

NATIONAL BUREAU OF STANDARDS REPORT

2100

**DETERMINATION
OF
THE SELF-IGNITION TEMPERATURE
OF
COMBUSTIBLE LIQUIDS**

by

N. P. Setchkin



**U. S. DEPARTMENT OF COMMERCE
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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

1002-10-1030

December 9, 1952

NBS REPORT

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DETERMINATION OF THE SELF-IGNITION TEMPERATURE OF COMBUSTIBLE LIQUIDS

ABSTRACT

A review is presented of methods which have been used to measure ignition temperatures of liquids. The fact is mentioned that many of the previous investigations in this field have not been conducted in apparatus and under thermal conditions likely to exhibit very low ignition temperatures. A description is presented of the various stages of development of an insulated spherical flask type of ignition apparatus. Using this apparatus, an extensive study has been performed on the ignition characteristics of combustible liquids. The results are presented in narrative graphical and tabular form.

1. INTRODUCTION

1.1 Purpose and Scope

The ignition of combustible materials by contact with flame and other ignition sources is a common yet most complex natural phenomenon. The research reported here was concerned only with self-ignition resulting from reaction with oxygen of air. Such ignition may be started by initial heating of normally stable materials to an elevated temperature. While the results are mainly of interest from the standpoint of fire and explosion hazards, the study of various phases of ignition phenomenon may also be of interest to workers in other fields. Each substance is usually characterized by physical and chemical properties such as density, viscosity, conductivity, solubility, molecular weight, etc.

Most of these properties are either of such a basic or fundamental nature or the arbitrary conditions for their measurement have been so well established that consistently reproducible results can be obtained in their measurement by different workers. However, one thermochemical property of a substance pertaining to ignition remains undefined in spite of its great importance not only for the evaluation of fire hazards but also for many other practical considerations. The self-ignition temperature (SIT) defines only general ignition characteristics of material comparable in type with others and this characteristic is a function of many governing conditions which are not yet standardized.

The scope of this work comprises a general study of the ignition phenomenon of combustible liquids and the conditions which control its measurement. A study was first made of the various test methods and experimental apparatus that had been previously applied for determination of ignition temperature. This was important since widely different results are obtained, depending upon the test method and the assumed definition of self-ignition temperature.

Having arrived at a concept or definition of self-ignition temperature that appeared logical, the next step was concerned with development of apparatus and test methods. Requirements for such a test include the elimination of all extraneous sources of ignition or accelerators of the ignition reaction. The effect of these can be studied separately. No external heat must be applied to the reacting mixture after a degree of self-heating has set in that of itself will result in ignition. The combustible mixture must also be isolated as far as possible against loss of heat to the surroundings so that the reacting portions of it can follow their natural thermal processes.

The work reported also includes the presentation of ignition characteristics of many commonly known combustible liquids in apparatus designed to measure an exceptionally low value of ignition temperature.

1.2 Criterion for Self-Ignition Temperature

(a) Early Methods and Apparatus

The ignition behavior of various substances has been studied by many investigators with various test methods and equipment constructed to obtain information on ignition under

some specific set of conditions or in conformity with a given requirement. Many of the conditions which have been used were not advantageous for obtaining a low ignition temperature. There also has been no unanimity in views as to the definition of ignition temperature. A large number of terms have been used by different investigators to define different stages of the ignition reaction. For example, the following terms designate early stages of reaction: "Temperature of Thermal Reaction (T.T.R.)" (1); "Temperature Initial Combustion (T.I.C.)" (2); "Critical Inflection Temperature (C.I.T.)" (3); and terms designating the stage from which the reaction is definitely accelerated to ignition: "Spontaneous Ignition Temperature" (4,5); "Autogeneous Ignition Temperature" (6). Many other terms are indicated by Dr. C. R. Brown in his thesis "The Determination of the Ignition Temperature of Solid Materials" (7).

In the study of early methods and apparatus, the following two basic methods of test procedure were considered: the "Rising Temperature Method" and the "Constant Temperature Method". In the first method the temperatures of the ignition apparatus and the specimen being tested are continually increased until ignition occurs. Dr. C. R. Brown, on page 23 (7) gives references for 16 different methods which have been used to define ignition temperature when the rising temperature method is used. However, recently the self-ignition temperature has been considered as that temperature at which self-heating, leading to ignition, is initiated. This temperature is usually indicated either by the point at which the time-temperature line for the material departs from a straight line or by its point of intersection with the time-temperature curve of the air in the testing device (8). The rising temperature method has been applied more frequently for solids than for liquids because slowly heated combustible mixtures of vapor and air often form relatively stable compounds at comparatively low temperatures which are ignitable only at higher temperatures than occur with the constant temperature method. Moreover, this method is subject to certain experimental difficulties in maintaining a small thermal gradient within the specimen and between it and its surroundings. Ignition temperatures determined with this method vary with the rate of temperature rise and therefore are not reproducible without elaborate control equipment to maintain a fixed rate of heating.

With the "Constant Temperature Method" the temperature of the apparatus is kept constant during the test. The test is repeated at different initial temperatures and with different samples of the same substance until self-ignition occurs. All initial temperatures can be precisely adjusted and recorded before the test. With a few exceptions, the initial temperature of a heating bath of the wall of the ignition vessel, or of the air inside the vessel necessary to promote ignition is generally recognized as the "Ignition Temperature."

Several test methods may be briefly described as follows:

(1) Oil drop method. Early determinations of ignition temperature with the so-called "oil drop method" were made by Holm (9) in 1913 with a heated porcelain surface. Moore (10) used a platinum crucible submerged in molten metal or embedded in a steel block. Sortman and Beatty (11) made a small cylindrical cavity of 43 ml capacity in a stainless steel block and provided for circulation of preheated air. Jentzsch and Von Zerbe (12) also used a steel block with four cylinders (7.1 ml) and circulation of oxygen or air. A modified type of Moore apparatus, heated electrically, has been widely used by many investigators (13). The initial temperature of the bath or wall of the ignition vessel leading to ignition is usually considered as the self-ignition temperature. The values of ignition temperatures given in table 1, which is reproduced from reference 13, show appreciable variations for any given liquid because of differences in details of test procedures and apparatus.

(2) Dynamic tube method. In this method, a pyrex tube is heated in a conventional electric furnace to the desired temperature indicated by a thermocouple in contact with the outside surface of the tube. A combustible substance, being preheated separately or together with air or oxygen, is allowed to pass through the tube. The tests are repeated at different temperatures of the tube until evidence of ignition is observed. Apparatus of this type has been used by Dixon in 1909 and 1934 (14, 15), also by Masson and Wheeler (16), Coward (17), and by many others. Coward limited his test to 15 seconds. Callendar (2) and Moureu (18) made a study of slow combustion and determined the "Temperature of Initial Combustion" (T.I.C.) in an improved apparatus. This

Table 1. Ignition temperature (in degree C) of various combustible liquids determined with "oil-drop" method (13)

Material	Investigators									
	Holm	Moore	Tausz and Shulle	Masson and Hamilton	Thompson	Edgerton and Gates	Sortman and Beatty	Jentzsch and Von Zerbe		
n-Heptane	---	451	---	---	---	430	259	560		
n-Hexane	---	---	---	520	248	---	---	560		
n-Pentane	---	579	487	579	308	515	418	580		
Benzene	520	566 656	740	656	580	700	625	720		
Toluene	---	516 633	810	633	553	780	630	730		
Carbon disulfide	---	---	---	343	125	120	---	---		
Ethyl ether	410	347	343	487	193	440	---	500		
Ethyl alcohol	510	518	558	568	420	515	---	575		

temperature was defined as the tube temperature necessary to provide the first appearance of products of combustion (steam, carbon dioxide, aldehyde, etc.), or was determined by chemical analysis of samples taken periodically during various phases of the reaction.

This temperature has some relation to the "Temperature of Thermal Reaction" (T.T.R) introduced by Estradère (1) and "Critical Inflection Temperature" (C.I.T.) introduced by Lewis (3). All these temperatures are related to the "Temperature of Initial Oxidation" (19) or in other words to the temperature of incipient self-heating. Prettre defined the ignition temperature by appearance of "cold flame" (T.C.F.) and by normal flame at "Minimum Ignition Temperature" (M.I.T.). A tabulation of ignition temperatures measured by this method is included in table 2, which is reproduced from reference 19.

(3) Evacuated vessel method. In this method a combustible mixture is suddenly admitted into an evacuated vessel which was preheated to the desired temperature. This method was originated by Mallard and Le Chatelier in 1880 and was used subsequently by Masson and Wheeler (16) and Townend (20). Ignition was indicated by rapid rise in pressure. Lewis and also Pidgeon and Edgerton (21) modified this method by admission of the cold combustible mixture into an evacuated vessel heated at a steady rate (rising temperature method).

(4) Bomb method. The bomb method was used by Neuman (22) and other investigators for determination of the ignition temperature of combustible mixtures at elevated pressures.

(5) Adiabatic compression method. Heating of a combustible mixture to the ignition point by adiabatic compression was used by Tizard and Pye (23) and Pignot (24). It is hardly likely that ignition temperatures measured by this method, which involves the use of rising temperature and pressure, are directly comparable to those measured at constant pressure.

(6) ASTM standard method. Committee D-2 on Petroleum Products and Lubricants of ASTM in 1930 adopted the standard method and apparatus (D286-30) (6) for the determination of the "Autogeneous Ignition Temperature." The standard apparatus consists of a conical pyrex flask of 160 ml capacity,

Table 2. Ignition temperature (in degree C) of liquids determined with different methods (19)

Material	Temperature initial oxidation		Cold flame T.C.F.	Minimum ignition temperature			Adiabatic compression	
	T.I.C.			(D)	(E)	(F)		(G)
	(A)	(B)						
Tube method		Evacuated vessel		Bomb	Adiabatic compression			
n-Pentane	295	255	225			254	510	225
			243	263	548	237		
n-Hexane	265	230	220	253	285	222	300	
			230		570	232		
n-Heptane	---	209	220	256	---	225	283	
n-Octane	---	197	210	248	---	320	278	
n-Nonane	205	193	---	---	---	---	---	
Isoöctane	---	---	500	---	---	---	---	
Cyclohexane	---	---	235	262	---	324	---	
			260					
Benzene	670	---	570	695	---	---	---	
Toluene	550	---	600	585	---	---	---	

Investigators: (A) Callendar; (B) Lewis; (C) Estradère; (D) Prettre; (E) Townend and Cohen; (F) Dumanois and others; (G) Tizard and Pye.

submerged in a molten alloy heated by a gas burner. A few drops of the liquid to be tested are allowed to fall into the flask, heated to different initial temperatures until ignition is observed. The ignition temperature is defined as the temperature of the solder bath, indicated by a thermocouple placed in a silica protection tube submerged in the bath near the flask necessary to cause ignition of the specimen. This thermocouple has an appreciable time lag in response to sudden changes in the bath temperature.

(b) Adopted Concept and Definition of Self-Ignition Temperature

The ignition reaction is a thermochemical process in which the thermal phase has a predominant effect upon the direction and intensity of chemical developments because not only does heat generated from the exothermic reaction lead to ignition, but also heat dissipation to the surroundings determines whether acceleration to ignition will occur. This important fact has frequently been overlooked in studying the problem of ignition. The above criteria can be illustrated by the time-temperature curves shown on figure 1, representing the thermal effects of ignition and nonignition reactions of a combustible substance with oxygen of air. After the injection of a dispersed charge of combustible liquid into a closed vessel, the temperature of the mixture of vapor and air at first falls below the initial temperature because of heat absorption. If the initial temperature (t_0) of air in the vessel is below the temperature of incipient self-heating (t_x), then after a certain time lag, the temperature recovers mainly by means of heat supplied from the walls. At a higher initial temperature (t_1), the temperature of the combustible mixture after an initial drop gradually rises due to combined effects of the heated wall and the exothermic reaction until the temperature (t_1) is reached. At the point (a) no heat is supplied by the wall and the rate of temperature rise represents the rate of heat generation by the exothermic reaction. During further increase in temperature of the gas mixture, the generated heat is partly absorbed by the wall, partly carried away through the wall to a medium surrounding the ignition vessel, and a very small part of the heat is used to raise the temperature of the gas mixture. The rise in temperature of the mixture continues only in cases where the rate of heat generation increases faster than the rate of heat dissipation. Otherwise, both rates become equal and the temperature of the combustible mixture for a time will

be constant and equal to (t_1'), before falling to the initial level at (t_1). A similar phenomenon has been observed at other higher initial temperatures (t_2, t_3, t_4). However, at certain initial temperatures (t_5) the inducing reaction is continually accelerated and at the point (t_f) evidence of ignition is observed in the form of flame or explosion. Temperature (t_f) is sometimes called "the ignition point." This temperature has no definite and reproducible value due to its rapid rate of change and often it is below the maximum temperature (t_4) observed at lower initial temperatures. Self-ignition at still higher initial temperatures (t_6 , etc.) usually occurs with shorter ignition time lag and with more violent evidence of ignition.

The initial temperature of air (t_5) is taken as the self-ignition temperature (SIT) of the material tested. This results in the following definition:

As used in this paper the self-ignition temperature (SIT) of a liquid is the minimum initial temperature of any combustible mixture with air at or above which it will pass into a condition of observable combustion under specific conditions.

1.3 Governing Conditions

(a) Thermal Characteristics of the Apparatus

The influence of the heating bath and ignition chamber wall on the trend of the ignition reaction and thus the measured ignition temperature has often been ignored. During the preliminary stage of the test, the bath supplies heat to the wall of the ignition chamber and maintains constant temperature in the apparatus. As soon as the temperature of the reacting mixture increases above the wall temperature, due to an exothermic reaction, the direction of heat flow is reversed and the observed rate of the ignition reaction is appreciably affected by the rate of heat loss to the surroundings or by the heat capacity and conductivity of wall and bath. The higher the rate of heat loss, the higher is the initial temperature required to accelerate the reaction to ignition.

(b) Dimensional Characteristics of the Ignition Chamber

The size, shape and material of the ignition chamber also have an effect on the observed rate of the ignition reaction and the value of the self-ignition temperature because the dimensional characteristics of the ignition chamber are interrelated with their thermal characteristics.

(c) Pressure and Uniformity of Temperature

The observed self-ignition temperature of a combustible gas mixture is probably affected by pressure in the ignition chamber. The tests reported here were conducted under atmospheric pressure without correction for barometric pressure changes.

Undoubtedly, ignition develops from molecular interaction of the combustible substance with oxidation agents. Ignition probably initiates in the most highly energized molecules of the mixture and propagates throughout the whole mass (Mareck and Hahn (25)). Not all the molecules present are in the same energy state. However, the more uniform the temperature distribution in this mass, the more favorable conditions will be for rapid propagation of the ignition reaction. Because of this, special attention was given to control of the temperature in the ignition vessel.

The control of the uniformity of the temperature within the flask was studied over the range of temperatures from 200°C to 600°C by means of tests conducted in the 1000 ml ignition apparatus provided with a number of thermocouples. This made it possible to measure the temperature at various points of the flask surface and air space and to control the heat input in different coils in such a manner that the uniformity of the temperature can be brought to within 2 degrees C.

As indicated below, the exploration tests clearly demonstrated the effect of heat loss through the exposed neck of the flask on the uniformity of temperature. With a non-insulated neck the variation of temperature in the flask reached 13 degrees C. These variations were reduced to 9 degrees C with asbestos insulation and to about 2 degrees C with the heating coils extended around the neck (Fig. 2). However, an additional exploration test with single or triple thermocouples in various parts of the air space showed that

variations in the temperature throughout the flask could be reduced to even one degree C.

The temperature of the combustible mixture varies more or less uniformly during the ignition reaction as is indicated by the time-temperature curves observed simultaneously in different zones of the flask. These curves exhibited substantially the same pattern, as will be shown later on Figures 20 and 42.

(d) Combustible Mixture

The ratio of combustible to air of the combustible mixture has an appreciable effect upon the minimum ignition temperature. Excessively rich or lean mixtures usually increase the ignition temperature. Carbon and soot deposits also affect the value of the minimum ignition temperature. Therefore, the effects of these factors should be considered in the determination of the lowest self-ignition temperature.

(e) Effective Temperature for Ignition

The method of determination of the effective temperature for ignition has an influence on the value of the observed ignition temperature. The initial temperature of the solder bath or the temperature of a metal block is often considered as the effective temperature for ignition. These temperatures differ appreciably from the initial temperature of air or the combustible mixture inside the ignition chamber. This fact has been recognized in the present method for measurement of ignition temperature. This temperature is measured by a thermocouple inserted in the lower portion of the ignition chamber, which is also extensively used during the test for observation of temperature changes during reaction and for the study of other thermal effects of the ignition phenomena.

(f) Evidence of Ignition

Ignition is generally indicated by visual evidence, the intensity of which varies with the initial temperature. At high initial temperatures, self-ignition usually occurs in a more or less violent form such as a bright flash of flame and audible expulsion of gases (explosion). In the medium range of temperature a mild flame is often observed, while at the lowest ignition temperatures a very dull violet or blue flame is visible, often only under dark room conditions.

These latter can be easily confused with cold flame or chemiluminescence which is not generally recognized as evidence of ignition in spite of the rapid rise in temperature of the reacting mixture. Therefore, test conditions should make observation of the lowest value of the ignition temperature possible.

Some investigators have limited their tests to 10 or 15 seconds only. In such cases it should be remembered that ignition lag is an inverse function of the ignition temperature. At high temperatures, the lag may be only a fraction of a second, while the lag at the lowest temperature may amount to minutes, depending upon test conditions. For example, the ignition lag of methyl cyclohexane at 275°C was found in the 1000 ml flask to be 30 seconds; at 248°C the lag was as long as 20 min 10 sec.

The occurrence of ignition for many liquids can also be determined by comparison of the time-temperature curves observed for the ignition and nonignition reactions. It is interesting to note that two adjacent typical ignition and nonignition reactions, illustrated by curves 5 and 4 on Figure 1, proceeded substantially with the same rate up to a certain transition point, after which one reaction rapidly accelerated to ignition and the other changed its course to a certain maximum temperature (t_4') and eventually cooled down. These typical curves are usually reproducible to within a few degrees C of the initial temperature in the same apparatus under identical conditions. Moreover, the thermal effect of the reaction observed under different controllable conditions is also reproducible with the same accuracy. Therefore, observed effects can be correlated with the factors representing the test conditions. Because of this, particular attention was given to observation of not only visible and audible evidences of ignition but also to the thermal effects of different reactions in terms of time-temperature curves.

(g) Effect of Extraneous Stimuli of Ignition

As stated in the introduction, the effect of all extraneous stimuli of ignition such as flame, spark, detonators, overheated surface or catalytic agents should be eliminated from the first phase of this study and the ignition reaction allowed to take its natural course within the combustible mixture. The effects of the above stimuli should be studied separately in relation to naturally

developed ignition, because of the complexity of the superimposed effects. For example, the catalytic effect of certain metals used in construction of the ignition chamber is usually superimposed by an additional thermal effect of metal masses. The relative effect of the thermal conductivity of the wall is considerably greater than the effect of heat capacity; therefore, the elimination of the first effect in the experiments makes the catalytic effect relatively more noticeable.

In the present study an investigation was made of the catalytic effect of the thermocouples placed inside the ignition chamber. Heat losses by conduction were practically eliminated and only the small effect of heat capacity of wires was left together with the possible catalytic action. This action of the thermocouple wires was not detected in comparative tests conducted with the thermocouple placed inside the ignition chamber and removed just before injection of the charge of different liquids. Neither was it detected with an additional 10 gr of wire placed in the chamber. Only a slight retarding effect on the ignition reaction was noticed because part of the heat generated by the exothermic reaction was absorbed by the mass of wires in increasing their temperature. As a result, the ignition temperature was found to be slightly higher with longer wires than with short thermocouple wires or without wires or thermocouples of any kind. For example, the minimum self-ignition temperatures of furnace oil No. 2 were obtained with 10 gr of bare thermocouple wires at 240°C; with three thermocouples in porcelain tubes at 236°C; with a single thermocouple in the tube at 234°C; with a bare single thermocouple at 233°C and without a thermocouple at 232°C. Similar results were found with other liquids.

Callendar (26) experimented with different metals placed in a test tube in a manner similar to that mentioned. His results did not show any catalytic action of these metals with the exception of platinum black. On the other hand, different values of ignition temperatures obtained by Thompson (27) and especially by Matson and Dufour (28) in chambers made of different metals definitely varied with the heat conductivity of the metal which has a predominant effect on the ignition temperature.

2. TEST APPARATUS AND PROCEDURE

2.1 Construction of Apparatus

Having arrived at a concept and definition of self-ignition temperature that appears logical, the next step was concerned with the development of equipment and an experimental method capable of furnishing ignition data with the desired degree of accuracy.

Initial experiments were conducted with the ASTM standard ignition apparatus (6) with solder bath and gas burner. Because of difficulties in controlling temperatures and poor reproducibility of the results, this apparatus was modified to include electrical heating elements, a 200 ml spherical pyrex flask, a stirring arrangement in the bath, and direct measurement of temperature in the flask. In order to eliminate large heat loss to the solder bath and to improve uniformity of temperature control in the flask, the solder bath was later replaced with two sets of heating elements made of nichrome wire in an asbestos sleeve wound around the upper and lower halves of the spherical flask and protected with alundum cement. The final design of the ignition apparatus consisted of a 1000 ml spherical pyrex flask, as shown in Figure 3, placed concentrically inside a refractory casing so that a 1/2-in. air space was provided between the flask and the casing for further reduction of heat loss during tests. The heating wires in the asbestos sleeve were wound around the upper and lower halves of the casing and the neck with independent control of electric current. Temperatures of the three heaters were indicated by three thermocouples made of chromel alumel (26 B & S gage) wire, placed behind each group of heating coils. Two additional thermocouples were placed in contact with the upper and lower surfaces of the flask. The sixth thermocouple, insulated by glass sleeves and also of 26 (B & S gage) wire, was placed in the lower part of the flask for indicating the temperature inside the flask. The flask neck was closed with a cement-asbestos stopper having two passages, one for the thermocouple wires and the other for injection of the charge.

Most of the tests reported in this paper were performed in the 1000 ml capacity apparatus shown in Figure 3. A few additional determinations were made in the 200 and 12,000 ml apparatus of similar construction.

The effect of different sizes of apparatus on the observed self-ignition temperature was studied in the 200, 1000, 12,000 and 15,000 ml capacity spherical pyrex flasks. These were constructed substantially in the same manner as shown in Figure 3 with the exception of the 15,000 ml flask which was made of vitreosel about 3/8 in. thick and without an air space between the flask and heating coils. The heat-absorbing capacity of this flask was higher than that of the 12,000 ml flask, the thickness of which was only 3/32 inch. Results of tests of two liquids in these various ignition apparatus are presented in table 3. From these data it is evident that flask size as well as other factors influence the measured ignition temperature.

The effect of the thermal properties of the apparatus on the measured self-ignition temperature was studied with three apparatus equipped with spherical pyrex flasks of the same capacity (1000 ml) and having the following types of casings: (1) 5/8 inch thick copper casing directly connected with the pyrex flask (2) a refractory casing with 1/2 inch air space, as shown in Figure 3, and (3) a refractory casing with mirrored inner surface for reflection of radiant heat back to the flask through 5/8-inch air space. The results of this study are given in table 9 of Section 3.6.

2.2 Test Procedure

(a) Preheating of the Apparatus

The ignition apparatus was preheated to the required temperature by electric current passing through a rheostat or variac connected with the heating coils wound around the various portions of the flask. The current was adjusted in such a manner that a constant temperature was maintained in the flask within limits of about $\pm 2^{\circ}\text{C}$.

(b) Admission of Charge

A constant amount of liquid charge (about 0.2 ml per 1000 ml of air) was usually injected. This was done by use of a hypodermic syringe and a fine needle providing good dispersion of liquid droplets essential for rapid evaporation and uniform initiation of the reaction throughout the whole of the spherical flask. The tests were usually repeated with the same charge until the minimum self-ignition temperature was obtained. Then a few additional tests were made with smaller and larger charges, in order to determine the most favorable combustible-air mixture for the lowest self-ignition temperature.

Table 3. Ignition characteristics of low ignition temperature liquids obtained in apparatus of different sizes

Material	200 ml			1000 ml			12,000 ml			15,000 ml		
	'SIT'	Lag	'Evi-' 'dence'	'SIT'	Lag	'Evi-' 'dence'	'SIT'	Lag	'Evi-' 'dence'	'SIT'	Lag	'Evi-' 'dence'
	'°C	'min sec'	'°C	'min sec'	'°C	'min sec'	'°C	'min sec'	'°C	'min sec'	'°C	'min sec'
Carbon disulfide	120	0 08	5	110	0 14	5	190	0 20	5	196	0 20	6
Ethyl ether	180	0 20	3	170	0 25	4	160	1 40	6	162	1 08	6

*Key for Evidence of Ignition

- 3 Flame
- 4 Mild Explosion
- 5 Explosion
- 6 Violent Explosion

In order to eliminate the effect of carbon or soot deposits on the measurements, the products of decomposition were blown out by a jet of air after each test and the interior flask surface cleaned regularly. The final determinations were made with a thoroughly cleaned surface. Liquids producing sooty residues (oils, lacquer, paints, etc.) or solids with low melting temperatures (gum, wax, tar, etc.) were usually placed in a small crucible held by a thin wire in the lower part of the flask. This arrangement prevents excessive accumulation of deposits; however, the minimum ignition temperature obtained in this manner was either corrected for the cooling effect of the additional mass of the crucible or final determinations were made without this arrangement.

(c) Observation of Temperature Changes

The temperature of the heating coils, flask surface and air in the flask were observed in terms of "emf", prior to admission of the charge, by means of a type "K" potentiometer and galvanometer and recorded in millivolts during a sufficient length of time for indication of stabilization of temperature throughout the apparatus. For a convenient and accurate recording of temperature during important phases of the thermal process in the combustible mixture, special attention is usually given to the readings of "emf" of the thermocouple located within the flask. These readings were made every 15 or 20 seconds, immediately after injection of the charge and continued until either ignition took place or the trend of the process or other phenomena of particular interest were definitely established. The graphical recording of the temperature on the millivolt and time scale was used for a consistent visual presentation of the thermal process taking place within the flask. The temperatures of coils and flask surface were observed at 3 to 5 minute intervals, because these temperatures change only slowly.

For observation of uniform changes of temperature inside the flask during the ignition reaction, three thermocouples were placed in the upper, central and lower portions of the flask. Successive readings of these thermocouples were taken and were graphically recorded as fast as possible. Chromel alumel wire of 26 (B & S) gage was generally used in all tests with exceptions made in some cases which required high precision data. In these cases 32 (B & S) gage wire was used with a small junction for higher sensitivity of the thermocouple.

(d) Observation of Evidence

Audible or visible evidence of ignition (explosion, flame, and puff) were usually observed in conjunction with corresponding changes in the time-temperature curves. In the absence of these, definitely nonignition reactions were also well indicated by the shape of the curves. The mild form of visual and audible evidence corresponding to the lowest self-ignition temperature was usually observed under dark room conditions through a periscope placed above the flask opening. With the exception of a few liquids, even a very dull flame was distinctly visible. Ignition of liquids producing dense smoke was indicated by illumination of the white clouds which was also distinctly visible through the periscope.

3. TEST RESULTS

The following ignition characteristics of combustible liquids were observed under the specified test conditions:

1. Minimum self-ignition temperature.
2. Character and intensity of the evidence of ignition.
3. Favorable fuel-air mixture ratio for minimum ignition temperature.
4. Time-temperature curves and ignition lags for different initial temperatures.
5. Character of the ignition and nonignition reaction.

The following groups of combustible liquids were subjected to the ignition tests:

1. Low ignition temperature liquids.
2. Petroleum products.
3. Pure petroleum fractions.
4. Reference fuels.
5. High ignition temperature liquids.
6. Paints, varnishes, oils and miscellaneous liquids.

3.1 Low Ignition Temperature Liquids

The characteristics of two liquids ignitable at comparatively low temperatures are shown in table 3.

The self-ignition temperature of these liquids varies with the size and thermal properties of the apparatus. However, the higher heat capacity of the 15,000 ml vitreosol flask as compared with the 12,000 ml pyrex flask has a more important effect on the self-ignition temperature than the effect of size.

(a) Carbon Disulfide

The self-ignition of carbon disulfide is usually indicated by a violent explosion accompanied by flame and a very rapid rise in temperature, shown on Figure 4. The pre-ignition reaction of this material, in contrast with that of other liquids, is of a very mild form indicated by a gradual rise in temperature, even for temperatures just below the ignition region. Consistent fluctuations in the time-temperature curves may result from secondary reactions caused by rich mixtures or gases evolved from yellow-brownish deposits on the flask surface left from previous tests. Both these factors may have a retarding effect on the ignition reaction. Normally the lowest self-ignition temperatures for combustible liquids were observed when using charges of 0.2 to 0.25 ml per 1000 ml of air. However, self-ignition temperatures of carbon disulfide show a rapid drop as the fuel charge is reduced from 0.2 to 0.05 ml/1000ml of air and remain almost constant for charges below 0.03 ml, as shown in Figure 5.

The carbon disulfide-air mixture has one critical ratio for each initial temperature above which the mixture remained nonignitable. For example, the critical charge for the initial temperature of 150°C is about 0.18 ml. With a charge of 0.25 ml, the reaction was not accelerated to ignition during the 2-1/2 min test period. If at the end of this nonignition reaction a fresh charge of air was admitted, then shortly a violent ignition occurred. This ignition was probably caused by reduction of concentration of the mixture below the critical value of 0.18 ml per 1000 ml.

(b) Ethyl Ether

Self-ignition of ethyl ether is usually indicated by a violent explosion accompanied by a large flame and rapid rise in temperature. Typical time-temperature curves are shown in Figure 6.

The nonignition reaction of this liquid, in contrast to that of carbon disulfide is characterized by a slow rise of temperature for a considerable time after injection of the charge. During the first period of the exothermic reaction, extending from 5 to 10 seconds, the pressure inside the flask increased slightly and gases were expelled from the neck with a just barely audible sound. The temperature of the mixture continued to rise and in about 10 or 15 min reached its maximum (25 degrees C above the initial temperature). However, at slightly higher initial temperatures ignition occurred at a time when the thermocouple indicated a lower temperature of the mixture than the maximum observed in the preceding test. This fact seems to indicate that either development of ignition is not a simple function of gas temperature, or the thermocouple and temperature-indicating system could not accurately follow the rapid temperature changes at the point within the gas where ignition actually takes place. On the other hand, the initial temperature can be accurately measured and defines the ignition or nonignition state; therefore, the initial temperature of the mixture is accepted as the representative temperature for self-ignition.

Self-ignition of combustible liquids usually occurred at lower temperatures in the larger apparatus. Data obtained in the 12,000 and 15,000 ml flasks (table 3) do not follow this general trend; however, the above relationship can be maintained only in apparatus of similar construction. Actually the 15,000 ml flask has larger heat capacity and higher heat loss per unit of volume than the 12,000 ml flask; therefore, the effects of the thermal characteristics of the apparatus are superimposed and affect the dimensional characteristics.

The effects of various sizes of ignition chamber on the ignition and nonignition reactions of ethyl ether are shown by the set of typical time-temperature curves in Figure 7 and the effect of various charges injected at the same initial temperatures at 160°C in Figure 8. In the determination of the lowest self-ignition temperature, it is obvious that ignition chamber size and thermal properties as well as fuel-air ratio should be considered.

3.2 Petroleum Products

The ignition characteristics of petroleum products, determined in different ignition apparatus, are given in Table 4. Some liquids were tested in four different sizes of apparatus and some liquids only in the apparatus of 1000 ml capacity, which was tentatively selected as the standard for tests reported here.

(a) Motor Gasoline (65 octane)

The ignition reactions of various gasolines (kerosene, cleaner's solvent and a few other refined petroleum products) usually proceed with characteristically shaped time-temperature curves which are different from those of other combustible liquids of non-petroleum origin. Well reproducible variations of these curves occur as the initial temperature is raised. These seem to indicate that both ignition and nonignition reactions of these liquids progress as a two-stage exothermic reaction. This is shown by the set of time-temperature curves in Figure 9, obtained in the 1000 ml ignition apparatus with constant charges of 0.20 ml. Somewhat similar characteristics were also found for other charges (0.10, 0.25 and 0.30 ml/l in the 200 and 12,000 flasks). Data for charges of 0.25 ml/l in the 200 and 12,000 flasks are shown in Figures 10 and 11.

The injection of the charge was usually made into a flask uniformly preheated to the required temperature. Immediately after injection of the charge, a considerable drop in temperature of the gas mixture was observed due to evaporation of liquid. However, the temperature was shortly increased by heat supplied from the wall and the exothermic reaction, which usually continued about one or two minutes depending on the level of the initial temperature. The other stage of reaction was indicated by a fall of temperature, which was probably due either to an interrupted exothermic reaction or to some endothermic process. The next stage of the exothermic reaction was initiated after a certain time interval and continued either until the temperature of the reacting mixture reached its maximum, at which time the rate of heat generation and heat dissipation to the surroundings were equal, or to a transition point from which the rate of heat generation accelerated faster than the rate of heat dissipation. Therefore, ignition resulted.

Table 4. Ignition characteristics of petroleum products obtained in flasks of different sizes

	Flask sizes															
	200 ml				1000 ml				12,000 ml				15,000 ml			
	S.I.T.	Lag	'S.I.T.	Lag	'S.I.T.	Lag	'S.I.T.	Lag	'S.I.T.	Lag	'S.I.T.	Lag	'S.I.T.	Lag		
	°C	'min	sec	°C	'min	sec	°C	'min	sec	°C	'min	sec	°C	'min	sec	
Gasoline (65 oct.)	248	2	30	243	4	30	224	10	50	240	8	15	240	8	15	
Gasoline (73 oct.)	---	-	-	258	5	00	---	---	---	252	3	35	---	---	---	
Gasoline (87 oct.)	---	-	-	412	0	06	---	---	---	---	---	---	---	---	---	
Varsol	237	1	52	235	3	00	215	6	48	---	---	---	---	---	---	
Kerosene	233	1	30	227	2	55	210	7	25	215	5	55	215	5	55	
Cleaners' solvent	---	-	-	243	2	44	224	9	42	235	4	25	---	---	---	
Crude oil	---	-	-	262	0	35	---	---	---	---	---	---	---	---	---	
Diesel fuels:																
41 Cetane	---	-	-	233	3	00	---	---	---	---	---	---	---	---	---	
55 Cetane	---	-	-	230	2	30	---	---	---	---	---	---	---	---	---	
60 Cetane	---	-	-	225	2	40	---	---	---	---	---	---	---	---	---	
68 Cetane	---	-	-	226	1	45	---	---	---	---	---	---	---	---	---	
Furnace oil No.2	242	0	55	233	2	40	226	2	55	230	2	30	---	---	---	
Lubricating oils:																
USN No.2075	---	-	-	241	2	15	---	---	---	---	---	---	---	---	---	
USN No.8190	---	-	-	271	0	15	---	---	---	---	---	---	---	---	---	
Chlorinated																
paraffin oil	---	-	-	414	0	03	---	---	---	---	---	---	---	---	---	
Motor oil	357	0	05	351	0	04	313	0	35	320	0	48	---	---	---	
Benzene	579	1	05	559	0	48	---	---	---	---	---	---	---	---	---	
Toluene	538	0	45	519	0	55	482	3	40	---	---	---	---	---	---	

Comparison of two adjacent ignition and nonignition reactions shows that the rate of formation of stable compounds in the nonignition reaction seems to be greater than in the ignition reaction; therefore, in spite of the fact that the temperature of the reacting mixture increased above the transition-ignition point, self-ignition did not occur. Moreover, these stable compounds were not ignitable either by spark or flame or by additional heating of the mixture up to about 400°C, unless the mixture was diluted with fresh air.

It is interesting to note that ignition of gasoline usually occurred during the last stage of reaction, in contrast with kerosene and cleaner's solvent for which, as will be shown later, ignition occurred at the first stage. The time interval between stages of the exothermic reaction was gradually diminished with increased initial temperature and finally in the high temperature region both stages seemed to proceed simultaneously along one smooth line; under these conditions, it is difficult to estimate at which stage ignition occurred.

The intensity of the evidence of ignition varied with the initial temperature. At the lower range of temperatures with some grades of gasoline (high octane number) ignition with a very dull blue flame was observed under dark room conditions or through the periscope attached to the flask neck. Gasoline of low octane number generally ignited with a mild orange flame accompanied by audible expulsion of gases ("puff"). Both types of evidence were well correlated with rapid rise in temperature, as is indicated in Figures 9, 10 and 11. Ignition at a higher initial temperature is usually indicated by a more violent flash of flame or by audible expulsion.

It is also interesting to point out that the temperature of a mixture after ignition or nonignition reaction rapidly falls close to the initial one with the exception of the high ignition temperature region, where the temperature of the mixture remains high for a comparatively long time. Moreover, the surface of the flask after these tests was more readily covered by soot and carbon deposits than after the tests at lower temperatures. These conditions prevailed for very small charges, 0.05 ml/l, as well as for 0.30 ml/l.

Ignition lags were found to be well correlated with the ignition temperature, as shown in Figure 12. The lowest self-ignition temperature was usually determined from the tests conducted with different charges, as shown in Figure 13.

Analysis of the time-temperature curves obtained at various initial temperatures and in different ignition apparatus (Figs. 9, 10, 11) indicates that:

- (1) The thermal effects of the ignition and nonignition reactions, recorded in terms of temperature changes with time, are well reproducible for the same initial temperature.
- (2) Observed changes in each stage of the thermal process or the patterns of the time-temperature curves are not accidental but seem to represent a definite part of the thermal process continuously and orderly progressing with the time.
- (3) These patterns are also related to the composition of the combustible mixture and the test conditions; therefore, some mechanisms of chemical reactions may be correlated with definite patterns obtained with the predetermined compositions.

For example (a) the timing and magnitude of the second drop in temperature consistently diminished with increased initial temperature and reduced size of the ignition chamber. (b) The ignition of gasolines always occurred in the second stage of the exothermic reaction and the minimum self-ignition temperature always increased and ignition lag decreased with smaller sizes of the ignition chamber. (c) Both ignition and adjacent nonignition reactions proceeded in all three apparatus substantially in the same pattern to the transition point, from which one reaction rapidly accelerated to ignition and the other turned to stabilization without ignition at certain maximum temperatures.

(b) Other Gasolines and Varsol

The characteristics of other gasolines and varsol are substantially the same as motor and aviation gasolines (Supply of 1937) with a two-stage reaction and with ignition occurring at the second stage of reaction.

(c) Kerosene and Cleaner's Solvent

Kerosene and cleaner's solvent belong to another group of petroleum products, the ignition of which seems to occur at the first stage of reaction in spite of the fact that the nonignition reaction proceeded with a two-stage reaction. Typical time-temperature curves are shown in Figures 14 and 15. "After burning" of cleaner's solvent in the region of high ignition temperatures was more pronounced than with other fuels and ignition at all temperatures was indicated by mild flame and hardly audible expulsion of gases.

(d) Crude Oil

Langonillas crude oil of gravity 17 A.P.I., flash point 15°C, and sulphur content 1.91 percent, was tested in connection with the study of the explosion of an oil tanker. This oil was tested under various conditions and for the presence of various agents supposed to stimulate ignition. However, self-ignition occurred with a violent explosion at the lowest temperature, 262°C, after 35 seconds in the absence of any accelerating agents.

The character of the ignition and nonignition reaction of crude oil is appreciably different from that of the gasoline and kerosene group of fuels. The reaction proceeds in a one-stage pattern with considerable self-heating for the nonignition reaction and a rapid increase of temperature after violent ignition, as shown in Figure 16.

(e) Diesel Fuels

The physical properties and ignition characteristics of four Diesel fuels determined in the 1000 ml flask are given in table 5.

The time-temperature curves determined for these fuels are shown in Figures 17 and 18. Both ignition and nonignition reactions of all four fuels are of single-stage pattern. However, some reduction of the rate of reaction was observed before more rapid acceleration to ignition or to maximum temperature of the stabilized state.

Table 5. Physical properties and ignition characteristics of Diesel fuels

Cetane number	41	55	60	68
Type	Cracked distillate	Straight run	Straight run	Doped 55 cetane
Specific gravity AP 1	33.7	32.8	38.3	38.2
Viscosity Syb	34.7	50.4	43.0	36.2
Flash point °F	185	213	151	130
Boiling point °F	405	415	323	221
Sulphur content %	0.29	0.23	0.10	0.14
S.I.T. °C	233	230	225	226
Ignition lag	3 min 00 sec	2 min 30 sec	2 min 30 sec	1 min 45 sec
Evidence*	1	5	4	3

*Key for Evidence of Ignition

- 1 Mild flame
- 3 Flame
- 4 Mild explosion
- 5 Explosion

The two upper curves shown on Figure 18 were obtained for the straight-run fuel (55 cetane); the two lower curves correspond to the same fuel doped with 1 percent of ethyl nitrate. A small addition of a dope reduces the ignition temperature from 230° to 226°C, and the ignition lag from 2 1/2 min to 1 3/4 min and the intensity of ignition from explosion to normal flame.

(f) Furnace Oil No. 2

General ignition characteristics of furnace oil No. 2 are substantially the same as Diesel fuels of 41 and 55 cetane number, i.e. single stage reaction with medium self-heating before ignition, which occurred at 233°C with mild flame after 2 min 40 sec.

(g) Lubricating Oils

Lubricating oils generally represent a complex mixture of different hydrocarbon components having different affinity for oxygen. Because of this, the self-ignition of oil vapor does not always proceed in a definite order and as consistently as is the case with other combustible liquids. Oils having a comparatively low ignition temperature such as U.S. Navy No. 2075 and 8190 were ignited more or less in a definite and reproducible manner. However, chlorinated paraffin oils and motor lubricating oils used for internal combustion engines usually ignited irregularly in the zone of minimum ignition temperatures. Above this zone, ignition can be observed regularly and below it the oil vapors are definitely not ignitable. For chlorinated paraffin oil this doubtful zone covers a range of about 10 degrees C but for motor oil it amounts to about 35 degrees C.

The causes of the irregularity of ignition of these two oils were not exactly established; however, some explanation may be offered on the basis of the studies of the time-temperature curves and observation of smoke clouds through the neck.

The time-temperature curves obtained in the 1000-ml flask with motor lubricating oil are shown in Figure 19. These show a rapid increase of temperature due to exothermic reaction observed at temperatures far below the ignition temperature. This increase in temperature was often accompanied by expulsion of smoke, which can be confused with the

"Puff" corresponding to ignition. The appearance of flame can be observed through the mirror placed above the neck of the flask only in cases where ignition occurred in the upper layers of the flask. Observation through the periscope attached to the neck, however, often permits the observer to see the illumination of clouds by flame in the lower part of the flask.

Irregularities in ignition usually increase with the charge. For charges of 0.05 or 0.10 ml per 1000 ml of air, irregularities are considerably less than for charges over 0.20 ml, for which "double" or "triple" ignitions were often observed at high temperatures and the time-temperature curves showed fluctuation especially in the large flask (Figure 20).

Observation under strong flashlight of the reacting gasses through the neck covered by the pyrex glass indicated that oil projected into the flask rapidly evaporates with formation of dense clouds which are not properly mixed with air due to the high viscosity of oil vapors. Ignition usually occurred locally with a flash of flame and locally the products of combustion become transparent. Other portions of the flask are filled with unburned dense clouds slightly disturbed by the force of ignition. At higher initial temperatures, ignition usually occurred with violent audible flash (explosion), causing turbulence in unburned clouds and repeated ignition. At minimum ignition temperatures the vapor mixture usually ignited with a very weak flame, which is difficult to observe through dense clouds even with the periscope. Moreover, nonuniform mixtures of oil vapor and air at the region of lowest ignition temperature did not always produce favorable conditions for acceleration of reaction to ignition.

The temperature distribution in the 15,000 ml flask during the nonignition reaction, shown in Figure 20 by the three time-temperature curves, was observed at the same time in the top, center and bottom regions of the flask. Maximum variation of these temperatures was only about 5 degrees C.

(h) Benzene

Samples of pure benzene (C_6H_6) were subjected to self-ignition tests in 200 and 1000-ml flasks. The time-temperature curves obtained in the 1000-ml flask are shown in

Figure 21. Appreciable self-heating of the reacting mixture was observed 50 degrees C below the self-ignition temperature. At the initial temperature of 557°C, the mixture was self-heated to 690°C. However, at the initial temperature of 565°C, actual ignition was observed at 603°C or about 87 degrees C below the maximum temperature of the preceding test. Here again evidence is presented of the fact that for ignition the initial temperature from which the exothermic reaction proceeds in a certain order is more important than the instantaneous temperature of the reacting mixture. It is interesting to note that the maximum temperatures for each reaction fall on a smooth curve. The shape of the nonignition reaction time-temperature curve is not quite that of a single-stage reaction.

In spite of a considerable and rapid increase of temperature during the nonignition reaction, ignition was indicated by a barely audible expulsion of dense smoke and mild flame which was not always visible without the periscope.

(i) Toluene

The determination of the minimum self-ignition temperature of toluene was also difficult because of the very mild form of ignition which was hardly visible through the dense smoke. Moreover, rapid self-heating of the reacting mixture was observed below the ignition region and an early expulsion of smoke similar to that observed in previous cases (benzene, lubricating oil, etc.) caused confusion in correctly judging the time of actual ignition. Therefore, the illumination of dense smoke even by dull flame, visible through the periscope, was considered as evidence of ignition.

The two-stage pattern of the reaction of toluene is not clearly shown on the time-temperature curves obtained in the 1000-ml apparatus. However, the "slow down" of the non-ignition reaction is similar to that observed for benzene. The two-stage reaction is more definitely indicated in the 12,000-ml apparatus, particularly at lower temperatures which is gradually transformed into "slow down" reaction at higher temperatures, as shown in Figure 22.

3.3 Pure Petroleum Fractions

Three groups of pure hydrocarbons, listed in table 6, were supplied by the division of thermochemistry. The ignition characteristics of these hydrocarbons were determined in the Bureau's 1000-ml apparatus.

Table 6. Physical properties and ignition characteristics of pure petroleum fractions

Fractions	Formula	Carbon atoms	Ratio H/C	Boiling point	Ignition characteristics		
					S.I.T.	Lag	Evidence*
(a) Normal fractions (chain type)							
n-Pentane	C ₅ H ₁₂	5	3.60	36.1	258	1 00	1
n-Hexane	C ₆ H ₁₄	6	2.33	68.7	240	1 30	1
n-Heptane	C ₇ H ₁₆	7	2.28	69.4	223	0 45	5
n-Nonane	C ₉ H ₂₀	9	2.22	150.7	211	1 25	3
n-Decane	C ₁₀ H ₂₂	10	2.20	174.0	206	2 10	1
n-Dodecane	C ₁₂ H ₂₆	12	2.17	216.5	203	2 17	5
n-Cetane	C ₁₆ H ₃₄	16	2.12	287.5	202	2 35	5
(b) Normal fractions (ring type)							
Cyclohexane	C ₆ H ₁₂	6	2.0	81.4	246	17 15	1
Methylcyclohexane	C ₇ H ₁₄	7	2.0	163.0	248	20 10	1
(c) Isomers							
Trimethylbutane	C ₇ H ₁₆	7	2.28	80.9	421	1 26	2
Isooctane	C ₈ H ₁₈	8	2.25	99.3	420	1 20	2

The time-temperature curves for the above liquids are given in figures 23 to 29.
 * Key for Evidence of Ignition - 1 Mild flame 2 Blue flame 3 Flame 5 Explosion

(a) Normal Fractions of the Chain Type

The pattern of the time-temperature curves for non-ignition reactions for fractions of the chain type are substantially the same, with the exception of the curves, for dodecane (Fig. 24) and cetane (Fig. 26), the non-ignition reaction of which has a "slow down" portion similar to two-stage reaction. The rate of the inducing reaction preceding ignition gradually decreases and the ignition lag increases with carbon content.

The self-ignition temperature of liquids of the chain type consistently diminished with an increasing number of carbon atoms up to 16 ($C_{16}H_{34}$) along the curve shown in Figure 27. The curve for fractions of larger carbon content was not determined exactly, because of very limited quantities of rare fractions. However, tests of very small amounts of dotriacontane ($C_{32}H_{66}$) indicate that the self-ignition temperature is somewhere above $300^{\circ}C$. In other words, the curve seemed to turn upward after carbon number 16. Additional tests will be necessary to confirm the shape of this curve.

(b) Normal Fractions of Ring Type

The time-temperature curves for the two-ring type fractions tested have similar shapes for ignition and non-ignition reactions (Figs. 28 and 29). It is interesting to note that in each case exothermic reactions initiated at temperatures differing by only one degree C were started with the first stage of reaction and proceeded further with the second stage at substantially constant temperature. After about 12 or 15 min delay, rapid self-heating initiated, which in one case accelerated to ignition and in another case reached equilibrium at the nonignition state. At higher initial temperatures, ignition of both cyclohexane and methylcyclohexane occurred at the end of the second stage. This two-stage pattern of reaction is identical with the pattern obtained for motor and aviation gasolines at the same region of initial temperatures as shown in Figure 30.

(c) Isomers

Trimethylbutane (Triptane). The determination of the minimum self-ignition temperature of this isomer involved difficulties due to the very mild form of the evidence of

self-ignition. The shape of the time-temperature curves, shown in Figure 31, was substantially the same for the ignition and nonignition reactions. Ignition in this case could not be judged by the shape of the time-temperature curve. The expulsion of gases or "puff" in the lower temperature region was also very weak and did not provide an indication of ignition. The intensity of visual evidence of ignition changed with initial temperature. At high temperatures, a bright orange flame was usually distinctly visible through the mirror placed above the neck of the reaction vessel. However, at lower temperatures approaching 421°C a blue-violet flame could be observed. The intensity of this flame was gradually diminished to approach a cold flame at 419°C and to chemiluminescent light at 414°C which was distinctly visible through the periscope placed above the open neck of the ignition flask.

Isooctane (2,3,4 - Trimethylpentane). The ignition characteristics of Isooctane obtained in the 1000-ml flask were substantially the same as for Trimethylbutane. The exothermic reaction became pronounced at about 150 degrees C below the self-ignition temperature and the shapes of the time-temperature curves were also similar for the ignition and nonignition reactions. The expulsion of gases was so weak that it could be noticed only by odor. Moreover, the observed reproducibility of blue and cold flame or chemiluminescent light was very poor and was affected by deposits on the flask wall, by direction of the charge stream, and by relative humidity of air. Injection of the charge along the side of the neck wall usually stimulated ignition at slightly lower temperatures than injection directly to the bottom of the flask. Ignition of Isooctane, indicated by dull blue flame was usually observed under dark room conditions (through a periscope). Minimum self-ignition temperatures obtained in this manner at different times during three months varied between 408°C and 425°C. It is likely that these variations were due to the combined effects of different humidity conditions and barometric pressure changes. In view of such variations, the more reproducible value of minimum self-ignition temperature was selected as 420°C with corresponding ignition lag of 1 min 20 sec.

Similar difficulties were encountered when the test was performed in the 200- and 12,000-ml flasks. The reproducibilities of self-ignition temperature were slightly better and the band of uncertainty in the 200-ml flask was within 12 degrees C and in the 12,000-ml flask even as low as 4°C.

More or less regular ignition was obtained in the 200-ml flask at 431°C after 35 seconds and in the 12,000-ml flask at 376°C after 1 min 45 sec. The factors affecting such poor reproducibility of the ignition of Isooctane should be studied more thoroughly.

3.4 Reference Fuels

Primary and secondary reference fuels have been used for the rating of various gasolines. The Primary Reference Fuels consist of mixtures of Isooctane and n-Heptane in various concentrations. The Secondary Reference Fuels are composed of mixtures of three specific gasolines in the following two groups: mixtures of gasoline A₆ with gasoline C₁₂ and gasoline C₁₂ with F₃.

According to the ASTM standard method, the performance of a gasoline in the CFR (Cooperative Fuel Research Committee) engine, operated under arbitrarily selected standard conditions, is matched with the similar performance of an Isooctane-n-Heptane mixture. The percentage of Isooctane in this mixture is then taken as the octane number of the fuel in being tested. Four different ASTM methods (motor, research, aviation, and supercharging) have been widely used for the rating of gasolines suitable for different purposes and one method for Diesel fuels. The octane rating of a particular gasoline may vary appreciably with the ASTM test method selected; because of this it is necessary to consider the test method when comparing ratings of different fuels.

(a) Primary Reference Fuels

The ignition characteristics determined in the 1000-ml flask of a number of Primary Reference Fuel mixtures are shown in Figures 32, 33 and 34. The shape of the time-temperature curves of these mixtures varies with the concentration.

It is interesting to note that the self-ignition temperatures and ignition lags changed at a gradual rate for mixtures varying in composition from 0 to 70% Isooctane (Fig. 35). The intensity of ignition also changed gradually from explosion to mild flame. Moreover, audible expulsion of gases ("puff") without flame was observed for mixtures containing 50 to 70% Isooctane at lower temperatures than in

cases where the "puff" was accompanied by flame (ignition). The temperature curve, corresponding to the first appearance of the "puff", consistently rose with the Isooctane concentration and at the same time the intensity of the "puff" diminished.

Study of the ignition characteristics of mixtures containing from 0 to 70% Isooctane indicates that the predominant effect of the n-Heptane component is gradually diminished until its concentration becomes 70%, at which point its effect reached "critical significance." For this mixture, in the temperature range of 260 to 280°C, the effect of n-Heptane seems still to predominate. However, at higher temperatures the effect of the Isooctane component becomes stronger and ignition in this region is defined by a blue flame. Moreover, ignition over a considerable range of temperatures is not well reproducible as was reported for pure Isooctane. At the intermediate range of temperatures from 294°C to 343°C, the mixture seems to have a peculiar balance between the effects of both components, as a result of which ignition of the mixture becomes erratic as it was observed through the periscope only. Moreover, this instability also spreads to other mixtures of lower concentration forming a so-called "secondary nonignition zone" as shown in Figure 35.

The secondary nonignition zone was observed also by Prettre (19) with pentane and hexane, by Townend (20) with hexane, by Sortman and Beatty (11) with heptane and cetane, and by many others. Nonignition zones were not observed for these liquids in the present investigation; therefore, this zone seems to be affected more by the apparatus and test conditions than by the nature of the substance in question.

(b) Secondary Reference Fuels

The first group of secondary reference fuels is composed of mixtures of gasoline A₆ (39.6 octane number) and C₁₂ (78.9 octane number). The self-ignition temperatures of these mixtures varied in direct proportion to the concentration, as is indicated by line II on Figure 36. The second group of reference fuels is composed of mixtures of gasolines C₁₂ (78.9 octane number) and F₃ (99.1 octane number). With these, ignition temperatures varied substantially in the same manner as for the Primary Reference Fuels. (Curve III). It was

found that self-ignition temperatures of mixtures up to 35% of fuel (C_{12}) varied linearly with the mixture. Ignition temperatures of mixtures of higher concentration rapidly increased up to 50% of fuel (C_{12}) at which concentration the mixture becomes nonignitable from 305°C to 382°C. This apparent secondary nonignition zone also spread to other mixtures of lower concentration, as is shown by a dotted line in Figure 36. The self-ignition temperature of mixtures containing larger concentrations of fuel (F_3) varied in a linear fashion with concentration, and ignition in this region was indicated by dull blue flame. The expulsion of gases ("puff") without flame was observed at lower temperatures, as shown by the dotted line (between 50% and 90% concentration).

The octane ratings of various mixtures of both groups of Secondary Reference Fuels were calculated from the concentration of fuels A_6 and C_{12} and fuels C_{12} and F_3 . The self-ignition temperatures of these mixtures were plotted against their octane ratings together with the Self-ignition temperatures of Primary Reference Fuels, as shown in Figure 37. Comparison of both self-ignition temperature curves obtained for the Primary Reference Fuels and Secondary Reference Fuels mixtures shows the following important facts:

(1) Both curves indicate that the self-ignition temperature is a discontinuous function of concentration of reference mixtures or corresponding cooperative fuel research committee ratings because of the secondary nonignition zone.

(2) Primary and Secondary Reference Fuel mixtures of the same cooperative fuel research committee ratings have different self-ignition temperature and ignition characteristics with the exception of the two end fuels (A_6 and F_3).

(3) The ignition characteristics of samples of two other gasolines are also not well correlated with the characteristics of corresponding mixtures of Primary and Secondary Reference Fuels, as shown in Figure 37. For example, the self-ignition temperatures of samples S_{18} (87 octane) and S_{19} (73 octane) are far away from the curve of the Primary Reference Fuels. Only S_{17} lies within the blue-flame zone of the rated mixture.

This poor correlation may be due to the fact that the appearance or intensity of knock and ignition lag, affecting the cooperative fuel research committee engine ratings, is dependent not only on the molecular structure, stability and other characteristics of fuel, but also on the operating engine conditions, such as compression ratio, air manifold and water jacket temperatures, speed and other factors which affect different fuels in different ways.

Poor correlation of the cooperative fuel research committee engine ratings with the ignition characteristics determined in other laboratory test apparatus have also been observed by other investigators (Jentzsch, Eckert, Zerbe and Carhart).

The presence of a combustion accelerator or dope in gasoline affects not only the octane rating but also the ignition characteristics and shape of the time-temperature curves. In the lower part of Figure 38, a typical time-temperature curve for fuel (C₁₂) (78.9 octane) is shown. The upper portion of the same chart contains time-temperature curves of the same fuel (C₁₂) with 1.25 ml tetra-ethyl lead per gallon of gasoline. The shape of these curves changed entirely and many additional stages of reaction developed before the reaction finally accelerated to ignition.

3.5 High Ignition Temperature Liquids

A few liquids ignitable at high temperatures were subjected to regular ignition tests in apparatus of different capacities. The ignition characteristics of these liquids are given in table 7 and the shapes of the time-temperature curves are shown in Figures 39, 40, and 41. The first five liquids given in table 7 have substantially the same shapes in time-temperature curves and comparatively short ignition lag. These curves are similar to those for acetone shown in Figure 39.

Both the ignition and nonignition reactions rapidly accelerated during the few seconds after injection to ignition or to maximum temperature. Methyl alcohol has a slightly different shape in the time-temperature curves shown in Figure 40, with the nonignition reaction lasting for several minutes. Glycerine has an extremely violent exothermic reaction even in the nonignition region, as shown in Figure 41.

Table 7. Ignition characteristics of high ignition temperature liquids

Material	Size of flask					
	200 ml	1000 ml	12,000 ml	S.I.T.	Lag	Lag
	°C	min	sec	°C	min	sec
Acetone	519	0	26	491	0	40
Acetic acid	505	0	08	488	0	13
Ethyl alcohol	402	0	28	391	0	40
Ethylene glycol	---	-	--	398	0	23
Methyl formate	---	-	--	467	0	25
Methyl alcohol	441	1	10	428	1	30
Glycerine	---	-	--	389	0	31
				(371)*	(0	36)*

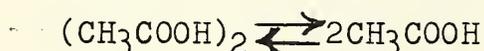
* In 15,000-ml flask.

(a) Acetone

Acetone ignites at the minimum temperature in an unusual manner observable through the periscope. The flame is very often either initiated by a small, red, glowing center of carbonized deposit of acetone on the flask wall and a blue-violet light spreads from this red center throughout the whole gas mass or it is initiated without this glowing center. The light usually appeared without audible manifestation and continued to be visible for about 20 seconds at 491°C and about 15 seconds at 505°C. The intensity of this light gradually increased from dull blue-violet at 491°C up to blue-pink at 515°C and to a regular pink-violet flash with an audible explosion at higher temperatures. The initial blue-violet light is similar to chemiluminescence, and when first observed it was questioned whether this could be taken as an indication of ignition. However, in consideration of the very sharp increase in the time-temperature curve (Fig. 39) at 491°C, this temperature was accepted as a minimum self-ignition temperature.

(b) Acetic Acid

Ignition of acetic acid occurred so irregularly that it was very difficult to define the lowest self-ignition temperature. One explanation of such irregularity may result from the fact that it is possible that acetic acid may exist in two interchangeable states, "dimer" and "monomer", which can be expressed by the following relationship:



It is possible that uncontrolled variables cause acetic acid to take either one or the other form, the ignition temperatures of which may be different.

In contrast to acetone, the glowing center usually was observed for only 15 seconds with definitely nonignition reactions. Ignition of acetic acid, in spite of existing irregularities, was defined by distinctly audible and visible evidence, which usually occurred about 8 seconds after injection of the charge. Ignition was initiated with blue flame which, at the end of the ignition period, changed to a pink color. Appearance of this color may be connected

with another phenomenon observed during ignition of acetic acid in the spherical flask of 35-ml capacity. Due to the very small size of the ignition chamber, the minimum self-ignition temperature was found at 517°C, at which temperature the flask walls were dull red. Normal ignition was indicated by a blue flame; however, at a temperature slightly below 515°C a pink light was observed without audible evidence. Study of this light through the periscope indicated that, at the end of exothermic reaction (nonignition) or about 15 sec after injection of the charge, clouds or fog formed in the transparent gas mixture which was illuminated by the reflection from the dull red walls of the ignition chamber. This phenomenon gave an erroneous impression of pink light or flame. Ignition in the 1000-ml flask occurred at 491°C, at which time the wall of the chamber was a very dull red color. The formation of clouds or fog at the end of the reaction may also be confused with the appearance of pink flame.

(c) Ethyl Alcohol

The shape of the time-temperature curve for ethyl alcohol was similar to that of acetone (Fig. 39). Due to the rapid increase of temperature (and pressure) at the time of evaporation, an audible expulsion of gases was observed before ignition. The actual ignition at 391°C after 40 seconds was accompanied by blue flame with a second expulsion of gas.

Ethyl alcohol-water mixtures were also found to be readily ignitable. The self-ignition temperature rapidly increased from 391°C to 444°C as the water content of the mixture approached 70%. Very weak flame was observed at 467°C even with 80% water.

(d) Ethylene Glycol

Ethylene glycol was subjected to ignition tests in connection with a determination of the fire hazard of anti-freeze in aircraft installations. The ignition of pure ethylene glycol in the 1000-ml flask was indicated at 398°C by orange-blue flame and hardly audible expulsion of gases. However, the same liquid with 3% of antirusting ingredient (triethanolamine phosphate) ignited at 395°C with violent audible flash. Furthermore, ethylene glycol was tested in solution with different percentages of water. It is interesting to report that ignition was observed at 460°C in a highly dilute solution (90% water). However, ignition of solutions with more than 40% water was so weak that the flame could be observed only through the periscope.

Two antifreezing liquids, R-19 and R-19d, were tested in the same manner and the results indicate that these liquids are highly ignitable. Both liquids are a petroleum distillate (kerosene type). Liquid R-19 is a pure product and R-19d is a mixture with a special ingredient for prevention of softening of rubber hose in engine installations. The self-ignition temperature of R-19 is 211°C and ignition lag 3 min 50 sec, while R-19d ignites at 223°C after 1 min 30 sec. Ignition of both liquids occurred suddenly without preliminary self-heating at only 3 degrees C above the initial temperature and was indicated by violent audible explosion; therefore, both liquids were considered high fire hazards.

(e) Methyl Formate

Ignition of methyl formate was indicated regularly by a mild explosion and rapid rise in temperature similar to that for acetone (Fig. 39).

(f) Methyl Alcohol

The shape of the time-temperature curves for methyl alcohol, shown in Figure 40, are slightly different from those of the previously described liquids. The curves for the ignition reaction are distinctly different from the nonignition reaction and give supplemental evidence of a very mild form of ignition, which is usually indicated by a dull blue flame and weak expulsion of clear gas.

(g) Glycerine

Ignition of glycerine was indicated by a very violent explosion accompanied by long flame and smoke expelled from the neck of the ignition apparatus. A very rapid rise in temperature of the gas mixture was recorded immediately after injection of the charge for both ignition and nonignition reactions, as shown in Figure 41.

Progressive development of the different stages of the ignition reaction was observed through the mirror and periscope. Immediately after injection of the charge, viscous glycerine droplets accumulated on the bottom surface of the flask and rapidly evaporated with dense white clouds. These clouds later (about 20 sec) became clear either due to superheating or partial oxidation. The next stage usually began about 5 sec later with the appearance of a small blue

flame with a pink center. Due to rapid propagation of flame, gases were expelled from the neck of the flask with considerable force.

The shapes of the time-temperature curves of a nonignition reaction adjacent to the ignition region were studied simultaneously in different parts of the 15,000-ml flask. In spite of the comparatively high rate of reaction, the temperature distribution within the flask was not far from uniform, as shown in Figure 42. The shapes of the time-temperature curves are substantially the same in the top, central and bottom portions of the flask. Continuous recording would probably show still better uniformity in temperature distribution through the whole cycle.

(h) Paint, Varnishes, Oil and Miscellaneous Materials

A number of combustible materials of commercial grade were tested in the 1000-ml ignition apparatus. Ignition characteristics of these materials are given in table 8.

(1) Black enamel. Noticeable decomposition of synthetic automobile black enamel (601) was indicated at 270°C by the appearance of smoke. At a temperature of about 445°C, carbonized residue of the charge was self-heated to the glow state. However, self-ignition occurred at 478°C with audible expulsion of a large flame and smoke. As a result of ignition, all the carbon residue was burned out and the flask surface became clear.

The temperature curves for black enamel are shown in Figure 43, and are typical of many materials of this class.

(2) Pine tar. Pine tar of commercial grade, due to its low "fluidity" was preheated in boiling water before injection by hypodermic syringe. The exothermic reaction of a mixture of pine tar vapor with air also initiated far below the ignition temperature. The shape of the time-temperature curves is substantially the same as for black enamel. Ignition was indicated by flame and mild expulsion of smoke. The flask surface after ignition was usually covered by a brownish coating and tar residue cooked to a hard carbon deposit removable only with a scraper. However, the residue after ignition of pine oil was soft and easily removable from the surface.

Table 8. Ignition characteristics of miscellaneous liquids

Material	Grade	S.I.T.	Lag	Evidence*
		°C	min sec	
Black enamel	Synthetic (601)	478	0 06	4
Pine tar	Commercial	439	0 10	3
Pine oil	do	316	0 07	4
Linseed oil (raw)	do	425	0 04	3
Castor oil	do	409	0 24	3
Varnish (interior)	TT-V-71	359	0 02	6
Varnish (spar)	TT-V-121a	350	0 03	3
Lacquer (red)	Nitrocellulose	349	0 25	3
Lacquer (clear)	do	342	0 14	3
Lacquer (thinner)	Commercial	298	0 12	5
Turpentine	Commercial	250	0 40	3

* Key for Evidence of Ignition

- 3 Flame
- 4 Mild explosion
- 5 Explosion
- 6 Violent Explosion

Table 9. The values of the self-ignition temperature of different liquids found in the 1000-ml ignition apparatus of different thermal characteristics

Liquids	Type of casing		
	Metal	Refractory	Mirror surface
	<u>°C</u>	<u>°C</u>	<u>°C</u>
Acetic acid	501	488	474
Acetone	505	491	---
Ethyl alcohol	405	391	385
Gasoline (motor)	249	243	238
Isooctane	431	420	409
Toluene	529	519	---
Varsol	237	235	234
Ethyl ether	172	170	---

(3) Linseed oil. Ignition characteristics of linseed oil are similar to lubricating oils and appreciable self-heating of the vapor-air mixture was observed at temperatures far below the ignition temperature.

(4) Varnish and lacquer. The ignition characteristics of varnish and lacquers are substantially the same, particularly in the nonignition region. Self-heating of the vapor-air mixture was initiated far below the self-ignition temperature. As the initial flask temperature approached the ignition temperature, the reaction became almost violent. A few degrees below self-ignition temperature, self-heating of the mixture often is 20 or 25 degrees C above the initial temperature. Ignition of these liquids, with the exception of interior varnish and lacquer thinner, is very mild; both the lacquer thinner and interior varnish ignited with an audible explosion.

(5) Turpentine. The time-temperature curves for turpentine are very similar to those for kerosene and even had the same two-stage nonignition reaction with ignition definitely in the first stage, as shown in Figure 44.

3.6 Effect of Thermal Characteristics of the Apparatus

The effect of thermal characteristics of the ignition apparatus described in section 2.1 on the observed self-ignition temperature of combustible liquids is shown in table 9. Results of further study and analysis of this effect are reserved for a future paper.

4. CONCLUSIONS

The following conclusions are presented as a result of the work reported:

- (1) Thermo-chemical processes occurring during the ignition of combustible liquids can be presented by means of time-temperature curves together with visual and audible evidence of ignition.
- (2) The shape, size, and thermal properties of the ignition vessel together with the details of the test procedure have an important effect on the observed ignition characteristics.

- (3) Ignition temperatures measured with the new apparatus described are lower than those observed by most other workers.
- (4) With the apparatus used in these tests, the experimental results have proved highly reproducible.
- (5) Changes in the observed ignition temperatures of a given liquid measured in different apparatus are correlated with changes in size and thermal properties of these apparatus.

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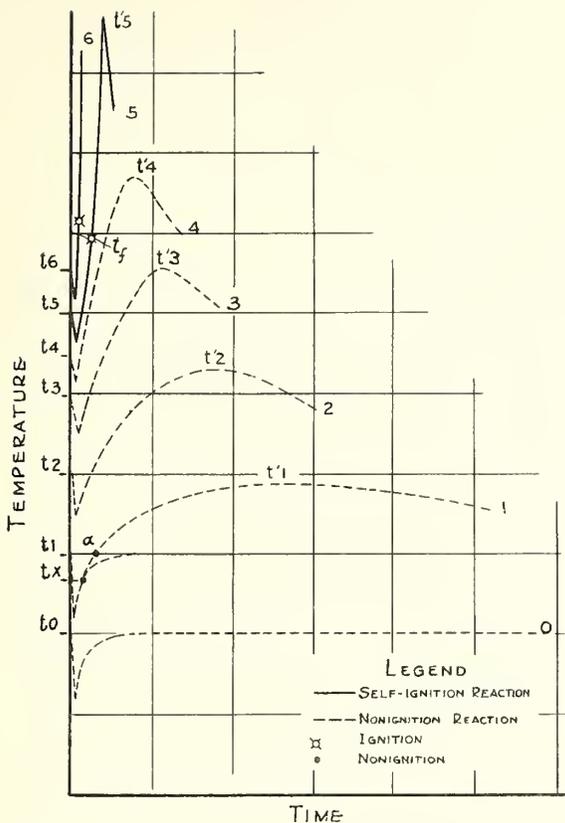


Fig. 1 Idealized Time-Temperature Curves for Self-Ignition and Non-Ignition Reactions of Combustible Liquids.

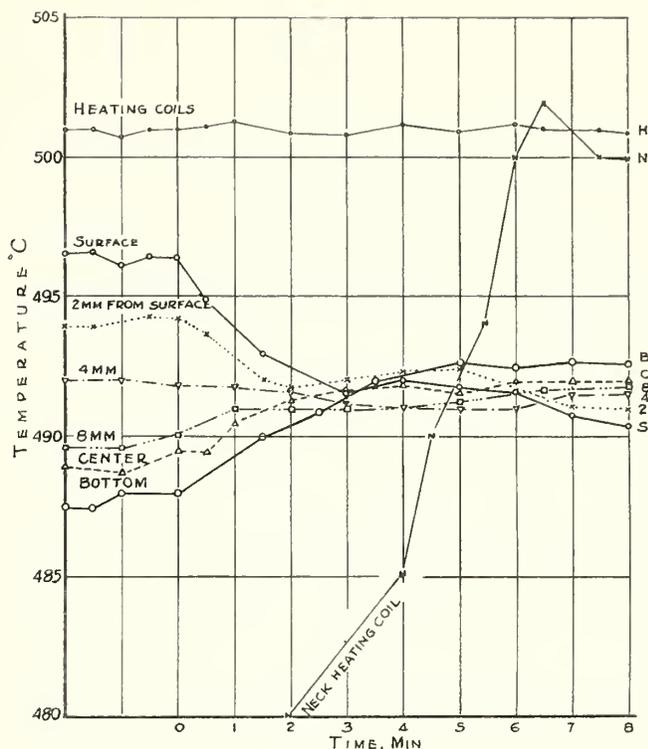


Fig. 2 Effect of Heating Neck on Uniformity of Temperature in the 1000 ml Spherical Flask.

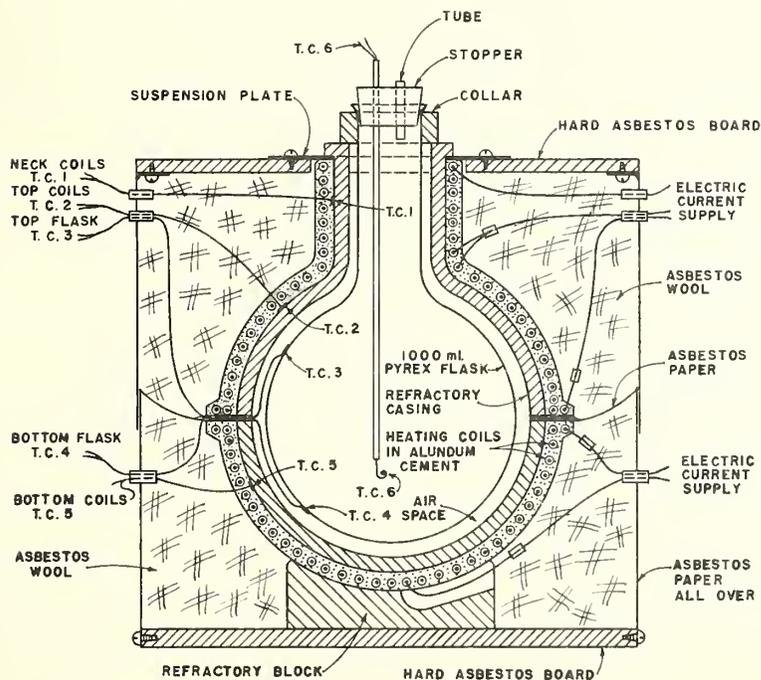


Fig. 3 1000 ml Spherical Pyrex Flask Ignition Apparatus for Liquids with Air Space and Refractory Casing.

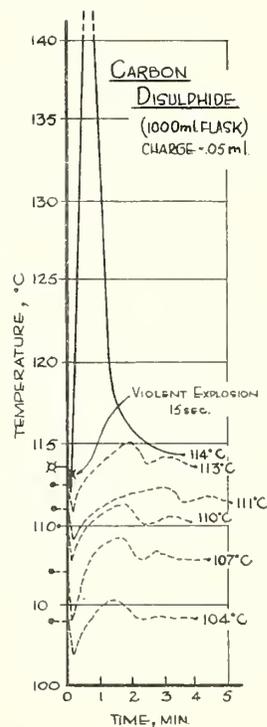


Fig. 4

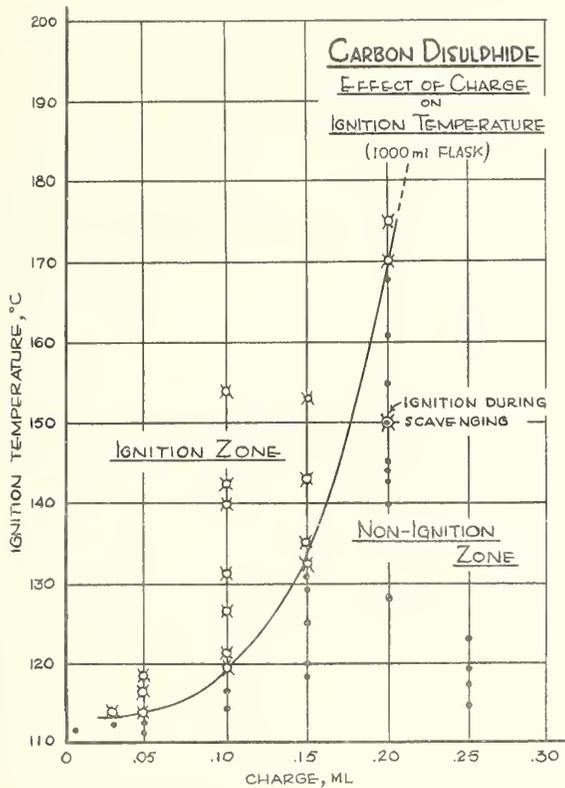


Fig. 5

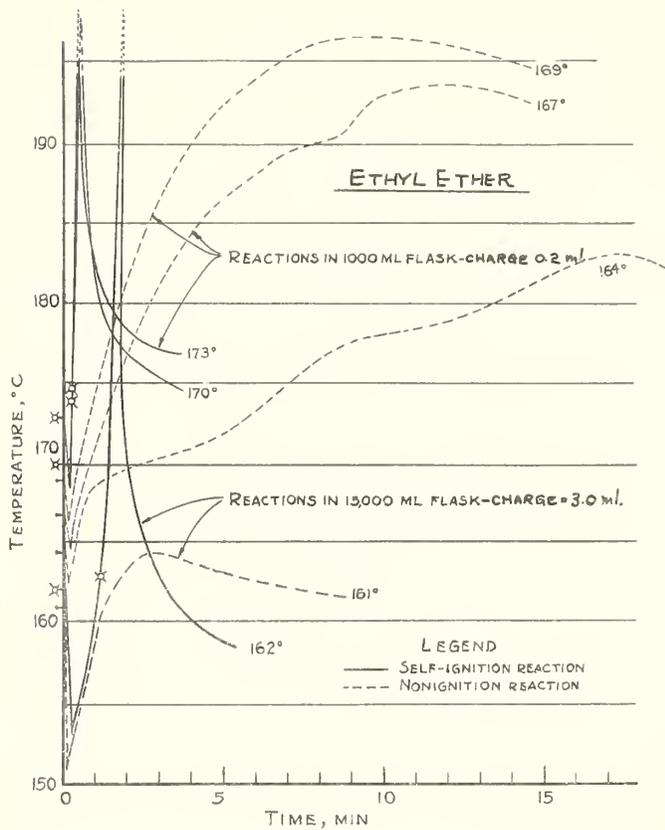


Fig. 6

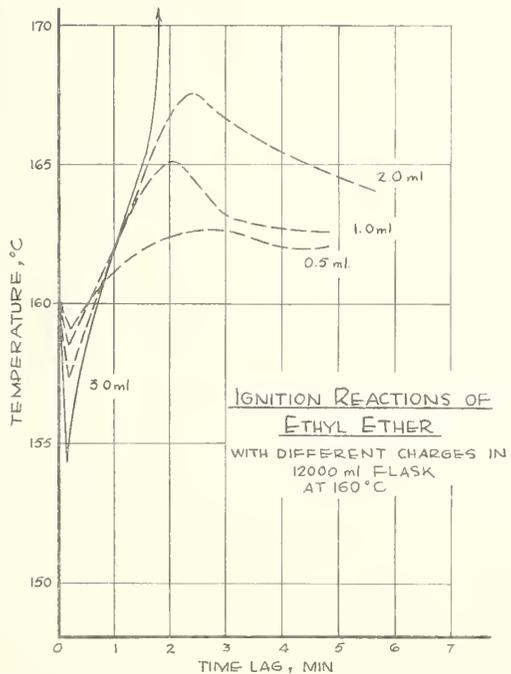


Fig. 8

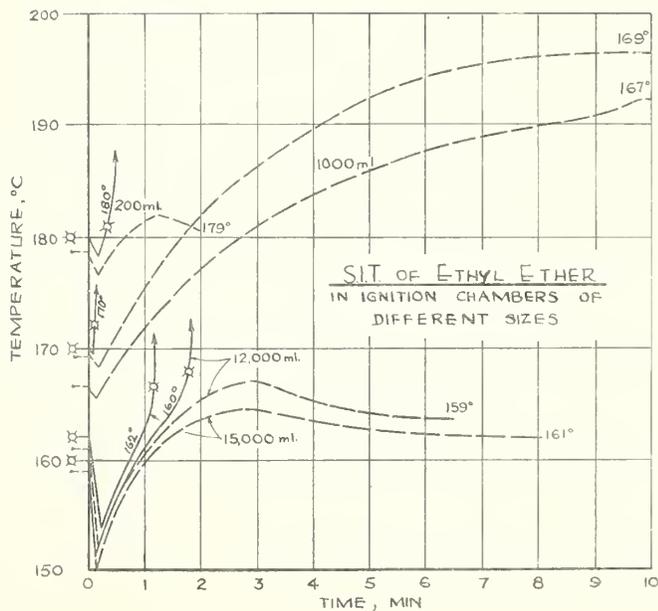


Fig. 7

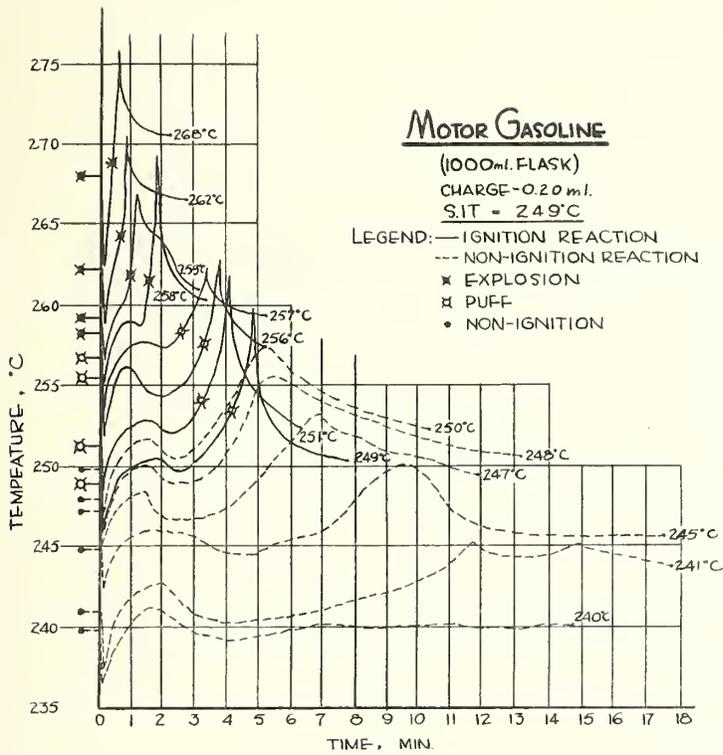


Fig. 9

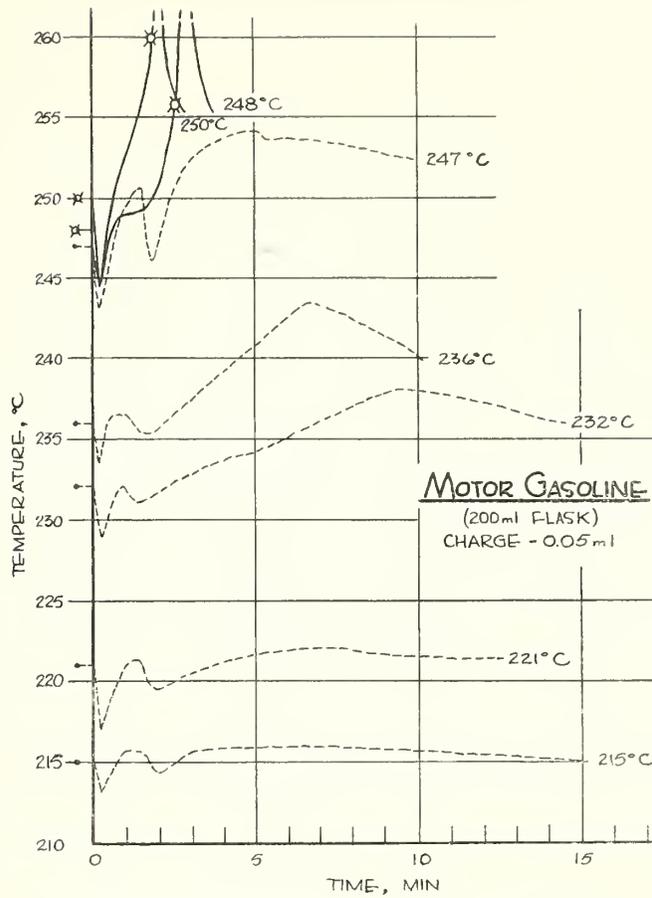


Fig. 10

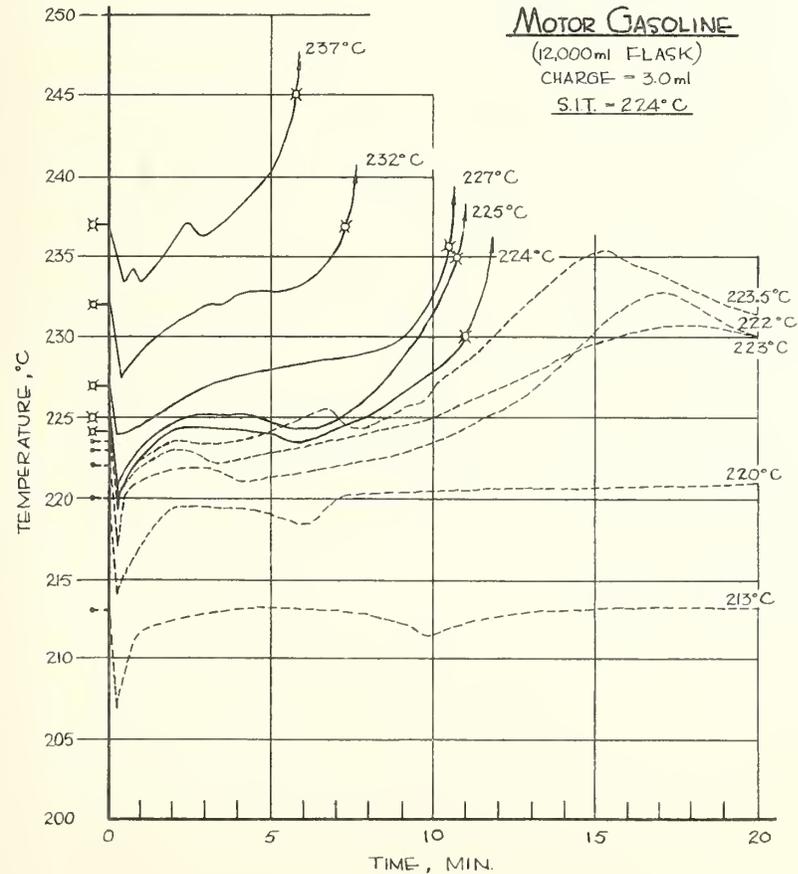


Fig. 11

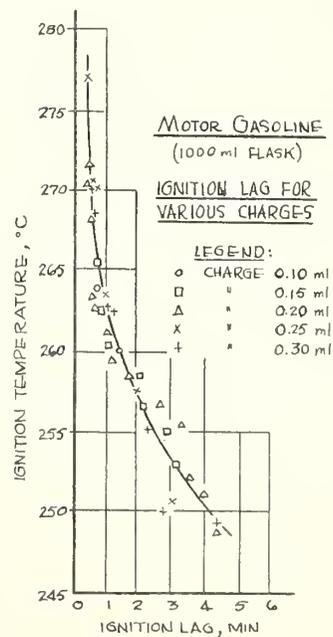


Fig. 12

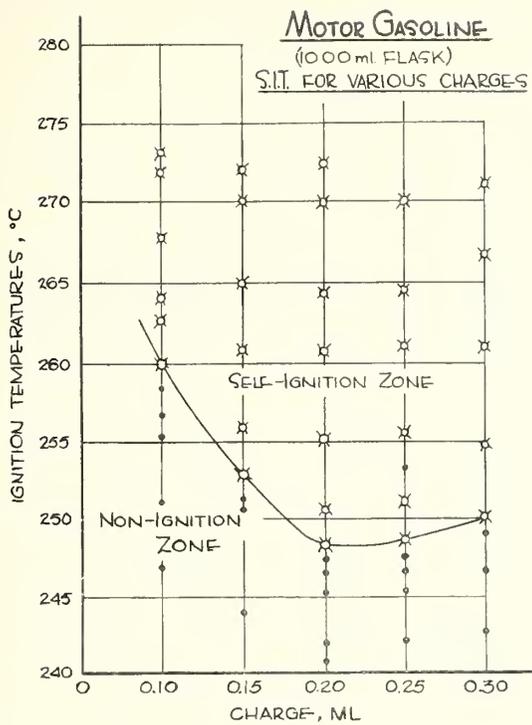


Fig. 13

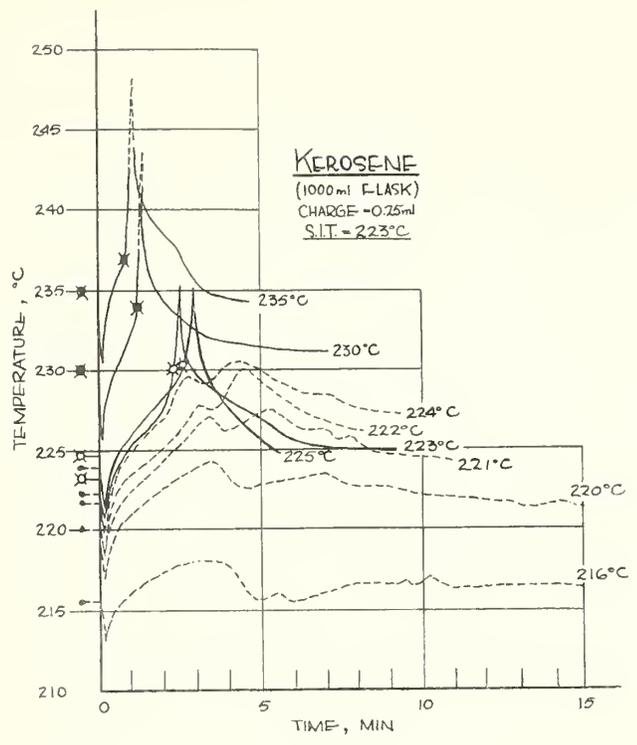


Fig. 14

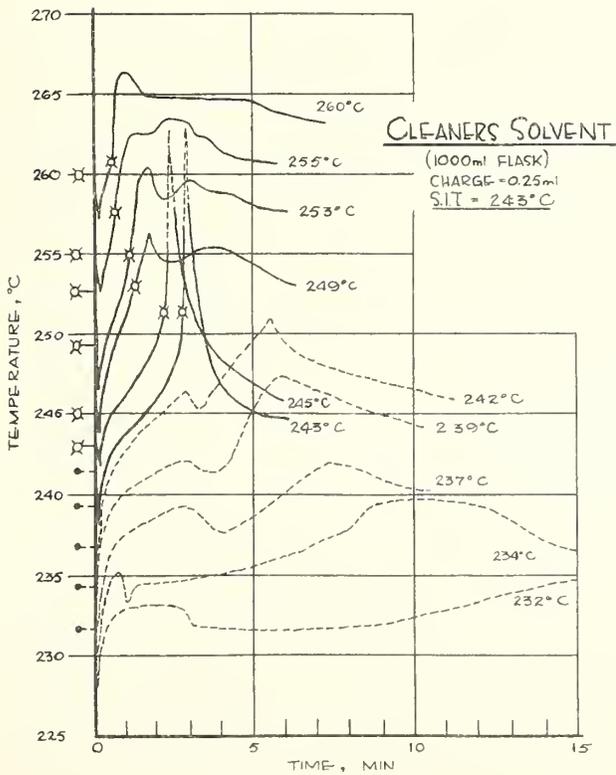


Fig. 15

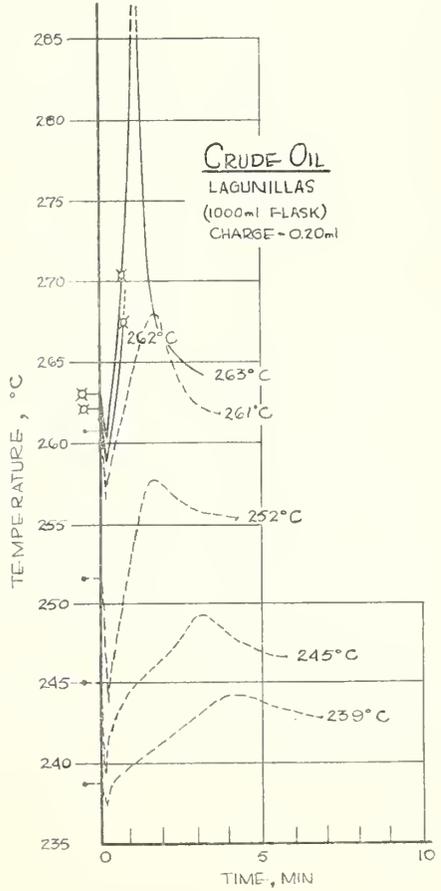


Fig. 16

MOTOR LUBRICATING OIL
(1000 ml. FLASK)
CHARGE = 0.2 ml.

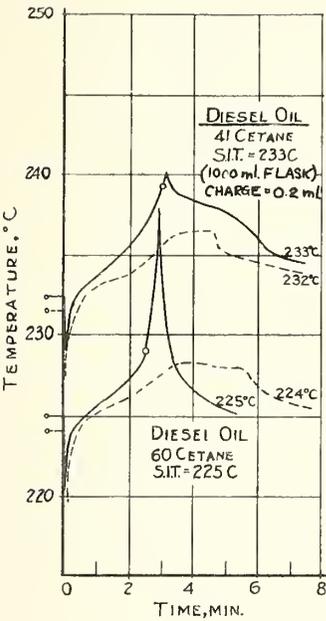


Fig. 17

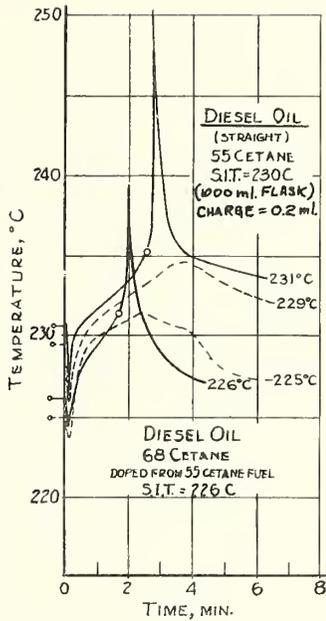


Fig. 18

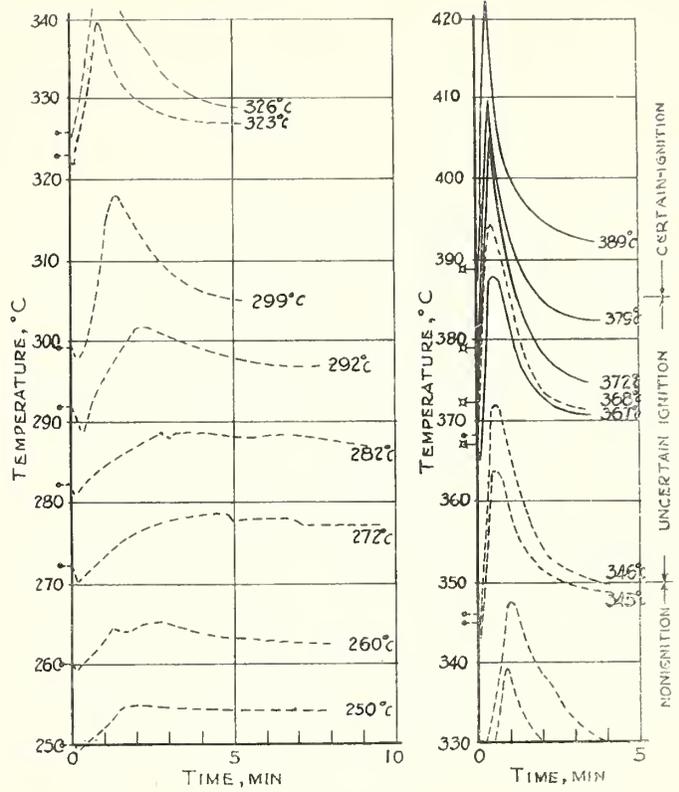


Fig. 19

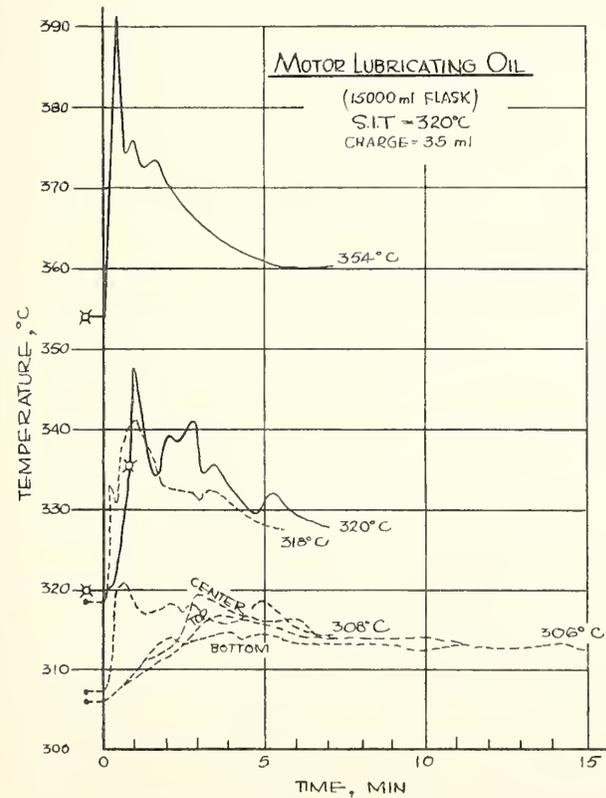


Fig. 20

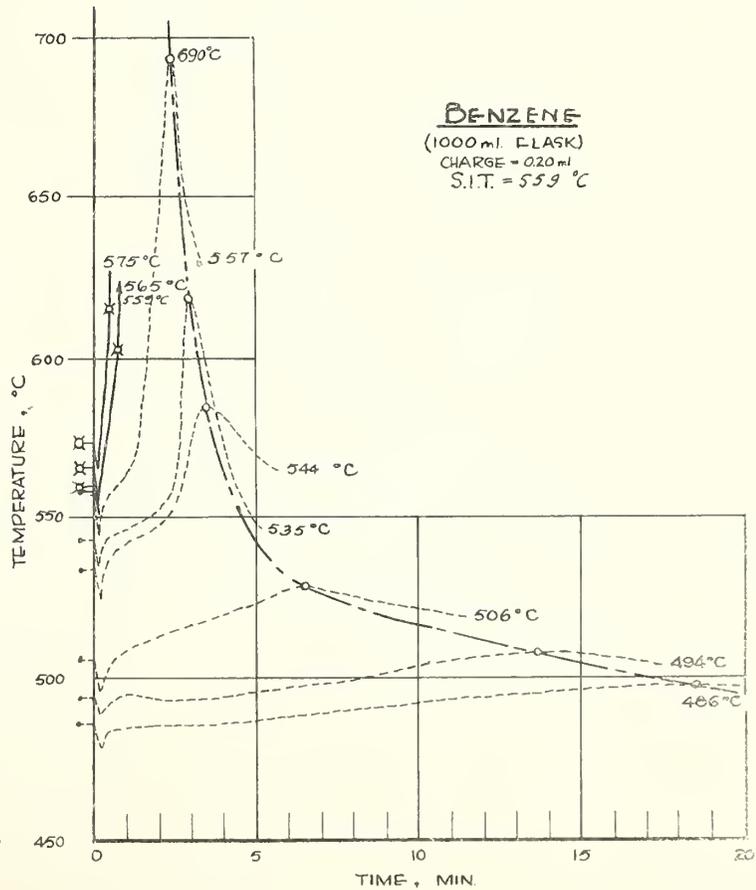


Fig. 21

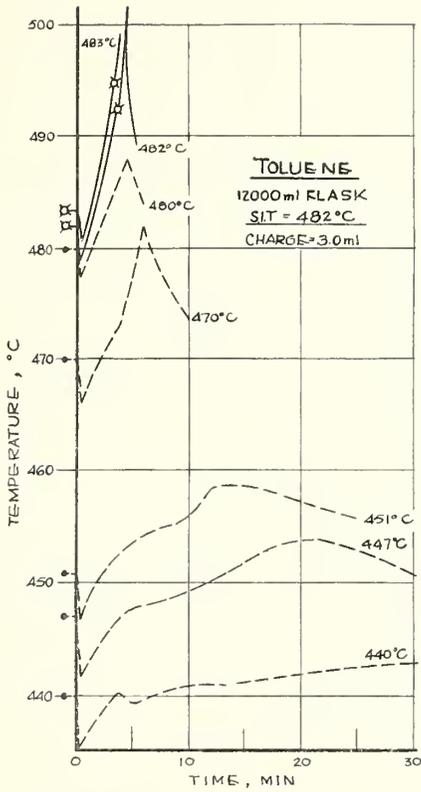


Fig. 22

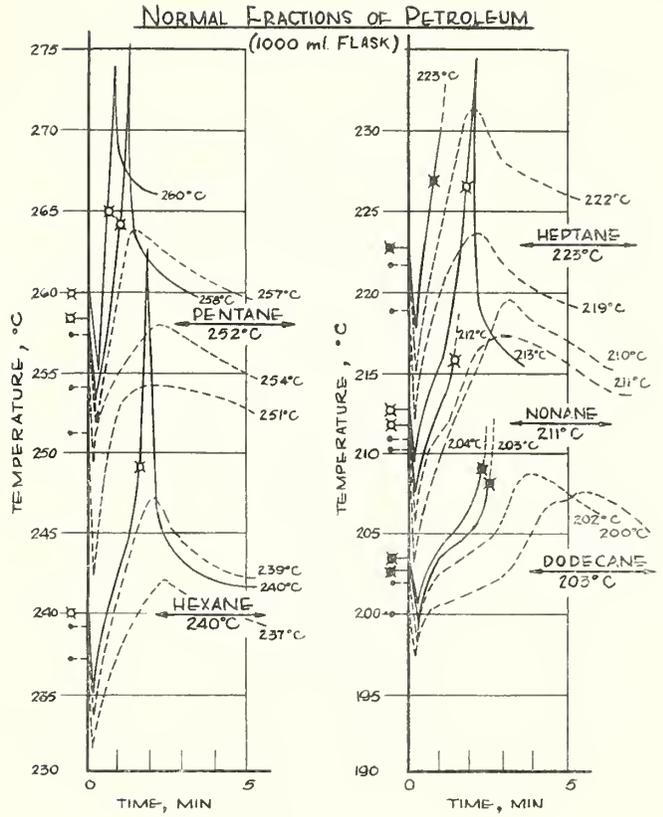


Fig. 23

Fig. 24

NORMAL FRACTIONS OF PETROLEUM
(1000 ml. FLASK)

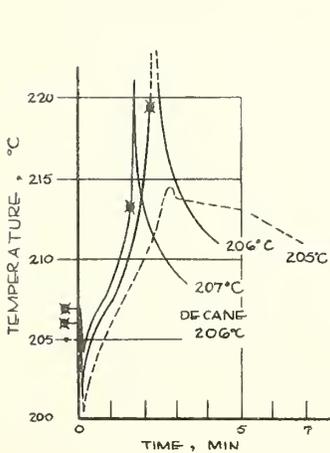


Fig. 25

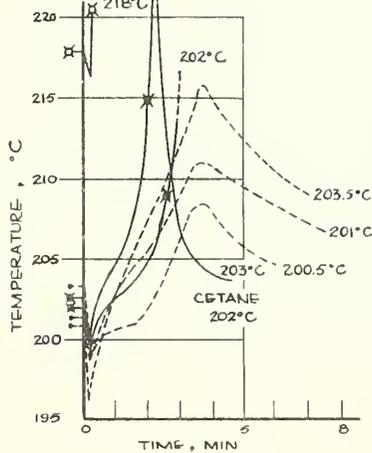


Fig. 26

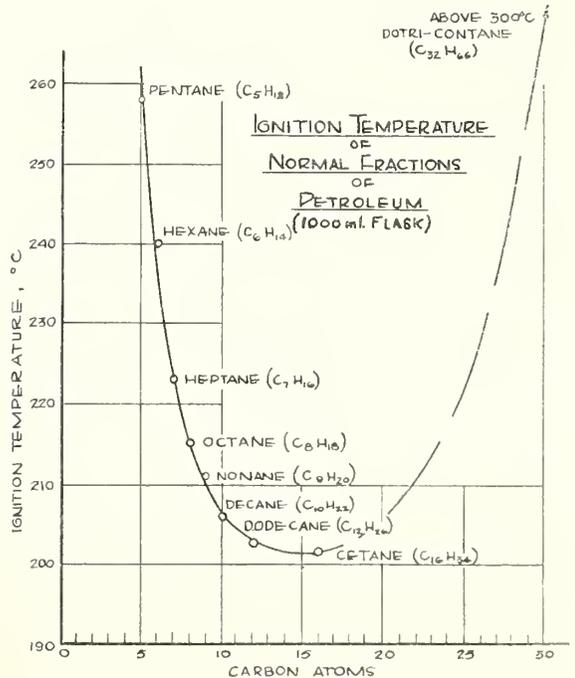


Fig. 27

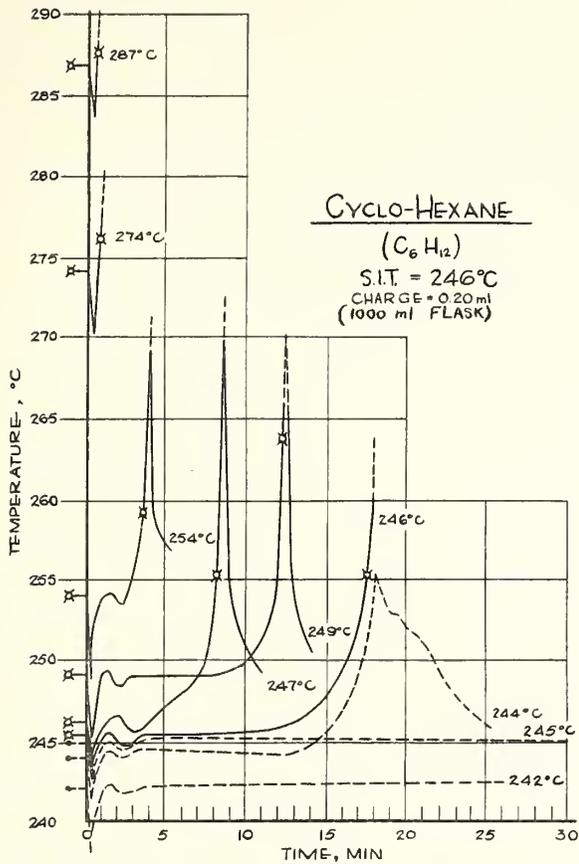


Fig. 28

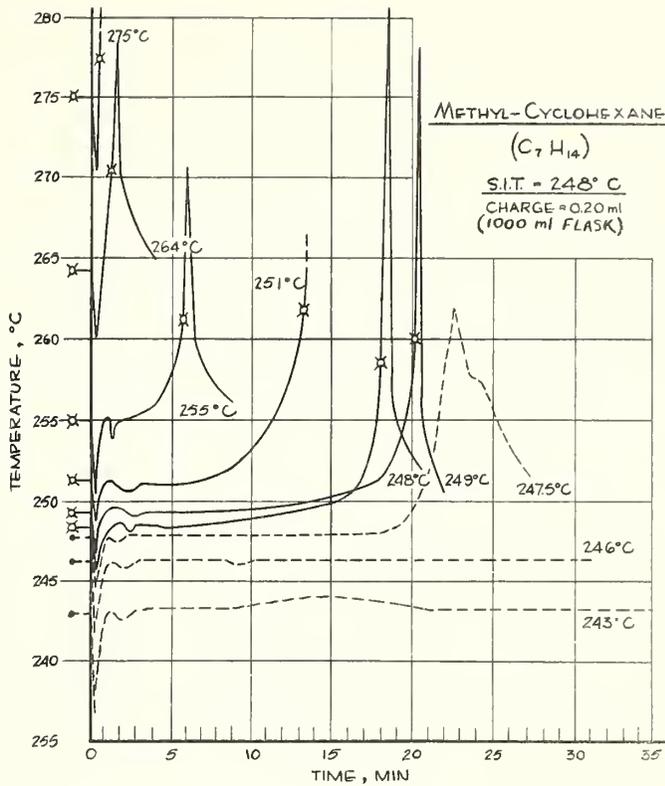


Fig. 29

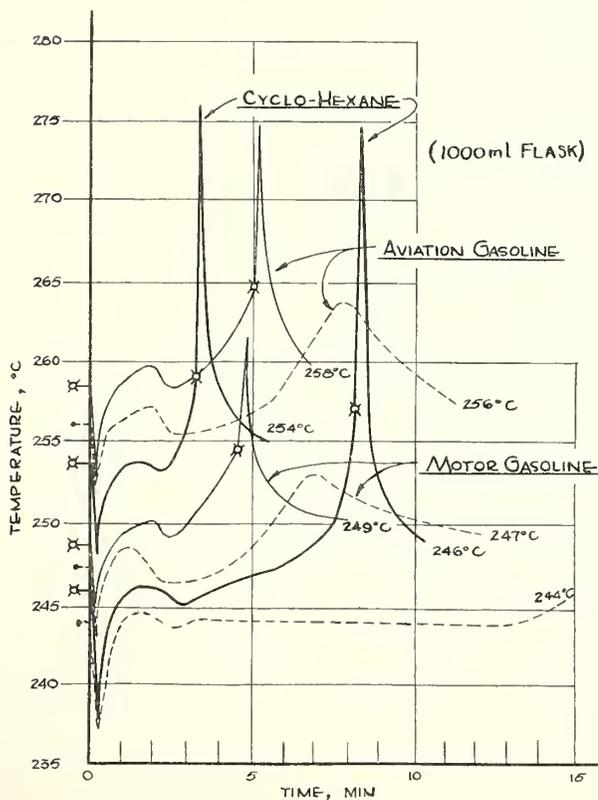


Fig. 30

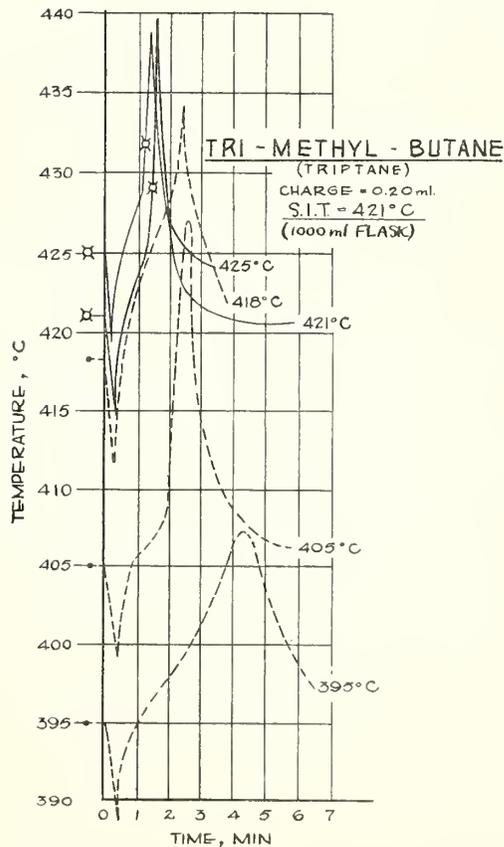


Fig. 31

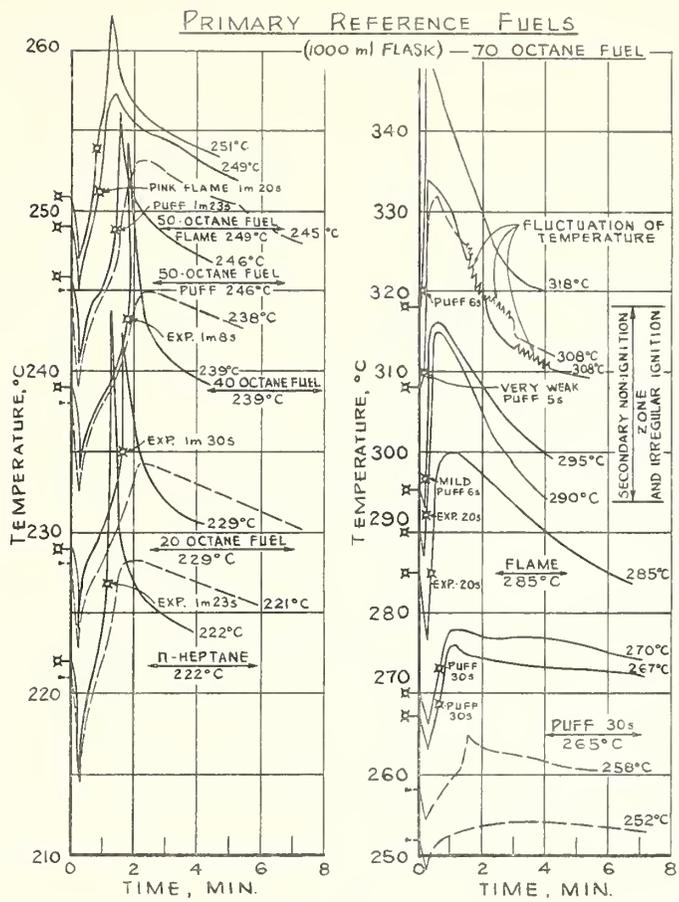


Fig. 32

Fig. 33

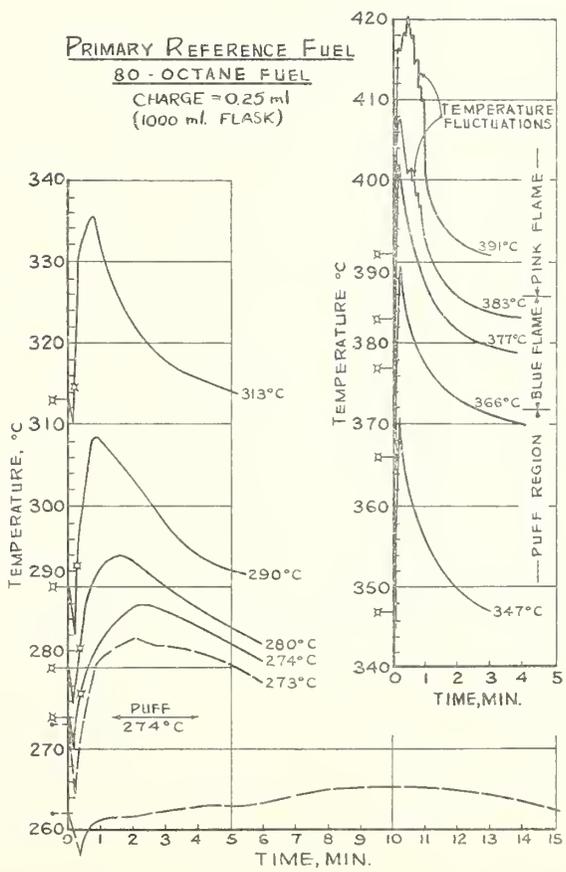


Fig. 34

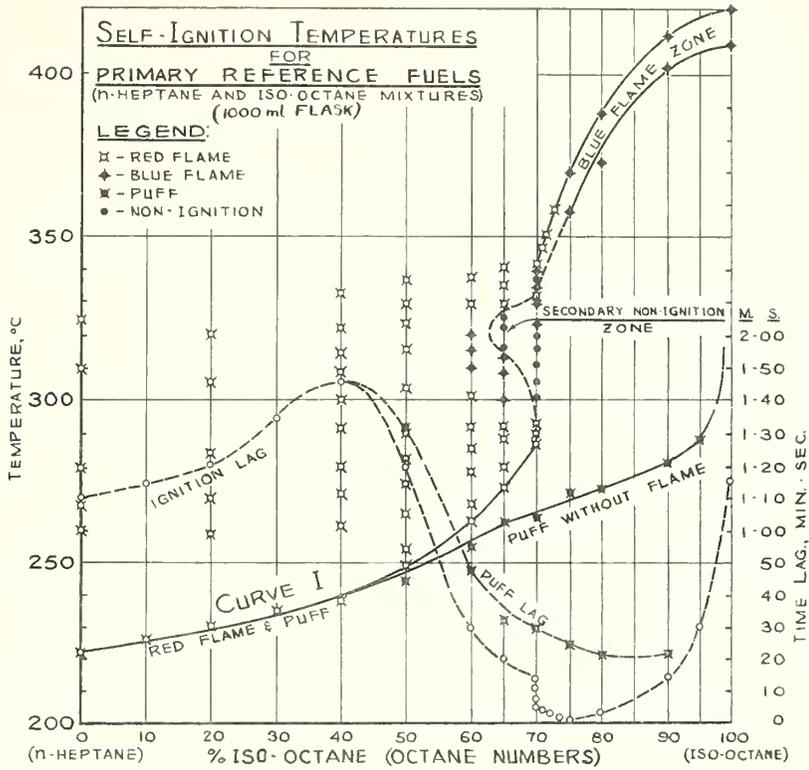


Fig. 35

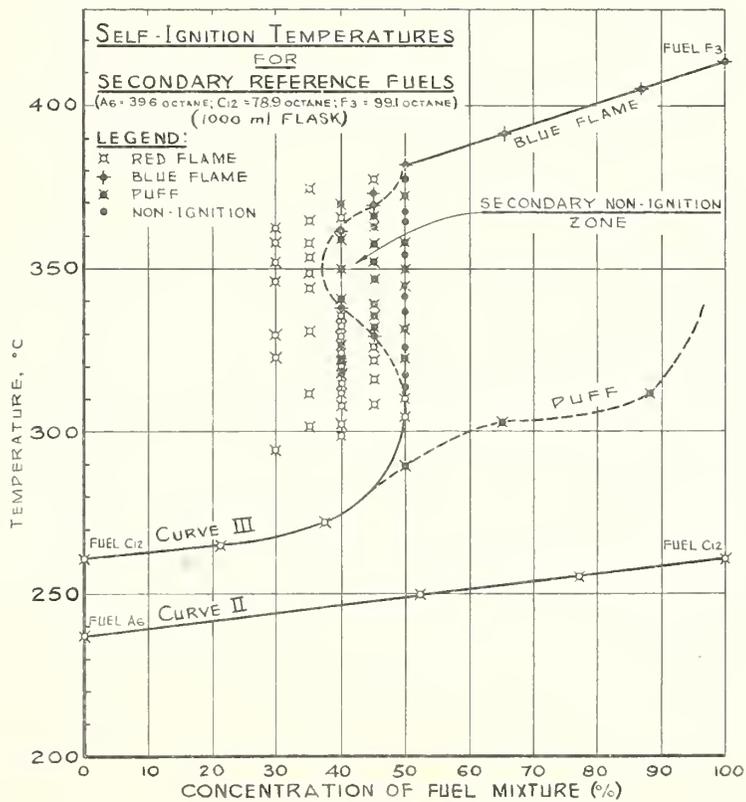


Fig. 36

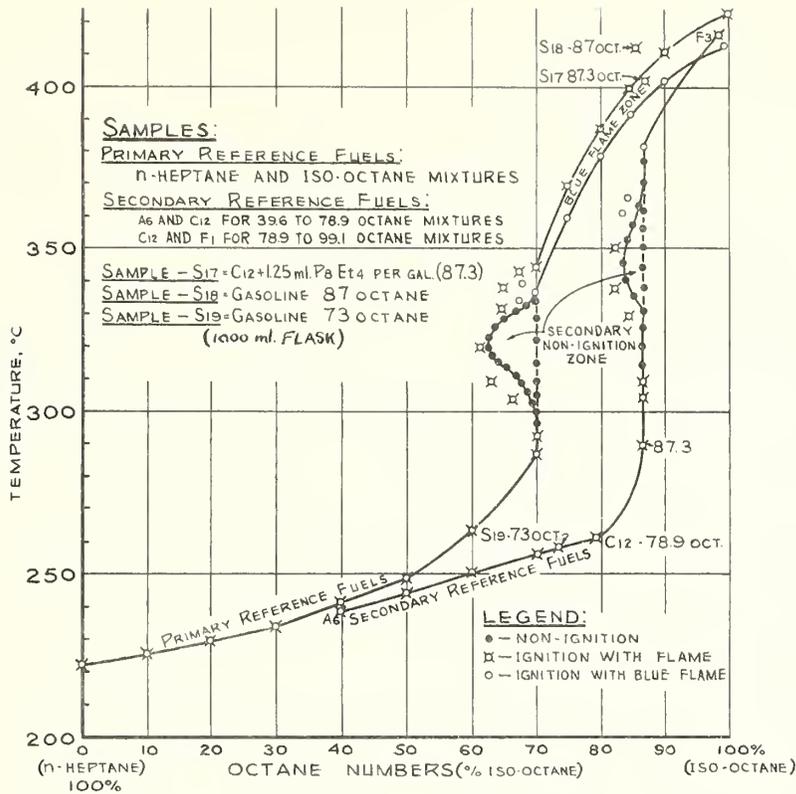


Fig. 37

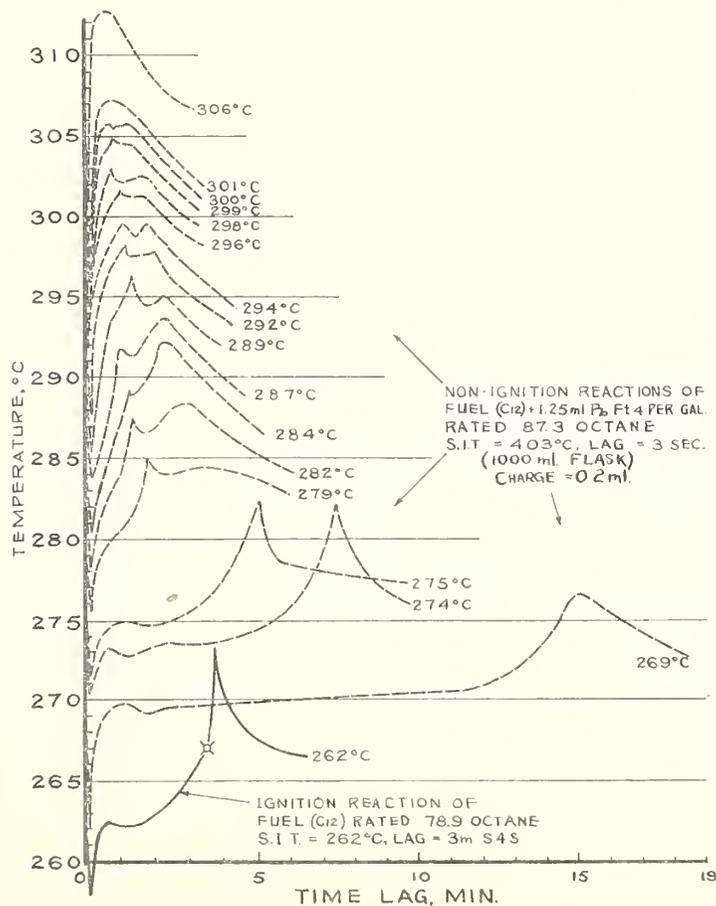


Fig. 38

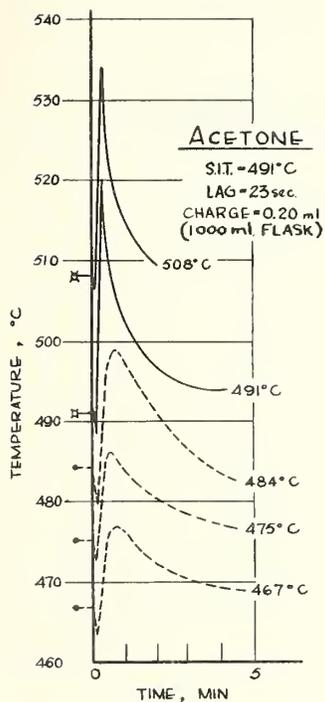


Fig. 39

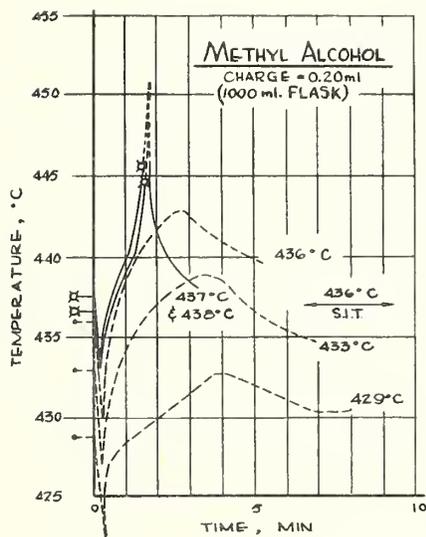


Fig. 40

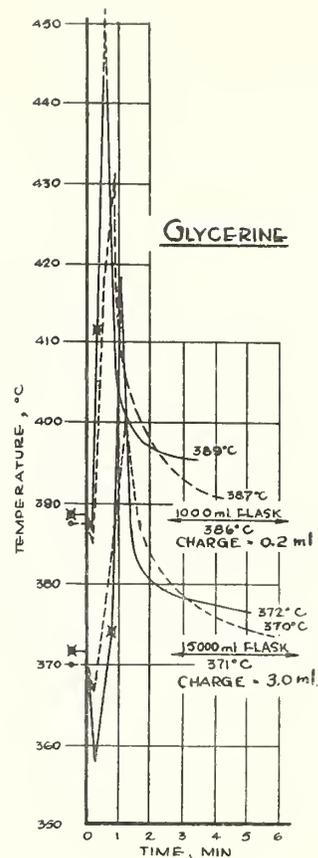


Fig. 41

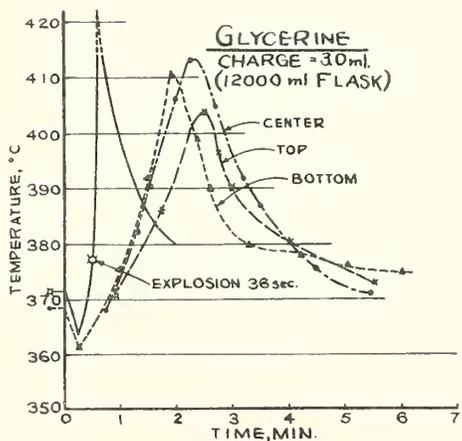


Fig. 42

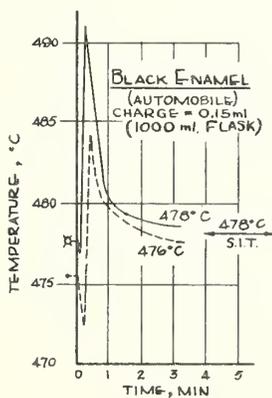


Fig. 43

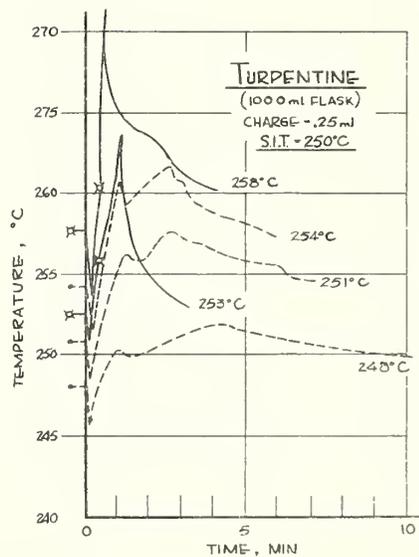


Fig. 44

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards (\$1.00). Information on calibration services and fees can be found in NBS Circular 483, Testing by the National Bureau of Standards (25 cents). Both are available from the Government Printing Office. Inquiries regarding the Bureau's reports and publications should be addressed to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C.

