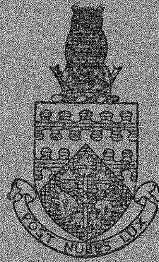


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THE COLLEGE OF AERONAUTICS
CRANFIELD



SPONTANEOUS-IGNITION DATA OF HYDROCARBONS
AND AVIATION FLUIDS

by

E. M. GOODGER

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CRANFIELD

Spontaneous - Ignition Data of Hydrocarbons and Aviation Fluids [⊗]

- by -

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SUMMARY

The standard A.S.T.M. method has been used to determine comparative spontaneous-ignition characteristics of 29 hydrocarbons and aviation fluids. Reasonable correlation is found with results from more precise methods. Ignition temperature levels are similar in the case of paraffins, olefins, and naphthenes, but are slightly higher with alcohols, and much higher with aromatics. Ignition temperature of petroleum-based aviation fluids show a general reduction with increase in specific gravity.

⊗ This note includes work reported in a thesis submitted by F/O. P. Susilvorn, R.T.A.F., in June, 1957 (ref. 7), as part of the requirements for the award of the Diploma of the College of Aeronautics, the research being under the supervision of the author.

SPONTANEOUS-IGNITION DATA OF HYDROCARBONS AND AVIATION FLUIDS

(by A.S.T.M. Method D 286-30)

Introduction

Part of the research activity at the College of Aeronautics consists of a broad series of investigations into the characteristics of spontaneous ignition and inflammability, and their relationship with engine combustion and aircraft fire problems. A comprehensive survey of spontaneous-ignition test techniques is given by Mullins (ref.1) together with an extensive collection of data covering a wide variety of materials. Examination of this data shows, as expected, considerable lack of agreement (e.g. 580 to 740°C for benzene, and 247 to 451°C for n-heptane), due to the differences between the apparatus and procedures used. Jackson (ref.2) and Frank and Blackham (ref.3) have presented comparative data for a number of pure hydrocarbons and commercial fluids, but the apparatus used in each case is somewhat specialised and not widely available in other laboratories. An attempt has been made, therefore, to present a body of information concerning the spontaneous ignition characteristics of typical pure hydrocarbons and aviation fluids, determined by the same operator, using the standard A.S.T.M. technique.

Procedure

The apparatus was set up as outlined in A.S.T.M. method D 286-30 'Autogenous Ignition Temperatures of Petroleum Products' (fig.1). An abridged version of the procedure is given in App.1. Heat was supplied by means of a Calor gas burner ring, and this was augmented by a kerosine blow lamp for temperatures in excess of about 450°C. Fuel was introduced into the flask by means of a 1 ml. hypodermic syringe, instead of the more usual pipette, since this gave a closer control over fuel quantity and a more precise instant for the commencement of the delay period. In some cases, a mirror mounted above the mouth of the flask was found helpful for the determination of ignition. Smoke puffs, without the appearance of luminous flame, were classed as non-ignition. In the A.S.T.M. method, the minimum ignition temperature[§] only is required to be recorded. In the present tests, it was considered of value to construct temperature-delay curves up to temperatures considerably in excess of the minimum value, since this would give some indication of ignition temperatures at shorter delay periods, and also show any marked variations in the temperature-delay relationship.

§ (described as the 'autogenous' ignition temperature.)

Results

Spontaneous ignition temperature-delay curves are presented in figs. 2 to 7 for representative paraffin, naphthene, aromatic, alcohol, glycol and glycol-ether hydrocarbons, and for typical aviation fluids. The fuel charges used for these curves were those which gave minimum ignition temperatures, as in the A.S.T.M. procedure. In most cases, these charges were found to be 0.05 ml. Based on a flask volume of 150 ml., this corresponds to mixture strengths considerably richer (5x to 10x) than stoichiometric, assuming no loss of vapour during the delay period.

The minimum values of spontaneous-ignition temperature are tabulated, together with their associated delays, in table 1, and are plotted against numbers of carbon atoms/molecule in fig.8. A comparison is made between the latter curves and those of Jackson and others, presented in fig.9.

Discussion

A rapid reduction in delay period is noted over the first 20 or 30°C rise in temperature above the minimum ignition value. Thereafter, the curves flatten out progressively. This characteristic is evident with all the fluids tested, but the gradients differ in magnitude (e.g. hydraulic fluid in fig.6). The effects of isomerism are clearly indicated in figs. 2 and 4, and those of special blends and non-hydrocarbon materials in figs. 6 and 7. The curves in fig.8 confirm the general reduction in minimum ignition temperature with increase in molecular weight. General agreement is noted between these results and those of Jackson (fig.9), obtained with the flask buried in a metal heater block. A detailed comparison between the two sets of data is included in table 1, and this shows that Jackson's results give a trend towards lower temperatures and longer delays, which reflects the greater precision possible by Jackson's method.

Frank and Blackham (ref.3) also used an ignition chamber buried in a metal block, but the provision of a continuous air current (125 cc./minute) permitted complete chamber flushing within the two minute period between tests. Fuel charges of about 0.04 gm. (i.e. same order as present tests) were found to be required, and similar delay periods (30 to 60 seconds) were experienced. Results, included in table 1 and fig. 9, are generally higher than the present results, but direct comparisons are difficult in the absence of quoted delays, and due to the presence of flushing air. It is to be noted that a reduction in air flow of 80% lowered the ignition temperature by about 3 to 8°C. The paraffin curve included in fig. 9 shows an increase in minimum ignition temperature beyond the C₁₆ molecule. This was due to the lower volatility, which made

necessary an increase in fuel charge, and gave rise to longer delays.

O'Neal (ref.4) used the basic flask system of the A.S.T.M. method, and incorporated it into a pressure-tight container. Minimum ignition temperatures obtained at 1 atmosphere pressure, which are included in table 1 and fig. 9, show a slightly closer agreement with the present results.

The principal advantages of the solid block type apparatus, as used by Jackson and by Frank and Blackham, lie in the uniformity of temperature distribution throughout the chamber (ref.5), and the ease of heating at higher temperature levels. Greater precision is possible, therefore, resulting in lower temperature associated with longer delays. Using Jackson's results as reference values, the present A.S.T.M. results show an average increment in ignition temperature of 19°C (fig.10), and a reduced average delay of about 22%.

Fig. 10 shows also the effect of catalysis when a platinum chamber is used. Mixture elements contacting the platinum surface are consumed rapidly. The remaining mixture becomes contaminated with oxidised diluents, and a higher chamber temperature is necessary to effect true ignition. Catalysis is seen to be more marked with the more ignitable fuels. With oxidisable metals, Frank and Blackham show that the oxide film gives an increasing catalytic effect at higher ignition temperatures.

Conclusions

Spontaneous ignition data obtained for the 29 materials show a reasonable correlation with results from more precise methods. A decreasing reduction is found in delay with increase in temperature, and in minimum ignition temperature with increase in molecular weight. An apparent increase in minimum ignition temperature has been observed elsewhere with the heavier materials, due to the rate of vaporization falling below the rate of reaction. Minimum ignition temperature levels are similar in the case of paraffins, olefins and naphthenes. Alcohols ignite at slightly higher temperatures, and aromatics at much higher temperatures. Isomerism raises the minimum ignition temperature level, and may shorten or lengthen the delay. The hydroxylation of ethane to ethanol apparently makes a marked reduction in minimum ignition temperature. The effect of further hydroxylation to ethylene glycol is negligible.

With petroleum-based aviation fluids, the minimum ignition temperature curve falls smoothly with increase in specific gravity.

Special blends tend to give rise to a departure from this curve, and synthetic fluids exhibit higher minimum ignition temperatures than their petroleum-based counterparts.

REFERENCES

1. Mullins, B.P., Spontaneous Ignition of Liquid Fuels. AGARDograph 4. Butterworths Sci. Pubs. London, 1955.
2. Jackson, J.L., Spontaneous Ignition Temperatures of Pure Hydrocarbons and Commercial Fluids. NACA RM E50J10. (Also Ind. Eng. Chem. 43, 1951, p.2869).
3. Frank, C.E., and Blackham, A.U., Investigation of Hydrocarbon Ignition. NACA TN.2549, 1952.
4. O'Neal, C., Effect of Pressure on the Spontaneous Ignition Temperature of Liquid Fuels. NACA TN.3829, 1956.
5. Scott, G.S., Jones, G.W., and Scott, F.E., Determination of Ignition Temperatures of Combustible Liquids and Gases. Anal. Chem., vol.20, No. 3, March 1948, p.238.
6. Masson, H.J., and Hamilton, W.F., A Study of Autoignition Temperature: Pure Compounds. Ind. Eng. Chem. 20. 1928.
7. Susilvorn, P., Fuels and Fire Risks. College of Aeronautics Thesis, June, 1957.

TABLE 1. MINIMUM SPONTANEOUS-IGNITION TEMPERATURES, AND DELAYS

FLUID	PRESENT TESTS		JACKSON (2)		FRANK(3)	O'NEAL(4)
	°C.	SECS.	°C.	SECS.	°C.	°C.
n-Heptane	248	18.4	247	30	250	250
n-Octane	230	20	240	54	-	-
2:2:4 Trimethyl Pentane	467	12.6	447	12	515	467
Cyclo Hexane <i>NONE</i>	315	22	270	102	-	-
Benzene	588	30	592	42	645	626
Toluene	592	19.4	568	48	635	-
o-Xylene	504	26.4	501	30	551	-
m-Xylene	587	22	563	54	652	-
p-Xylene	598	16.4	564	42	657	-
Cumene	486	18.4	468	6	-	-
Methanol	489	14	-	-	-	-
Ethanol	439	13.8	-	-	425	-
Propanol	420	14.4	-	-	441	-
iso-Propanol	454	15.4	-	-	498	-
Butanol	392	15.4	358	18	-	-
Ethylene Glycol	436	17.4	-	-	-	-
Oxitol \ast	241	12	-	-	-	-
Dioxitol Δ	224	26.6	-	-	-	-
Liquid Paraffin	363	10.7	-	-	-	-
73 Avgas <i>NONE</i> (2485)	315	6.6	-	-	-	-
100/130 Avgas (2485)	500	5	451	6	-	-
Avtag (2486)	255	25.8	-	-	-	272 (A)
Avtur (2482)	254	28.4	249	66	-	-
Avcat (2488)	261	35.8	-	-	-	247 (B)
Gas Oil	247	30.8	-	-	-	-
Lubricating Oil (2472)	234	37.2	-	-	-	-
Lubricating Oil (2479)	236	34.4	-	-	-	-
Lubricating Oil (Synthetic) (2487)	293	5.6	-	-	-	-
Hydraulic Oil (DTD.585)	258	58	-	-	-	-

\ast Ethylene glycol monoethyl ether $C_4H_{10}O_2$

(A) JP4

Δ Diethylene glycol monoethyl ether $C_6H_{14}O_3$

(B) JP5

APPENDIX 1.

AUTOGENOUS IGNITION TEMPERATURE (ASTM. D 286 - 30)

- Abridged description -

This method is suitable for liquid and semi-liquid petroleum products.

Procedure

1. Melt the alloy in the solder bath, and partially submerge the flask so that the bottom of the flask is $\frac{3}{4}$ " from the bottom of the pot. Centralise the flask in the pot. Check that the thermocouple bead is about $\frac{3}{4}$ " from the bottom of the pot and $\frac{1}{4}$ " from the side of the flask. Place the draught shield in position, and bring the temperature of the bath to a level near that of the probable ignition temperature of the sample under test.
2. Admit various amounts of the sample to the flask from the pipette until an amount is found to produce ignition. Allow at least 2 minutes to elapse after each addition, and displace the gases completely each time by means of a slow stream of clean air.
3. When ignition takes place, lower the temperature by about 50° and repeat the process, starting with the number of droplets that ignited in the first instance. A larger and smaller number of droplets should be tried also in order to be sure that the volume of sample giving the lowest temperature of ignition is included in the tests.
4. Proceed in this fashion until an indicated temperature is found at which ignition takes place, but at 50° below which ignition fails to take place. The minimum indicated ignition temperature may then be determined by repeated trials between these two temperatures.

Precision

Results should be duplicable to within $\pm 20^{\circ}$.

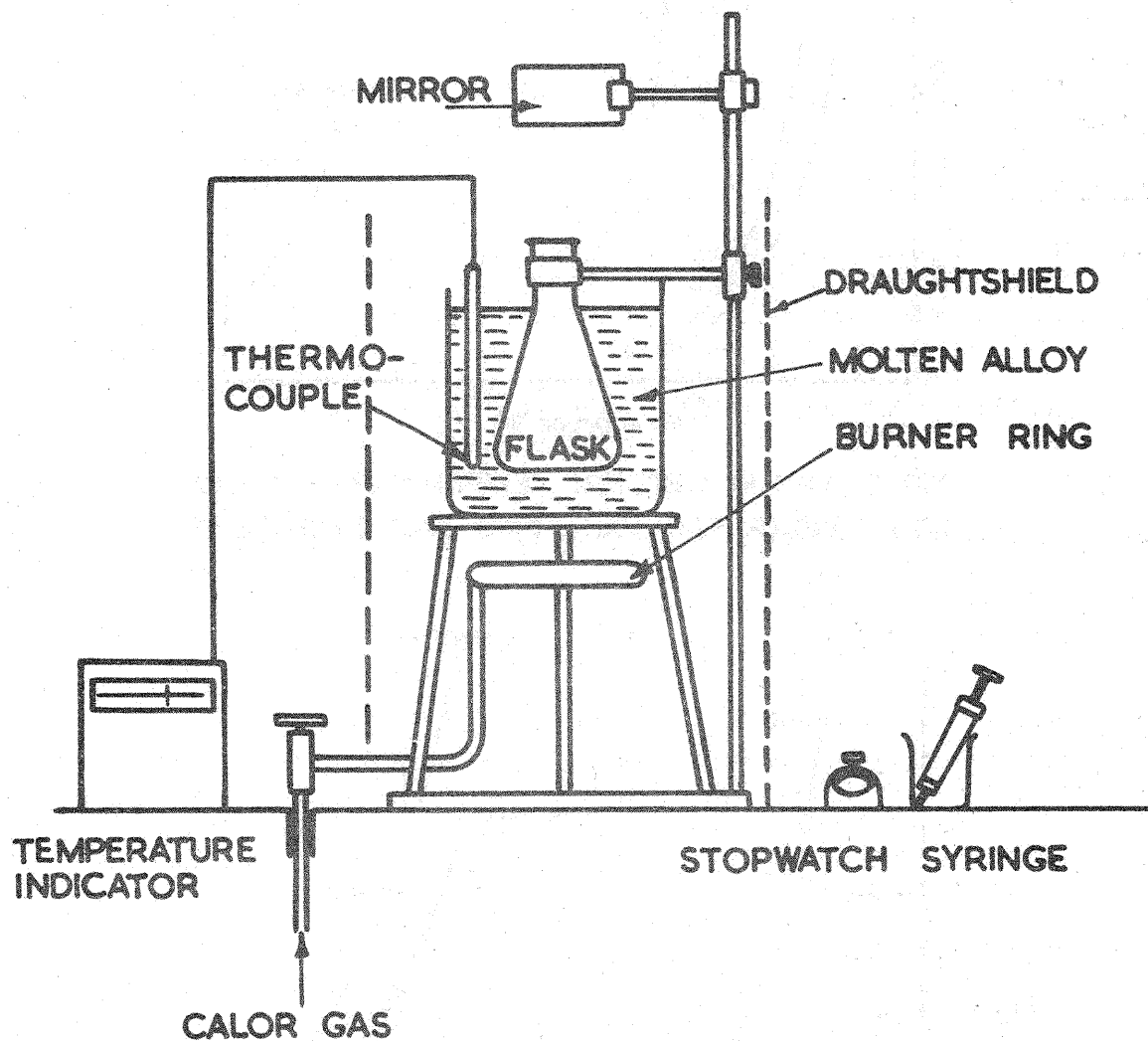


FIG. I. A.S.T.M. AUTOGENOUS IGNITION APPARATUS (D. 286 - 30) AS USED IN PRESENT TESTS.

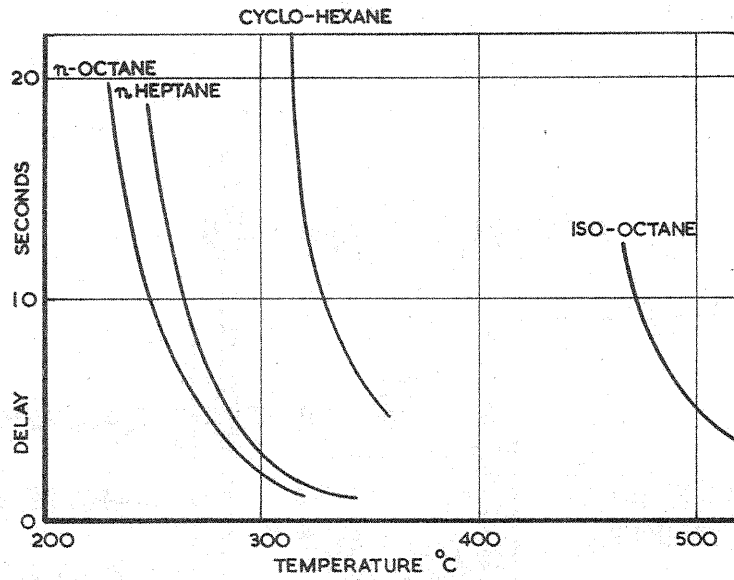


FIG. 2. A.S.T.M. IGNITION TEMPERATURE - DELAY RELATIONSHIP FOR PARAFFINS AND NAPHTHENES

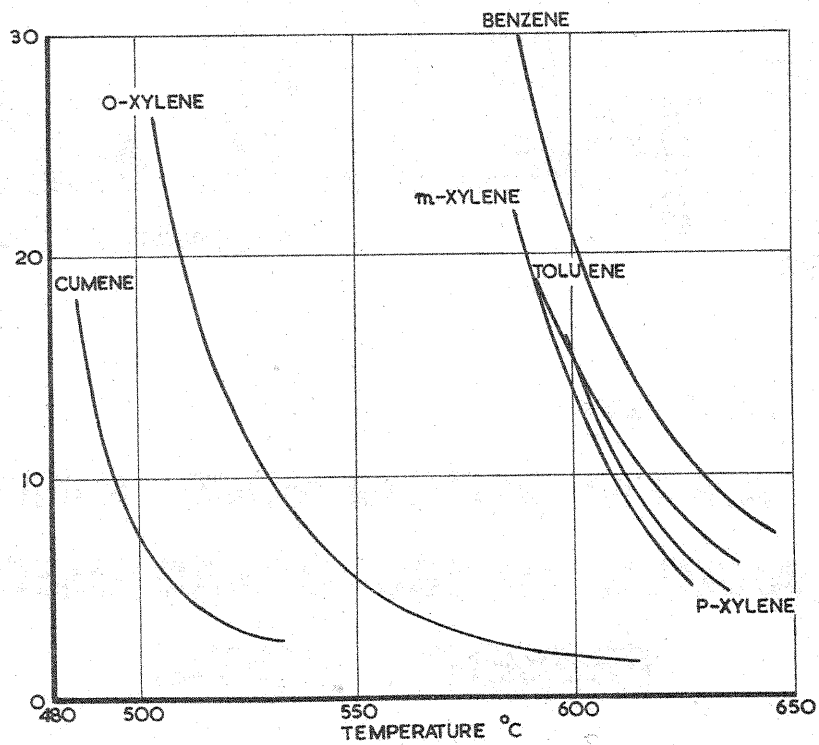


FIG. 3. A.S.T.M. IGNITION TEMPERATURE - DELAY RELATIONSHIP FOR AROMATICS

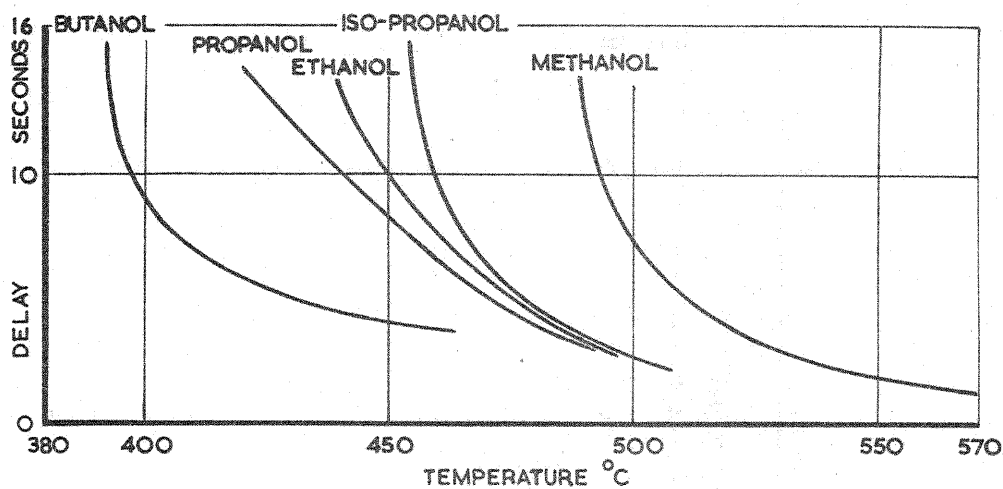


FIG. 4. A.S.T.M. IGNITION TEMPERATURE-DELAY RELATIONSHIP FOR ALCOHOLS

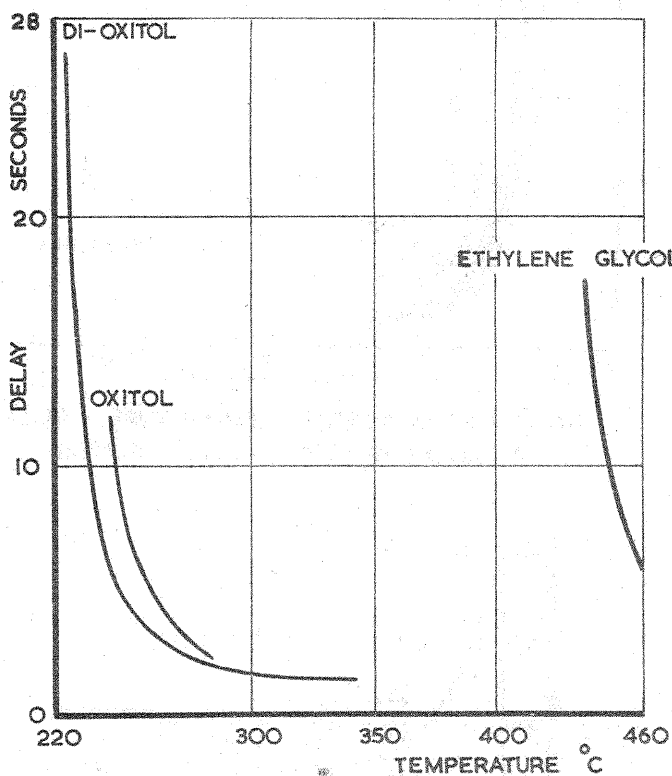


FIG. 5. A.S.T.M. IGNITION TEMPERATURE-DELAY RELATIONSHIP FOR GLYCOL AND GLYCOL ETHERS

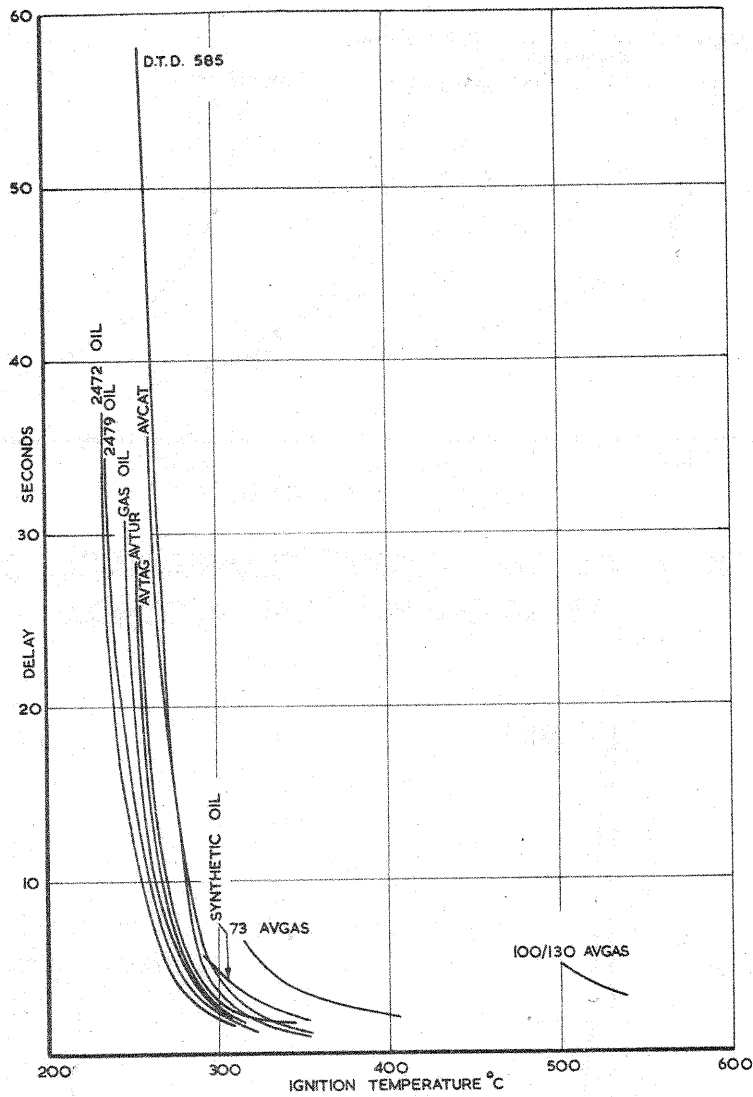


FIG. 6 A.S.T.M. IGNITION TEMPERATURE - DELAY RELATIONSHIP FOR AVIATION FLUIDS

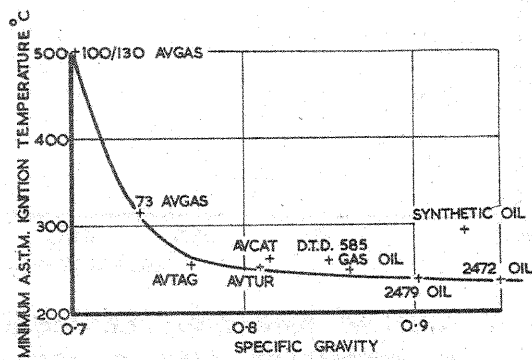


FIG. 7. VARIATION IN MINIMUM A.S.T.M. IGNITION TEMPERATURE WITH SPECIFIC GRAVITY (AVIATION FLUIDS)

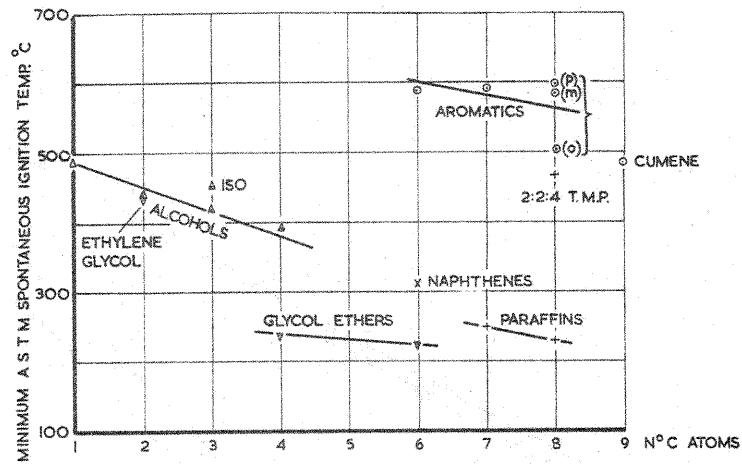


FIG. 8. EFFECT OF MOLECULAR STRUCTURE UPON MINIMUM A.S.T.M. SPONTANEOUS IGNITION TEMP.

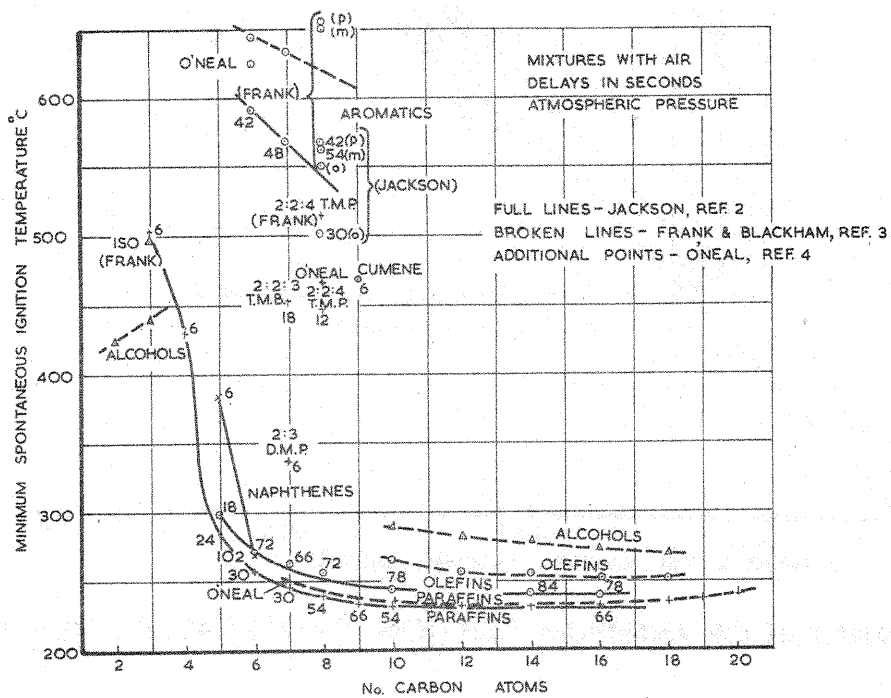


FIG. 9 EFFECT OF MOLECULAR STRUCTURE UPON MINIMUM SPONTANEOUS IGNITION TEMP. (PUBLISHED DATA)

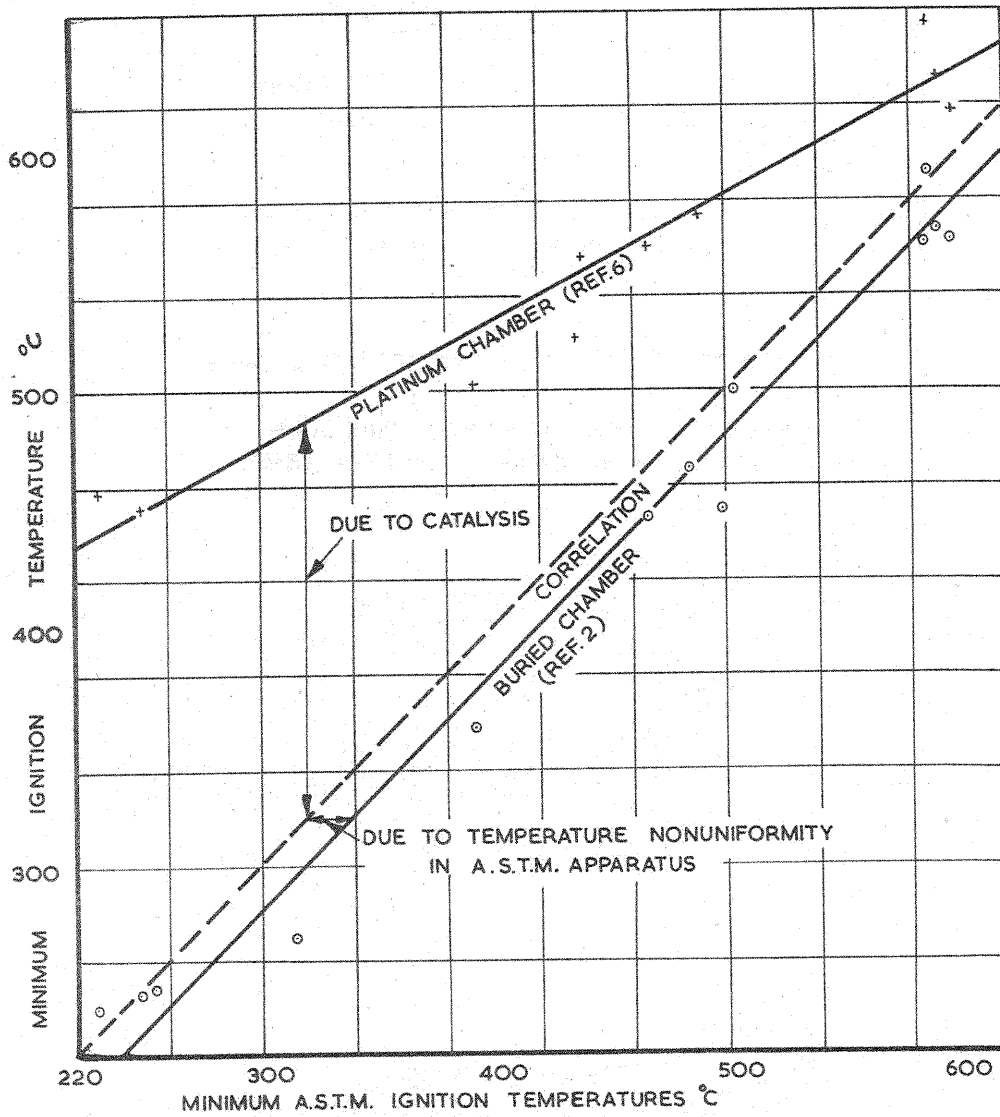


FIG. 10 COMPARISON OF MINIMUM IGNITION TEMPERATURE RESULTS