

inversely with approximately the square of pressure. With increasing temperature, they decrease roughly by a factor of 2 for a 100° C temperature change (69). The low ignition energy requirements of combustible vapor mixtures are of great concern since sparks or arcs from ordinary electrical equipment have much greater energies (order of joules); even spark energies from static electricity are often greater (order of tens of millijoules) than MIE values, as discussed under theory and definition. Applications of spark ignition data to safety engineering, including intrinsic safety, are elaborated on by Litchfield (67).

Quenching Distances

Minimum ignition quenching distances for the combustible vapors in normal ambient air or oxygen are included in table 14. These data were obtained by the above-cited authors and refer to quenching of the spark flame kernel between flat plate electrodes. As with MIE values, minimum quenching distances occur at near-stoichiometric fuel-air ratios and fall in a narrow range (~1.5 to 2.5 mm) for many combustibles. Notable exceptions again are acetylene, carbon disulfide, and hydrogen, which are the most readily ignitable; other exceptions are ammonia and some of the halogenated materials, which are least ignitable.

Although corresponding data in oxygen are less available, the minimum quenching distances are much lower, being only a few tenths of a millimeter for hydrocarbons and hydrogen (table 14). For most combustibles, quenching distances vary inversely with the first power of pressure but with an ill-defined power of temperature (69). A useful correlation for estimating the minimum ignition quenching

Table 14. — Comparison of minimum spark ignition quenching distances and maximum experimental safe gaps (MESG) of combustible vapors in air at 25° C and 1 atm¹

Combustible	Ignition quenching ² distance, mm	MESG ³ , mm
HYDROCARBONS		
Methane	2.03 (0.30 in O ₂)	1.14
Ethane	1.5	.91
Propane	1.75	.92
n-Butane	2.4 (0.15 in O ₂)	.98
n-Hexane	1.5 (0.20 in O ₂)	.93
Acetylene64 (0.18 in O ₂)	.37
Ethylene	1.22 (0.23 in O ₂)	.65
1,3-Butadiene	1.25	.79
Cyclopropane	NA	.91
Benzene	1.95	.99
HALOGENATED HYDROCARBONS		
Allyl chloride	<2.75	1.17
n-Butyl chloride	2.2	1.06
Methylene chloride	5.46	NA
Ethylene chloride	4.57	1.8
Vinyl chloride	NA	.96
OTHER COMBUSTIBLES		
Ammonia	NI	3.18
Carbon disulfide55	.20
Carbon monoxide	NA	.91
Ethyl ether	1.85	.83
Isopropyl ether	3.0	.94
Ethylene oxide	1.18	.59
Hydrogen64 (0.25 in O ₂)	.20
Methanol	1.5	.92
Methyl amine	NA	1.10
Propylene oxide	1.3	.70
Vinyl acetate	2.35	.94

NA Not available. NI No ignition at 1 J.

¹Mixture composition—stoichiometric or near-optimum for ignition.

²Reference 8, 66 (p. 323), and 67-69.

³Reference 71.

distance from the MIE, or vice versa, is given graphically by figure 47 (102). This figure is a composite of Bureau data for various combustible-oxidant-diluent mixtures over a wide range of pressures and oxygen concentrations; here, the MIE varies approximately with the square of the quenching distance. Quenching diameters obtained in tubes are about 1.5 times greater than these flat plate quenching distances.

Such ignition quenching data are useful in predicting flame propagation hazards of combustible mixtures and designing flame arresting devices. An effective flame arrester must quench the propagating flame at the arrester face and remove sufficient heat from the product gases to prevent ignition beyond the arrester; thus, both flame velocity and arrester physical specifications are important. In practice, flame velocities can be much greater than those developed in the above quenching distance experiments. Palmer (81) found the approach velocity of the flame to be most critical and developed semiempirical expressions for predicting the effectiveness of various flame arresters.

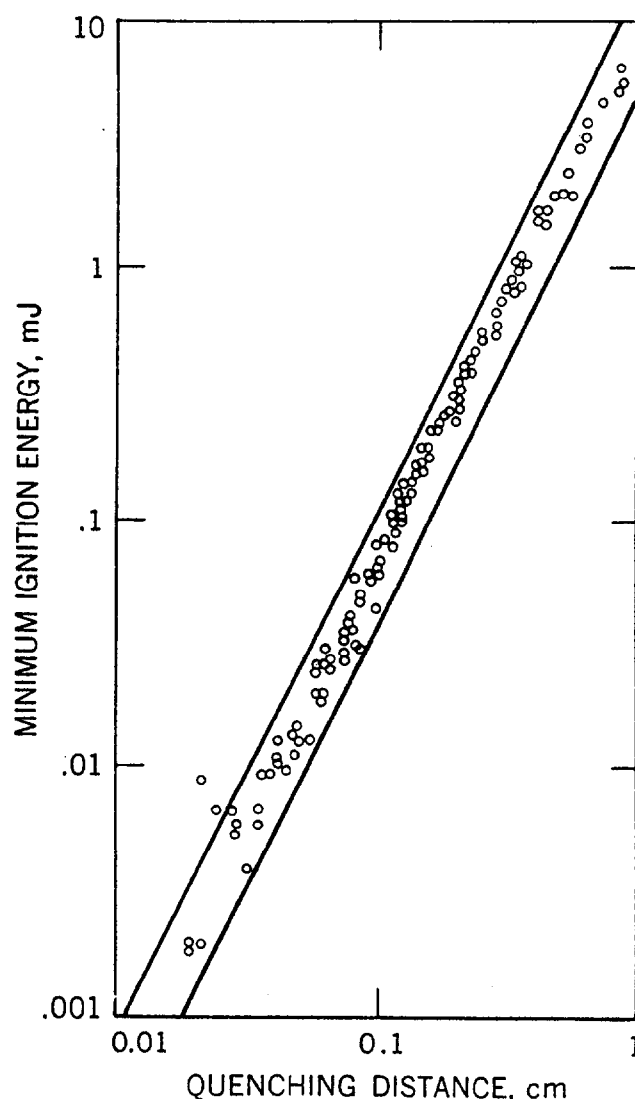


Figure 47.—Correlation of minimum ignition energy with minimum quenching distance for a large variety of combustibles.

Based on this work and others, a simple relationship is given in a British guide (73) for predicting the critical approach velocity:

$$v = 0.5 a y/d^2, \quad (65)$$

where v is flame velocity (ft/s), y is arrester thickness (in), d is diameter of apertures (in), and a is the face area not blocked by the arrester material (wire gauze, metal ribbon, etc.). This expression is primarily applicable to ordinary flame propagations and to moderate pressures.

In the case of explosionproof enclosures, ignition quenching distance data are not sufficiently conservative to protect against the high-velocity jets of flame or hot gas that can be produced at high explosion pressures. Instead, it is necessary to use the maximum experimental safe gap (MSEG) data, which are designed to prevent ignition by any jets of hot gas escaping through the flange gap of such enclosures; hot gas ignition temperatures are given in the next section. The MSEG values included in table 14 are proposed by British Government laboratories (71) and were obtained at an initial pressure of 1 atm and gap passage length of 2.54 cm (1 in). Underwriters' Laboratories (15) in this country reports lower MSEG values for some of the combustibles, particularly acetylene, hydrogen, carbon disulfide, and ammonia. Their lower values reflect the effects of a shorter gap length (3/4 in) and more severe explosion pressures that were developed by using turbulent mixtures and a long flame runup to simulate pressure piling.

Ignition Temperatures

Minimum autoignition temperatures (AIT's) are widely relied upon for assessing the ignitability hazard of combustible vapors in a heated environment without an external ignition source. Relatively complete listings of AIT's for liquid and gaseous compounds in atmospheric air are given in appendix A. These listings also update any previously reported data that could not be confirmed, including the widely cited values for methane (540° C) and hydrogen (400° C). The data refer to ignitions under static conditions that were obtained in open glass vessels, usually of at least 200 cm³ volume and with induction or contact times (ignition delays) of the order of minutes; data obtained in smaller vessels or with shorter contact times are less conservative for safety applications. Appearance of any flame was normally used as the criterion of ignition in such determinations. Precision of these data can be assumed to be approximately $\pm 10^\circ$ at 300° C. They should not be confused with flashpoints, which relate to the volatility and not the ignitability of the combustible.

AIT's of combustibles are lower in oxygen than in air, but the differences are not great for most hydrocarbon combustibles. Selected data from Bureau (23, 110, 112) and NFPA (72, 78) compilations are given in table 15 for some representative organic and inorganic combustibles at atmospheric pressure. The effects of chemical structure are evident from the data in this table and appendix A. Generally, the AIT's of straight-chain hydrocarbons decrease with increasing number of carbon atoms and increase with chain branching (note isobutane) and ring formation (note cyclopropane); Zabetakis (112) showed they can be correlated with the average chain length. Similar trends occur with the various families of hydrocarbon derivatives, although the data are less consistent, depending upon the functional group. The AIT's of most hydrocarbons and their derivatives in air fall between the values for

Table 15. — Minimum autoignition temperatures (AIT's) of combustible gases and liquids in air and oxygen at 1 atm

Combustible	Minimum AIT, °C	
	Air ¹	Oxygen ²
HYDROCARBONS		
Methane	630	555
Ethane	515	505
Propane	450	NA
n-Butane	370	285
Isobutane	460	320
n-Pentane	260	260
n-Hexane	225	220
n-Heptane	225	210
n-Octane	220	210
n-Decane	210	200
Acetylene	305	295
Ethylene	490	485
Propylene	460	425
1,3-Butadiene	420	335
Cyclopropane	500	455
Gasoline (100/130)	440	315
Kerosene	230	215
HALOGENATED HYDROCARBONS		
Ethyl chloride	520	470
n-Butyl chloride	250	245
Methylene chloride	615	535
Ethylene chloride	440	430
Methyl chloroform	485	470
Trichloroethylene	420	405
OTHER COMBUSTIBLES		
Acetaldehyde	175	160
n-Amyl acetate	360	235
Carbon disulfide	~100	<105
Carbon monoxide	610	590
Ethyl ether	195	180
Glycerol	370	320
Hydrazine	270	150
Hydrogen	520	~400
Hydrogen sulfide	260	220
Propanol	440	330
Vinyl ether	360	165

NA Not available.

¹References 72, 110, and 112.

²References 23 and 78.

methane (630° C) and n-decane (210° C); notable exceptions are acetaldehyde, methyl hydrazine, and various alkyl ethers, nitrites, or nitrates, which can autoignite below 200° C. Among inorganic compounds, the AIT's are lowest for carbon disulfide and diborane ($\leq 100^\circ$ C) and highest for carbon monoxide and ammonia ($>600^\circ$ C); the updated values for hydrogen are 520° C in air and 400° C in oxygen. With nitrogen tetroxide as the oxidant, the AIT's are comparable to those in oxygen for such paraffins as butane, hexane, and heptane, but lower by 100° to 200° C for hydrogen and highly chlorinated hydrocarbons (23); also, hydrazine fuels are hypergolic with this oxidant.

Figure 48 (57) illustrates the dependence of ignition delays on autoignition temperatures in stagnant air for various hydrocarbon fuels, including cyclics and aromatics. Although the data display an exponential dependence as predicted by the Semenov theory (equation 29), the temperature dependence for each fuel changes to a less sensitive one (decreased slope) at some high temperature; this indicates a change in reaction mechanisms or rate-controlling factors. Global activation energies (E) derived from the slopes and use of equation 29 are 11 to 22 kcal/mol in the high-temperature region and 33 to 46 kcal/mol in the low-temperature region for most of these fuels. Similar data under flow conditions, where contact times can be of the order of milliseconds, are rather meager for individual compounds. The following expressions from the above Bureau work (57) give the approximate estimation of ignition delay

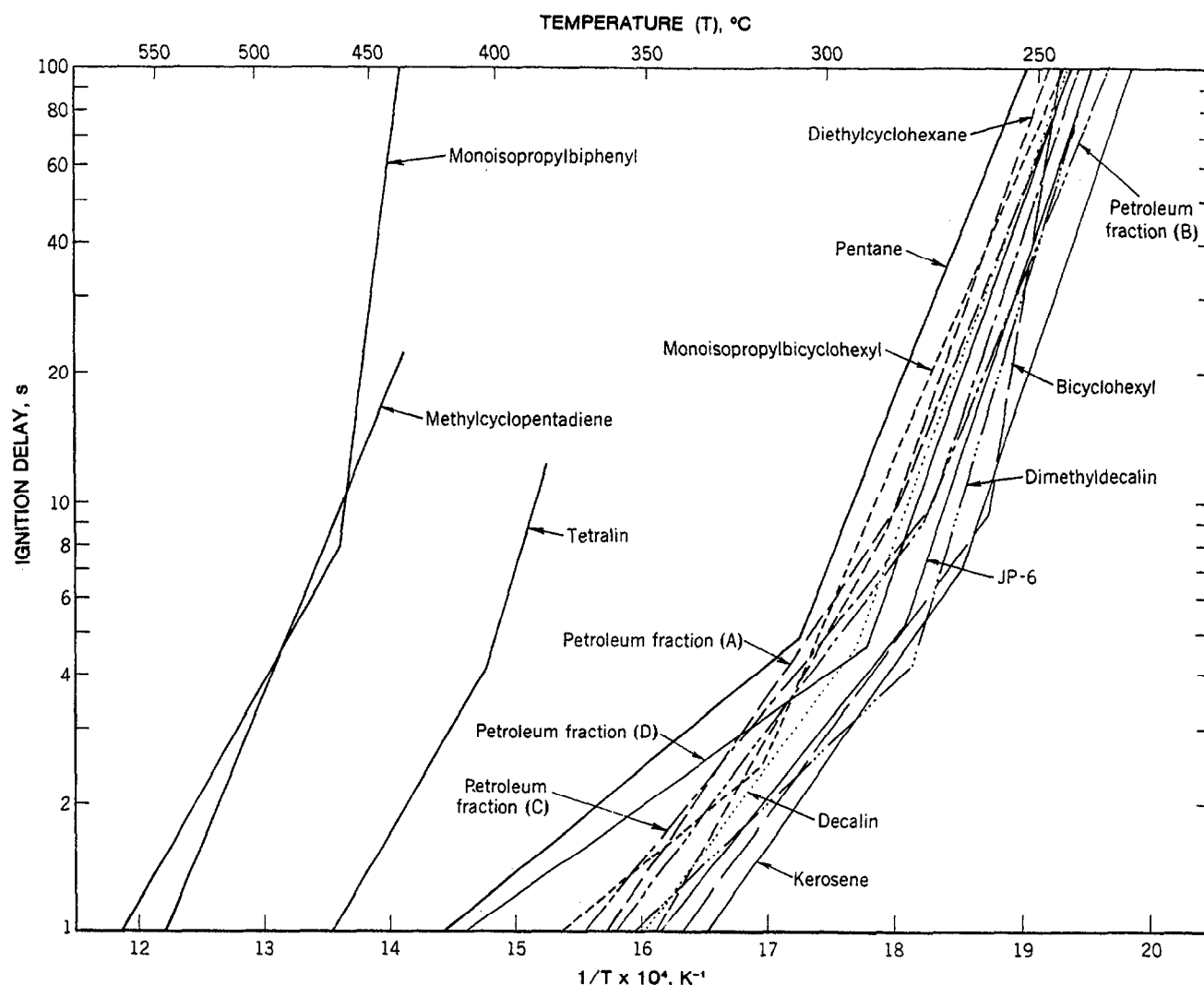


Figure 48.—Autoignition temperatures and corresponding ignition delays of hydrocarbon fuels under static conditions in air at atmospheric pressure.

(τ , ms) with temperature (T , K) for *n*-pentane (C_5H_{12}) and decalin ($C_{10}H_{18}$) in heated air streams at 2 atm:

$$\text{Pentane (350°-650° C)} \dots \ln \tau = 5400/RT + 1.13 \quad (66)$$

$$\text{Decalin (370°-600° C)} \dots \ln \tau = 6600/RT - 0.37 \quad (67)$$

where R is 2 cal/(K·mol). The low gross activation energies indicate that physical factors rather than chemical factors were rate controlling.

Autoignition temperatures decrease with increasing pressure, but the decrease is often small for moderate pressure changes, depending upon the combustible and oxidant. According to data for high-molecular-weight hydrocarbons (57), their AIT's in air at 5 atm roughly approximate their corresponding values in oxygen at atmospheric pressure (table 15), i.e., an atmosphere of equivalent oxygen partial pressure. Also, the values in air for hydrocarbons of low AIT ($\sim 250^\circ\text{C}$) are approximately doubled when the pressure is reduced to 0.5 atm (57, 112). However, as shown by Furno (23) for selected paraffins, chlorinated hydrocarbons, and hydrazine fuels, the pressure effect is greatly diminished by the use of large vessels ($4,900\text{ cm}^3$).

Ignitions by any heated surface are a function of the heat source dimensions. For autoignitions in heated vessels, a vessel diameter of at least 5 cm or surface-volume ratio (S/V) less than 1 cm^{-1} is required to obtain the AIT values given in appendix A. With larger vessels, Setchkin (94) has shown that the AIT's do not decrease greatly, although the size effect can still be significant for some combustibles. Heated wire, rod, or tube ignition temperatures are normally much higher than the heated vessel AIT's; such data are compared in table 16 for some representative combustibles. Figure 49 was obtained by Kuchta (50) and illustrates the dependence of ignition temperature on surface area of the heat source with different sources and combustibles; heat source diameters ranged from 0.8 to 7.5 cm for the vessels (cylindrical) and from 0.04 to 2.5 cm for the wires or rods. For the three paraffins in this figure, their ignition temperatures (T , $^\circ\text{C}$) in air are given by the following expressions for heat source surface areas (A , cm^2) less than 80 cm^2 :

$$\text{n-Hexane} \quad T = 951 - 98.5 \ln A; \quad (68)$$

$$\text{n-Octane} \quad T = 921 - 96.0 \ln A; \quad (69)$$

$$\text{n-Decane} \quad T = 893 - 89.5 \ln A. \quad (70)$$

Table 16. — Comparison of hot surface and hot gas ignition temperatures of hydrogen, carbon monoxide, and hydrocarbon fuels in air at 1 atm

Combustible	Ignition temperature, °C			
	Heated ¹ glass vessel (~4.5-cm diam)	Heated ² Inconel wire (1-cm diam)	Heated ³ Nichrome wire (0.1-cm diam)	Heated ⁴ air jet (1-cm diam)
Methane	630	NA	1,220	1,040
Ethane	515	NA	980	840
Propane	450	NA	1,050	885
n-Butane	370	NA	1,010	910
n-Hexane	225	670	900	765
n-Octane	220	660	860	755
n-Decane	210	650	835	750
Acetylene	305	NA	850	655
Ethylene	490	NA	900	765
Propylene	460	NA	1,090	930
Isobutylene	445	NA	1,060	960
Carbon monoxide	610	NA	780	785
Hydrogen	520	NA	750	640
JP-6 fuel	230	695	930	805
MIL-L-7808 oil	390	585	695	750

NA Not available.

¹AIT data from table 15 and appendix A.

²Reference 50.

³References 50 and 103.

⁴References 51 and 103.

Linear correlations extending to the larger surface areas (~180 cm²) associated with heated vessel AIT's appear to occur only with combustibles requiring high autoignition temperatures; note data for the engine oil.

Heat source dimensions are equally important in ignitions by jets of hot gases that may come into contact with a combustible vapor-air mixture. Comprehensive studies on hot gas ignitions have been made by Vanpee and Wolfhard (103-104, 108). Their results on the effect of jet diameter on ignition temperature with heated laminar air jets are shown in figure 50 for hydrogen and the lower members of the alkane and alkene series; similar data for higher alkane members are also available (51). Minimum ignition temperatures obtained with a 1-cm-diam heated air jet are included in table 16 for the various combustibles. As noted, the hot gas ignition temperatures correlate best with the heated wire or rod ignition temperatures, all of which are noticeably higher than the heated vessel AIT's. In comparing all such ignition temperatures for a given combustible, Kuchta (51) found the differences are not necessarily great

when they are compared at the same heat source diameter. Hot gas ignition temperatures are especially useful in evaluating the ignition hazard of possible hot gases evolved from flame arrestors, explosionproof seals, and permissible explosive firings in mines.

FLAME TEMPERATURES AND BURNING RATES

Flame Temperatures

Assessment of the potential heat release and pressure development in the combustion of gaseous mixtures requires a knowledge of flame temperatures. Table 17 includes such data for the constant-pressure combustion of various combustibles in ambient air at atmospheric pressure; the

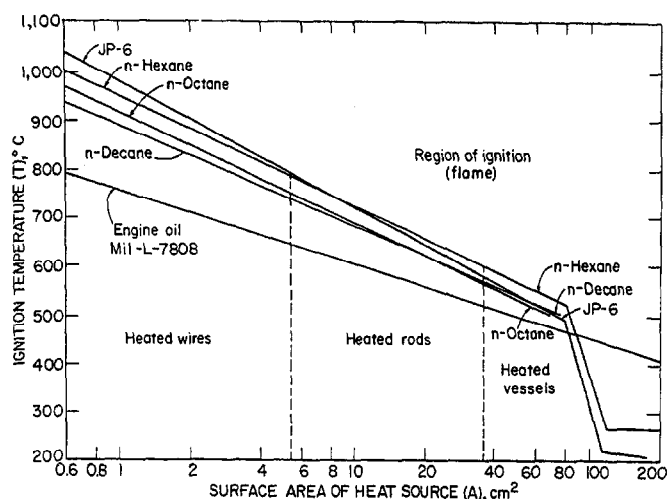


Figure 49.—Hot surface ignition temperatures as a function of heat source surface area for hydrocarbon fuels and an engine oil in air at 1 atm.

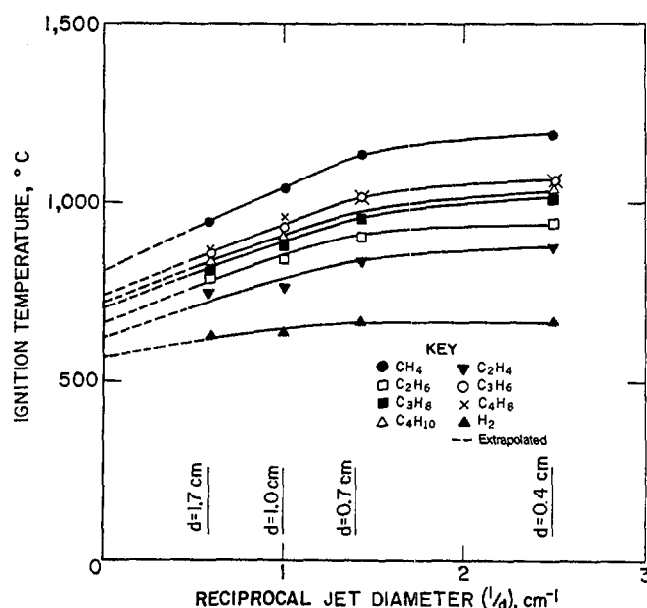


Figure 50.—Hot gas (air) ignition temperatures as a function of reciprocal jet diameter for hydrogen and various hydrocarbons at atmospheric pressure.

Table 17. — Limit flame temperatures, maximum flame temperatures, and maximum burning velocities of gaseous combustibles in air at 1 atm

Combustibles	Limit flame temperature, (T _f) _L		Maximum flame ¹ temperature, (T _f) _M		Maximum burning ² velocity (S _u), cm/s
	Diffusion ³ , °C	Premixed ⁴ , °C	Measured, °C	Calculated, °C	
HYDROCARBONS					
Methane	1,518	1,377 (1,260)	1,875	1,927	45
Ethane	1,363	1,327 (1,230)	1,895	1,922	47.5
Propane	1,422	1,367 (1,310)	1,925	1,967	45.5
n-Butane	1,434	1,492 (1,390)	1,895	2,007	46
n-Pentane	NA	1,362	NA	2,002	44.5
n-Heptane	NA	~1,400 (1,370)	NA	2,002	42.5
Acetylene	NA	1,002	2,325	2,307	157
Ethylene	1,335	1,202	1,875	2,067	74.5
Propylene	1,489	1,337	1,935	2,047	51
Butylene	1,494	NA	1,930	NA	43
1,3-Butadiene	NA	1,317	NA	2,104	54.5
Cyclopropane	NA	1,377	NA	2,077	55.5
Cyclohexane	NA	NA	NA	1,952	43.5
Benzene	1,540	1,442	NA	2,092	48
Natural gas	NA	~1,350	NA	1,950	38.5
OTHER COMBUSTIBLES					
Acetone	NA	1,427	NA	1,934	42.5
Acrolein	NA	1,267	NA	2,067	66
Carbon monoxide	1,177	NA	2,100	2,032	52
Ethanol	1,405	NA	NA	NA	NA
Ethyl ether	1,386	1,337	NA	2,032	50
Ethylene oxide	NA	1,242	NA	2,152	89.5
Hydrogen	811	712	2,045	2,072	326
Methanol	1,258	NA	NA	1,862	57
Propylene oxide	NA	1,282	NA	2,087	67

NA Not available.

¹References 66, p. 705 (measured values) and 2, 18, and 95 (calculated values); values for near-stoichiometric mixtures.

²References 2, 25, and 95; values for near-stoichiometric mixture.

³Reference 103 (diffusional burner flame method).

⁴Reference 18 (flammability tube method); parenthetical values from reference 115.

maximum flame temperatures were obtained with near-stoichiometric mixtures. Measured values by Lewis (66, p. 628) differed only slightly (<100° C) from calculated values for common hydrocarbons in spite of the lack of adiabatic conditions in measuring such temperatures. Calculated data by Fenn (18), Simon (95), and others (2) are included in table 17. Excluding acetylene (2,325° C), the maximum flame temperatures of hydrocarbons and their derivatives fall in a narrow range, nominally between 1,900° and 2,100° C; hydrogen and carbon monoxide also fall within this temperature range. Corresponding flame temperatures under constant-volume conditions are about 20 pct higher, largely because of the heat capacity differences of the gaseous products under constant volume and constant pressure; see equations 40 and 42.

Limit flame temperatures for the constant-pressure propagation of combustible vapor-air mixtures (lower limit mixtures) are also included in table 17. It is evident that the premixed flame data by Fenn (18) and Zabetakis (115) are more conservative than the diffusional flame data by Vanpee (103). A temperature of at least 1,200° C is required by most of these combustibles, excluding acetylene (~1,000° C) and hydrogen (~800° C). Lowest flame temperatures occur at the lower flammability limit that correspond to upward propagation and constant-pressure combustion. However, in the special case of hydrogen, which has a very high diffusivity coefficient, the calculated flame temperature for its lower limit in air with upward propagation (4.0 pct) would be less than 400° C. Thus, a value of 700° to 800° C is more meaningful and would be characteristic of the concentration required for downward propagation (~8 pct). The variation of theoretical flame temperatures and pressure rises for the adiabatic combustion of hydrogen, methane, and carbon monoxide in atmospheric air is shown

in table 18 as a function of combustible concentration. Furno (22) and Burgess (5) showed that the experimental and theoretical explosion pressures come into agreement only when upward and downward propagation can occur. Knowing the flame temperature at constant volume, the explosion pressure can be estimated by use of equation 48. Thus, for a 5 pct methane-air mixture, the calculated explosion pressure is

$$P_2 = P_1 \frac{n_2}{n_1} \frac{T_2}{T_1} = 1 \times 1 \times \frac{1,810}{300} = 6.03 \text{ atm}, \quad (71)$$

where P is in atm, T is in K, and n_2/n_1 is 1. A maximum P_2/P_1 ratio of approximately 8 is typical of near-stoichiometric mixtures.

Table 18. — Calculated flame temperatures and pressure rises for adiabatic combustion of hydrogen, methane, and carbon monoxide in air at 25° C (5)

Fuel concentration, vol pct	Pressure rise (ΔP), psig	Flame temperature (T _f), K	
		Constant volume	Constant pressure
H ₂ -air:			
4	21.4	746	628
6	30.9	951	788
8	39.8	1,151	944
12	56.2	1,528	1,249
15	67.2	1,794	1,472
CH ₄ -air:			
4.5	68.5	1,688	1,382
5	74.6	1,810	1,485
6	86.0	2,040	1,683
7	96.4	2,248	1,870
8	105.4	2,425	2,043
CO-air:			
10	53.2	1,450	1,194
11	57.4	1,547	1,275
12	61.5	1,643	1,355
13	65.4	1,736	1,434
14	69.2	1,828	1,512

Burning Velocities

Like flame temperatures, burning velocity (S_u) of a flammable mixture is a fundamental property and depends primarily upon the temperature, pressure, and composition of the mixture. The burning velocities of limit vapor-air mixtures are only a few centimeters per second and become maximum at near-stoichiometric combustible concentrations. Figure 51 illustrates the combustible concentration effect obtained by Gibbs (25) for several paraffins in air at ambient temperature and pressure. Maximum S_u values are given for these and other combustibles in table 17. The maximum values for the paraffins and most of their derivatives fall in the 40- to 50-cm/s range, whereas those for unsaturated hydrocarbons are usually greater. Values for acetylene (155 cm/s), hydrogen (325 cm/s), ethylene (75 cm/s), and ethylene oxide (90 cm/s) stand out among the fast-burning combustibles.

With the addition of inert diluents, burning velocities decrease depending upon the concentration and heat capacity of the diluent. Figure 52 (92) shows the effect of added nitrogen on both burning velocity (S_u) and flame speed (S_f) of methane-air- N_2 mixtures. Greater S_u reduction occurs with inerts of greater heat capacity than N_2 and even more so with diluents that are chemical flame inhibitors; Johnson (39) found that 2.4 pct Halon 1301 (CF_3Br) gave approximately the same S_u reduction (~85 pct) as 34 pct N_2 for CH_4 -air flames at near-atmospheric pressure. Assuming nonturbulent flames, the maximum flame speeds of most combustibles at optimum fuel-air ratios can be roughly estimated by

$$S_f = 8 S_u, \quad (72)$$

where 8 approximates the expansion ratio (see equation 45) for combustion at 25° C and atmospheric pressure.

Burning velocities are much higher in oxygen than in air. For the paraffins, the maximum values at normal ambient conditions are about an order of magnitude greater in oxygen, as shown in figure 53 from the work by Singer (96). For such fuels as acetylene, hydrogen, and carbon monoxide, the corresponding values are about 7, 4, and 2-1/2 times greater, respectively, in oxygen than in air.

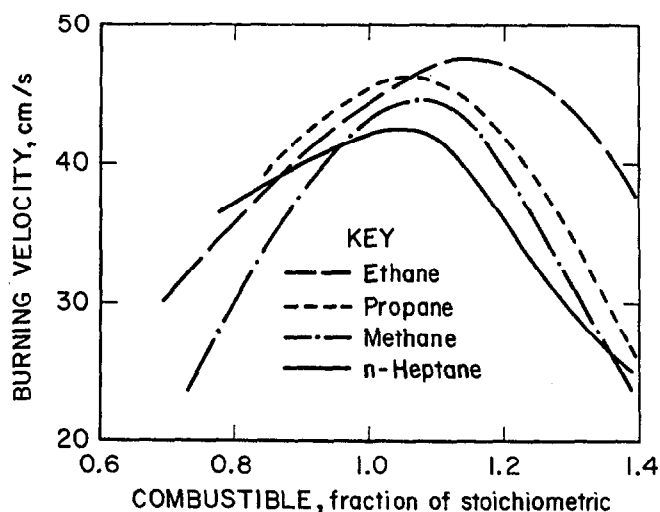


Figure 51.—Burning velocities of methane-, ethane-, propane-, and n-heptane-air mixtures at atmospheric pressure and room temperature.

These data are summarized in the comprehensive works by Lewis (66, p. 705) and Gaydon (24, p. 56), who have developed basic theories on flame propagation. With increasing temperature, the burning velocities increase (fig.

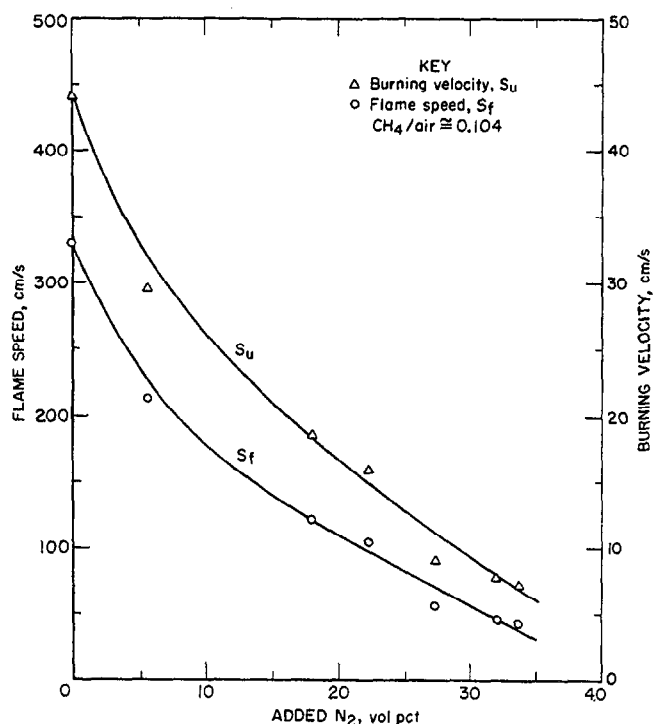


Figure 52.—Burning velocity and vertical flame speed versus added N_2 for combustion of CH_4 -air- N_2 mixtures in a 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

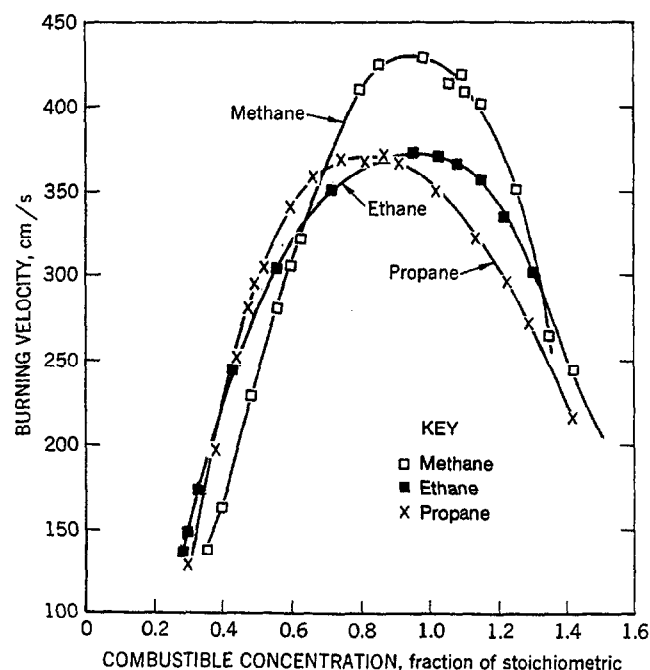


Figure 53.—Burning velocities of methane-, ethane-, and propane-oxygen mixtures at atmospheric pressure and room temperature.

54). The following expression by Dugger (16) has been found reliable for at least paraffinic hydrocarbons in ambient air:

$$S_u = 10 + 0.000342 T^2 \quad (73)$$

where S_u is in cm/s and T is in K. Pressure effects on S_u are more difficult to predict. Data summaries (24, 66, 110) indicate that S_u decreases with increased pressure for low-burning-velocity mixtures (<50 cm/s) and increases for high-velocity mixtures (>100 cm/s); intermediate mixtures display little effect of pressure.

Detonation Velocities

Detonations involve supersonic propagation rates and are more likely to occur in oxygen than in air. Figure 55 gives the detonation velocities obtained by Morrison (74) for vapors of various paraffins in oxygen as a function of combustible concentration. Maximum velocities are 2,500 to 2,700 m/s for these combustibles. For acetylene, hydrogen, and ammonia, the maximum values are closer to 3,000 m/s or more (66, p. 524). In all cases, the maximum values occur at combustible concentrations greater than stoichiometric.

Many combustibles can also undergo detonation in air, although this requires much higher initiation energies, higher pressures, or conditions that promote turbulent combustion and pressure piling. Propagations in long tunnels, especially with irregular wall surfaces, offer favorable conditions for detonations. Although detonations of the paraffins are obtained most readily with the higher members, even methane-air mixtures have been found detonable in recent work. Table 19 lists the detonation velocities obtained by Burgess (6) in an air atmosphere for a few hydrocarbon fuels; data for methane and hydrogen are taken from references 46 and 66, p. 524. Although the velocities in air are lower than in oxygen, they are all above 1,500 m/s over the given range of concentrations, below or above which they decrease as the detonability limits are approached; detonability limits normally fall within flammability limits but can be wider for some combustibles with the use of large booster (initiator) charges. In addition to the initiator strength, the length and diameter (or l/d ratio) of the explosion container can be critical for the development of a detonation at a given pressure; detailed discussions of these factors are given in references 66 and 110.

Table 19. — Detonation velocities of several combustibles in air at 25° C and atmosphere pressure¹

Combustible	Combustible concentration, vol pct	Initiator	Detonation velocity, m/s
Acetylene	19-77	10 g PETN	1,950-2,100
Ethylene oxide . . .	10-18	10 g tetryl	1,890-1,910
	20.5-22	100 g tetryl	2,300-2,350
Hydrogen	~30	NA	1,975
Methane	7-13	50-70 g Amatol . .	1,550-1,600
Propane	4-7	10 g PETN	1,800-1,890
MAPP gas ²	6-8	10 g PETN	1,800-1,850

NA Not available.

¹Based upon data in references 6, 46, and 66, p. 524.

²Methylacetylene, propadiene, and propane of near-equal fractions.

Additional detonation velocities for various combustible mixtures are listed in table 20. Although these data were compiled by Laffitte (61) almost 50 years ago, they are in fair to good agreement with more recent data, including those given in figure 55 for the paraffins. Where data

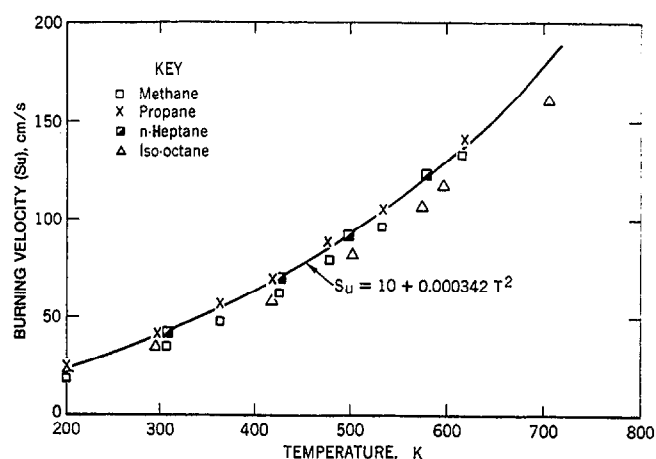


Figure 54.—Effect of temperature on burning velocities of four paraffins in air at atmospheric pressure.

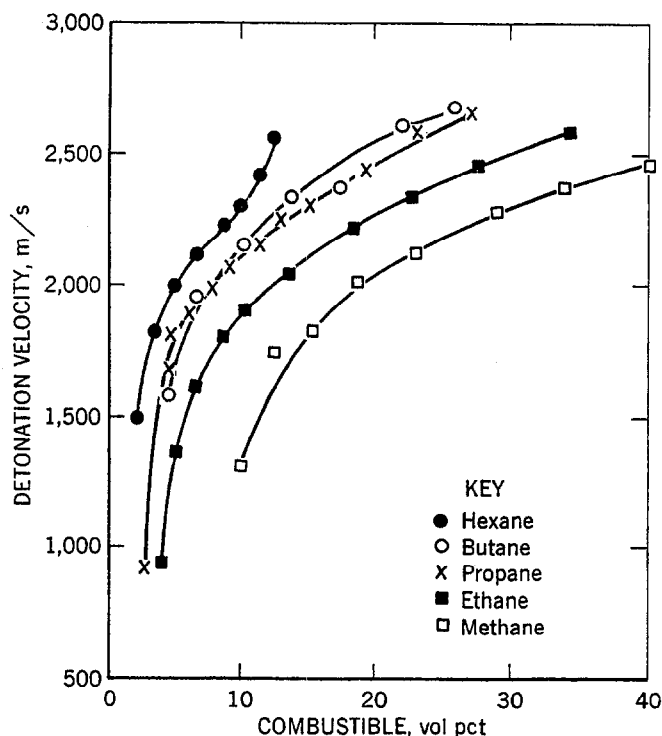


Figure 55.—Detonation velocities of methane-, ethane-, propane-, butane-, and hexane-oxygen mixtures at atmospheric pressure.

discrepancies occur, the values in table 20 are on the low side. It is worth noting that the detonation velocities of benzene and ethyl alcohol at stoichiometric oxygen concentrations are comparable to those of most hydrocarbons, excluding acetylene. Other combustibles such as carbon monoxide and carbon disulfide have relatively low detonation velocities in oxygen even at stoichiometric concentrations; the value for carbon monoxide (1264 m/s) is near marginal for a true detonation. Because of the magnitude of detonation velocities, explosion protection systems designed to protect against deflagrations (subsonic) can hardly be expected to be effective against detonations (supersonic).

Table 20. — Detonation velocities of various combustible mixtures at 25° C and atmospheric pressure (61)

Mixture	Detonation velocity, m/s	Mixture	Detonation velocity, m/s
2 H ₂ + O ₂	2,821	C ₃ H ₈ + 3 O ₂	2,600
2 CO + O ₂	1,264	C ₃ H ₈ + 6 O ₂	2,280
CS ₂ + 3 O ₂	1,800	i-C ₄ H ₁₀ + 4 O ₂	2,613
CH ₄ + 2 O ₂	2,146	i-C ₄ H ₁₀ + 8 O ₂	2,270
CH ₄ + 1.5 O ₂ + 2.5 N ₂	1,880	C ₃ H ₁₂ + 8 O ₂	2,371
C ₂ H ₆ + 3.5 O ₂	2,363	C ₃ H ₁₂ + 8 O ₂ + 24 N ₂	1,680
C ₂ H ₄ + 3 O ₂	2,209	C ₆ H ₆ + 7.5 O ₂	2,206
C ₂ H ₄ + 2 O ₂ + 8 N ₂	1,734	C ₆ H ₆ + 22.5 O ₂	1,658
C ₂ H ₂ + 1.5 O ₂	2,716	C ₂ H ₅ OH + 3 O ₂	2,356
C ₂ H ₂ + 1.5 O ₂ + N ₂	2,414	C ₂ H ₅ OH + 3 O ₂ + 12 N ₂	1,690

Liquid Burning Rates

Whereas burning velocities of combustible gases are relevant to explosion hazard evaluations, burning rates of combustible liquids—including liquefied gases—are important in assessing their fire hazards. The burning rate of a liquid pool is normally defined as a linear regression rate but can also be expressed as a mass or molar consumption rate per unit area. Data uncertainties are greatest for cryogenic fuels, which represent the extreme in vaporization rates.

Burgess (7) defined the liquid regression rates of various combustibles in ambient air as a function of pool diameter (fig. 56). With increasing pool diameter, the regression rates increase because of increased radiation feedback to the burning pool, resulting in greater vaporization and reaction. A pool diameter of about 1 m is required before the rates become maximum and level off for most of the fuels. Burgess gives the following expression for predicting the maximum burning rates:

$$v_{\infty} = 0.0076 \Delta H_c / \Delta H_v \quad (74)$$

where v_{∞} is the extrapolated rate at infinite pool diameter (cm/min) and $\Delta H_c / \Delta H_v$ is the ratio of net heat of combustion and sensible heat of vaporization (ΔH_v). For most hydrocarbon fuels, $\Delta H_c / \Delta H_v$ is about 100. This equation has been found to underestimate the burning rates of liquefied natural gas (LNG) in full-scale tests with 6-m-diam pools.

Table 21 (7) lists the calculated or experimental v_{∞} values for various liquid fuels and the corresponding fractions of thermal energy that may be radiated in large-diameter pool fires. For hydrocarbon flames, the fraction of heat radiated to the surroundings can be expected to be between 25 and 40 pct, as compared to only 17 pct for methanol flames. Note that the burning rate of LNG is roughly comparable to that of butane, hexane, and gasoline. (See also figure 56.) The data for liquid hydrogen, which has by far the highest burning rate (1.4 cm/min), indicate that only about 25 pct of the thermal energy is radiated; however, these data are uncertain because of the limited range of testing. The special hazards associated with liquid hydrogen fires and explosions are summarized by Zabetakis (11).

Table 21. — Burning rates and radiative characteristics of burning liquid pools (7)

Combustible	Linear burning rates ¹ (v_{∞}), cm/min	Thermal output		
		Total, kcal/(cm ² -min)	Radiative, kcal/(cm ² -min)	pct
n-Butane ...	0.79	5.1	1.4	28
n-Hexane73	5.1	2.0	39
Ethylene ...	NA	NA	NA	38
Benzene60	5.1	1.8	35
Xylene58	5.0	NA	NA
Gasoline ...	NA (~0.8)	NA	NA	NA
LNG66 (~0.9)	3.2	.8	25
Methanol17	.64	.11	17
Hydrogen ...	1.40	2.8	.7	25
UDMH38	2.2	.6	27

NA Not available.

¹Computed rates for infinite diameter; parenthetical values from tests with 3-m diam pools.

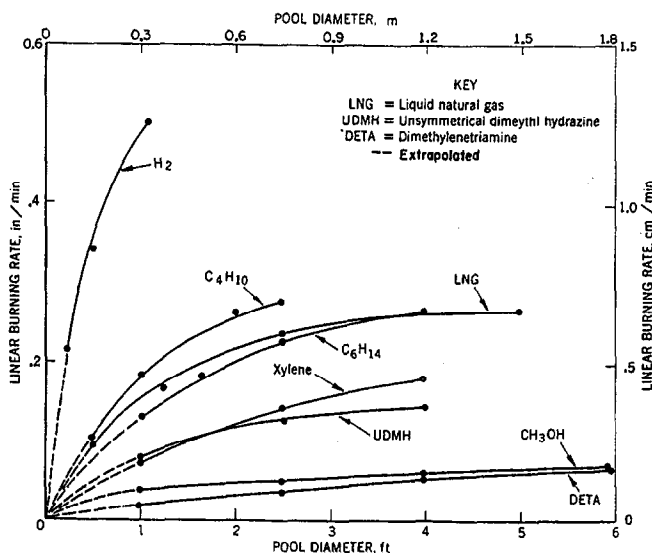


Figure 56.—Linear burning rates of combustible liquids as a function of pool diameter at ambient temperature.

PROPERTIES OF GASOLINES, JET FUELS, HYDRAULIC FLUIDS, AND LUBRICANTS

This section summarizes the combustion properties of composite liquid fuels, hydraulic fluids, and lubricating oils. Most of the data are derived from Bureau studies sponsored by the Air Force. Table 22 gives some of the common physical and combustion properties of various gasolines, diesels, and jet fuels. Table 23 gives correspond-

ing combustion data for hydraulic fluids and lubricating oils. The flashpoints, minimum AIT's, and limits of flammability were determined by the same or modified methods previously described for the neat organic and inorganic combustibles.

Table 22. — Summary of combustion properties of gasolines, diesels, and jet fuels: Gaseous combustion in air at atmospheric pressure¹

Fuel	Mol wt (av)	Sp gr (water = 1)	BP (90 pct), °C	C _{st} ² (in air), vol pct	ΔH_c (net, 25° C)		Flash-point, °C	Minimum AIT, °C	Flammable limits	
					Btu/lb	cal/g			L ₂₅ , vol pct	U ₂₅ , vol pct
JP-1	151	0.81	210	1.3	18,480	10,265	46	230	NA	NA
JP-3	112	.76	227	(2.6)	18,710	10,395	NA	240	1.4	7.9
JP-4	125	.78	199	(2.4)	18,710	10,395	— 18	240	1.3	8.2
JP-5	169	.83	238	1.1	18,440	10,245	66	225	3.6	34.5
JP-6	147	.84	260	(1.3)	18,620	10,345	38	230	3.7	34.8
JP-8	164	.8	238	NA	18,400	10,225	46	225	NA	NA
Jet A	NA	.8	249	NA	18,590	10,328	47	225	(4)	(4)
Jet B	NA	.8	199	NA	18,780	10,435	— 7 to — 18	230	(5)	(5)
Kerosene	NA	.8	254	(1.3)	18,600	10,335	52	230	3.7	34.8
Gasoline 100/130	NA	.7	116	(2.4)	19,000	10,555	— 45	440	1.3	7.1
Gasoline 115/145	NA	.7	120	(2.2)	19,000	10,555	— 45	470	1.2	7.1
Diesel fuel (60 cetane)	NA	.8	~325	NA	NA	NA	40 to 55	225	NA	NA

NA Not available.

¹Flammability data from references 41-42, 47, and 114; physical property values are average or typical.

²Values in parentheses calculated by $C_{st} = L_{25}/0.55$.

³Values at 100° to 150° C.

⁴Similar to JP-5.

⁵Similar to JP-4.

Table 23. — Summary of combustion properties of hydraulic fluids and lubricating oils¹

Fluid	Sp gr (water = 1)	Flash-point, °C	Fire point, °C	Minimum AIT, °C
MINERAL OILS				
MIL-H-5606 (oil)	0.9	90	107	225
MIL-2190 (oil)	.86	232	NA	350
MLO-60-294 (oil)	.88	196	221	370
Mobil DTE-103 (oil)	.92	199	NA	370
Pyrogard D (invert emulsion)	NA	NA	NA	>315
GLYCOLS				
Propylene glycol	NA	110	113	445
Houghto-Safe 271 (water-glycol)	1.05	NA	NA	410
Ucon 50 HB-260 (polyglycol)	1.04	235	260	395
PHOSPHATE ESTERS				
Cellulube 220 (ester base)	1.15	235	352	560
Skydrol (ester base)	NA	182	243	>700
Pydraul 150 (ester base)	1.13	193	243	525
Pydraul AC (ester base)	1.35	232	396	595
Houghto-Safe 1055 (aryl ester)	1.15	263	360	550
Tricresyl phosphate	1.17	243	NA	600
POLYOL AND DIBASIC ACID ESTERS				
MIL-L-7808 (acid diester)	NA	225	238	390
MIL-L-9236 (polyol ester)	NA	221	246	390
MLO-54-581 (acid diester)	NA	224	246	390
Plexol 201 (acid diester)	.91	216	232	~380
SILANES				
MLO-56-280 (diphenyl-dodecyl)	NA	291	329	415
MLO-56-610 (decyl-dodecyl)	NA	279	302	400
SILICATES AND SILICONES				
MLO-54-540 (silicate)	NA	163	221	375
MLO-54-856 (silicate)	NA	157	227	380
Oronite 8200 (silicate)	.93	196	227	380
Versilube F-50 (silicone)	1.05	288	338	480
Dow Corning 400 (siloxane)	NA	124	138	320
Dow Corning 500 (siloxane)	≤.95	243	NA	480
Dow Corning 550 (silicone)	1.07	316	NA	NA
CHLORINATED SILICONES AND HYDROCARBONS				
MLO-53-446 (silicone)	NA	304	377	420
Arachlor 1248 (diphenyl)	1.41	193	>315	~640
Pydraul A-200 (hydrocarbon)	1.42	177	360	650
AROMATIC ETHERS				
5P4E (polyphenoxy)	NA	293	349	610
OS-124 (polyphenyl)	1.20	288	349	600
MCS-293	1.19	220	270	490
MISCELLANEOUS FLUIDS				
SAE No. 10 lube oil	<1.0	171	193	380
SAE No. 60 lube oil	<1.0	249	327	380
Linseed oil	.95	224	279	440

NA Not available.

¹Based upon data in references 47 and 52 and vendors' literature.

VAPOR PRESSURES AND FLASHPOINTS

Jet aircraft fuels can be classified as low- or high-volatility petroleum mixtures. The low-volatility grades are typically kerosenes, such as JP-1, JP-5, JP-6, and JP-8, which have a 10 pct boiling point of at least 177° C (350° F); commercial Jet A fuel also falls in this category. The high-volatility grades are blends of kerosene and high-octane aviation gasoline, such as JP-3 and JP-4, which have a 10 pct boiling point of about 110° C (230° F) or lower; commercial Jet B fuel and motor gasolines also fall in this category. In practice, the compositions of the different grades of fuels can vary with the sources and seasonal period of production. Their vapor compositions will necessarily depend upon the fractional distillation of the lighter ends that comprise such fuels.

Reid vapor pressure curves and flashpoint data are given for representative grades of aviation gasoline and five jet fuels in figure 57 (47). The Reid vapor pressures are normally determined at 38° C (100° F) and are slightly lower than true vapor pressures because the vapor-liquid ratio is not ideal in Reid determinations. The flashpoints are at least 38° C (100° F) for the low-volatility fuels and about -18° C (0° F) or less for high-volatility fuels. Diesel fuels fall in the flashpoint range of the low-volatility fuels. Thus, the vapors of the low-volatility fuels, including Jet A, which is used on most commercial passenger aircraft, will not form homogeneous flammable vapor-air mixtures at a normal ambient temperature of 20° C (68° F) and atmospheric pressure. However, flammable mists can form below the flashpoints of the liquids; see figure 6 and discussion. Assuming ideal behavior, the lower limit fuel concentrations at the flashpoint temperatures can be calculated

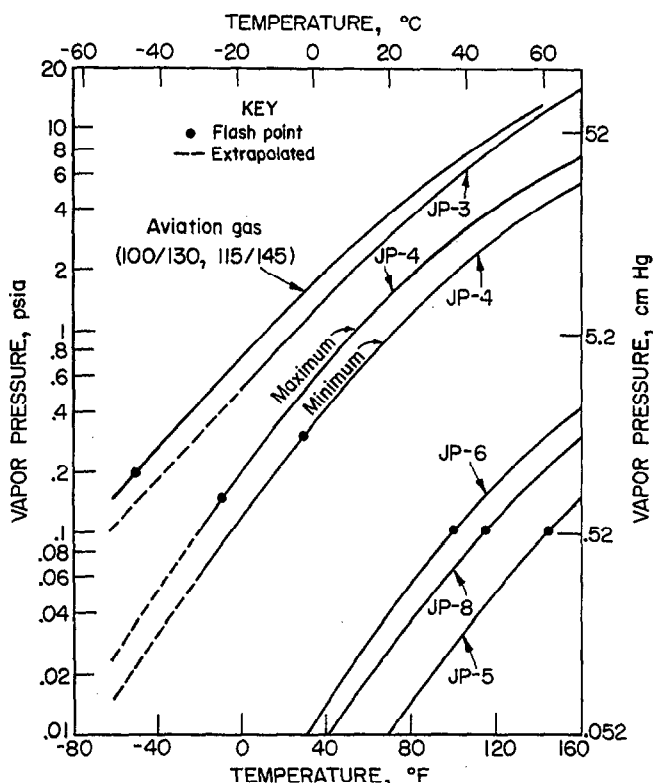


Figure 57.—Vapor pressure (Reid)-temperature curves and flashpoints for aviation gas and five jet fuels.

from the vapor pressure data and equation 4. These may be compared to the experimental values given in table 22, which generally represent the limits of the completely vaporized fuels.

Both flashpoint and firepoint data are listed in table 23 for the hydraulic fluids and lubricating oils. The firepoint is the temperature at which flame can be sustained after the vapors have been ignited; differences between flashpoints and firepoints tend to be great for combustible liquids of low volatility and high fire resistance (high AIT). The flashpoints of hydraulic fluids and lubricating fluids are much higher than those of gasolines and jet fuels. Flashpoints of about 200° C or more are typical of the highly fire-resistant fluids for each chemical class of fluids. In the case of mineral-oil-based fluids, their flashpoints will be largely determined by the paraffinic and naphthenic constituents that are present; MIL-H-5606 oil, which has a flashpoint of only 90° C, is largely paraffinic and presents the greatest flammability hazard among these fluids. In the case of water-glycols, flashpoints will not exist until the excessive water has been removed. It is evident from these data that a high-temperature environment is required to realize a flashpoint hazard with the vapors of these fluids at normal pressure conditions.

FLAMMABILITY LIMITS IN AIR

Limits of flammability of completely vaporized fuel blends can differ from those obtained only with their lighter fractions, as in flashpoint determinations, since the limits vary inversely with the molecular weights of the combustible vapors. Data reported here are mainly those obtained with all fractions of the composite fuel present. As with flashpoint, the flammability limits of the gasolines and jet fuels in table 22 fall into two separate groups. The fuels of high volatility have a flammability range of approximately 1.3 (L_{25}) to 8 (U_{25}) vol pct or less in normal ambient air; those of low volatility have a limiting range of approximately 0.6 to 5 vol pct at ambient temperatures (100° or 150° C) above their flashpoints. These limits are comparable to those found for high-molecular-weight paraffins ($>C_4$) and the benzenes or naphthalenes (appendix A).

Bureau investigators have determined the flammability limits of aircraft-type fuels in air under various environmental conditions. Their data on the effects of mixture temperature and pressure for various gasolines and jet fuels are summarized in tables 24 and 25, respectively. Table 24 shows that the flammability limits of such fuel vapor-air mixtures on a weight basis vary only slightly with a moderate temperature increase; the lower limits at 25° C were at least 48 mg/L and the upper limits were at

Table 24. — Effect of temperature on flammability limits of gasolines and jet fuels in air at atmospheric pressure¹

Fuel	Flammability limits, mg/L ²			
	25° C		150° C	
	Lower	Upper	Lower	Upper
Av gas 100/130	56	350	53	348
Av gas 115/145	56	330	48	337
JP-1	NA	NA	48	380
JP-3	61	370	48	387
JP-4	48	330	47	330
JP-6	NA	NA	³ 46	290

NA Not available.

¹Based upon data in references 41, 57, and 114.

²Mg fuel per liter of air at 0° C and at 1 atm.

³Data at 100° C.