature characteristics of aircraft or hydrocarbon type combustibles for predicting environmental heating conditions under which explosion hazards may exist in the use of the combustibles. Ignition temperatures depend upon a number of variables including the nature and dimensions of the heat source which effects ignition. Most of the autoignition temperature (AIT) data available for aircraft combustibles are primarily applicable to situations in which a flammable mixture contacts a relatively large heated surface, such as the walls of a fuel tank. Ignition may also result in small heated containers and in situations where the heat source is a heated wire or a jet of hot air or other gases. Accordingly, hot surface and hot gas ignition temperatures of the combustibles were determined in air and various oxygen-nitrogen atmospheres as a function of heat source dimensions. Reaction rate studies were also conducted to develop semi-empirical expressions for predicting critical ignition conditions from rate parameters and ignition temperature data. "Hot" and "cool" flame ignitions were examined in the above studies and in limit-of-flammability experiments at elevated temperatures. The combustibles included n-hexane, n-octane, n-decane, JP-6 jet fuel, adipate diester (MIL-L-7808) and sebacate diester (H-1026) engine oils, and other hydrocarbon type fuels.

Generally, the autoignition or vessel ignition temperatures of combustible mixtures decrease as the diameter of the vessel is increased (Ref 1). Wire ignition temperatures display a similar dependence on heat source diameter (Ref 2). However, little information is available for most combustibles on the correlation of these hot surface ignition temperatures over a wide range of heat source dimensions. In the present work, the heat sources consisted of heated cylindrical and spherical glass vessels and Nichrome wires and rods or tubes. Since minimum ignition temperatures were of primary interest, stagnant and near stagnant flow conditions were employed. The results indicated that these temperatures correlate over a greater range of heat source dimensions when the surface area of the heat source rather than diameter is used. Expressions, based on thermal ignition theory (Refs 3, 4), are given for predicting the hot surface ignition temperatures of the hydrocarbon combustibles.

Little information is available on the hot gas ignition temperatures of combustibles, other than the data of Wolfhard, Vanpee, and Bruszak (Refs 5, 6). These ignition temperatures are reported to be much higher than corresponding AIT's. However, according to data found here with 1/8 to 3/4-inch diameter air jets (laminar), the differences between such ignition temperatures are not necessarily great when the diameter of the heat source and the ignition criterion are the same. Jet temperature and concentration profiles were also obtained to compare the extent of reaction and the heat requirements for the initial luminous or "cool" flame reactions and subsequent "hot" flame ignitions which occurred.

Vapor phase reaction rate studies provided information on the slow oxidation of n-octane and JP-6 fuel in various size vessels at reduced pressures

and at temperatures near critical for "cool" flame ignitions. The effect of total pressure on the rates of pressure rise was greater than that of oxygen partial pressure. The temperature dependency of these rates were consistent with ignition delay-AIT data, indicating the possible use of such rate data for predicting the AIT's of the combustible mixtures.

The data obtained in the various phases of this three-year program are summarized in this report and include many of the results reported in the two previous annual reports on this work (Refs 7, 8). For convenience, the work is divided into four parts.

1. Hot Surface Ignition Temperatures of Hydrocarbon Type Combustibles.

2. Hot Gas Ignition Temperatures of Hydrocarbon Type Combustibles.

3. Reaction Rate Experiments with n-Octane and JP-6 Fuels.

4. Autoignition Temperature and Flammability Limits of New Aircraft Combustibles.

EXPERIMENTAL APPARATUS AND PROCEDURE

1. Hot Surface Ignition Temperature Experiments

Autoignition temperatures of the combustibles were determined in quiescent air and various oxygen-nitrogen (or helium) atmospheres using a modified ASTM ignition temperature apparatus (Ref 9). The apparatus is described in Appendix I and was equipped with spherical Pyrex vessels of 0.94 to 2.93-inch diameter (0.3 to 13.0 in^3 volume) and with cylindrical Pyrex vessels of 0.3 to 1.38-inch diameter (0.46 to 8.3 in^3 volume) and 6 inches long. Pyrex vessels were used since they gave the lowest AIT values in preliminary trials; the values were only slightly higher in stainless steel vessels but they were at least 100°F higher in aluminum, carbon steel, and copper vessels (0.5-inch diameter tubes). In all cases, ignition was evidenced by the appearance of flame. The AIT values were reproducible to within ±5° at low temperatures ($\sim$ 500°F) and ±20° at high temperatures ($\sim$ 1000°F).

Wire ignition temperatures were determined under flow conditions using electrically heated Nichrome and Inconel wires (or rods and tubes) of 0.016 to 1.0-inch diameter mounted perpendicular to the flow of the combustible vapor-oxidant mixture. The apparatus is described in Appendix II. Mixture flow rate was maintained at 17.8 in^3/min (N.T.P.) which corresponded to a linear velocity of approximately 0.1 in/sec in the 2-inch diameter tube. Preliminary experiments indicated that the ignition temperatures vary little with mixture flow rate between 0 and 200 in^3/min. In addition, they did not vary greatly with wire material although the values obtained with carbon steel wires of 0.08-inch diameter were consistently higher (30° to 100°F) than those for Nichrome, copper and stainless steel wires. The initial mixture or oven temperature was 300°F for the fuels and 500°F for the engine oils which contained higher boiling point constituents. The appearance of

flame was also the ignition criterion in these experiments. Most of the wire ignition temperatures were reproducible to within ±25°F.

The neat hydrocarbons used in this work were of chemically pure grade. The JP-6 jet fuel contained about 85 percent saturated hydrocarbons and 14 percent aromatic hydrocarbons according to a sample analysis; its flash point was 100°F. The MIL-L-7808 (0-60-18) engine oil consisted primarily of adipate diesters which vaporized at temperatures between 480° and 780°F; its flash point was 435°F. The main constituents of the H-1026 oil were 94.4 weight percent Plexol 2101-J (di-2-ethyl hexyl sebacate), 5 percent tricresyl phosphate and 0.5 percent phenothiazine.

2. Hot Gas Ignition Temperature Experiments

The hot gas ignition temperature experiments were conducted with 1/8 to 3/4-inch diameter jets of hot air injected into combustible vapor-oxidant mixtures under near stagnant flow conditions. Appendix III describes the apparatus employed in these determinations. The initial mixture temperature was 350°F for the fuels and 600°F for the engine oil; higher temperatures were used than in the wire ignition experiments in order to obtain data at higher combustible concentrations. The mixture flow rate was 365 in^3/min (about 1 in/sec) and the jet flow rate was 185 in^3/min ($\geq$ 50 in/sec), both at N.T.P. conditions, in the ignition temperature experiments with 1/8, 1/4, 3/8 and 1/2-inch diameter jets; the jet flow rate was 365 in^3/min (about 50 in/sec) with a 3/4-inch size jet. These jet flow rates appeared to be optimum for ignition of the mixtures in the 4-inch diameter reaction chamber.

Normally, a faintly visible precursor flame or luminous column formed above the base of the jet when the jet temperature was within 100° to 200°F of that required for ignition (Figure 1). This flame extended to a height of 6 inches or less above the jet base and was a pale blue. The height at which ignition occurred decreased with increasing jet temperature. Motion picture records of the ignition of n-octane vapor-air mixtures indicated that ignition with a 1/2-inch diameter jet at 1400°F occurs about 3 inches above the jet base within 10 to 60 seconds after the mixture is admitted. The minimum ignition temperature values reported here refer to the jet base temperatures required for flame propagation throughout the mixture. They were reproducible to within ±25°.

To compare heat requirements for the hot gas ignition reactions, axial and radial temperature profile measurements were made for 1/2-inch diameter jets of hot air flowing into preheated air and into preheated combustible vapor-air mixtures. In making these measurements, jet base temperatures were selected to produce the luminous and the "hot" flame reactions under the given flow conditions. However, ignition reactions were usually quenched when the temperature probe (36 gage Pt/Pt-Rh thermocouple) was inserted at a distance between 0 and 4 inches above the jet base; under such conditions, ignitions occurred only when the height of the probe was greater than 4 inches. Although heat loss to the probe influenced the absolute temperature

values, this error would tend to be minimized in comparing the differences between the temperatures with and without combustible. Corresponding axial concentration profiles were measured by sampling at various heights above the jet base with a quartz probe having a throat diameter of about 0.015-inch; the sampling rate was about 0.01 in^3/sec. Analyses of the noncondensable reactant and product gases were made by a mass spectrometer or gas chromatograph.

3. Reaction Rate Experiments

The vapor phase oxidation of n-octane and JP-6 was investigated at reduced pressures ($\geq$ 0.6 psia) and at various temperatures (390° to 590°F) in the apparatus described in Appendix IV. The static method was employed here with spherical reaction vessels (Pyrex) of 518 cc (31.6 in^3), 222 cc (13.5 in^3), 106 cc (6.47 in^3), 55 cc (3.36 in^3), and 32 cc (1.95 in^3) volume. Reaction of the fuel vapor-oxygen-nitrogen mixtures was followed primarily by pressure rise measurements. Sampling runs were also made at selected conditions to compare the consumption of reactants and formation of gaseous products with the pressure rise data.

4. Limits of Flammability

Limit-of-flammability determinations were made at atmospheric pressure and elevated temperatures under near stagnant flow conditions in a 2-inch diameter tube (Bureau of Mines F-11 apparatus - Appendix V). At reduced pressures, the determinations were performed by the partial pressure method in a 12-liter spherical Pyrex vessel, 11.2 inches in diameter; an exploding copper wire was employed as the ignition energy source.

RESULTS AND DISCUSSION

1. Hot Surface Ignition

Autoignition or Vessel Ignition Temperatures in Quiescent Air

The minimum autoignition temperatures (AIT's) found for n-hexane, n-octane, n-decane, JP-6 jet fuel and MIL-L-7808 engine oil in air with various cylindrical and spherical Pyrex vessels are given in Table 1. These were obtained with nonuniform mixtures at an optimum fuel-air weight ratio (F/A) for ignition. The apparent F/A ratio was 0.35 $\pm$ 0.1 in most cases and much greater than the stoichiometric value (< 0.07) required for complete combustion of the hydrocarbons; the effect of F/A ratio was most pronounced at low ratios when the AIT's tended to be higher. Consistent with most AIT data, the AIT's in Table 1 increased with decreasing vessel size. Figures 2 and 3 show these ignition temperatures plotted vs the surface area to volume ratio (S/V) of the vessel. At comparable S/V ratios, the AIT's tend to be higher in spherical vessels than in cylindrical vessels 6 inches long, but the latter are of greater volumes. The opposite behavior is observed if the data are compared

at equal vessel volumes. This is not surprising since, at equal volumes, the spherical vessels had the larger diameters (d) and their S/V ratios (6/d) were less than the S/V values (4/d + 2/L) of the corresponding cylindrical vessels. The approximate critical vessel dimensions above which the AIT's increased greatly for most of the combustibles were as follows:

Cylindrical Vessels S/V - 5.0 in^{-1} V - 3.7 in^3(60 cc) d - 0.9 in

Spherical Vessels S/V - 3.8 in^{-1} V - 2.0 in^3(33 cc) d - 1.6 in

To obtain the lowest AIT's, vessels of at least 12.2 in^3(200 cc) are required. It was also observed that the ignition temperatures increase when the vessels are packed with glass rods or beads since the S/V ratio also was increased. However, for spherical or cylindrical vessels of equal volume, the AIT's are more dependent on effective vessel diameter than on S/V ratio for packed and unpacked vessels.

Since it is of interest to know the critical vessel diameter below which ignition will not occur, vessels of smaller diameter than cited above were also used. With a cylindrical quartz vessel of 0.16-inch diameter and 8-3/4 inches long, the minimum AIT was about 1500°F in air for all the combustibles in Table 1 and for benzene, toluene and xylene (high AIT combustibles). With a vessel of 0.08-inch diameter, no ignitions were observed at temperatures up to about 1700°F, the limiting temperature of the apparatus.

The data for the neat hydrocarbon materials are consistent in that the AIT's increased with decreasing molecular weight. The AIT values for the engine oil are much higher than those for all the fuels at large vessel volumes, i.e., at temperatures below about 800°F, whereas they are comparable or lower at small vessel volumes. Apparently, the adipate esters which largely make up this oil break down to form more thermally unstable species with increasing temperature than do the hydrocarbon fuels. In a few exploratory experiments, the thermal stability of the H-1026 oil (which contains fewer additives than MIL-L-7808) was examined with a Perkin-Elmer Differential Scanning Calorimeter (DSC-1). Shown in Figure 4 are two sets of thermograms (temperature rise-time curves) obtained in heating 4.5 mg samples of oil in air and nitrogen atmospheres at 20°F/min. The temperature at which an initial exothermic reaction occurred in the liquid was essentially the same (530° to 540°F) with either atmosphere. These results agree fairly well with the decomposition temperature of 543°F (Ref 10) reported for bis (2-ethylhexyl) sebacate, the main constituent of this oil. However, an endothermic rather than exothermic reaction would most likely be favored if one assumes that a carboxylic acid and an olefin is formed initially. Nevertheless, the decomposition temperature of this type (MIL-L-7808 or H-1026) of oil appears to be nearly comparable to its minimum AIT ($\sim$500°F) when pressure rise is the ignition criterion (Ref. 11). Further studies should be made to investigate the possible relationships which may exist between such temperatures for various classes of aircraft lubricants.

Autoignition Temperatures in Various Oxygen-Nitrogen Mixtures

The minimum AIT's of the combustibles decreased when the oxygen content of the oxygen-nitrogen mixture was varied from 5 to 100 volume percent. Table 2 gives the data obtained in a 13.0 in^3 spherical Pyrex vessel; they are also shown in Figure 5. The greatest variation of AIT was observed when the oxygen was increased from 10 to 21 percent for the hydrocarbon fuels and from 21 to 100 percent for the engine oil. For all the combustibles, the AIT's were reduced by at least a factor of 1/2 over the range of increasing oxygen concentration.

TABLE 2. - Minimum Autoignition Temperatures of Hydrocarbon Fuels and an Engine Oil in Oxygen-Nitrogen Atmospheres at Atmospheric Pressure.
Spherical Pyrex Vessel - 13 in^3 volume
Ignition Criterion - Appearance of flame
Fuel-Oxygen Weight Ratio - Approximately 1

Oxygen	Autoignition Temperature, °F			
Vol.%	n-Hexane	n-Octane	JP-6	MIL-L-7808 Oil
5	1040	1100	995	1020
10	920	925	945	855
21	462	440	470	765
100	428	400	432	518

In autoignitions, the fuel contact time or ignition delay tends to be maximum at minimum AIT conditions. According to thermal or chain ignition theory (Ref 12), a linear relationship should exist between the logarithm of ignition delay and reciprocal ignition temperature. The data obtained in the above experiments display such relationships in Figure 6, at least for the ignitions in atmospheres of 5, 10 and 100 percent oxygen. With 21 percent oxygen, the plots are not linear over the entire range of temperatures because of an apparent change in the reaction mechanisms; such observations are common for many hydrocarbons and, in some cases, may be attributed to a transition from a "cool" flame to a "hot" flame operative mechanism. The following expressions describe the variation of ignition delay, τ (seconds), with autoignition temperature, T(°R), for the combustibles in Table 2:

All Combustibles	$\ln\tau = 32{,}900/T - 20.9$	5% O_2	(1)
All Combustibles	$\ln\tau = 30{,}700/T - 20.7$	10% O_2	(2)
Hexane and Octane	$\ln\tau = 25{,}600/T - 24.3$	21% O_2	(3)
JP-6	$\ln\tau = 27{,}700/T - 25.7$	"	(4)
MIL-L-7808 Oil	$\ln\tau = 22{,}300/T - 17.2$	"	(5)
Hexane	$\ln\tau = 30{,}700/T - 29.6$	100% O_2	(6)
Octane	$\ln\tau = 30{,}300/T - 29.8$	"	(7)
JP-6	$\ln\tau = 36{,}500/T - 35.5$	"	(8)
MIL-L-7808 Oil	$\ln\tau = 72{,}000/T - 69.4$	"	(9)

TABLE 1. - Minimum Autoignition Temperatures of Hydrocarbon Fuels and an Engine Oil in Cylindrical and Spherical Vessels with Quiescent Air at Atmospheric Pressure.
Ignition Criterion - Appearance of flame
Fuel-air Weight Ratio - Approx. 0.35

Vessel Volume, cc	Vessel Volume, $in.^3$	Vessel Diameter, in.	S/V[1/], $in.^{-1}$	S, $in.^2$	Minimum Autoignition Temperature, °F				
					n-Hexane	n-Octane	n-Decane	JP-6	Engine Oil MIL-L-7808
Cylindrical Pyrex Vessels (6-inch length)									
7.5	0.46	0.315	13.03	5.97	1164	1117	1116	1105	1076
10	0.61	0.365	11.44	6.98	1117	1081	1089	1036	1035
23	1.41	0.54	7.58	10.70	1006	941	914	903	883
41	2.50	0.75	5.66	14.15	808	720	703	766	833
45	2.75	0.78	5.46	15.00	810	720	612	707	826
60	3.66	0.89	4.95	18.15	511	450	435	471	795
135	8.25	1.38	3.23	26.55	509	441	417	468	790
200	12.21	(1.76)[2/]	(2.34)	(28.55)	453	428	406	449	759
Spherical Pyrex Vessels									
5	0.305	0.94	7.19	2.18	1110	1025	1000	1000	1020
10	0.61	1.05	5.73	3.49	950	875	800	805	880
15	0.915	1.20	4.98	4.56	915	835	770	755	810
33	2.015	1.60	3.85	7.74	640	535	490	525	780
50	3.05	1.80	3.35	10.20	570	500	470	500	780
104	6.35	2.30	2.61	16.50	485	450	425	485	755
213	13.00	2.93	2.05	26.60	460	440	420	470	755

1/ Surface area to volume ratio of vessel.
2/ Erlenmeyer - Equivalent diameter of a 5-inch cylinder with a 12.21 $in.^3$ volume.

To some extent, the lack of a complete correlation of the hot surface ignition temperatures over the full range of heat source dimensions can be explained by the fact that the lengths of the cylindrical vessels (6 inches) and the wires or rods (2 inches) were not the same. Therefore, the correlation should improve, as was found here, by plotting the ignition temperatures against the surface area (A) of the heat source (semilog plot of Figure 9). For the engine oil, the variation of T with $\log_e A$ is approximately linear over the entire range of surface areas. The straight regression lines drawn to represent the data are given below:

Hexane	$T = 1415 - 177 \log_e A$;	$0.1 < A < 11$;	$S_{y/x} = 43$	(13)
Octane	$T = 1365 - 173 \log_e A$;	" ;	" = 56	(14)
Decane	$T = 1340 - 161 \log_e A$;	" ;	" = 61	(15)
JP-6	$T = 1430 - 201 \log_e A$;	" ;	" = 37	(16)
MIL-L-7808 Oil	$T = 1175 - 115 \log_e A$;	$0.1 < A < 29$;	" = 65	(17)

where T is in °F and A is in square inches. $S_{y/x}$ is the standard error of estimate and is a measure of the vertical scatter of the data about the regression line; most of the data fall within $\pm S_{y/x}$.

It is not altogether surprising that the hot surface ignition temperatures for the engine oil correlated over the entire range of heat source surface areas, since relatively high temperatures (> 750°F) are required for its ignition. Thus, the oxidation reactions involved are primarily of the high temperature type. Data for such high AIT materials as benzene and toluene also correlate well with heat source dimensions. In comparison, the ignition temperature data for the low AIT hydrocarbon fuels involve low and high temperature oxidation reactions. Therefore, "cool" and "hot" flames can be involved and probably account for the sudden change of the slopes of the curves for these fuels in Figure 9.

The above expressions do not take into account variations which may arise due to varying oxygen concentration, a, and initial mixture temperature, T_o (pertinent in wire ignitions). In this connection, a modified expression of those given by Semenov (Ref 4) should be applicable:

$$(a)^n A \frac{T}{T-T_o} = k e^{E/RT} \qquad (18)$$

where T is the ignition temperature and the other terms have their previous meanings. For the case of vessel ignitions, the term $T/T-T_o$ is not applicable and is omitted. According to this equation, a linear relationship should exist between the logarithm of the terms on the left and 1/T. Therefore, such a correlation was attempted using ignition temperature data obtained in air and various oxygen-nitrogen atmospheres with the heated wires and with the cylindrical and spherical vessels. A value of 0.75 was used for n for the effect of oxygen concentration $(a)^n$, based on our findings in the reaction rate studies with n-octane. Admittedly, this value may be primarily applicable to the reduced total pressures used in the rate studies,

two different types of ignition; this may be attributed largely to the different heat source dimensions and corresponding temperatures associated with the ignitions in each case.

TABLE 3. - Minimum Hot Surface Ignition Temperatures of the Hydrocarbon Fuels (300°F) and an Engine Oil (500°F) in Air at a Mixture Flow Rate of 17.8 in^3/min (N.T.P.).
Ignition Criterion - Appearance of flame
Pyrex Reaction Vessel - 2-inch ID, 8 inches long
Fuel-Air Weight Ratio - 0.3 to 0.5

Diameter of Heat Source, inch	Minimum Ignition Temperature, °F				
	n-Hexane	n-Octane	n-Decane	JP-6	Engine Oil MIL-L-7808
			Nichrome Wires (2-inch length)		
0.016	1830	1820	1775	1880	1550
0.032	1720	1670	1650	1770	1295
0.051	1590	1500	1440	1630	1275
0.081	1570	1430	1400	1530	1160
0.102	1530	1440	1355	1540	1165
			Nichrome Rod (2-inch length)		
0.20	1400	1360	1330	1435	1190
			Inconel Tubes (2-inch length)		
0.50	1190	1185	1160	1235	1040
0.75	1060	1000	1040	1085	1015
1.00	960	980	960	985	1010

TABLE 4. - Minimum Wire Ignition Temperatures of Hydrocarbon Fuels (300°F) and an Engine Oil (500°F) in Various Oxygen-Nitrogen Atmospheres with a 0.081-inch Diameter Nichrome Wire.
Mixture Flow Rate - 17.8-in^3/min
Fuel-Oxygen Weight Ratio - 1.9

Oxygen, Vol.%	Ignition Temperature, °F				
	n-Hexane	n-Octane	n-Decane	JP-6	Engine Oil H-1026
2.5	>2050	1885	--	1660	>2050
5	1585	1570	1545	1560	>2050
10	1560	1560	--	1535	1560
21	1570	1430	1400	1530	1215
100	1360	1060	960	1170	1010

Relationships Between Hot Surface Ignition Temperatures and Heat Source Dimensions

According to thermal theory, the ignition of a combustible mixture by a heated surface is governed by the rate of heat release from chemical reaction and by the rate of heat loss from the system. In AIT experiments, the gaseous mixture and the walls of the heated vessel are ordinarily at a uniform temperature; therefore, ignition should occur in the center of the vessel where heat reaction losses are minimum. In wire ignition temperature experiments, the temperature of the wire is usually much greater than that of the confining vessel and the combustible mixture not in contact with the heated surface. Thus, in such cases, ignition should take place at or close to the heated surface, as was observed in the present work. Figure 7 shows motion picture records from two identical wire ignition experiments in which octane vapor-air mixtures ignited close to the downstream surface of the heated wire. Flame speeds measured about 5 ft/sec during the early stages (0 to 15 millisec) and 1.6 ft/sec subsequently.

For the case of thermal ignition in cylindrical vessels, Frank-Kamenetskii (Ref 3) derived the following expression:

$$r = \left[\frac{2\lambda}{QE}\ \frac{RT^2}{Z\ e^{-E/RT}}\right]^{1/2} \qquad (10)$$

where r is the vessel radius, Q is heat of reaction of the mixture with thermal conductivity λ, R is the universal gas constant, E is the activation energy, Z is a rate collision factor, and T is the ignition temperature. It is applicable primarily to ignitions in small vessels and where convective heat transfer may be neglected. Semenov derived a similar expression for the case of thermal ignition by heated wires (Ref 4). In both cases, the expressions predict that, as a first approximation, a plot of $\log_e r$ vs 1/T should be linear over a limited range of temperatures and heat source dimensions.* The wire and rod ignition temperature data of the present work (Table 3) appear to obey such a relationship but the AIT data do not (Figure 8). The following expression may be used to describe the approximate variation of the wire ignition temperatures (T, °R) with the wire radius (r) between 0.008 and 0.25-inch:

$$\log_e r = 21000/T - k \qquad (11)$$

where k is 14.41 for decane, 14.30 for octane, and 13.50 for JP-6 and hexane. Similarly, for the MIL-L-7808 oil, the following equation is applicable for r values between 0.008 and 0.375-inch:

$$\log_e r = 25800/T - 18.53 \qquad (12)$$

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* "r" is the radius of the vessel in the autoignitions and the radius of the wire in the wire ignitions.

These expressions are primarily applicable to a temperature range of at least 100° to 150° and starting slightly above the minimum AIT of the given combustible mixture. The ignition delay values appeared to vary inversely with $[O_2]^{1.5}$ for the data found with 5 to 21 percent oxygen but the data were not very consistent.

Wire Ignition Temperatures in Flowing Combustible-Air Mixtures

Minimum ignition temperature data obtained for flowing combustible vapor-air mixtures (17.8 in^3/min) with electrically heated Nichrome wires and rods or tubes (2-inch lengths) are summarized in Table 3. These data are similar in many respects to those found with the heated vessels. The ignition temperature values increase with a decrease of heat source diameter and molecular weight of the neat hydrocarbon fuels; also minimum values occurred at high fuel-air weight ratios (0.3 to 0.5) and were influenced little by fuel-air ratio except at low ratio values where they increased appreciably. Furthermore, the ignition temperatures for the engine oil are lower than those for any of the 4 hydrocarbon fuels; this behavior is consistent with the AIT data found in small cylindrical vessels of 1.41 in^3 or less capacity (0.54-inch diameter). However, the JP-6 values are higher than those for n-hexane, whereas the opposite is the case in the autoignition experiments. An explanation for this trend would require a study of the ignition characteristics of various distilled fractions of the JP-6 fuel.

The length as well as the diameter of the heated wire can influence the wire ignition of the combustible mixtures. Here, the ignition temperatures increased noticeably when the L/d ratio of a 0.081-inch diameter wire (2 inches long) was decreased from 20 to 3. Thus, the reported ignition temperatures should be minimum for wires $\leq$ 0.1-inch diameter. Those listed for wires between 0.1 and 1-inch diameter may be slightly higher than the values possible with wires of greater length than 2 inches.

These wire ignition temperatures can also vary with the initial mixture temperature, which was 300°F for the fuels and 500°F for the engine oil in the above determinations. With increasing mixture temperature, the wire ignition temperature decreases until the minimum AIT of the particular combustible is reached. It was also observed that wire ignitions of the combustibles, JP-6 and MIL-L-7808 oil particularly, could result at initial mixture temperatures lower than their flash points under flow conditions such as were used here.

Wire Ignition Temperatures in Various Oxygen-Nitrogen Mixtures

Table 4 gives the minimum wire ignition temperatures of the combustibles found in oxygen-nitrogen mixtures containing 2-1/2 to 100 percent oxygen at a mixture flow rate of 17.8 in^3/min. A Nichrome wire of 0.08-inch diameter was used and the fuel-oxygen weight ratio was about 1.9. These data are also shown on the semi-log plot in Figure 5 with corresponding AIT data from experiments in a 13.0-in^3 spherical vessel. As expected, the ignition temperatures increased with decreasing oxygen concentration. However, the variation of ignition temperature with oxygen concentration was not the same for the

which are discussed later, and also not necessarily to all the combustibles of this work. In addition, the ignition delay was assumed constant since the values were not available for all the ignition temperature conditions; since ignition delay varied with temperature, oxygen concentration (see Figure 6), and heat source size, its effect is partly included.

According to Figures 10, 11, 12, 13 and 14, the semi-log plots of the ignition temperature data for each of the combustibles were not linear over the entire range of different ignition conditions. In particular, the wire ignition data display greater temperature sensitivity than the vessel ignition data. Nevertheless, most of the data for each combustible appear to follow a consistent trend indicated by the curves drawn to represent the data; the ignition temperatures in 100 percent oxygen deviate the most from the curves. Considering the wide range of heat source dimensions, temperatures, and oxygen concentrations, some inconsistencies should be expected in such correlations. Computer solutions of equation (18) or others utilizing oxidation rate data should be explored to compare experimental ignition temperature data with those which may be predictable from chemical kinetics.

2. Hot Gas Ignition

Hot Gas (Air) Ignition Temperatures of Flowing Combustible Mixtures

The temperature required to ignite a combustible vapor-air mixture with a jet of hot gas depends on the jet dimensions as well as on the composition and velocity of the jet and combustible mixture. Since jets of hot air were used here, the combustible mixture was diluted by the air jet, particularly along the interface between the two moving fluids. Accordingly, high fuel concentrations and low jet flow rates which provide long contact times should be optimum for ignition. The results of the present work were consistent in this connection.

Generally, a fuel-air weight ratio of approximately 0.5 was required to obtain minimum ignition temperatures; this ratio corresponds to 11.6 volume percent for a fuel like n-octane. As in the hot surface ignition temperature determinations, the effect of fuel-air ratio was not great. The effect of jet velocity on minimum ignition temperature also was not great. Table 5 shows data obtained for MIL-L-7808 oil vapor-air mixtures with a 1/2-inch diameter jet. The ignition temperature increased 60°F at most when the jet velocity was varied from 36.5 to 81.0 in/sec with a constant mixture velocity of 1 in/sec. The variation of ignition temperature was also small when mixture velocity was varied between 0.7 and 1.5 in/sec and the jet velocity/mixture velocity ratio was constant, slightly above 50. Although a jet velocity of approximately 50 in/sec was near optimum for ignition of the mixtures with 1/2 and 3/4-inch diemter jets, higher jet velocities were required with the smaller size jets to provide ideal heat inputs for ignition.

TABLE 5. - Effect of Jet and Mixture Velocity on the Minimum Hot Gas Ignition Temperature of MIL-L-7808 Engine Oil Vapor-Air Mixtures With a 1/2-inch Diameter Hot Air Jet.

Fuel-Air Weight Ratio - 0.55

Jet Velocity / Mixture Velocity	36.5	52.1	52.5[1/]	52.7	54.7	81.0
Mixture Velocity, in/sec	1.0	0.7	1.0[1/]	1.3	1.5	1.0
Ignition Temperature, °F	1240	1255	1250	1270	1315	1300

1/ Mixture flow rate - 365 in^3/min; jet flow rate - 185 in^3/min (N.T.P.)

Table 6 lists the minimum hot gas ignition temperatures found for the hydrocarbon fuel (350°F) and engine oil (600°F) vapor-air mixtures with the various size jets of hot air. These data are also shown graphically in Figure 15 where the ignition temperatures are plotted against the jet diameter.

TABLE 6. - Minimum Hot Gas Ignition Temperatures of the Hydrocarbon Fuels and Engine Oil (Fuel Vapor-Air Mixtures) With Various Hot Air Jets.

Mixture Flow Rate - 365 in^3/min (N.T.P.)
Fuel-Air Weight Ratio - Approx. 0.5
Ignition Criterion - "Hot" Flame Propagation

Diameter of Jet, inch	Jet Flow Rate, in^3/min	Ignition Temperature, °F				
		n-Hexane	n-Octane	n-Decane	JP-6	Engine Oil MIL-L-7808
1/8	185	1910	1875	1890	1985	1605
1/4	185	1630	1610	1600	1670	1530
3/8	185	1450	1440	1440	1500	1410
1/2	185	1280	1250	1220	1410	1250
3/4	365	1210	1220	1170	1290	1210

For all the fuels, the ignition temperatures decreased close to 700°F when the jet diameter was increased from 1/8 to 3/4-inch; for the engine oil, the temperature values decreased only approximately 400°F. Consistent with the wire ignition data in Table 3, the values for the JP-6 fuel were the highest in all cases while those for the engine oil were the lowest for jet diameter less than 1/2-inch. The values for the paraffin hydrocarbons varied little at a given jet diameter.

Comparison of Hot Gas and Hot Surface Ignition Temperatures

A comparison was made of the autoignition, wire ignition, and hot gas ignition temperatures of various combustibles, including those of the present work. Table 7 lists the temperature values found in air with cylindrical heat sources of about 0.4-inch diameter; minimum AIT values found in a 12.2 in^3 Pyrex Erlenmeyer are also listed.

The hot gas ignition temperatures of all the combustibles except hydrogen, are noticeably higher than their corresponding hot surface ignition temperatures. For the paraffin hydrocarbons, they are about 200°F higher than the wire ignition temperatures and 300° to 500°F higher than the cylindrical vessel AIT's. Of course, the AIT's found in the Erlenmeyer ($\sim$1.7-inch diameter) are the lowest ignition temperature values, although the variation tends to be at least for high AIT materials like methane, benzene, and hydrogen.

Figures 16 and 17 show comparisons of these ignition temperatures at various heat source diameters for the five combustibles of the present work. Again, the hot gas ignition temperatures are the highest and their variation with reciprocal heat source diameter (1/d) resembles most closely that displayed by the AIT's. At 1/d values between 1 and 2-$inch^{-1}$, the hot gas and wire ignition temperatures differed only slightly; heat source diameters greater than 1 inch appear to be required for these ignition temperatures to approximate the minimum AIT values. In these correlations, the hot surface ignition temperatures referred to any visible flame whereas the hot gas temperatures referred only to "hot" flame ignitions. According to our observations, luminous or precursory flame reactions may occur at jet temperatures 100° to 200°F below those required for "hot" flame ignitions. Furthermore, the hot gas temperatures were measured near the jet base but were at least 200° lower at the plane where ignition occurred above the jet base (Table 8). Thus, although the hot gas ignition temperatures are generally higher than the hot surface ignition temperatures, the differences are not necessarily great if the ignition criterion and the heat source dimensions are the same.

Thermal Considerations of Hot Gas Ignitions

Hot gas ignitions are unique in that surface effects are essentially absent and pre-ignition reactions may be observed at high temperatures and for long durations (several seconds). Such ignitions should occur at the hottest point in the jet stream and where the heat generated is greater than the heat lost. If radial convection is assumed negligible and axial convection most important, the heat balance equation can be reduced to the following expression (Refs 6, 14):

$$Q = \rho C_p v_y \left[\frac{\partial T}{\partial y} - \left(\frac{\partial T}{\partial y} \right)_{Q=0} \right] \qquad (19)$$

where Q is rate of heat release by chemical reaction, ρ is density of gas jet, C_p is specific heat, v_y is axial velocity and T is jet temperature.

TABLE 7. - Comparison of Hot Surface and Hot Gas Ignition Temperatures of Hydrocarbon Combustibles and Hydrogen with Air at Atmospheric Pressure.

Fuel-air Ratio - Optimum for ignition
Ignition Criterion - Appearance of flame

Combustible \ Heat Source	Ignition Temperature, °F			
	Pyrex Erlenmeyer (1.7 in.diam) 5 in.long [1/]	Cylindrical Pyrex Vessel 0.4 in.diam. 6 in.long	Inconel Wire 0.4 in.diam. 2.0 in.long	Air Jet 0.4 in.diam. > 4 in. long
MIL-L-7808 oil	760	1030	1085	1380
JP-6 fuel	450	1040	1285	1480
n-Decane	405 (Ref 13)	1085	1200	1380
n-Octane	430 (")	1085	1220	1390
n-Hexane	455 (")	1120	1240	1410
n-Butane	760 (")	1165	--	1670 [2/] (Ref.6)
Ethane	960 "	1075	--	1545 "
Methane	1000 "	1375	--	1905 "
Benzene	1045 "	1265	--	(N_2 jet) 1870 "
Hydrogen	1030	1175	--	1185 "

1/ Minimum AIT values obtained in 12.2 in^3 Erlenmeyer (equivalent cylinder diameter of 1.7 inch).

2/ Values from Ref 6 obtained with hot air jet injected into pure fuel except for benzene; values of present research obtained with hot air jet injected into fuel vapor-air mixture.

Since $\rho C_p v_y$ varies slightly with temperature, the heat release can be determined by measuring axial jet temperature profiles with combustible $(\partial T/\partial y)$ and without combustible $(\partial T/\partial y)_{Q=0}$. Such measurements were made here initially with a 1/2-inch diameter hot air jet at a jet flow rate of 185 in^3/min and mixture flow rate of 365 in^3/min. Radial temperature profiles were essentially flat up to a radial distance of about 0.05 inch for jet heights up to about 2 inches. However, axial temperature gradients were much greater because of the low jet flow rates employed to obtain these data at minimum ignition temperature conditions. Thus, the Q values are only applicable to low jet heights and the center of the jet and should be considered only as relative values because of experimental uncertainties.

The above measurements were made at a fuel-air weight ratio of 0.25 to 0.30. The temperature differences observed with and without combustible became significant at heights equal to or greater than about 1-1/2 inches above the jet base. Without the temperature probe present, ignitions occurred at temperatures critical for ignition. The critical jet temperature which may produce "hot" and luminous reactions were determined for each of the combustibles. The reference temperature was taken at a jet height of 1-1/2 inches in all cases. The gas velocity required in equation (19) was determined from photographs of particle tracks of dust entrained in the jet stream and illuminated at selected time intervals. Particle velocities were of the order of 70 in/sec near the center of the jet at distances between 1 and 2 inches above the jet base.

In Table 8, one observes significant differences between the temperatures which define the two ignition conditions for each combustible. In comparison, the axial heat flux values ($A_{Q=0}$) obtained without combustible for each temperature condition varied little. The rates of heat release (Q_2) correspond to observed temperature rises between 10° and 40°F at the jet height of 1-1/2 inches. If equation (19) is applicable, temperature rises of 160° to 180°F would appear to have been required to overcome the heat losses indicated by the axial temperature gradients observed. Ordinarily ignitions resulted before temperature rises of this magnitude were noted.

Since the jet flow rate (185 in^3/min) used for comparing the above ignition temperature conditions produced steep axial temperature gradients, other similar measurements were made at a higher jet flow rate of 365 in^3/min ($\sim$100 in/sec). Figure 18 shows that at the higher jet flow the axial temperature drop was not more than approximately 100°F at a height of 2 inches for 1/2-inch diameter air jets flowing into heated air at 350°F (jet base temperatures were 1315° and 1350°F); in comparison, the temperature drops at the lower jet flow were over 200°F at a jet height of 1-1/2 inches and similar jet base temperatures (Table 8). It is also noted in Figure 18 that initial exothermal reaction occurs at jet heights $\geq$ 1-1/2 inches and that the jet temperature varies little with jet height when the combustible is present (n-octane vapor-air mixtures).

TABLE 8. - Critical Temperature and Heat Flux Data for Luminous Reactions and "Hot" Flame Ignitions With 1/2-inch Diameter Hot Air Jet Flowing Into Various Combustible Vapor-Air Mixtures.

Jet Flow Rate - 185 in^3/min
Mixture Flow Rate - 365 in^3/min
Fuel-Air Weight Ratio - 0.25 to 0.30

Combustible	T_{base} °F	T_1 1/ °F	$A_{Q=o} \times 100$ Btu/in^3-sec	T_{base} °F	T_2 1/ °F	$A_{Q=o} \times 100$ Btu/in^3-sec	Q_2 2/ Btu/in^3-sec
n-Hexane	1350	1100	5.55	1455	1190	5.60	1.25
n-Octane	1150	900	5.35	1330	1085	5.50	1.25
n-Decane	1060	750	5.30	1265	1065	5.45	2.15
JP-6 Fuel	1265	1035	5.45	1415	1195	5.55	2.45
MIL-L-7808 Oil	1320	1130	5.55	1415	1155	5.55	0.60

1/ Jet temperatures above which luminous reactions (T_1) and "hot" flame ignitions (T_2) can occur; measured at 1-1/2 inches above jet base.
2/ Heat release determined from axial convection with and without combustible ($A_{Q\neq o} - A_{Q=o}$) at T_2.

Similar data were obtained at the jet flow rate of 365 in^3/min for various n-hexane vapor-oxygen-nitrogen mixtures. Figure 19 shows the effect of fuel-air weight ratio on the axial temperature change or rise observed with and without combustible present at various jet heights and jet base temperatures (1350° to 1500°F). The temperature rises increased with increasing jet temperature (slightly) and as the fuel-air ratio of the combustible mixture was varied from 0.22 to 0.5. They also increased with increasing distance above the jet base although the rises were nil at a jet height of 1.75 inch, regardless of fuel-air ratio; at a fuel-air ratio of 0.4 and jet height of 2.5 inches, the temperature rises were in excess of 60°. In general, the temperature rises associated with the pre-ignition reactions appear to display a linear dependence on fuel-air ratio between 0.2 and 0.5. Without the temperature probe present, ignitions were obtained at the higher fuel-air ratios with jet base temperatures greater than about 1350°F.

The effect of oxygen concentration on the hot gas ignition of n-hexane vapor-oxygen-nitrogen mixtures was practically negligible under the above jet flow conditions. The axial temperature profiles of the 1/2-inch diameter hot air jets varied little when the oxygen content of the mixture was varied from 5 to 25 volume percent. Apparently, the high air jet flow rate used (365 in^3/min) insured an adequate supply of oxygen in the jet reaction zone.

According to axial concentration profiles obtained for n-hexane vapor-air mixtures, the extent of reaction was not great at jet temperatures between 100° to 200°F below those critical for ignition. Table 9 and Figure 20 show data from measurements made at a fuel-air weight ratio of 0.5 and

at jet base temperatures of 1200° and 1300°F. The oxygen consumption increased with increasing jet height up to about 3 inches, above which they decreased (T_{base} = 1200°F) or leveled off (T_{base} = 1300°F). The concentra- of CO and CO_2 were maximum at a jet height of 2 or 3 inches, consistent with the observed oxygen consumption. The concentration of unreacted fuel (n-hexane) increased with jet height and also tended to level off at the higher jet heights (4-5 inches) where mixing of the jet and combustible gas would be greater. Jet temperatures $\geq$ 1350°F would have been required to produce ignition in these experiments. The applicability of equation (19) to the data obtained at this higher jet flow rate (365 in^3/min) was not determined since data on the radial temperature and velocity profiles were incomplete.

TABLE 9. - Analyses of Carbon Monoxide, Carbon Dioxide, Oxygen, and n-Hexane at Various Jet Heights in a 1/2-inch Diameter Hot Air Jet Flowing Into n-Hexane Vapor-Air Mixtures (350°F) at 1200° and 1300°F Jet Base Temperatures.
Fuel-Air Weight Ratio - 0.5

Distance above jet base, inches	Gas Concentration, volume percent			
	CO	CO_2	O_2	$n\text{-}C_6H_{14}$
	Jet Base Temperature, 1200°F			
0	--	--	20.89	--
1	0.07	0.21	20.21	0.60
2	1.00	0.40	18.02	1.30
3	1.00	0.38	17.76	1.45
4	0.83	0.30	17.92	2.13
5	0.55	0.31	18.54	2.14
	Jet Base Temperature, 1300°F			
0	--	--	20.89	--
1	0.13	0.29	20.28	0.18
2	1.08	0.77	17.86	0.94
3	1.11	0.53	17.76	1.47
4	1.04	0.47	17.83	1.85
5	1.08	0.52	17.70	2.18

3. Reaction Rate Experiments With n-Octane and JP-6 Fuels

The ignitions of combustible-oxidant mixtures are generally controlled by slow oxidation reactions which are characterized by relatively low rates of pressure rise. In the present oxidation rate studies, n-octane was used to obtain rate data for possible use in predicting the ignition behavior of hydrocarbon type fuels at reduced pressures and in various size reaction vessels (1.95 to 31.6 in^3 spherical Pyrex vessels); such data were also

obtained with the JP-6 fuel for comparison in some of the experiments. Pressures between 0.6 and 13 psia and temperatures between 392° and 590°F were employed.

n-Octane Vapor-Oxygen-Nitrogen Mixtures

Initial oxidation of n-octane vapor-air mixtures at 1 atmosphere pressure occurs at about 400°F. The oxygen consumption increases uniformly at temperatures up to about 660°F with CO_2 as the primary gaseous product below 520°F and CO as the predominant one above this temperature (Ref 15). Thus, rate of pressure rise measurements, as were made here, should be suitable for following the rate of oxidation. Figure 21 shows the pressure rise versus time observed in the oxidation of 5 percent n-octane vapor-air mixtures (volume percent) at 482°F in various size vessels and for various initial pressures. Similar measurements were made at other temperatures and fuel concentrations between 1.65 and 30 percent. In general, the maximum pressure rises occurred during the early stages of reaction ($\leq$ 5 minutes) and the induction periods were only a few seconds, except at the lowest initial pressures or temperatures employed in this work. Thus, the initial or maximum rates of pressure rise were most significant and these were determined from the point of initial pressure rise to that attained within approximately 3 minutes or less.

The pressure rise data were compared with the consumption of oxygen and formation of gaseous products in some of the experiments performed in the 31.6 in^3 vessel with 5, 10, 20 and 30 percent n-octane vapor-air mixtures; the temperature was 482°F and the total pressure was 1.16 psia. Figure 22 shows that the oxygen consumption increased with increasing pressure rise and with increasing fuel concentration from 5 to 20 volume percent. Also the oxygen consumption curves displayed approximately the same variation with pressure rise as the curves for CO and CO_2. However, the data found with 30 percent fuel display less oxygen consumption or CO and CO_2 formation at a given pressure rise than observed with 5 to 20 percent fuel; apparently, larger concentrations of other gaseous products formed in the oxidations with the 30 percent fuel mixture. Methane was detected in concentrations less than 1 percent and could not account for the oxidation behavior observed with this mixture.

In the experiments with n-octane vapor-air mixtures, the total pressure required to produce an abrupt pressure rise increased with decreasing temperature, fuel concentration, and vessel size. Generally, pressure rises greater than 0.1 psi (5 mm Hg) were required before an abrupt pressure rise or rapid reaction was observed. Table 10 lists the minimum total pressures required for rapid reaction of 5 percent n-octane vapor-air mixtures at various temperatures and for various vessel sizes. Here, the critical pressures varied from 2.18 to 8.40 psia when the vessel volume was decreased from 31.6 in^3 (518 cc) to 1.95 in^3 (32 cc) and the temperature was constant (482°F); also they varied from 1.41 to 13.0 psia when the temperature was decreased from 536° to 410°F at a given vessel volume (31.6 in^3). Consistent with AIT data, the effect of vessel size is small above 13.5 in^3, the approximate volume required to obtain minimum AIT's in spherical vessels (Table 1).

TABLE 10. - Critical Total Pressures for Rapid Reaction of 5 Percent n-Octane Vapor-Air Mixtures at Various Temperatures and Vessel Sizes.

Temperature °F	Vessel Volume in^3	Vessel Volume cc	Vessel Diameter inch	Critical Total Pressure psia
482	31.6	518	3.84	2.18
"	13.5	222	2.94	2.36
"	6.47	106	2.30	3.85
"	3.36	55	1.87	6.11
"	1.95	32	1.60	8.40
536	31.6	518	3.84	1.41
482	"	"	"	2.18
428	"	"	"	7.05
410	"	"	"	13.0

At 590°F, an abrupt pressure rise was not observed up to a pressure of 9.5 psia. Thus, the reaction mechanism apparently changed between 536° and 590°F, which is consistent with that reported by others (Ref 15). At or below 536°F the abrupt pressure rises may be considered indicative of reactions capable of forming "cool" flames; also, they occurred at temperatures and corresponding pressures below those normally required to produce autoignition of the given mixture. The data presented in the following discussions were all obtained in the 31.6 in^3 vessel.

The rates of pressure rise $\emptyset$ increased with increasing total pressure (P_t) as shown by the log-log plot in Figure 23 for the data obtained with 5 percent n-octane vapor-air mixtures at temperatures between 410° to 590°F; data at 392°F are not included because of the little reaction observed. The variation of log $\emptyset$ with log P_t tends to be linear over the range of pressures where slow oxidation was observed at initial temperatures of 410°, 428°, 482°, and 536°F. At these temperatures, the slopes of the curves corresponding to the slow oxidation stage are 1.4 ± 0.15. In a similar plot (Figure 24), the rates of pressure rise also increased linearly with fuel concentrations (P_f) between 5 and 30 volume percent; the temperature was 482°F and the total pressures were 50, 80 and 90 mm Hg (0.96, 1.55, and 1.74 psia). The slopes of the curves lie between 0.34 and 0.42 for the above data. However, rates found with 1.65 percent fuel appeared inconsistent and lower than would be expected from the other data shown.

An Arrhenius plot was also made for the rate data obtained at various temperatures with the 5 percent fuel mixture at a total pressure of 1.16 psia (60 mm Hg). It is evident from Figure 25 that the temperature dependency of the rates obeys an exponential law up to about 550°F. Therefore, if the above total pressure and fuel concentration effects hold over these temperature conditions, the following expression may be written:

$$\phi \text{ (psi/min)} = k\,(P_f)^{0.38}\,(P_t)^{1.4}\,\exp\frac{-24.9}{RT} \qquad (20)$$

where k is a constant, R is the universal gas constant and equal to 2 cal/°K-mole, T is temperature in °K, and 24.9 is the apparent activation energy in kcal/mole. It is interesting to note that the above exponential term is equivalent to exp $\frac{-22.5}{T}$ with T in °R. The value of 22.5 is in fair agreement with the value 25.6 obtained from AIT data for n-octane vapor-air mixtures (see equation 3).

The effect of oxygen partial pressure (P_{O_2}) on the rate of oxidation of n-octane was less than that of total pressure (P_t). Figures 26 and 27 show the data obtained with 5 percent n-octane vapor-oxygen-nitrogen mixtures at 1.16 psia (60 mm Hg) total pressure and 482°F temperature. In the log-log plot of Figure 27, the variation of the rate of pressure rise with oxygen partial pressure is linear over the range of oxygen concentrations (4.8 to 40 percent) where slow oxidation was observed; the slope of the curve is 0.75. Accordingly, the following expression may be written for the oxidation of this fuel at 482°F:

$$\phi \text{ (psi/min)} = k\,(P_f)^{0.38}\,(P_{O_2})^{0.75}\,(P_t)^{1.4} \quad . \qquad (21)$$

Thus, the rate is influenced to a greater extent by the total pressure than by either the partial pressure of oxygen or of the fuel. A test of these rate expressions for predicting critical conditions for "cool" flame ignitions should be considered in future work.

JP-6 Fuel Vapor-Air Mixtures

The JP-6 fuel (vapors) appeared to be more resistant to oxidation than n-octane under the temperature and pressure conditions employed in this work. Figure 28 shows the pressure rise data obtained for 5 percent JP-6 fuel vapor-air mixtures at 482° in various size vessels and for various initial pressures. Minimum pressure for rapid reaction or abrupt pressure rise was defined only in the experiments performed with the largest reaction vessel (31.6 in^3). The critical pressure for this size vessel was between 8.63 and 9.13 psia and much higher than the value of 2.18 psia found for n-octane. Conditioning the vessels by heating did not appear to influence the results greatly. In addition, it was particularly difficult to obtain reproducible data in the smaller size vessels.

4. Autoignition Temperatures and Flammability Limits of New Aircraft Combustibles

Minimum Autoignition Temperatures in Air

Table 11 and Figure 29 compare the minimum AIT data obtained in the BuMines I-8 apparatus for 5 new aircraft jet fuels (SF6-6209, TSF-6314, F64-17, F65-3 and F64-12A) in air at initial pressures of 1/2, 1 and 1-1/2

atmospheres; included in Table 11 are the optimum fuel volumes for ignition, ignition delay times, and maximum pressure rises observed at ignition. The AIT's at 1-1/2 atmospheres were found in a 460 cc steel vessel with sudden pressure rise as the ignition criterion and those at 1/2 and 1 atmosphere in a 500 cc Pyrex vessel with flame or pressure rise as the ignition criterion. At 1-1/2 atmosphere pressure, the F64-12A fuel had the lowest AIT (388°F) and the TSF-6314 fuel had the highest value (455°F). As may be noted, data obtained with pressure rise as the ignition criterion show little effect of initial pressure on the minimum AIT values; the observed temperature differences were not greater than 16°F for any fuel. In contrast, the effect of pressure is seen to be very noticeable when the appearance of flame is the ignition criterion. With flame as the criterion, the AIT values at 1/2 atmosphere are about 400°F higher than those at 1 and 1-1/2 atmosphere. Of course, for maximum safety, the lowest ignition temperature values should be utilized in predicting explosion hazards which may be encountered in the use of these fuels. The AIT characteristics of the above fuels do not differ greatly from those of the JP-6 jet fuel whose minimum AIT is 440°F at 1 atmosphere (Ref 16).

Similar AIT data are given in Table 12 for a hydraulic fluid (MIL-H-6083B) in air at 1 and 34 (500 psig) atmosphere pressure. The AIT was 470°F at 1 atmosphere and 435°F at 34 atmospheres. This small effect of pressure is reasonably consistent with that observed for a similar hydraulic fluid, MIL-O-5606; its AIT decreased from 442°F at 1 atmosphere to only 428°F at 9.5 atmospheres (Ref 17).

Limits of Flammability in Air

The lower limits of flammability of the 5 new aircraft jet fuels were determined in air at 1 atmosphere pressure (210°F) in a 2-inch diameter flammability tube and at 1/15 or 1/25 atmosphere (75° or 100°F) in a 11.2-inch diameter spherical vessel. These data are given in Table 13 together with the flash point data obtained for the fuels; the flash points varied between 125° and 195°F. Since flammable mixtures were not formed with the F64-12A and the F65-3 fuels at ambient temperature and 1/15 atmosphere, the reduced pressure experiments with these fuels were made at 1/25 atmosphere. It is evident that the lower limits of the fuels varied slightly (0.75 to 0.82 volume percent) at 1 atmosphere pressure. They are comparable to the reported value of 0.7 volume percent for the JP-6 jet fuel (Ref 16) but lower than the value of 1.3 percent for the JP-4 fuel (Ref 18). Figure 30 shows that the effect of reduced pressure is negligible and consistent with that observed for the JP-4 fuel.

The lower and upper limits of flammability of the MIL-H-6083B hydraulic fluid at 400°F were 4.6 and 31.8 weight percent or 62 and 601 mg of combustible per liter of air (32°F and 1 atm) respectively at 1 atmosphere pressure. Corresponding values for the MIL-L-7808 engine oil at 500°F were 3.3 and 15.0 weight percent or 45 and 238 mg of combustible per liter of air. These data were obtained in the F-11 apparatus (2-inch diameter tube) at mixture temperatures $\geq$ 400°F because of the relatively high flash points and low vapor pressures of these materials. The flash points were 255°F for the hydraulic fluid and 445°F for the engine oil.

TABLE 11. - Minimum Autoignition Temperatures (AIT's) of Five Aircraft Jet Fuels in Quiescent Air at Various Initial Pressures.
500 cc Spherical Pyrex Vessel - 0.5 and 1 atmosphere
460 cc Cylindrical Stainless Steel Vessel - 1.5 atmosphere

Initial Pressure, atm.	Fuel Volume, cc	AIT °F	Ignition Delay, sec	Ignition Criterion		
				Flame	Pressure Rise, mm Hg	psi
			Jet Fuel SF6-6209			
0.5	0.09	446	206	--	45	0.87
0.5	0.09	830	1	Flame	(125)	(2.4)
1 1/	0.16	446	131	Flame	--	--
1.5	0.20	451	114	--	735	50
			Jet Fuel TSF-6314			
0.5	0.07	439	147	--	23	0.44
0.5	0.07	828	1	Flame	(120)	(2.3)
1 1/	0.10	451	144	Flame	--	--
1.5	0.17	455	92	--	>1470	>100
			Jet Fuel F64-17			
0.5	0.10	424	66	--	35	0.68
0.5	0.05	860	3	Flame	(120)	(2.3)
1 1/	0.10	428	105	Flame	--	--
1.5	0.20	414	97	--	>1470	>100
			Jet Fuel F65-3			
0.5	0.07	410	57	--	30	0.57
0.5	0.04	800	3	Flame	(85)	(1.7)
1 1/	0.10	433	154	Flame	--	--
1.5	0.10	421	100	--	>1470	>100
			Jet Fuel F64-12A			
0.5	0.10	383	76	--	37	0.72
0.5	0.04	805	3	Flame	(95)	(1.8)
1 1/	0.10	417	62	Flame	--	--
1.5	0.25	388	293	--	882	60

1/ Open vessel ignition.

TABLE 12. - Minimum Autoignition Temperatures (AIT's) of MIL-H-6083B Oil in Air at 1 and 34 Atmospheres Pressure.
200 cc Pyrex Erlenmeyer Vessel - 1 atmosphere
460 cc Cylindrical Stainless Steel Vessel - 34 atmospheres

Initial Pressure atm	Fuel Volume cc	Fuel-Air[1/] Weight Ratio	AIT °F	Ignition Delay sec	Ignition Criterion
1	0.07	0.46	470	80	Flame
34	1.30	0.10	435	14	Pressure Rise

1/ Calculated values based on volume of liquid oil injected into vessel.

TABLE 13. - Lower Limits of Flammability of Five Aircraft Jet Fuels in Air at Various Initial Pressures.

Initial Pressure atm	Temperature, °F	Lower Limit[1/] Wt.%	Vol.%	Flash Point[2/] °F
		SF6-6209		
1/15	75	--	0.82	--
1	210	3.6	0.71	125
		TSF-6314		
1/15	75	--	0.77	--
1	210	4.1	0.81	135
		F64-17		
1/15	75	--	0.75	--
1	210	3.8	0.75	155
		F64-12A		
1/25	100	--	0.77	--
1	210	3.8	0.75	185
		F65-3		
1/25	100	--	0.76	--
1	210	3.9	0.78	195

1/ 1/15, 1/25 atm. - Determined in an 11.2-inch diameter spherical Pyrex vessel.
1 atm - Volume % calculated assuming an average molecular weight of 147; determined in BuMines F-11 apparatus with a 2-inch diameter Pyrex tube.
2/ Determined in a Cleveland Open Cup Tester.

Effect of Initial Temperature on Upper Limits of Flammability

Generally, the flammable range or concentrations of combustible vapor-air mixtures increases with increasing mixture temperature. Furthermore, many hydrocarbons are capable of forming "cool" flames at relatively high fuel concentrations, depending on the mixture temperature. In assessing explosion hazards, the possible occurrence of "cool" flames cannot be neglected since the temperature rises and corresponding pressure rises may be greater than can be tolerated; e.g., in a thin-walled fuel tank. Figures 31, 32, and 33 show that the temperature rises associated with the "cool" flames of n-hexane, n-octane, and n-decane vapor-air mixtures can be of the order of 400° to 500°F; these temperature rises were measured with a 36-gage iron-constantan thermocouple and the "cool" flames were not visible to the naked eye in many instances.

Table 14 gives a list of upper limit values found at various initial mixture temperatures for the paraffins, propane to n-decane, and the JP-6 fuel in air at 1 atmosphere pressure. These data are also shown graphically in Figure 34. Here, it is seen that the upper limits of flammability of propane, n-butane, and n-pentane increased consistently with increasing temperature but not as greatly as that observed with the other combustibles. The upper limit values for the higher molecular weight paraffins increased abruptly at temperatures in excess of about 200° to 250°F and were characteristic of "cool" flame propagation. The highest upper limit (30.5 volume percent) was obtained with n-octane at a mixture temperature of 355°F; at higher temperatures, the limit decreased apparently because of noticeable oxidation of the fuel prior to testing (igniting) the mixture. The limit values of the JP-6 fuel increased abruptly above 355°F. According to these data, the range of flammable concentrations for all of the above fuels can be noticeably greater than that which is generally reported for these materials at ambient or slightly elevated temperatures.

TABLE 14. - Effect of Initial Mixture Temperature on the Upper Limits of Flammability of Various Hydrocarbon Fuel Vapor-Air Mixtures at Atmospheric Pressure.
F-11 Apparatus - 2-inch diameter tube

Fuel	Temp. °F	Vol. %	Temp. °F	Vol. %	Temp. °F	Vol. %	Temp. °F	Vol. %	Temp. °F	Vol. %
Propane	75	9.5[1/]	--	--	--	--	355	12.9	550	16.5
n-Butane	75	8.4[1/]	250	9.9	--	--	355	10.6	550	12.7
n-Pentane	75	7.8[1/]	210	8.8	--	--	--	--	390	13.8
n-Hexane	75	7.4[1/]	140	8.6[1/]	250	9.3	325	17.5	390	26.6
n-Heptane	75	6.7[1/]	200	7.1[1/]	--	--	--	--	390	25.3[1/]
n-Octane	140	6.1	250	20.5	300	26.5	355	30.5	390	19.5
n-Decane	185	5.6	250	15.7	--	--	355	18.4	--	--
JP-6 Fuel[2/]	210	5.4	250	5.5	--	--	355	5.9	410	10.3

1/ Values obtained from Bureau of Mines Bull. 627, 1965.
2/ Values calculated assuming an average molecular weight of 147.

CONCLUSIONS AND RECOMMENDATIONS

The autoignition and wire ignition temperatures of hydrocarbon combustible mixtures, such as those employed in this work, can be expected to increase with decreasing oxygen concentration, fuel contact time, total pressure, and vessel or wire diameter. Pyrex vessels and Nichrome wires tend to give the lowest ignition temperatures for the heat source materials investigated. For heat sources of varying length, the hot surface ignition temperatures correlate over a greater range of heat source dimensions when the surface area of the heat source rather than the radius is used. High AIT combustibles like the engine oils can be less thermally stable than low AIT hydrocarbons at relatively high temperatures. Hot gas ignition temperatures obtained for hydrocarbon combustibles with jets of hot air are not necessarily much greater than their corresponding hot surface ignition temperatures when the heat source diameter and ignition criterion are the same. The dependence of hot gas ignition temperatures on heat source diameter resembles that displayed by autoignition temperature data.

The slow oxidation of n-octane vapor-air mixtures between 428° and 536°F is approximately 0.4 order with respect to fuel concentration and 1.4 with respect to total pressure ($\sim$ 0.6 to 8 psia); the apparent activation energy is close to 25 kcal/mole and consistent with AIT data. The reaction was less dependent on oxygen partial pressure ($P_{O_2}^{0.75}$) than on total pressure. Also, the critical pressures for "cool" flame reactions increased with decreasing vessel size and temperature. With increasing temperature, the upper limits of flammability of the hydrocarbon combustibles increased noticeably and indicated that, at near AIT conditions, the range of flammable concentrations can be much greater than that usually reported in the literature for relatively low ambient temperatures.

The following recommendations are made for future work:

1. Hot Surface and Hot Gas Ignition Temperatures

Determine minimum AIT's of aircraft lubricants in air atmospheres at elevated pressures to 15,000 psig and of any new aircraft fuels at pressures between about 1/16 and 5 atmospheres. Extend hot gas ignition temperature data for aircraft jet fuels to hot air jets of greater diameter than 3/4-inch.

2. Limits of Flammability

Determine "hot" flame and "cool" flame limits of aircraft combustibles of interest at elevated temperatures to near the minimum AIT of the given combustible.

3. Thermal and Oxidative Stability

Conduct oxidation and decomposition rate experiments to define the minimum oxidation or decomposition temperatures and pressures of aircraft jet fuels and lubricants. Continue efforts to correlate such rate parameters and ignition temperature data with heat source dimensions for predicting ignition behavior of hydrocarbon type combustibles under various heating conditions.

4. Fuel Foams and Mists

Investigate the formation of hydrocarbon fuel foams or mists and their flammability characteristics under simulated flight conditions of varying temperature and pressure. Low and high volatility fuels should be included. In addition, the effectiveness of various flame arrestors should be explored.

PUBLICATIONS

The following publications were based upon the work that is summarized in this report:

1. Kuchta, J. M., A. Bartkowiak and M. G. Zabetakis, Hot Surface Ignition Temperatures of Hydrocarbon Fuel Vapor-Air Mixtures. J. Chem. Eng. Data, Vol. 10, July 1965, p. 282.

2. Kuchta, J. M. and R. J. Cato, Comparison of Hot Surface and Hot Gas Ignition Temperatures. Combustion and Flame, Vol. 8, December 1964, p. 349.

3. Kuchta, J. M. and R. J. Cato, Hot Gas Ignition Temperatures of Hydrocarbon Fuel Vapor-Air Mixtures. Bureau of Mines Report of Investigations to be published.

LIST OF REFERENCES

1. Setchkin, N. P. Self-Ignition Temperatures of Combustible Mixtures. J. Res. NBS, Res. Paper 2516, Vol. 53, No. 1, 1954.

2. Guest, P. G. Ignition of Natural Gas-Air Mixtures by Heated Surfaces. U. S. BuMines Tech. Paper No. 475, 1930, 59 pp.

3. Frank-Kamenetskii, D. A. Diffusion and Heat Exchange in Chemical Kinetics. Princeton University Press, Princeton, N. J., 1955, p. 209.

4. Semenov, N. N. Thermal Theory of Combustion and Explosion. NACA Tech. Memo 1024, Washington, D. C., 1942, p. 41.

5. Wolfhard, H. G. The Ignition of Combustible Mixtures by Hot Gases. Jet Propulsion, December 1958, p. 798.

6. Vanpee, M. and A. E. Bruszak. The Ignition of Combustible Mixtures by Laminar Jets of Hot Gases. U. S. BuMines Rept. of Investigations 6293, 1963, 84 pp.

7. Kuchta, J. M., A. Bartkowiak, R. J. Cato, and M. G. Zabetakis. Ignition Characteristics of Fuels and Lubricants. Air Force Aero Propulsion Laboratory, TDR No. APL-TDR-64-25, December 1963.

8. Kuchta, J. M., and R. J. Cato. Ignition Characteristics of Fuels and Lubricants. Air Force Aero Propulsion Laboratory Tech. Report AF-APL-TR-65-18, March 1965.

9. Zabetakis, M. G., A. L. Furno, and G. W. Jones. Minimum Spontaneous Ignition Temperatures of Combustibles in Air. Ind. and Eng. Chem., Vol. 46, October 1954, p. 2173.

10. Blake, E. S., et al. Thermal Stability as a Function of Chemical Structure. J. Chem. Eng. Data, Vol. 6, January 1961, p. 87.

11. Kuchta, J. M., et al. Flammability Characteristics of High Temperature Hydrocarbon Fuels. Air Force Systems Command TDR No. ASD-TDR-62-328, April 1962.

12. Semenov, N. N. Chemical Kinetics and Chain Reactions. Oxford University Press, London, 1935, p. 86.

13. Zabetakis, M. G., G. S. Scott, and G. W. Jones. Limits of Flammability of Paraffin Hydrocarbons in Air. Ind. and Eng. Chem., Vol. 43, September 1951, p. 2120.

14. Bruszak, A. E., D. Burgess and M. H. J. Wijnen. Reaction Kinetics in Hot Gas Ignition of Ethane-Air. Combustion and Flame, Vol. 7, September 1963,

15. Pope, J. C., F. J. Dykstra, and G. Edgar. The Mechanism of the Vapor Phase Oxidation of Isomeric Octane: Normal Octane. J. Am. Chem. Soc., Vol. 51, 1929, p. 1875.

16. Kuchta, J. M., A. Bartkowiak, and M. G. Zabetakis. Autoignition of Hydrocarbon Jet Fuel. U. S. BuMines Rept. of Investigations 6654, 1965, 25 pp.

17. Zabetakis, M. G., et al. Research on the Flammability Characteristics of Aircraft Hydraulic Fluids. WADC Tech. Report 57-151, Supplement 1, December 1957.

18. Jones, G. W., et al. Research on the Flammability Characteristics of Aircraft Fuels. WADC Tech. Report 52-35, Supplement 1, January 1954.

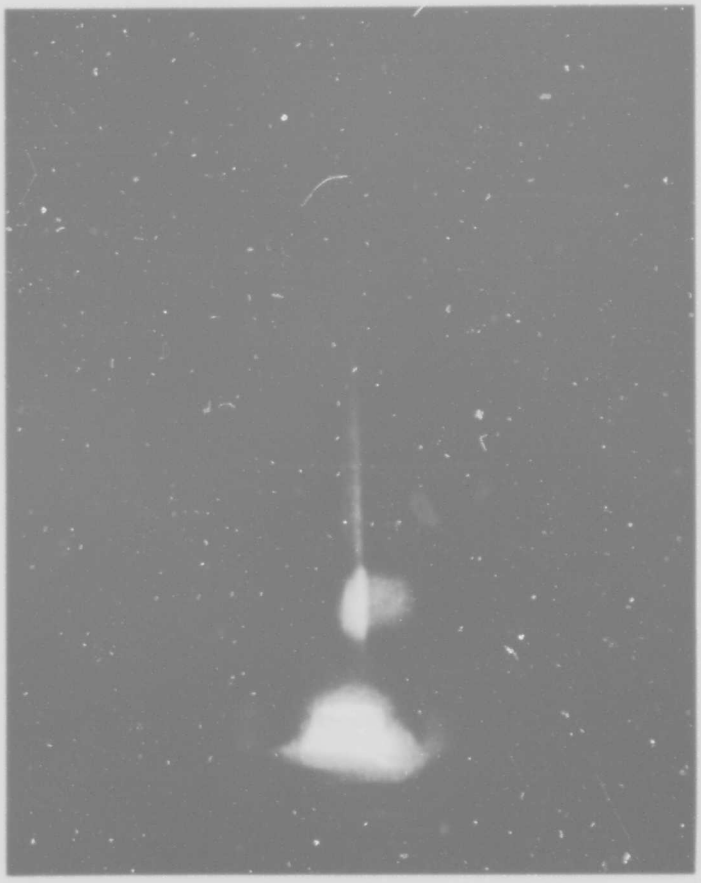


Figure 1. - Precursory flame formed in pre-ignition reaction of 1/4-inch diameter hot air jet (1670° F) with a uniform octane-vapor-air mixture at 350° F.
Jet flow rate - 185 in^3/min Fuel-air weight ratio - 0.14
Mixture flow rate - 365 in^3/min Scale: 1 inch = 0.935 inch

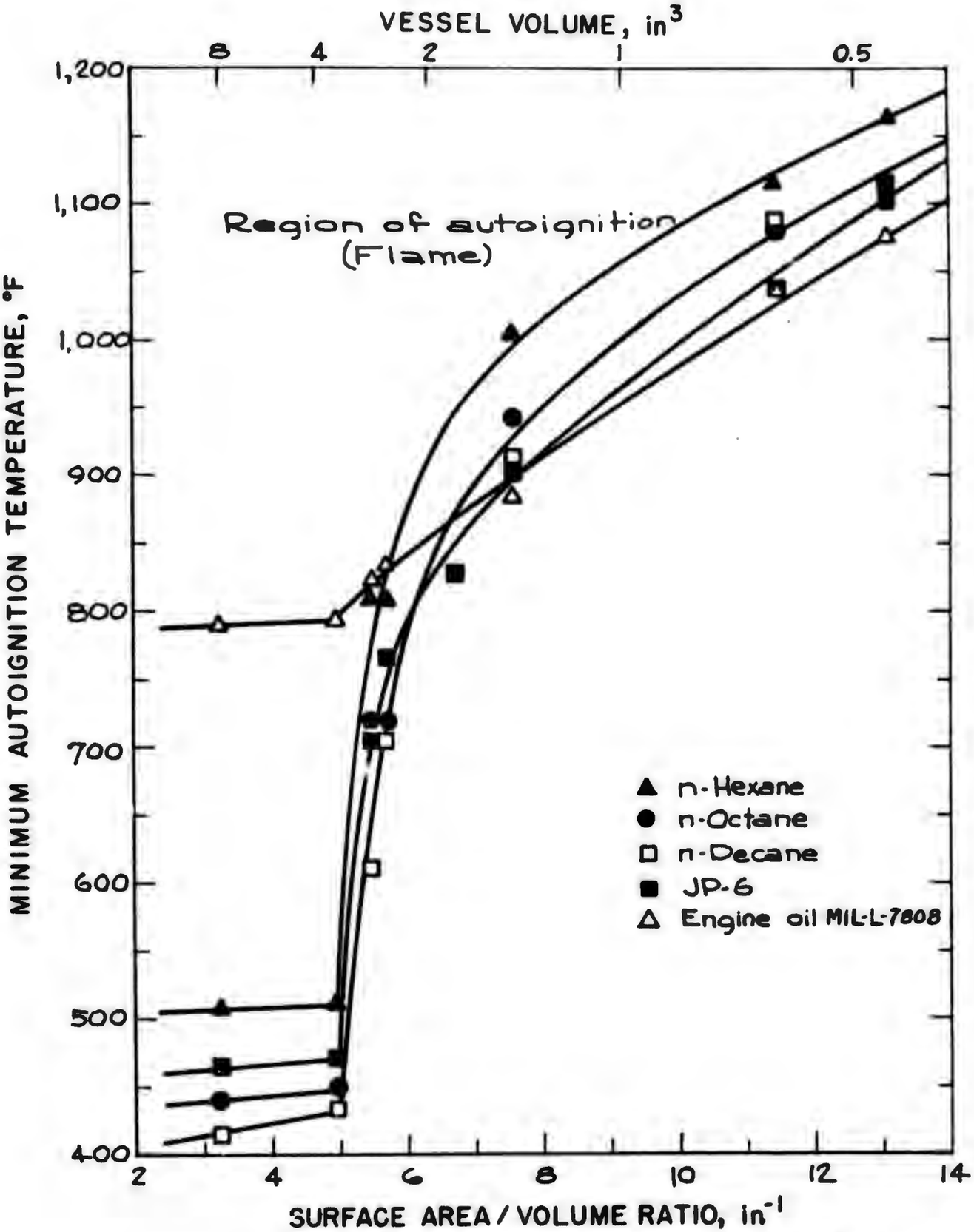


Figure 2. - Effect of vessel surface-volume ratio on minimum autoignition temperatures of various hydrocarbon fuels and engine oil in quiescent air (Pyrex cylinders 6-inches long).

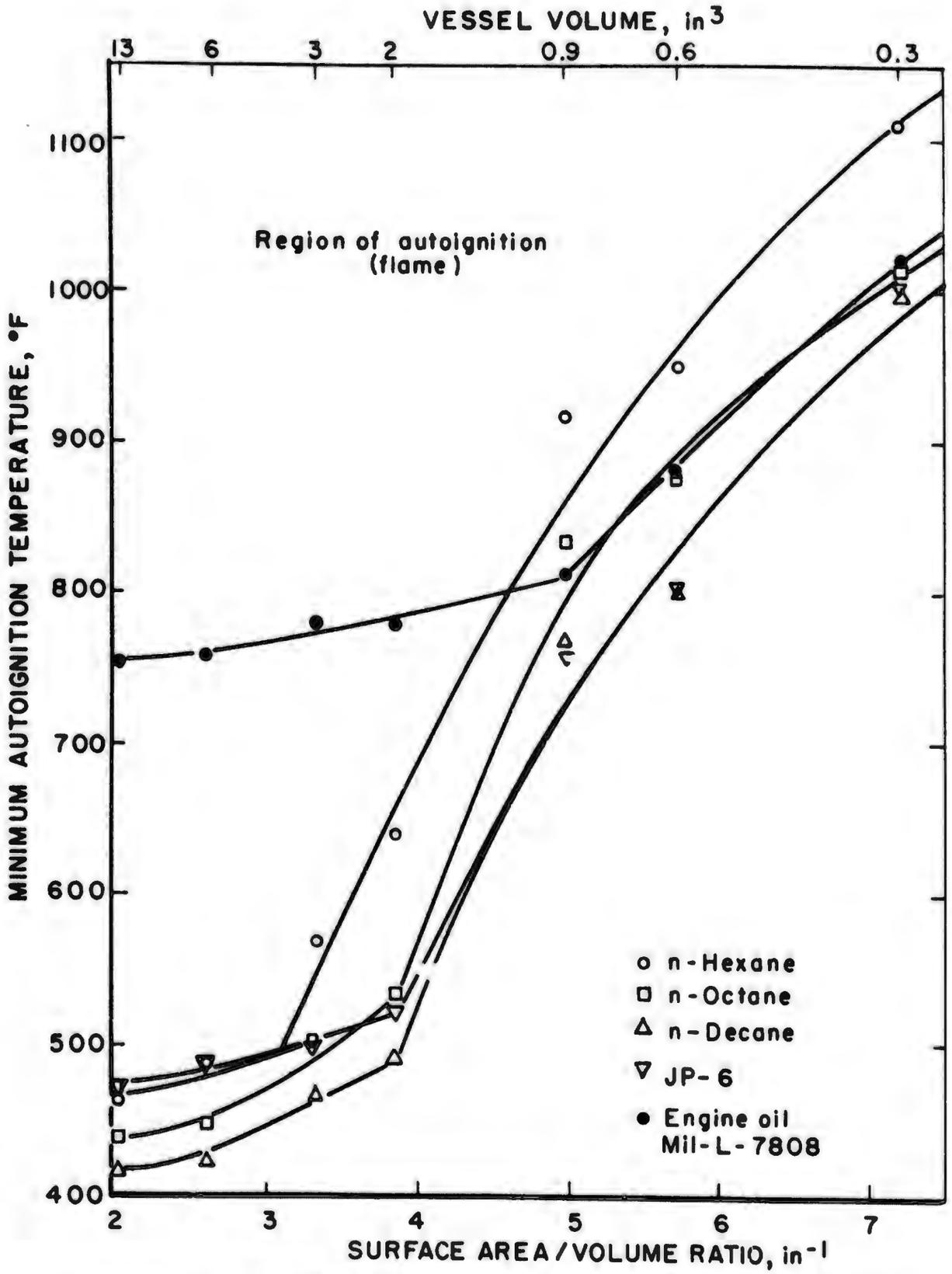


Figure 3. Effect of vessel surface area/volume ratio on minimum autoignition temperatures of various hydrocarbon fuels and an engine oil in quiescent air.
(Spherical Pyrex vessels)

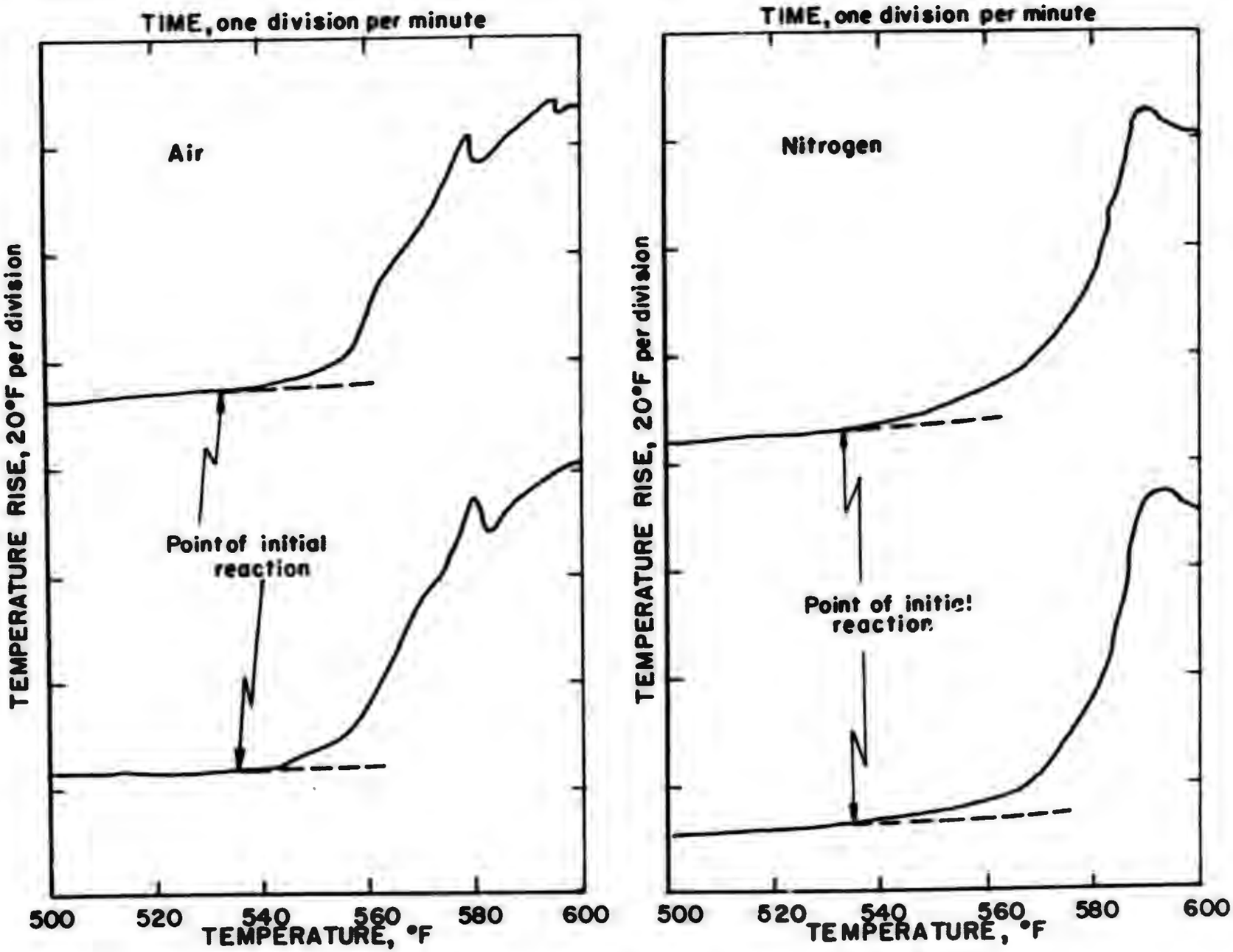


Figure 4. - Representative thermograms from DTA experiments with H-1026 engine oil in air and nitrogen atmospheres.

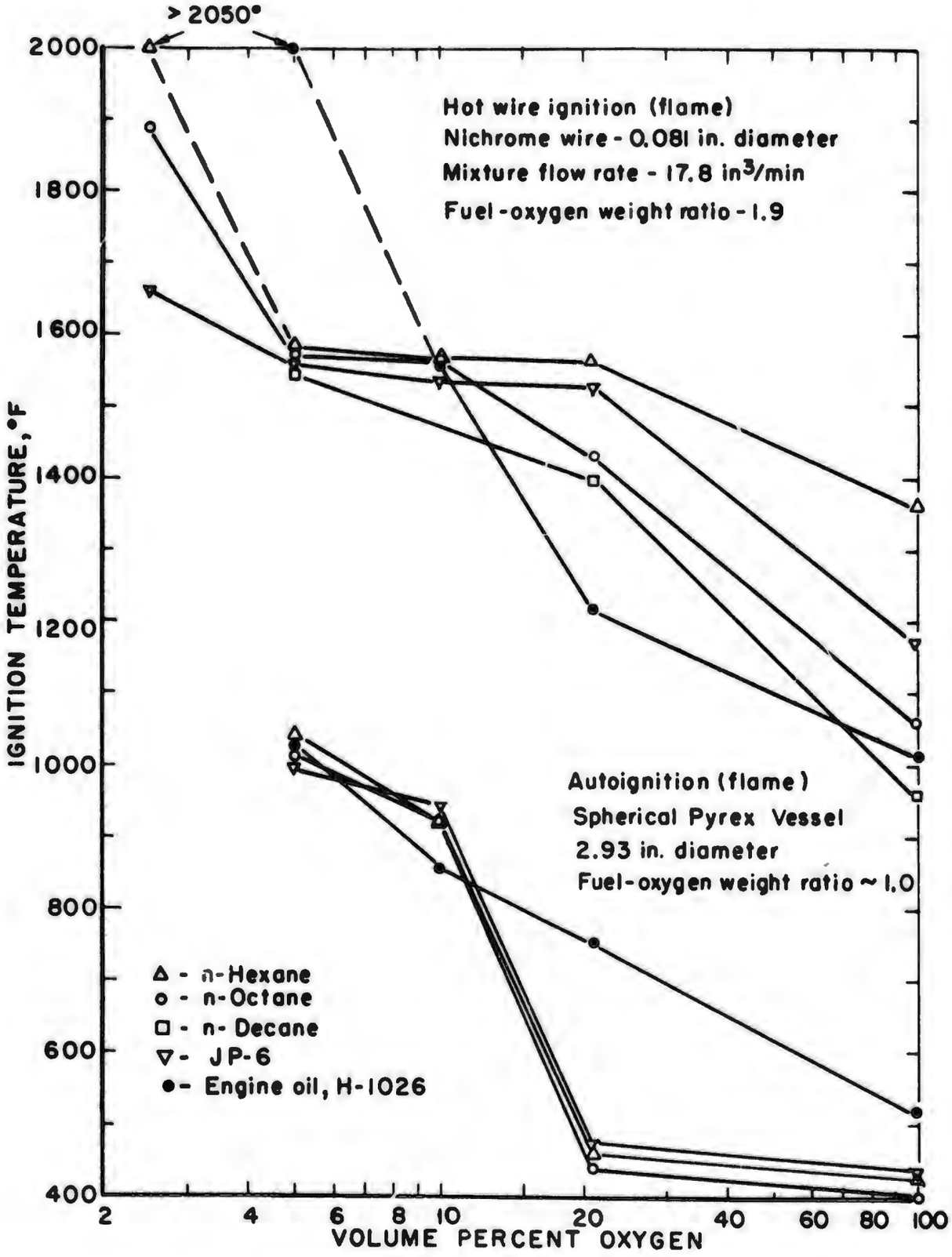


Figure 5. - Effect of oxygen content on autoignition and wire ignition temperatures of various hydrocarbon fuels and an engine oil in oxygen-nitrogen atmospheres.

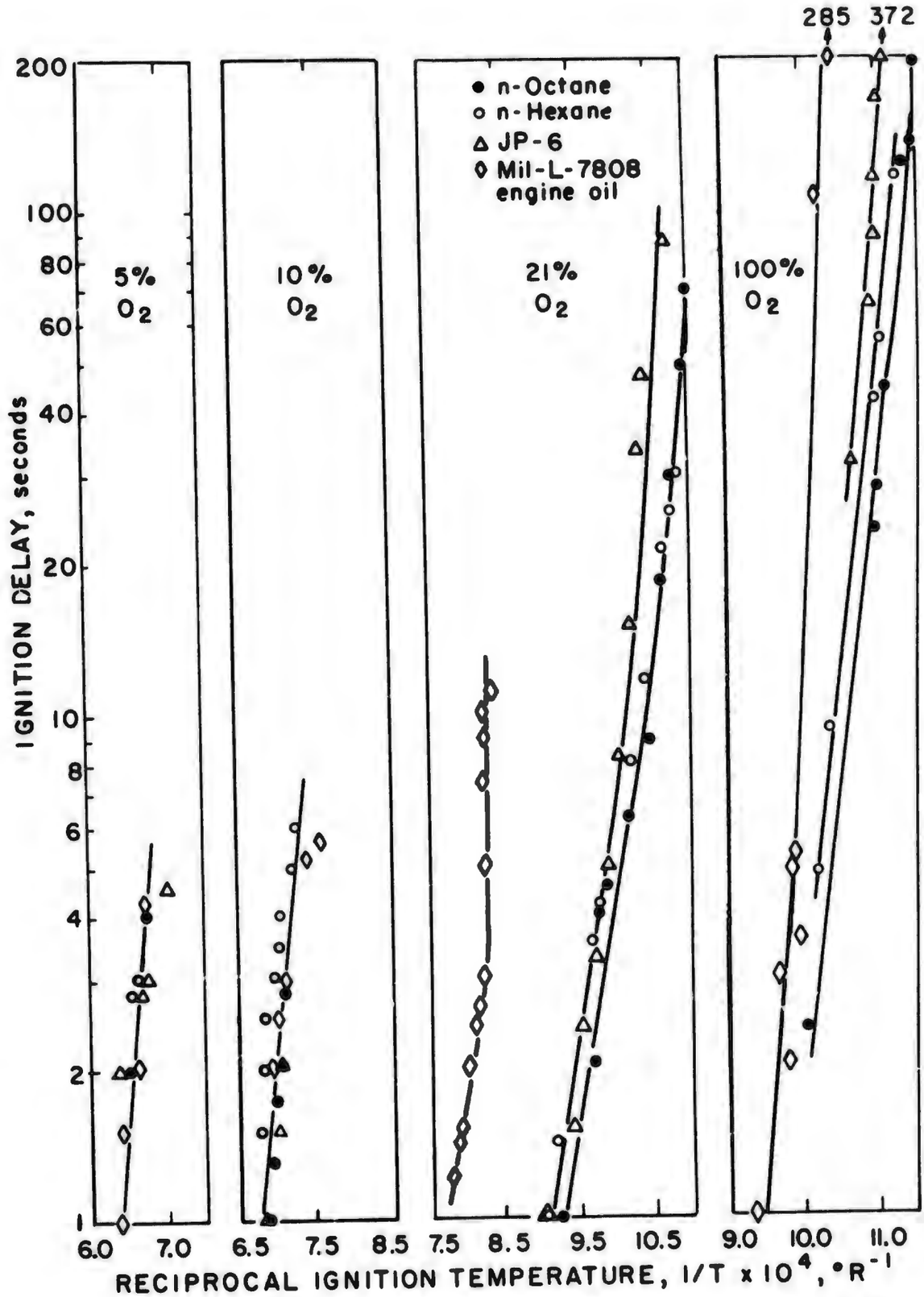


Figure 6. - Variation of ignition delay with reciprocal autoignition temperature for n-Octane, n-Hexane, JP-6 fuel, and MIL-L-7808 engine oil in various oxygen-nitrogen atmospheres. (13 in^3 spherical Pyrex vessel)

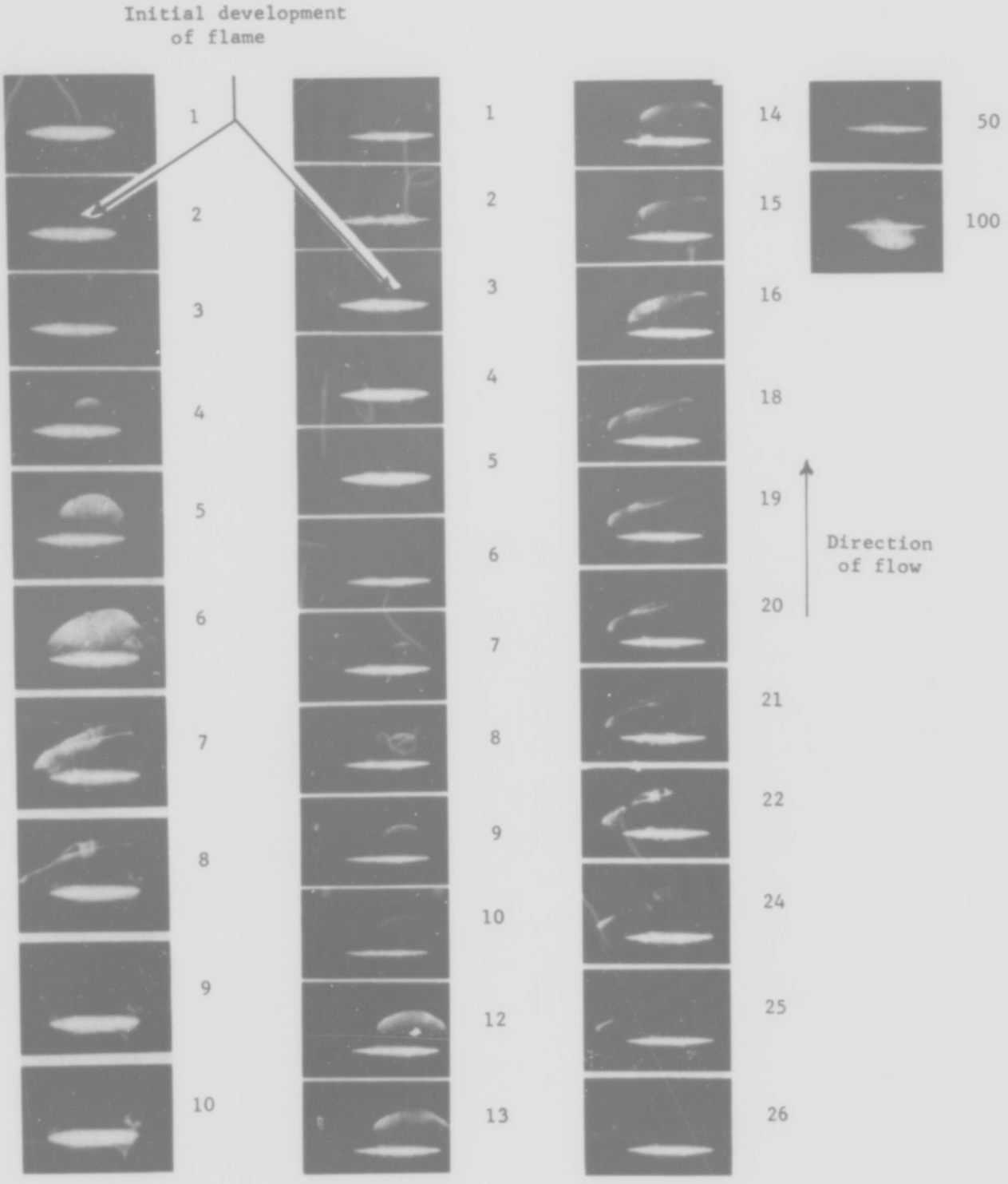


Figure 7. - Motion picture records from 2 experiments showing the ignition of octane vapor-air mixtures with a heated Nichrome wire (2 inches long and 0.102-inch diameter) at 1900° F.
Mixture flow rate - 17.8 in^3/min (N.T.P.)
Fuel air-weight ratio - 0.42 Scale: 1 inch = 3.1 inches

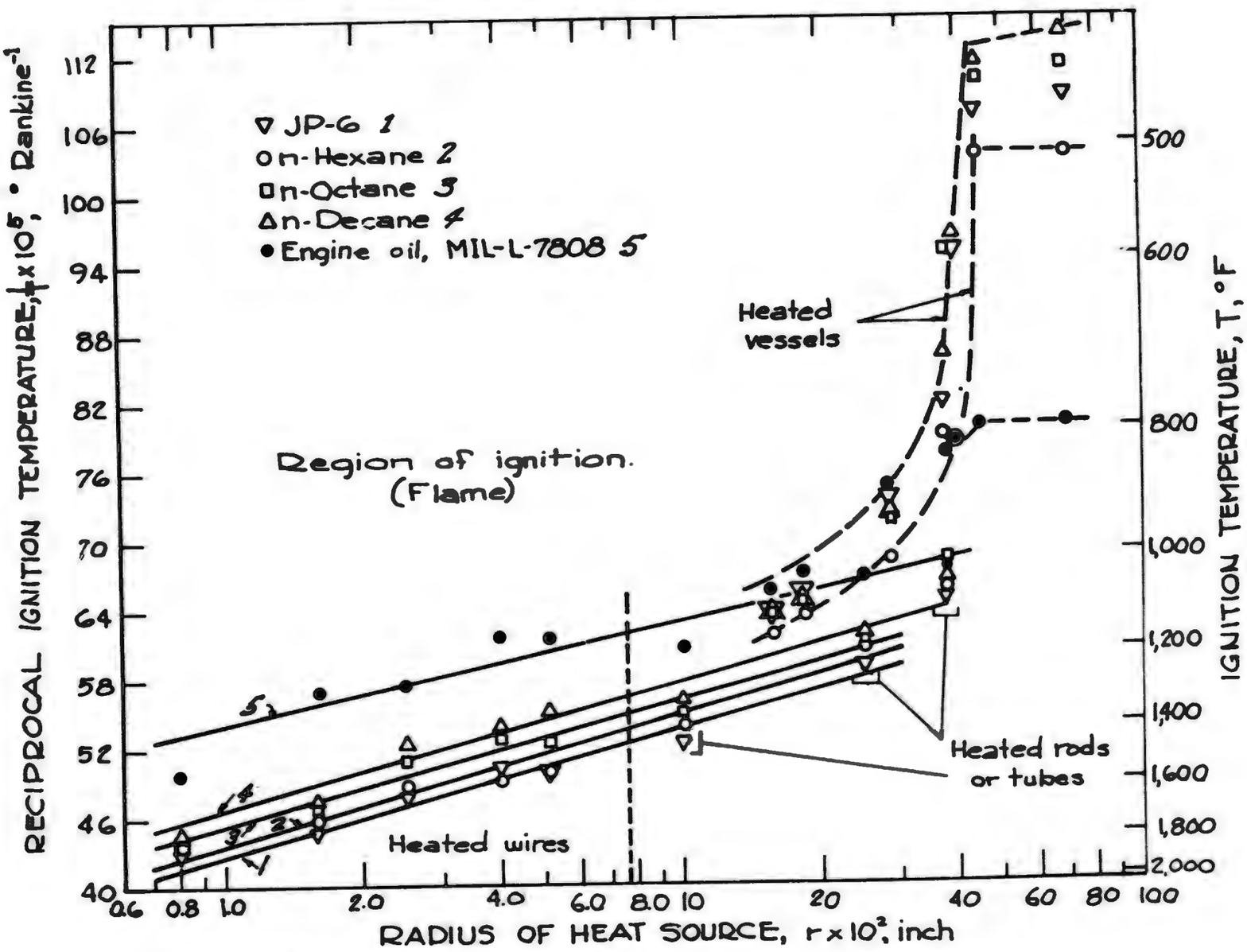


Figure 8. - Reciprocal hot surface ignition temperature as a function of the radius of the heat source for various hydrocarbon fuels and an engine oil in air.

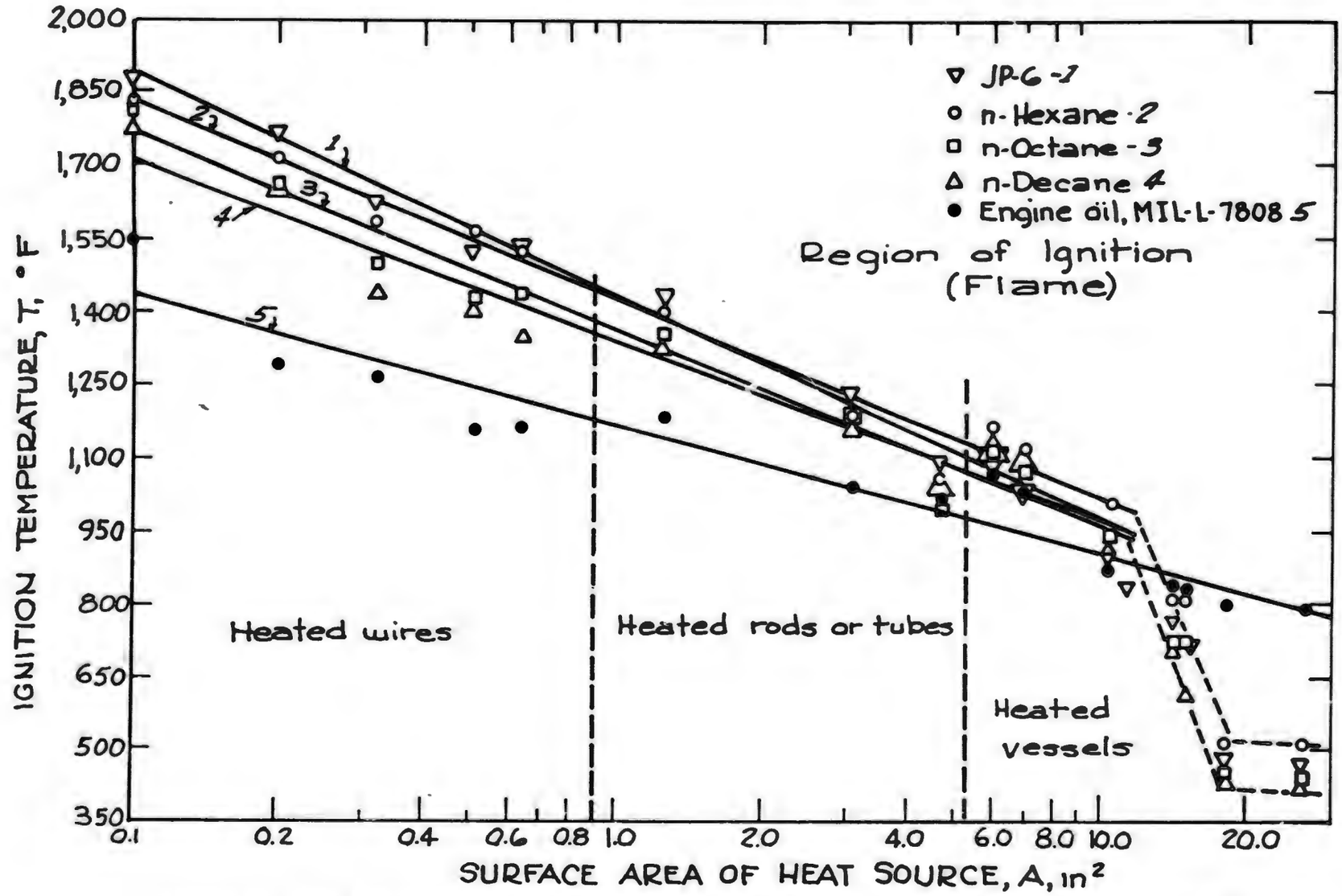


Figure 9. - Hot surface ignition temperature as a function of the surface area of the heat source for various hydrocarbon fuels and an engine oil in air.

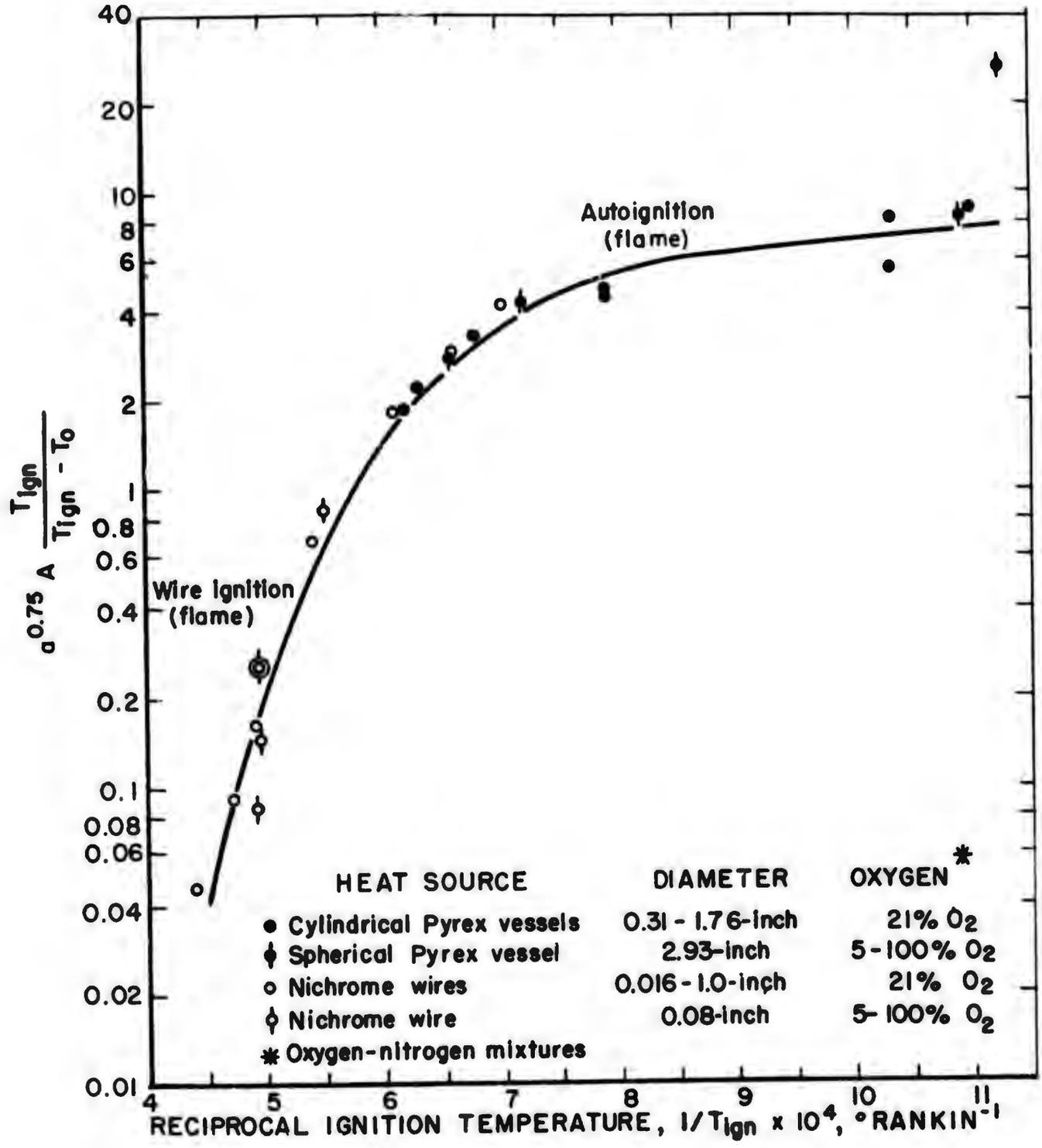


Figure 10. - Correlation of ignition temperatures (T_{ign}) of n-hexane with surface area (A) of the heat source for varying oxygen concentration (a) and initial mixture temperatures (T_o).

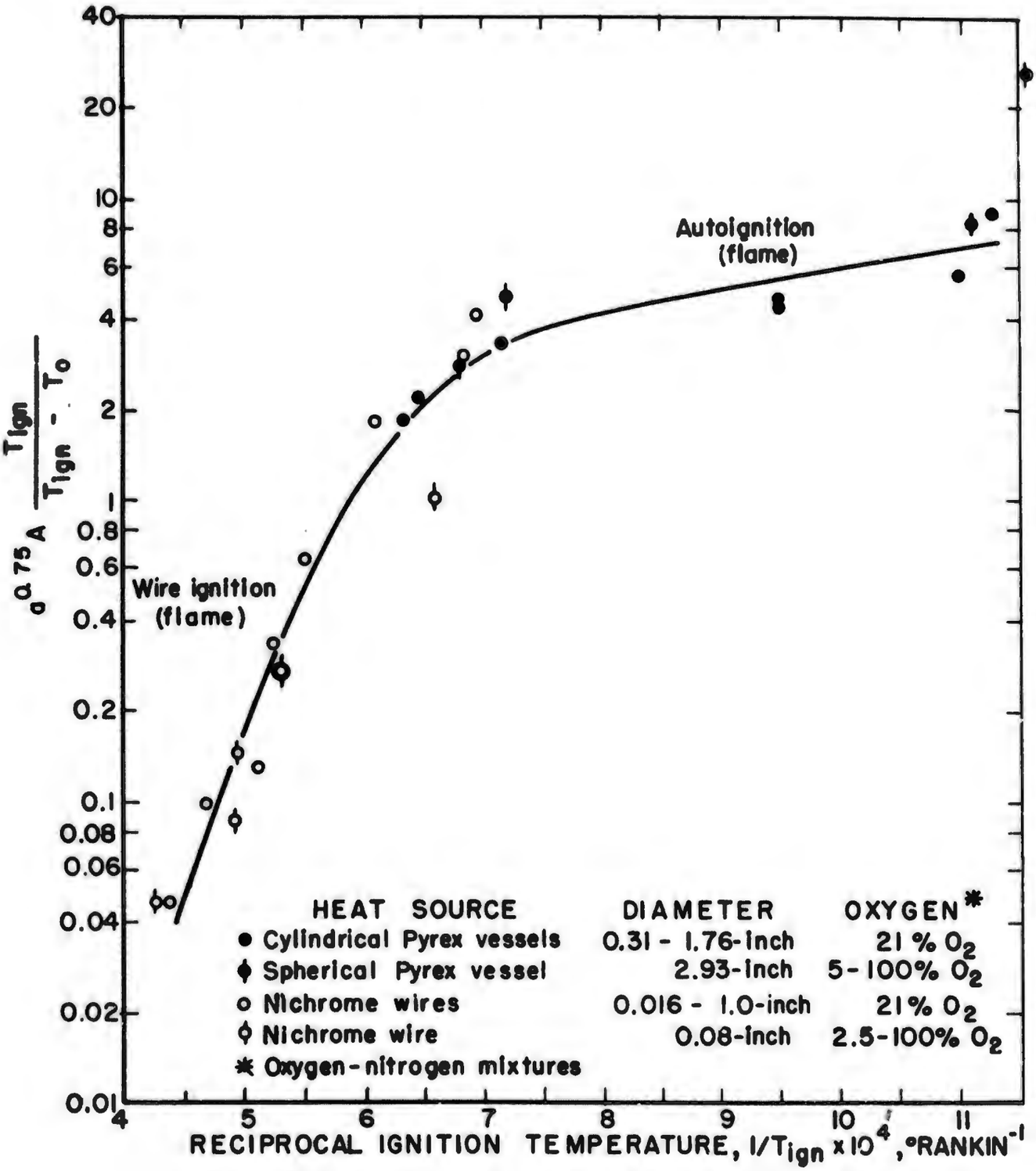


Figure 11. - Correlation of ignition temperature (T_{ign}) of n-octane with surface area (A) of the heat source for varying oxygen concentration (a) and initial mixture temperature (T_o).

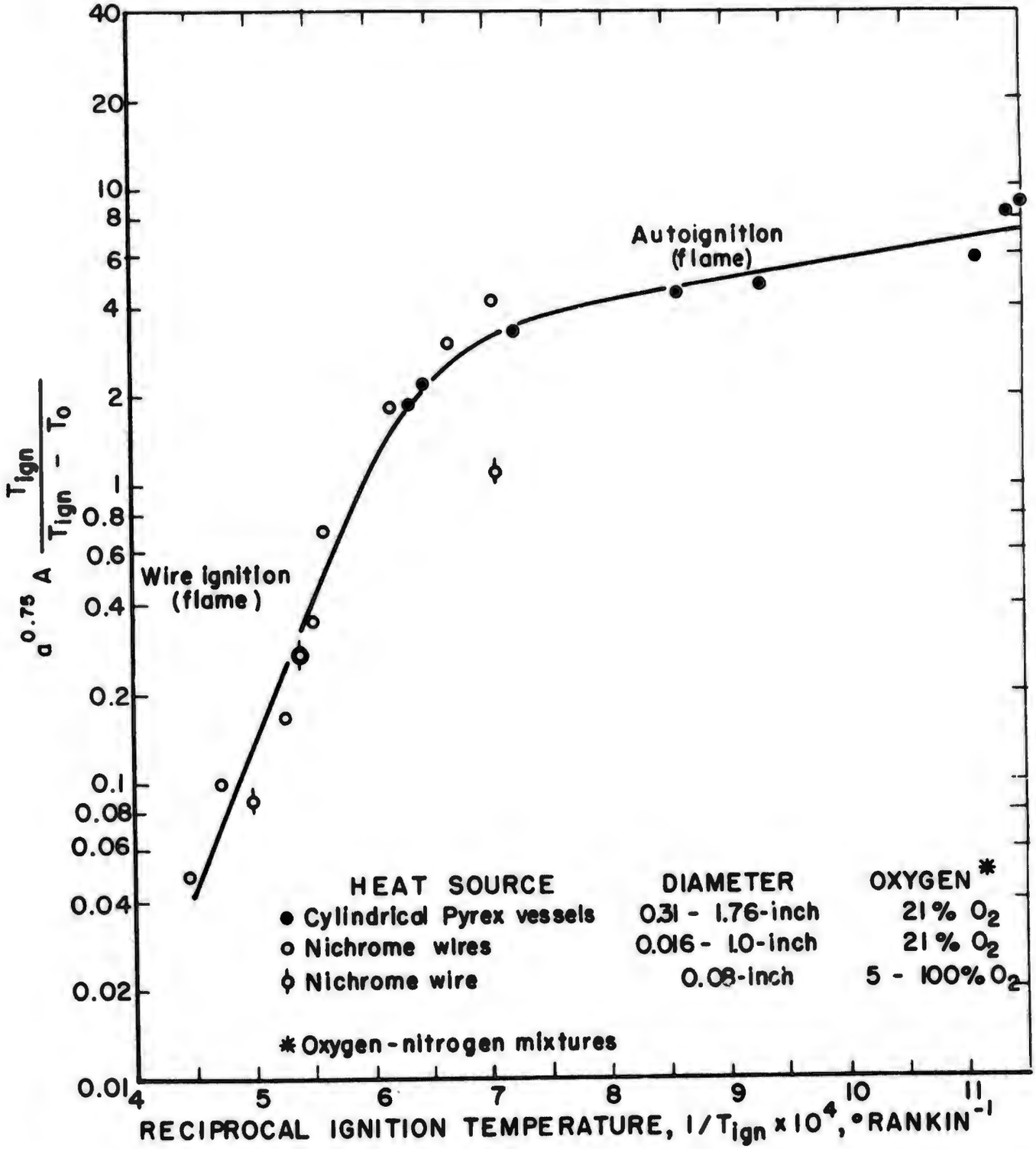


Figure 12. - Correlation of ignition temperature (T_{ign}) of n-decane with surface area (A) of the heat source for varying oxygen concentration (a) and initial mixture temperature (T_o).

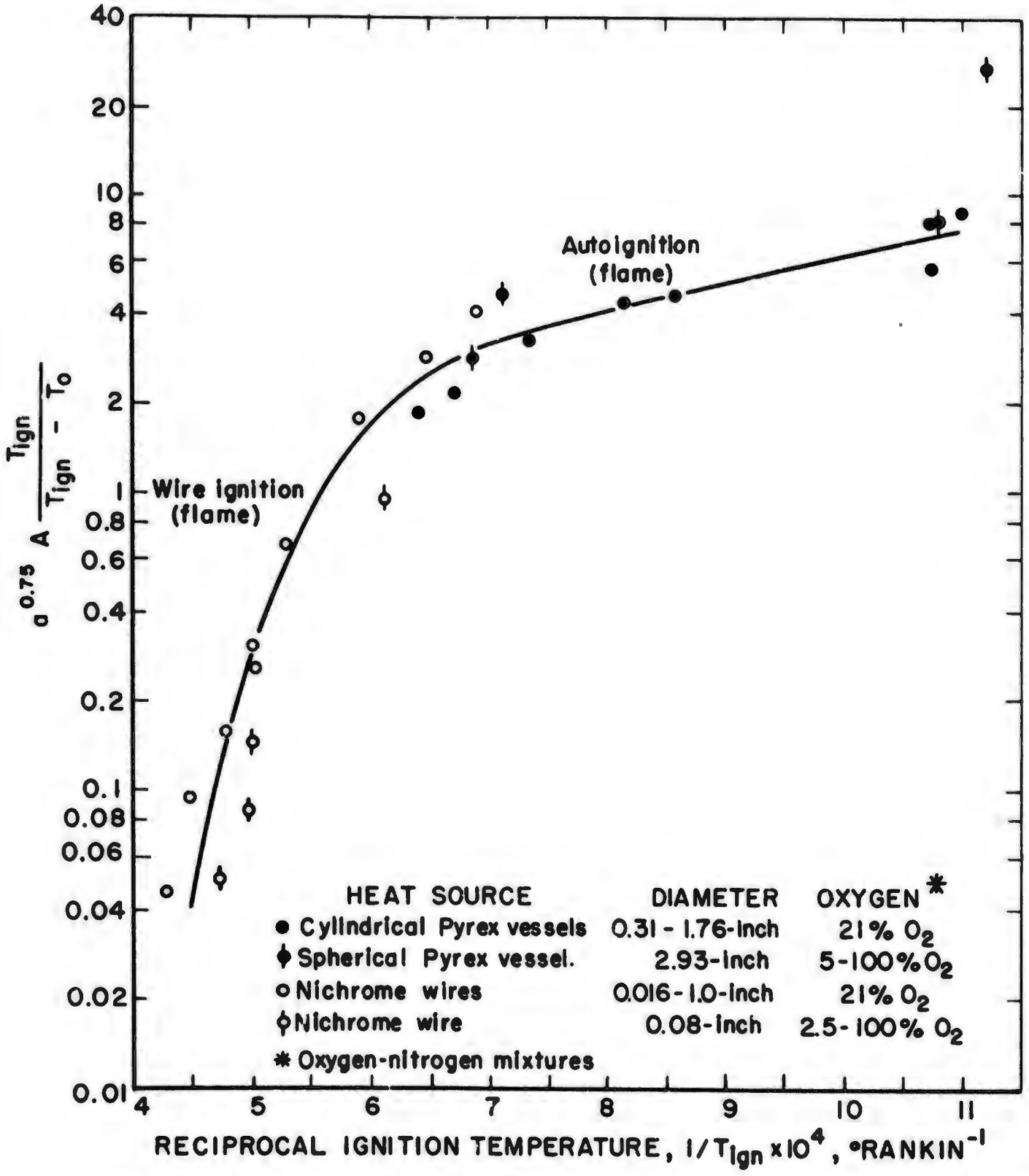


Figure 13. - Correlation of ignition temperature (T_{ign}) of JP-6 fuel with surface area (A) of the heat source for varying oxygen concentration (a) and initial mixture temperatures (T_o).

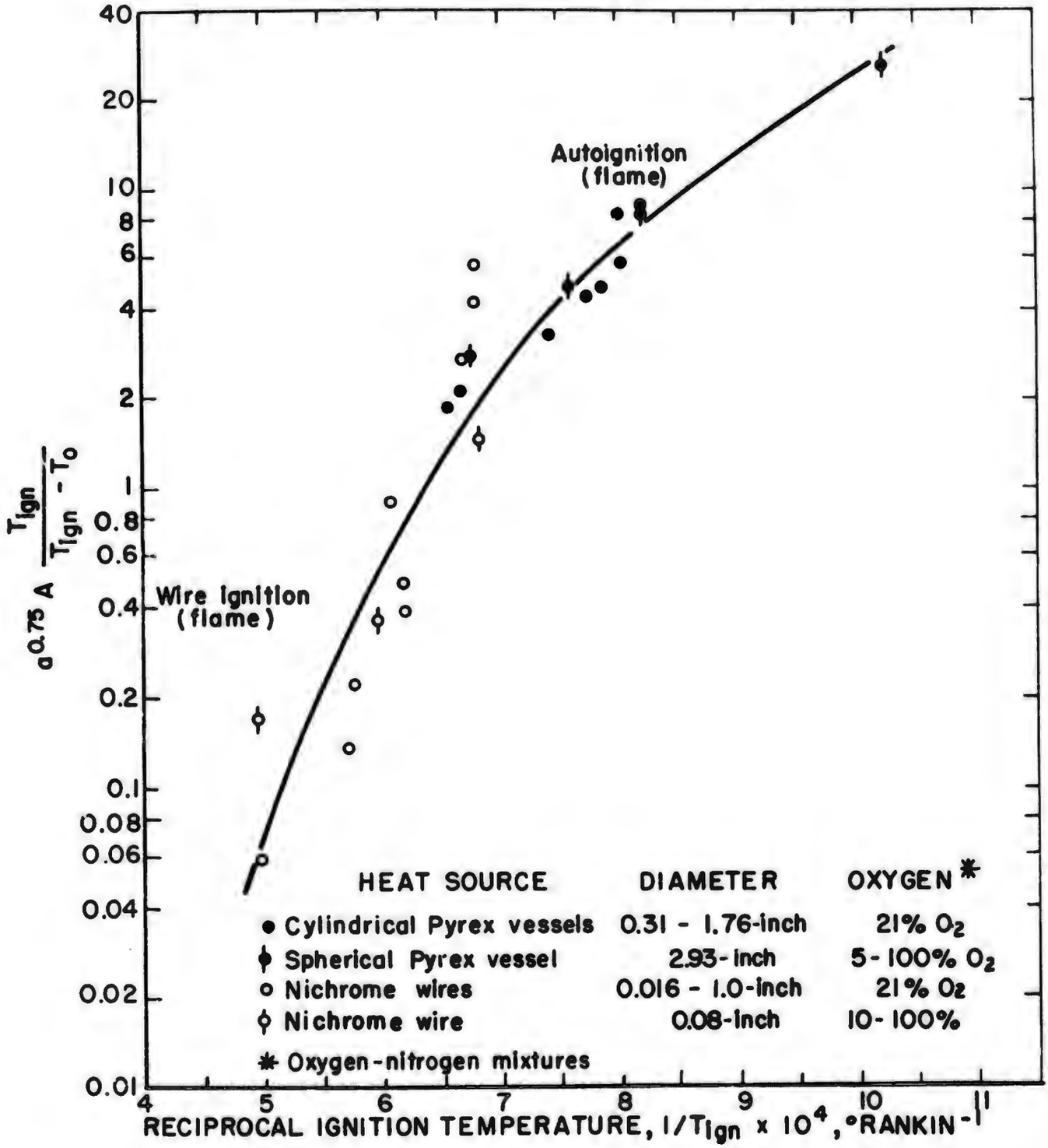


Figure 14. - Correlation of ignition temperature (T_{ign}) of MIL-L-7808 engine oil with surface area (A) of the heat source for varying oxygen concentration (a) and initial mixture temperatures (T_o).

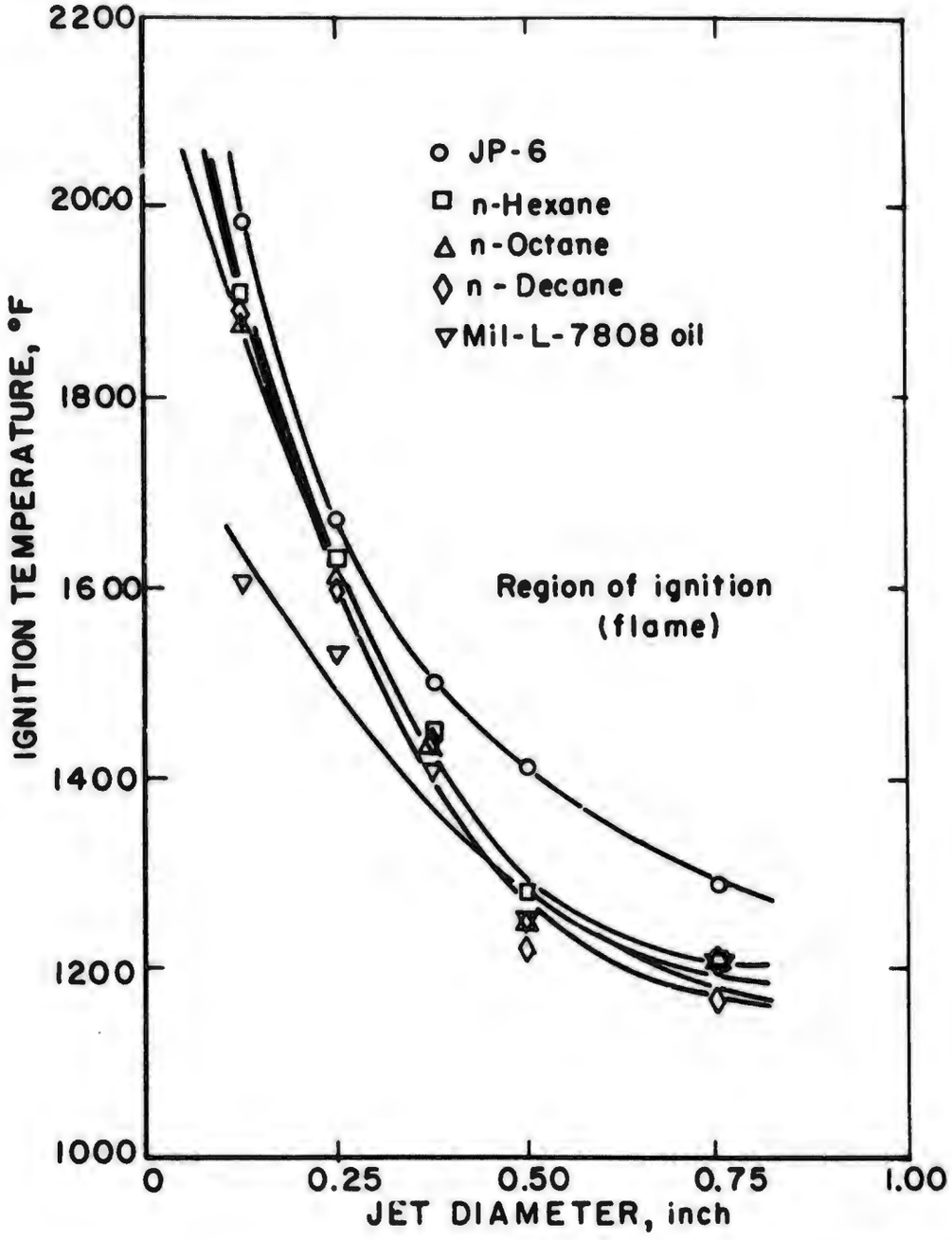


Figure 15. - Effect of jet diameter on the minimum hot gas ignition temperature of various hydrocarbon fuels and an engine oil in air.
(Jet flow rate - 185 in^3/min)

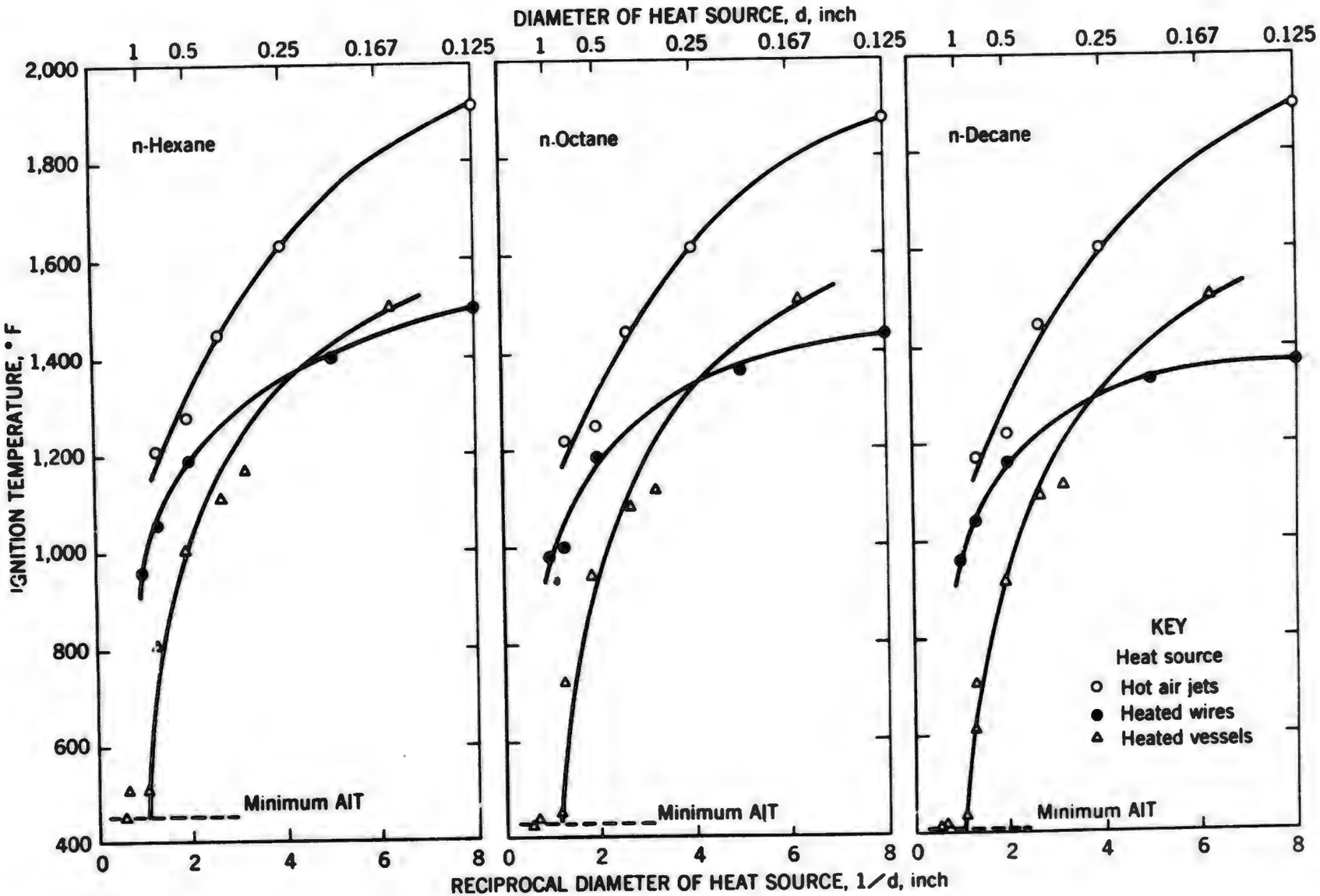


Figure 16. - Variation of hot gas and hot surface ignition temperature with reciprocal diameter of heat source for n-hexane, n-octane, and n-decane vapor-air mixtures.

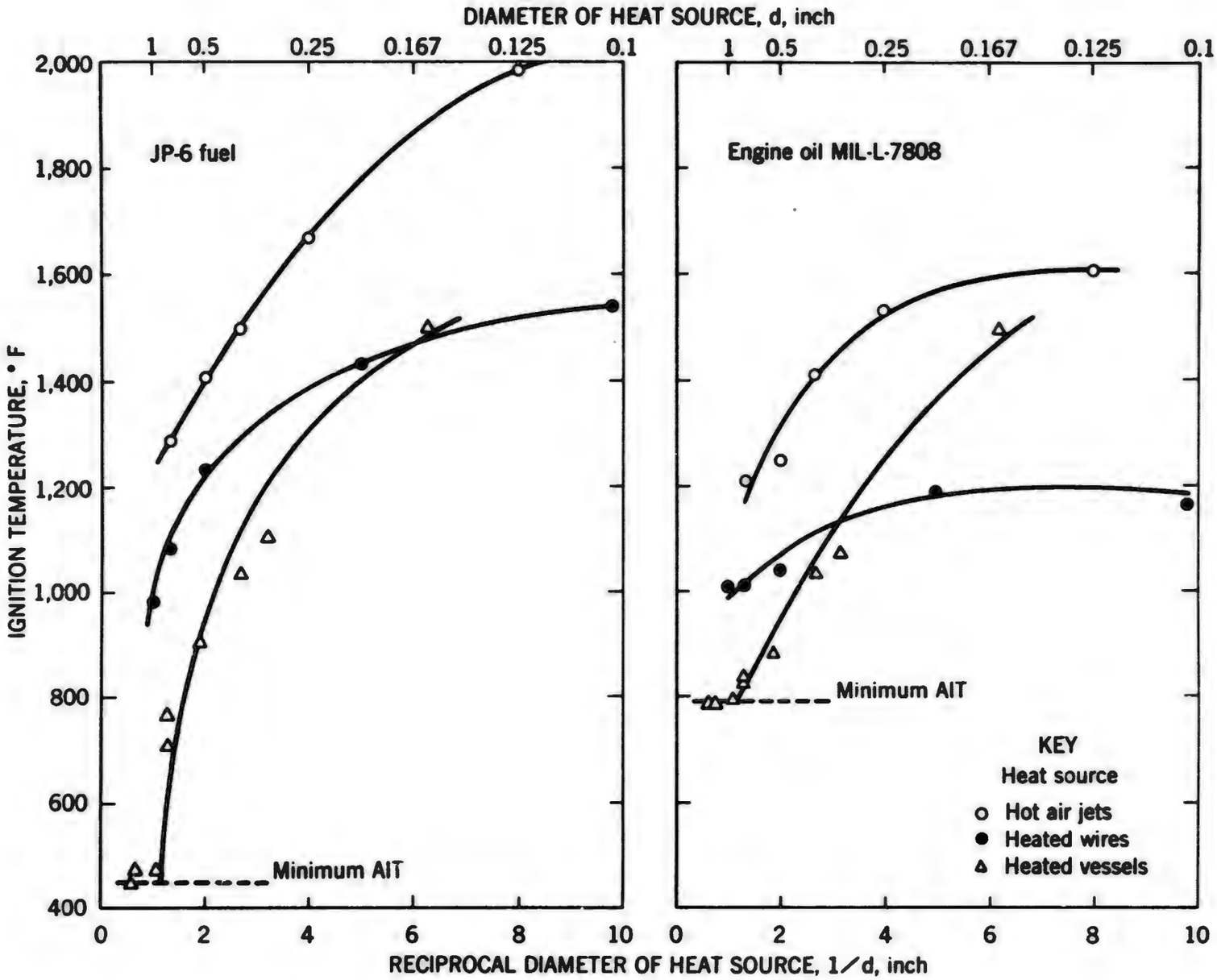
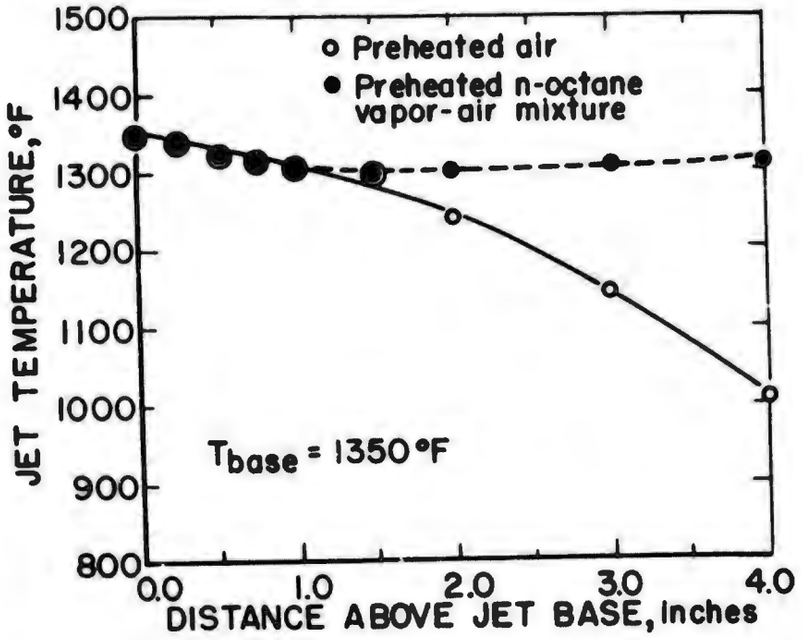


Figure 17. - Variation of hot gas and hot surface ignition temperature with reciprocal diameter of heat source for JP-6 and MIL-L-7808 engine oil vapor-air mixtures.



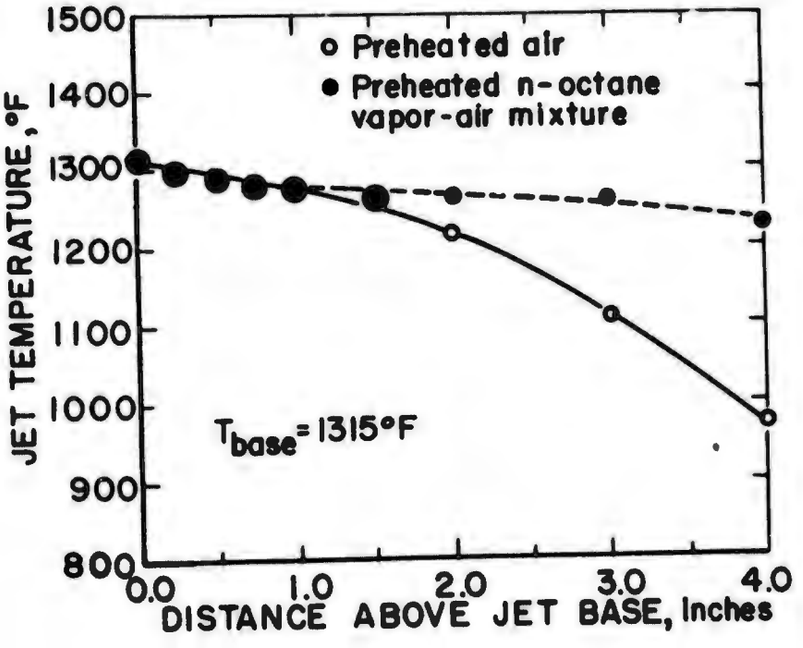


Figure 18. - Axial temperature profiles for 1/2-inch diameter jets of hot air flowing at 365 in^3/min, (N.T.P.) into preheated air and n-octane vapor-air mixtures at 350°F. Fuel-Air Weight Ratio - 0.25

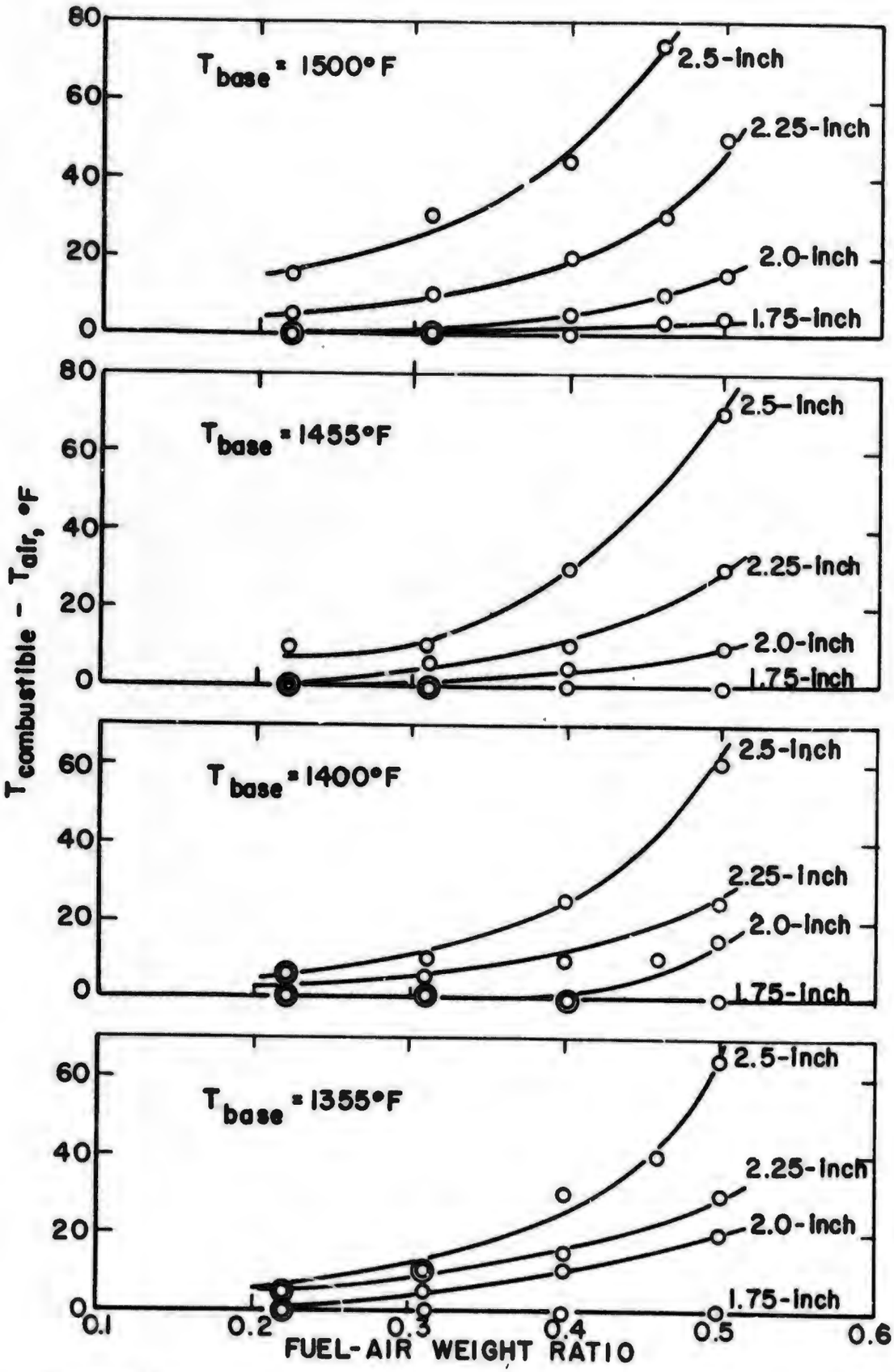


Figure 19. - Axial temperature change at various heights above jet base for 1/2-inch diameter jets of hot air flowing at 365 in^3/min, (N.T.P.) into n-hexane vapor-air mixtures at 350°F.

$T_{combustible}$-Temperature with combustible vapor-air mixture.

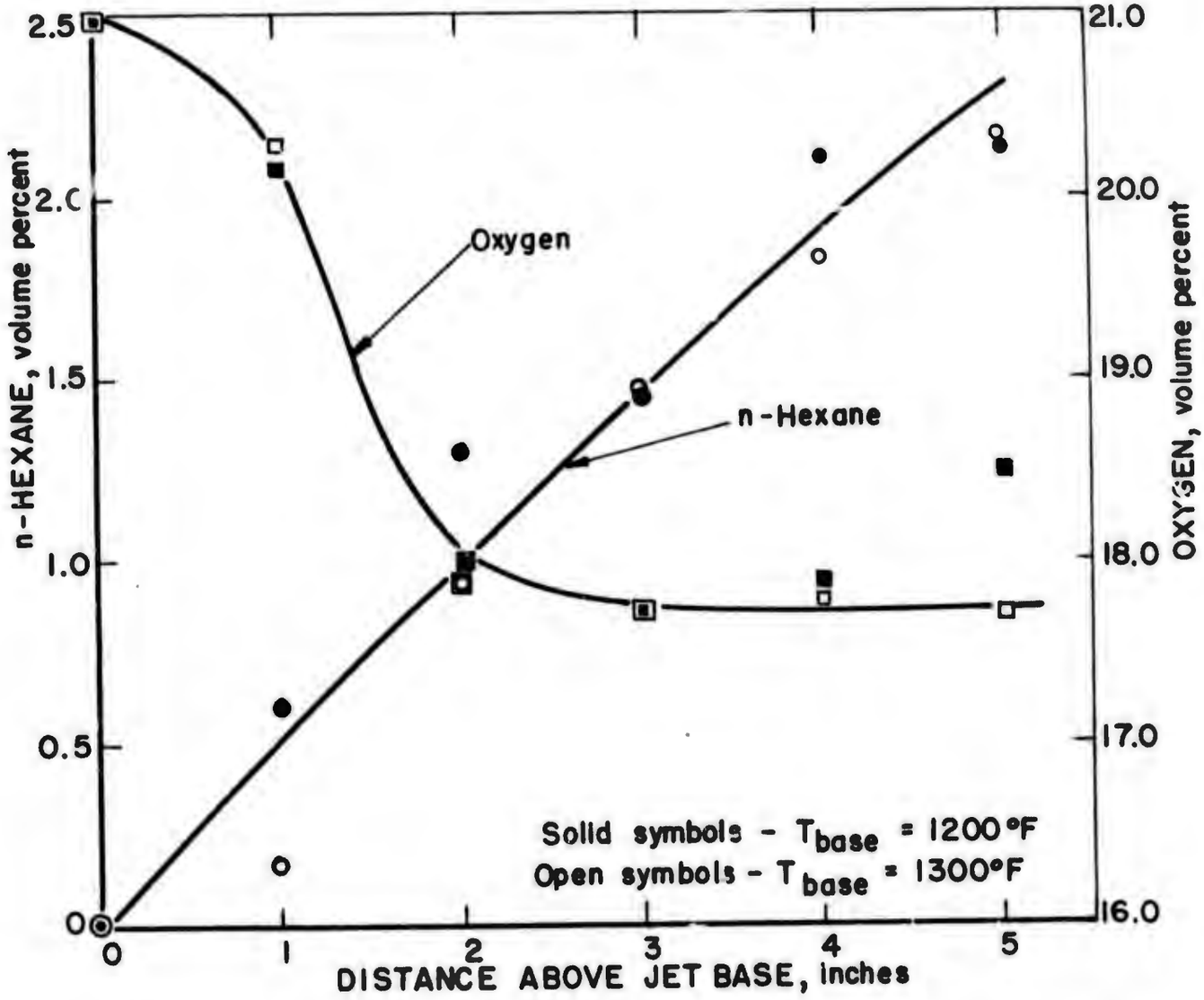


Figure 20. - Axial concentration profiles of oxygen and n-hexane for 1/2-inch diameter jets of hot air flowing at 365 in^3/min into n-hexane vapor-air mixtures at 350°F.
Fuel-air weight ratio - 0.5

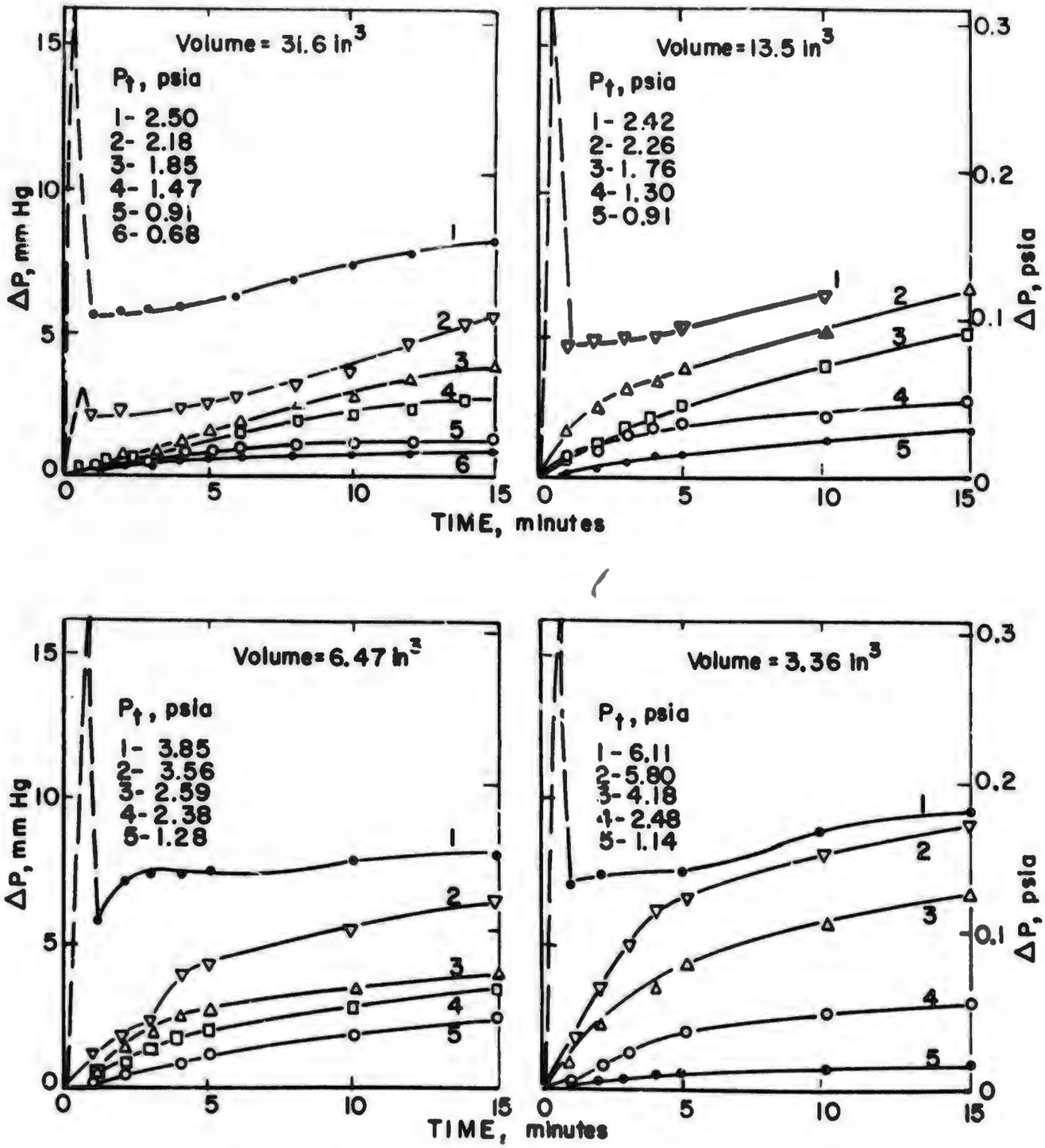


Figure 21. - Effect of vessel size on pressure rise vs time in oxidation of 5 percent n-octane vapor-air mixtures at 482°F and various initial pressures.

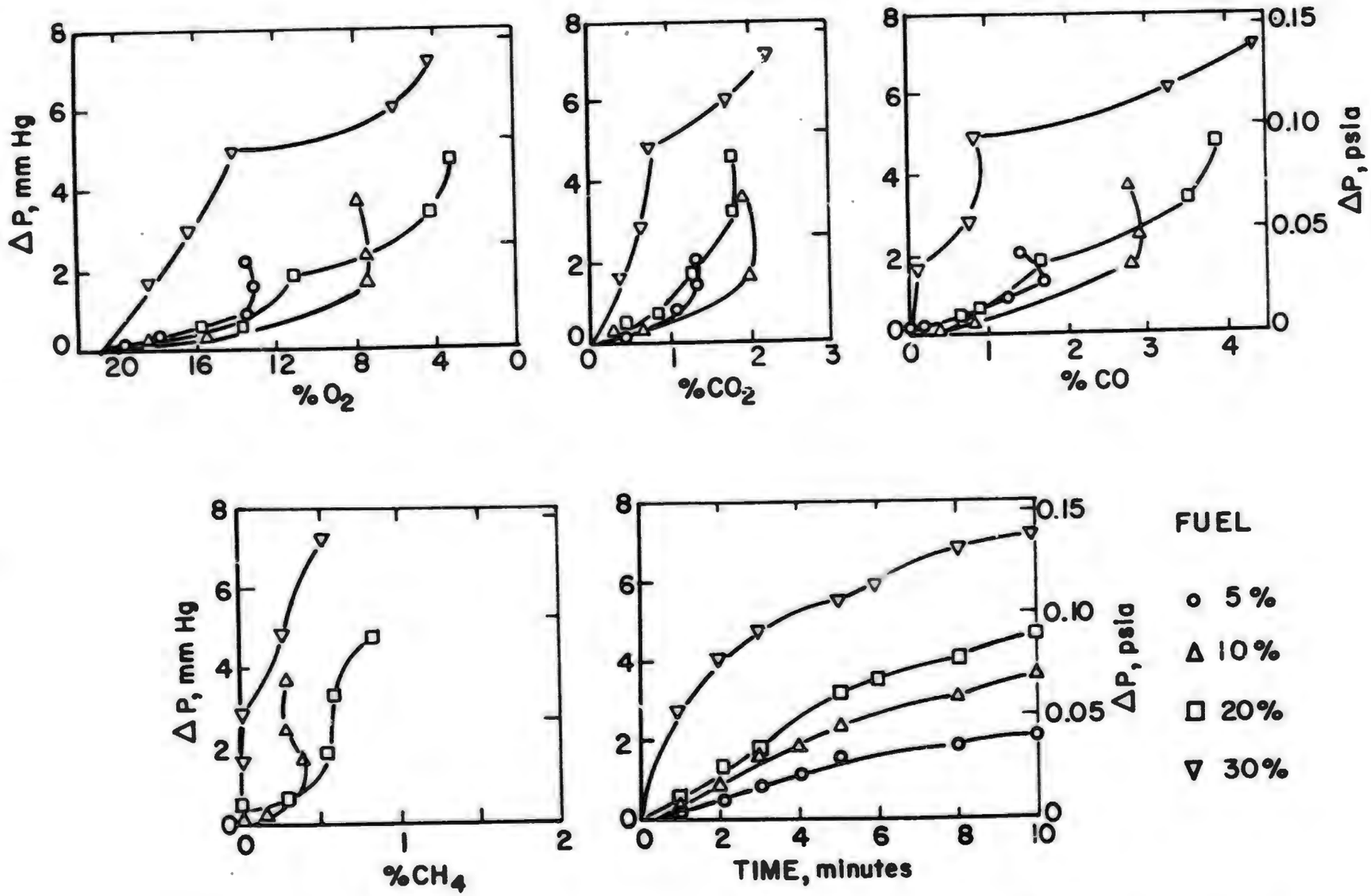


Figure 22. - Comparison of pressure rise data with the depletion of oxygen and formation of gaseous products for 5, 10, 20, and 30 percent n-octane vapor-air mixtures at 482°F and 1.16 psia initial pressure.

31.6 in^3 Spherical Pyrex Vessel

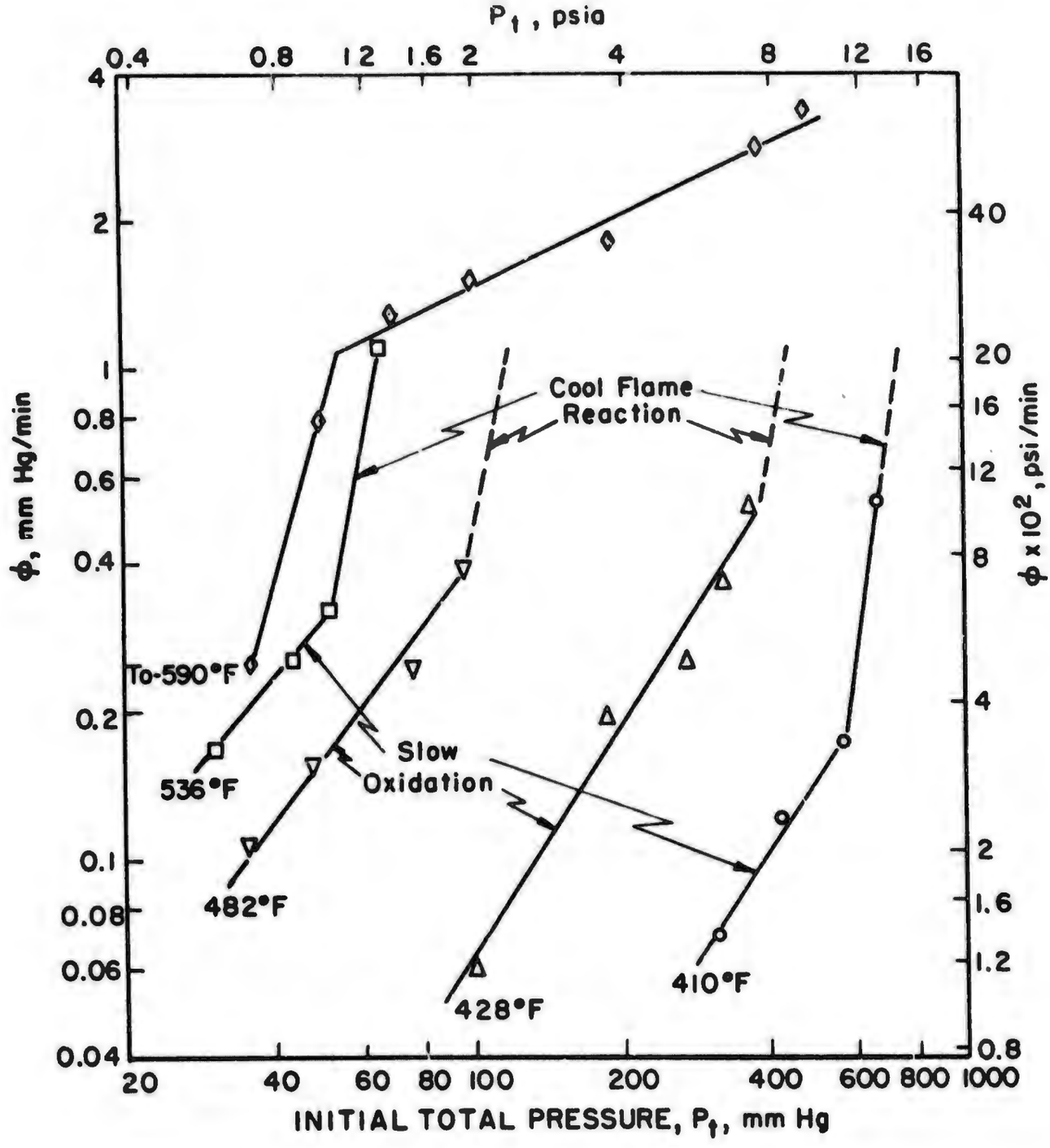


Figure 23. Rate of pressure rise vs initial total pressure in oxidation of 5 percent n-octane vapor-air mixtures at various temperatures.
(31.6 in^3 Spherical Pyrex vessel)

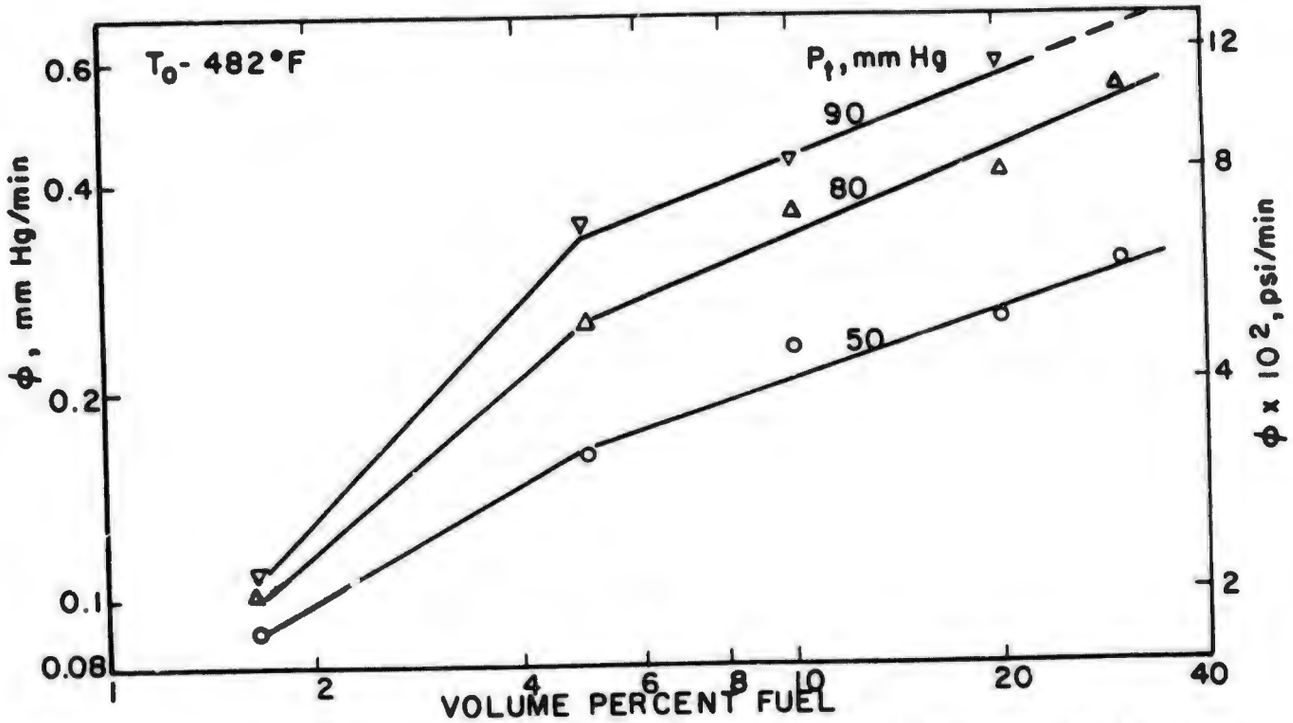


Figure 24. - Rate of pressure rise vs percent fuel in oxidation of n-octane vapor-air mixtures at 482°F and at various initial total pressures.

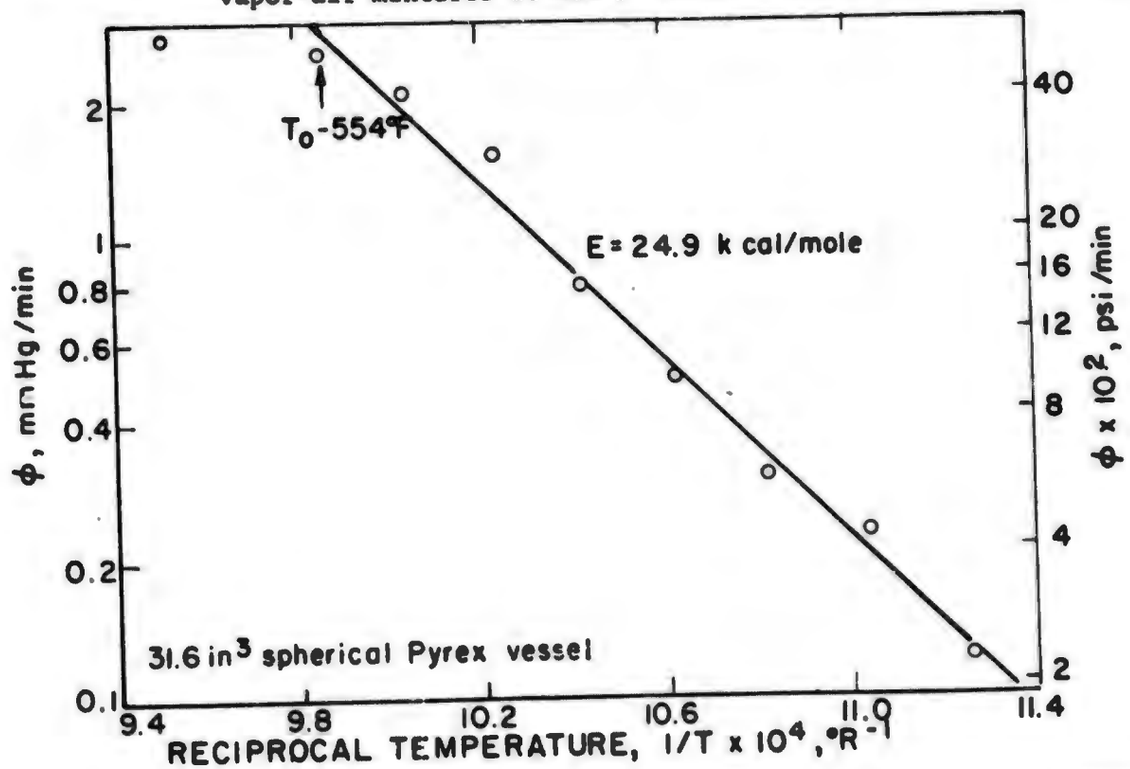


Figure 25 - Arrhenius plot of rate of pressure rise and reciprocal temperature for oxidation of 5 percent n-octane vapor-air mixtures at a total pressure of 60 mm Hg (1.16 psia).
(31.6 in^3 Spherical Pyrex vessel)

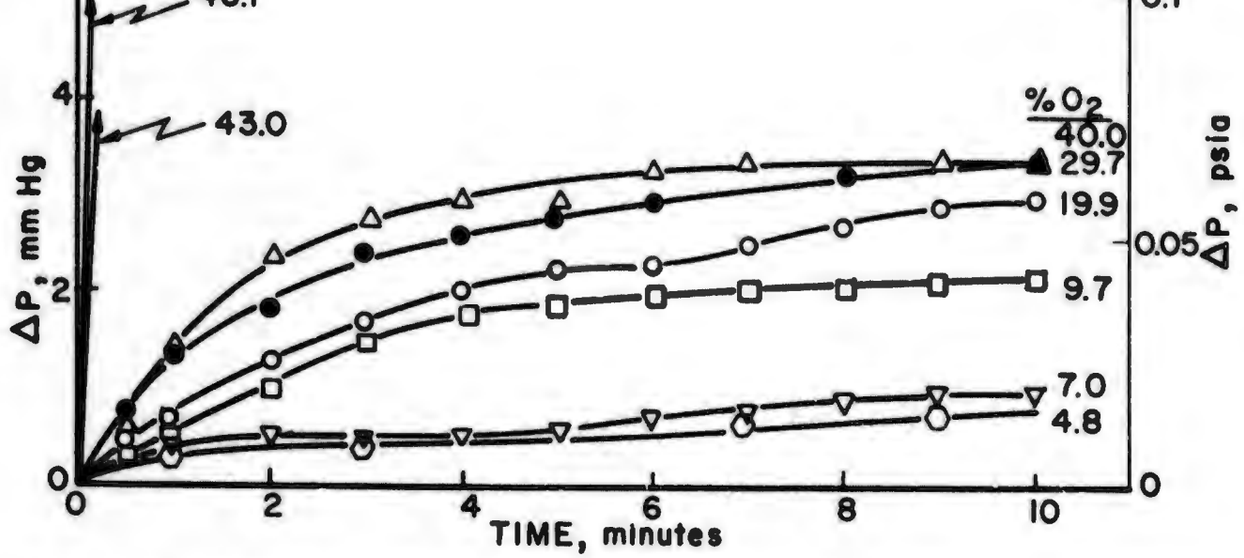


Figure 26.- Pressure rise vs time in oxidation of 5 percent n-octane vapor-oxygen-nitrogen mixtures at various oxygen concentrations; total initial pressure of 60 mm Hg (1.16 psia) and temperature of 482°F.

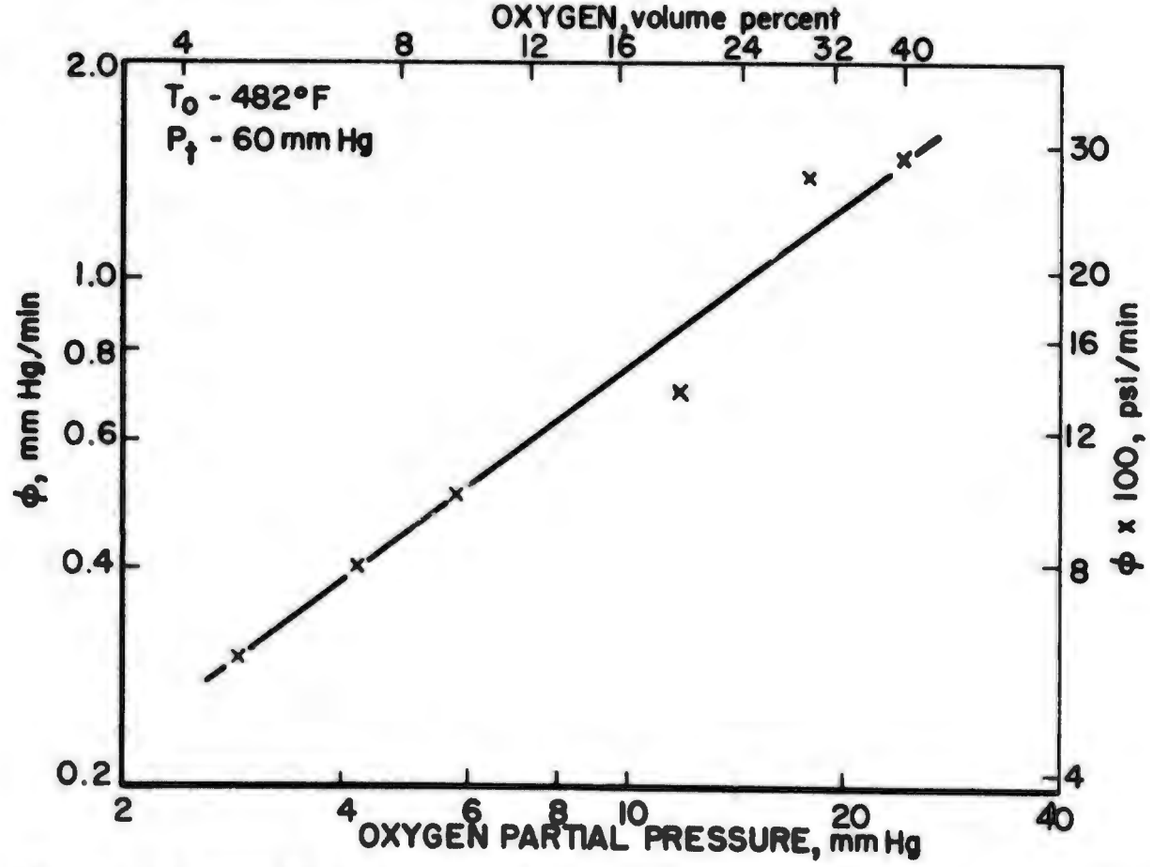


Figure 27.- Rate of pressure rise vs oxygen partial pressure in oxidation of 5 percent n-octane vapor-oxygen-nitrogen mixtures at various oxygen concentrations; total initial pressure of 60 mm Hg (1.16 psia) and temperature of 482°F. (31.6 in^3 Spherical Pyrex vessel)

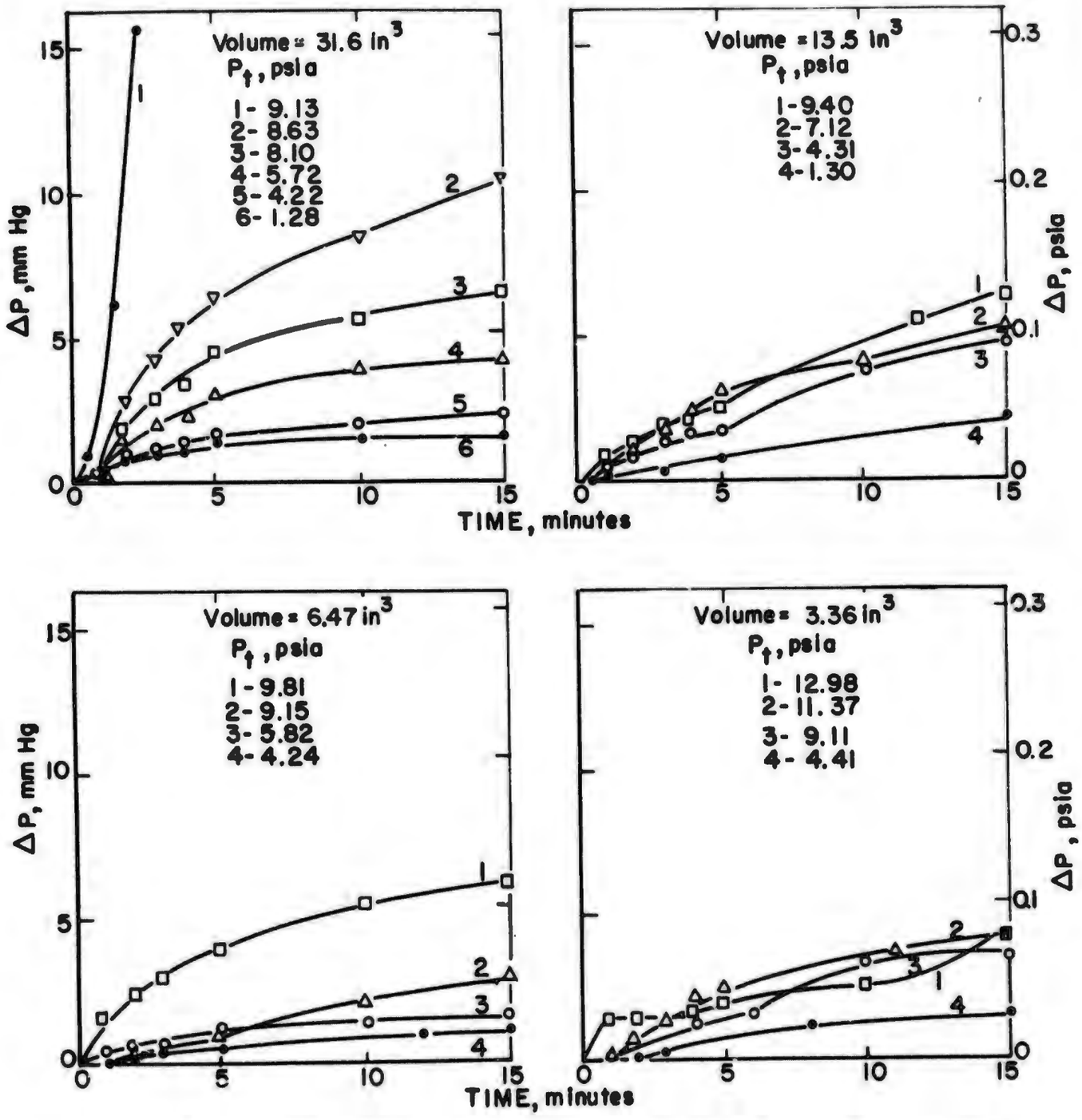


Figure 28. - Effect of vessel size on pressure rise vs time in oxidation of 5 percent JP-6 vapor-air mixtures at 482°F and various initial pressures.

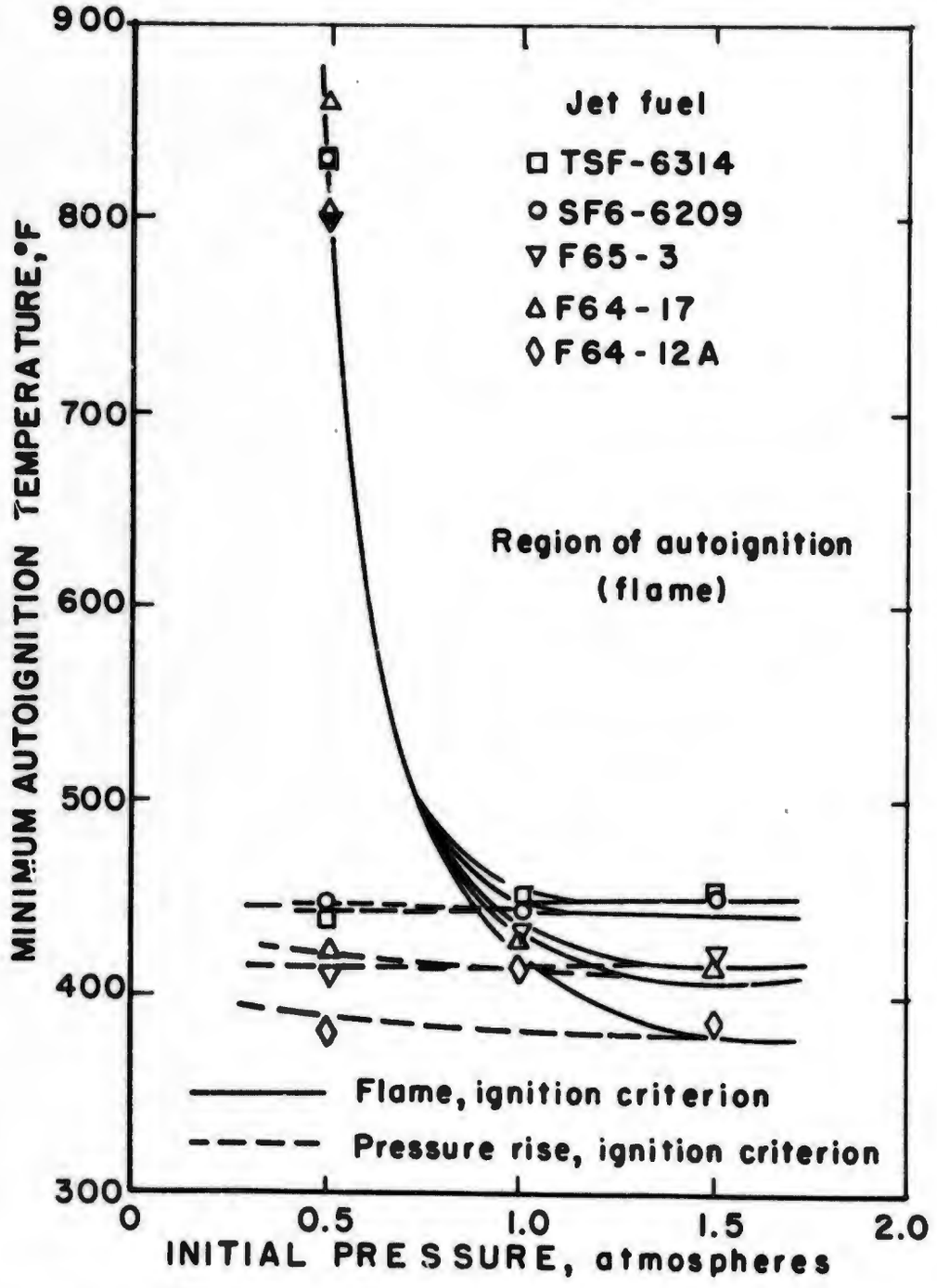


Figure 29.- Effect of initial pressure on the autoignition temperature of five aircraft jet fuels in quiescent air.

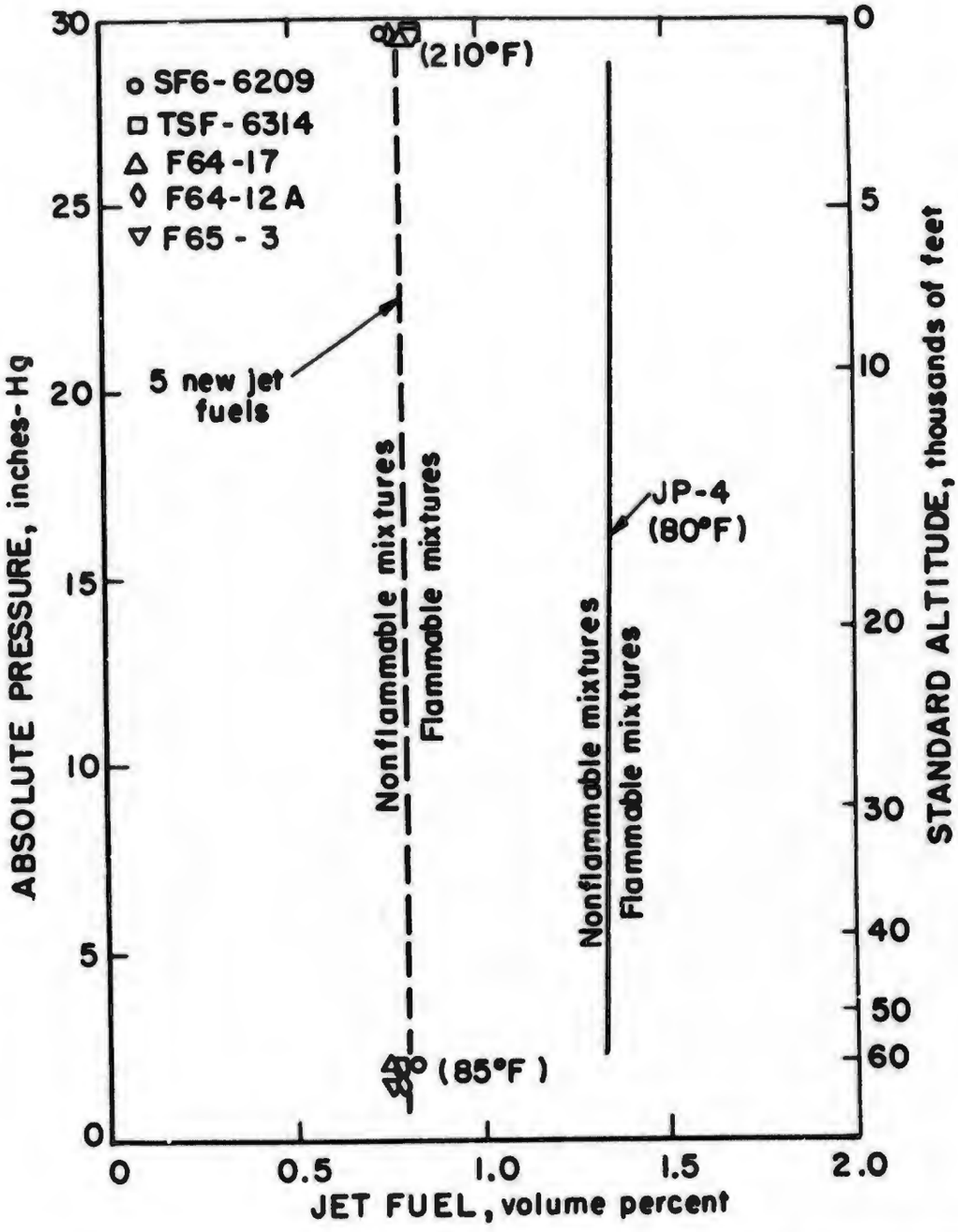


Figure 30.- Lower limits of flammability of six hydrocarbon jet fuels in air at various initial pressures.

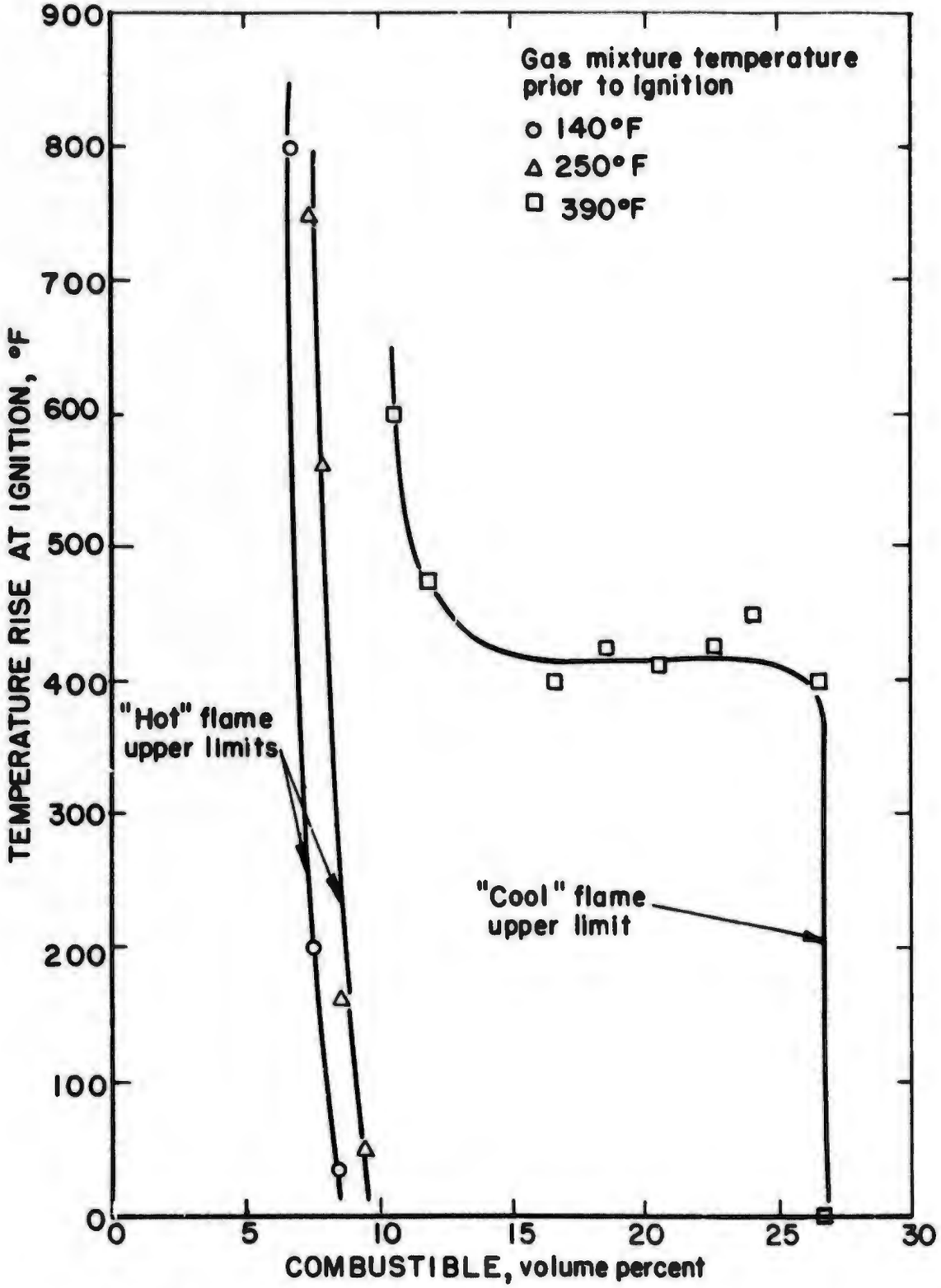


Figure 31.- Temperature rise associated with the flammability of n-hexane vapor-air mixtures at initial mixture temperatures between 140 and 390°F and at atmospheric pressure.
(2-inch diameter flammability tube)

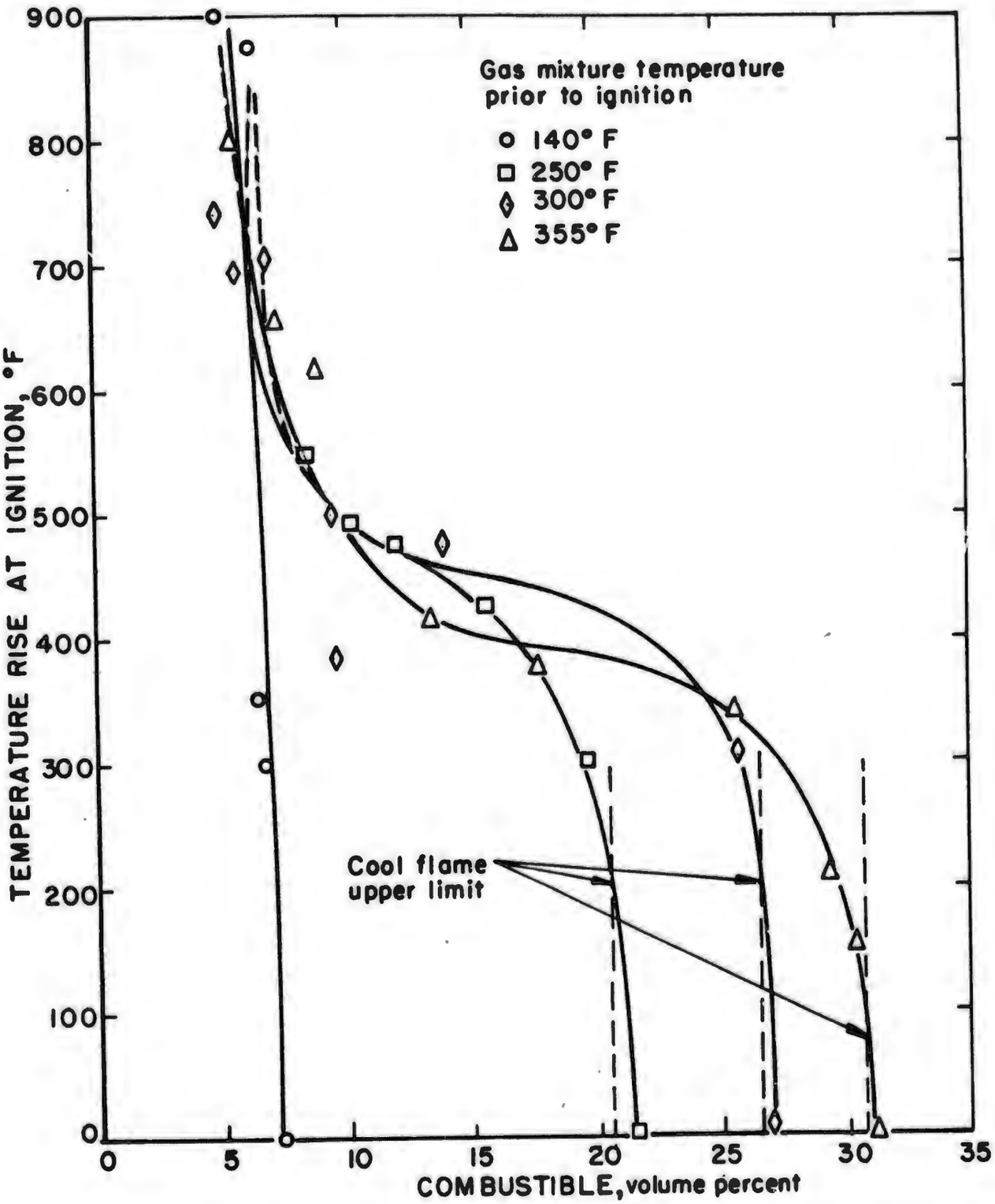


Figure 32.- Temperature rise associated with the flammability of various n-octane vapor-air mixtures at initial mixture temperatures between 140° and 355°F and at atmospheric pressure. (2-inch diameter flammability tube)

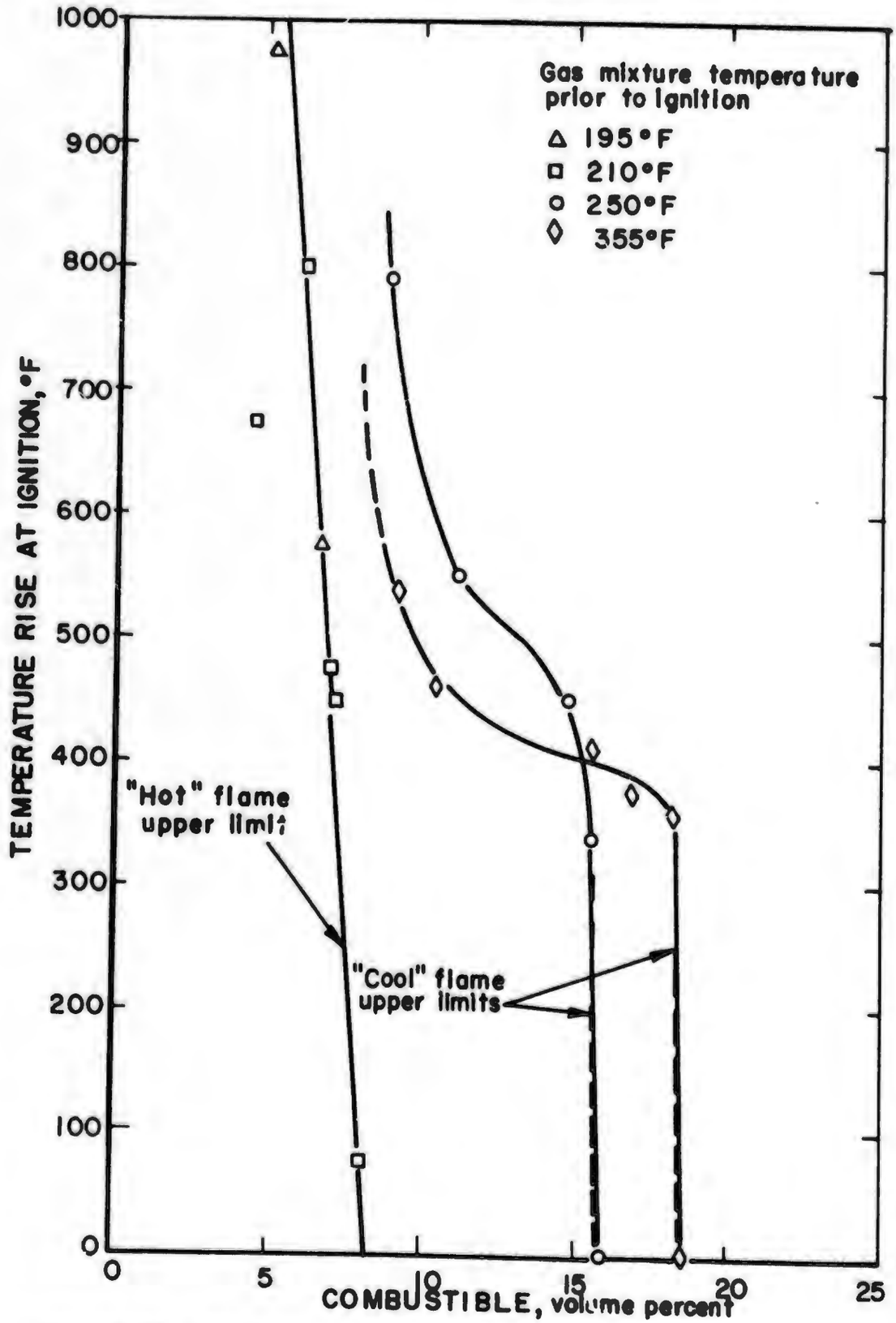


Figure 33.- Temperature rise associated with the flammability of n-decane vapor-air mixtures at initial mixture temperatures between 195 and 355°F and at atmospheric pressure.
(2-inch diameter flammability tube)

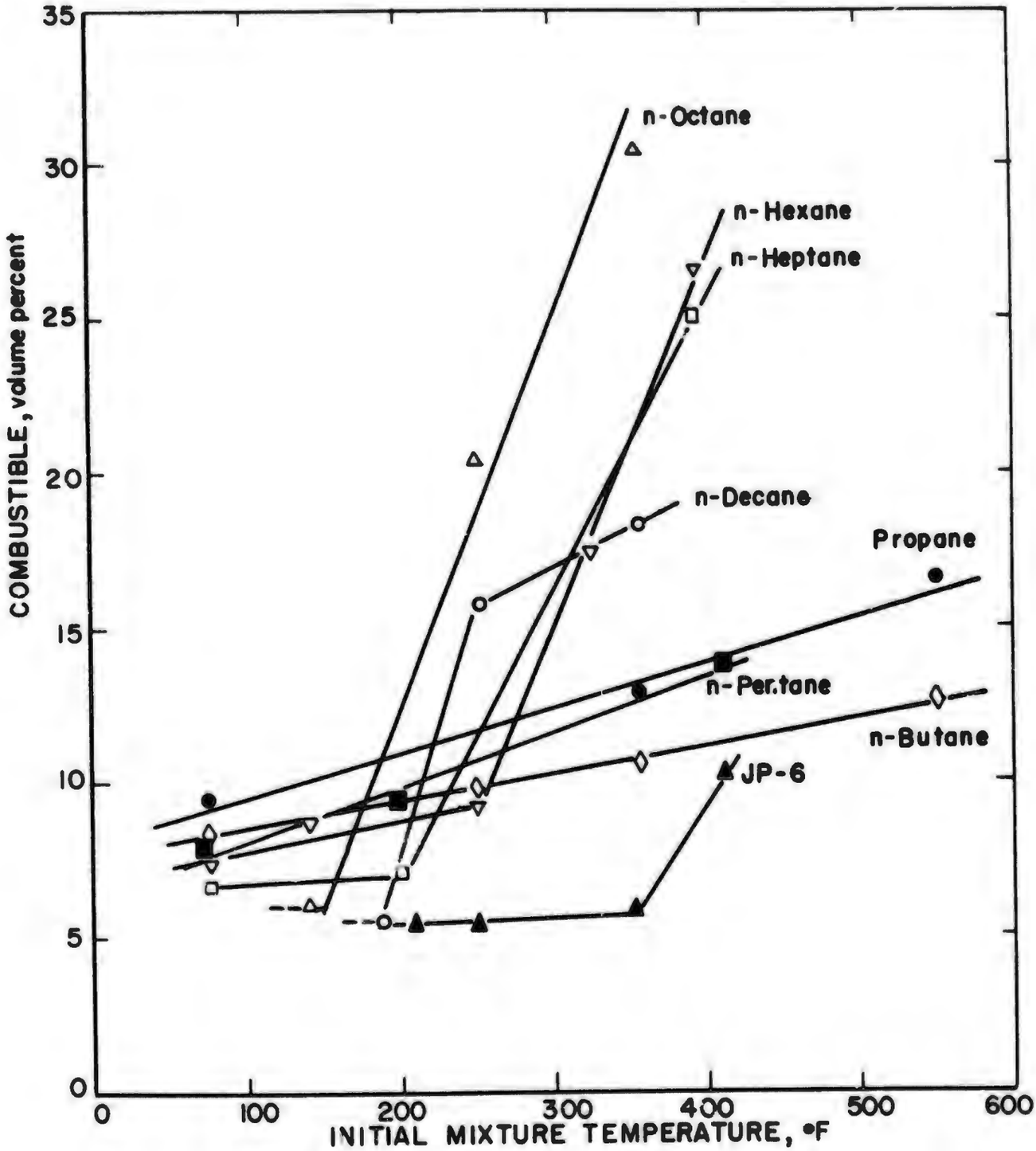


Figure 34. - Effect of initial mixture temperature on the upper limits of flammability of various hydrocarbon fuel vapor-air mixtures at atmospheric pressure. (2-inch diameter flammability tube)

APPENDIX I

The I-8 Spontaneous Ignition Temperature Apparatus

The I-8 apparatus (Figure 35) is a modified ASTM spontaneous ignition temperature unit (Ref 9). It consists of a crucible furnace with heater f wound on an alundum cylinder p. As the operating temperatures at the top and bottom of the crucible well are below the temperature at the mid-section, a neck heater e and base heater q were added to the furnace. A transite ring n keeps the reaction flask a in place and supports the ceramic insulators m. The temperatures at the neck, mid-section, and base are measured by means of iron-constantan thermocouples b, c, and d, respectively. These temperatures are recorded on three channels of a 12-channel electronic temperature recorder. The temperatures of the three heaters are varied by means of three autotransformers connected to the heaters.

In making a determination at atmospheric pressure, flask a is initially flushed with the oxidant to be used and the three autotransformers are adjusted to bring the vessel to the desired temperature. A measured amount of the sample is then injected into the flask with a hypodermic syringe. An electric timer is switched on when the sample is injected and stopped at the first appearance of flame in the flask. The inside of the flask is observed by means of a mirror placed at an appropriate angle above the flask. It is often necessary to darken the room in order to see the flames which are rather light blue in color. If no flame appears within 5 minutes, the experiment is then repeated at higher temperatures and/or at various volumes of combustible until the minimum spontaneous ignition temperature is found.

For determinations at reduced pressures, a modified flask is used which is equipped with a neck extension having a 3-way stopcock. Evacuation and addition of gases is made through the stopcock. The addition of fuel is made through a side port equipped with a rubber septum. Otherwise, the procedure is the same as described above.

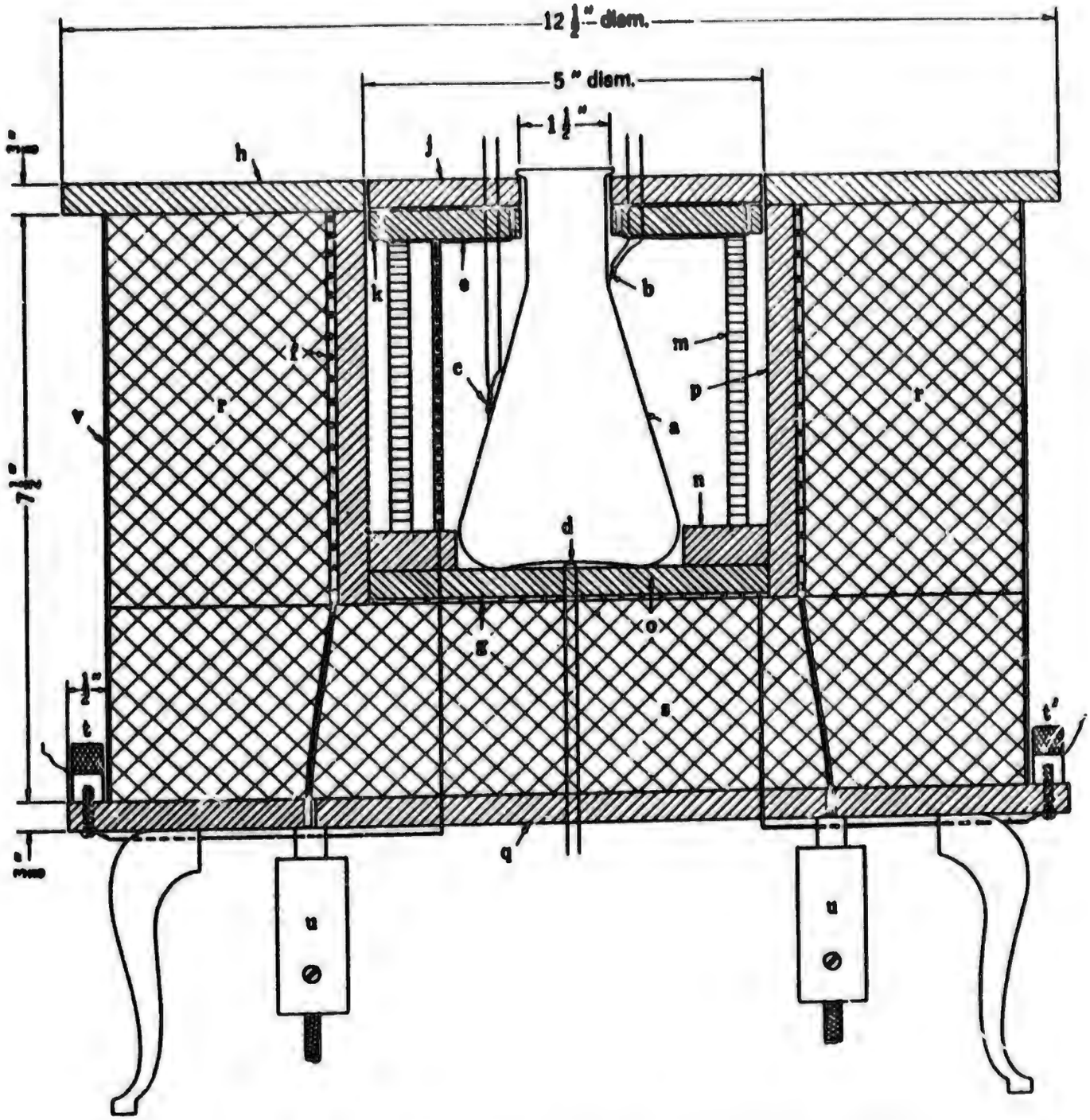


Figure 35. - Detailed drawing of I-8 ignition-temperature apparatus.

APPENDIX II

Wire Ignition Temperature Apparatus

The wire ignition temperature apparatus is shown in Figure 36. This apparatus is equipped with liquid fuel- and air-feed assemblies capable of providing pre-mixed fuel vapor-air mixtures at a uniform rate to a heated reaction chamber - a Pyrex tube 2 inches ID and 8 inches long (33.2 in^3 volume). Figure 37 is a photograph of the reaction chamber; in use it is normally mounted in a small oven equipped with an observation window. Two side arms at the middle of the tube are fitted with brass adapters for use in mounting the wires (or tubes and rods) normal to the direction of flow. These adapters are spaced 2 inches apart, the length of wire that is heated electrically in each trial. The wire temperature can be varied in large or small increments by using a control switch to adjust a motor-driven autotransformer.

To conduct an experiment, the wire is first heated to a predetermined surface temperature which is measured with a Leeds & Northrup optical pyrometer, calibrated against a General Electric standard lamp. The fuel vapor-air mixture is then passed over the heated wire at a designated flow rate and, depending on whether or not ignition occurs, the wire temperature is decreased or increased in succeeding trials until the lowest temperature at which ignition occurs is found. Minimum wire ignition temperatures are obtained at various fuel-air ratios; these are generally repeatable to within ±25°F. In each case, ignition is evidenced by the appearance of flame and by a sudden rise of the gas mixture temperature. These temperatures are measured with two chromel-alumel thermocouples (28-gage) located 1 inch above and below the heated wire. The gas mixture temperatures are recorded continuously on an oscillograph during each run.

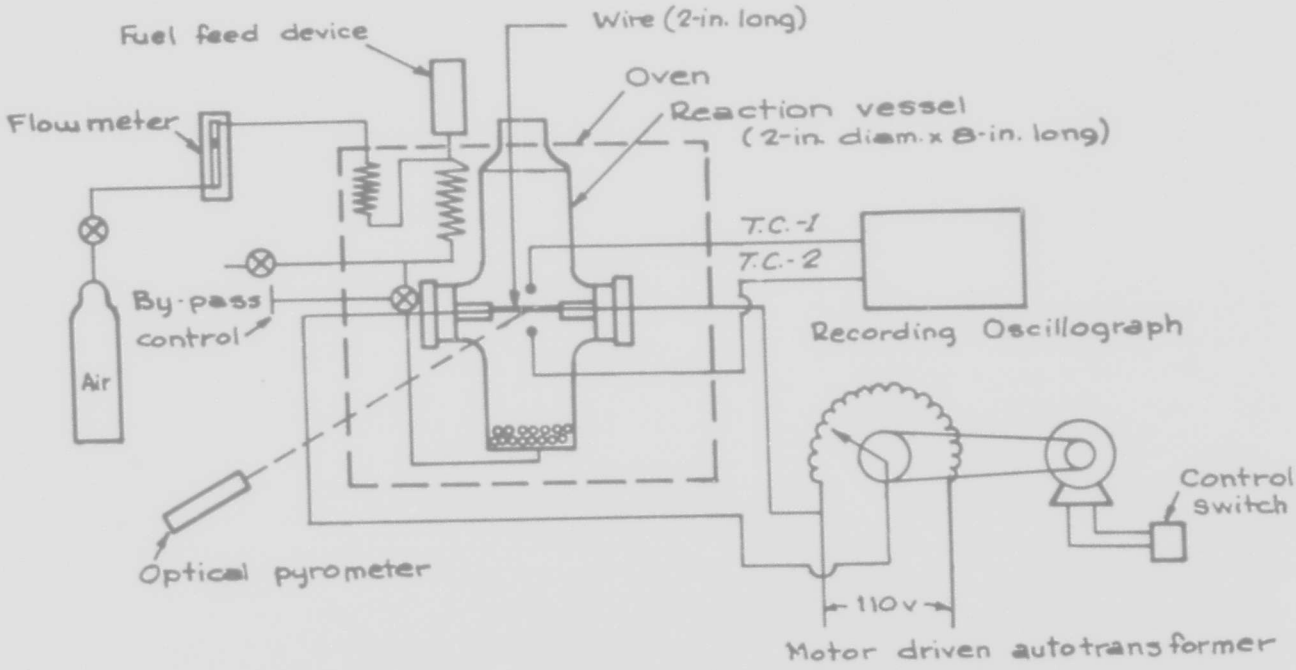


Figure 36. - Wire ignition temperature apparatus.

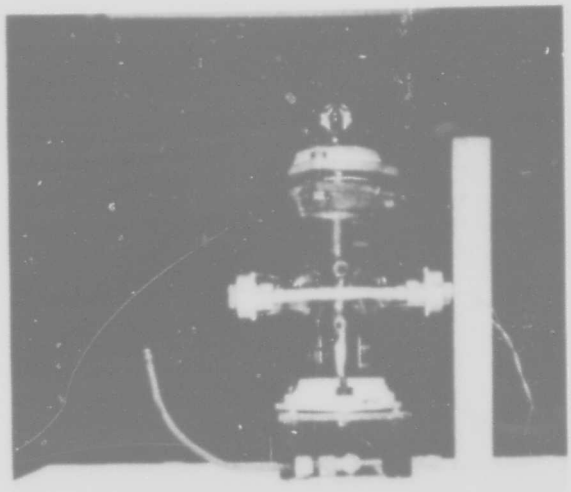


Figure 37.- Reaction vessel of wire ignition temperature apparatus fitted with a Nichrome tube.

APPENDIX III

Hot Gas Ignition Temperature Apparatus

The apparatus used for the hot gas ignition temperature experiments is similar to that employed by Wolfhard (Ref 5) except for some minor modifications and is shown in Figure 38. Basically, the apparatus consists of a tubular ceramic furnace that is used to heat the air stream, a cylindrical reaction chamber into which is fed the hot air jet and the combustible mixture, and the feed assemblies that provide the desired combustible vapor-air mixture at a uniform rate. The tubular furnace is wound externally with platinum-rhodium wire and is enclosed in a cylindrical Nichrome-wire furnace (3-inch ID) which serves as a pre-heater. The reaction chamber consists of a 4-inch diameter Pyrex pipe (26 inches long) that is also heated by a Nichrome-wound furnace designed to maintain the combustible mixture at a given temperature. Narrow slits are located on both sides of the enclosed pipe along its longitudinal axis to permit visual observation of the reaction. The combustible vapor-air mixture is fed to the reaction chamber through a "mixing ring" by the fuel- and air-feed assemblies (Figure 39). This ring is located just below the base of the hot jet; a water jacket is positioned between the ring and the ceramic tubular furnace to help maintain the mixture at a uniform initial temperature. Jet temperatures are measured with a 33-gage platinum-90% platinum + 10% rhodium thermocouple at a point of about 1/4-inch above the jet base. The temperature of the combustible vapor-air mixture is measured with three Chromel-Alumel thermocouples (28-gage) spaced 3 inches apart as shown in Figure 38. Recorded temperature differences were usually not in excess of ±25°.

To conduct an experiment, the temperatures of the hot air jet and ambient atmosphere in the reaction chamber are measured initially. The thermocouples are then removed and the combustible mixture of interest is introduced, flowing coaxially with the hot jet. If ignition does not occur, the temperature of the hot air jet is increased in successive increments until ignition is evidenced by the propagation of flame throughout the combustible mixture. Fuel residence time and fuel-air ratio are varied to obtain the minimum ignition temperatures with each size of hot air jet used.

The temperature probe could be adjusted to make axial and radial temperature measurements at various heights within the hot gas jet. Adjustment of the probe was made by rotating a micrometer in contact with a movable plate supporting the probe. The thermocouple bead of the probe for these measurements was made with 36-gage Pt/Pt-Rh wire and was coated with a ceramic material recommended by the Bureau of Standards; addition of the coating resulted in slightly lower ($\leq$ 25°F) jet temperatures. To obtain jet concentration profiles, the temperature probe was replaced with a quartz sampling probe having a throat diameter of 0.015 inch.

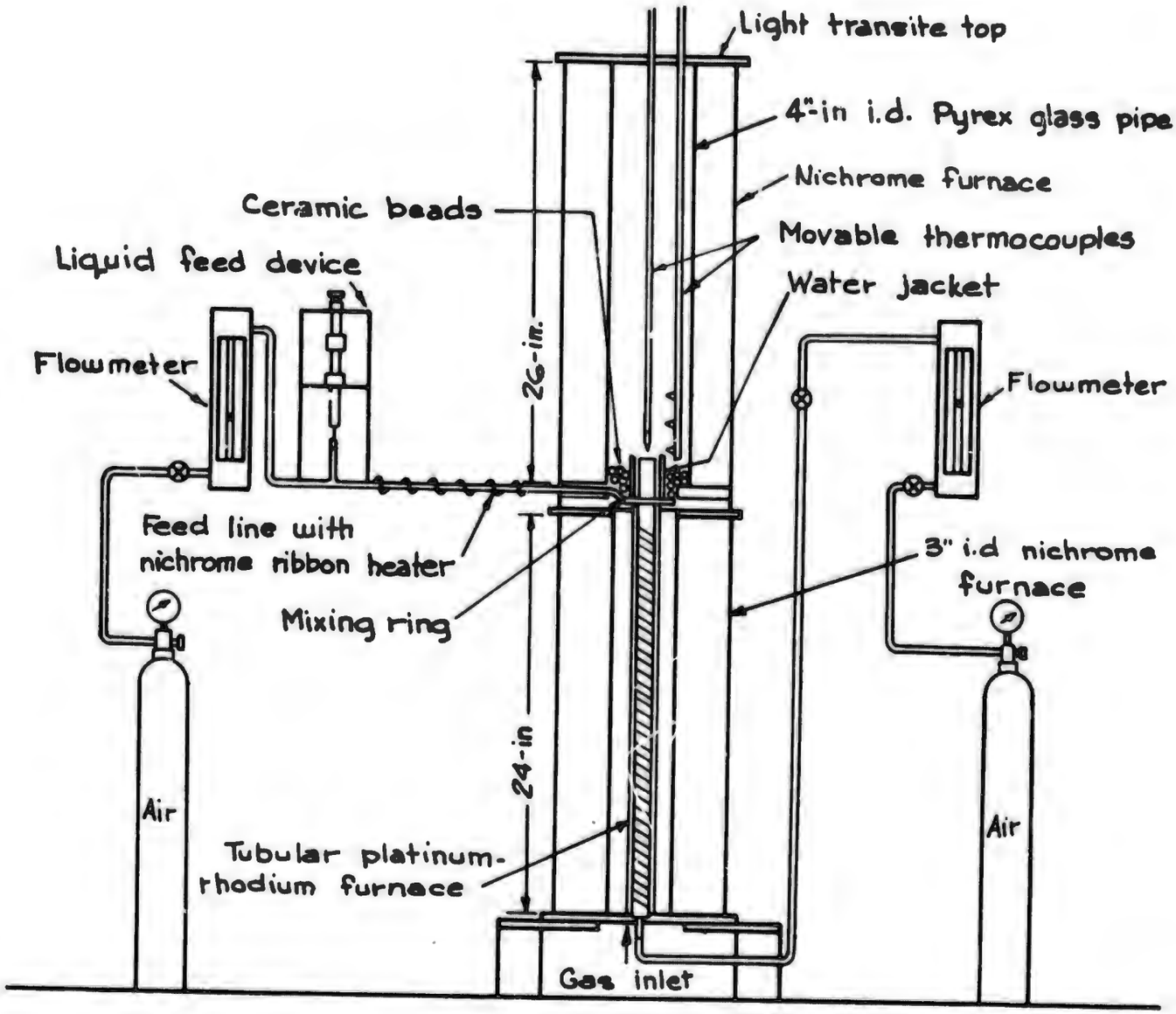


Figure 38. - Hot gas ignition temperature apparatus.

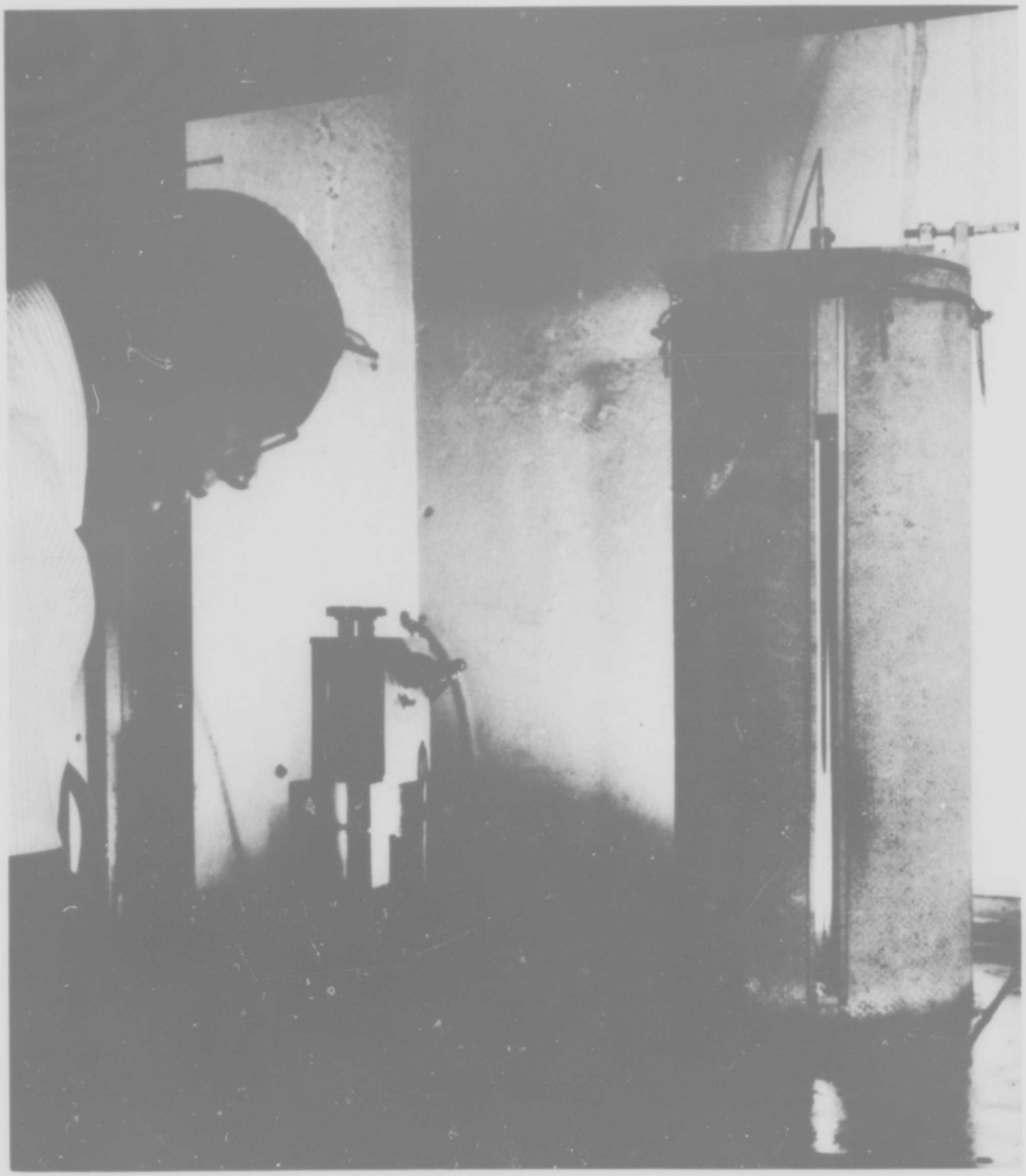


Figure 39. - Operator adjusting fuel-air feed assembly of hot gas ignition apparatus.

APPENDIX IV

Reaction Rate Apparatus

A schematic diagram of the apparatus used for oxidation rate experiments is shown in Figure 40. The apparatus consists of an all-glass system in which fuel vapor-oxidant mixtures are prepared in a heated 122-in^3 (2000 cc) vessel and transferred through heated tubing to either a Pyrex or a quartz reaction vessel; the supply vessel and all tubing were maintained at 266° and 212°F, respectively in the present experiments to prevent condensation of the reactant and product gases. The reaction vessel is installed in an oven which is capable of maintaining the desired vessel wall temperature to within ±1°F. Test mixtures were made up in the 122-in^3 supply vessel by initially introducing the desired quantity of moisture-free air and subsequently injecting the liquid fuel into the heated vessel by means of a hypodermic syringe. The fuel vapor-air mixtures were allowed to mix for at least four hours prior to transfer to the reaction vessel, which was pretreated with a 5 percent hydrofluoric acid solution. Reaction of the mixture is followed by a capillary mercury manometer or by a spiral glass gage which eliminates possible contamination by mercury vapors; pressure variations of at least 0.1 mm mercury (Hg) could be detected.

Provisions were also made for gas sampling to follow the consumption of reactants and formation of gaseous products. For this purpose, a dry ice bath was employed to remove condensable fuel vapor and product gases. The gases were collected at various reaction times in 1.52 in^3 (25 cc) sample bulbs at approximately 1/12 atmosphere pressure and then analyzed by a mass spectrometer.

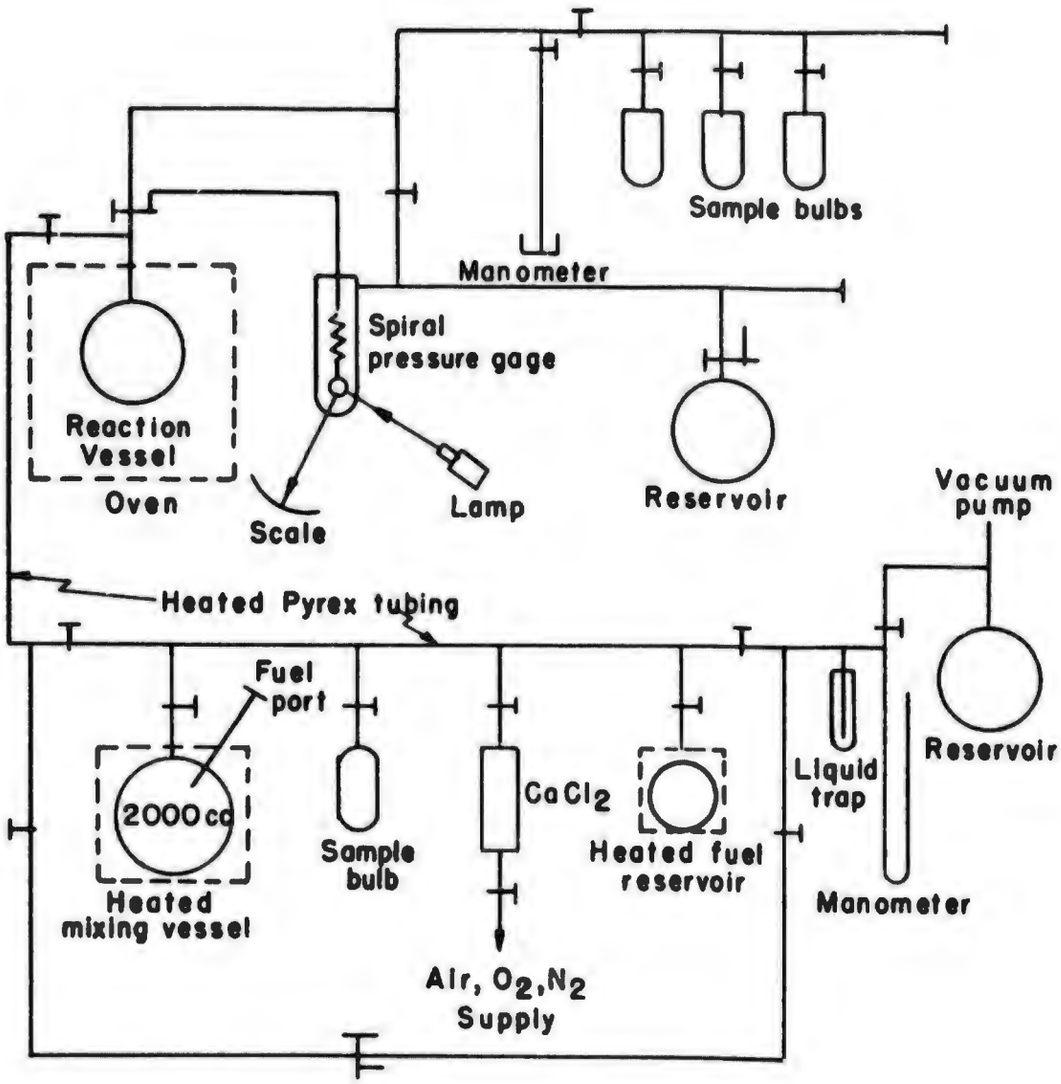


Figure 40. - Schematic diagram of reaction rate apparatus.

APPENDIX V

The F-11 Elevated Temperature Limit-of-Flammability Apparatus

The Bureau of Mines F-11 apparatus (Ref 13) (Figure 41) is a flow-type unit housed in a temperature-controlled oven to allow determination of limits of flammability at elevated temperatures ($\leq$ 650°F). The oxidant is introduced into the system at a. It then passes through flow regulator b, drier c, wet test gas meter d, flow meter g, preheater m and into flammability tube o. The tube is of 2-inch diameter Pyrex although other size tubes can be employed. Valve r, gas bottle s, and calibrated tube t are used to calibrate the wet test gas meter prior to a series of experiments. Liquid fuels are introduced into the flow stream through openings h, i, and l with motor-driven liquid feed devices j and k. The preheater, m, vaporizes the liquid at the rate it is supplied by the feed devices. Preheater m', wound with glass-covered Nichrome ribbon, is electrically heated to the furnace temperature. The test mixtures are examined for flammability under near quiescent conditions (flow rates are less than one foot per minute) in a darkened room by passing a high-voltage spark between platinum electrodes n spaced 1/4-inch apart. Mixture compositions are calculated from the volume of gas and weight of liquid introduced into the system. Where the fuel is a gas, the liquid feed device is not needed and the fuel is introduced into the system through the flow assembly. A mixture was considered flammable if flame was observed (visually) to propagate throughout the mixture.

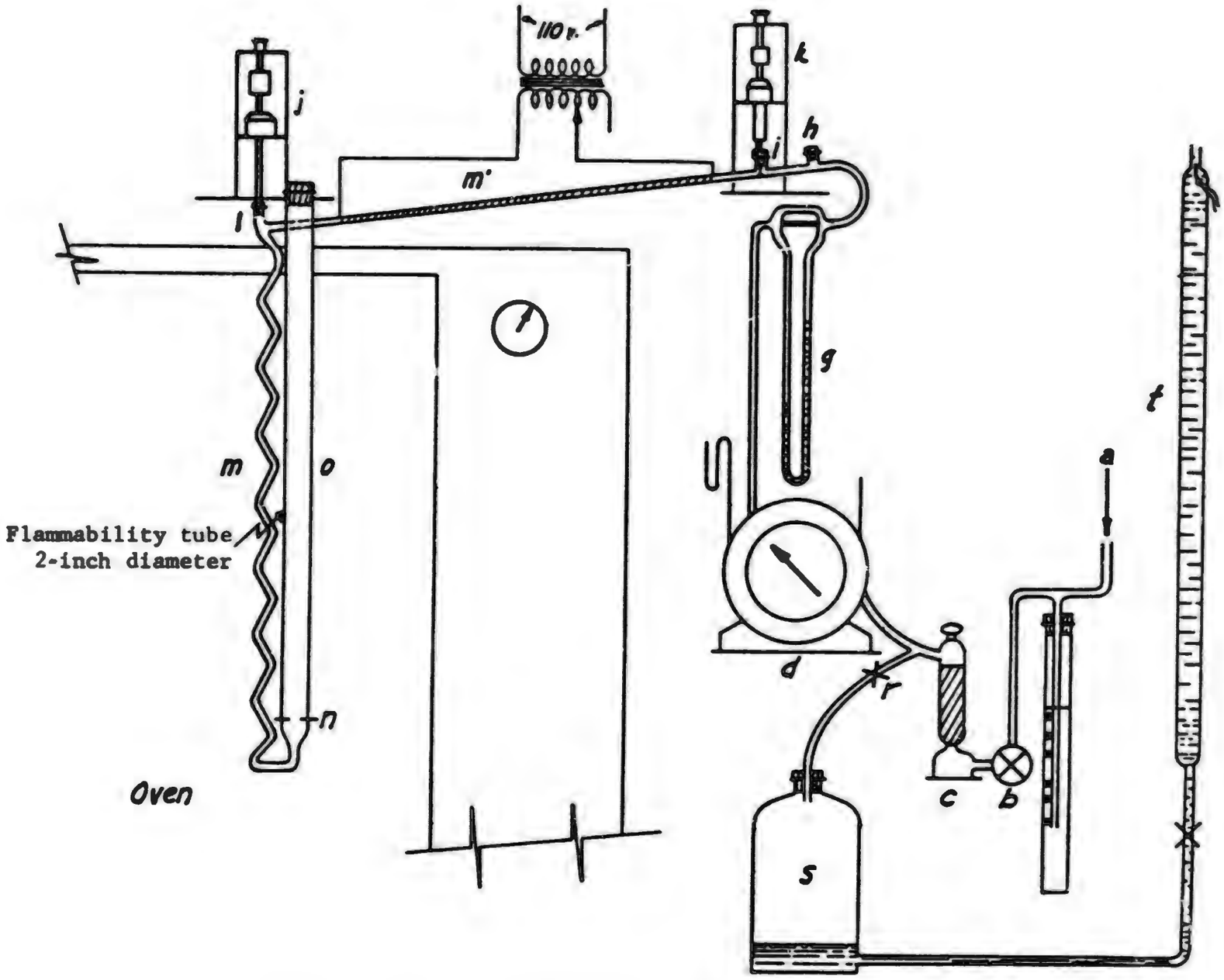


Figure 41.- F-11 limit-of-flammability apparatus.
(2-inch diameter flammability tube).

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