General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)
Fuels Research Studies at NASA Lewis

Albert C. Antoine
Lewis Research Center
Cleveland, Ohio

Prepared for the
Fifty-fourth Annual Convention of the National Technical Association, Inc.
Baltimore, Maryland, August 2-7, 1982
FUELS RESEARCH STUDIES AT NASA LEWIS

Albert C. Antoine
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

ABSTRACT

Fuels research studies are being carried out at the NASA Lewis Research Center in a variety of areas related to aviation propulsion, ground transportation, and stationary power generation systems. The major efforts are directed to studies on fuels for jet aircraft. These studies involve fuels preparation, fuels analysis, and fuel quality evaluations. In this brief report the scope and direction of research activities in these areas will be discussed, descriptions of Lewis capabilities and facilities given, and results of recent research efforts reported.

INTRODUCTION

The NASA Lewis Research Center has for a number of years been actively engaged in aircraft engine research and technology. For many of those years Lewis has also been engaged in a variety of energy-conversion processes and systems, both for aerospace and terrestrial applications. Improving the efficiency of most present-day energy-conversion processes has become extremely important because of the uncertainty regarding future fuel supplies. Research on fuels is an important element in improving the efficiency of many of these energy-conversion processes, as the characteristics of fuels can have severe limiting effects on the performance and durability of propulsion or power systems. Future supplies of petroleum fuels may have characteristics different from those of present-day fuels, and fuels derived from alternate sources such as oil shale and coal may differ also. In reference 1 a comparison is given of the physical properties and chemical compositions of some synthetic crudes with those of typical petroleum crudes.

In order to identify the potential changes in jet aircraft fuels, Lewis has acquired the capability to produce small quantities of research fuels from both conventional and alternative sources. These fuels are prepared in laboratory-scale synthesis facilities using processing techniques found in typical modern refineries. After preparation, the research fuels are subjected to a broad spectrum of physical and chemical property analyses. The fuels analysis facilities at Lewis are capable of conducting most of the American Society for Testing and Materials (ASTM) specification tests for jet fuels. In addition to the specification tests, various other instrumental analyses are used to gain more detailed descriptions of the chemical compositions and molecular structures of fuels. Current work in these analytical areas will be described, together with a review of the new analytical methods being investigated.

In addition to chemical composition and physical property analyses, a variety of performance tests are used to characterize fuel quality. These include tests for fuel characteristics such as storage and thermal
stability, and smoking tendency. At Lewis, research is underway to examine the validity of these performance tests as fuel properties change.

**FUELS PREPARATION**

The facilities at Lewis are designed and scaled to produce small quantities of distillate fuels. The processing involved is similar to the petroleum processing conducted in modern refineries. A distillation unit for crude or product processing is shown in figure 1. The unit has a 72-liter (19-gal) capacity and may be operated at pressures from atmospheric to $2.67 \times 10^5$ (2 torr). The crude oil which is being processed may be separated into several boiling-range fractions or the pretreated, or dewatered, crude may be sent directly to the hydroprocessing apparatus. The Lewis hydroprocessing facility is shown in figure 2. Hydroprocessing, which is the catalytic addition of hydrogen, increases the hydrogen content of the crude and also reduces the content of organic nitrogen, oxygen, and sulfur. The extent of the hydroprocessing reactions, or severity, is controlled by varying the pressure, temperature, or flow through the reactors.

Since synthetic crudes derived from oil shale or coal are likely to be introduced in the future, some effort has been placed on producing transportation fuels from these sources. The hydroprocessing facility was used to prepare jet fuels from two shale oil feedstocks, and to study the effect of hydroprocessing severity on the products produced (ref. 2). Samples for the feedstocks were obtained from the TOSCO II process and the Hayashi process. Jet A boiling-range fuels, 121° to 321° C (250° to 620° F), were produced by hydroprocessing the shale oil distillates and their properties were measured to characterize the fuels. Table I shows some of the results obtained from the study. With increasing severity, hydrogen content is increased and aromatics and nitrogen content decreased. The specific gravity of the fuel is also decreased with increased hydroprocessing severity.

**FUELS ANALYSIS**

The American Society for Testing and Materials (ASTM) lists a number of specification tests an aviation turbine fuel must meet before being accepted for civil use (ref. 3). Most of these tests can be conducted in the Lewis fuels analysis facilities. These tests are listed and described in table II, together with several other ASTM tests, not required for specification but needed for fuels analysis and characterization. In addition, other analytical techniques are used to supplement those listed.

**Elemental Analysis**

Fuels are mainly mixtures of compounds which contain carbon and hydrogen only. The amounts of each element are often measured since carbon-hydrogen ratios are used in aircraft engine combustor design and performance calculations. One method of measurement involves combustion of the fuel and determination of the amounts of carbon dioxide and water produced. This analysis can be performed with the apparatus pictured in figure 3, in which a small sample of fuel undergoes combustion in an oxygen atmosphere. Figure 4 shows the apparatus used for the determination of hydrogen content only. In this method, the fuel is not combusted.
Rather, a low resolution, continuous-wave, nuclear magnetic resonance spectrometer is used, which is tuned to measure the resonance from hydrogen atoms. The method provides a fast, accurate, and precise measurement of the hydrogen content.

Though fuels are mainly composed of carbon and hydrogen, petroleum fuels also contain low concentrations of sulfur-containing compounds. The amount of sulfur in the fuel is usually determined by oxidation of the sulfur and measurement of the resulting sulfate by titration or precipitation. Another method determines sulfur by measuring the intensity of X-rays emitted from the sulfur atoms after excitation. The use of an ion chromatograph, pictured in figure 5, is under evaluation at Lewis (ref. 4). In this method the fuel undergoes combustion in an oxygen bomb and the sulfate ion formed is separated and measured with the chromatograph. The method may be more sensitive than some other methods for determining sulfur, as well as enabling other elements to be determined virtually simultaneously.

Petroleum crudes usually contain very small amounts of nitrogen-containing compounds and the amount of nitrogen in petroleum-derived fuels is usually not measured. The amount of nitrogen in synthetic crudes is often significantly higher and the amounts that could be present in the fuels derived therefrom could be of concern. An accurate determination of nitrogen content is needed, even at very low levels. Several methods are available to effect such a determination. One method in use at Lewis involves pyrolysis of the fuel in a hydrogen atmosphere and detection and measurement of the ammonium ions formed in a microcoulometric titration cell. The apparatus is pictured in figure 6. The method is applicable to fuels containing as little as 0.0002 wt percent (2 ppm) total nitrogen.

Traces of many other elements may be found in fuels, bound as organometallics or existing as inorganic compounds. Spectral methods are often used in attempting to measure the low concentrations of these elements. One method uses an atomic absorption flame photometer. The technique involves the aspiration of a solution of the sample into a flame and the measurement of individual elements by spectral absorption. Another method uses an optical emission spectrometer. In this technique the fuel sample is oxidized to remove carbon and hydrogen and the resulting ash is incorporated into an electrode. A DC arc is produced from the electrode in a controlled-atmosphere chamber (fig. 7, ref. 5). Twenty elements can be determined in a short time with high sensitivity.

The traces of metallic elements found in fuels are most often present in the original crude from which they were prepared. However, the presence of some may result from contamination during processing and handling. In analyzing for trace elements it is imperative that sample-handling procedures do not add to any contamination. To aid in reducing the possibility of contamination, a special controlled-flow, clean-air hood, shown in figure 8, has been fabricated at Lewis.

A primary concern in trace-element analysis is that the precision in measurements between laboratories and analytical techniques is very often quite poor. In reference 6 a review of the techniques used at Lewis is presented, as well as the design of an Interlaboratory Study being conducted by the Lewis Center. Conclusions will be drawn from a statistical analysis of the results and research efforts directed toward improving interlaboratory analytical precision and accuracy.
Hydrocarbon Group Type Analysis

Hydrocarbon compounds may be divided into groups based on their structure and composition. The groups found primarily in fuels are paraffins, cycloparaffins (naphthenes), olefins, and aromatics. Because of their behavior on burning, storage, and effect on materials, limits are placed on the amounts of olefins and aromatics many fuels can contain. For jet fuels the aromatics concentration must be determined. The Fluorescent Indicator Adsorption (FIA) method is used to determine the amounts of aromatics, saturates (paraffins and cycloparaffins), and nonaromatic olefins present in several types of fuels. In the method the fuel is separated on a column, shown in figure 9, into aromatic, olefin, and saturate zones. Some fluorescent dyes which are introduced with the sample are also separated selectively with the hydrocarbon types and make the zones visible under ultraviolet light. The method is routinely used in analyzing jet fuels to determine if specifications are being met.

Recently, however, there has been concern expressed about the applicability of the method to fuels other than gasolines for which the method was developed. These concerns are heightened if the use of broadproperty petroleum jet fuels and jet fuels prepared from alternate sources is planned. With the development of high performance liquid chromatography (HPLC), suggestions are being made that this technique can be used effectively to separate hydrocarbon group types in fuels. In this technique the hydrocarbon groups are separated on a column and measured by spectrophotometers or refractometers as they leave the column. One HPLC system is shown in figure 10. A comparison of results for FIA and HPLC analyses of some fuels from oil shale and coal was made (ref. 7) and the results indicated that HPLC could afford a rapid, precise measurement of hydrocarbon group type. Research is being conducted to develop the method for general use with fuels. A central problem is involved with the preparation of standards that can be used with a wide variety of fuels. Efforts are being directed toward using standards prepared directly from the fuels. This will lead to improved precision and accuracy of the general technique, and extension of the range of its applicability.

Another analytical technique using infrared spectroscopy is being evaluated for hydrocarbon group type determination in jet fuels (ref. 8). The concentration of hydrocarbon types is measured using a computerized infrared spectrophotometer. The spectrophotometer is calibrated using a fuel of known aromatic and olefinic content. Once calibration is completed other fuels can be rapidly analyzed by means of the computer program. Application to conventional fuels, synthetic fuels, oils, and other organic mixtures is being evaluated.

A more detailed analysis of fuel composition can be made when necessary. For example, the aromatics group can be analyzed for single-, double-, and triple-ring compounds. This can be done by mass spectrometry. Even further details can be obtained by combining a gas chromatograph with a mass spectrometer. Another technique, nuclear magnetic resonance spectrometry, can provide a detailed analysis of hydrocarbon types in fuels.

FUEL QUALITY EVALUATION

Certain properties of fuels have significant effects on the performance and durability of aircraft propulsion-system and fuel-system compone-
ents. Some properties are related to the combustion of the fuel. Others affect the storage and thermal stabilities of the fuel. Still others are related to the behavior of the fuel at temperatures close to the freezing point. Thus, certain tests are required which measure the quality of the fuel.

A determination of fuel thermal stability is made by the Jet Fuel Thermal Oxidation Tester (JFTOT) procedure. This is a standard laboratory method which subjects the fuel to conditions which can be related to those occurring in gas turbine engine fuel systems. A schematic of the test apparatus is shown in figure 11. Fuel is passed at a constant rate over a heated tube at a given temperature. At the conclusion of the test, the tube is removed and a rating is assigned based on the amount and color of any fuel deposit stain on the surface of the tube. The tube can be examined visually, as shown in figure 12, and rated or it can be rated by an instrumental light-reflection method. If sufficient deposit has formed, the fuel is determined to be unacceptable. Also, if sufficient particles are formed to create a significant pressure drop across the filter during the test, the fuel is determined to be unacceptable.

The JFTOT test is used for qualifying the thermal stability of aviation turbine fuels but at Lewis it is also used as a research tool for studying thermal instability processes. Some recent results are described in references 9 and 10. In the former, the effect of some nitrogen compounds on the thermal stability of Jet A, a common commercial jet fuel, is described. The results show that the type of nitrogen compound used has a distinctive effect, particularly on the placement of deposits on the tube used for testing. In the latter reference, a description is given of a modified JFTOT procedure used to evaluate deposit and sediment formation for four pure hydrocarbon types. The fuel types were a normal alkane, an alkene, a naphthene, and an aromatic. The results show that each fuel exhibited certain distinctive deposit and sediment formation characteristics.

Further research is being conducted to study the mechanisms of thermal instability processes. The goal is to obtain a complete description of the several chemical reactions associated with the processes. In one approach in studying the problem the basic fuel stability test apparatus has been modified. Pictured in figure 13 is a gas chromatograph which has been incorporated into a special JFTOT apparatus. The apparatus is being used to identify and measure specific components in the fuel, beginning with the initial reaction of the fuel component with oxygen dissolved in the fuel. The chemistry of deposit formation can be determined, as the rates of formation and degradation of deposit precursors are measured.

To further study thermal instability processes, the deposits which are formed are examined. Since deposits are more easily examined on a flat surface, a modified test section with a flat surface has been prepared for the JFTOT apparatus. More than one technique can be used to examine the deposits. To get details of surface character, a scanning electron microscope, pictured in figure 14, can be used. To determine the elemental composition of the deposit particles, the energy dispersive X-ray analyzer capability can be used. Further information on elemental composition and functional groups can be derived by use of an X-ray photoelectron spectroscope and a Fourier transform infrared spectrophotometer.
A determination of combustion quality is achieved by measuring the flame radiation and smoking tendency of a fuel in laboratory burner equipment. One such piece of equipment, shown in figure 15, measures the smoke point of aviation turbine fuels. The smoke point, defined as the maximum height of flame that can be attained without smoking, can be related to combustion behavior in full-scale engines.

Other aspects of fuel quality evaluation are also being investigated. These involve both analytical and experimental studies. For example, in regard to synthetic fuels, use of petroleum-based methods and correlations are being evaluated. In reference 11 an evaluation was made of the applicability, to some synthetic fuels, of some gas chromatographic methods now under development for use with petroleum-based fuels for the determination of fuels properties. In reference 12 the use of petroleum-based correlations and estimation methods for hydrogen content and heat of combustion was evaluated for use with synthetic fuels.

Experimental studies in both fundamental and applied combustion research, which is closely related to the fuels-research program, are being conducted. A wide variety of combustion test facilities are used, together with a large number of experimental fuels. For example, as reported in ref. 13, the combustion of some industrial turbine liquid fuels prepared from solvent-refined coals was studied. The experiment was conducted in a small burner rig and the response of some superalloys to exposure to the combustion gases was determined. Further, an equilibrium thermodynamic analysis was employed to predict the chemical composition of the deposits. The agreement between predicted and observed compounds was excellent. The results of this and similar studies will enable the influence of fuel property variation on the performance and life of combustion systems to be identified.

CONCLUDING REMARKS

The purpose of this report was to describe briefly some of the fuels research capabilities and activities at the Lewis Research Center. These include the facilities for fuels preparation, fuels analysis, and fuel quality evaluation. The emphases of the research efforts are in analytical methods evaluation and development to meet the needs as fuels properties change.

REFERENCES

<table>
<thead>
<tr>
<th>Property</th>
<th>Feedstock (from Parafo Process)</th>
<th>Processing severity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Hydrogen content, wt %</td>
<td>12.05</td>
<td>13.66</td>
</tr>
</tbody>
</table>
| Aromatics content, vol %         | ------                           | 17.7                | 15.5                | 8.1
| Sulfur content (mercaptan), wt % | 0.0016                           | 0.0006              | <0.0003             | <0.0003 |
| Sulfur content (total), wt %     | 0.81                             | 0.02                | 0.02                | 0.02
| Nitrogen content, wt %           | 1.53                             | 0.71                | 0.0602              | 0.0005 |
| Naphthalenes content, vol %      | ------                           | 2.0                 | 31                  |
| Flashpoint, °C (°F)              | ------                           | 42 (107)            | 38 (100)            | 35 (95) |
| Gravity (API, 15° C)             | 29.8                             | 40.3                | 41.6                | 44.8
<p>| Gravity (specific, 15/15° C)     | 0.8767                           | 0.8232              | 0.8160              | 0.8026 |</p>
<table>
<thead>
<tr>
<th>ASTM procedure</th>
<th>Test description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D 56, D 92, D93</td>
<td>Flash points</td>
</tr>
<tr>
<td>D 86</td>
<td>Distillation of petroleum products</td>
</tr>
<tr>
<td>D 97</td>
<td>Pour point</td>
</tr>
<tr>
<td>D 129</td>
<td>Total sulfur (bomb method)</td>
</tr>
<tr>
<td>D 323</td>
<td>Reid vapor pressure</td>
</tr>
<tr>
<td>D 445</td>
<td>Kinematic viscosity (dynamic viscosity)</td>
</tr>
<tr>
<td>D 677</td>
<td>Aniline point</td>
</tr>
<tr>
<td>D 974</td>
<td>Acid number by color indicator</td>
</tr>
<tr>
<td>D 1094</td>
<td>Water reaction test</td>
</tr>
<tr>
<td>D 1218</td>
<td>Refractive index</td>
</tr>
<tr>
<td>D 1298</td>
<td>API and specific gravity</td>
</tr>
<tr>
<td>D 1319</td>
<td>Fluorescent Indicator Adsorption method for aromatics, olefins, saturates</td>
</tr>
<tr>
<td>D 1322</td>
<td>Smoke point</td>
</tr>
<tr>
<td>D 1740</td>
<td>Luminometer number</td>
</tr>
<tr>
<td>D 1840</td>
<td>Vol. % naphthalenes</td>
</tr>
<tr>
<td>D 2382</td>
<td>Heat of combustion (high precision)</td>
</tr>
<tr>
<td>D 2386</td>
<td>Freezing point</td>
</tr>
<tr>
<td>C 2887</td>
<td>Boiling point range distribution by simulated distillation</td>
</tr>
<tr>
<td>D 3241</td>
<td>Thermal oxidation stability</td>
</tr>
<tr>
<td>D 3431</td>
<td>Nitrogen content by microcoulometric method</td>
</tr>
<tr>
<td>D 3701</td>
<td>Hydrogen content by low resolution NMR</td>
</tr>
</tbody>
</table>
Figure 3. - Microcombustion elemental analyzer.

Figure 4. - Nuclear magnetic resonance spectrometer for hydrogen analysis.
Figure 5. - Ion chromatograph used to determine the sulfur content of fuels.

Figure 6. - Microcoulometric titration analyzer for nitrogen content of fuels.
Figure 7. - Controlled atmosphere DC arc chamber.

Figure 8. - Clean air facility.
Figure 9. - Fluorescent indicator adsorption column for hydrocarbon group type analysis.

Figure 10. - High-performance liquid chromatograph.
Figure 11. - Jet fuel thermal oxidation tester schematic.

Figure 12. - Examination of JFTOT tube.
Figure 13. - Jet fuel thermal oxidation test apparatus coupled to gas chromatograph.

Figure 14. - Scanning electron microscope with energy dispersive X-ray analyzer capability.
Figure 15. - Apparatus for ASTM smoke point measurement.