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# HYDROGEN CONTENT AS A MEASURE OF THE COMBUSTION PERFORMANCE OF HYDROCARBON FUELS

AIR FORCE AERO PROPULSION LABORATORY

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*CHARLES R. MARTEL*

*LEONARD C. ANGELLO*


TECHNICAL REPORT AFAPL-TR-72-103

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13. ABSTRACT

Previous work by various investigators has shown that the hydrogen content of a hydrocarbon jet fuel is the primary variable affecting the combustion performance of the fuel; i.e. the amount of heat radiated during the combustion of the fuel within the jet engine combustor. The results of statistical correlations of fuel data are presented wherein the hydrogen content of fuels is correlated with other fuel combustion measurements including smoke point, luminometer number, and net heat of combustion. Also, the hydrogen content of fuel is correlated with the specific gravity and aniline point measurements.

The report concludes that the fuels' hydrogen content can be calculated with sufficient accuracy to eliminate the need for measuring smoke points, luminometer numbers, and net heat of combustion. For conventional jet fuels (JP-4, JP-5, JP-8, Jet A, Jet A-1, and Jet B) a minimum allowable hydrogen content of 13.5% by weight is recommended.

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*CHARLES R. MARTEL*
*LEONARD C. ANGELLO*

# FOREWORD

This report was prepared by the Fuels Branch, Fuels and Lubrication Division of the Air Force Aero Propulsion Laboratory. The report uses experimental data obtained from a variety of sources.

The report was prepared during the Spring and Summer of 1972 and was submitted by the authors on 11 August 1972.

This technical report has been reviewed and is approved.

ARTHUR V. CHURCHILL
Chief, Fuels Branch
Fuels and Lubrication Division

## ABSTRACT

Previous work by various investigators has shown that the hydrogen content of a hydrocarbon jet fuel is the primary variable affecting the combustion performance of the fuel; i.e. the amount of heat radiated during the combustion of the fuel within the jet engine combustor. The results of statistical correlations of fuel data are presented wherein the hydrogen content of fuels is correlated with other fuel combustion measurements including smoke point, luminometer number, and net heat of combustion. Also, the hydrogen content of fuel is correlated with the specific gravity and aniline point measurements.

The report concludes that the fuels' hydrogen content can be calculated with sufficient accuracy to eliminate the need for measuring smoke points, luminometer numbers, and net heat of combustion. For conventional jet fuels (JP-4, JP-5, JP-8, Jet A, Jet A-1, and Jet B) a minimum allowable hydrogen content of 13.5% by weight is recommended.

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# SECTION I

# INTRODUCTION

The primary purpose of this report is to document the investigation of using the hydrogen content of a hydrocarbon jet fuel as a measure of the fuel's combustion properties. A secondary purpose is to compare calculated values of a fuel's hydrogen content with measured values and to determine if calculated values are adequate for fuel quality control.

# SECTION II

# BACKGROUND

## 1. COMBUSTION TEST METHODS

Early in the development of jet engines the effect of fuel composition on a fuel's combustion performance was recognized. Carbon deposits in jet engine combustors, combustor life, and exhaust plume smoke were found to be directly affected by fuel composition with the amount of hydrogen present in the fuel as the key parameter (Reference 1). Smoke point measurements, based on tests originally developed for illuminating or lamp oils, were also found to correlate with the fuel combustion performance. Subsequently, smoke point measurements were adopted as the means for specifying and controlling the fuel's combustion properties.

Current jet fuel specifications use one or more of the following test methods for specifying and controlling fuels' combustion properties:

a. Smoke Point - ASTM D-1322

Using a simple wick lamp, the maximum flame height obtainable without smoking is measured.

b. Luminometer Number - ASTM D-1740

This method is basically an automated smoke lamp in which flame temperature at a fixed flame radiation is measured in relation to known fuels. A simple wick lamp is used.

c. Smoke Volatility Index

The sum of the smoke point and 0.42 times the percent of fuel distilled below 400°F is the smoke volatility index; i.e., SVI = SP + 0.42 (% distilled off under 400°F). This method was adopted when early jet engine combustors and fuel injection systems were found to perform better with low volatility fuels. However, fuel combustion in a current jet engine is little affected by fuel volatility (Reference 3).

d. Smoke Point and Percent Naphthalenes

A lower smoke point may be allowed if the maximum percent naphthalenes is limited (naphthalenes have been found to be difficult to burn completely and tend to result in exhaust plume smoke). For example, for Jet A fuel the minimum allowable smoke point is 25 mm; however, if the percent naphthalenes is limited to a maximum of 3%, then the minimum allowable smoke point is 20 mm.

One major shortcoming of smoke point measurements is that existing smoke point lamps burn with a diffusion flame. Schirmer (Reference 2) has shown that the tendency of a fuel to smoke is also a function of the type of flame. For example, a diffusion flame burns cleanest with normal paraffin hydrocarbons while premixed flames burn cleanest with isoparaffin hydrocarbons. Typically, jet engine combustors have a turbulent diffusion flame (i.e., a flame which is partially premixed and partially diffusion), and isoparaffin and normal paraffin fuels burn about equally well.

Another shortcoming of the smoke point type of measurement is the inability to use it with highly volatile and high viscosity fuels. Highly volatile fuels evaporate too rapidly making it difficult to obtain a controlled, stable flame. High viscosity fuels will not flow up the wick fast enough.

2. HYDROGEN CONTENT AS A COMBUSTION PERFORMANCE PARAMETER

The combustion performance of a fuel has often been interpreted to mean the tendency of a fuel to form carbon deposits within the combustors, to affect the magnitude of exhaust plume smoke, to affect the radiation of heat energy to the combustor and other exposed engine components, or combinations of these factors. Recent work has shown that carbon deposition and exhaust smoke formation can be controlled through engine design (Reference 6). Thus, for the remainder of this report, fuel combustion performance is hereby defined as pertaining only to the fuel's luminosity; i.e., the radiation of heat from the burning fuel to surrounding components.

Schirmer (References 2, 3, 4, and 5), Shayeson and Macauly (Reference 6), and Horstman and Jackson (Reference 7) have conclusively shown that the hydrogen content of a fuel is the best measure of the fuel's combustion performance. That hydrogen content (or conversely, carbon content) of a fuel is an accurate measure of its combustion performance is not unexpected. The oxidation of carbon yields much visible and infrared radiation, and unburned carbon particles incandesce and add to the radiation. The oxidation of hydrogen, however, emits no visible radiation and less infrared radiation than the oxidation of carbon. Thus, the higher the hydrogen content, the lower is the radiant energy emitted by the combustion of the fuel. Schirmer has presented several graphic examples of flame radiant energy for fuels of varying hydrogen content (Reference 3).

Combustion pressures and temperatures also affect the magnitude of flame radiation. Schirmer states, "The problem of flame radiance increases markedly as the severity of the turbine-inlet conditions increase. At 25 atmospheres and 2100°F, a severe flame-radiance problem is anticipated. Flame radiance is slightly sensitive to fuel quality at the mild turbine-inlet conditions of five atmospheres and 1300°F, but as the turbine-inlet conditions increase in severity, the beneficial effects of increasing hydrogen content are also increased." Schirmer also notes that as turbine-inlet conditions increase in severity, the exhaust smoke problem essentially vanishes regardless of fuel quality (Reference 5).

Despite the excellent work already accomplished, the hydrogen content of fuel is not used for specifying a jet engine fuel's combustion characteristics. Recent work by the American Society of Testing and Materials, Committee D-2, Technical Division J, has produced excellent statistical data correlating smoke point, luminometer number, smoke volatility index, percent naphthalenes, and percent hydrogen by weight. The data clearly indicates that the hydrogen content measurement is more precise than the other measurements; i.e., the repeatability and reproducibility were superior.

## 3. HYDROGEN CONTENT AS AN ESTIMATE OF OTHER FUEL PROPERTIES

### a. Net Heat of Combustion

The heat of combustion of a hydrocarbon fuel is directly affected by its hydrogen content. Hydrogen oxidation liberates more energy than does carbon oxidation. Thus, the higher the hydrogen content of the fuel, the higher the fuel's heat of combustion. The presence of unsaturated carbon bonds found in aromatic and olefin molecules also affect the heat of combustion. However, as current jet fuel specifications limit the percentages of olefins and aromatics allowed, a reasonably good correlation can be obtained between the heat of combustion and hydrogen content for current jet fuels. Thus, indirectly, current specifications require a minimum hydrogen content by specifying a minimum allowable net heat of combustion.

### b. Aromatic and Olefin Content

By specifying a maximum allowable aromatic and olefin content for jet engine fuels, the minimum hydrogen content of the fuel is also controlled. Saturated paraffinic and single-ring naphthenic compounds have a minimum hydrogen content of 14.3% by weight, while aromatic compounds will typically be considerably below 14%. Olefins usually contain about 14% hydrogen while diolefins are well below 14%.

The limitations on aromatics and olefins also serve other purposes. Both aromatics and olefins are strong solvents and their effect on rubbers and other elastomers is controlled by limiting their allowable concentrations in the fuel. Olefins are also believed to be largely responsible for gum formation in fuels, and being stronger solvents than aromatics, their allowable concentrations are usually less than aromatics.

## 4. CALCULATION OF COMBUSTION PERFORMANCE PARAMETERS

The British Institute of Petroleum has recently proposed to ASTM Committee D-2, Technical Division J, Section VII, that smoke points, luminometer numbers, and hydrogen content of fuels be calculated from the measured specific gravity and aniline point values (Reference 8).

This proposal merits consideration from a cost savings standpoint. For several years the net heat of combustion has been calculated for jet fuels using the aniline point and the specific gravity (ASTM D-1405). Preliminary data provided by the Institute of Petroleum indicates that calculated smoke points and luminometer numbers are comparable in accuracy to the measured values (Reference 8).

# SECTION III

# DISCUSSION OF RESULTS

## 1. CORRELATION OF MEASURED COMBUSTION PARAMETERS

This section of the report compares measured values of fuel hydrogen content with smoke points, luminometer numbers, and net heats of combustion. The data sources mentioned refer to those discussed in the Appendix .

### a. Percent Hydrogen versus Smoke Point

Table I lists the various correlation equations obtained between weight % hydrogen and smoke point. The smoke point was selected as the independent variable as present fuel specifications use smoke point rather than % hydrogen. Figure 1 is a visual comparison of the correlation equations listed in Table I and the letters identifying the curves and correlation equations refer to the data sources described in the Appendix.

At first glance the seven correlation curves do not agree very well. There are two obvious reasons for this disagreement. First, only data sources B, E, F, G, and J primarily reflect the properties of conventional jet fuels. Data Sources A and C include fuels of widely varying composition and some pure hydrocarbons. This explanation may explain why correlation curves A and C do not correlate well with the other curves. Secondly, the reproducibility of smoke point measurements is about 10% while the reproducibility for hydrogen content measurements is about 2%. This may partially explain the discrepancy between correlation curve G and curves B, E, F, and J.

Further inspection of Figure 1 shows that curves B, E, and J correlate quite well and curve F correlates well at smoke points between about 20 and 30. It is the authors' opinion that the correlation from data source B is the preferred correlation. Thus, correlation curve B is selected as the "best estimate" as it is based upon the statistical analysis of results gathered by the ASTM during a round-robin involving

TABLE I

CORRELATION EQUATIONS OF SMOKE POINT VERSUS PERCENT HYDROGEN BY WEIGHT

| DATA SOURCE * | CORRELATION EQUATIONS (PHM = percent hydrogen by weight, SPM = smoke point in mm) | NUMBER DATA POINTS | CORRELATION COEFFICIENT | STANDARD ERROR OF ESTIMATE | |
|---|---|---|---|---|---|
| | | | | SPM | PHM |
| C | PHM = 11.37 + 0.0946 (SPM) | 12 | 0.883 | 5.26 | 0.56 |
| A | PHM = 4.54 + 3.03 $LOG_e$ (SPM) | 6 | 0.996 | - | .12 |
| B | PHM = 11.884 + 0.08254 (SPM) | 8** | .98 | 1.4 | .12 |
| E | PHM = 12.33 + 0.06916 (SPM) | 7 | 0.96 | 1.91 | 0.14 |
| F | PHM = 12.99 + 0.040 (SPM) | 47 | 0.417 | 3.82 | 0.367 |
| G | PHM = 12.49 + 0.074 (SPM) | 35 | 0.753 | 2.2 | 0.22 |
| J | PHM = 12.14 + 0.0779 SPM | 22 | 0.95 | 2.2 | 0.18 |

* APPENDIX

** 15 Duplicate, Independent Measurements of eight Fuels

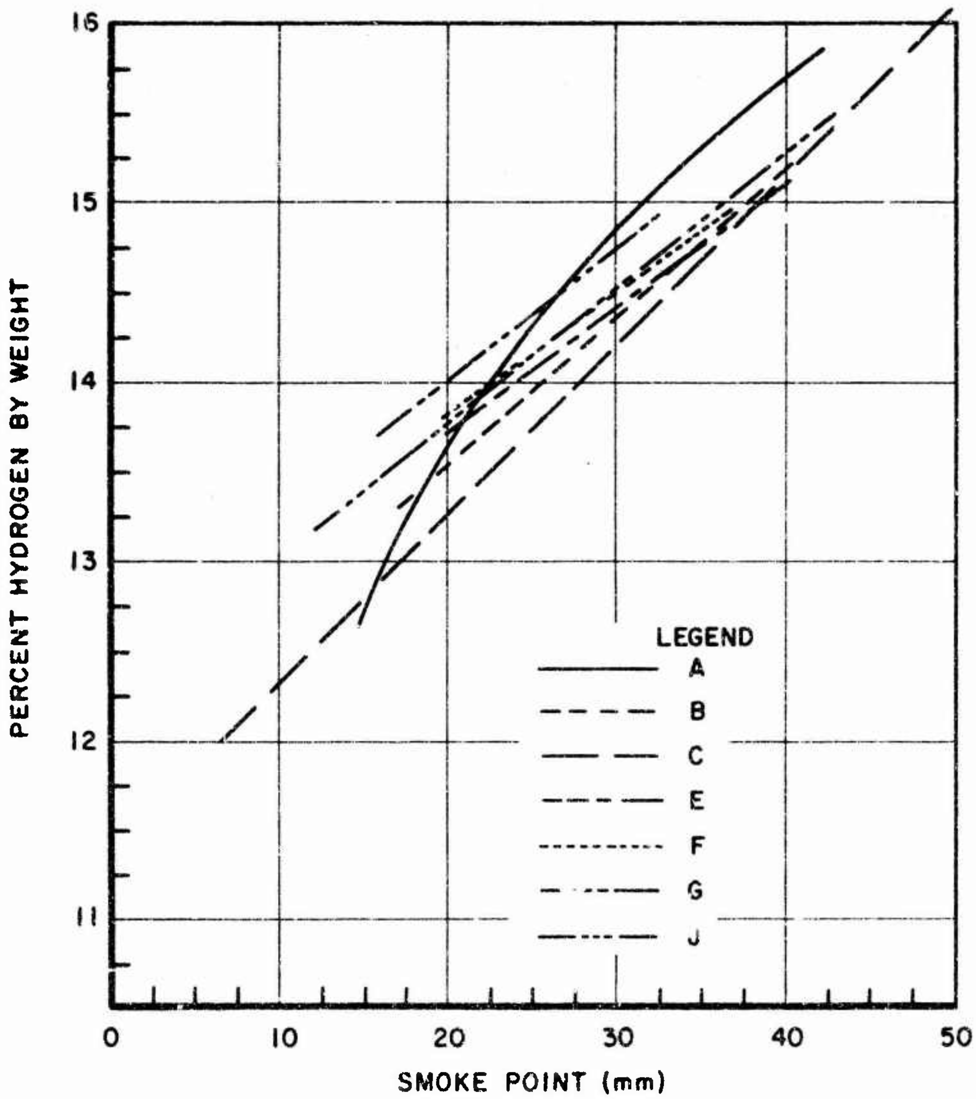


Figure 1. Percent Hydrogen versus Smoke Point.

eight JP-4 type fuels with 15 independent laboratories making duplicate measurements. This choice is reinforced by the excellent agreement with the correlation curves obtained from data sources E and J and the fair agreement with the other data sources C, F, A, and G. Correlation equation B also has one of the lowest standard error of estimate values and a high correlation coefficient (Table I).

b. Percent Hydrogen versus Luminometer Number

Correlations have been obtained between weight percent hydrogen and luminometer number. All correlation equations are semi-log with the exception of the ASTM data source B, which was a linear correlation (Table II and Figure 2). It is likely that an even better correlation using data source B could have been obtained if a semi-log equation had been used.

The data from source D is the only set of data which significantly deviates from the others. The age of the data (1959) may be a factor as the luminometer number test method was not issued as an ASTM standard test method until 1960. Thus, slight variations in procedure may account for the observed differences.

Table II lists the various correlation curves obtained, the number of data points used, the correlation coefficients obtained, and the standard errors of estimate. Data source D was the only set of data giving a correlation coefficient below 0.95, but data source D fuels are not representative of conventional jet fuels. The correlation curves obtained from data sources C, E, and G appear to enclose the other correlations quite well, yet these two curves differ by only about 0.3% hydrogen content over the range of interest (45 to 75 lum Nr). Taking the mean of these curves, the following percent hydrogen contents are the "best estimate" values obtained for the luminometer numbers of special interest:

| Luminometer Number | Equivalent Percent Hydrogen by Weight |
|---|---|
| 45 | 13.6 |
| 50 | 13.8 |
| 60 | 14.1 |
| 75 | 14.5 |

Note that over this range of luminometer numbers all correlation curves except for data source D agree to within about ± 0.15% by weight hydrogen. This value of ± 0.15% hydrogen also agrees well with the standard error of estimate values calculated for each correlation.

c. Percent Hydrogen versus Net Heat of Combustion

Table III lists the various correlation equations obtained for weight weight % hydrogen versus the net heat of combustion. Figure 3 is a plot of these correlation curves over their applicable range (based on the minimum and maximum hydrogen contents found in the data). Inspection of Figure 3 shows that data sources C, D, E, G, I, and J agree quite well over the range of interest of 13.0 to 15.0% hydrogen.

An average of the correlation curves over the range of interest results in the following values:

| Heat Combustion | Percent $H_2$ |
|---|---|
| 18,300 | 12.6 |
| 18,400 | 13.05 |
| 18,700 | 14.4 |

These values are selected as being a reasonable "best estimate" for correlating hydrogen content with the wet heat of combustion.

TABLE II

CORRELATION EQUATIONS OF LUMINOMETER NUMBER VERSUS PERCENT HYDROGEN BY WEIGHT

| DATA SOURCE | CORRELATION EQUATIONS LMN = Luminometer Nr.; PHM = % Hydrogen | NUMBER DATA POINTS | CORRELATION COEFFICIENT | STANDARD ERROR OF EST. | |
|---|---|---|---|---|---|
| | | | | LMN | PHM |
| B | PHM = 12.03 + 0.0342 (LMN) | 8 * | 0.99 | 2.28 | 0.08 |
| C | PHM = 7.62 + 1.581 $LOG_e$ (LMN) | 12 | 0.975 | 1.18 | 0.268 |
| D | PHM = 6.74 + 1.674 $LOG_e$ (LMN) | 41 | 0.766 | 1.2 | 0.390 |
| E | PHM = 6.47 + 1.89 $LOG_e$ (LMN) | 7 | 0.975 | 1.1 | 0.109 |
| J | PHM = 7.32 + 1.662 $LOG_e$ (LMN) | 24 | 0.966 | 1.0 | 0.15 |
| E ** | PHM = 6.076 + 1.96 $LOG_e$ (LMN) | 21 | 0.985 | 1.2 | .406 |
| G | PHM = 9.12 + 1.216 $LOG_e$ (LMN) | 35 | 0.748 | 1.2 | 0.23 |

* 15 Duplicated, Independent Measurements of eight Fuels

** Includes seven JP-7 Fuels and 14 Pure Hydrocarbons

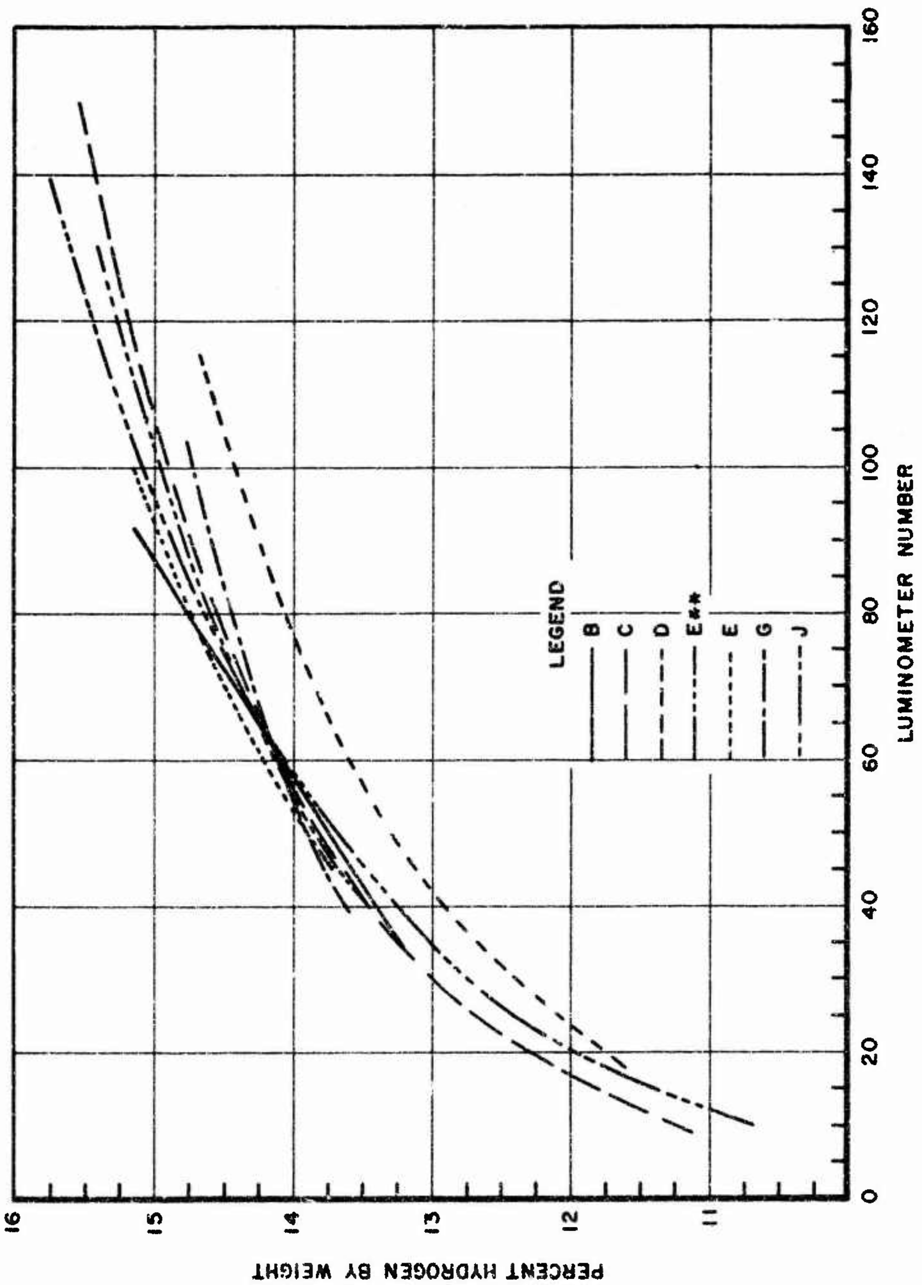


Figure 2. Percent Hydrogen versus Luminometer Number.

TABLE III

CORRELATION EQUATIONS OF NET HEAT OF COMBUSTION VERSUS PERCENT HYDROGEN BY WEIGHT

| DATA SOURCE | CORRELATION EQUATIONS<br>HCM = Net Heat Combustion (Measured)<br>PHM = % Hydrogen (Measured) | NUMBER DATA POINTS | CORRELATION COEFFICIENT | STANDARD ERROR OF EST. | |
|---|---|---|---|---|---|
| | | | | HCM | PHM |
| C | HCM = 14,805 + 267.9 PHM | 12 | 0.991 | 44 | 0.16 |
| D | HCM = 15,443 + 223 PHM | 41 | 0.868 | 77 | 0.30 |
| F | HCM = 17,027 + 115 PHM | 47 | 0.525 | 75 | 0.34 |
| G | HCM = 16,360 + 162 PHM | 35 | 0.646 | 65 | 0.26 |
| I | HCM = 15,358 + 234.8 PHM | 134 | 0.93 | 51 | 0.20 |
| J | HCM = 14,563 + 288 (PHM) | 24 | 0.984 | 32 | 0.11 |
| E | HCM = 15,657 + 211.6 (PHM) | 7 | 0.747 | 92 | 0.32 |

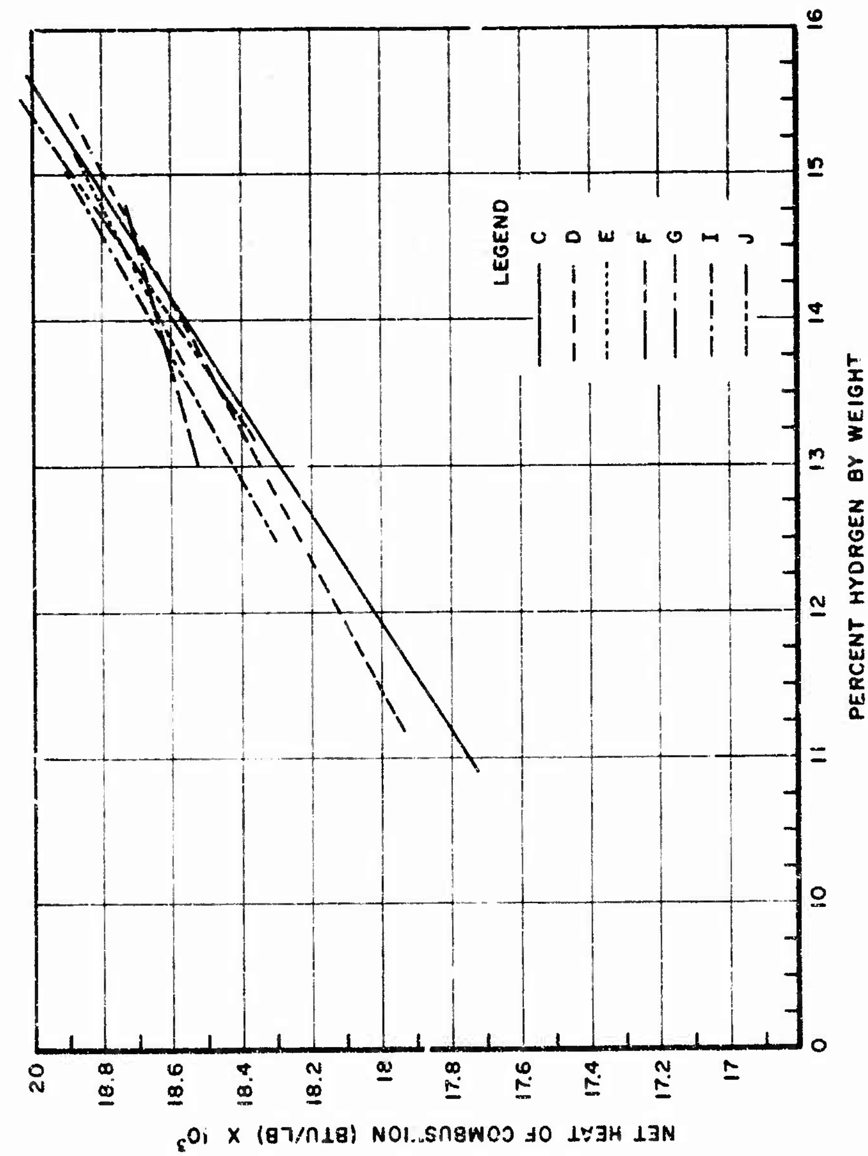


Figure 3. Net Heat of Combustion versus Percent Hydrogen

2. CORRELATION OF FUEL HYDROGEN CONTENT WITH EXISTING SPECIFICATION REQUIREMENTS

The fuel combustion requirements of jet fuel specifications MIL-T-5624 (JP-4 and JP-5), MIL-T-38219 (JP-7), proposed MIL-T-38133 (JP-8), and ASTM D-1655 (Jet A, A-1, and B) have been extracted and are presented in Table IV below.

TABLE IV

FUEL COMBUSTION REQUIREMENTS OF JET FUELS

| Fuel Type | Net Heat Combustion (Btu/Lb) Minimum | Smoke Point (mm) (Minimum) | Luminometer Number (Minimum) | Smoke Volatility Index* (Minimum) |
|---|---|---|---|---|
| JP-4 | 18,400 | - | 60 or | 52 |
| Jet B | 18,400 | - | 50 or | 54 |
| JP-5 | 18,300 | 19 or | 50 | - |
| Jet A & A-1 | 18,400 | 25** or | 45 | - |
| JP-8 | 18,400 | 25** or | 45 | - |
| JP-7 | 18,700 | - | 75 | - |

* SVI = Smoke Point + 0.42 (% fuel evaporated below 400°F)
** Smoke Point Minimum drops to 20 mm if % naphthalenes is below 3%

By the definition of the Smoke Volatility Index (SVI), the minimum allowable smoke points for JP-4 and Jet B fuels could be as low as 10 mm and 12 mm respectively, assuming 100% of the fuel evaporates below 400°F, which is not unusual. These very low values of smoke points are completely out of line with other specified smoke points and luminometer numbers for similar or identical fuels. As these fuels are limited to a maximum of 25% aromatics and 5% olefins, it is probably impossible to blend a JP-4 or Jet B fuel having a smoke point as low as 10 or 12 mm.

It is the opinion of the authors that SVI values are no longer appropriate and have little or no value in specifying fuels for modern jet engines. No further attempt will be made to correlate Smoke Volatility Index with the fuel's hydrogen content.

Examination of Table IV reveals that the different fuel specifications do not agree on the relative values of smoke points and luminometer numbers. For example, the JP-5 specification equates a 19 mm smoke point with a 50 luminometer number while JP-8 and Jet A specifications equate a 25 mm smoke point with a 45 luminometer number. Evidently the problem of correlating smoke points and luminometer numbers is not new.

Most Air Force jet engines are designed to operate using JP-4 fuel, but usually JP-5, Jet A, Jet A-1, and Jet B are alternate fuels. Similarly, most Navy jet aircraft are designed for use with JP-5 fuel but may also use JP-4, Jet A, Jet A-1, and Jet B fuels. Thus, the combustion performance of JP-4, JP-5, JP-8 Jet A, Jet A-1, and Jet B cannot differ greatly or there would be operational and maintenance problems when using alternate fuels. (Note, however, that there are other substantial differences in fuels which do affect their uses in specific aircraft; for example, freezing point, volatility, and flash point).

Considerable differences in fuel specifications in terms of allowable smoke points, luminometer numbers, and net heat of combustion have been shown in Table IV. Some differences are found in terms of average properties; for example, 19 JP-4 fuels had an average hydrogen content of 14.35% while 16 Jet A fuels had an average hydrogen content of only 13.98%. Yet, some JP-4 fuels had hydrogen contents about as low as the lowest Jet A fuels (Appendix, Data Source G).

Assuming that JP-4, JP-5, JP-8, Jet A, Jet A-1, and Jet B fuels do have sufficiently similar combustion performance requirements so that they can be lumped together, the minimum acceptable values of combustion performance parameters for this group of fuels would be:

Minimum Luminometer Number = 45 (Jet A, Jet A-1, and JP-8 fuels)

or a

Minimum Smoke Point = 19 mm (JP-5 fuel)

and a

Minimum Net Heat of Combustion = 18,300 Btu/lb (JP-5)

Table V equates the weight percent hydrogen of the fuel, calculated using the correlation equations obtained in Section III.1, with the specified values of smoke point, luminometer number, and net heat of combustion. Also listed are the "best estimate" values obtained in the preceding sections for these correlations. Using these "best estimate" values, a luminometer number of 45 is equivalent to 13.6 wt % hydrogen; a 19 mm smoke point is equivalent to 13.45 wt % hydrogen; and a net heat of combustion of 18,300 Btu/lb is equivalent to 12.6 wt % hydrogen.

Note that either the luminometer number or the smoke point specified requires a significantly higher fuel hydrogen content than does the specified net heat of combustion. Thus, either the luminometer number or the smoke point will determine the lowest acceptable fuel hydrogen content. This was found to be 13.45 wt % above. Rounding this value to 13.5 wt % hydrogen gives the minimum allowable hydrogen content recommended for JP-4, JP-5, JP-8, Jet A, Jet A-1, and Jet B fuels.

JP-7 is a "high luminometer number" fuel; i.e., its luminosity during combustion is to be less than that of conventional fuels. The minimum allowable luminometer number of 75 for JP-7 fuel is equivalent to 14.5 wt % hydrogen, and the minimum allowable net heat of combustion of 18,700 Btu/lb is equivalent to 14.4 wt % hydrogen using the "best estimate" values shown in Table V. Comparing these values it is evident that the luminometer number is the controlling specification. Thus, the minimum recommended hydrogen content for JP-7 fuel is 14.5 wt %.

TABLE V

WEIGHT PERCENT HYDROGEN EQUIVALENTS

| COMBUSTION PARAMETER | | DATA SOURCES (APPENDIX) A | B | C | D | E | F | G | H | I | J | Best Est. Value**** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Net Heat of Comb. (Btu/lb) | 18,300 (JP-5) | - | - | 13.0 | 12.8 | 12.55 | 13.05 | 12.0 | - | 12.5 | 13.0 | 12.6 |
| | 18,400 Jet B JP-4 JP-8 Jet A, JetA-1 | - | - | 13.35 | 13.3 | 13.0 | 13.3 | 12.6 | - | 13.0 | 13.3 | 13.05 |
| | 18,700 JP-7 | - | - | 14.45 | 14.6 | 14.35 | 14.1 | 14.4 | - | 14.2 | 14.4 | 14.4 |
| Luminometer Number | 45 JP-8, Jet A, JetA-1 | - | 13.55 | 13.64 | 13.1 | 13.3 | - | 13.75 | - | - | 13.64 | 13.6 |
| | 50 JP-5 | - | 13.75 | 13.80 | 13.3 | 13.5 | - | 13.9 | - | - | 13.8 | 13.8 |
| | 60 JP-4 | - | 14.10 | 14.09 | 13.6 | 14.0 | - | 14.1 | - | - | 14.1 | 14.1 |
| | 75 JP-7 | - | 14.60 | 14.45 | 13.95 | 14.6 | - | 14.36 | - | - | 14.5 | 14.5 |
| Smoke Point (mm) | 19 JP-5 | 13.4 | 13.45**** | 13.18 | - | 13.6 | 13.75 | 13.9 | - | - | 13.6 | 13.45 |
| | 20* Jet A, A-1 | 13.6 | 13.53**** | 13.26 | - | 13.7 | 13.79 | 13.99 | - | - | 13.7 | 13.53 |
| | 25 Jet A, JP-8 Jet A-1 | 14.5 | 13.95**** | 13.75 | - | 14.1 | 14.0 | 14.36 | - | - | 14.1 | 13.95 |
| | Number Data Points | UNKNOWN | ** | 12 | 41 | 21*** | 47 | 35 | - | 134 | 22 | - |

* 20 mm Smoke Point permitted if fuel contains less than 3% naphthalenes.
** Eight fuels with duplicated analyses by 15 laboratories.
*** Only seven data points for smoke point correlation.
**** Best estimate values are those selected in Section III.1. of this report.

3. COMPARISON OF CALCULATED AND MEASURED VALUES OF FUEL HYDROGEN CONTENT

The British Institute of Petroleum (Reference 8) has proposed a simple method for calculating the hydrogen content of jet fuels using the fuel's aniline point and gravity. We have developed similar correlations using the measured hydrogen content, the aniline point, and the gravity of the various fuels in data sources F, G, I, and J from the Appendix. The resulting correlation equations are presented in Table VI and have been plotted in Figures 4 and 5. Figure 4 graphically depicts the correlations at 13.5 weight percent hydrogen and Figure 5 at 14 weight percent hydrogen.

Data sources F, G, and I represent conventional type jet fuels; i.e., JP-4, JP-5, and Jet A, and A-1 fuels. Thus, the correlations derived from these data sources should be representative of conventional jet fuels. It can be seen from Figures 5 and 6 that the agreement is not good. However, by grouping these three data sources, a new correlation was derived (combined F, G, and I) which agrees closely with the correlation from data source H; i.e., the correlation presented by the Institute of Petroleum (Reference 8).

Data source J includes both conventional and unconventional fuels and is not considered to be representative of conventional jet fuels.

Note that at different hydrogen contents the correlation curves shift places to some degree, especially correlation F (Figures 4 and 5). However, the combined correlation curve (F, G, and I) continues to agree reasonably well with correlation H as seen in Figure 6 which plots these two correlations at 13.5%, 14.0%, and 14.5% hydrogen content. It is concluded that either of these two correlations (correlation H or the correlation developed using combined data sources F, G, and I) is representative of conventional jet fuels.

In comparing calculated values of fuel hydrogen content with measured values of hydrogen content, smoke point, and luminometer number, the precision obtainable must be considered. Table VII lists the established

TABLE VI

CORRELATION EQUATIONS FOR WEIGHT PERCENT HYDROGEN AS FUNCTION OF ANILINE POINT AND GRAVITY

| SOURCE OF DATA | CORRELATION EQUATIONS<br>PH = % hydrogen by weight<br>APF = aniline point °F<br>API = gravity (°API) | NUMBER DATA POINTS | CORRELATION COEFFICIENT | STANDARD ERROR OF ESTIMATE PH |
|---|---|---|---|---|
| F | $PH = 10.932 + 0.04168\ API + 0.00764\ APF$ | 47 | 0.531 | 0.35 |
| G | $PH = 9.629 - 2.941\ LOG_e\ (API) + 0.00123\ (API)^2 + 2.625\ LOG_e\ (APF)$ | 35 | 0.8415 | 0.195 |
| H | $PH = 8.124 + 0.0586\ (API) + 0.02165\ APF$ | | | |
| I | $PH = 8.096 + 0.0776\ (API) + 0.061\ (APF)$ | 121 | 0.956 | 0.147 |
| J | $PH = 19.228 - 2.24\ LOG_e\ (API) + 0.00125\ (API)^2 + 0.00004\ (APF)^2$ | 24 | 0.984 | 0.12 |
| F, G and I | $PH = 8.572 + 0.06412\ (API) + 0.0170\ (APF)$ | 203 | 0.869 | 0.23 |

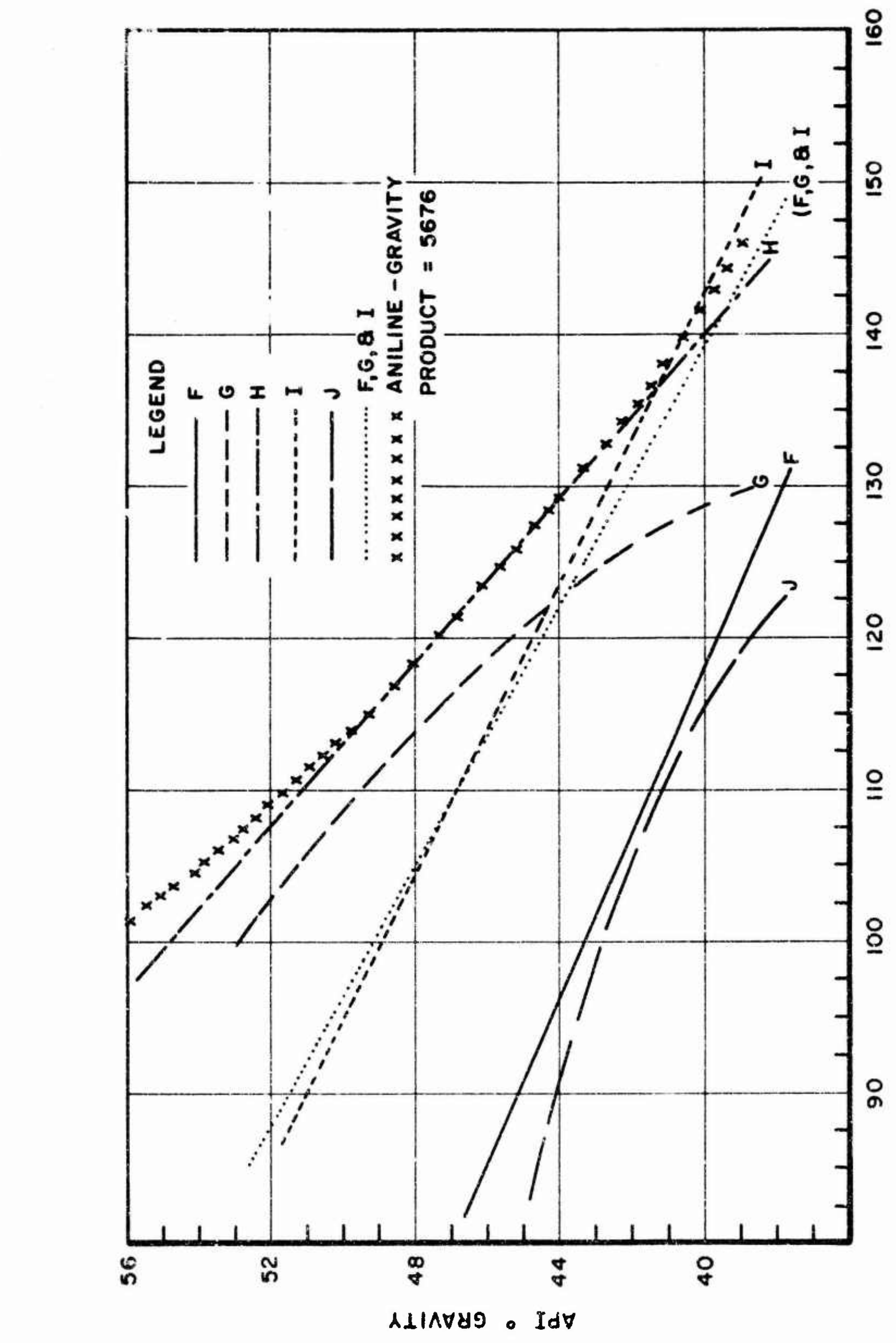


Figure 4. Correlation Curves for 13.5 Weight Percent Hydrogen

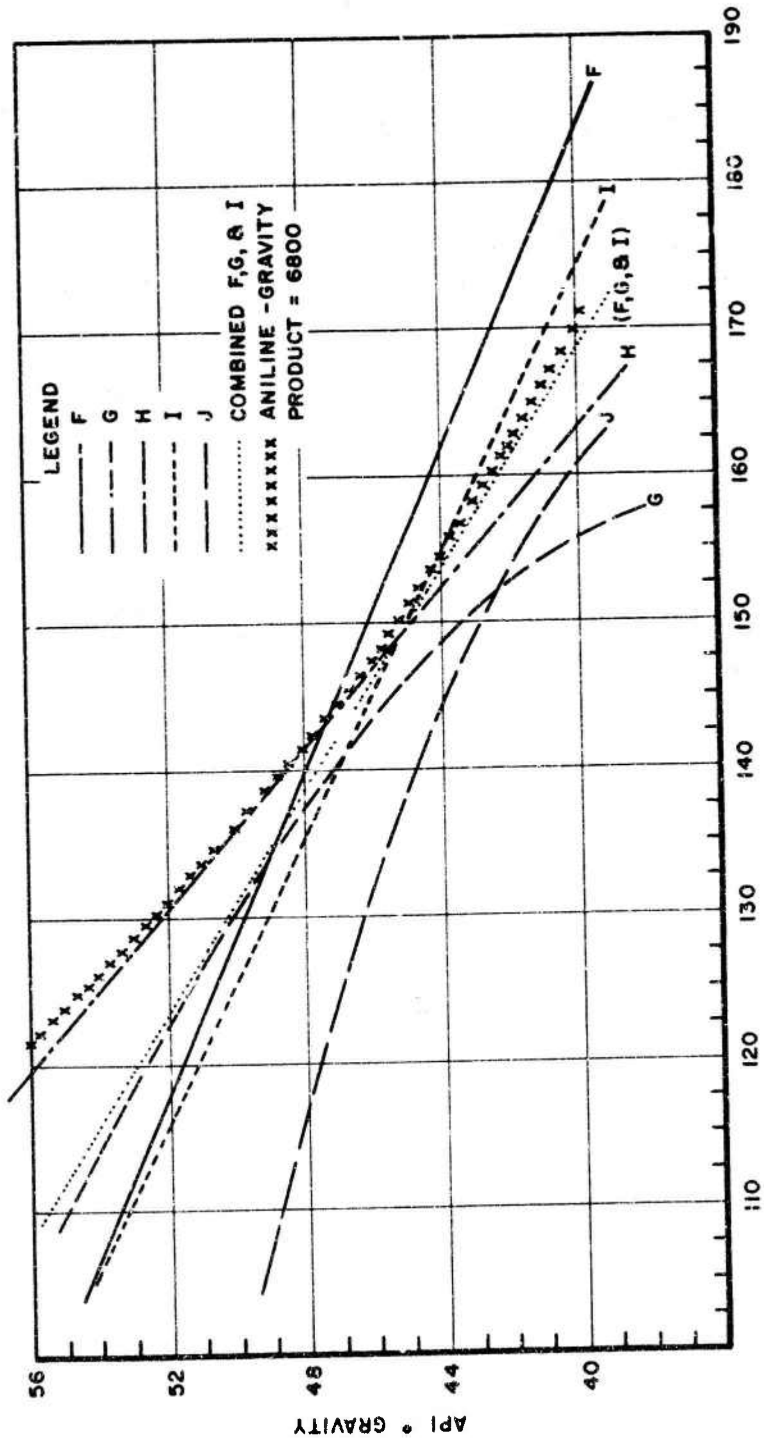


Figure 5. Correlation Curves for 14.0 Weight Percent Hydrogen

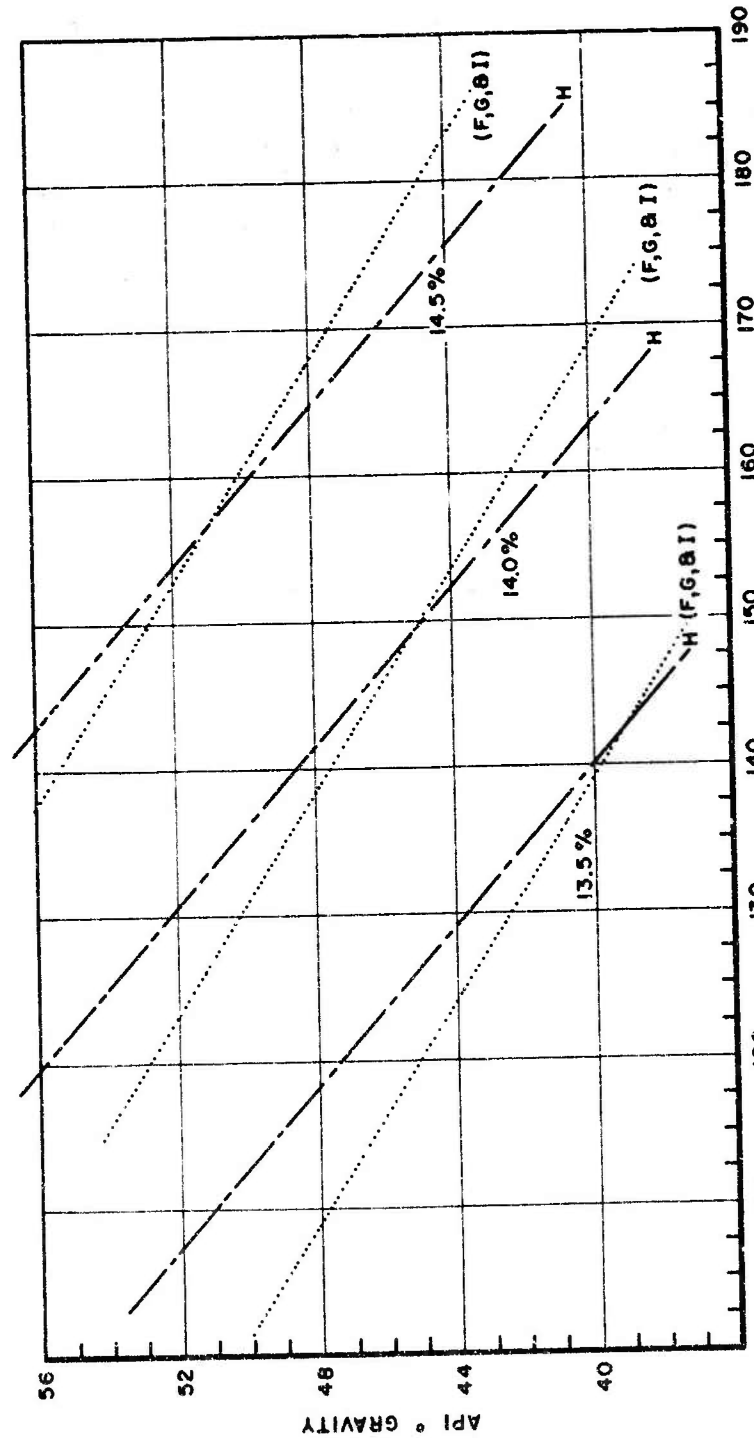


Figure 6. Correlation Curves for 13.5, 14.0, and 14.5 Weight Percent Hydrogen

precision limits for smoke point, luminometer number, and percent hydrogen by weight. Also listed is the equivalent percent error for a hydrogen content of 13.5% and the estimated precision values for calculated hydrogen contents. Although the measured hydrogen values are much more precise than calculated values, the calculated values of hydrogen are about a factor of two more precise than the measured smoke point and luminometer number. Thus, calculated hydrogen contents should be sufficiently precise for use in jet fuel specifications.

Figures 4 and 5 also have a curve plotted based on a specific aniline-gravity product. Aniline-gravity products are presently permitted as a substitute for net heat of combustion measurements in existing fuel specifications, and as noted in Section III.1.C, the net heat of combustion correlates well with a fuel's hydrogen content. It is found that an aniline-gravity product value of 6800 is roughly equivalent to 14.0% hydrogen in the 46 to 52 °API range, and a value of 5,676 is roughly equivalent to 13.5% hydrogen in the 42 to 50 °API range. The aniline-gravity product would be a good first estimate of a fuel's hydrogen content. For example, if the aniline-gravity product exceeds 5,676, then the fuel equals or exceeds 13.5% hydrogen and would be acceptable. If the aniline-gravity product is less than 5,676, then a calculated or measured hydrogen content would be required.

## 4. VALIDATION OF CALCULATED HYDROGEN CONTENT AS FUEL COMBUSTION PARAMETER

Figure 7 plots the aniline point and gravity of various JP-4, JP-5, Jet A, and Jet A-1 fuels listed by the Bureau of Mines (Reference 9). Figure 7 also includes two curves calculated from the correlation equations which were selected in Section III.3. These two curves show the correlation between the aniline point and gravity for fuel containing 13.5% hydrogen by weight. Note that all of the JP-4 fuels fall above both correlation curves as do all but three JP-5's and two Jet A's. The five fuels which fall below the 13.5% hydrogen curves have smoke points of 19 and 20 mm. The two JP-4 fuels which fall above, but closest to the 13.5% line have smoke points of 21 and 19 mm. Thus, it appears

TABLE VII

PRECISION LIMITS FOR COMBUSTION TEST METHODS

| TEST METHOD | RANGE | REPEATABILITY | REPRODUCIBILITY | EQUIVALENT ERROR AT 13.5% HYDROGEN |
|---|---|---|---|---|
| Smoke Point ASTM D-1322 | Up to 20<br>20 to 30<br>30 to 40 | 1<br>1<br>1 | 2<br>3<br>4 | ± 10% |
| Luminometer Number ASTM D-1740 | 40 to 70<br>70 to 100<br>100 to 120 | 4 to 5<br>5 to 6<br>6 to 7 | 6 to 8<br>8 to 9<br>9 to 10 | ± 13% |
| Weight Percent Hydrogen ASTM D-1018 | 11 to 16 | 0.11 | 0.18 | ± 1.3% |
| Calculated Weight % Hydrogen Data Source H | 13 to 15 | 0.01* | 0.04* | ± 5.8%** |

* Based on the precision of the aniline point test (D611) and the API gravity test (D1298).

** Based on three times the standard error of estimate for the correlation.

that the 13.5% hydrogen line (H data source) is an acceptable correlation and will separate fuels according to their combustion characteristics. The F, G, and I data sources curve is adequate for the low volatility fuels but not for the JP-4 fuels.

Examination of Figure 7 also indicates that, in general, JP-4 fuels have higher hydrogen contents than do JP-5, Jet A, and Jet A-1 fuels, and that JP-5 may be slightly inferior to the Jet A and A-1 fuels.

Figure 8 is a plot of 19 JP-4 and 16 Jet A and A-1 fuels presently under study as part of two jet fuel survey programs. Only one of the fuels (a Jet A fuel) falls below the 13.5% hydrogen line (H data source correlation curve). The one Jet A fuel below the line had an analyzed hydrogen content of 13.58%. As the hydrogen analysis accuracy is in the neighborhood of 0.3%, this may explain this slight anomaly.

Figures 9 and 10 are plots of 200 JP-4 fuels (100 fuels per plot) selected at random from fuels delivered to the Air Force early in 1972. Note, that in Figure 9, 93 of the fuels greatly exceed the 13.5% hydrogen line with only seven JP-4 fuels having a calculated hydrogen content of about 13.5%. In Figure 10 all but three fuels are well above the 13.5% hydrogen line. The seven JP-4 fuels from Figure 9 and the three JP-4 fuels from Figure 10 which are close to or below the 13.5% hydrogen line are from only three refineries.

A sample of fuel was obtained from one of the three refineries suspected of delivering marginal fuel (Figures 9 and 10). Table VIII compares this fuel (identified at JP-4-H) with another JP-4 fuel which was found to obey the aniline-gravity-hydrogen correlation. According to the ASTM (Reference 10), the aniline point increases with increasing molecular weight and decreases with increased percentages of naphthenic and aromatic constituents. Note in Table VIII that the JP-4-H has a lower average molecular weight and a higher volumetric percentage of naphthenic and aromatic compounds, all of which tend to lower the aniline point in comparison to the other JP-4 fuel.

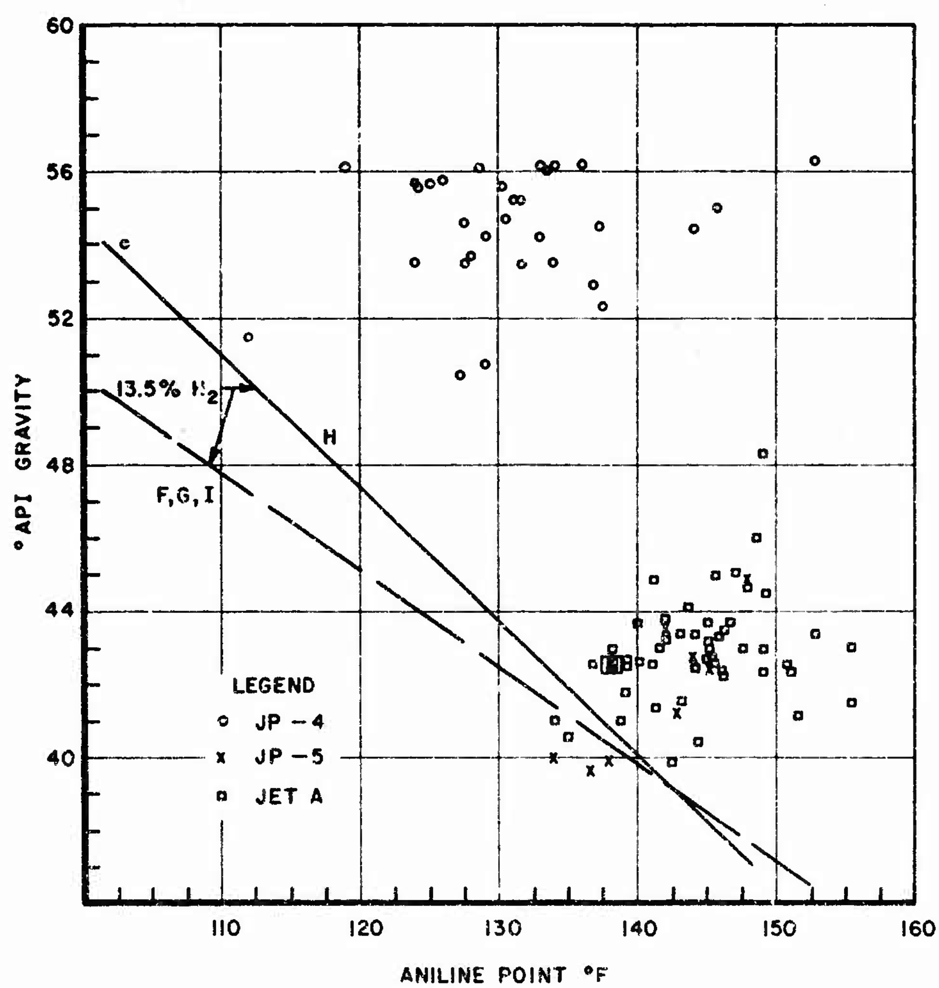


Figure 7. Correlation of Hydrogen Content with Aniline Point and API Gravity for 1971 Aviation Turbine Fuels

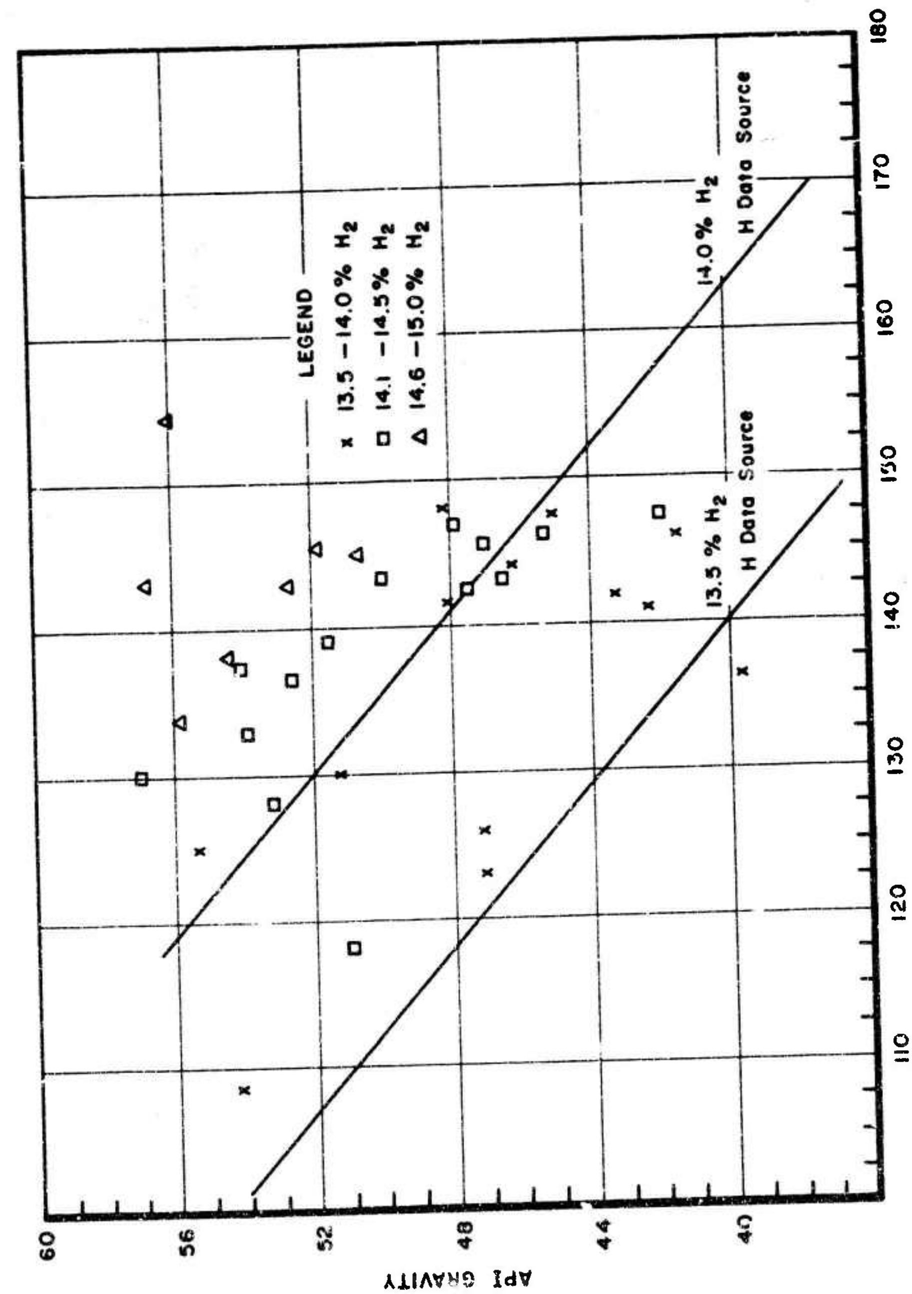


Figure 8. Hydrogen Content versus Aniline Point and API Gravity for JP-4 and Jet A Survey Fuels

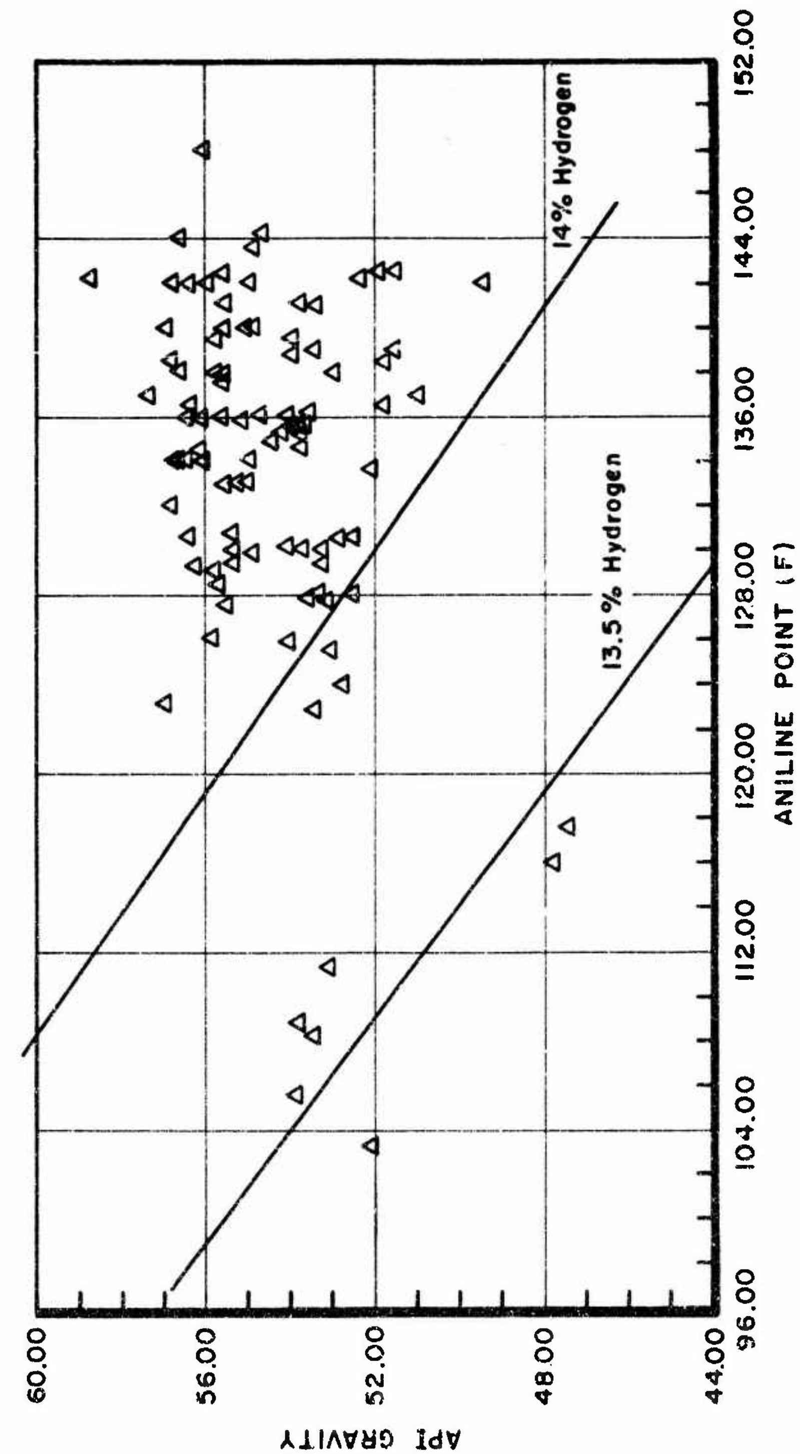


Figure 9. Hydrogen Content versus Aniline Point and API Gravity fcr One Hundred 1972 JP-4 Fuels Batch 1

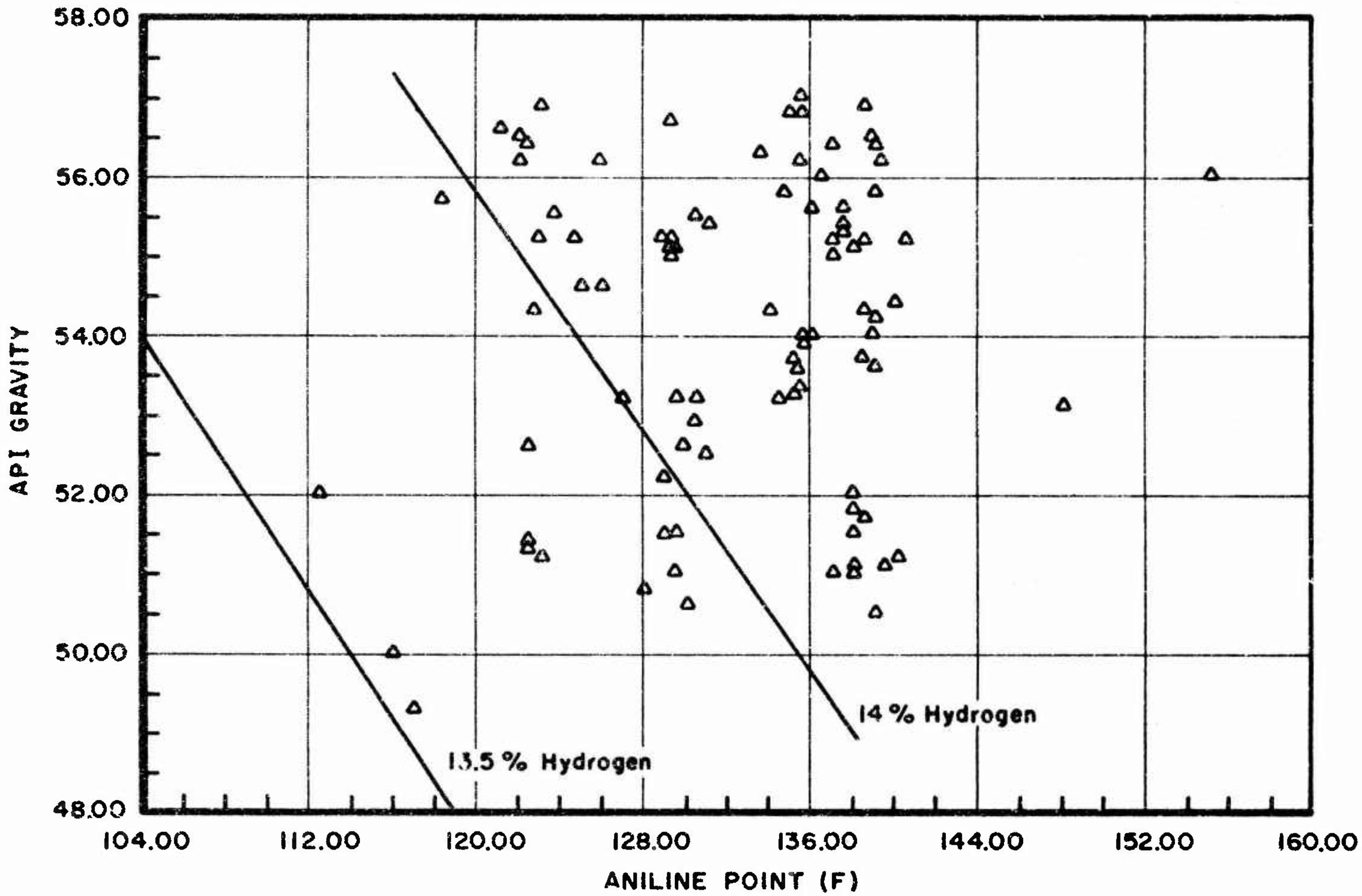


Figure 10. Hydrogen Content versus Aniline Point and API Gravity for One Hundred 1972 JP-4 Fuels Batch 2

TABLE VIII

PROPERTIES OF TWO JP-4 FUELS

| FUEL COMPOSITION (Vol. %)* | JP-4-H | JP-4-9 |
|---|---|---|
| Paraffins | 45.3 | 53.1 |
| Monocycloparaffins | 36.6 | 23.6 |
| Dicycloparaffins | 1.2 | 5.1 |
| Alkylbenzenes | 16.1 | 16.0 |
| Indans - Tetraline | 0.1 | 1.7 |
| Naphthalenes | 0.5 | 0.5 |
| **OTHER FUEL PROPERTIES** | | |
| Gravity °API | 55.2 | 51.3 |
| Aniline Point °F | 111.5 | 130. |
| % Hydrogen by Wt. (Measured) | 14.3 | 13.9 |
| % Hydrogen by Wt. (Calculated **) | 13.7 | 13.9 |
| Average Carbon Number of all Paraffins | 8.0 | 9.3 |
| Average Carbon Number of all Aromatics | 7.4 | 8.8 |

* Excluding olefin content which was 1% or less for the two fuels.

** Calculated using the aniline-gravity-%-hydrogen correlation from data source H.

Table VIII also shows that the calculated hydrogen content of JP-4-H is considerably less than the measured hydrogen content. In the case of the JP-4-H fuel, the error between the calculated and measured hydrogen content is on the conservative side. The question arises, however, as to the probability of having JP-4 fuels which give high calculated hydrogen contents but actually have low hydrogen contents. Based on the parameters which affect the aniline point, this would require a fuel having: (1) a high molecular weight, and (2) a fuel having relatively low concentrations of naphthenic compounds. This might best be illustrated by a fuel composed primarily of high boiling point paraffin fractions and high boiling point aromatics with little or no naphthenic compounds. The probability of encountering such a fuel is not known.

The large difference between the calculated and measured hydrogen contents for the JP-4-H fuel is discouraging and tends to discredit the aniline-gravity-hydrogen correlation. However, the difference between the calculated and measured hydrogen contents is less than 4 1/2%; considerably less than the reproducibility of the measured smoke point and luminometer number.

Further examination of Figures 7, 8, 9, and 10 indicate that almost all of the JP-4 fuels have calculated hydrogen contents of 14% or more. For example, 87% of the fuels in Figures 10 and 11 have hydrogen contents of 14% or greater. Thus, at a small penalty in terms of availability and cost, the JP-4 specification could be significantly upgraded in terms of combustion performance.

Figure 7 indicates, however, that Jet A and JP-5 do not have much of a "cushion" available, and that a minimum of 13.5% hydrogen by weight is a reasonable requirement. To upgrade the combustion performance of Jet A and JP-5 would greatly limit the availability and increase the cost of the fuel.

# SECTION IV

# CONCLUSIONS

1. Early investigators have conclusively shown that the hydrogen content of a jet fuel is a better predictor of the fuel's combustion performance than either the smoke point or the luminometer number.

2. Excellent correlations have been found between : (a) luminometer number and hydrogen content of the fuel, (b) smoke point and the hydrogen content of the fuel, and (c) hydrogen content and the net heat of combustion.

3. The smoke volatility index is an obsolete, ineffective method for specifying a jet fuel's combustion performance in modern jet engines.

4. The precision of hydrogen content measurements is much better than the precision of either the smoke point or the luminometer number.

5. The hydrogen content of a fuel can be calculated using the fuel's measured aniline point and gravity with better precision than can the fuel's smoke point or luminometer number be measured.

6. Existing jet fuel specifications measure the fuel's combustion performance using the smoke point, the luminometer number, or the smoke volatility index. Most of the existing specifications do a poor job of specifying equivalent values of smoke points, luminometer numbers, and smoke volatility indices.

7. Existing jet fuel specifications for JP-4, JP-5, JP-7, JP-8 and Jet A, A-1 and B, specify a minimum net heat of combustion. However, these specification limits on the net heat of combustion are not needed as other specification requirements are more stringent and thereby ensure adequate heats of combustion.

8. A fuel's hydrogen content can be calculated significantly cheaper than can the smoke point or luminometer number be measured.

# SECTION V

# RECOMMENDATIONS

It is recommended that jet fuel specifications be changed to specify a minimum allowable fuel hydrogen content in lieu of smoke point, luminometer number, smoke volatility index, and/or percent naphthalenes as a measure of the fuel's combustion characteristics. Current jet fuel specifications should be changed as follows:

(1) Specify a minimum of 13.5% hydrogen by weight for JP-4, JP-5, JP-8, Jet A, Jet A-1, and Jet B fuels.

(2) Specify a minimum of 14.5% hydrogen by weight for JP-7 fuels.

(3) Delete all references to smoke point, smoke volatility index, luminometer number, percent naphthalenes, and net heat of combustion from the specifications.

(4) ASTM D-1018 should be listed as the referee method for measuring the hydrogen content of a jet fuel.

(5) For conventional jet fuels, calculated values of the fuel's hydrogen content should be permitted. One suitable method for calculating the hydrogen content of a conventional jet fuel uses the measured values of the fuel's gravity and aniline point (Section III.3).

(6) For JP-7 fuels it is suggested that only measured values of the fuel's hydrogen content be permitted initially. However, calculated values should be reported. If calculated values are found to correlate with measured values as well as is anticipated, then calculated values could also be approved for JP-7 fuels.

# APPENDIX

## SOURCES OF DATA FOR CORRELATIONS INVOLVING FUEL HYDROGEN CONTENT, LUMINOMETER NUMBER, SMOKE POINT, AND NET HEAT OF COMBUSTION

A. ASTM Test Method D-1322 - Smoke Point. Method D-1322 uses six blends of isooctane and toluene as reference fuels for the calibration of the smoke point apparatus. The percent hydrogen by weight for these six blends has been calculated and plotted against the specified smoke points (Figure 11). However, the resulting curve is biased as isooctane is a branched paraffin, and branched paraffins in a diffusion flame (such as the flame used for smoke point measurements) will not burn as cleanly as will a normal paraffin (Reference 2). Thus, the correlation curve tends to give a high value of percent hydrogen by weight for a given smoke point. This bias, however, does not prevent the isooctane-toluene blends from being suitable reference fuels.

B. ASTM 1966 Combustion Properties of Aviation Turbine Fuels, Project 0611. The ASTM Committee D-2, Technical J, Division VII, conducted a correlation program in 1966 using eight different JP-4 type fuels tested by 15 independent laboratories. The smoke point, luminometer number, percent hydrogen by weight, smoke volatility index, and percent naphthalenes were measured by each laboratory, in duplicate, and the results statistically analyzed. The fuels selected covered a wide range of properties and good correlations between the measured properties were obtained.

C. ASD-TDR-62-682, "Combustion Characteristics of Special Hydrocarbon Jet Fuels," July 1962. This program conducted by Shell Oil Company for the US Air Force evaluated the combustion properties of 12 hydrocarbon fuels. The fuels represented extremes of composition and combustion characteristics. Good correlations have been obtained from the published data for these fuels when comparing percent hydrogen by weight with luminometer number, smoke point, and net heat of combustion.

D. WADC-TR-59-327, "Evaluation of Hydrocarbons for High Temperature Fuels," December 1961. This program was conducted for the US Air Force by Monsanto Research Corporation. Of the hydrocarbon products examined about 45 were given HTF designations. Data from 41 of these products have been analyzed to compare measured luminometer numbers with percent hydrogen by weight and net heat of combustion with percent hydrogen by weight. These products exhibit a wide variety of compositions - some are pure hydrocarbons, others are blends.

E. Phillips Petroleum Company Report 4230-65R, "Effect of JP Fuel Composition on Flame Radiation and Hot Corrosion," November 1965. This program was conducted for the US Navy. Twenty-five fuels of which seven were JP-5 type blends were burned in a 2-inch combustor device. Correlations obtained by Phillips have been included in this report as well as the use of their data for other correlations.

F. US Bureau of Mines - Aviation Fuels Data for Years 1958, 1966, 1967, 1968, and 1969. Data for jet fuels which included percent hydrogen by weight, smoke points, and net heat of combustion were extracted from these reports. Correlations were calculated using this date. Note, however, that some of the data points have been thrown out as the percent hydrogen measurements were obviously in error.

G. Coordinating Research Council Jet A and the Air Force JP-4 Fuel Surveys, 1971, 1972. Nineteen samples of JP-4 and 16 samples of Jet A fuels are being used by the AF and the CRC involving the JFTOT coker. Extensive analysis of these fuels provided another ready source of data for comparing combustion parameters.

H. "Jet Fuels Combustion Properties and Quality Control," by the Institute of Petroleum and presented to the December 1970 meeting of ASTM D-2. This paper presented proposed equations for calculating the smoke point, the luminometer number, and the percent hydrogen by weight for jet fuels using the aniline point and the specific gravity. The exact fuels used to establish these correlations is not clear, but were of jet fuel types.

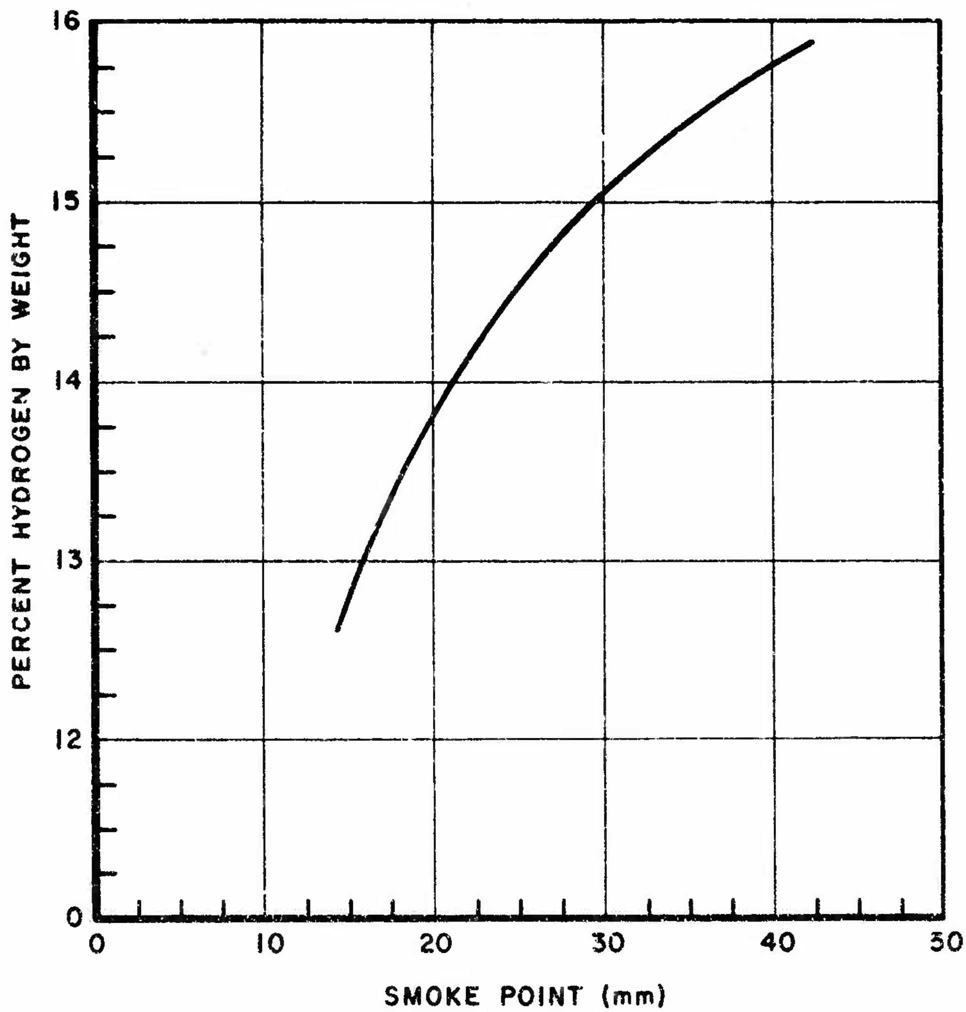


Figure 11. ASTM D-1322 Reference Fuel Blend Smoke Point Data

I. "Net Heat of Combustion and Other Properties of Kerosines and Related Fuels," Journal of Chemical Engineering Data, National Bureau of Standards, 1962. Over 100 kerosine type fuels including distillates, alkylates, and some special experimental fuels were used to establish the correlations between the net heat of combustion and the measured values of aniline point and specific gravity. This data has been used to obtain other correlations reported on herein.

J. "Air Force Fuel Bank." For over ten years the Air Force has maintained a bank of reference fuels in cold storage. These fuels include both conventional jet fuel types as well as experimental jet fuels having a wide variety of compositions. Analysis data on these fuels have been used to obtain correlations between various combustion properties.

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