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RESEARCH MEMORANDUM

EFFECT OF DIFFUSION PROCESSES AND TEMPERATURE

ON SMOKING TENDENCIES OF LAMINAR

DIFFUSION FLAMES

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NATIONAL ADVISORY COMMITTEE
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EFFECT OF DIFFUSION PROCESSES AND TEMPERATURE ON SMOKING

TENDENCIES OF LAMINAR DIFFUSION FLAMES

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SUMMARY

The effects of diffusion processes on the smoking tendencies of eight laminar diffusion flames were investigated by varying the rate and concentration of air and oxygen supplied to the flame. Increasing the rate at which air was supplied permitted rather limited increases in the smoke-free burning rate. Increasing the concentration of oxygen from 21 to 45 percent increased the smoke-free fuel flow for pentene-1, neopentane, isobutane, ethylene, and n-butane, but decreased the smoke-free burning rate for butene-1, cyclopropane, and propene in the range of 25 to 40 percent oxygen. Increasing the flame temperature caused the smoke-free fuel flow to increase except for butene-1, cyclopropane, and propene, where initial rates were lower. The variations in smoke formation with oxygen enrichment were tentatively explained by considering the effect of temperature on the initial decomposition reactions of the fuel molecule.

INTRODUCTION

Several factors which affect the smoking tendencies of laminar diffusion flames are fuel type, pressure, diffusion, and possibly temperature. The effect of fuel type and a proposed explanation for the variations in smoke formation with fuel type were reported in reference 1. Studies of the effect of pressure on smoke formation have been reported and interpreted in references 2 and 3. Similar investigations of the effects of diffusion and temperature on the smoking tendencies of diffusion flames have not been made. It is, of course, known that flames burning in an inadequate supply of air will produce more smoke and carbon than those burning with a sufficient quantity of air. The industrial production of carbon black is based on this principle (ref. 4).

The present investigation was conducted to obtain a more comprehensive understanding and evaluation of the effectiveness of reducing smoke

formation by varying the diffusion processes between the fuel and oxygen. Combining this information with that already reported in the literature may give further insight into the mechanisms which govern the formation of smoke.

The effect of diffusion processes on smoke formation was studied by determining the maximum relative rate at which eight pure gaseous hydrocarbon compounds could be burned from a 9-millimeter burner tube without smoking when air flowed past the flame at rates which were increased by gradual steps. In addition to air, mixtures of oxygen and nitrogen of increasing oxygen enrichment were used to determine the variation in smoke formation as the oxygen concentration was changed. The effect of flame temperature was investigated by preheating the fuel and also by substituting argon-oxygen mixtures for the nitrogen-oxygen mixtures.

The fuels used in this investigation were butene-1, cyclopropane, propene, pentene-1, neopentane, isobutane, ethylene, and n-butane. These fuels were selected because their smoking tendencies were in a range which was convenient to measure and their vapor pressures were sufficiently high to permit burning in the gas phase.

APPARATUS AND PROCEDURE

To study the effect of diffusion processes on smoke formation, the apparatus shown in figure 1 was used. The eight hydrocarbons studied were burned from a stainless steel burner tube 9 millimeters in diameter (see fig. 1(a)). The burner tube was enclosed by a pyrex glass tube 40 millimeters in diameter and 760 millimeters in height. All of the air supplied to the flame was admitted through perforated holes in a cylindrical chamber sealed into the base of the pyrex tube. Both the fuel and air were metered through flowmeters before entering the tubes. At each selected air flow, a determination was made of the maximum rate of fuel which could be burned without causing the flame to smoke. A visual observation was used to detect the first smoke which issued from the flame.

Since the vapor pressure of pentene-1 was not sufficiently high at room temperature to give the needed fuel flow, a heated bomb was used to hold the vaporized liquid, which was then burned in the gas phase in the same manner as the gaseous compounds (fig. 1(b)). However, to determine the fuel flow rate in this case, the bomb plus the sample were weighed before the fuel was burned and were then reweighed after the fuel had burned at its incipient smoking point for a given interval of time. From the loss in weight over this time interval, the maximum smoke-free fuel flow could be obtained.

To study the effect of preheating a fuel, the apparatus shown in figure 1(c) was used. The 9-millimeter burner tube 700 millimeters in length was jacketed by an electric heating coil controlled by a Variac transformer. To stabilize the flame a chimney 47 millimeters in diameter and 300 millimeters high was placed with the bottom edge level with the port of the burner tube. After the burner tube temperature had reached a constant value, with a small air flow passing through it, the maximum rate of fuel which could be burned without smoking was measured. The temperature was then raised until a higher equilibrium value was reached and the smoke-free fuel flow again determined.

RESULTS AND DISCUSSION

Since diffusion flames burning in an inadequate supply of air produce more smoke and carbon than those burning with a sufficient quantity of air, it would be expected that smoke formation could be eliminated by increasing the amount of air supplied to the flame. It might also be expected that fuels which burn with very smoky flames such as the aromatics and olefins might burn as smoke-free as the normal paraffins if they were supplied with a sufficiently larger quantity of air. However, the results of this investigation show that only relatively small gains in the rate of fuel flow which will burn smoke-free can be obtained by increasing the air supplied to laminar diffusion flames. Figure 2 shows the variation in smoke-free fuel flow with increasing air flow for eight pure hydrocarbon compounds. As the rate of air flow past the flame is increased, the rate of fuel flow which will burn without smoking is increased proportionally; however, a limiting fuel flow is shortly reached. Once this maximum, limiting fuel flow is obtained, additional increases in the air flow do not permit further increases in the fuel flow for smoke-free burning. Therefore, increasing the rate of air flow past a laminar butene-1 diffusion flame, for example, will never permit it to burn as much fuel smoke-free as an isobutane flame except in the very low fuel flow region. Of course, all these fuel flows, even the highest, are still in the laminar region and a different maximum limit would be expected if turbulent flames were studied (ref. 5).

While increasing the rate of air flow to a diffusion flame will increase the chances for diffusion of oxygen into the flame, a greater quantity of oxygen could enter the flame if enriched oxygen-nitrogen mixtures were used. Consequently, oxygen-nitrogen mixtures with oxygen concentrations ranging from 25 to 45 percent were substituted for air. Attempts were made to use oxygen-enriched mixtures up to 100 percent oxygen, but oxygen concentrations higher than 45 percent led to two important experimental difficulties.

One of these difficulties was the formation of solid carbon on the port of the burner tube. This carbon formed when certain fuels burned in an environment of 50 percent oxygen or greater. Figure 3 shows a propene flame with solid carbon formation around its base. The growth of the solid carbon was very rapid and proceeded in a spiral fashion around the flame until the flame was finally choked. A carbon-hydrogen analysis of this carbon showed it to be 99.73 percent carbon and 0.04 percent hydrogen. A similar observation was made by Parker and Wolfhard (ref. 2) while burning acetylene in pure oxygen. Since the presence of this solid carbon may have some influence on the smoking tendency of the flame, no oxygen-enriched mixtures above 45 percent oxygen - 55 percent nitrogen were used.

A second difficulty was that the experimental accuracy in detecting an exact smoke point becomes extremely poor as the oxygen concentration is increased. A description of the change in flame structure with oxygen enrichment will perhaps explain why the smoke point is harder to detect. A diffusion flame about 28 millimeters high burning just above its incipient smoke point in air is shown in figure 4(a). The first smoke emitted from the tip of this flame is very dark in appearance and only a very small change in fuel flow is necessary to indicate a definite change from a nonsmoking to a smoking flame. A diffusion flame burning in an environment of 35 percent oxygen is shown in figure 4(b). This flame is also burning just above its incipient smoke point, but as indicated in the figure the smoke is now issuing from the tip of the sheath of flame extending above the top of the flame proper. The lines on the figure indicate the position where smoke first appears. In this extended sheath of flame, small carbon particles can be seen moving upward even when no smoke is issuing from the flame. Apparently this upper portion of the flame affords the carbon particles an additional chance for oxidation. The first smoke which eventually issues from the flame also appears to have been partly consumed in its travel since it is micro size and appears white or light gray. This light smoke is much harder to detect than the heavy, black smoke issuing from flames burning in air, and appreciable variations in the fuel flow are necessary to indicate a definite change from nonsmoking to smoking. In addition, for high fuel flows and consequently for tall flames, the extended sheath of flame becomes so tall that it no longer remains erect and stable. For those flames where the accuracy in detecting the smoke point was very poor, the fuel flow rates are only reported as being greater than a certain value. It was definitely believed that no smoke appeared below this reported value.

The effect on the smoke-free fuel flow obtained by substituting oxygen-enriched mixtures of oxygen and nitrogen for air is shown in figure 5 for eight pure hydrocarbons. With the initial increase in the flow rate of a given oxygen-enriched mixture, the maximum smoke-free fuel flow also increased. The fuel flow, however, reached a limiting

value which is usually greater than that for air although for some
fuels the limiting fuel flow with oxygen enrichment is actually less
than for air. To show more readily the variations of the maximum
limiting fuel flow with oxygen enrichment, a cross plot of the data is
shown in figure 6.

For propene, cyclopropane, and butene-1 (fig. 6(a)), the limiting
fuel flow is the same for 21 percent oxygen - 79 percent nitrogen and
25 percent oxygen - 75 percent nitrogen, but decreases for 30 and 35
percent oxygen mixtures. An increase is again observed for the 45-
percent concentration. For isobutane, neopentane, and pentene-1
(fig. 6(b)), the limit fuel flow continuously increases with increasing
oxygen enrichment. This was also true for ethylene and n-butene
(fig. 5(g) and (h)), but these limits were subject to the experimental
problem of smoke detection as explained previously.

The decrease in smoke-free fuel flow with oxygen enrichment as
shown by propene, cyclopropane, and butene-1 seems contrary to what
would be expected. A tentative explanation for this observation may
perhaps be found by considering the structure of the fuels involved and
also the variation in flame temperature. The three fuels in question
showed lower smoke-free fuel flows in still air experiments than the
other five compounds studied (ref. 1). In reference 1 the variation in
smoking tendency among different fuel types was related to the stability
of the carbon chain or skeleton. It was proposed that molecules with
highly stable carbon skeletons could readily undergo dehydrogenation
reactions, and the partly or totally dehydrogenated carbon skeletons
so formed could simultaneously polymerize to form smoke (ref. 6). Since
the three fuels which show decreasing fuel flow with increasing oxygen
concentration are also the smokiest and, as discussed in reference 1,
the most thermally stable with respect to the carbon skeleton and there-
fore easily dehydrogenated, any factor which would aid the dehydrogena-
tion process would promote smoke formation. One such factor which should
be taken into consideration is temperature, since in air diffusion flames
the fuel is heated to a temperature of the order of 800° C before coming
into contact with oxygen (ref. 2).

As the concentration of oxygen in the oxygen-nitrogen mixture is
increased, the temperature of the flame also increases, and consequently,
diffusion and temperature are being varied simultaneously. The increase
in temperature may, for certain fuel types which possess very stable
carbon skeletons, increase the dehydrogenation process and therefore
advance the formation of smoke to a greater extent than the oxygen
diffusion processes can later overcome.

An experiment to separate the diffusion and temperature effects
was therefore undertaken. This was accomplished by substituting argon
for nitrogen in the oxygen-enriched mixtures. The lower specific heat
of argon will appreciably increase the flame temperature and yet allow
the concentration and diffusion of oxygen to be held relatively constant.

Unpublished NACA data by R. S. Brokaw indicate that the substitution of
argon for nitrogen will increase the flame temperature $250°$ to $400°$ C.
Another method of increasing the flame temperature without changing the
oxygen concentration or diffusion processes is by preheating the fuel.
However, only relatively small increases in flame temperature can be
obtained by this technique as compared to the argon substitution. In
fact, preheating a propene flame to about $190°$ C had no effect on the
smoking tendency.

The effect of enriched oxygen-argon mixtures is shown in figure 5
and the limit fuel flows are plotted against percentage oxygen in figure
6. For propene, cyclopropane, and butene-1 (fig. 6(a)), the limit fuel
flows for 21 percent oxygen - 79 percent argon and 24 percent oxygen -
76 percent argon are less than for the corresponding oxygen-nitrogen
mixtures. Since the oxygen concentrations are approximately the same,
the decrease in smoke-free fuel flow is attributed to the increase in
temperature. For isobutane, neopentane, and pentene-1, the limit fuel
flows for 21 percent oxygen - 79 percent argon and 24 percent oxygen -
76 percent argon are about the same as or slightly greater than the fuel
flows for similar oxygen-nitrogen concentrations. These three fuels are
apparently not greatly affected by the increased temperature. The small
increase observed may result from the slight increase in diffusion which
accompanies the increasing temperature. Butene-1 and cyclopropane show
about the same fuel flow limit for 34 percent oxygen - 66 percent argon
as for the 35 percent oxygen - 65 percent nitrogen mixture. The other
fuels, however, exhibit an appreciable increase in the fuel flow limit
for 34 percent oxygen - 66 percent argon. The increasing temperature now
appears to promote reactions which decrease the formation of smoke. For
a 44 percent oxygen - 56 percent argon mixture all of the fuels are
burning at a much higher smoke-free fuel flow than for the similar oxygen-
nitrogen mixture. Although the experimental error in measuring the
smoke point of the 44 percent oxygen - 56 percent argon mixture is fairly
large, all the fuels seem to have about the same limit fuel flow for
this mixture. Increasing the oxygen concentration to 44 percent and the
flame temperature to that obtained by a 44 percent oxygen - 56 percent
argon mixture probably permits butene-1 to burn smoke-free at a rate
equivalent to isobutane.

Why the increase in temperature encountered by going from 21 per-
cent oxygen - 79 percent nitrogen to 21 percent oxygen - 79 percent
argon should decrease the smoke-free fuel flow for butene-1 whereas the
increase in temperature obtained by going from 44 percent oxygen - 56
percent nitrogen to 44 percent oxygen - 56 percent argon should increase
the smoke-free fuel flow can only be speculated upon. The initial
temperature increase with the 21 percent oxygen - 79 percent argon mix-
ture is perhaps sufficient to promote only dehydrogenation reactions
whereas the temperature rise with 44 percent oxygen - 56 percent argon
is so severe that no preferential dehydrogenation occurs. At the much

higher temperatures all the bonds in the molecule are probably broken at similar rates and a more complete decomposition is obtained. Consequently, the decrease in smoke-free fuel flow for propene, cyclopropene, and butene-1 with initial increasing oxygen enrichment probably results from the increase in temperature which accompanies the increase in oxygen concentration. This increase in temperature may advance decomposition reactions, such as dehydrogenation, which are responsible for promoting the formation of smoke. For fuels such as isobutane and neopentane, the initial thermal decomposition of the molecule probably proceeds to a greater extent through breaking of carbon-carbon bonds rather than by dehydrogenation reactions. Increasing temperatures therefore continue to promote decomposition by a mechanism which is not so highly conducive to smoke formation.

The effect of flame temperature is obviously very important and appears to overshadow the effect of diffusion. The exact manner by which temperature exerts its effect is certainly not clearly understood. Since fuel type is also important, the tentative explanation which has been proposed is based primarily on the effect which temperature might have on the initial decomposition reactions of the fuel molecule.

SUMMARY OF RESULTS

In an investigation of the effect on the smoking tendency of eight laminar diffusion flames by increasing the rate and concentration of oxygen supplied to the flame, the following results were obtained:

1. Increasing the air flow past a diffusion flame increased the rate at which the fuel could be burned smoke-free until a maximum rate was reached at which the fuel would burn smoke-free.

2. When mixtures of oxygen and nitrogen, with oxygen concentrations ranging from 25 percent to 45 percent, were used in place of air, the smoke-free fuel flow increased for pentene-1, neopentane, isobutane, ethylene, and n-butane, but decreased for butene-1, cyclopropane, and propene over the range of 25 to 40 percent oxygen.

3. Substituting oxygen-argon mixtures for oxygen-nitrogen mixtures, to increase the flame temperature, showed that the fuel flow generally increased with increasing temperature except for butene-1, cyclopropane, and propene where initially the fuel flow rates decreased.

4. The variations in smoke formation with oxygen enrichment were tentatively explained by considering the effect of temperature on the initial decomposition reactions of the fuel molecule.
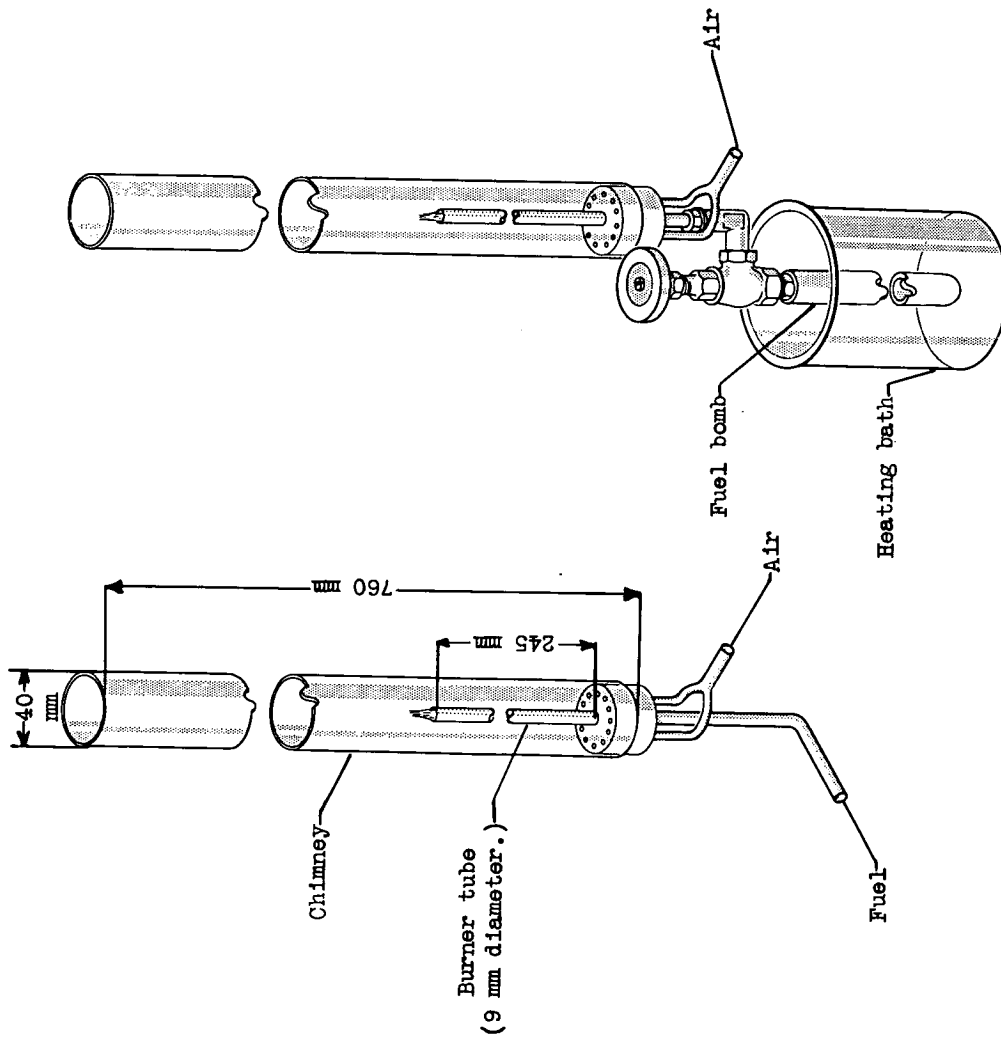

Lewis Flight Propulsion Laboratory
    National Advisory Committee for Aeronautics
        Cleveland, Ohio, October 8, 1953

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6. Porter, George: Carbon Formation in the Combustion Wave. Fourth Symposium (International) on Combustion, The Williams and Wilkins Co., 1953, pp. 248-252.

300 mm

47 mm

Heated burner
tube
9 mm. diameter

700 mm. length

Chimney

Fuel

CD-3178
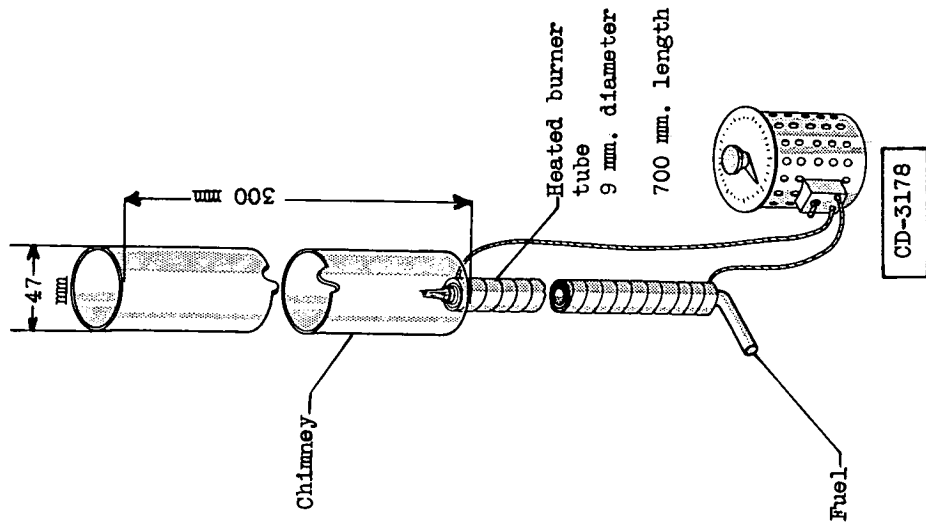
(c) Apparatus modified for
preheating fuels.

Air

Fuel bomb

Heating bath

(b) Apparatus modified for
vaporized liquid fuels.

760 mm

40 mm

245 mm

Chimney

Burner tube
(9 mm diameter.)

Air

Fuel

(a) Burner tube.

Figure 1. - Diagram of apparatus.
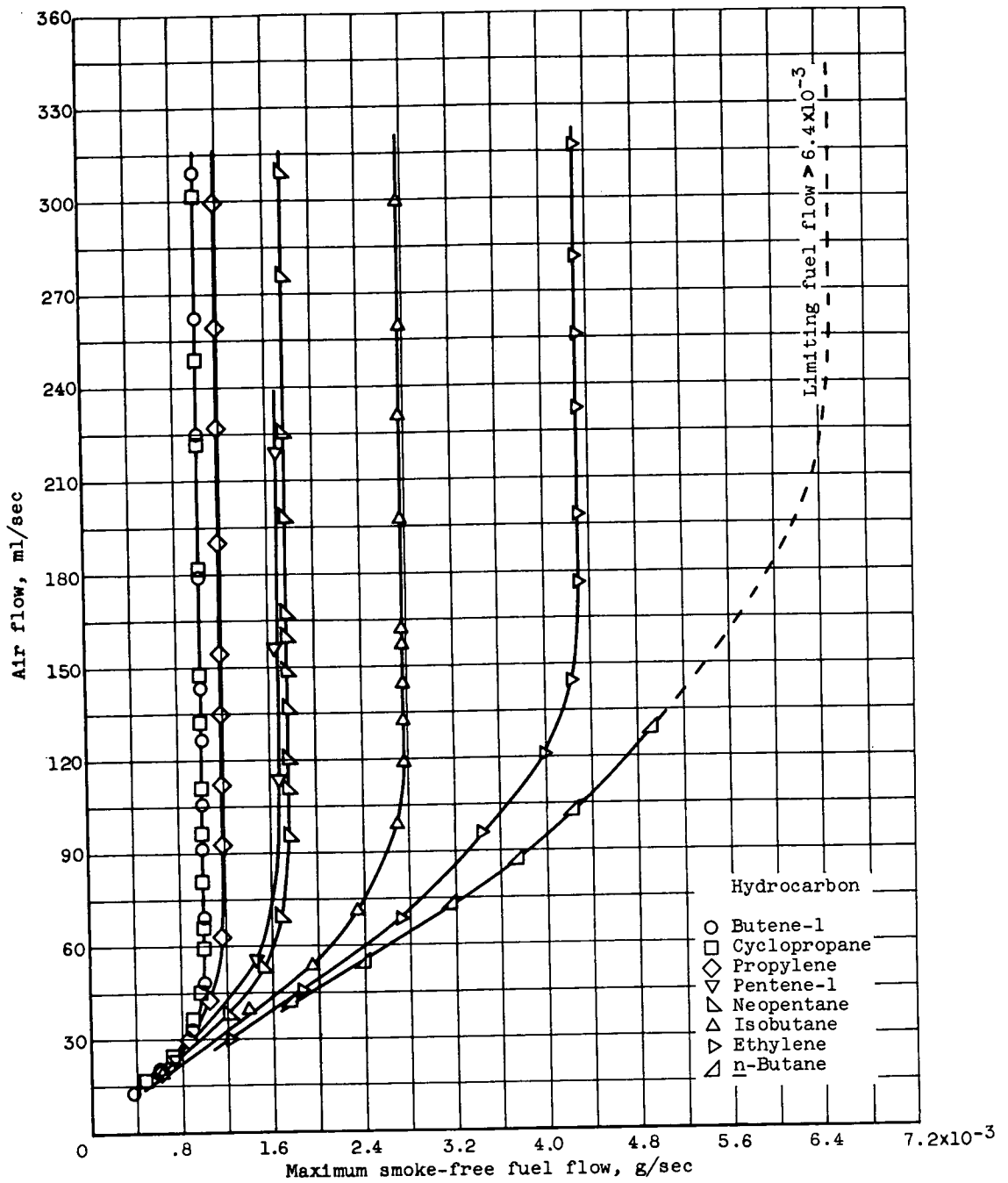
Figure 2. - Variation in smoke-free fuel flow with air flow.

Figure 3. - Propylene diffusion flame burning in 50 percent oxygen, showing formation of solid carbon at base of flame.

C-33934
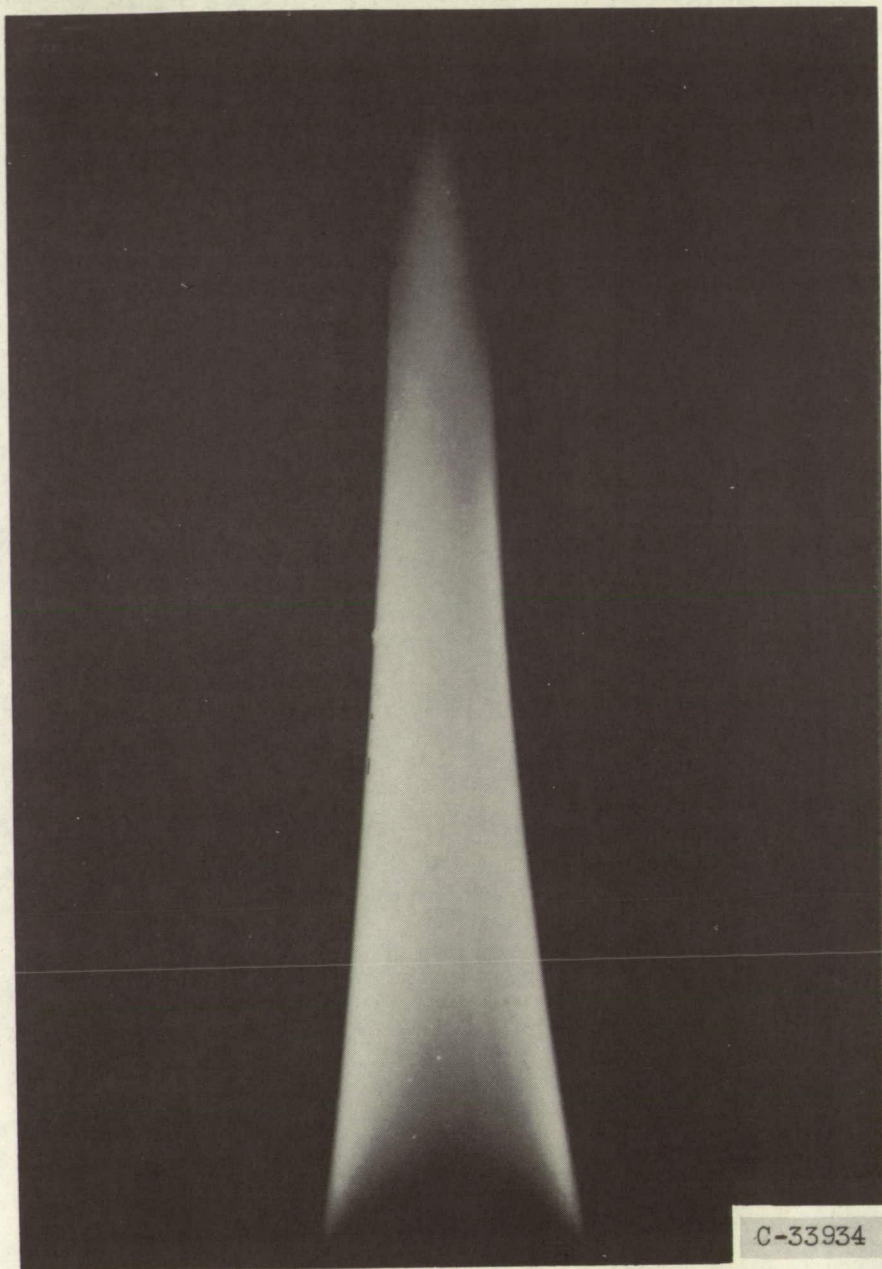
(a) In air

Figure 4. - Diffusion flames.

Smoke first appears

C-33935
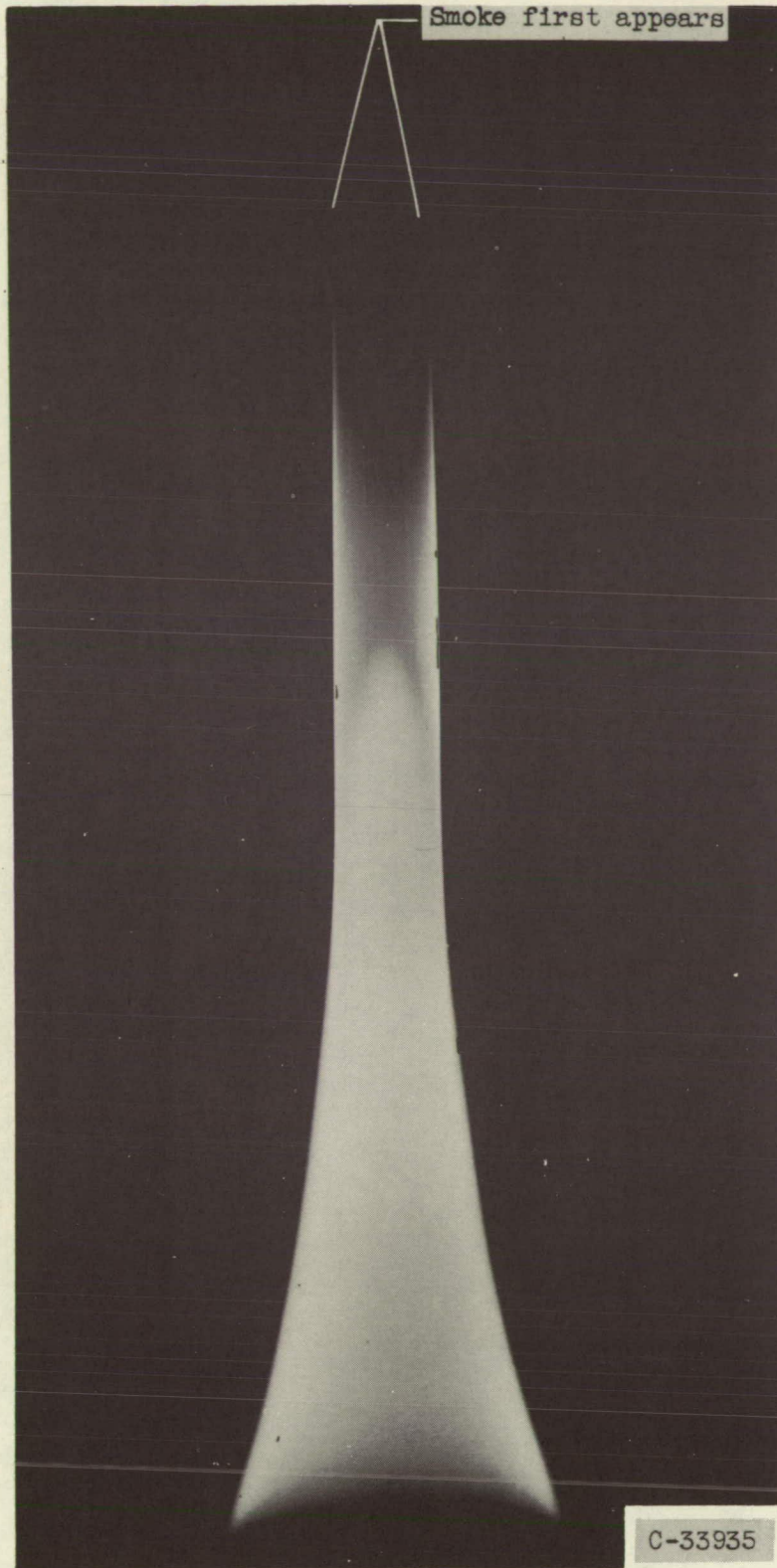
(b) In 35 percent oxygen - 65 percent nitrogen.
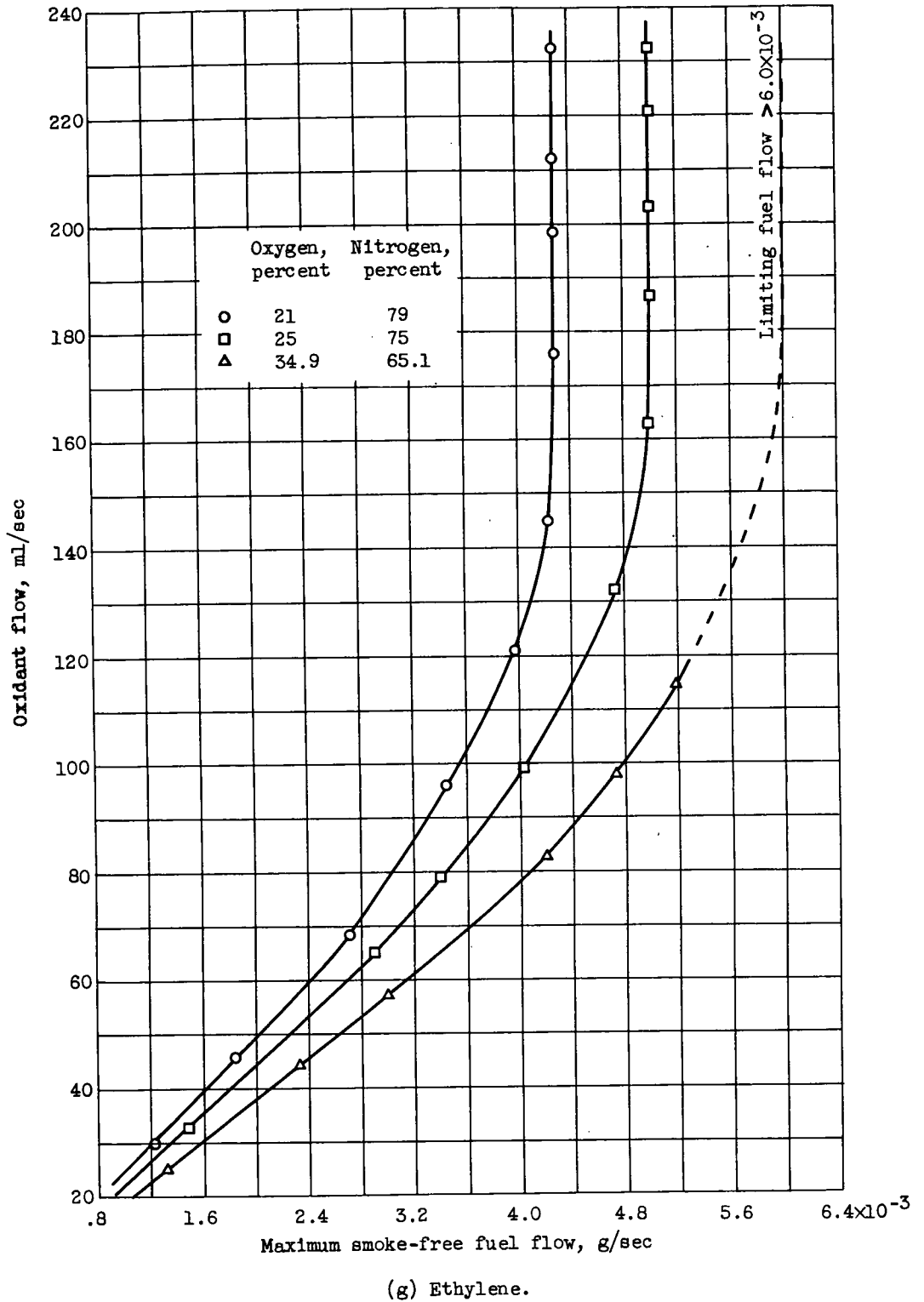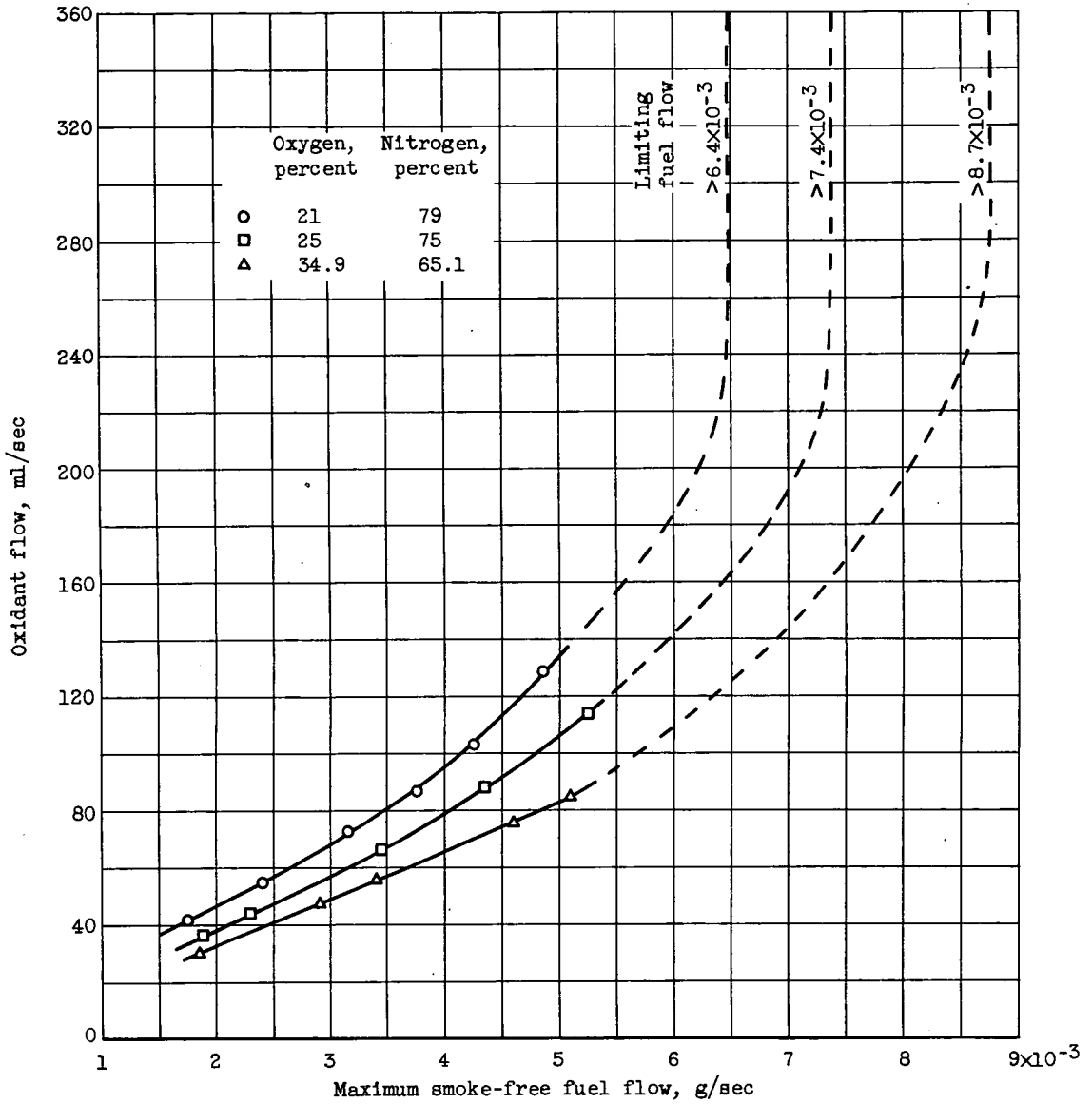
Figure 4. - Concluded. Diffusion flames.
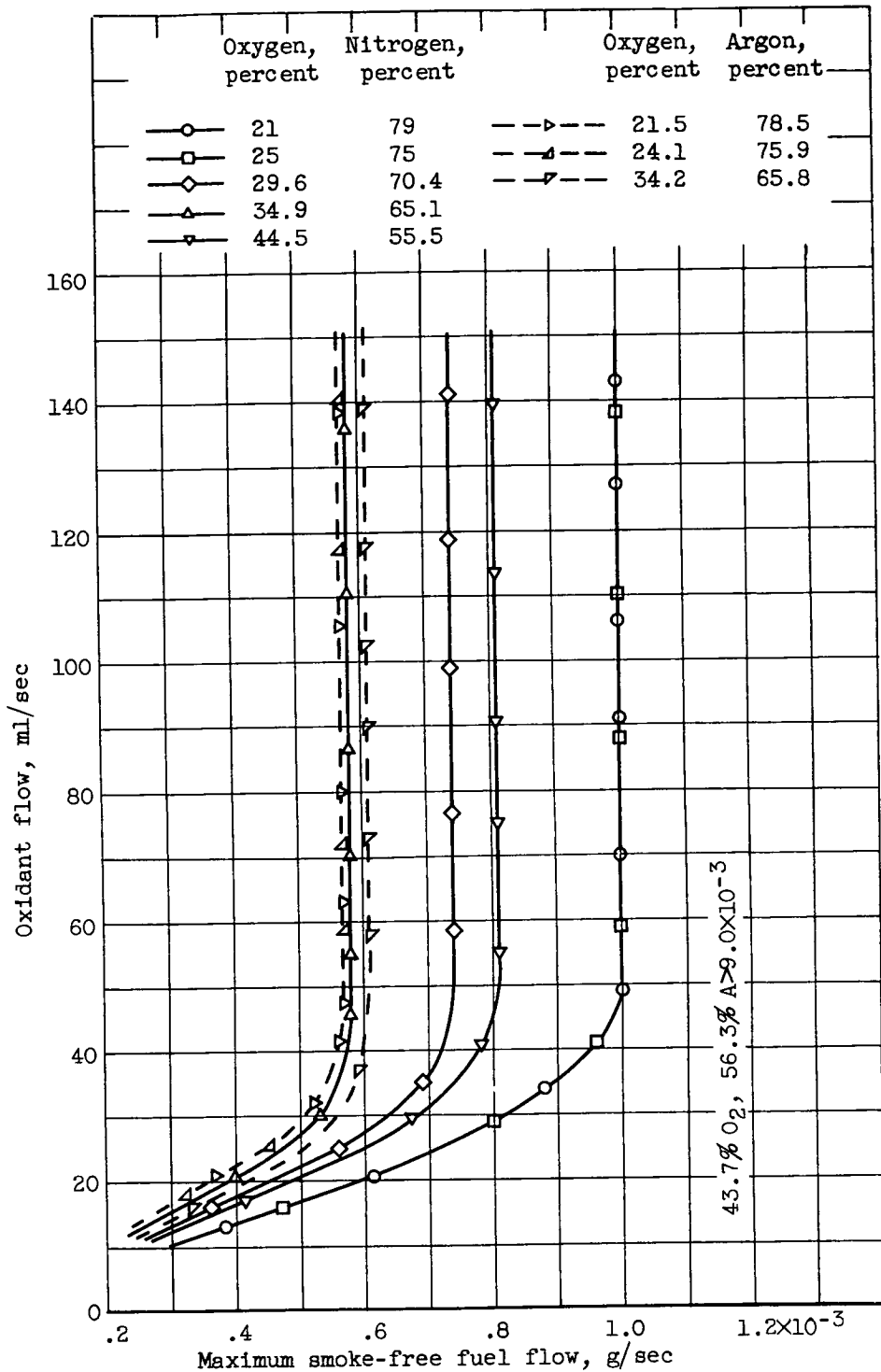
(a) Butene-1.

Figure 5. - Variations in maximum smoke-free fuel flow
with oxygen-enriched mixtures.
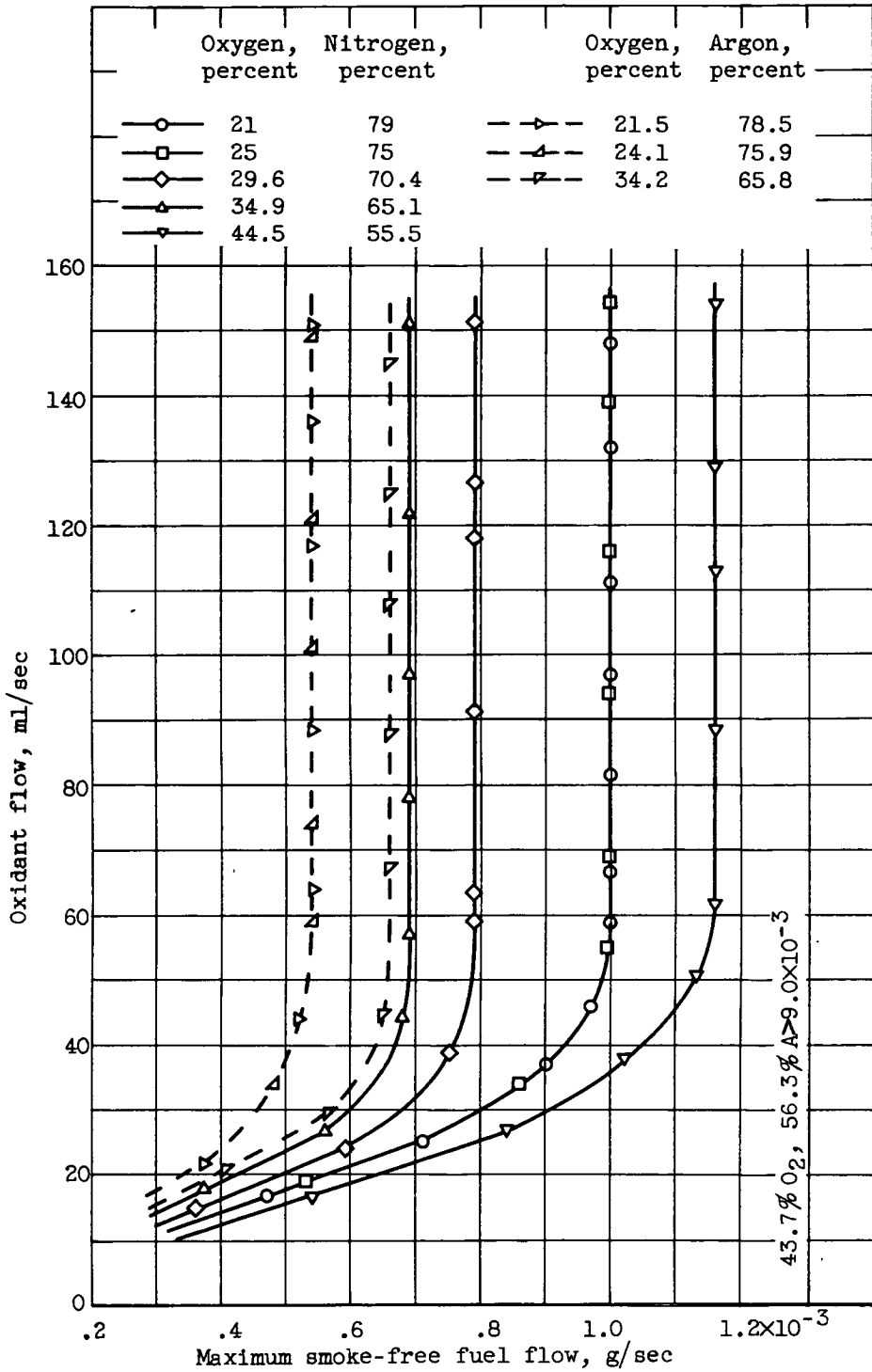
(b) Cyclopropane.

Figure 5. - Continued. Variations in maximum smoke-free fuel
flow with oxygen-enriched mixtures.
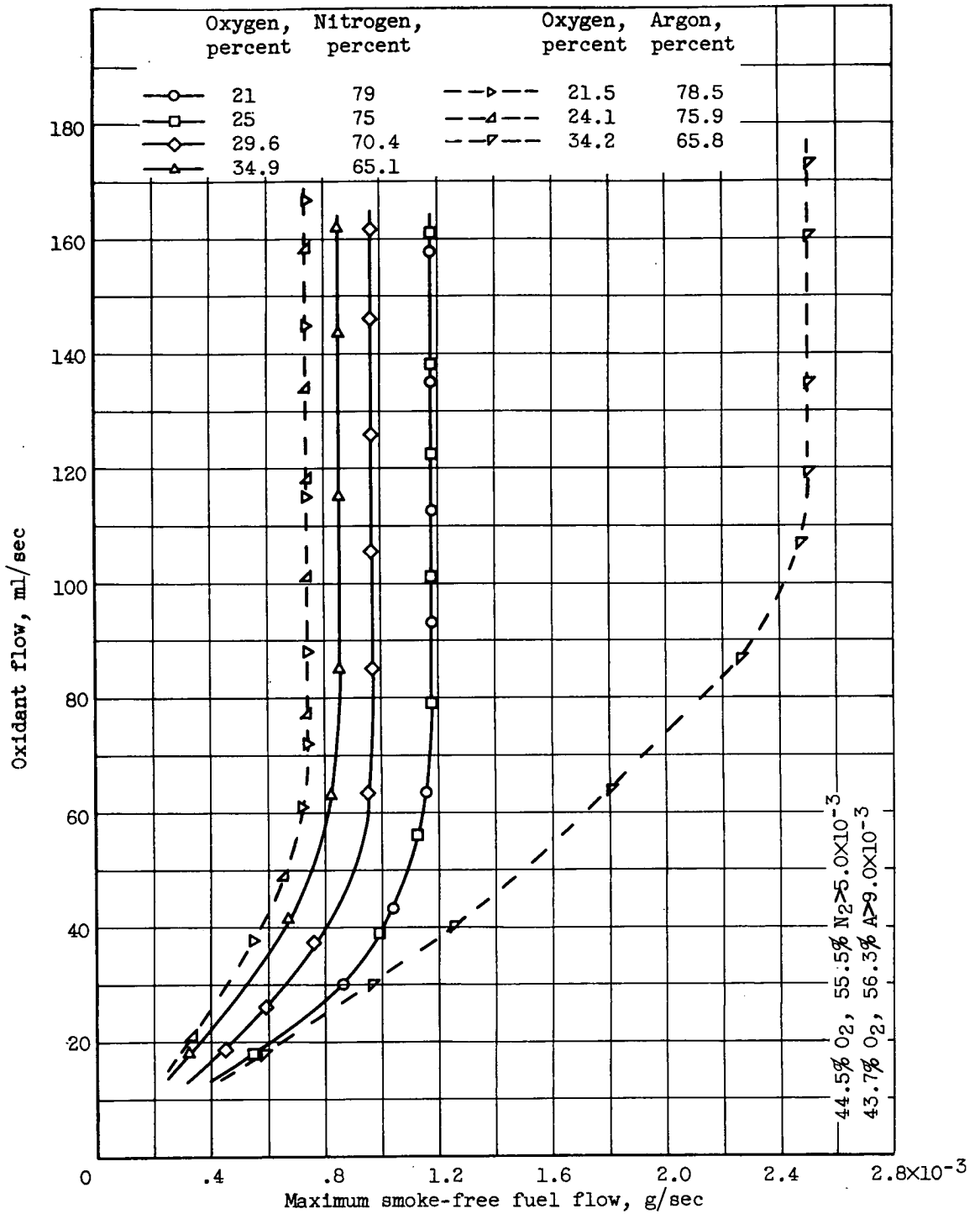
(c) Propene.

Figure 5. - Continued. Variations in maximum smoke-free fuel flow
with oxygen-enriched mixtures.
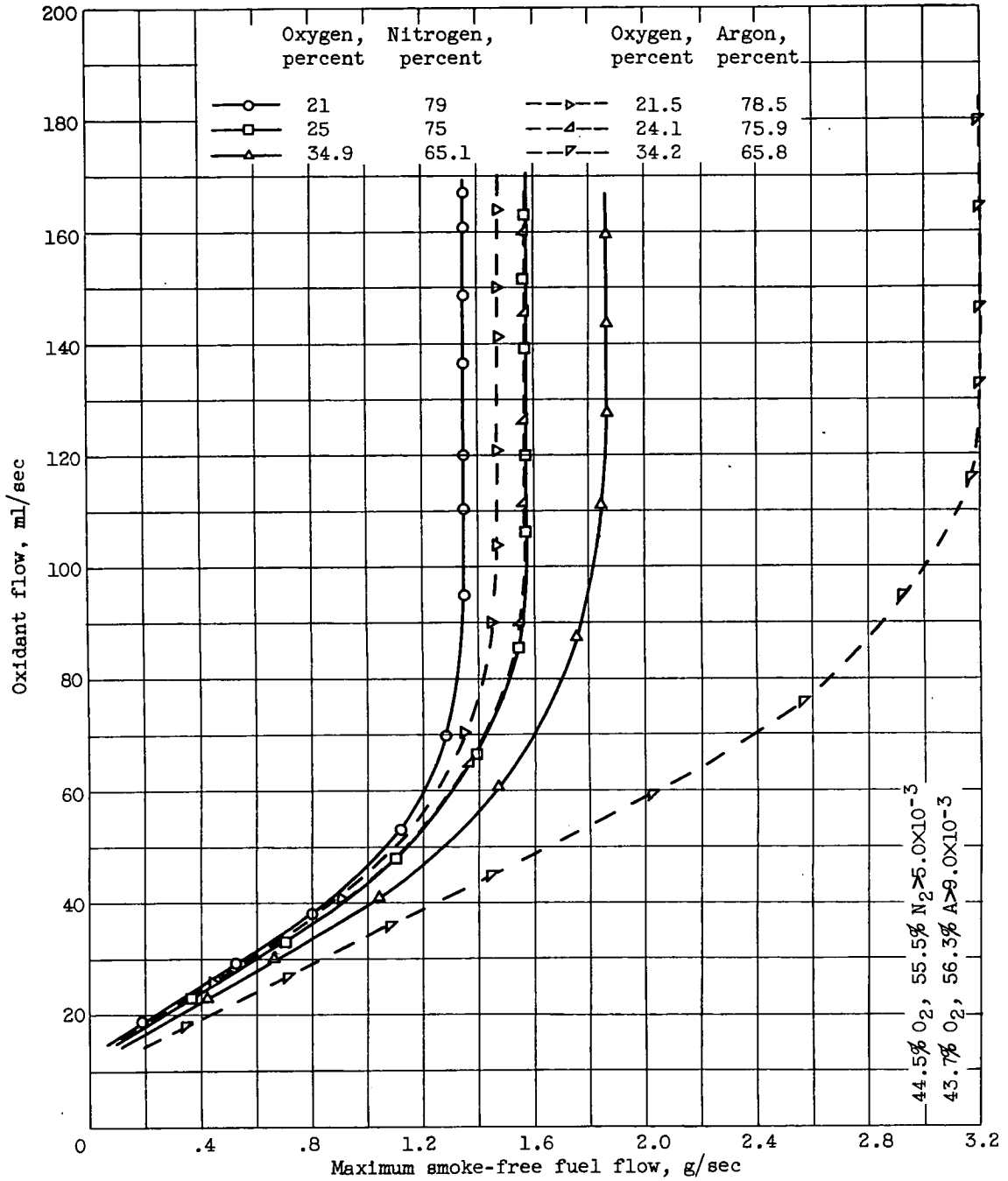
(d) Neopentane.

Figure 5. - Continued. Variations in maximum smoke-free fuel flow with oxygen-enriched mixtures.

(e) Isobutane.
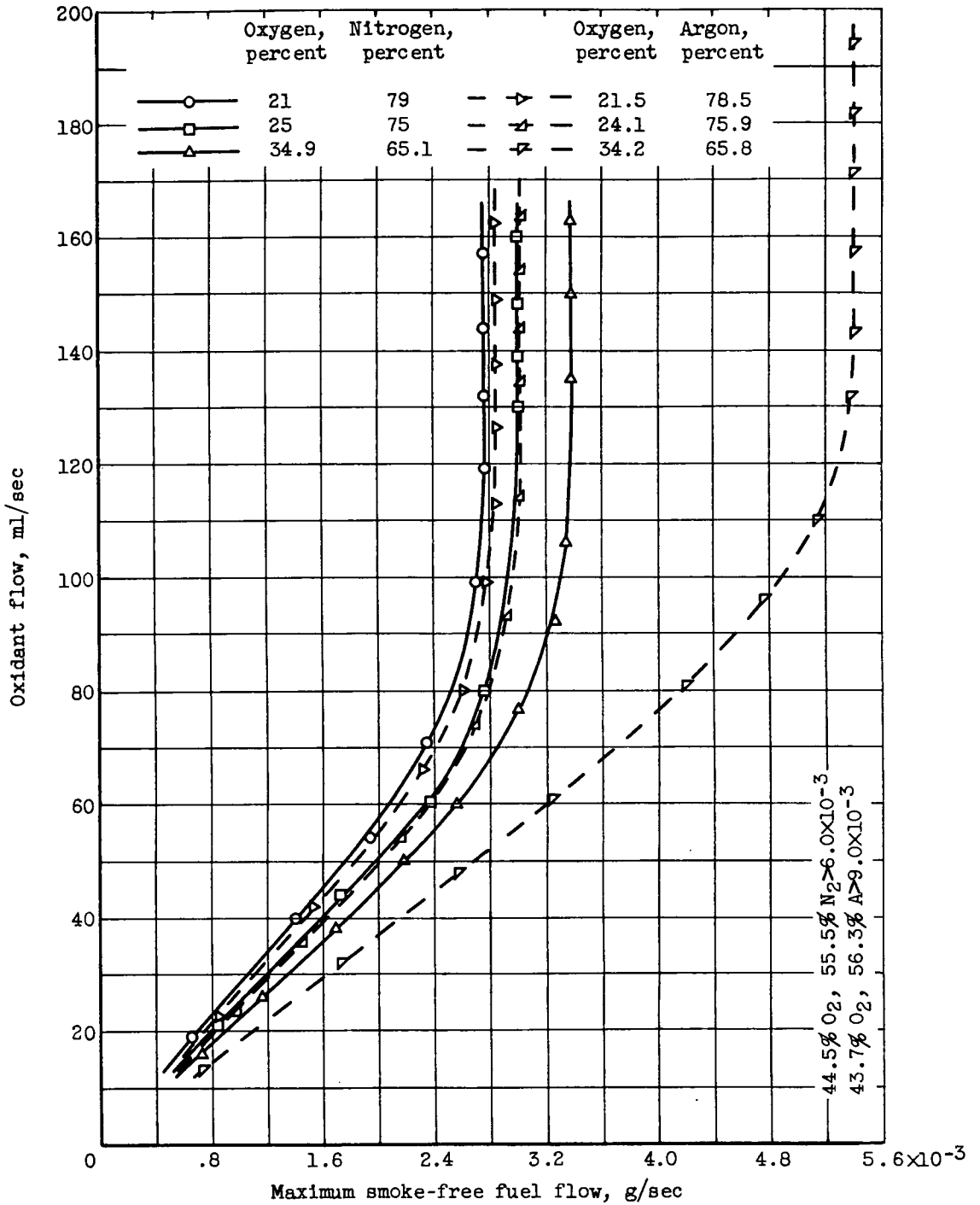
Figure 5. - Continued. Variations in maximum smoke-free fuel flow
with oxygen-enriched mixtures.

(f) Pentene-1.

Figure 5. - Continued. Variations in maximum smoke-free fuel flow with oxygen-enriched mixtures.

(g) Ethylene.
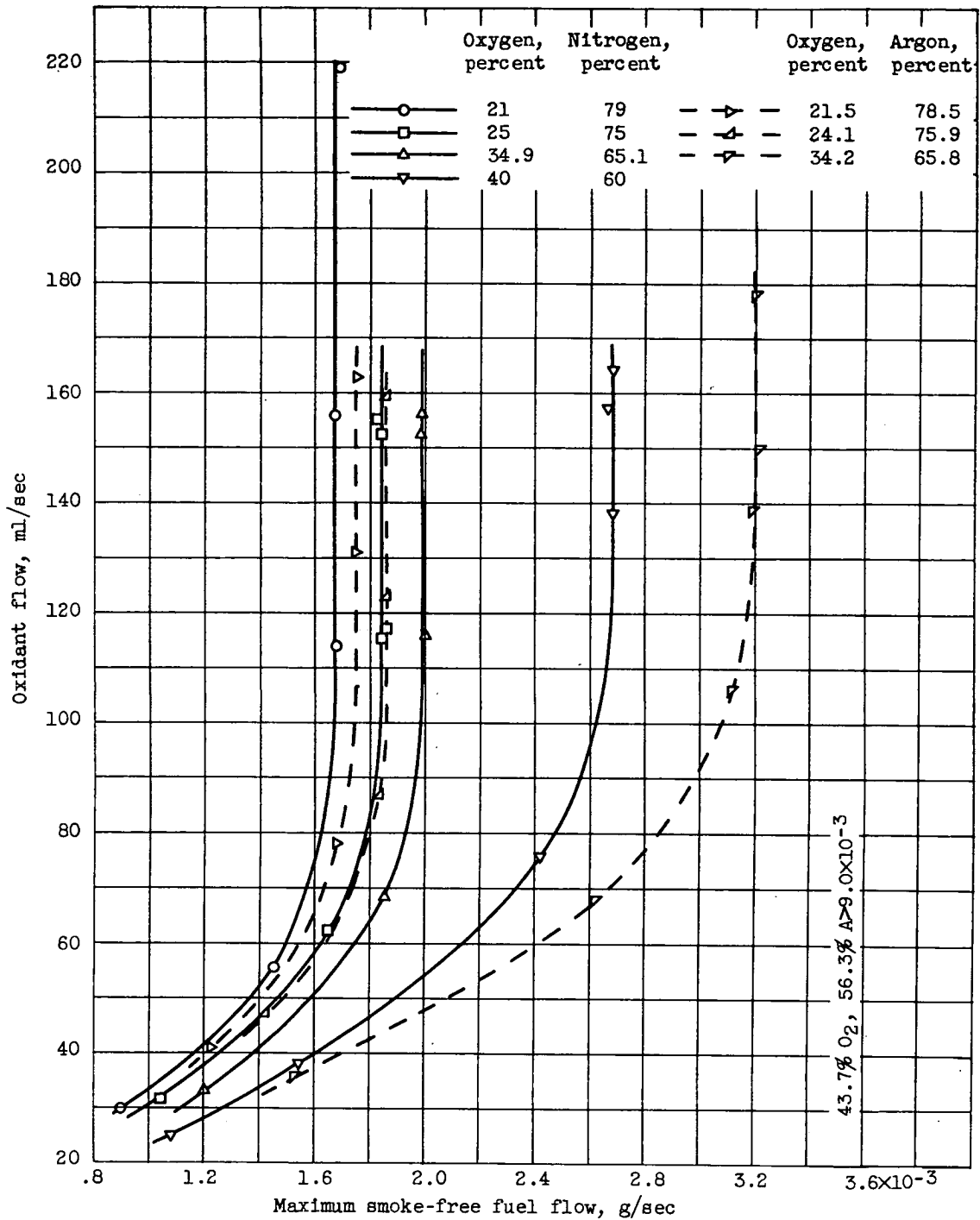
Figure 5. - Continued. Variations in maximum smoke-free fuel flow with oxygen-enriched mixtures.

(h) n-Butane.

Figure 5. - Concluded. Variations in maximum smoke-free fuel flow with
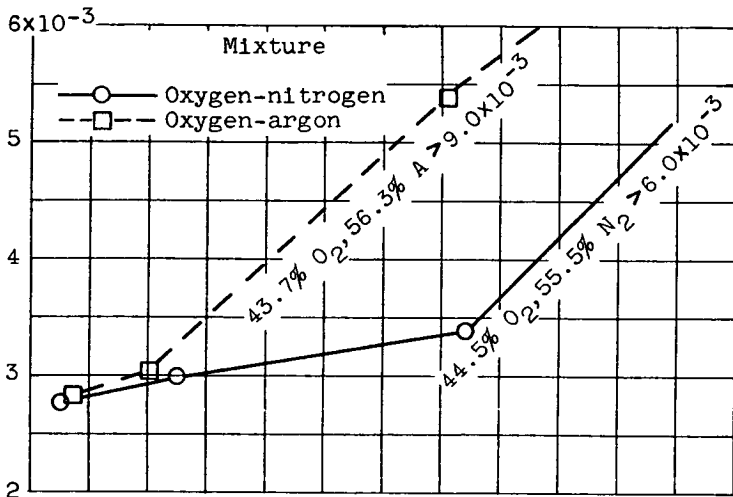   oxygen-enriched mixtures.
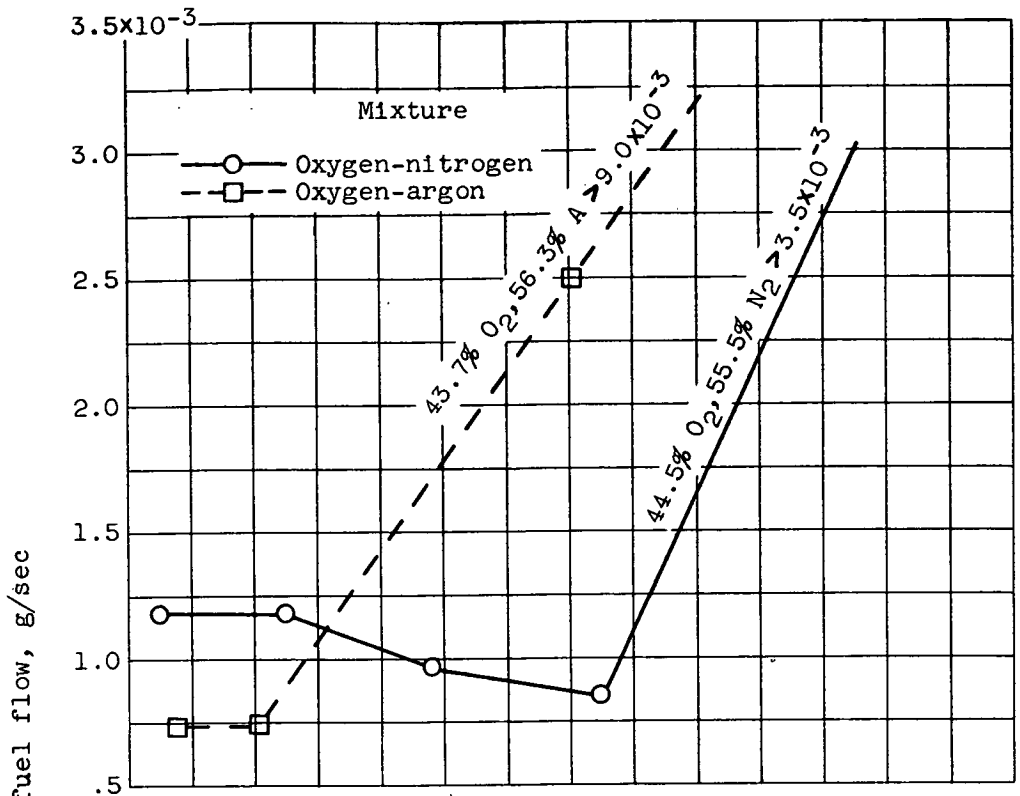
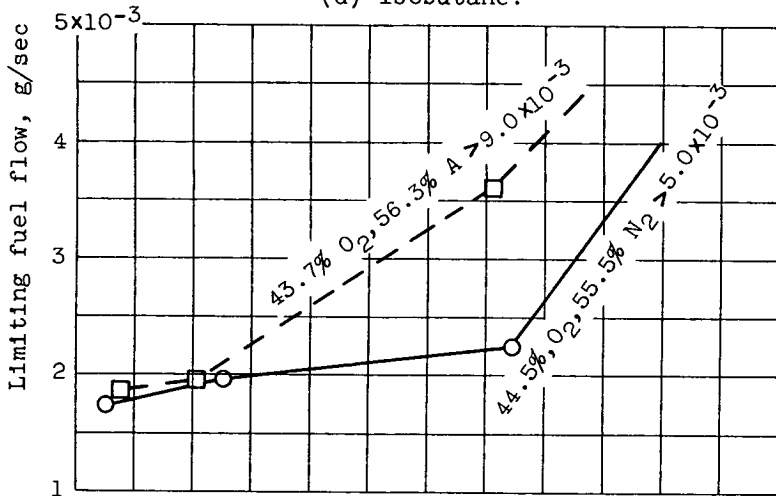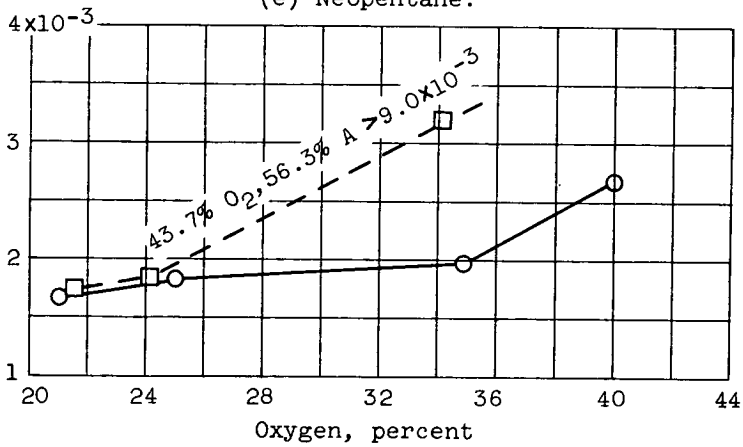(a) Propene.
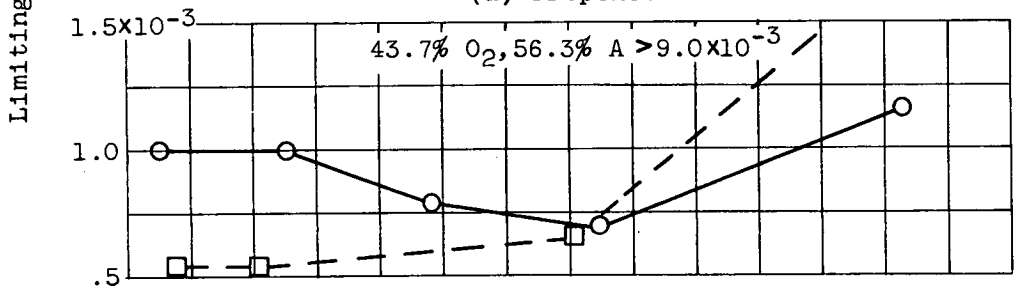
(b) Cyclopropane.
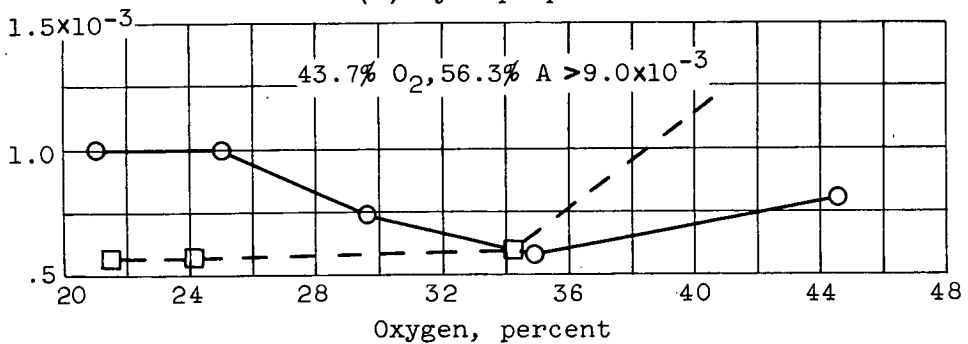
(c) Butene-1.

Figure 6. - Variation in limiting fuel flow with
oxygen enrichment.

(d) Isobutane.

(e) Neopentane.

(f) Pentene-1.

Figure 6. - Concluded. Variation in limiting
fuel flow with oxygen enrichment.