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Applications of High Pressure Differential Scanning Calorimetry to Aviation Fuel Thermal Stability Research

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APPLICATIONS OF HIGH PRESSURE DIFFERENTIAL SCANNING CALORIMETRY
TO AVIATION FUEL THERMAL STABILITY RESEARCH

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SUMMARY

High pressure differential scanning calorimetry (DSC) was studied as an alternate method for performing high temperature fuel thermal stability research. The DSC was used to measure the heat of reaction versus temperature of a fuel sample heated at a programmed rate in an oxygen pressurized cell. Pure hydrocarbons and model fuels were studied using typical DSC operating conditions of 600 psig of oxygen and a temperature range from ambient to 500 °C. The DSC oxidation onset temperature was determined and was used to rate the fuels on thermal stability. Kinetic rate constants were determined for the global initial oxidation reaction. Fuel deposit formation was measured, and the high temperature volatility of some tetralin deposits was studied using thermogravimetric analysis. Gas chromatography and mass spectrometry were used to study the chemical composition of some DSC stressed fuels.

INTRODUCTION

The purpose of this study was to investigate the high temperature thermal stability of hydrocarbon fuels and the kinetic mechanisms of fuel degradation. High temperature thermal stability is a measure of a fuel's resistance to degradation and deposit formation as it encounters the hot metal surfaces in an engine fuel system.

The high temperatures of the fuel injectors can cause the fuel to degrade and form adherent deposits in the fuel spray nozzles. This clogging can restrict the fuel flow or distort the fuel spray pattern. A distorted spray pattern will cause hot spots in the combustor, which can decrease the lifetime of the combustor liner or the turbine stator blades.

Currently deposit formation is not a major concern because present aircraft turbine engine fuels possess high thermal stability. However in the future thermal stability may become a significant problem. Aircraft fuels produced from alternate sources, such as shale oil or coal, will be less thermally stable unless they are highly refined. Advanced engines with higher pressure ratios and higher combustor temperatures will put increased heat loads on the aircraft fuel, leading to greater deposit formation. To be able to prevent these potential problems with fuel thermal stability, it is important that we understand the mechanisms leading to deposit formation.

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The jet fuel thermal oxidation tester (JFTOT) is an instrument that has been used to study high temperature thermal stability. The fuel is subjected to conditions similar to those of a jet engine and evaluated on the basis of the amount of deposit produced. This method has been used to study both real fuels (ref. 1) and pure hydrocarbons or model fuels (refs. 2 to 5). High pressure differential scanning calorimetry (DSC) has been used as an alternate method for studying high temperature thermal stability. For example, high pressure DSC has been used to study the thermal oxidative stability of lubricating oils and greases (refs. 6 to 8). Recently this method has been applied to the thermal stability of aviation fuels (ref. 9). High pressure DSC is used for thermal stability research to measure the heats of reaction of a fuel sample as it is heated at a constant rate in an oxygen pressurized cell.

In the present work, high pressure DSC was used in an exploratory study to obtain a variety of data on fuel thermal stability. The fuels studied were pure hydrocarbons and binary mixtures which simulate practical jet fuels. The hydrocarbons used were n-dodecane, tetralin, 2-ethylnaphthalene, and indene. Using the DSC, the fuels were subjected to 600 psig oxygen pressure and temperatures from ambient to 500 °C. The DSC oxidation onset temperature was determined for the fuels; it is a measure of the fuel's resistance to autoxidation. Kinetic rate constants were determined for the global initial oxidation reaction. The gum (high molecular weight oxidation products) to fuel weight ratio was determined for some of the fuels. Some of the gums were further studied using thermogravimetric analysis to determine their high temperature volatility. A few DSC stressed fuels were analyzed with gas chromatography and mass spectrometry to determine their chemical composition.

EXPERIMENTAL

Fuels

A complete list of fuels studied is presented in table I. Instead of studying actual jet fuels, we focused our attention on pure hydrocarbons and model fuels. This greatly simplifies the chemical analysis and the interpretation of the results. n-Dodecane was chosen as a standard n-alkane fuel, as it is a major constituent of JP-5 and Jet A fuels. Tetralin and 2-ethylnaphthalene were chosen as typical aromatic fractions. A sample of aged 2-ethylnaphthalene was also studied. Indene was included due to its high production of gum, although it would not be present in actual jet fuels. The model fuels were binary mixtures of n-dodecane and an aromatic hydrocarbon, mixed on a volume basis. 90/10 Dodecane/tetralin was proposed by Daniel as a model fuel, as it has been found to exhibit stability behavior similar to a real fuel (ref. 10). Jet A fuel was studied for comparison purposes.

All of the fuel samples, except for indene, were redistilled before use. Although the indene was not redistilled, it was obtained at 99+ percent purity from Aldrich Chemical Company. After redistillation, a sample of 2-ethylnaphthalene was aged for 60 days at about 50 °C in an incubator. During aging, the sample was opened to the air and then shaken daily to maintain the dissolved oxygen supply. All of the fuel samples were refrigerated, but they were not stored under nitrogen.

DSC Procedure

The DSC experiments were performed using the DuPont DSC pressure cell with the DuPont 1090 Thermal Analyzer. A cut-away view of the DSC pressure cell is presented in figure 1. In the DSC cell, the fuel sample and an empty reference pan are heated at a known rate in a controlled environment. The difference between the sample and reference pan temperatures will be constant unless a heat related change takes place in the sample. With the DuPont DSC, the temperature difference is directly related to the differential heat flow between the sample and the reference. The differential heat flow is plotted against temperature or time to produce the thermogram, the thermal history of the sample. Using the thermogram, it is possible to determine heats of reaction, the onset of the reactions, and various kinetic data.

DuPont hermetic sample pans were used to prevent the loss of sample by spattering. The pans were covered but unsealed. Except where noted, a gold pan was used for the research, since gold is relatively inert towards hydrocarbon oxidation. The gold pan was cleaned for reuse by heating it in the DSC until complete combustion of the fuel sample was achieved. For our operating conditions of 600 psig oxygen and 10 °C/min, a temperature of 500 °C was found to be sufficiently high for complete combustion. At this point no soot or gum was visible. The pan was finally immersed in acetone and ultrasonically cleaned.

For a typical test run, the fuel sample weighed 1 to 3 mg. An empty pan was used as the inert reference. The DSC cell was normally pressurized to 600 psig oxygen to suppress any spattering or evaporation of the fuel. The pressure cell was used statically with no flow or purge during the test runs. Heating the cell increased the pressure during the tests, but this did not exceed 50 psid.

There are two DSC test procedures commonly in use today for studying oxidation, the induction time method and the onset temperature method. The induction time method is carried out isothermally at elevated temperatures. An example thermogram for this method for tetralin is shown in figure 2. The induction time is found from the intersection of the extrapolated leading edge of the peak and the heat flow baseline. This is the most straightforward and reproducible way to describe the onset of a peak, or in this case, the beginning of oxidation.

In the onset temperature method the sample is heated at a programmed rate for a specified temperature range. Thermogram for this method are shown in figures 3 to 11. The oxidation onset temperature is determined in the same manner as the induction time, by using the extrapolated leading edge of the first exothermic peak. The heat of reaction is determined from the area between the curve and an extrapolated baseline. Our studies were done using a heating rate of 10 °C/min. Although faster heating rates give stronger peak signals, slower rates give better resolution. The rate of 10 °C/min was chosen as a compromise between high resolution and the time required for a run. Our method was similar to that used by May and Bsharah to study the oxidation of pure hydrocarbons by high pressure differential thermal analysis (ref. 11).

In order to measure the amount of gum produced by the fuels, a number of runs was made using DuPont silicate-coated, aluminum, hermetic pans. The runs were made with a 10 °C/min temperature ramp and a typical maximum temperature

of 300 °C. Immediately after completion of the test, the sample pan was reweighed to determine the amount of gum remaining.

TGA Procedure

Several gum samples produced in the DSC were tested further by thermogravimetric analysis (TGA). This test gives the change in weight versus temperature for a sample heated at a constant rate. Example TGA plots for fresh tetralin and two tetralin gum samples can be seen in figures 12 to 14. The TGA test method is similar to DSC, except that in TGA weight is measured instead of differential heat flow. The TGA plot provides an indication of the volatility of the gum and its high temperature decomposition products as a function of temperature. This TGA study simulates the heating of gum on hot surfaces to form insoluble, adherent deposits. The gums were produced in the DSC in uncovered, uncoated, aluminum pans. The DSC was run isothermally with 600 psig of oxygen for 60 min. The TGA would not accept the DSC sample pans so the gum was dissolved in acetone, and transferred to the platinum TGA sample pan via a syringe. It should be noted that only the soluble gum could be tested. Time was allowed for the solvent to evaporate before the test was begun. The runs were made under a flowing nitrogen atmosphere with a temperature ramp of 25 °C/min, beginning at 25 °C and ending typically at 900 °C.

GC Procedure

To study some of the precursors leading to gum formation, two DSC stressed fuels were analyzed by gas chromatography. The stressed fuels were produced in the DuPont aluminum, hermetic pans by stopping the DSC test run in the middle of the first oxidation peak. At this point there was still liquid remaining in the sample pan. The contents of the pan were dissolved in methylene chloride and analyzed using a capillary gas chromatograph equipped with a hydrogen flame ionization detector and a split injector. The column was 60 ft fused silica with an internal diameter of 0.25 mm, and was coated with methyl silicon oil. The oven was heated at 2 °C/min for a temperature range of 50 to 280 °C. The carrier gas was helium with a flow rate of 1 ml/min. The operating conditions allowed good resolution of nonpolar compounds and the detection of some oxygenated compounds (ref. 5).

GCMS Procedure

A sample of DSC stressed 90/10 dodecane/tetralin was analyzed by GC mass spectrometry (GCMS) using a quadrupole mass spectrometer with 70 V electron impact ionization. A 30 ft SP-2100 column was used for the test. The temperature program was the same as for the other gas chromatography work (2 °C/min, 50 to 280 °C). Potential identities were determined for the GC peaks by comparing their mass spectra with a computerized library of data.

DISCUSSION AND RESULTS

DSC Experiments

Induction time. - The DSC induction time method did not prove to be very useful for our thermal stability research. The method demonstrated that the oxidation induction time increases from run to run as the isothermal temperature is decreased. However, assuming Arrhenius kinetics, this is always true. The induction time could have been used as a measure of thermal stability, but this quantity was often difficult to determine. The peaks became very broad and flat so that the induction time could not be accurately determined. Only isothermal temperatures close to the oxidation onset temperature gave a strong enough signal to accurately determine the induction time. Our results showed that the isothermal method was only useful as a means of producing gum for later analysis. This is in agreement with the findings of some DSC thermal stability work done at NBS with real fuels (ref. 9).

Onset temperature. - The thermograms resulting from the onset temperature tests are shown in figures 3 to 11. As can be seen, the thermograms typically consist of several peaks, many of which are actually unresolved combinations of peaks. This shows that the fuel oxidation takes place in specific stages. The first peak(s) represent the oxidation reactions leading to gum and deposit formation. The last peak(s) represent the complete combustion of the deposit to gaseous products such as carbon monoxide and steam. The shapes of the thermograms can be used to illustrate the similarities or differences between the fuel samples. There is an obvious similarity between the thermograms for n-dodecane, 90/10 dodecane/tetralin, 90/10 dodecane/2-ethylnapthalene, and Jet A fuel (figs. 3 and 9 to 11). The thermograms for fresh and aged 2-ethylnapthalene (figs. 5 and 6) are similar, except that the initial peak is smaller for the aged sample. The total heat of reaction is given on the figures. Due to unavoidable weight loss during the tests, these values are neither accurate nor very reproducible.

The oxidation onset temperature can be found on the thermograms as well. The fuels studied are listed in order of increasing onset temperature (increasing thermal stability) in table II. These values should be accurate to within ± 5 °C, although this was not checked due to the exploratory nature of this study. The lowest onset temperature by far was for indene. This result was expected since indene is known to be an excellent gum producer at low temperatures (ref. 12). Also, indene is especially susceptible to oxidation due to the double bond in its 5-membered ring. Tetralin followed indene in thermal instability, as determined by the oxidation onset temperature. The onset temperatures of n-dodecane, 90/10 dodecane/tetralin, 90/10 dodecane/2-ethylnapthalene, and Jet A fuel were all within a narrow 5 °C range. This indicates that under the DSC conditions the four fuels have similar thermal stability. The onset temperature of 50/50 dodecane/tetralin was found to be between those determined for tetralin and dodecane, as one might expect. The oxidation onset for both the fresh and aged 2-ethylnapthalene were considerably higher than for the other fuels. This may be due to the high resistance of 2-ethylnapthalene's aromatic structure to oxidation.

DSC Kinetics. - A Borchardt and Daniels kinetic analysis (ref. 13) was performed on the thermal data from some of the onset temperature test runs. The kinetic analysis was done for the first exothermic peak of the thermograms, which represents the initial oxidation reactions. The analysis method assumes

a simple peak representing a single reaction. However for our study, the first peak was assumed to represent a global initial oxidation reaction. This global reaction represents a spectrum of reactions, from the initial autoxidation and peroxide formation to gum and deposit formation (table III).

The analysis was done using a kinetics data analysis program commercially available for the DuPont 1090 Thermal Analyzer. The kinetic analysis method developed by Borchardt and Daniels uses the heat of reaction as a measure of the extent of the reaction. The general rate equation based on this analysis method is given below (ref. 13).

$$\frac{d\alpha}{dt} = k(T) \cdot (1 - \alpha)^n$$

where

α fraction of heat release
 $k(T)$ specific rate constant at temperature T
n reaction order.

Besides the specific rate constant and the reaction order, the kinetics program provides the activation energy of the reaction and the Arrhenius pre-exponential factor.

The kinetic data for six of the fuels is presented in table IV. The data are very approximate and should only be considered qualitatively. The inaccuracy of the data is due to the unresolved nature of the thermogram peaks. The analysis requires that the reaction peak be completely distinct from its neighboring peaks. Unfortunately this was not the case with our data, so approximations in extrapolating the baseline had to be made. Data are not given for the tetralin or the two 2-ethylnaphthalene runs because of the poor peak resolution.

The kinetic data were used along with the Arrhenius equation to calculate the specific rate constant at 130 °C (and 600 psig of oxygen). These values are presented in table V along with the corresponding DSC onset temperatures. As can be seen, there is a very high correlation between the 130 °C rate constant and the onset temperature. However, the strong dependence of the rate constant on temperature is expected from the Arrhenius equation. From the rate equation, the initial rate of reaction ($\alpha = 0$) is equal to the kinetic rate constant. Therefore the global initial rate of oxidation (or the kinetic rate constant) at a given temperature and the DSC onset temperature are synonymous measures of thermal stability. The onset temperature is the better measure of the two as it can be determined more easily and more precisely.

The 130 °C global initial rate of oxidation for the fuels was also compared to the rates of oxygen consumption and gum formation measured at 130 °C by Mayo, et al. (ref. 12). There was no correlation between our calculated global initial rate of oxidation and the measured rates of oxygen consumption and gum formation. This is not unexpected because the tests were run with different atmospheric conditions. The oxygen consumption and gum formation tests were done in a standard air atmosphere, while the DSC data are for a 600 psig oxygen atmosphere.

Gum/Fuel Weight Ratio. - The relative amounts of gum produced by some of the fuels in the DSC are presented in table VI. All of the results presented

are for a maximum DSC temperature of 300 °C, except for 2-ethylnaphthalene. A maximum temperature of roughly 370 °C was used for 2-ethylnaphthalene because of its high oxidation onset temperature. It should be noted that the results were not very reproducible, and that time was not allowed for remaining volatiles to evaporate. As can be seen in the table, there is a fair correspondence between the amount of gum formed and the fuel's hydrogen to carbon ratio. Only indene produced a great amount of gum. The other aromatic fuels produced a moderate amount, while the fuels with a low aromatic content produced little. This is to be expected since fuel deposits are known to consist of highly aromatic structures.

Thermogravimetric Analysis

Thermogravimetric analysis was performed on several tetralin gums produced isothermally in the DSC. The TGA tests were made on tetralin gums produced at 120, 130, 140, and 170 °C. The TGA plots for the 120 and 170 °C gums are presented in figures 14 and 15. A TGA plot for fresh, unoxidized tetralin is shown in figure 13 for comparison. The low temperature gums produced plots similar to that of the fresh tetralin, except that the weight loss was over a broader range. Unlike the low temperature gums both the 140 °C gum and the 170 °C showed significant weight loss near 100 °C, before the evaporation of tetralin. This suggests the presence of tetralin fragments, most likely from the rupture of tetralin's saturated ring. The high temperature gums also showed significant weight loss at high temperatures as well. The high temperature weight loss indicates the presence of high molecular weight oxidation products. Presumably these are dimers and trimers of tetralin.

Two methods were used to quantify the upper temperature limit of the gum's boiling point range. The first method was to take it as the temperature where 95 wt % of the sample had evaporated. The second method assumed the upper limit to be the temperature where the rate of weight loss dropped to 1 wt %/min. The upper boiling points for the tetralin gums are given in table VII. As can be seen, the second method generally gives a lower temperature due to the very gradual weight loss at higher temperatures. The table illustrates that higher DSC temperatures lead to higher production of high molecular weight products.

Other TGA tests with indene and 50/50 dodecane/tetralin gums gave similar results to the tetralin gum tests. As with the tetralin gum, there was evidence of fuel fragments and high molecular weight oxidation products.

Gas Chromatography

Samples of fresh 2-ethylnaphthalene and 90/10 dodecane/tetralin were stressed in the DSC and then studied using gas chromatography. The gas chromatographs for the DSC stressed samples are presented in figures 15 and 16 along with related chromatographs from reference 5. The chromatographs for the DSC stressed samples were produced at a different sensitivity than those of reference 5. This is the reason for the difference in the chromatographs in the figures.

The 2-ethylnaphthalene chromatographs are presented in figure 15. As expected, the chromatograph for the DSC stressed sample is markedly different from those for the unstressed and the JFTOT stressed samples. Although they

are unsimilar, the DSC and JFTOT stressed fuels both exhibit low carbon number species. These are presumably degradation products from the oxidation of the 2-ethylnaphthalene. The DSC and JFTOT stressed samples also contain two high carbon number species, possibly dimers of 2-ethylnaphthalene. Overall, the DSC stressed fuel shows more similarity to the aged fuel, whether JFTOT stressed or not. The samples are similar because they both contain several species with carbon numbers near 2-ethylnaphthalene.

The 90/10 n-dodecane/tetralin chromatographs are shown in figure 16. As with the 2-ethylnaphthalene, the DSC stressed sample is unlike the unstressed or JFTOT stressed samples. It is particularly interesting that the DSC stressed fuel chromatograph did not indicate the presence of tetralin. As with the 2-ethylnaphthalene, the DSC stressed fuel chromatograph indicates the presence of considerably fewer chemical species than in the JFTOT stressed fuel.

It is not surprising that the DSC and JFTOT stressed fuels were found to be different. Unlike the JFTOT, the fuel conditions in the DSC do not resemble the fuel conditions in a jet engine. In the DSC, the amount of oxygen dissolved in the fuel is much greater than with the JFTOT. The fuel in the DSC is not flowing, and it is exposed to high temperatures much longer than in the JFTOT. Perhaps most importantly, the JFTOT stressing is dominated by surface reactions while the DSC stressing is probably dominated by the bulk liquid phase reactions.

GC Mass Spectrometer Analysis

The GC mass spectrometer chromatograph for the DSC stressed 90/10 dodecane/tetralin is presented in figure 17. Possible identities for the labelled peaks are given in table VIII.

The first peak was not identified by the mass spectrometer as n-dodecane, although it was known to be so from its size and location. However the chromatogram produced by the standard GC showed three small peaks appearing as shoulders on the dodecane peak. These did not appear on the GCMS chromatograph because of the mass spectrometer's shorter column and lower resolution. From this it was concluded that the peak was unresolved and represented n-dodecane and three or more minor compounds.

The mass spectrometer identified the second peak as a tetralone. This is in good agreement with the known autoxidation process.

The following three peaks have been previously identified using gas chromatography to study JFTOT stressed n-dodecane by Hazlett, et al. (ref. 2). These results show that the first peak represents 6-, 5-, and 4-dodecanones; the second peak represents 3-dodecanone; and the third peak represents 2-dodecanone. The five corresponding dodecyl radicals have been observed in n-dodecane radical studies done using electron spin resonance (ref. 14). Our mass spectrometer results further support these identities.

The identities of the remaining peaks are considerably more vague. Peak F appears to represent a phenol, and peak H seems to be a tolyl ether. The mass spectrum for peak G best matches with various biphenyl amines. However this is unlikely since the nitrogen was only present as a contaminant of the DSC atmosphere. Although the identities for the last peaks are unclear, it is

reasonable to assume that they represent various tetralin degradation products. As previously mentioned, upon oxidation tetralin's saturated ring is broken creating various alkylbenzenes.

SUMMARY OF RESULTS

Nine hydrocarbon fuels were oxidized in a high pressure differential scanning calorimeter (DSC) to determine their relative thermal stability. The fuels studied were primarily pure hydrocarbons or binary mixtures of pure hydrocarbons mixed on a volume basis. The fuels were heated in gold sample pans, under 600 psig of oxygen, at 10 °C/min for a temperature range of 50 to 500 °C. The fuels were then rated on thermal stability on the basis of their DSC oxidation onset temperature. The oxidation onset temperature is the temperature marking the beginning of the exothermic autoxidation reaction, based on the DSC's measurement of the sample's differential heat flow.

Indene demonstrated its low thermal stability with the lowest onset temperature, 120 °C. Tetralin and 50/50 dodecane/tetralin followed with respective onset temperatures of 168 and 178 °C. n-Dodecane, 90/10 dodecane/tetralin, 90/10 dodecane/2-ethylnaphthalene, and Jet A fuel gave oxidation onset temperatures within the range of 207 to 212 °C. This indicates that they are similarly resistant to oxidation for the DSC operating conditions used. 2-Ethylnaphthalene showed the highest resistance to oxidation, with onset temperatures of 263 and 272 °C for the aged and fresh samples, respectively.

Borchardt and Daniels kinetics were applied to the DSC heat flow data for some of the fuels. The analysis was very qualitative, but the results have proven to be meaningful. The activation energy and the Arrhenius pre-exponential factor were determined for the global initial oxidation reaction. The data were used with the Arrhenius equation to calculate the kinetic rate constant at 130 °C (and 600 psig of oxygen). The 130 °C rate constant, which is equal to the initial decomposition rate, was found to show a very strong inverse dependence on the onset temperature of the reaction.

Therefore indene had the highest oxidation reaction rate, with a kinetic rate constant of $1.2 \times 10^{-2} \text{ sec}^{-1}$. The lowest rate constants, those for n-dodecane, 90/10 dodecane/tetralin, 90/10 dodecane/2-ethylnaphthalene, and Jet A fuel were in the range of 1.0×10^{-16} to $2.6 \times 10^{-15} \text{ sec}^{-1}$.

Gums (high molecular weight oxidation products) were produced in the DSC for some of the fuels. They were produced by heating the fuel in silicate-coated, aluminum pans, at 600 psig oxygen, at 10 °C/min for a temperature range of 50 to 300 °C. A maximum temperature of 370 °C was used for 2-ethylnaphthalene due to its high onset temperature. The relative amount of gum produced by a fuel was in fair correlation with its hydrogen to carbon ratio. Only indene produced a large amount, with an average gum to fuel weight ratio of 0.80. Tetralin, 2-ethylnaphthalene, and 50/50 dodecane/tetralin had respective gum to fuel weight ratios of 0.28, 0.20, and 0.08. The weight ratios for 90/10 dodecane/tetralin and 90/10 dodecane/2-ethylnaphthalene measured less than 0.01.

The high temperature volatility of several tetralin gums was studied using thermogravimetric analysis (TGA). The gums were produced in uncovered, uncoated, aluminum pans under 600 psig of oxygen at various isothermal temperatures. TGA revealed the presence of low molecular weight products, most

likely tetralin fragments. It also showed the presence of high molecular weight oxidation or pyrolysis products, presumably dimers and trimers of tetralin. The gums produced at higher DSC temperatures contained more low and high molecular weight products than the low temperature gums.

The chemical composition of two DSC stressed fuels was studied using gas chromatography. The fuels were stressed in the DSC by heating them only part way through the first oxidation peak. They were produced in silicate-coated, aluminum pans, under 600 psig of oxygen, with a heating rate of 10 °C/min. The composition of the DSC stressed 2-ethylnaphthalene was found to be somewhat similar to that of aged 2-ethylnaphthalene, either stressed in a JFTOT or unstressed. However the chromatograph for the DSC stressed 2-ethylnaphthalene was unlike that for JFTOT stressed 2-ethylnaphthalene. Similarly, the DSC stressed 90/10 dodecane/tetraline was unlike its JFTOT stressed counterpart in chemical composition. The majority of the compounds represented by the GC peaks were not identified.

Mass spectrometry was used to further analyze a sample of DSC stressed 90/10 dodecane/tetralin. Based on the results of the mass spectrometer, the DSC stressed fuel was determined to contain n-dodecane, tetralone(s), 6-, 5-, 4-, 3-, and 2-dodecanones, and several unidentified tetralin fragments.

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TABLE I. - RESEARCH FUELS STUDIED

Pure Hydrocarbons	Model fuels (mixed on a volume basis)	Real fuels
n-Dodecane (Dod) Tetralin (Tet) 2-Ethyl-naphthalene (Etn) Aged 2-ethyl-naphthalene (60 days, 50 °C) Indene	50/50 Dodecane/tetralin 90/10 Dodecane/tetralin 90/10 Dodecane/2-ethyl-naphthalene	Jet A

TABLE II. - DSC OXIDATION
ONSET TEMPERATURE^a

Fuel	T ₀ , °C
Indene	120
Tetralin	168
50/50 Dod/Tet	178
Jet A	207
90/10 Dod/Tet	207
Dodecane	210
90/10 Dod/Etn	212
Aged Etn	263
2-Ethyl-naphthalene	272

^aGold pan; 10 °C/min;
600 psig O₂, but 500
psig for Jet A.

TABLE III. - ACCEPTED MECHANISM FOR FUEL
DEGRADATION VIA AUTOXIDATION (REF. 2)

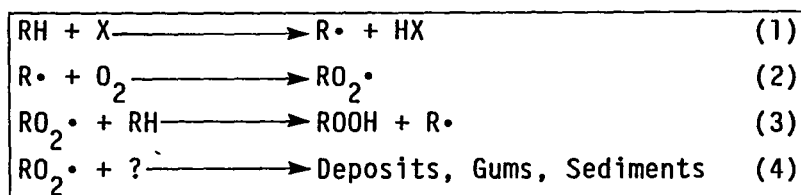


TABLE IV. - DSC KINETICS DATA FOR THE INITIAL OXIDATION PEAK^a

Fuel	Reaction order, n	Arrhenius activation energy, E, kJ/mol	Arrhenius pre-exponential factor, log ₁₀ Z, min ⁻¹	Heat of reaction, ΔH, J/g
Indene	3.36	279	36.0	5263
50/50 Dod/Tet	1.21	189	20.8	3098
Dodecane	3.21	552	58.7	8433
Jet A	2.56	592	63.5	2037
90/10 Dod/Tet	3.42	600	64.3	3903
90/10 Dod/Etn	3.03	609	64.7	1262

^aGold pan; 10 °C/min; 600 psig O₂, but 500 psig for Jet A.

TABLE V. - 130 °C KINETIC RATE
CONSTANTS VERSUS DSC
ONSET TEMPERATURE^a

Fuel	$k_{130\text{ °C}}, \text{ s}^{-1}$	$T_0, \text{ °C}$
Indene	1.2×10^{-2}	120
50/50 Dod/Tet	3.4×10^{-6}	178
Dodecane	2.6×10^{-15}	210
Jet A	1.0×10^{-15}	207
90/10 Dod/Tet	6.3×10^{-16}	207
90/10 Dod/Etn	1.0×10^{-16}	212

^aGold pan; 10 °C/min; 600 psig O₂,
but 500 psig for Jet A.

TABLE VI. - GUM TO FUEL WEIGHT RATIO

Fuel	Gum to fuel weight ratio	Hydrogen to carbon number ratio H/C
Indene	0.80	0.9
Tetralin	.28	1.2
2-Ethyl-naphthalene	.20	1.0
50/50 Dod/Tet	.08	---
90/10 Dod/Tet	.00	---
90/10 Dod/Etn	.00	---
Dodecane	----	2.0

TABLE VII. - TGA UPPER BOILING POINT
FOR TETRALIN GUM

Temperature, °C		
T, DSC	T, 95 wt %	T, 1 wt %/min
Fresh	160	160
120	250	220
130	350	280
140	480	320
170	>800	520

TABLE VIII. - GCMS ANALYSIS OF A SAMPLE
OF DSC STRESSED 90/10 Dod/Tet^a

Peak	Proposed Identity
A	Dodecane + ?
B	Tetralone(s)
C	6-, 5-, and 4-Dodecanones
D	3-Dodecanone
E	2-Dodecanone
F-H	Tetralin fragments

^aRefer to figure 17.

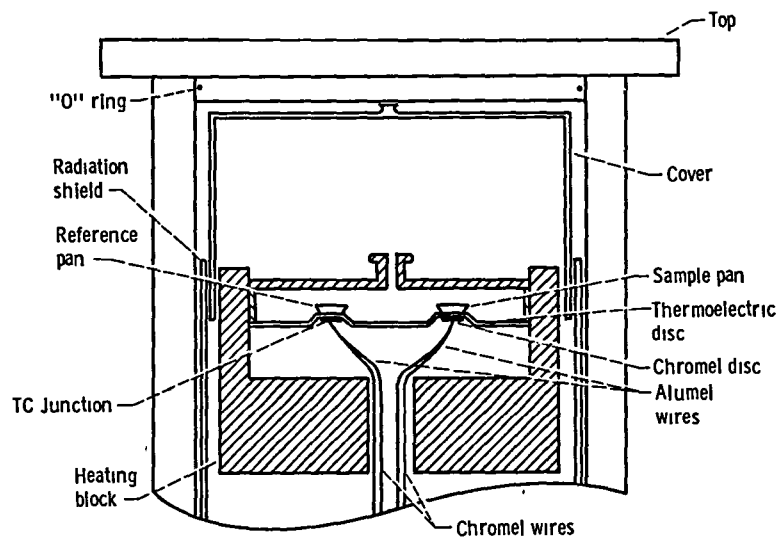


Figure 1. - Schematic of DSC cell (ref. 8).

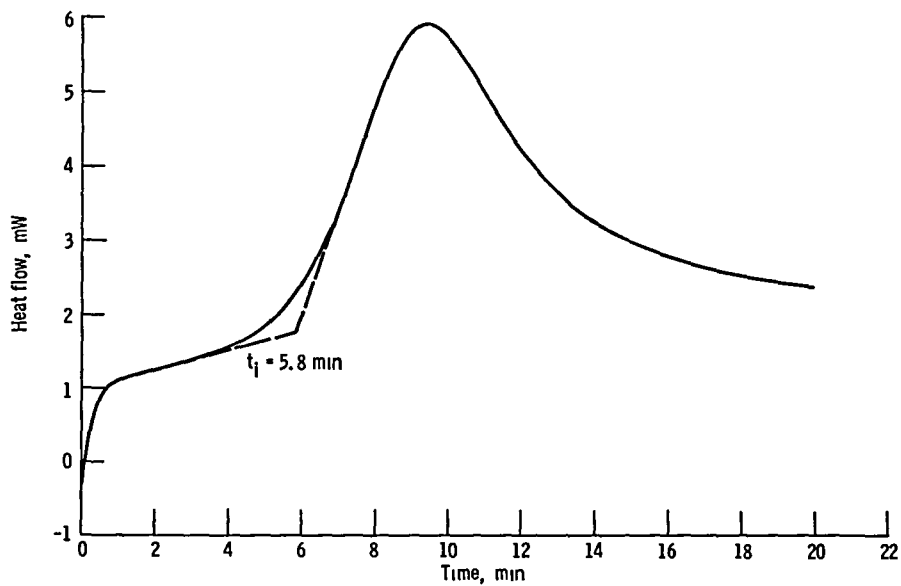


Figure 2. - Oxidation induction time thermogram for tetralin.

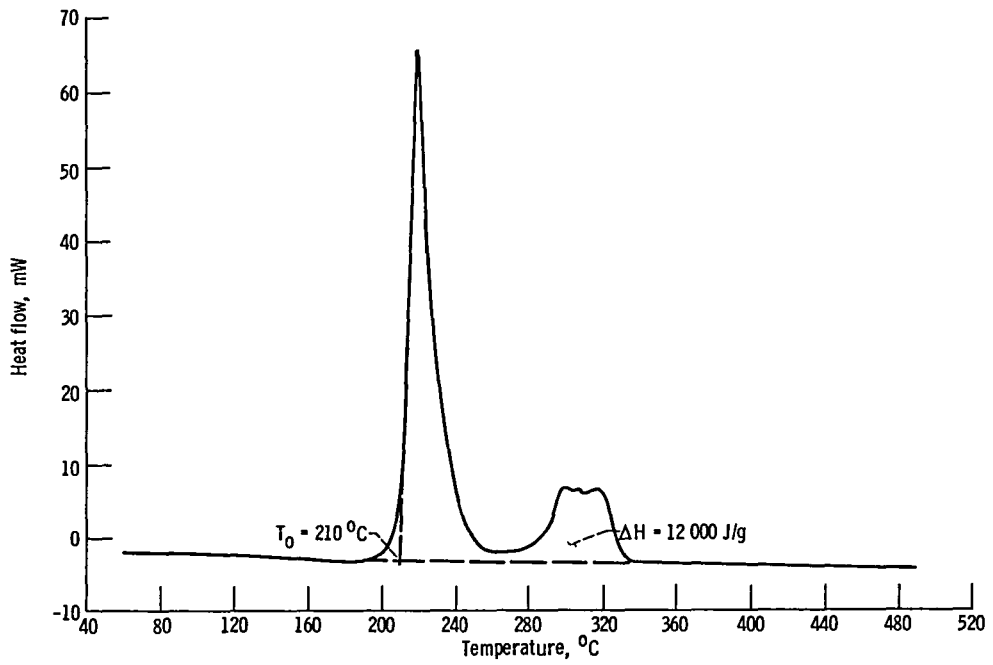


Figure 3 - Oxidation onset temperature thermogram for n-dodecane.

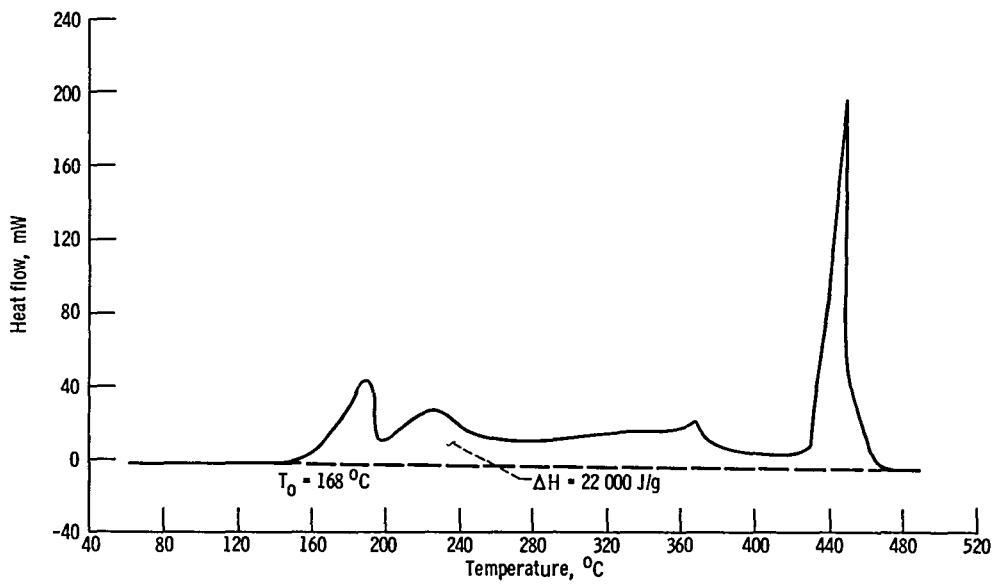


Figure 4. - Oxidation onset temperature thermogram for tetralin

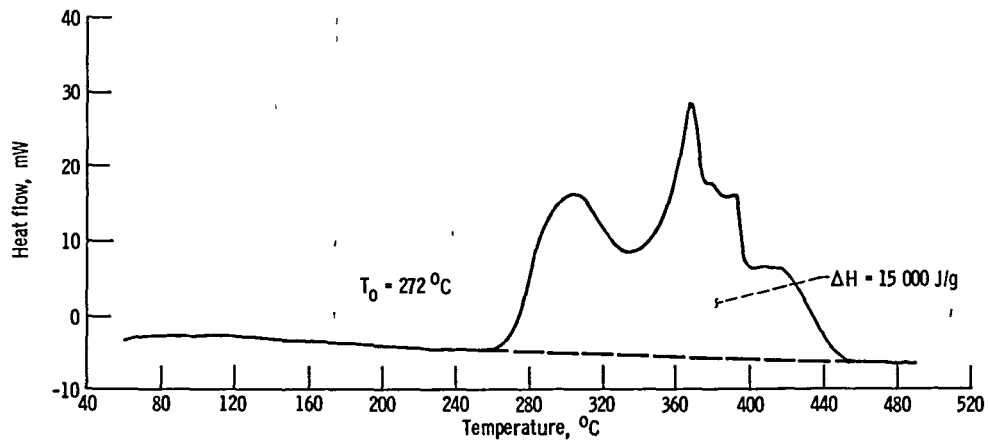


Figure 5. - Oxidation onset temperature thermogram for 2-ethylnaphthalene.

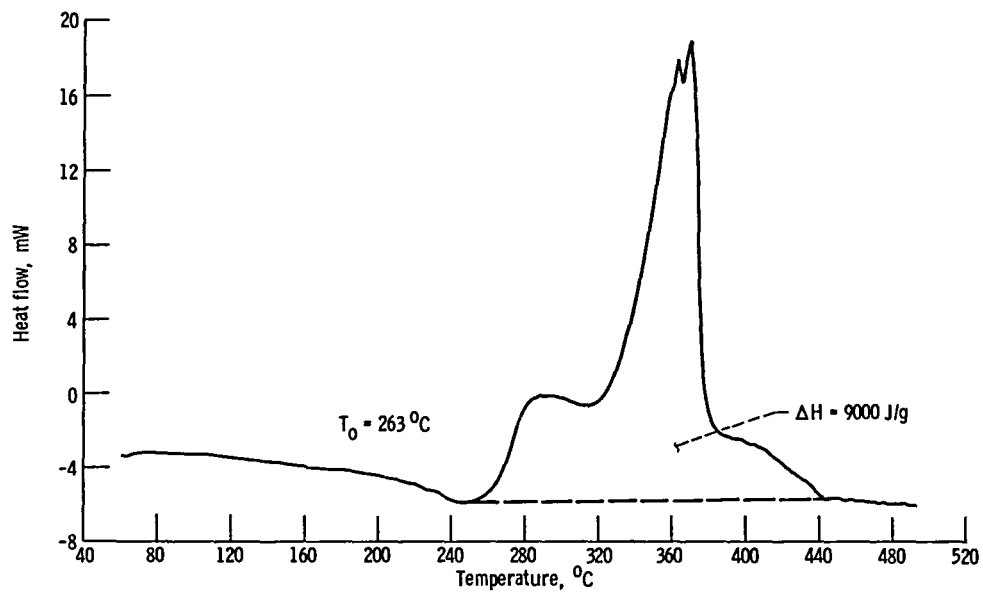


Figure 6 - Oxidation onset temperature thermogram for aged 2-ethylnaphthalene (60 days, 50 °C).

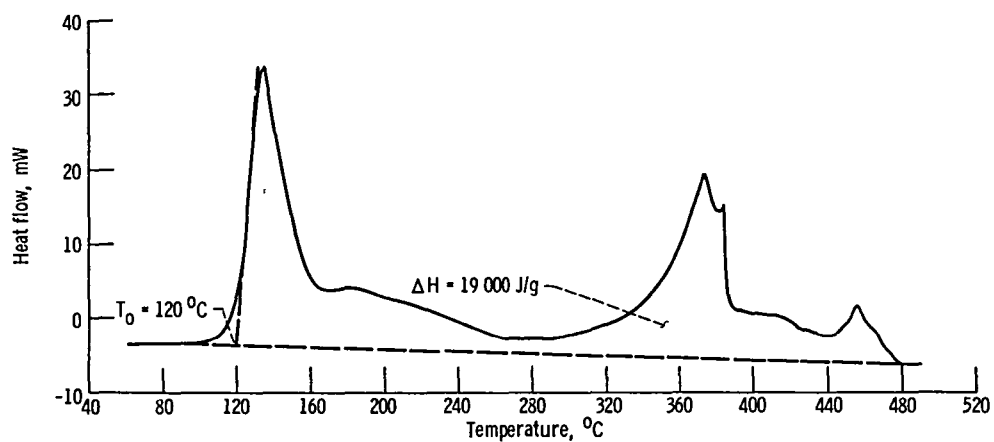


Figure 7 - Oxidation onset temperature thermogram for indene.

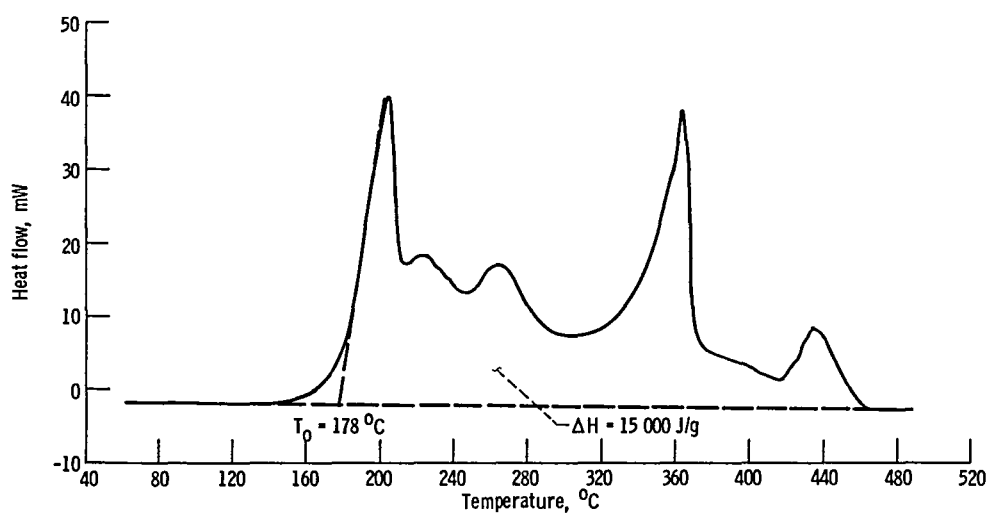


Figure 8. - Oxidation onset temperature thermogram for 50/50 n-dodecane/tetralin.

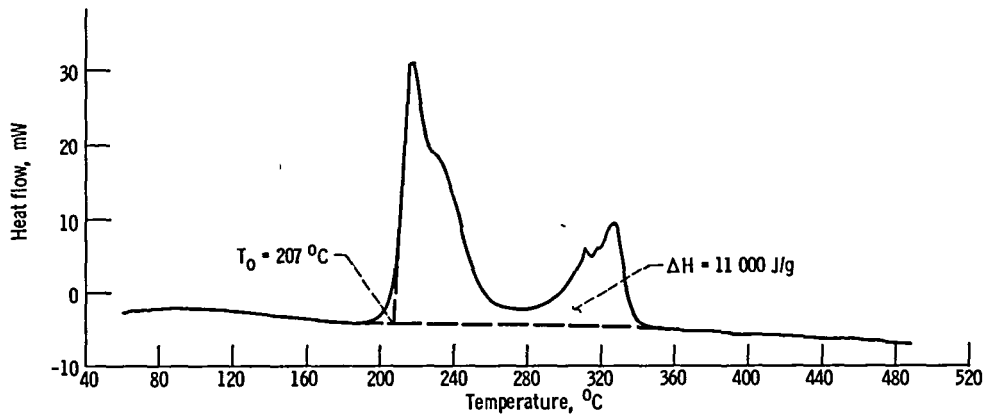


Figure 9. - Oxidation onset temperature thermogram for 90/10 n-dodecane/tetralin

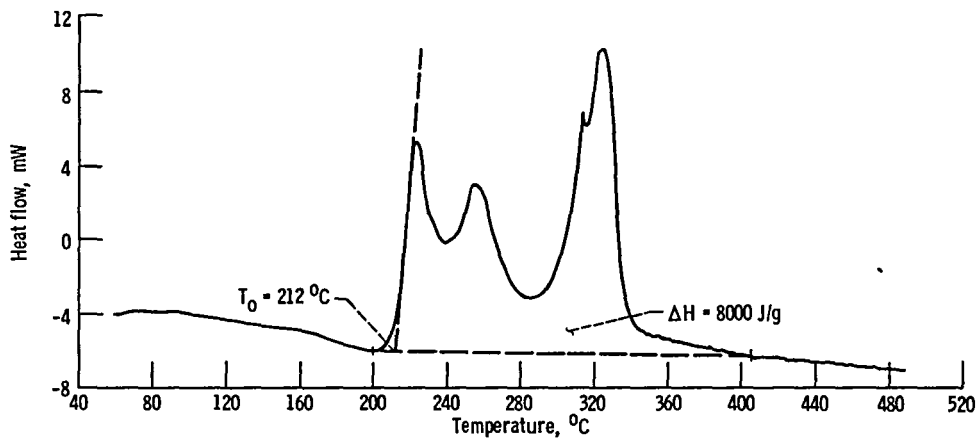


Figure 10. - Oxidation onset temperature thermogram for 90/10 n-dodecane/2-ethylnaphthalene.

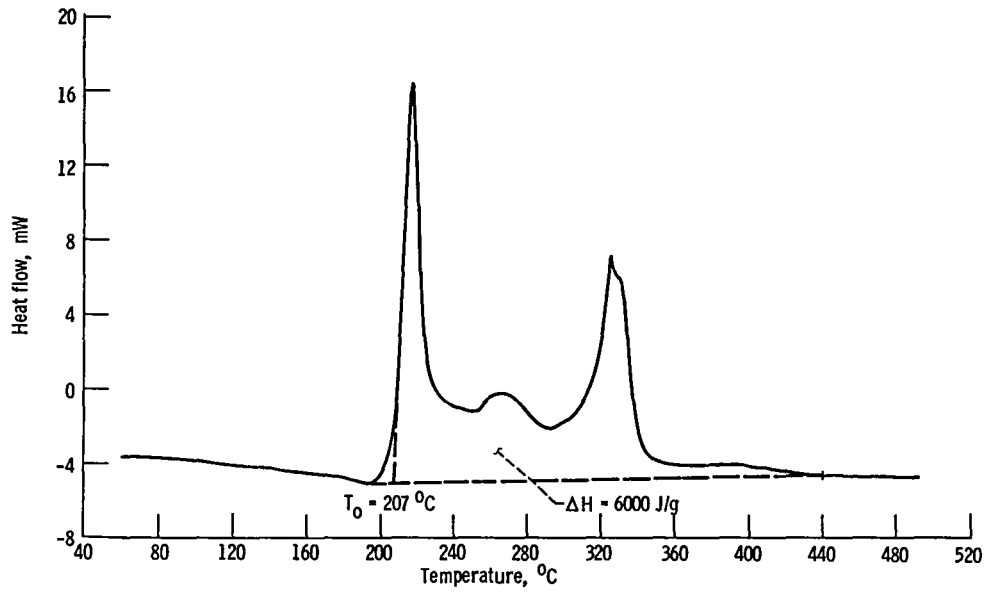


Figure 11. - Oxidation onset temperature thermogram for Jet A fuel.

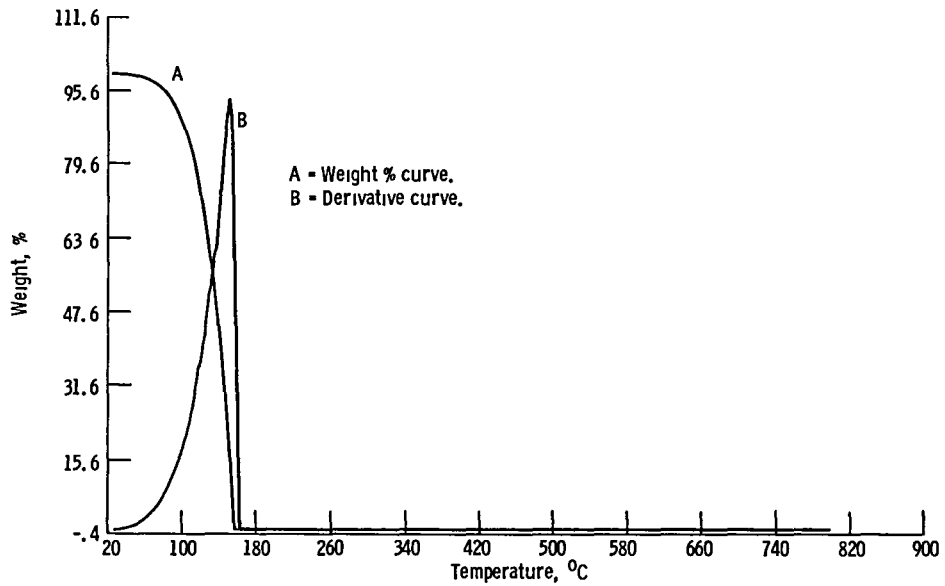


Figure 12. - TGA plot for fresh tetralin.

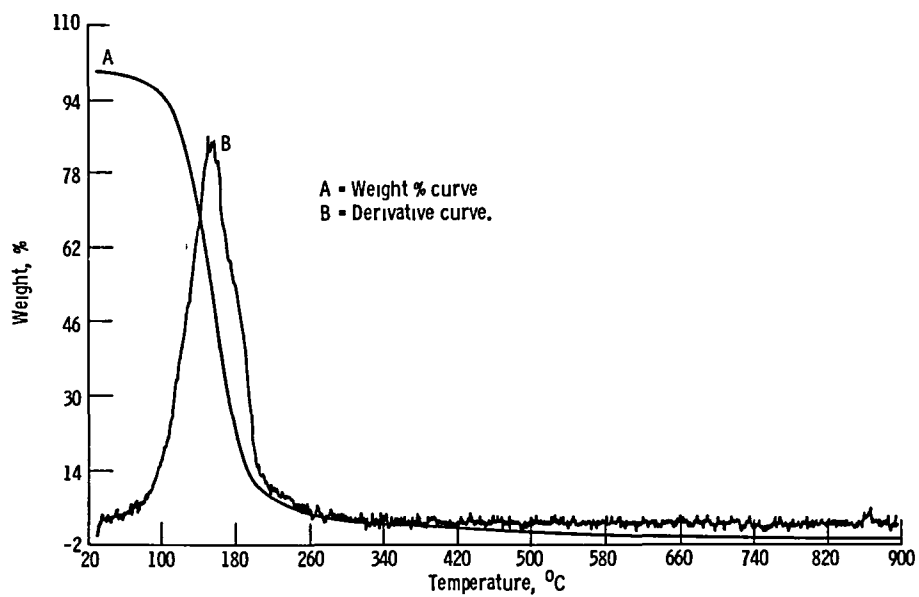


Figure 13. - TGA plot for 120 °C tetralin gum.

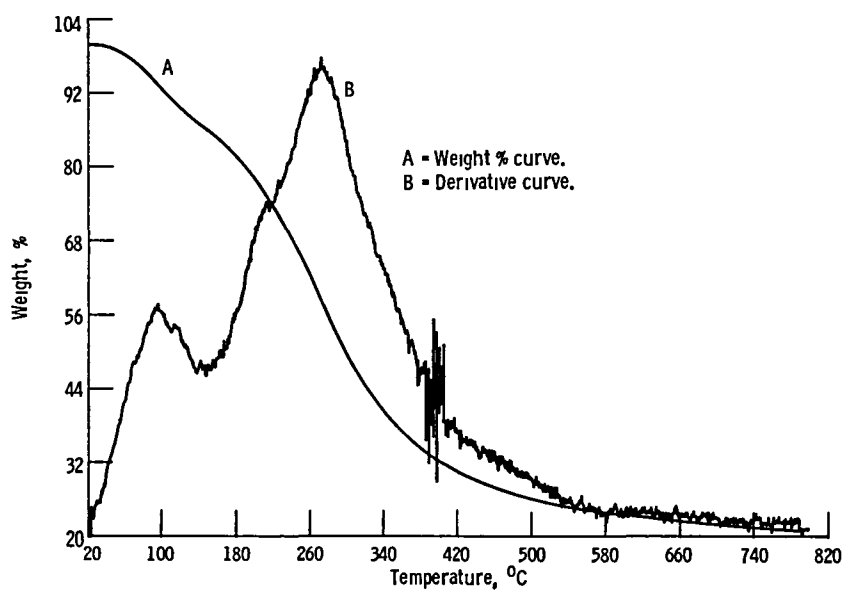


Figure 14. - TGA plot for 170 °C tetralin gum.

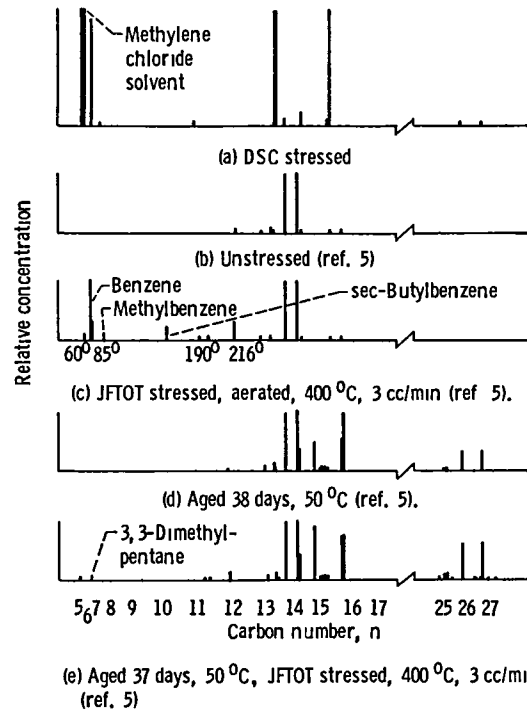


Figure 15 - Gas chromatograph profile of 2-ethylnaphthalene.

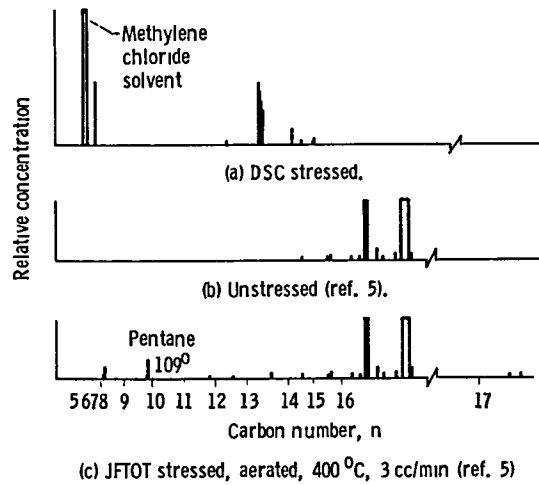


Figure 16. - Gas chromatograph profile of 90/10 n-dodecane/tetralin.

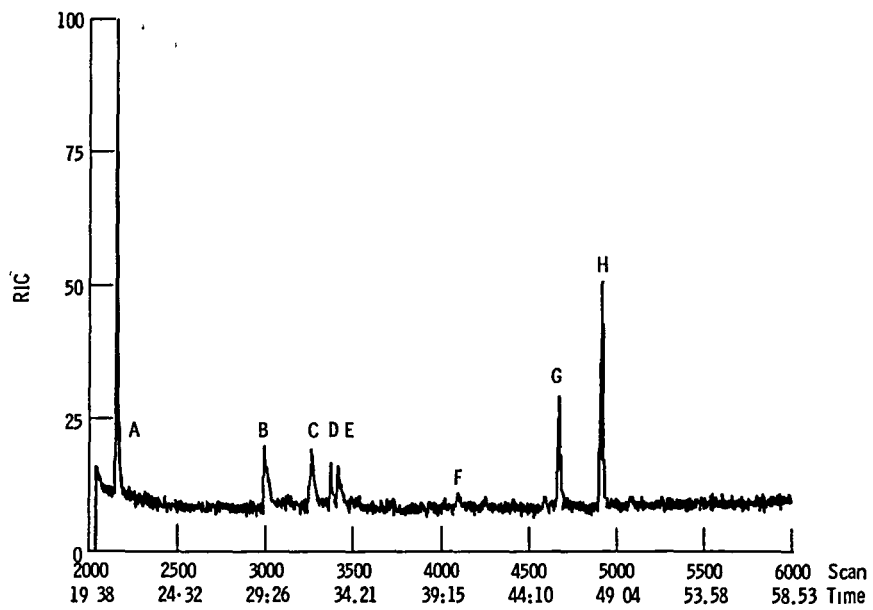


Figure 17. - GCMS gas chromatogram of DSC stressed 90/10 n-dodecane/tetralin (refer to Table 8).

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16 Abstract High pressure differential scanning calorimetry (DSC) was studied as an alternate method for performing high temperature fuel thermal stability research. The DSC was used to measure the heat of reaction versus temperature of a fuel sample heated at a programmed rate in an oxygen pressurized cell. Pure hydrocarbons and model fuels were studied using typical DSC operating conditions of 600 psig of oxygen and a temperature range from ambient to 500 °C. The DSC oxidation onset temperature was determined and was used to rate the fuels on thermal stability. Kinetic rate constants were determined for the global initial oxidation reaction. Fuel deposit formation was measured, and the high temperature volatility of some tetralin deposits was studied using thermogravimetric analysis. Gas chromatography and mass spectrometry were used to study the chemical composition of some DSC stressed fuels.					
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