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# SUMMARY OF IGNITION PROPERTIES OF JET FUELS AND OTHER AIRCRAFT COMBUSTIBLE FLUIDS

U.S. BUREAU OF MINES  
PITTSBURGH MINING AND SAFETY RESEARCH CENTER

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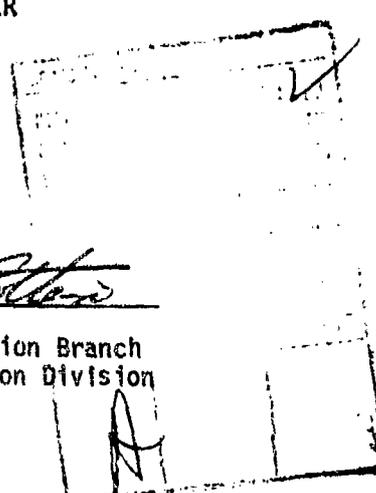
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following types of ignition sources: Electrical sparks or arcs, frictional sparks, heated vessels or tubes, heated wires or rods, heated metal targets, jets of hot gases, shock wave and adiabatic compression, incendiary ammunition and self-heating.

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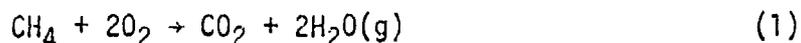
## INTRODUCTION

In an aircraft environment, jet fuels are exposed to various temperatures and pressures under which flammable vapor-air mixtures may form and be ignited when heated by the surroundings or an external heat source. Other aircraft combustible fluids, such as engine oils, lubricating oils, and hydraulic fluids, also can form hazardous vapor-air mixtures, although the required temperatures are generally higher than for the jet fuels. To assess their ignition hazard level in various practical situations, it is necessary to have a knowledge of the ignition properties of the combustibles when exposed to different types of heat sources. Although such information has been reported for various aircraft combustible fluids, the data are found scattered among many publications. Accordingly, this report was prepared at the request of the Air Force to discuss gaseous ignition processes and to provide compilations of available data on the ignition properties of the aircraft fuels or fluids. The data were taken largely from reports of Air Force sponsored work, including a fire and explosion manual (ref. 1) that was recently prepared by the Bureau of Mines.

## THEORY AND DEFINITIONS

### A. Combustion

Combustion is normally defined as an oxidation process in which a fuel and oxidant, such as air or oxygen, react to produce heat with or without the emission of visible light. The potential amount of heat production can be predicted from thermodynamic considerations but the combustion intensity at a given time will depend upon the chemical kinetics and heating conditions. For example, the maximum heat of reaction ( $\Delta H$ ) for the following reaction (1 atm., 75°F)



is 344,000 Btu per lb. mole or 192 kcal per g mole of methane. If the oxidation of these reactants occurs at high temperatures such that the final or intermediate products are rapidly elevated to their excited states, flaming combustion can readily occur; this is the case of normal hot flame ignition of a flammable gas mixture where the temperature or rate of heat input of the heat source is sufficient to promote a branched-chain explosion. However, if the oxidation occurs at relatively low temperatures, the heat liberated will not necessarily be sufficient to produce a self-accelerating chain reaction which depends upon such factors as temperature, pressure, and concentration of the reactants; this low intensity combustion is the case of cool flame ignition or low temperature oxidation where luminosity may or may not be observed. Thus, combustion may involve rapid or slow oxidation processes, as well as a combination of both types. The maximum temperatures and pressures realized in practice will depend upon the above cited factors and the heat transfer and mass transport processes influencing the reacting system.

In both hot flame and cool flame ignitions, a finite reaction time is required before the chemical heat release is sufficient to produce flaming combustion. Such ignitions of combustible gas mixtures involve highly complex reactions but are frequently characterized as two-stage processes,

$$\tau = \tau_1 + \tau_2 \quad (2)$$

where  $\tau$  is the total ignition delay and includes the initial or low temperature stage ( $\tau_1$ ) and the final or high temperature stage ( $\tau_2$ ). The reaction velocity ( $k$ ) associated with either stage can be expressed in terms of the well known Arrhenius law,

$$k = Z e^{-E/RT} \quad (3)$$

where  $Z$  is a collision frequency factor ( $\text{time}^{-1}$ ),  $T$  is absolute temperature,  $R$  is the molar gas constant, and  $E$  is the activation energy ( $\text{cal/mole}$ ) that determines what fraction of molecular collisions will take part in the chemical reaction. If one assumes that the ignition delay corresponds to the time required for a fraction of the reaction to be completed, such that  $\tau \propto 1/K$ , then equation 2 can be written as follows:

$$\tau = z_1' e^{E_1/RT_1} + z_2' e^{E_2/RT_2} \quad (4)$$

where the frequency factors ( $z_1'$  and  $z_2'$ ) are expressed as reciprocals of the conventional  $Z$ . Thus, we see that the  $\tau$  for each stage may have a different  $E$  value but both are defined by exponential functions of temperature. However, if any stage is controlled by physical rather than chemical processes, its ignition delay will not necessarily be a strong function of temperature.

Cool flames are formed in air by many hydrocarbon fuels including ethers, aldehydes and most paraffinic hydrocarbons. These flames are ordinarily pale blue and are believed to be characterized by aldehyde and/or peroxide formation. They occur over a limited range of temperature and pressure that is usually below that required to produce normal autoignition of the particular combustible gas mixture. However, they can also occur when the mixture is exposed to a very high temperature source. Generally, they are most often found with fuel-rich mixtures that are outside the normal flammability limits of the fuel vapor-air system. Since these flames have very low burning velocities, they propagate largely only in the upward direction. It is possible that their propagation is partly supported by preferential diffusion which appears to be a plausible mechanism for explaining the wider upper limits (fuel-rich) of many hydrocarbon fuels when comparing their upward and downward propagation limits; however, the propagation of such flames is complicated by buoyancy effects which also tend to widen the propagation limits. Because only a small fraction of the available enthalpy is involved in producing cool flame ignitions, their temperature rises are relatively small and seldom more than 100° or 200° (Fahrenheit). In comparison, normal hot flame ignitions yield much higher temperature rises, depending upon the mixture composition; for near-limit mixtures of hydrocarbon fuels in air (1 atm), their adiabatic flame temperatures are of the order of 2200°F. Since cool flames can develop into normal ignitions when they come into contact with an optimum fuel vapor-air composition, their possible formation cannot be ignored.

Combustion is not necessarily limited to reactions in an oxidant atmosphere. Some endothermic compounds, such as acetylenic hydrocarbons, are thermally unstable and can produce a decomposition flame in the absence of oxygen above certain temperatures and pressures. However, these materials are not typical of aircraft fuels or fluids and will not be emphasized in this report.

#### B. Thermal Ignition

The thermal ignition of a combustible solid or combustible gas mixture can be considered as a reaction initiated with or without external heating and accelerated to the point of ignition by the heat release from chemical reaction. Since the concept of "ignition temperature" is basic to the theory of thermal ignition and has practical usefulness, two widely known thermal theories are briefly discussed below to indicate expected trends in such temperatures.

## 1. Semenov Theory

In this simplified theory (ref. 2), it is assumed that the rate of chemical reaction for a combustible gas mixture follows the Arrhenius law,

$$W = Z a^n e^{-E/RT} \quad (5)$$

where  $W$  is the rate per unit volume,  $a$  is initial reactant concentration such as moles per unit volume,  $n$  is order of reaction, and the other terms are the same as in equation (3). The rate of chemical heat release ( $q_1$ ) in a specific volume ( $V$ ) is given by  $VQW$ , that is,

$$q_1 = VQZ a^n e^{-E/RT} \quad (6)$$

where  $Q$  is the heat of reaction per mole. This theory further assumes that the temperature distribution throughout the reacting system is uniform and that the heat loss is localized at the boundaries (walls) of the system. In practice, only well stirred reactors would satisfy the above condition. Nevertheless, the rate of heat loss ( $q_2$ ) is expressed as,

$$q_2 = \alpha S (T - T_0) \quad (7)$$

where  $\alpha$  is a heat transfer coefficient,  $S$  is surface area of the reactor walls,  $T_0$  is wall temperature, and  $T$  is the reactant gas temperature.

It is evident from equations (6) and (7) that the heating condition for ignition should become more favorable with decreasing  $S/V$  ratio of the reaction vessel. The critical heating condition is defined as that temperature and pressure when the chemical heat release is equal to the heat loss from the system, that is  $q_1 = q_2$ . Figure 1 illustrates the theoretical case where the wall temperature is varied and the heat loss rates are compared to a single heat release rate at constant pressure. The critical condition for ignition is reached at the intermediate wall temperature,  $T_2$ , when the heat loss rate ( $q_2$ ) becomes tangent to the heat release rate ( $q_1$ ). Below this wall temperature,  $q_2 > q_1$  after the initial heating stage and the reaction can never reach the ignition point ( $T_i$ ).

Based on this theory, the following expression is obtained for the ignition temperature ( $T$ ) of a combustible mixture as a function of pressure ( $P$ ) by equating equations (6) and (7) and replacing the concentration term ( $a$ ) with  $P/RT$ .

$$\log_e \frac{P}{\tau^{1+2/n}} = \frac{A}{T} + \log_e B \quad (8)$$

where  $A = E/nR$ ,  $B$  is a system constant, and the ignition delay is fixed. The variation of ignition delay ( $\tau$ ) with temperature and pressure, as derived from thermal or chain theory, is given by

$$\tau P^n = B' e^{E/RT} \quad (9)$$

which at constant pressure yields

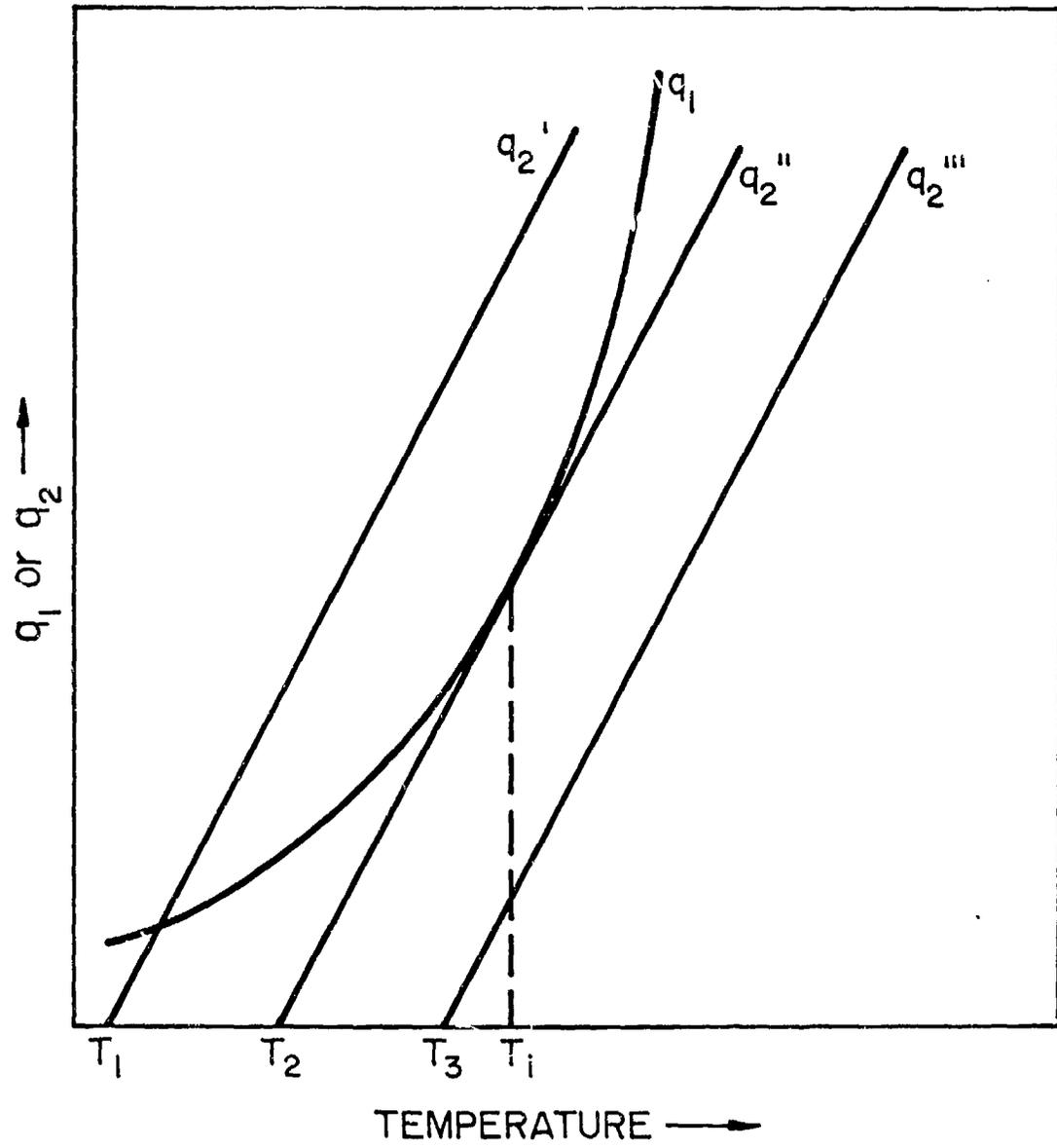


Figure 1. - Schematic of heat gain ( $q_1$ ) and loss ( $q_2$ ) to surroundings at three different wall temperatures.

$$\log_e \tau = \frac{A'}{T} + \log_e B' \quad (10)$$

Thus, the ignition delay and ignition or explosion pressure should vary exponentially with the system temperature. The derivations of the above expressions assume that the temperature rise and reactant consumption during the pre-ignition period are very small and that the reaction order (n) and activation energy (E) do not change; these conditions are usually not fully satisfied in practice. Thus, although the ignition temperature behavior of many combustible-oxidant mixtures may be estimated by such relationships, great uncertainties exist relating to their chemical kinetic significance.

## 2. Frank-Kamenetskii Theory

A more rigorous thermal ignition theory is one developed by Frank-Kamenetskii (Ref. 3). It assumes that the temperature distribution in the reacting system is nonuniform and that heat loss is by conduction with infinite heat transfer at the boundaries of the system; also, ignition is taken to occur at the center of the reacting material. This theory is particularly suitable for predicting the critical size of combustible solids required for self-ignition under adiabatic conditions but is also applicable to ignitions of combustible gas mixtures. Here, the self-heating rate ( $q$ ) is assumed to be equal to the sum of the chemical heat release rate ( $q_1$ ) and the (negative) conductive heat loss rate ( $q_2$ ):

$$\rho c \frac{\partial T}{\partial t} = \rho Q Z e^{-E/RT} + \lambda \nabla^2 T \quad (11)$$

where  $\rho$  is density,  $c$  is specific heat,  $T$  is absolute temperature,  $Q$  is heat of reaction,  $Z$  is rate frequency factor,  $E$  is activation energy,  $R$  is molar gas constant, and  $\lambda$  is the thermal conductivity - all with respect to the reacting material;  $\nabla^2$  is the Laplacian differential operator. For steady state conditions ( $\partial T/\partial t = 0$ ),  $q_1$  is equal to  $q_2$  and the one dimensional solution yields

$$r_c = \left[ \frac{\delta_c \lambda R T^2}{E \rho Q Z e^{-E/RT}} \right]^{1/2} \quad (12)$$

where  $r_c$  is the critical radius of combustible material that will self-ignite at temperature,  $T$ , and  $\delta_c$  is a shape factor that is equal to 3.33 for a sphere, 2.0 for a cylinder, and 0.88 for a plane-parallel slab. If adiabatic conditions are assumed ( $\partial T/\partial x = 0$ ),  $q$  is equal to  $q_1$  and the rate of temperature rise at the self-heating condition is

$$\frac{\partial T}{\partial t} = \frac{QZ}{c} e^{-E/RT} \quad (13)$$

Integration of this equation leads to an expression that defines the exponential dependence of the ignition or explosion time, similar to the ignition delay equation (10) given in the previous section.

## C. Classification of Ignitions

Normal ignition of a fuel vapor-air mixture can occur only if the mixture composition is flammable and some critical volume is sufficiently

heated to produce an exothermic reaction that propagates flame beyond the point of initiation. The required level of heating can be achieved by elevating the ambient temperature of the environment or by introducing an external source of heating. Since ignitions can be initiated by various methods, they are generally classified according to the type of heat or energy source. A listing of representative sources is given below:

1. Electrical sparks or arcs
2. Lasers
3. Hot surfaces
  - a. Frictional sparks
  - b. Incendiary particles
  - c. Heated wires, rods, or fragments
  - d. Heated vessels or tubes
4. Hot gases
  - a. Shock compression
  - b. Adiabatic compression
  - c. Hot gas jets
  - d. Pilot or burner flames
5. Self-heating
6. Pyrophoricity or catalytic reaction

The temporal and spatial characterization of heat sources is useful in differentiating between initiating processes. Figure 2 illustrates the general trend expected between the time scale of heating and the size of the heat source for typical electrical and hot surface ignition sources. In the case of an electrical spark, the source is highly localized in space and the duration of heating can be as little as a few microseconds; here, temperatures are always very high and ignition is determined by the amount and rate of energy input to the gaseous mixture. Lasers also fall into this category although their energy is not readily absorbed by gases. In comparison, a heated vessel represents a much more spatially distributed source and the duration of heating can be as much as several minutes; here, temperature rather than energy is the critical factor and is minimum when the heating duration or corresponding ignition delay is maximum. The latter are referred to as minimum autoignition temperatures (AIT's) and are normally determined in quiescent air. Both temperature and heating rate tend to be important with such small hot surface sources as heated wires, metal fragments and frictional sparks. Generally, the ignition temperature of a mixture increases with a decrease in the size or surface area of the heat source. Incendiary ignitions may be considered a special case of hot surface particle ignition where the chemical reactivity of the heat source is an added factor in determining ignition.

The heat sources associated with hot gas ignitions also differ in their temporal and spatial characteristics. Shock wave heating is the most localized in space and time (e.g.  $<1$  millisecond), whereas adiabatic compression heating is the most spatially distributed and, therefore, can

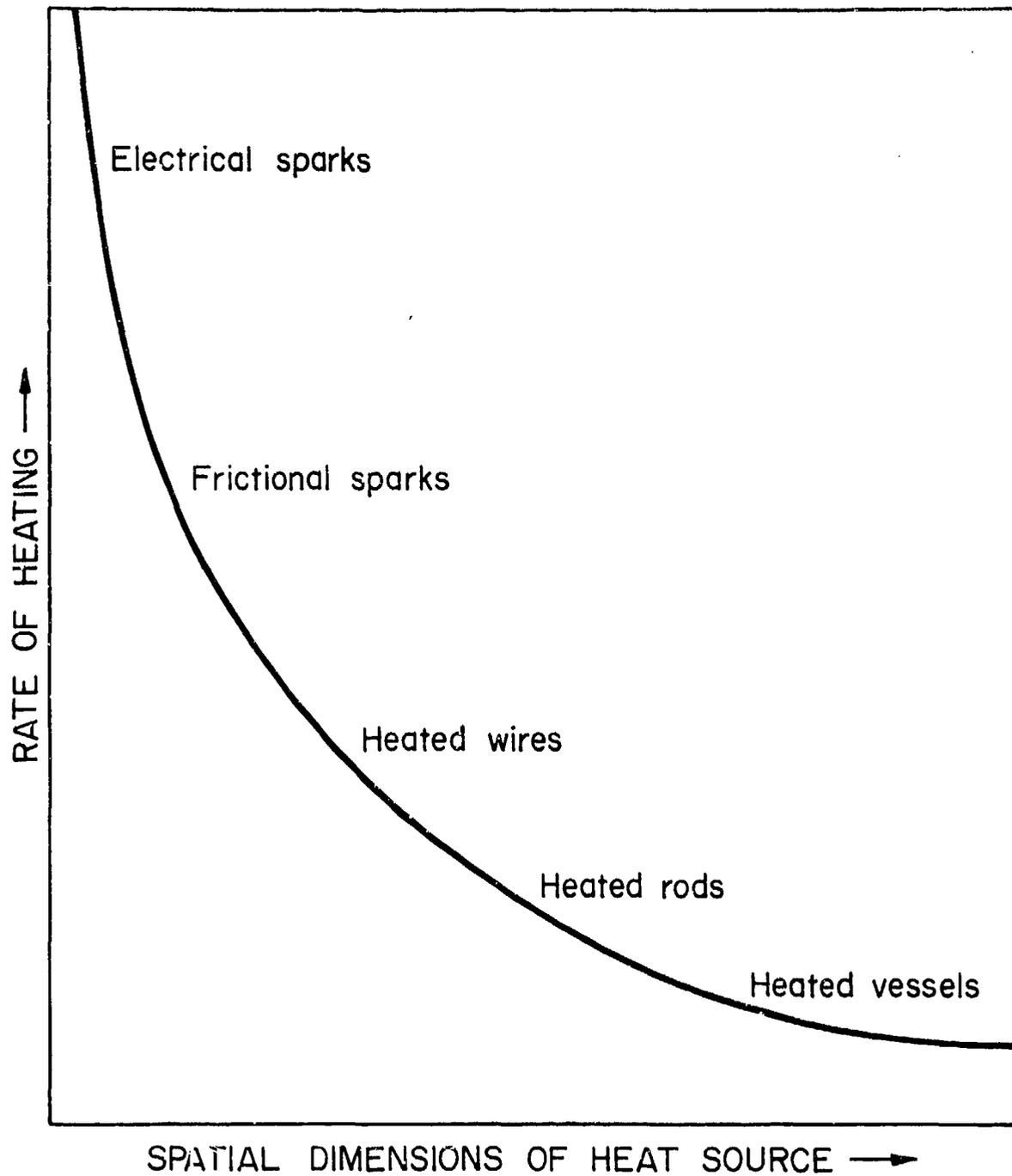


Figure 2. - Temporal and spatial characterization of electrical and hot surface ignition sources.

effect ignition at much lower temperatures than is possible by shock compression. Adiabatic compression ignition temperatures are usually of the order of heated vessel autoignition temperatures that are found at relatively short heating times, that is, a few seconds. Other sources such as jets of hot gas or flame are intermediate on the temporal and spatial scale of heating by hot gases. Ignition temperatures with these sources will vary with the jet composition and dimensions and tend to be of the order of those obtained with heated wires or particles at comparable heat fluxes. Here again, the ignitions are more complicated when the heat source is chemically reactive (a flame), as opposed to an inert hot gas source.

Self-heating is a special case of autoignition in which an exothermic reaction is possible without any external heating. This involves slow oxidation or decomposition of the combustible and requires hours or even days for ignition to occur, depending upon heat losses and chemical reactivity of the system. Pyrophoric reaction may also be considered as a special case of autoignition without external heating. However, in this case, the combustible reacts directly with moisture or other contaminants in air and the reaction times are much shorter (seconds) than in normal self-heating.

#### IGNITION BY ELECTRICAL SPARKS OR ARCS

##### A. Minimum Spark Ignition Energies

Electrical ignitions may be classified as high voltage or electrostatic type and low voltage or break spark type. The energy of electrostatic discharge is given by

$$E_c = 1/2 CV^2 \quad (14)$$

where E is energy (joules), C is material capacitance (farads) and V is the potential difference (volts). By this expression, a man with a capacitance of  $300 \times 10^{-12}$  farads could conceivably produce a static discharge of  $1.5 \times 10^{-2}$  joules (15 mj) if he is charged to 10,000 volts. Most petroleum products are capable of accumulating a static charge and, thereby, present a spark ignition hazard. The minimum electrostatic spark energy required for ignition of a flammable gaseous mixture is determined at an optimum length of spark gap. This energy is much less than that required with a break spark or arc, which is produced by opening an electrical switch or by separation of current carrying conductors. The energy of a break spark is given by

$$E_b = 1/2 LI^2 \quad (15)$$

where L is inductance (henries) and I is the current (amperes). Minimum ignition energy (MIE) values by the break spark method can be nearly of the order of MIE's associated with the capacitance spark method if very fine wires and rapid separations are used. Nevertheless, the capacitive spark discharge data are relied upon here for the MIE's.

Most spark ignition energy data have been obtained for hydrocarbon compounds and other so called "neat" fuels. Figure 3 (Ref. 4) shows that the spark ignition energy is a function of the fuel-air ratio and that the MIE's for the paraffins with the exception of methane tend to occur at fuel vapor concentrations greater than stoichiometric; the indicated trend can be attributed to the increasing differences between the diffusivities of the fuel and oxygen with increasing fuel molecular weight. As noted, the MIE is approximately 0.25 millijoule for the given paraffins in air at normal ambient temperature and pressure. Aircraft hydrocarbon fuels have comparable MIE values and can be assumed to behave similar to the higher molecular weight paraffins, such as n-hexane or n-heptane. Noticeably lower MIE's are found under the same ambient conditions for such unsaturated hydrocarbons as ethylene (0.07 mj) and acetylene (0.02 mj) and for hydrogen (0.02 mj).

In a flight environment, the minimum ignition energy will increase with altitude. The variation of MIE with ambient pressure (P) may be expressed as

$$\text{MIE} = (\text{MIE})_0 (P/P_0)^{-n} \quad (16)$$

where n is approximately 2 for hydrocarbon type fuels (Ref. 5). With increasing temperature, the MIE's decrease roughly by a factor of 2 for a 150°(F) temperature change. They are also sensitive to oxygen concentration, being reduced by more than an order of magnitude when the atmosphere is changed from air to oxygen. Figure 4 (Ref. 1) illustrates the effect of mixture pressure and oxygen concentration on the MIE of propane-oxygen-nitrogen mixtures. Most important in applying these data is the fact that the MIE's are small compared to the electrical energies that could result from most accidental arcs or sparks in an aircraft. Note that even static discharge from a human body can generate energies ( $\leq 15$  mj) that can be hazardous, particularly when the most ignitable mixtures are present.

The ignition energy requirements are greater for fuel sprays than for homogeneous vapor-air mixtures. With increasing fuel temperature, the ratio of fuel vapor to spray increases and, therefore, the ignition energy should decrease. Figure 5 (Ref. 1) shows such data for the sprays ( $\sim 10\mu$ ) of three jet aircraft fuels. The following expressions define the minimum ignition energies (MIE, mj) as a function of the fuel temperature (T, °F):

$$\text{MIE} = 23.2 e^{-.042T} \quad \text{JP-4} \quad (17)$$

$$\text{MIE} = 139 e^{-.034T} \quad \text{JP-5} \quad (18)$$

$$\text{MIE} = 111 e^{-.037T} \quad \text{JP-8} \quad (19)$$

#### B. Minimum Ignition Quenching Distances.

In assessing the ignitability hazard of a fuel-air mixture, both the ignition energy and the quenching distance can be useful. Excluding the

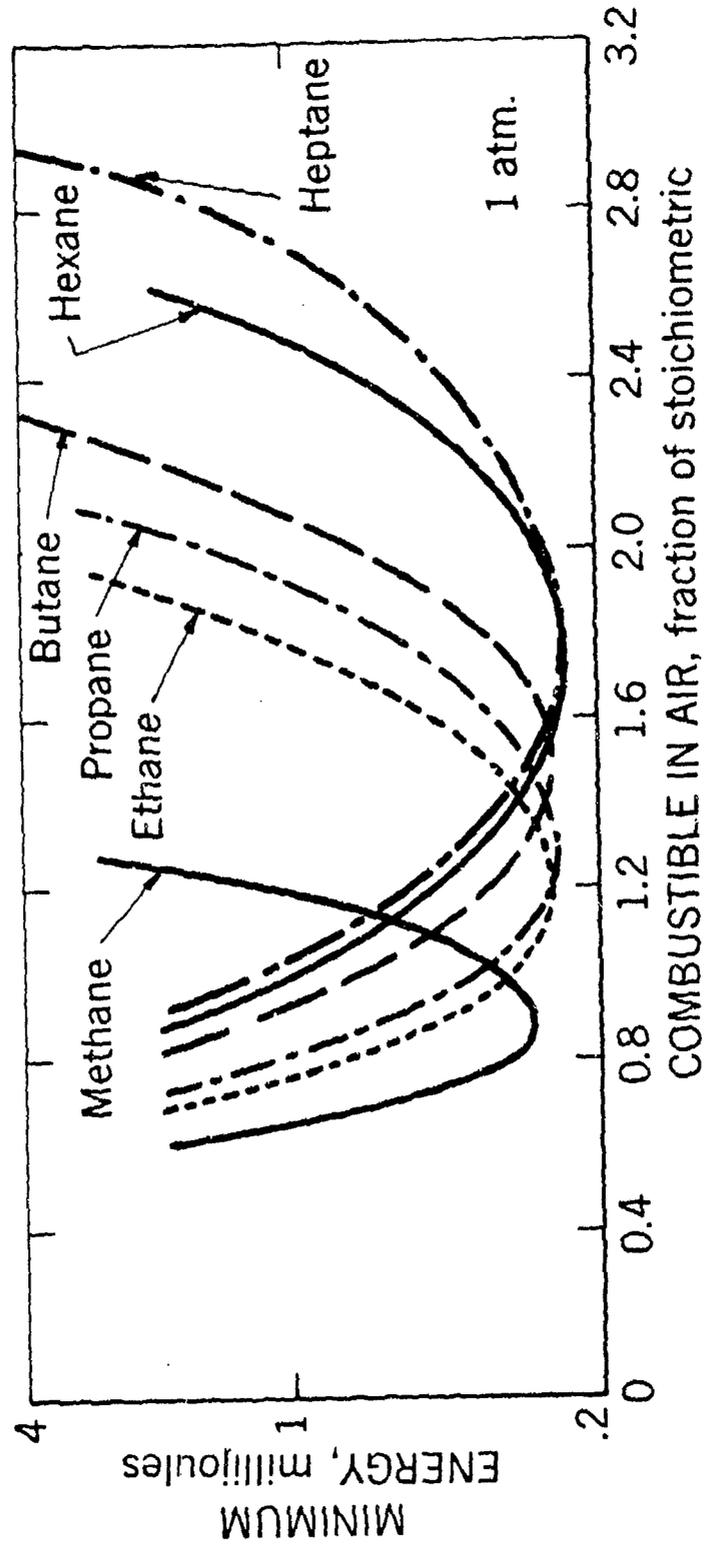


Figure 3. - Spark ignition energy vs mixture composition for mixtures of various straight chain saturated hydrocarbons with air at 1 atmosphere.

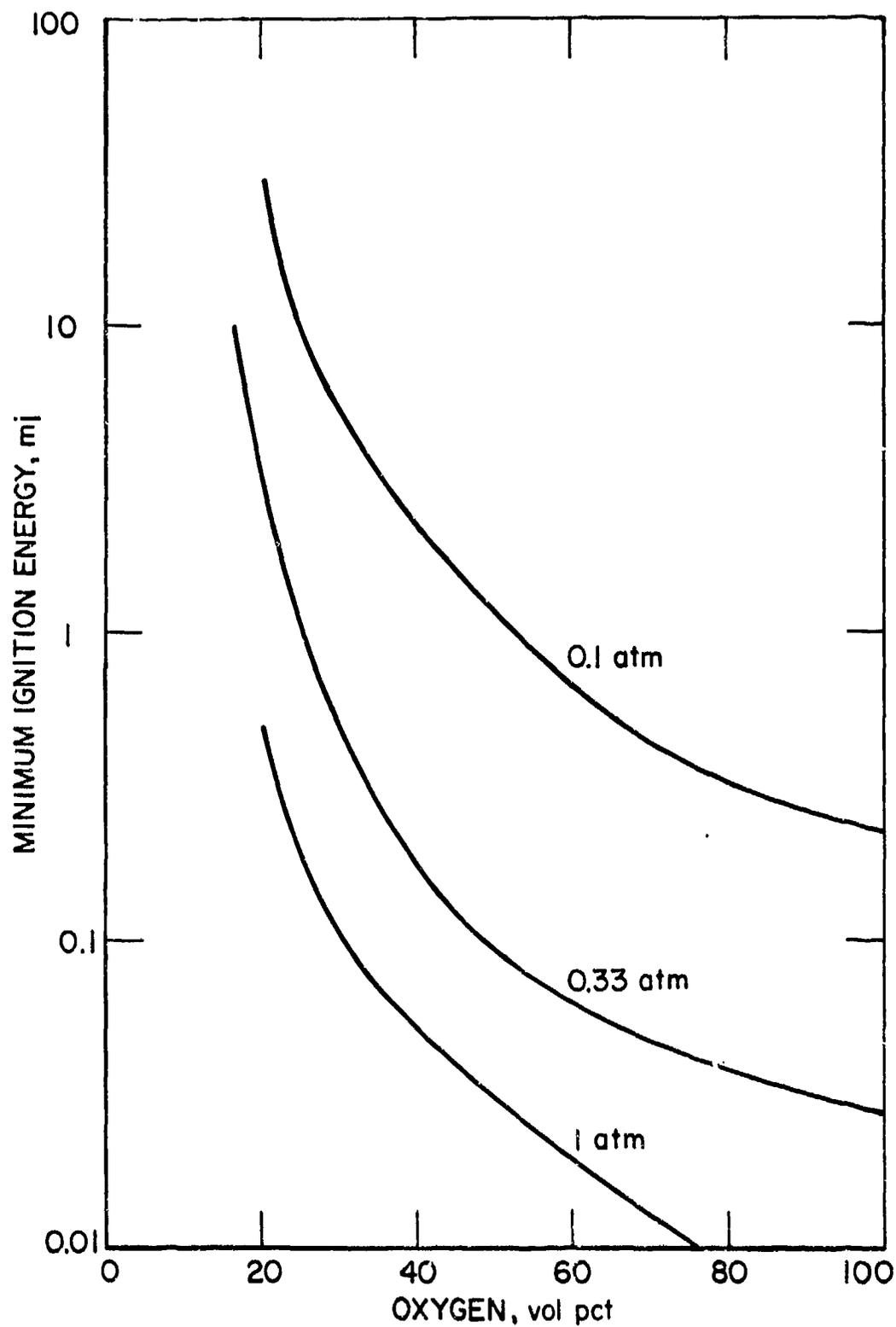


Figure 4. - Minimum ignition energy of propane-oxygen-nitrogen mixtures as a function of oxygen concentration and mixture pressure.

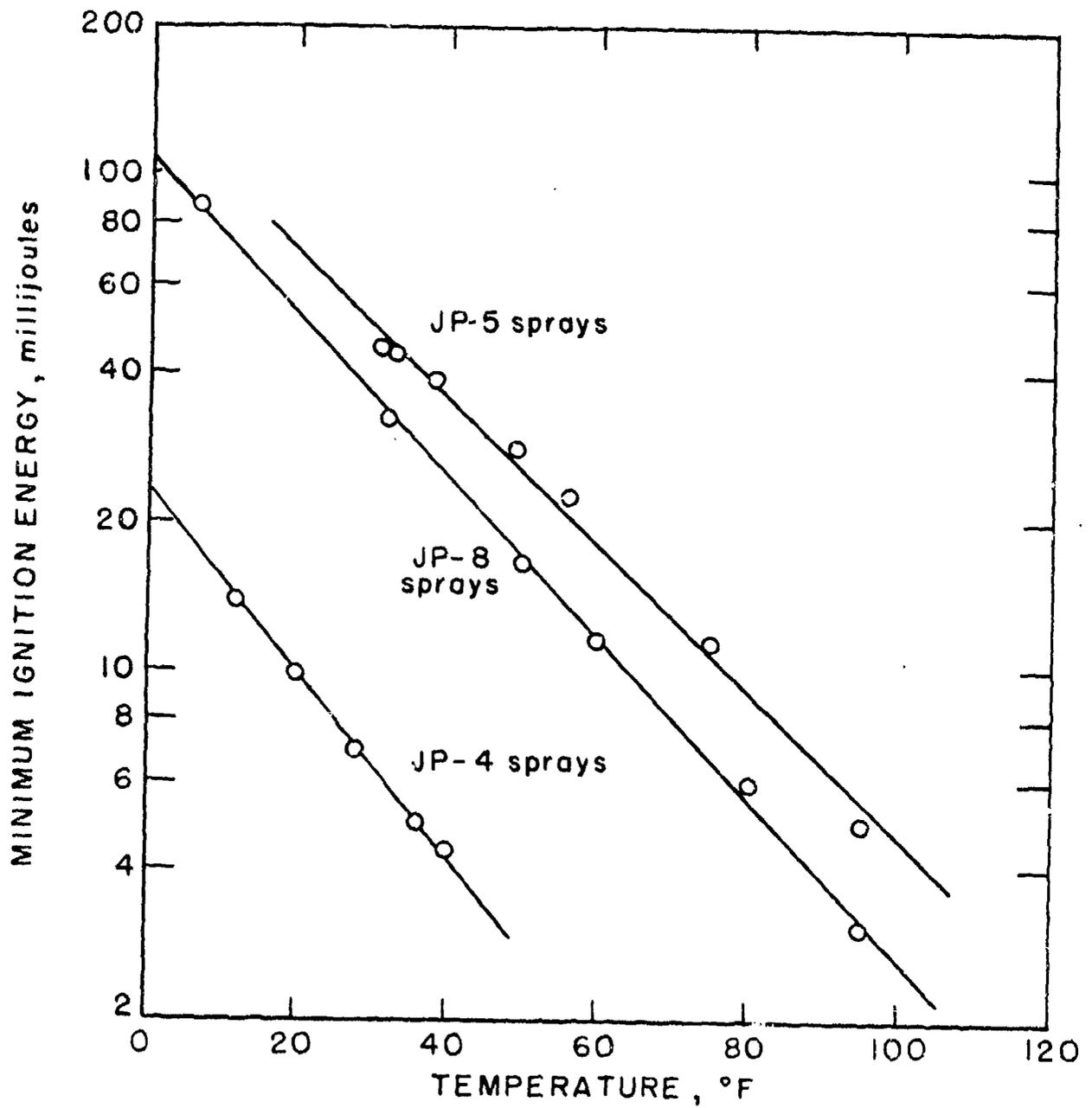


Figure 5. - Minimum spark ignition energy of the sprays ( $\sim 10\mu\text{m}$  diameter) of three jet fuels at various temperatures.

higher energy fuels such as hydrogen and the acetylenic hydrocarbons, the minimum ignition quenching distance for most conventional hydrocarbon fuel vapor-air mixtures at atmospheric pressure is between 0.05 and 0.1 inch. Table 1 summarizes ignition quenching distances and corresponding ignition energies for a number of fuels in air or oxygen at ambient temperature and atmospheric pressure; mixture ratio was stoichiometric or near-optimum for combustion. As with MIE's, the quenching distances decrease with increasing pressure and are roughly proportional to  $(P/P_0)^{-1}$  for many fuel-air mixtures.

Although ignition quenching distance data provide a measure of fuel mixture ignitability, they should not be confused with maximum safe gaps that are used in the design of permissible electrical equipment. The latter values relate to quenching of flame and hot gas jets produced under severe explosion conditions and have been compiled for a number of fuels by the Underwriters Laboratories (Ref.8). Maximum experimental safe gaps are of the order of 50% less than corresponding ignition quenching distances of table 1.

## AUTOIGNITION IN UNIFORMLY HEATED CONTAINERS

### A. Minimum Autoignition Temperatures

The most widely used property for evaluating the ignitability hazard of a fuel is its minimum autoignition temperature, that is, minimum AIT or SIT. This property defines the lowest temperature at which flammable mixtures of a fuel (vapor) and air, or other oxidant of interest, will ignite when heated in a container of uniform temperature. It depends upon such factors as fuel concentration, oxygen concentration, mixture pressure, fuel injection pressure, fuel contact time before ignition (ignition delay), and the size, shape and composition of the container. The ignition criterion is also an important factor. Normal ignitions are evident by the presence of visible flame but cool flames or marginal ignition are more difficult to detect and, therefore, temperature rise or pressure rise is also used as the ignition criterion. Visible flame was the ignition criterion for the AIT data presented here, unless specified otherwise.

In autoignitions, the time scale of heating can extend over a wide range but is about 5 minutes or less at the minimum AIT condition for most fuels in air at atmospheric pressure. Thus, the ignition delays can be assumed to be maximum for any minimum AIT data given in this report.

The AIT's of most combustibles do not vary greatly with fuel concentration except at the near critical concentrations required to sustain flame propagation. Generally, the optimum fuel-air ratio is on the rich side of stoichiometric and is of the order of 0.1 (weight basis) or more for aircraft jet fuels. In an aircraft fuel tank, one must assume that a wide range of fuel-air ratios can be present at any given time.

Table 1. - Minimum Ignition Energies and Quenching Distances of Various Combustibles in Air and Oxygen at Atmospheric Pressure<sup>a/</sup>

Combustible	Ignition Energy, mj		Quenching Distance, in.	
	Air	Oxygen	Air	Oxygen
Methane	0.30	0.003	0.08	0.012
Ethane	0.25	0.002	0.09	-
n-Butane	0.25	0.009	0.095	0.006
n-Hexane	0.29	0.006	0.06	0.008
n-Heptane	0.24	-	0.07	-
Ethylene	0.07	0.001	0.05	0.009
Propylene	<0.28	-	0.08	-
Acetylene	0.02	0.0002	0.025	0.007
Cyclohexane	0.22	-	0.07	-
Benzene	0.22	-	0.07	-
Hydrogen	0.02	0.0012	0.018	0.009

a/ Data from references 1, 5, 6 and 7

## 1. Effect of Vessel Material and Size.

AIT values of hydrocarbon type fuels are affected only slightly by the material composition of the container. The lowest values are normally found in glass vessels, as recommended by the standard ASTM method (Ref. 9), or in stainless steel vessels; aluminum containers may give comparable results but tend to be less reliable at high temperatures, as well as with halogenated type fuels. Surface material effects can be expected to be greatest with fuels of high reactivity or poor thermal stability.

Consistent with thermal theory, AIT's decrease with increasing vessel volume and decreasing surface area to volume ratio of the vessel. The effect of vessel dimensions on minimum AIT is shown by the data in figure 6 (Ref. 10) for n-hexane, n-octane, n-decane, JP-6 jet fuel and MIL-L-7808 engine oil. These data were obtained in air with cylindrical vessels and indicate that AIT's increase greatly above an S/V ratio of  $5.0 \text{ in}^{-1}$ , or diameter less than 0.9 inch; the critical S/V ratio with spherical vessels was  $3.8 \text{ in}^{-1}$  or a diameter of 1.6 inches. Thus, it is appropriate that vessels of about 2-inch diameter or more are recommended for minimum AIT determinations. For vessels of equal volume, the AIT will be lowest in a spherical vessel because of its smaller S/V ratio, although this difference is small when the vessels are large. According to British investigators (Ref. 11), the following relationship may be used to predict the AIT's of kerosene fuels in large diameter vessels that are uniformly heated:

$$T = T_0 + kr^{-1/2} \quad (20)$$

where T is the AIT ( $^{\circ}\text{F}$ ) in a vessel of radius r (in); k is a constant and  $T_0$  is the AIT ( $^{\circ}\text{F}$ ) at an infinite r. For a jet fuel having a minimum AIT of  $460^{\circ}\text{F}$  in a 2-inch diameter vessel,  $T_0$  is  $380^{\circ}\text{F}$  and k is 82.5.

## 2. Effect of Fuel Composition

The minimum AIT's of organic fuels vary noticeably with chemical structure and do not correlate with their corresponding minimum ignition energy values. Tables 1-A, 2-A, and 3-A in the appendix of this report give the minimum AIT's of various hydrocarbons, aircraft fuels and hydraulic fluids or lubricants, respectively, in air at atmospheric pressure. As noted in Table 1-A, the AIT's of paraffins are between  $400^{\circ}$  and  $1000^{\circ}\text{F}$  and decrease with increasing carbon chain length. Zahetakis (Ref. 12) has shown that the AIT's of straight and branched chain paraffins can be correlated with the average carbon chain length ( $L_{ave}$ ):

$$L_{ave} = \frac{2 \sum_i^n g_i N_i}{M(M-1)} \quad (21)$$

where  $g_i$  is number of possible chains,  $N_i$  is number of carbon atoms in each chain and M is the number of methyl groups. For example, 2,2,3,3-tetramethyl pentane has a maximum of 4 chains with 3 carbon atoms, 8 chains with 4 carbon atoms, 3 chains with 5 carbon atoms, and a total of 6 methyl groups, which yields a  $L_{ave}$  of 3.9; in comparison, n-nonane is a straight chain

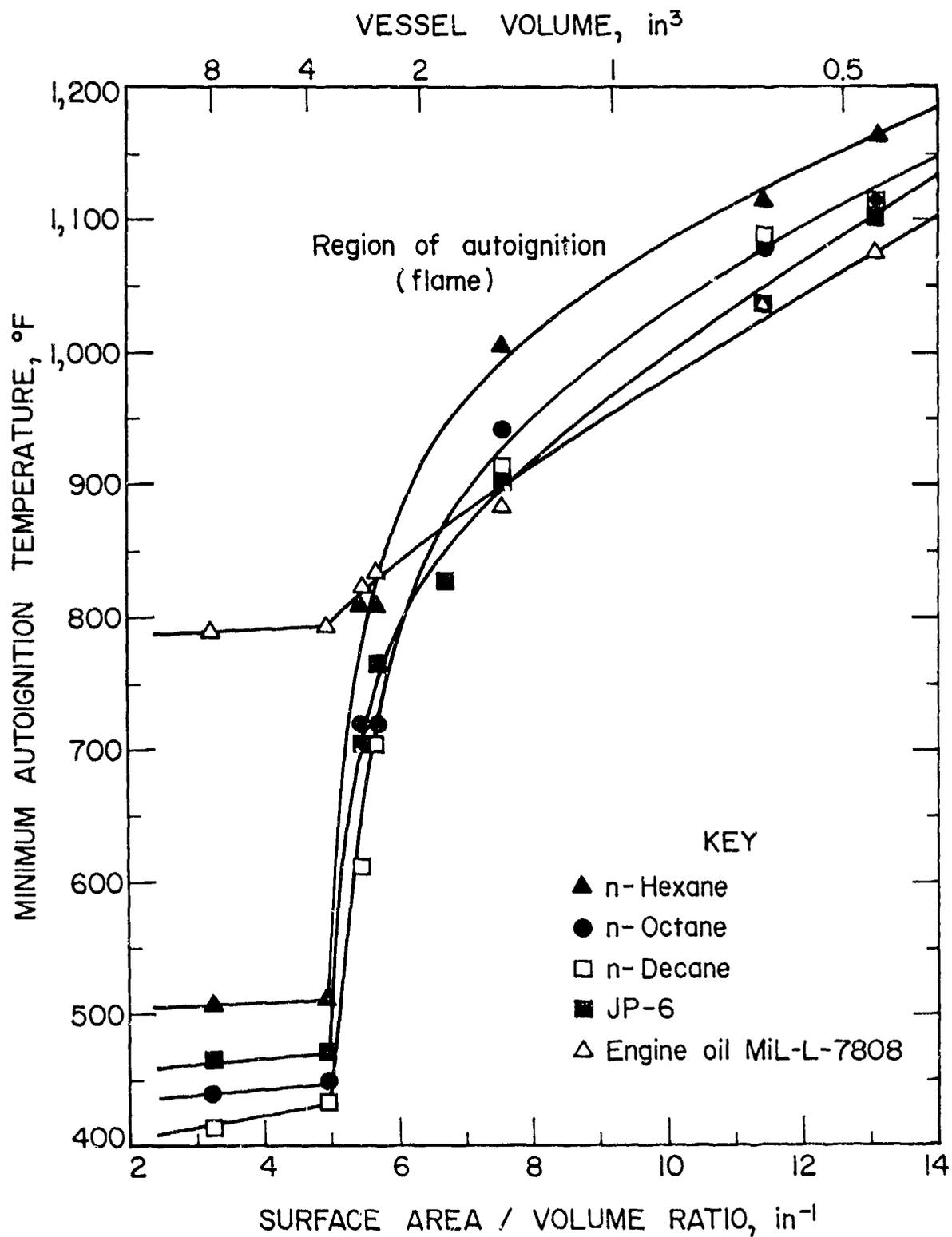


Figure 6. - Effect of vessel surface-volume ratio on minimum auto-ignition temperatures of various hydrocarbon fuels and engine oil in quiescent air (Pyrex cylinders 6-inches long).

paraffin with a  $L_{ave}$  of 9 and is typical of a low AIT fuel. Generally, increased branching of a paraffin increases the AIT, as shown in figure 7. This correlation is similar to that found when comparing the critical compression ratio of the fuels, which provides a measure of their "knock" tendency. Thus, low molecular weight and branched chain paraffins tend to have high critical compression ratios.

Aromatic hydrocarbons have relatively high resistance to oxidation and, therefore, have minimum AIT's that fall in the high temperature range ( $>700^{\circ}\text{F}$ ) of figure 7. The AIT of benzene ( $1040^{\circ}\text{F}$ ) is comparable to that of methane ( $1000^{\circ}\text{F}$ ) but that of a substituted benzene can be of the order of  $750^{\circ}\text{F}$ , depending upon the substituted group. Other combustibles such as ethers, alcohols and the unsaturated hydrocarbons tend to have lower ignition temperatures than their corresponding paraffins.

All jet aircraft fuels have minimum AIT's of less than  $500^{\circ}\text{F}$  in air (Table 2-A), whereas those for Avgas (100/130 or 115/145) are in the  $800^{\circ}$  to  $900^{\circ}\text{F}$  range. This indicates that the autoignition of jet fuels is largely controlled by the presence of paraffins having a  $L_{ave}$  of less than 5 (see figure 7), which is typical of any kerosene base fuel.

Most hydraulic fluids, engine oils and lubricating fluids have higher AIT's (Table 3-A) than the jet fuels; mineral oil-based fluids are an exception. The aromatic ether and aromatic phosphate ester fluids, as well as the halogenated hydrocarbons, are among the fluids having the highest AIT's and are followed by the halogenated and non-halogenated silicones. The fluids with an aliphatic base pose a greater autoignition hazard than those with an aromatic base. Table 2 indicates the approximate minimum AIT range of such fluids according to their chemical class (Ref. 13).

### 3. Effect of Mixture Pressure and Oxygen Concentration

Since the chemical reaction rate of a combustible mixture usually increases with increased pressure, its ignition temperature should vary inversely with pressure. For jet fuels, the minimum AIT's in air, as determined in the standard ASTM apparatus (200 cc), are nearly doubled when the pressure is decreased from 1 to  $1/2$  atmosphere (Table 3); paraffins such as n-pentane display a similar pressure effect. In comparison, the same trend cannot necessarily be the same for the aircraft hydraulic fluids or lubricants because of their widely different compositions. As shown in figure 8 (Ref. 13), the AIT of the MIL-O-5606 mineral oil is very sensitive to mixture pressure, whereas that of the chlorinated silicone fluid (MLO-53-466) is only slightly affected and those for the 5 other synthetic fluids are moderately affected by the pressure change,  $1/4$  to 1 atmosphere (Ref. 13). Generally, the pressure effect is less noticeable when the reaction chamber is sufficiently large, e.g. 5000 cc ( $305\text{ in}^3$ ), to minimize wall effects.

The above data were obtained at near zero injection pressure. If the fluids were injected into a heated container at high fluid injection

Table 2. - Approximate Minimum Autoignition Temperature Range of Various Classes of Hydraulic Fluids or Lubricants.

AIT Range °F	Fluid Class
1000-1200	{ Halogenated hydrocarbons Aromatic ethers or phosphate esters
800-900	{ Silicones Halogenated silicones
600-800	{ Water glycols Aliphatic silanes or silicate esters Hydrocarbon polyol esters Sebacate esters Mineral oils
400-550	{ Aliphatic phosphate esters Mineral oils

Table 3. - Minimum AIT's of Jet Fuels and Other Combustibles in Air at Various Pressures.

Combustible	Ignition criterion - visible flame		
	1/4 atm.	Minimum AIT, °F 1/2 atm.	1 atm.
JP-1	-	865	440
JP-3	-	840	460
JP-4	-	830	445
JP-6	1135	925	450
Avgas 100/130	-	1030	825
Avgas 115/145	-	1060	880
Kerosene	1100	865	≥445
n-Pentane	1145	935	500

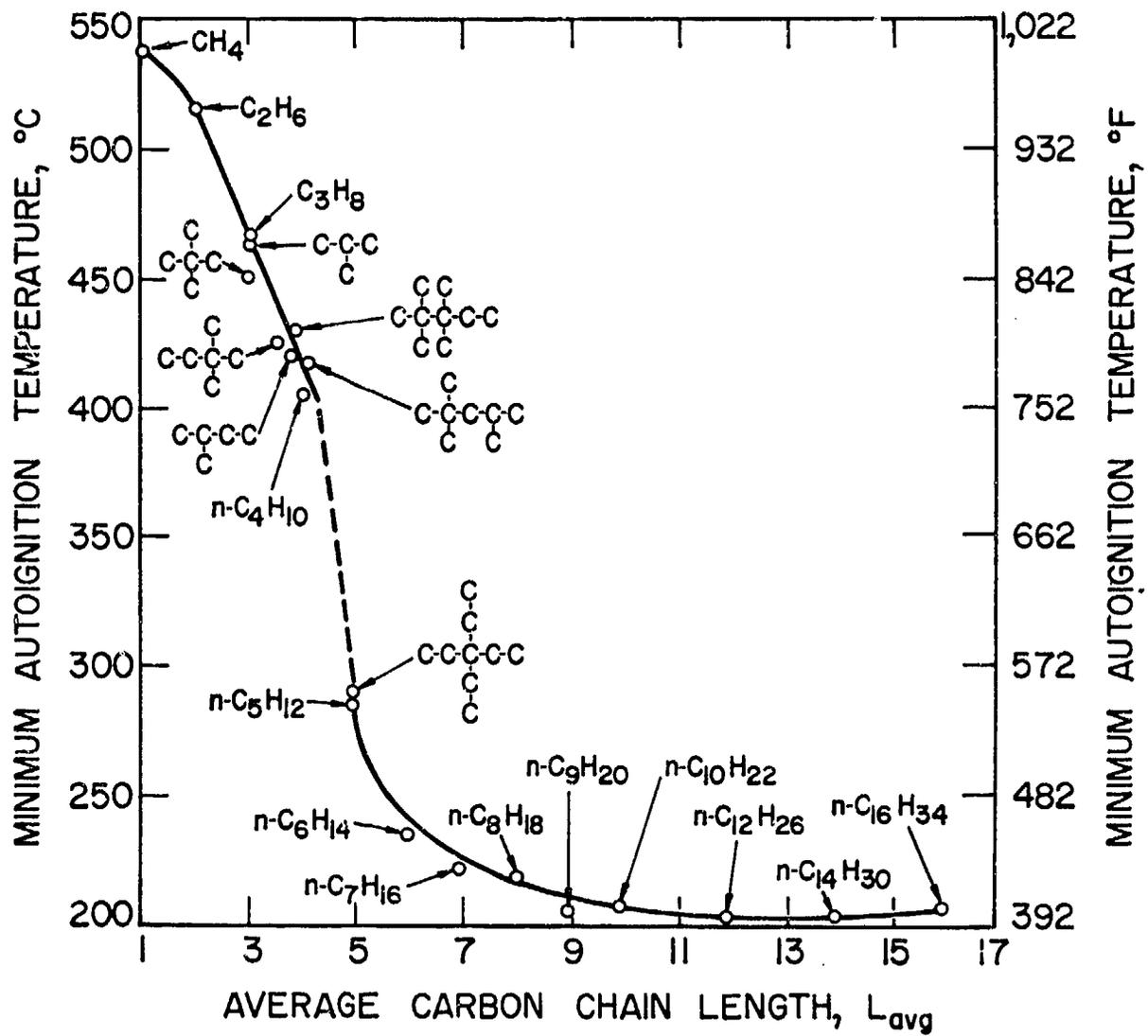


Figure 7. - Variation of minimum autoignition temperature of paraffinic hydrocarbons in air with average carbon chain length.

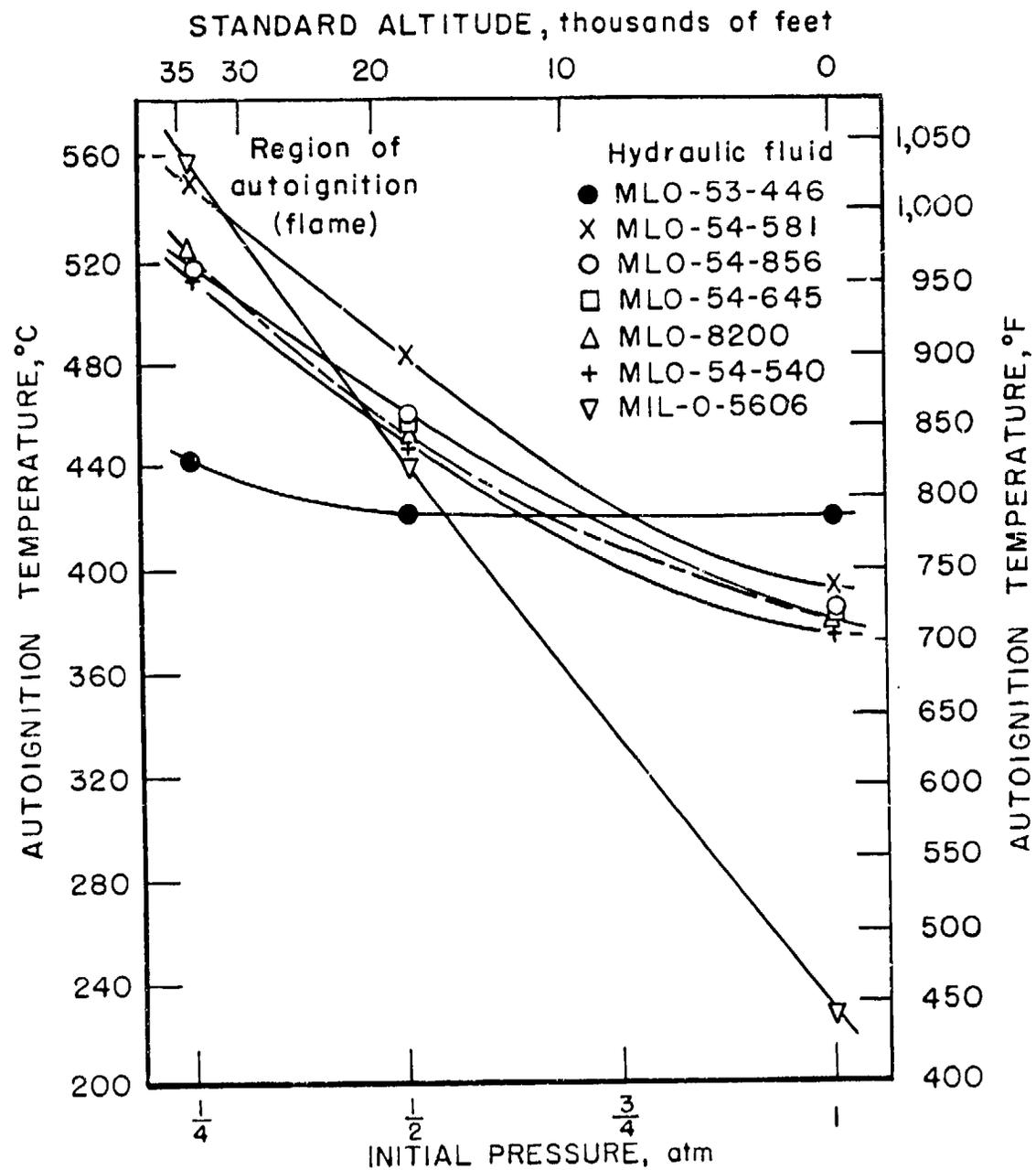


Figure 8. - Minimum autoignition temperatures of seven hydraulic fluids in air at various initial pressures.

pressures, they might ignite at lower temperatures than their minimum AIT's in quiescent air. Figure 9 shows the effect of injection pressure on the autoignition of the same hydraulic fluids and lubricants discussed above (Ref. 13). The AIT's of the mineral oil (MIL-H-5606) and chlorinated silicone (MLO-53-446) fluids were unaffected over the range of injection pressures, 0 to 5000 psig. However, the values for the dibasic acid ester (MLO-54-581) and silicate-type (MLO-54-856, MLO-8200, MLO-54-645, MLO-54-540) fluids decreased markedly when injection pressure was increased to 500 psig; above this injection pressure, the AIT's varied little. Similar results have been observed with the MIL-7808 engine oil, a sebacate-adipate diester fluid.

At elevated pressures, the ignition hazard is greater because AIT's are generally lower and the resultant explosion pressures are greater. For such lubricants as shown in figure 10 (Ref. 13), the AIT's decrease consistently with increasing pressure to at least 100 atmospheres, above which they tend to level off. It is also noted that the phosphate ester fluids fall into a noticeably higher temperature region of autoignition than the mineral oil and water glycol fluids. Similar data from a more recent study (Ref. 1) are shown in figure 11. Here, the critical pressure above which the AIT was essentially constant was about 300 atmospheres for the phosphate ester fluid (Houghto 1055) and the petroleum base fluid (Mobil DTE-103) and about 100 atmospheres for the dibasic acid ester fluid (MIL-L-7808). Differences in the AIT values in figures 10 and 11 for the Houghto 1055 fluid at atmospheric pressure can be partly attributed to differences in the ignition criterion (flame vs pressure rise). Over the pressure range where the AIT varies, the data in these figures appear to be consistent with the pressure effect predicted by thermal theory. For example, plots of  $\log P/T_{ign}$  vs  $1/T_{ign}$  for such data have been shown to be approximately linear (Ref. 12), which is predictable by equation 8.

As expected, the autoignition hazard in oxygen-enriched atmospheres is also greater for most combustibles. Table 4 compares the minimum AIT's of several combustibles in air and oxygen at atmospheric pressure. As a rule, combustibles having high AIT's in air display a greater effect of oxygen concentration than those having low AIT's. However, exceptions to this rule are found as illustrated by the data in figure 12 for various hydraulic fluids (Ref. 13). It is seen that the data for five of the fluids having the highest AIT's are noticeably affected by increasing oxygen concentration to about 50 percent, whereas the data for the other high AIT fluid (MLO-53-446) are unaffected over the entire range of oxygen concentrations; the results for the mineral oil (MIL-H-5606A) are typical for fluids having low AIT's. Increasing the oxygen concentration tends to have somewhat the same effect on AIT as increasing the injector pressure (Fig. 9).

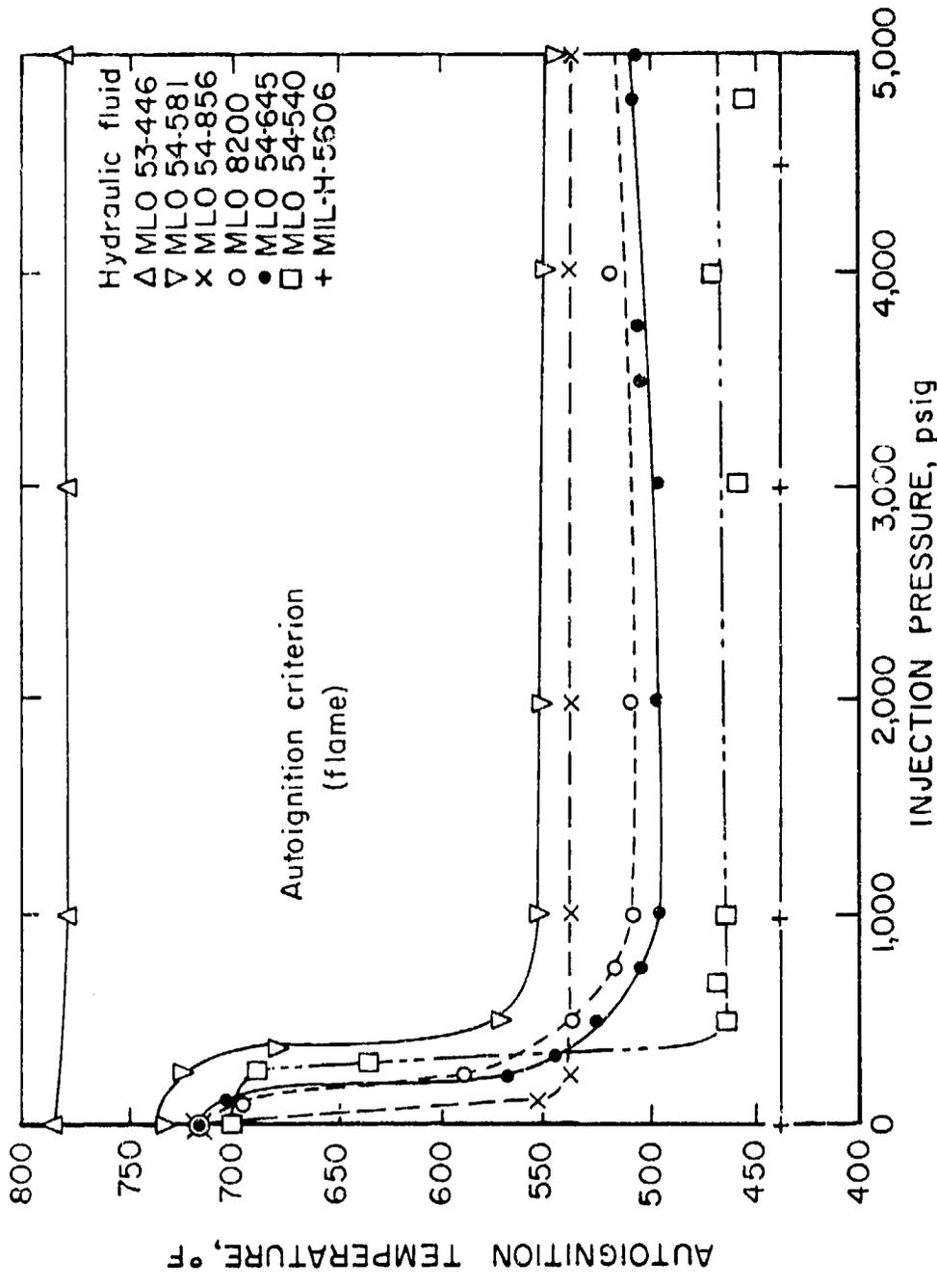


Figure 9. - Minimum autoignition temperatures of seven hydraulic fluids in air at one atmosphere pressure in contact with a Pyrex glass surface as a function of diesel injector pressure (200 cc Pyrex vessel).

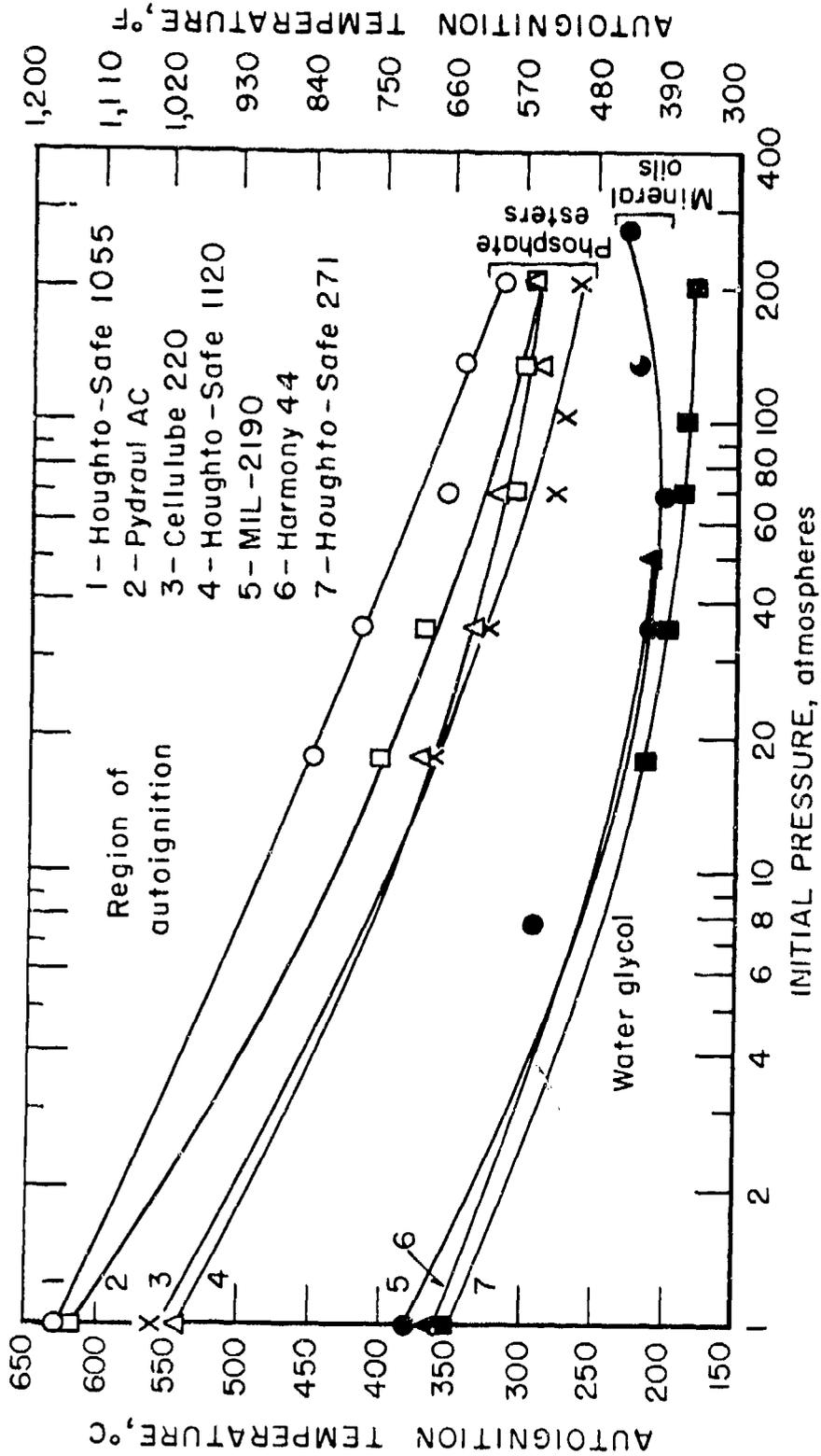


Figure 10. - Minimum autoignition temperatures of phosphate ester, mineral oil, and water-glycol lubricants in air at various initial pressures.

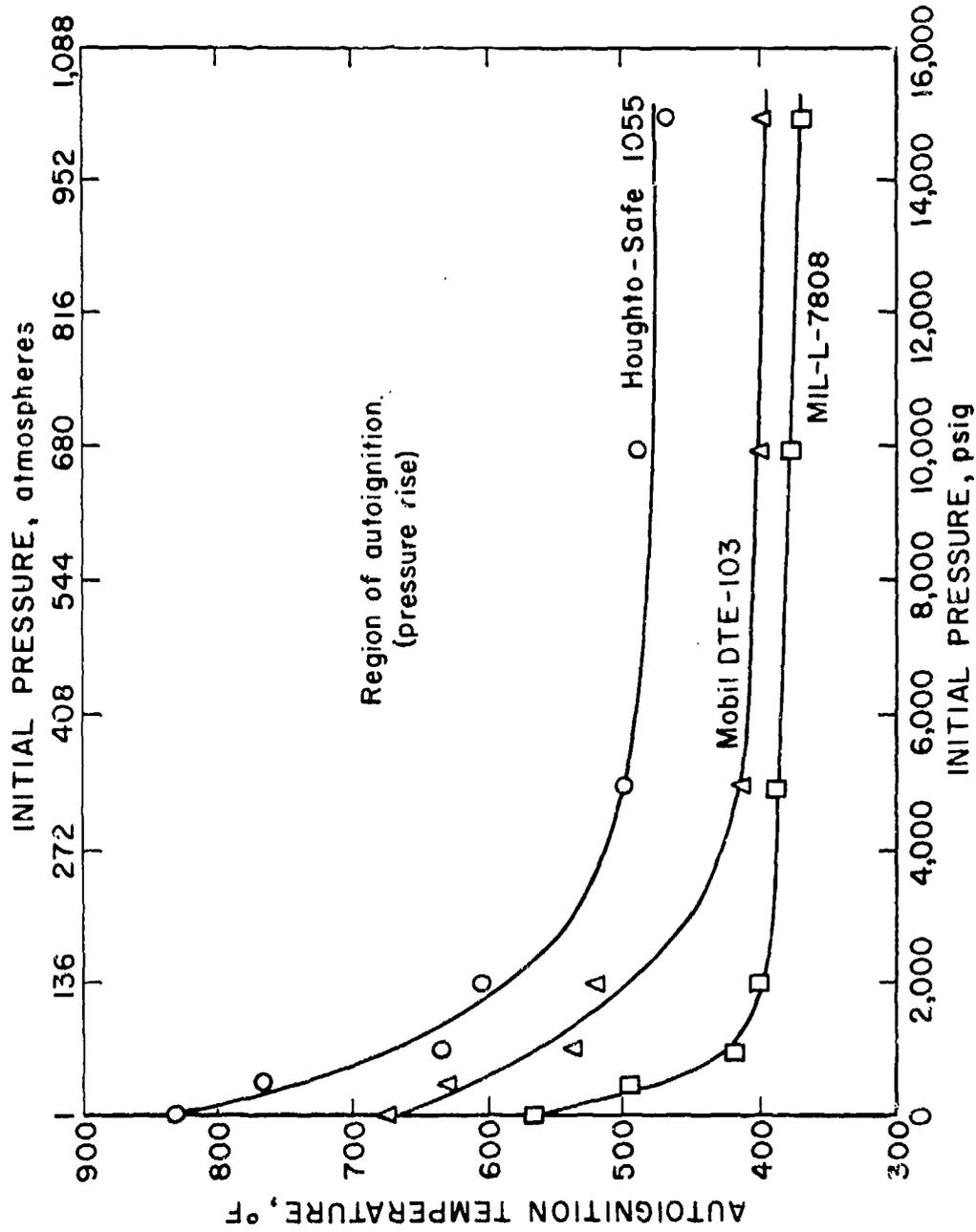


Figure 11. - Minimum autoignition temperatures of Houghto-Safe-1055, Mobil DTE-103, and MIL-L-7808 lubricants in air at various initial pressures.

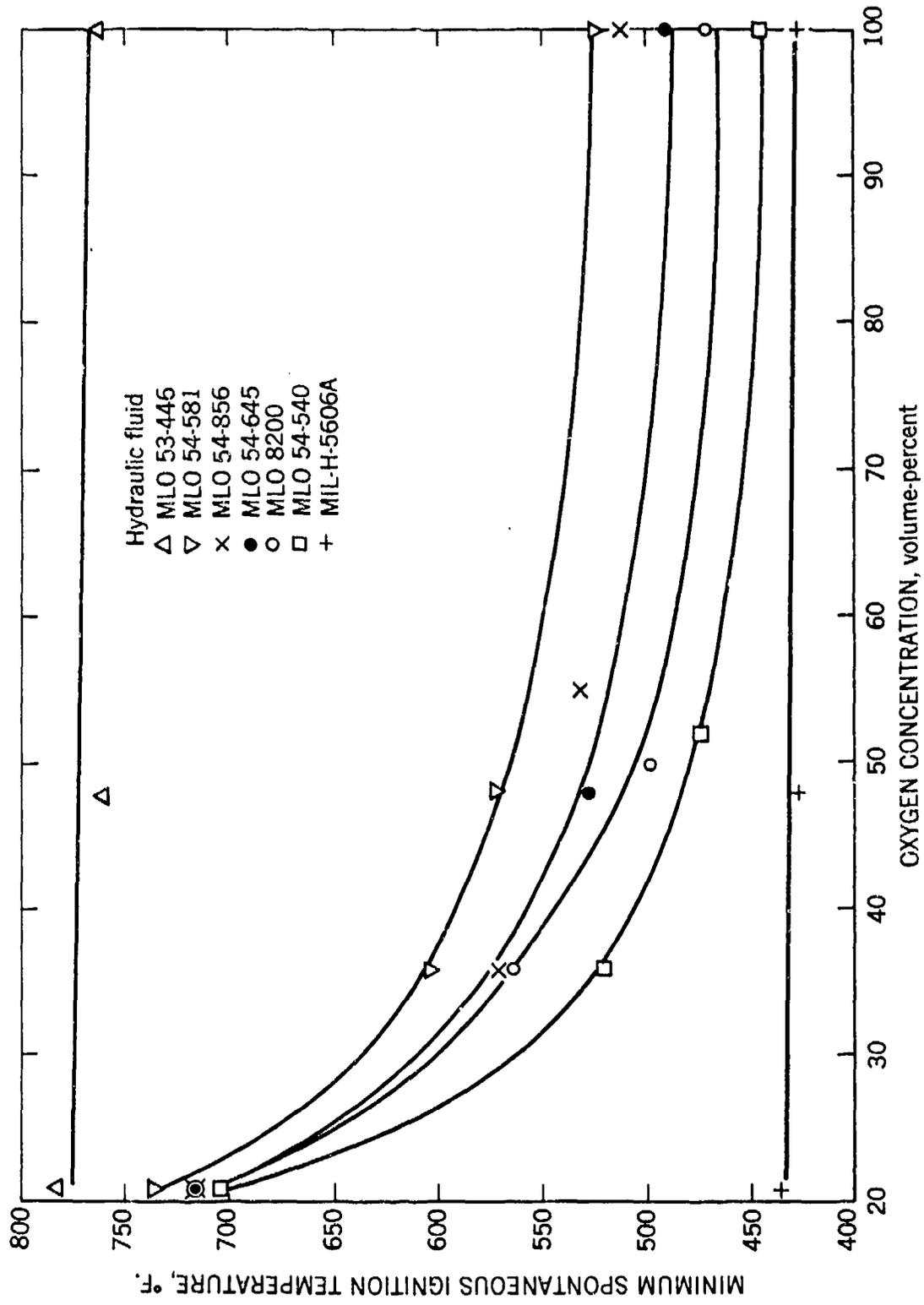


Figure 12. - Effect of oxygen concentration on the minimum auto-ignition temperature of seven hydraulic fluids in oxygen-nitrogen mixtures (1 atm) under static conditions.

Table 4. - Minimum AIT's of Several Combustibles in Air and Oxygen at Atmospheric Pressure.

Ignition criterion - visible flames					
Oxidant	n-Hexane	Minimum AIT, °F			
		n-Octane	JP-6	MIL-7808	MIL-H-5606
Air	462	440	470	755	437
Oxygen	428	400	432	518	428

Generally, the effect of oxygen concentration on AIT is greatest in atmospheres of low oxygen partial pressures. This is illustrated in figure 13 where data are shown for JP-6 in various O<sub>2</sub>-N<sub>2</sub> mixtures at reduced and elevated pressures (Ref. 14). These data were obtained in vessels of at least 12 in<sup>3</sup> capacity with flame as the ignition criterion and indicate that the critical P<sub>O2</sub> above which the AIT of JP-6 increases greatly is about 3 psia (≈0.2 atm); this critical P<sub>O2</sub> is typical for many hydrocarbon fuels. Figure 14 shows a similar correlation of AIT with P<sub>O2</sub> for various lubricants (Ref. 13). Here, pressure rise was the ignition criterion in most cases and the critical P<sub>O2</sub> varied with the lubricant composition; note that the data for the MIL-0-5606 fluid are very similar to those of the JP-6 jet fuel. In the application of these data, one cannot assume that all the ignitions observed at small P<sub>O2</sub> values will necessarily propagate a normal flame. The critical oxygen concentrations required for normal flame propagation of hydrocarbon vapor-air-nitrogen mixtures will generally be greater than 10 volume percent. Thus, ignitions at lower oxygen concentrations (<10 pct) will be more typical of cool flame reactions in which only a small fraction of the available enthalpy is converted to heat.

#### 4. Variation of Ignition Delay with Temperature

Ignition delay is the total time associated with the chemical and physical processes that occur between the instant of fuel exposure to heated surroundings and the time of ignition. Whether chemical or physical processes are controlling is frequently determined by the temperature of the reacting system. In any event, the variation of ignition delay with temperature can be useful in predicting the AIT of combustible liquids under static or dynamic conditions.

According to equation 10 of the Semenov thermal theory, a plot of the logarithm of ignition delay ( $\tau$ ) vs the reciprocal of temperature (1/T) should be linear and the slope should indicate the nature of the controlling process. However, this linear relationship usually holds only over a limited

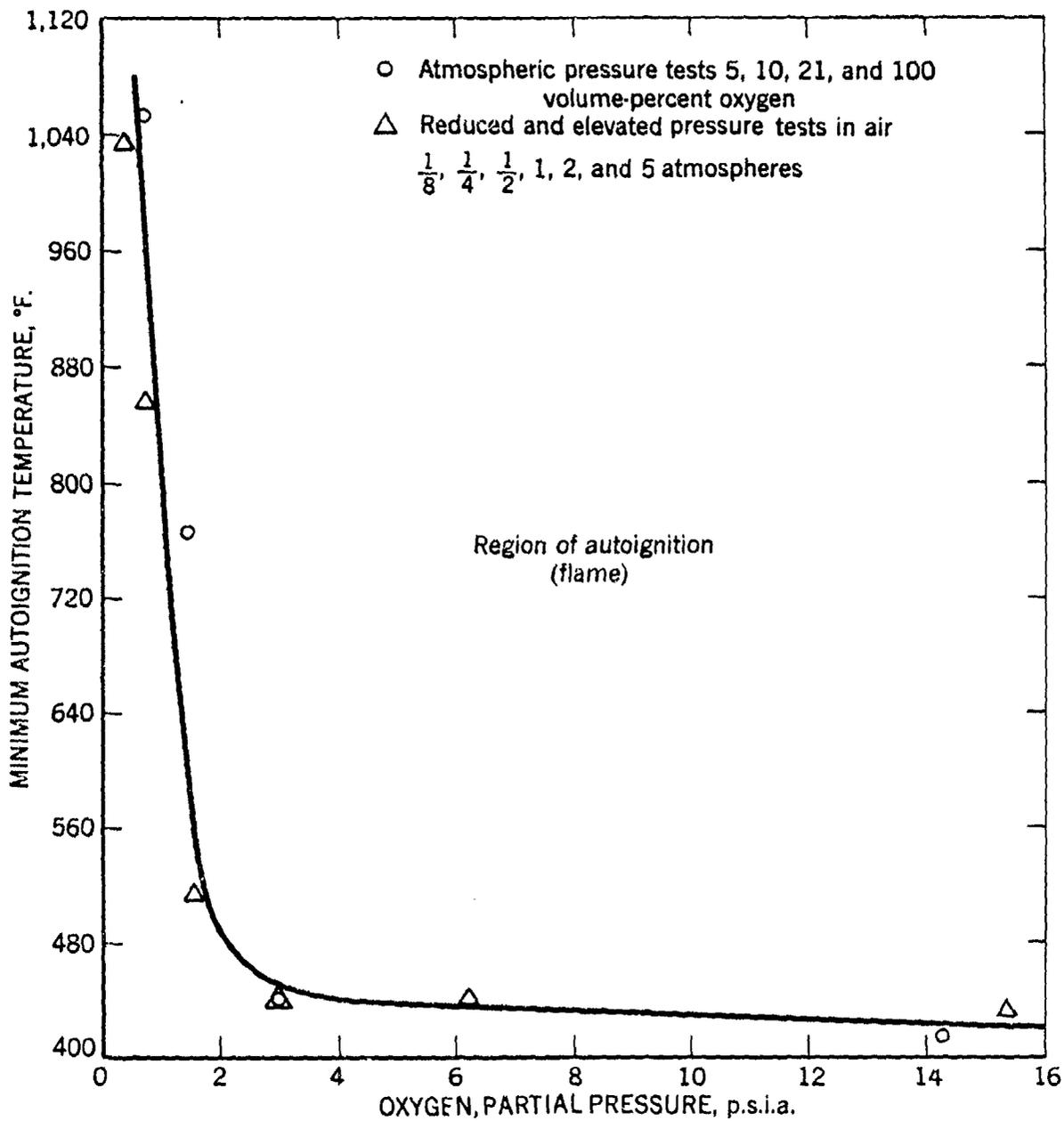


Figure 13. - Effect of oxygen partial pressure on the minimum auto-ignition temperature of JP-6 fuel vapor-oxygen nitrogen mixtures at various total pressures under static conditions.

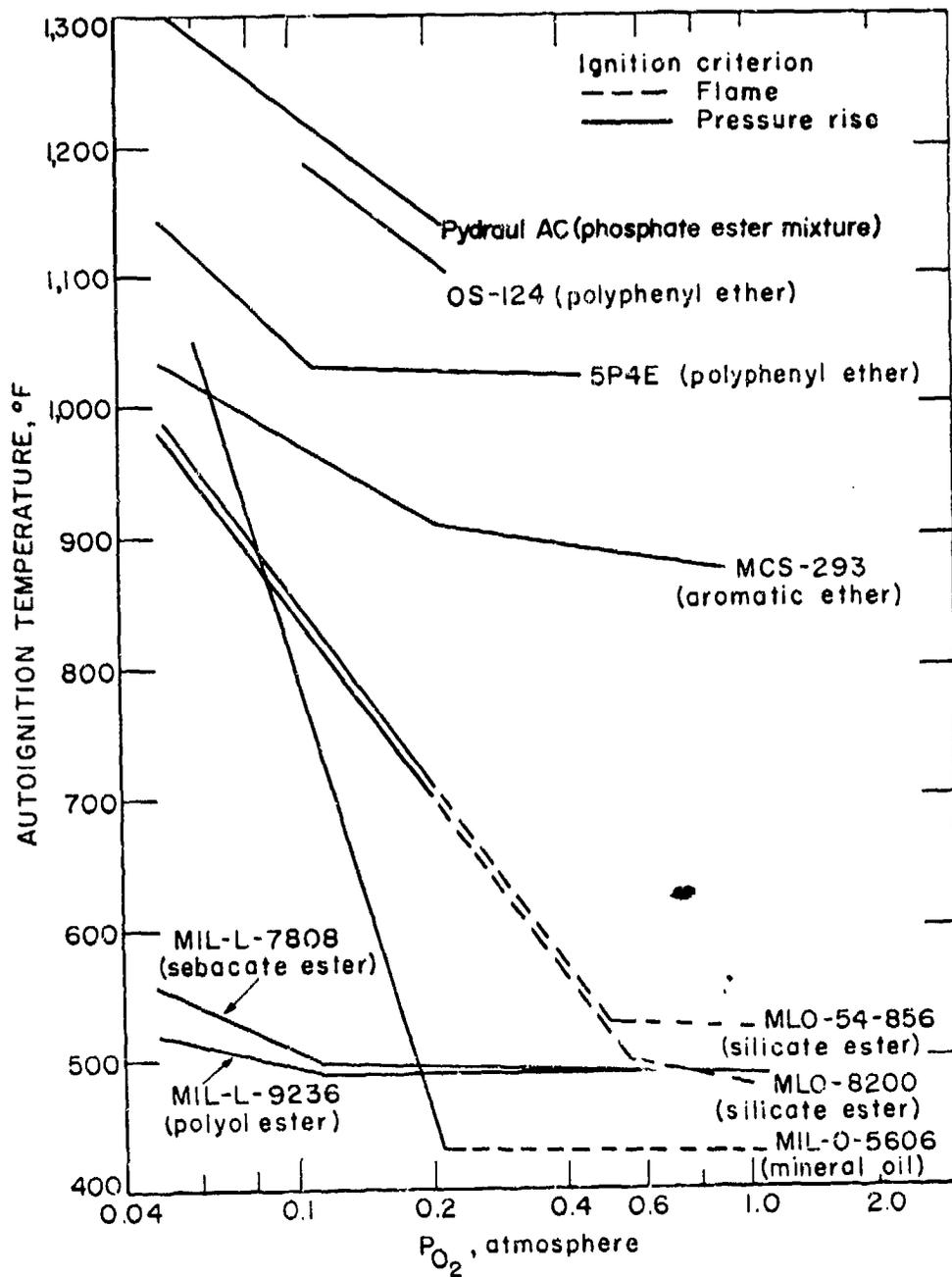


Figure 14. - Variation of minimum autoignition temperature with oxygen partial pressure ( $P_{O_2}$ ) for various lubricants.

temperature range since the reaction mechanism tends to change with temperature. For example, the semi-log plots in figure 15 (Ref. 14) for the 1 atmosphere data are linear only for the JP-4 jet fuel over the entire range of test temperatures; these data were obtained in quiescent air in a 13 in<sup>3</sup> Erlenmeyer flask. The data for the JP-4 fuel below 600 F and JP-6 fuel below 550°F can be expressed as follows:

$$\ln \tau = 34,000/T - 32.2 \quad \text{JP-4 (21\% O}_2\text{)} \quad (22)$$

$$\ln \tau = 36,000/T - 34.65 \quad \text{JP-6 (21\% O}_2\text{)} \quad (23)$$

where  $\tau$  is in seconds and  $T$  is in °R. Comparable temperature coefficients of ignition delay are found for JP-150, kerosene, and similar hydrocarbon fuels in low temperature autoignitions and are characteristic of a chemical controlling process, such as oxidation.

At a fixed temperature, ignitions delays are expected to increase with decreasing pressure (see fig. 15) but the available data are meager for aircraft fuels. Similarly, they should be greater when the oxygen concentration is decreased. The data shown in figure 16 for n-octane, n-hexane, JP-6, and the MIL-L-7808 engine oil are consistent in this respect (Ref. 10). However, the effect of fuel composition on ignition delay appears to be negligible at reduced O<sub>2</sub> concentrations, that is, at high temperatures. For example, the 10 percent O<sub>2</sub> data for all combustibles in figure 16 can be approximated by the following expression:

$$\ln \tau = 30,700/T - 20.7 \quad \text{All 4 fuels (10\% O}_2\text{)} \quad (24)$$

where  $\tau$  is in seconds and  $T$  in °R. In comparison, the 100 percent O<sub>2</sub> data varied as follows:

$$\ln \tau = 30,700/T - 29.6 \quad \text{Hexane (100\% O}_2\text{)} \quad (25)$$

$$\ln \tau = 30,300/T - 27.8 \quad \text{Octane (100\% O}_2\text{)} \quad (26)$$

$$\ln \tau = 36,500/T - 35.5 \quad \text{JP-6 (100\% O}_2\text{)} \quad (27)$$

$$\ln \tau = 72,000/T - 69.4 \quad \text{MIL-L-7808 (100\% O}_2\text{)} \quad (28)$$

where  $T$  is less than 1020°R(560°F). The AIT of each combustible was reduced by at least 1/2 by increasing the O<sub>2</sub> concentration from 5 percent to 100 percent.

If a fuel leakage occurs in the engine compartment of an aircraft, the fuel contact time with a heated surface can be relatively short and, therefore, AIT's are of interest under flow conditions. Such data are included in figure 17 for the JP-6 fuel on a semi-log plot where the ignition delays were obtained from autoignition in heated air streams (Ref. 14); air velocity was between 20 and 160 ft/sec. It is seen that relatively high temperatures ( $\leq 1150^\circ\text{F}$ ) are required for ignitions under such flow conditions and that the

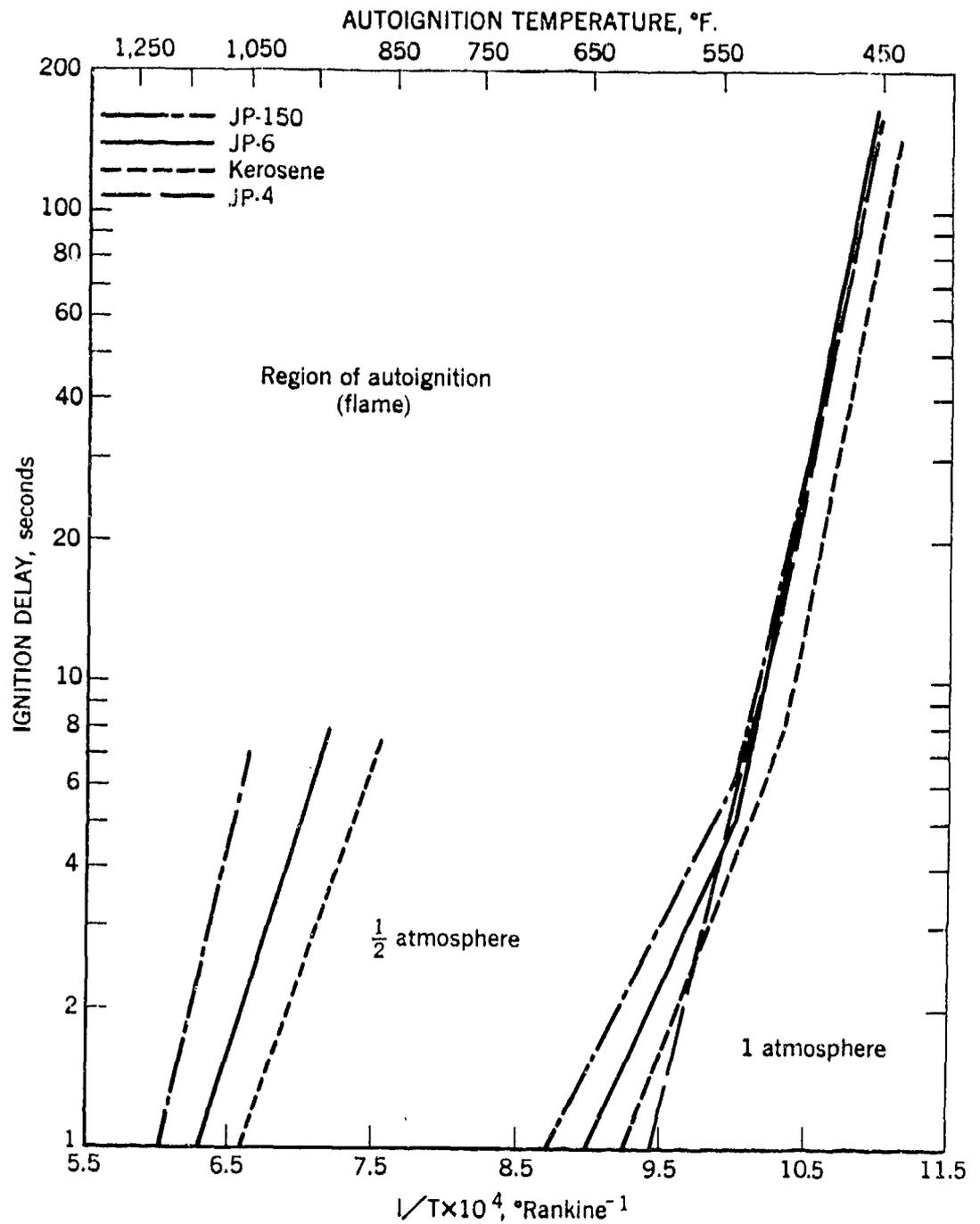


Figure 15. - Variation of ignition delay with reciprocal temperature in autoignition of four aircraft fuels in stagnant air at 1/2 and 1 atmosphere.

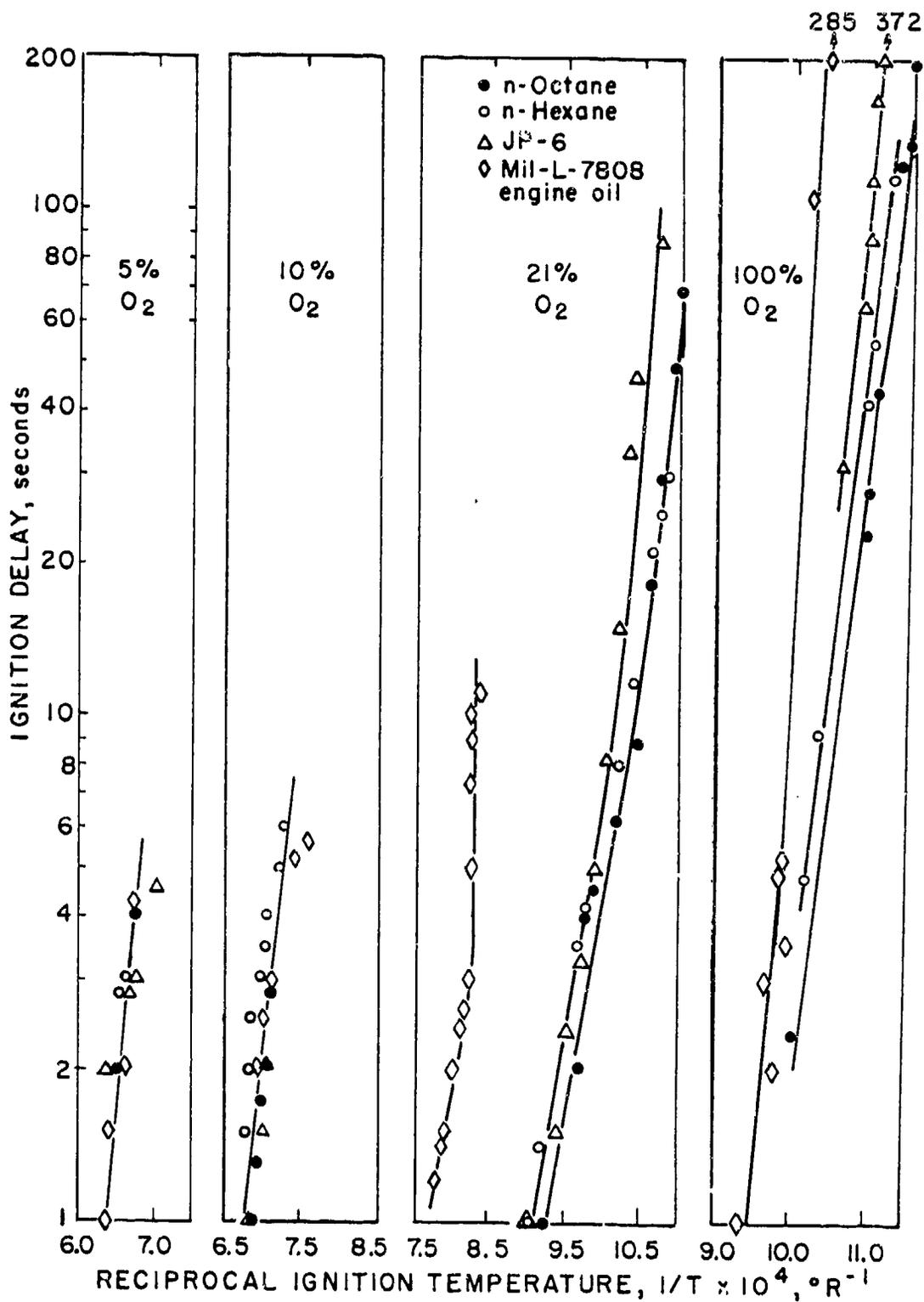


Figure 16. - Variation of ignition delay with reciprocal autoignition temperature for n-Octane, n-Hexane, JP-6 fuel, and MIL-L-7808 engine oil in various oxygen-nitrogen atmospheres. (13 in<sup>3</sup> spherical Pyrex vessel).

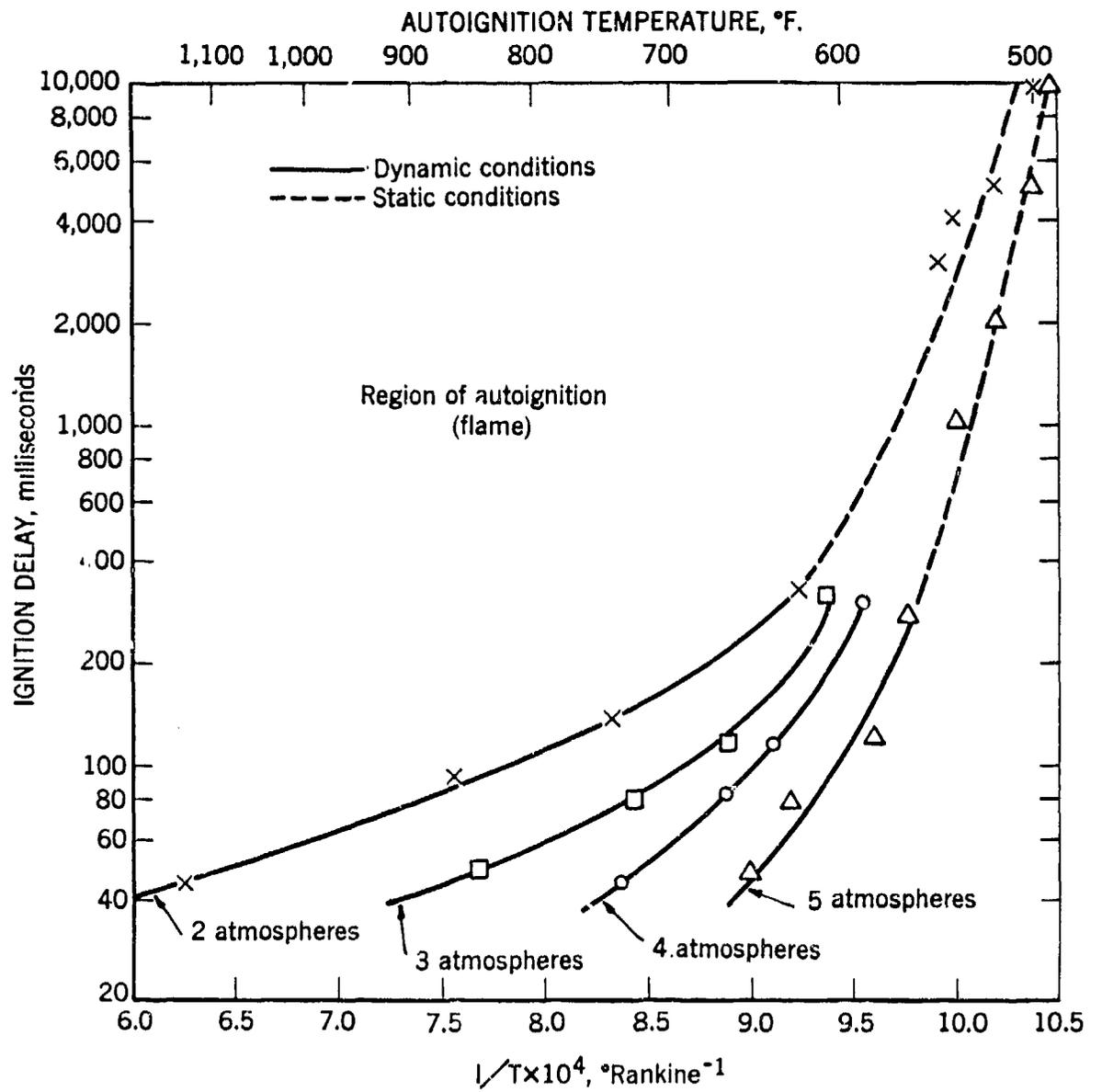


Figure 17. - Variation of ignition delay with reciprocal temperature in autoignition at JP-6 fuel in air under static and dynamic conditions.

ignition delays are of the order of milliseconds. Also, with increasing pressure, the ignition delays decrease and their temperature dependence becomes more pronounced, tending to approach that observed under static conditions below 600°F. In the high temperature region (700°-1150°F), the following expressions may be used to predict the variation of ignition delay ( $\tau$ , ms) with temperature ( $T$ , °R) under static and dynamic conditions at 1 or 2 atmosphere pressures:

$$\ln \tau = 4100/T + 3.13 \quad \text{Static (1 atm)} \quad (29)$$

$$\ln \tau = 6000/T - 0.04 \quad \text{Dynamic (2 atm)} \quad (30)$$

Since  $\tau$  is inversely proportional to air velocity, such data can be used to predict the air flow requirements to prevent ignition of flowing JP-6 fuel vapor-air mixtures in heated compartments. The JP-4 fuel would be expected to give similar results.

### IGNITION BY OTHER HOT SURFACE SOURCES

#### A. Metal Target Ignition Temperature

In many situations, ignition may result when the fuel vapor-air mixture is exposed to a relatively small heated surface which heats the mixture non-uniformly. As in heated vessel ignitions, the ignition temperatures can vary greatly with the size or surface area of the heat source. Figure 18 (Ref. 1) shows that the ignition temperatures of 5 aircraft fuels or fluids are at least 1000°F when the combustibles are injected upon a 2 inch diameter by 24 inch long steel target under low velocity conditions (<9 ft/sec). These ignition temperatures would be much higher under the flow conditions possible in an aircraft engine bay. However, they also decrease with increasing target diameter and tend to approximate ignition temperatures obtained with such fuels in heated tubes at comparable fuel contact times (Figure 19). Heated metal configurations which tend to trap or confine the fuel, thus increasing the fuel contact time, can be expected produce ignitions at lower temperatures than in figure 19.

Table 5 compares the ignition temperatures of the 5 aircraft fluids in quiescent air with a heated steel target and a heated glass vessel; flash points of the fluids are also listed to indicate fluid volatility.

#### B. Wire or Rod Ignition Temperatures

Ignitions by a heated wire or rod depend upon similar factors as described above for the cylindrical targets and, therefore, require higher temperatures. Generally, the wire radius required for ignition is an exponential function of temperature, as predicted by thermal theory. Equations 31 and 32 describe the relationship between the wire radius ( $r$ , inch) and ignition temperature ( $T$ , °R) for JP-6 fuel and MIL-L-7808 engine oil (optimum vapor-air mixtures) under near-stagnant conditions (Ref. 10).

Table 5. - Comparison of Minimum Ignition Temperatures of 5 Aircraft Fluids in Quiescent Air with a Heated Steel Target and a Heated Glass Vessel.

Aircraft Fluid	Flash Point °F	Ignition Temperature	
		Heated Target <sup>a/</sup> °F	Heated Vessel <sup>b/</sup> °F
JP-4	0	920	445
JP-8	115	900	435
MIL-H-5606	195	960	437
MIL-H-83282	340	1080	670
HIL-L-7808	437	1010	728

a/ Ignition with a 4-inch diameter cylindrical target.

b/ Ignition with a 13 in<sup>3</sup> vessel.

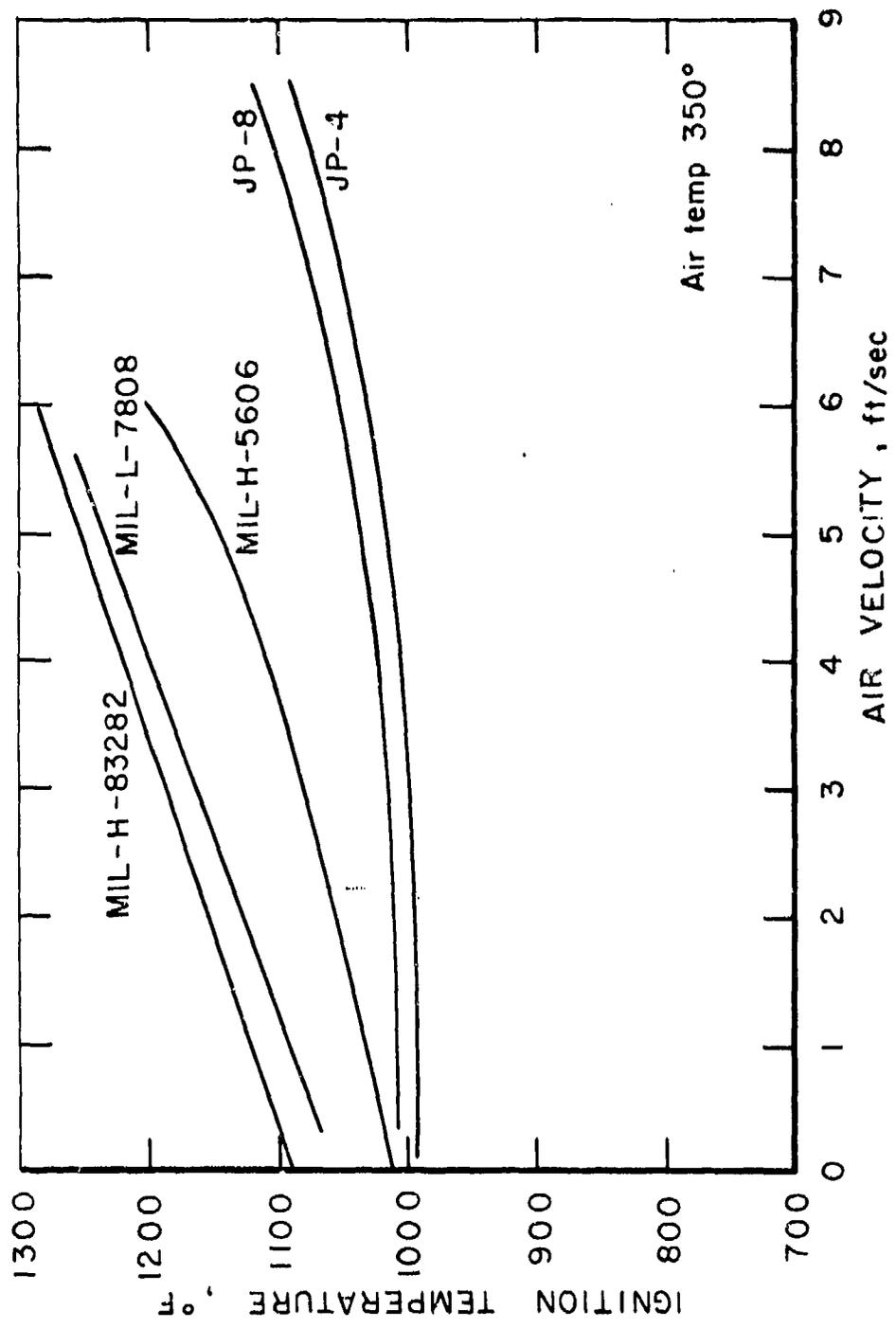


Figure 18. - Comparison of ignition temperatures of aircraft fuels or fluids at various air velocities with a heated 2-inch diameter by 24-inch long steel target.

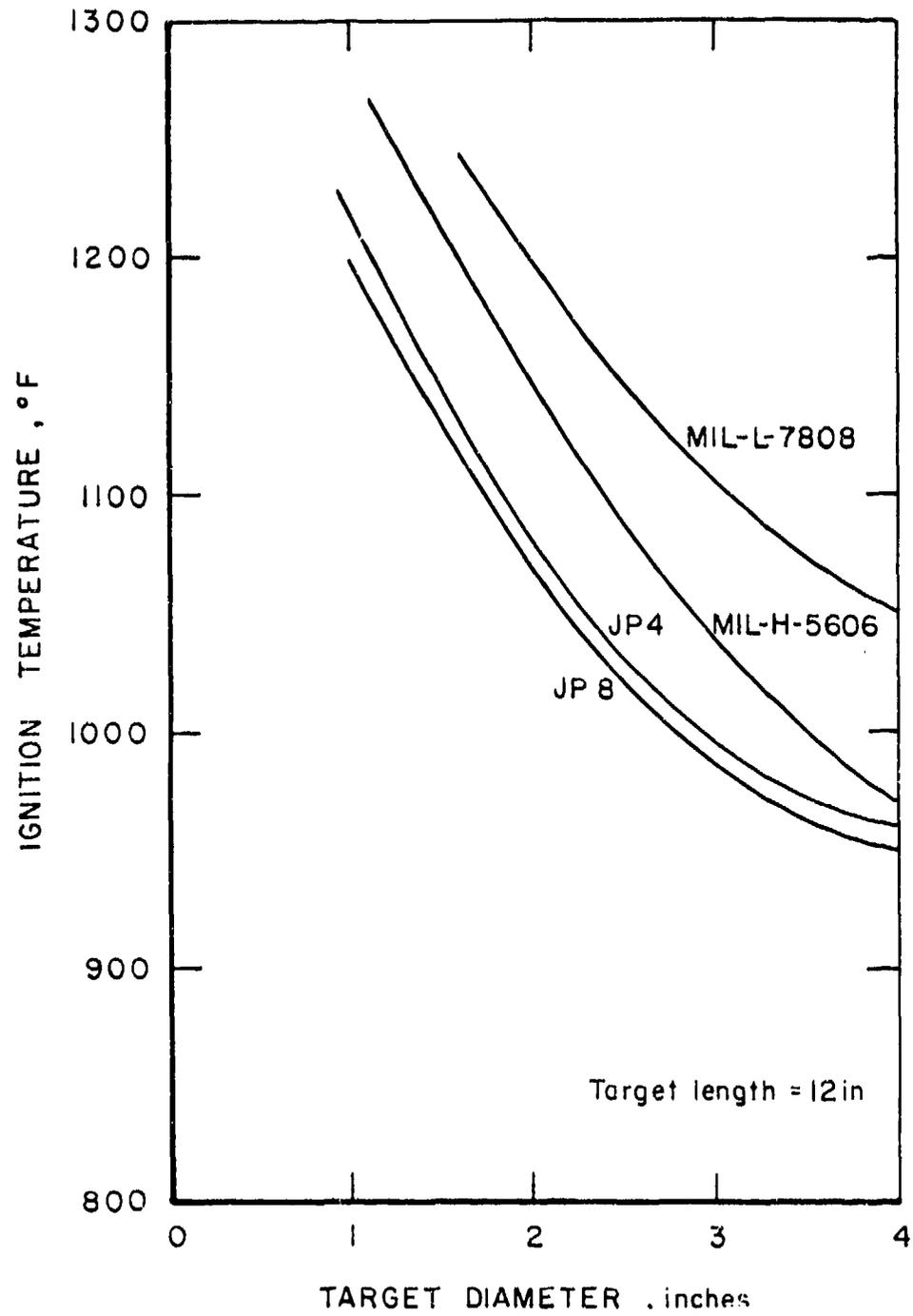


Figure 19. - Ignition temperature vs target diameter for various aircraft fuels or fluids at an air velocity of 2 ft/sec and air temperature of 80°F.

$$\ln r = 21000/T - 13.50 \quad \text{JP-6} \quad (31)$$

$$\ln r = 25800/T - 18.53 \quad \text{MIL-L-7808} \quad (32)$$

where  $r$  is between 0.008 and 0.4 inch; nichrome wires were used.

Such ignition temperatures correlate best with the surface area of the heat source when the length and geometry of the source are not fixed (Fig. 20). Figure 20 compares data obtained at optimum fuel-air ratios with the nichrome wires or rods and heated glass vessels. It is seen that ignition of the engine oil involved predominantly high temperature reactions over the range of heat source dimensions used. In comparison, the JP-6 jet fuel is capable of "cool" and "hot" flame reactions at relatively low temperatures, which accounts in part for the transition in the JP-6 curve but not in the curve for the engine oil; the data for n-hexane, n-octane and n-decane also displayed the same trend as JP-6. For each combustible, the ignition temperature ( $T$ , °F) variation with heat source surface area ( $A$ , in<sup>2</sup>) is

$$T = 1430 - 201 \ln A \quad \text{JP-6; } 0.1 < A < 11 \quad (33)$$

$$T = 1175 - 115 \ln A \quad \text{MIL-L-7808; } 0.1 < A < 29 \quad (34)$$

$$T = 1415 - 177 \ln A \quad \text{Hexane; } 0.1 < A < 11 \quad (35)$$

$$T = 1365 - 173 \ln A \quad \text{Octane; } 0.1 < A < 11 \quad (36)$$

$$T = 1340 - 161 \ln A \quad \text{Decane; } 0.1 < A < 11 \quad (37)$$

The wire ignition temperatures of these combustibles vary only slightly with moderate changes in the O<sub>2</sub> concentration (Ref. 10).

### C. Frictional Ignition

Frictional sparks and impact sparks are well recognized as possible sources of ignition when metals or other hard substances come into contact forcibly with each other. The sparks are abraded particles that have been heated to incandescence by the conversion of the frictional or impact energy into heat and by any oxidation or burning of the hot particles. The incendiarity of such localized heat sources will depend primarily upon the thermal energy imparted to the abraded particles and their chemical reactivity; material properties such as hardness, melting point, heat conductivity and specific heat are important in the formation of these sparks. Frictional sparks generated by hand tools striking a metal surface may be considered less incendiary than those possible with powered tools or machines. Hot spots are also produced at the point of origin of the frictional and impact sparks and may be sufficient alone to cause ignition of a flammable gas mixture in some instances.

Aluminum materials appear to have a low frictional spark ignition hazard in an aircraft crash situation. In simulated full-scale drag tests on concrete and asphalt runways, Campbell (Ref. 16) reported

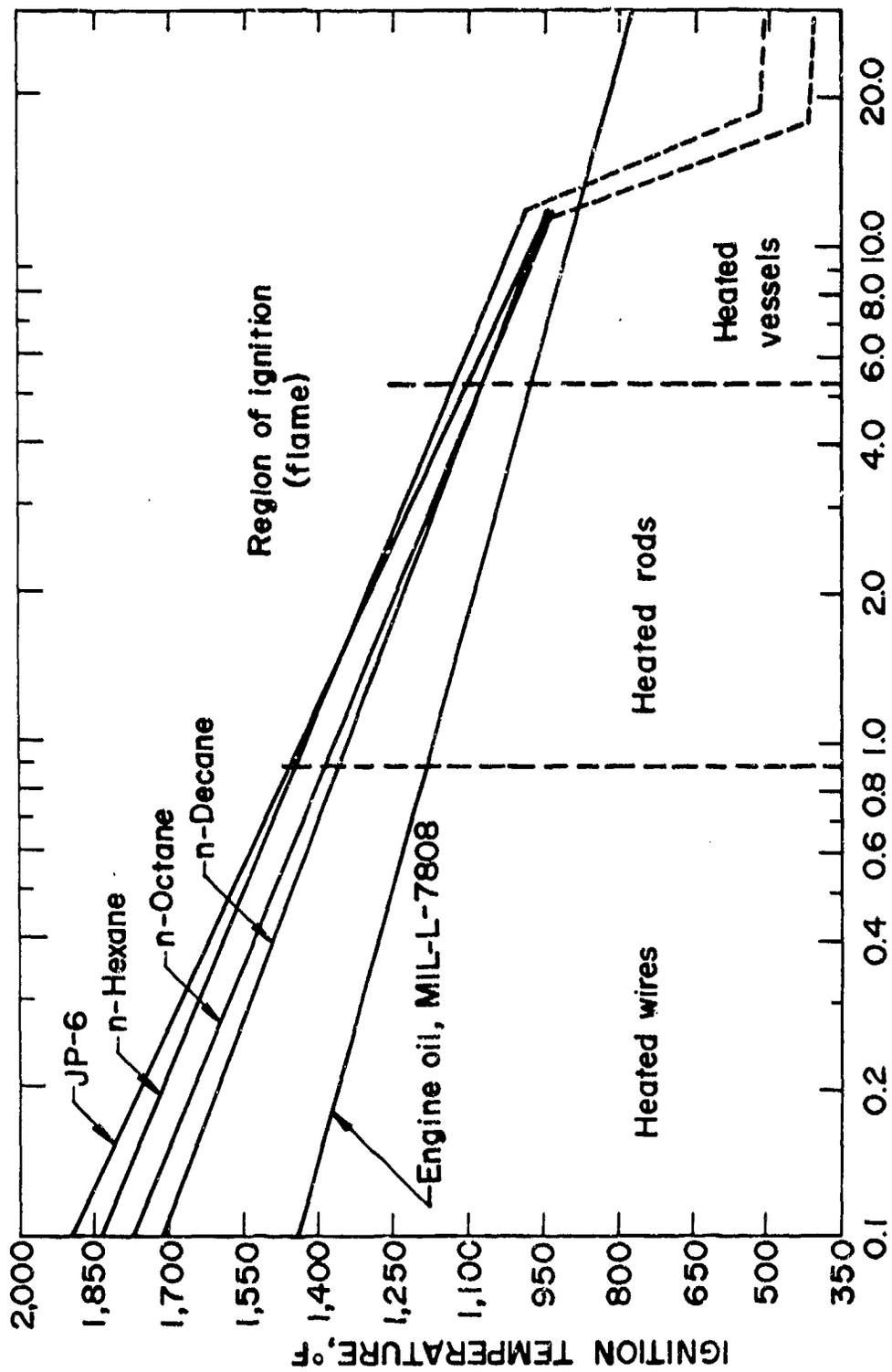


Figure 20. - Hot surface ignition temperature as a function of the surface area of the heat source for various hydrocarbon fuels and an engine oil in near-stagnant air.

no ignitions of fuel sprays with an aluminum alloy (2024-T3) at bearing pressures up to 1455 psi and slide speeds up to 40 miles per hour; the fuels were gasoline, JP-4, kerosene and preheated SAE No. 5 lubricating oil. In comparison, frictional spark ignitions were readily obtained with a titanium alloy (Ti-100A), magnesium alloy (FSI), chrome-molybdenum steel (SAE-4130) and stainless steel (AISI-347) at bearing pressures as low as 20 to 50 psi and slide speeds below 50 miles per hour; titanium ignited the fuel mists most readily.

The results of other investigators, as summarized in reference 16, show that the impact ignition hazard is great for titanium on steel and for light metal alloys on rusted steel. The probability of impact ignition for aluminum alloys on rusted steel appears to vary linearly with the magnesium content of the alloy and was about 9% at a 5% (weight) magnesium concentration in a drop weight test with an 8.2% (volume) methane-air mixture.

#### D. Incendiary Ignitions

Aircraft fuel tank ignitions by incendiary particles are of particular concern wherever gun firings may be encountered, such as in an hostile environment. The energy flux provided by this type of heat source is far greater than that of most hot surface sources. The burning incendiary powder can produce temperatures of the order of 4000°F or more, similar to those of an exploding wire such as Pyrofuze. Thus, incendiary ignitions of optimum fuel vapor-air mixtures would usually be expected to have extremely short ignition delays, e.g. a few milliseconds or even less. Furthermore, the ignitions can occur at multiple sites in a fuel tank, depending upon the extent that the incendiary particles are dispersed.

Because of the excessive energy provided by incendiary sources, they are capable of producing ignitions in fuel tanks under liquid fuel temperature conditions which normally would not be conducive to the formation of flammable mixtures. For example, Manheim (Ref. 17) obtained ignitions with JP-8 jet fuel in vertical gun firings (50 caliber API) through a 92 gallon tank at fuel temperatures as low as 10°F; JP-8 has a flash point of 115°F. Also, similar ignitions occurred with the low flash point JP-4 fuel (0°F) at fuel temperatures as high as 130°F; although the upper temperature limit of flammability of this fuel (~70°F) appeared to be greatly extended, the observed effect is only partly due to the incendiary source because equilibrium fuel vapor concentrations were not attained throughout the test chamber. Figure 21 (Ref. 17) shows typical pressure histories that were obtained in the above gun firing tests at two initial pressures and 70°F; the muzzle velocity with the 50 caliber API ammunition was 2800 ft/sec.

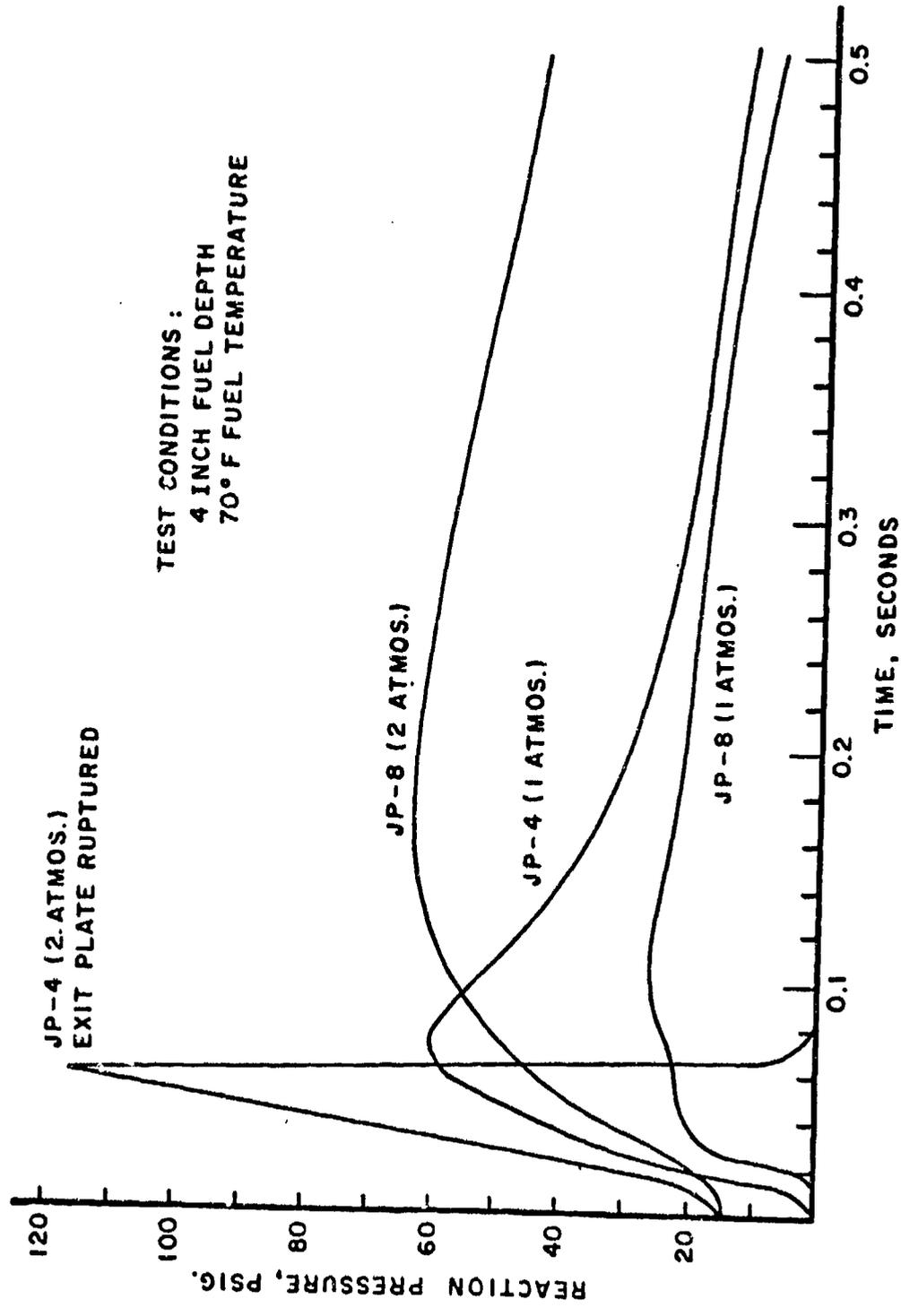


Figure 21. Typical pressure-time profiles from incendiary firings into a 92 gallon fuel tank containing JP-4 and JP-8 jet fuels. (50 caliber API, type M-8, ammunition).

To quench incendiary ignitions of fuel vapor-air mixtures, noticeably more quenchant or inert is necessary than in ignitions by heated wires, heated vessels and electrical sparks. As noted in figure 22 (Ref. 18) nearly 10% Halon 1301 ( $\text{CF}_3\text{Br}$ ) was required to reduce the pressure rise rates to less than 50 psi/sec in fuel tank ignitions with an IM-11 incendiary ammunition; the pressure rises in the 75 gallon fuel tank at these critical conditions were of the order of 1 to 3 psi. With an electrical spark source, the same fuel vapor-air mixtures could be inerted with about 1/2 of the Halon concentration required in the incendiary ignition.

## IGNITION BY HOT GASES

### A. Hot Gas Jet Ignition Temperatures

Ignition by a jet of hot gas is unique in that wall or surface effects are usually not a factor. Such ignitions may occur as a result of an oil seal failure or a pin hole leak in lubricating systems and are also of interest in designing flame arrestors and explosion proof equipment. These ignitions can involve jets of heated air or inert gas that are discharged into the fuel or fuel-air mixture, or jets of heated fuel into an air atmosphere. The ignition temperatures are not greatly sensitive to fuel stoichiometry and, therefore vary only slightly when the jet and outside mixture components are interchanged. However, they are noticeably dependent upon jet diameter.

Similar to hot surface ignition temperatures, the hot gas ignition temperatures increase with decreasing diameter of the heat source. Figures 23 and 24 compare such data for 3 paraffins and 2 aircraft fuels or fluids, respectively (Ref. 10), under optimum flow conditions for ignition. It is important to note that although the MIL-L-7808 engine oil has a relatively high minimum AIT in air, its ignition temperatures with heated air jets, wires, rods or vessels are lower than those for JP-6 fuel over most of the range of heat source dimensions investigated. This behavior is not unexpected since the jet fuel has the greater thermal stability; the paraffinic hydrocarbons also behave as the JP-6 fuel for the same reason. Figures 23 and 24 also show that any comparison of ignition temperatures can not ignore the size of the heat source; furthermore, one must recognize that heated vessel ignition temperatures will tend to increase drastically when the vessel diameter is close to the ignition quenching diameter ( $\sim 0.1$  to 0.15 inch for most hydrocarbons). At a given heat source diameter, hot gas ignition temperatures may be considered as greater than hot surface ignition temperatures in evaluating the ignitability hazard of aircraft fuels or fluids. If hydrogen is the fuel in question, little difference in such temperatures should be expected.

### B. Shock and Compression Ignition Temperatures

The rapid pressurization that is encountered in reciprocating engines, air compressors, or in high pressure systems where quick-

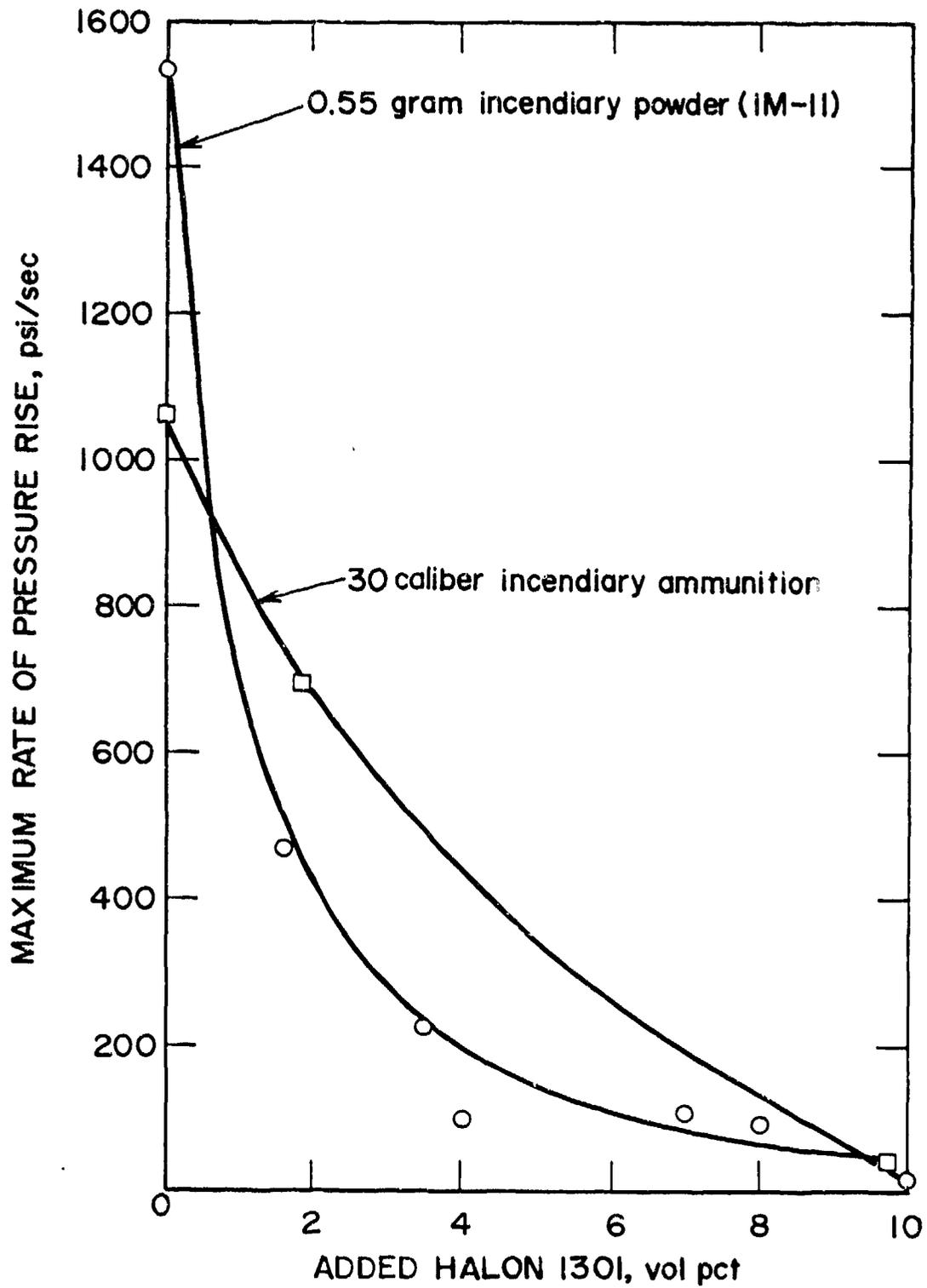


Figure 22. - Effectiveness of Halon 1301 in quenching incendiary ignitions of near-stoichiometric n-pentane-air mixtures (1 atm) in a 74 gallon fuel tank at 75°F.

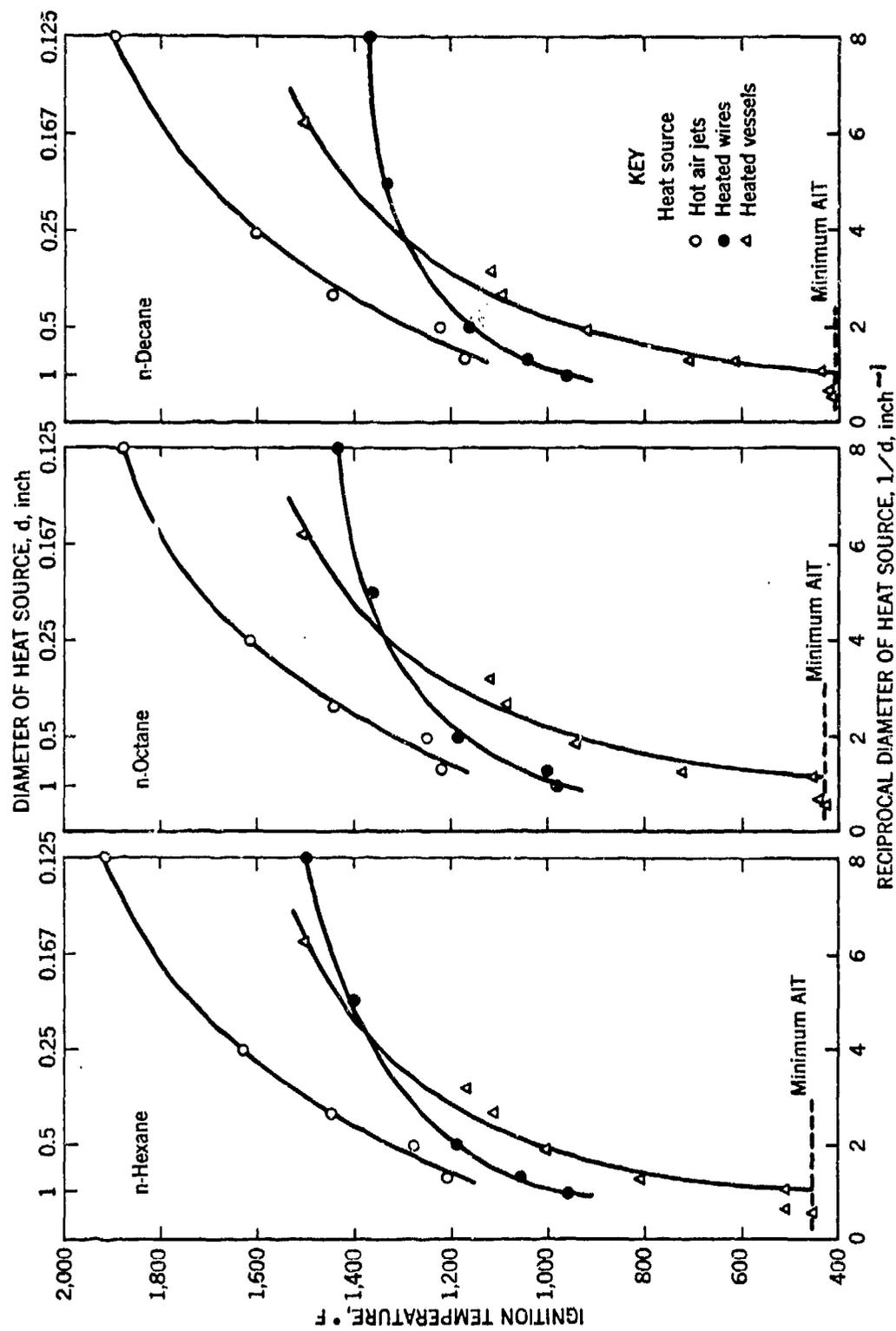


Figure 23. - Variation of hot gas and hot surface ignition temperatures with reciprocal diameter of heat source for n-Hexane, n-Octane, and n-Decane vapor-air mixtures.

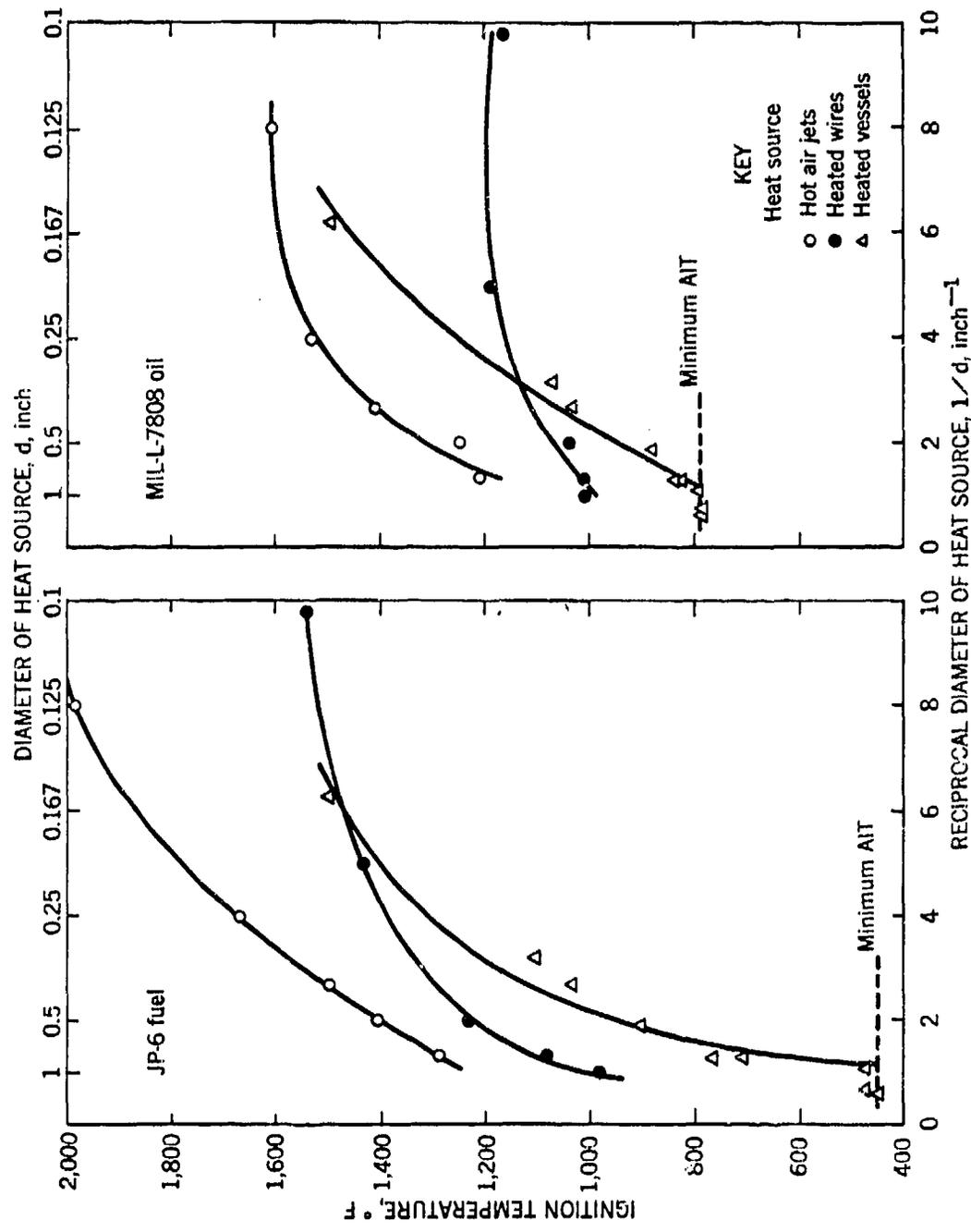


Figure 24. - Variation of hot gas and hot surface ignition temperatures with reciprocal diameter of heat source for JP-6 fuel and MIL-L-7808 engine oil vapor-air mixtures.

opening valves are used can result in ignition of a combustible mixture by shock or adiabatic compression. The theoretical gas temperatures ( $T_2$ ) which can result from shock and adiabatic compression of air initially at 32°F and atmospheric pressure are compared in table 6 for various compression ratios ( $P_2/P_1$ ). At a  $P_2/P_1$  ratio of 50, the adiabatic compression temperature (970°F) would appear adequate for autoignition of most hydrocarbon fuels in air. However, this will depend upon the rate of pressure rise and container dimensions and can only occur if the high temperature ( $T_2$ ) condition is maintained for a duration that exceeds the required ignition delay, as discussed earlier. Figure 25 illustrates the ignition requirements for a typical phosphate-ester base lubricant (Cellulube 220) and a mineral-oil base lubricant as a function of rate of pressure rise, compression ratio and initial temperature (Ref. 19) As noted, the rate of pressure rise required for ignition increases sharply below some critical compression ratio which decreases with increasing initial temperature; here, the critical compression ratios were greatest for the phosphate-ester base fluid and nearly doubled when the initial temperature varied from 210°F(B) to 75°F(A). Generally, the required rates of pressure rise for such ignitions are noticeably lower when the pipe or container diameter is increased.

The case of shock compression is more complicated, particularly because of the small volume of gas mixture that is heated and the very short duration of heating. Thus, a shock wave with a compression ratio of 10 and  $T_2$  of 810°F would hardly be expected to produce ignition of a mixture having an AIT of 800°F.

#### SELF-HEATING AND PYROPHORICITY

##### A. Spontaneous Heating Temperatures

Spontaneous or self-heating refers to the incipient stage of combustion which generally involves slow oxidation over a period of several hours or more. Thus, minimum spontaneous heating temperatures should not be confused with minimum AIT's which are associated with short reaction times and much higher temperatures; the former are usually of the order of normal ambient temperatures, depending upon the combustible composition and the physical factors affecting the rate of reaction (heat gain) and rate of heat loss.

Materials capable of self-heating include those derived from animal and vegetable oils. According to equation 12 from thermal theory, the critical temperature for such reaction is necessarily a function of the size or mass of material. Gross and Robertson (Ref. 20) utilized kinetic constants obtained at elevated temperatures to calculate the critical sizes for several materials at various ambient temperatures. The critical radii (inches) for the self-heating of 6 different oils at 68°F were as follows:

Table 6. - Shock Wave and Adiabatic Compression Temperatures

$P_1 = 14.7$  psia;  $T_1 = 32^\circ\text{F}$

Compression Ratio $P_2/P_1$	Gas Compression Temperature	
	Shock Wave $T_2, ^\circ\text{F}$	Adiabatic Compression $T_2, ^\circ\text{F}$
2	144	134
5	406	306
10	810	467
50	3610	970
100	6490	1250
1000	33,940	2615

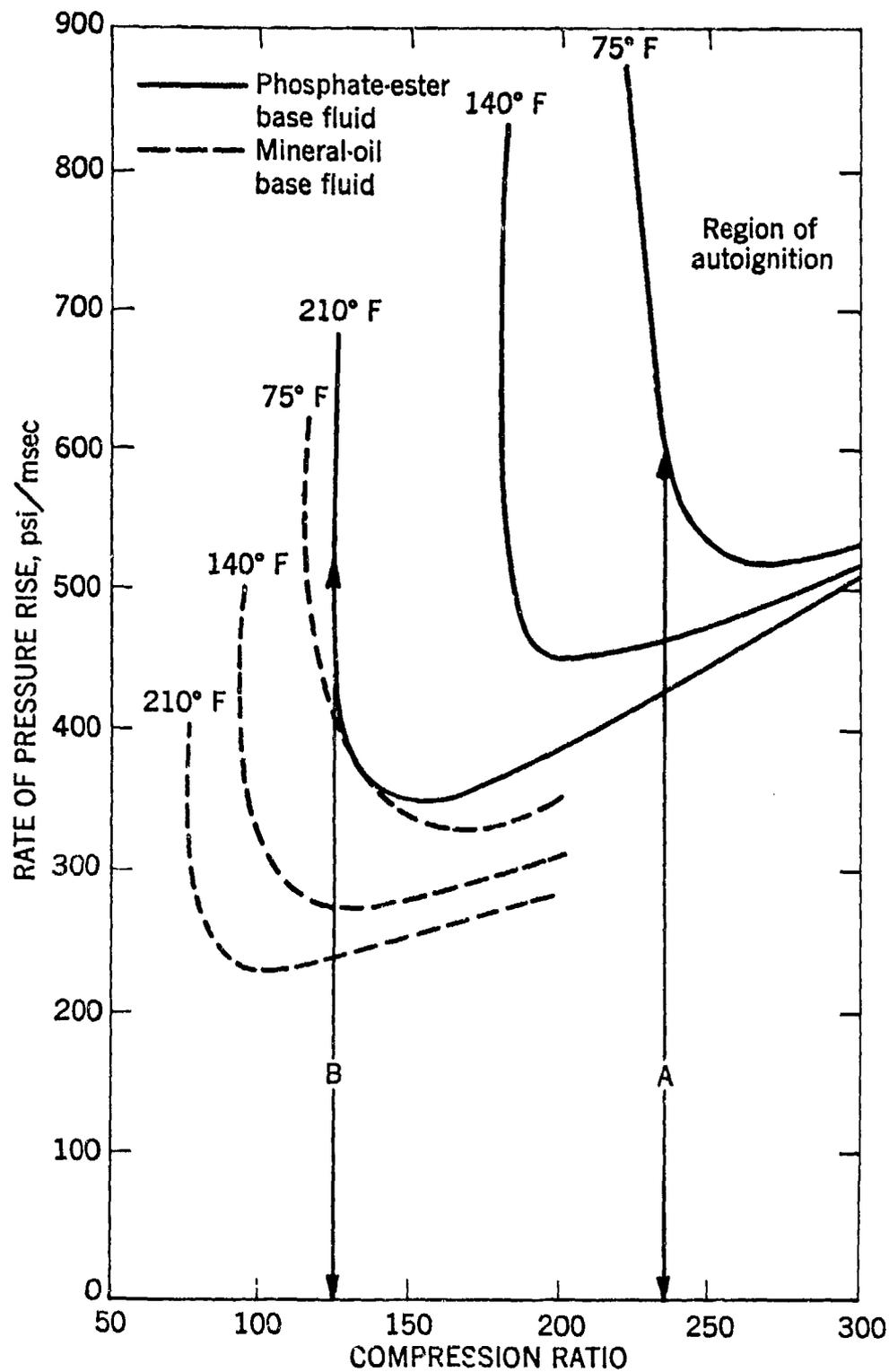


Figure 25. - Rate of pressure rise required for ignition of a phosphate-ester base lubricant (Cellulube 220) and a mineral-oil base lubricant (MIL-290 TEP) as a function of compression ratio at various temperatures in a 1-foot length of 3/8-inch diameter pipe.

raw linseed - 2.6, rapeseed - 2.8, cottonseed - 4.0, olive - 4.3, sperm - 5.6 and castor - 45.7; here, these radii refer to a spherical mass of porous or fibrous material, such as cotton gauze, to which the sample oil was applied. It is evident from these data that the probability of self-heating at room temperature should be high for 5 of the oils when compared to castor oil.

Generally, aircraft fuels or fluids have good oxidative stability at ambient temperature. However, some aircraft oils or lubricants are capable of self-heating type reactions at temperatures noticeably below their minimum AIT's in air. For example, the SAE No. 10 oil was observed to undergo exothermic reaction at temperatures as low as 350°F when mineral wool or calcium silicate insulation was soaked with this oil and heated in a vessel (Ref. 21); this oil has a minimum AIT of about 700°F. Similarly, the MIL-L-7808 engine oil appears to display some evidence of exothermicity in heating tests at temperatures as low as 490°F, whereas its AIT is close to 730°F (Ref. 13). Aircraft fluids having lower decomposition temperatures than their minimum AIT's should be suspected as being possibly capable of this type of behavior.

#### B. Pyrophoric Ignitions

Most pyrophoric materials are solids, such as the alkali metals and their hydrides, although a few liquids also fall into this class of high reactivity. No aircraft combustible fluids or solids are pyrophoric.

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APPENDIX

Table 1-A. - Properties of Hydrocarbons and Miscellaneous Combustibles<sup>a/</sup>

Combustible	Mol. Wt.	Specific Gravity (Air=1)	Boiling Point °F	Vapor Press. (70°F) psia	Heat Capacity <sup>b/</sup> C <sub>p</sub> (70°F) Btu/lb.-°F	Net Heat of Combustion Btu/lb	Cst. in air Vol. %	Flash Point °F	AIT in air °F	Flamm. Limits in Air LL Vol. %	UL Vol. %
Methane	16.04	0.55	-259	---	0.529(g)	21,500	9.48	Gas	1,000	5.0	15.0
Ethane	30.07	1.04	-128	560	0.414 "	20,420	5.65	Gas	959	3.0	12.4
Propane	44.09	1.52	-44	124.	0.393 "	19,930	4.02	Gas	871	2.1	9.5
n-Butane	58.12	2.01	31	33.	0.402 "	19,670	3.12	Gas	761	1.8	8.4
n-Pentane	72.15	2.49	97	8.4	0.402 "	19,500	2.55	<- 40	743	1.4	7.8
n-Hexane	86.17	2.98	156	2.5	0.403 "	19,240	2.16	- 7	433	1.2	7.4
n-Octane	114.22	3.94	258	0.2	0.404 "	19,100	1.65	56	428	0.95	6.5
iso-Octane	114.22	---	211	0.80	0.404 "	19,080	---	10	779	1.1	6.0
n-Decane	142.28	4.91	345	0.03	0.405 "	19,020	1.33	115	406	0.75	5.6
Ethylene	28.05	0.97	-155	882	0.366(g)	20,290	6.53	Gas	840	2.7	36
Propylene	42.08	1.45	-53	151	0.358 "	19,690	4.45	Gas	856	2.4	11
Acetylene	26.04	0.9	-118	645	0.399 "	20,740	7.72	Gas	580	2.5	100
Cyclohexane	84.16	2.91	179	1.55	0.304(g)	18,680	2.27	- 4	473	1.3	7.8
Benzene	78.11	2.69	176	1.5	0.245 "	17,270	2.72	12	1,040	1.3	7.9
Toluene	92.13	3.18	231	0.45	0.264 "	17,450	2.27	40	896	1.2	7.1
o-Xylene	106.16	3.67	292	0.1	0.295 "	17,610	1.96	90	887	1.1	6.4
Naphtha	---	---	95-140	---	---	---	---	<	550	1.1	5.9
Turpentine	---	---	300	---	0.411 "	---	---	95	488	0.8	---
Methyl alcohol	32.04	1.11	147	1.85	0.600(l)	8,580	12.25	52	725	6.7	36
Ethyl alcohol	46.07	1.59	173	0.85	0.581 "	11,550	6.53	55	689	3.3	19
Propyl alcohol	60.09	2.07	207	0.3	0.586 "	13,190	4.45	77	824	2.2	14
Ethylene glycol	62.07	---	387	0.0	0.573 "	7,340	---	232	752	3.2	---
Propylene glycol	76.09	---	370	---	---	9,350	---	210	700	2.6	12.5
Methylether	46.07	1.59	- 11	---	---	12,340	6.53	---	662	3.4	27
Ethylether	74.12	2.56	95	8.7	0.547(l)	14,560	3.37	- 49	356	1.9	36
Acetone	58.08	2.01	134	3.6	0.528 "	12,280	4.97	0	869	2.6	13
Methylethylketone	72.10	2.49	21	---	0.549 "	13,490	3.67	21	960	1.9	10
Methyl acetate	74.08	2.56	14	3.3	0.468 "	8,700	5.65	14	935	3.2	16
Ethyl acetate	86.10	3.04	24	1.45	0.459 "	10,300	4.02	24	800	2.2	11
Carbon monoxide	28.0	0.97	-313	---	0.248(g)	4,340	29.50	Gas	1,128	12.5	74
Hydrogen	2.02	0.07	-423	---	3.412 "	51,600	29.53	Gas	752	4.0	75
Ammonia	17.08	0.59	- 28	129	0.52 "	8,000	21.83	Gas	1,204	15	28

<sup>a/</sup> Reference 1.

<sup>b/</sup> Values for gas (g) and liquid (l)

Table 2-A. -Properties of Aviation Fuels<sup>a/</sup>

Fuel	Av. Mol. Wt.	Sp. Gr. (Water = 1)	Boiling Pt. 10% °F	Boiling Pt. 90% °F	Reid Vapor Press. (100°F) psi	Net Heat of Combustion Btu/lb	C <sub>st</sub> in air Vol. %	b/ C <sub>st</sub> in air Vol. %	Flash point °F	AIT in air °F	Flamm. Limits in Air LL Vol. %	UL Vol. %
JP-1	151	0.81	350	410	<0.1	18,480	1.3	1.3	115	440	---	---
JP-3	112	0.76	160	440	6.0	18,710	(2.5)	(2.5)	---	460	1.4	7.9
JP-4	125	0.78	210	390	2.6	18,710	(2.4)	(2.4)	0	445	1.3	8.0
JP-5	169	0.83	380	460	<0.1	18,440	1.1	1.1	150	435	0.6	4.5
JP-6	147	0.84	350	500	0.1	18,620	(1.3)	(1.3)	100	450	0.7	4.8
JP-8	164	0.8	370	460	<0.1	18,400	---	---	115	435	---	---
Jet A	---	0.8	370	480	<0.3	18,590	---	---	105-140	435	Similar to JP-5	---
Jet B	---	0.8	230	390	2.4	18,780	---	---	0-20	450	Similar to JP-4	---
Gasoline 100/130	---	0.7	140	240	7.0	19,000	(2.4)	(2.4)	-45	825	1.3	7.1
Kerosene	---	0.8	380	490	<0.1	18,600	(1.3)	(1.3)	125	480	0.7	4.8

<sup>a/</sup> Reference 1.

<sup>b/</sup> Values in parenthesis, calculated by C<sub>st</sub> = LL/0.55

Table 3-A. - Properties of Lubricants and Hydraulic Fluids<sup>a/</sup>

Fluid	Specific Gravity (Water=1)	Net Heat of Combustion Btu/lb.	Flash Point °F	Minimum AIT °F
Hydraulic Fluid				
MIL-H-5606C H-515 OHA (mineral oil)	0.86	18,240	195	437
MIL-H-83282 MLO-73-93	0.84	17,870	385	670
Chevron M2V MLO-71-45	0.94	13,730	208	698
MIL-2190 (mineral oil)	0.86	-	450	665
Mobil DTE 103 (mineral oil)	0.92	-	390	702
Cellulube 220 (phosphate ester)	1.15	-	455	1038
Harmony 44 (mineral oil)	0.88	-	460	680
Houghto-Safe 271 (water glycol)	1.05	-	-	767
Houghto-Safe 1055 (phosphate ester)	1.15	-	505	1020
Pydraul 150 (phosphate ester)	1.13	-	380	975
Pydraul AC (chlorinated ester)	1.36	-	450	1148
Skydrol (phosphate ester)	-	-	360	>1300
Lubricating Oils				
MIL-L-7808G O-148 LGT (sebacate-adipate diester)	0.92	14,790	405	728
MIL-L-23699B O-156 (polyester)	0.99	13,060	440	725
Monsanto OS-124	1.20	-	550	1112
SAE No. 10	<1	-	340	720
SAE No. 60	<1	-	480	770

<sup>a/</sup> Data from reference 1, 13 and private communication with Air Force Aero Propulsion Laboratory.