

HIGH TEMPERATURE GAS PHASE PYROLYSIS OF JP-8

by

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Gas phase pyrolysis of JP-8 (NATO designation F-34), neat and with a thermal stability additive (JFA-5) is reported. Experiments were conducted in a quartz test cell to minimize catalytic effects. Data were collected isothermally at 50 degree intervals from 350°C (662°F) to 850°C (1562°F) and at mean residence times in the range of 0.3 to 3.0 seconds. Products were analyzed using gas chromatography with mass selective and flame ionization detectors, GC/MS and GC/FID, respectively. The low molecular weight decomposition products, from C₁ to C₇, are identified. The onset of decomposition and formation of decomposition products were observed under these conditions. The products of thermal decomposition and the time and temperature relationship of the decompositions are discussed and compared to the decomposition products of pure compounds. The results obtained from the jet fuel thermal oxidation tester (JFTOT) for the same fuels are also discussed. The JFA-5 additive had almost no effect on the thermal decomposition over this temperature range.

INTRODUCTION

The chemical composition of aviation fuels determines the thermal stability of the fuel. The temperatures and times required for a fuel to degrade determine the limits of aircraft performance and how much of the advantage gained from more efficient engines can actually be achieved. Thermal stability and thermal decomposition products of aviation fuels will play an important role in the design of future aircraft systems.

The thermal stability of aviation turbine fuels was first recognized as a problem in the 1950's. In conventional turbine engines, aviation fuels encountered high temperatures in the lubrication oil heat exchanger and the combustor manifold and nozzles[1]. Exposure of the fuel to these high temperatures resulted in the thermal degradation of the fuel and formation of deposits on critical engine parts.

With the development of high-Mach aircraft and more efficient engines, thermal stability of fuels has become even more crucial. The fuel in these aircraft and systems may reach temperatures of 538°C (1000°F), or higher[2]. This increased thermal stress may increase the thermal degradation and the deposits formed on critical engine parts and in fuel systems. Therefore, a better understanding of the thermal stability characteristics of current United States Air Force and NATO jet fuels is needed.

Previously, the pyrolysis of several alkanes, branched alkanes, and alkylated cycloalkanes within a carbon number range of 8 to 14 was reported[3]. These classes were chosen for study because they number among the major components of a typical JP-8. Comparison of individual component pyrolysis behavior with the pyrolysis behavior of JP-8 will yield a better understanding of JP-8 thermal stability.

A systematic study of the thermal decomposition of JP-8 (NATO designation F-34) from 600°C to 1000°C has been accomplished. JP-8 is typically a petroleum distillate cut from 177°C to 266°C (kerosenes) and commonly contains certain classes of compounds that may lower thermal stability. The rates at which individual components decompose and products form, *i.e.*, the temperatures and times necessary for pyrolysis to occur, are important factors in understanding the general thermal stability of a jet fuel.

EXPERIMENTAL

Apparatus

The system for thermal diagnostic studies (STDS)[4], developed at the University of Dayton Research Institute, is a continuous system consisting of three in-line units: the thermal decomposition unit, an analytical gas chromatograph (GC) for separation of parent compounds and pyrolysis products, and hydrogen flame ionization and mass selective detectors (FID and MSD, respectively)[5][6].

The thermal decomposition unit has a test-cell control module and an interchangeable test-cell assembly. The test-cell assembly has a quartz reaction cell heated by a hinged tube furnace (Linberg) over a temperature range of 250°C to 1150°C. The test-cell assembly is housed in a GC oven (Hewlett-Packard 5890A) for temperature control of the transfer lines, e.g., -100°C to +400°C.

Chromatographic separation was performed in a GC (Hewlett-Packard 5890A) with two separate chromatographic columns. Initial experiments were performed on a 30-meter Hewlett-Packard Ultra-5 column that was fed from the reactor cell assembly to the MSD (Hewlett-Packard 5970B). The Hewlett-Packard Ultra-5 column was then replaced with a 12-meter Hewlett-Packard Ultra-1 column that was fed from the reactor cell assembly to the FID. Ultra-high purity helium (99.999%) was used in the reactor cell assembly and as the carrier gas for chromatographic analysis.

Reagents

Thermal stability enhanced JP-8 was prepared from a WRDC/POSF standard JP-8 and 30 mg/l of JFA-5, obtained from the DuPont Company. Standard mixtures of C₂ to C₆ alkenes and C₁ to C₆ normal alkanes were obtained from Scott Specialty Gases for identification standards and quantitation.

Procedure

A 0.03 μl sample was injected into the test-cell assembly resulting in a gas-phase concentration of 1.78 × 10⁻⁴ moles/l. Both a neat JP-8 and a JP-8 standard containing 30 mg/l of JFA-5 were tested. The reaction temperature was governed by the tube furnace temperature. Temperatures were monitored before, within, and after the reaction zone using chromel/alumel thermocouples. The sample was held at 200°C before and after isothermal exposure (±1°C) to the experimental temperature in the reactor. Residence time at temperature was controlled by changing the mass flow. Unreacted sample and decomposition products were swept through a heated transfer line—to prevent condensation—after emerging from the test-cell and were captured at the head of the analytical chromatographic column, held at -60°C. During the first 6 minutes, separation of the C₁ to C₄ products occurred on the column. After the initial 6 minutes, the analytical GC was temperature programmed at 15°C/min to 285°C to allow for chromatographic separation of the remaining decomposition products and the jet fuel sample. The GC eluents were detected qualitatively by the MSD and quantitatively by the FID.

RESULTS AND DISCUSSION

JP-8 is composed of thousands of compounds, among which normal alkanes, branched alkanes, and alkylated cycloalkanes have the largest concentration, with smaller amounts of aromatic and unsaturated compounds. Trace components, such as nitrogen-, sulfur-, and oxygen-containing species and dissolved oxygen and metals, are present in the fuel and may act as initiators in free radical decomposition of the fuel components[7][8]. Thermal decomposition of JP-8 was not observed at temperatures below 650°C. Thermal decomposition of alkanes at high temperatures (500°C or higher)[9] occurs via a radical-chain mechanism[10]. Other pyrolysis experiments with low molecular weight alkanes at 660°C[11][12] produced the same products as JP-8, but the higher molecular weight hydrocarbons in JP-8 require higher temperatures to produce similar decompositions[13]. This is supported by the trends observed for individual component decomposition[3].

JP-8 was subjected to pyrolysis to determine its overall thermal decomposition and the thermal decomposition characteristics of individual components in a complex mixture at various mean residence times. In Table 1, the reactor residence times necessary for one, five, ten, fifteen, and twenty percent decomposition of neat JP-8 have been calculated from the experimental data for temperatures from 600°C to 1000°C. In Figure 1, the gas chromatograms of the neat JP-8, subjected to temperatures from 500°C to 1000°C with a mean residence time of 1 second, illustrate typical behavior observed from the thermal decomposition. Additional chromatograms showing similar behavior were collected at reactor residence times between 0.3 and 3.0 seconds.

While data were collected over a range of residence times, 0.3 to 3.0 seconds, within the temperature range of 500°C to 1000°C, the typical patterns of formation and decomposition observed are shown in Figures 2 through 9, using a residence time of 1.0 second. The C₁ to C₆ compounds in Figures 2 to 5 are not present in the unstressed JP-8. The C₇ and higher carbon number compounds in Figures 5 to 9 are present at differing

concentrations in the unstressed JP-8. The concentrations of the decomposition products relative to the initial JP-8 concentration are also given in Figures 2 through 9.

Inspection of Figures 2 through 4 indicates that for temperatures less than 750°C, the lighter hydrocarbons (C₁ through C₄) are the principal products. At higher temperatures, the rate of decomposition for C₂ and higher carbon number compounds competes with their rate of formation until the formation of methane dominates above ~900°C. Higher molecular weight aromatic compounds are observed chromatographically, but were not quantitatively measured. These higher molecular weight compounds include alkylated benzenes, naphthalenes, and multiple-aromatic-ring compounds identified by the MSD.

Methane and ethene increase in concentration up to 800°C, where the rate of formation no longer increases with temperature (Figure 2). Propene and propyne each reach a maximum at 800°C and 900°C, respectively, and then fall off in concentration (Figure 3). 1,3-Butadiene and 1-butene reach maxima at 750°C and 800°C, respectively, before decreasing in concentration (Figure 4). Finally, the two primary aromatic species formed are benzene and methylbenzene (Figure 5). These aromatic species reach their maxima at 750°C and 825°C, respectively. Their formation is a potential indicator of deposit precursor formation[14], and may provide a link to the degradation kinetics.

The normal and branched alkanes found in JP-8 show similar behavior in most cases. Nonane and decane can be formed through pyrolysis of higher molecular weight alkanes, and therefore show maxima before rapidly decreasing at 650°C (Figure 6). Slightly higher in molecular weight and thermal stability, the concentrations of undecane and dodecane are fairly constant until they reach a breakpoint after which their concentration decreases (Figure 7). The branched alkanes shown in Figure 8 have very different behavior resulting from their formation from the decomposition of higher molecular weight species. 2-Methyldodecane behaves similar to nonane and decane, with a maximum at 650°C. At 800°C, 2-methylundecane coeludes with naphthalene, which begins to dominate as a more favorable by-product of decomposition and addition reactions at higher temperatures, because the naphthalene concentration increases up to 1000°C. The concentrations of tetradecane and pentadecane decrease linearly in concentration as temperature increases (Figure 9).

The addition of 30 mg/l of the JFA-5 additive into JP-8 increased the JFTOT breakpoint temperature from 280°C to 360°C using a 2.5 hour duration test[15]. Comparisons of 1.0 second residence time data within the 650°C to 1000°C temperature range show a slightly greater decomposition occurring for the JP-8 with additive compared to the neat JP-8 (Figure 10). Other thermal oxidative inhibitors have been reported to enhance thermal stability at moderate temperatures and decrease stability at much higher temperatures[16]; inhibiting radical formation at moderate temperatures and acting as a radical initiator at much higher temperatures. Additional tests above 650°C with varied amounts of the radical-inhibitor JFA-5 will be needed to determine its effectiveness for extremely high temperatures.

Although the STDS contained an oxygen-free environment, as noted previously, oxygen was most likely present as small amounts of dissolved oxygen and oxygenated species, approximately 55 ppm. This results in an oxygen concentration of approximately 1.65 ppb in the reactor. The presence of oxygen affects the pyrolysis behavior; oxygen readily supports the formation of radical species that are important in the decomposition of hydrocarbon compounds. Even so, the typical behavior of an average JP-8 at these temperatures was observed. The kinetics of thermal decomposition of JP-8 are complex, and remain unresolved.

CONCLUSIONS

The maximum temperature and minimum times at various temperatures, at which a fuel will resist thermal degradation in the presence of small amounts of oxygen, have been approximately determined. To obtain a ten percent decomposition using reactor residence times of 0.3 to 3.0 seconds, temperatures from 680°C to 600°C, respectively, were required. For a one second residence time, a temperature of 636°C was needed for ten percent decomposition of JP-8. The addition of 30 mg/l of the JFA-5 additive did not change the temperature required for equivalent decomposition in the neat JP-8. This information will provide the basis for determining the limits of thermal stability and developing methods that will be used to enhance thermal stability of future jet fuels[17].

The major components of JP-8 are normal and branched alkanes. The majority of other components have alkyl groups attached to them. The decomposition products are formed by the cracking of alkanes and

cleaving alkyl groups. Additionally, dehydrogenation and isomerization occurs at temperatures above 850°C and reformed products undergo further cracking and cleavage. The major low molecular weight products formed from 600°C to 1000°C are the methane, ethene, propene, propyne, and the butenes. From 600°C to 700°C, terminal alkenes are formed preferentially. From 700°C to 850°C, alkylated cycloalkanes and alkenes dominate the higher molecular weight products. Above 850°C, the major products become alkylated benzenes, naphthalenes, and multiple-aromatic-ring compounds.

Further work needs to be accomplished before the kinetics can be resolved. The pyrolysis studies of more single components and simple mixtures of these single components are required before the mechanisms and kinetics will be understood. Pure compound studies are planned to attempt to unravel the kinetic complexity of JP-8 decomposition.

The JFA-5 additive had the effect of increasing the thermal oxidative stability at lower temperatures (up to 350°C); yet, it had almost no effect on the thermal stability of JP-8 from 600°C to 1000°C at a residence time of 1.0 second.

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Table 1. Temperature Versus Reactor Residence Time Required for One, Five, Ten, Fifteen, and Twenty Percent Decomposition of Neat JP-8.

T (°C)	$t_{(1\%)}$	$t_{(5\%)}$	$t_{(10\%)}$	$t_{(15\%)}$	$t_{(20\%)}$
600	0.56	1.64	2.38	2.64	2.75
650	0.06	0.37	0.71	0.92	1.13
700	<0.01	0.02	0.21	0.32	0.47
750	<0.01	<0.01	0.06	0.11	0.19
800	<0.01	<0.01	0.02	0.04	0.08

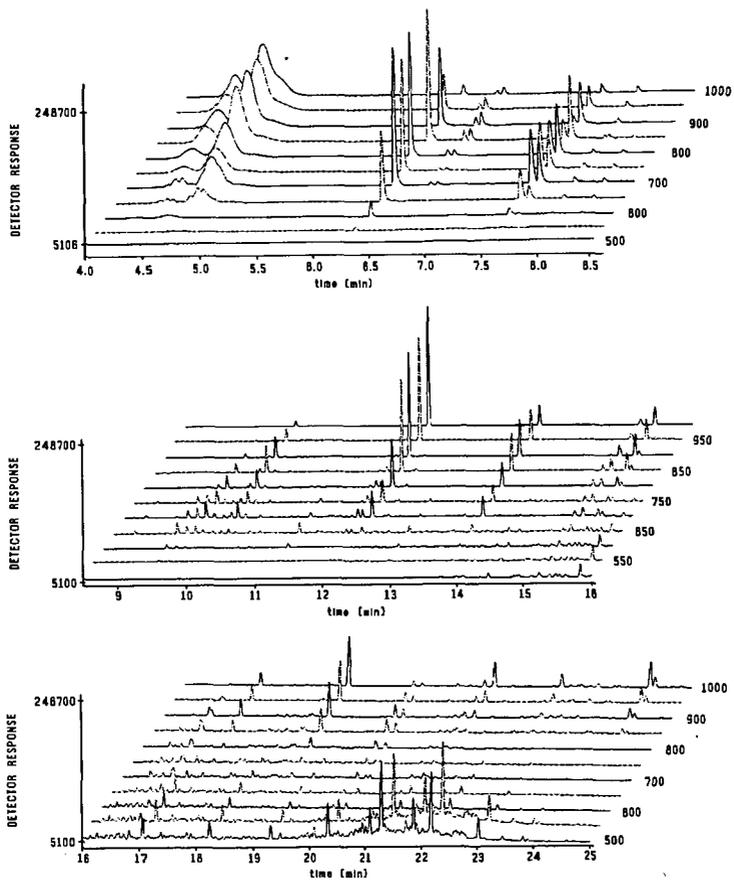


Figure 1. Gas Chromatograms of JP-8 from 500°C to 1000°C with a 1 Second Residence Time.

Compounds not initially present in JP-8.

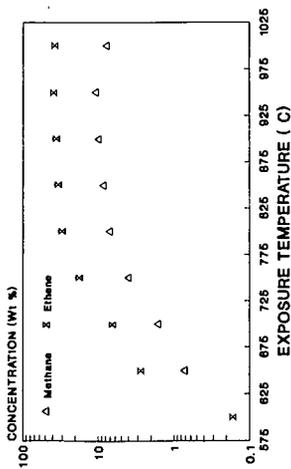


Figure 2. Formation of CH4 and C2H4.

Compounds not initially present in JP-8.

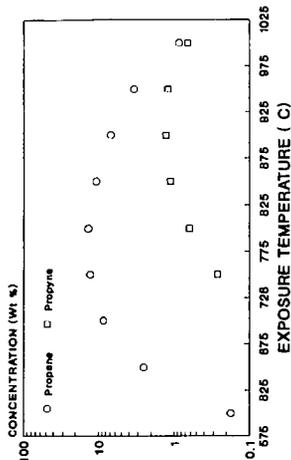


Figure 3. Formation of C3 Species.

Compounds not initially present in JP-8.

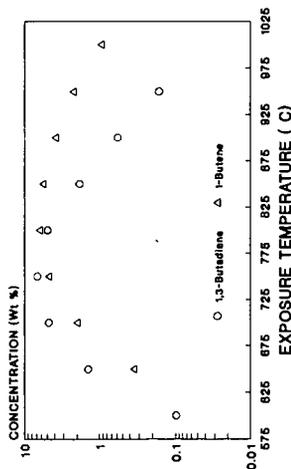


Figure 4. Formation of C4 Species.

Benzene is not initially present in JP-8.

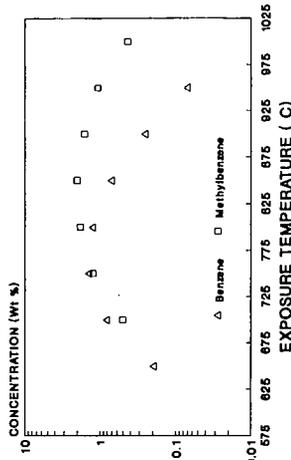


Figure 5. Formation of C6-C7 Aromatics.

Changes in amounts present in JP-8.

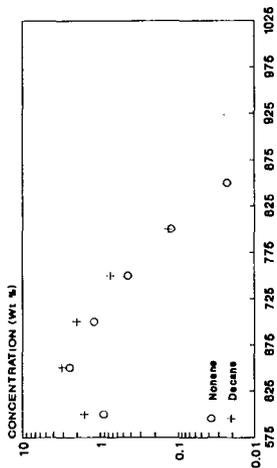


Figure 6. Decomposition of C9 and C10.

Changes in amounts present in JP-8.

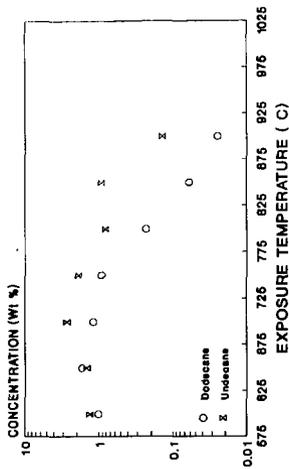


Figure 7. Decomposition of C11 and C12.

Changes in amounts present in JP-8.

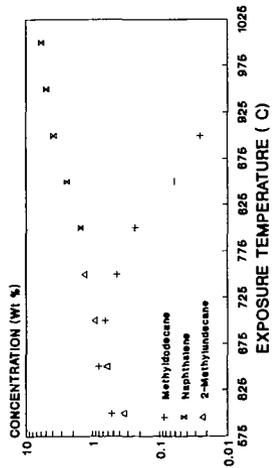


Figure 8. Behavior of Branched Alkanes and Formation of Naphthalene.

Changes in amounts present in JP-8.

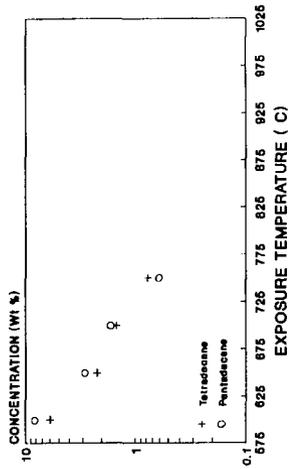


Figure 9. Decomposition of C14 and C15.

Samples run at 1 second residence time.

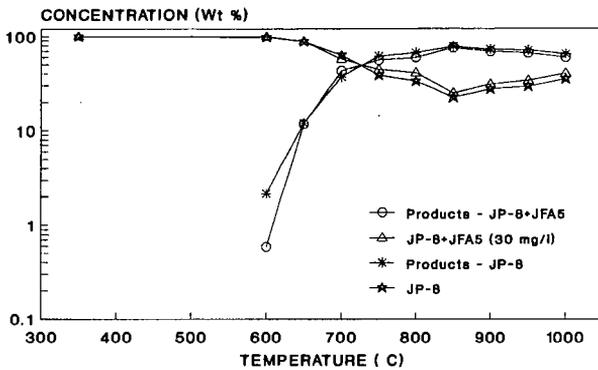


Figure 10. JP-8 versus JP-8 + JFA-5.