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RESEARCH MEMORANDUM

VARIATION OF SPONTANEOUS IGNITION DELAYS WITH TEMPERATURE

AND COMPOSITION FOR PROPANE-OXYGEN-NITROGEN MIXTURES

AT ATMOSPHERIC PRESSURE

By Joseph L. Jackson and Richard S. Brokaw

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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SUMMARY

The ignition delays of propane-oxygen-nitrogen mixtures as a function of temperature and composition have been determined in a flow system. The variation of the ignition lag τ at constant temperature can be represented by the equation

$$1/\tau = k \left[C_3H_8\right] \left[O_2\right]^{1/4}$$

where k is a constant. The temperature dependence of this equation over the range investigated (525° to 740° C) is given within 30 percent by the empirical equation:

$$\tau \left[C_3H_8\right] \left[O_2\right]^{1/4} = 0.030 + 5.4\times10^{-9}\, e^{14,500/T}$$

with concentrations expressed as mole fractions and temperature as degrees Kelvin.

INTRODUCTION

Spontaneous ignition processes manifest themselves in many reactions that are studied under the general classification of combustion. These processes may be deleterious, as when they produce preignition in a reciprocating engine or create fires in the storing and handling of combustible materials, or they can be beneficial by serving as the ignition source in a diesel engine or promoting smoother burning in a turbojet combustor. Some of the thermal theories of flame propagation propose that a flame is propagated by virtue of continuous spontaneous ignition occurring on the leading edge of the flame front. In any combustion process where self-ignition can occur, the time lapse before the flame appears is an important factor. Since the time delay of ignition is an

inverse measure of the rate at which the reaction proceeds, a study of
the factors influencing the delays may provide information on the kine-
tics and mechanism that prevail in the ignition process. This paper
reports a study of the effect of temperature and fuel-oxidant ratio on
the ignition lag of propane.

One of the earliest and perhaps simplest types of apparatus for
spontaneous ignition work is the "drop method", a modification of which
has been chosen as the A.S.T.M. standard for the determination of auto-
genous ignition temperatures (ref. 1). This test determines the lowest
temperature of an air-filled cavity that will cause ignition when drops
of liquid fuel are introduced into it, with delays measured by a stop
watch. The results obtained by this method are markedly affected by the
size and shape of the cavity. A fuel-concentration gradient exists from
the bottom of the vessel, where evaporation takes place, to the opening
at the top where dilution with the ambient air occurs, while the tem-
perature may vary in like manner throughout the region. Although no
strict control of fuel-air ratio can be exercised, it was found in
previous work (ref. 2) that the amount of fuel generally has to be in-
creased to obtain ignition as the temperature is lowered. A calculation
of the fuel concentration from the size of the ignition vessel and the
number of drops of fuel indicates a mixture which may contain over 50
percent fuel at the minimum spontaneous ignition temperature.

With the aim of a better understanding of the combustion processes
in a reciprocating engine, several workers designed systems to determine
ignition temperatures and lags in rapid-compression machines. Much of
the work by this method was done at high pressure, with special emphasis
on conditions which produce cool flames and zones of nonignition. Dixon
and Crofts (ref. 3) reported that the ignition temperature of hydrogen-
air mixtures steadily increases with fuel concentration, while Jost
(ref. 4) reported that the lag of the first region is relatively inde-
pendent of fuel concentration for heptane-air mixtures. More recent
experiments, with isooctane (ref. 5), show minimum delays for stoichio-
metric compositions. In this type of apparatus, independent control of
temperature and pressure is difficult and the temperature and the pres-
sure at which ignition occurs may be quite different from those at which
the initiating reaction begins.

Work has been done in constant-volume or constant-pressure systems,
where premixed gases are admitted to heated vessels. The results of
different investigators are in many cases contradictory. For example,
in the book by Jost (ref. 6), a curve by Prettre on page 39 shows a mini-
mum in the ignition temperature - composition plot for CO-air mixtures at
about 25 percent fuel, while a curve by Bloch on page 41 gives a minimum
at about 70 percent CO. In the summary table on page 45 of this refer-
ence, it is noted that lower temperatures are generally reported for
richer mixtures of hydrocarbons, although Mason and Wheeler (ref. 7)

reported that a minimum temperature for methane-air mixtures was found at about 5 percent methane. Newitt and Thornes (ref. 8) found that the maximum rate of oxidation as measured by the rate of pressure increase in the ignition of propane was at about 55 volume percent fuel in oxygen.

In order to allow the combustibles to be preheated separately to the desired temperature, various flow systems have been employed. Dixon (ref. 9) used two concentric tubes with fuel flowing through the inner section and air or oxygen passing through the annulus. Heating was accomplished by winding resistance wire around the outside of the inner tube. With this type of apparatus Dykstra and Edgar (ref. 10) found a lowering of the ignition temperature with increasing fuel concentration for gasolines or octanes. On the other hand, for very lean mixtures Mullins (ref. 11) observed no effect of fuel concentration on the ignition lag when fuel was injected from a small port in the center of a large duct of heated air. In the work of Olson (ref. 12), where an attempt at rapid mixing was made, a definite shortening of the ignition lag with increasing heptane concentrations was noted.

The program reported in the present paper was started in an attempt to clarify the effect of fuel concentration on the ignition lag in particular, and with the hope of elucidating the chemistry of the ignition reaction. The initial results reported were run with propane-oxygen-nitrogen mixtures at atmospheric pressure and at temperatures from 525° to 740° C. A flow system has been chosen because it permits control of temperature and pressure from the time of mixture preparation until ignition occurs.

The reactants were preheated separately and were mixed at the desired temperature in a time very much shorter than the ignition lag. The reaction chamber was a 3-foot length of 25- or 50-millimeter Vycor tubing. Runs were made with 9.5, 20.9, and 39.5 percent oxygen in the oxygen-nitrogen mixtures with a wide range of fuel percentages.

APPARATUS AND PROCEDURE

For this research, an apparatus was desired which would accomplish the following:

(1) Preheat the gases, air, and combustibles separately to any predetermined temperature

(2) Mix the gases at this temperature in a time very much shorter than the ignition lag

(3) Provide a reaction volume with the predetermined temperature constant throughout the region where ignition can result

(4) Permit complete control over the fuel-air ratio

These requirements dictated a flow system; since none of the apparatus reported in the literature met these specifications, a new setup was designed, as shown in the schematic sketch of figure 1.

Fuel was supplied from a cylinder through a pressure regulator to a critical flow orifice. The size of the orifice and upstream pressure determined the flow rate. A three-way solenoid valve located just ahead of the test section normally by-passed into the exhaust line. When the valve was energized, the fuel was diverted into the mixer.

Air was supplied from the laboratory line through a pressure regulator and critical flow orifices to another three-way solenoid. This valve normally passed the air to the mixing chamber but exhausted into the room when energized. The air line could also be connected to cylinders containing various oxygen-nitrogen mixtures.

A drawing of the mixer is given in figure 2. Fuel and air were supplied to separate concentric chambers where temperature equilibrium was established with the system. The 16 holes drilled tangentially into the small inner cup were connected alternately with the two chambers. This inner cup was fitted with a thermocouple and had a volume of about 1 cubic centimeter. The temperature of the unit was controlled with a heating element and variable transformer.

From the inner cup the gases passed through a 3/16-inch hole and expanded to the wall of the tube through a diffuser fitted with 200-mesh stainless-steel screens to remove the swirl. The ignition zone consisted of a 25- or 50-millimeter Vycor tube 36 inches long (see fig. 1). The exhaust fitting at the top of the unit contained a movable thermocouple probe to check the temperature axially through the reaction volume. A constant temperature throughout the reaction volume was accomplished by wrapping resistance heaters in ascending sections on a metal tube surrounding the Vycor. Each section was individually controlled by a variable-voltage transformer. The original design had viewing windows in the outer insulating jacket and 3/4-inch slits on the metal tube which permitted visual observation to provide added information about phenomena occurring in the reaction chamber. Metal-to-glass seals were formed with compression fittings utilizing asbestos and talc as a packing medium at the mixer and exhaust couplings. Several runs were made with this feature to observe the ignition and subsequent events. However, it was decided to forego this feature in favor of a positive seal between the reaction vessel and the surroundings. This modification entailed the replacement of the metal tube by one without the viewing slits. The seals at the mixer and exhaust sections were then made with soft copper gaskets. Figure 2 shows this arrangement as well as the nozzle and screen adapters connecting the swirl cup to the 25- or 50-millimeter Vycor tubes. It was now possible to change the tube sizes without removing the insulating jacket. The results obtained were the same with either arrangement, suggesting that no appreciable leakage through the metal-to-glass seal occurred.

The bulk of the heat required was supplied by air from a 25-kilowatt electric heater. This air was injected upwards from a ring at the bottom of the chamber between the ignition tube and the insulating jacket (fig. 1) and exhausted by a collector ring at the top. The heating elements on the metal tube were adjusted to remove any temperature gradients. The pressure in the heating chamber was kept equal to that in the ignition section (atmospheric). The unit required 2 to 3 hours to establish a desired temperature in the mixer and throughout the reaction volume, but once established, it did not drift with time.

Ignition lags were measure by a photocell relay and electric timer or by a pressure recorder. When an ignition was indicated by both units, the results were identical. If the flame-to-background light intensity ratio was low (weak flames, or high-temperature operation), the photocell sometimes failed to indicate; whereas, the pressure recorder always responded. With either system, the timing cycle was started automatically on introduction of a combustible mixture into the mixer. Only the pressure recorder could be used after modification of the apparatus. In general, lags were reproducible within about ±5 percent.

The customary procedure was to set the air flow through the burner while bypassing the fuel to the exhaust. When constant-temperature conditions were reached, as indicated by the movable thermocouple probe, the fuel solenoid was energized, which diverted the flow to the mixer and started the electric timer and the recorder time-indicator. When the flame or pressure pulse appeared, the fuel valve was de-energized and the ignition delay recorded. Three or four runs were made before the fuel-air ratio was changed. A constant total flow of mixture was usually maintained for all points at a given temperature unless the delay time changed sufficiently to require a change in flow rate in order to keep the ignition within the center two thirds of the tube length.

The electrical connections were later changed to permit alternate procedures to be used. The first modification allowed the introduction of air into fuel rather than fuel into air. With either of these methods, a fuel-oxygen gradient existed within the interfacial region. In order to eliminate this concentration gradient, the second modification allowed metered nitrogen to be sent through a solenoid into the mixing cavity. In this way, all oxygen was swept out of the system. A single switch cut off the nitrogen flow, diverted fuel and air into the mixer, and started the time cycle. The fuel-oxygen ratio was thus kept the same in the interface as in the mixture.

RESULTS AND DISCUSSION

Ignition lags observed under a variety of experimental conditions are contained in tables I to IV. In the following sections, the effect of the individual variables on ignition lag will be examined.

Effect of Apparatus Parameters

Flow rate. - Runs in which ignition lags were determined at varying flow rates are contained in tables I and II. Results of a typical series of experiments are graphed in figure 3, and it is seen that the position of the minimum in the lag - flow rate plot shifts toward higher flow rates for richer mixtures. Investigations in which temperatures and tube size were varied suggested that these parameters do not affect the volumetric flow rate giving minimum lag.

Tube size. - Under comparable conditions of volumetric flow rate, fuel-air ratio, and temperature, lags observed in the 25-millimeter tube were on the average very slightly higher than in the 50-millimeter tube (e.g., see fig. 3). However, this difference was well within the experimental error, and in many cases the order was reversed. In obtaining the data of tables III and IV, an attempt was made to select flow rates such that the position of the ignition (as calculated from flow rate and ignition lag) was in the central two thirds of the tube. For the 50-millimeter tube, these conditions corresponded closely to the flow rates for minimum induction period; however, in the 25-millimeter tube, somewhat lower flows were employed and lags were correspondingly longer.

Mode of introduction of reactants. - As described in the experimental section, the apparatus was designed to permit introduction of fuel and air to the reaction tube in three different ways. Figure 4 shows typical pressure-time traces obtained by these methods; ignition is indicated by the first sharp rise in pressure. For some of the richer mixtures pressure pulses were very weak, so the recorder was used at maximum gain, as indicated in the figure.

In the first procedure, which was employed in all the runs of tables I to IV, the desired air flow through the ignition tube was first established. Next, propane was introduced, and the time required for appearance of a flame was determined. In this method the interfacial region between the leading air and the following fuel-air mixture must contain mixtures of all fuel-air ratios leaner than the one under investigation. Should any leaner mixture have a shorter lag, a spurious result might be obtained. Since richer mixtures had shorter lags by this method (see pressure-time traces of fig. 4), it was felt that the measurements were meaningful. However, to verify this point, a few experiments were performed with the order of air and fuel introduction reversed.

When the propane precedes the air, the interfacial region contains mixtures of higher fuel-air ratio only. If, as suggested previously, richer compositions have shorter delays, lags determined by this procedure (fuel lead) might be expected to correspond to the shortest lags measured in the alternate manner (air lead). In most cases, it was

impossible to make delay measurements when the fuel-lead method was em-
ployed, since there was no sharp appearance of flame or pressure pulse
marking ignition (e.g., see fig. 4; propane lead, 20 and 30 percent).
At fuel concentrations above 30 percent, no flames were observed, al-
though a definite temperature rise at the top of the tube indicated that
some reaction was taking place. With less fuel in the final mixture, a
luminous zone appeared shortly after air admission which became more
distinct as the interface passed up the tube (and the region near the
mixer became leaner) until finally a well defined flame was formed.
Presumably, the ignition reactions were started before an explosive
mixture (that is, a mixture capable of reacting rapidly enough to give
a sharp pressure pulse) entered the tube. In a few cases the delay
characteristic of the rich region was sufficiently long to permit an
explosive mixture to enter the tube during the induction period. In
these experiments lags observed were similar to those obtained for richer
mixtures by the air-lead method. (See 10-percent, propane-lead experi-
ment of fig. 4.) It appears, then, that the shorter delays observed by
the propane-lead method are characteristic of the richer interfacial
region rather than of the following fuel-air mixture.

In the third experimental method, a flow of nitrogen preceded both
reactants into the tube; propane and air were introduced and the nitrogen
was shut off simultaneously. Here fuel-oxidant ratio must be constant
through the interface, with nitrogen concentration as the only variable.
Lags observed with this technique have been recorded for many of the runs
in tables II to IV and it may be seen that, in general, ignition delays
were the same as lags obtained by the air-lead method. (Compare also
nitrogen and air-lead columns of fig. 4.) Nevertheless, close scrutiny
of the data reveals a trend of slightly shorter lags for mixtures leaner
than 15 percent fuel, and slightly longer delays at higher propane con-
centrations. Furthermore, at high flow rates, the nitrogen was not ade-
quately preheated so that some cooling of the system occurred, giving
rise to increased lags. However, the generally good agreement between
results of the nitrogen and air-lead methods indicates that measurements
by the latter technique are characteristic of the mixture rather than
the interface.

On the other hand, the nature of the interface has a marked effect
on the composition range over which ignition is observable. With an air
lead, sharp pressure pulses and flames were noted at all fuel-air ratios,
although the violence of the explosion decreased gradually as the propane
concentration increased. However, with a nitrogen lead the intensity of
the pressure pulse diminished rapidly with increasing fuel content, and,
in general, no pulse was detectable when the propane concentration ex-
ceeded 40 percent by volume. If the fuel flow was continued after igni-
tion, stationary flames were seated in the tube for mixtures containing
as much as 30 percent fuel in air.

These experiments indicate that the rate of the initiating reaction, as measured by the ignition delay, is characteristic of the regions of highest fuel-air ratio, even though a homogeneous mixture of the same fuel concentration may be incapable of supporting a flame. When a flammable mixture exists near a region of very high propane concentration (as in the case of air-lead experiments), it may be ignited by reactions initiated in the richer zone.

The phenomena obtaining in very rich mixtures appear to be analogous to those observed by Prettre (ref. 13) in studying the oxidation of pentane in a static system at 250° to 360° C. Three types of pressure-time curves were observed. One type was characterized by an induction period followed by explosion. In a second type, the induction period preceded an extremely rapid reaction, which did not, however, lead to ignition. Presumably, it was the lag for this type of reaction which was measured in the present investigation in the case of very rich propane mixtures with an air lead. The final type of curve observed by Prettre was one in which rate of pressure rise was slow through the entire course of the reaction.

Inasmuch as the air-lead method gave results comparable to those obtained with the nitrogen lead, it was employed in obtaining the data discussed in the following sections, since sharper indications of ignition were observed by this technique and better temperature control could be maintained at high flow rates (no cooling by the leading gas).

Effect of Propane Concentration

When only fuel-oxidant ratio was varied, ignition lags decreased with increasing propane concentration. Figure 5 shows typical logarithmic plots of ignition lag for propane-air mixtures against volume percent propane at various temperatures in 25- and 50-millimeter tubes. In general, these plots are linear, so that the dependence of ignition delay on propane concentration may be expressed by an equation of the type

$$1/\tau = \text{const}\left[C_3H_8\right]^n \tag{1}$$

where

τ the ignition lag, sec

$\left[C_3H_8\right]$ propane concentration

n a constant

The slopes of the straight lines (given by n in eq. (1)) lie between the extremes of 0.74 and 1.0, with an average of 0.93. For half the runs, the slopes are unity, and there does not seem to be any trend in the slope variations.

Effect of Oxygen Concentration

In order to determine the dependence of ignition lag on oxygen concentration, delays were obtained for mixtures in which the volume percent of propane was held constant while oxygen-nitrogen mixtures containing 9.5, 20.9 (air), and 39.5 percent oxygen were employed. In figure 6, ignition lag is plotted against $[O_2]/([O_2]+[N_2])$ for four different propane concentrations. It is seen that the dependence of ignition delay on the oxygen content of the oxygen-nitrogen mixture is slight, being somewhat more pronounced at the higher propane percentages. The dependence at constant fuel concentration is given approximately by

$$1/\tau = \text{const } [O_2]^{1/4} \qquad (2)$$

where $[O_2]$ is the mole fraction of oxygen in the total mixture, although an equation of the form

$$1/\tau = \text{const } [O_2]/\left(1 + k[O_2]\right)^2 \qquad (2a)$$

where k is a constant describes the results somewhat better, by implying a greater dependence of lag on oxygen concentration in richer mixtures. The constant k has a value of approximately 4 when concentrations are expressed as mole fractions.

Combining equations (1) and (2) results in

$$1/\tau = \text{const } [C_3H_8]^n [O_2]^{1/4} \qquad (3)$$

which should apply for variations of both fuel and oxygen concentration. In figure 7 data obtained in a 25-millimeter tube at 666° C are plotted according to equations (1) and (3), and it is seen that the latter equation, which accounts for the effect of varying oxygen concentration, fits the experimental data somewhat better.

Effect of Temperature

Ignition lags decreased with increasing temperature, as might be expected since chemical reaction rates are accelerated as temperature is raised. Data at constant temperature may be fairly well represented by

equation (3) with the exponent n taken as unity. The effect of tem-
perature on lag is illustrated in figure 8 in which the quantity
$\tau \left[C_3H_8 \right] \left[O_2 \right]^{1/4}$ is plotted against reciprocal temperature on semi-
logarithmic paper. The open symbols refer to the data of tables III
and IV; solid symbols are obtained from the shortest lags of tables I
and II. The nonlinearity of the plot illustrates the fact that the tem-
perature dependence is not of the simple Arrhenius type with a constant
activation energy. In lower-temperature ignition studies, two induction
periods are often observed: the first one for the appearance of cool
flames, followed by a second time lag to explosion. If the ignition lags
observed in this research are also the sum of two delays, then an Arr-
henius type of temperature dependence is not to be expected (see, for
example, ref. 14). Alternatively, the nonlinearity of figure 8 might
be a result of a change in mechanism with changing temperature, or may
perhaps be due to some effect of the apparatus.

The mean line of figure 8 is given by the empirical expression

$$\tau \left[C_3H_8 \right] \left[O_2 \right]^{1/4} = 0.030 + 5.4 \times 10^{-9} \, e^{14,500/T} \tag{4}$$

where concentrations are expressed as mole fractions, temperature in
degrees Kelvin, and ignition lag in seconds. This equation represents
the data within 30 percent.

Interpretation in Terms of Slow Reaction Kinetics

While the slow oxidation of propane has been the subject of con-
siderable research (refs. 8 and 15 to 18), most of this work has been
concerned with reaction rates and product analysis. The induction
period prior to the onset of rapid reaction has not been closely scru-
tinized; indeed, in many instances it has been deliberately altered
either by the addition of aldehydes or by treatment of vessel walls.
The ignition-delay measurements described in this report have been
carried out at higher temperatures (525° to 740° C) than can be employed
in slow oxidation (280° to 475° C) studies. Kinetic measurements have
not been made at higher temperatures since the induction period is
followed by explosion in which the reaction proceeds to completion with
a considerable temperature rise. Rates are, by present methods, im-
measurably high and analysis of final products cannot be expected to
yield information on reaction intermediates and thereby the chain of
reactions involved in the explosion.

In considering the events leading to the thermal ignition of
propane-oxygen-nitrogen mixtures an examination must therefore be made
of the reactions proposed to explain the products in the partial oxida-
tion of propane-oxygen mixtures at the highest temperature for which

measurements have been carried out. Satterfield and Wilson (ref. 19) suggest a scheme involving some 20 reactions in order to indicate the origin of all reaction products. The propyl radical is a key intermediate and may react with oxygen in two ways: (1) to form propylene and HO_2, and (2) to form oxygenated organic products. At 375° C, it is suggested that approximately 60 percent of the propyl radical - oxygen reaction proceeds by the first path; at 475° C this increases to 90 percent. For simplicity, then, the second mode of reaction will not be considered significant at the higher temperatures at which ignition lag measurements have been made.

In general, kinetic analysis of explosion phenomena has been concerned with the existence or nonexistence of a finite reaction rate (the steady state). Such considerations serve to define the conditions of temperature, pressure, and so forth under which explosion may occur, that is, the limits for spontaneous inflammation.

The ignition lag, on the other hand, is a measure of the time required to achieve the unsteady state (explosion). The kinetic scheme adopted must therefore be one in which no steady-state solution exists. The following reactions, selected from reference 19, can serve to explain, at least qualitatively, the ignition lags of this report.

$$C_3H_8 + O_2 \xrightarrow{k_1} C_3H_7 + HO_2 \tag{i}$$

$$C_3H_7 \xrightarrow{k_2} C_2H_4 + CH_3 \tag{ii}$$

$$C_3H_7 + O_2 \xrightarrow{k_3} C_3H_6 + HO_2 \tag{iii}$$

$$C_3H_8 + HO_2 \xrightarrow{k_4} C_3H_7 + H_2O_2 \tag{iv}$$

$$C_3H_8 + CH_3 \xrightarrow{k_5} C_3H_7 + CH_4 \tag{v}$$
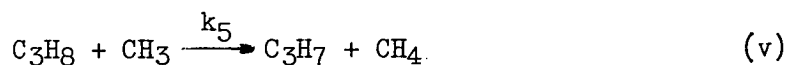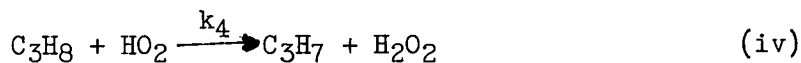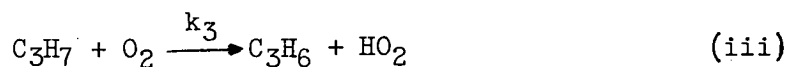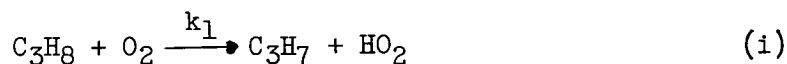
In this scheme, the initiating reaction is the only chain-branching step. The propyl and methyl radicals are highly reactive, so that a steady state in these species is assumed. (That is, the rate of production is equal to the rate of destruction.) On the other hand, the HO_2 radical is assumed to be chemically less active, so that its concentration builds up during the induction period. These considerations lead to the following expressions for the rates of change of propane and HO_2 concentration:

$$-\frac{d[C_3H_8]}{dt} = \left(1 + \frac{k_2}{k_3[O_2]}\right)\left(k_1 [C_3H_8] [O_2] + k_4 [C_3H_8] [HO_2]\right) \quad (5)$$

$$d[HO_2]/dt = 2k_1 [C_3H_8] [O_2] \quad (6)$$

Equation (6) is easily integrated if it is assumed that during the preignition period the propane and oxygen concentrations are substantially constant. Equation (5) becomes:

$$-\frac{1}{[C_3H_8]} \frac{d[C_3H_8]}{dt} = k_1\left(k_2/k_3 + [O_2]\right)\left(1 + 2k_4 [C_3H_8]t\right) \quad (7)$$

This equation describes the observed lags if it is assumed that $k_4 [C_3H_8] \gg 1$ and that ignition occurs when the fractional rate of propane consumption reaches a critical value characteristic for a given temperature and pressure. If this is so, then

$$\left(k_2/k_3 + [O_2]\right) [C_3H_8]\tau = \text{const} \quad (8)$$

The first assumption is reasonable since reaction (iv) is an exothermic radical reaction and therefore probably has a large rate constant. The postulate that a critical fractional rate of propane consumption is attained at the time of ignition is not so easily justified. However, if the explosion is thermal in origin (that is, if heat is generated by the slow reaction more quickly than it is dissipated by conduction to the surroundings so that temperature rises and, with it, reaction rates), it might be expected that more propane should be required to prereact in rich mixtures for the following reasons: First, in richer mixtures, initial reaction of propane to give cracked products (methane and ethylene) will occur more frequently relative to partial oxidation (to propylene and hydrogen peroxide). This may result in less heat generated per molecule of propane consumed. Second, for a given heat evolution, the resultant temperature rise will be lower at higher propane concentrations because of the higher heat capacity and thermal conductivity of rich mixtures.

The dependence of ignition lag on oxygen concentration as given by equation (8) is qualitatively correct if k_2/k_3 is of the order of unity. (e.g., if $k_2/k_3 = 1$ and $[O_2] \cong 0.2$, the variation would be $[O_2]^{1/6}$.) However, experimentally the effect of oxygen concentration was more pronounced for mixtures of low oxygen-nitrogen ratio (best described by eq. (2a), while eq. (8) predicts the opposite).

The variation of ignition lag with temperature should involve principally the energies of activation of reactions (i) and (ii). Reaction (i) is endothermic by roughly 50 kilocalories, so its activation energy must be at least that large. However, the observed variation of ignition delay with temperature is not compatable with such a high energy of activation, unless nonkinetic factors are playing a dominant role in the temperature effect.

Alternatively, the effect of propane and oxygen concentration on ignition delay might be explained in terms of initiation by means of a bimolecular surface reaction between propane and oxygen. If the induction period varies inversely with the initiation rate, then

$$1/\tau \propto \text{initiation rate} = k'\theta_{O_2}\;\theta_{C_3H_8} \qquad (9)$$

where θ_{O_2} and $\theta_{C_3H_8}$ are the fractions of the surface covered by oxygen and propane, respectively, and represent surface concentrations; k' is a constant. For monolayer adsorption on a homogeneous surface, with oxygen moderately adsorbed, θ_{O_2} is given by

$$\theta_{O_2} = \frac{k''p_{O_2}}{1 + k''p_{O_2}} = \frac{k[O_2]}{1 + k[O_2]} \qquad (10)$$

where p_{O_2} is the partial pressure of oxygen (see ref. 20). When the mole fraction of oxygen is used as a concentration unit, the constant of equation (10) is pressure-dependent. If propane is weakly adsorbed, its surface concentration will be proportional to its gas phase partial pressure and to the bare surface $(1 - \theta_{O_2})$.

$$\theta_{C_3H_8} = a(1 - \theta_{O_2})\,[C_3H_8] = \frac{a[C_3H_8]}{1 + k[O_2]} \qquad (11)$$

Substitution of (10) and (11) into equation (9) yields an expression for the ignition delay:

$$1/\tau \propto \frac{[O_2]\,[C_3H_8]}{\left(1 + k[O_2]\right)^2} \qquad (12)$$

Note that the dependence of lag on propane and oxygen concentration is as given in equations (1) and (2a), respectively.

It might at first appear surprising that lags observed in the 25- and 50-millimeter tubes are the same if a surface reaction is involved. This might be explained by the fact that while the smaller tube (with a larger surface-volume ratio) gives greater surface concentrations of reactants per unit volume of gas, the smaller tube also offers more surface per unit volume for the removal of heat or the destruction of chain carriers.

SUMMARY OF RESULTS

The variation of spontaneous ignition delays of propane with temperatures, fuel concentration, and oxygen concentration at atmospheric pressure has been studied in a flow system. The reactants were mixed in a time much shorter than the ignition lag at the temperature of the reaction chamber. Ignition delays were measured with a photocell relay and timer, or alternatively with a pressure recorder.

Ignition lags were found to be:

1. Inversely proportional to the 0.74 to 1.0 power of the propane concentration

2. Inversely proportional to approximately the 0.25 power of the oxygen concentration

3. Decreased by increasing temperature

4. Unaffected by changing tube size under comparable flow conditions. Over the range of temperatures investigated, ignition delays τ in seconds were given within 30 percent by the empirical relation

$$\tau \left[C_3H_8\right]\left[O_2\right]^{1/4} = 0.030 + 5.4 \times 10^{-9} \, e^{14,500/T}$$

with concentrations expressed as mole fractions and temperature T in degrees Kelvin.

Lewis Flight Propulsion Laboratory
        National Advisory Committee for Aeronautics
                Cleveland, Ohio, February 23, 1954

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TABLE I. - EFFECT OF FLOW RATE ON IGNITION DELAY AT VARIOUS TEMPERATURES AND OXYGEN

CONCENTRATIONS IN 25-MILLIMETER REACTION TUBE

Temperature, 560° C; date, 8/26/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
18	560	1.0	0.209	10	3.8
17	568	2.0			2.65
16	560	4.0			2.5
15	563	8.0			[a]14
19	560	8.0			12.0
20	560	16.0			6.2
14	560	16.0			8.0
1	560	.5		20	3.2
2	558	1.0			2.7
3	557	2.0			2.05
4	566	4.0			1.55
7	560	4.0			1.6
5	557	8.0			1.7
6	560	16.0			4.4
11	560	.5		40	1.61
10	560	1.0			1.19
9	557	2.0			.94
8	566	4.0			.78
12	563	8.0			.96
13	566	16.0			1.06

Temperature, 629° C; date, 9/20/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
9	632	2.0	0.209	5	2.44
8	632	4.0			1.90
7	632	8.0			1.93
6	632	16.0			3.96
1	638	1.0		10	1.74
2	632	2.0			1.29
3	632	4.0			1.04
4	632	8.0			1.04
5	632	16.0			1.37
19	632	2.0		20	.74
10	632	2.0			.714
11	632	4.0			.549
12	629	9.0			.502
18	632	9.0			.53
17	629	16.0			.62
13	629	16.0			.596
16	627	4.0		40	.344
15	624	8.0			.313
14	632	15.0			.290
21	627	2.0	.095	10	1.79
22	627	4.0		10	1.53
20	627	4.0		20	.90

Temperature, 685° C; date, 9/1/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
1	685	1.0	0.209	20	0.52
2	682	1.0			.50
3	685	2.0			.46
4	688	4.0			.38
5	682	8.0			.35
6	682	16.0			.40
7	679	32.0			.53
8		32.0		10	[b]1.24

Temperature, 685° C; date, 9/9/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
13	685	0.5	0.209	10	0.57
12	685	1.0			.51
11	688	2.0			.57
10	682	4.0			.66
9	690	8.0			.70
8	690	16.0			.77
7	688	32.0			1.18
1	685	1.0		20	.48
2	685	2.0			.46
3	690	4.0			.38
4	688	8.0			.35
5	685	16.0			.40
6	690	32.0			.52
14	685	1.0		40	.25
15	682	2.0			.17
16	688	4.0			.16
17	688	8.0			.18
18	685	16.0			.18

Temperature, 743° C; date, 9/21/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
10	741	2.0	0.209	5	[c]>30
8	741	4.0			1.16
9	741	8.0			1.22
7	746	8.0			[d]1.24
6	743	16.0			1.47
1	743	1.0		10	[e]>30
2	743	2.0			[f]10.7
3	738	4.0			7.7
4	749	8.0			.580
5	743	16.0			.629
11	743	2.0		20	[e]>30
12	741	4.0			.291
13	743	9.0			.295
14	743	16.0			.378
17	743	4.0		40	.128
16	743	8.0			.096
15	749	15.0			.098
22	746	1.0	.095	10	.68
18	735	2.0		20	.397
19	746	4.0			.437
20	746	9.0			.421
21	738	16.0			.493
23	743	1.0	.395		[g].45
24	746	2.0			[h].26
25	743	4.0			.214
26	743	9.0			.226
27	743	16.0			.307

[a] Temperature rise, in 2.7 sec.
[b] Mixer heater burned out.
[c] No ignition.
[d] May be too long.
[e] No pressure pulse; temperature rise in mixer.
[f] Small temperature rise in mixer.
[g] Flash in mixer.
[h] Weak pulse; strong at 0.64 sec.

TABLE II. – EFFECT OF FLOW RATE ON IGNITION DELAY AT VARIOUS TEMPERATURES IN 50-MILLIMETER REACTION TUBE

Temperature, 529° C; date, 9/24/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay, sec — Air lead	Ignition delay, sec — N_2 lead
7	532	1.16	0.209	5	18.2	
6	529	2.0			a22.8	
5	527	4.0			b35.2	
8	532	.6		10	14.8	
1	529	1.0			11.0	
2	529	2.0			9.0	
3	524	4.0			8.8	
4	527	8.0			c>30	
9	527	.5		20	8.7	
10	524	1.0			7.0	
11	529	2.0			6.2	
12	529	4.0			5.2	
13	529	9.0			4.7	
14	527	16.0			d>40	
19	532	1.0		40	3.3	
18	529	2.0			2.3	
17	529	4.0			2.3	
16	535	8.0			2.45	
15	521	16.0			3.2	
20	527	1.5		80	2.2	
21	527	2.0			1.9	
22	532	4.0			1.77	
23	532	8.0			1.52	

Temperature, 577° C; date, 8/17/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay, sec — Air lead	Ignition delay, sec — N_2 lead
4	579	1.0	0.209	10	2.87	2.43
3	574	2.0			2.50	2.45
2	577	4.0			1.99	2.36
9	577	4.0			1.74	2.18
5	582	8.0			1.99	2.32
6	585	16.0			2.18	2.40
8	582	32.0			2.30	2.62
7	582	28.7		11.1	1.99	2.28
12	574	1.0		20	1.91	1.83
11	574	2.0			1.28	1.41
10	577	4.0			1.02	1.34
1	574	4.0			1.11	
16	574	4.0			1.07	1.41
13	579	8.0			.87	1.31
14	574	16.0			1.07	1.36
15	579	32.0			1.15	1.34
19	577	1.0		40	1.19	
18	577	2.0			.91	
17	574	4.0			.72	.83
22	574	4.0			.72	
20	574	8.0			.62	
21	574	16.0			.59	

Temperature[e], 632° C; date, 9/16/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
10	632	1.0	0.209	5	2.15
9	632	2.0			1.87
8	630	4.0			1.71
7	635	8.0			2.06
6	632	16.0			2.33
1	630	1.0		10	2.19
2	630	2.0			1.41
3	632	4.0			1.01
4	627	8.0			.99
5	632	16.0			1.15
11	632	1.0		20	1.04
12	632	2.0			.78
13	632	4.0			.60
14	632	8.0			.50
15	632	9.0			.50
16	632	16.0			.55
17	632	32.0			.76
21	632	2.0		40	.481
20	632	4.0			.359
19	632	8.0			.281
18	632	15.0			.256

Temperature, 685° C; date, 9/2/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
10	690	2.0	0.209	2.5	2.0
11	682	4.0			2.4
12	685	10.0			2.5
13	688	20.0			3.6
3	688	2.0		10	.70
2	688	4.0			.60
8	685	4.0			.64
7	690	10.0			.67
1	685	10.0			.68
5	688	20.0			.85
6	696	35.0			1.14
19	685	1.0		20	.61
18	682	2.0			.434
20	685	4.0			.42
21	685	8.0			.36
22	685	16.0			.40
23	685	32.0			.52
4	685	.4		25	.60
9	685	.4			f.53
17	685	2.0		40	.275
16	685	4.0			.243
14	688	16.0		47	.180
15	688	9.1			.177

Temperature, 740° C; date, 9/14/53

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay with air lead, sec
12	746	2.0	0.209	5	1.8
13	743	4.0			1.14
14	738	8.0			1.05
15	743	16.0			1.11
16	743	32.0			1.97
11	746	1.0		10	1.45
10	738	2.0			.85
9	740	4.0			.540
8	738	8.0			.498
7	738	16.0			.62
6	746	32.0			.90
1	740	1.0		20	g.59
2	743	2.0			g.30
3	743	4.0			.24
4	743	8.0			.28
5	746	16.0			.39
18	743	6.4		25	.21
20	738	4.0		40	.131
19	738	8.0			.107
17	743	14.0			.088

aTemperature rise before ignition, 10° to 30° C.

bTemperature rise, 30° C; pulse after shut off. Only one ignition.

cTemperature rise, 20° C.

dTemperature rise, 25° C.

eNumber 6 heater out, reducing tube length to 23 in.

fTemperature rise in mixer.

gNo sharp pressure pulses.

TABLE III. - EFFECT OF TEMPERATURE AND OXYGEN CONCENTRATION ON IGNITION DELAY IN

25-MILLIMETER REACTION TUBE

Left panel

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay, sec — Air lead	N2 lead
Temperature, 546° C; date, 3/3/53						
6	549	1.0	0.209	7.5	6.6	6.5
7	549	2.0		7.5	7.9	8.2
5	546	1.0		10	6.0	5.9
4	543	1.0		15	4.28	4.3
3	546	2.0		15	3.39	3.35
8	546	2.0		15	4.32	
2	543	2.0		20	2.57	2.63
1	543	2.0		30	1.93	1.94
9	546	2.0		30	2.12	
10	546	2.0		40	1.59	1.64
11	546	2.0		50	1.25	1.28
12	546	2.0		75	.97	
Temperature, 554° C; date, 6/30/53						
5	557	1.0	0.209	6	8.3	8.2
4	557	1.0		7.5	5.3	4.7
3	554	1.0		10	4.2	3.8
12	554	2.0		10	4.0	3.8
2	551	1.0		15	3.3	2.8
1	549	1.0		20	2.7	2.5
6	554	1.0		20	2.5	2.4
7	554	2.0		20	2.1	2.0
8	554	2.0		30	1.50	1.40
9	554	2.0		40	1.21	1.20
10	554	2.0		60	.91	1.0
11	554	2.0		80	.80	
Temperature, 563° C; date, 4/23/53						
11	563	1.0	0.209	5.5	6.4	4.7
10	563	1.0		7.5	5.3	4.4
9	566	2.0		7.5	4.5	4.3
12	566	1.0		10	4.1	4.0
8	566	2.0		10	3.20	3.22
17	563	2.0		10	4.3	
25	566	2.0		10	4.4	
7	566	2.0		15	2.35	2.32
13	568	1.0		20	2.32	2.24
14	563	2.0		20	1.92	
1	563	2.0		20	1.98	2.08
6	566	2.0		20	1.91	
2	563	2.0		30	1.51	
3	566	2.0		40	1.18	1.24
4	566	2.0		60	.92	1.02
5	563	2.0		80	.81	
23	568	2.0	.095	10	4.7	
22	568	2.0		20	[a]2.39	
21	568	2.0		40	[b]1.27	2.30
16	563	2.0	.395	10	5.1	
18	563	2.0		10	4.8	5.2
24	568	2.0		10	4.9	
15	563	2.0		20	1.98	1.80
19	563	2.0		40	1.07	1.08
20	563	2.0		80	.68	
Temperature, 568° C; date, 4/7/53						
4	568	1.0	0.209	15	2.11	2.16
1	568	1.0		20	1.60	1.61
2	568	1.0		25	1.26	1.25
3	568	1.0		30	1.06	1.07
Temperature, 579° C						
20	582	2.0	0.209	8	3.06	3.10
14	577	2.0		8.3	2.82	2.88
19	582	2.0		10	2.33	2.40
18	582	2.0		12.5	1.88	1.93
17	582	2.0		15	1.50	1.60
16	579	2.0		20	1.21	1.29
13	577	.50		25	1.52	
15	579	2.0		30	.83	.90
Temperature, 593° C; date, 7/2/53						
12	593	2.0	0.209	5	3.4	
11	593	2.0		7.5	2.67	2.40
10	593	2.0		10	2.01	1.87
9	596	2.0		15	1.33	1.32
1	593	2.0		20	1.12	1.24
7	593	2.0		20	[c].98	
8	593	2.0		20	[d]1.05	1.20
13	596	2.0		20	1.05	
24	596	2.0		20	1.03	
2	593	2.0		30	.76	.70
3	593	2.0		40	.57	.60
4	593	2.0		60	.46	
5	593	2.0		80	.43	
16	593	2.0	.095	5	3.7	2.6
15	593	2.0		10	2.14	
14	593	2.0		20	1.31	
17	596	2.0		40	.95	
23	596	2.0	.395	5	3.4	
22	593	2.0		10	1.96	
21	593	2.0		20	.96	
18	593	2.0		40	.43	
20	599	2.0		60	.40	

Right panel

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay, sec — Air lead	N2 lead
Temperature[e], 593° C; date, 6/28/53						
1	593	2.0	0.209	20	1.21	1.26
2	593	2.0		30	.89	.92
3	593	2.0		40	.71	.72
4	593	2.0		60	.56	
Temperature, 621° C; date, 5/15/53						
7	624	2.0	0.209	3	3.2	2.9
6	624	2.0		5	2.54	2.04
5	621	2.0		7.5	1.58	1.50
4	621	2.0		7.5	1.74	1.56
3	621	2.0		10	1.36	1.44
8	621	2.0		10	1.44	
20	621	2.0		10	1.23	
2	621	2.0		15	.99	.90
1	621	2.0		20	.79	.70
9	621	2.0		20	.77	
10	621	2.0		30	.54	[f].58
11	621	2.0		40	.44	.48
19	621	2.0		40	.44	
14	621	2.0	.095	10	1.66	1.56
13	621	2.0		20	[g].90	
12	621	2.0		40	[h].48	
15	621	2.0	.395	10	1.17	1.03
16	624	2.0		20	.79	.68
17	624	2.0		33.3	.48	.66
18	624	2.0		40	.36	.38
Temperature, 666° C; date, 4/14/53						
8	666	2.0	0.209	2.5	2.46	2.00
7	666	2.0		3.5	2.01	1.76
6	663	4.0		3.5	2.22	2.00
5	663	4.0		5	1.62	1.30
23	666	4.0		5	1.46	
4	663	4.0		7.5	1.13	.96
3	663	4.0		10	.88	.70
9	666	2.0		10	.87	.94
2	663	4.0		15	.644	.55
1	663	4.0		20	.502	.47
10	666	4.0		20	.481	.47
11	666	4.0		30	.344	.34
12	666	4.0		40	.288	.30
22	666	4.0		40	.282	
13	666	4.0		50	.235	
18	666	4.0	.095	5	1.84	
19	666	4.0		10	1.07	
20	666	4.0		20	.614	
21	666	4.0		40	.429	
17	666	4.0	.395	5	1.45	
16	666	4.0		10	.78	
15	666	4.0		20	.424	
14	668	4.0		40	.247	
Temperature, 679° C; date, 6/29/53						
5	682	4.0	0.209	5	1.55	1.10
4	679	4.0		7.5	1.02	.74
3	677	4.0		10	.78	.53
2	677	4.0		15	.53	.46
1	674	4.0		20	.43	.46
6	679	4.0		20	.40	.43
8	677	2.0		20	.48	
7	682	6.0		40	.23	
Temperature, 685° C; date, 6/29/53						
7	685	2.5	0.209	2.5	3.8	3.2
6	688	2.5		5	1.61	1.45
5	685	2.5		10	.88	.82
4	685	8.0		10	.92	1.04
3	685	8.0		15	.63	.68
2	682	8.0		20	.455	.49
1	679	7.75		25	.376	.44
9	685	2.50		25	.409	.38
10	685	6.0		25	.380	.47
11	685	6.0		30	.316	.34
12	685	5.0		40	.249	
13	685	4.0		50	.227	
14	685	2.66		75	.257	
Temperature, 738° C; date, 4/21/53						
5	738	4.0	0.209	5	1.10	
4	735	4.0		7.5	.75	
3	732	4.0		10	.582	0.39
2	732	4.0		15	.354	.30
1	732	4.0		20	.291	.32
6	738	4.0		20	.281	
9	738	4.0		20	.294	
8	738	6.0		20	.328	
7	738	8.0		20	.418	
12	738	4.0	.095	5	1.12	
11	738	4.0		10	.69	
10	738	4.0		20	.404	
14	738	4.0	.395	5	.97	
13	738	4.0		10	.490	
15	738	4.0		20	.243	

[a] First pulse weak; second at 2.80.

[b] First pulse weak; second at 1.73.

[c] Run immediately after extremely rich trial; may be in error because of soot on tube.

[d] Run 20 minutes after above.

[e] Discovered after 4 runs that 25-mm. tube was broken; not known how long it had been so.

[f] On N2 lead; no visible flash but definite pressure pulse.

[g] First pulse weak; second at 1.04.

[h] First pulse weak; second at 0.68.

TABLE IV. – EFFECT OF TEMPERATURE AND OXYGEN CONCENTRATION ON IGNITION DELAY IN 50-MILLIMETER REACTION TUBE

Run	Temperature, °C	Total flow rate, l/min	$O_2/(O_2+N_2)$ (by vol.)	Volume percent propane	Ignition delay, sec — Air lead	Ignition delay, sec — N_2 lead
Temperature, 521 °C; date, 10/10/52						
10	524	5.0	0.209	9	12.0	
9	521	5.0		11	7.0	
11	527	5.0		12.5	5.7	
8	521	5.0		15	4.8	
15	527	1.0		15	11.1	
7	521	5.0		20	3.80	
6	521	5.0		24.6	3.20	
1	516	25.0		25	>30	
14	529	1.0		25	5.07	
12	527	5.0		40	2.01	
13	527	1.0		40	3.27	
2	516	25.0		40	>30	
3	516	25.0		52	>30	
4	518	10.0		55	1.70	
5	518	10.0	↓	70	1.35	
Temperature[a], 538° C; date, 1/20/53						
13	546	2.5	0.209	6	7.5	
11	543	5.0		6	7.8	
1	527	5.0		9	8.8	
2	535	5.0		11	5.35	
10	543	5.0		11	3.20	
12	543	2.65		11.2	3.51	
3	532	5.0		12.5	[b]4.55	
4	532	5.0		15	[b]2.97	
5	538	5.0		17.5	[b]2.45	
6	540	4.87		18	[c]2.20	
7	540	5.0		20	[c]1.75	
8	543	5.0		25	[c]1.45	
9	546	5.0	↓	30	[c]1.21	
Temperature, 554° C; date, 7/5/53						
6	554	4.0	0.209	3.75	9.0	8.4
5	554	4.0		5	6.8	6.5
4	554	4.0		7.5	4.6	5.4
3	554	4.0		10	4.0	3.5
7	554	4.0		10	3.2	
2	554	4.0		15	2.24	2.50
1	551	4.0		20	1.76	2.04
8	554	4.0		20	1.60	1.92
14	554	4.0		20	1.55	1.76
23	554	4.0		20	1.54	
9	554	4.0		30	1.18	1.40
10	554	4.0		40	.97	1.06
11	557	15.0		40	.88	1.08
12	557	15.0		60	.65	
13	557	15.0	↓	80	.59	
22	554	4.0	.095	5	6.3	
21	554	4.0		10	3.5	
20	554	4.0	↓	20	[d]1.76	
19	554	4.0		40	[e]1.08	
17	554	4.0	.395	5	5.9	
16	554	4.0		10	2.8	
15	554	4.0		20	1.42	1.76
18	554	4.0	↓	40	.84	1.04
Temperature, 607° C; date, 7/7/53						
9	607	10.4	0.209	1.25	[f]8.8	14
8	610	7.4		1.75	5.7	
7	607	5.22		2.50	4.3	
6	607	3.8		3.75	3.1	
5	607	3.8		5	2.4	
4	610	4.0		7.5	1.70	
3	607	4.0		10	1.21	
2	607	4.0		15	.87	
1	607	4.0		20	.74	
10	607	4.0		20	.67	.68
15	607	4.0		20	.67	.76
24	610	4.0		20	.63	
30	607	4.0		20	.64	
11	610	30.0		21.6	.66	
12	607	30.0		32.1	.41	
13	607	30.0		42.3	.36	
14	607	30.0	↓	62.3	.28	
19	607	5.2	.095	2.5	4.6	4.8
18	607	4.0		5	2.5	2.6
17	610	4.0		10	1.43	1.50
16	607	4.0	↓	20	.93	.94
20	607	5.2	.395	2.5	3.3	
21	610	4.0		5	1.90	1.78
22	607	4.0		10	1.03	
23	607	4.0	↓	20	.57	.58
Temperature[g], 613° C; date, 10/17/52						
1	610	10.0	0.209	1.5	6.45	
2	610	10.0		3	3.6	
3	610	10.0		6	2.05	
4	613	10.0		10	1.22	
5	613	10.0		15	.92	
6	616	10.0		22.5	[h].63	
7	616	10.0		60	[i]1.32	
8	616	10.0		80	[j].27	
9	618	10.0	↓	90	[j].26	
Temperature, 624° C; date, 10/2/52						
13	621	10.0	0.209	1.5	[k]6.6	
14	621	10.0		2	[k]5.1	
15	627	10.0		3	[k]3.4	
6	618	5.0		3	3.8	
7	627	10.0		5	1.95	
16	627	10.0		6	[k]1.8	
8	621	5.0		7	1.33	
19	624	2.0		7	[k]4.10	
1	599	2.0		7	2.62	
2	602	2.0		8.5	1.92	
3	607	2.0		10	1.99	
17	624	10.0		10	[k]1.04	
4	610	2.0		12.5	1.58	
9	621	5.0		12.5	.81	
5	616	2.0		15	1.14	
10	624	5.0		15	.75	
18	627	10.0		15	[k].75	
11	624	5.0		20	[k].5	
12	624	5.0	↓	30	[k].4	
Temperature, 679° C; date, 7/9/53						
10		10.8	0.209	1.25	6.5	8.3
9	682	9.0		1.75	[l]3.9	6.7
8	682	6.0		2.50	[m]2.2	4.5
7	682	9.0		2.50	[n]2.7	4.6
6	679	9.0		3.75	1.91	2.90
5	679	9.0		5	1.39	2.32
4	679	12.0		7.5	1.02	1.64
3	679	12.0		10	.76	1.20
2	679	12.0		15	.52	.80
1	679	12.0		20	.40	.56
17	679	12.0		20	.37	
26	679	12.0		20	.38	
11	682	12.0		20	.38	
12	682	30.0		20	.46	
13	679	30.0		30	.21	
14	682	30.0		40	.10	
16	679	30.0		40	..11	
15	677	30.0	↓	60	.10	
22	679	9.0	.095	2.5	3.3	
23	677	9.0		5	1.76	
24	677	12.0		10	1.00	
25	677	12.0	↓	20	.50	
21	673	9.0	.395	2.5	2.9	
20	679	9.0		5	1.50	
19	677	12.0		10	.72	
18	679	12.0	↓	20	.36	
Temperature, 738° C; date, 7/10/53						
9	735	11.5	0.209	3.75	[o]1.66	
8	735	11.6		5	[p]1.30	
7	738	11.9		7.5	.90	
6	738	12.0		10	.69	
5	738	12.0		15	.42	
4	735	12.0		20	.32	
10	735	12.0		20	.29	
1	740	30.0		20	.35	
2	738	30.0		30	.19	
3	738	30.0	↓	40	.11	

[a]Poor temperature control in this set.
[b]Persistent flame.
[c]Very faint blue flame seated, 4 in. above mixer.
[d]First pip weak; second at 2.19 sec.
[e]First pip weak; second at 1.80 sec.
[f]First pip weak; second at 11.0 air lead; 16.0 N_2 lead.
[g]On this set, photocell did not detect some flames that were visible to the eye.
[h]Instantaneous temperature rise, 250° C.
[i]Small instantaneous temperature rise.
[j]No instantaneous temperature rise.
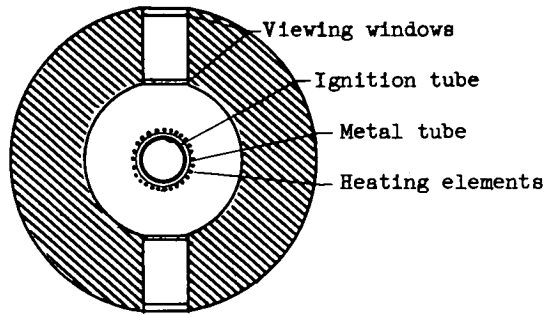[k]Photocell failed; manual shut-off of timer.
[l]First pip weak; second at 4.5 air lead; 7.2 N_2 lead.
[m]First pip weak; second at 2.6 air lead; 4.8 N_2 lead.
[n]First pip weak; second at 3.1 air lead; 5.0 N_2 lead.
[o]First pip weak; second at 1.86.
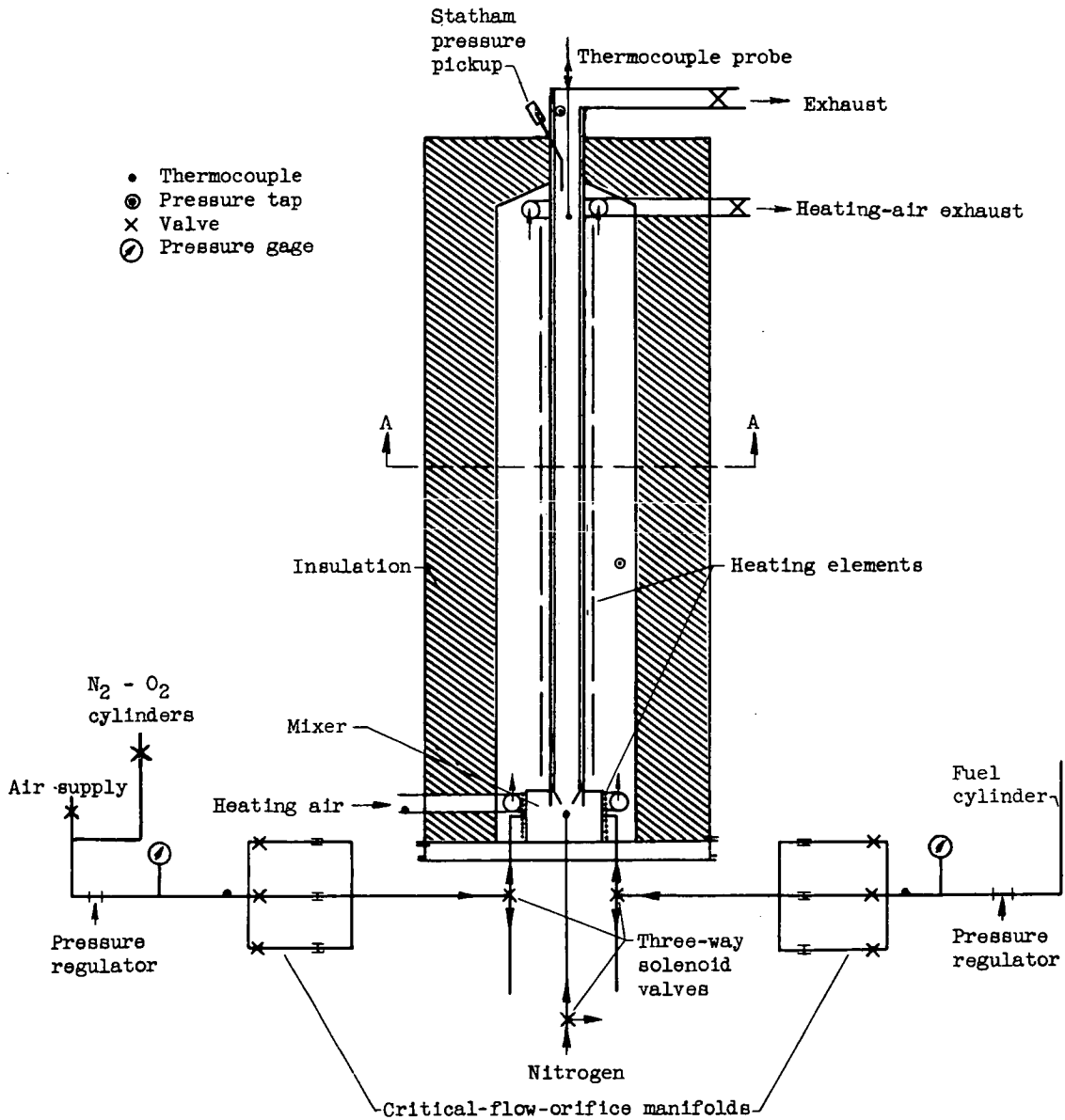[p]First pip weak; second at 1.50.

Figure 1. - Schematic drawing of spontaneous ignition apparatus.
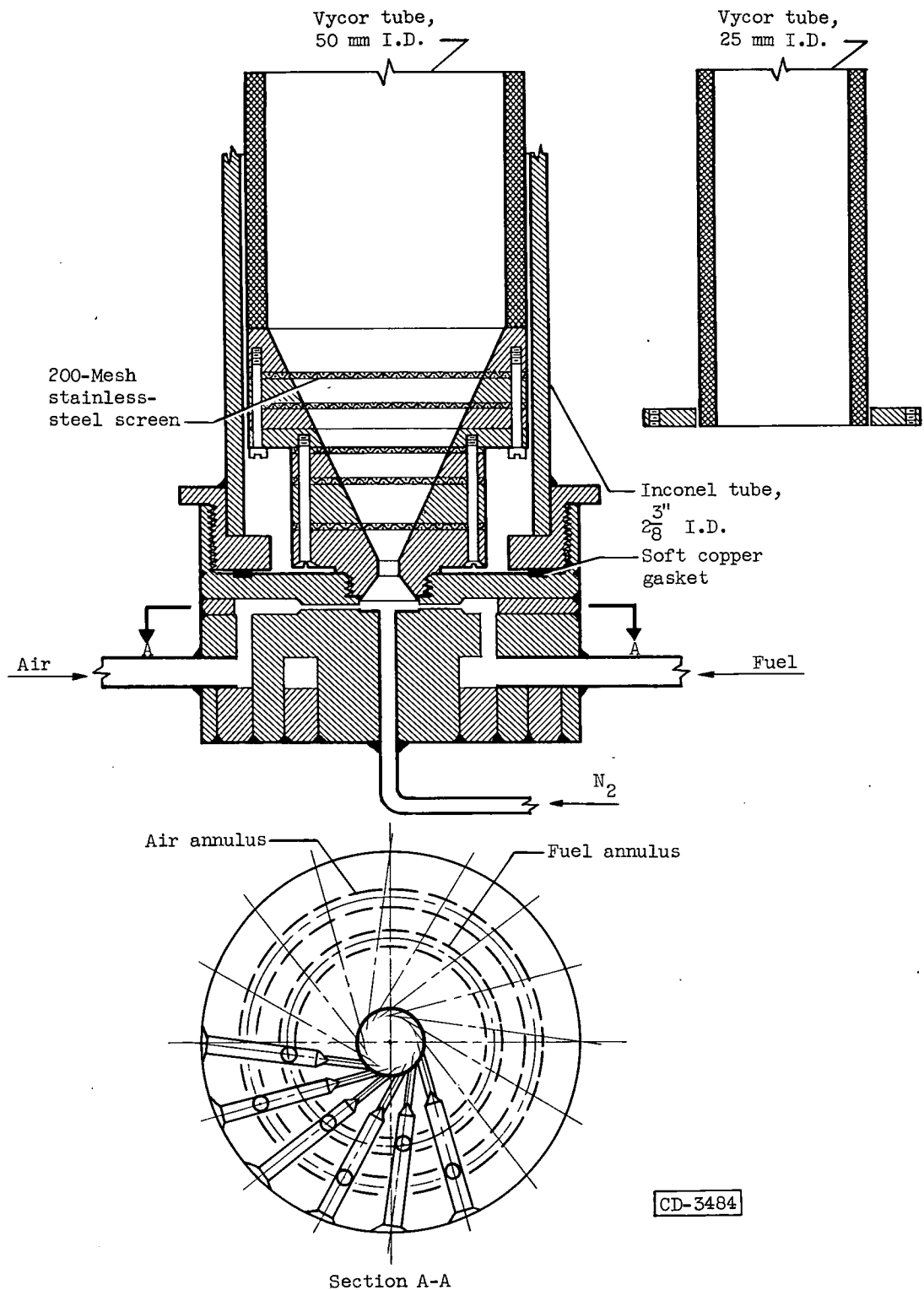
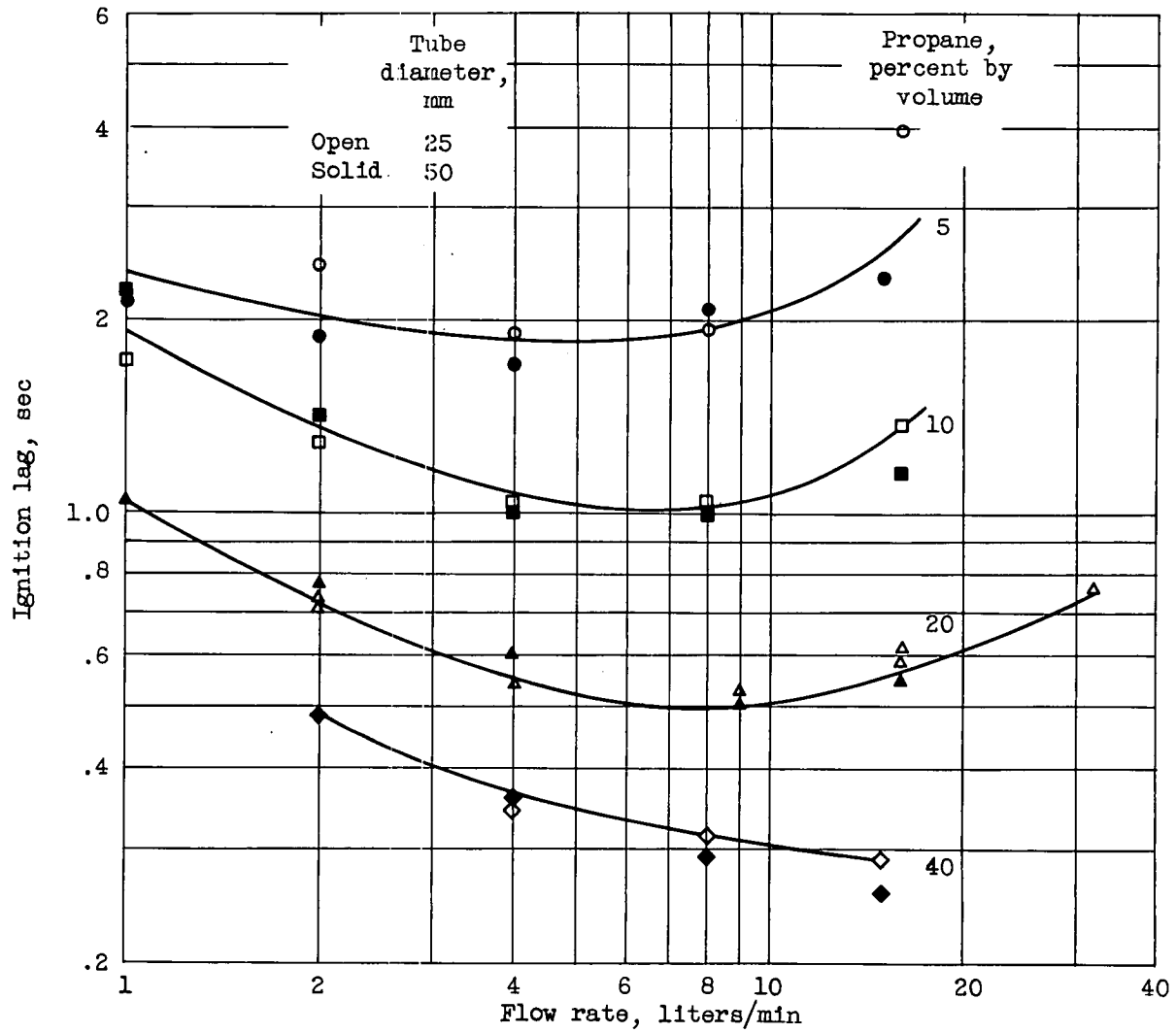Figure 2. - Mixing chamber for spontaneous ignition apparatus.

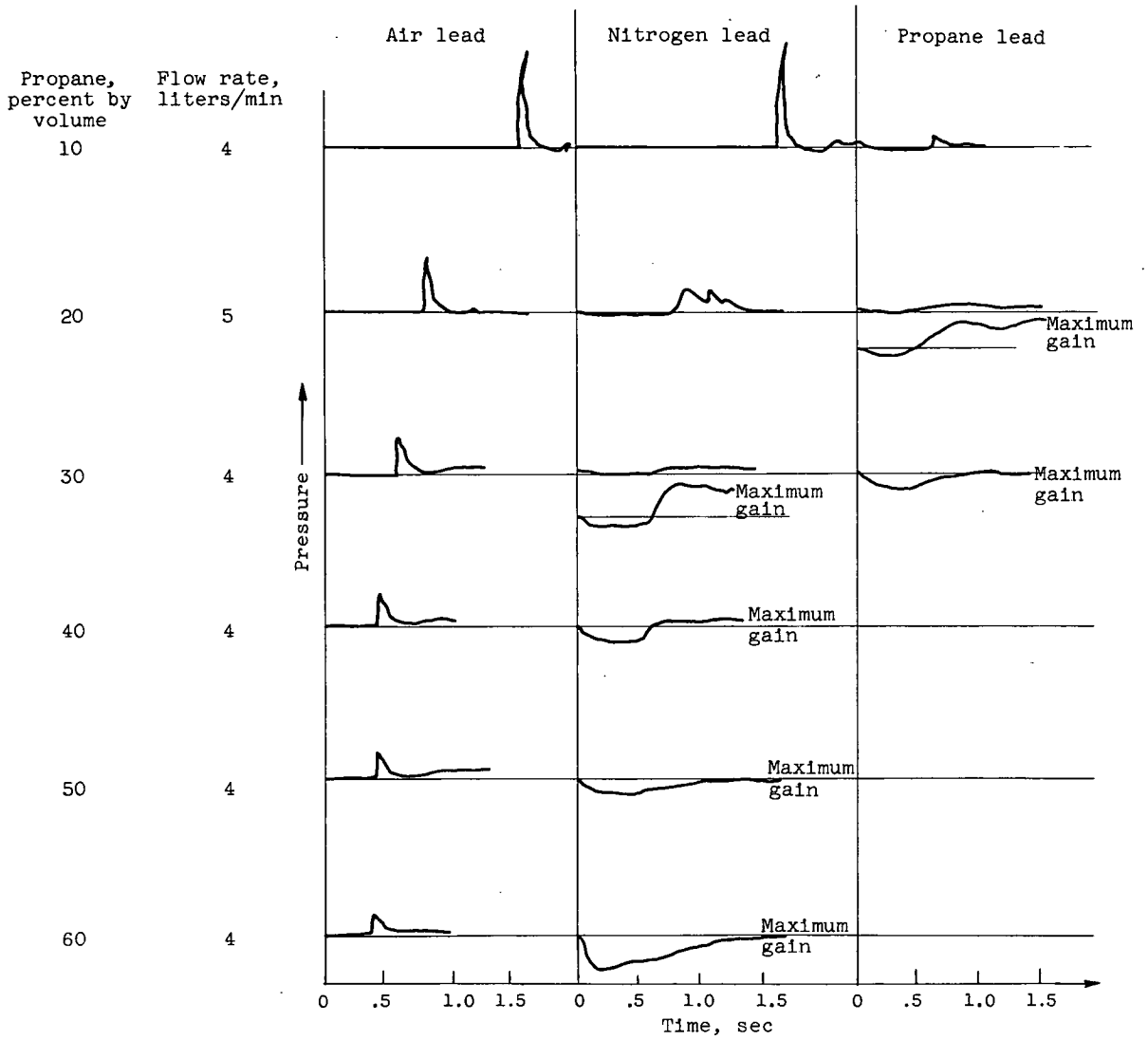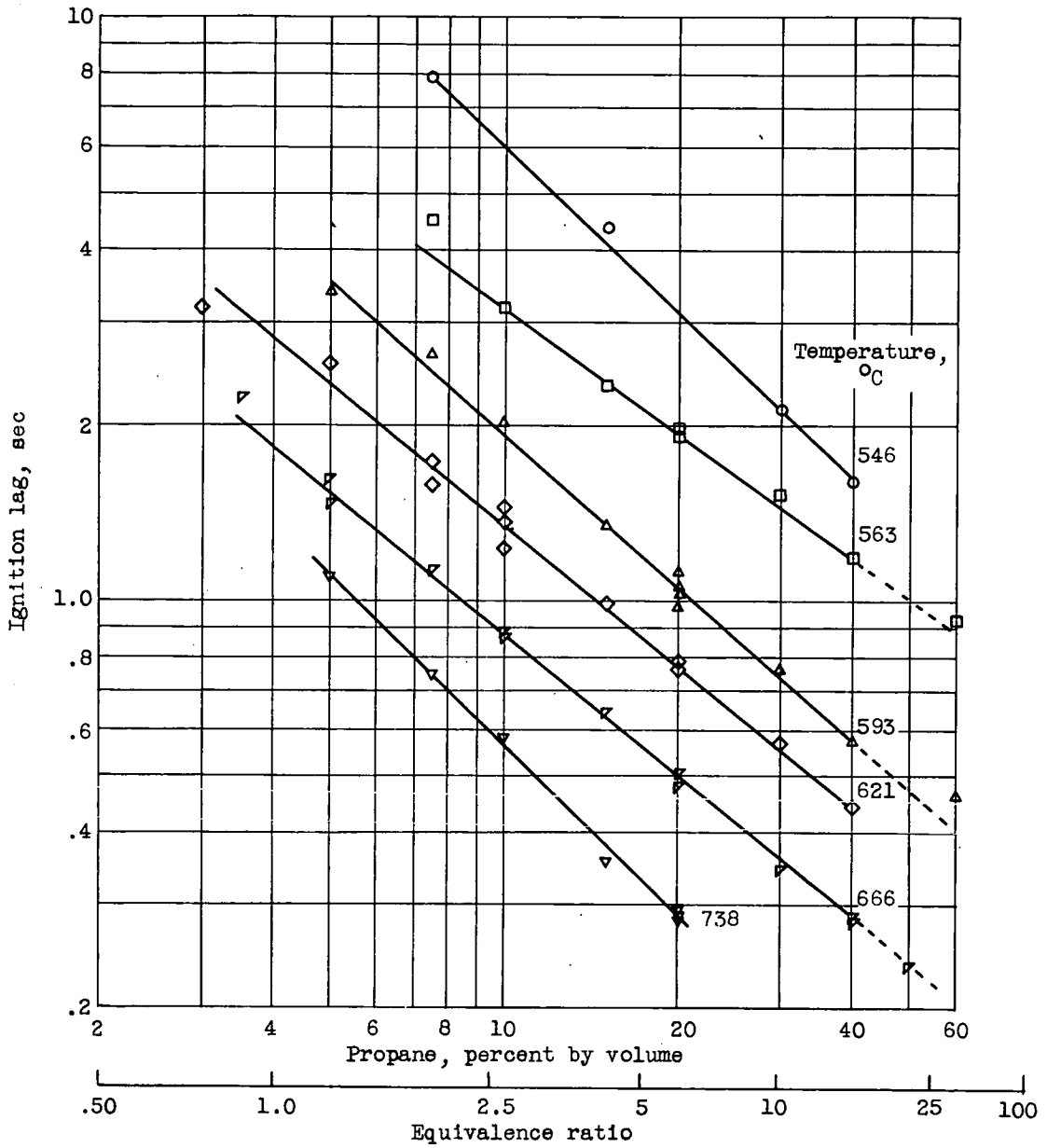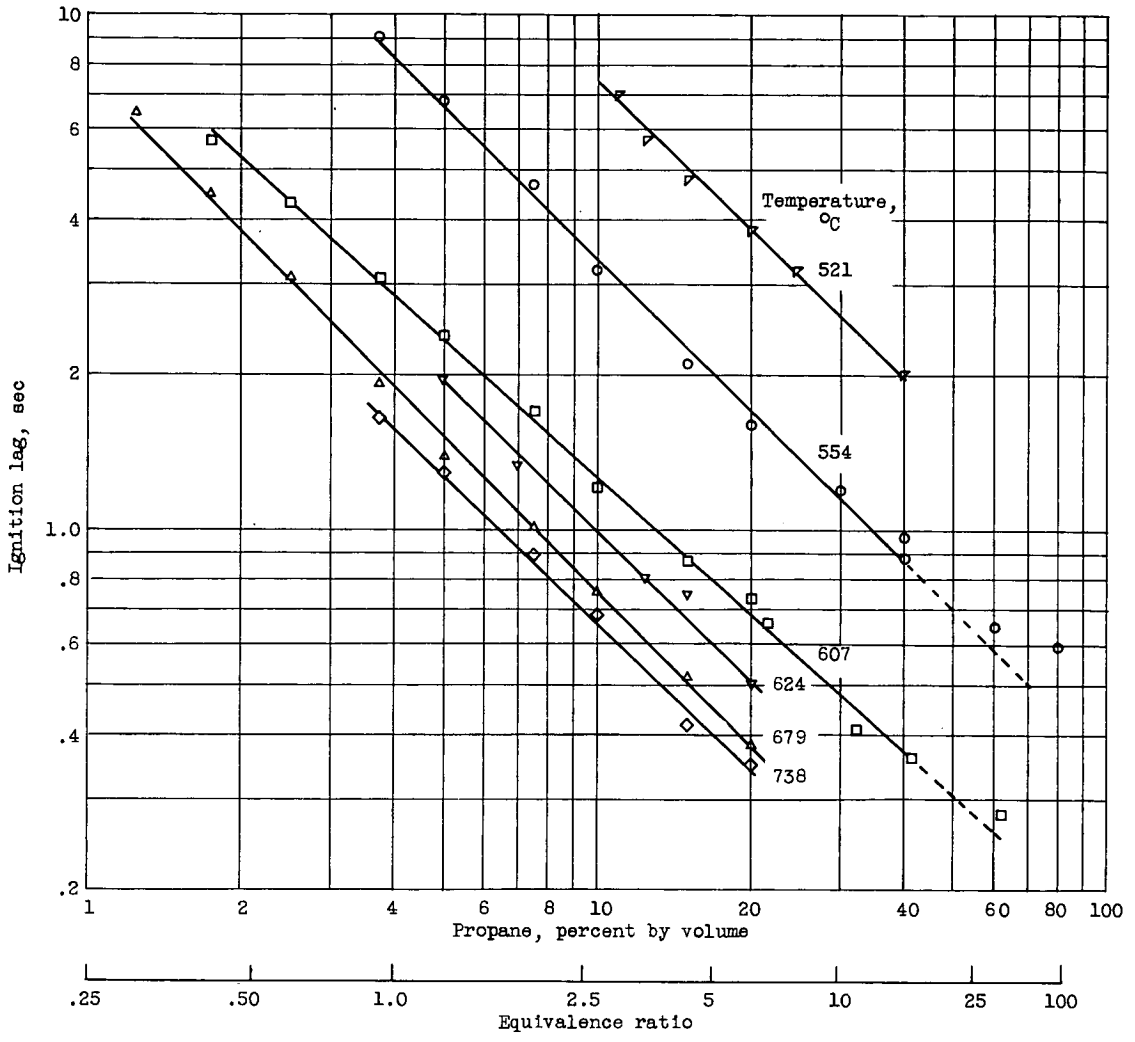Figure 3. - Effect of flow rate on ignition lag. Temperature, 629° C.

Figure 4. - Typical pressure traces for ignition of propane-air mixtures.

(a) Tube diameter, 25 millimeters.

Figure 5. - Variation of ignition lag with propane concentration.

(b) Tube diameter, 50 millimeters.

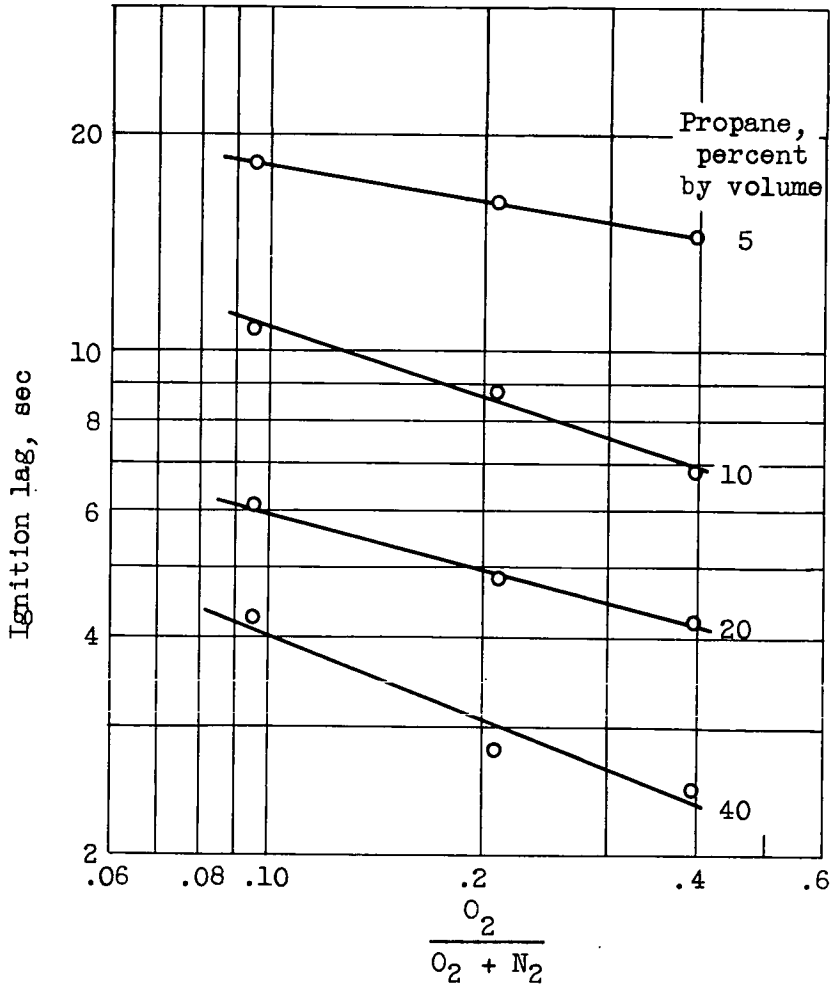Figure 5. - Concluded. Variation of ignition lag with propane concentration.

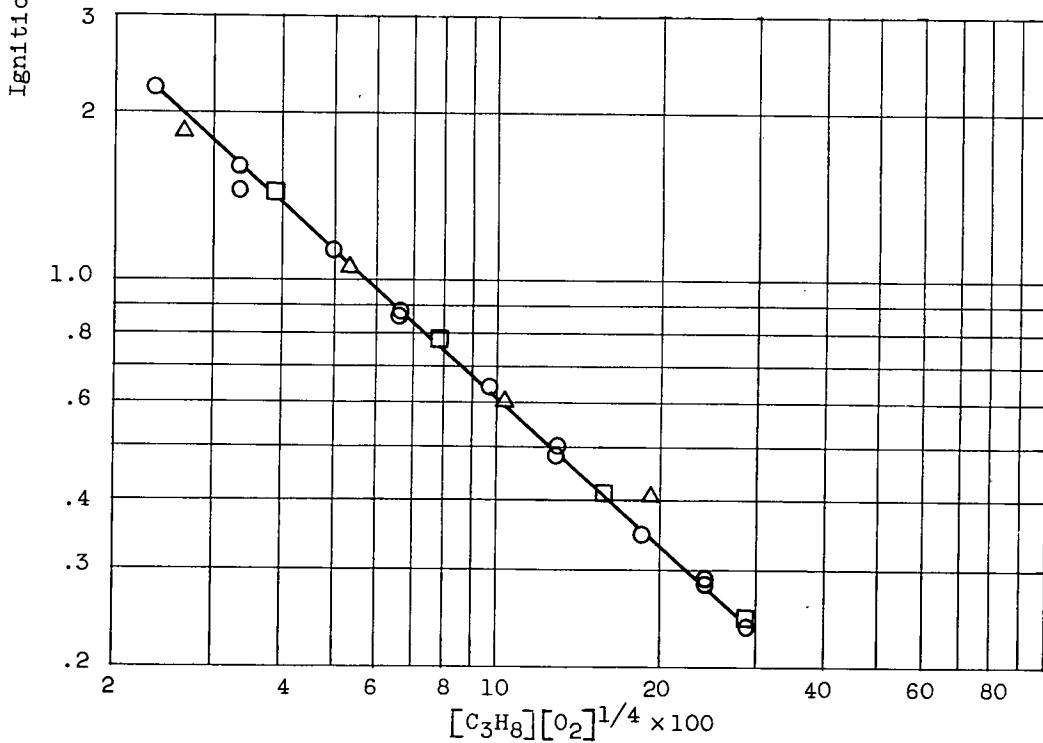Figure 6. - Variation of ignition lag with oxygen concentration in 25-millimeter tube. Temperature, 666° C.

(a) Neglecting oxygen concentration (eq. (1)).
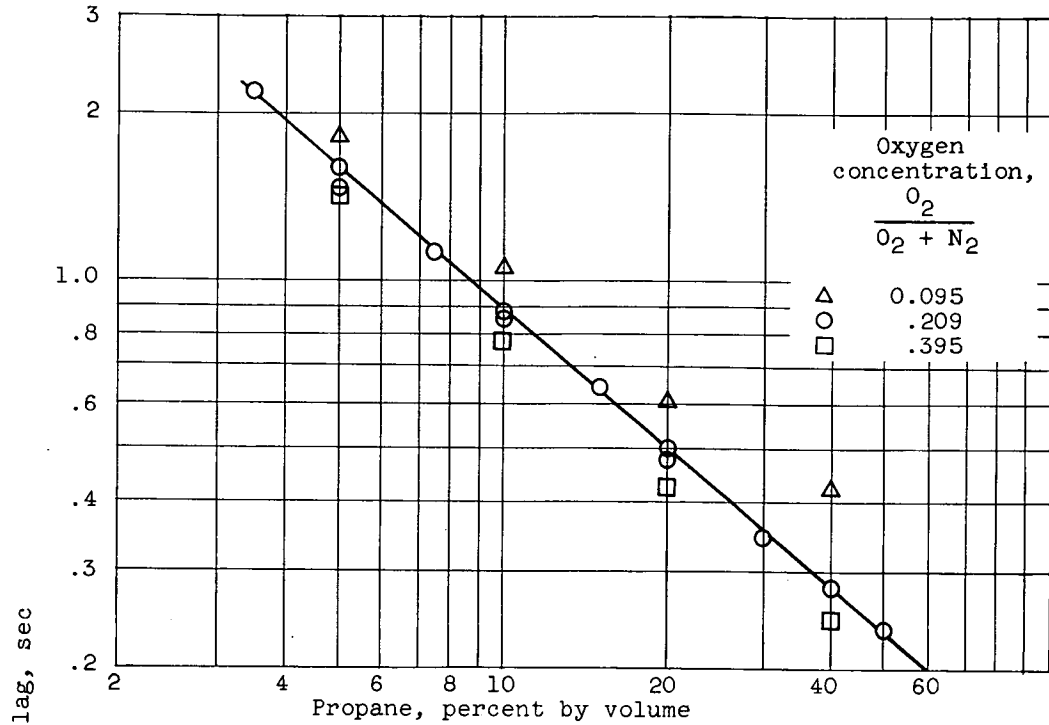
(b) Including oxygen concentration (eq. (3)).

Figure 7. - Variation of ignition lag with propane and oxygen
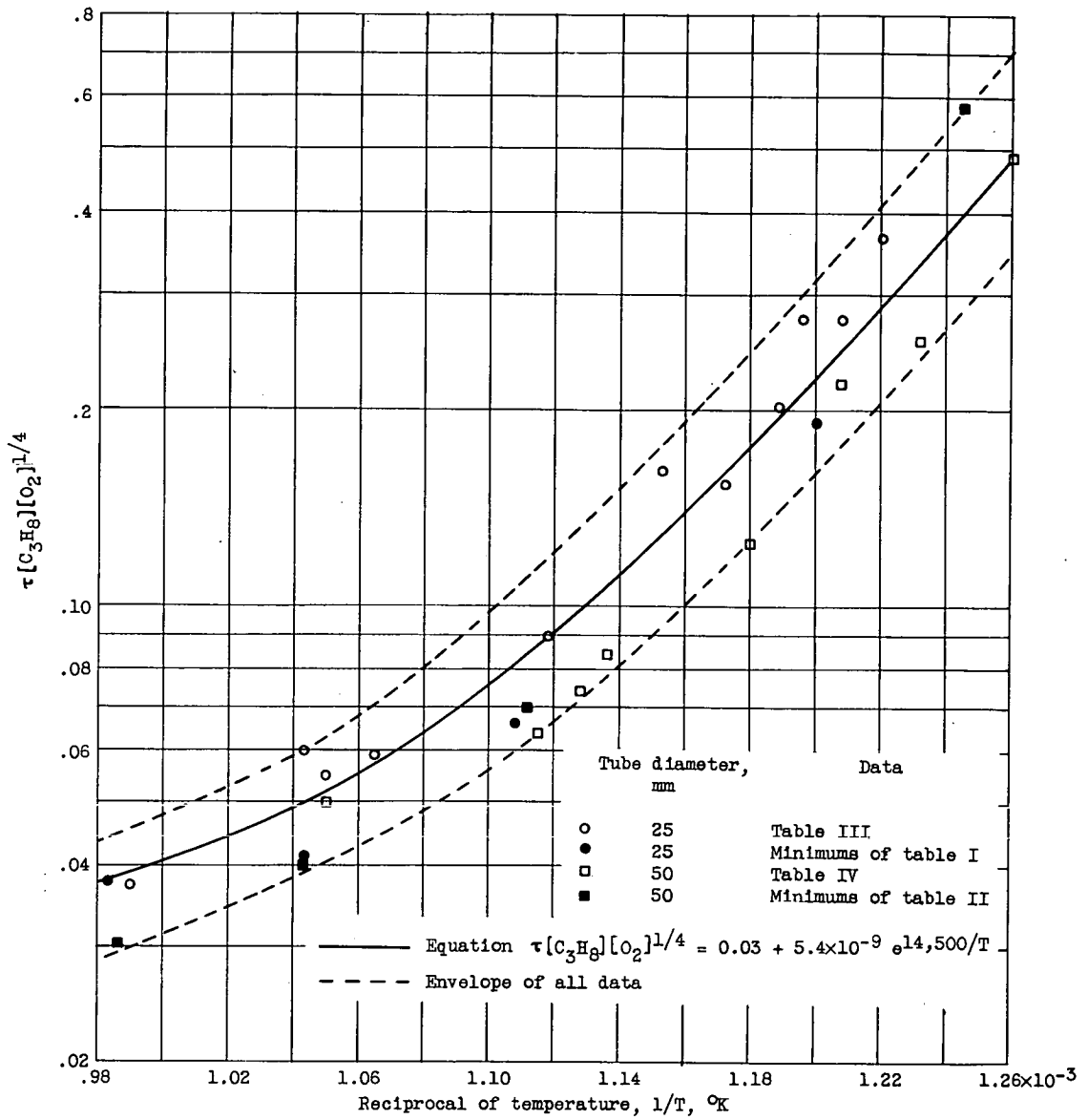concentrations in 25-millimeter tube. Temperature, 666° C.

Figure 8. - Variation of parameter $\tau[C_3H_8][O_2]^{1/4}$ with reciprocal of temperature.