THERMAL STABILITY OF JET FUELS: KINETICS OF FORMING DEPOSIT PRECURSORS

By
David W. Naegeli
U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
P.O. Drawer 28510
San Antonio, Texas

For
NASA/Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135

June 1997

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Thermal Stability of Jet Fuels[1]
Kinetics of Forming Deposit Precursors

I. ABSTRACT

The focus of this study was on the autoxidation kinetics of deposit precursor formation in jet fuels. The objectives were (1) to demonstrate that laser-induced fluorescence is a viable kinetic tool for measuring rates of deposit precursor formation in jet fuels, (2) to determine global rate expressions for the formation of thermal deposit precursors in jet fuels, and (3) to better understand the chemical mechanism of thermal stability. The fuels were isothermally stressed in small glass ampules in the 120 to 180°C range. Concentrations of deposit precursor, hydroperoxide and oxygen consumption were measured over time in the thermally stressed fuels. Deposit precursors were measured using laser-induced fluorescence (LIF), hydroperoxides using a spectrophotometric technique, and oxygen consumption by the pressure loss in the ampule. The expressions,

$$I.P. = 1.278x10^{-11}\exp(28,517.9/RT)$$

and

$$R_{dp} = 2.382x10^{17}\exp(-34,369.2/RT)$$

for the induction period, I.P. and rate of deposit precursor formation, R_{dp}, were determined for Jet A fuel. The results of the study support a new theory of deposit formation in jet fuels, which suggest that acid catalyzed ionic reactions compete with free radical reactions to form deposit precursors. The results indicate that deposit precursors form only when aromatics are present in the fuel. Traces of sulfur reduce the rate of autoxidation but increase the yield of deposit precursor. Free radical chemistry is responsible for hydroperoxide formation and the oxidation of sulfur compounds to sulfonic acids. Phenols are then formed by the acid catalyzed decomposition of benzylic hydroperoxides, and deposit precursors are produced by the reaction of phenols with aldehydes, which forms a polymer similar to Bakelite. Deposit precursors appear to have a phenolic resin-like structure because the LIF spectra of the deposit precursors were similar to that of phenolic resin dissolved in TAM.[2]

---

[1] Superscript numbers in parenthesis refer to literature citations.

[2] TAM is a mixture containing equal volumes of toluene, acetone and methanol.

1

II. INTRODUCTION

Advances in engine technology are imposing higher operating temperatures on fuel nozzles and heat exchangers. The added heat stress increases the rate of fuel oxidation and pyrolysis, which increases the rate and degree of deposit formation in the fuel systems. The deposits clog narrow passages in fuel nozzles and insulate surfaces in heat exchangers. The goal in furthering the state of the art of thermal stability, as seen by workers at NASA and Wright-Patterson AFB, is to develop a more basic way of predicting deposit formation in aircraft-engine fuel systems.

The formation of deposits may be treated as a two-step mechanism: first, the chemical formation of deposit precursors by fuel oxidation; and second, the mass transport of deposit precursors to fuel system parts. The purpose of the present study is to understand the chemical mechanism and determine the global rate expression for the formation of deposit precursors in jet fuels. Complex models utilizing chemical kinetic rate equations and mass transport properties have been developed.[1,2] However, these model are incomplete because there is little rate data available, and the chemical mechanism is poorly understood.

III. BACKGROUND

With advances in jet-engine technology and the quest to reach higher mach numbers, fuel stability is expected to play a significant role in the thermal management of modern aircraft. As system temperatures increase, the fuel autoxidation process that forms peroxides, gums and deposits will accelerate. Fuels will be exposed to high temperatures for longer periods of time because there will be an increased demand on the cooling capacity of the fuel. Although heat exchanger wall temperatures will be maintained below a "breakpoint" temperature, at which deposits form rapidly in the JFTOT [3], the temperatures will be higher than in conventional systems. The fuel could thus become contaminated with relatively high concentrations of peroxides and gums by the time it reaches the atomizer.

---

[3] JFTOT stands for "Jet Fuel Thermal Oxidation Tester."

The conclusion of most studies on fuel stability, e.g., Mayo and Lan[3-5], is that gums are the precursors to deposit formation. Basically, most workers expect the rate of formation of deposits to be proportional to fuel's propensity to autoxidize and form gums. However, recent work has shown an anomalous relationship between the rate of autoxidation at moderate temperatures (<150°C) and the rate of surface deposition at high temperatures (>200°C). It has been observed that fuels which autoxidize quickly tend to form fewer deposits, or require higher temperatures to form deposits, than fuels that are relatively resistant to autoxidation. Hardy, et al.[6] measured insolubles formed in a JFTOT rig and the peroxide potentials of 13 jet fuels. They used the weight of insolubles as a measure of thermal stability, and the concentration of peroxides formed as a measure of the oxidation rate. Figure 1 shows a very nonlinear relationship between thermal deposition and peroxide potential. It appears that fuels which are resistant to oxidation have a greater tendency to form deposits.
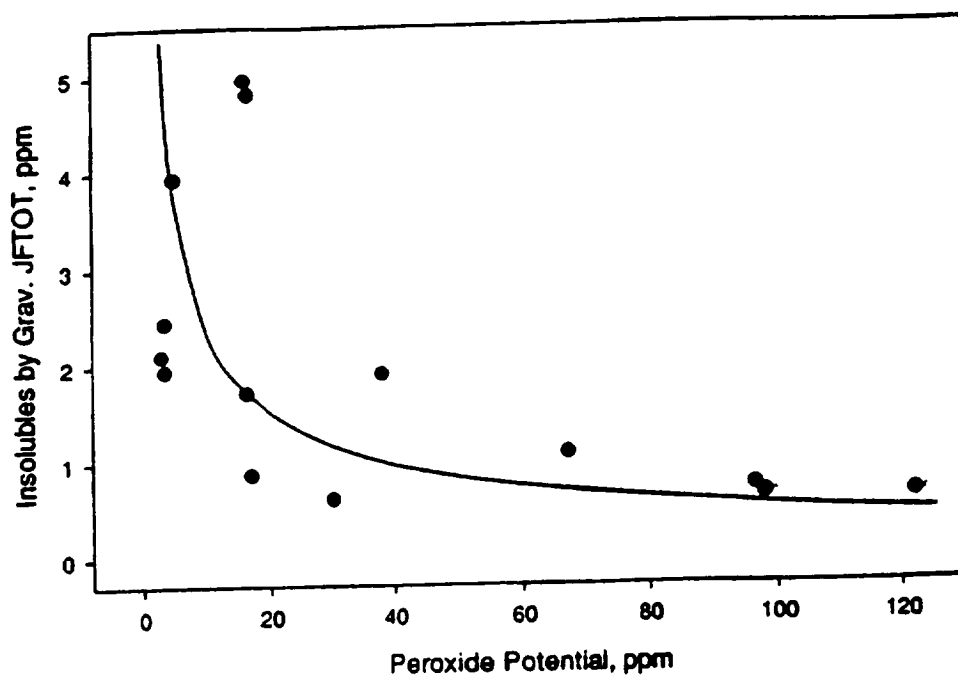
Figure 1. The Inversed Relationship Between Rate of Autoxidation
and Thermal Deposition

The results of Hardy, et al.[6] suggest that the pathway to deposits is not necessarily linked to the formation of gums, because fuels which autoxidize quickly also form gums. Basically, there is not enough information to conclude without a doubt that gums and deposits are not related. The problem requires a more in-depth investigation of the mechanisms of formation of gums and deposits.

The mechanism of deposit formation in jet fuels is a complex process involving several chemical reactions, mass transport effects and surface interactions. In the most general case, deposits form as a result of fuel oxidation, producing peroxides and relatively insoluble species of higher molecular weight known as gums. Gums are rich in oxygen and often contain sulfur and nitrogen in much higher concentrations than are originally present in the fuel. Because of their high heteroatom content and high molecular weight, gums have limited solubility in the fuel. They are characterized as both soluble and insoluble because a portion is dissolved in the fuel, while the remainder precipitates and adheres to reaction vessel walls. It is believed gums contain the precursors that form varnish or lacquer-type deposits on heat exchanger surfaces and fuel atomizer orifices in gas turbine engines.

The kinetics of gum formation in jet fuels has always been a challenging problem because the procedure for measuring gum concentration (ASTM D 381) is not only lengthy and tedious, but lacks sensitivity. Laser-induced fluorescence (LIF) has shown promise in the detection of soluble gums in jet fuels.[7] Thermally stressed fuels contain a fluorescent material that correlates with the soluble gums in jet fuels. LIF seems to be effective in following the concentration of gums formed in a single fuel. Since gums tend to vary with fuel composition, some gums are more fluorescent than others. Thus, it has not been possible to measure absolute gum concentrations without calibrating the LIF-gum response of each fuel. On the other hand, LIF appears to be an excellent tool for studying the kinetics of gum formation in a single fuel.

It is not known for sure whether LIF actually detects gums in fuels or something else that forms as the result of fuel autoxidation. Results of the present study indicate that LIF detects phenolic resins, which may represent a fraction of the gum in jet fuels. The rate of gum formation in fuels generally

4

increases in direct proportion to the rate of autoxidation, which suggests that fuels that oxidize rapidly have lower thermal stability. If it is assumed that gums are the precursors to deposits, the latter statement is in question because Hardy, et al.[6] showed that fuels with high rates of oxidation formed fewer deposits than fuels with lower rates of oxidation.

The relationship between thermal stability and peroxide formation in Figure 1, is similar to the relationship between LIF sensitivity to soluble gums and the rate of oxygen consumption shown in Figure 2.[7] The LIF sensitivities were calculated as the fluorescence intensity per unit concentration (mg/dL) of gum. The results in Figure 2 include 13 test fuels, stressed at 100°C. Figure 2 shows that fuels with low oxidation rates form gums that are substantially more fluorescent than fuels with high rates of oxidation. The similarity in Figures 1 and 2 suggests that the LIF sensitivity to soluble gums is a measure of thermal stability. In other words, LIF seems to be detecting the deposit precursor in gum.
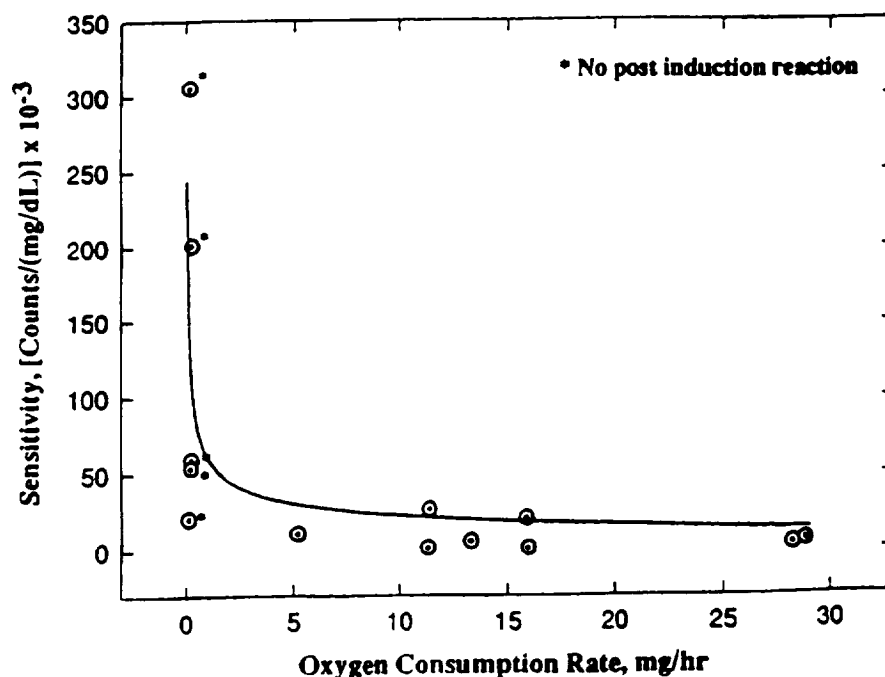
Figure 2. **Effect of Autoxidation Rate on LIF Response to Gum Concentration**

IV. EXPERIMENTAL DESIGN

A. Test Fuels

The test fuels included Jet A, hydro-treated coal liquid, cumene and tetradecane. The main focus of the work was to develop rate expressions for deposit precursor formation in Jet A fuel. Experiments on hydro-treated coal liquid, cumene and tetradecane were performed to provide more insight into the mechanism of deposit precursor formation. The sulfur content of the Jet A was 262 ppm, while that of the hydro-treated coal liquid was about 2 ppm. Hydro-treating removed most of the sulfur and lowered the aromatic content of the coal liquid to about 10 wt.%. Chemically pure samples of tetradecane ($C_{14}H_{30}$), a straight chain saturated hydrocarbon, and cumene (C_9H_{12}), also known as isopropyl benzene, were obtained from Aldrich Chemical Company. The purpose of examining them was to determine the effect of fuel molecular structure on deposit precursor formation.

A break-point of 286°C was determined for the Jet A fuel by ASTM method D 3241. The break-point of the Jet A was relatively sharp, providing readings of 2 and 4 tube on the JFTOT tubes at 282°C and 290°C respectively.

When the Jet A and hydro-treated coal liquid fuels were received, they contained traces of fluorescent material, which probably formed through autoxidation while the fuels were in storage. Since the fluorescent material interfered with the detection of deposit precursors formed when the fuels were thermally stressed, the fluorescent material was removed by filtering the fuels through 30/60 mesh Attapulgus clay. Clay filtering would also remove the fluorescent deposit precursor that formed when the fuels were thermally stressed. The clay filtering increased the break-point of the Jet A to about 318°C. All experiments on the kinetics of thermal stressing were performed with the clay filtered Jet A.

6

B. Fuel Stressing Apparatus

The objectives of the work were to better understand the mechanism and determine rate expressions for the formation of deposit precursor in jet fuel stressed at high temperatures. The fuel stressing apparatus shown in Figure 3 is a solid aluminum cylinder, 4 inches in diameter and 5 inches in height, containing 10 ports arranged symmetrically about the central axis. The ports house glass ampules that contain fuel samples. A cartridge heater is placed in the central port and the thermocouple is placed between two of the ampule ports to monitor fuel temperature. The cartridge heater and thermocouple are wired to a Watlow series 965 controller which maintains the apparatus at a constant temperature.
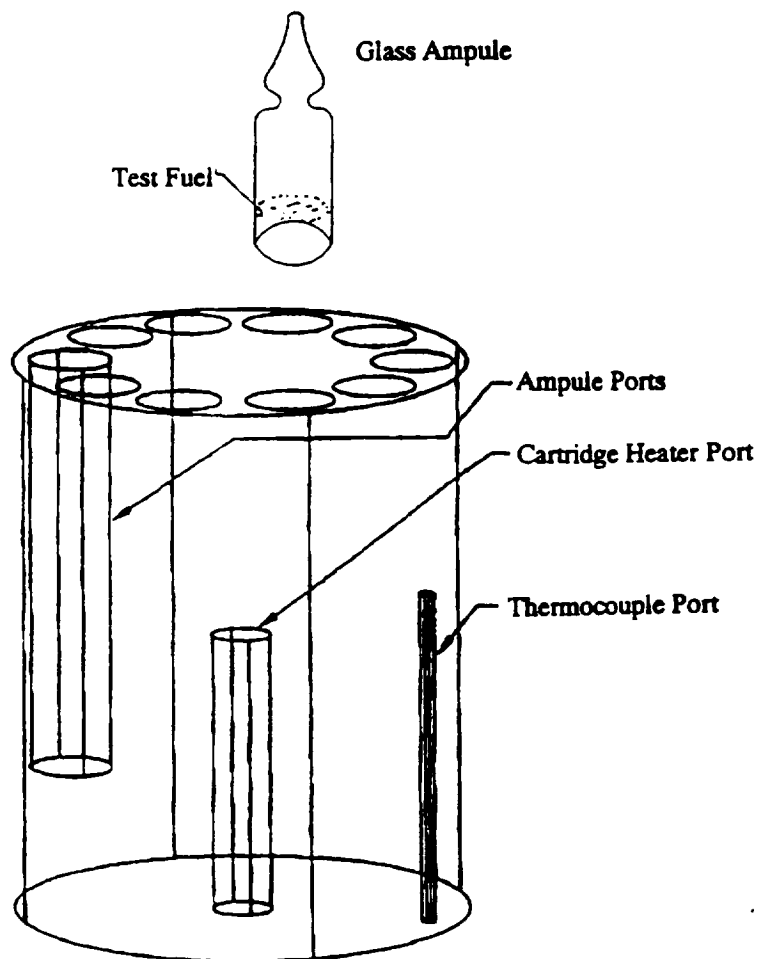
Figure 3. Static Reactor for Stressing Jet Fuels

Fuel samples of 5 mL were placed in flame-sealed glass ampules having a total volume of about 14.5 mL. Before the ampules were sealed, the fuel and head space were purged with oxygen. The ampules were then inserted into the ports of the fuel stressor. After a 7-minute warm-up period the "kinetic clock" was started. The warm-up period was determined by inserting an RTD[4] into an open ampule containing mineral oil and measuring the time required to heat the fuel to within a few degrees of the test temperature.

Experiments on Jet A fuel were performed at 10°C increments in the range of 120 to 180°C. The run time for the autoxidation of Jet A fuel was about 60 minutes at 180°C. In each run, ampules were removed for analysis at regular intervals.

V. ANALYTICAL MEASUREMENTS

Stressed fuel samples were analyzed for the presence of deposit precursor, hydroperoxides, and the amount of oxygen remaining in the head space of the ampules. Laser induced fluorescence was used to determine relative concentrations of deposit precursor in the stressed fuel. A spectrophotometric method was developed to measure hydroperoxides in the fuel. Oxygen consumption was determined by a technique developed to measure the oxygen pressure in an ampule.

A. Deposit Precursor

Experiments have shown that when jet fuels are thermally stressed, a fluorescent material forms which correlates with gum formation.[7] Since gums are considered precursors to deposits[3-5], the present study assumes that the LIF signal from stressed jet fuels measures a relative deposit precursor concentration in the fuel. The LIF measurements were performed with an optical setup similar to that in Figure 4. An air-cooled model Argon ion laser emitting at 488 nm was used to induce fluorescence in the thermally stressed fuels. The laser light was passed through a glass

---

[4] An RTD is a Resistance Temperature Detector.

8
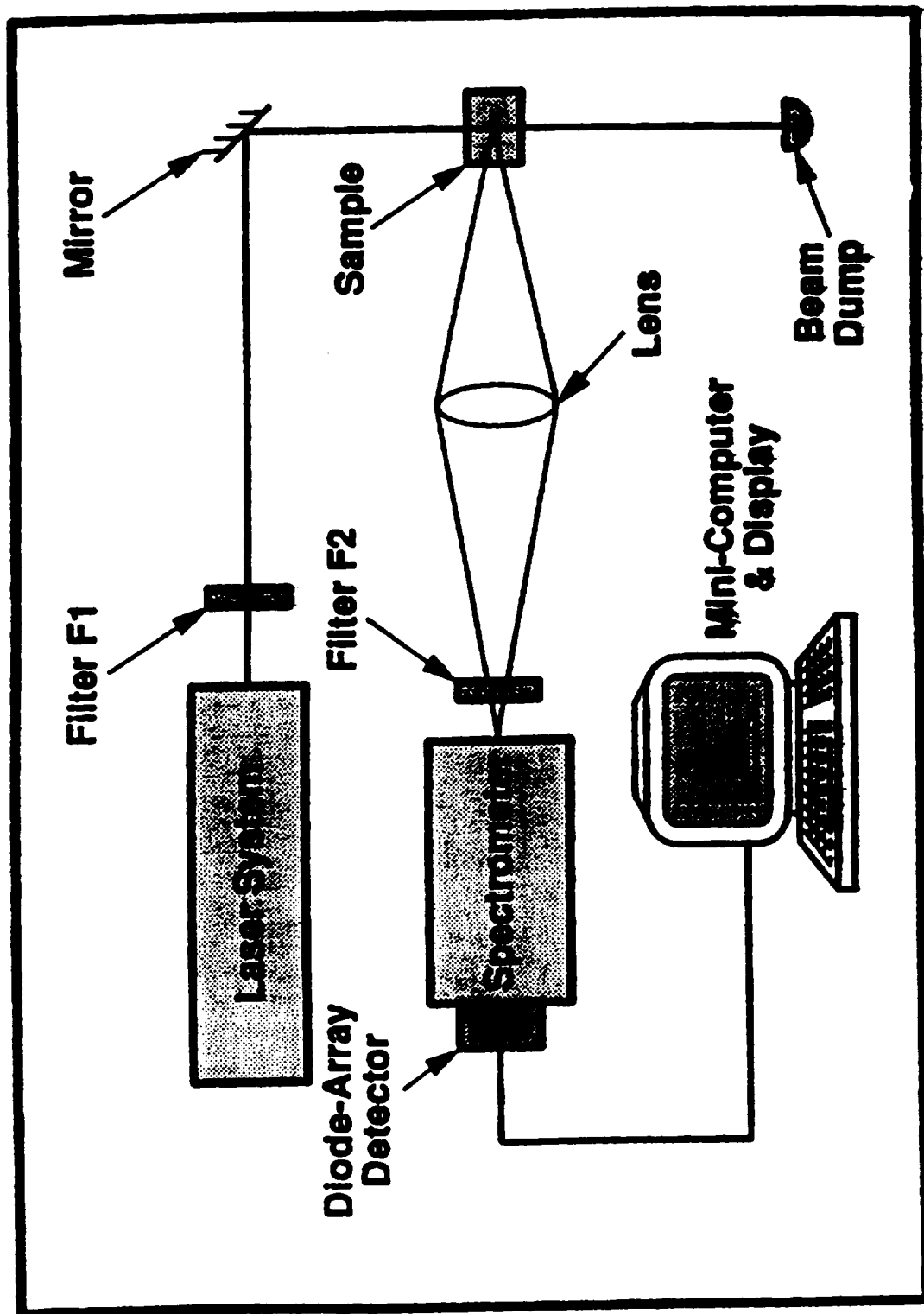
Figure 4. Optical Arrangement and Instrumentation for Laser-Induced Fluorescence Measurements

9

with fuel sample and the fluorescence normal to the laser beam was collected with a fiber optic cable. It was then fed to a model 640 Monochromator made by ISA Instruments Inc., equipped with photomultiplier detector. The fluorescence signal was sent to a computer equipped with ISA Jobin Yvon-Spex software, " SpectraMax." where it was converted to a spectrum similar to that shown in Figure 5.

Fluorescence intensity measurements on fuel samples were made over a 30-second time scan at the peak fluorescence intensity. The wavelengths of the peak fluorescence intensities of the fuels were similar, ranging from 520 to 530 nm.
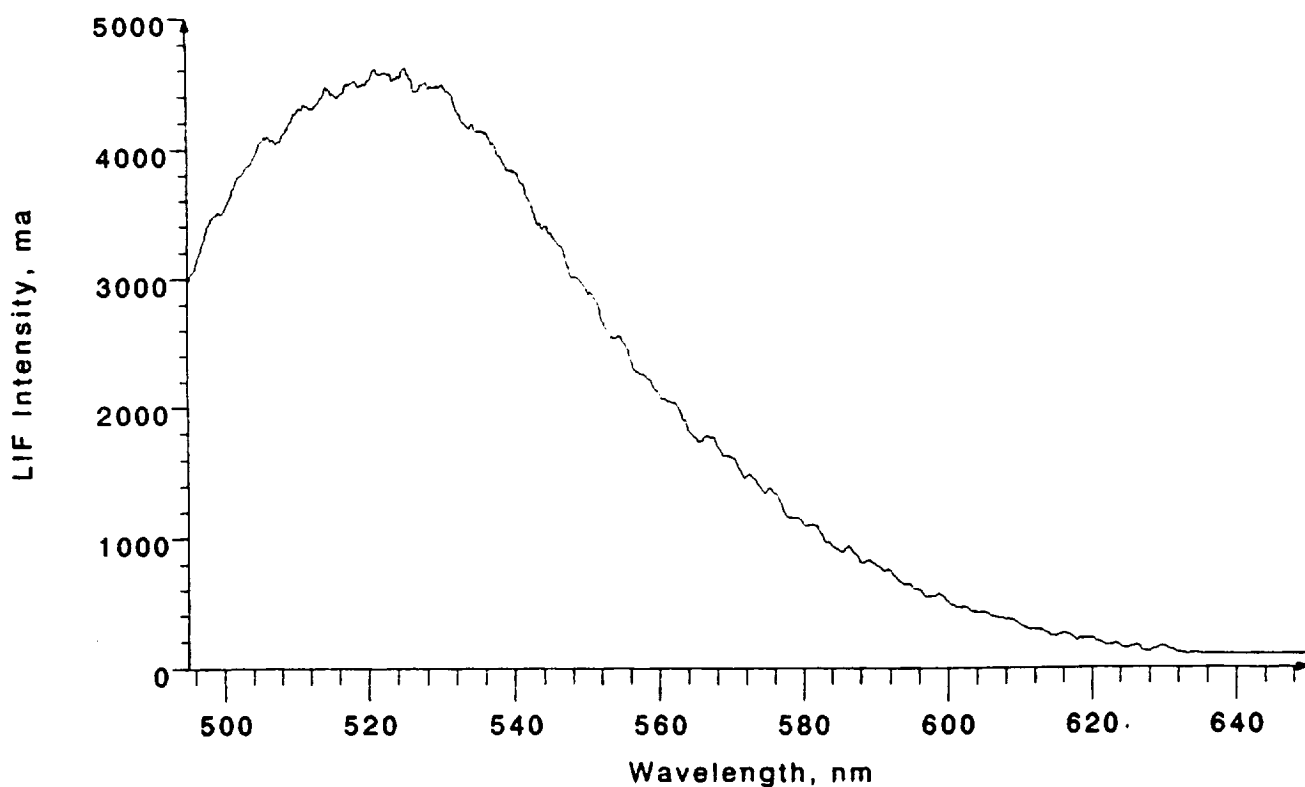
Figure 5. The LIF Spectrum of Stressed Jet A

10

B. Oxygen Consumption

Oxygen consumption was determined by measuring the gas pressure inside the ampule. It was assumed that autoxidation converted oxygen in the head space of the ampule to liquid phase oxygenates, and no gaseous products such as CO_2 were produced.

The technique involved breaking the ampule within an enclosure and measuring the pressure with a manometer. Figure 6 shows the apparatus used to measure the gas pressure in the ampule. The ampule envelope shown in the figure fits over the tip of the ampule and is sealed to the main body of the ampule with a section of heat-shrinkable tubing. A heat gun is used to shrink the tubing onto the envelope and ampule, forming a flexible seal between them. The envelope-ampule unit is then attached to the manometer, and the ampule tip is broken by applying perpendicular force to the ampule envelope, holding the ampule in a fixed position. The fluid used in the manometer was dodecane. The pressure, P_1, in the ampule calculated in units of [mm of dodecane] is,

$$P_1 = \frac{(P_A - H)(V_1 - \pi r^2 H) - V_2 H}{V_1} \tag{1}$$

where P_A is the atmospheric pressure, V_1 is head space volume in the ampule, V_2 is the combined volume of the manometer tube and ampule envelope, H is the height of the dodecane column, and r is the radius of the manometer tube.

C. Hydroperoxides

Hydroperoxides were determined by a spectrophotometric method similar to one described by Egerton, et al.[8] using titanous chloride ($TiCl_3$) reagent. This method is well suited for measuring hydroperoxides in aqueous solutions, but does not work in non-aqueous media. Attempts to modify the method were met with moderate success.
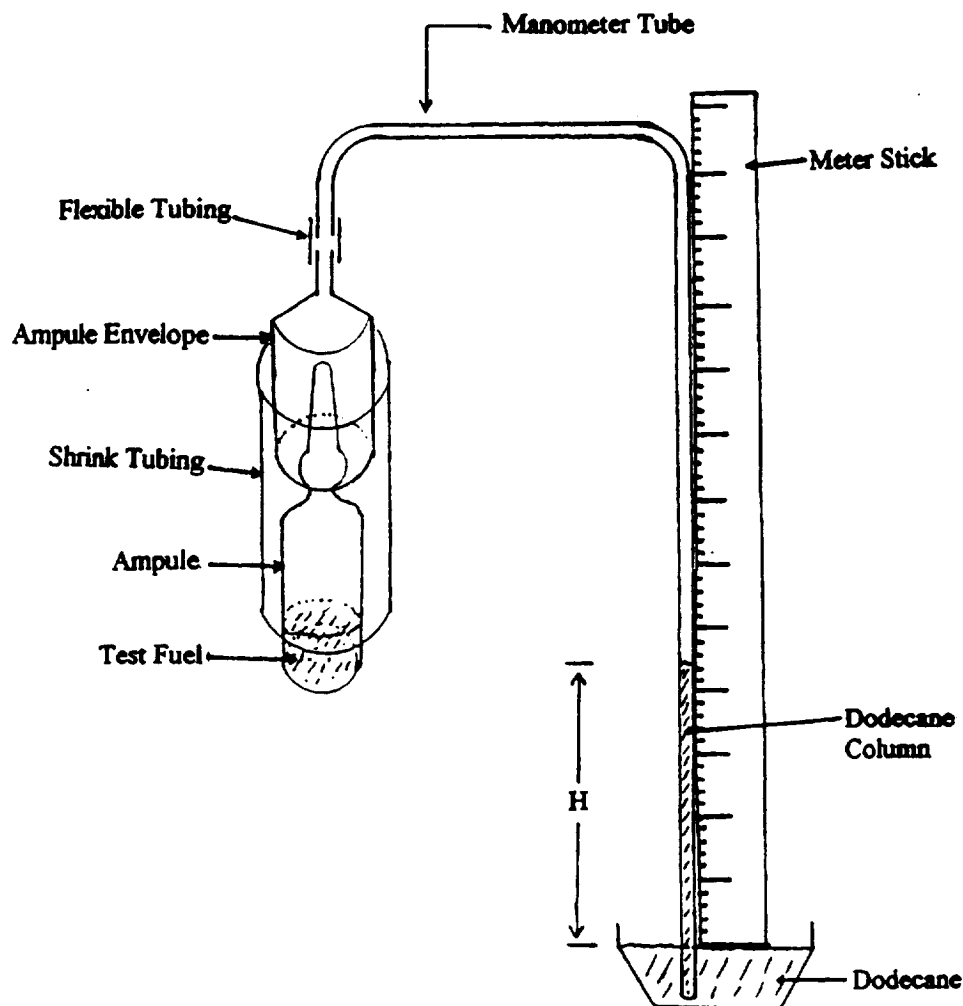
Figure 6. Apparatus for Measuring Oxygen Pressure in Ampules

After several trials, a titanous chloride reagent for non-aqueous media was prepared by blending 1 mL of titanous chloride (19 wt.% solution) with 50 mL of concentrated hydrochloric acid and 150 mL of concentrated acetic acid. The hydroperoxide analysis was performed by mixing 5 mL of titanous chloride reagent with 1 mL of fuel and agitating the mixture for 30 seconds. The samples were agitated because the fuel was only sparingly soluble in the titanous chloride reagent. After agitation, the samples separated into two phases with the fuel on top. Aqueous solutions of hydroperoxides produced a yellow coloring with a peak absorption at 410 nm. Hydroperoxide was evident in the lower layer as an orange hue that had a peak absorption at 428 nm.

12

The analysis was always performed on 12 samples, i.e., 10 stressed fuel samples, and 2 unstressed baseline samples. The unstressed samples were used as blank and baseline in the spectrophotometer. Before the optical densities could be measured, the samples were centrifuged to remove a haze of fuel micro-droplets in the lower layer. The micro-droplets were separated by a Sorvall model SS-3 Automatic Superspeed centrifuge with a capacity of 12 plastic test tubes, operated at 12000 rpm for 10 minutes. The lower layer of the each sample was decanted and placed in a cuvette for the optical density reading. The color was reasonably stable but would eventually fade, so it was important to read the optical densities in a timely manner.

The method was calibrated using several mixtures of cumene hydroperoxide in Jet A fuel. Cumene hydroperoxide (80 wt. % in cumene) was obtained from Aldrich Chemical Company. Figure 7 shows a linear relationship between absorbance and the cumene hydroperoxide concentration. A correlation of absorbance with cumene hydroperoxide concentration was used to calculate the hydroperoxide concentrations in the thermally stressed fuel samples.
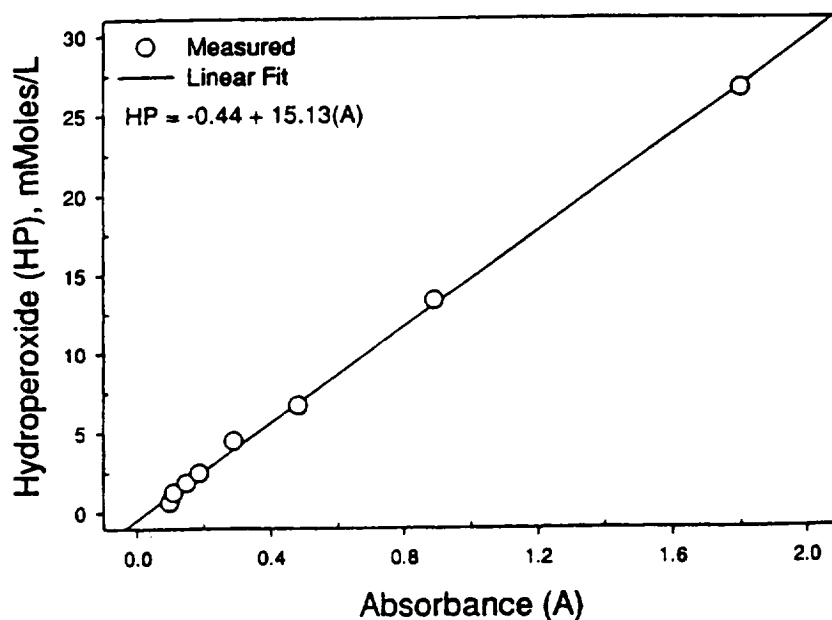
Figure 7. Correlation of Absorbance with the Concentration of Cumene Hydroperoxide Dissolved in Jet A Fuel

13

VI. RESULTS AND DISCUSSION

A. LIF Spectra & Fuel Effects

Early in the project, the test fuels and pure compounds were thermally stressed to determine their tendencies to form fluorescent material and to characterize their spectra. Tetradecane and cumene were compared with clay-treated Jet A to determine if pure compounds produced deposit precursors similar to those found in a natural fuel. The fuels and compounds were stressed at 150°C until a noticeable increase in fluorescence appeared. In other words, ampules were removed and then returned to the stressor periodically to determine if significant amounts of fluorescent material had formed. Deposit precursor formed relatively quickly in both Jet A and the hydro-treated coal liquid, but would not form at all in tetradecane. It formed very slowly in pure cumene, requiring a stress duration of about 10 times that of Jet A to develop an equivalent fluorescence intensity.

Figure 8 shows the LIF spectra of the deposit precursors in Jet A, coal liquid and cumene. The spectra are very similar, indicating that deposit precursors originate in fuels that contain aromatic molecules. This is supported by the fact that fluorescent material will not form in straight-chain hydrocarbons such as tetradecane.

Kauffman[9] showed that sulfur compounds cause phenols to form when jet fuels are thermally stressed. Sulfur-free fuels showed little evidence of phenol formation. It is interesting that the infrared spectra of deposits also show the presence of aromatic C-O bonds[10,11] similar to those observed in the spectra of phenols. These observations suggested that deposits could have a phenolic resin type structure. To test this hypothesis, the fluorescence spectrum of thermally stressed Jet A was compared with that of a phenolic resin. Figure 9 shows the fluorescence spectra of thermally stressed Jet A and phenolic resin dissolved in TAM. The phenolic resin solution was made by soaking a piece of the resin in TAM for several days. The strong similarity of the spectra suggests that the deposit precursors have a phenolic resin structure.

14
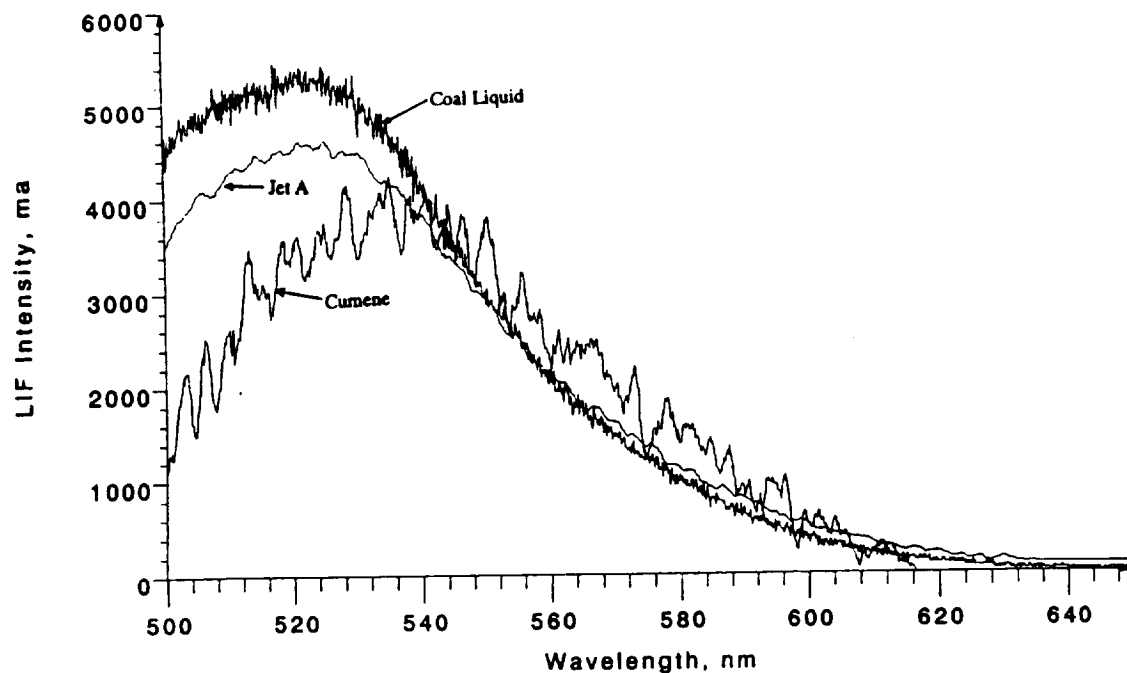
Figure 8. LIF Spectra of Jet A, Coal Liquid and Cumene Stressed at 150°C
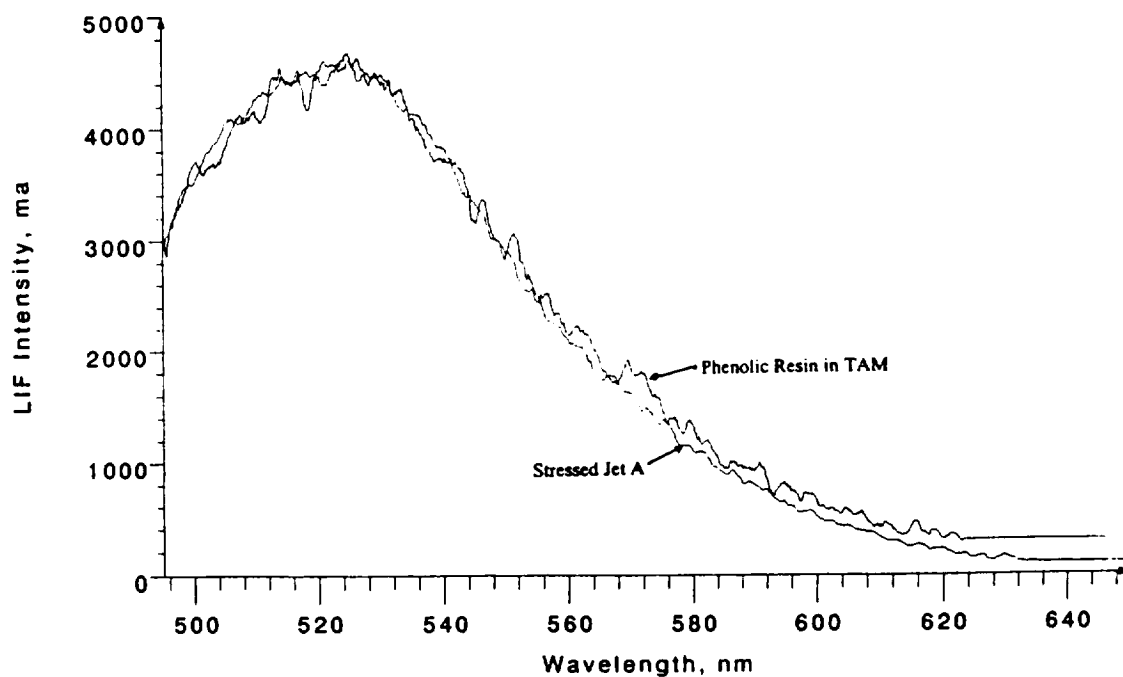
Figure 9. LIF Spectra of Stressed Jet A and Phenolic Resin Dissolved in TAM

B. Jet A Experiments

Concentration profiles over time of deposit precursor formation, hydroperoxide formation, and oxygen consumption were measured in thermally stressed Jet A and hydro-treated coal liquid. Experiments on the coal liquid were performed only at 150°C, while those on Jet A were performed in 10°C increments over the range of 120 to 180°C. Figures 10-16 show plots of concentration versus time for the Jet A experiments. The scale on the left represents the relative deposit precursor concentration in terms of LIF intensity; the scale on the right represents either the absolute concentration of hydroperoxide or the amount of oxygen consumed. The right-hand scale gives the total micro-moles of hydroperoxide in the 5 mL fuel sample and the total amount of oxygen removed from the head space in the ampule.

Clay Treated Jet A Stressed @ 120°C in Atmospheric O$_2$
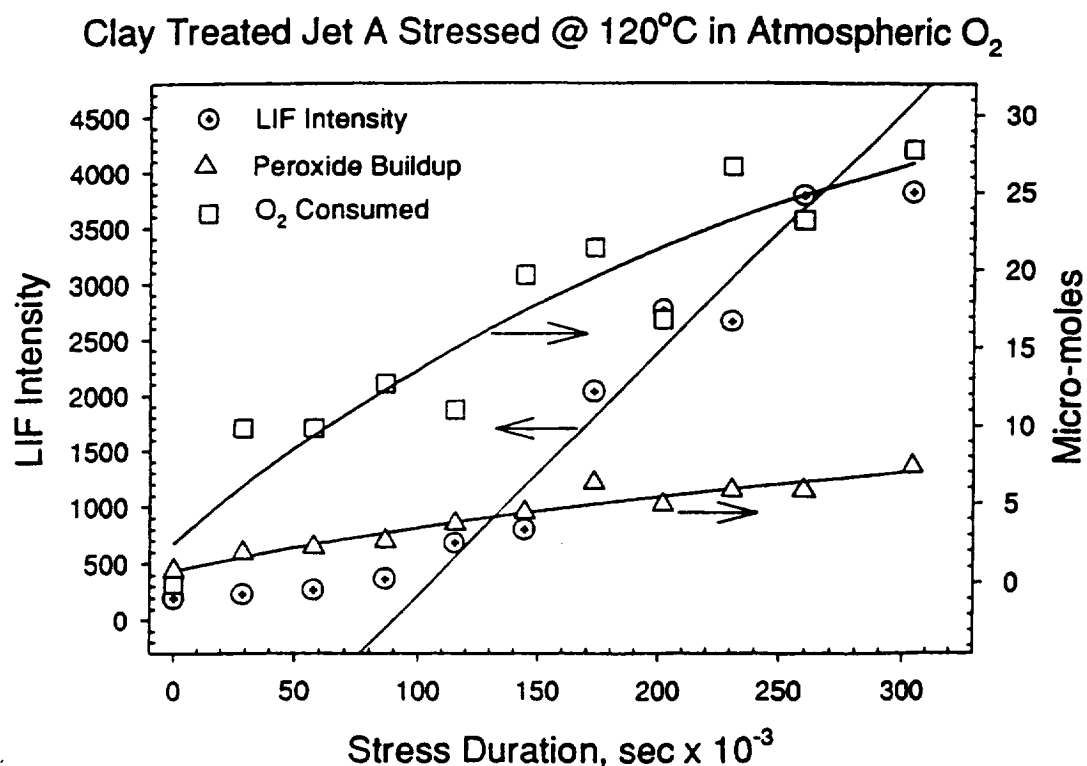
Figure 10. Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 120°C

16

Clay Treated Jet A Stressed @ 130°C in Atmospheric O_2

LIF Intensity

- ⊙ LLIF Intensity
- △ Peroxide Buildup
- □ O_2 Consumed

Stress Duration, sec x 10^{-3}
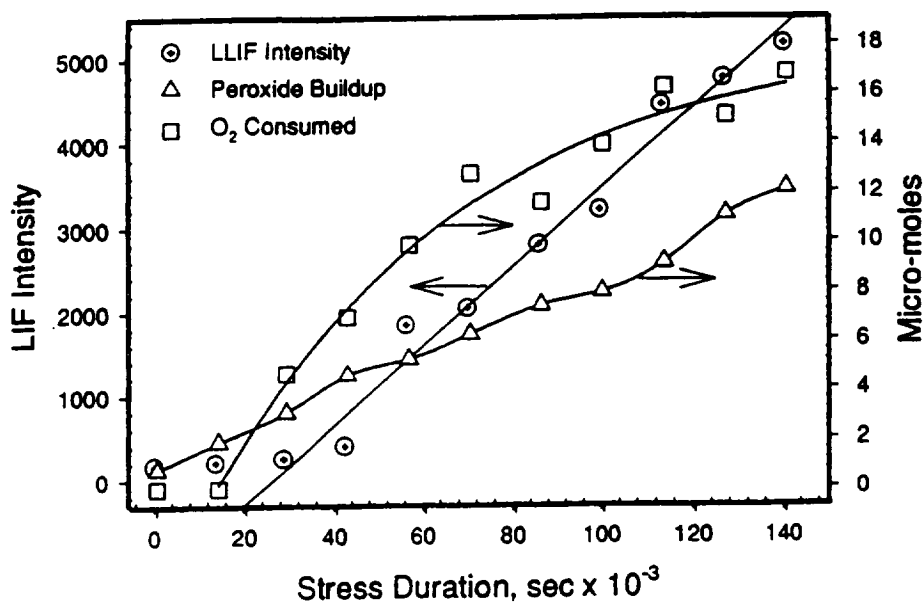
Figure 11. <u>Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 130°C</u>

Clay Treated Jet A Stressed @ 140°C in Atmospheric O_2

LIF Intensity

- ⊙ LIF Intensity
- △ Peroxide Buildup
- □ O_2 Consumed

Stress Duration, sec
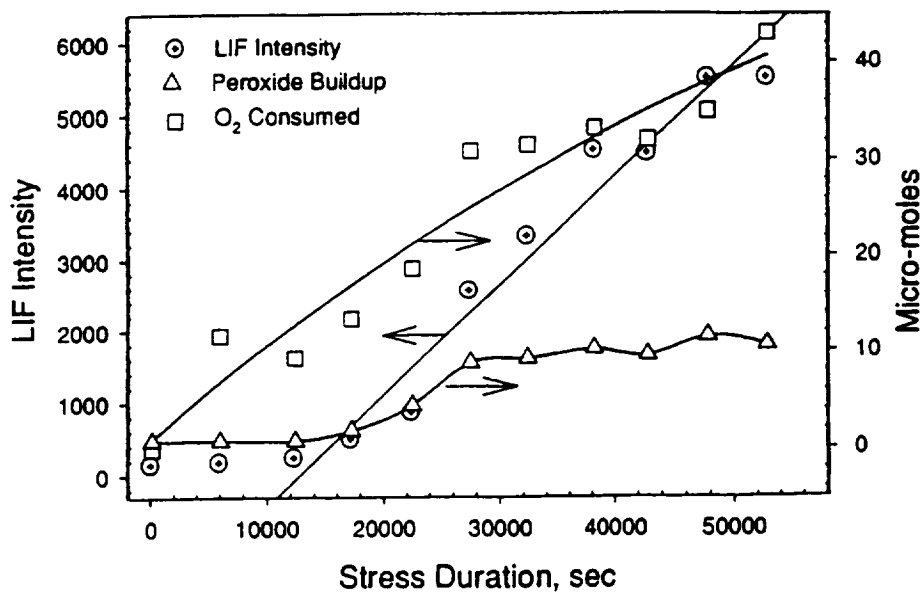
Figure 12. <u>Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 140°C</u>

17
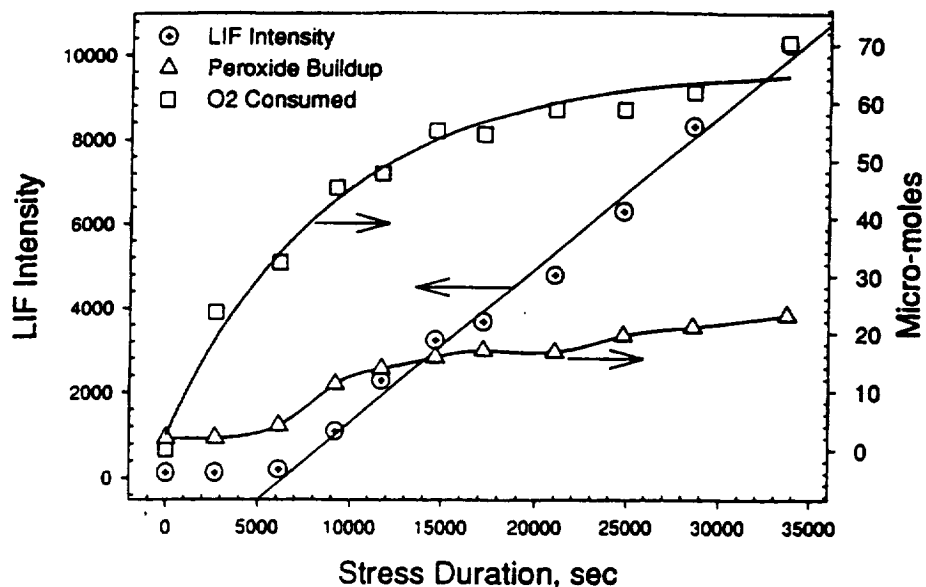
Figure 13. Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 150°C
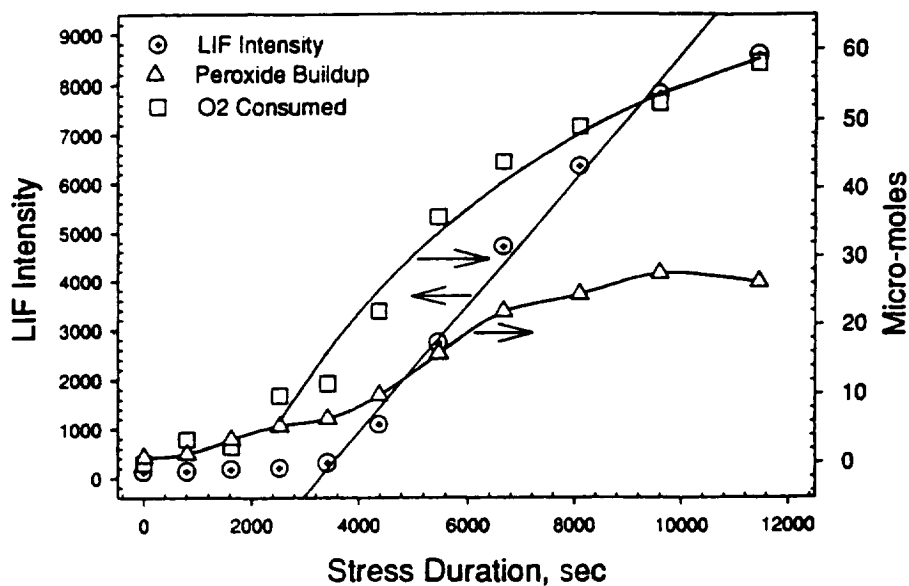
Figure 14. Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 160°C
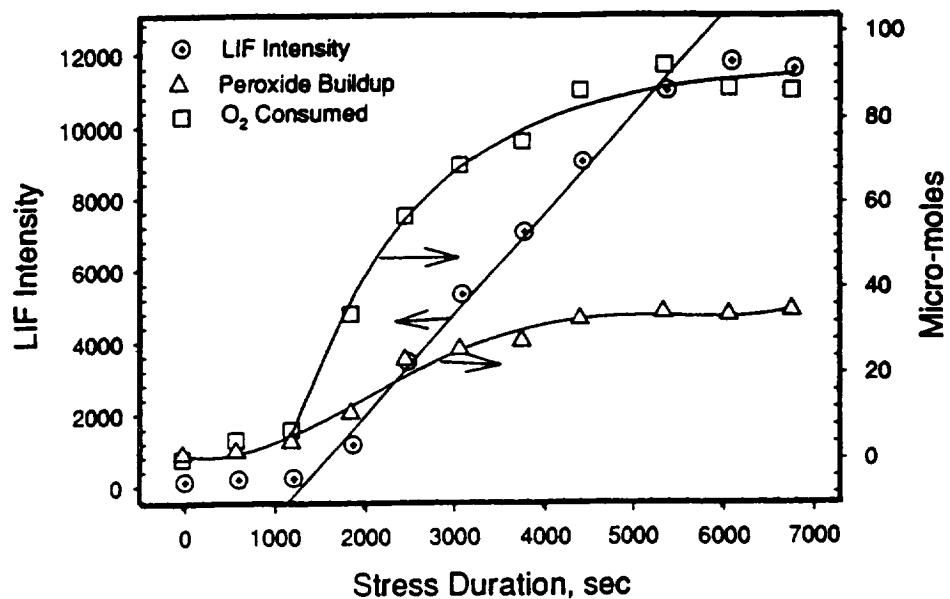
Figure 15. Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 170°C
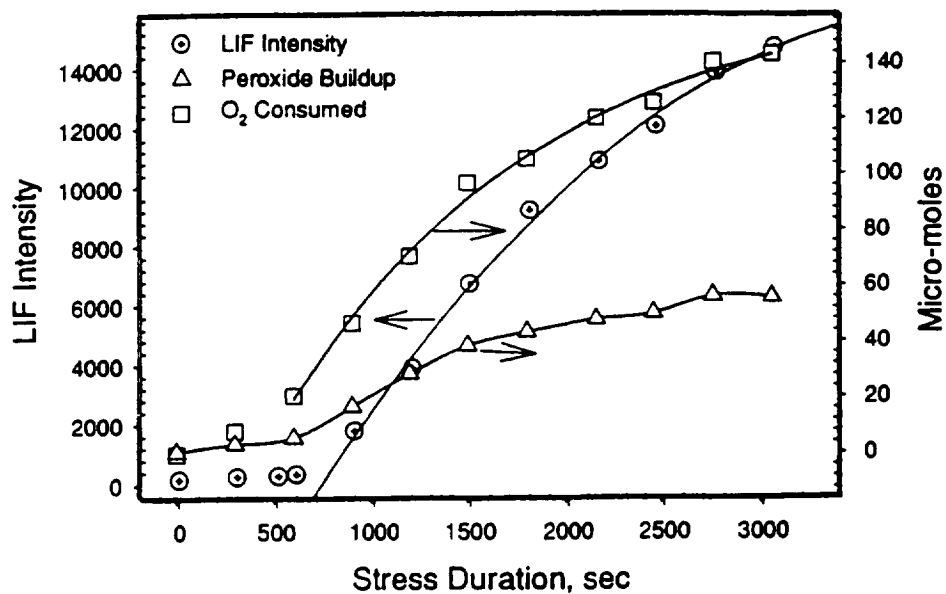
Figure 16. Time Dependence of Species Concentrations in JetA - Stressed in an Oxygen Atmosphere at 180°C

A calibration was not performed to determine the LIF response to deposit precursor. If the weight of deposit precursor could have been measured at some point, it would have been possible to determine a response factor with units such as mg of deposit precursor and microamp of LIF.

Figures 10-16 show that the autoxidation of Jet A has an induction period. The induction period is an initial stage of the autoxidation during which very little oxygen is consumed, and no hydroperoxide or deposit precursor is formed. The induction period is followed by a post-induction reaction during which hydroperoxide and deposit precursor start to build up, and the oxygen consumption rate sharply increases. Throughout the post-induction reaction, the deposit precursor builds up linearly, while oxygen consumption and hydroperoxide formation increase rapidly at first, taper off, then reach a plateau. It appears that the rate of deposit precursor formation is not strongly dependent on the oxygen concentration because it remains relatively constant over the course of the reaction.

The hydroperoxide seems to approach a steady-state concentration, and the rate of oxygen consumption slows to a snail's pace while the deposit precursor continues to grow. From the standpoint of oxygen consumption, the post-induction reaction seems to die out prematurely, because the rate of oxygen consumption becomes very low after only a fraction of the available oxygen is consumed. For example, in Figure 15 it appears as if the reaction has run out of oxygen at the 90 micro-mole level, when in fact the available oxygen at the start of the reaction was 383 micro-moles. This premature fall-off in the autoxidation rate suggests that something is formed early in the post-induction reaction that inhibits the process.

Figure 17 shows Arrhenius-type plots of the rate of deposit precursor formation during the induction period and the post-induction reaction. Since the Arrhenius plots are linear, it is concluded that the rate-controlling reactions in the autoxidation process remain the same throughout the 120 to 180°C range. A change in the slope, e.g., at 150°C, would have indicated a change in the mechanism of deposit precursor formation at that temperature.
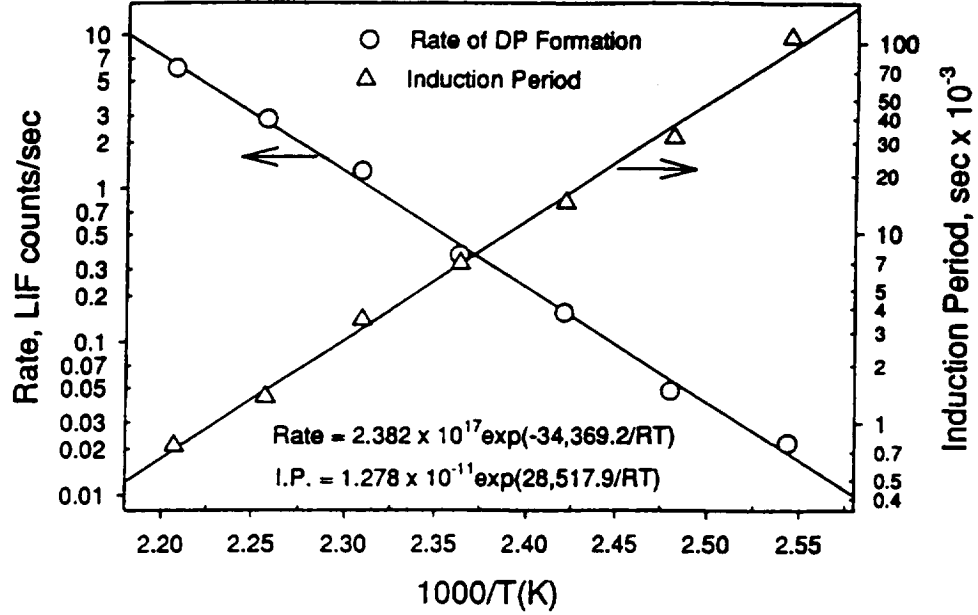
Figure 17. <u>Arrhenius Plots of the Induction Period and the Post-Induction Rate of Formation of Deposit Precursor</u>

The induction period, I.P., given in units of [seconds] is expressed as

$$I.P. = 1.278 x 10^{-11} \exp(28,517.9/RT) \qquad (2)$$

and the rate of deposit precursor formation, R_{dp} given in units of [LIF-intensity counts per second] is expressed as

$$R_{dp} = 2.382 x 10^{17} \exp(-34,369.2/RT) \qquad (3)$$

where R is the ideal gas constant in units of cal/mole-°K, and T is the absolute temperature.

C. High Temperature Predictions

Table 1 gives predicted induction periods (I.P.), rates of deposit precursor formation (R_{dp},) and estimates of the residence time (t_d) required to make deposits at various temperatures. These properties were calculated using Equations 2 and 3. The estimated residence time for deposition (t_d) was calculated from I.P. and R_{dp} assuming that the concentration of deposit precursor required to cause deposition was equivalent to a LIF intensity of 5000 microamps. At that concentration, a deposit film would form on the ampule wall after a few days.

The calculations in Table 1 show that the induction period determines the time when deposition begins. Once the induction period is over, the deposit precursor forms relatively quickly, so deposition takes place in a relatively short period, unless mass transport effects are rate-controlling. The trend shown in Table 1 helps predict the way deposits might be formed in a single-tube heat exchanger.

Table 1. Calculated Induction Periods, Rates of Deposit Precursor Formation, and Estimated Residence Times, t_d, for Deposit Formation in Jet A fuel.			
Temperature °F[°K]	I.P. (sec)	R_{dp} (Counts/sec)	t_d (sec)
400[477]	145.1	44.0	258.7
450[505]	27.8	322.3	43.3
500[533]	6.3	1,919.2	8.9
550[561]	1.7	9,577.5	2.2
600[589]	0.5	41,066.0	0.6

Flow experiments on Jet A fuel in a single-tube heat exchanger show that deposition occurs abruptly over a relatively short section of the tubing.[12] A stainless-steel single-tube heat exchanger of 0.4 cm I.D. and a 50 cm length was used in the experiments. The tube was resistance heated using an

arc-welder power supply. The initial fuel temperature upon entering the tube was about 250°F[394 K], and the flow rate was 10 mL/minute. The fuel heated up at a constant rate (dT/dx = constant) as it flowed through the tube. The Renold's number increased from 35 at the tube inlet to approximately 160 at the start of deposition. Deposition occurred abruptly over a 3 to 5 cm section of the tube. The position in the tube where the deposition started depended on the rate of heat input or fuel temperature gradient (dT/dx) in the tube.

Some results of the single-tube heat exchanger experiments are shown in Table 2. Temperatures along the length of the tube were measured with several thermocouples welded to the outside wall. The experiments were performed at low flow rates so there would be ample time for the fuel and tube wall temperatures to equilibrate. Fuel temperatures measured at the core of the flow were less than 10°K below the wall temperature.

Table 2. Results of Deposit Formation on Jet A Fuel in a Single Tube Heat Exchanger.					
Heat Input (watts)	dT/dx (°K/cm)	Flow Rate (cm³/sec)	Deposit Start Temperature (K)	Measured Deposit Start (cm)	Calculated Deposit Start (cm)
146	8.54	0.167	553	18.6	19.3
89	5.25	0.167	537	28.6	29.5
231	14.87	0.167	558	7.6	11.9
240	14.44	0.167	562	8.3	12.2
175	10.94	0.167	548	14.1	15.6

The calculated positions for the start of deposit were performed by numerically integrating Eqns. 2 and 3 over the temperature-time history of the flow in the tube. The calculations show that the induction period determines the start of deposition, and that deposits form rapidly over about one centimeter of tube length. Note that these calculations are based on Equations 2 and 3, determined for clay-filtered Jet A, which had a higher break-point than the Jet A used in the deposition experiments. In other words, the start of deposition in clay-filtered Jet A should have occurred later

than in the Jet A used in the deposition experiments.

The Fortran code, used to make the calculations (see Appendix A), makes some simplifying assumptions which may explain the good agreement. The linear flow rate in the tube was assumed constant, which if allowed to vary would have increased the calculated position of deposition. Equations 2 and 3 are based on data obtained using pure oxygen in the ampules, so the concentration of dissolved oxygen was about 5 times greater than the air-saturated Jet A used in the single tube heat exchanger experiment. The calculated position of deposition may have increased if the effect of oxygen concentration had been taken into account. Both effects, linear flow rate and oxygen concentration, tend to compensate for the increased break-point of the clay-filtered Jet A, so the good agreement in Table 2 may not be as fortuitous as orginally thought.

D. Coal Liquid Experiments

The experiments on the hydro-treated coal liquid fuel were performed at 150°C. Figures 18 and 19 show plots of the species concentration profiles over time for hydro-treated coal liquid and Jet A respectively. It is seen that the production of hydroperoxides and the amount of oxygen consumed in the coal liquid are about five times greater than in Jet A. There is no induction period in coal liquid autoxidation, and essentially all the oxygen is consumed while only about 20 percent is used in Jet A. Clearly, the coal liquid autoxidizes much more rapidly than Jet A. The absence of an induction period in the autoxidation of the coal liquid suggests that all the antioxidants were removed by the hydro-treatment.

The relative deposit precursor concentration increased in a linear way with time in the coal liquid, similar to Jet A. Deposit precursor formed more rapidly in the coal liquid than in Jet A. However, it appears that the yield of deposit precursor relative to oxygen consumption was much lower in the coal liquid than in Jet A. Figure 20 compares the ratios of deposit precursor to the amount of oxygen consumed in the coal liquid with that in Jet A. Jet A makes much more efficient use of oxygen in making deposit precursor than the coal liquid.
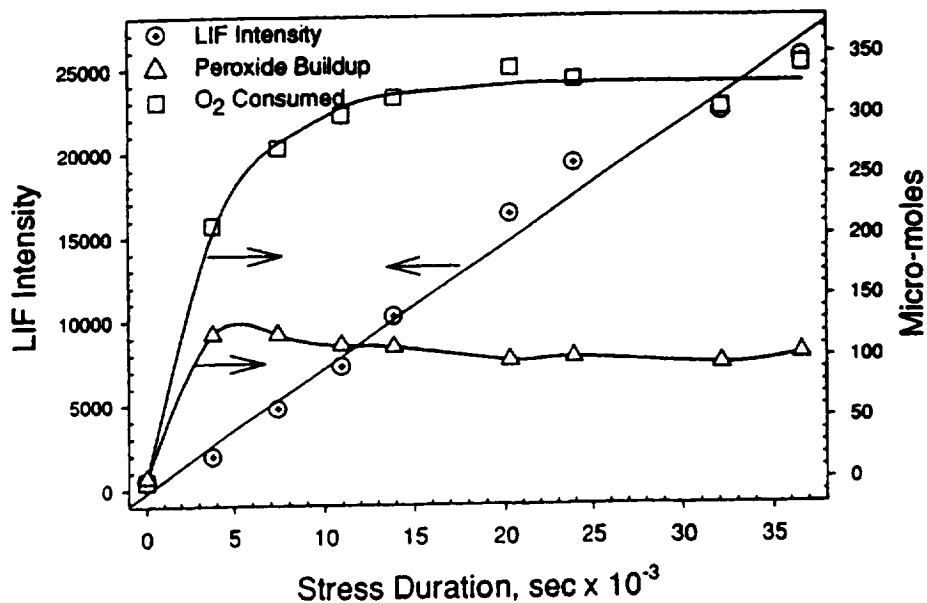
Figure 18. Time Dependence of Species Concentrations in Hydrotreated Coal Liquid - Stressed in an Oxygen Atmosphere at 150°C
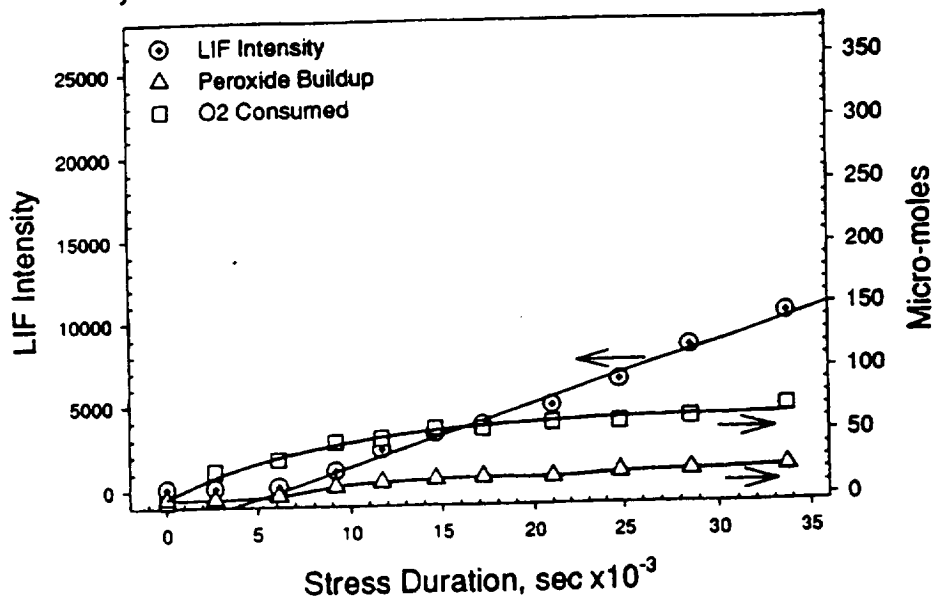
Figure 19. Time Dependence of Species Concentrations in Jet A- Stressed in an Oxygen Atmosphere at 150°C

Deposit Precursor Yield Based on O_2 Consumption
"Comparing Jet A with Hydrotreated Coal Liquid"
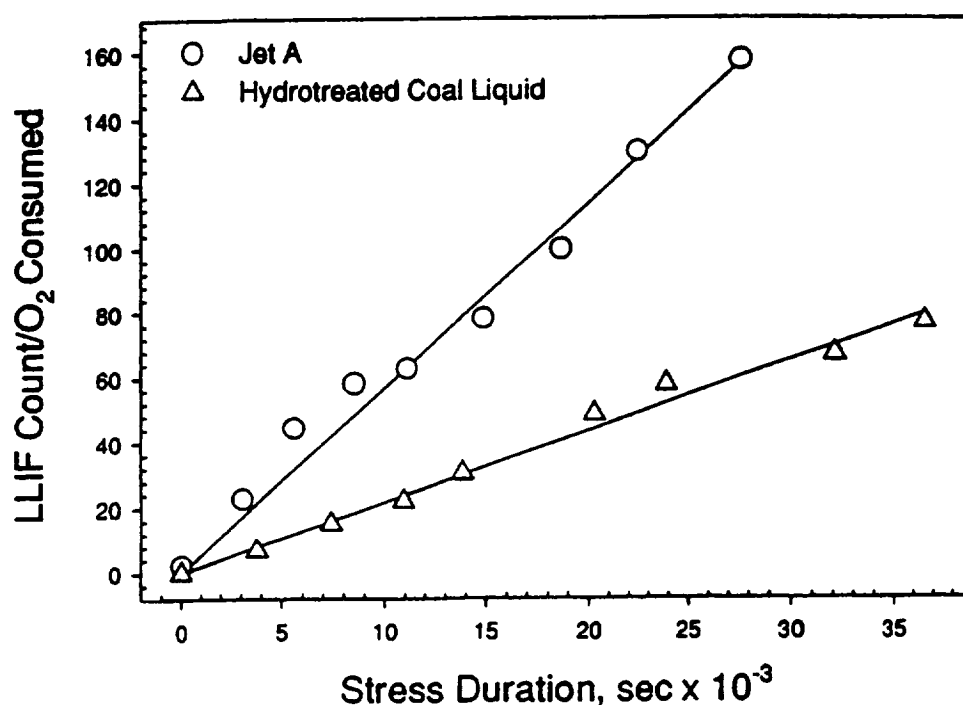
Figure 20. Yields of Deposit Precursor Relative to the Amount of Oxygen Consumed in Jet A and Hydrotreated Coal Liquid

It has been observed in thermal stability tests that fuels which oxidize rapidly tend to form less deposit than those that show resistance to oxidation. The amount of oxygen available in thermal stability tests, e.g., the JFTOT, is limited to that dissolved in the fuel. Since the dissolved oxygen is very small compared to the amount of oxygen available to the fuel in the ampules, the efficient use of oxygen in producing deposit precursor may have a greater influence in a standard thermal stability test.

It is important to note that, in comparing the coal liquid experiments with those of Jet A, it is assumed that the deposit precursors in both fuels have the same LIF response. In the above discussion, the question of LIF response to deposit precursor is very important. Unfortunately, the LIF response factors for the fuels were not measured in the present study. Determining LIF response

26

factors for deposit precursor is surely a subject for further study. It is uncertain how the response factor should be determined, because it appears to be dependent not just on the mass of deposit precursor, but also on the molecular weight and degree of polymerization. A previous study[7] showed that the LIF response to gums in fuels increased as the gums aged. The gums were aged in a solvent in the absence of oxygen. Since high molecular weight species tend to have greater absorption cross sections than lighter molecules, it seems that the increased fluorescence from aged gums is caused by increased agglomeration and cross linking of the higher molecular weight species. It is these high molecular weight species that tend to be least soluble and thus the most favorable deposit precursor candidates.

E. Mechanism

The autoxidation kinetics of Jet A and hydro-treated coal liquid were found to be significantly different. There was a substantial induction period in the autoxidation of Jet A and essentially none in the hydro-treated coal liquid. The induction period in Jet A is attributed to naturally occurring antioxidants in the fuel. The coal liquid had no induction period because the antioxidants, which may have been present originally, were removed by the hydro-treating process along with the sulfur and some of the aromatics.

The Jet A contained sulfur compounds, while the coal liquid was sulfur free. The post-induction reaction in Jet A started swiftly, then rapidly slowed. It appeared as if all the oxygen in the ampule had been consumed. In fact, only about 20 percent of the oxygen was consumed in Jet A, while the coal liquid consumed all the oxygen in the ampule much more rapidly. The Jet A results suggest that an intermediate species builds up in the early stages of the post-induction reaction which inhibits the autoxidation process. It is believed that sulfur causes the inhibiting species to form, because Kauffman[8] showed that sulfur compounds caused phenols to form in jet fuels. Phenols make excellent antioxidants and are known to inhibit the autoxidation of jet fuels.[13] It seems that phenols play an important role in the formation of deposits because both the infrared and LIF spectra of gums and deposits indicate a phenolic resin-like structure.

Free Radical Chemistry

The free radical mechanism for hydrocarbon autoxidation is well-founded, but it does not completely explain the anomalous relationship between the rate of autoxidation and the deposit-forming tendencies of jet fuels. Recall the work of Hardy, et al. [6], which showed a reciprocal relationship between the rate of autoxidation and the tendency to form deposits. The rational theory is that while free radical autoxidation is a prerequisite, deposits result from ionic-type reactions that require an acid catalyst. Strong acids are formed by the oxidation of sulfur compounds, whereas weaker acids are formed by the oxidation of aldehydes. Sulfur compounds form sulfonic acids[14], while aldehydes form relatively weak carboxylic acids. In the mechanism discussed below, it is proposed that acids catalyze the decomposition of benzylic hydroperoxides to phenols, which in turn react with aldehydes and polymerize into phenolic resins.

Autoxidation

The autoxidation of jet fuels is based on a free-radical mechanism[15-19], which includes the familiar radical initiation, propagation, chain branching, chain breaking, and termination reaction steps. While a relatively complex sequence of reaction steps is conceivable in the overall autoxidation of hydrocarbon fuels, the formation of hydroperoxides (ROOH) and the role of antioxidant inhibitors (AH) may be described succinctly by the following mechanism:

Initiation	$RH + O_2 = R\bullet + HO_2\bullet$	(1)
	$ROOH = RO\bullet + OH\bullet$	(2)
Radical exchange	$OH\bullet + RH = HOH + R\bullet$	(3)
	$RH + HO_2\bullet = R\bullet + H_2O_2$	(4)
Aldehyde formation	$R'CH_2\bullet + O_2 = R'CHO + HO_2\bullet$	(5)
Chain propagation	$R\bullet + O_2 = RO_2\bullet$	(6)
	$RO_2\bullet + RH = ROOH + R\bullet$	(7)

Chain branching	$H_2O_2 = \bullet OH + \bullet OH$	(8)
	$ROOH = RO\bullet + OH\bullet$	(2)
Chain breaking	$RO_2\bullet + AH = ROOH + A\bullet$	(9)
Radical termination	$RO_2\bullet + RO_2\bullet = Products$	(10)
	$A\bullet + A\bullet = A_2$	(11)
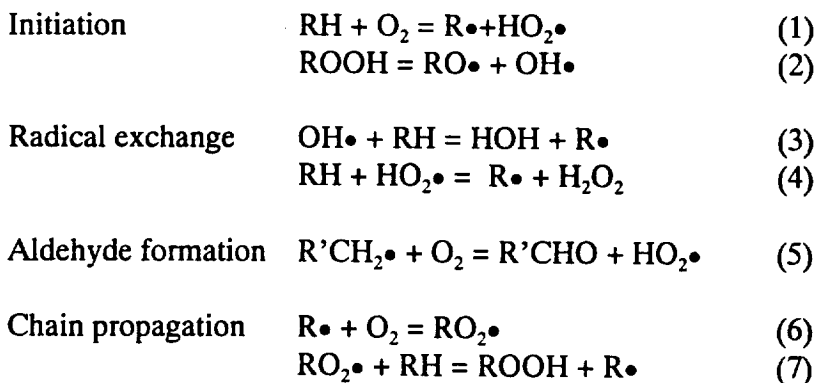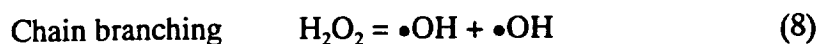
where $R\bullet$, $RO\bullet$, $OH\bullet$, $HO_2\bullet$, $RO_2\bullet$ and $A\bullet$ are free radicals. RH represents the fuel hydrocarbons, ROOH is the hydroperoxide, and $A\bullet$ is a relatively stable radical that forms when antioxidants (AH) neutralize free radicals *via* Reaction 9. In the absence of antioxidants, free radicals are terminated principally by the recombination of $RO_2\bullet$ radicals in Reaction 10.

Hydroperoxide decomposition in Reaction 2 plays an important role in both the radical initiation [13] and chain branching. Since fuels almost always contain at least a trace of ROOH, Reaction 1 often seems to be of little importance in free radical initiation. However, when ROOH formation is strongly inhibited, as it appears to be in the autoxidation of Jet A (see section B), Reaction 1 may also be a significant contributer to free radical production.

It is proposed in the present study that aldehydes and benzylic hydroperoxides formed by the autoxidation process are the principle ingredients for deposit formation. This will be revealed in the forthcoming discussion.

Antioxidant Effects

Autoxidation in jet fuels usually proceeds in two steps, i.e., the induction period and the post-induction reaction. The induction period is characterized by a slow or near-zero rate of oxygen consumption with little or no formation of hydroperoxides or deposit precursor. During the post-induction reaction, oxygen is consumed, so hydroperoxides and deposit precursor build up rapidly.

Induction periods occur frequently in the autoxidation of jet fuels. However, some jet fuels, and more often pure hydrocarbons, exhibit little or no induction period. The induction period is believed

to be caused by naturally occurring antioxidants in the fuel. Experiments on adding antioxidants to fuels have shown that the induction period is extended roughly in proportion to the amount added.[13] In the above mechanism, Reaction 9 inhibits autoxidation by exchanging reactive free radicals with less reactive radicals. In this way, the antioxidants prevent the build-up of the reactive free radicals and maintain a near zero oxidation rate. Antioxidants are consumed during the induction period and have no effect on the rate of the post-induction reaction unless they are later formed by an alternative reaction mechanism. The most common antioxidants are substituted phenols, which are found in jet fuels [9] and are manufactured commercially to increase fuel stability.

Kauffman[9] found that sulfur compounds promoted the formation of phenols in jet fuels. More recently, Mushrush, et al.[14] showed that sulfonic acids are formed in the autoxidation of jet fuels that contain sulfur compounds. They found that only specific sulfur compounds, such as mercaptans or thiols, oxidized to form sulfonic acids. Based on their results shown in Figure 21, they concluded that the sulfur compounds acted as antioxidants, which reduced hydroperoxide formation in jet fuels.
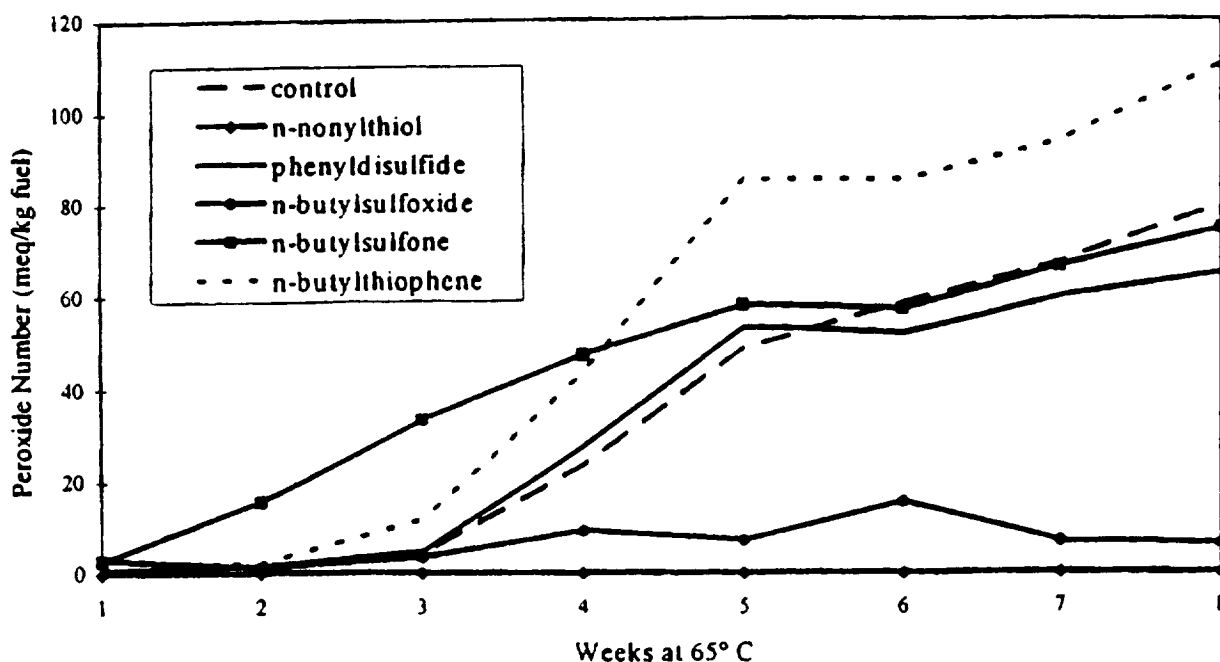
Figure 21. Peroxidation of Shale JP-5 in the Presence of Organosulfur Compound Dopants [14]

30

Figure 21 shows that nonyl thiol, which oxidized to the sulfonic acid, resulted in the lowest rate of hydroperoxide formation. It is well known that benzylic hydroperoxides, which appear to form abundantly in jet fuels, decompose into phenols, if an acid catalyst is present. The classic example of the reaction is the synthesis of phenol and acetone from cumene hydroperoxide [18] as shown below.
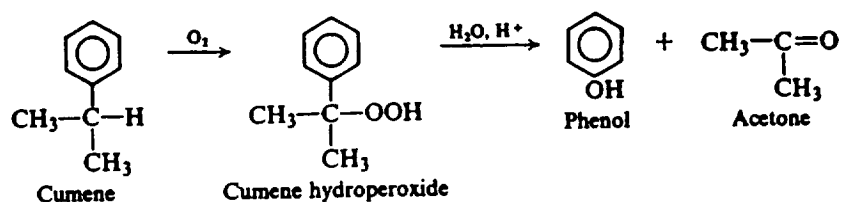
In jet fuel autoxidation, it is very probable that alkyl substituted phenols form by a similar acid catalyzed decomposition of benzylic hydroperoxides. Since alkyl substituted phenols are potent antioxidants, they inhibit free radical formation and supress any future formation of hydroperoxides. Therefore, it is contended that, while nonyl thiol acted as an antioxidant, the main cause of hydroperoxide supression in Figure 21 was the formation phenolic antioxidants. Nonyl thiol was the only compound they tested that strongly suppressed the formation of hydroperoxides and produced significant amounts of sufonic acid.

Deposit Formation

In light of the similarity between the LIF and infrared spectra of deposit precursors and phenolic resins, it is proposed that deposit precursors are formed by the polymerization of phenols and aldehydes. The reaction is similar to the way in which phenolic resins are produced by the reaction of phenol with formaldehyde.[20] The reaction of phenol with formaldehyde, as shown below, requires an acid or base catalyst, so it stands to reason that sulfonic acids also play an important role in the formation of deposits.

o-Hydroxymethylphenol
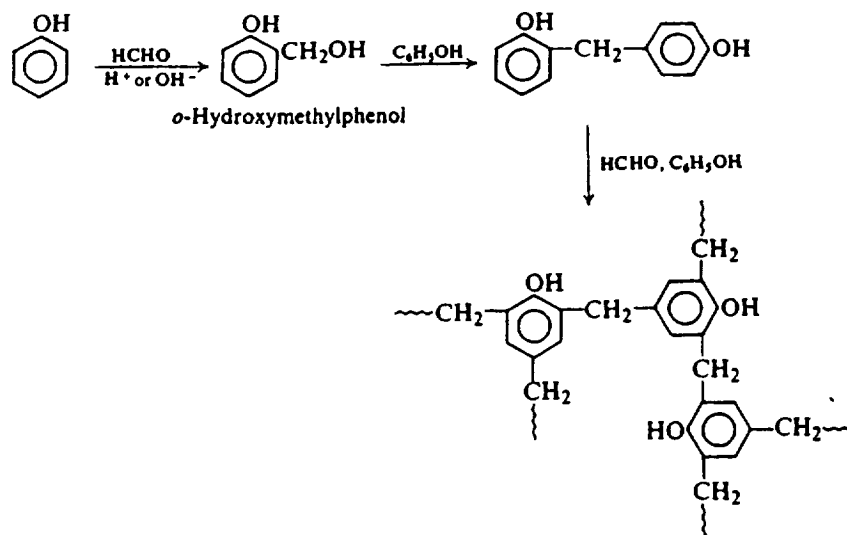
Other phenols and other aldehydes (e.g., furfural, acetaldehyde, benzaldehyde) are used for commercial production of resins; the reactions involved are similar to those above.[21] Similar reactions are expected to occur between the phenols and aldehydes that form in the autoxidation of jet fuels.

Deposits have a complex composition, consisting of carbon, hydrogen, oxygen, sulfur and nitrogen. They seem to be composed of everything that is insoluble in the stressed fuel. However, the key ingredient is the phenolic resin because it serves as the glue that holds the deposit together and gives it its adhesive properties. Sulfur and nitrogen appear to be entrapped in the deposit as insoluble salts formed by acid-base reactions.

VII. CONCLUSIONS

Laser induced fluorescence spectroscopy was found to be a viable kinetic tool for following the build up of deposit precursors in jet fuels. The following expressions for the the induction period, I.P., and the rate of deposit precursor formation, R_{dp},

$$I.P. = 1.278x10^{-11}\exp(28,517.9/RT)$$

$$R_{dp} = 2.382x10^{17}\exp(-34,369.2/RT)$$

were determined from deposit precursor concentration versus time data in the 120 to 180°C range. A simplified model incorporating the expressions for I.P. and R_{dp} provided a reasonable prediction of the onset of deposition in a relatively high-temperature single-tube heat exchanger experiment. The model demonstrated that the mechanism proposed to explain the results in the 120 to 180°C range was also applicable at temperatures above 200°C.

Deposit precursors in jet fuels are formed from aromatic compounds that contain benzylic hydrogens. Deposits were detected in cumene, Jet A and coal liquid, but were not observed in paraffins such as tetradecane. The LIF spectra of deposit precursors in Jet A and a phenolic resin dissolved in TAM were similar. Since sulfur compounds are known to increase both the formation of phenols[9] and the potential for deposits[22], it is concluded that they oxidize to sulfonic acids which catalyze the decomposition of benzylic hydroperoxides into phenols. Phenols then react with aldehydes and polymerize into phenolic resins similar to Bakelite. Phenols also have antioxidant properties which inhibit the free radical mechanism and slow down the rate of oxygen consumption. It is concluded that the formation of phenols slows down, and nearly stops, hydroperoxide formation and oxygen consumption in Jet A fuel. In fuels that are sulfur free, such as the coal liquid, oxygen is consumed completely and at a much greater rate than in Jet A.

The proposed mechanism explains the anomalous relationship between oxidation rate and deposit formation observed by Hardy, et al.[6] While phenols inhibit the free radical oxidation, they nevertheless react with aldehydes to form deposits, so fuels that have lower thermal stability tend to oxidize more slowly. On the other hand, fuels that do not form phenols have a much higher rate of oxidation and a lower deposit forming potential. The mechanism proposed in this study suggests that an acid-buffering type additive, such as an amine carbonate, would arrest the formation of deposits in jet fuels.

VIII. SUGGESTIONS FOR FURTHER STUDY

The present study has led to a theory of deposit formation that could greatly aid the development of fuel additives. The Betz additive, which is currently used to suppress deposit formation at high temperatures, contains a surfactant that degrades the efficiencies of the filter coalescers. A better understanding of the mechanism of deposit formation may lead to a new class of fuel additives, e.g., acid buffers, that do not have surfactant characteristics. In the present study, only a limited number of parameters were investigated. The theory and experiment were consistent, but the effects of fuel composition, acid catalysis, and higher temperatures need to be examined more comprehensively before the theory can be validated.

Experiments similar to those performed on Jet A need to be done on other fuels of different composition and with different deposit forming tendencies. Fuels of different deposit forming tendencies need to be run in the single-tube heat exchanger to determine the position, time, and temperature where deposits begin to form. Kinetic experiments need to be performed in the static flow reactor to determine rate expressions for the induction period, rate of deposit precursor formation and oxygen consumption. The rate expressions should then be used to predict the single-tube heat exchanger results to validate their effectiveness in models for fuel system design.

To further understand the mechanism, it is necessary to determine the effects of sulfur and sulfonic acids on the kinetics of deposit precursor formation. Tests should be conducted on pure alkyl benzenes such as cumene. Cumene contains no sulfur and forms deposit precursor very inefficiently. The effect of acid catalysis on the formation of deposit precursor can be tested by doping cumene with sulfonic acids. The effects of sulfonic acid on the deposit forming tendencies of fuels needs further study. The base fuel in these experiments should be sulfur free, since only traces of sulfonic acid may have a significant effect on deposition. A surrogate fuel blend of dodecane, and cumene with varying amounts of a thiol type sulfur compound, would serve to demonstrate the proposed theory of deposit formation.

Sulfur could be removed from a fuel to see if the kinetics of oxidation and deposit precursor formation changes significantly. The Jet A used in the present study could be lightly hydro-treated to remove the sulfur. Kinetic experiments similar to those performed on the Jet A in the present study would then be repeated on the hydro-treated Jet A. Without sulfur, the Jet A should consume oxygen more quickly and give a lower yield of deposit precursor, and its deposit forming tendency in the single tube heat exchanger should be reduced. Rate expressions for the induction period, rate of deposit precursor formation and oxygen consumption for the hydro-treated Jet A could then be used to predict deposit formation in a single-tube heat exchanger.

Higher Temperature Measurements

Figure 22 illustrates the concept of a flow reactor proposed for measuring kinetic rates at temperatures above 180°C. Since fuels need to be isothermally stressed, the time required to reach the test temperature must be short relative to the stress duration. In Figure 22, the test fuel is pumped through a preheating tube made of 0.062 inch I.D. electro-polished nickel or silico-steel tubing. Calculations, as well as measurements, have shown that the fuel will reach the test temperature in less than 10 seconds if the preheater tube is about 30 cm in length and the flow rate is similar to that used in a JFTOT. Once the fuel is raised to the test temperature in the pre-heater tube, it flows at constant temperature through a larger-diameter tube where it has a relatively long residence time. From there it is quickly cooled and passed to the optical cell where it is radiated with a 488 nm laser light. A fiber optic probe, normal to the laser beam, collects fluorescent light from deposit precursor and delivers it to a monochromator. Fuel samples will be extracted from the flow for analysis of oxygen, hydroperoxides, and phenols. The flow reactor will allow kinetic measurements up to 250°C. The flow reactor will be similar to the "Near Isothermal Flowing Test Rig" used by Jones and Balster,[23] but should provide a more isothermal reaction environment.

Power
Supply

Stressed
Fuel

Temperature
Controller

Monochromator

Heat Block

Fiber Optic

Cartridge
Heater

6 mm I.D. Tubing

Flow Through
Optical Cell

Laser

1.5 mm I.D. Tubing

Cooling
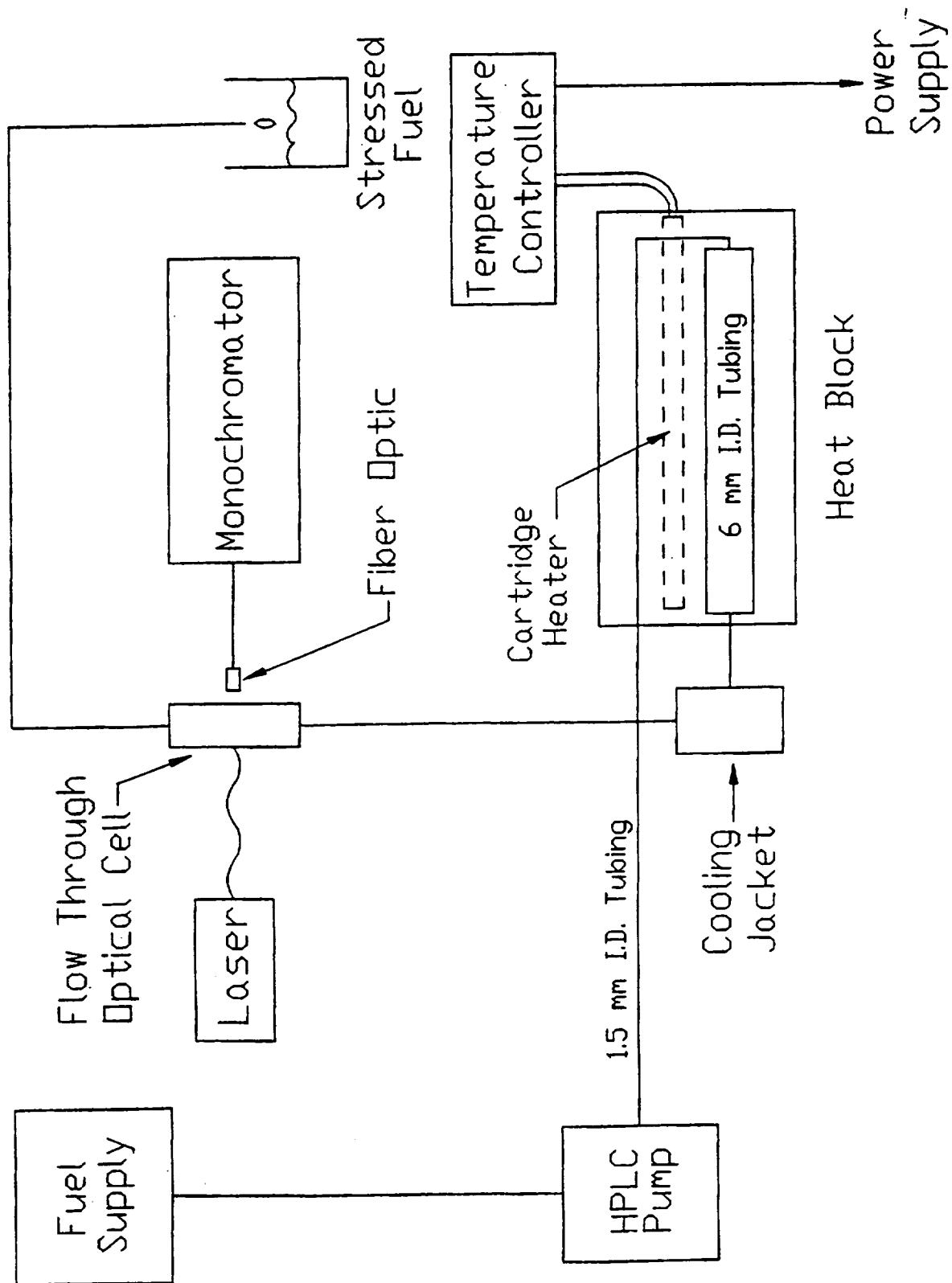Jacket

Fuel
Supply

HPLC
Pump

Figure 22. High Temperature Flow Reactor for Stressing Jet Fuels

IX. LIST OF REFERENCES

1. Roquemore, W.M., Pearce, J.A., Harrison, W.E., III, Krazinski, J.L. and Vanka, S.P., "Fouling in Jet Fuels: A New Approach," Symposium on the Structure of Future Jet Fuels II, Presented before the Division of Petroleum Chemistry, Inc., American Chemical Society, Miami Beach Meeting, September 10-15, 1989.

2. Krazinski, J.L., Vanka, S.P., Pearce, J.A. and Roquemore, W.M., "A Computational Fluid Dynamics and Chemistry Model for Jet Fuel Thermal Stability," ASME Paper No. 90-GT-99.

3. Mayo, F.R., Buttrill, S.E., Jr., Lan, B.Y., St. John, G.A., and Dulin, D., "Oxidation and Formation of Deposit Precursors in Hydrocarbon Fuels," Preprints, Division of Fuel Chem.27(2), 76, (1982).

4. Mayo, F.R. and Lan, B.Y., "Gum and Deposit Formation from Jet Turbine and Diesel Fuels," presented before Division of Petroleum Chemistry, Inc. American Chemical Society, Washington, D.C. meeting, 28 August-2 September (1983).

5. Mayo, F.R. and Lan, B.Y., "Gum and Deposit Formation From Jet Turbine and Diesel Fuels at 130°C," Ind. Eng. Chem. Prod. Res. Dev.25, p.333 (1986).

6. Hardy, D.R., Beal, E.J. and Burnett, J.C. "Title", Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, US Department of Energy, Washington, D.C. (1991) p. 260

7. Naegeli, D.W. and Hill, R.H., "Laser Induced Fluorescence Detection of Gums in Jet Fuels," Final Report, SwRI 03-3685, February 10, 1992.

8. Egerton, A.C., Everett, A.J., Minkoff, G.J., Rudrakanchana, S., and Salooja, K.C., "The Analysis of Combustion Products: I. Some Improvements in the Methods of Analysis of Peroxides," Analytica Chimica Acta, Vol. 10, p. 422 (1954).

9. Kauffman, R.E., "The Effects of Different Sulfur Compounds on Jet Fuel Oxidation and Deposition," ASME Paper No. 95-GT-222, Presented at the International Gas Turbine and Aeroengine Congress & Exposition, Houston, Texas - June 5-8 (1995).

10. Kauffman, R.E., University of Dayton Research Institute, Dayton, Ohio, Private Communication, July 13, 1995.

11. Power, A.J., "Accelerated Oxidation of Diesel Distillate," Fuel 65, 133 (1986).

12. Moses, C.A., NASA Proposal and Technical Report. (1996).

13. Fodor, G.E., Naegeli, D.W. and Turner, L.M., "Inhibition of Peroxide Formation by Hindered Phenols in Jet Fuels," To be presented at the 203rd ACS National Meeting, Division of Petroleum Chemistry, Symposium on Structure of Jet Fuels, San Francisco, CA, April 5-10 (1992).

14. Mushrush, G.W., Beal, E.J., Slone, E., and Hardy, D.R., "Reaction of Organosulfur Compounds with Naturally Occurring Peroxides in Jet Fuel," Energy & Fuels 10, 504 (1996).

15. Fodor, G.E.; Naegeli, D.W.; Kohl, K.B., "Peroxide Formation in Jet Fuels", Energy & Fuels, 1988, 2, 729-734.

16. Frost, A.A.; Pearson, R.G., Kinetics and Mechanism; Wiley: New York, 1961, pp. 248-251.

17. Walling, C., Free Radicals in Solution; Wiley: New York, 1957, Chapter 9.

18 Hine, J., Physical Organic Chemistry; McGraw-Hill: New York, 1956.

19. Nixon, A.C. In Autoxidation and Antioxidants; Lundberg, W.O., Ed.; Interscience: New York, London, 1962; Chapter 17.

20. Morrison, R.T., and Boyd, R.N., Organic Chemistry, 2nd Ed., Allyn and Bacon, Inc. Boston (1966).

21. Royals, E.E., **Advanced Organic Chemistry**, p. 504, Prentice-Hall Chemistry Series, Englewood Cliffs, New Jersey, Copyright 1954, 5th printing (1961).

22. Taylor, W.F., and Wallace, T.J., "Kinetics of Deposit Formation from Hydrocarbons: Effect of Trace Sulfur Compounds," I&EC 7(3), p.198 (Sept. 1968).

23. Jones, E.G. and Balster, W.J., "Surface Fouling in Aviation Fuel: Short- vs Long- Term Isothermal Tests," Energy and Fuels 9, 610-615 (1995).

APPENDIX A
Program Deposit

PROGRAM DEPOSIT

The program "DEPOSIT" calculates the position, time, and temperature where fuel deposit begins to form in a single-tube heat exchanger. The calculation is based on kinetically determined expressions for the induction period and rate coefficient for the formation of deposit precursor in JetA fuel. The induction period, I.P. and Rate are expressed as

$$IP = 1.278E\text{-}11*EXP(28517.9/(R*T))$$

$$Rate = 2.382E\text{+}17*EXP(-34369.2/(R*T))$$

where R is the ideal gas constant and T is the absolute temperature.
Assumptions:

1. The fuel temperature and tube wall temperature are equal.
2. Fuel density does not change with temperature.
3. The induction period is proportional to the antioxidant concentration in the fuel. When antioxidant is depleted, the induction period is over.
4. The chemical kinetics of deposit precursor formation is the rate controlling step in deposition. Mass transport and adherence of deposits to the walls is assumed to be fast.

Definitions:

pi = 3.14156
x = position (cm) in the tube starting from zero.
time = time in seconds
F = fraction of antioxidant consumed during induction period.
DP = concentration of deposit precursor in milliamps of detector current.
TI = initial fuel temperature at x = 0 in degrees K.
Q = flow rate in mL/minute.
D = inside diameter of single-tube heat exchanger in cm.
G = temperature gradient, dT/dx.
dx = position increment: dx = 0.0001 cm small enough.
dt = time increment in seconds.
v = linear flow velocity in cm/sec.

  REAL R, TI, Q, D, G, x, dx, time, dt, v, F, DP, pi

  R = 1.987
  pi = 3.14156
  x = 0.0
  time = 0.0
  F = 0.0

41

```
     DP = 0.0
INPUT INITIAL TEMPERATURE, FLOW RATE, TUBE I.D. AND dT/dx

     WRITE(6,*) 'ENTER INITIAL TEMPERATURE (K):'
     READ(5,*) TI
     WRITE(6,*) 'ENTER FLOW RATE (mL/min):'
     READ(5,*) Q
     WRITE(6,*) 'ENTER TUBE I.D.(cm):'
     READ(5,*) D
     WRITE(6,*) 'ENTER dT/dx (degrees K/sec):'
     READ(5,*) G
     WRITE(6,*) 'ENTER dx (cm):'
     READ(5,*) dx

     Q = Q/60
     T = TI
   LOOP
2  x = x + dx
     T = T + G*dx
     v = Q/(pi*(D/2)**2)
     dt = dx/v
     time = time + dt
     F = F + dt/(1.278E-11*EXP(28517.9/(R*T)))
     IF(F.GE. 1.00) go to 5
     go to 2
5 Continue
     write(6,*) '    position  Induction time  Temperature (K)'
     write(6,*) x, time, T
   LOOP
6  x = x + dx
     T = T + G*dx
     v = Q/(pi*(D/2)**2)
     dt = dx/v
     time = time + dt
     DP = DP + 2.382E+17*EXP(-34369.2/(R*T))*dt
     IF(DP .GE. 5000.0) go to 7

     go to 6
7  continue
     write(6,*) '    position  total time  Temperature (K)'
     write(6,*) x, time, T
     end
```

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 1997	Final Contractor Report

4. TITLE AND SUBTITLE

Thermal Stability of Jet Fuels: Kinetics of Forming Deposit Precursors

6. AUTHOR(S)

David W. Naegeli

5. FUNDING NUMBERS

WU–538–06–12
C–NAG3–1739

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
P.O. Drawer 28510
San Antonio, Texas

8. PERFORMING ORGANIZATION REPORT NUMBER

E–10720

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA CR–202340

11. SUPPLEMENTARY NOTES

Project Manager, C.J. Marek, Turbomachinery and Propulsion Systems Division, NASA Lewis Research Center, organization code 5830, (216) 433–3584.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 07

This publication is available from the NASA Center for AeroSpace Information, (301) 621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The focus of this study was on the autoxidation kinetics of deposit precursor formation in jet fuels. The objectives were (1) to demonstrate that laser-induced fluorescence is a viable kinetic tool for measuring rates of deposit precursor formation in jet fuels, (2) to determine global rate expressions for the formation of thermal deposit precursors in jet fuels, and (3) to better understand the chemical mechanism of thermal stability. The fuels were isothermally stressed in small glass ampules in the 120 to 180 °C range. Concentrations of deposit precursor, hydroperoxide and oxygen consumption were measured over time in the thermally stressed fuels. Deposit precursors were measured using laser-induced fluorescence (LIF), hydroperoxides using a spectrophotometric technique, and oxygen consumption by the pressure loss in the ampule. The expressions, $I.P. = 1.278 \times 10^{-11} \exp(28,517.9/RT)$ and $R_{dp} = 2.382 \times 10^{17} \exp(-34,369.2/RT)$ for the induction period, I.P. and rate of deposit precursor formation, R_{dp}, were determined for Jet A fuel. The results of the study support a new theory of deposit formation in jet fuels, which suggest that acid catalyzed ionic reactions compete with free radical reactions to form deposit precursors. The results indicate that deposit precursors form only when aromatics are present in the fuel. Traces of sulfur reduce the rate of autoxidation but increase the yield of deposit precursor. Free radical chemistry is responsible for hydroperoxide formation and the oxidation of sulfur compounds to sulfonic acids. Phenols are then formed by the acid catalyzed decomposition of benzylic hydroperoxides, and deposit precursors are produced by the reaction of phenols with aldehydes, which forms a polymer similar to Bakelite. Deposit precursors appear to have a phenolic resin-like structure because the LIF spectra of the deposit precursors were similar to that of phenolic resin dissolved in TAM.

14. SUBJECT TERMS

Laser diagnostics; Jet–A; Coking; Kinetics

15. NUMBER OF PAGES

48

16. PRICE CODE

A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102