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RESEARCH MEMORANDUM

LIMITS OF FLAMMABILITY OF PURE HYDROCARBON-AIR MIXTURES AT REDUCED PRESSURES AND ROOM TEMPERATURE

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
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SUMMARY

A systematic study was undertaken to determine the effect of molecular structure on the flammability limits of pure hydrocarbon-air mixtures at reduced pressures and room temperature. This report presents results obtained for 17 pure normal paraffins, branched paraffins, and mono-olefins.

Limit determinations were made in a closed tube with hot-wire ignition. It was found that the low-pressure limit of propagation of about 34 millimeters of mercury was relatively unaffected by molecular weight, branching, or unsaturation. The fuel-rich limit of propagation, when expressed as percent stoichiometric fuel, increased markedly with increased molecular weight; whereas the lean limit of propagation narrowed slightly with molecular weight. Branched paraffins had a slightly decreased range of composition limits when compared to straight-chain isomers. The effect of branching was most evident when two methyl groups were substituted for hydrogen atoms on the same carbon atom. Unsaturation in the form of one double bond (ethylene excepted) had no significant effect when mono-olefins were compared to analogous saturated hydrocarbons. Flammability-limit curves were characterized by a two-lobe form. The formation of the fuel-rich lobe was attributed to cool-flame phenomena.

INTRODUCTION

The performance of a fuel in a jet engine is related to the combustion characteristics of the fuel. In an effort to understand the effect of molecular structure on fuel combustion characteristics, a program directed to the measurement of fundamental combustion properties of representative fuel types was undertaken at the NACA Lewis laboratory. Reports on flame velocity (reference 1) and minimum ignition energy (reference 2) have been published previously. This report contains a systematic study of the flammability limits of 17 normal paraffins, branched paraffins, and mono-olefins at reduced pressures and room temperature. Limit determinations were made in a vertical glass tube 2 inches in diameter and 4 feet long. Ignition was accomplished by a hot-wire source located at the lower end of the tube.

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Bone and Townend (reference 3) define a flammable mixture as one through which a flame can propagate indefinitely, independently of, and away from the original source of ignition. A limit mixture then, may be considered as a mixture capable of releasing only the energy necessary for the independent propagation of flame. At any pressure above a limiting value, there are at least two limits of flammability, a lean limit containing the minimum concentration of fuel, and a rich limit containing the maximum concentration of fuel that will permit independent flame propagation.

Previous information regarding flammability limits has been rather limited and selective. Coward and Jones (reference 4) report limit data for many hydrocarbons and other fuels at atmospheric pressure. Burgess and Wheeler (reference 5) determined the lean limit of propagation for some of the normal paraffins in air. Burrell and Robertson (reference 6) and Mason and Wheeler (reference 7) studied the effect of temperature and pressure on the flammability limits of methane-air mixtures. Payman and Wheeler (reference 8) determined limits for downward, horizontal, and upward propagation. Van der Hoeven (reference 9) reports a complete flammability-limit curve for propane and air at reduced pressures, in a narrow explosion burrette.

The list of references presented is only a small fraction of the work that has been done on flammability limits; however, no data are present in the literature that give complete limit curves at reduced pressures for homologous series of hydrocarbons.

A systematic study of the effect of molecular structure on flammability limits at reduced pressures is reported in this paper.

APPARATUS AND PROCEDURE

The essential components of the apparatus were a flame tube, a hot-wire ignition system, and a combustible-mixture reservoir which are illustrated in figure 1.

The flame tube was a glass cylinder 4 feet long, and 2 inches in diameter. The tube was closed at both ends with rubber stoppers.

The ignition coil consisted of about 14 inches of Brown and Sharpe 26 gage Nichrome wire wound in a 1/2-inch helix. Spark and gun-cotton ignition were also investigated and will be discussed in a following section. Ends of the coil were soldered to copper leads that extended through a rubber stopper at the lower end of the tube. Electric power to the coil was kept constant by a constant-voltage transformer. A wattmeter was used to measure power input, and an electric timer indicated the interval of time during which current was applied. A constant 60-watt power level was maintained for the tests reported.

Hydrocarbon-air mixtures were prepared in a 47-liter glass carboy. The hydrocarbon was introduced as a gas or vapor and its pressure measured with a metal Bourdon gage which covered a range of 0 to 50 millimeters of mercury. Total pressure, after air had been admitted to the carboy, was measured with an absolute mercury manometer. Mixing of hydrocarbon vapor and air was accomplished with a bellows-type stirrer. The stirring rod extended through the center of a copper bellows located at the neck of the carboy. A reciprocating motion was imparted to the stirrer by means of a cam operated by an electric motor.

Hydrocarbon fuel as a gas or vapor was admitted to the evacuated carboy and its partial pressure determined with the Bourdon gage. Air was then admitted through Ascarite, to remove carbon dioxide, and Anhydrone, to remove water vapor, to give a desired composition. The gases were then mixed to homogeneity with a bellows-sealed stirrer. Propagation in the flame tube was attempted at various pressures until the lowest pressure that would support flame travel was found. Pressure limits were determined to within ±2 millimeters. That is, two pressures were found that differed by 4 millimeters, the higher of which permitted flame propagation. The limit recorded was the average of the two pressures. Propagation of flame through the entire length of the flame tube was the criterion for flammability. Determinations were repeated at the limit as a check on reproducibility.

The maximum error in the preparation of hydrocarbon-air mixtures was ±2 percent. This error is based on ability to determine the partial pressure of the fuel. The partial pressure of air was large; therefore, the percent error for this measurement was not as great. Pressure limits were reproducible to about ±4 percent. Deviations were greatest at the extremely rich or lean portions and at the point of inflection of the limit curve.

The purity and source of the compounds used in the investigation appear in table I. Any trace of impurities present was not considered to be of a chemical nature that would significantly affect flammability limits.

RESULTS

Experimental Variables

Ignition source. - The source of ignition is known to affect flammability limits (reference 10). Figure 2 shows the limits obtained for hot-wire, spark, and gun-cotton ignition. The hot-wire source has been described in a previous section. The sparks used were of two types, an induction or long-duration spark, and a capacitance or short-duration spark. The induction spark was produced by discharging 25,000 volts A.C. across pointed stainless-steel electrodes spaced 1/4 inch apart. The capacitance spark was produced by discharging an 0.1-microfarad condenser system having a 10,000 volt potential, across the same electrodes. The gun-cotton platinum-wire system was similar to the one used by Jones and Scott (reference 11). Approximately one milligram of gun cotton was ignited by fusing electrically a 1/8-inch helix of platinum wire.

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The striking two-lobe form of the limit curves shown will be discussed in a following section. Inspection of the data points of figure 2 shows that the hot-wire source gave wider composition and lower pressure limits than any of the other sources. The induction spark, which resembled a glow discharge at low pressure, gave limits that were very close to those obtained with hot-wire ignition. It is significant that the capacitance spark was unable to ignite mixtures that contained more than 200-percent stoichiometric fuel. Several unsuccessful ignitions were attempted at 206-, 230-, and 240-percent stoichiometric fuel over a pressure range of 200 to 400 millimeters of mercury. Although the lean- and rich-composition limits found with gun-cotton ignition were in close agreement with the hot-wire limits, the low-pressure limit of propagation was roughly twice the limit determined with the other sources.

Inasmuch as the widest limits were obtained with the hot-wire source, it was used to obtain the data reported herein.

Further experiments were conducted with a hot-wire source to determine the effect of power input (watts) on flammability limits. The results illustrated in figure 3 show that at 30 watts the composition limits were narrower, and the pressure limits higher, than the limits obtained when 45 and 60 watts were impressed upon the coil. Figure 4 shows the relation between power input or watts, and coil temperatures as determined with an optical pyrometer. The temperatures at 30, 45, and 60 watts are, respectively, 810° C, 930° C, and 1040° C. Black-body conditions did not prevail, therefore the recorded temperatures are slightly low. A 60-watt power level was maintained for all further limit determinations.

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Open or closed tube. - Another experimental factor to be considered is the use of a closed flame tube for pressure-limit determinations. Figure 5 shows limit curves for propane-air mixtures determined in an open and closed flame tube. For the open tube experiments, a 47-liter carboy was connected to the lower end of the flame tube through a 3/4-inch-bore stopcock. The pressure in the carboy was made equal to the pressure in the flame tube. Just before ignition, the stopcock connecting the two vessels was opened so that propagation occurred under constant-pressure conditions. The limit curves determined in open and closed tubes have the same characteristic shape but are displaced slightly from one another. A closed tube was used for the data reported herein because of simplicity and ease of operation.

Direction of propagation. - The effect of upward and downward propagation on the flammability limits of pentane-air mixtures is shown in figure 6. The previously described hot-wire source of ignition was used for each limit curve. The lean-composition limit shows no appreciable change with direction of propagation, but the rich limit was decreased greatly for downward propagation. It was possible to ignite rich mixtures with the coil located at the top of the tube, but the flames initiated would not travel down the tube. Upward propagation was selected for this investigation because of the wider limits that result.

Tube dimensions. - The flame-tube dimensions were taken from data presented by Coward and Jones (reference 4) which show that there is a negligible increase in composition limits at atmospheric pressure for tube diameters larger than 2 inches. It is quite possible, however, that a 2-inch diameter tube is not large enough to prevent inhibition of propagation at low pressures by wall effects. It will be shown in a following section that it is possible to relate variation in limits with pressure to surface quenching.

A 4-foot tube length was chosen on the assumption that any energy supplied to the combustible mixture in excess of the amount required for ignition would be dissipated to the tube walls and in the relatively large volume of burned gas before the flame reached the top of the tube.

Experimental Observations

Limit-flame characteristics. - The physical nature of the limit flames varied considerably over the composition range studied. Figure 7 shows a typical limit curve that has eight characteristic flames superimposed at regions that were common to their appearance. A possibly significant physical characteristic is that the flames of the fuel-lean lobe are predominantly blue and fill the cross section of the tube, whereas the flames of the fuel-rich lobe are predominantly green and do not fill the tube. Elston and Laffitte (reference 12) also have reported flames similar to those of the rich lobe observed in this work. Some flames, especially those near the lean- and rich-composition limits, as well as those at the point of inflection of the limit curve, travelled up the tube about half way before being extinguished. Payman and Wheeler (reference 8) observed the same behavior and stated that it was more difficult to differentiate between a "flame cap" and independent propagation for the lean limit than for the rich limit. Flames at the point of inflection of the limit curve flashed up the tube in rapid oscillations and then vanished. Raising the pressure as little as 4 millimeters, however, resulted in rapid propagation of a large green flame for the full length of the tube. The tube used by Payman and Wheeler was only 2 feet in length which may account for difficulty they experienced.

Flammability limit curves. - Flammability limit curves for the normal alkanes appear in figure 8. The data are plotted as limit pressure against the composition expressed as percent stoichiometric fuel. Percent stoichiometric fuel is defined as the actual fuel-air ratio divided by the stoichiometric fuel-air ratio. The composition limits become wider as the molecular weight of the hydrocarbon increases from methane to hexane. The low-pressure limit of propagation shows no change with molecular weight. All the limit curves except methane have the characteristic two-lobe shape.

The effect of unsaturation for a two-carbon-atom molecule is shown in figure 9 where limit curves for ethane and ethylene appear. The lean-composition and low-pressure limit show little change, but the rich-composition limit for ethylene is more than twice the limit for ethane. Figures 10 and 11 have limit curves plotted for some alkenes with their corresponding alkanes.

The effect of unsaturation in the form of one double bond is inconsistent. Butene-1 and pentene-1 exhibit slightly wider composition limits than butane and pentane, respectively, but propene and hexene-1 have narrower limits than propane and hexane. The differences are small, however, and may be insignificant.

The effect of branching on flammability limits is shown in figures 12, 13, and 14 in which branched alkanes are compared to straight-chain isomers. The only appreciable reduction in composition limits occurs when two methyl groups are substituted for hydrogen atoms on the same carbon atom. This effect can be seen in figure 13 where 2,2-dimethylpropane and 2,2-dimethylbutane are compared with n-pentane and n-hexane, respectively.

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DISCUSSION

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A flammable or explosive mixture may be defined as one through which a flame can be propagated indefinitely, independently of, and away from the original source of ignition (reference 3). The propagation of flame is dependent upon the transfer of energy from the burned to the neighboring unburned gas. In a limit mixture, the amount of energy available for transfer is the minimum required for the maintenance of flame.

Wall quenching. - Inasmuch as an energy balance is probably established between the flame and its surroundings, the flammability limit may be controlled by wall-quenching effects. On the assumption that the pressure limits are a wall-quenching phenomenon, Friedman and Johnston (reference 13) estimate that the minimum tube diameter for propagation of propane flames at 35 millimeters would be 1.6 inches based on experiments made to determine the minimum quenching distances as a function of pressure. This result is in rough agreement with the low-pressure limit of 34 millimeters obtained for propane with a 2-inch tube in this research. Belles (reference 14) also has investigated wall effects and found that the low-pressure limit of propagation varied directly with the surface-to-volume ratio for a series of cylindrical tubes.

Two-lobe phenomenon. - Perhaps the most striking feature of the limit curves is their two-lobe characteristic. One would expect the curves to exhibit only one minimum. Spence and Townend (reference 15) as well as White (reference 16) postulate that the point of inflection of the limit curve is actually the intersection of two curves, one forming the limits for normal flames, and the other forming the limits for cool flames.

The cool-flame hypothesis for the formation of the rich lobe is further substantiated in this investigation inasmuch as:

(1) Methane, which has but one lobe to its limit curve, does not support cool-flame combustion (reference 17).

(2) Jost (reference 18) reports that cool flames propagate at a rate of about 10 to 20 centimeters per second. The flames of the rich lobe of the limit curve also travelled at about 10 to 20 centimeters per second.

(3) White (reference 16) found that it was impossible to initiate cool-flame combustion with a capacitance spark. A capacitance spark was also unable to initiate flame for rich propane-air mixtures in this investigation.

(4) White (reference 16) was unable to propagate the cool flames of ether and acetaldehyde downward. Flames of the rich lobe of the limit curves determined in this investigation were also unable to propagate downward.

SUMMARY OF RESULTS

From the results of the 17 hydrocarbons investigated under the conditions described, the following statements are made:

(1) The low-pressure limit of flame propagation was relatively unaffected by the molecular weight, branching, or unsaturation.

(2) Limit curves of pressure against composition were characterized by a two-lobe form. The formation of the second, or rich, lobe was attributed to cool-flame phenomena.

(3) When expressed as percent stoichiometric fuel, the range of flammability (rich minus lean limit) increased with increased molecular weight.

(4) Branched paraffins exhibited composition limits that were slightly narrower when compared with straight-chain isomers. An appreciable reduction in limits occurred only when two methyl groups were substituted for hydrogen atoms on the same carbon atom.

(5) Unsaturation in the form of one double bond (ethylene excepted) had no significant effect when compared to analogous saturated compounds.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, March 12, 1951.

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TABLE I - SOURCE AND PURITY OF COMPOUNDS USED

Compound	Source	Purity (mol percent)
Methane	M[1]	99
Ethane	P[2]	99.9
Propane	P	99
Butane	P	99
Pentane	NACA[3]	99.3
Hexane	NACA	97
2-Methylpropane	P	99
2-Methylbutane	NACA	99.4
2,2-Dimethylbutane	NACA	98
2,3-Dimethylbutane	NACA	----
2,2-Dimethylpropane	P	99
2-Methylpentane	NACA	99.3
Ethylene	O[4]	99.5
Propene	P	99
Butene-1	P	99
Pentene-1	NACA	----
Hexene-1	NACA	----

[1]Matheson Co., Inc.

[2]Phillips Petroleum.

[3]NACA. Prepared jointly by National Bureau of Standards and NACA.

[4]Ohio State Univ. Res. Foundation, A.P.I. Res. Proj. 45.

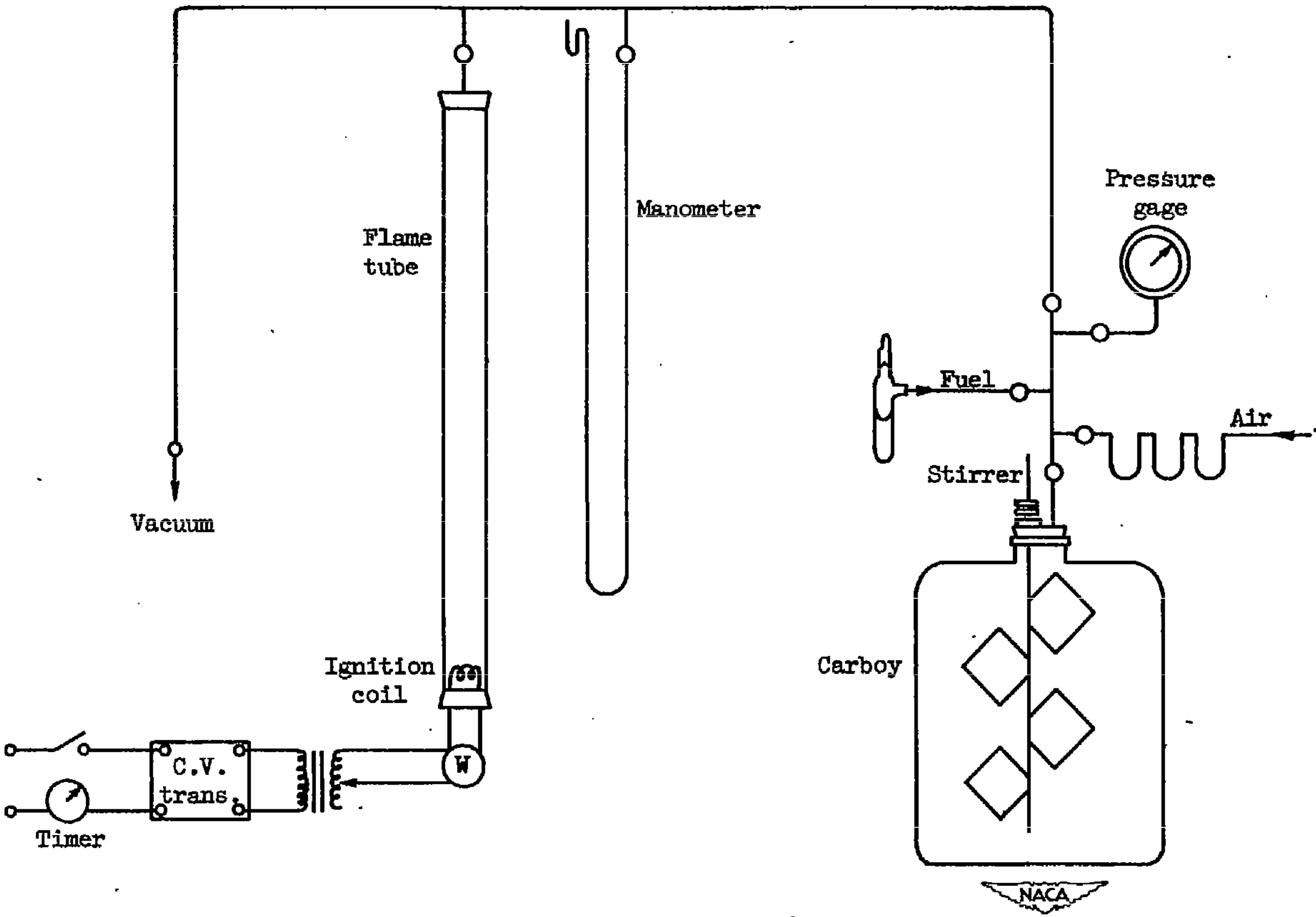

Figure 1. - Flammability limit apparatus.

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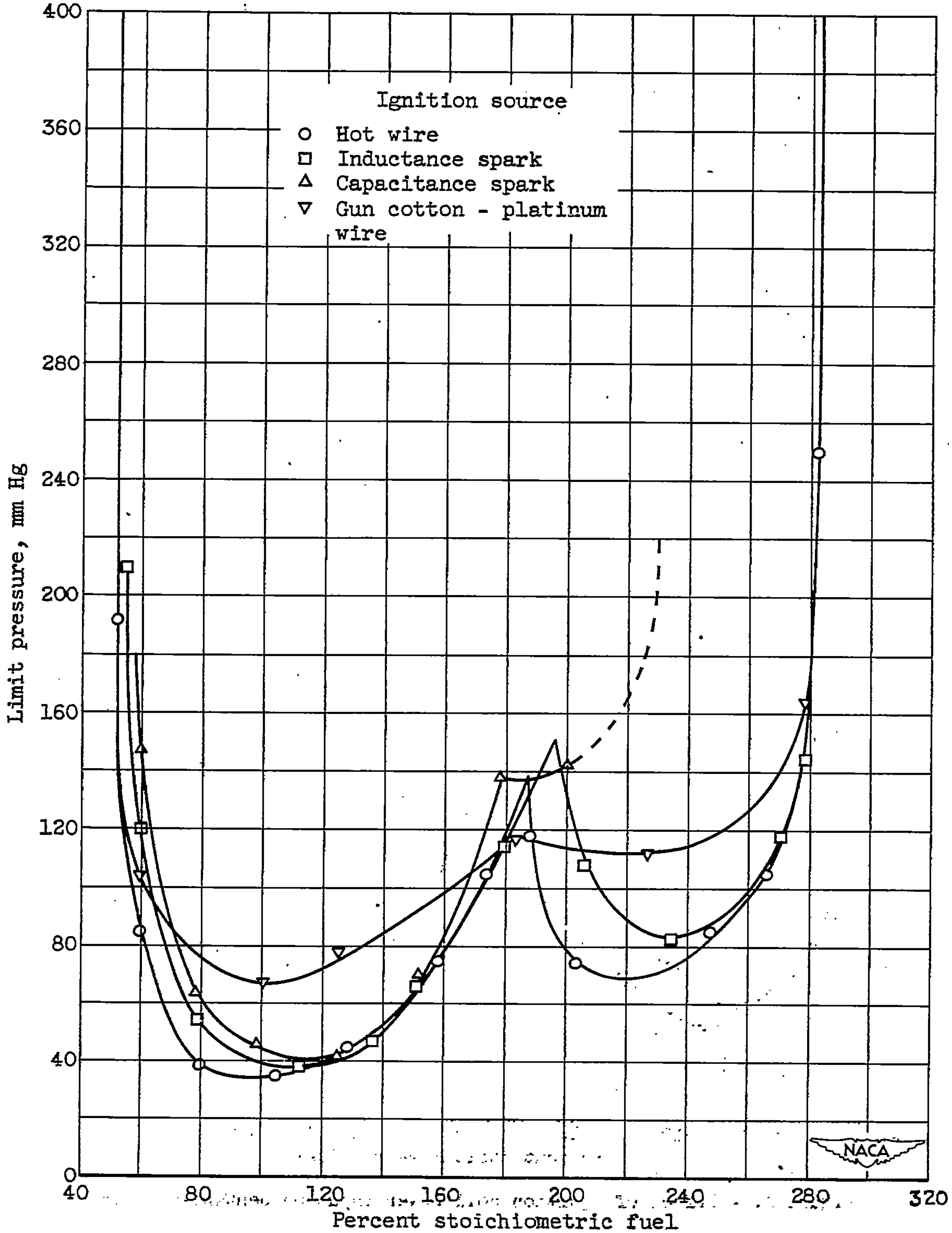

Figure 2. - Effect of ignition source on propane-air limits.

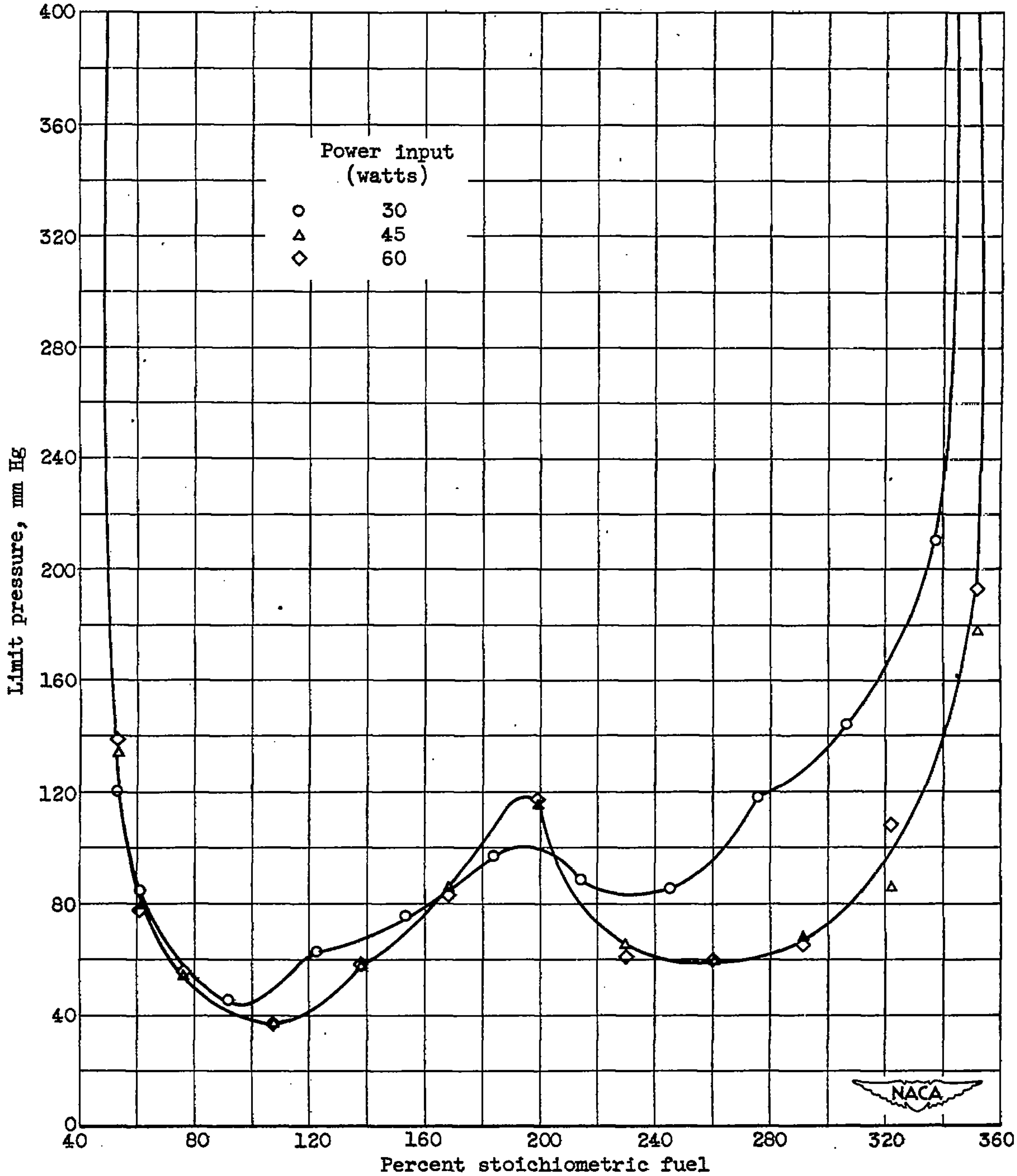

Figure 3. - Effect of ignition coil power input on pentane-air limits.

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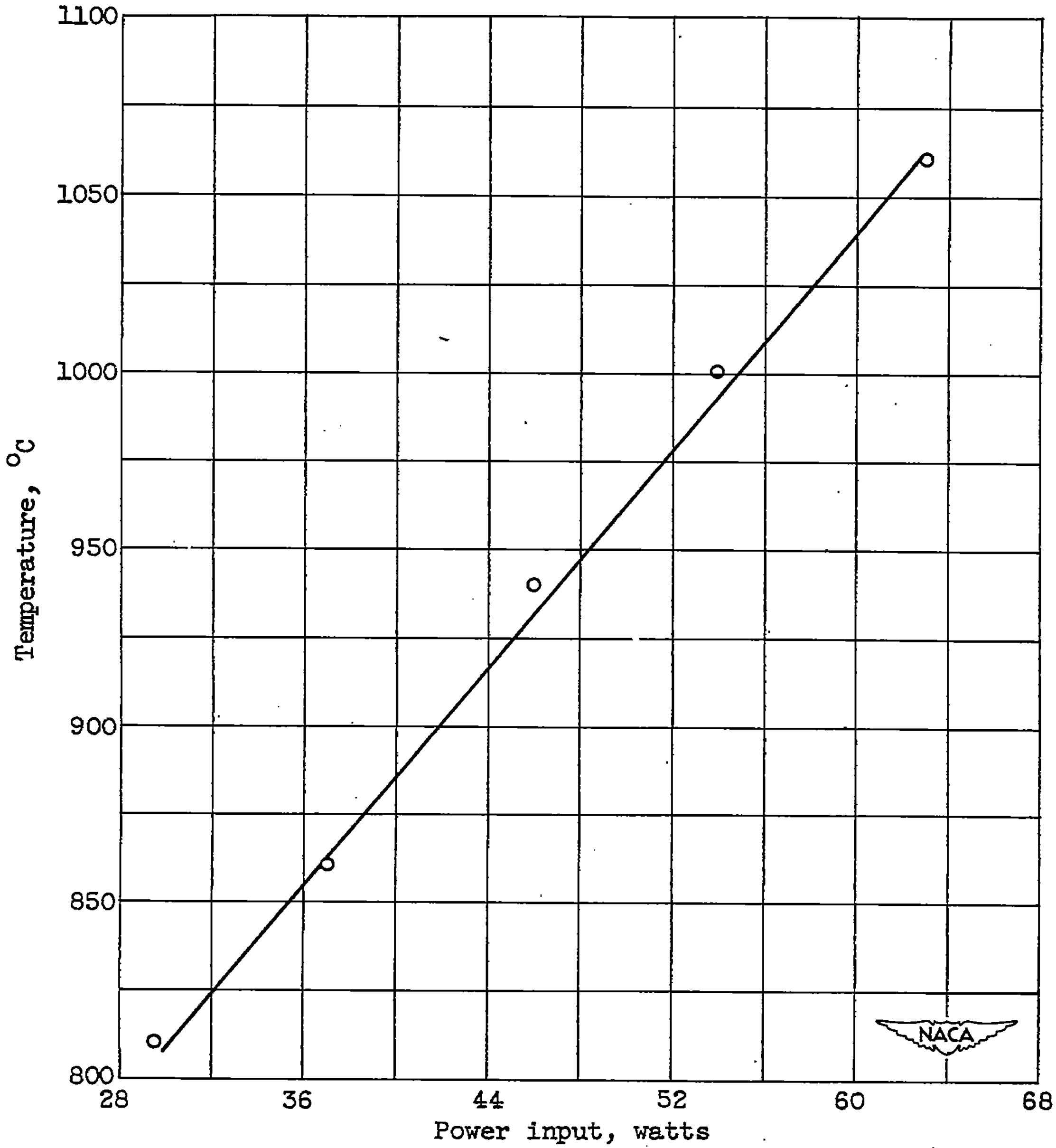

Figure 4. - Ignition coil power input against temperature.

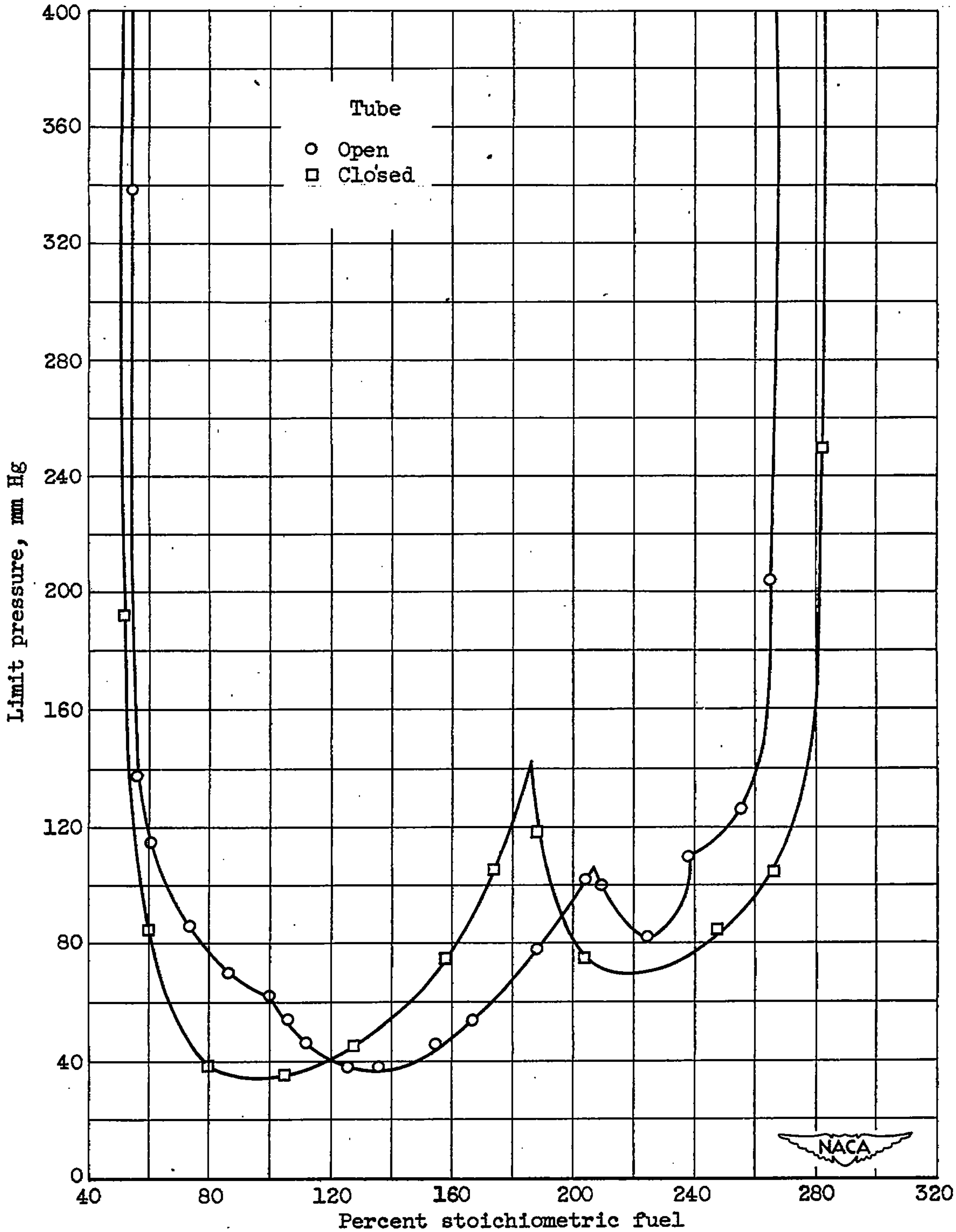

Figure 5. - Effect of open or closed tube propagation on propane-air limits.

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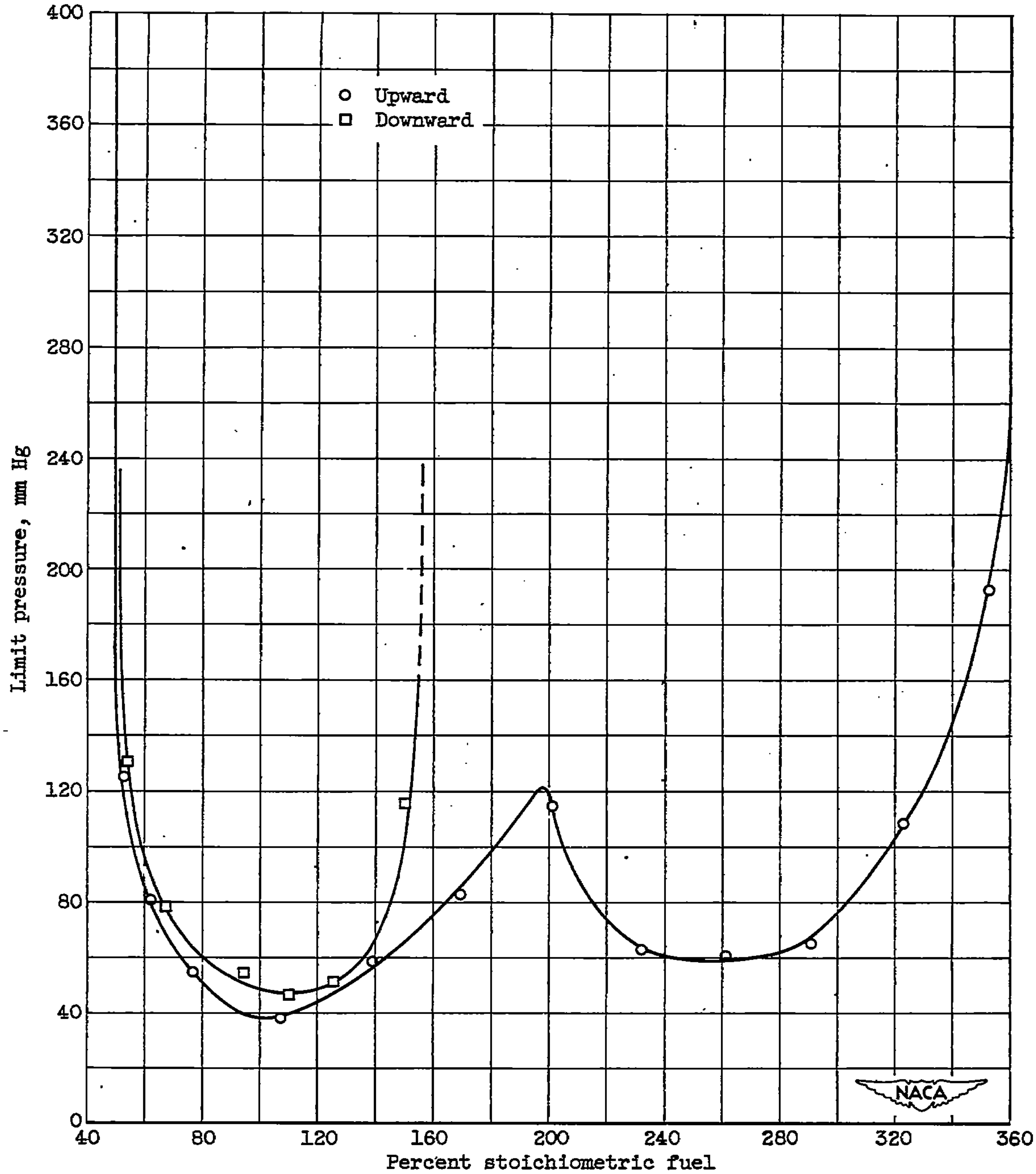

Figure 6. - Effect of upward and downward propagation on pentane-air limits.

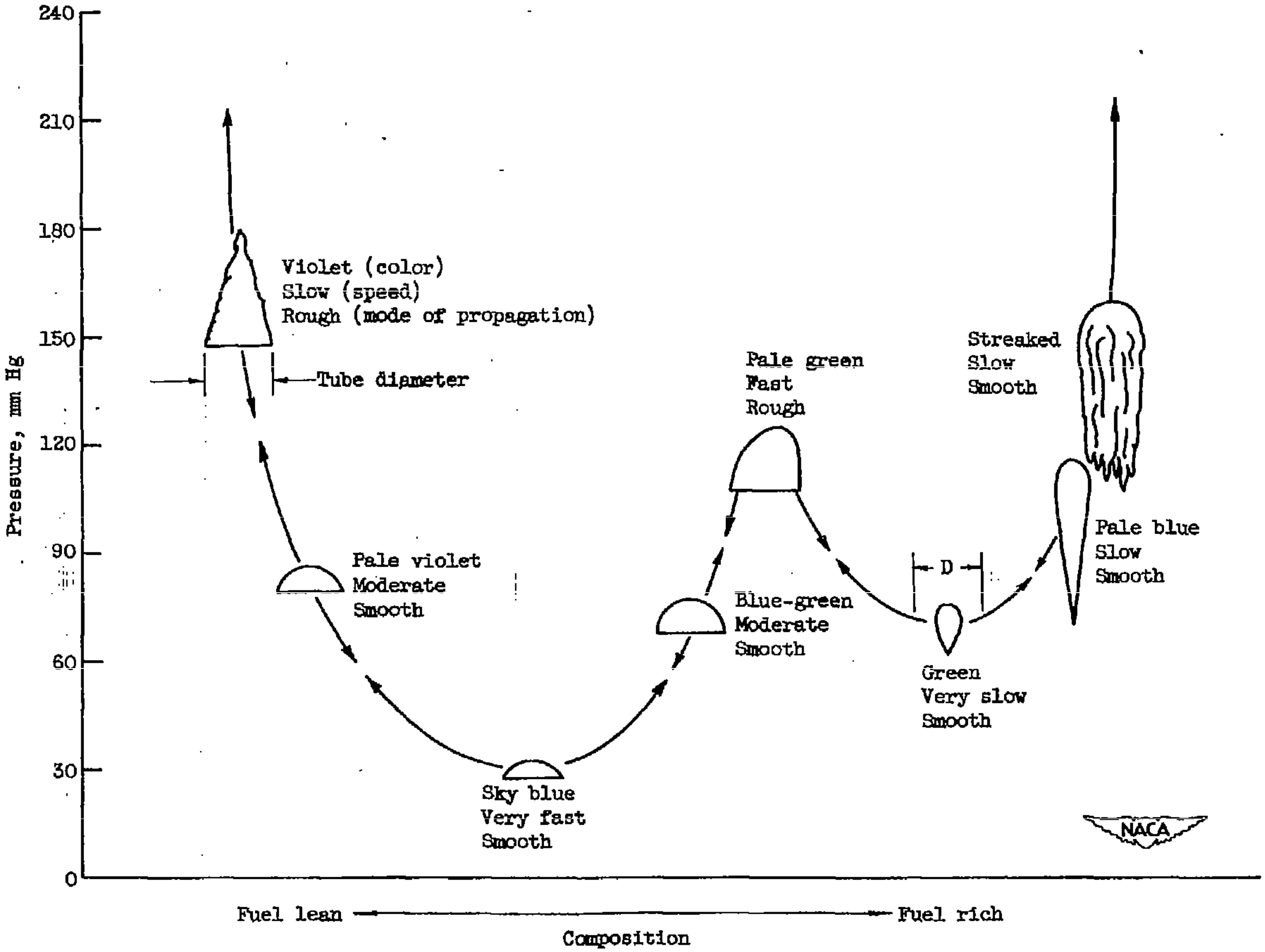

Figure 7. - Character of flames near limits.

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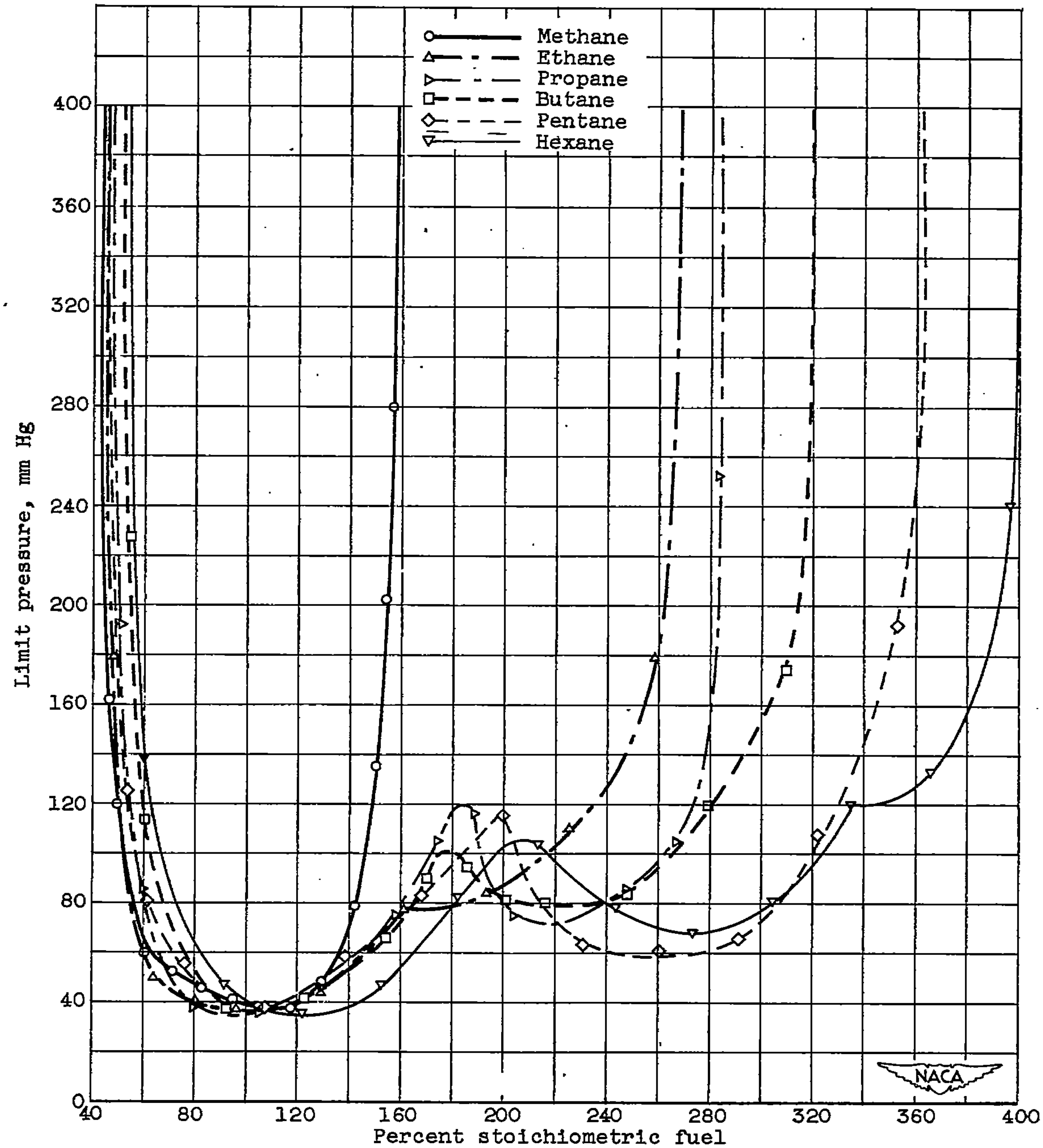

Figure 8. - Effect of molecular weight on flammability limits.

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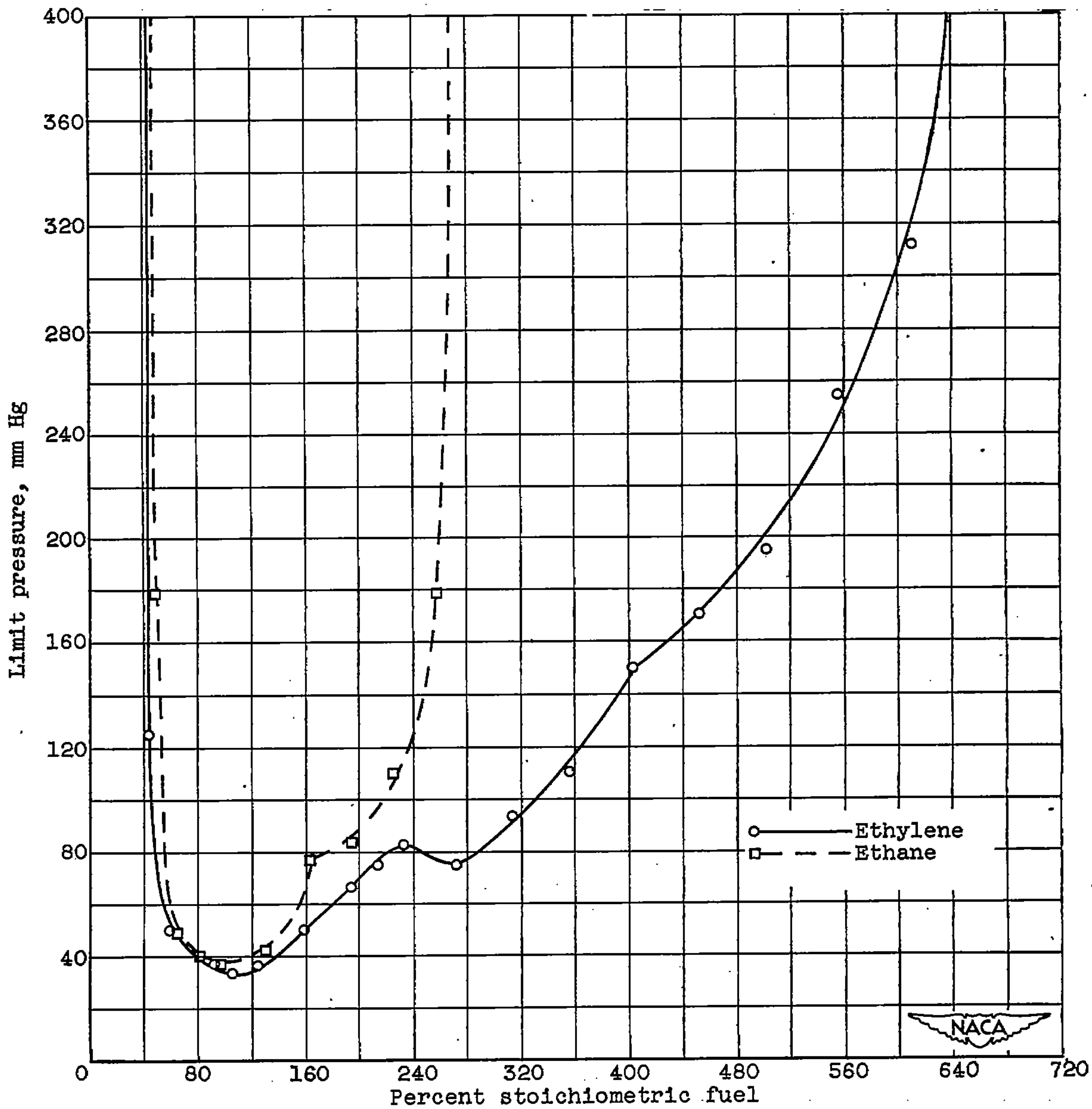

Figure 9. - Flammability limit curves for ethylene and ethane.

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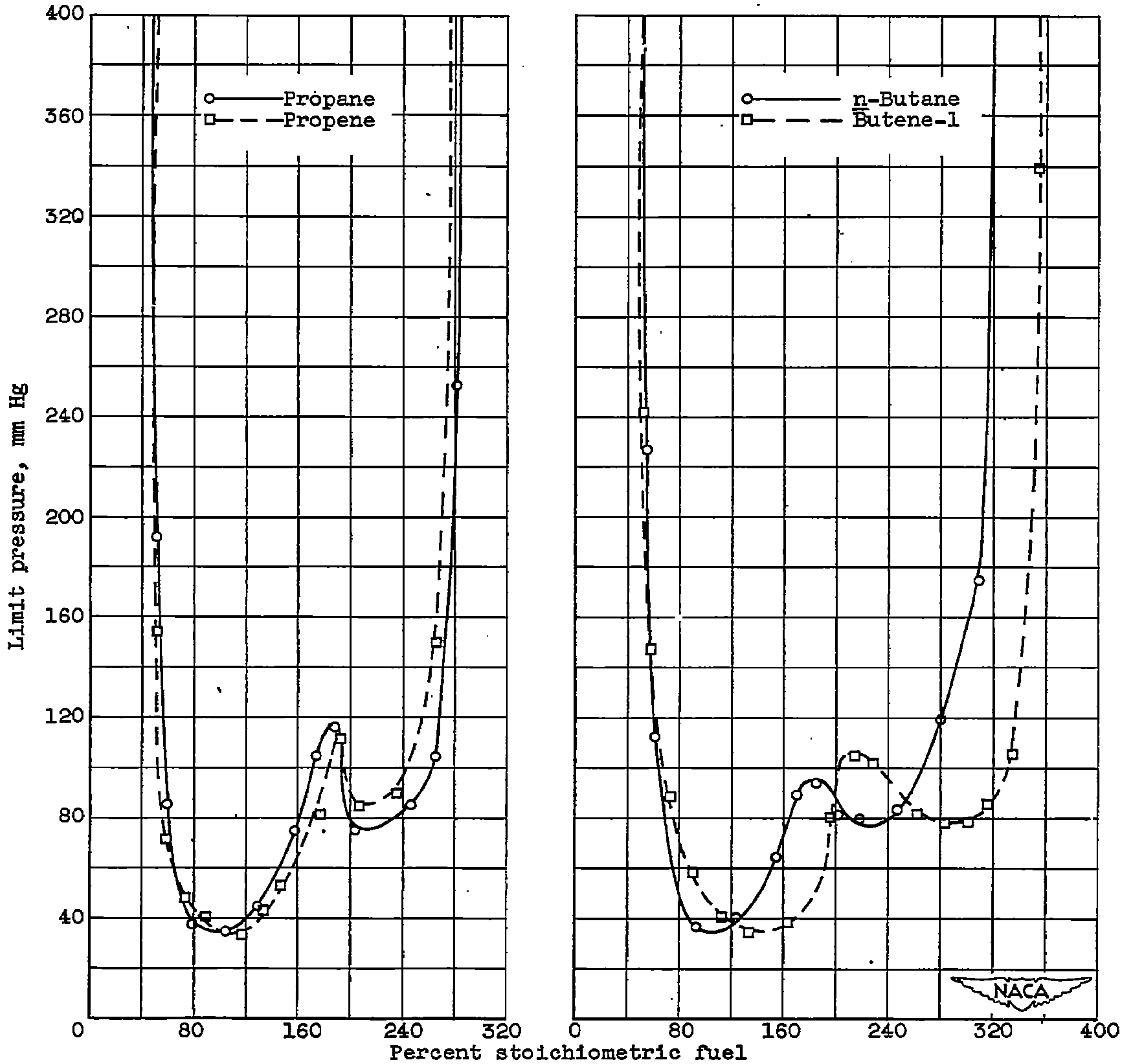

Figure 10. - Limit curves for propane, propene, n-butane, and butene-1.

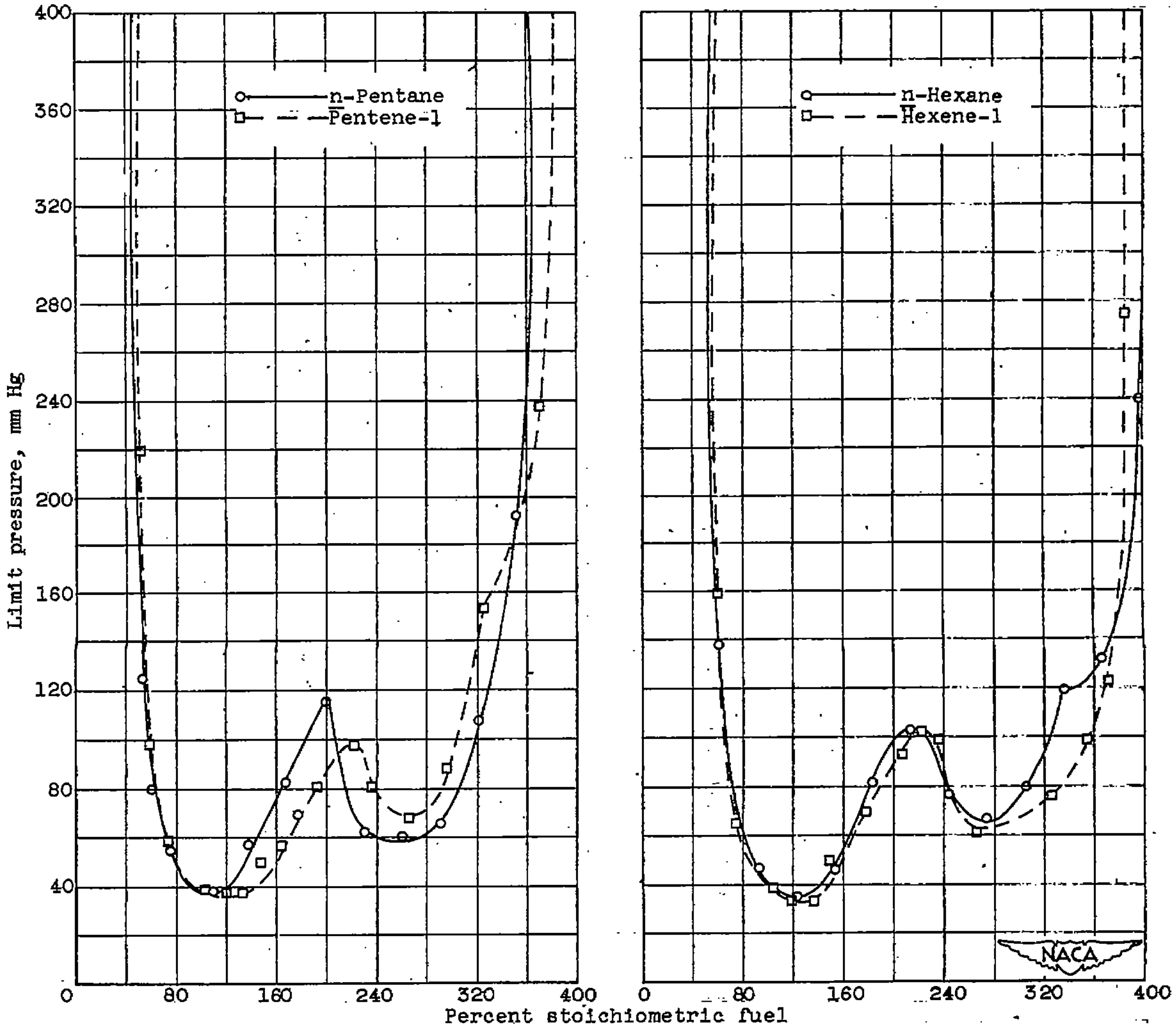

Figure 11. - Limit curves for n-pentane, pentene-1, n-hexane, and hexene-1.

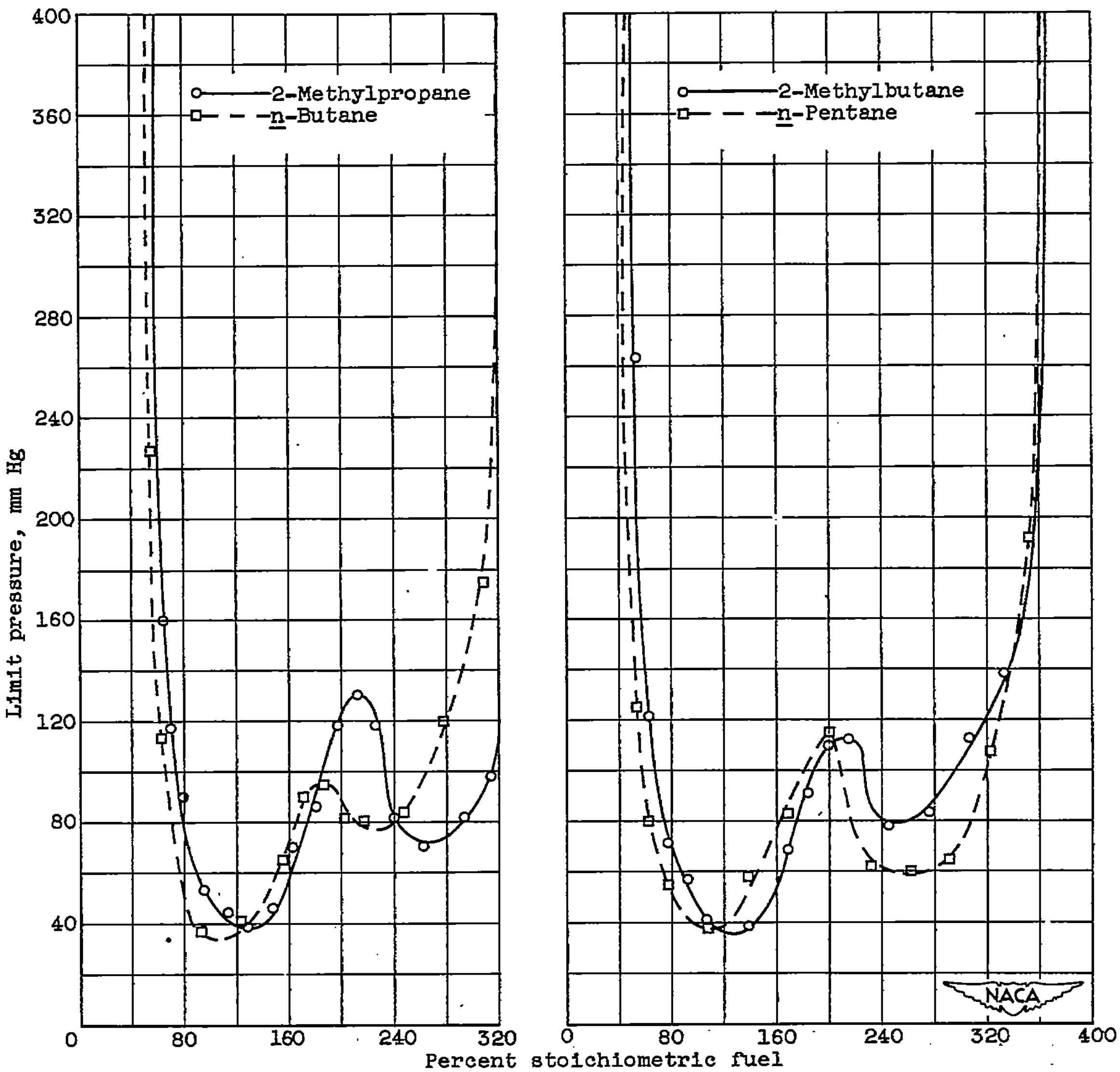

Figure 12. - Effect of branching on flammability limits for butane and pentane isomers.

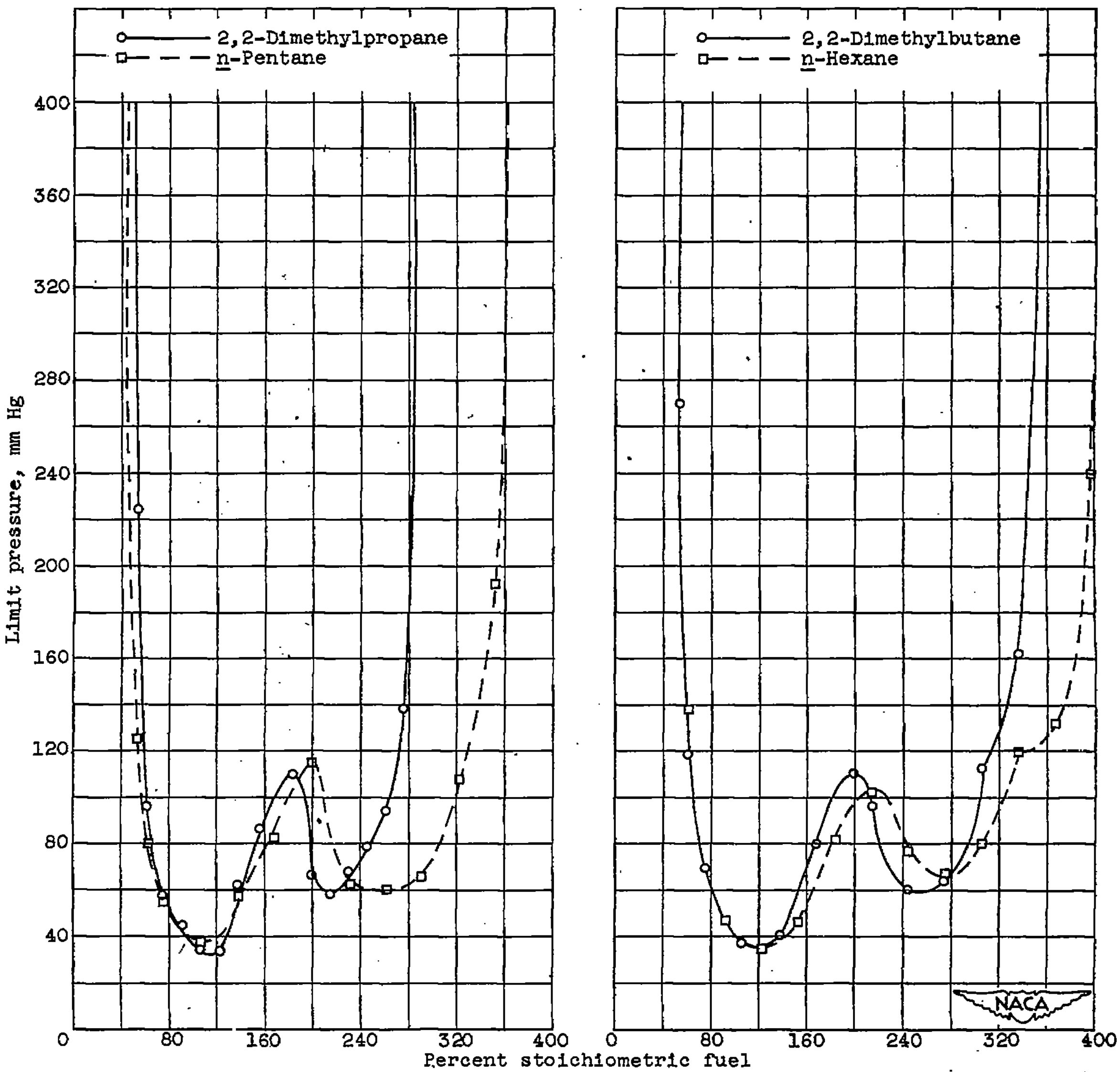

Figure 13. - Effect of branching on flammability limits for pentane and hexane isomers.

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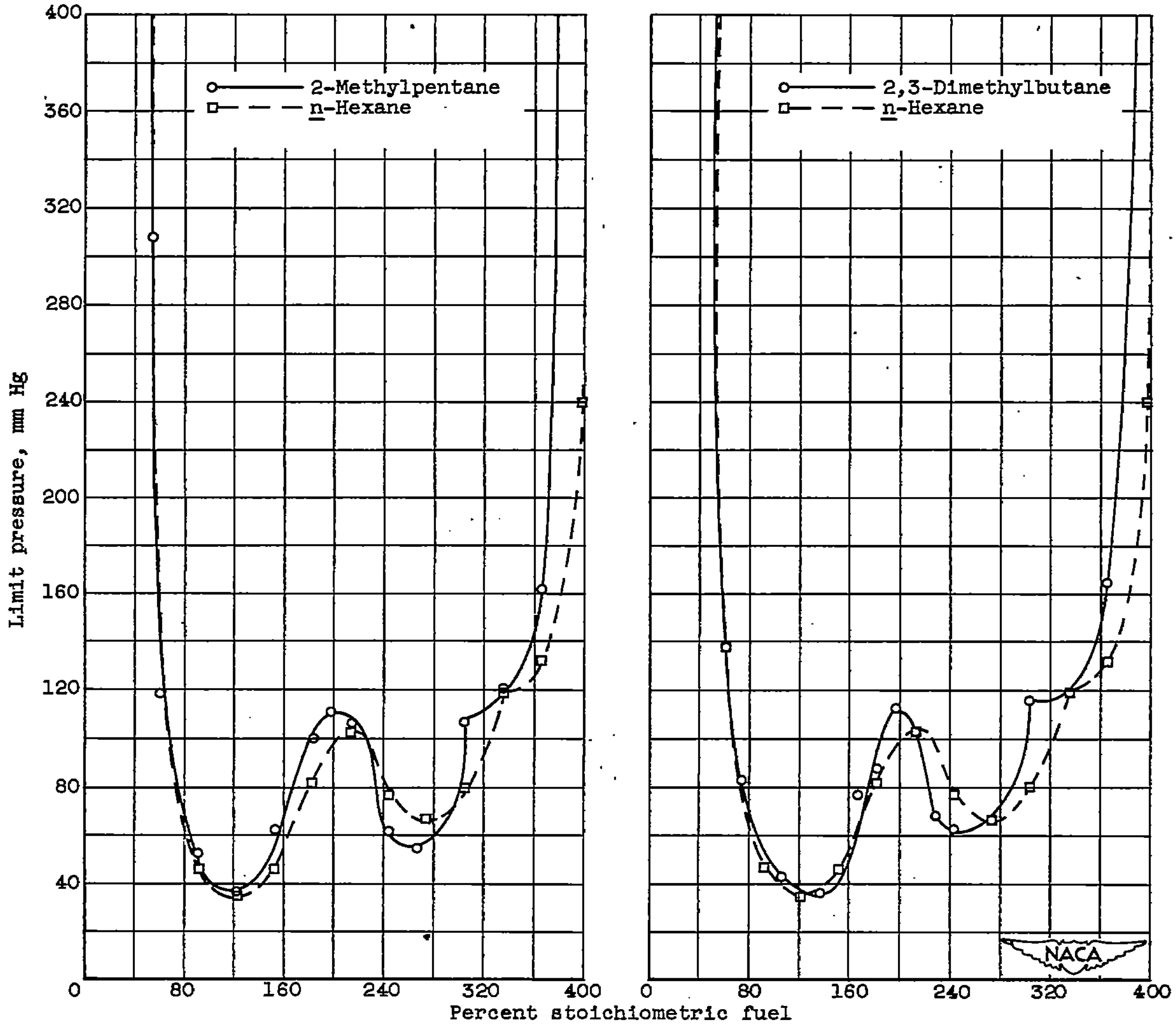

Figure 14. - Effect of branching on flammability limits for hexane isomers.