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# RESEARCH MEMORANDUM

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## A STUDY OF THE COMBUSTION RATES OF HYDROCARBON FUELS WITH RED FUMING NITRIC ACID IN A SMALL ROCKET ENGINE

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

# A STUDY OF THE COMBUSTION RATES OF HYDROCARBON FUELS WITH RED FUMING NITRIC ACID IN A SMALL ROCKET ENGINE*

By Louis Baker, Jr.

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## SUMMARY

The relative combustion rates of eight hydrocarbon fuels with red fuming nitric acid (19-percent nitrogen dioxide) were determined in a 40-pound-thrust rocket engine with rapid liquid-phase mixing. The combustion rates were determined in short (30 in. L*) and long (240 in. L*) combustion chambers. Seven of the fuels were pure hydrocarbons and represented several chemical classes, while the eighth fuel was JP-4.

The results indicated that there was little effect of chemical type. An analysis, based upon the concept of mixed-droplet vaporization, gave the correct general shape of the experimental characteristic-exhaust-velocity - mixture-ratio curves. The order of combustion rates, toluene > heptane, heptene > JP-4, methylcyclopentane > triptane > tetradecene or tetradecane, was thought to be due to physical differences and was interpreted in light of the vaporization model of combustion.

Heat-transfer measurements were made using water-cooled, copper chambers. A value of 0.8 Btu per second per square inch was obtained for smooth runs with hydrocarbon fuels regardless of the fuel over a wide mixture-ratio range. Screaming runs and additional runs with JP-X (40-percent unsymmetrical dimethylhydrazine by weight in JP-4 fuel) and hydrazine fuels gave heat-transfer rates ranging up to 2.1 Btu per second per square inch.

## INTRODUCTION

The propellant combination, jet fuel with fuming nitric acid, has several attractive properties for a storable system. It has been chosen for a number of different applications. The design of combustion chambers for hydrocarbon - fuming-nitric-acid systems would be aided if a reaction-rate index were available. Such data for individual jet-fuel components

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would indicate which fuel blends can give the most efficient combustion in combustors of minimum size and weight.

Previous studies at the NACA Lewis laboratory have shown that it is possible to differentiate between the combustion rates of various fuel-acid combinations in a 40-pound-thrust rocket engine using a high-speed mixing head (ref. 1). The relative combustion rates of six self-igniting fuels with red fuming nitric acid were determined. The characteristic length $L^*$ required to reach 97 percent of the maximum characteristic exhaust velocity $c^*$ was used as a measure of reactivity. The combustion rates of the fuels varied in the following order: hydrazine > trimethyltrithiophosphite > furfuryl alcohol > unsymmetrical dimethylhydrazine > allylamine > o-toluidine. (The symbols used in this report are defined in appendix A.)

This report describes a similar study of the relative combustion rates of jet fuel and jet-fuel components with red fuming nitric acid (RFNA). The jet-fuel components studied were paraffinic, olefinic, napthenic, and aromatic hydrocarbons. The effect of fuel molecular weight and degree of branching was also investigated.

Heat-transfer measurements were made using water-cooled combustors, and the measured heat losses were used to correct theoretical $c^*$ values. Heat-transfer measurements were also made with JP-X fuel (40-percent unsymmetrical dimethylhydrazine by weight in JP-4) and hydrazine.

A swirl-cup-type injector was used to produce efficient liquid-phase mixing. This injector was identical to the one used in reference 1, therefore, the results should be comparable. Combustion chambers were various lengths of 1.5-inch-diameter pipe. The results were interpreted in terms of a vaporization model of the combustion process.

## APPARATUS AND PROCEDURE

The apparatus and instrumentation are described in detail in reference 1. A schematic diagram of the 40-pound-thrust rocket engine and injector is shown in figure 1. Water-cooled, copper chambers were used to measure heat transfer; most of the runs, however, were made in uncooled steel-pipe chambers having an inside diameter of 1.5 inches. The 1.5-inch-diameter chambers were used rather than the 1-inch-diameter chambers of reference 1 because it was possible to obtain larger $L^*$ values without excessive chamber length. It was reasoned that large $L^*$ values would be required for the hydrocarbon fuels because of their relative inertness toward RFNA in the liquid phase. The larger chamber also had

less tendency to bow when overheated. The chamber lengths and corresponding $L^*$ values are given in the following table:

| Uncooled chambers, 1.5-in. diam | | Cooled chambers, 1.60-in. diam | |
|---|---|---|---|
| Length, in. | $L^*$, in. | Length, in. | $L^*$, in. |
| 1.5 | 30 | 2.6 | 60 |
| 2.4 | 47 | 4.4 | 100 |
| 4.9 | 97 | 8.8 | 200 |
| 7.1 | 140 | 12.1 | 275 |
| 12.2 | 240 | | |

## Operation

None of the hydrocarbon fuels studied ignited spontaneously with RFNA. Ignition was achieved with an 8- to 10-cubic-centimeter slug of unsymmetrical dimethylhydrazine (UDMH). Extreme care was necessary to avoid destructive explosions which resulted when small quantities of hydrocarbon fuel preceded the UDMH into the chamber.

The 8- to 10-cubic-centimeter slug of UDMH was sufficient to operate the engine as long as 1 second for runs with low fuel-flow rates. A total run time of at least 3 seconds was used to ensure complete removal of UDMH before measurements were made near the end of the run. The complete removal of UDMH was further verified by cold-flow tests using dyed UDMH solutions.

The experiments were conducted at a nominal chamber pressure of 300 pounds per square inch and total flow rates that varied from 0.20 to 0.30 pound per second.

## Fuels and Acid

The red fuming nitric acid used throughout the study contained from 18- to 19-percent nitrogen dioxide ($NO_2$) and from 0.2- to 2.5-percent water ($H_2O$).

In addition to JP-4, the following pure hydrocarbon fuels were used in this study:

(1) Straight-chain paraffins: n-heptane, $C_7$; n-tetradecane, $C_{14}$



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(2) Branched-chain paraffin: 2,2,3-trimethylbutane, (triptane), $C_7$

(3) Straight-chain olefins: n-heptene-1, $C_7$; n-tetradecene-1, $C_{14}$

(4) Napthenic: methylcyclopentane, $C_6$

(5) Aromatic: toluene, $C_7$

The density of each fuel was measured and compared to literature values in table I. The physical characteristics of the JP-4 fuel are given in table II. The JP-X fuel used for heat-transfer measurements was a mixture of 60-percent JP-4 fuel and 40-percent commercial-grade UDMH proportioned by weight. The hydrazine was commercial anhydrous hydrazine.

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## Treatment of Data

The characteristic length $L^*$ was calculated from chamber volume and nozzle-throat area; characteristic exhaust velocity $c^*$ was calculated from (chamber pressure)(nozzle-throat area)/(total-flow rate). The mixture ratio o/f was acid weight flow/fuel weight flow. To compare different fuels, the parameter $\beta = (o/f)/(o/f)_{st}$ was used.

The heat-transfer rates were calculated from the water-coolant flow rate and the temperature rise of the water. The values are average rates over the length of the chamber but do not include heat transferred in the nozzle.

## CHARACTERISTIC EXHAUST-VELOCITY-PERFORMANCE RESULTS

The characteristic exhaust velocity $c^*$ is shown in figure 2 as a function of mixture ratio and $L^*$. Three fuels: toluene, heptane, and heptene were run in five different chamber lengths. Analysis of the data showed that no well-defined differences existed in the $L^*_{97}$ values for the three fuels. The small differences in fuel ratings depended upon the mixture ratio chosen for comparison and upon the reference percentage of maximum experimental $c^*$. In addition, the fuels did not reach a maximum $c^*$ below an $L^*$ of 240 inches. It was thus decided to compare the fuels on the basis of their performance in the shortest and longest chamber ($L^*$ of 30 and 240 in., respectively), and the remaining fuels therefore were run only in these two chambers.

The reproducibility of the data was tested by repeating toluene runs in the 30- and 240-inch chamber lengths. The original data were obtained early in the experimental program; the repeat runs (fig. 2(a)) were made near the close of the experimental program and were found to agree well with the original data.

The short-chamber, $L^*$ of 30 inches, data are compared in figure 3. The apparent order of combustion rates is toluene > heptane, heptene > JP-4, methylcyclopentane > triptane > tetradecene or tetradecane for values of $\beta$ from 0.6 to 0.7. The order depended somewhat on mixture ratio. The long-chamber, $L^*$ of 240 inches, data are compared in figure 4. The long-chamber $c^*$ values fell in a band which was approximately 200 $c^*$ units wide, and as a result differentiation among the fuels was virtually impossible.

## Screaming Runs

High-frequency combustion oscillations (screaming) occurred frequently in chambers having an $L^*$ greater than 200 inches (chamber lengths exceeding 8.8 in.). Screaming (identified by the audible screech) was not associated with a particular fuel but occurred randomly with each fuel. In the cooled chambers screaming invariably gave increased heat-transfer rates.

Screaming reduced $c^*$ for heptane and for fuel-rich mixtures of heptene probably because of increased heat losses. With acid-rich mixtures of heptene $c^*$ increased during screaming. In this case, the increased combustion efficiency associated with screaming more than offset the increased heat losses. Screaming runs were not considered in the determination of the $c^*$ performance curves.

## Comparison of Long-Chamber Performance to Theoretical

No theoretical data could be found that applied precisely to the acid and fuel compositions used in the present study. Calculations were therefore made for two values of mixture ratio: $\beta = 0.8$, corresponding approximately to peak $c^*$, and $\beta = 1.0$, stoichiometric. The details of the calculations are presented in appendix B. Calculations apply only to fuels having the empirical formula $CH_2$. These include JP-4, heptene, methylcyclopentane, and tetradecene. The experimental data are compared with both uncorrected theoretical data and theoretical data corrected for heat transfer in table III. It is seen that long-chamber $c^*$ performance ranged from 94 to 99 percent of theoretical when corrected for heat losses.

## Effect of Chemical Type

The fuel heptene has a reactive double bond while heptane has no such point of attack within the molecule; however, there is no significant difference in the short-chamber performance of these two fuels (fig. 3). Similarly, tetradecene gave $c^*$ values only slightly greater than tetradecane.

There were, however, very great differences in performance between heptene and tetradecene and between heptane and tetradecane. These differences appear to be due to differences in fuel physical properties. It was shown in reference 2 that the fuel molecular weight has little effect on burning velocity in premixed fuel-air flames. This indicates that the c* differences cannot be attributed to differences in gas-phase reaction rates. An attempt was therefore made to account for performance differences in terms of the physical properties of the fuels and the acid.

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## ANALYSIS OF DROPLET BURNING

### Vaporization Model

Recent studies with the hydrocarbon - liquid-oxygen propellant combination have shown that the vaporization of fuel droplets is an important rate-limiting step (refs. 3 and 4). Droplet vaporization was also found to be an important rate-controlling step in the combustion of furfuryl alcohol - aniline mixtures with RFNA (ref. 5). It was concluded in reference 5 that heat generation inside mixed droplets of fuel and acid increased their evaporation rate, thereby increasing combustion performance in short chambers.

The furfuryl alcohol - aniline fuel mixtures studied in reference 5 undergo rapid liquid-phase reactions with fuming nitric acids. This is evidenced by the fact that the system is self-igniting. The hydrocarbon fuels used in the present study are not self-igniting with fuming nitric acids and do not undergo rapid heat-generating reactions. The degree of liquid-phase reactivity of hydrocarbons with RFNA can be judged by the rate of temperature rise on rapid mixing of the two liquids. Reference 6 reported that JP-4 - RFNA mixtures gave a temperature rise of only $50^{\circ}$ F in 0.6 second. With octane, a temperature decrease was obtained. The most reactive hydrocarbon reported was octene-2 which gave a $97^{\circ}$ F rise in 0.6 second. In order to be effective within an engine, heat liberation within the mixed drop must be of the same order of magnitude as the heat transferred to the drop, and this heat liberation must occur in a few milliseconds. It is reasonable to suppose that chemical heat generation within mixed hydrocarbon-acid droplets is not an important factor in rocket combustion.

Accordingly, the vaporization model of rocket combustion was interpreted assuming negligible liquid-phase reactivity.

## Vaporization of Mixed Droplets

This analysis assumed that the injector produces a spray of droplets of finely dispersed fuel and acid and that the two liquids are completely immiscible. A mixture of two immiscible liquids will boil when the sum of their vapor pressures is equal to the ambient pressure. They will distill at a constant weight ratio $r$ as follows (ref. 7):

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$$r = \frac{P_o M_o}{P_f M_f} \tag{1}$$

where $P$ is vapor pressure, and $M$ is molecular weight.

Liquid droplets injected into a hot-gas stream will reach a steady-state temperature somewhat below the boiling point at the prevailing pressure (ref. 8). The boiling points of the acid and fuels at 200 pounds per square inch absolute were estimated from references 9 and 10 and are given in table I. The acid is more volatile than any of the fuels. For simplicity, it was assumed that the mixed-droplet temperature would be the boiling point of pure acid at 200 pounds per square inch, that is, 260° F. Estimated vapor pressures of the fuels at 260° F are given in table I. From the vapor pressures, fuel molecular weights, and an assumed acid molecular weight of 60, the vaporization ratios $r$ of each fuel-acid combination were calculated from equation (1) and are shown in table IV.

This idealized mixed-droplet model of combustion then leads to the conclusion that there is a more or less constant and calculable mixture ratio in the vaporized gas for the entire burning process until one of the components is completely vaporized.

## Calculation of $c^*$

A method of calculating $c^*$, assuming that evaporation is the only limiting factor in the combustion process, is given in reference 11. The following equation is derived in reference 11:

$$c^*_{exp} = \left[c^*_{th}, (o/f)_v\right] K \tag{2}$$

where $(o/f)_v$ is the mixture ratio of vaporized propellant, and $K$ is the fraction of total propellant vaporized. The mixture ratio of vaporized material $(o/f)_v$ is equal to the vaporization ratio $r$ if idealized mixed-droplet vaporization occurs and if neither propellant is completely vaporized. Then $c^*_{exp}$ can be calculated from equation (2) for any input mixture ratio $o/f$ and for any assumed value of the fraction of propellant evaporated $K$ if theoretical $c^*$ values are available.

A typical $c^*$ mixture-ratio diagram is shown in figure 5 using the theoretical values of $c^*$ of reference 12. The $c^*$ values were calculated for white fuming nitric acid (WFNA) and octane combination and were assumed to apply approximately to the fuel-acid combinations used in the present study. The diagram shows the expected $c^*$ values for various values of the fraction of propellants vaporized for the idealized case of mixed-droplet vaporization.

## Comparison of Results to Idealized Droplet Model

The experimental data indicated little effect of chemical type, and the injector produced rapid liquid-phase mixing (ref. 1), and thus to test the vaporization model it is necessary only to compare the experimental results with the theoretical $c^*$ curves predicted by the model.

## Fraction of Propellants Vaporized

It is necessary to consider what variations of $K$, the fraction of propellants vaporized, would result from variations in fuel volatility and mixture ratio. The fraction of material evaporated must also depend upon the initial droplet-size distribution, the residence time of the droplets in the chamber, and the heat-transfer rate from the gases to the droplets. As a first approximation for a given fuel, $K$ might be considered to depend only upon the chamber length. The experimental data should then parallel the lines of constant $K$ on the diagrams. Diagrams for each fuel are shown in figure 6 with the experimental data superimposed. The diagrams in figures 6(f) and (g) represent the limiting cases of a totally nonvolatile fuel and a very volatile fuel, respectively.

## Volatile Fuels

The fuels methylcyclopentane and triptane were the most volatile fuels studied. Figures 6(a) and (b) show that there is no region on the diagram corresponding to complete acid vaporization. The mixed-droplet model predicts a sharp break in $c^*$, corresponding to the region of complete fuel vaporization. The experimental data follow the expected trend.

## Fuels of Intermediate Volatility

The vaporization ratios of the fuels heptene, heptane, and toluene are in the region of mixture ratios corresponding to maximum theoretical performance. The constant $K$ lines on the diagrams for heptene and heptane, figures 6(c) and (d), are horizontal over a wide range of mixture

ratio. The experimental $c^*$ for the two fuels is also constant over the range except for an anomalous $c^*$ increase occurring at fuel-rich mixture ratios of heptene.

The data for toluene are shown in figure 6(e). The mixed-droplet model predicts an increasing $c^*$ in fuel-rich mixtures and a decreasing $c^*$ in acid-rich mixtures. The experimental data show the expected trends, but the positions of the sharp breaks do not correspond accurately to the predicted values.

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## Nonvolatile Fuels

The vaporization ratios for tetradecane and tetradecene are over 200. This implies that practically all of the acid must be vaporized before any fuel can evaporate. There is, therefore, no region of constant $c^*$ in the $c^*$ mixture-ratio diagram of figure 6(f). Because the acid must evaporate first, a maximum followed by a sharp decrease in $c^*$ with increasing mixture ratio is predicted since relatively more acid has to be vaporized in acid-rich mixtures. The experimental data show the expected trend, but the slope is not as extreme as predicted. The mixed-droplet model implies, moreover, that burning cannot occur at all for extremely nonvolatile fuels in very short chambers. The burning that does occur would depend on fuel being present as pure fuel droplets so that fuel vapor is present for combustion. Possibly, a nonmixing-type injector would be preferable for combustion involving nonvolatile fuels. The same reasoning would apply for very volatile fuel. In this case, complete fuel vaporization would be required as shown in figure 6(g).

## Order of Combustion Rates

For each fuel $K$ was evaluated by dividing the experimental $c^*$ value in the linear region by $c^*_{th,(o/f)_v}$. The results are shown in table V and are reasonably constant indicating that 65 to 75 percent of the propellants are vaporized in 30-inch $L^*$ chambers. It might be expected that toluene would have a slightly increased $K$ value since the vapor coming from a mixed droplet of toluene and RFNA has a mixture ratio close to stoichiometric and would have the highest combustion temperature. Heptene and heptane both have lower temperature and $K$ values than that of toluene. Methylcyclopentane and triptane would have still lower temperatures; however, methylcyclopentane is exceptional in that it has a high value of $K$. Values of $K$ were estimated for the longer chambers with heptene, heptane, and toluene and are shown in figure 7. The $K$ values show a regular increase with chamber $L^*$.

JP-4 Performance

No attempt was made to account for the observed performance data for JP-4 fuel in terms of the evaporation theory. The evaporation ratio would increase with the amount of evaporation for a given mixed droplet because of differential distillation. The JP-4 data shown in figure 3 are similar to those for the volatile fuels, triptane and methylcyclopentane.

## HEAT-TRANSFER RESULTS AND DISCUSSION

Heat-transfer measurements were made with heptane in four water-cooled chambers of different lengths. The results, shown in figure 8, are average heat-transfer rates over the chamber length. The shortest cooled chamber, $L^*$ of 60 inches, gave only a slightly higher heat-transfer rate, 1.0 Btu per second per square inch than the longer ones, 0.8 Btu per second per square inch. Data for the other fuels were obtained only in the longer chambers, either $L^*$ of 200 inches, or $L^*$ of 275 inches.

The data for all of the hydrocarbon fuels are shown in figure 9. The data for the nonscreaming runs indicated a value of 0.8 Btu per second per square inch, which was relatively independent of the fuel and the mixture ratio. Heat-transfer rates from 0.6 to a peak of 1.3 Btu per second per square inch were reported in reference 13 for WFNA and JP-3 fuel at a chamber pressure of 300 pounds per square inch. The experimental data are compared with calculated values given in reference 13 in table VI. The engine used in reference 13 had a somewhat lower contraction ratio which would lead to an increased chamber gas velocity and an increased heat-transfer rate.

Reference 13 reported that a carbon layer was gradually formed, which after several seconds of running resulted in a decreased heat-transfer rate. No significant amount of carbon was found after runs in the present program, possibly, because the short running times did not exceed 4 seconds.

Heat-transfer rates under screaming conditions showed a maximum of 2.1 Btu per second per square inch in the stoichiometric region and dropped off sharply for fuel-rich mixtures below a $\beta$ of 0.6 (fig. 9). It is remarkable that the heat-transfer data under screaming conditions formed a continuous curve and that no heat-transfer points of intermediate value were obtained.

Heat-transfer measurements were also made for JP-X fuel and anhydrous hydrazine. The data are shown in figure 10; both fuels show a marked dependence of heat-transfer rate on mixture ratio. Values up to 2.1 Btu

per second per square inch were obtained that were of the order of the values obtained for hydrocarbons under screaming conditions.

## CONCLUDING REMARKS

The principal feature of the combustion model developed in this report is that it depends only on the assumption that evaporation is the rate-limiting step and not on the detailed nature of the vaporization process. This feature can be expressed as follows: The less volatile propellant droplets, acid or fuel, cannot reach temperatures favorable to their evaporation if they are intimately mixed with the more volatile component. Combustion then occurs at an unfavorable mixture ratio rich in the more volatile propellant and starved for the less volatile propellant.

Considerably more research is required to fully clarify the role of mixed droplets in fuel - nitric-acid combustion. The preliminary results indicate, however, that a mixing-type injector should be avoided if either a very volatile or a very nonvolatile fuel is to be used with fuming nitric acid. For fuels that undergo liquid phase reaction with nitric acid with release of substantial amounts of heat, a mixing-type injector would be desirable to take advantage of the heat liberation (ref. 14).

## SUMMARY OF RESULTS

The relative combustion rates of eight hydrocarbon fuels with RFNA were determined in short and long chambers ($L^*$ of 30 and 240 in., respectively) as a function of mixture ratio. The experiments were conducted in a 40-pound-thrust rocket engine using a swirl-cup injector. An analysis was made of the idealized combustion of mixed fuel-acid droplets with the assumption that vaporization is the only rate-determining step. The results of the investigation may be summarized as follows:

1. The experimental $c^*$ mixture-rate variations were generally predicted by an analysis based on the concept of mixed-droplet vaporization.

2. The combustion rates of the fuels generally decreased over most of the mixture-ratio range in the following order: toluene > heptane, heptene > JP-4, methylcyclopentane > triptane > tetradecene or tetradecane.

3. As acid-fuel ratio was increased, the short-chamber performance of (1) the volatile fuels, methylcyclopentane and triptane, increased sharply, and (2) the nonvolatile fuels, tetradecane and tetradecene, decreased sharply. The fuels of intermediate volatility, heptane, heptene, and toluene, gave the highest performance. The short-chamber performance of heptene and heptane was largely independent of mixture ratio; the

short-chamber performance of toluene increased at low values of the acid-fuel ratio.

4. Long-chamber performance ranged from 94 to 99 percent of theoretical after corrections for heat losses.

5. A heat-transfer rate of 0.8 Btu per second per square inch was obtained for nonscreaming runs with hydrocarbon fuels over a wide mixture-ratio range. Values up to 2.1 Btu per second per square inch were obtained for screaming runs with hydrocarbon fuels and nonscreaming runs with JP-X and hydrazine fuels.

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Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, April 28, 1958

# APPENDIX A

## SYMBOLS

| | |
|---|---|
| $c^*$ | characteristic exhaust velocity, ft/sec |
| $c^*_{th,(o/f)_v}$ | theoretical $c^*$ evaluated at vapor phase o/f |
| $c_p$ | specific heat at constant pressure, cal/mole, $^oK$ |
| $\sum H$ | total enthalpy of combustion products |
| $\Delta H_{loss}$ | enthalpy loss due to heat transfer |
| K | fraction of propellants vaporized |
| $L^*$ | characteristic length, in. |
| $L^*_{97}$ | characteristic length required to reach a $c^*$ of 97 percent of the maximum experimental $c^*$ |
| M | molecular weight |
| o/f | acid-fuel weight ratio, $\dot{w}_o/\dot{w}_f$ |
| $(o/f)_{st}$ | stoichiometric acid-fuel weight ratio |
| $(o/f)_v$ | acid-fuel weight ratio of vaporized propellant |
| P | vapor pressure, lb/sq in. |
| $Q_f$ | heat of formation at 300° K |
| R | universal gas constant, cal/mole, $^oK$ |
| r | mixture ratio of vapor coming from mixed droplet of fuel and acid |
| $T_c$ | temperature of combustion products, $^oK$ |
| $\dot{w}_f$ | fuel-flow rate, lb/sec |
| $\dot{w}_o$ | acid-flow rate, lb/sec |
| $\beta$ | fraction of stoichiometric o/f, $[o/f/(o/f)_{st}]$ |
| $\gamma$ | ratio of specific heats |

# APPENDIX B

## CALCULATIONS OF THEORETICAL PERFORMANCE

### Method

The general method of calculation of the gas composition and the required thermodynamic data are given in reference 15. The following steps were performed in the calculation:

1. By taking 1 gram of fuel and o/f grams of RFNA, the number of atoms of carbon, hydrogen, oxygen, and nitrogen (atom balance) was calculated.

2. Several temperatures were chosen, for example, 2600°, 2800°, and 3000° K, and composition calculations made by a trial and error procedure for each temperature. Calculations were continued until each of the atom balances checked to within 0.1 percent and until the total pressure, calculated from the average molecular weight, was within 0.1 percent of 350 pounds per square inch absolute. The results are given in table VII.

3. Characteristic exhaust velocity $c^*$ was calculated from the approximate equation for frozen expansion (ref. 16) for each mixture at the assumed temperature:

$$c^* = \frac{\sqrt{\frac{\gamma RT_c}{M}}}{\gamma\sqrt{\left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma+1}{\gamma-1}}}}$$

The mean specific-heat ratio $\gamma$ is defined by the following equation for perfect gases:

$$\gamma = \frac{c_p}{c_p - R}$$

where $c_p$, the mean specific heat of the mixture is

$$c_p = \frac{\sum H_{T_c} - \sum H_{T_c - 300^\circ\ K}}{300^\circ\ K}$$

4. The over-all heat balance, relating the high-temperature mixtures to the cold propellants, is

$$\sum Q_f, \text{ reactants, } 300^\circ \text{ K} + \Delta H_{loss} = \sum Q_f, \text{ products, } 300^\circ \text{ K} + \sum(H_{T_c} - H_{300^\circ \text{ K}})$$

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## Results

The calculations give values of $c^*$ and temperature $T_c$ as a function of $(\sum Q_f, \text{ reactants, } 300^\circ \text{ K} + \Delta H_{loss})$. The results for two mixture ratios, $\beta = 0.8$ and $\beta = 1.0$, for fuels having the empirical formula $CH_2$ are plotted in figure 11. Values of the theoretical adiabatic temperature and $c^*$ can be obtained by interpolation using the heats of formation of the acid and of particular fuels. Values for the four $(CH_2)_n$ fuels studied in the present research are indicated in figure 11. These $c^*$ values are also given in table III.

The heats of formation of the pure fuels were obtained from reference 10. The heat of formation of JP-4 was calculated from measured values of the heat of combustion. The heat of formation of RFNA was estimated to be -653 calories per gram from standard values of the pure components, $HNO_3$, $NO_2$, and $H_2O$ with corrections for the heat of solution of $H_2O$ in $HNO_3$ and $NO_2$ in $HNO_3$ given in reference 17.

## Correction for Heat Loss

Presentation of the results of the calculations in the form of figure 11 allows a simple correction for heat lost to the combustion chamber walls. It is only necessary to estimate $\Delta H_{loss}$ per gram of fuel (negative value), add it to the sum of the heats of formation of the acid and fuel, and look up corrected values of $T_c$ and $c^*$ on a plot of the type shown in figure 11.

Corrected data shown in figure 11 and table III were obtained assuming a heat-transfer rate of 0.8 Btu per second per square inch and an average total propellant-flow rate of 0.220 pound per second, giving values of $\Delta H_{loss}$ of 0.70 and 0.84 kilocalorie per gram of fuel for the mixture ratios $\beta = 0.8$ and $\beta = 1.0$, respectively.

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TABLE I. - PHYSICAL PROPERTIES OF FUELS AND ACID

| Material | Density, gm/cm$^3$ at 20° C | | Boiling point, °F (a) | Vapor pressure, lb/sq in. (b) | Molecular weight |
|---|---|---|---|---|---|
| | Observed | Ref. 10 | | | |
| Red fuming nitric acid | ----- | ------ | 260 | 200.0 | [c]60 |
| Methylcyclopentane | 0.748 | 0.7486 | 375 | 61.2 | 84.2 |
| Triptane | .689 | .6900 | 403 | 47.3 | 100.2 |
| Heptene | .696 | .6968 | 422 | 35.6 | 98.2 |
| Heptane | .684 | .6837 | 432 | 31.5 | 100.2 |
| Toluene | .865 | .8670 | 460 | 22.7 | 92.1 |
| Tetradecene | .778 | ------ | 772 | .3 | 196.4 |
| Tetradecane | .764 | ------ | 775 | .2 | 198.4 |

[a]Estimated at 200 lb/sq in. (refs. 9 and 10).
[b]Estimated at 260° F (refs. 10 and 11).
[c]Assumed.

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TABLE II. - PHYSICAL CHARACTERISTICS

OF JP-4 FUEL

| | |
|---|---|
| Fuel boiling point, °F<br>Percent evaporated | |
| 0 | 157 |
| 5 | 224 |
| 10 | 246 |
| 20 | 263 |
| 30 | 273 |
| 40 | 282 |
| 50 | 291 |
| 60 | 301 |
| 70 | 312 |
| 80 | 324 |
| 90 | 345 |
| 95 | 364 |
| 100 | 418 |
| Residue | 1.1 |
| Loss | .5 |
| Reid vapor pressure, lb/sq in. | 2.6 |
| Specific gravity, 60/60 °F | 0.763 |
| Hydrogen-carbon ratio by weight | .171 |
| Net heat, Btu/lb | 18,700 |
| Aniline point, °F | 134.9 |

TABLE III. - COMPARISON OF EXPERIMENTAL LONG-CHAMBER PERFORMANCE

WITH THEORETICAL DATA[a] FOR $CH_2$ FUELS

| Fuel | Mixture ratio, β | Characteristic exhaust velocity, $c^*$, ft/sec | | | Percent of corrected theoretical |
|---|---|---|---|---|---|
| | | Theoretical uncorrected | Theoretical corrected | Experimental | |
| Heptene | 0.8 | 5120 | 4980 | 4690 | 94.2 |
| | 1.0 | 4980 | 4850 | 4560 | 94.0 |
| Tetradecene | .8 | 5100 | 4960 | 4790 | 96.6 |
| | 1.0 | 4960 | 4830 | 4660 | 96.5 |
| Methylcyclopentane | .8 | 5090 | 4940 | 4770 | 96.6 |
| | 1.0 | 4960 | 4825 | 4770 | 98.9 |
| JP-4 | .8 | 5080 | 4930 | 4740 | 96.1 |
| | 1.0 | 4950 | 4820 | 4740 | 98.3 |

[a]See appendix B.

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TABLE IV. - VAPORIZATION RATIO OF RED FUMING

NITRIC ACID WITH VARIOUS FUELS

| Fuel | Stoichiometric mixture ratio, $(o/f)_{st}$ | Vaporization ratio | |
|---|---|---|---|
| | | $r^a$ | $r/(o/f)_{st}$ |
| Tetradecane | 5.51 | 251 | 45 |
| Tetradecene | 5.44 | 227 | 42 |
| Toluene | 4.95 | 5.74 | 1.16 |
| Heptane | 5.57 | 3.81 | .684 |
| Heptene | 5.44 | 3.44 | .631 |
| Triptane | 5.57 | 2.53 | .454 |
| Methylcyclopentane | 5.44 | 2.33 | .428 |

[a] $r = P_oM_o/P_fM_f$

TABLE V. - FRACTION OF PROPELLANTS VAPORIZED

IN CHAMBERS WITH 30-INCH

CHARACTERISTIC LENGTH

| Fuel | Fraction of propellant vaporized, K |
|---|---|
| Toluene | 0.741 |
| Heptane | .674 |
| Heptene | .677 |
| Triptane | .654 |
| Methylcyclopentane | .725 |

TABLE VI. - COMPARISON OF CALCULATED AND EXPERIMENTAL HEAT-TRANSFER RATES AT 300 POUNDS PER SQUARE INCH PRESSURE

| Fuel | Maximum rate of heat transfer, Btu/(sec)(sq in.) | Engine contraction ratio[a] | Reference |
|---|---|---|---|
| Hydrocarbons | 0.8 | 20.2 | Present study |
| JP-3 | 1.3 | 14.2 | 13, Experimental |
| Octane | 1.1 | 14.2 | 13, McAdams equation |
| Octane | 1.6 | 14.2 | 13, Humble equation |

[a]Contraction ratio = chamber cross-sectional area/nozzle cross-sectional area.

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TABLE VII. - EQUILIBRIUM COMPOSITION OF TWO PROPELLANT MIXTURES

AT VARIOUS ASSUMED TEMPERATURES

[Acid: Red fuming nitric acid (78.5-percent nitric acid, 19.0-percent nitrogen dioxide, 2.5-percent water)
Fuel: $(CH_2)_n$].

| Component | Partial pressure of component, lb/sq in. | | | | | |
|---|---|---|---|---|---|---|
| | $\beta = 1.0^a$ | | | $\beta = 0.8^b$ | | |
| | Temperature of combustion products, $T_c$, $^oK$ | | | | | |
| | 3200 | 2800 | 2400 | 3000 | 2800 | 2600 |
| $H_2O$ | 135.8 | 157.6 | 168.2 | 145.0 | 150.4 | 152.3 |
| $CO_2$ | 61.4 | 87.3 | 102.9 | 58.6 | 63.2 | 65.6 |
| $N_2$ | 60.0 | 65.1 | 67.8 | 57.6 | 58.8 | 59.3 |
| CO | 37.5 | 17.5 | 5.0 | 56.8 | 53.7 | 51.9 |
| $O_2$ | 16.8 | 8.3 | 2.7 | 1.7 | .5 | .1 |
| $H_2$ | 10.9 | 4.6 | 1.4 | 19.4 | 18.7 | 18.9 |
| OH | 15.6 | 5.8 | 1.4 | 6.0 | 2.8 | 1.1 |
| NO | 4.8 | 2.2 | .7 | 1.2 | .5 | .2 |
| H | 3.6 | .7 | .1 | 2.7 | 1.4 | .6 |
| O | 3.6 | .6 | .1 | .6 | .1 | .03 |
| Total | 350.0 | 349.7 | 350.3 | 349.6 | 350.1 | 350.0 |

[a]$\beta = 1.0$, o/f = 5.427.
[b]$\beta = 0.8$, o/f = 4.342.

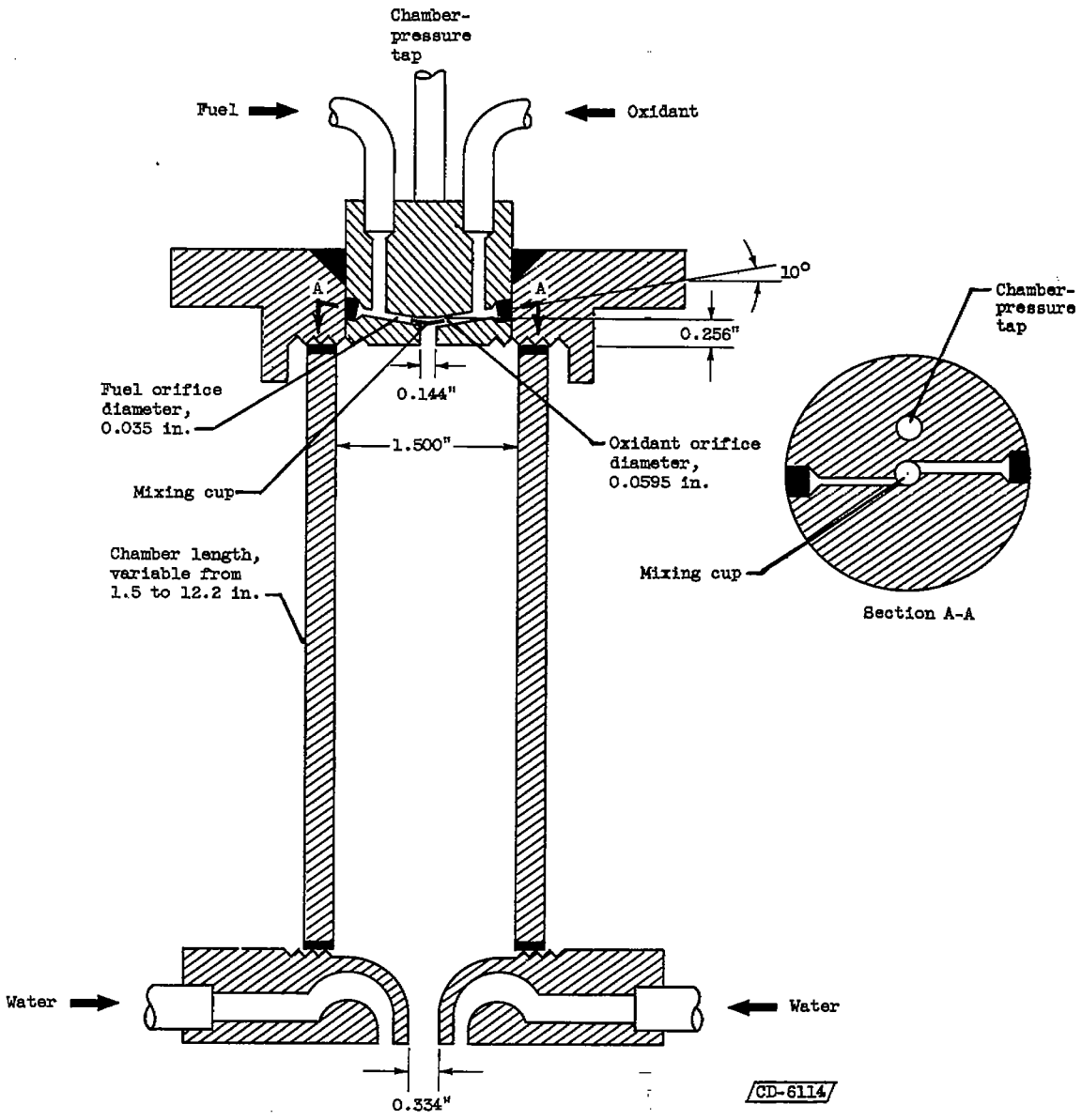


Figure 1. - Schematic drawing of 40-pound-thrust rocket engine.

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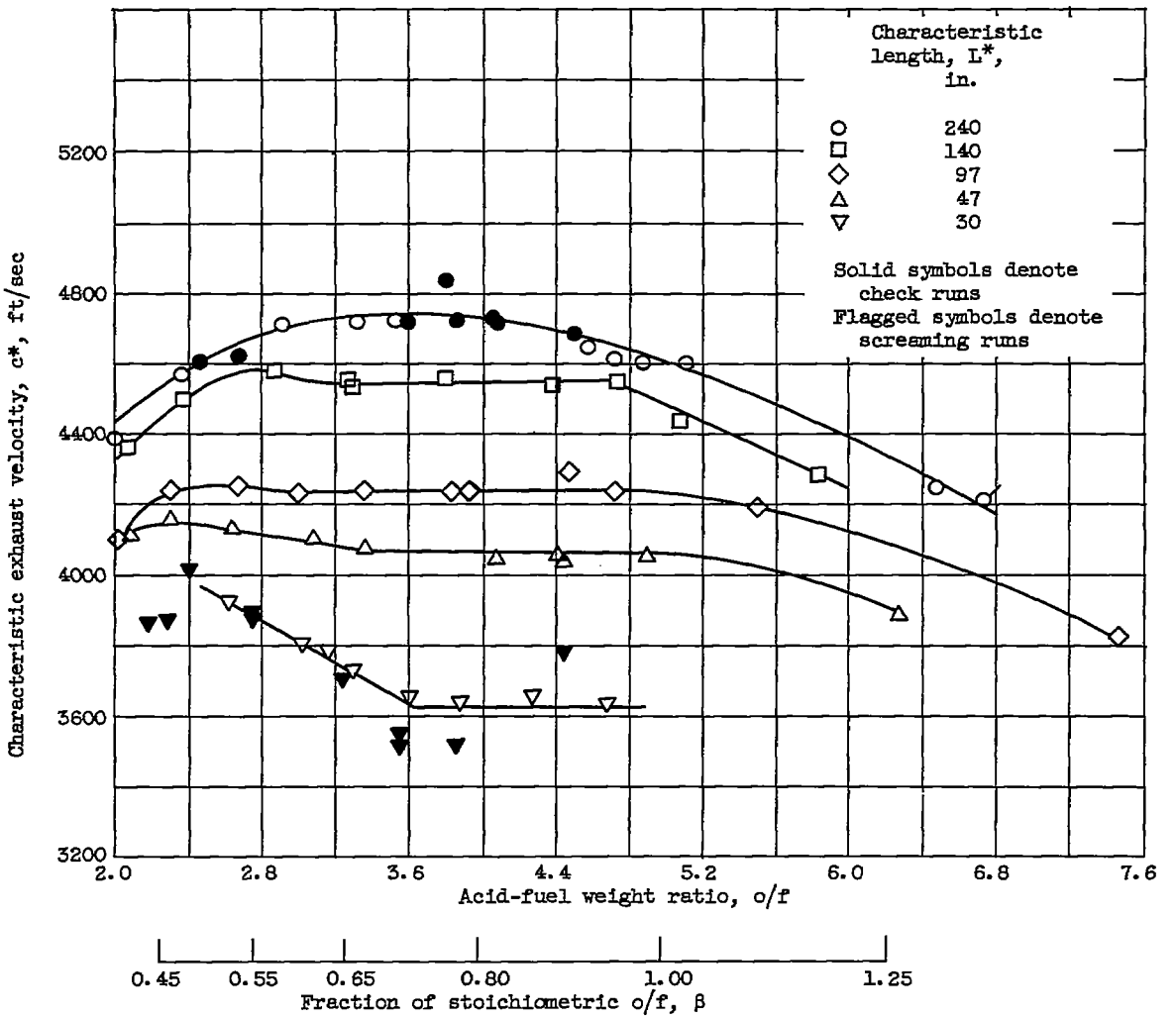
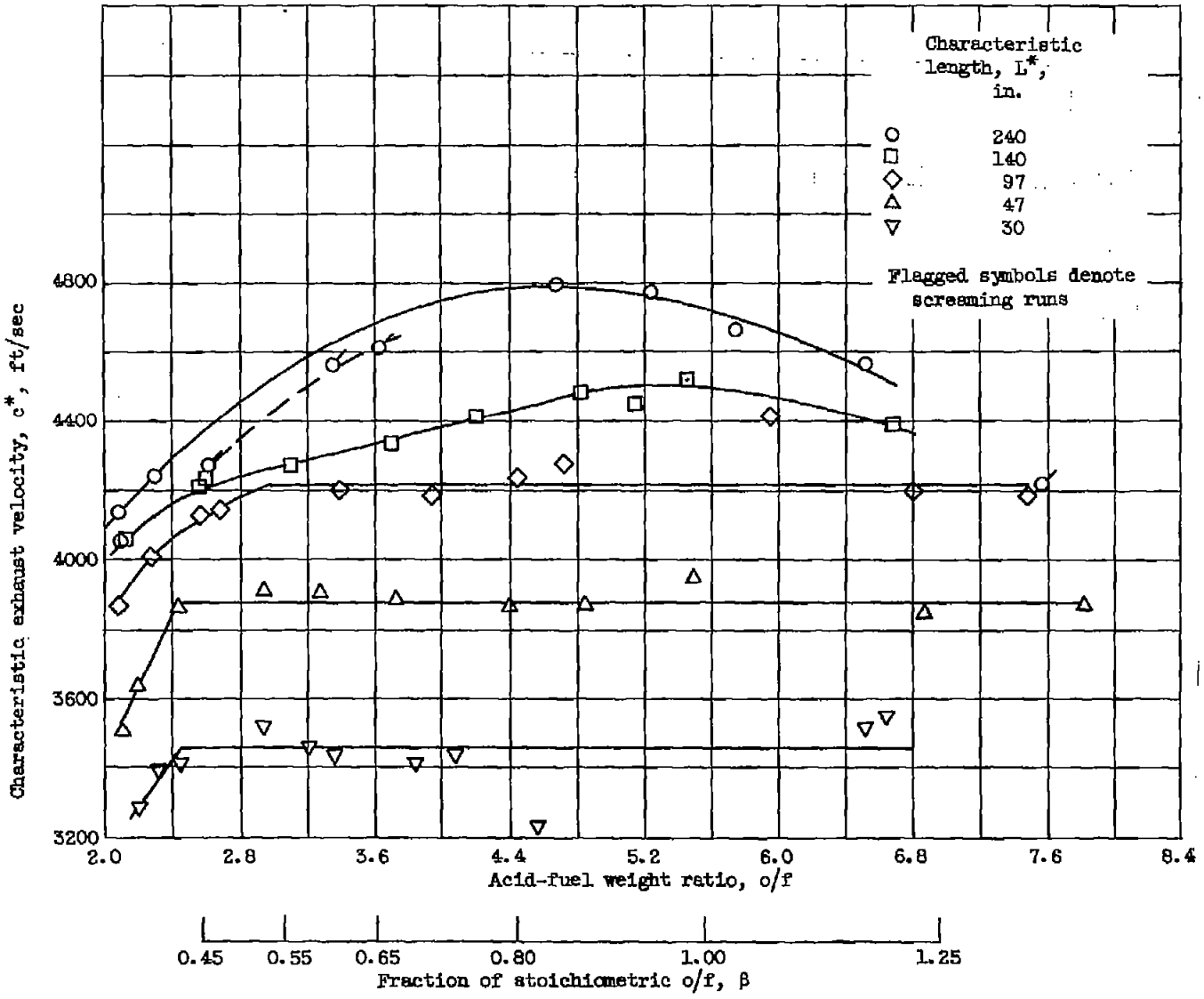



(a) Toluene.

Figure 2. - Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.




(b) n-Heptane.

Figure 2. - Continued. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.

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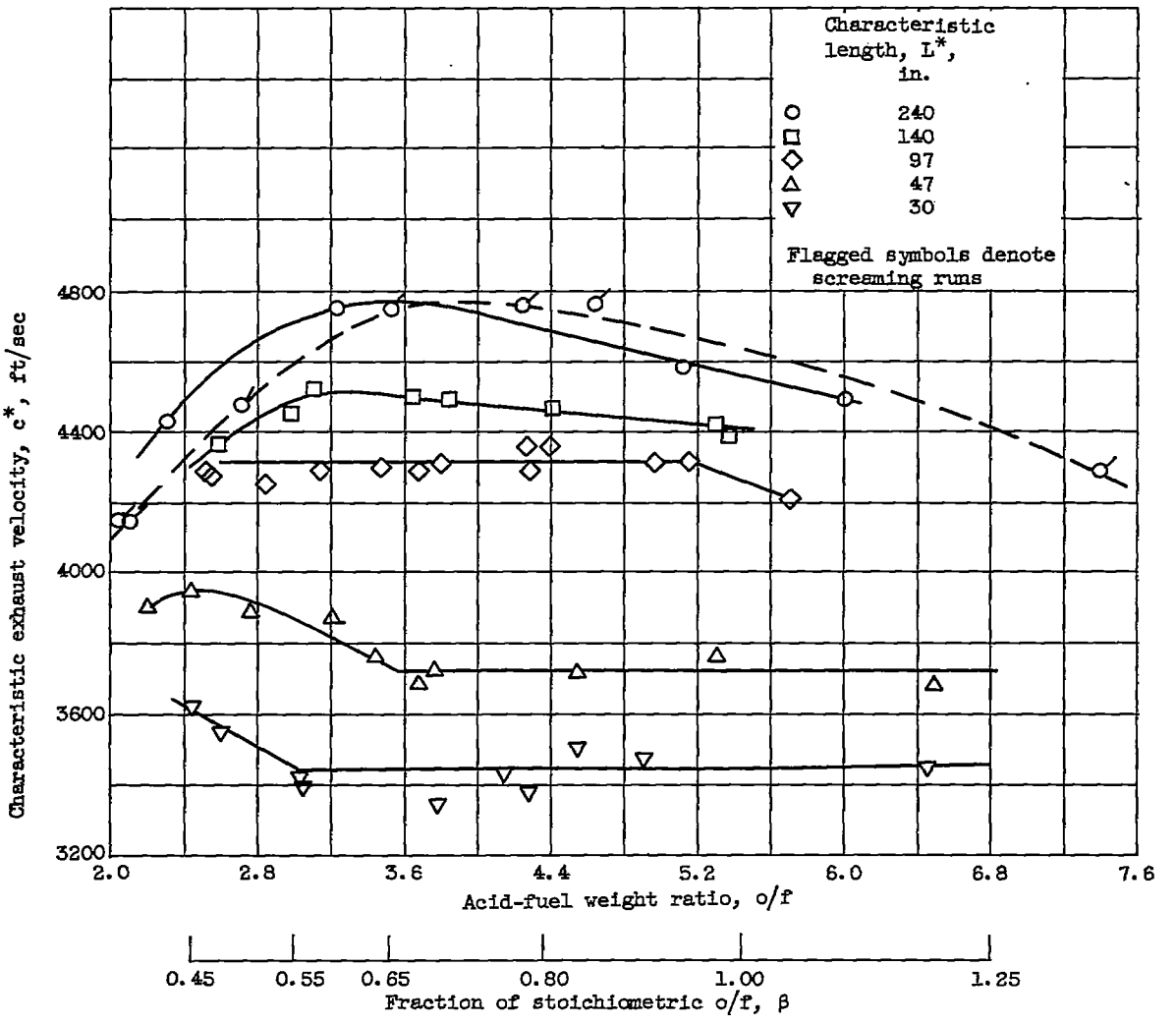
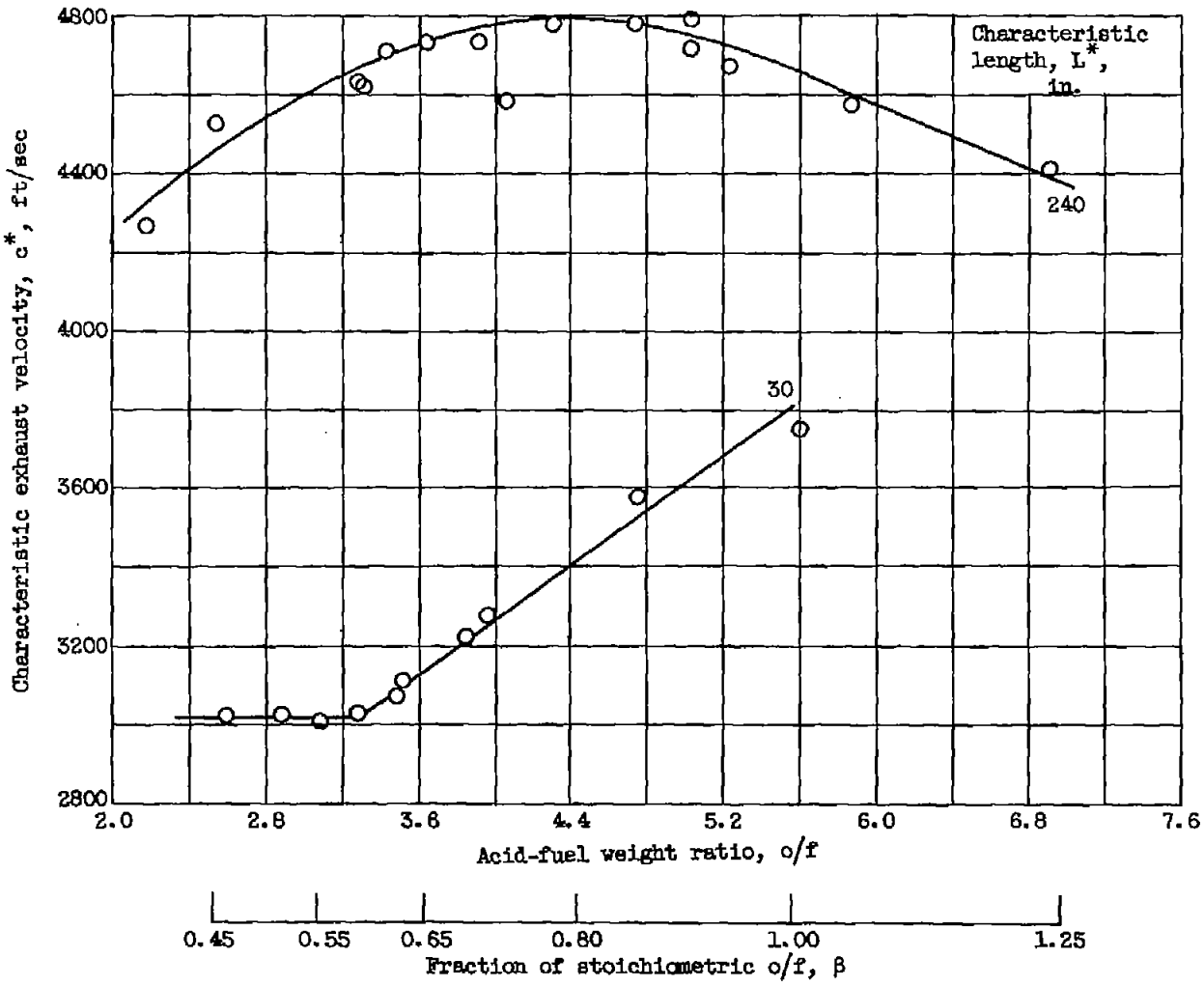



(c) n-Heptene-1.

Figure 2. - Continued. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.




(d) Triptane.

Figure 2. - Continued. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.

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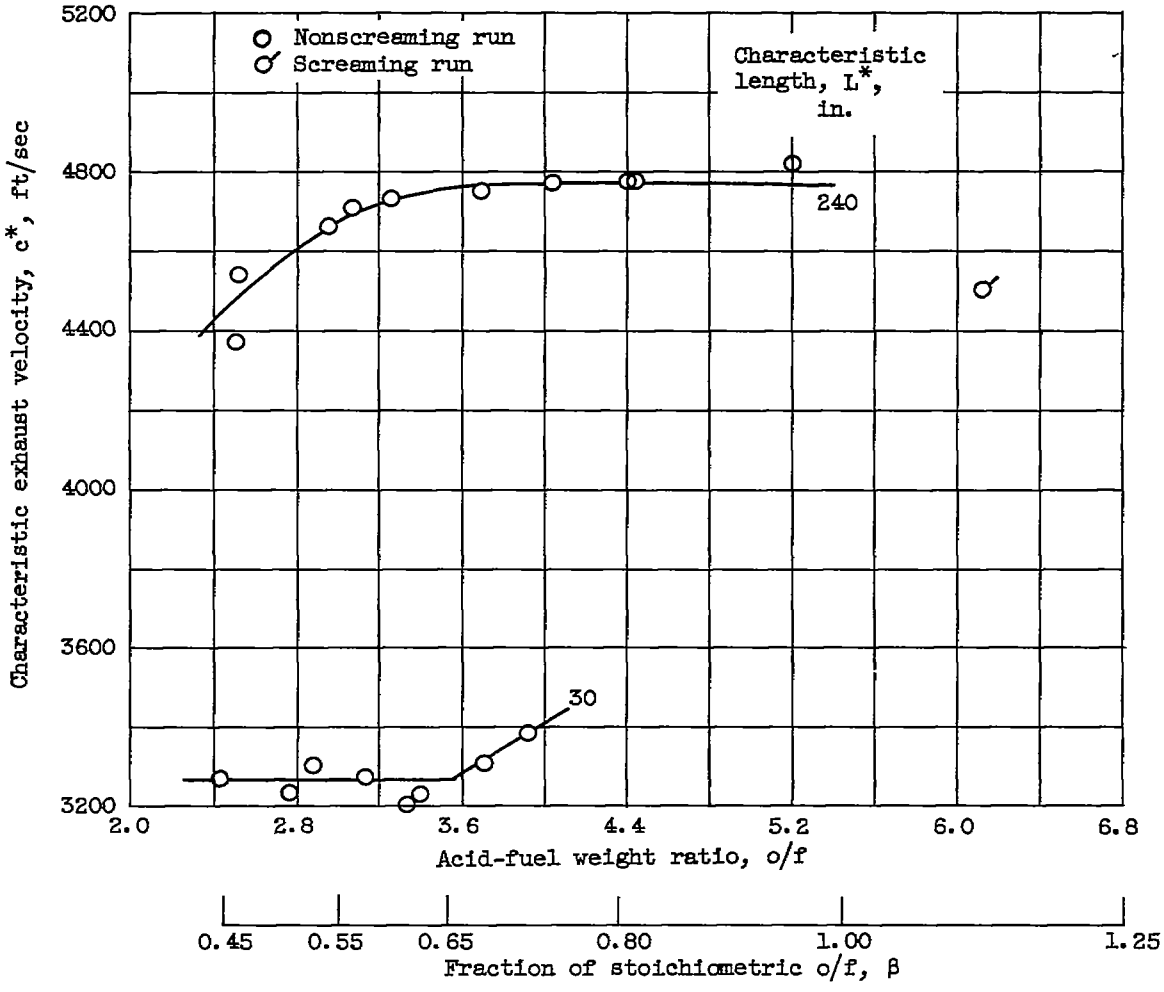
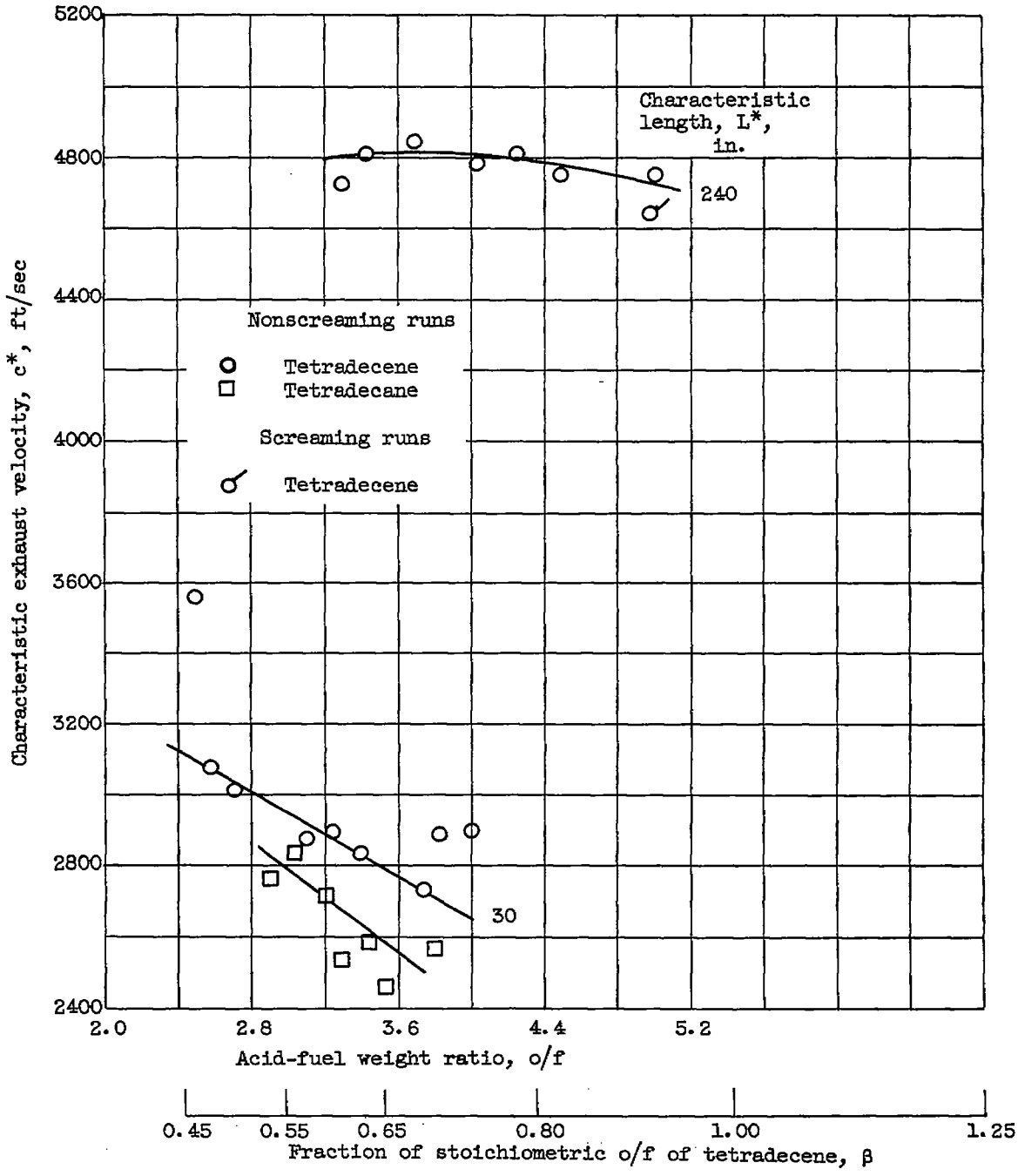



(e) Methylcyclopentane.

Figure 2. - Continued. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.




(f) Tetradecene and tetradecane.

Figure 2. - Continued. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.

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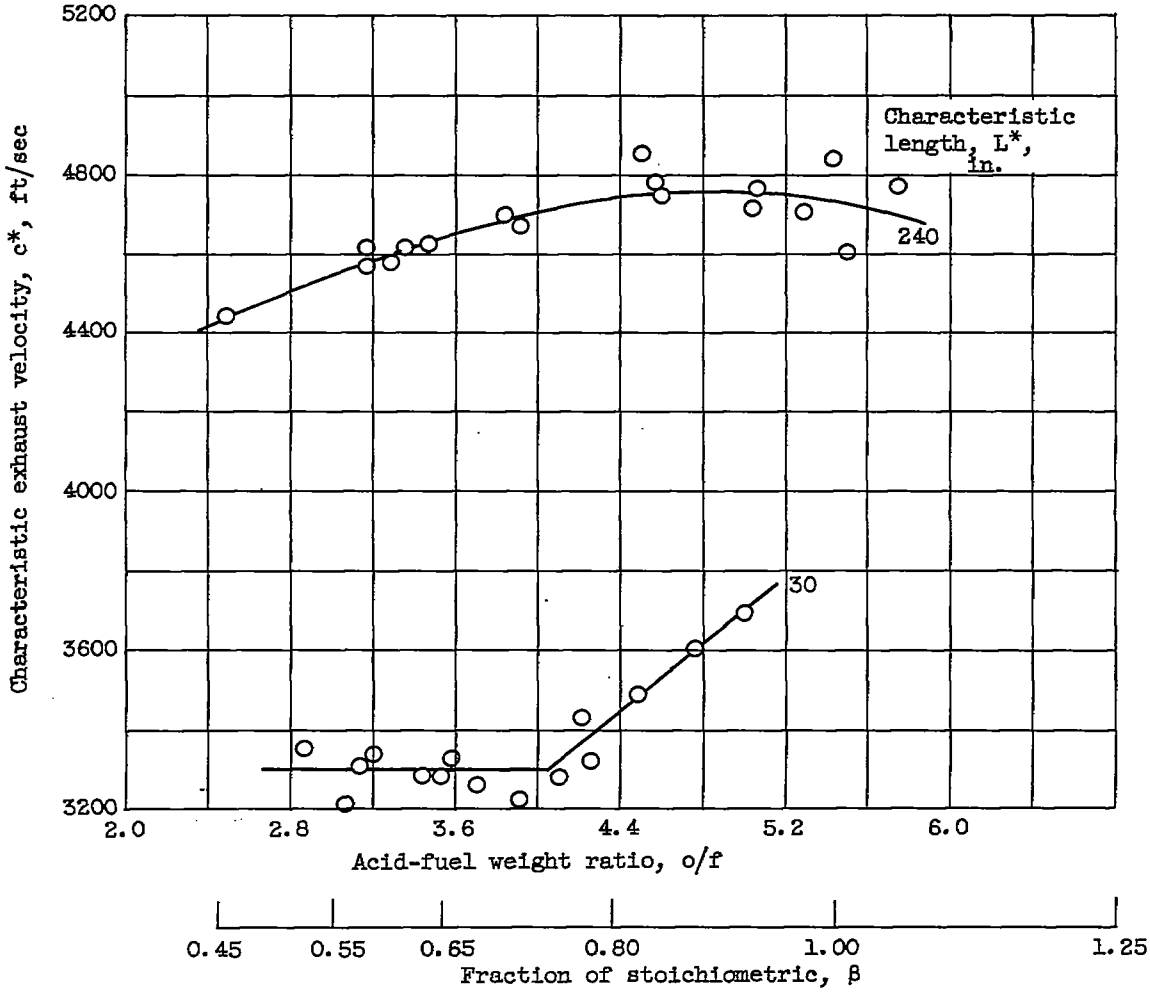


(g) JP-4.

Figure 2. - Concluded. Characteristic exhaust velocity as a function of the mixture ratio and characteristic length for hydrocarbon fuels.

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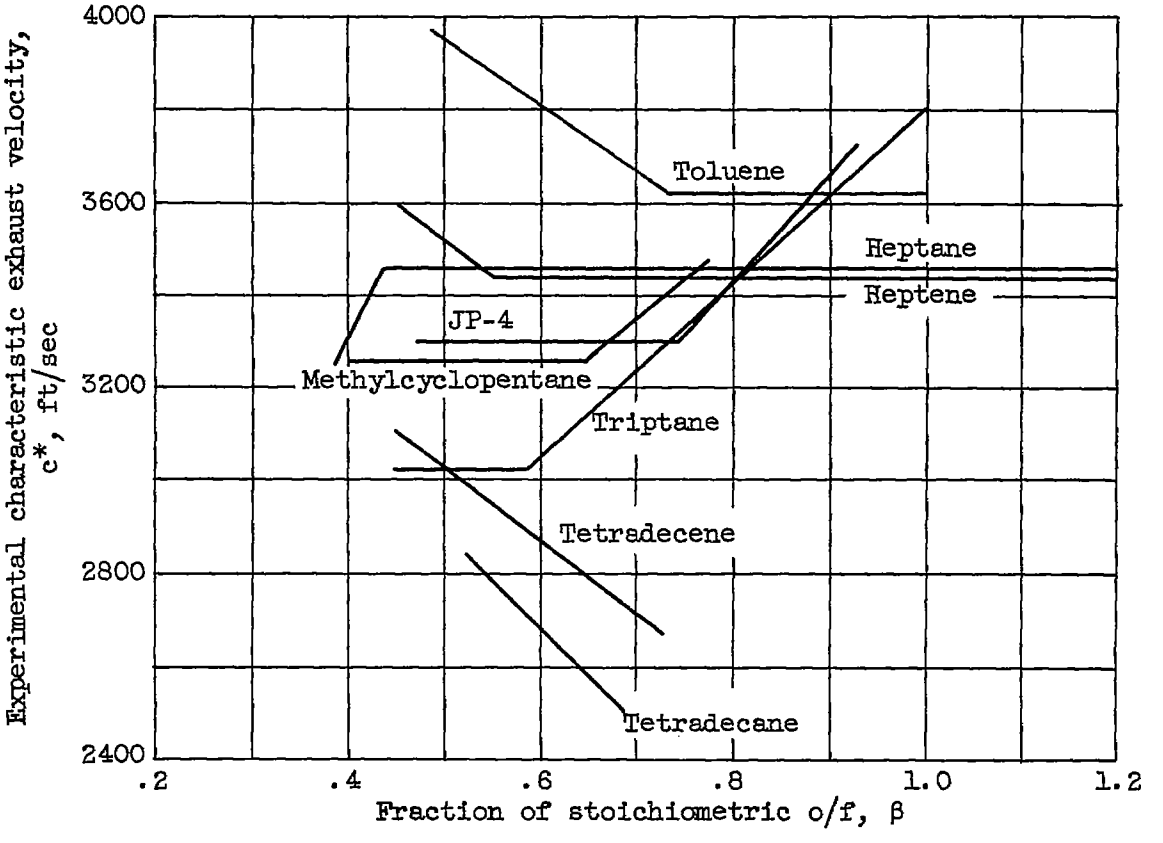


Figure 3. - Comparison of short-chamber (30-in. $L^*$) performance of the various fuels.

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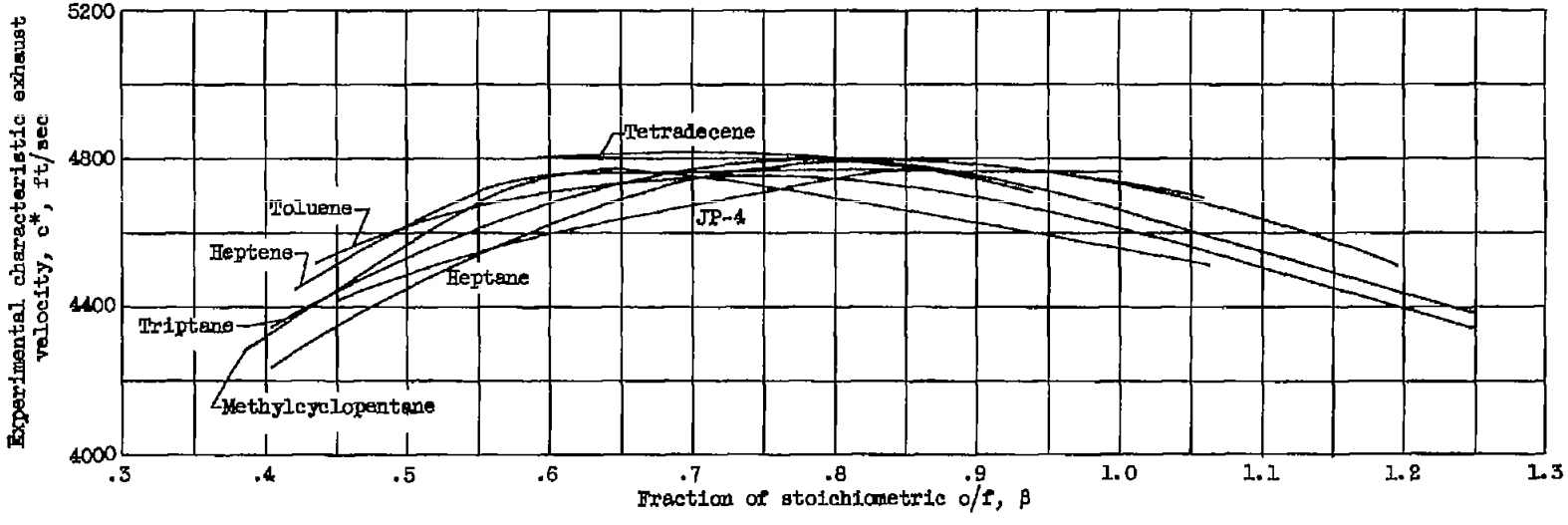


Figure 4. - Comparison of long-chamber performance (240-in. L*) of the various fuels.

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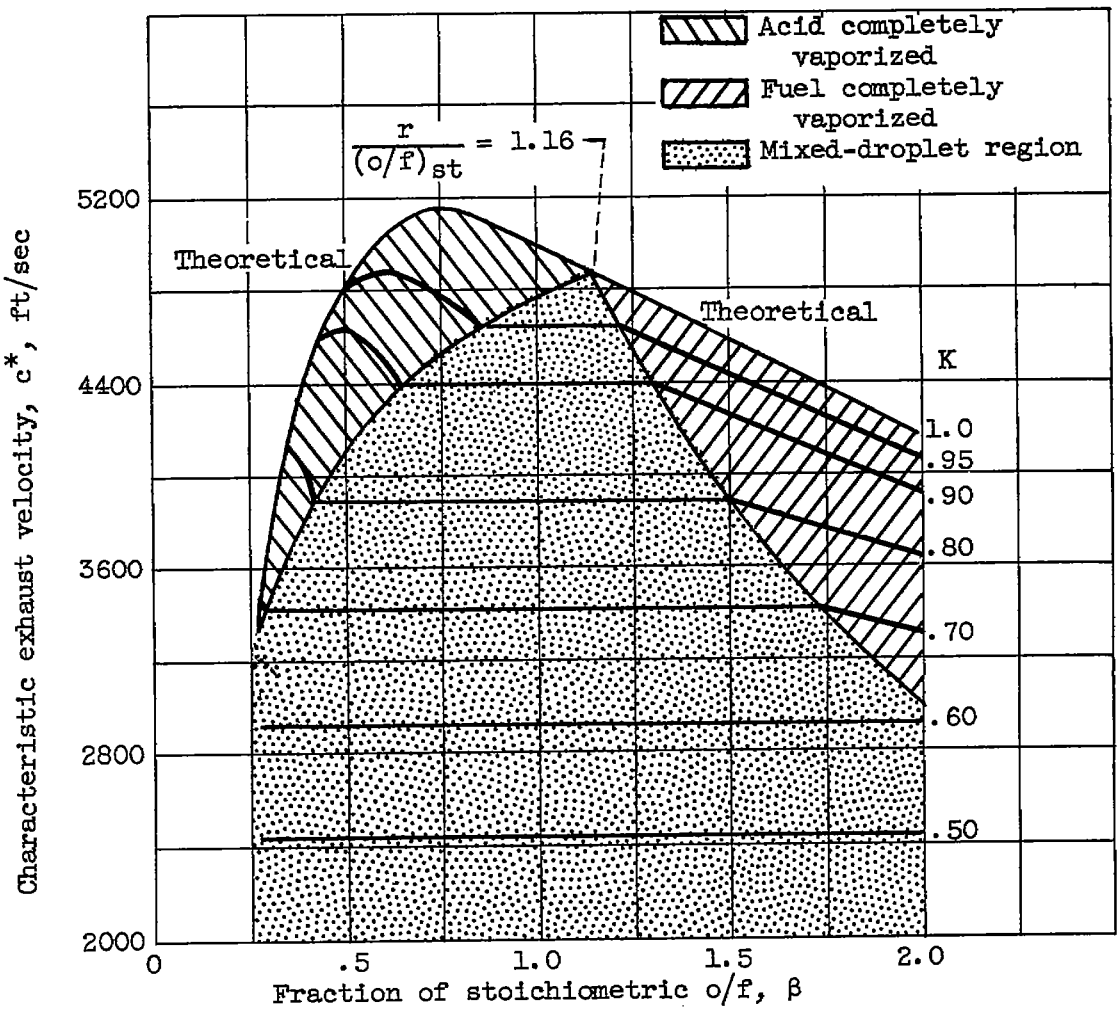


Figure 5. - Characteristic-exhaust-velocity mixture-ratio diagram for toluene according to the idealized mixed-droplet model showing lines of constant K, fraction of vaporized propellants.

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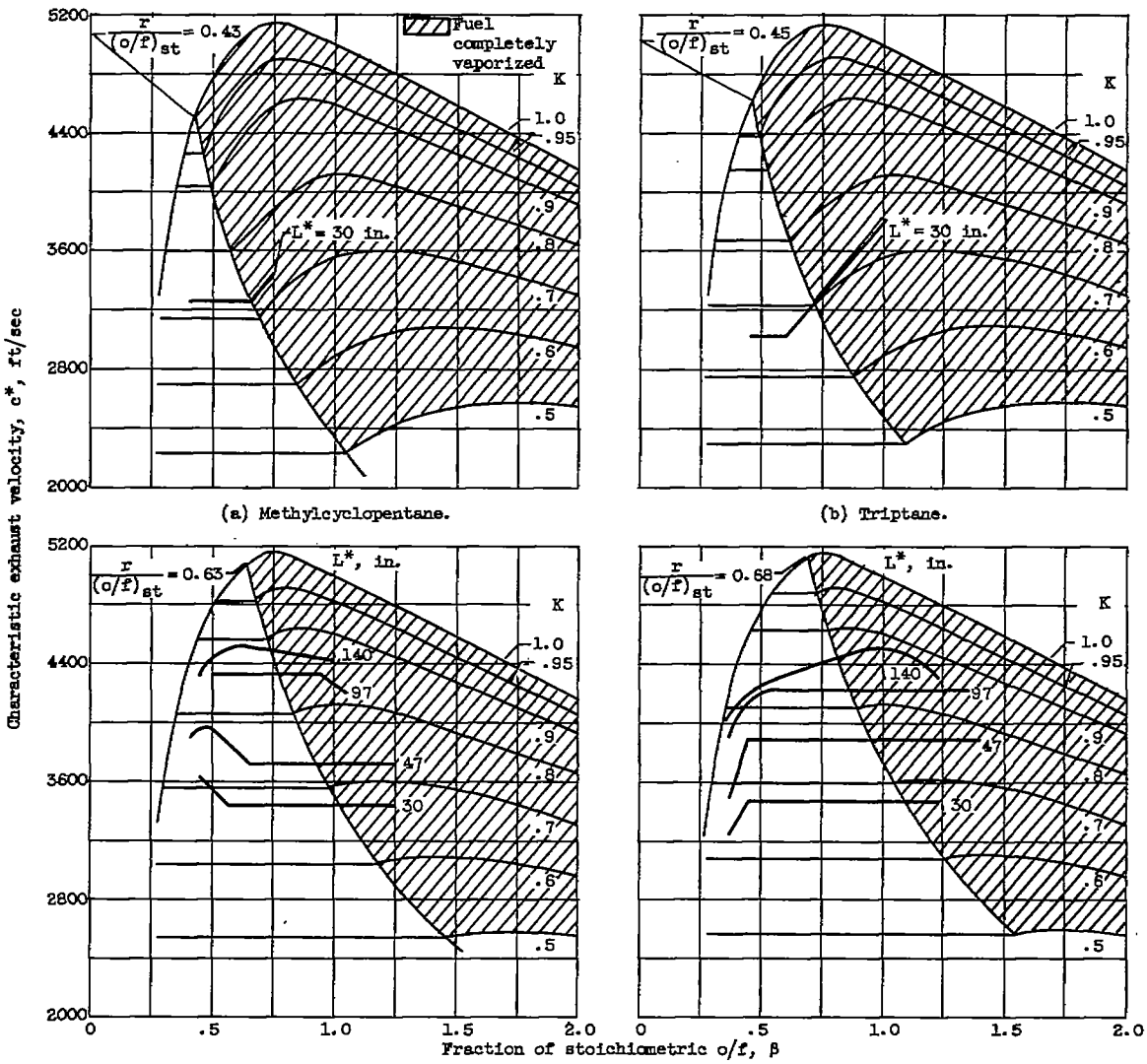


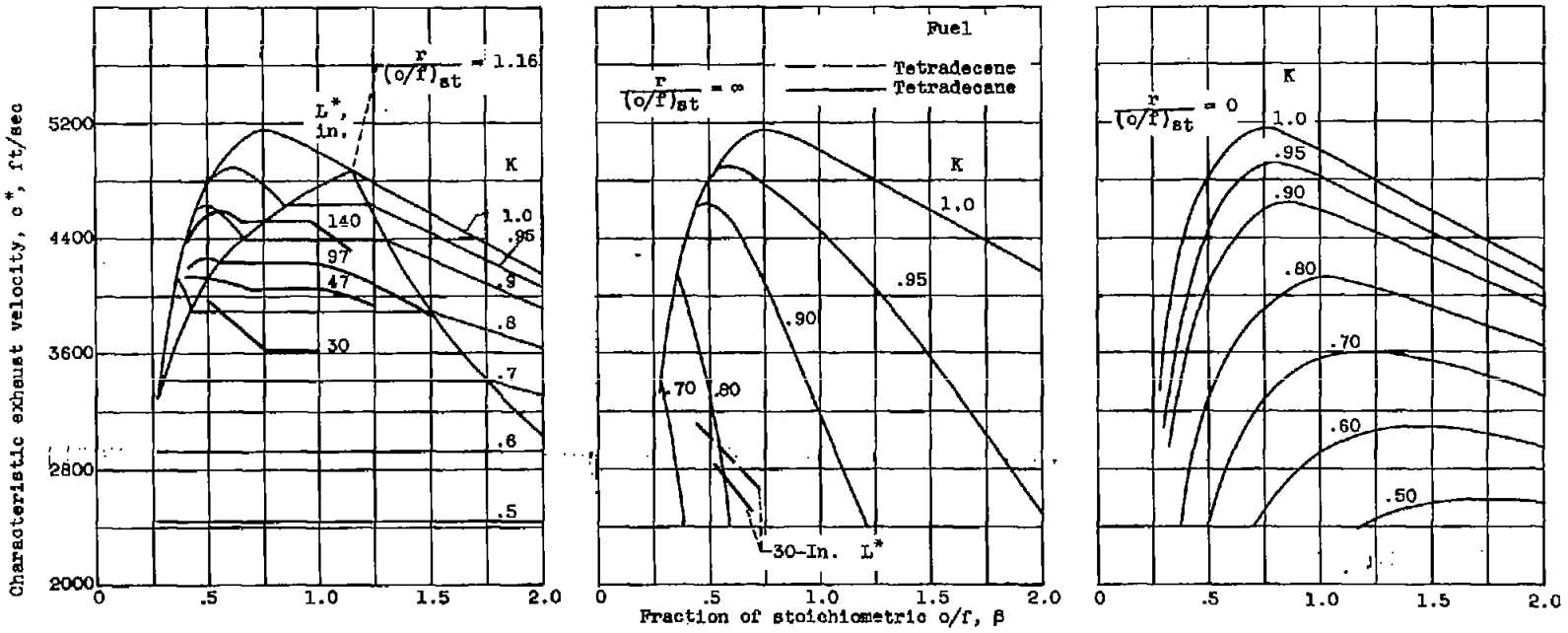

(a) Methylcyclopentane.

(b) Triptane.

(c) Heptene.

(d) Heptane.

Figure 6. - Idealized c* mixture-ratio diagrams with superimposed experimental data.




(e) Toluene.

(f) Nonvolatile fuel; acid completely evaporated.

(g) Volatile fuel; fuel completely evaporated.

Figure 6. - Concluded. Idealized $c^*$ mixture-ratio diagrams with superimposed experimental data.

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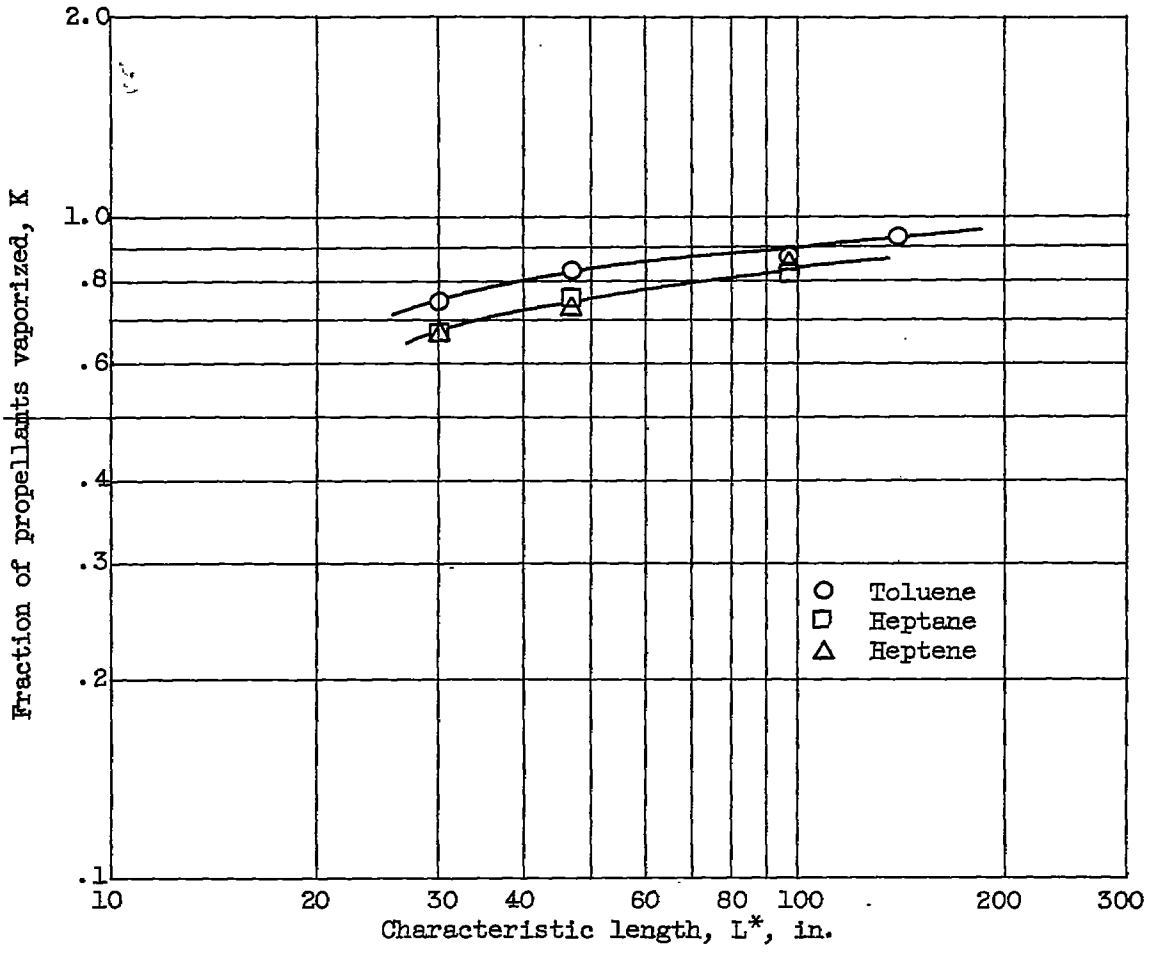


Figure 7. - Fraction of propellant vaporized as a function of characteristic length; fuels: toluene, heptane, and heptene.

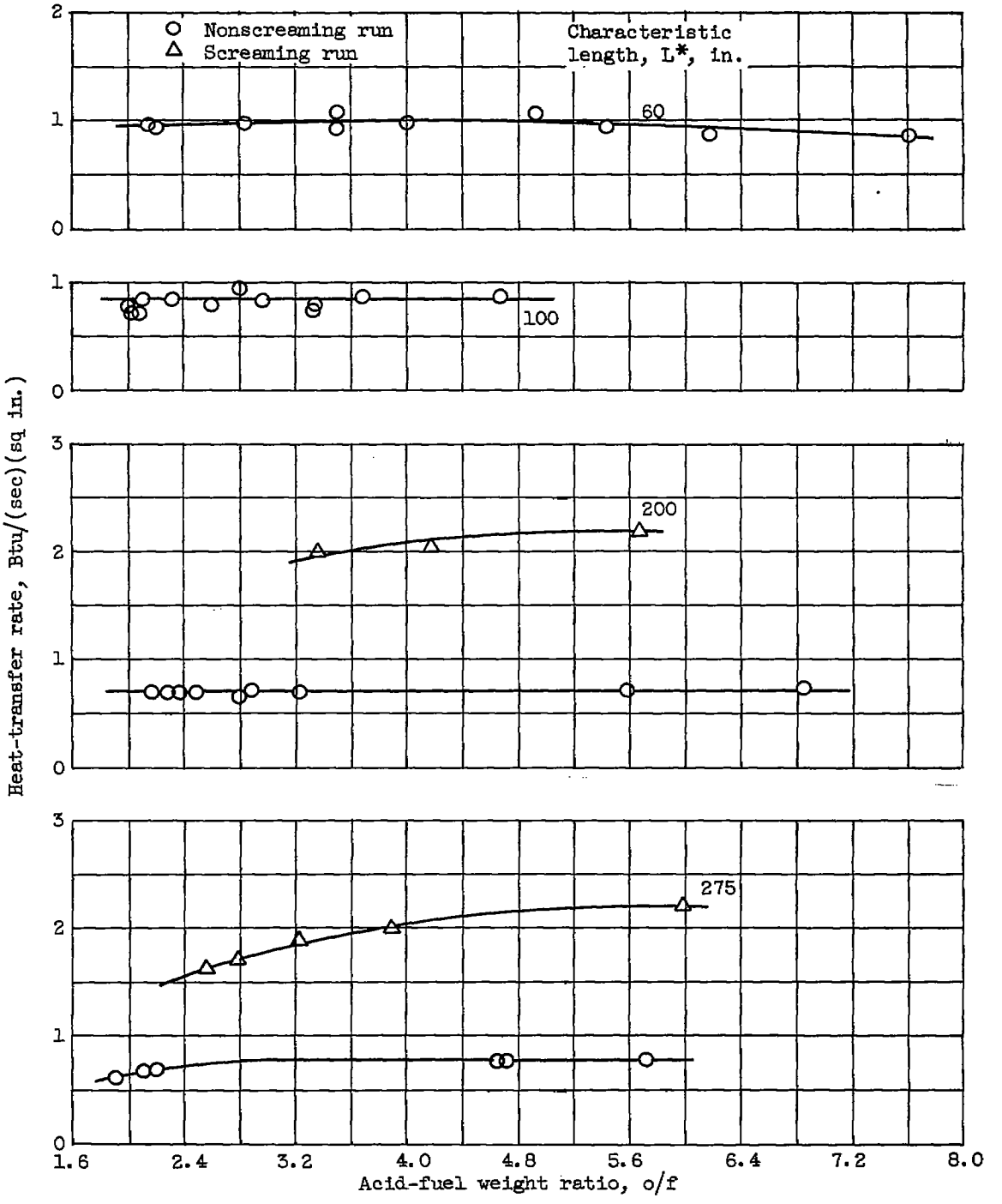


Figure 8. - Heat-transfer rate as a function of weight ratio and characteristic length; fuel: heptane.

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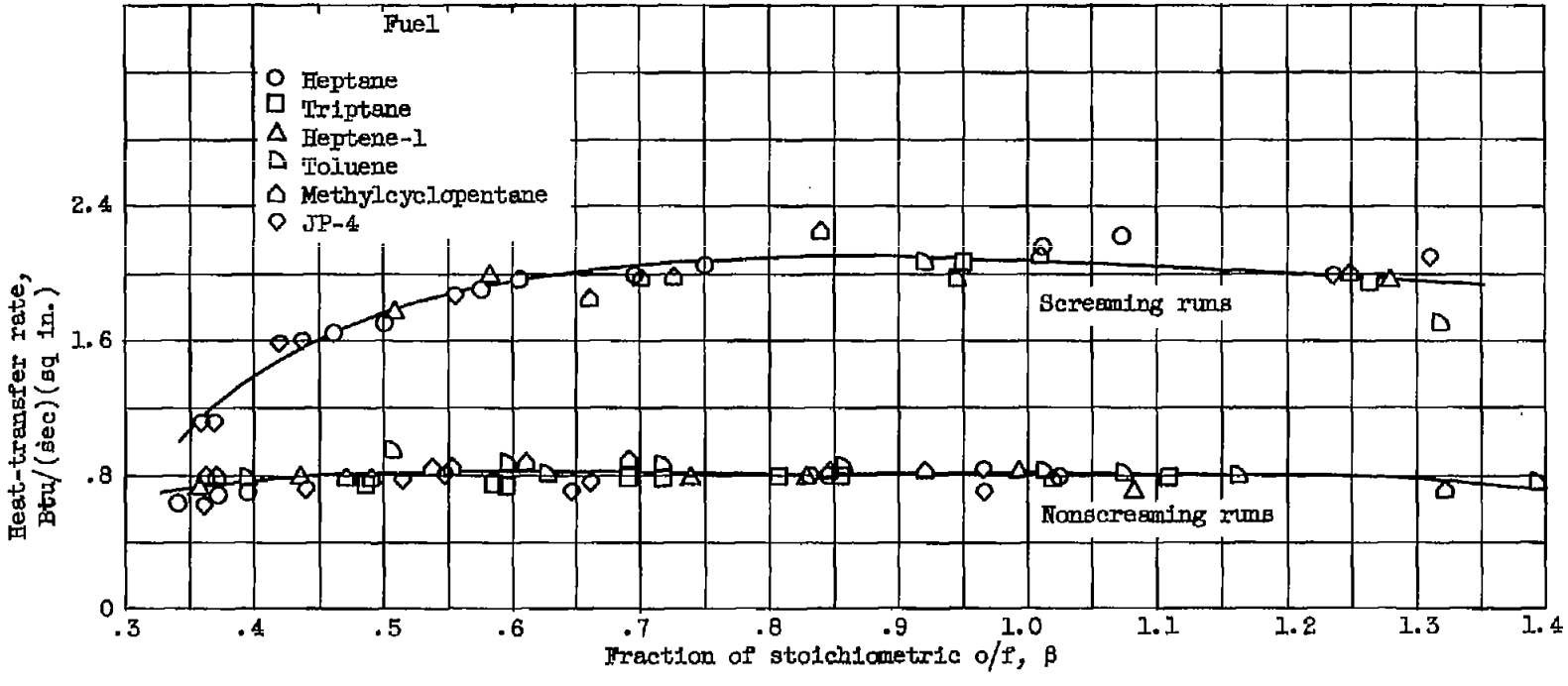


Figure 9. - Heat-transfer results for hydrocarbon fuels.

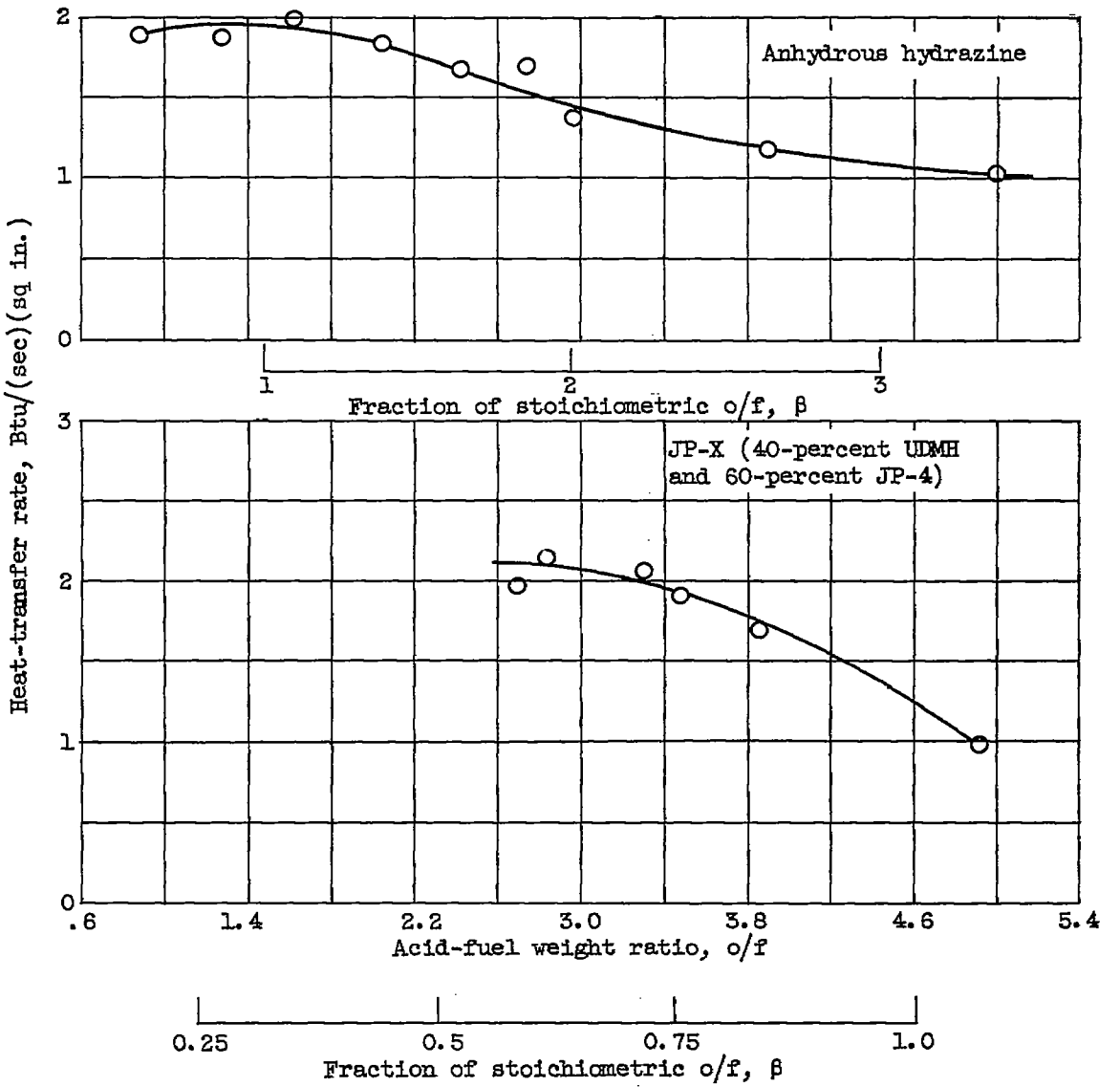


Figure 10. - Heat-transfer rate as a function of mixture ratio in 200-inch L* chambers; fuels: anhydrous hydrazine and JP-X.

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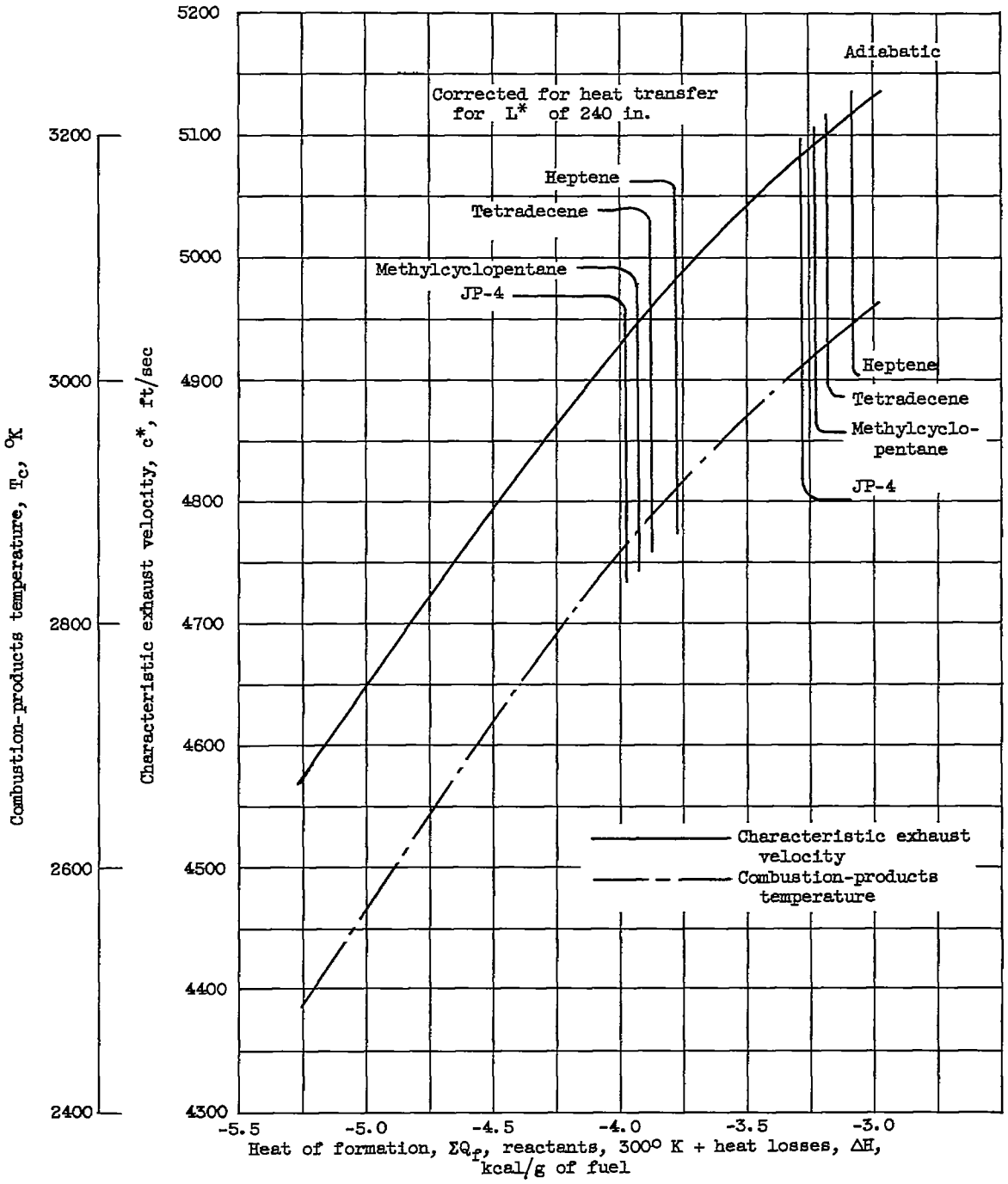
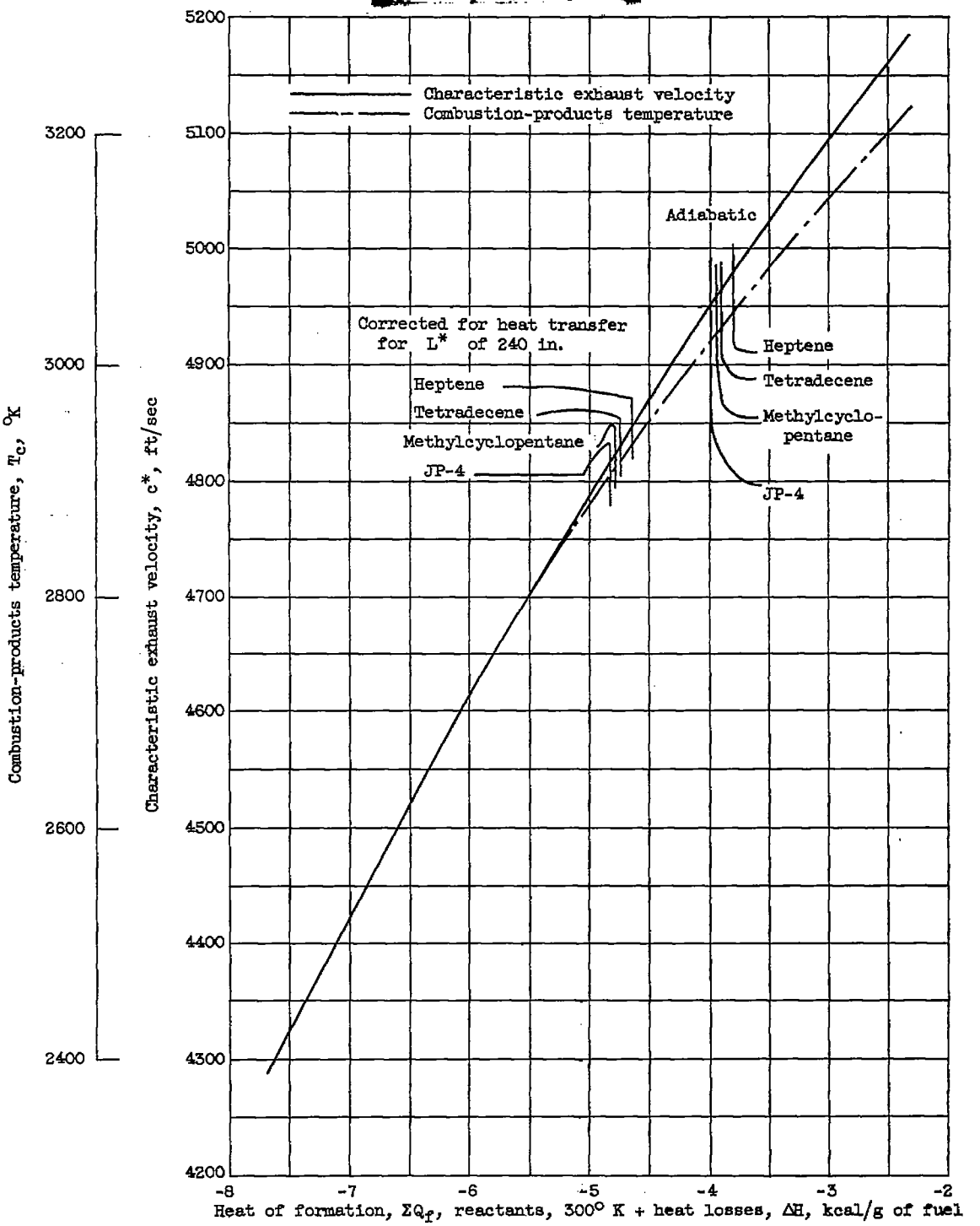



(a) Mixture ratio; β, 0.8.

Figure 11. - Theoretical characteristic exhaust velocity and combustion-products temperature for $CH_2$ fuels as a function of the heats of formation (at 300° K) and heat losses.




(b) Mixture ratio, β, 1.0.

Figure 11. - Concluded. Theoretical characteristic exhaust velocity and combustion-products temperature for $CH_2$ fuels as a function of the heats of formation (at 300° K) and heat losses.



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