Effect of Hydrocarbon Fuel Type on Fuel Thermal Stability

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Summary

A modified jet fuel thermal oxidation tester (JFTOT) procedure was used to evaluate deposit and sediment formation for four pure hydrocarbon fuels over the temperature range 150° to 450° C in 316-stainless-steel heater tubes. Fuel types were a normal alkane, an alkene, a naphthene, and an aromatic. Each fuel exhibited certain distinctive deposit and sediment formation characteristics.

The effect of aluminum and 316-stainless-steel heater tube surfaces on deposit formation for the fuel n-decane over the same temperature range was investigated. Results showed that an aluminum surface had lower deposit formation rates at all temperatures investigated.

By using a modified JFTOT procedure the thermal stability of four pure hydrocarbon fuels and two practical fuels (Jet A and home heating oil no. 2) was rated on the basis of their breakpoint temperatures. Results indicate that this method could be used to rate thermal stability for a series of fuels.

Introduction

This report describes a study of the effect of individual fuel components on hydrocarbon fuel thermal stability. This work is part of a research program whose purpose is to obtain a better understanding of the chemistry of hydrocarbon fuel thermal degradation.

Previous investigators (refs. 1 to 3) have reported that fuel composition is one of many important factors determining fuel stability. The present report describes the effect of pure hydrocarbon fuel type on deposit and sediment formation. Four hydrocarbon types were selected: an n-alkane, an alkene, a naphthene, and an aromatic. An alkene was selected, even though alkenes are not usually a major component of jet fuels, because they are produced when an alkane fuel undergoes pyrolysis at temperatures of 350° C and higher. Because practical fuels are complex mixtures of hydrocarbons and other species, the chemistry of their thermal degradation is exceedingly complex. Therefore pure hydrocarbon fuels were used to simplify the reacting system for easier chemical interpretation of the results.

Materials, Apparatus, and Procedure

Fuels

Both pure and practical hydrocarbon fuels were used in this investigation. The pure hydrocarbon fuels were
(1) n-Decane, pure grade (99 mole percent, minimum), from the Phillips Chemical Co.

(2) Cyclohexane, Fisher certified American Chemical Society (ACS) (99 mole percent, minimum), from the Fisher Scientific Co.

(3) 1-Hexene, pure grade (99 mole percent, minimum), from the Phillips Chemical Co.

(4) Benzene, Fisher certified ACS (99 mole percent, minimum), from the Fisher Scientific Co.

The practical hydrocarbon fuels were

(1) Jet A

(2) Home heating oil no. 2

Apparatus

A commercially available JFTOT (from Alcor, Inc.), shown in figure 1, was used to thermally stress the fuel. Alcor standard JFTOT 316-stainless-steel heater tubes were used, except for one series of tests. For this series both aluminum and 316-stainless-steel tubes were used to study the effect of surface material on deposit formation for the fuel n-decane.

An Alcor, Inc., Mark 8 tube deposit rater (TDR) operating on a light reflectance principle was used to rate the amount of fuel deposit on heater tube surfaces (refs. 4 and 7). Deposit was expressed in terms of a net TDR value as a function of tube position. The amount of fuel sediment was determined by the standard JFTOT procedure of measuring the pressure drop ΔP across a test filter as a result of sediment collecting on the filter (refs. 4 and 7).

Procedure

The standard JFTOT procedure consists of flowing 3 cm³/min of an aerated fuel at 3447-kPa (500-psig) nitrogen gas pressure and 260° C for 2½ hours over a tubular aluminum test surface (ref. 4). For this study we modified this procedure so that it consisted of operation at one of the temperatures (150°, 250°, 350°, 400°, or 450° C) for 40 minutes. Fuel flow rate, pressure, and aeration were the same as for the standard test. For the temperature range of interest it was necessary to use 316-stainless-steel tubes instead of aluminum tubes, which became distorted at 450° C.

As stated previously, the Mark 8 TDR readings were used as a measure of fuel deposit on the heated tube surface. The TDR rating scale is calibrated so that a zero reading is an indication of a clean tube and a reading of 50 (maximum value) represents excessive deposit formation. The net TDR readings are obtained by subtracting from readings measured after a run, background readings made on each clean tube before it is mounted in the JFTOT. For a petroleum fuel, previous work (ref. 7) has shown that a maximum net TDR value of 13 or below indicates that a fuel has passed the standard stability test. This value of 13 is supported by the fact that a tube with such a value would also have received a pass rating by two other tube deposit rating methods. One is the Exxon Research and Engineering method (ref. 13), and the other is the ASTM visual color standard technique (refs. 7, 10, and 13).

Fuel thermal sediment formation is monitored by using a mercury manometer to measure the pressure drop across a test filter. A fuel is considered to pass the standard test if its ΔP value does not exceed 3.3 kPa (25 torr) before the end of a JFTOT 2½-hour test (ref. 7).

For this study we have adopted the concept of using break point temperatures $T_B$ to rate the thermal stability of a series of fuels, as was done in reference 7. Although our test conditions are different, we are also defining $T_B$ for a fuel as that temperature at which its maximum TDR value equals 13 on a plot of maximum TDR value against test temperature. As was done in reference 7, $T_B$ is alternatively defined as that temperature at which sediment formation for a fuel is such that its ΔP value equals 3.3 kPa (25 torr) at the end of a test run of 40 minutes, if this situation occurs. Previous JFTOT results, combined with chemical analyses (ref. 12), have shown that hydrocarbon oxidation rates are about 20 percent higher for 316-stainless-steel tubes than for aluminum tubes. This suggests that both deposit and sediment formation should be more severe for 316-stainless-steel tubes. For a given JFTOT temperature and fuel we have observed that 316-stainless-steel tubes form more deposits; the actual comparisons are given later in this report. For this reason we can apply the same pass-fail criteria of the longer standard JFTOT test to our much shorter test procedure. The effect of shorter time is offset by our use of stainless-steel tubes, for which deposit formation is much higher than for aluminum tubes.

Results and Discussion

Temperature Profiles for 316-Stainless-Steel Heater Tubes

Figure 2 shows typical temperature profiles for a 316-stainless-steel heater tube at its test section for a range of test temperatures during the early portion of a JFTOT run with the fuel n-decane. For each test temperature, referred to as a nominal temperature in figure 2, there exists a temperature gradient so that only a small portion of the tube surface is at that test temperature. The tube test section is such that the fuel enters at the bottom (position, 0) and exits at the top (position, 60 mm). Note that the maximum, or nominal, temperatures are all at about the same position on the test section.
Tube Deposit and Sediment Formation for Four Pure Hydrocarbons

Deposit formation. – Tube deposit amounts, expressed as net TDR values, for four hydrocarbon fuels over the temperature range 150° to 450° C for 316-stainless-steel heater tubes are plotted against tube position in figure 3. At the lower temperatures of 150° and 250° C all four fuels produced deposits with TDR values of less than 5, which is considered a small amount of deposit. At 350° C the olefinic fuel, 1-hexene, formed the largest amount of deposit, and cyclohexane the second largest. Both n-decane and benzene formed much less deposit, with maximum TDR values of 14 and 26. In general most of the deposit was located on the upper half of the tube test section for all fuels used. It is not surprising that 1-hexene formed the most deposit. This can be attributed to its susceptibility to oxidation and polymerization. At the higher temperatures of 400° and 450° C all fuels except benzene formed deposits with TDR values of 40 to over 50. Most of these deposits for all four fuels were again located in the upper half of the tube test section. It is interesting that benzene formed much less deposit than the other three fuels. This may be attributed to the benzene aromatic structure, which is very resistant to oxidation (ref. 2).

Figure 4 shows the effect of temperature on deposit formation for the four pure hydrocarbon fuels. Although these black-and-white photographs do not give a completely accurate depiction of the actual tube deposit, certain general distinctive features can be observed. This figure shows visually the differences in deposit formation for these fuels that were indicated graphically in the previous figure. The most significant difference is between benzene and the other three fuels. Even at the higher 400° and 450° C temperatures benzene showed no intense dark deposit. Its deposit at 350°, 400°, and 450° C is characterized by a series of darker rings located at the lower portion of the light deposit coating. At 350°, 400°, and 450° C n-decane showed a deposit that was relatively uniform in shading, but the other three fuels had deposit formation that displayed various light and dark shadings or numerous darker rings. On the actual tubes these rings in many cases showed a peacock type of coloring. This photograph also shows that even at 350° C the tube deposit for cyclohexane expanded to cover the entire top half of the test section. For the other fuels the deposits expanded downward toward the lower (upstream) portion of the tube as temperature was increased from 350° to 400° and 450° C.

Sediment formation. – Sediment formation, expressed as Δp in kilopascals (torr), for the four fuels, is shown in figure 3. For these fuels only benzene showed any significant Δp increase. The final Δp varied from 0.4 kPa (3 torr) at 250° C to 2.5 kPa (19 torr) at 450° C. This is a significant increase. Thus the aromatic fuel benzene tends to form much sediment but little deposit.

Tube Deposit and Sediment Formation for Two Practical Fuels

Deposit formation. – Figure 5 shows deposit formation plotted against tube position for Jet A and home heating oil no. 2. In general, these practical fuels formed much more deposit at 250° C than did the pure hydrocarbon fuels (fig. 3). This can be attributed to the fact that practical fuels usually contain certain deposit-promoting species that are absent in a pure hydrocarbon. At the lower temperature the heating oil formed more deposit than Jet A. The maximum TDR value for the heating oil at 200° C was just slightly less than the value for Jet A at 250° C. At 350° C the maximum TDR value for the heating oil (45) was much higher than the maximum TDR value for Jet A (31). At 400° C both fuels had high TDR values of 45 to 50 or over, but the heavy deposit formed by the heating oil covered more of the tube test section.

Figure 6 shows the effect of temperature on deposits for the two practical fuels. This photograph emphasizes visually that, as temperature was increased, the deposit coating expanded toward the lower portion of the tube. For both fuels deposits were nonuniform in shading. For Jet A this nonuniform portion was very narrow and located at the lower portion of each deposit for temperatures of 350°, 400°, and 450° C. For the heating oil most of the deposit was nonuniform even at 250° C. (See the second tube from the right in the heating oil tubes in fig. 6.) At 350° and 400° C the nonuniform portion moved to the lower portion of each deposit. On the actual tubes the nonuniform portions for both fuels were peacock colored. It should be pointed out that the photography of figures 4 and 6 was done at different times and under different lighting and processing conditions. Therefore any comparisons between the two figures should be made with this fact in mind.

These data showing Jet A forming less deposit than the heating oil are consistent with our observations for the pure hydrocarbons. Table I, which lists fuel components for these two fuels, shows that Jet A has a high proportion of alkanes and much lower concentrations of less-stable olefins and aromatics.

Sediment formation. – Figure 5 shows that Jet A formed no sediment at any temperature but that the heating oil formed large amounts of sediment even at 250° C. At higher temperatures of 350° and 400° C sediment amounts decreased significantly. This somewhat surprising result must be verified by further work. The higher sediment formation for the heating oil can be attributed to its much higher aromatic content (table I).
Comparison of Deposit Formation on Aluminum and 316-Stainless-Steel Tubes

Figure 7 shows deposit formation on aluminum and 316-stainless-steel tubes for n-decane over the temperature range 150° to 450° C. The 316-stainless-steel data are from figure 3. At 150° and 250° C no deposit was formed on the aluminum tube. Even at 450° C deposit formation attained a TDR value of only about 33. This confirms some unpublished previous findings that deposit formation for an aluminum tube is significantly lower than that for a 316-stainless-steel tube. Even at 450° C, when pyrolysis reactions would be more important than oxidation (ref. 12), deposit formation for an aluminum tube was much lower. This suggests that, if both oxidation and pyrolysis are important to tube deposit formation, an aluminum surface may inhibit pyrolysis as well as the oxidation process (ref. 12) during fuel thermal degradation. An additional factor affecting deposit formation may be the different thermal conductivities of the two metals. This will cause the fuel to be subjected to different temperature gradients in the two tubes and may have an effect on deposit formation.

Breakpoint Temperature Estimates

On the basis of the two criteria described previously, breakpoint temperatures were estimated for the series of fuels investigated. Only deposit formation data were used to evaluate \( T_B \) because sediment formation for each fuel was never severe enough to yield a lower \( T_B \) value. Figure 8 shows a plot of maximum net TDR values against nominal temperatures for each fuel in 316-stainless-steel tubes. This plot is used to derive \( T_B \) values. For the fuel n-decane an aluminum heater tube was also used.

In 316-stainless-steel tubes, n-decane is most stable, followed in turn by benzene, cyclohexane, 1-hexene, Jet A, and the heating oil. For the pure hydrocarbon fuels the order of stability agrees with their oxidative-polymerization reactivities. The two practical fuels, Jet A and the heating oil, are much less stable, which is to be expected because of the presence of certain deposit promoters.

A comparison of our \( T_B \) values for Jet A and the heating oil with those reported in the literature is shown in Table 11. This comparison shows that our \( T_B \) values for Jet A and the heating oil are in reasonable agreement with those reported in references 9 and 14. This, in combination with the reasonable \( T_B \) values obtained for the four pure hydrocarbon fuels, shows that this modified JFTOT procedure could be used to rate fuel thermal stability. Using this modified JFTOT technique could reduce significantly the amount of both fuel and time needed to conduct a stability test.

From figure 8 breakpoint temperatures in aluminum and 316-stainless-steel tubes can be compared for the fuel n-decane. The \( T_B \) of 376° C for an aluminum surface is considerably higher than the \( T_B \) of 341° C for a 316-stainless-steel surface. This is consistent with our previous result, which showed more deposit formation on 316-stainless-steel tubes than on aluminum tubes.

Significance of Tube Deposit Rater Values

In this study we found that at the lower temperatures of 150° and 250° C the deposits for the pure fuels n-decane and benzene were light coatings (TDR of 26 or less) that were relatively uniform in appearance. For this condition a TDR could be used to estimate relative deposit amounts. At 350° C and higher, deposits for the two other pure fuels, 1-hexene and cyclohexane, were heavy coatings (TDR of 38 and over) and very nonuniform in appearance. For the latter condition the TDR may not be too useful for estimating relative deposit amounts. Nevertheless, we believe that the TDR can still serve a useful purpose by characterizing deposit formation for a series of fuels, as we have done in this study.

Concluding Remarks

The present study has shown that the four major hydrocarbon fuels have quite different deposit and sediment formation characteristics. These differences could be related to the different chemical reactions occurring in each thermally stressed fuel. One way to confirm this is to obtain chemical kinetic information involving the various stressed fuels’ reaction products and relate these data to deposit and sediment characteristics. Such knowledge will eventually lead to a better understanding of the fuel thermal degradation process.

Summary of Results

Four pure, aerated hydrocarbon fuels and two aerated practical fuels were thermally stressed by using a modified jet fuel thermal oxidation tester (JFTOT) procedure over a temperature range of 150° to 450° C and a pressure of 3447 kPa (500 psig) at a fuel flow rate of 3 cm³/min. Heater tubes made of 316 stainless steel were used in this study. Most of our findings are very qualitative but nevertheless appear to be meaningful in obtaining a better understanding of thermal fuel degradation.

Each of the four hydrocarbon fuels exhibited the following sediment and deposit properties:

1. n-Decane, an alkane fuel, formed a uniform dark deposit with tube deposit rater (TDR) values of over 50 at 400° and 450° C. No sediment was observed at any temperature.
2. Cyclohexane, a naphthenic fuel, formed a nonuniform dark deposit with peacock coloring at 350°, 400°, and 450° C. and TDR values of 35 to 50 were obtained. Small amounts of sediment formation (Δp, 0.13 to 0.33 kPa (1 to 2½ torr)) were observed at 400° and 450° C.

3. 1-Hexene, an olefin fuel, formed a nonuniform dark deposit with peacock coloring at 350°, 400°, and 450° C. and TDR values of over 50 were obtained. Small amounts of sediment formation (Δp, 0.27 kPa (2 torr)) were observed at 450° C.

4. Benzene, an aromatic fuel, formed a nonuniform lighter deposit with TDR values of 25 to 40 at 350°, 400°, and 450° C. Sediment formation increased from a Δp of 0.40 kPa (3 torr) at 250° C. to 2.5 kPa (19 torr) at 450° C.

Each of the two practical fuels had the following deposit and sediment characteristics:

1. Jet A formed a uniform deposit with a maximum TDR value of 14 at 250° C. This deposit was larger than those formed by any of the four pure fuels at this temperature. At 350°, 400°, and 450° C the deposit was nonuniform with peacock coloring. The maximum TDR values ranged from 31 to over 50. No sediment was observed at any temperature.

2. Home heating oil no. 2 formed a nonuniform deposit with peacock coloring at 250° C. The maximum TDR value was 29. At 350° and 400° C the deposit was similar, but the maximum TDR values ranged from 45 to 50. Sediment formation was greatest at 250° C (Δp, 11.2 kPa (84 torr)) and decreased to 0.53 to 1.60 kPa (4 to 12 torr) at 400° C.

A modified JFTOT procedure was evaluated for rating thermal stability by means of breakpoint temperatures for a number of fuels. Breakpoint temperatures obtained for these fuels were in reasonable agreement with their expected deposit formation tendencies as reported in the literature and on the basis of their chemical reactivities.

A comparison of 316-stainless-steel and aluminum tube surface effects on deposit formation for n-decane fuel showed that an aluminum surface produced significantly less deposit.

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National Aeronautics and Space Administration
Cleveland, Ohio, January 26, 1982

References


TABLE I. - FLUORESCENCE INDICATOR ABSORPTION
ANALYSES OF JET A AND HOME HEATING OIL NO. 2

<table>
<thead>
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<th>Fuel</th>
<th>Alkanes</th>
<th>Olefins</th>
<th>Aromatics</th>
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<tr>
<td></td>
<td>Content, wt%</td>
<td></td>
<td></td>
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<tr>
<td>Jet A</td>
<td>84</td>
<td>0.8</td>
<td>15</td>
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<tr>
<td>Home heating oil no. 2</td>
<td>57.5</td>
<td>2.5</td>
<td>40</td>
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TABLE II. - COMPARISON OF BREAKPOINT TEMPERATURES FOR JET A AND HOME HEATING OIL NO. 2

<table>
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<th>Breakpoint temperature, T&lt;sub&gt;B&lt;/sub&gt;, °C</th>
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<tr>
<td></td>
<td>Present study</td>
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<tr>
<td>Jet A</td>
<td>246</td>
</tr>
<tr>
<td>Home heating oil no. 2</td>
<td>208</td>
</tr>
</tbody>
</table>

<sup>a</sup>From ref. 9.
<sup>b</sup>From ref. 14, for a series of five standard JFTOT runs.
Figure 1 - Jet fuel thermal oxidation tester (JFTOT).

Figure 2 - Temperature profiles for Alcoa JFTOT 316 stainless-steel heater tubes.
(a) n-Decane, $\Delta p = 0$.
(b) Cyclohexane, $\Delta p = 0.33$ kPa (2.5 torr) at 450°C.
(c) 1-Heptene, $\Delta p = 0.27$ kPa (2 torr) at 450°C.
(d) Benzene, $\Delta p = 0.40$ kPa (3 torr) at 250°C, 0.80 kPa (6 torr) at 350°C, 1.9 kPa (14 torr) at 400°C, and 2.5 kPa (19 torr) at 450°C.

Figure 3. Tube deposit and sediment formation for four hydrocarbon fuels.
Figure 4 - Effect of temperature on lube deposits for four fuel components: \( \text{Benzene, 1-Hexene, Cyclohexane, Decane} \). 316-Stainless-steel tubes; temperatures 250, 350, 450, and 550°C, right to left.

Figure 5 - Tube deposit and sediment formation for two practical fuels.
Figure 6. - Effect of temperature on tube deposits for two practical fuels. Temperatures, 250°, 350°, 400°, and 450° C for jet A and 200°, 350°, 350°, and 400° C for home heating oil no. 2, right to left.
Figure 7. Comparison of deposit formation for aluminum and 316-stainless-steel tubes. Fuel, n-decane.

Figure 8. Breakpoint temperature estimates derived from tube deposit formation.