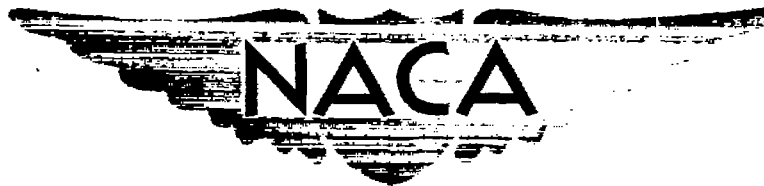874

NACA

RESEARCH MEMORANDUM

SPONTANEOUS IGNITION TEMPERATURES OF PURE HYDROCARBONS

AND COMMERCIAL FLUIDS

By Joseph L. Jackson

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

December 20, 1950

2013

NACA RM E50J10

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

SPONTANEOUS IGNITION TEMPERATURES OF PURE HYDROCARBONS

AND COMMERCIAL FLUIDS

By Joseph L. Jackson

SUMMARY

The spontaneous ignition temperatures of 94 pure hydrocarbons and 15 fuels and commercial fluids were determined by a crucible method. The resulting data for the pure compounds are presented as functions of hydrocarbon structure.

An increase in molecular weight results in a decrease in spontaneous ignition temperature for both normal alkanes and normal alkenes; in general, increased branching increases the ignition temperature of alkanes and alkenes. Aromatics have considerably higher spontaneous ignition temperatures than most alkanes or alkenes, with benzene having the highest value for any of the hydrocarbons tested.

INTRODUCTION

In conjunction with the aircraft-fire problem and as a corollary to the combustion research at the NACA Lewis laboratory, it was desirable to have self-consistent data on spontaneous ignition temperatures of pure hydrocarbons and aircraft fluids. The spontaneous ignition temperature of a substance has been defined (reference 1) as the lowest temperature at which that substance will ignite in air or oxygen without the application of a source of ignition. The spontaneous ignition temperature is different from the flash point of a liquid. (The flash point is the lowest temperature of a liquid that will permit its ignition by an external source.) Spontaneous ignition temperatures of fuels are of some significance in the performance of reciprocating engines because, in general, fuels for spark-ignition engines should have high ignition temperatures, and fuels for compression-ignition engines should have low spontaneous ignition temperatures. This property of the fuel probably influences the combustion characteristics of the fuel in continuous combustion apparatus, such as aircraft gas-turbine engines or ram-jet engines. The spontaneous ignition temperature is also a factor in rating the inflammability hazards in handling

combustibles. Knowledge of the spontaneous ignition temperature of a variety of fuels may also aid in determining the mechanism by which fuels are ignited and burned.

Four general methods have been used to determine spontaneous ignition temperatures:

1. Crucible methods in which a small amount of fuel is dropped into a heated cavity

2. Dynamic methods in which mixtures of the fuel and air or oxygen are passed through heated tubes and raised to the ignition temperature

3. Bomb methods, which permit the determination of ignition temperatures at elevated pressures

4. Adiabatic compression methods in which fuel and air mixtures are rapidly compressed to varying compression ratios to determine the minimum ignition temperature

A survey of the methods used for the determination of ignition temperatures is given in reference 1 and more recent studies are reported in references 2, 3, and 4. In general, the value obtained for the spontaneous ignition temperature of any substance will depend on the pressure, the nature of the igniting surface, the ratio of the combustible to air or oxygen, the movement of the mixture relative to the surface, and the time allowed for ignition to occur. Small amounts of contaminants in the substance or in the atmosphere may markedly affect the results. Both the individual and the relative ignition temperatures of different substances vary widely in the data reported by different investigators. For example, the values quoted in the literature for the spontaneous ignition temperature of benzene in air vary from 370° to 1062° C (698° to 1944° F) (reference 1).

Compilations of spontaneous ignition temperatures are presented in references 3 and 5, but these are composed of data determined by many investigators using a variety of methods. Because different methods were used, there was no basis for comparing the ignition temperatures of the combustibles listed in these references and it appeared desirable to redetermine the spontaneous ignition temperatures of a variety of pure hydrocarbons and other liquids using a single procedure. The spontaneous ignition temperatures of 94 pure hydrocarbons and 15 commercial fluids as determined by one investigator using a crucible method are reported herein.

2013

APPARATUS AND PROCEDURE

The apparatus used in this work was the Scott, Jones, and Scott (reference 3) modification of the A.S.T.M. (reference 6) crucible method. In the A.S.T.M. method, a pyrex Erlenmeyer flask is supported in a molten metal bath (solder or other low-melting alloy) and the minimum bath temperature that will cause ignition when a few drops of the combustible are dropped into the flask is determined. Because there are experimental difficulties in the use of this method at high temperatures, the Scott, Jones, and Scott apparatus in which a quartz flask is placed in a hole in a solid metal block was used. This apparatus (fig. 1) consists of an electrically heated Inconel block, 8 inches in diameter by $5\frac{1}{4}$ inches deep. A 125-milliliter quartz Erlenmeyer flask rests on the bottom of a $2\frac{5}{8}$-inch diameter by 3-inch deep hole drilled axially into the block. Temperatures are measured by a thermocouple in a well, drilled from the side of the block and with the junction 1/2 inch below the bottom of the flask.

Spontaneous ignition temperatures were determined by raising the temperature of the block and periodically dropping a few drops of the combustible into the flask until ignition was observed. The temperature of the block was then slowly decreased and the amount of added combustible was varied until the lowest temperature for ignition was found. It is shown in reference 2 that zones of nonignition appear for some compounds at temperatures above the minimum ignition temperatures. Inasmuch as these zones may not appear for all fuel-air ratios, the fuel-air ratio was varied over wide limits with repeated trials at lower temperatures to eliminate the interference of these zones. Two minutes was allowed for ignition to occur and the flask was purged with air after each test.

The time required for ignition to occur was measured by a stop watch and varied from about 1 second to almost 2 minutes. This time lag is not an independent variable in spontaneous-ignition testing. For a given combustible, time lag increases as temperature is decreased. The time lag at the minimum ignition temperature varies widely for various types of combustible. Although it is possible to select some relatively short time lag and determine the ignition temperatures of all combustibles at this selected lag, the data presented herein are the minimum ignition temperatures for this apparatus. The time lags reported are those at this minimum temperature.

RESULTS AND DISCUSSION

The spontaneous ignition temperatures were reproducible to $\pm5^{\circ}$ F. When the results obtained in this work are compared with those obtained by Scott, Jones, and Scott using substantially identical apparatus and procedure, considerably greater deviations are found in the spontaneous ignition temperatures. Ten hydrocarbons were common to both investigations and, as shown in table I, differences as great as 41° F were observed. The reasons for these differences are not known, but it emphasizes the undesirability of comparing ignition-temperature data from different sources.

The spontaneous ignition temperatures and the time lags of the pure hydrocarbons are given in table II. Also listed in table II are the estimated purity of the pure hydrocarbons, most of which, with the exception of the cycloparaffins and butenes, were prepared by either the National Bureau of Standards or the Lewis laboratory.

The variation of spontaneous ignition temperature with the number of carbon atoms in the molecule for the normal alkanes and alkenes is shown in figure 2. After a rapid decline in the ignition temperature from 940° F for propane to 544° F for pentane, the values tend toward a constant figure, falling only 3° between decane and hexadecane, with an ignition temperature of 446° F. The values for the normal alkenes roughly parallel those of the alkanes, the alkenes being 20° to 30° F higher.

The variation of spontaneous ignition temperature with the number of carbon atoms in the molecule for the branched alkanes, with the curve for the normal alkanes shown for comparison, is presented in figure 3. For molecules having a chain length shorter than eight carbon atoms, branching raises the ignition temperature. The position of the first side chain has little effect, but a molecule having two side chains on the same carbon atom has a higher ignition temperature than one having two side chains on adjacent carbon atoms. In general, the higher the degree of branching, the higher the ignition temperature. For molecules having a chain length of eight carbon atoms or longer, however, one side chain can cause a slight lowering of the ignition temperature below that of the corresponding normal compound.

The variation of spontaneous ignition temperature with the number of carbon atoms in the molecule for the branched alkenes, with the curve for the normal alkenes shown for comparison, is shown in figure 4. The conclusions drawn for the shorter chain branched alkanes hold for the branched alkenes, but the introduction of the double bond moderates the effect of branching.

2013

Data on the cycloparaffins are insufficient to establish many trends in this class of compound. It is apparent from table II, however, that cyclohexane, methylcyclohexane, and ethylcyclohexane have fairly constant ignition temperatures, whereas the methyl-tert-butylcyclohexanes have substantially higher values.

The aromatic hydrocarbons have higher spontaneous ignition temperatures than most paraffins. The highest value for any hydrocarbon was 1097° F for benzene. A plot of the ignition temperature against the number of carbon atoms is shown in figure 5. When only one side chain is present, the degree of branching can greatly influence the ignition temperature, as in the butylbenzenes. Where there are ortho, meta, and para isomers of the compound, the ignition temperature of the meta isomer is usually lower than the para, and the ortho isomer is substantially below the others. This difference is illustrated by the xylenes, with values of 1048°, 1045°, and 934° F for the para, meta, and ortho isomers, respectively.

The spontaneous ignition temperatures for representative samples of various commercial fluids are listed in table III. Gasoline of 100/130 grade falls where expected in view of its high content of short-chained highly branched constituents, whereas kerosene has a low-ignition temperature owing to its long-chain characteristics. The high values of the lubricating oils can probably be explained by their substituted cycloparaffinic constituents. The use of tricresyl phosphate, chlorinated diphenyls, and hexachlorobutadiene as bases for less-flammable hydraulic fluids is suggested by the relatively high ignition temperatures of these materials. The ignition temperatures of completely fluorinated and chlorinated compounds indicate that perhaps no completely nonflammable organic compound can be found.

SUMMARY OF RESULTS

From an investigation of the spontaneous ignition temperatures of 94 pure hydrocarbons and 15 fuels and commercial fluids by the crucible method, the following results were obtained:

1. The spontaneous ignition temperatures for normal alkanes decreased with increasing molecular weight from 940° F for propane to 446° F for hexadecane.

2. The spontaneous ignition temperatures of normal alkenes decreased with increasing molecular weight from 569° F for 1-pentene to 464° F for 1-hexadecene.

3. In general, branching increased the spontaneous ignition temperatures of both alkanes and alkenes.

4. Aromatics, in general, had higher spontaneous ignition temperatures than either alkanes or alkenes with benzene having the highest temperature of any of the hydrocarbons examined.

Lewis Flight Propulsion Laboratory,
    National Advisory Committee for Aeronautics,
        Cleveland, Ohio.

REFERENCES

1. Anon.: Science of Petroleum. Vol. IV. Oxford Univ. Press, 1938, pp. 2970-2975.

2. Sortman, Charles W., Beatty, Harold A., and Heron, S. D.: Spontaneous Ignition of Hydrocarbons. Zones of Nonignition. Ind. and Eng. Chem. (Ind. ed.), vol. 32, no. 3, March 1941, pp. 357-360.

3. 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, pp. 238-241.

4. Taylor, C. F., Taylor, E. S., Livingood, J. C., Russell, W. A., and Leary, W. A.: Ignition of Fuels by Rapid Compression. SAE Quart. Trans., vol. 4, no. 2, April 1950, pp. 232-270; discussion, pp. 271-274.

5. The Associated Factory Mutual Fire Insurance Cos.: Properties of Flammable Liquids, Gases, and Solids. Ind. and Eng. Chem. (Ind. ed.), vol. 32, no. 6, June 1940, pp. 880-884.

6. Anon.: Standard Method of Test for Autogeneous Ignition Temperatures of Petroleum Products. (Adopted 1930.) A.S.T.M. Designation: D 286-30. A.S.T.M. Standards on Petroleum Products and Lubricants, Nov. 1948, pp. 199-200.

TABLE I - COMPARISON OF SPONTANEOUS-IGNITION-TEMPERATURE DATA

Hydrocarbon	Spontaneous ignition temperature in air ($^\circ$F)		
	Reference 3	NACA	Difference
Butane	766	807	41
2,3-Dimethylbutane	788	790	2
Ethylbenzene	891	860	-31
Heptane	446	477	31
2-Methylbutane	788	800	12
2-Methylpropane	864	890	26
Octane	424	464	40
Pentane	554	544	-10
Propane	920	940	20
2,2,4-Trimethylpentane	813	837	24

2013

TABLE II - SPONTANEOUS IGNITION TEMPERATURES OF PURE HYDROCARBONS

Hydrocarbon	Spontaneous ignition temperature (°F)	Time lag at last ignition (min)	Estimated purity (percent)
Propane	940	0.1	98+
Butane	807	.1	98+
Pentane	544	.4	98+
Hexane	501	.5	98+
Heptane	477	.5	98+
Octane	464	.9	98+
Nonane	453	1.1	98+
Decane	449	.9	98+
Hexadecane	446	1.1	98+
2-Methylpropane	890	.3	98+
2,2-Dimethylpropane	853	.05	98+
2-Methylbutane	800	.1	98+
2,2-Dimethylbutane	824	.2	98+
2,3-Dimethylbutane	790	.2	98+
2,2,3-Trimethylbutane	849	.3	98+
2-Methylpentane	585	.1	98+
3-Methylpentane	580	.2	98+
2,3-Dimethylpentane	640	.1	98+
2,2,3-Trimethylpentane	816	.4	98+
2,2,4-Trimethylpentane	837	.2	98+
2,3,3-Trimethylpentane	806	.2	98+
2,2,3,3-Tetramethylpentane	845	.7	98+
2,3,3,4-Tetramethylpentane	818	.4	98+
2,4-Dimethyl-3-ethylpentane	734	.2	98+
3,3-Dimethylheptane	626	.06	98+
2-Methyloctane	440	1.1	98+
3-Methyloctane	442	1.0	98+
4-Methyloctane	450	.1	98+
2,3-Dimethyloctane	447	1.2	98+
4-Ethyloctane	458	.9	98+
2-Methylnonane	418	1.7	98+
1-Pentene	569	0.3	98+
1-Hexene	521	1.2	98+
1-Heptene	505	1.1	98+
1-Octene	493	1.2	98+
1-Decene	471	1.3	98+
1-Tetradecene	463	1.1	98+
1-Hexadecene	464	1.3	95+

NACA

2013

TABLE II - SPONTANEOUS IGNITION TEMPERATURES OF

PURE HYDROCARBONS - Continued

Hydrocarbon	Spontaneous ignition temperature ($^\circ$F)	Time lag at last ignition (min)	Estimated purity (percent)
3-Methyl-1-butene	706	0.1	98+
2-Methyl-1-pentene	582	.1	95+
4-Methyl-1-pentene	580	.2	98+
2-Ethyl-1-butene	615	.1	95+
2,3-Dimethyl-1-butene	697	.1	98+
2,3-Dimethyl-2-butene	764	.1	98+
2,3,3-Trimethyl-1-butene	721	.2	98+
2,4,4-Trimethyl-1-pentene	788	.2	98+
2,4,4-Trimethyl-2-pentene	587	.5	98+
2,3,4-Trimethyl-1-pentene	495	.2	95+
3,4,4-Trimethyl-2-pentene	626	.4	98+
Cyclopentane	725	0.1	90+
Methylcyclopentane	614	.1	95+
Cyclohexane	518	1.7	98+
Methylcyclohexane	509	1.8	99+
Ethylcyclohexane	507	1.9	98+
1-Methyl-2-tert-butylcyclohexane	597	.2	99+
1-Methyl-3-tert-butylcyclohexane (high boiling isomer)	580	.2	99+
1-Methyl-3-tert-butylcyclohexane (low boiling isomer)	556	.4	99+
Alpha-pinene	506	1.0	98+
dl-Limonene	505	.5	98+
Benzene	1097	0.7	99+
Toluene	1054	.8	99+
1,3-Dimethylbenzene (m-xylene)	1045	.9	99+
1,4-Dimethylbenzene (p-xylene)	1048	.7	99+
1,2-Dimethylbenzene (o-xylene)	934	.5	99+
1,3,5-Trimethylbenzene	1039	.8	99+
1,2,4-Trimethylbenzene	970	.4	99+
1,2,3-Trimethylbenzene	895	.4	99+
Ethylbenzene	860	.3	99+
1-Methyl-3-ethylbenzene	905	.3	99+
1-Methyl-4-ethylbenzene	902	.2	99+
1-Methyl-2-ethylbenzene	836	.3	99+

TABLE II - SPONTANEOUS IGNITION TEMPERATURES OF

PURE HYDROCARBONS - Concluded

Hydrocarbon	Spontaneous ignition temperature (^{o}F)	Time lag at last ignition (min)	Estimated purity (percent)
1,2-Diethylbenzene	759	0.1	99+
1,3-Diethylbenzene	851	.2	99+
1,4-Diethylbenzene	844	.2	99+
Propylbenzene	853	.2	99+
Isopropylbenzene	873	.1	99+
Butylbenzene	821	.1	99+
Isobutylbenzene	853	.2	99+
Secbutylbenzene	836	.3	99+
Tertbutylbenzene	891	1.2	99+
1-Methyl-3,5-diethylbenzene	861	.2	99+
1-Methylnaphthalene	1017	.4	---
Biphenyl	1071	.6	99+
2-Methylbiphenyl	936	.2	99+
2-Ethylbiphenyl	840	.3	99+
2-propylbiphenyl	845	.3	99+
2-butylbiphenyl	811	.2	99+
Diphenylmethane	962	.3	99+
1,1-Diphenylethane	909	.1	99+
1,1-Diphenylpropane	870	.1	99+
1,1-Diphenylbutane	863	.1	99+
1-Ethylnaphthalene	898	.1	99+
Tetrahydronaphthalene	794	.1	95+
Decahydronaphthalene	521	.3	95+

2013

TABLE III - SPONTANEOUS IGNITION TEMPERATURES OF FUELS

AND COMMERCIAL FLUIDS

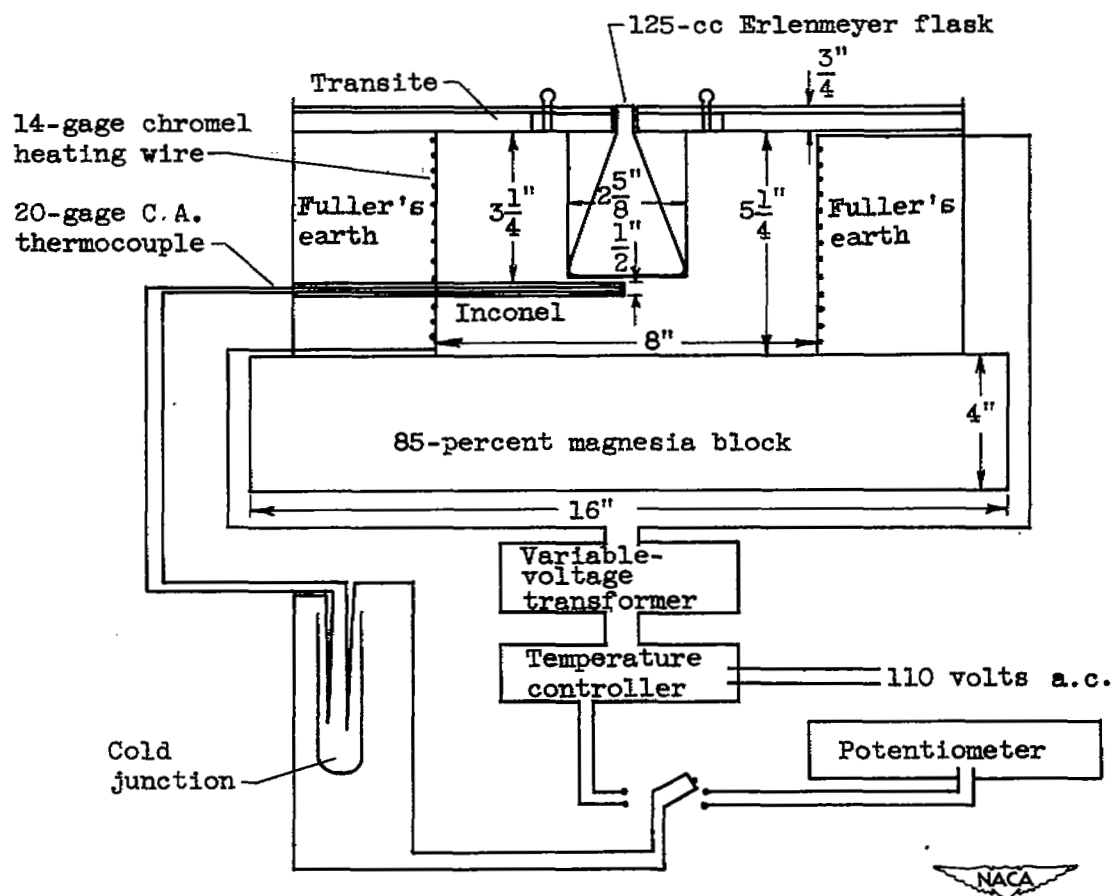| Material	Spontaneous ignition temperature ($^{\circ}$F)	Time lag at last ignition (min)
Aniline	1100	0.1
Chlorinated wax	770	.1
Diphenyloxide	1195	.2
Hexachlorobutadiene	1144	.1
Hexachlorodiphenyloxide	1163	.01
Butyl alcohol	678	.3
Perfluorodimethylcyclohexane	1204	.1
Tricresylphosphate	1112	----
Tetraarylsilicate	1070	.1
Aviation fuel; 100/130 grade		
Gasoline	844	.1
Low-volatility		
(49 percent aromatic)	943	.1
Low-volatility		
(20 percent aromatic)	900	.2
Kerosene	480	1.1
S.A.E. No. 10 Lube oil	720	.02
S.A.E. No. 60 Lube oil	770	.08

NACA

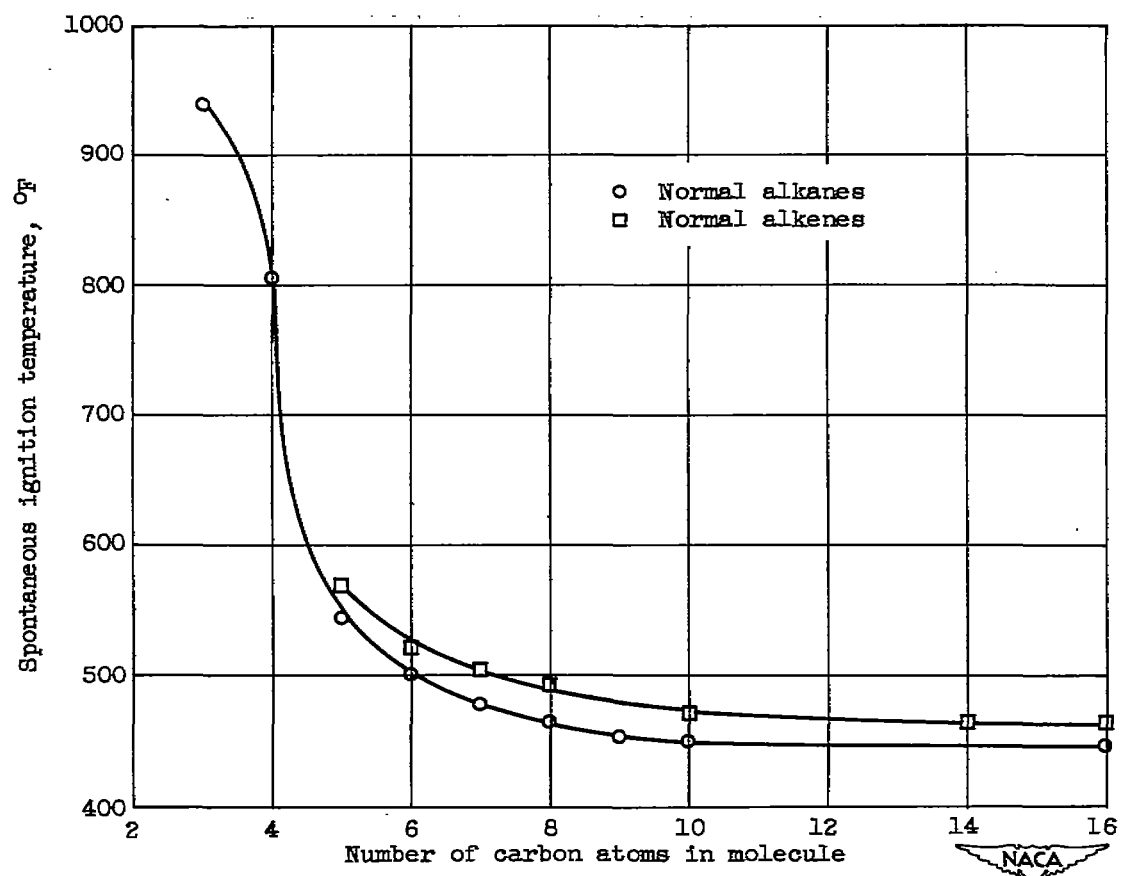Figure 1. - Spontaneous-ignition-temperature apparatus.

2013

Figure 2. - Variation of spontaneous ignition temperature with number
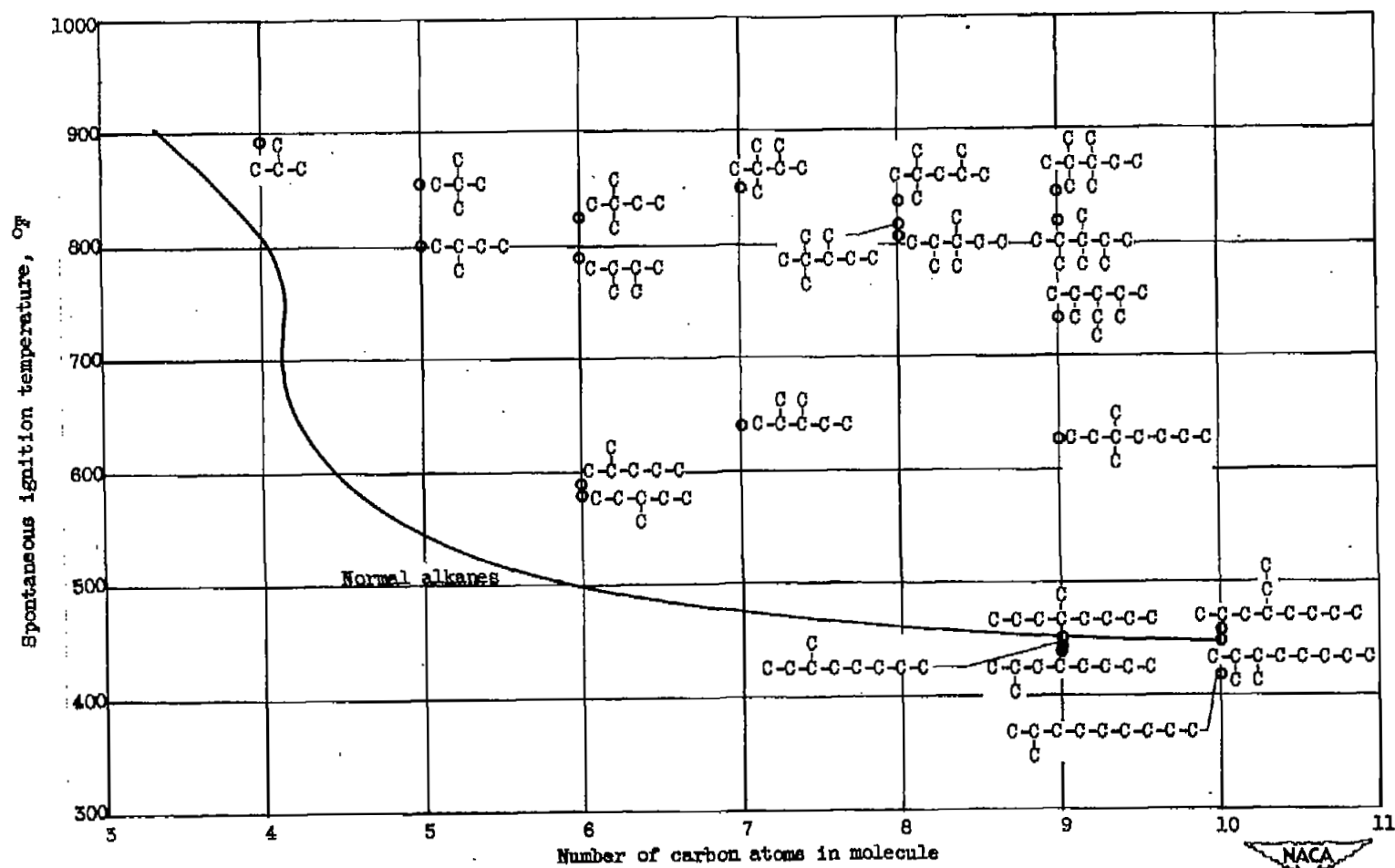of carbon atoms in molecule for normal alkanes and alkenes.

Figure 3. – Variation of spontaneous ignition temperature with number of carbon atoms in molecule for branched alkanes.
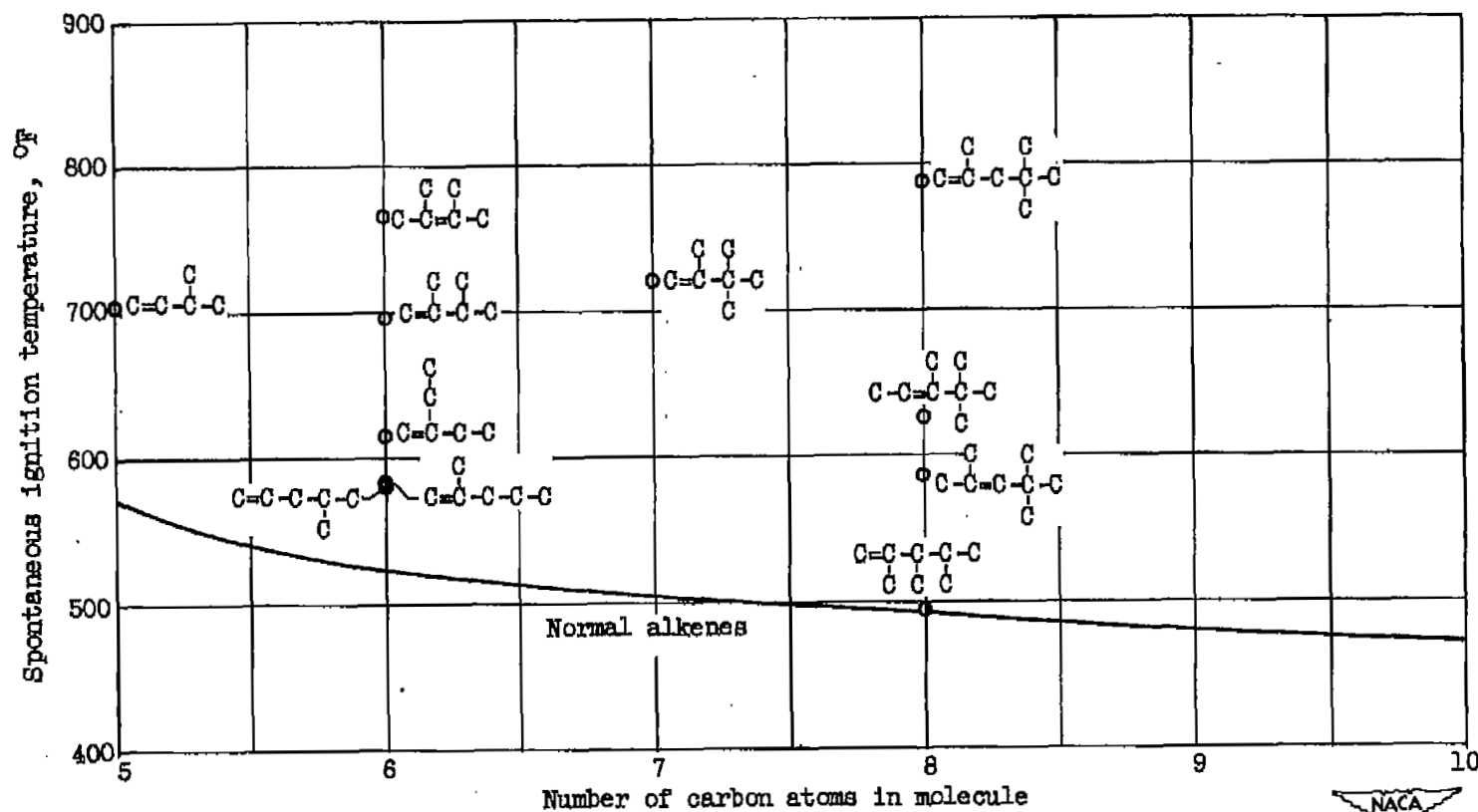
Spontaneous ignition temperature, °F

900

800

700

600

500

400

$C \, C$
$\phi C-C=C-C$

$C \, C$
$\phi C=C-C-C$
C

$\phi C=C-C-C$
C

$C=C-C-C-C$
C
$C=C-C-C-C$

$C \, C$
$\phi C=C-C-C$
C

$C \, C$
$\phi C=C-C-C-C$
C

$C-C=C-C-C$
ϕ
C

$C \, C$
$\phi C-C=C-C-C$
C

$C=C-C-C-C$
$C \, C \, C$

$\phi C=C-C-C$

Normal alkenes

5   6   7   8   9   10

Number of carbon atoms in molecule

NACA

Figure 4. - Variation of spontaneous ignition temperature with number of carbon atoms in molecule for branched alkenes.

15

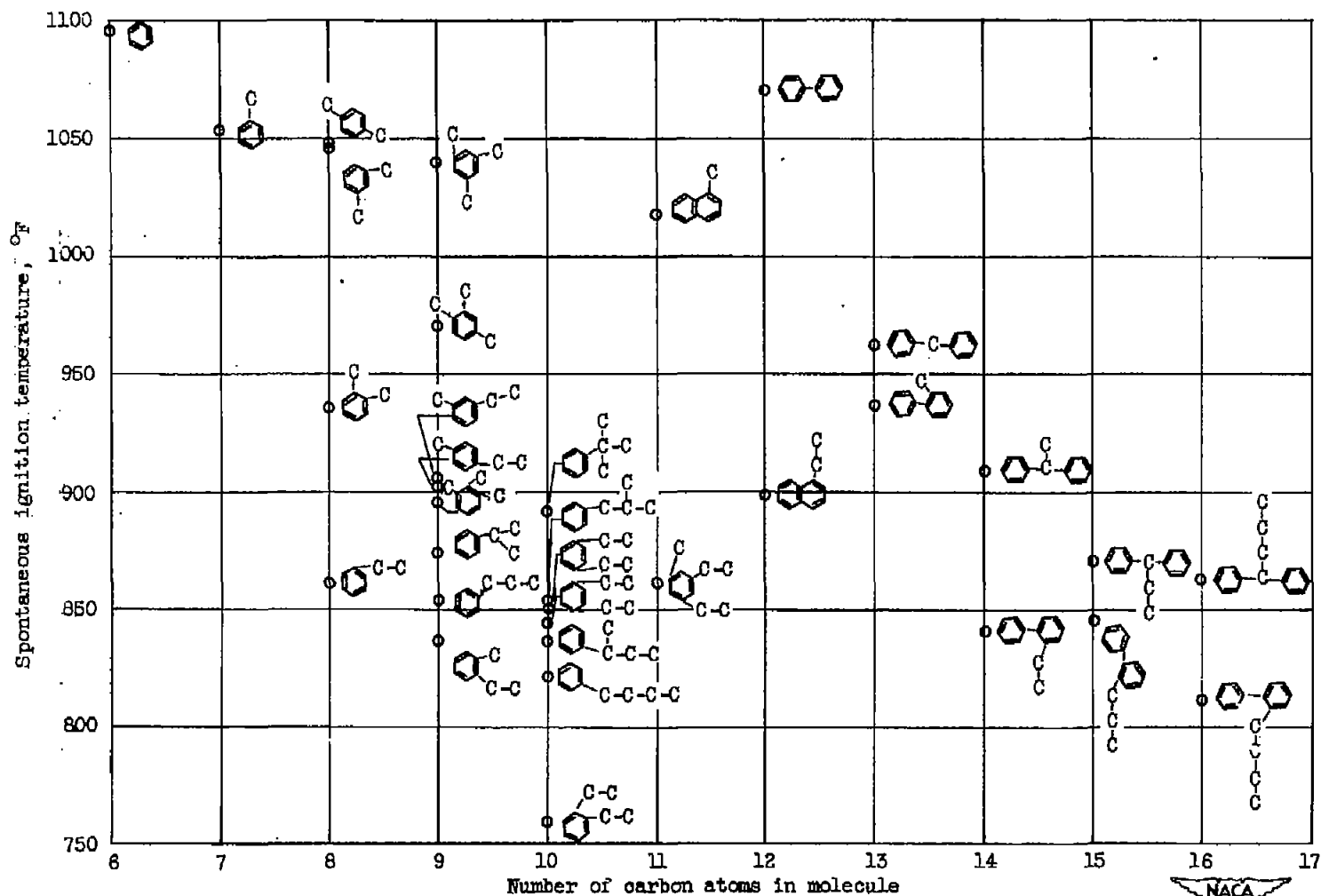Figure 5. - Variation of spontaneous ignition temperature with number of carbon atoms in molecule for aromatics.