

THE CATALYTIC THERMOCOUPLE METHOD OF  
DETERMINING SELF-IGNITION TEMPERATURES

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## PREFACE

The present study of the self-ignition temperatures of fuels was made possible through a grant made by the United States Army Air Corps to the Research Foundation of the Oklahoma Agricultural and Mechanical College. The object of the investigation was to devise a method of determining self-ignition temperatures that would not reflect the degree of catalysis occurring at the wall of the chamber.

The writer is indebted to Drs. Luis H. Bartlett and Charles L. Nickolls for their valuable guidance in this project, as well as to the remainder of the staff of the School of Chemical Engineering at the Oklahoma Agricultural and Mechanical College for their assistance and co-operation. In particular, the author is grateful to Mr. Eugene McCroskey for his skillful aid in constructing the equipment, and to Mr. Robert Maddox for generously preparing the photographs that appear in this thesis.

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## THEORIES OF SELF-IGNITION

If the temperature of a combustible mixture held at constant pressure is gradually increased, or if the pressure is increased while holding the temperature constant, the velocity of reaction is increased until combustion occurs.

In the early attempts to explain this phenomenon of spontaneous ignition, the erroneous assumption was made that there existed a temperature below which no reaction occurred between the fuel and the oxidant, and above which explosion took place.<sup>67</sup> This assumption was contrary to the results of many subsequent experiments, including those of Callendar,<sup>7</sup> Naylor and Wheeler,<sup>41</sup> Pease,<sup>43</sup> and one of the first to take note of this fact in modernizing the theory of self-ignition was van't Hoff.<sup>62</sup> With the realization that reactions occurred in fuel-air mixtures below the temperature of self-ignition, two theories were developed to explain the phenomenon. These are generally known as the thermal and the chain theories of self-ignition.

### The Thermal Theory

The thermal theory states that self-ignition is due to the increase in the rate of heat liberation caused by the progressively faster reaction. At some point, the rate of

heat liberation will start to exceed the rate of heat lost to the surroundings. As a result, there is a progressive self-heating of the combustible mixture that leads to a still greater speed of reaction. This results in an almost instantaneous development of heat of reaction within the mixture which is known as combustion.<sup>52</sup>

The concept of this limiting condition of self-ignition was used by van't Hoff to define the temperature of self-ignition as follows:

The ignition temperature is the temperature at which the initial loss of heat, due to conduction etc., is equal to the heat evolved in the same time by the chemical reaction.<sup>63</sup>

This definition explained why an increase in temperature would ultimately change a slow reaction into combustion, and it also implied that the combustion should be preceded by a period of relatively slow increase in the velocity of the reaction corresponding to the slow rise in the temperature. This period, which is usually referred to as the induction period or the self-ignition lag, is indeed known to exist, but at times it is hardly noticeable.<sup>5,12</sup>

According to this theory, the larger the vessel in which the reaction takes place, the less will be the heat lost per unit volume of the mixture, given a constant temperature. Thus, according to the thermal theory, the temperature of self-ignition is a function of the size of the container and is higher in small vessels than in large ones. This hypothesis has been corroborated by the work of such

men as Naylor and Wheeler<sup>41</sup> and by Dixon and his co-workers.<sup>16,17</sup>

Although van't Hoff gave no quantitative formulation of the ignition phenomenon, his evaluation of the physical nature of self-ignition still represents closely the thermal theory of self-ignition. Of particular note is the following passage:

By inflammation we shall understand here not only the phenomena of combustion, but also any complete chemical transformation which occurs in consequence of a local elevation of the temperature to the so-called temperature of ignition.

In every change of this kind the following conditions are fulfilled: --

- 1. The reaction which produces the inflammation evolves heat.
- 2. The reaction occurs more or less rapidly below the temperature of ignition.
- 3. The reaction is accelerated by an elevation of temperature.<sup>64</sup>

For some forty years after van't Hoff advanced his views on self-ignition, no important improvement was made on the thermal theory of self-ignition. In 1927-28, Semenov gave a mathematical formulation corresponding to van't Hoff's theory:

In a reaction in the gaseous phase with velocity  $w$ , measured by the number of molecules of the product appearing per second per unit volume, the amount of heat given off per second in the entire volume  $v$  of the vessel is

$$q_1 = v Q' w$$

where  $Q'$  is the heat liberated by each elementary process of the reaction; that is,  $Q' = Q/N$ , where  $Q$  is the heat of the reaction for one gram-mol of the product, and  $N$  the Avogadro number... As has been shown, the velocity of the reaction at the initial stage as a function of the absolute temperature  $T$  and the number of molecules  $a$  of the initial substance per unit volume is equal to

$w = k_1 a e^{-E/RT}$  for monomolecular, and  $k_2 a^2 e^{-E/RT}$  for bimolecular reactions, so that

$$q_1 = \frac{v Q k a^n e^{-E/RT}}{N}$$

where for monomolecular reactions  $n = 1$ , and for bimolecular reactions  $n = 2$ .

The amount of heat conducted away by the walls of the vessel will be

$$q_2 = X (T - T_0) S$$

where  $X$  is the coefficient of heat conductivity,  $T$  the temperature of the reacting gas,  $T_0$  the vessel-wall temperature applied from the outside, and  $S$  the area of the walls.<sup>50</sup>

Semenoff proceeds to demonstrate that at the temperature of self-ignition, not only will  $q_1 = q_2$ , but also their partial derivatives with respect to temperature will be equal. Thus, the two following equations are obtained:

$$\frac{v Q k a^n e^{-E/RT_1}}{N} = X (T_1 - T_0) S$$

and

$$\frac{v Q k a^n E e^{-E/RT_1}}{NRT_1^2} = XS$$

from which, by eliminating  $XS$  and solving for  $T_1$ , one obtains the equation

$$T_1 = \frac{1 \pm \sqrt{1 - \frac{4RT_0}{E}}}{2 R/E}$$

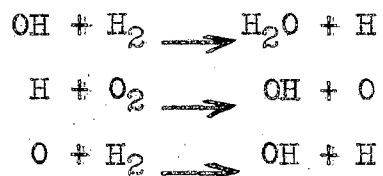
Although this equation is of little value in predicting the ignition temperature of the mixture, it indicates that the self-ignition temperature is dependent on the energy of

activation,  $E$ , of the mixture.

### The Chain Theory

Most explosion and ignition phenomena could be explained by the thermal theory. The discovery of some discrepancies, however, in the explanation of negative catalysis led Christiansen to formulate a workable chain theory of combustion.<sup>11</sup> In 1927-28, this theory was applied to the study of the reactions leading to the inflammation by such men as Gibson,<sup>23</sup> Hinshelwood,<sup>24</sup> and Semenov.<sup>49</sup> Since then, the chain reaction theory has come into extensive use in such reactions as the explosion of azomethane<sup>1</sup> and of hydrogen-oxygen mixtures<sup>30,47,58</sup> and has become firmly established as at least a partial explanation of those reactions.

According to the chain theory, the reaction of two gases such as hydrogen and oxygen does not occur directly, but rather proceeds through intermediate compounds such as the chain proposed by Lewis and von Elbe:<sup>32,34</sup>



In the three reactions, the active substances H, OH, and O are chain carriers. Furthermore, since the second and third reactions result in an increase in the number of chain carriers, they may be called chain-branching reactions. Those latter reactions, under favourable circumstances, cause

such a rapid increase in the rate of reaction that explosion occurs in a short time. Other reactions result in the destruction of chain carriers, and these may occur in sufficient number to prevent explosion from occurring. It would consequently be under very particular circumstances that the rate of occurrence of chain-branching reactions would be greater than that of chain-breaking reactions and that explosion would occur.

In addition to chain reactions caused by substances that are active by their nature, another chain mechanism has been proposed that consists of chain carriers that are active by their energy state rather than by their physical nature.<sup>28</sup> These "energy chains" would consist of molecules activated by the transfer of energy liberated by the reaction.

When two molecules react, a relatively large amount of energy is liberated, which consists of the energy of activation and the energy of reaction. This energy will be transmitted to a relatively few molecules immediately around the reacting ones, and it is only after a number of collisions that the energy so liberated will be relatively evenly distributed among the other molecules in the system. Thus, for a short time at least, each reacting molecule will have activated other molecules, thereby enabling several of them to react in turn and to multiply the rate of reaction.

There is no experimental evidence that allows one to discard or to adopt entirely the thermal theory or either version of the chain theory. However, the present consensus of investigators appears to be that the material chain type of reaction is the one that occurs most frequently, and that most reactions are affected to a greater or lesser degree by all three mechanisms.



## METHODS USED BY PREVIOUS INVESTIGATORS

The problem of determining experimentally the true temperature of self-ignition has long troubled investigators. According to Bridgeman and Marvin in their survey of the work done in this field, the following experimental variables affect the results obtained:

1. The materials in contact with the fuel mixture.
2. The volume of the ignition chamber.
3. The concentration of oxygen in the inflammable mixture.
4. The time lag before ignition occurs.
5. The pressure of the system.
6. The composition of the fuel.<sup>4</sup>

The nature of the effect of many of these variables is complex, and the interpretation of their effect on the ignition temperature varies with the investigator.

In many methods used, the investigators attempted to eliminate or to diminish the effect of some of the above-mentioned variables. Other methods are purely arbitrary in nature and do not represent an attempt to determine a self-ignition temperature reproducible by any other method. The methods used hertofore can be classified into the following categories:

1. The explosive mixture flows through a tube of known temperature.<sup>6,7,43,44,45,46</sup>

2. The mixture is introduced into a container of known temperature.<sup>35,41,55</sup>
3. The gaseous mixture is compressed adiabatically and the temperature is computed from the thermodynamic relations between the initial and final volumes or pressures.<sup>17,18,22,61</sup>
4. The gases are heated separately to the ignition temperature and then mixed.<sup>5,12,13</sup>
5. A drop of liquid fuel is introduced into a container of known temperature.<sup>20,48,57</sup>
6. The mixture is introduced into a soap bubble and ignited by contact with a hot wire of known temperature.<sup>40,66</sup>
7. A drop of liquid is ignited by contact with a body of known temperature.<sup>26,36,38,54</sup>
8. Two gases are mixed in a closed vessel and gradually brought to the ignition temperature.<sup>27</sup>
9. The mixture is ignited by dropping spheres heated to a known temperature through the container.<sup>42,51</sup>

It is generally recognized that there is a catalytic effect of the materials in contact with the combustible mixture that causes changes in the value found for the ignition temperature. This is seen in the work of such men as Dixon,<sup>13</sup> Paterson,<sup>42</sup> and N. J. Thompson.<sup>57</sup>

Gaseous materials are also known to influence the temperature of self-ignition. Schumacher,<sup>47</sup> Gibson and Hinshelwood,<sup>23</sup> and Thompson and Hinshelwood<sup>59</sup> found that traces

of nitrogen dioxide cause a large decrease in the ignition temperature of hydrogen-oxygen mixtures and that large amounts of that gas cause an increase in the ignition temperatures determined. Naylor and Wheeler also found that argon and helium cause an increase in the temperature of ignition.<sup>41</sup> On the other hand, Dixon and Crofts,<sup>17</sup> Dixon,<sup>13</sup> and Falk<sup>18</sup> found little difference in the ignition temperatures of hydrogen in oxygen and of hydrogen in air.

The size of the reaction chamber has been found by many investigators to affect materially the ignition temperatures determined. Naylor and Wheeler,<sup>41</sup> and Taffanel and LeFloch<sup>55</sup> have shown the temperature of ignition to vary inversely with the size of the reaction chamber. Dixon showed that a limit is reached in the chamber size beyond which any further increase causes no decrease in the ignition temperature.<sup>13</sup>

The influence of induction periods has been investigated by Mulcahy,<sup>39</sup> Bullock<sup>5</sup> and many others, and the ignition temperature has been found to decrease as the induction period is increased, but the various investigators do not agree on the extent of that variation.

Kane and co-workers,<sup>29</sup> Mondain-Monval and Quanquin,<sup>37</sup> and others have shown that a change in pressure causes an inverse change in the ignition temperature.

The influence of the many variables, and the nature of the ignition data reported in literature clearly show

that the temperature of self-ignition of a combustible mixture has so far depended to a great extent on the method used to determine it. This is manifested by the following ignition temperatures found for hydrogen:

TABLE I  
IGNITION TEMPERATURES OF HYDROGEN IN AIR

Author	Mixture strength	Time Lag seconds	Ignition temperature OF
Bullock <sup>5</sup>	Stoichiometric	0.26-0.53	1284-1330
Cottle <sup>12</sup>	Stoichiometric	0.21-0.44	1056-1092
Dixon <sup>13</sup>	---	0.50-15	1060-1165
Dixon and Crofts <sup>17</sup>	28.5% H <sub>2</sub>	---	1060
Dixon et al <sup>16</sup>	---	---	990-1000
Falk <sup>18</sup>	---	---	1480-1505
Gershanik <sup>22</sup>	Stoichiometric	---	1070
McDavid <sup>40</sup>	---	---	1260-1395
Scott et al <sup>48</sup>	---	---	1060
White and Price <sup>66</sup>	---	---	1320-1580

## EVOLUTION OF THE IGNITION APPARATUS

At the outset of this project, it was proposed that a method of determining ignition temperatures be developed that would require small amounts of fuel and that would be as free as possible from the harmful effects of catalysis.

From the survey made of relevant literature, it was manifest that catalysis would most readily be avoided if a flow-type system were chosen; that is, an apparatus should be designed in which the conditions favourable to self-ignition would be produced in a flowing mixture of gases. In order to limit the quantity of fuel used in such a system, it was necessary that the fuel-immitting tube be made small, and the choice made was of austenitic stainless steel capillary tubing. Because of the small quantities of fuel and air entering the ignition space, the problem of maintaining in the jets a temperature sufficiently high to cause ignition dictated the choice of a heated tube for the ignition chamber.

Early experiments with the apparatus so built indicated strongly the existence of some catalytic action at the walls of the ignition chamber. This catalysis could not be eliminated without re-designing the apparatus and thereby losing some of the desirable characteristics. Consequently, it was proposed that the idea of avoiding catalysis should be discarded, and rather that it should

be used in such a manner as to eliminate the element of uncertainty contingent upon its occurrence only in loci on the chamber walls where its total effect could not be determined exactly. The reasoning used was as follows:

If catalysis occurs in the ignition chamber, it is likely to be uneven in its action and to be most marked in relatively small areas. This unevenness would be due to the roughness of the chamber walls, to the lack of homogeneity of the material of which the chamber is made, or to some other factor of similar nature. Those areas of localized catalysis would thus become hot enough to cause the ignition of the combustible mixture, while the mixture itself and the rest of the chamber walls would be at temperatures below the true ignition temperature. Thus, if the temperature of the combustible mixture at the moment of ignition were taken as the true ignition temperature, the amount of error involved could be large.

If, on the other hand, the temperature of the catalytic area itself were the quantity measured, the likelihood of the true ignition temperature's being obtained would be much greater, for, unless some error exist in the reasoning, the ignition would have been caused by the fact that the catalytic area had reached a temperature high enough that the reaction rate in the combustible mixture had become self-propagating in the immediate vicinity of the catalytic area.

The idea of finding the area of most intense catalytic

action and then determining its temperature is absurd, not only because of the difficulties involved in locating that area, but also because the mere fact of determining its temperature could cause a sufficient decrease in the intensity of catalysis to allow another area to become the most active catalyst. Thus, it was preferred to make the point of temperature measurement become the most active catalytically rather than vice versa. This result could be achieved by using as pyrometer a bare thermocouple made of metals more catalytic than any substance in the ignition chamber.

According to the above reasoning, the following facts should be true:

1. The ignition temperature determined should be independent of the nature of the catalyst used in the thermocouple, provided that it remain more catalytic than any part of the ignition chamber.
2. The ignition temperature determined should be independent of the temperature of the walls of the ignition chamber.
3. The ignition temperature determined should be independent of the bulk temperature of the combustible mixture over wide ranges of temperature.

Experiments designed to verify the above hypotheses were carried out using hydrogen as fuel, and all the arguments held true. This was considered sufficient proof of the validity of the method, and it was adopted for all subsequent work.

## DESCRIPTION OF THE APPARATUS

For the sake of simplicity of explanation, the apparatus can be described in the following order: the fuel stream, the air stream, the ignition chamber, the thermometric section, the inert gas stream, and the calibrating section.

### The Fuel Stream

When hydrogen was used as fuel, the compressed gas was taken from a cylinder, its pressure was reduced by a pressure-regulating valve (C on Figure 2), and the gas then led into a six-foot length of quarter-inch copper tubing. The hydrogen pressure was indicated by a bourdon-type gauge reading in pound divisions up to 30 pounds per square inch gauge. The other end of the copper tubing was connected by means of a reducing connection to a twelve-foot length of capillary tubing having internal and external diameters of 0.025 and 0.060 inches respectively (J on Figure 1). This capillary tubing led the hydrogen through a Hoskins electric muffle furnace of 5 kilowatt maximum capacity (K on Figure 1), and then into the ignition chamber. Except in certain check runs, the muffle furnace was unheated.

When a liquid fuel was used, it was stored in a one-gallon steel flask built in the same manner as a wash



bottle (D on Figure 1). Compressed hydrogen was introduced above the liquid by means of a quarter-inch steel pipe welded into the top of the flask and connected to the hydrogen cylinder through the pressure-regulating valve and a length of quarter-inch copper tubing and the necessary tube-to-pipe connections. The pressure so induced inside the flask forced some of the liquid through another quarter-inch pipe opening near the bottom of the flask, through a waste-cloth filter (L on Figure 1), through a quarter-inch copper tubing lead, through a flushing section (I on Figure 1), and then through the muffle furnace and into the ignition chamber (G on Figure 1), as in the case of the hydrogen.

The flushing section in the liquid fuel line (J on Figure 1) was simply a connection between the fuel line and the compressed air with two valves so located that the flow of fuel could be stopped and air could be made to blow the remaining fuel out of the capillary tube. The sole reason for this device was to prevent the stoppage of the capillary by the carbonization of the fuel inside the muffle furnace when it was hot.

#### The Air Stream

The air was taken from a compressed air tank at pressures between 100 and 120 pounds per square inch. As with the hydrogen, the air pressure was reduced by means of a pressure-regulating valve, and it was led into capillary

tubing ( E on Figure 1). In much of the early work, one capillary tube was used for the air; three capillaries were later used. For some check determinations, the air capillary led through the muffle furnace and into the ignition chamber. Later with the single capillary, and always with the triple capillaries, the muffle furnace was by-passed.

The connection between the air line and the fuel line was made some six inches ahead of the capillaries, and the same distance beyond the pressure indicator -- a bourdon-type gauge measuring pressures in two-pound divisions up to 100 pounds per square inch gauge.

#### The Ignition Chamber

This chamber (G on Figure 1) consisted of a mullite tube, 0.75 inch in diameter and six inches long, around which was wound a 50 foot nichrome resistance coil which, by means of a thirty-point transformer, allowed from 15.7 to 279 watts to be used for heating the tube. One end of the tube was closed by a soft steel plug (F on Figure 1) 2.75 inches long through which were drilled holes for the fuel and air capillaries. Half an inch of this plug was inserted in the mullite tube, the remainder being outside to dissipate some of the heat generated inside the ignition chamber and to maintain the plug end of the chamber at a slightly lower temperature than that of the rest of the tube. The capillaries introduced through the steel plug were so arranged that the gas jets emitted by them would

impinge one inch from the end of the plug.

Through the open end of the mullite tube was introduced a platinum-platinum rhodium thermocouple, the junction of which was centered in the tube two inches beyond the point of impingement of the fuel and air jets (H on Figure 1).

In the early experiments with hydrogen, the ignition chamber used was a copper tube with an internal diameter of  $1\frac{5}{8}$  inches, a wall thickness of  $\frac{7}{32}$  inch, and a length of 3 inches. This tube was heated by means of two bunsen burners, and its temperature was determined by means of a thermocouple inserted into a  $\frac{1}{8}$  inch hole drilled half-way down the inner surface of the chamber. The end of the tube through which the fuel and air capillaries were introduced was pressed against the muffle furnace and closed with asbestos cement. The catalytic thermocouple was introduced through the open end of the tube, and had its junction one inch from the point of impingement of the fuel and air jets.

#### The Thermometric Section

At various times, three platinum-platinum rhodium thermocouples were used. These were: the catalytic thermocouple used in the ignition chamber, the thermocouple set in the wall of the first ignition chamber, and a thermocouple used to determine the temperature of the muffle furnace. These thermocouples were made of one-foot lengths of 24 gauge platinum and platinum 10% rhodium wire joined together at one end by means of a weld. The unwelded ends were connected to a cold junction and to a potentiometer (D on Figure 3) by means of insulated copper wire.

The cold junction consisted of a six-inch thermocouple of similar nature to the ones described above, with the welded join immersed in an ice bath (A on Figure 3).

The potentiometer used was sensitive to 0.002 millivolts. The electromotive force generated by any one thermocouple could be measured on the potentiometer by connecting the required hot junction to the cold junction via the potentiometer.

#### The Inert Gas Stream

Inert gas was used only in a few preliminary determinations made with hydrogen as the fuel. The inert gas stream differed from the hydrogen stream in only two ways:

1. Five capillaries were used for the inert gas as compared to one for the hydrogen.
2. The inert gas was introduced in a swirling stream around the inner walls of the ignition chamber rather than in the center of the chamber as with the hydrogen.

The inert gas bottle was changed according to whether argon or nitrogen was desired.

#### The Calibrating Section

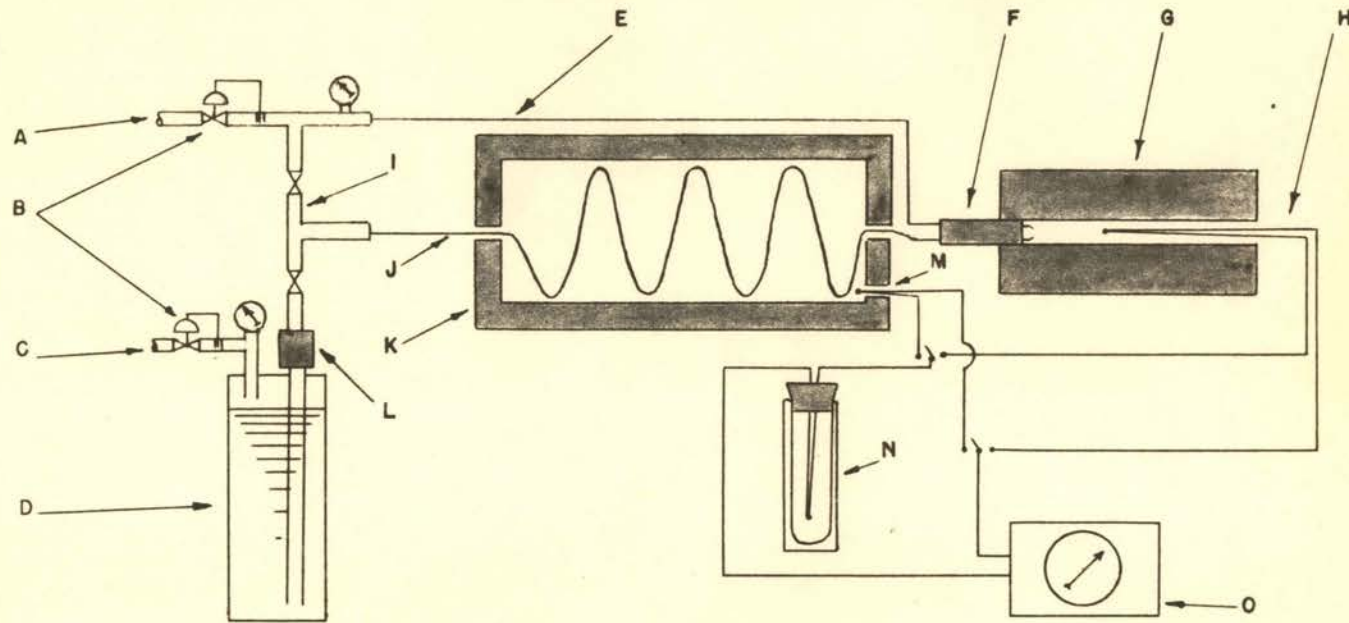
The system used to calibrate the air and the hydrogen streams was the same. A narrow-necked one-liter flask was filled with water and inverted in a water bath. The air or hydrogen flow could then be measured by determining the time required for that gas to replace the water in the inverted

flask.

In the case of liquid fuels, the capillaries were led to a water-cooled, glass condenser (B on Figure 4). The water in the cooling jacket of the condenser was circulated from an ice bath by means of a pump (C on Figure 4), and the condensate was collected in an erlenmeyer flask partially immersed in ice-water (D on Figure 4). The condensate was then weighed on an analytical balance sensitive to 0.0001 gram.

FIGURE I

SCHEMATIC FLOW DIAGRAM OF THE IGNITION APPARATUS



LEGEND

A AIR LINE  
 B PRESSURE REGULATORS  
 C HYDROGEN LINE  
 D FUEL FLASK  
 E AIR CAPILLARY

F SOFT STEEL PLUG  
 G TUBE FURNACE  
 H CATALYTIC THERMOCOUPLE  
 I FLUSHING SECTION  
 J FUEL CAPILLARY

K MUFFLE FURNACE  
 L WASTE CLOTH FILTER  
 M FURNACE THERMOCOUPLE  
 N GOLD JUNCTION FLASK  
 O POTENTIOMETER

DRAWN BY: L. E. MARC DE CHAZAL

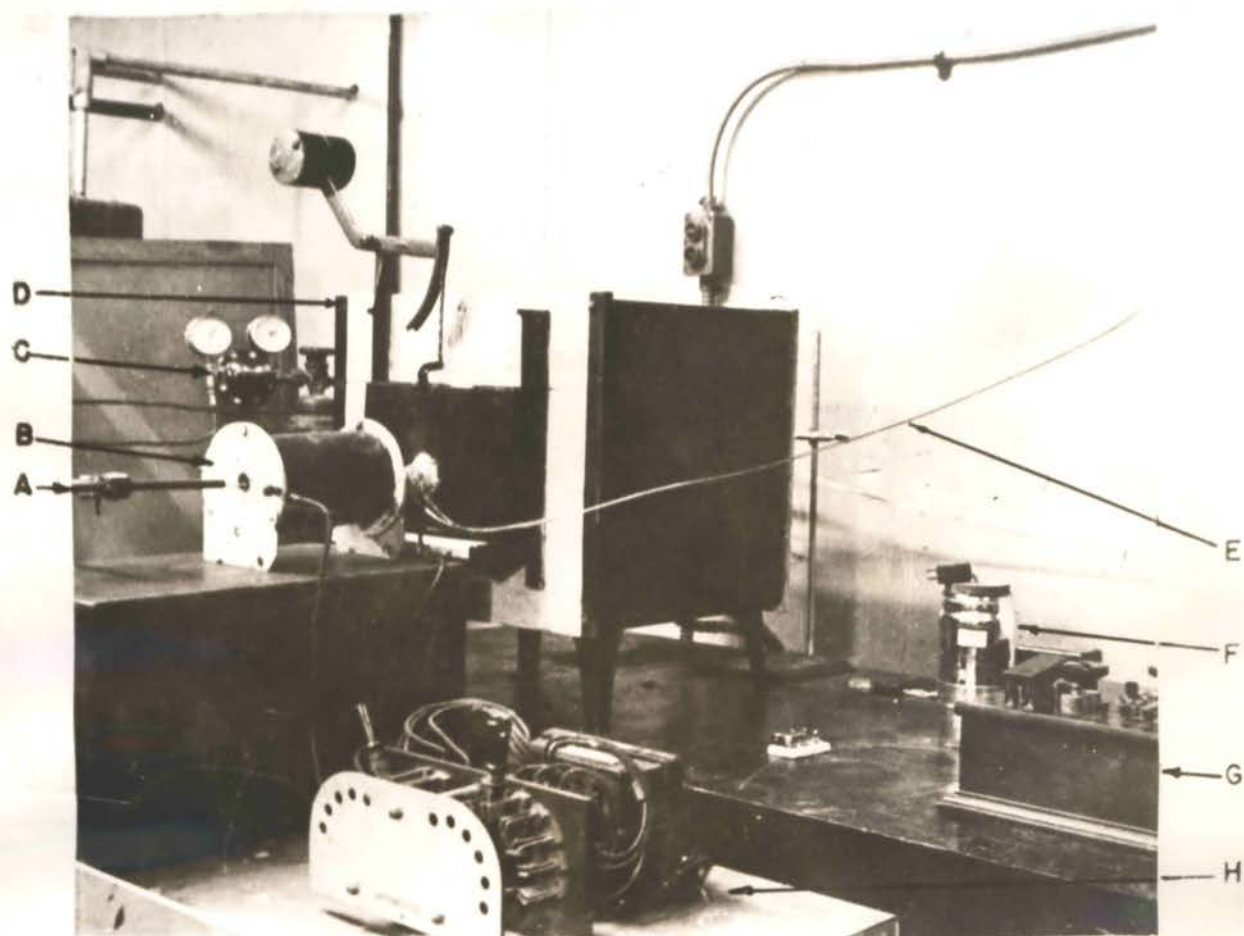


FIGURE 2  
THE IGNITION APPARATUS

LEGEND

- A CATALYTIC THERMOCOUPLE
- B TUBE FURNACE
- C HYDROGEN PRESSURE REGULATOR
- D MUFFLE FURNACE
- E AIR CAPILLARIES
- F THERMOCOUPLE COLD JUNCTION
- G POTENTIOMETER
- H TUBE FURNACE TRANSFORMER

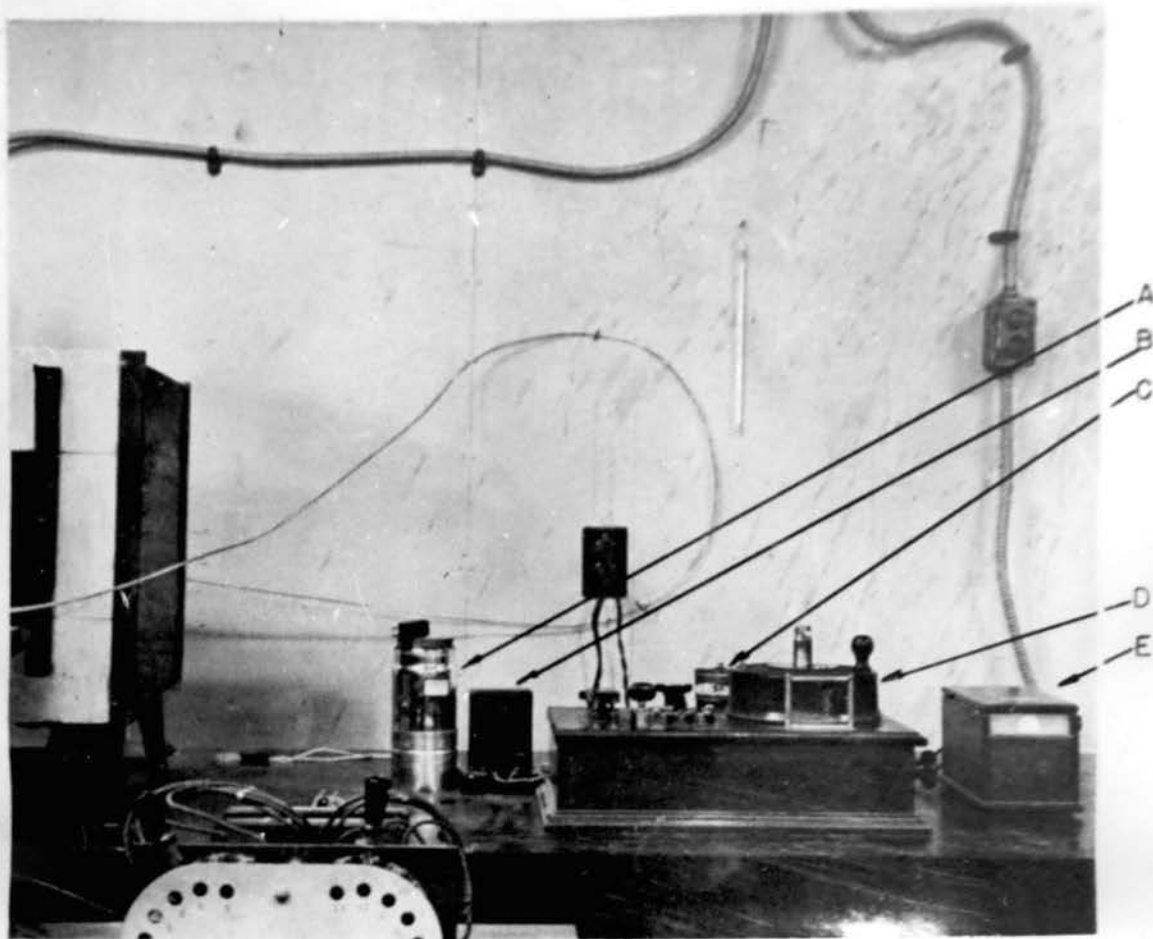


FIGURE 3  
THE THERMOMETRIC SECTION

LEGEND

- A THERMOCOUPLE COLD JUNCTION
- B STANDARD CELL
- C POTENTIOMETER BATTERY
- D POTENTIOMETER
- E GALVANOMETER



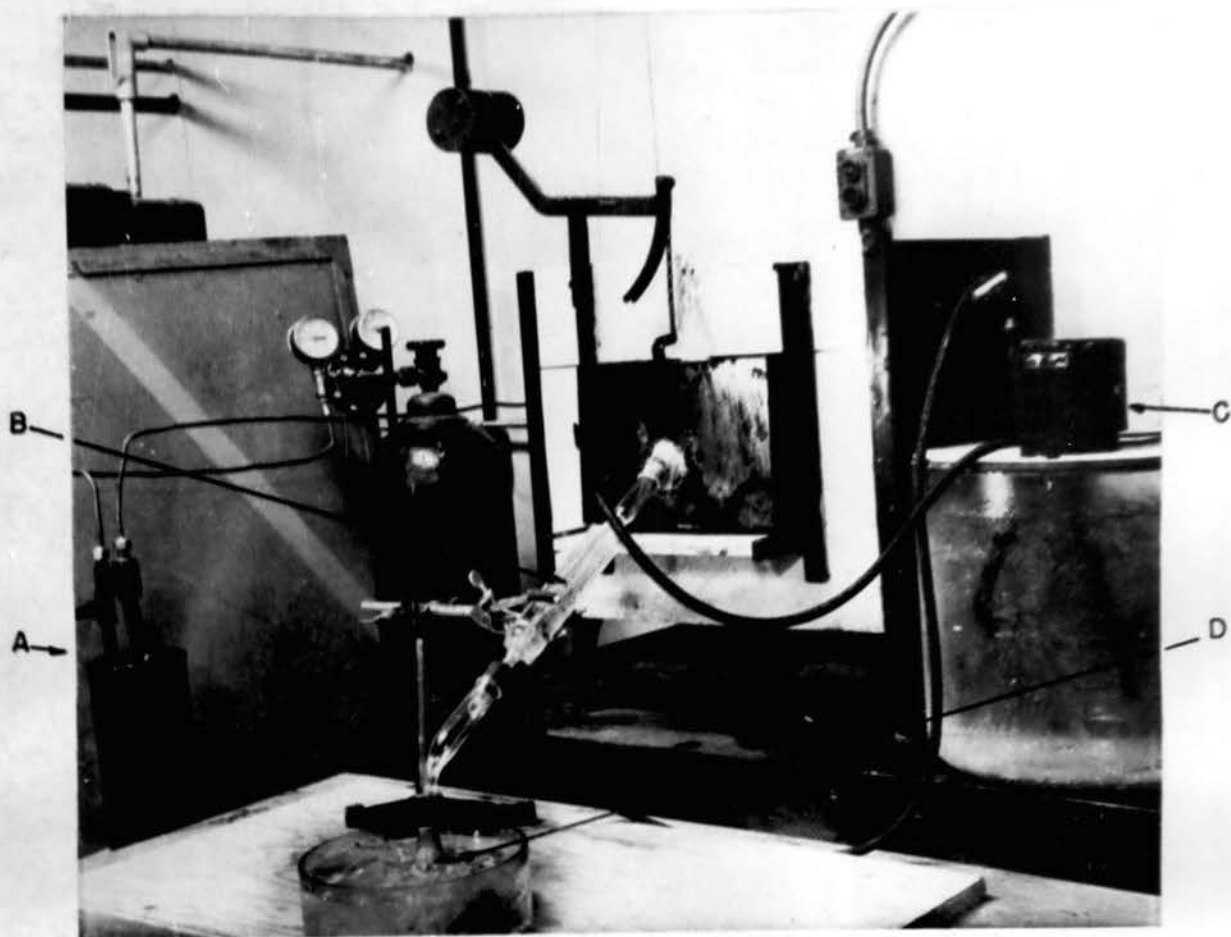


FIGURE 4  
LIQUID FUEL CALIBRATION

LEGEND

- A FUEL FLASK
- B FUEL CONDENSER
- C COLD WATER CIRCULATOR
- D CONDENSED FUEL COLLECTOR

## PROCEDURE

When self-ignition temperature determinations were made with a liquid fuel, the following procedure was used:

1. The muffle furnace was brought to an equilibrium temperature of  $975^{\circ}\text{F}$  plus or minus  $20^{\circ}\text{F}$ . Because of the large heat capacity of the furnace insulation, this took a minimum of three hours.
2. When the furnace had reached the equilibrium temperature, the flow of liquid fuel was started by imposing a hydrogen pressure above the liquid in the flask. The pressure used varied between four pounds per square inch and ten pounds per square inch, depending on the fuel.
3. The flow of air was started, and the air pressure was regulated to the desired value -- generally between 20 and 100 pounds per square inch gauge.
4. The tube furnace was started and allowed to heat on maximum voltage up to  $500^{\circ}\text{F}$  as indicated by the catalytic thermocouple. The voltage to the furnace was then changed to give a temperature rise of  $5^{\circ}\text{F}$  or less per minute until ignition occurred.
5. Periodically, the ignition chamber was inspected visually in order to ensure that the junction of the catalytic thermocouple was hotter than any

other part of the ignition chamber. This was readily determined by the greater brightness of the thermocouple after the glowing stage had been reached.

6. When ignition occurred, this phenomenon was signalled by an explosion and by an immediate drop in the thermocouple voltage. The voltage indicated by the potentiometer at the instant immediately prior to the explosion was noted.
7. If the explosion was not followed by steady combustion, the voltage of the catalytic thermocouple was followed until another explosion occurred, at which time another voltage reading was noted. This procedure was repeated until a total of five readings was made.
8. If the explosion was followed by steady combustion, the air flow was stopped; and the flame, which now burned outside, was extinguished. The tube furnace was disconnected from the source of electricity and allowed to lose the heat gained by the combustion. After about one minute, the tube furnace was re-connected and the air flow was resumed. This procedure was repeated until a total of five readings was obtained.
9. After the five readings were obtained, the tube furnace was allowed to cool to 500°F, and the air rate of flow was changed by altering the

setting of the pressure regulator in the air line. The new air pressure was noted, and five more ignition temperature determinations were made.

10. The air pressure was altered and ignition temperature readings were made for each pressure until the pressure was found for which the ignition temperature was a minimum.
11. The tube furnace was then removed and replaced by the condenser, and the condensed fuel was collected for exactly one hour in a tared erlenmeyer flask. The flask was then weighed in order to determine the weight rate of flow of the fuel.
12. The muffle furnace was shut off, the fuel flow was stopped, and the fuel remaining in the line was blown out with compressed air.
13. The fuel system was then drained, cleaned, and dried in readiness for another fuel.
14. The groups of five voltage readings made for each air pressure were averaged, and the average was converted to the ignition temperature by means of the conversion tables.<sup>31</sup>
15. The fuel-air ratio for each air pressure was calculated in terms of the fraction of the fuel used compared to the stoichiometric requirements, and a graph of the ignition temperature versus the fuel-air ratio was made.

When hydrogen was the fuel used, the procedure varied

only in two ways:

1. The muffle furnace was not heated, since a more accurate calibration of the hydrogen flow could be obtained with the capillary at room temperature.
2. The calibration of hydrogen flow was made in the same manner as was that of air, and all determinations made with hydrogen were carried out with a pressure of 10 pounds per square inch gauge.

During the preliminary runs made with the hydrogen, certain other differences existed in the procedure. In some runs, the furnace temperature was altered from room temperature. In addition, when the burner-heated ignition chamber was used, the tube temperature was recorded. Finally, in some of those determinations, inert gas was used.

## RESULTS

On the following pages, the data obtained during the course of this research are interpreted and presented in tabular and graphical form. In the tables are presented first the experimental justification of the method used, and then the ignition temperatures found by that method. The graphs show the variation of the ignition temperatures with the fuel ratio.

### TABLE II

#### PRELIMINARY TESTS MADE TO VERIFY THE METHOD

Fuel Used: Hydrogen

Fuel Rate: 0.0383 Cu. Ft. per Min. at 32°F, 760 mm Hg.

Air Supply: Surroundings

Muffle Furnace Temperature °F	Shield Temperature °F	Catalyst Used on the Thermocouple	Ignition Temperature °F	Ignition Followed by Steady Combustion
84	682	Platinum	no ignition	no
84	697	"	1677	no
84	749	"	1677	yes
84	910	"	1676	yes
475	700	"	1677	no
805	700	"	1677	no
952	700	"	1675	yes
84	1034	Nickel	no ignition	no
84	1183	Nickel	1676	yes

TABLE III  
 IGNITION TEMPERATURES OF HYDROGEN DETERMINED IN  
 COPPER TUBE IGNITION CHAMBER

Inert Gas Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature OF
	1.58	1540
	1.38	1528
Argon	1.19	1525
	1.03	1520
	0.92	1524
	1.58	1660
	1.38	1583
Nitrogen	1.19	1532
	1.03	1507
	0.92	1523

TABLE IV  
 IGNITION TEMPERATURES DETERMINED IN THE TUBE FURNACE  
 USING A SINGLE AIR TUBE

Fuel Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature °F
Ethanol	1.54	1399
	1.34	1365
	1.16	1345
	1.01	1337
	0.89	1345
Iso-propanol	1.37	1492
	1.16	1474
	0.99	1464
	0.88	1467
	0.80	1470
N-propanol	1.38	1713
	1.21	1690
	1.07	1683
	1.01	1680
	0.96	1685
Tertiary butanol	1.19	1593
	1.05	1577
	1.00	1573
	0.95	1580
	0.85	1600
N-Butanol	1.13	1775
	1.06	1739
	1.00	1717
	0.95	1719
	0.90	1730



Fuel Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature OF
	1.12	1425
	1.06	1392
Ethyl Acetate	0.99	1375
	0.94	1380
	0.89	1385
	1.22	1879
	1.06	1860
Toluene	1.00	1858
	0.94	1865
	0.85	1875

TABLE V

IGNITION TEMPERATURES DETERMINED IN THE TUBE FURNACE  
USING THREE AIR TUBES

Fuel Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature °F
Methanol	1.14	1120
	1.03	1100
	1.01	1095
	0.95	1097
	0.80	1135
Ethanol	1.15	1188
	1.05	1162
	1.00	1155
	0.96	1160
	0.81	1182
N-Propanol	1.11	1298
	1.01	1287
	0.92	1290
	0.78	1321
	0.68	1448
N-Butanol	1.19	1372
	0.99	1350
	0.91	1352
	0.83	1370
	0.73	1430
N-Pentanol	1.17	1556
	1.07	1523
	0.99	1502
	0.92	1508
	0.86	1530
N-Hexanol	1.08	1545
	0.99	1538
	0.95	1543
	0.91	1550
	0.79	1570

Fuel Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature °F
N-Heptanol	1.11	1638
	1.05	1625
	1.01	1623
	0.98	1638
	0.94	1650
N-Octanol	1.13	1692
	1.04	1658
	1.00	1654
	0.96	1677
	0.83	1708
N-Decanol	1.22	1745
	1.06	1718
	1.00	1702
	0.98	1704
	0.95	1708
Iso-Butanol	1.11	1503
	1.03	1477
	1.00	1472
	0.96	1473
	0.84	1508
Iso-Pentanol	1.22	1687
	1.06	1633
	0.99	1623
	0.93	1619
	0.83	1626

TABLE VI

IGNITION TEMPERATURES OF HYDROGEN DETERMINED IN THE  
TUBE FURNACE WITH VARYING NUMBERS OF AIR CAPILLARIES

Number of Air Capillaries Used	Amount of Fuel as Fraction of Stoichiometric Requirements	Ignition Temperature °F
1	1.28	1527
	1.13	1512
	1.06	1508
	1.00	1505
	0.89*	1532
2	1.31	1438
	1.05	1423
	1.00	1415
	0.96	1423
	0.88	1428
3	1.10	1402
	1.04	1397
	1.01	1392
	0.98	1395
	0.88	1408

\*This value was obtained by extrapolation.

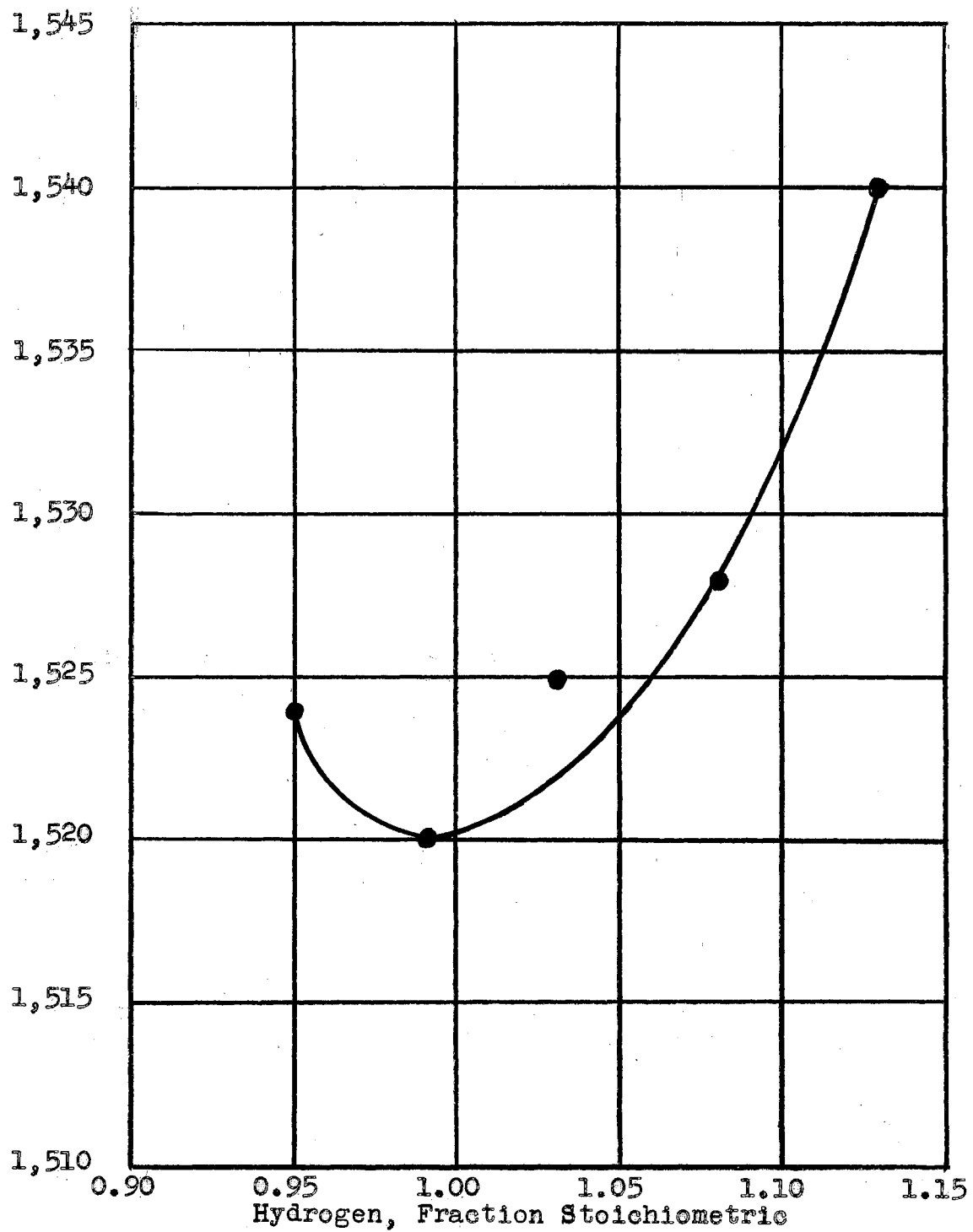


FIGURE 5

SINGLE-AIR-TUBE IGNITION OF HYDROGEN WITH ARGON AS INERT GAS

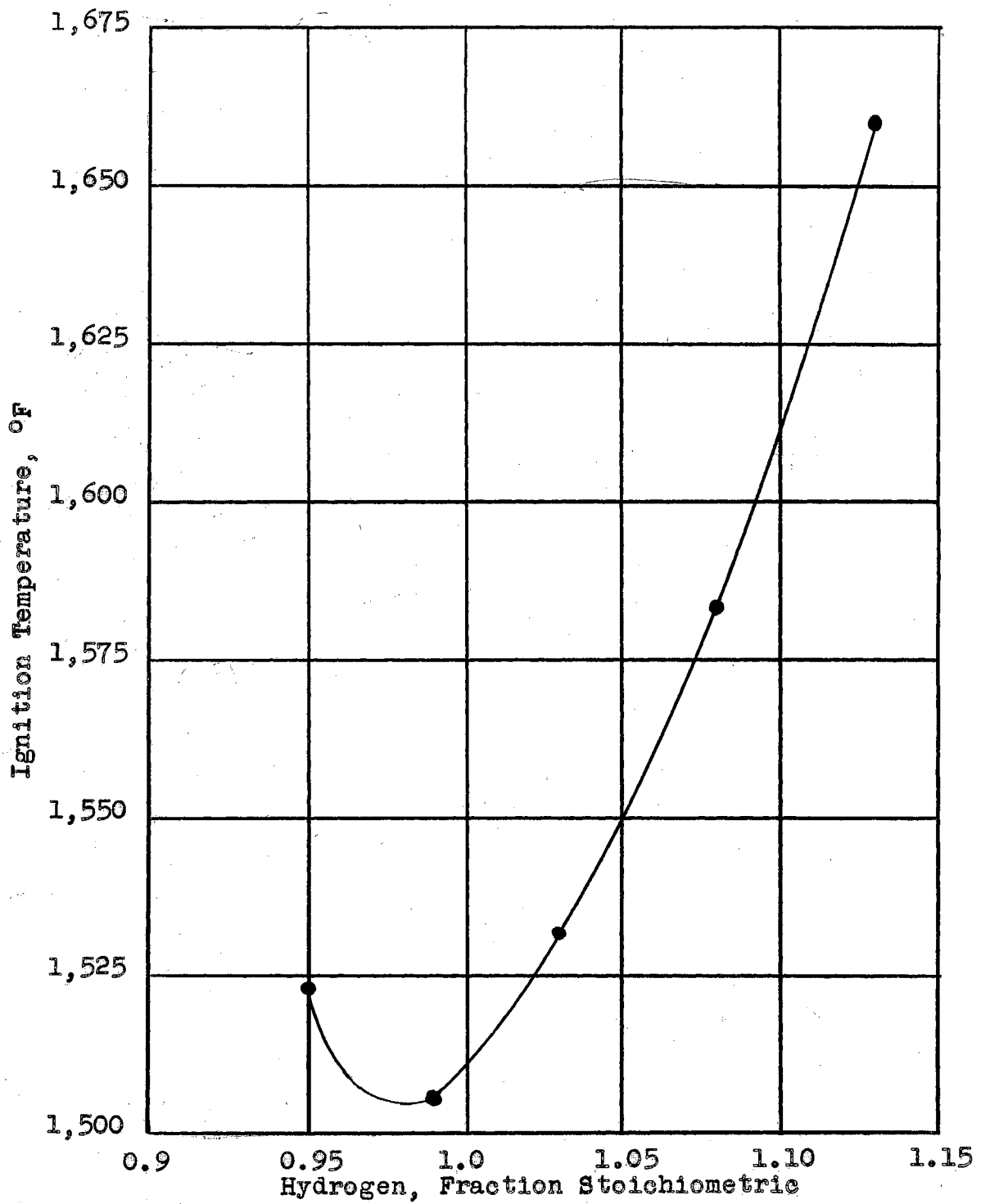


FIGURE 6

SINGLE-AIR-TUBE IGNITION OF HYDROGEN WITH  
NITROGEN AS INERT GAS

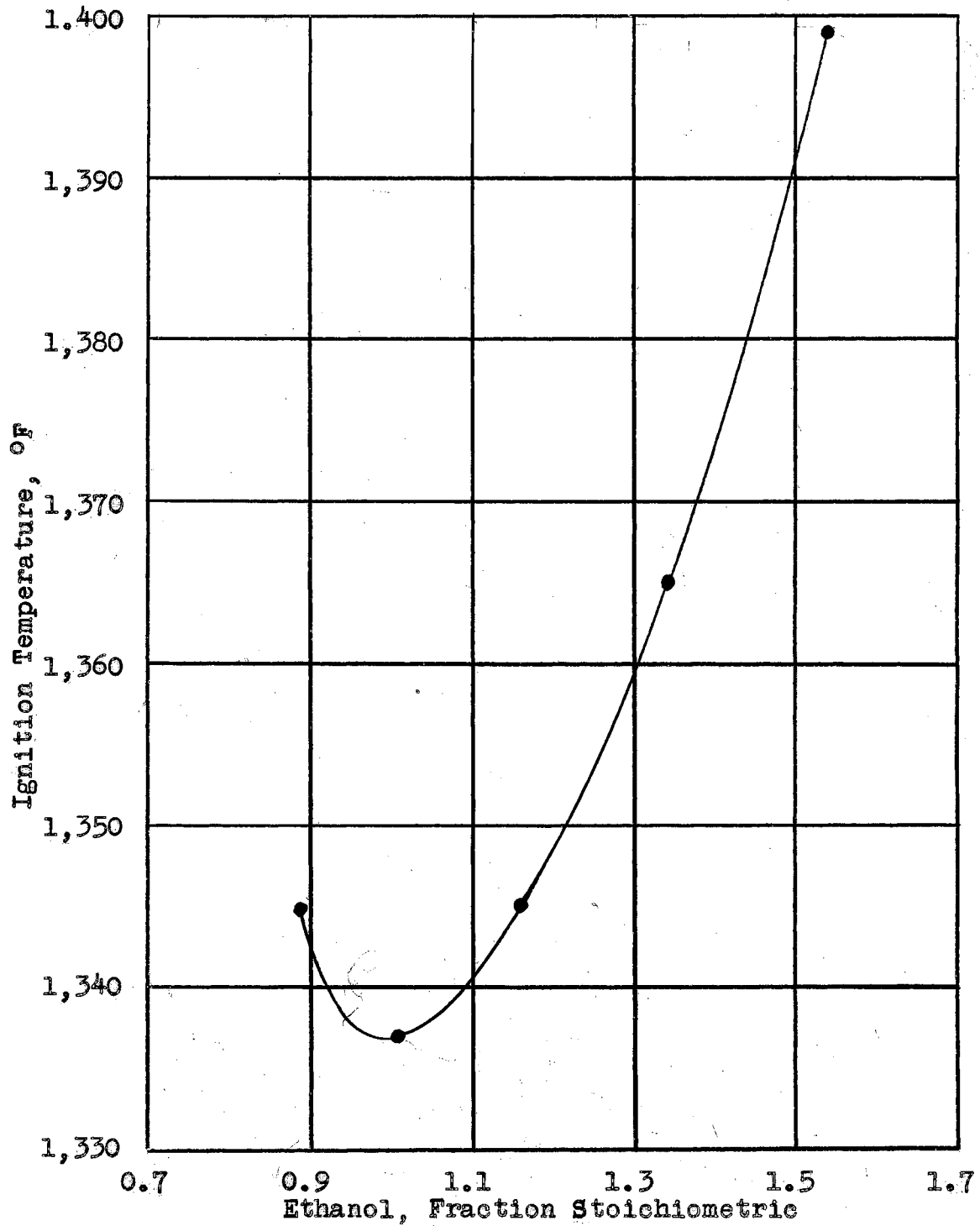


FIGURE 7

SINGLE-AIR-TUBE IGNITION OF ETHANOL

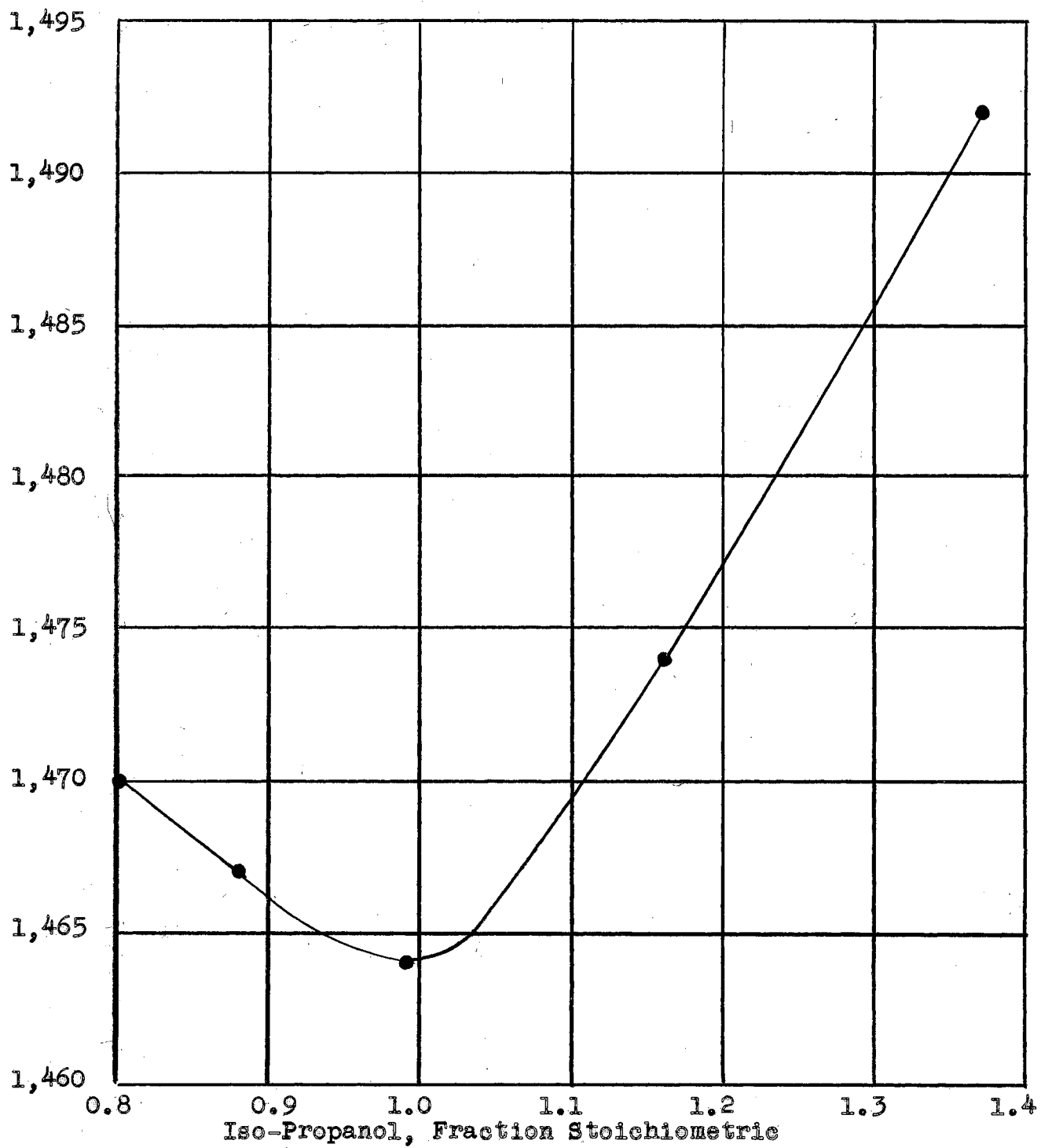


FIGURE 8

SINGLE-AIR-TUBE IGNITION OF ISO-PROPANOL



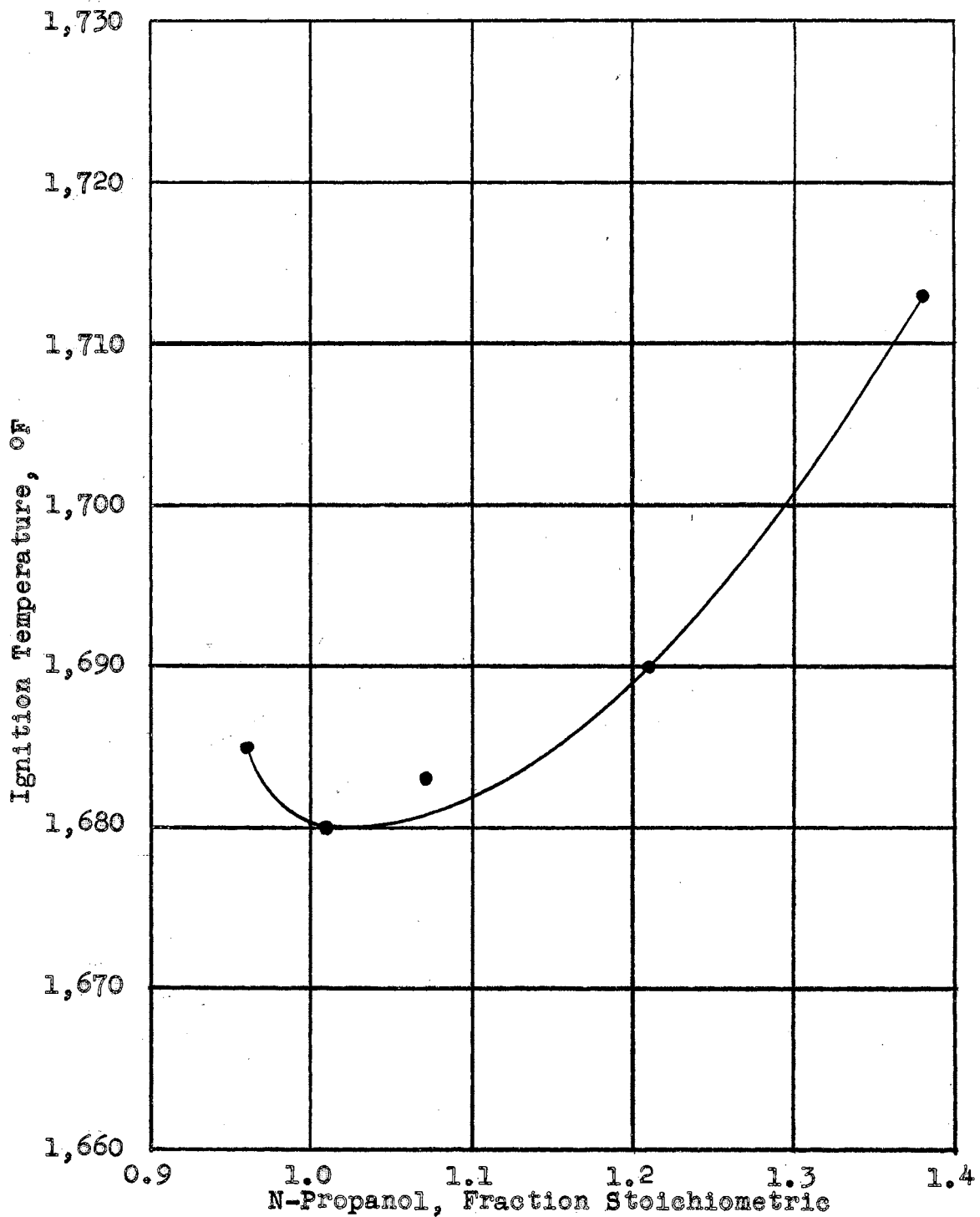


FIGURE 9

SINGLE-AIR-TUBE IGNITION OF N-PROPANOL

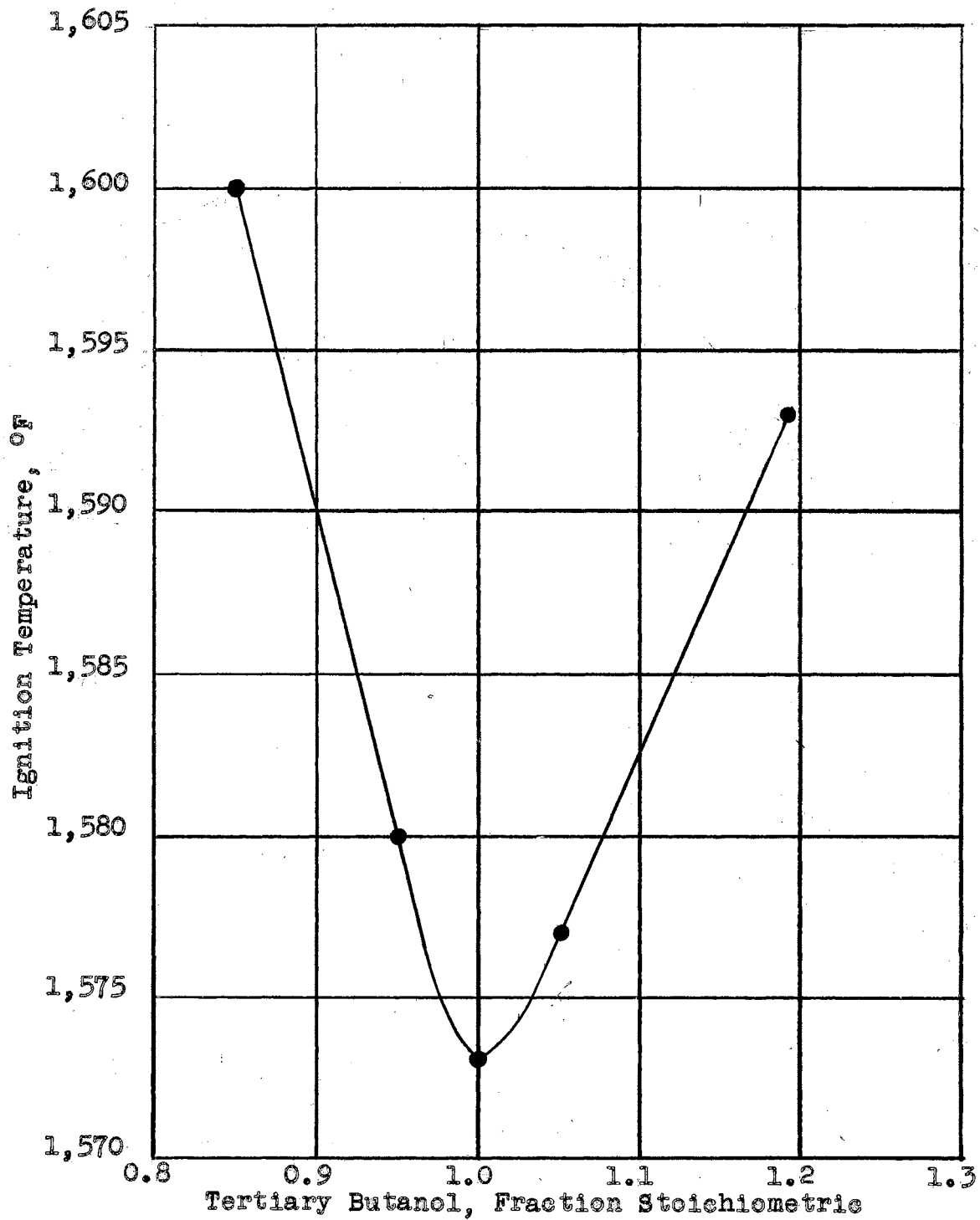


FIGURE 10

SINGLE-AIR-TUBE IGNITION OF TERTIARY BUTANOL

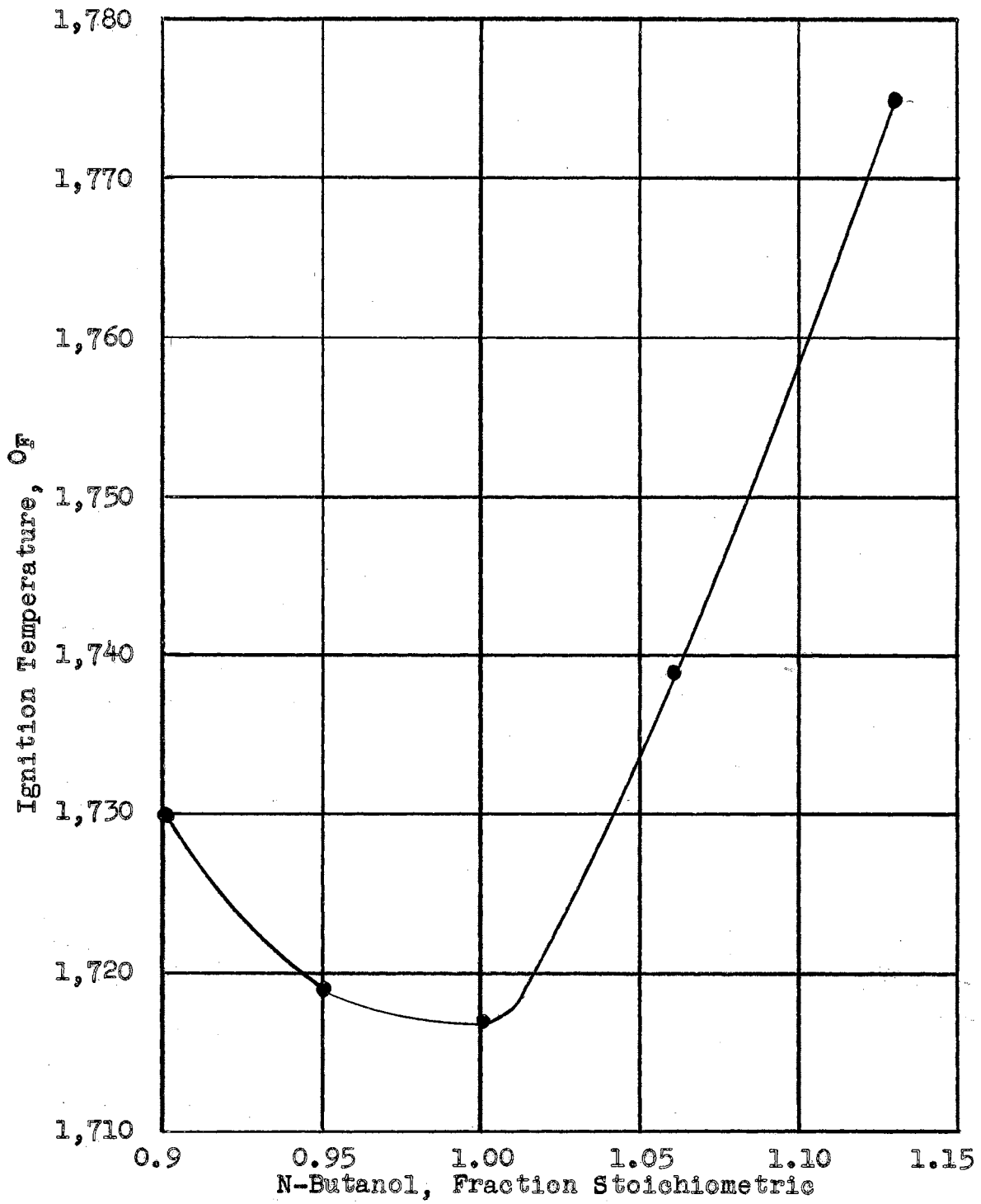


FIGURE 11

SINGLE-AIR-TUBE IGNITION OF N-BUTANOL

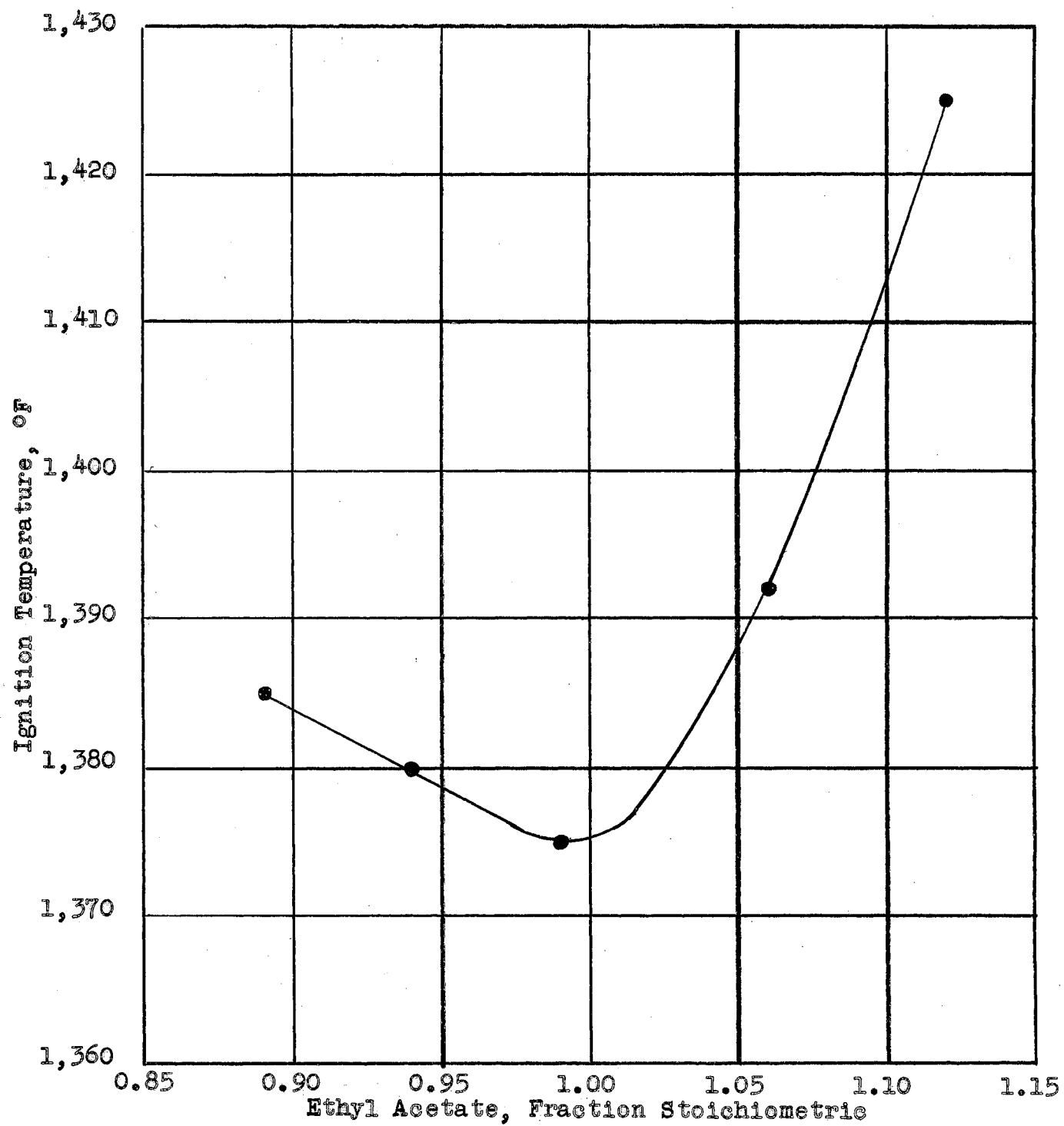


FIGURE 12

SINGLE-AIR-TUBE IGNITION OF ETHYL ACETATE

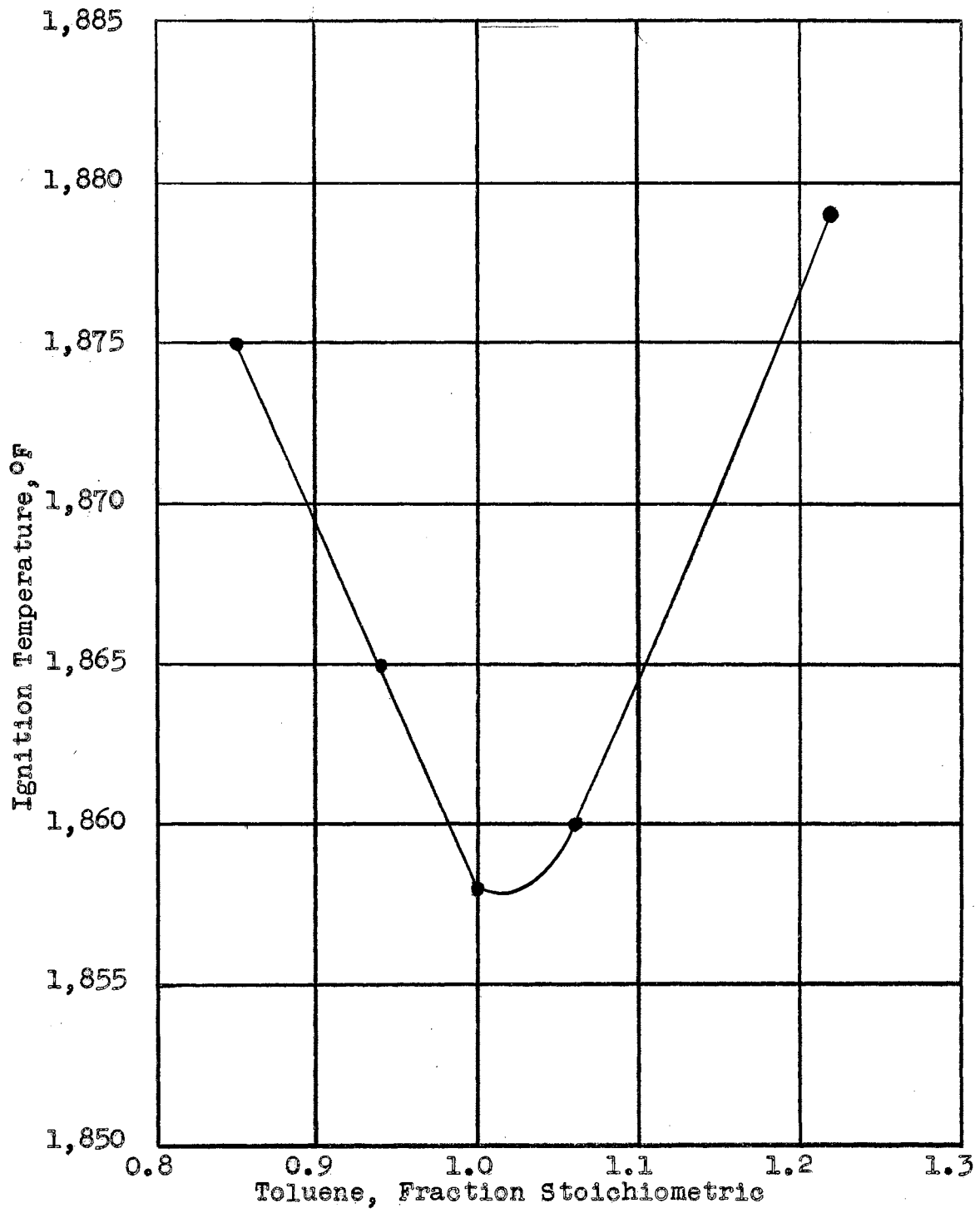


FIGURE 13

SINGLE-AIR-TUBE IGNITION OF TOLUENE

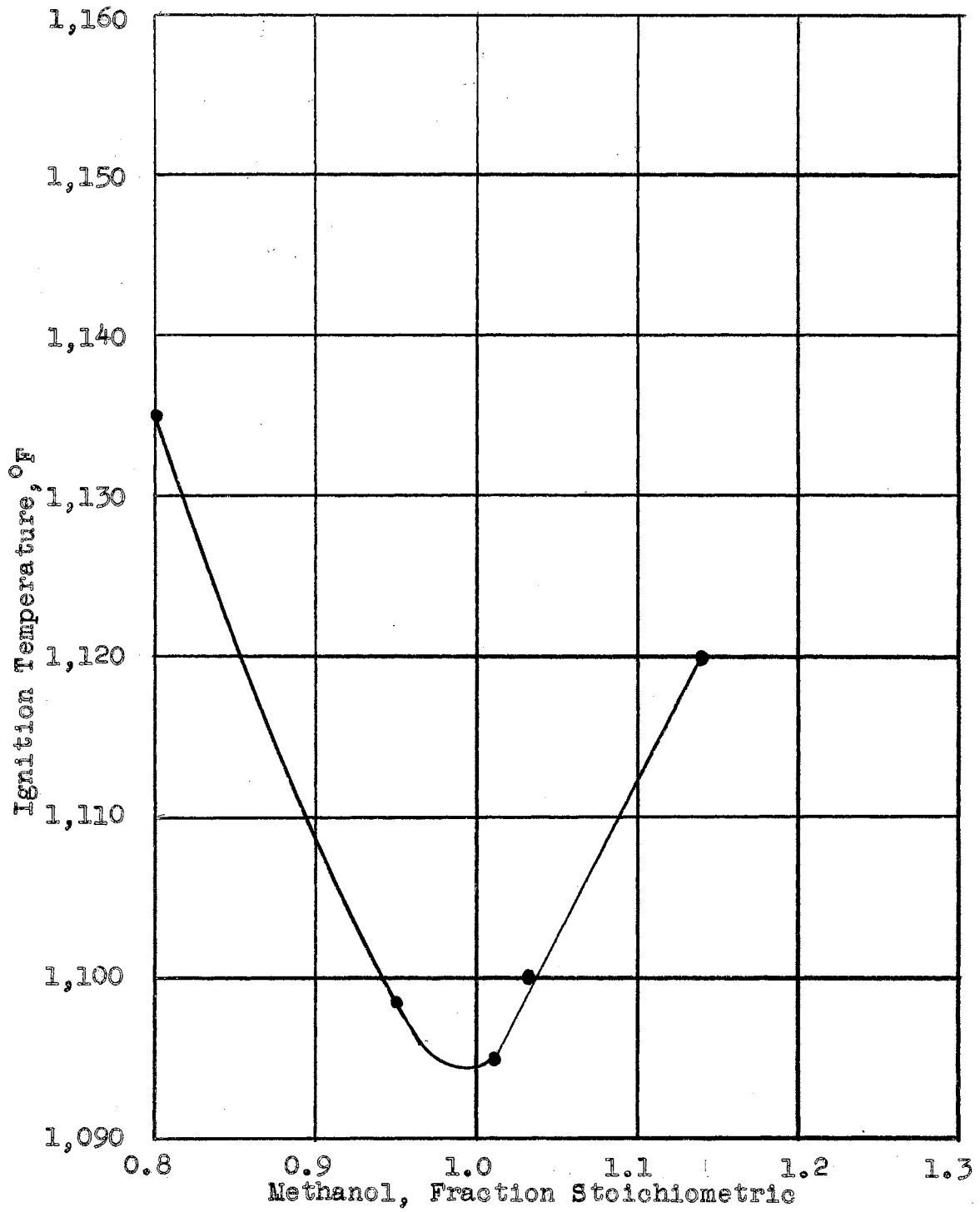


FIGURE 14

TRIPLE-AIR-TUBE IGNITION OF METHANOL

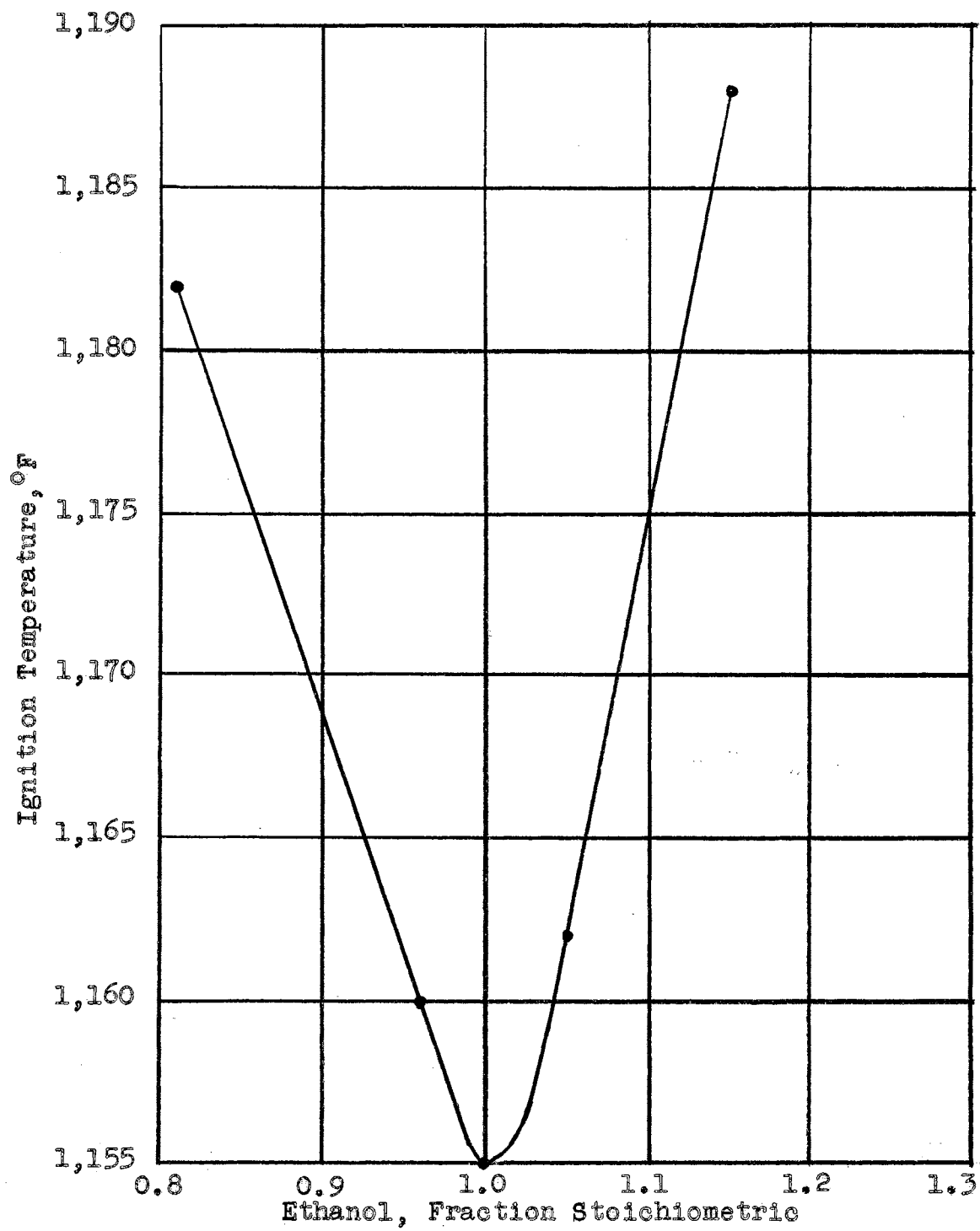


FIGURE 15

TRIPLE-AIR-TUBE IGNITION OF ETHANOL

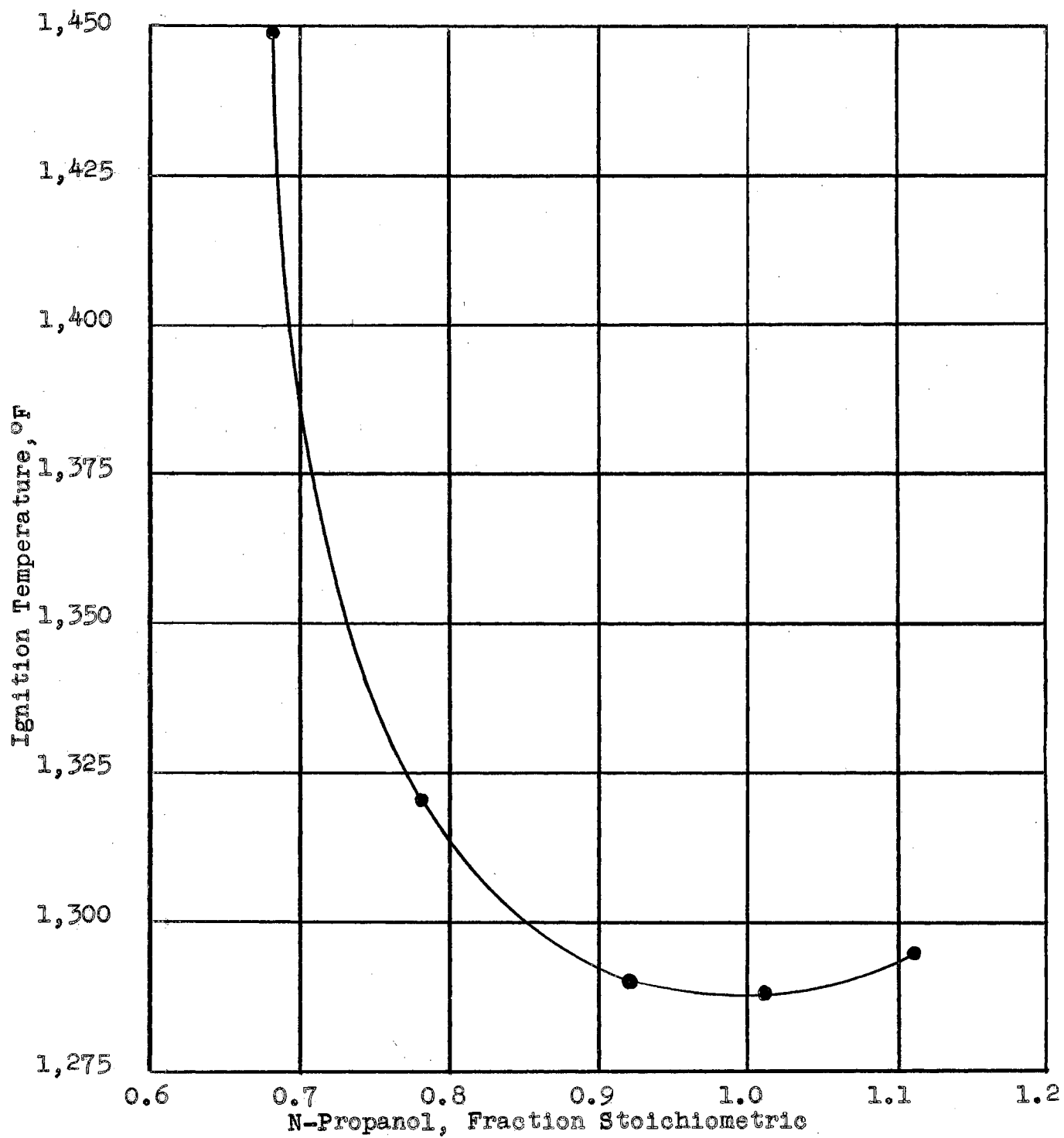


FIGURE 16

TRIPLE-AIR-TUBE IGNITION OF N-PROPANOL



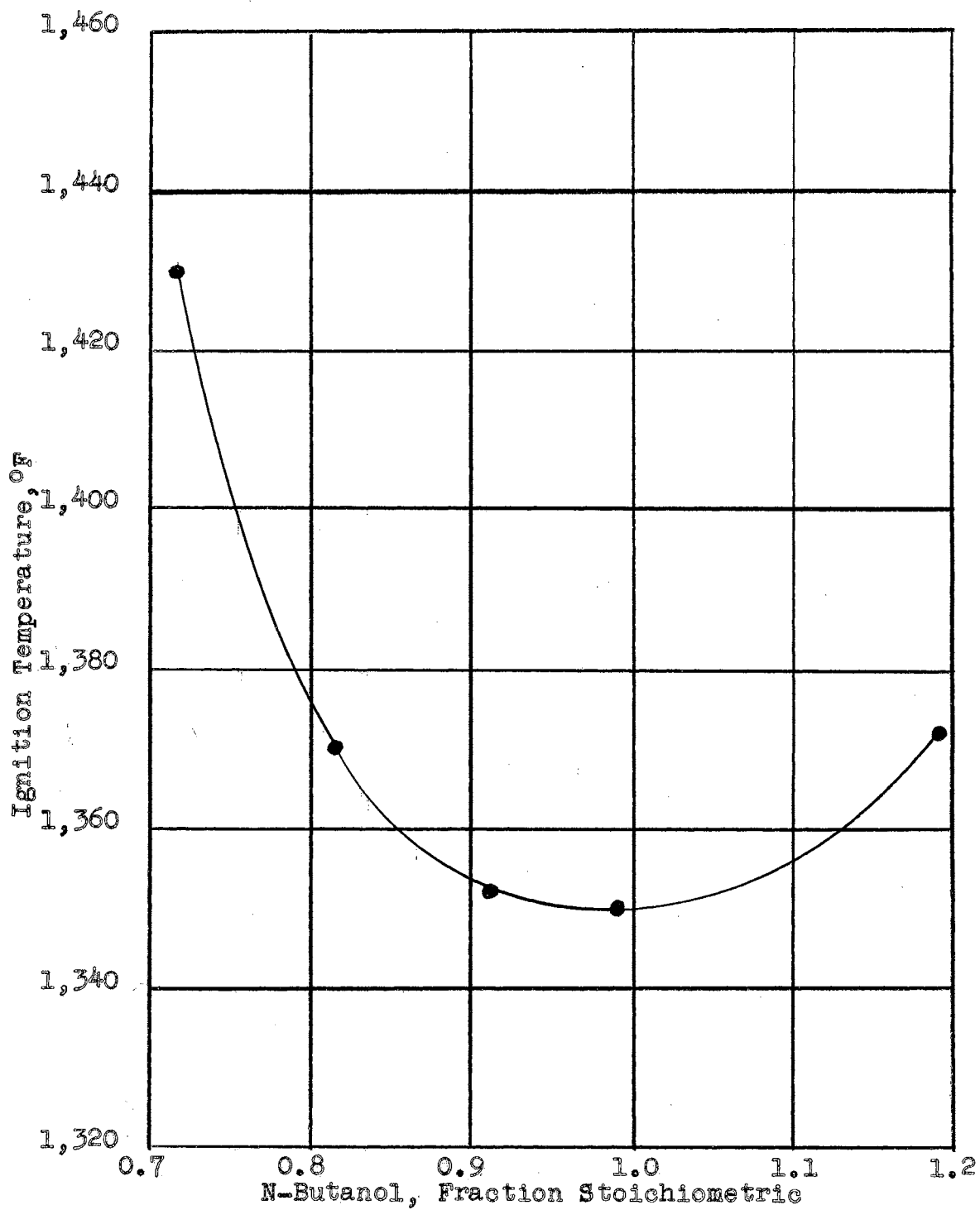


FIGURE 17

TRIPLE-AIR-TUBE IGNITION OF N-BUTANOL

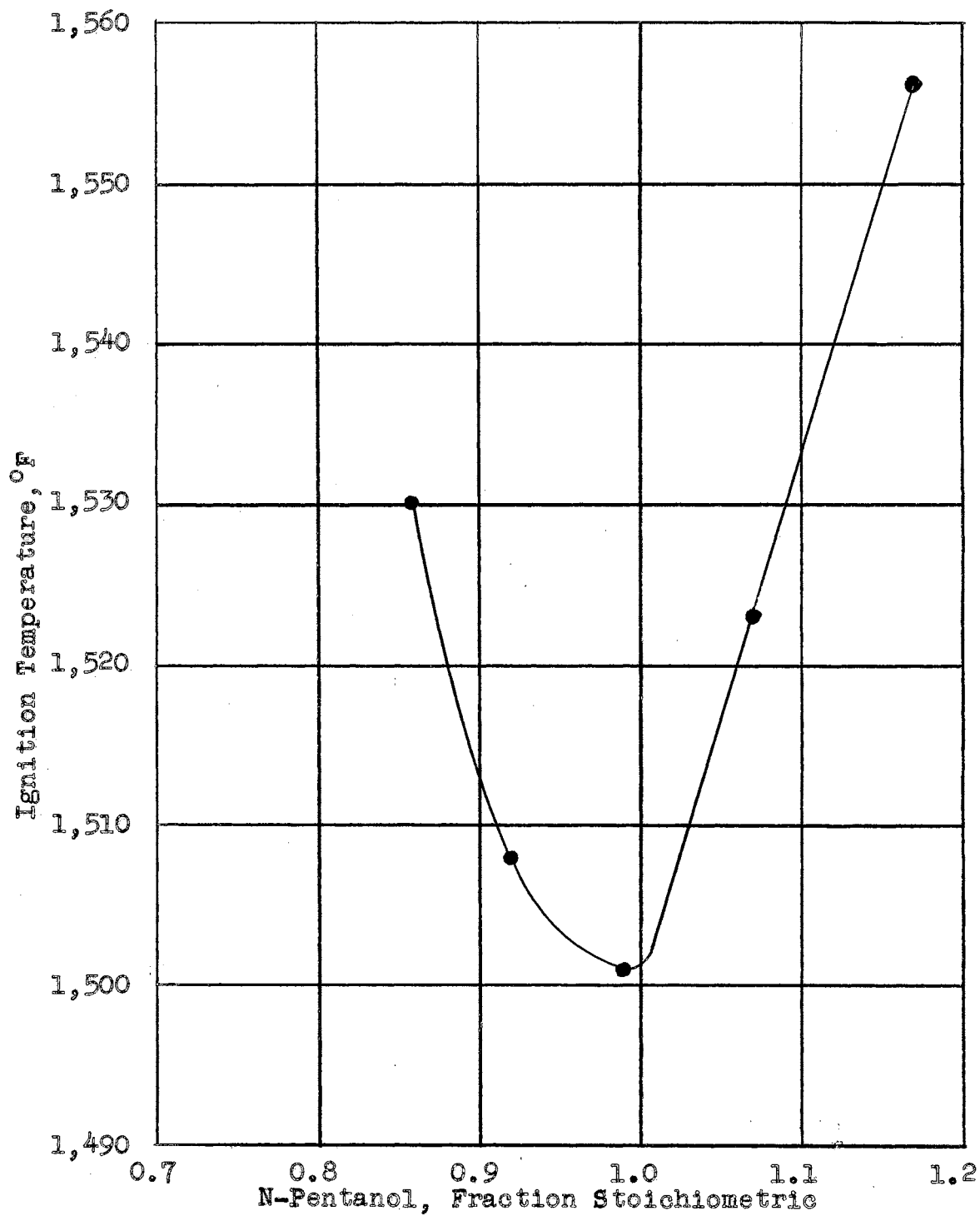


FIGURE 18

TRIPLE-AIR-TUBE IGNITION OF N-PENTANOL

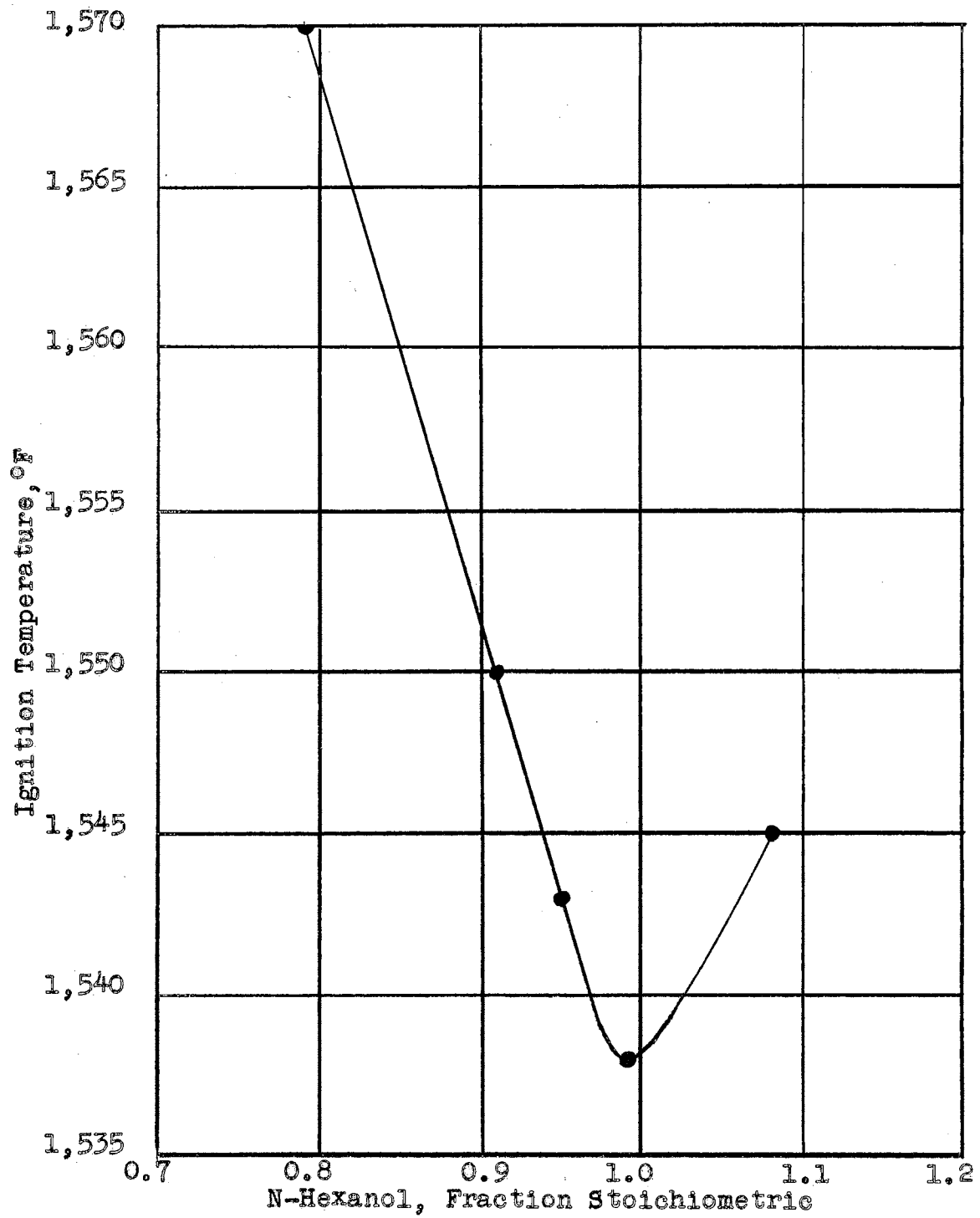


FIGURE 19

TRIPLE-AIR-TUBE IGNITION OF N-HEXANOL

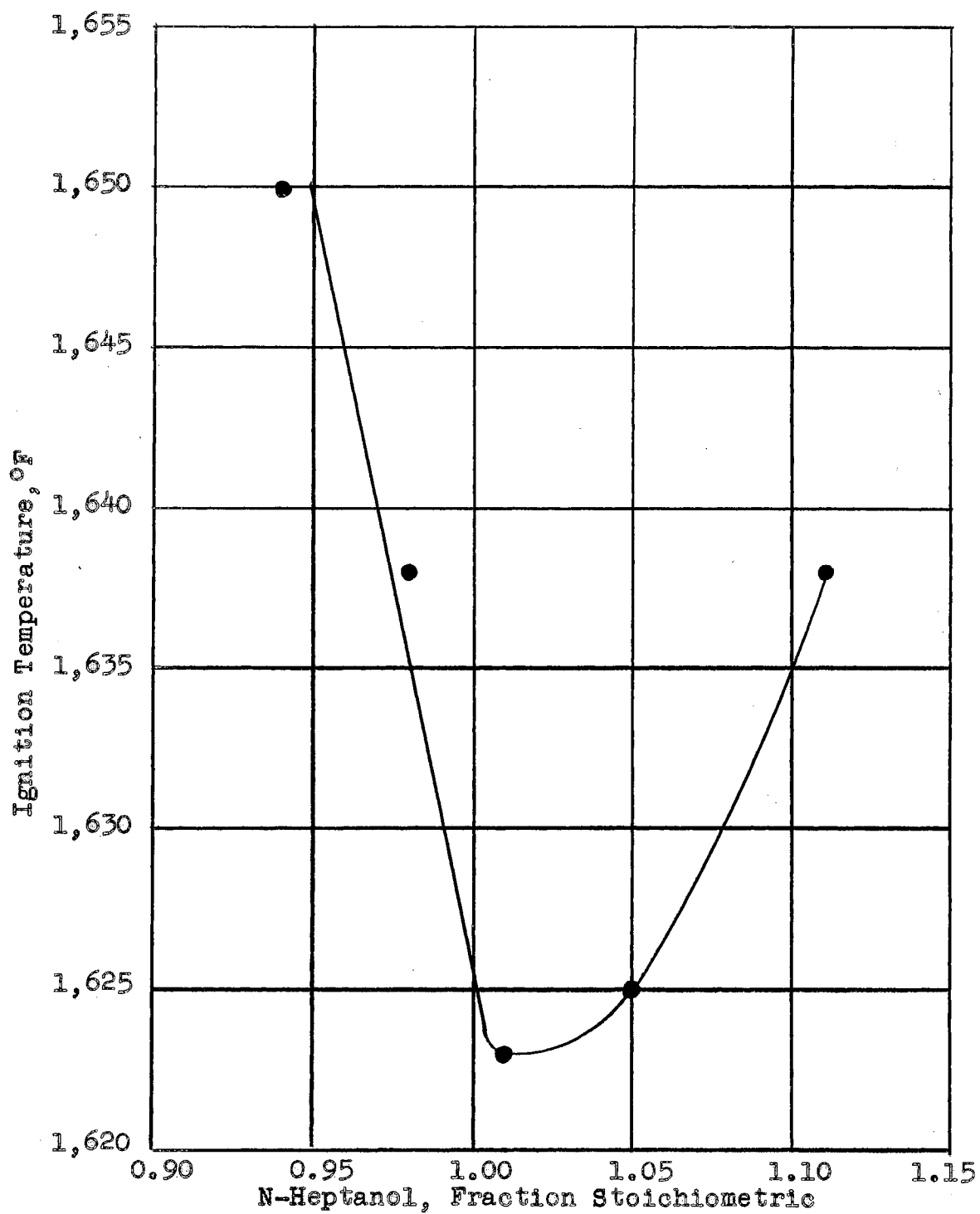


FIGURE 20

TRIPLE-AIR-TUBE IGNITION OF N-HEPTANOL

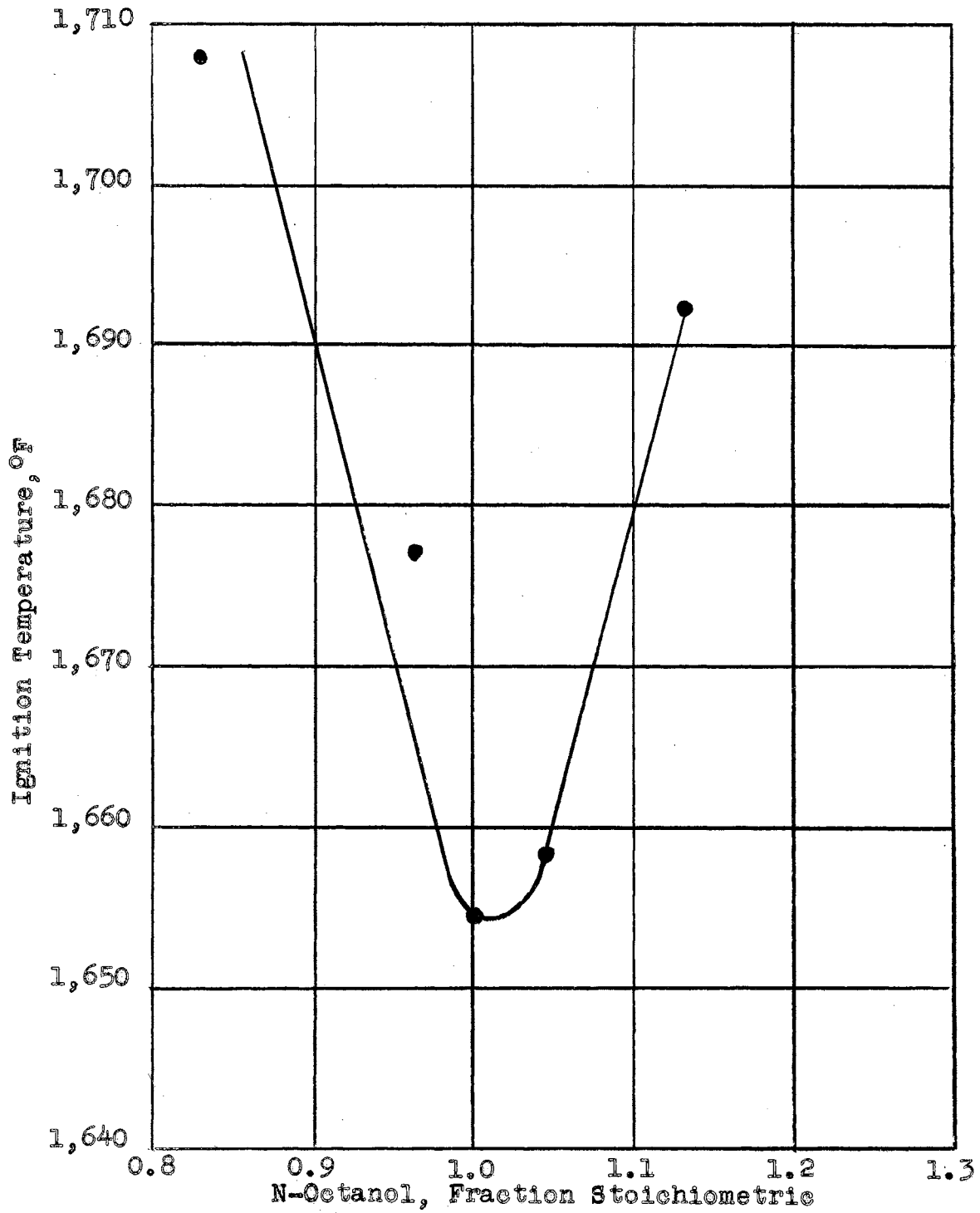


FIGURE 21

TRIPLE-AIR-TUBE IGNITION OF N-OCTANOL

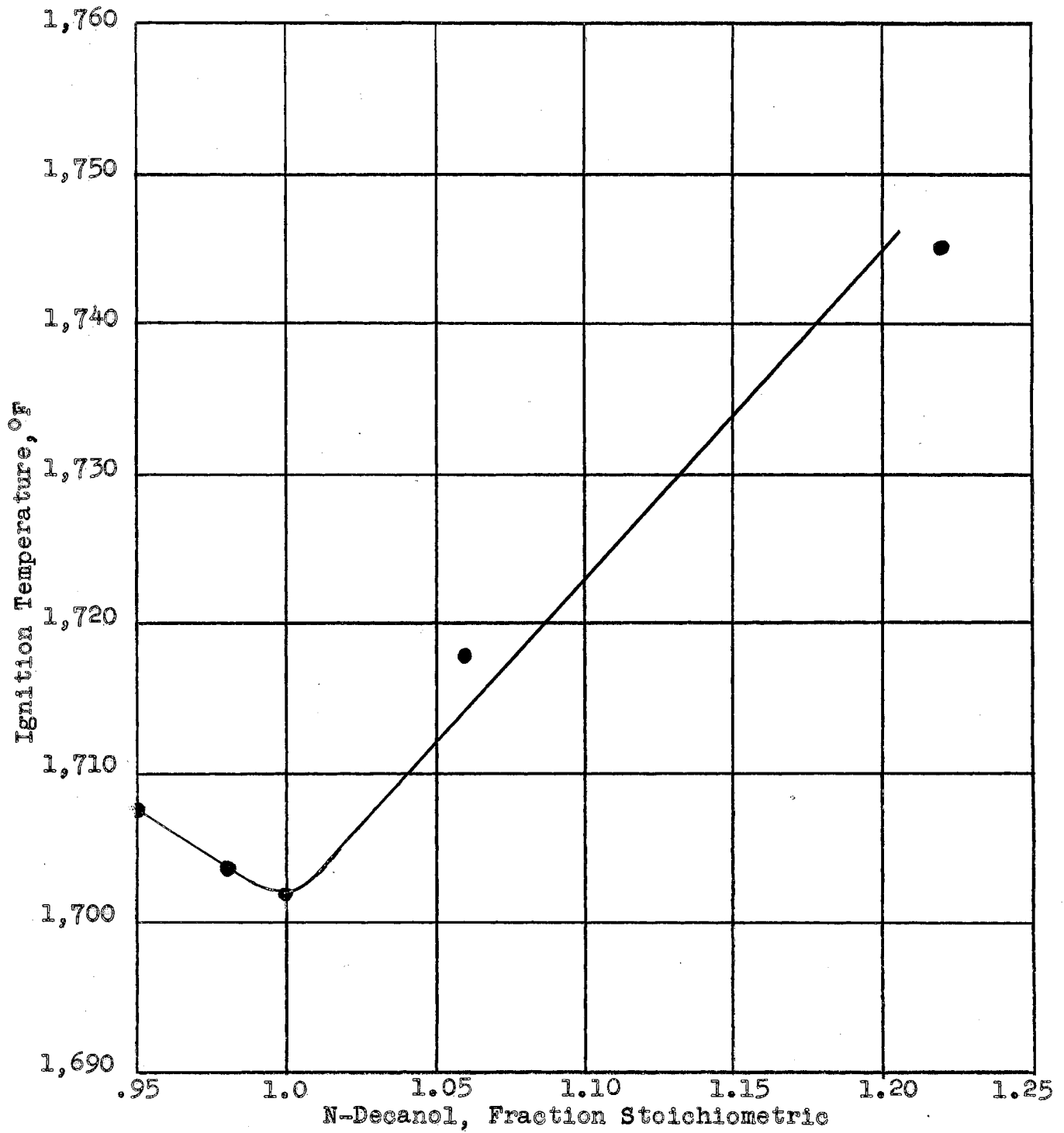


FIGURE 22

TRIPLE-AIR-TUBE IGNITION OF N-DECANOL

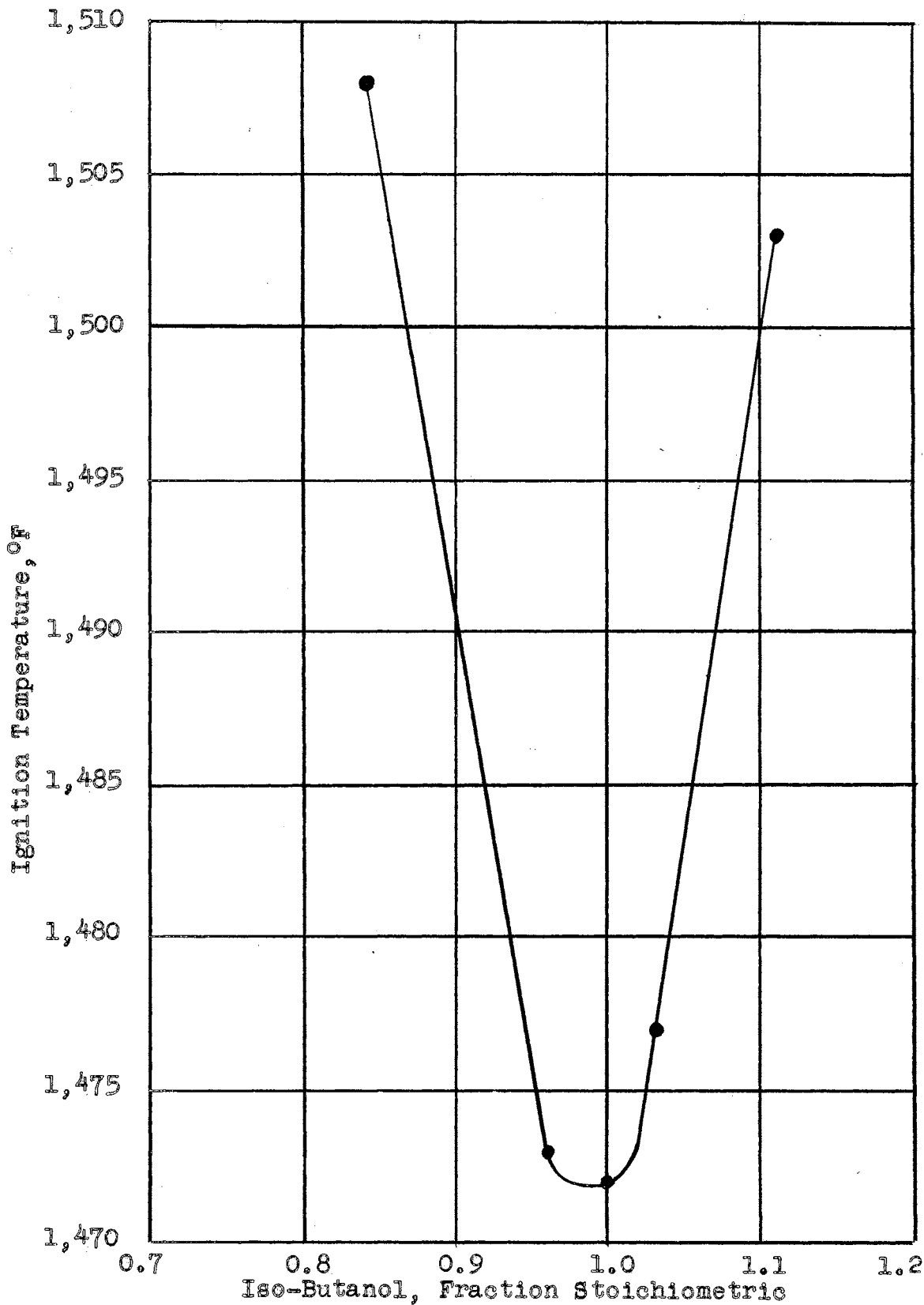


FIGURE 23

TRIPLE-AIR-TUBE IGNITION OF ISO-BUTANOL

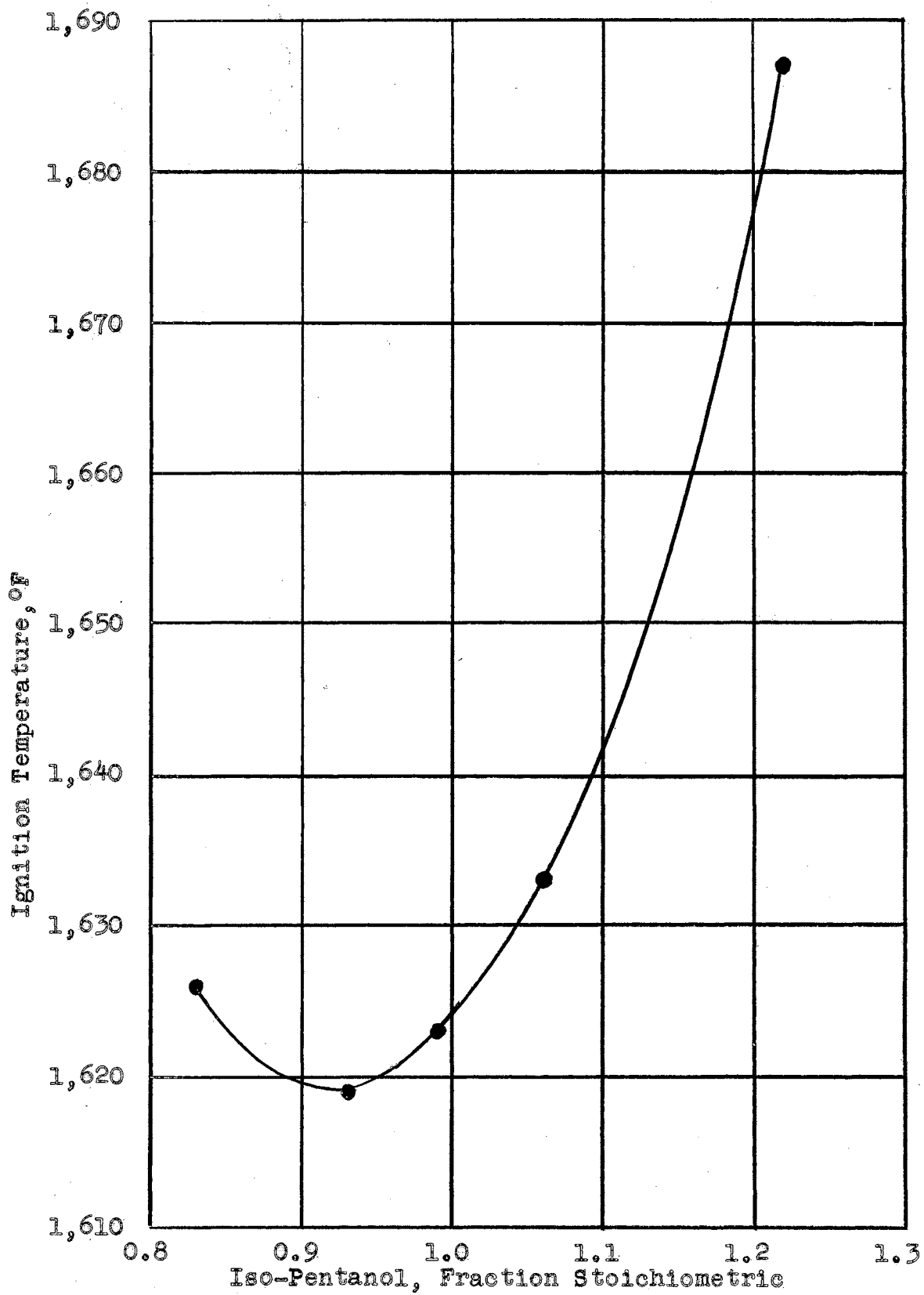


FIGURE 24

TRIPLE-AIR-TUBE IGNITION OF ISO-PENTANOL



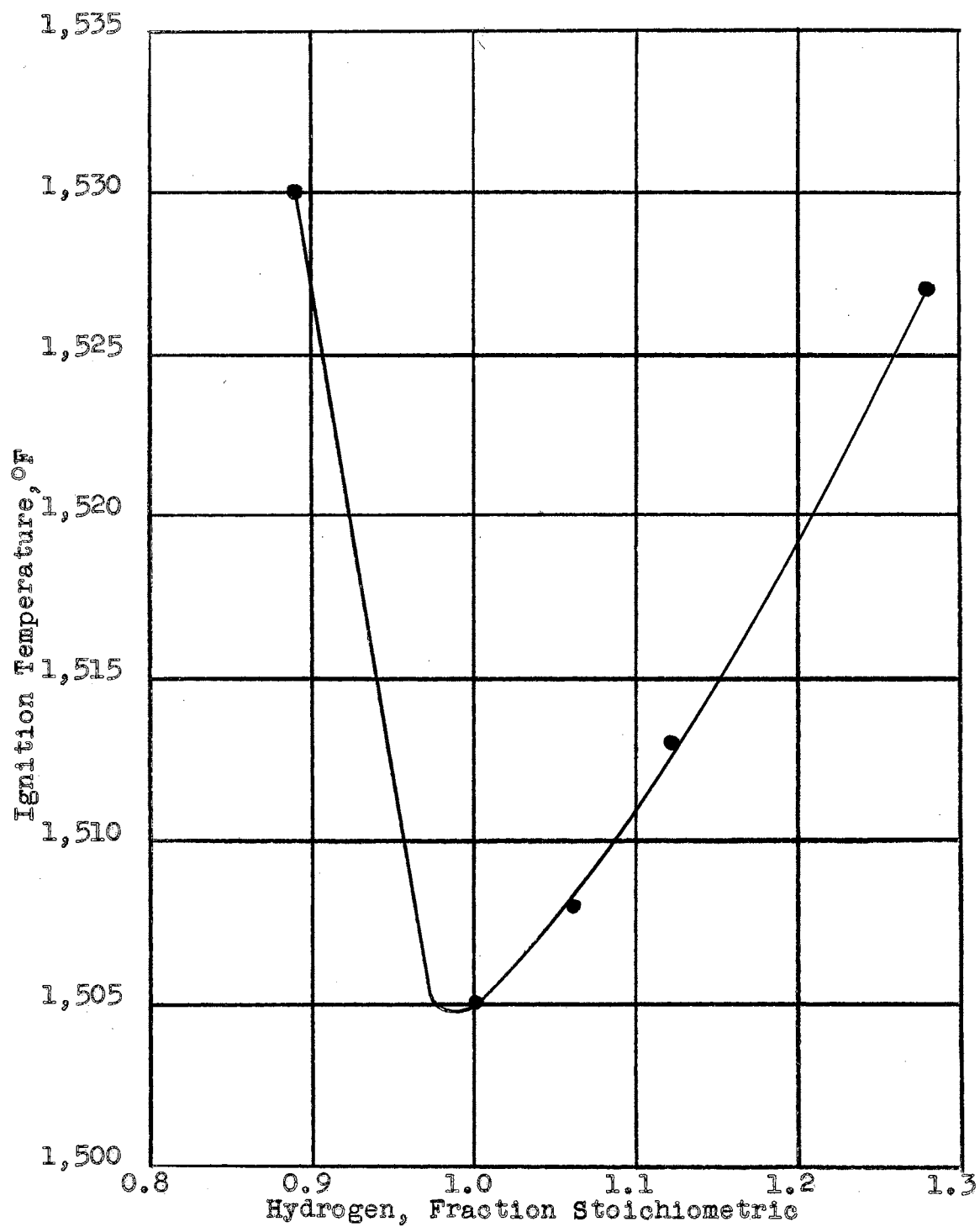


FIGURE 25

SINGLE-AIR-TUBE IGNITION OF HYDROGEN IN TUBE FURNACE

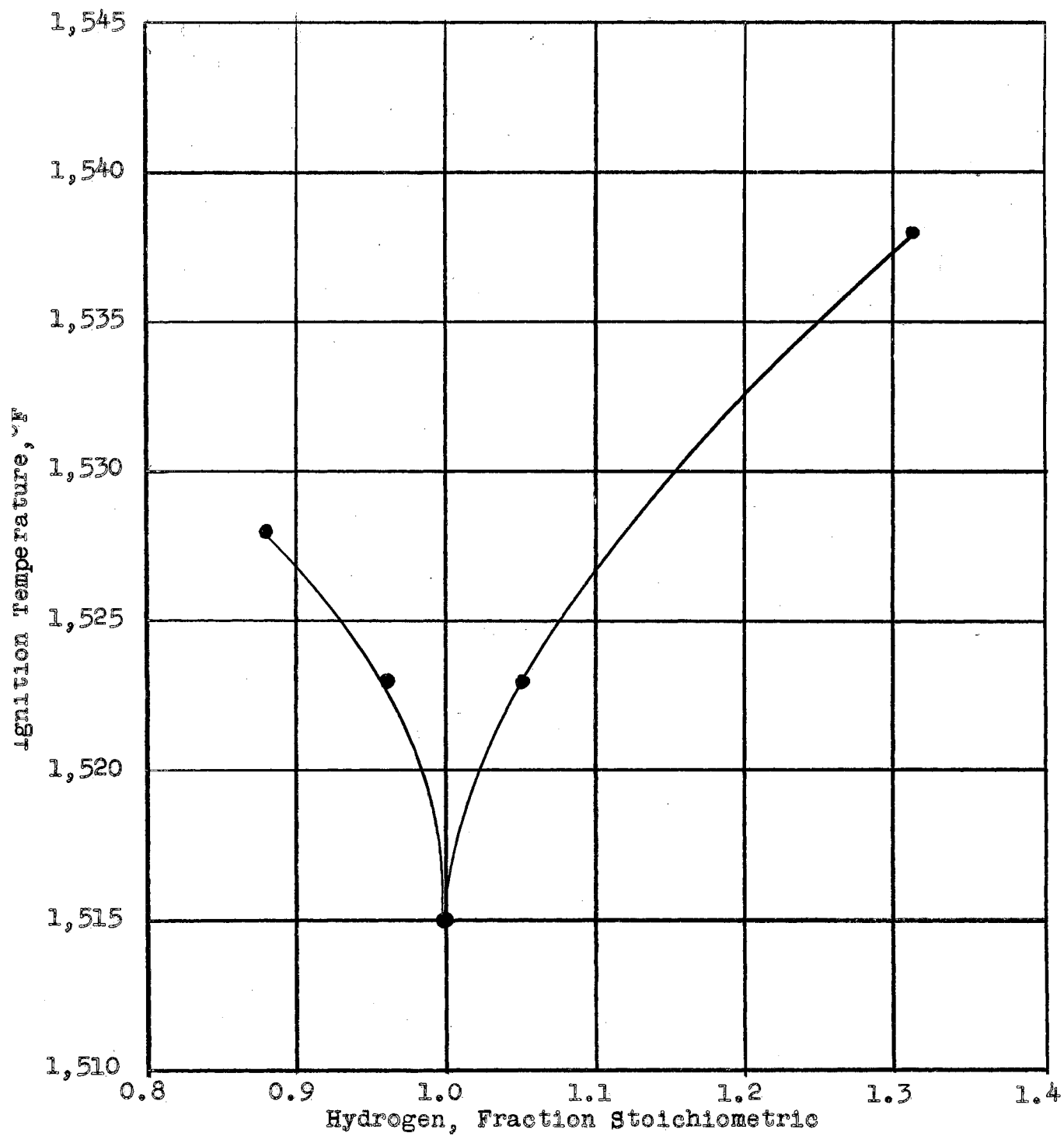


FIGURE 26

DOUBLE-AIR-TUBE IGNITION OF HYDROGEN

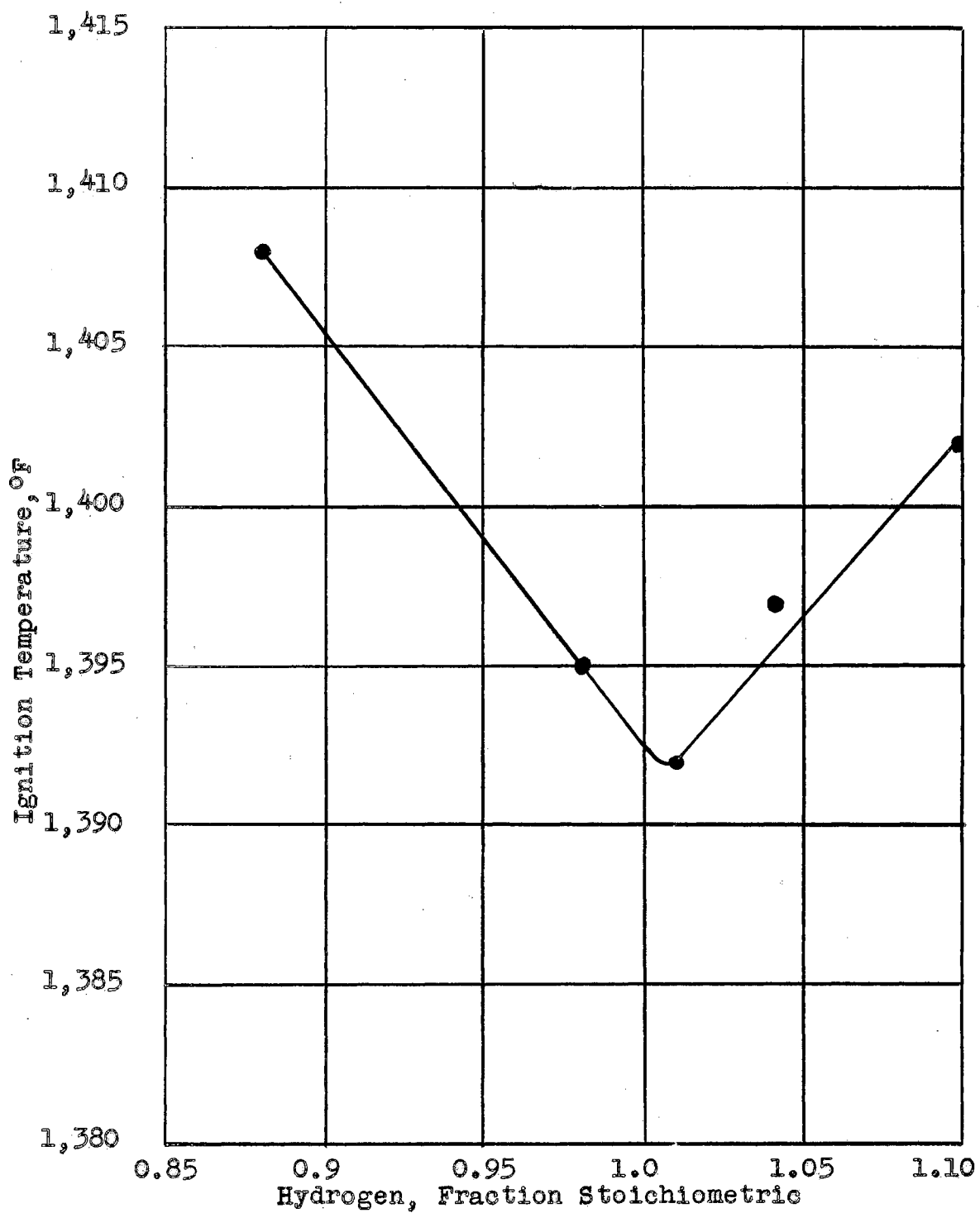


FIGURE 27

TRIPLE-AIR-TUBE IGNITION OF HYDROGEN

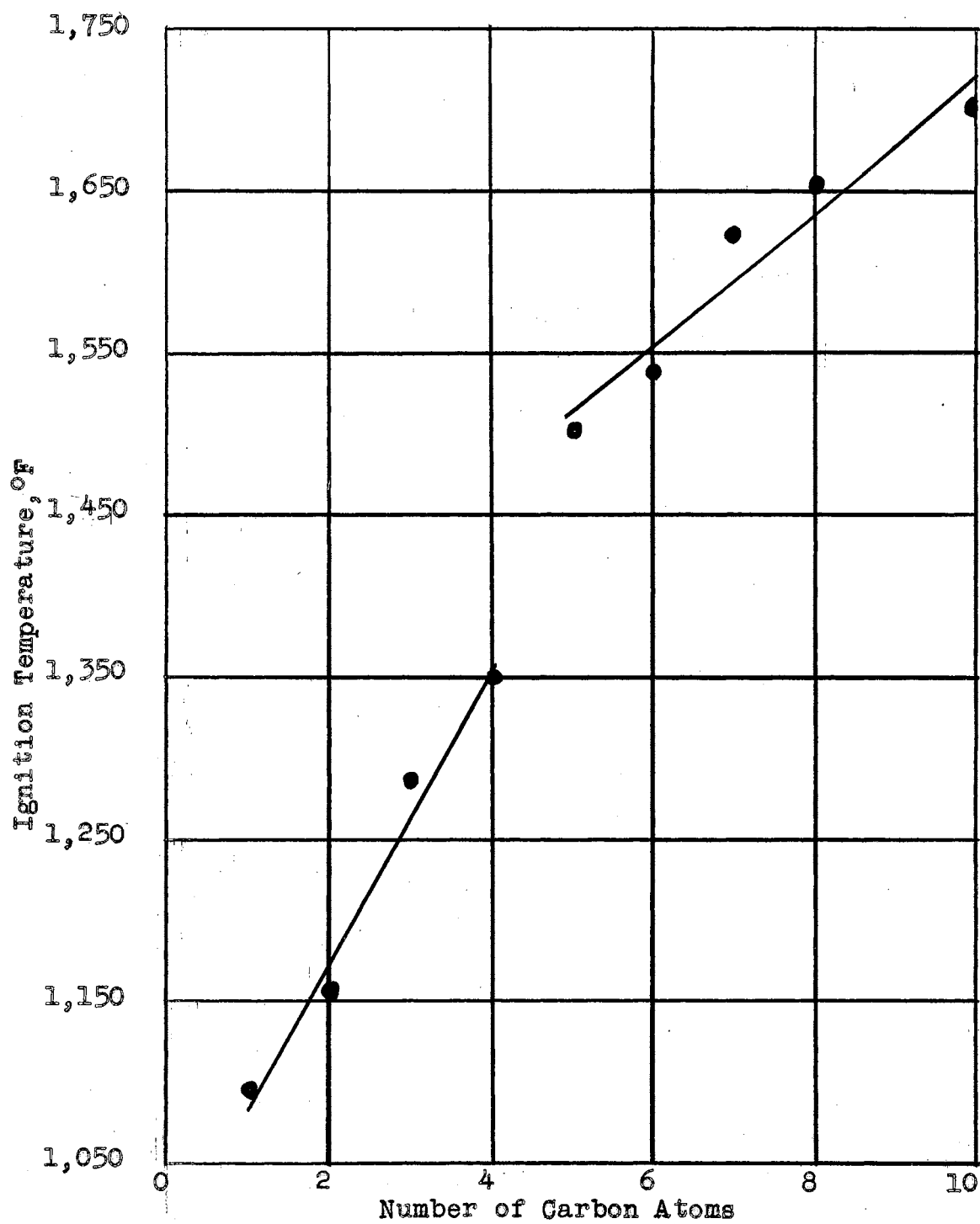


FIGURE 28

MINIMUM IGNITION TEMPERATURES OF THE NORMAL ALCOHOLS

## DISCUSSION OF RESULTS

In the preliminary determinations made to establish the validity of the method used, it was found, as shown in Table II, that the results obtained by this method are independent within limits from the temperature of the ignition chamber, the temperature of the combustible mixture, and the catalyst used.

The influence of the temperature of the ignition chamber appears to be purely one of heat transfer. In other words, if the temperature of the ignition chamber is too low, the rate of heat radiated from the thermocouple will be so high that the rate of heat liberated to the thermocouple by the reaction will not suffice to raise the temperature to that of ignition. By the same count, if the chamber temperature were too high, the thermocouple temperature should rise so fast as to reach the temperature of ignition almost instantaneously; this was indeed found to be true.

The influence of the temperature of the gaseous mixture is not as readily determined. Apparently, the only real influence of the gas temperature is to determine in part whether the initial explosion will be followed by steady combustion. Otherwise, since a variation of 900°F caused an apparent change of only two degrees in ignition temperature, the ignition temperature may be considered to remain constant when the temperature of the combustible mixture varies

over wide ranges.

When nickel was used as a catalyst instead of platinum, no change in the ignition temperature resulted. However, the temperature to which the ignition chamber had to be heated before ignition occurred was considerably higher than was necessary when platinum was the catalyst. When heat transfer is considered, this fact is a clear indication that nickel is by no means as good a catalyst as platinum for the oxidation of hydrogen. Thus, the similar ignition temperatures obtained with the two catalysts cannot be attributed to similar degrees of catalytic action, and hence the nature of the catalyst at the thermocouple junction can be considered not to influence the ignition temperature determined.

When ignition temperature determinations were made using hydrogen as fuel and argon or nitrogen as inert gas, it was found that the ignition obtained for the stoichiometric mixture was lower when nitrogen was the inert gas rather than when argon was used. This was in agreement with the results of Naylor and Wheeler.<sup>41</sup>

A striking result obtained was the variation between the ignition temperatures obtained in the tube furnace when one air tube was used and when three air tubes were used. The drop in the ignition temperatures when three air tubes were used was so great for ethanol and iso-propanol that additional determinations were made using hydrogen as fuel. The results thus obtained are listed in Table VI, and show a decrease of more than 100°F as the number of air tubes

was increased from one to three. Since the hydrogen rate of flow was maintained constant for the three runs, the only logical explanation for this variation is the poor mixing of the fuel and air in the ignition chamber when a single air tube was used. Unfortunately, no more capillary tubes were available, and it was not possible to determine the influence of additional air tubes on the temperature of ignition. However, since the drop in the ignition temperature between the determinations made with two and three air tubes is only a quarter as great as the drop between one and two air tubes, it may be supposed that perfect mixing was being rapidly approached.

When the lowest ignition temperatures obtained with three air tubes for the normal alcohols were compared, it was found that they did not fit any simple curve. A general increase in the ignition temperature with the number of carbon atoms was evident, and two equations were found by the method of least squares that fitted the results within 30°F. These equations are:

$$t = 995.5 + 89.7C \quad C \leq 4$$

and

$$t = 1330 \times 10^{0.01125C} \quad 5 \leq C \leq 10$$

In most cases, the lowest ignition temperature determined was for a fuel-air mixture close to the calculated stoichiometric ratio. This was not true for iso-pentanol, for which the optimum mixture was almost ten per cent richer in oxygen than the stoichiometric ratio. This may

have been caused by some particular impurity in the fuel, but it is unlikely in view of the results obtained with the other compounds.

Although there is little in the method used that would allow one to determine which of the theories on combustion is the most applicable, one fact was observed which could be used as a basis of reasoning: after the initial explosion, steady combustion would result only if the chamber walls were above a certain temperature, or if the combustible mixture were sufficiently hot.

The combination of these two possibilities represents good evidence against the thermal theory. This is obviously so, since any reaction that liberates enough heat to be self-propagating must of necessity liberate enough to be self-sustaining. Thus, according to the thermal theory, any combustion that originates in a cold, gaseous, combustible mixture should not be ephemeral if a source of fuel and air exist. Consequently, since explosions were commonly not followed by steady combustion, the thermal theory does not explain adequately the ignition behaviour observed.

The chain theory, on the other hand, does offer an explanation for the extinction of the flame. If enough chain-branching reactions are initiated at the catalytic thermocouple, the explosion will radiate from that point. This will leave an inert atmosphere around the thermocouple and prevent any further chain-branching reactions



from being initiated there. When the explosion front reaches the comparatively cold chamber wall, a sufficient number of chain-breaking reactions may occur to halt the explosion.

The fact that, for a given chamber temperature, a hot gaseous mixture continues to burn while a cold one does not, may be considered as an argument in favor of the energy chain as opposed to the material chain, but it presents no conclusive argument.

TABLE VII  
COMPARISON OF EXPERIMENTAL IGNITION TEMPERATURES  
WITH LITERATURE VALUES

Fuel Used	Ignition Temperature of Stoichiometric Mixture, °F	Maximum Literature Value, °F	Minimum Literature Value, °F
Hydrogen	1387 - 1520	1580 <sup>66</sup>	979 <sup>17</sup>
Methanol	1095	1065 <sup>36</sup>	878 <sup>48</sup>
Ethanol	1155-- 1337	1054 <sup>36</sup>	737 <sup>57</sup>
N-Propanol	1287 - 1680	1004 <sup>36</sup>	610 <sup>57</sup>
Iso-Propanol	1464	1180 <sup>57</sup>	853 <sup>48</sup>
N-Butanol	1350 - 1717	697 <sup>57</sup>	653 <sup>48, 57</sup>
Iso-Butanol	1472	1007 <sup>36</sup>	813 <sup>48</sup>
Tert-Butanol	1573	1113 <sup>57</sup>	892 <sup>48</sup>
N-Pentanol	1502	---	---
Iso-Pentanol	1619	---	---
N-Hexanol	1538	572 <sup>48</sup>	572 <sup>48</sup>
N-Heptanol	1623	---	---
N-Octanol	1654	---	---
N-Decanol	1702	555 <sup>20</sup>	555 <sup>20</sup>
Ethyl Acetate	1375	903 <sup>48</sup>	903 <sup>48</sup>
Toluene	1858	1172 <sup>36</sup>	960 <sup>38</sup>

## SUMMARY AND CONCLUSIONS

The purpose of this investigation was to develop a method of determining ignition temperatures that would require small amounts of fuels and that would be free from the harmful effects of catalysis. To this effect the method used was devised, in which small streams of gaseous (or vapourized) fuel and air were injected into a tubular ignition chamber by means of stainless steel capillary tubes. The ignition chamber was heated to below the ignition temperature, and the ignition was initiated at the junction of a catalytic thermocouple. The temperature of the thermocouple at the instant of ignition was considered to be the true ignition temperature.

Preliminary tests demonstrated the method to yield results independent of the temperature of the ignition chamber walls, the temperature of the combustible mixture, and the nature of the catalyst used on the thermocouple.

In subsequent determinations, the ignition temperatures of hydrogen, ethyl acetate, toluene, and thirteen alcohols ranging from methanol to n-decanol were determined for various fuel-air mixtures. In general, the lowest temperature of ignition for any fuel occurred at or near the calculated stoichiometric ratio.

Determinations made with a varying number of air

capillaries demonstrated that the first ignition temperature determinations were much too high, probably because improper mixing of the fuel and air occurred when a single air capillary was used.

The ignition temperatures of stoichiometric mixtures of the normal alcohols showed an increase in the temperatures of ignition that could be represented by the following two equations with an accuracy of 30°F:

$$t = 995.5 + 89.7C \quad C \leq 4$$

$$t = 1330 \times 10^{0.01125C} \quad 5 \leq C \leq 10$$

The behaviour of the flame after ignition had occurred led to the conclusion that the method of flame propagation was more likely to be through chain-branching reactions than through heat conduction. Whether the chains involved are material or of the energy type is not determined, but there is a slight indication in favour of energy chains.

The method used in this research is of importance because of its novel approach and because catalytic influence of the temperature of self-ignition has been eliminated. However, the matter of obtaining a truly homogeneous mixture has not been attempted.

The following modifications of the apparatus are therefore suggested if further work is contemplated:

1. More than three air capillaries should be used.

Enough tubes should be added, one at a time, that any further increase would not result in

a lowering of the ignition temperature. Thus, a correlation between the number of air tubes and the degree of mixing could be obtained.

An interesting possibility would be to use this method to develop a satisfactory method of determining the degree of mixing of gaseous fluids.

2. Variations should be made in the tube furnace as follows:

a. The tube furnace should be made longer, with a long mixing section heated only to a few degrees above the boiling point of any liquid fuel used, and a short ignition section that could be heated to whatever temperature may be required to cause the thermocouple to ignite the mixture.

b. The tube should be so devised that a sleeve could be inserted so as to determine whether the diameter of the chamber has a strong bearing on the ignition temperature. If the tube is long, the flow rates could be determined so as to have the same period of induction in both tubes.

A possibility that should also be kept in mind is that the present method could be used as an accurate and rapid

means of determining the comparative degree of catalytic effects of various methods. This could be determined as a function of the minimum temperature of the tube walls required to cause ignition.

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APPENDIX

APPENDIX A

CALIBRATION OF HYDROGEN AND AIR STREAMS

TABLE VIII

## CALIBRATION OF AIR FLOW IN SINGLE CAPILLARY

Air Line Pressure psi.	Air Temperature °F	Barometric Pressure mm. Hg.	Time Required to Displace One Liter of Water, Seconds	Calculated Flow Rate Gm. Mols O <sub>2</sub> per Hour
20	62.6	757.3	84.5	0.366
30	62.6	757.3	53.0	0.582
40	62.6	757.3	42.8	0.722
50	62.6	757.3	34.0	0.915
60	62.6	757.3	29.7	1.045
70	61.7	757.3	25.5	1.22
80	61.7	757.3	22.2	1.40
90	61.7	757.3	19.7	1.58
100	61.7	757.3	17.7	1.77

TABLE IX

## CALIBRATION OF AIR FLOW IN TRIPLE CAPILLARY

Air Line Pressure psi	Air Temperature °F	Barometric Pressure mm. Hg	Time Required to Displace One Liter of Water, Seconds	Calculated Flow Rate Gm. Mols O <sub>2</sub> per Hour
20	73.0	730	23.6	1.31
30	72.5	730	18.7	1.65
40	72.5	730	15.0	2.06
50	72.0	730	12.5	2.48
60	71.5	730	10.6	2.94
70	71.5	730	9.2	3.38
80	71.5	730	8.0	3.86
90	71.0	730	7.2	4.33

TABLE X

## CALIBRATION OF HYDROGEN FLOW

Hydrogen Pressure psi	Hydrogen Temperature °F	Barometric Pressure mm. Hg.	Time Required to Displace One Liter of Water, Seconds	Calculated Flow Rate Gm. Mols H <sub>2</sub> per Hour
10	62.6	757.3	51.0	2.89
15	62.6	757.3	42.2	3.50
20	62.6	757.3	30.0	4.92
25	62.6	757.3	23.0	6.42
30	62.6	757.3	18.5	7.98

APPENDIX B

LIQUID FUEL COMPOSITIONS AND FLOW RATES

TABLE XI

## COMPOSITION OF THE FUELS

Methanol

Acidity (maximum) . . . . .	0.02%
Assay . . . . .	99.5% by volume
Non-volatile matter . . . . .	0.001%
Alkalinity (maximum) . . . . .	0.0003%
Solubility in water . . . . .	passes test
Boiling range . . . . .	64.0 - 65.0°C
Substances darkened by sulfuric acid . . .	passes test
Substances reduced by $\text{KMnO}_4$ . . . . .	none
Acetone and aldehydes . . . . .	0.003%

Ethanol

Commercial grade, 95% ethanol.

Iso-Propanol

Boiling range . . . . .	0.2°C
Non-volatile matter . . . . .	0.0008%
Acidity as acetic acid . . . . .	0.002%
Solubility in water . . . . .	passes test
Water content . . . . .	0.05%

N-Propanol

Boiling range . . . . .	96 - 97.1°C
Non-volatile matter . . . . .	0.000%
Acidity as acetic acid . . . . .	0.002%
Substances precipitated by water . . . . .	none

Iso-Butanol

Acidity as butyric acid . . . . .	0.003%
Boiling range . . . . .	107 - 109°C
Non-volatile matter . . . . .	0.000%
Solubility in water . . . . .	passes test
Water content . . . . .	passes test



N-Butanol

Boiling range . . . . .	116 - 118°C
Free acid . . . . .	0.00%
Non-volatile matter . . . . .	0.00%

Tert-Butanol

Matheson Co. lot number 5048  
Chemically pure. No analysis reported

N-Pentanol

Practical. Boiling range 135 - 137°C

Iso-Pentanol

Boiling range . . . . .	129 - 132°C
Non-volatile matter . . . . .	0.004%
Acids and esters . . . . .	0.030%
Aldehydes . . . . .	none
Pyridine . . . . .	0.001%
Substances darkened by sulfuric acid . . . . .	passes test

N-Hexanol

Practical  
Minimum content of n-hexanol . . . . . 95%  
Boiling range . . . . . 155 - 158°C

N-Heptanol

Highest purity.  
Boiling range . . . . . 174 - 176°C

N-Octanol

Highest purity.  
Boiling range . . . . . 191 - 194°C

N-Decanol

Practical.  
Minimum content of n-decanol . . . . . 90% plus  
Melting point range . . . . . 1 - 5°C

Ethyl Acetate

Minimum content of ethyl acetate . . . . .	99.5%
Free acid as acetic acid . . . . .	0.01%
Non-volatile matter . . . . .	0.005%

Toluene

Non-volatile matter . . . . .	0.001%
Acid or alkali . . . . .	0.000%
Substances darkened by sulfuric acid . . . . .	passes test
Sulfur compounds as S . . . . .	0.003%
Water content . . . . .	passes test

Hydrogen

Commercial grade bottled hydrogen.

TABLE XII

## CALIBRATION OF FUEL RATES

Fuel Used	Weight of Empty Flask Grams	Weight of Flask and Fuel, Grams	Weight Rate of Fuel Flow Grams per Hour
Methanol	63.2106	113.2332	50.0226
Ethanol (Run No. 1)	66.5368	85.0417	18.5049
Ethanol (Run No. 2)	63.2038	99.6121	36.4083
N-Propanol (Run No. 1)	63.5433	86.0855	22.5422
N-Propanol (Run No. 2)	64.2207	94.6314	30.4107
Iso-Propanol	66.6682	80.8507	14.1825
N-Butanol	63.2411	93.5314	30.2903
Iso-Butanol	63.2218	103.4336	40.2118
Tert-Butanol	65.6549	81.0793	15.4244
N-Pentanol	66.2258	100.3441	34.1183
Iso-Pentanol	63.2217	105.3060	42.0843
N-Hexanol	64.2236	94.6441	30.4205
N-Heptanol	63.2160	95.2153	31.9993
N-Octanol	66.2418	96.6621	30.4203
N-Decanol	64.2468	107.5331	43.2863
Ethyl Acetate	62.1185	89.8193	27.7008
Toluene	63.4122	78.6441	15.2319

APPENDIX C

IGNITION TEMPERATURE DATA

TABLE XIII

## PRELIMINARY DETERMINATIONS MADE TO VALIDATE THE METHOD

Fuel Rate: 0.0383 Cu. Ft. per Minute

Air Supply: Surroundings

Shield Thermocouple Millivolts	Furnace Thermocouple Millivolts	Nature of Catalyst on Thermocouple	Catalytic Thermocouple Millivolts at Ignition
2.88	0.17	Platinum	No Ignition
2.96	0.17	Platinum	8.60 n*
			8.59 n
			8.58 n
			8.61 n
			8.60 n
3.23	0.17	Platinum	8.60 c**
			8.59 c
			8.59 c
			8.60 c
			8.59 c
4.10	0.17	Platinum	8.58 c
			8.59 c
			8.57 c
			8.60 c
			8.58 c
2.98	1.83	Platinum	8.60 n
			8.59 n
			8.58 n
			8.61 n
			8.60 n
2.98	3.53	Platinum	8.59 n
			8.61 n
			8.58 n
			8.55 n
			8.62 n

\* n = Initial explosion not followed by steady combustion

\*\* c = Initial explosion followed by steady combustion.

Shield Thermocouple Millivolts	Furnace Thermocouple Millivolts	Nature of Catalyst on Thermocouple	Catalytic Thermocouple Millivolts at Ignition
2.98	4.33	Platinum	8.58 c 8.57 c 8.57 c 8.59 c 8.57 c
4.78	0.17	Nickel	No Ignition
5.63	0.17	Nickel	8.59 c 8.58 c 8.56 c 8.57 c 8.58 c

TABLE XIV

## HYDROGEN IGNITION DETERMINATION, NUMBER ONE

Number of Air Capillaries: One

Inert Gas: Argon

Fuel Rate: 0.0383 Cu. Ft. per Minute

Shield Thermocouple Millivolts	Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
3.70	50	7.74
		7.75
		7.74
		7.74
		7.75
3.79	60	7.67
		7.68
		7.68
		7.67
		7.67
3.89	70	7.64
		7.65
		7.65
		7.64
		7.67
4.04	80	7.61
		7.63
		7.61
		7.61
		7.63
4.22	90	7.65
		7.64
		7.64
		7.65
		7.63

TABLE XV

## HYDROGEN IGNITION DETERMINATION, NUMBER TWO

Number of Air Capillaries: One

Inert Gas: Nitrogen

Fuel Rate: 0.0383 Cu. Ft. per Minute

Shield Thermocouple Millivolts	Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
3.10	50	8.50
		8.52
		8.51
		8.52
		8.52
3.10	60	8.15
		8.14
		8.13
		8.16
		8.15
4.16	70	7.69
		7.72
		7.71
		7.70
		7.69
4.24	80	7.55
		7.56
		7.54
		7.55
		7.54
4.24	90	7.63
		7.65
		7.64
		7.66
		7.63



TABLE XVI

## HYDROGEN IGNITION DETERMINATION, NUMBER THREE

Number of Air Capillaries: One

Fuel Rate: 0.0383 Cu. Ft. per Minute

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
70	7.64
	7.66
	7.66
	7.65
	7.67
80	7.58
	7.55
	7.57
	7.58
	7.56
85	7.53
	7.55
	7.56
	7.55
	7.54
90	7.52
	7.54
	7.53
	7.53
	7.54
100	7.71
	7.68
	7.69
	7.68
	7.67

TABLE XVII

## HYDROGEN IGNITION DETERMINATION, NUMBER FOUR

Number of Air Capillaries: Two

Fuel Rate: 0.0383 Cu. Ft. per Minute

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
30	7.13
	7.11
	7.14
	7.15
	7.12
40	7.02
	7.04
	7.01
	7.03
	7.03
43	7.00
	6.98
	6.98
	6.99
	6.98
45	7.05
	7.02
	7.03
	7.02
	7.04
50	7.11
	7.10
	7.08
	7.08
	7.10

TABLE XVIII

HYDROGEN IGNITION DETERMINATION, NUMBER FIVE

Number of Air Capillaries: Three

Fuel Rate: 0.0383 Cu. Ft. per Minute

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
20	6.91
	6.91
	6.90
	6.93
	6.90
22	6.88
	6.89
	6.87
	6.88
	6.86
23	6.87
	6.86
	6.84
	6.85
	6.85
25	6.88
	6.86
	6.87
	6.86
	6.88
30	6.97
	6.95
	6.95
	6.96
	6.94

TABLE XIX

METHANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 50.0226 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
40	5.25 5.29 5.27 5.29 5.27
45	5.15 5.16 5.14 5.13 5.16
47	5.14 5.12 5.12 5.14 5.11
50	5.13 5.14 5.15 5.12 5.14
60	5.33 5.37 5.35 5.34 5.35

TABLE XX

ETHANOL IGNITION DETERMINATION, NUMBER ONE

Number of Air Capillaries: One

Fuel Rate: 18.5049 grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	6.73
	6.75
	6.72
	6.76
	6.74
60	6.53
	6.52
	6.55
	6.54
	6.54
70	6.41
	6.44
	6.43
	6.41
	6.42
80	6.36
	6.38
	6.37
	6.38
	6.37
90	6.42
	6.41
	6.43
	6.44
	6.42

TABLE XXI

ETHANOL IGNITION DETERMINATION, NUMBER TWO

Number of Air Capillaries: Three

Fuel Rate: 36.4083 grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
40	5.66
	5.65
	5.67
	5.67
	5.65
45	5.52
	5.51
	5.51
	5.50
	5.52
47.5	5.47
	5.46
	5.46
	5.48
	5.47
50	5.51
	5.50
	5.49
	5.48
	5.50
60	5.61
	5.63
	5.61
	5.62
	5.62

TABLE XXII

## N-PROPANOL IGNITION DETERMINATION, NUMBER ONE

Number of Air Capillaries: One

Fuel Rate: 22.5422 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
70	8.80
	8.83
	8.82
	8.81
	8.80
80	8.67
	8.65
	8.67
	8.66
	8.67
90	8.63
	8.64
	8.62
	8.63
	8.63
95	8.61
	8.63
	8.60
	8.61
	8.60
100	8.63
	8.65
	8.64
	8.65
	8.64

TABLE XXIII

## N-PROPANOL IGNITION DETERMINATION, NUMBER TWO

Number of Air Capillaries: Three

Fuel Rate: 30.4107 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
40	6.31
	6.29
	6.30
	6.31
	6.30
45	6.24
	6.23
	6.23
	6.22
	6.24
50	6.25
	6.27
	6.26
	6.25
	6.24
60	6.45
	6.42
	6.44
	6.43
	6.43
70	7.00
	6.98
	6.99
	7.01
	6.99



TABLE XXIV

ISO-PROPANOL IGNITION DETERMINATION

Number of Air Capillaries: One

Fuel Rate: 14.1825 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	7.28
	7.29
	7.29
	7.30
	7.28
60	7.18
	7.19
	7.19
	7.17
	7.18
70	7.11
	7.11
	7.12
	7.13
	7.12
80	7.13
	7.13
	7.14
	7.14
	7.13
90	7.15
	7.14
	7.16
	7.16
	7.17

TABLE XXV

N-BUTANOL IGNITION DETERMINATION, NUMBER ONE

Number of Air Capillaries: One

Fuel Rate: 19.95351 grams per hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
80	9.20
	9.18
	9.19
	9.21
	9.21
85	8.97
	8.99
	9.00
	8.98
	8.99
90	8.85
	8.83
	8.84
	8.85
	8.85
95	8.85
	8.86
	8.87
	8.86
	8.85
100	8.90
	8.93
	8.92
	8.93
	8.91

TABLE XXVI

## N-BUTANOL IGNITION DETERMINATION, NUMBER TWO

Number of Air Capillaries: Three

Fuel Rate: 30.2903 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
40	6.75
	6.72
	6.74
	6.73
	6.72
50	6.60
	6.59
	6.60
	6.61
	6.60
55	6.60
	6.61
	6.61
	6.60
	6.61
60	6.70
	6.73
	6.72
	6.71
	6.73
70	7.10
	7.08
	7.08
	7.07
	7.09

TABLE XXVII

TERTIARY BUTANOL IGNITION DETERMINATION

Number of Air Capillaries: One

Fuel Rate: 15.4244 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
70	7.90
	7.91
	7.91
	7.90
	7.89
80	7.79
	7.80
	7.82
	7.79
	7.80
85	7.76
	7.78
	7.77
	7.78
	7.77
90	7.82
	7.81
	7.81
	7.83
	7.81
100	7.95
	7.94
	7.93
	7.94
	7.95

TABLE XXVIII

## ISO-BUTANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 40.2118 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
60	7.52
	7.50
	7.54
	7.53
	7.53
65	7.35
	7.37
	7.36
	7.35
	7.36
67	7.32
	7.34
	7.33
	7.34
	7.33
70	7.35
	7.33
	7.35
	7.34
	7.33
80	7.55
	7.53
	7.55
	7.56
	7.57

TABLE XXIX

## N-PENTANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 34.1183 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	7.85
	7.84
	7.80
	7.86
	7.85
55	7.65
	7.62
	7.66
	7.65
	7.64
60	7.49
	7.52
	7.54
	7.50
	7.51
65	7.57
	7.56
	7.54
	7.57
	7.55
70	7.66
	7.69
	7.69
	7.68
	7.67

TABLE XXX

ISO-PENTANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 42.0843 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
60	8.65
	8.63
	8.66
	8.64
	8.66
70	8.30
	8.33
	8.32
	8.30
	8.31
75	8.27
	8.25
	8.26
	8.24
	8.24
80	8.24
	8.22
	8.23
	8.24
	8.23
90	8.28
	8.26
	8.27
	8.29
	8.25

TABLE XXXI

## N-HEXANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 30.4203 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	7.76
	7.79
	7.76
	7.78
	7.77
55	7.71
	7.74
	7.73
	7.73
	7.72
57.5	7.75
	7.76
	7.76
	7.75
	7.77
60	7.81
	7.79
	7.80
	7.81
	7.81
70	7.91
	7.94
	7.93
	7.91
	7.93



TABLE XXXII

## N-HEPTANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 31.9993 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	8.36
	8.33
	8.35
	8.34
	8.35
53	8.27
	8.28
	8.26
	8.28
	8.29
55	8.24
	8.25
	8.25
	8.26
	8.26
57	8.36
	8.34
	8.34
	8.36
	8.35
60	8.44
	8.40
	8.43
	8.43
	8.42

TABLE XXXIII

## N-OCTANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 30.4203 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
50	8.67
	8.70
	8.69
	8.68
	8.67
55	8.46
	8.47
	8.48
	8.46
	8.48
57	8.44
	8.45
	8.45
	8.44
	8.44
60	8.59
	8.58
	8.60
	8.59
	8.58
70	8.79
	8.76
	8.80
	8.80
	8.80

TABLE XXXIV

## N-DECANOL IGNITION DETERMINATION

Number of Air Capillaries: Three

Fuel Rate: 43.2863 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
70	9.01
	9.03
	9.00
	9.04
	9.02
80	8.84
	8.86
	8.85
	8.83
	8.85
85	8.74
	8.72
	8.75
	8.74
	8.75
87	8.76
	8.77
	8.75
	8.77
	8.76
90	8.76
	8.77
	8.80
	8.78
	8.79

TABLE XXXV

## ETHYL ACETATE IGNITION DETERMINATION

Number of Air Capillaries: One

Fuel Rate: 27.7008 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
80	7.05
	7.07
	7.03
	7.05
	7.04
85	6.85
	6.87
	6.83
	6.86
	6.85
90	6.75
	6.76
	6.75
	6.74
	6.75
95	6.78
	6.79
	6.77
	6.78
	6.78
100	6.80
	6.83
	6.81
	6.82
	6.80

TABLE XXXVI

## TOLUENE IGNITION DETERMINATION

Number of Air Capillaries: One

Fuel Rate: 15.2319 Grams per Hour

Air Pressure psig	Catalytic Thermocouple Millivolts at Ignition
70	9.91
	9.88
	9.89
	9.88
	9.90
80	9.75
	9.73
	9.76
	9.75
	9.74
85	9.73
	9.72
	9.74
	9.74
	9.73
90	9.78
	9.77
	9.80
	9.75
	9.77
100	9.87
	9.86
	9.90
	9.88
	9.86

APPENDIX D

SAMPLE CALCULATIONS AND NOMENCLATURE

## SAMPLE CALCULATIONS

### Flow Rate of Air

Data: Run used: Air calibration for flow in single capillary tube with an air pressure of 20 psig (see Table VIII).

Atmospheric pressure during run: 757.3 mm Hg.

Temperature of water displaced: 62.6°F.

Time required to collect one liter of wet air:  
84.5 seconds.

Volume of one gram-mol of gas at 760 mm Hg., and 492°R is 22.4 liters.

Vapor pressure of water at 62.6°F: 14.5 mm Hg.

Oxygen content of dry air: Taken as 20.9% by volume.

Calculations: Absolute temperature for run is

$$460 + 62.6 = 522.6^{\circ}\text{R.}$$

Flow rate of air in terms of oxygen:

$$\text{Flow rate} = 1 \frac{(757.3 - 14.5)}{760} \times \frac{492}{522.6} \times \frac{3600}{84.5} \times \frac{0.209}{22.4}$$

Flow rate = 0.366 gram mols of oxygen per hour.

### Flow Rate of Hydrogen

Data: Run used: Hydrogen calibration at 10 psig upstream pressure. (see Table X).

Atmospheric pressure during run: 757.3 mm Hg.

Temperature of water displaced: 69.4°F.

Time required to collect one liter of wet hydrogen  
was 51.0 seconds.

Vapor pressure of water at 62.6°F = 14.5 mm Hg.

1 cubic foot is equivalent to 28.32 liters

Calculations: Absolute temperature for run is

$$460 + 62.6 = 522.6^{\circ}\text{F.}$$

Molar flow rate:

$$\text{Flow rate} = \frac{1(757.3 - 14.5)}{760} \times \frac{492}{522.6} \times \frac{3600}{51.0} \times \frac{1}{22.4}$$

Flow rate = 2.89 gram mols per hour.

Volumetric flow rate, cubic feet per minute:

$$\text{Flow rate} = \frac{2.89 \times 22.4}{28.32} \times \frac{1}{60}$$

Flow rate = 0.0383 cubic feet per minute.

#### Fuel-Air mixture with hydrogen as fuel

Data: Run used: Hydrogen ignition using argon as inert gas, with air line pressure of 50 psig (see Table III).

From Table VIII, flow rate of oxygen = 0.915 gram mols of oxygen per hour.

From previous calculation, flow rate of hydrogen is 2.89 gram mols per hour.

The oxidation reaction is:  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

Calculations: The number of mols of hydrogen required to reduce 0.915 mols of oxygen per hour is thus:



Mols of hydrogen required =  $2(0.915) = 1.830$  mols  
per hour.

The amount of hydrogen supplied, as fraction of  
stoichiometric requirements is thus:

Hydrogen supply =  $\frac{2.89}{1.83} = 1.58$  stoichiometric  
requirements.

Molar rate of flow of liquid fuel

Data: Run used: Methanol (see Table XII).

Flow rate of methanol: 50.0266 grams per hour.

Formula weight of methanol: 32.04

Calculations:

Molar flow =  $\frac{50.0266}{32.04} = 1.563$  gram mols per hour.

Fuel-air mixture with a liquid fuel:

Data: Run used: Ignition of methanol using air at  
50 psig (see Table XIX).

From Table IX, flow rate of oxygen is 2.48  
gram mols per hour.

From previous calculations, flow rate of methanol  
is 1.563 gram mols of methanol per hour.

The oxidation reaction is:



Calculations: The number of mols of methanol required to  
reduce 2.48 mols of oxygen per hour is:

Mols of methanol required =  $\frac{2(2.48)}{3} = 1.65$

The amount of methanol supplied, as fraction of stoichiometric requirements is thus:

Methanol supply =  $\frac{1.563}{1.65} = 0.947$  stoichiometric requirements.

### Ignition temperature

Data: Run used: Ignition of methanol using air at 50 psig (see Table XIX).

Catalytic thermocouple readings at the moment of ignition were:

5.25, 5.29, 5.27, 5.29, 5.27 mv.

Calculations: Average reading is:

$$\frac{5.13 + 5.14 + 5.15 + 5.12 + 5.14}{5}$$

Average reading = 5.14 millivolts, rounded off to the second decimal place.

From the Platinum-platinum 10% rhodium conversion table with reference junction at 32°F:<sup>31</sup>

Millivolts at 1095°F = 5.126 mv.

Millivolts at 1100°F = 5.155 mv.

By linear interpolation, 5.14 corresponds to an ignition temperature of 1097°F.

Finding equations giving a satisfactory relation between the number of carbon atoms in the normal alcohols and their ignition temperatures:

From Table V:	Normal Alcohol number of carbon atoms	Lowest Ignition Temperature Determined
	1	1095
	2	1155
	3	1287
	4	1350
	5	1502
	6	1538
	7	1623
	8	1654
	10	1702

Using the first eight values, it is seen below that the differences never become constant:

1095	1155	1287	1350	1502	1538	1623	1654
	60	132	63	152	36	85	31
		72	-69	89	-116	49	-54
			-141	158	-205	165	-103
				299	-363	370	-268

This increasing divergence of the differences means that there is no unique polynomial that fits the points. In addition, an equation in the form of the sum of trigonometric functions was not considered desirable because of its length and of its lack of smoothness between the points.

By plotting the minimum ignition temperatures of the normal alcohols versus the number of carbon atoms in the molecules on Cartesian, semi-logarithmic, and logarithmic

graph paper, it was found that the data could be represented with a fair degree of accuracy by two lines: a straight line between methanol and butanol, and an exponential curve between pentanol and decanol.

Once the nature of the lines had been ascertained, the equations were determined by the method of least squares:

1. The straight line:

C	t	C <sup>2</sup>	Ct
1	1095	1	1095
2	1155	4	2310
3	1287	9	3861
4	1350	16	5400
10	4887	30	12666

From the above tabulation, the following two equations are obtained:

$$4a + 10b = 4887$$

$$10a + 30b = 12666$$

Solving them by Cramer's rule:

$$a = \frac{\begin{vmatrix} 4887 & 10 \\ 12666 & 30 \end{vmatrix}}{\begin{vmatrix} 4 & 10 \\ 10 & 30 \end{vmatrix}} = 995.5$$

$$b = \frac{\begin{vmatrix} 4 & 4887 \\ 10 & 12666 \end{vmatrix}}{\begin{vmatrix} 4 & 10 \\ 10 & 30 \end{vmatrix}} = 89.7$$

Thus, the equation of the straight line becomes:

$$t = 995.5 + 89.7C$$

A check of the equation against the experimental points showed the equation to fit the points to within  $\pm 25^{\circ}\text{F}$ .

2. The exponential curve:

C	Log t	C <sup>2</sup>	C Log t
5	3.17667	25	15.88335
6	3.18696	36	19.12176
7	3.21032	49	22.47224
8	3.21854	64	25.74832
10	3.23096	100	32.30960
36	16.02345	274	115.53527

whence:

$$5a + 36b = 16.02345$$

$$36a + 274b = 115.53527$$

Solving the equations for a and b:

$$a = 3.12372$$

$$b = 0.01125$$

Therefore:

$$\text{Log } t = 3.12372 + 0.01125C$$

or,

$$t = 1330 \times 10^{0.01125C}$$

A check of the equation against the experimental points showed the equation to fit the points to within  $\pm 30^{\circ}\text{F}$ .

## NOMENCLATURE

- a = a constant.
- b = a constant.
- C = the number of carbon atoms in a molecule of normal alcohol.
- E = the energy of activation.
- k = the reaction rate constant.
- N = Avogadro's number.
- n = a constant.
- Q = the heat of reaction per gram-mole of product.
- Q<sup>1</sup> = the heat of reaction per molecule of product.
- q<sub>1</sub> = the amount of heat liberated per second by the reaction.
- q<sub>2</sub> = the amount of heat conducted away per second by the vessel walls.
- R = the universal gas constant.
- S = the wall area of the reaction vessel.
- T = absolute temperature.
- t = temperature in degrees Fahrenheit.
- v = the volume of the reaction vessel.
- w = the velocity of the reaction in the gaseous phase.
- X = the coefficient of heat conductivity.
- °F = degrees Fahrenheit.
- °R = degrees Rankine.

## VITA

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