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**THE EFFECT OF COPPER, MDA, AND ACCELERATED AGING ON JET FUEL
THERMAL STABILITY AS MEASURED BY THE GRAVIMETRIC JFTOT**

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ABSTRACT

Thermally unstable jet fuels pose operational problems. In order to adequately identify such fuels, factors that realistically impact on thermal stability were examined. Evaluation was based on a quantitative method of measuring thermal stability, viz., NRL's recently developed gravimetric JFTOT. This method gives a quantitative measurement of both the strip deposit and filterables formed. The pertinent factors examined, included the individual and interactive effects of: soluble copper, MDA (metal deactivator), and aging. The latter was accelerated to simulate field conditions of approximately six months aging at ambient temperature and pressure. The results indicate that the individual and interactive effects of copper, MDA, and accelerated aging appear to be fuel dependent. Based on the results, the three test fuels examined (one JP-8 and two JP-5s) were categorized as exhibiting very good, typical, and poor thermal stabilities, respectively. For both the very good and poor thermal stability fuels, the effect of copper in conjunction with accelerated aging did not significantly increase the total thermal deposits of the neat fuels. In contrast, for the typical thermal stability fuel, the combined effects of copper and accelerated aging, did. Furthermore, the addition of MDA *prior* to aging of the copper-doped, typical stability fuel significantly counteracted the adverse effect of copper and aging. A similar beneficial effect of MDA was not observed for the poor stability fuel. These results focus on the compositional differences among fuels and the need to elucidate these differences (physical and chemical) for a better understanding and prediction of their performance.

Introduction

The deposits formed from jet fuels of poor thermal stability pose operational problems. These problems, which date back to the mid-1950s include: clogging of the injector nozzles, a decrease in the efficiency of the heat exchangers, and malfunction of the fuel metering controls.^{1a} However, although current commercial and military jet fuels usually exceed specification thermal stability requirements, intermittent incidents of fuels

of poorer thermal stability have continued to the present.² This problem is further exacerbated by the higher temperatures of current production engines - a consequence of improving efficiency² and increasing power demands.

To adequately identify current and future fuels of marginal to poor thermal stability, it is important to: (1) evaluate factors that realistically impact on thermal stability and (2) quantify the insolubles formed. Thermal stability was determined using the Naval Research Laboratory's (NRL) recently developed Gravimetric JFTOT,³ which gives a quantitative measurement of both the strip deposit and the filterables formed. Its operating conditions are similar to the current ASTM test method for determining the thermal oxidation stability of aviation fuels, viz., the Jet Fuel Oxidation Tester (JFTOT: ASTM D3241). Disadvantages of ASTM D3241 include both its criteria for assessing thermal deposits. For example, the amount of heater tube thermal deposit is based on a qualitative evaluation of the discoloration of a metal tube; furthermore, efforts to quantify heater tube thermal deposits suffer drawbacks.³ The other JFTOT criterion, a filter pressure drop limit of 3.3 kPa (25mm Hg), is not a direct measure of the amount of filterables, nor a sensitive enough measure.

The pertinent factors examined include both the individual and interactive effects of the following:

1) *soluble copper at approximately 400 ppb maximum concentration*. Dissolved copper has been found to be the most reactive of those metals that catalyze fuel oxidation,⁴⁻⁶ hence its examination. Sources of copper contamination in fuels include: a) nickel-copper alloys used in the fuel piping systems of U.S. aircraft carriers and air capable ships (ships that carry helicopters);^{7,8} and b) in the refinery copper sweetening process.⁹ The maximum concentration employed reflects the level of contamination found in typical field samples taken from aircraft carriers at the point of aircraft fueling.

2) *MDA (metal deactivator: N,N'-disalicylidene-1,2-propane diamine) at 5.8 ppm (w/v) concentration*. Its use as a metal deactivator for counteracting the catalytic effect of copper in gasoline was reported by Pedersen⁵ in 1949. Currently, this additive is approved for use in both civil and military fuels. The 5.8 ppm concentration employed is the same as the

level specified in the military specification, MIL-T-5624N, for JP-4 and JP-5 fuels (5.8 mg/L). The ASTM specification level for aviation turbine fuels is a maximum of 5.7mg/L.

3) *aging* - this was accelerated to simulate realistic field conditions, viz., approximately six months aging at ambient temperature and pressure.

Although the roles of copper and MDA on fuel thermal stability have been studied systematically and extensively,^{1b,10a} adequate quantification of the data, i.e., based on the weights of the deposits (strip and filterables) has not - hence the significance of this study.

Experimental Section

Materials.

Fuels: Of the three fuels examined, fuel A is a hydrotreated Jet A-1 containing JP-8 additives; and, fuels B and C are JP-5s. Both the accelerated aged and the non-aged fuels were filtered through two nylon filters (0.8 micron porosity; 47mm diameter), before testing. Otherwise, no additional purifications were performed.

Copper II ethylacetoacetate (Eastman Kodak) was used as received without further purification. The concentrations levels employed were generally 400 ppb copper, although smaller levels (approx. 100 ppb) were also used (*see* Tables). The amount needed was generally weighed to the nearest micro gram. It was added in powder form (to obviate the introduction of a solvent to the fuel) and the solution well mixed. Addition to the fuel was made just prior to conducting the test to minimize possible losses to the walls of the container on standing.

N,N'-salicyclidene-1,2-propane diamine commonly known as *MDA* (Pfalz and Bauer) is sold under the trade name, Du Pont DMD No.2. It, likewise, was used as received without further purification and was added as a powder. Concentration levels examined include 1 and 5.8ppm (*see* Tables).

Stainless steel strips, grade 302, (approximately 7cm long and 0.5cm wide) were cut from 0.025mm thickness shimstock (Lyon industries). They were pre-cleaned by immersion in trisolvant (equi-volumes of toluene, acetone, and methanol), dried (70 °C/30 min), cooled, and weighed before use.

Filters used were MAGNA nylon membranes of 0.8 micron porosity. Depending on the amount of filterables, the filter sizes used were 13mm or 47mm diameter (*see* below). Two filters were used for each filtration, including the test and control filters.

Weighings: Both the stainless steel strips and 13mm nylon filters were weighed to the nearest micro gram using a Cahn micro balance (model 29). In cases of large amount of deposits, often noted by cloudiness of the effluent, a larger filter size (47mm) was employed and weighed to the nearest 0.1mg. For correction purposes, a control filter was also employed. Averages of 3 weighings were employed in all cases.

Aging. This was accelerated using the Low Pressure Reactor (LPR) developed at the Naval Research Laboratory (ASTM D5304-92). The conditions employed were 90 °C/24 hr/50 psig air, which simulate approximately six months aging at ambient temperature and pressure. *Note*, accelerated aging in this paper refers specifically to aging conducted in the LPR; it does not include the gravimetric JFTOT.

Gravimetric JFTOT. A detailed description of the method has been published,³ hence only a brief outline is given. Using a reciprocating piston HPLC pump (e.g., Isco model 2350), the filtered fuel is pumped at a rate of 3 mL/min over a stainless steel strip contained in a strip holder, which is heated to a temperature of 260 °C. A backpressure of 500 psi is maintained throughout the run, via a micro valve at the fuel outlet. Duration of the run is 2.5 hr. The effluent (450 mL) is subsequently filtered using two pre-weighed 0.8 micron MAGNA nylon filters. The collected insolubles are washed with pre-filtered hexane, dried in an oven at 70 °C for 30 min, and weighed, on cooling. The control filters are treated similarly except for filtering a small amount (~50 mL) of the neat filtered fuel in lieu of the effluent.

Results and Discussion

Compared to the conventional JFTOT (ASTM D3241), the quantitative measurements of the gravimetric JFTOT were particularly valuable in examining the performance and subsequently, the roles of: copper, MDA, and simulated aging in fuels of different thermal stabilities. Differences in the thermal stabilities of the three test fuels in relation to both the individual factors examined and their interactive effects are addressed. Evaluation was based on the fuel's performance relative to the corresponding neat fuel as

well as on the amount of total deposits formed. Note, data have been repeated in the Tables to facilitate comparisons.

Neat Fuels. As shown in Table 1, the neat fuels A and B formed similarly low amounts of total deposits (0.2-0.3 mg/L) and thus appear to exhibit similarly high thermal stabilities. However, differences in their thermal stabilities with respect to, copper plus accelerated aging, further differentiate these two fuels: Fuel A appears to be very good, and fuel B, typical (*see below*). In contrast, the *neat* Fuel, C, formed a significantly large amount of total deposits (7 mg/L). Thus, it has been categorized as poor. This categorization of fuel C is based on the results of an earlier study in which Hardy *et al.*¹¹ found that for stable fuels, the maximum total deposit was 5 mg/L.

Individual effects of copper and accelerated aging in the LPR. For the three fuels examined, neither individual effect (Tables 1 and 2, respectively) significantly increased the amount of total deposits formed relative to the corresponding neat fuel.

Interactive effect of copper with accelerated aging in the LPR. The interactive effect of copper and aging - as defined (*see Experimental*), on fuel thermal stability was found to be fuel dependent. As shown in Table 3, relative to its corresponding neat fuel, the copper-doped fuels A and C again exhibited no significant increase in total deposits, on accelerated aging. However, for fuel B, the interactive effect of copper with accelerated aging did significantly increase the total deposits (9.4 mg/L). It is this striking difference between fuels A and B that led to our categorization of fuel A, as being very good, and fuel B, as typical. Also, decreasing the copper level in fuel B from 400 ppb to 109 ppb, with accelerated aging, did not decrease the total deposits formed. This 'no concentration effect' with copper supports a copper catalysis mechanism, which is discussed later.

The effect of aging on the thermal stability of fuels has previously been found to be fuel dependent, but the copper content of these fuels was not reported.^{10c} The apparent non-effect of copper in an aging fuel of very good thermal stability (Fuel A) suggests either the inherent presence of natural inhibitors or the absence of those species that are susceptible to copper catalysis, or both. The inherently poor thermal stability of fuel C,

which does not appear to deteriorate further - e.g., on aging in the presence of copper, suggests the converse, i.e., either the absence of natural inhibitors, or the inherent presence of precursors/species that promote thermal instability, or both. In addition, the non-effect of copper and accelerated aging in fuel C suggests that the thermal deposit precursors are limiting reagents under the test conditions employed.

In the case of fuel B (typical thermal stability), the deleterious effect of copper on aging of the fuel is likely attributable to copper catalyzed autoxidation during the accelerated aging. The combined effects of aging with copper present lead to the formation of precursors that promote thermal instability in the gravimetric JFTOT (*see below*). Data supporting a catalytic role by copper, on accelerated aging of fuel B, are as follows:

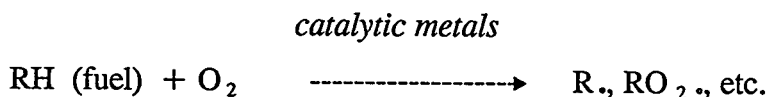
a) the amount of total deposits formed from copper alone (Table 1), or fuel aging alone (Table 2) were very low (1.2-1.3 mg/L) compared to that formed (9.4 mg/L: Table 3) from the interactive effect of accelerated aging with similarly small amounts (400 ppb) of copper;

b) the total gravimetric JFTOT deposits formed on decreasing the copper concentration further from 400 ppb to 100 ppb were also similar (Table 3);

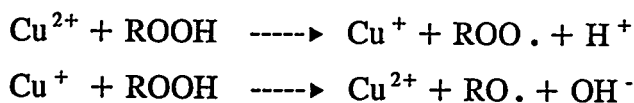
c) the small amount of insolubles formed from the copper-doped fuel on pre-addition of MDA, a reported copper chelant,^{4,5,10a,12} but not on post-addition (Table 4).

Additional data also support the interactive effect of copper and aging on fuel B to be synergistic. For example, the total gravimetric JFTOT deposits formed when copper was added *before* aging was significantly higher compared to that formed when copper was added *after* aging (9.4 versus 2.4 mg/L: Table 3). Furthermore, the total deposits formed when copper was added after aging appears to be the sum of that from aging alone and copper alone (Table 3).

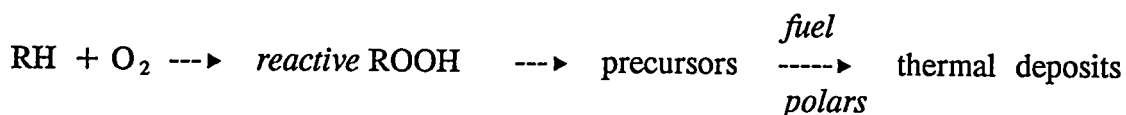
The catalytic role of copper in autoxidation has been reported to be twofold:^{10b}
 1) *at the initiation stage in autoxidation*;¹²⁻¹⁵ an increase in the rate of initiation of free radicals by metals is illustrated in the following equation proposed by Clark:¹²



2) *in the decomposition of hydroperoxides via copper catalysis*; the equations shown below are based on those proposed by Walling¹⁸ for dissolved metal ions with multiple valence states:



Fuel thermal deposits, however, do not appear to be directly related to the concentration of hydroperoxides.^{16,17} For example, in a separate study, Hardy *et al.*¹⁶ found fuels that formed high levels of hydroperoxides were relatively thermally stable, whereas fuels that formed lower hydroperoxide levels exhibited a wide range of thermal instabilities. These results reflect the differing stabilities/reactivities of fuel hydroperoxides, since these species would vary with the composition of the fuel. Nonetheless, thermal deposits are likely produced from interactions between the precursors that are formed during autoxidation (from the reactive hydroperoxides) and the fuel polars such as nitrogen and sulfur compounds, as represented below:



Clark¹² has suggested a similar pathway; but, that both autoxidation and the subsequent reactions occur during the JFTOT testing regime. As mentioned earlier, our data suggest that, for the fuels examined, copper catalyzed autoxidation leading to the formation of the precursors can also occur during accelerated aging. From a practical viewpoint, the combined tests of simulated aging with the gravimetric JFTOT are important: these tests realistically simulate the fuel pathways from the refinery to combustion in the engine as shown in the three stages below:

<u>Pathways</u>	<u>Simulated Test</u>
Stage I: <i>En route from the refinery to the aircraft via pipes/drums (ambient conditions at: t = wks)</i>	Storage
Stage II: <i>Circulation within the engine: heat exchangers and filters via stainless steel tubing (<160°C at: t = hrs)</i>	<div style="border: 1px solid black; padding: 2px; display: inline-block;"> Grav JFTOT JFTOT </div>
Stage III: <i>Combustors: nozzle coking (<300°C at: t = secs)</i>	<div style="border: 1px solid black; padding: 2px; display: inline-block;"> Grav JFTOT JFTOT </div>

The above postulates and observations focus on the significance of fuel composition on thermal stability. Fuel composition is a function of not only the inherent crudes' composition but the refining processes to which it has been subjected.^{10d}

Effects of MDA and its interactive effects with copper, and copper with accelerated aging in the LPR. These effects on the thermal stability of fuels B and C are given in Table 4. The effect of MDA with fuel A was not examined in view of its high thermal stability, even on aging with copper (0.41 mg/L). However, for fuels B and C, the results again indicate a fuel dependency. Thus, for typical fuel B, MDA appears to exhibit a beneficial effect on its thermal stability particularly at the recommended concentration level (5.8 ppm versus 1 ppm), but only when added prior to accelerated aging of the copper-doped fuel. In contrast, for fuel C, MDA appears to exhibit some increase in the total deposits formed versus the neat fuel in several cases; e.g., the non-accelerated aging fuel, and the copper-doped fuel without and with accelerated aging. For accelerated aging with no copper added, MDA exhibited an apparent small decrease in the total deposit relative to the aged neat fuel.

The generally beneficial effects of MDA in decreasing thermal deposits of fuels containing both defined and undefined metal content are well documented in two detailed reviews.^{1c,10e} The dramatic decrease in total deposits when MDA was added *before* accelerated aging of the copper doped fuel compared to when added *after* accelerated aging supports the well acknowledged mechanism of copper chelation^{4,19} to form a stable complex. Such data further indicate that the precursors of thermal deposits can also be formed during simulated aging.

A plausible explanation for the effectiveness of the MDA-copper chelate in counteracting copper's catalytic effect in autoxidation is likely related to unfavorable thermodynamics and kinetics for the redox reactions of the copper (II)-MDA complex. Though these values were not measured, this postulate is supported by the fact that depending on the ligand, both the kinetics and the oxidation potential of metal complexes/chelates in redox reactions are known to change.

With no added copper, the decrease in total deposits on MDA addition to fuel B (Table 4), both before (0.27 mg/L) and after aging (0.48 mg/L) versus the neat aged fuel (1.23 mg/L) suggests MDA possibly exhibits an additional role. In the absence of copper, its role as a surface passivator in the JFTOT has been proposed by Kendall *et al.*²⁰ and by Clark.¹² These authors also found the passivation mechanism to be less so, for longer tests, such as those conducted in the single-tube-heat-transfer rig (STHTR) versus the JFTOT. Additional studies by Clark *et al.*²¹ indicate that more than an adsorption mechanism is operative at elevated temperatures.

Recent studies by Schreifels *et al.*²² on the adsorption of MDA onto metal surfaces do not appear to support a passivation mechanism: very little MDA coverage (less than a monolayer) on stainless steel was found. Furthermore, the well acknowledged decrease in deposits obtained with aluminum versus stainless steel tubes in the JFTOT has been ascribed to magnesium migration. Both these factors of low MDA coverage on metal surfaces and possibly, a basicity effect by magnesium, in conjunction with - other data involving surface adsorbed acids - led Schreifels *et al.*²² to propose that: a) MDA adsorption on a metal surface is not a prerequisite for decreasing deposition; and b) MDA's role may be an interaction with acidic sites on the metal or deposit surface.

An important inference of the overall study is that for fuels of typical thermal stability, MDA should be added before aging in order to counteract the adverse effect of copper. This result is consistent with Pedersen's recommendation in 1949, that, for gasoline, metal deactivators should be added as early as possible.⁵ Also, the observed thermal stability differences among the fuels, e.g., with MDA between fuels B and C and others mentioned earlier, focus on the role of fuel compositional differences (physical and chemical).

Conclusions

In ascertaining meaningful assessments of jet fuel thermal stability, the results of this study highlight: a) the advantages of the gravimetric JFTOT in determining thermal stability, i.e., it is quantitative and much simpler than the conventional JFTOT; b) the importance of

using pertinent factors such as copper, simulated aging, MDA, and their interactive effects, when evaluating jet fuel thermal stability; and c) the judicious choice of fuels, i.e., having a wide range of thermal stabilities versus mere number of fuels.

Based on the diverse thermal stability range of the three fuels examined, the results suggest that the inherent stabilities of both the very good and the poor fuel do not change when exposed to adverse factors such as copper, aging, and their interactive effects. In contrast, the typical stability fuel does deteriorate significantly when exposed to the interactive, and apparently synergistic, effects of copper and accelerated aging. However, such deleterious effects are counteracted and effectively so by MDA, but, only when present in the fuel prior to aging. Thus, early addition of MDA to fuels of typical thermal stability appears to be recommended. It is interesting to note that in 1949, Pedersen⁵ made a similar recommendation for gasoline. However, MDA addition to fuels of poor thermal stability does not appear to be beneficial. These results focus on the inherent compositional differences among fuels and the need to elucidate these differences (physical and chemical) for a better understanding and prediction of their performance.

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Table 1. Effect of Copper on Fuel Thermal Stability for Three Jet Fuels

fuel	type	description	deposits (mg/L)		
			strip	filter	total
good:					
A	JP-8	neat	0.009	0.19	0.20
A	JP-8	+ ~372 ppb Cu/no LPR	0.031	0.54	0.57
		+ ~400 ppb Cu/no LPR rpt	0.042	0.52	0.56
		<i>avg</i>	0.037	0.53	0.57
typical:					
B	JP-5	neat	0.069	0.35	0.42
B		rpt	0.029	0.14	0.17
		<i>avg</i>	0.049	0.24	0.29
B	JP-5	+ 400 ppb Cu/no LPR	0.060	1.45	1.51
		rpt	0.036	1.11	1.15
		<i>avg</i>	0.048	1.28	1.33
poor:					
C	JP-5	neat	0.124	7.22 ^a	7.34
C	JP-5	+ 94 ppb Cu/no LPR	0.052	8.22 ^b	8.27

^a black tacky residue

^b tan colored residue

**Table 2. Effect of Aging on Fuel Thermal Stability for Three Jet Fuels
(No Copper Added)**

fuel	type	description	deposits (mg/L)		
			strip	filter	total
good:					
A	JP-8	neat	0.009	0.19	0.20
A	JP-8	LPR/no Cu	0.033	0.40	0.43
		rpt	0.000	0.14	0.14
		<i>avg</i>	0.017	0.27	0.28
typical:					
B	JP-5	neat	<i>avg</i> 0.049	0.24	0.29
B	JP-5	LPR/no Cu	0.031	1.04	1.08
		rpt	0.044	1.33	1.38
		<i>avg</i>	0.038	1.19	1.23
poor:					
C	JP-5	neat	0.124	7.22 ^a	7.34
C	JP-5	LPR/no Cu	0.110	8.00 ^b	8.11

^a black tacky residue

^b tan colored matte residue

Table 3. Effect of Copper and Aging on Fuel Thermal Stability for Three Jet Fuels

fuel	type	description	deposits (mg/L)		
			strip	filter	total
good:					
A	JP-8	neat	0.009	0.19	0.20
A	JP-8	+ ~372 ppb Cu/LPR	0.064	0.44	0.50
		+ ~400 ppb Cu/LPR	0.080	0.24	0.32
		<i>avg</i>	0.072	0.34	0.41
typical:					
B	JP-5	neat	<i>avg</i> 0.049	0.24	0.29
B	JP-5	+ 109 ppb Cu/LPR	0.086	10.54 ^a	10.62
		+ 400 ppb Cu/LPR	0.107	10.22 ^b	10.33
		rpt	0.087	8.44 ^b	8.53
		<i>avg</i>	0.097	9.33	9.43
B	JP-5	+ ~400ppb Cu added post LPR (effect of Cu on aged fuel)	0.178	2.22 ^c	2.40
poor:					
C	JP-5	neat	0.124	7.22 ^d	7.34
C	JP-5	+ 94 ppb Cu/LPR	0.086	7.33 ^c	7.42

^a black caked residue

^b brown glazed residue

^c tan colored matte residue

^d black tacky residue

Table 4. Effect of MDA and Its Interactive Effect with Copper on Fuel Thermal Stability: Without and With Aging For Two JP-5 Fuels

fuel	description		deposits (mg/L)		
			strip	filter	total
<i>typical:</i>	<u>no aging/no copper:</u>				
B	neat	avg	0.049	0.24	0.29
B	+ 1 ppm MDA/no LPR		0.024	0.10	0.13
	rpt		0.029	0.26	0.29
		avg	0.027	0.18	0.21
	<u>no aging/with copper:</u>				
	+ ~400ppb Cu/no LPR rpt:	avg	0.048	1.28	1.33
	+ 1 ppm MDA +419 ppb Cu/no LPR		0.020	0.67	0.69
	+5.7ppm MDA +396ppb Cu/no LPR		0.016	0.15	0.17
	<u>with aging/ no copper:</u>				
B	neat/LPR	avg	0.038	1.19	1.23
B	+1 ppm MDA/LPR/no Cu		0.033	0.67	0.70
	+5.7ppm MDA/LPR/no Cu		0.022	0.25	0.27
	post LPR + 5.7 ppm MDA (no Cu)		0.044	0.43	0.48
	<u>with aging and copper:</u>				
B	+ 400 ppb Cu/LPR	avg	0.097	9.33	9.43
	+1 ppm MDA + 419 ppb Cu/LPR		0.191	12.22 ^a	12.41
	5.7 ppm MDA + 396 ppb Cu/LPR		0.024	0.20	0.23
B	+420 ppb Cu/LPR + post LPR: + 5.7ppm MDA		0.113	7.56	7.67
<i>poor:</i>	<u>no aging/no copper:</u>				
C	neat/no LPR		0.124	7.22 ^b	7.34
	+5.8ppm MDA/no LPR		0.034	11.78 ^c	11.81
	<u>no aging/with copper:</u>				
C	+94 ppb Cu/no LPR		0.052	8.22 ^d	8.27
	+5.8ppm MDA +410ppb Cu/no LPR		0.010	10.42 ^d	10.43
	<u>with aging/ no copper:</u>				
C	neat: LPR/no Cu		0.110	8.00 ^d	8.11
	+ 5.8 ppm MDA/LPR/no Cu		0.022	6.67 ^c	6.69
	<u>with aging and copper:</u>				
C	+ 94 ppb Cu/LPR		0.086	7.33 ^d	7.42
	+410 ppb Cu + 5.8 ppm MDA/LPR		0.032	10.22 ^e	10.25

^a brown glazed residue; ^b black tacky residue; ^c light tan shiny residue with odor; ^d tan colored matte residue; ^e dark tan shiny residue.

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MECHANISM OF DEPOSIT FORMATION ON FUEL-WETTED METAL SURFACES

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Experiments were performed in a Single-Tube Heat Exchanger (STHE) apparatus and a Hot Liquid Process Simulator (HLPS) configured and operated to meet Jet Fuel Thermal Oxidation Tester (JFTOT) ASTM D 3241 requirements. The HLPS-JFTOT heater tubes used were 1018 mild steel, 316 stainless steel (SS), 304 stainless steel (SS), and 304 SS tubes coated with aluminum, magnesium, gold, and copper. A low-sulfur Jet A fuel with a breakpoint temperature of 254°C was used to create deposits on the heater tubes at temperatures of 300°C, 340°C, and 380°C. Deposit thickness was measured by dielectric breakdown voltage and Auger ion milling. Pronounced differences between the deposit thickness measuring techniques suggested that both the Auger milling rate and the dielectric strength of the deposit may be affected by deposit morphology/composition (such as metal ions that may have become included in the bulk of the deposit). Carbon burnoff data were obtained as a means of judging the validity of DMD-derived deposit evaluations. ESCA data suggest that the thinnest deposit was on the magnesium-coated test tube. The Scanning Electron Microscope (SEM) photographs showed marked variations in the deposit morphology and the results suggested that surface composition has a significant effect on the mechanism of deposition. The most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300° to 380°C, also verified in a single-tube heat exchanger. The results indicate that the deposition rate and quantity at elevated temperatures is not completely temperature dependent, but is limited by the concentration of dissolved oxygen and/or reactive components in the fuel over a temperature range. Experiments were done for several fuels using the Single-Tube Heat Exchanger (STHE) apparatus to evaluate deposit formation rates with fuel at measured temperatures. The STHE test tubes were 0.64 cm O.D., 304 SS test tubes, heated at 340°, 380°, 420°, 460°, 500°, and 540°C for 4 hours with a fuel flow of 10 mL/minute. The position of the fuel deposit in the tube versus the fuel temperature at various bath set temperatures very closely approximates what was observed for HLPS heater tubes. These data support the observation based on HLPS data that the depositing position on the tube is temperature dependent. Furthermore, the magnitude of the deposit is essentially the same at all three temperatures. Oxygen measurements in both HLPS and STHE tests, indicate that oxygen is depleted at temperatures below 260°C. At higher temperatures (set temperature of 420°C) for the STHE, methane generation is observed due to pyrolysis of the fuel. At pyrolysis temperatures, surface deposit formation is fuel composition dependent.

I. INTRODUCTION AND BACKGROUND

The effect of fuel system metallurgy on fuel stability is an important concern in the development of high efficiency/advanced engine technology such as adiabatic, low-heat rejection engines. Several studies have shown that trace metals adversely affect the thermal stability of hydrocarbon fuels.^{1,2} Metal concentrations as low as 15 ppb of copper, 25 ppb of iron, 100 ppb of zinc, and about 200 ppb of lead have been found to cause significant change in the thermal stability of jet

* Underscored number in parentheses refer to references at the end of this report.

fuels. These studies suggest that the slightest metallic contamination could cause a significant change in the thermal oxidative stability of hydrocarbon fuels. In fact, the theory has been advanced that all hydrocarbon autoxidations are trace metal catalyzed.³ Recent work,⁴ in which only limited data are available, suggests that aluminum tubes with magnesium-enriched surfaces tend to have lower deposit buildups than the standard aluminum tubes. If such minor changes in surface metallurgy cause significant differences in the rate of deposit formation, major changes in surface composition could dramatically effect processes such as deposit adherence and oxidation catalysis.⁵ Experiments with metal deactivator in dodecane using JFTOT equipment suggest that the effect on deposit reduction may be a consequence of interactions in the liquid-phase rather than a reduced adherence to the hot metal surface.⁶

One measure of the thermal stability of aviation fuels is the quantity of deposits formed on heated metal surfaces.⁷ In accelerated stability tests conducted in accordance with the JFTOT procedure (ASTM D 3241),⁸ the rating methods currently employed involve either visual comparisons or measurements of reflected light by the tube deposit rater (TDR), both of which are sensitive to deposit color and surface texture. Morris and Hazlett⁷ examined deposits formed on stainless-steel JFTOT heater tubes in several ways including TDR, gravimetric carbon combustion, and two new nondestructive techniques for determining deposit volumes based on dielectric strength and optical interference. Measurements of total carbon content by combustion were used as a reference. They found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the total TDR often gave misleading results.

The rate of deposit formation in and by fuels is generally both time and temperature dependent. The hotter the fuel, the lower the time needed to form deleterious products. However, the hotter the wall (surface) used to heat the fuel, the greater are the wall (surface) deposits, as long as adequate reactants remain available or are not depleted. Deleterious Products are:

- **Microparticulates:** Particulates Filterable by Porous Membranes.
- **Sediment:** Agglomerated particulates settled to the bottom.
- **Surface deposits:** Insoluble fuel products formed on heated walls by one of severable mechanisms.

Mechanisms of deposit formation include:

- **Autoxidation:** Self catalyzed oxidation not directly involving the container surface. This is typical in long-term storage environments and accelerated tests up to around 150 degrees C.
- **Thermal-Oxidative:** Fuel flowing over hot surfaces as in JFTOT or HLPS or STHE with set temperatures of 200 degrees C and hotter. Relates to deposits in higher temperature surfaces of heat exchanger/fuel nozzle-injector
- **Pyrolysis:** Decomposition of fuel and thermal-oxidative deposits on very hot surfaces. Relates to deposits on nozzle/injector tips & combustion chamber deposits.

Typical forms of deterioration related to fuel types are:

- Gasoline:
 - Autoxidation in the storage of fuel.
 - Rapid autoxidation and thermal oxidation, ie., engine induction system depositing (ISD) in vehicle fuel system.
- Diesel:
 - Storage autoxidation, condensation, esterification, and acid-base reactions forming fuel insoluble microparticulates and sediment (agglomerated microparticulates).
 - Thermal-oxidation forming surface deposits in injectors.
 - Pyrolysis forming deposits on injector tips and combustion chamber fuel wetted surfaces.
- Jet/Gas turbine:
 - Autoxidation forming soluble gum, peroxides, and color bodies.
 - Thermal-oxidation formation of deposits on fuel wetted hot surfaces of heat exchangers, control arms, divider valves, nozzles (during operation and shut-down soak-back)

In a previous paper "Quantitation of Fuel Deposition on Hot Metal Surfaces," at the 4th International Conference on Stability and Handling of Liquid Fuels, data for a Jet A fuel was presented which led to the following conclusions:¹³

- Under JFTOT D 3241 test conditions, thickness profiles of deposits formed on a variety of surfaces including mild steel, 304 SS, Al, Mg, Cu and Au, were compared using the DMD (dielectric breakdown voltage) and Auger milling.
- Except for gold and aluminum, the deposit thicknesses measured by DMD were substantially lower than those measured by Auger milling, and the disparity in the two methods seemed to grow with increased temperature and deposit thickness. The disparities in the thicknesses measured by DMD and Auger milling were most pronounced in the copper-coated heater tubes.
- Using carbon burnoff data for quantitation, allowed an observation that the deposit magnitude essentially the same, except it seemed dramatically lower for aluminum. The highest value was 416 μg for Mg at 380°C while the lowest value at 380°C was 153 μg C for aluminum.
- Aside from variations in the thickness of deposits due to metallurgy, the most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300 to 380°C. This effect was somewhat greater on the copper-coated tubes. Deposition rate is highly temperature dependent and may be quantitatively limited by the concentration of dissolved oxygen and/or reactive components in the fuel.
- Surface analysis by ESCA showed that the deposits consisted of a highly oxygenated aliphatic hydrocarbon film containing alcohol, ether, ester and carboxylic acid groups.
- The SEM photographs showed marked variations in the deposit morphology among the surface materials tested. The results suggested that surface composition has a significant effect on the mechanism of deposition. In general, it appears that insolubles coalesce in the fuel to form microspheres less than 1000 Å in diameter. The microspheres then either deposit directly onto the surface, forming a relatively smooth platelet-type structure or they agglomerate into macrospheres (1- to 3 μm in diameter) before adhering to the surface. The former is observed on aluminum and gold, while the latter is particularly evident in deposits

formed on magnesium. For copper, mild steel, and 304 SS, the deposits appear to form from several particle sizes ranging from micro to macrospheres.

- Single Tube Heat Exchanger Experiments using 304 SS tubing has confirmed the temperature dependence of fuel deposits and limited depositing capacity (with oxygen starvation) for the Jet A fuel based on HLPS data.

In this report, the earlier report is expanded by evaluating three additional fuels covering a wide range of composition from a very stable Jet A-1 to a Referee one percent No. 2 diesel fuel and emphasizes the utility of results of quantitation of fuel deposits on hot metal surfaces.

II. EXPERIMENTAL PROCEDURES

- A. Hot Liquid Process Simulator: Experiments were performed in an Alcor model HLPS300 Hot Liquid Process Simulator (HLPS), which is a modular version of the JFTOT apparatus used for the ASTM D 3241 method. The HLPS was operated to give conditions equivalent to D 3241 requirements except that Triton-treated fuel prefilters were not used. Preparation of JFTOT tubes for carbon burn-off involved removing both of the tube end grips using a fine tooth jeweler's saw. Special care is taken not to handle the test section of the tube. After SEM evaluation, the test section is then placed in a pre-labeled test tube and cleaned with toluene followed by n-hexane. After decanting the solvents, the test tube is placed in a vacuum oven and dried at 75°C for approximately one hour. The specimens are now ready for carbon burn-off analysis.
- B. Deposit Measuring Device: The deposit thickness measurement device (DMD) determines the thickness of a deposit on a conductive surface by applying a voltage across the deposit while measuring the dielectric breakdown of the layer at various points.⁹ The DMD used in this work was first reported in Reference 10. The DMD voltage measurements were shown to relate thickness of deposits with 350 volts equal to 1 micrometer.¹⁰ Methods for calculating deposit volume on JFTOT heater tubes were also discussed in Reference 10. This procedure was used to develop DMD data correlations to carbon burn-off values reported in Reference 7. Based on deposit density calculations, assuming that a density value of 1.0 to 1.5 g/cm³ is reasonable, deposit volumes greater than 0.0800 mm³ (and ranging up to 0.6365 mm³) by DMD seemed most reliable in this work. These DMD deposit volumes correspond to carbon burn-off values of 95 µg to 877 µg of carbon, respectively.
- C. Single Tube Heat Exchanger: Fig. 1 is a schematic description of the single tube heat exchanger (STHE). Fig. 2 summarizes the thermocouple measured fuel temperatures at various positions in the test tubes at the indicated bath temperatures. Prior to a run the test fuel is filtered and aerated according to the procedures outlined in ASTM D 3241, the JFTOT test. Prior to beginning a run, test fuel is pumped through the system for 15 minutes to flush the lines of all residue from the previous run or cleanup. The pumping is done with a standard HPLC pump set to deliver 10 mL/min. The pressure in the system fluctuates (due to the pulsing action of the pump) between 800 and 950 psig with the help of a back pressure regulator. A safety pressure relief valve is set at 1000 psig. The flush is performed with no heat applied to the heat exchanger tube. Once the flush is complete, the heating bath, a Techne Fluidized Bath Model SBL-2D, is raised into position around the heat exchanger tube. This point is the beginning of the 4 hour run. At this point also, a zero hour oxygen/methane analysis is made using gas chromatography. Additional oxygen/methane analyses

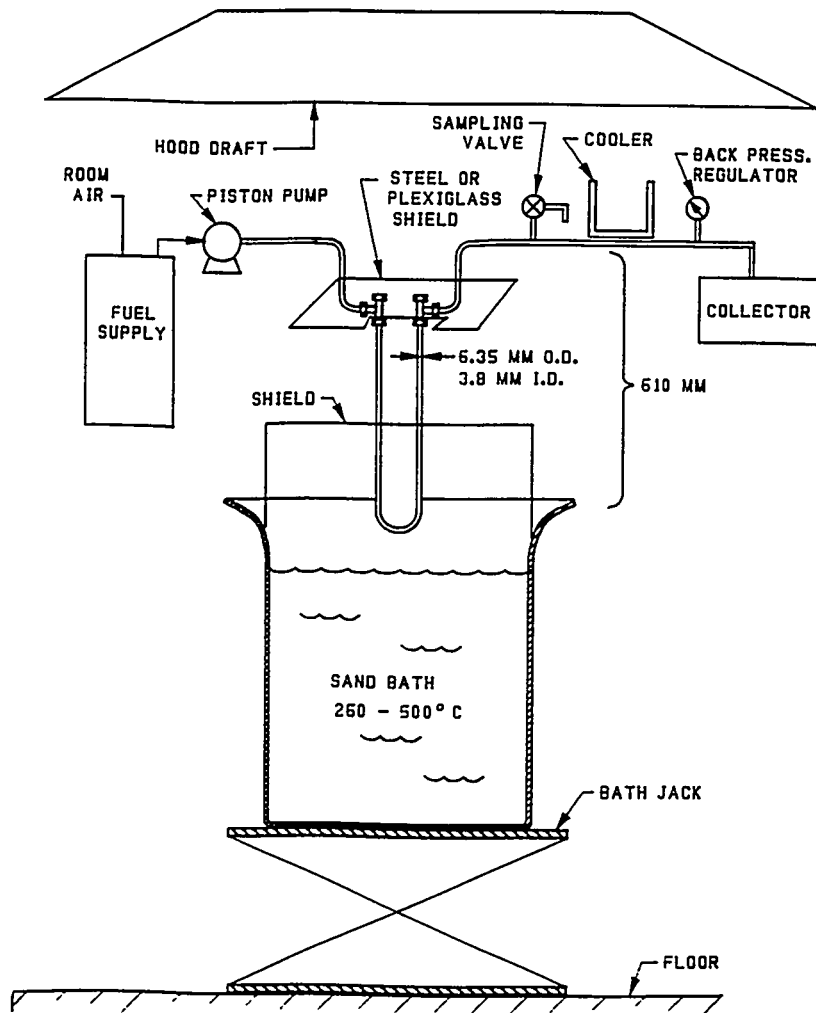


Figure 1. Schematic of Single Tube Heat Exchanger

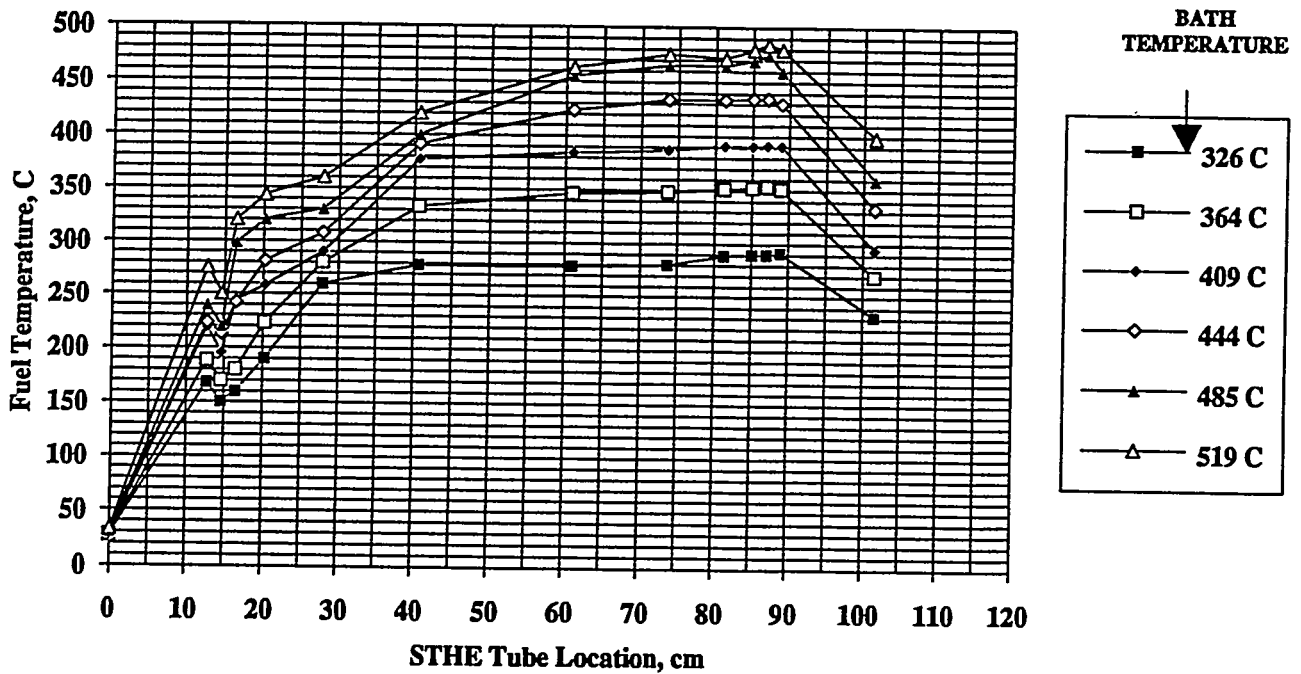


Figure 2. Fuel Temperature Versus Location in Single Tube Heat Exchanger

are conducted throughout the run, once every 10 minutes for the first hour and every 30 minutes thereafter. An end of test analysis, at ambient temperature, is also made for comparison purposes. At the end of a STHE run the heating bath is lowered away from the U-tube. Fuel is allowed to flow through the tube for approximately 10 more minutes to cool the tube. The pressure is released and the U-tube is removed from the STHE. Next the U-tube is rinsed with heptane and air dried. The tube is then clamped in a bench vise and straightened. The longitudinal center of the tube is marked. Measuring from the center point, marks are made at 3 inch (7.6 cm.) intervals along the entire length of the tube. Beginning at the inlet end of the tube, inscribe each marked-off section with a letter; starting with "A" and ending with "N." Cut the tube at each of the 3 inch scribe marks using a tubing cutter. Since the tubing cutter will tend to close the openings at each end of the 3 inch sections, use a 1/4" drill bit to open the holes to original diameter. The sections (B through M) are now ready for carbon burn-off analysis.

D. Carbon Burnoff Procedure: All analyses were conducted on Control Equipment Corporation Model 240XA Elemental Analyzer. Specially constructed quartz sample boats were used to inject the test specimen into the furnace of the analyzer. The combustion tube section of the analyzer is set at 950-975°C and the reduction tube section is set at 600-625°C. Calibration of the instrument is conducted using squalane and n-hexadecane. Analysis time is 250 seconds. Results are reported in micrograms of carbon ($\mu\text{g C}$).

E. Test Fuels: TABLE 1 provides fuel chemical and physical properties.

TABLE 1. Chemical and Physical Properties of Test Fuels

Property	Test Method	Reference No. 2 (Cat 1-H)				MIL-F-46162C 1% Sulfur
		West Coast Jet A AL-19471-F	Jet A-1 AL-19546-F	AL-19540-F	Reference Fuel w/o Additives AL-19854-F	
API Gravity	D 1298	40.8	50.4	33.6	31.1	
Density, kg/L	D 1298	0.8212	0.7776	0.8566	0.8698	
Flash Point, C	D 93	46	48	87	49	
Cloud Point, C	D 2500	---	---	-8	<-45	
Pour Point, C	D 97	---	---	-9	<-45	
Freeze Point, C	D 2386	-42	-57	---	---	
Kinematic Viscosity at 40 C, cSt	D 445	---	---	2.84	3.36	
Distillation, C	D 86					
IBP		153	163	208	180	
10 % Recovered		183	171	233	228	
50 % Recovered		214	181	263	274	
90 % Recovered		241	204	302	326	
End Point		261	232	349	372	
Residue, vol%		0.5	0.8	1.4	0.5	
Ash, wt %	D 482	---	---	0.01	0.03	
Carbon Residue, 10%						
Bottoms, wt %	D 524	---	---	0.12	0.12	
Particulate Contamination, mg/L	D 2276	1.2	0.8	1.5	1.7	
Accelerated Stability, mg/100 mL	D 2274	---	---	0.5	1.3	
Total Acid Number, TAN, mg KOH/g	D 974	0.001	0.009	0.08	0.16	
Copper Strip Corrosion	D 130	1a	1b	1a	1a	
Hydrogen, wt %		13.49	---	---	12.96	
Sulfur, wt %		0.04	0.008	0.39	1.02	
Net Heat of Combustion, MJ/kg	D 240	42.8	43.4	42.5	42.1	
BTU/lb	D 240	18406	18671	18260	18119	
Aromatics, wt %	D 1319	21.7	11.8	41.1	33.1	
Cetane Number	D 613	---	---	48.6	44.5	
Cetane Index	D 976	---	---	44.8	43.0	
Free Water and Particulate Contamination	D 4176	Sed/Bright	Clean/Bright	Sed/Bright	Sed/Bright	
Mercaptan Sulfur, wt%	D 3227	0.0004	---	---	0.2086	

III. DISCUSSION

Data in Fig. 3 obtained using the Hot Liquid Process Simulator (HLPS) at 380°C compares the Jet A fuel with three additional fuels; a very stable Jet A-1, a Reference No. 2 D diesel, and a referee 1 % Sulfur diesel No. 2. The test tube metallurgy included 316 SS, 304 SS aluminum plated on 304 SS, and magnesium plated on 304 SS. Note that for all the fuels except the Jet A, lower deposit levels were observed on the hot magnesium surface. Deposit levels are known to vary with fuel type and surface metallurgy.¹⁴

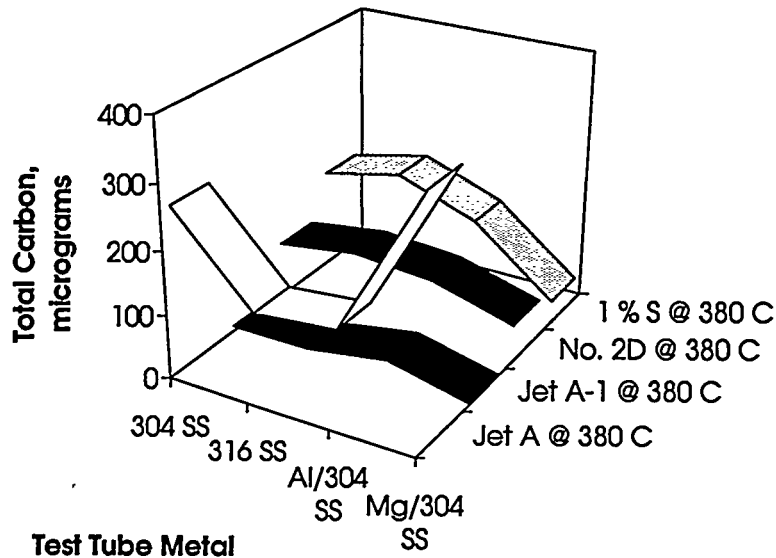


Figure 3. Carbon Data for Four Fuels on Various HLPS Metal Test Tubes

At both 300°C and 380°C as shown in Fig. 4, deposit formation is dramatically reduced to essentially no deposit when the 1 % Sulfur diesel fuel was purged with nitrogen as opposed to air, which showed significant deposit carbon burnoff values also in Fig. 4.

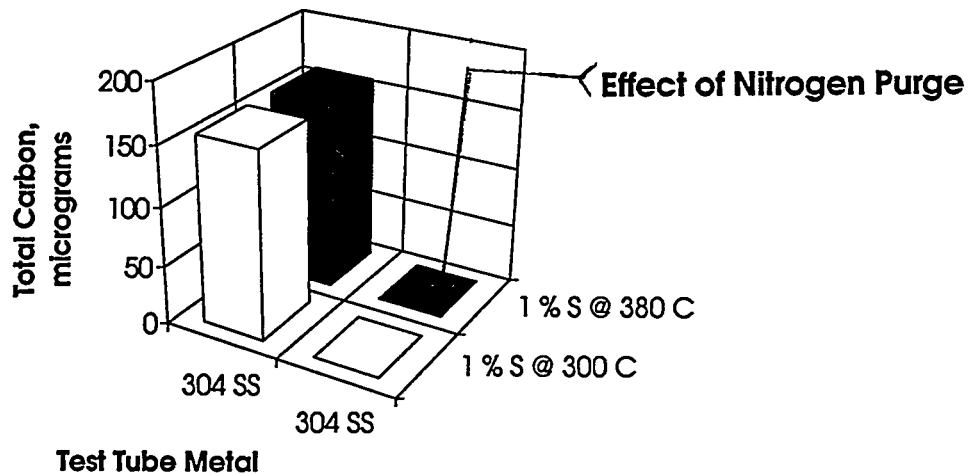


Figure 4. Fuel Nitrogen Purge Effect on Deposit Level on HLPS Metal Tubes

By measuring oxygen and methane in the test fuel, sampled as it exits the reactor, oxygen was depleted at 300-340°C and methane generation (indicative of pyrolysis) generally started at about 380°C depending on the fuel type as shown in Fig. 5. No methane was observed for the Reference No. 2 D fuel even at the upper test temperature of 460°C.

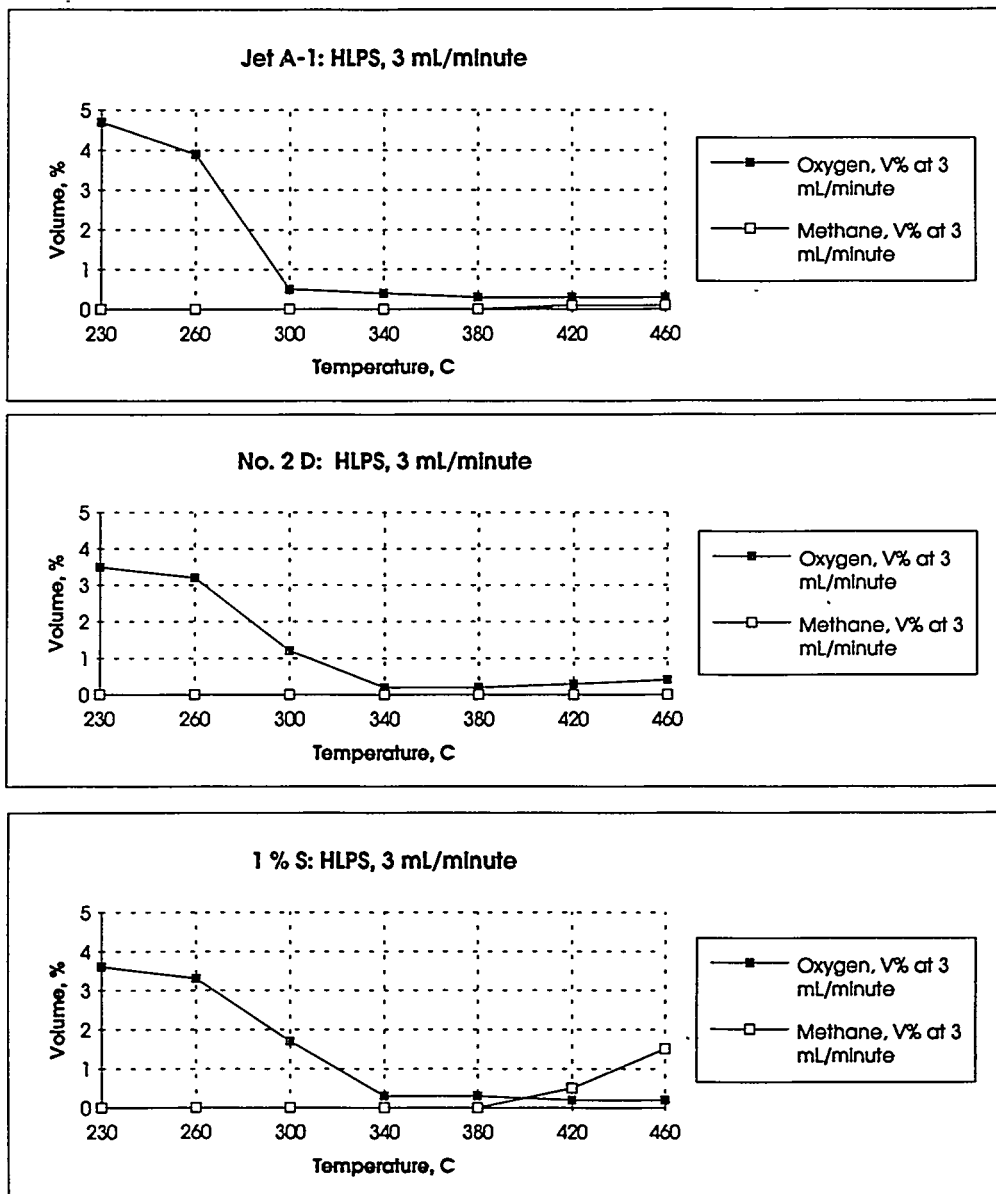


Figure 5. HLPS: Temperature Effects on Oxygen and Methane

The Single Tube Heat Exchanger (STHE) gave more consistent and definitive results in that the three reacted with all the available oxygen below a 260°C bath temperature, and formed methane in the temperature of 400-445°C, as shown in Fig. 6.

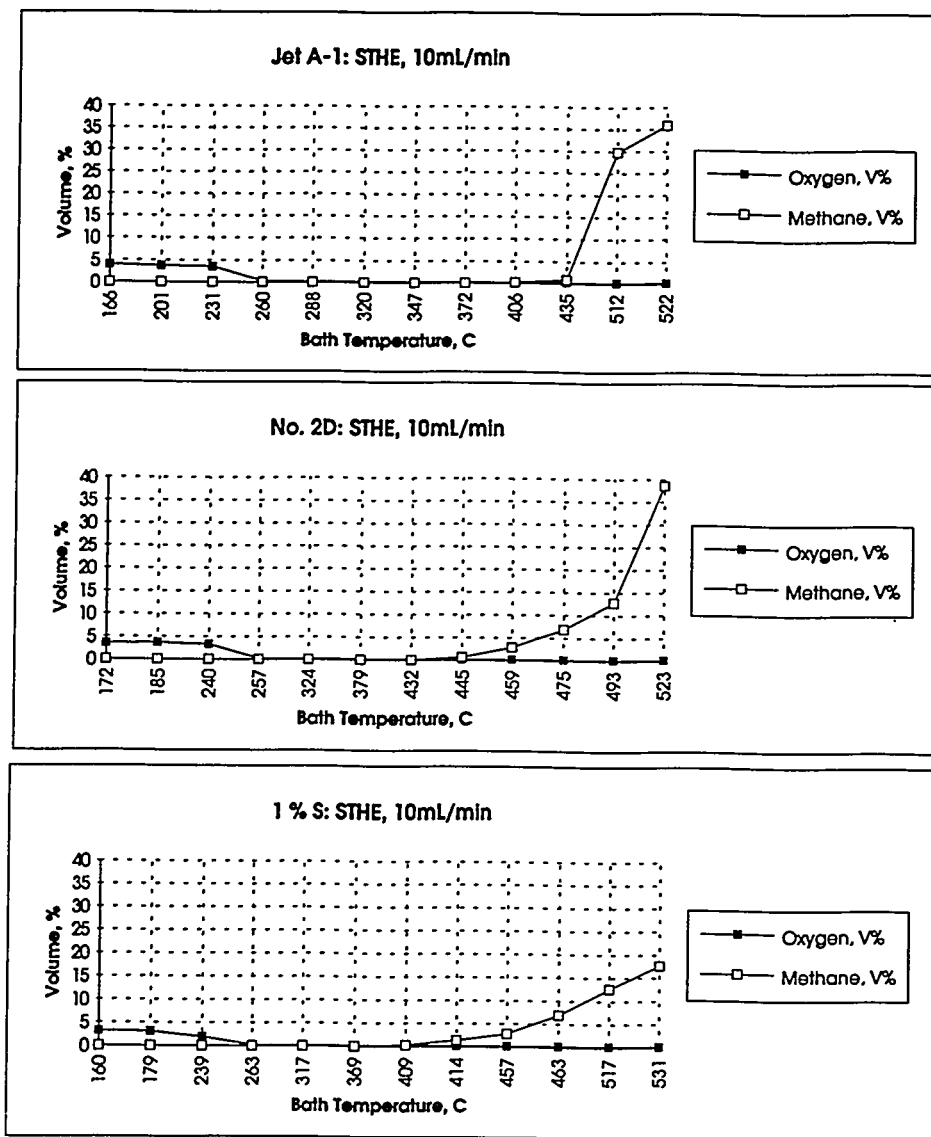


Figure 6. STHE: Temperature Effects on Oxygen and Methane

Deposit levels were measured as carbon burn-off values for both 304 SS and 316 SS test tubes in the STHE apparatus. This data is summarized in Fig. 7:

- Higher deposit levels were observed for Reference No. 2D on 304 SS compared to 316 SS.
- Deposits formed by the 1 % Sulfur fuel at pyrolysis temperatures on both 316 SS and 304 SS, but at higher tube locations. Deposits observed at lower tube locations in lower bath temperature experiments, were not present at the higher test temperatures.
- Deposits from the Jet A-1 were significantly higher on 316 SS, especially at the higher test temperatures.

Data for particulates, summarized in Fig. 8, were measured by filtering reacted test fuel (at room temperature) through porous membrane filters having a nominal pore size of 0.8 micrometer. The particulate level tended to be lower at the higher pyrolysis temperatures, and were not formed at all for the very stable Jet A-1.

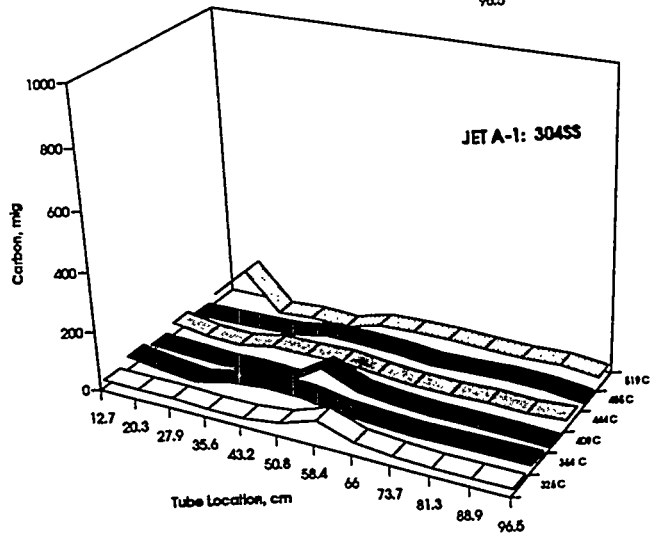
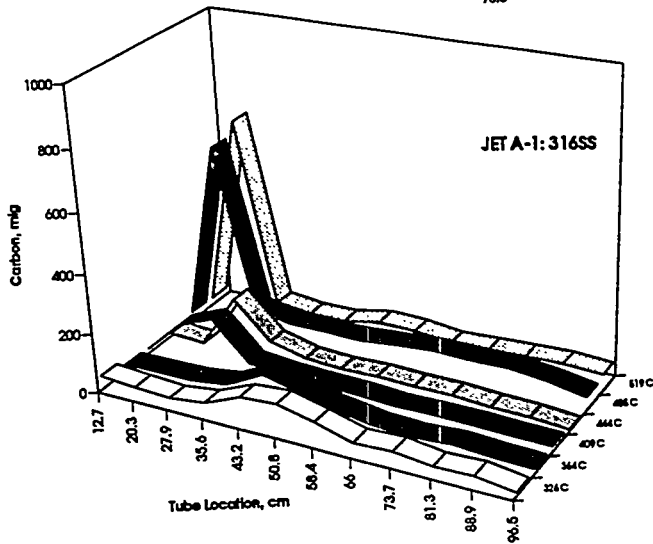
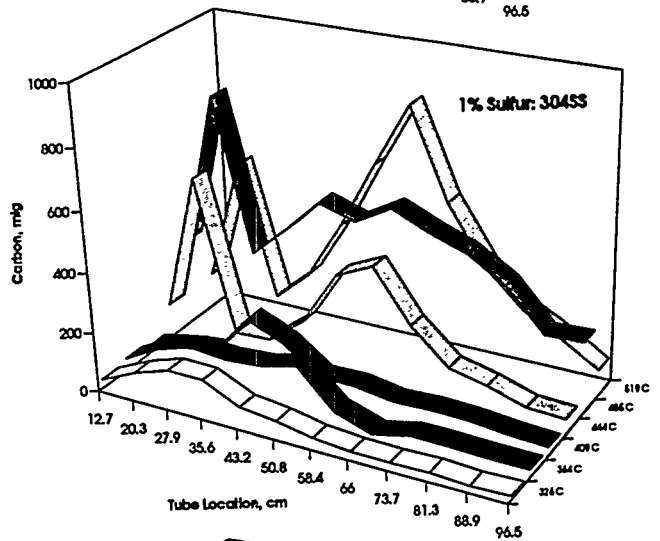
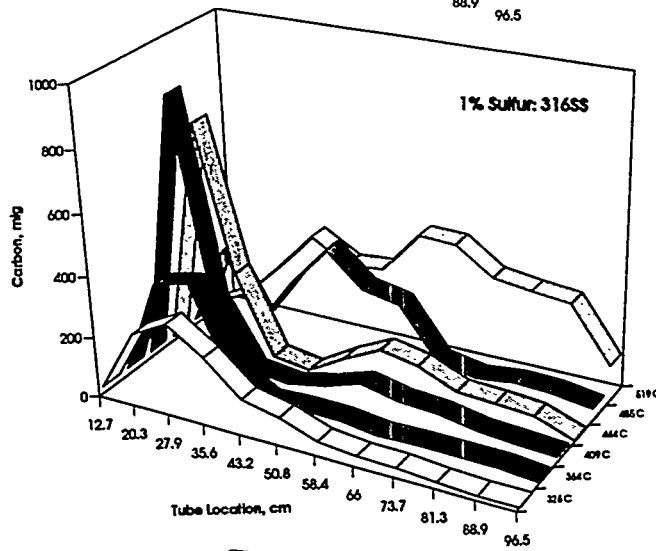
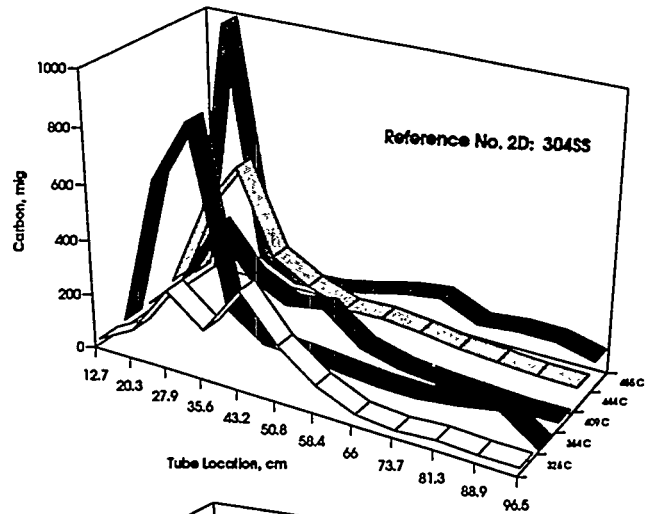
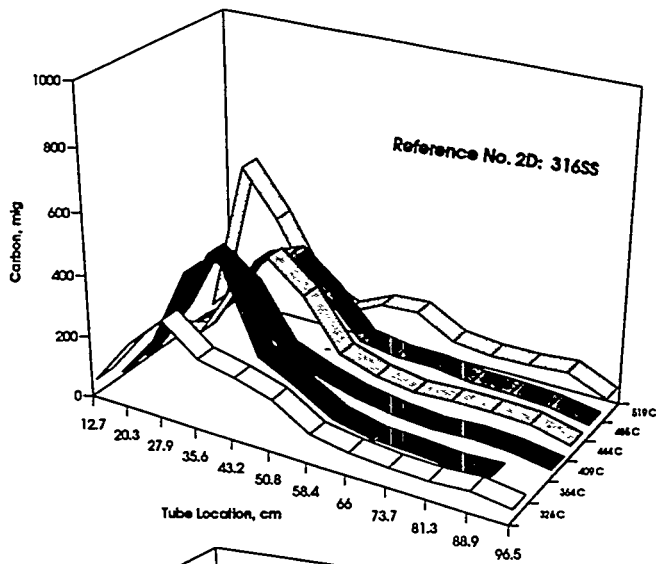
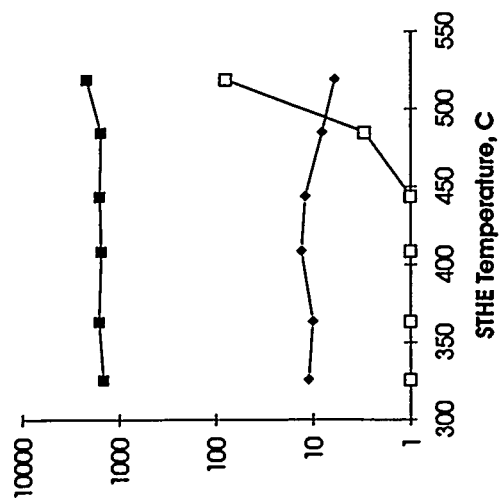
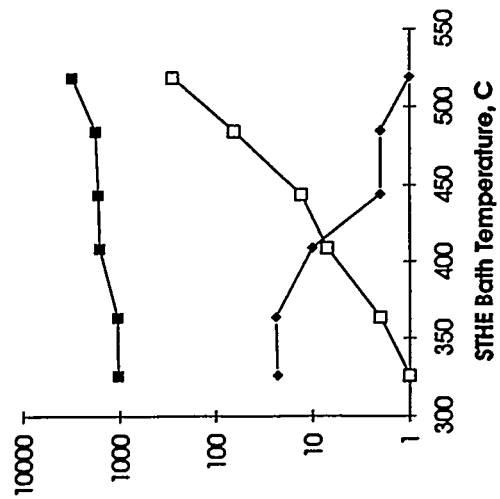


Figure 7. Carbon Data for Three Fuels at Various STHE Bath Temperatures

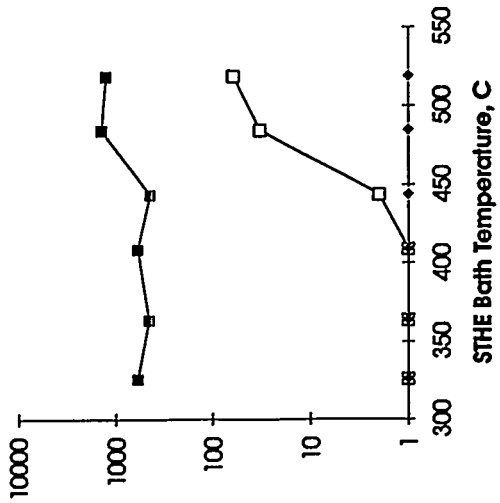
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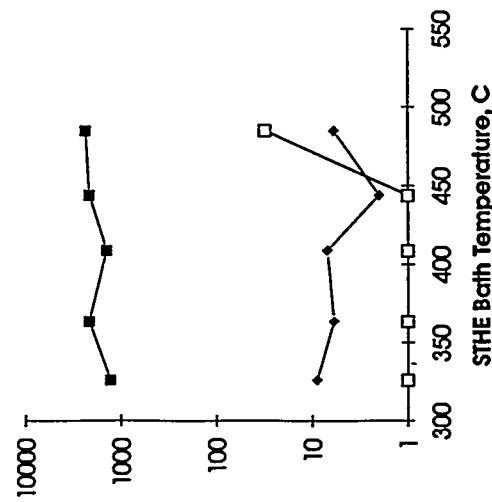
1 % Sulfur: 316SS



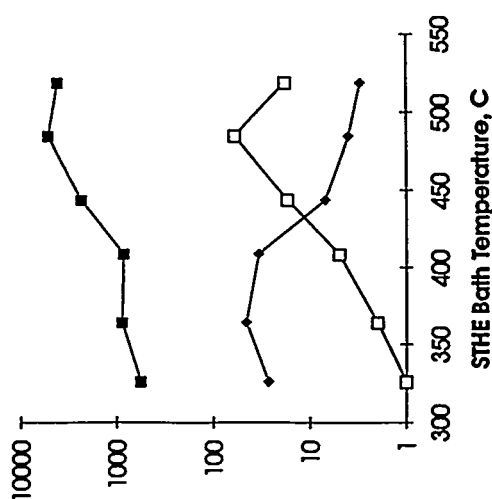
Jet A-1: 316SS



Cat 1-H: 304SS



1 % Sulfur: 304SS



Jet A-1: 304SS

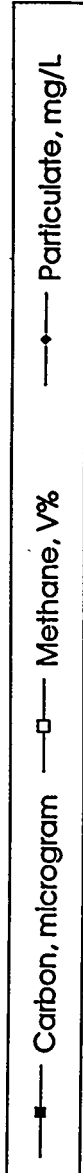
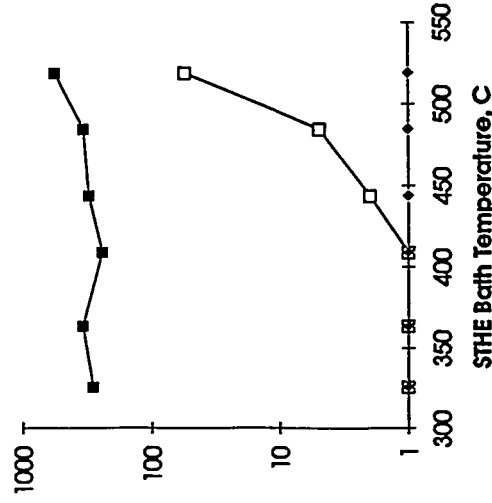


Figure 8. Fuel Microparticulate Levels after STHE Stressing at Various Temperatures Using 304 SS and 316 SS Test Tubes

When the 1 % Sulfur test fuel was passed through filters of various pore sizes, as the hot fuel exited the test tube, the data in Fig. 9 was obtained using a 17 micrometer stainless steel filter, a 5 micrometer silver filter and a 1.2 micrometer silver filter in separate tests. While no deposits were found on the 17 micrometer filter, significant quantities were observed on both the 5 and 1.2 micrometer filters. Removal of the particulates during high temperature filtration was not reflected in the room temperature particulate values. Small size particulates formed in the fuel at high temperatures may not cause equipment distress (compared to large particulates which would both plug injector filters and closely rubbing, highly loaded surfaces).

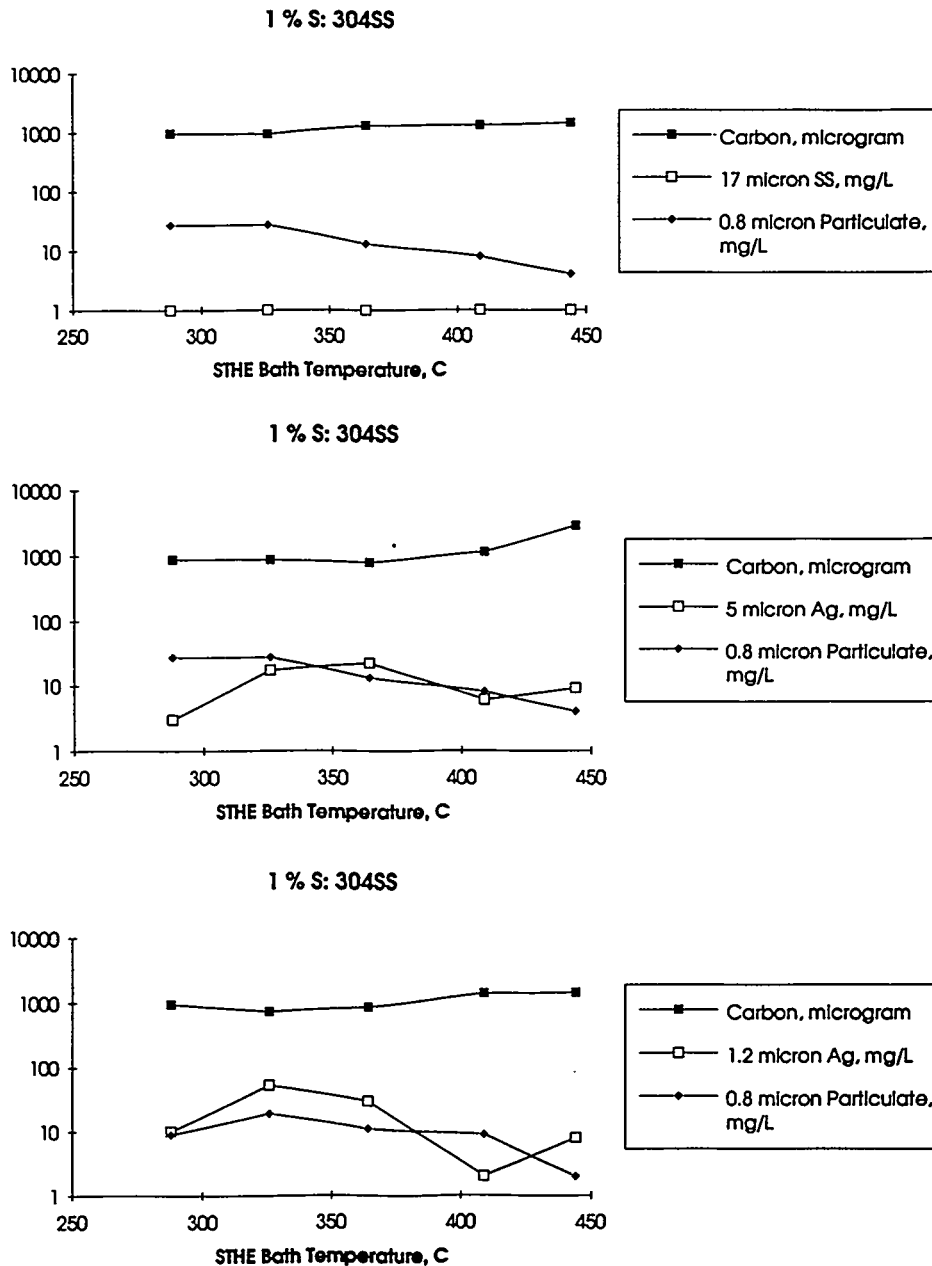


Figure 9. 1 % S Fuel Microparticulate Levels at Room Temperature after STHE Stressing at Various Temperatures and Flowing Through In-Line Metal Filters

When the 1 % Sulfur fuel was purged with nitrogen, deposit levels in Fig. 10 were significantly reduced from the aerated sample deposit level at 364°C.

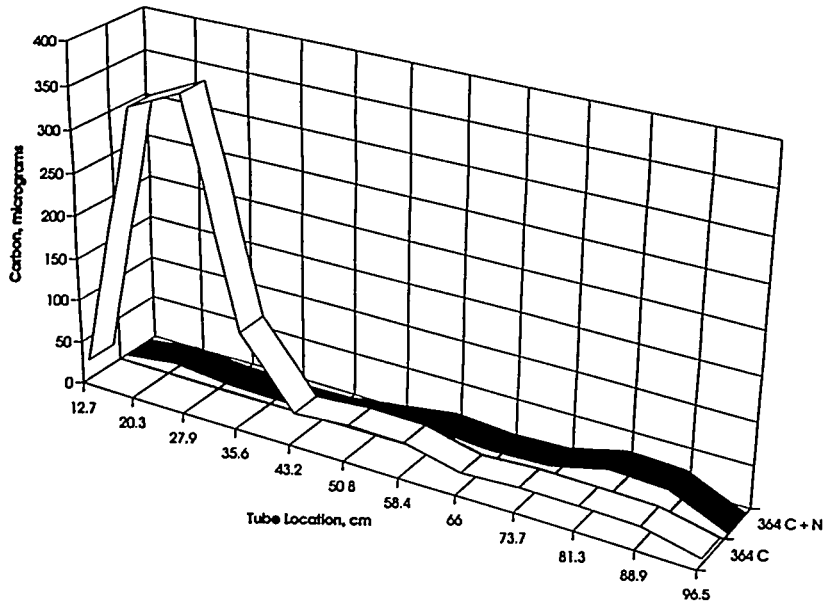


Figure 10. Nitrogen Purge Effect on 1 % S Fuel Deposit Level in STHE 316 SS Metal Tubes at 364 Degrees C

When two test tubes were used in series, very low deposit levels were observed on the second tube using the 1 % Sulfur and the Reference No. 2 D fuels. Figure 11 provides comparative data for the Reference No. 2 D fuel in both 316 SS and 304 SS test tubes, at 364 °C.

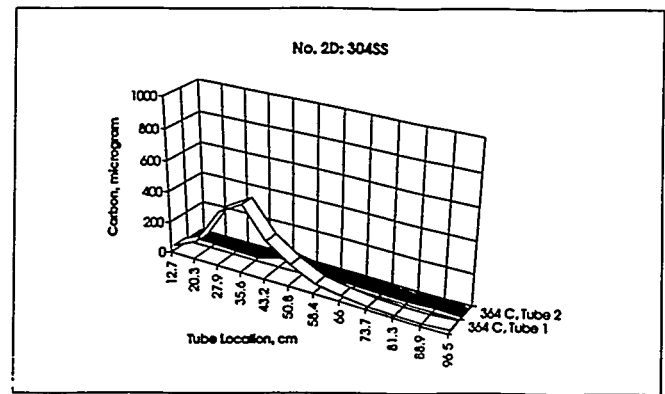
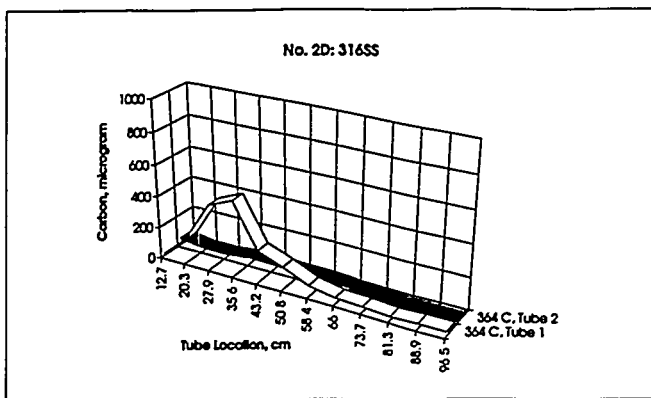


Figure 11. Reference No. 2D Fuel Deposit Level on STHE 316 SS and 304 SS Serial Metal Tubes at 364 Degrees C

Arrhenius activation energy values are summarized for the three fuels in Fig. 12 (for different sections of the test tubes covering the 5.6 to 35.6 cm, 35.6 to 96.5 cm, and 5.6 to 95.6 cm which was the whole tube). As would be expected, the values generally reflected the change in deposit quantity with temperature. Knowing that the oxygen was depleted at about 260°C, increases in deposit level with increase in temperature would not be expected to increase until pyrolysis temperatures were reached, and even then deposit levels would probably be lower as any deposit formed on the surface may subsequently pyrolyze.

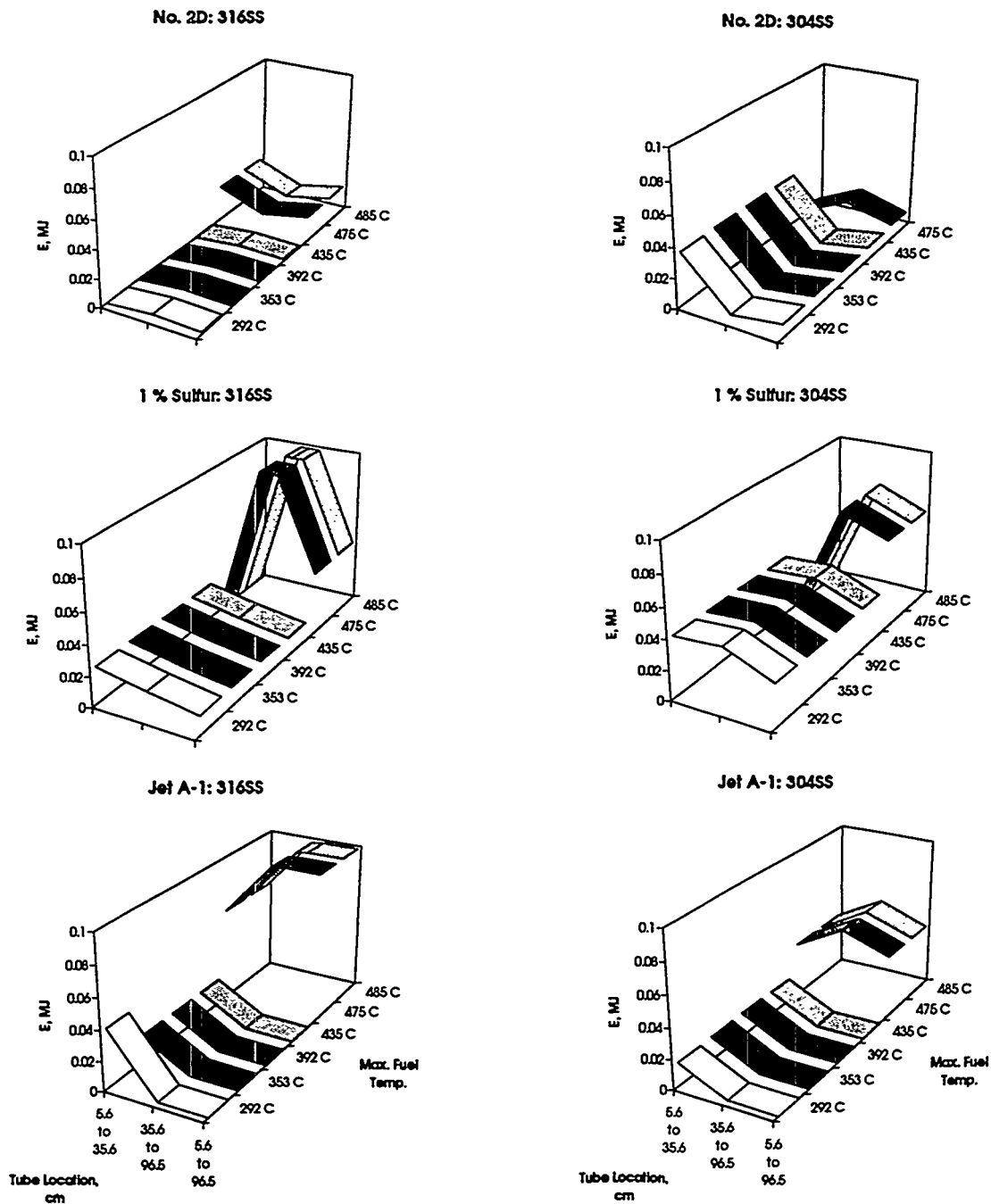


Figure 12. Arrhenius Energies of Activation For Three Fuels on 304 SS and 316 SS STHE Metal Tubes Using Carbon Levels for the Whole Tube and Two Sections of the Tube

IV. Conclusions

- The mechanism of deposit formation on fuel-wetted hot metal surfaces involves thermal-oxidation reactions which are limited by the available oxygen. Different fuels contain different amounts of reactive species capable of oxidizing and subsequently agglomerating to form fuel insolubles which attach to the hot surfaces. Formation of non-deleterious thermal-oxidative products can effectively deplete the available oxygen, thus preventing deleterious oxidation. Metal surface composition effects the quantity of surface deposition, depending on fuel composition and depending on whether the temperature is high enough for pyrolysis to occur.
- At higher pyrolysis temperatures, deposit levels are influenced by both the fuel composition and the surface composition.
- The STHE is a viable procedure for evaluating deposit formation from fuels at high temperatures.
- While the HLPS is a viable tool for evaluating the relative stability of fuels, the temperatures of the test tube are less effective than the bath temperature of the STHE, which more accurately reflects the bulk fuel temperature as it passes out of the heated section of the test tube. This is particularly true at STHE temperatures which caused fuel formation of methane, but no methane was observed at similar tube temperatures in the HLPS for at least one of the test fuels.
- Reduction of deposit can be accomplished by reducing oxygen or heat-pretreating the fuel.

V. Recommendations

- The Army Fuel System Design Guide in The Standard Army Refueling System¹⁵ should address reducing the replenishment of Oxygen in the fuel as this relates to the design of the tank venting system.
- An expanded test matrix, including both tube size and test time, should be evaluated to support conclusions reached in this report related to the mechanism of deposit formation in hot-fuel flowing systems. Test fuels should include additives, especially deposit modifiers, oxidation inhibitors, and detergent/dispersants.
- Fuel prestressing/cleanup systems and oxygen-reduction additives should be evaluated for eliminating thermal-oxidative deposits in hot fuel systems.

VI. Acknowledgement

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Development, and Engineering Center, Fort Belvoir, Virginia. Mr. T.C. Bowen (SATBE-FL) served as the contracting officer's representative, and Mr. M.E. LePera (SATBE-FL) was the project technical monitor. This paper represents only the views of the authors.

VII. REFERENCES

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EFFECT OF HIGH SURFACE AREA ACTIVATED CARBON ON THERMAL DEGRADATION OF JET FUEL

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Different solid carbons added to jet fuel during thermal stressing cause substantial changes in pyrolytic degradation reactions. Activated carbons, especially high surface area activated carbons were found to be very effective in suppressing solid deposition on metal reactor walls during stressing at high temperatures (425 and 450°C). The high surface area activated carbon PX-21 prevented solid deposition on reactor walls even after 5h at 450°C. The differences seen in the liquid product composition when activated carbon is added indicated that the carbon surfaces affect the degradation reactions. Thermal stressing experiments were carried out on commercial petroleum-derived JPTS jet fuel. We also used *n*-octane and *n*-dodecane as model compounds in order to simplify the study of the chemical changes which take place upon activated carbon addition. In separate experiments, the presence of a hydrogen donor, decalin, together with PX-21 was also studied.

Introduction

Jet fuel degradation occurs under long-term low-temperature (oxidative) storage conditions as well as short-term high-temperature (pyrolytic) stress. During both storage and exposure to high temperatures jet fuel decomposes, forming insoluble materials which could deposit in fuel lines or on other surfaces. The higher temperature that jet fuels may be exposed in the future, possibly in the range of 400–500°C, as a result of increased demands for "thermal management" on aircraft complicates the problem even further. Many chemicals have been used as additives, antioxidants, metal deactivators, dispersants and passivators for fuel applications in the oxidative regime. They should be used with caution in fuels taken into the pyrolytic region, since at high temperatures the oxygen plays very complex role and participates in many side reactions¹. Recently, Coleman et al.² reported the promising news that benzyl alcohol and 1,4-benzenedimethanol could retard the formation of carbonaceous solids in Jet A-1 fuel at 425°C in

nitrogen and air atmosphere. The performance of an additive depends on factors, such as type of fuel, fuel composition, additive concentration, and temperature of stressing. It is well known that a fuel that shows the highest degree of instability also has the highest free radical concentration³. Alfelli et al.⁴ reported that solid adsorbents, which they called "Fuel stability foam," produced from polyurethane were found to be effective in greatly improving diesel fuel stability.

We have studied the changes in degradation reactions when different carbons were added to JP-8 jet fuel during thermal stressing at 450°C (ref. 5). The solid carbons with the most disordered structure and the highest surface reactivity (*i.e.*, activated carbons) produced the most significant effect on preventing solid deposition on reactor surfaces. The addition of carbon black also prevented solid deposition, but the effect was not as evident as that seen with the activated carbon addition. The most ordered and the least reactive solid (SP-1 graphite) used did not have a significant influence on thermal reactions.

We assumed that the activated carbons added during thermal stressing of jet fuels promoted a variety of surface reactions because of their active surfaces. The reactivity of an activated carbon depends on the nature of the carbon surface, the presence of carbon-oxygen surface structures, the availability of the active sites and the surface area. Spiro⁶ studied the catalytic effect of carbons on reactions in solution and reported that the surface area played an important role on carbon catalytic activity. In our previous studies, we showed that the activated carbon surface area is an important parameter which determines to a high degree the effectiveness in suppressing solid deposition during thermal stressing at high temperatures⁷. For better understanding the role of activated carbon during thermal stressing, we used model compounds *n*-dodecane and *n*-octane. Using model compounds simplifies the study of the chemical changes upon activated carbon addition⁸.

The main objective of our work reported in the present paper was to study the thermal degradation of commercial petroleum-derived JPTS jet fuel (as well as model compounds *n*-dodecane and *n*-octane) in the presence of high surface area activated carbon PX-21.

Experimental Section

Thermal stressing experiments were carried out on 10 mL samples of a commercial petroleum-derived JPTS jet fuel at 425 and 450°C for 1 and 5h. The JPTS fuel is a thermally stable jet fuel, containing a proprietary additive JFA-5⁹. The experiments were carried out in microautoclave reactors purged with ultra-high purity (UHP) grade nitrogen five times to minimize the presence of dissolved oxygen and finally pressurized to 0.7 MPa with nitrogen or air. The *n*-dodecane, *n*-octane, and *cis/trans*-decalin used as model compounds were purchased from Aldrich and used without further purification. In some experiments, 5 or 50% decalin was added to the alkane model compounds. The experimental method for stressing and analyzing the model

compounds was the same as used for the authentic fuel. The high surface area activated carbon PX-21 was obtained from Amoco Oil Company. The influence of the amount of PX-21 carbon was studied by adding different quantities (50, 150, and 250 mg) during thermal stressing of the model compounds or the fuel.

Gas chromatography (GC) of liquid samples was conducted using a Perkin-Elmer 8500 GC with a fused silica capillary column. Quantitative analysis of the liquid products was performed based on the calibration curves obtained from external standards. Compounds in the liquid products were identified by capillary gas chromatography–mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with HP 5971A mass selective detector.

The gaseous products obtained after stressing were analyzed using a Perkin-Elmer AutoSystem gas chromatograph equipped with two different columns and detectors for quantifying the components. The gaseous products were identified by comparing their retention times with those of standard gases (Supelco), and quantified by using external standards.

The activated carbon PX-21 was characterized before and after stressing experiments by N₂ adsorption at 77K using a Quantachrome automated adsorption apparatus, Autosorb-1, model ASIT and the BET surface areas were calculated¹⁰. The activated carbon PX-21 and the deposits obtained after thermal stressing were examined using a polarized-light microscope, Nikon-Microphot FXA and a scanning electron microscope (SEM), ISI ABT, model SX-40A.

Results and Discussion

Thermal stressing of JPTS jet fuel with PX-21 activated carbon at 425 and 450°C in N₂ and air atmosphere. The thermal stressing experiments on JPTS jet fuel in the presence of high surface area activated carbon PX-21 were carried out at 425 and 450°C for 5h in nitrogen and air. Initially, the fuel is a clear, colorless liquid which became dark brown after 5h at 450°C. The liquid obtained after thermal stressing of 10 ml JPTS mixed with 100 mg PX-21 is much lighter and does not differ very much in color from the unstressed JPTS.

Tables I and II present the results for thermal stressing of JPTS with and without PX-21 at 425 and 450°C for 5h in nitrogen and air. When PX-21 is added, generally, higher liquid products yields and lower final reactor pressure are obtained with no solid deposition. The trends observed from thermal stressing at 450 and 425°C are essentially the same, except for lower liquid yields and higher reactor pressures with more solid deposition in the absence of PX-21 at higher temperature (Table II). The presence of oxygen (air) during stressing causes more degradation of jet fuel (Tables I and II).

Figures 1 and 2 show the yields of alkanes in the liquid products after stressing. The C₈ and C₁₄ alkanes are not shown because they are coeluted with other compounds. It is clear from

the figures that adding PX-21 gives lower concentrations of shorter chain alkanes (C₅-C₉) and C₁-, C₂-, and C₃-benzenes, and higher concentrations of longer chain alkanes (C₁₀-C₁₅), compared to the composition of the liquids produced without PX-21. Overall, addition of PX-21 appears to preserve the alkanes present in JPTS. A more extensive degradation in the presence of air is also noted from the lower concentrations of longer chain alkanes (Figure 2).

The differences seen in the liquid product compositions shows the active role of PX-21 in the degradation reactions. One possible explanation for the apparent increase in the stability provided by the activated carbon could be the stabilization of nascent free radicals on carbon surfaces. It is also apparent that the presence of oxygen limits the stabilizing effect of the added carbon upon stressing the fuel under the same conditions.

There are substantial differences also in the head-space gas yield and composition obtained after thermal stressing of JPTS with and without PX-21 in nitrogen, as shown in Table III. The major compounds in the gas sample obtained after thermal stressing of JPTS alone are methane, ethane coeluted with ethylene, and propane. Except for propylene and butene, the other C₃-C₆ gas species are in negligible concentrations. Lower methane and propylene and much higher propane and butene yields in the presence of PX-21 suggest significantly different reaction mechanisms of thermal degradation upon activated carbon addition.

The BET surface area of PX-21 is 2090 m²/g. It shows anisotropic microstructures (an unusual characteristic for activated carbons), since it is derived from a petroleum coke. Table IV shows the BET N₂ surface area of PX-21 after thermal stressing at 425 and 450°C in nitrogen and air atmosphere. The initial surface area of PX-21 activated carbon decreases substantially. The surface areas of PX-21 after thermal stressing at 450°C decrease more than after thermal stressing at 425°C. Most probably, the higher temperature contributes to more extensive interaction of carbon surface with jet fuel. It should be also noted that the surface area of PX-21 after thermal stressing in air is lower than in nitrogen. Clearly, oxygen also contributes to the adsorption/deposition processes. The scanning electron micrographs of PX-21 after stressing at 450°C show a thin layer of carbonaceous solid covering the activated carbon surface as well as a few discrete particles deposited on the surface. The PX-21 has a very microporous structure (2090 m²/g), and it is not possible to observe the micropores with scanning electron microscopy. Most probably, activated carbon micropores are also filled with liquid products or solid deposits.

Thermal stressing of *n*-octane mixed with 5% decalin and PX-21 activated carbon at 450°C for 1h in N₂ atmosphere. Song et al.⁷ reported that adding hydrogen donors, such as tetralin or decalin, to jet fuel reduced formation of solid deposit at 450°C and decreased the extent of fuel decomposition and gas formation. The increased stability of jet fuel in the presence of H-donors is attributed to the stabilization of the reactive radicals, which contributes to inhibiting radical decomposition, cyclization, aromatization, and condensation reactions. When

the activated carbon is present during thermal stressing of *n*-octane+decalin one might expect that the hydrogen-transferring pyrolysis mechanism to be different. Adding PX-21 considerably reduced the pressure increase during stressing of *n*-octane as well as the formation of lighter compounds, such as C₄ and C₅ alkanes. The final product of H-transfer from decalin when it acts as a hydrogen donor is naphthalene. The higher amount naphthalene and the lower amount of decalin identified in the liquid stressed with PX-21 indicates that PX-21 affects the H-transfer reactions. Figure 3 shows the naphthalene and tetralin concentrations in the stressed liquids upon adding different amounts of PX-21, indicating significant increases upon adding as little as 50 mg of PX-21 with the effect leveling off at 150 mg PX-21 addition. It is possible that most of the hydrogen is abstracted by the carbon surface and redonated to stabilize the free radicals arriving on the surface.

The specific structure of activated carbons can explain their role as a hydrogen carrier during thermal stressing of *n*-octane+decalin and *n*-dodecane+decalin at 450°C. Activated carbons have a structure consisting of sheets of aromatic condensed ring systems stacked in nonpolar layers. These sheets have edges, defects, dislocations and discontinuities. The carbon atoms at these places have unpaired electrons and residual valencies and are richer in potential energy. These carbon atoms are highly reactive and constitute active sites or active centers.

Considerable research has been dedicated to understand the nature of these active sites in the surface and catalytic reactions of carbons. Puri and Bansal^{11,12} studied the chlorination of coconut charcoals and observed that the chemisorbed hydrogen was eliminated in a number of steps, depending on the temperature of the treatment. This was attributed to the fact that hydrogen in charcoals was bonded at different types of sites associated with various energies of activation. The activation energy of adsorption at relatively more active sites is 7.4 kcal/mol. Sherman and Eyring¹³ made theoretical calculations of the energy of activation for dissociative chemisorption of hydrogen from a carbon surface and found the values to vary with carbon-carbon spacing.

Thermal stressing of *n*-dodecane mixed with 5% decalin and PX-21 activated carbon at 450°C for 1h in N₂ atmosphere. Figure 4 shows the variations of naphthalene, *cis*-decalin and *trans*-decalin concentrations of the liquids obtained after stressing of *n*-dodecane alone and with 50, 150 and 250 mg PX-21. The naphthalene concentration sharply increases when activated carbon is added. The concentration of naphthalene in the stressed liquids shows a linear dependence on the amount of activated carbon mixed with dodecane, and increases with the increasing carbon concentration from 50 to 250 mg. The amount of *cis*- and *trans*-decalin in the stressed liquids shows the opposite trend, *i.e.*, decreasing with the added PX-21 concentration. The decrease in decalin concentration is not as sharp as the increase in the concentration of naphthalene, suggesting that part of the naphthalene comes from the pyrolytic degradation that takes place during thermal stressing,

Dodecane → Alkylcyclohexenes → Alkylbenzenes → Naphthalene .

Figure 5 shows the changes in the concentrations of shorter chain alkanes and alkenes as a function of the amount of PX-21 added. The alkanes *n*-butane, *n*-pentane and *n*-hexane coelute with the corresponding alkenes and their area percents can not be calculated separately. There is a sharp drop in the percent area of *n*-butane+butene and *n*-pentane+pentene when activated carbon is added, as well as in the concentration of *n*-hexane+hexene and *n*-heptane. The amount of carbon does not seem to affect the concentration of shorter chain alkanes and alkenes, but it does affect the stability of dodecane, as can be seen from Figure 6. The area percent of dodecane stressed without carbon is 10% lower than with PX-21. There is an additional stabilization of dodecane when the amount of carbon increases from 50 to 250 mg. However, dodecane concentration does not differ very much in the stressed liquids, being 62.80% in the liquid with 50 mg PX-21 and 65.15% in the liquid with 250 mg PX-21.

Thermal stressing of *n*-dodecane mixed with 50% decalin and PX-21 at 450°C for 1h in N₂ atmosphere. Table V compares the experimental results obtained after stressing dodecane with 50% decalin and with 5% decalin. It was seen that the color of stressed liquid is darker and there is less liquid left after stressing of dodecane with 5% decalin than with 50% decalin. There is no deposit formation on the reactor walls when activated carbon is added in both cases, but there is a larger increase in the activated carbon weight when the decalin concentration is 5%. These results suggest that the degree of thermal degradation of dodecane depends on both the amounts of decalin and the activated carbon added. Most probably, activated carbon added to dodecane mixed with 5% decalin adsorbed more of the intermediates/or accumulated more deposits from the degradation reactions.

Table VI shows the main compounds identified in the liquids after thermal stressing of *n*-dodecane+decalin (50%) mixed with 50, 150 and 250 mg PX-21. The rest of the compounds identified are in negligible concentrations and are not listed in Table VI. From Table VI, the area percents of dodecane, decalin, naphthalene, and tetralin in the liquids obtained from thermal stressing of dodecane+50% decalin follow the same trends as those obtained after stressing of dodecane with 5% decalin. The concentrations of dodecane, naphthalene, and decalin increase with adding activated carbon. The increase depends slightly on the amount of carbon added. In accordance with the increase in naphthalene and tetralin concentration, the *cis*- and *trans*-decalin concentration decreases.

The data in Table VI for alkane concentration in the stressed liquids with and without PX-21 lead to the following speculations: The variation of product distribution with PX-21 is mainly due to distinction between different radicals. The lower concentration of light compounds C₄-C₈

and higher concentration of C₉-C₁₁ alkanes obtained from stressing of dodecane+decalin+50 (or 150) mg PX-21 suggest that the primary radicals were more stable than the secondary. However, with the increasing amount of PX-21, the alkane concentration increases, and, in the liquid stressed with 250 mg PX-21, the concentration of C₆-C₁₁ alkanes is even higher than the alkanes concentration from dodecane+decalin stressed without carbon. These results are in contradiction with the higher percent of dodecane preserved with increasing amount of PX-21 added. Most probably, the active sites of PX-21 carbon promote certain cracking reactions in addition to stabilizing the free radicals.

Conclusions

The high surface area activated carbon PX-21 during thermal stressing at high temperatures (425 and 450°C) suppressed solid deposition from jet fuel and model compounds *n*-dodecane and *n*-octane on the metal reactor walls. Higher concentrations of longer chain alkanes and lower concentration of alkylated aromatics were identified in the liquid products obtained from thermal stressing of JPTS in the presence of activated carbon. The activated carbon surfaces appear to be effective in stabilizing the free radicals or catalyzing recombination reactions. The presence of oxygen limits the stabilizing effect of the added carbon upon stressing the fuel under the same conditions.

Adding decalin as H-donor additionally reduced the extent of decomposition of *n*-dodecane and *n*-octane. The activated carbon addition also appears to promote H-transfer reactions during thermal treatment. The structure of the activated carbon PX-21 consists of sheets of aromatic condensed rings with edges and defects where the carbon atoms are highly reactive. Most probably, the active sites of PX-21 carbon act to stabilize the pyrolysis products, enhance the H-transfer reactions and to promote some cracking reactions.

Acknowledgments

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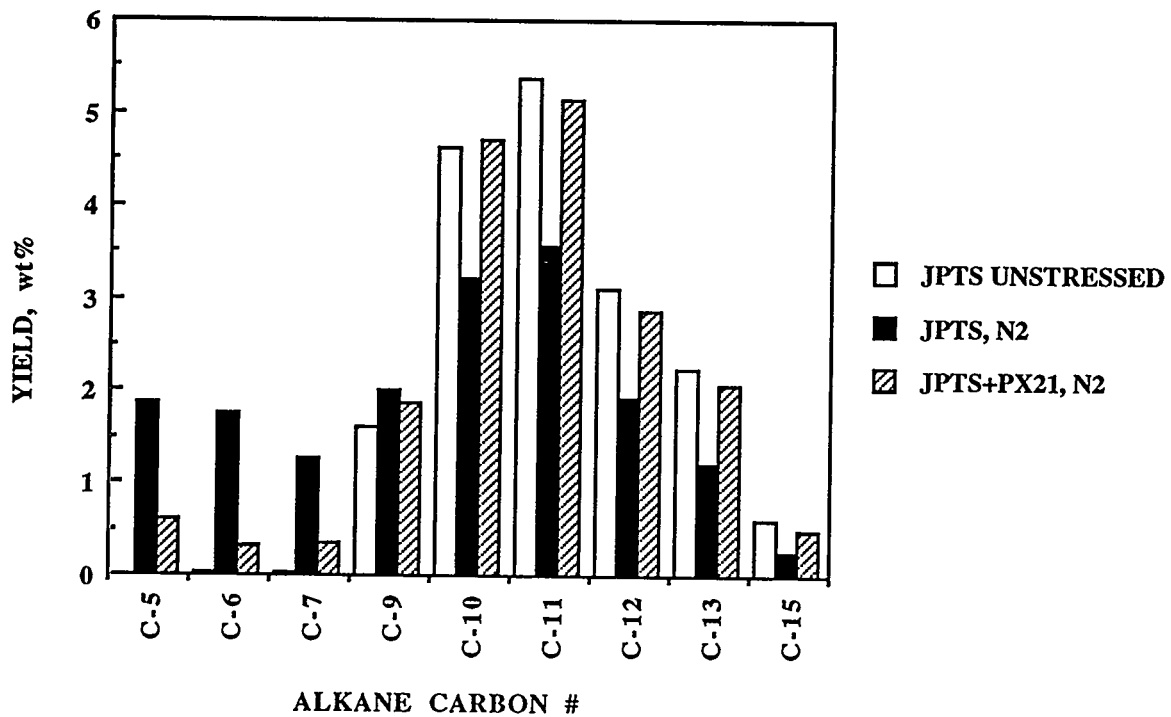


Figure 1. Yields of n-Alkanes from Thermal Stressing of JPTS Jet Fuel at 425°C for 5h in Nitrogen.

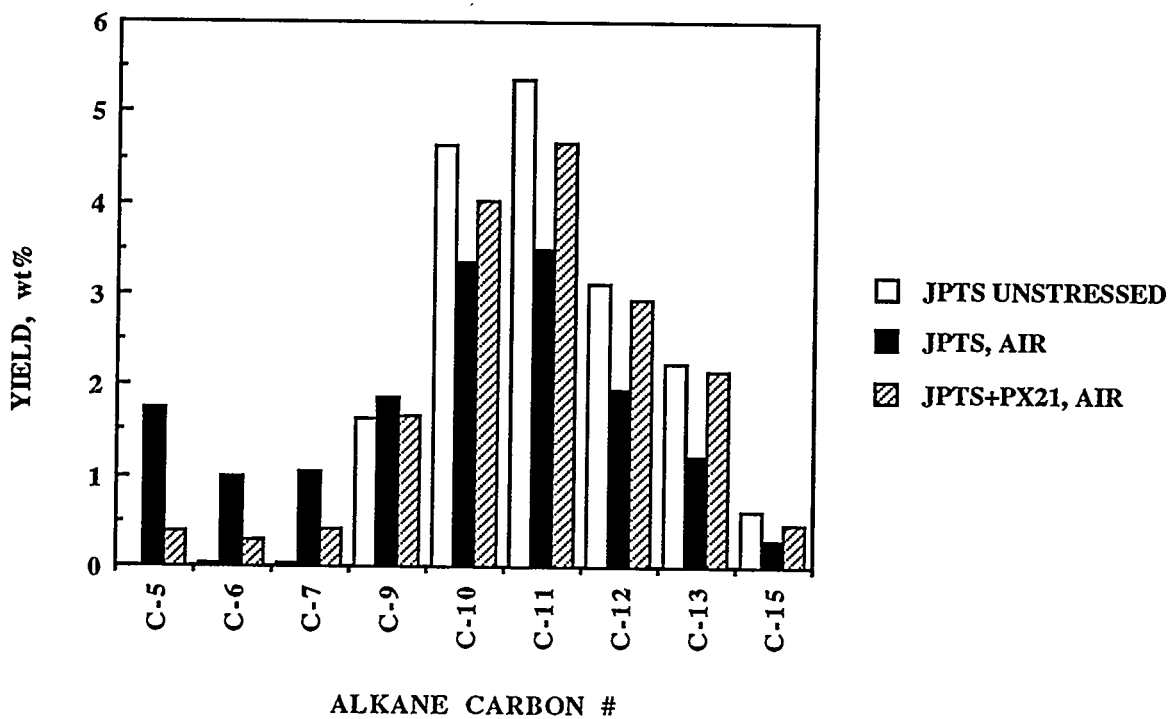


Figure 2. Yields of n-Alkanes from Thermal Stressing of JPTS Jet Fuel at 425°C for 5h in Air.

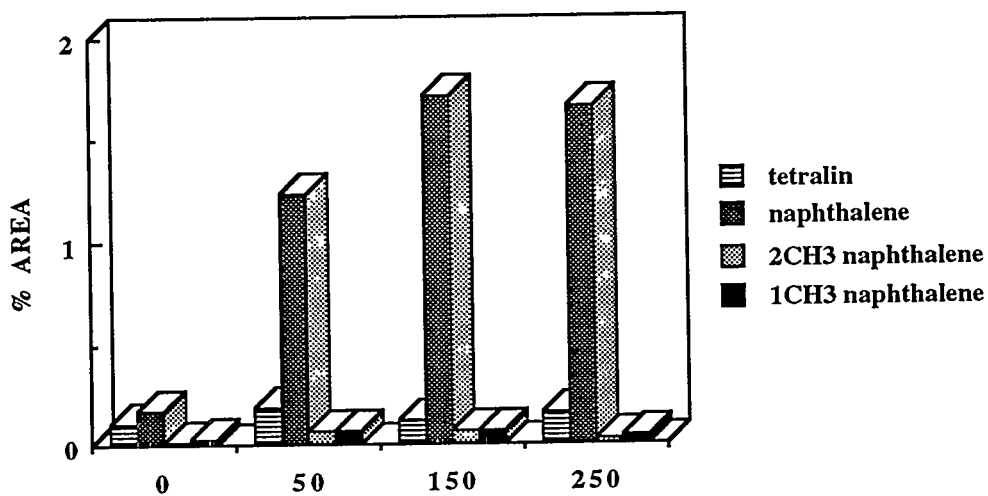


Figure 3. Effect of PX-21 Concentration on the Naphthalene and Tetralin Concentrations in the Liquids Obtained from Thermal Stressing of n-Octane with Decalin.

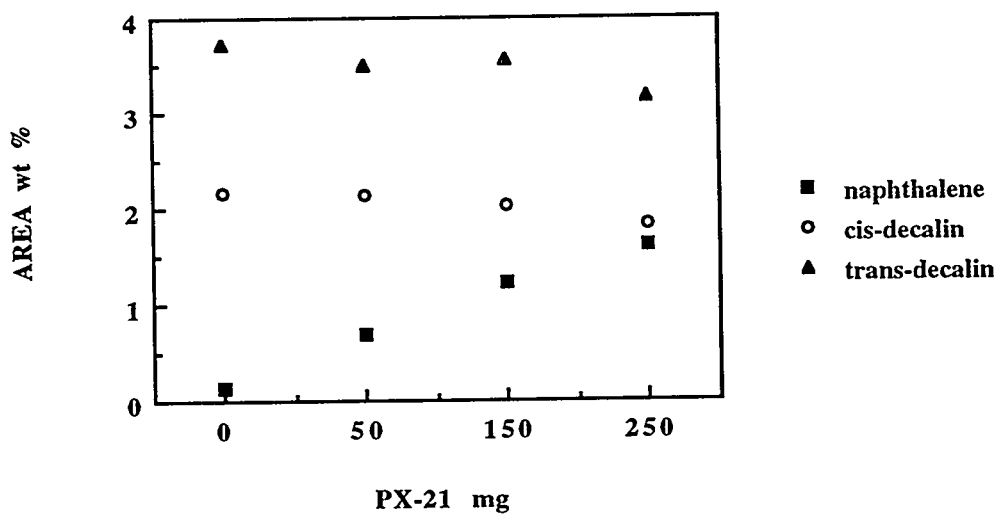


Figure 4. Effect of PX-21 Concentration on the Naphthalene and Decalin Concentrations in the Liquids Obtained from Thermal Stressing of n-Octane with Decalin.

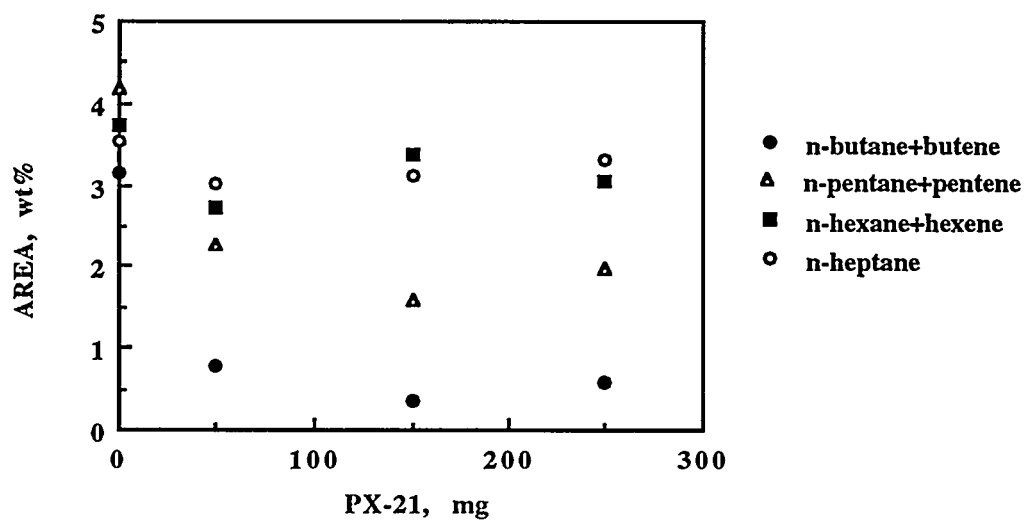


Figure 5. The Relative Concentrations of Shorter Chain Alkanes and Alkenes as a Function of the Amount of PX-21 Added.

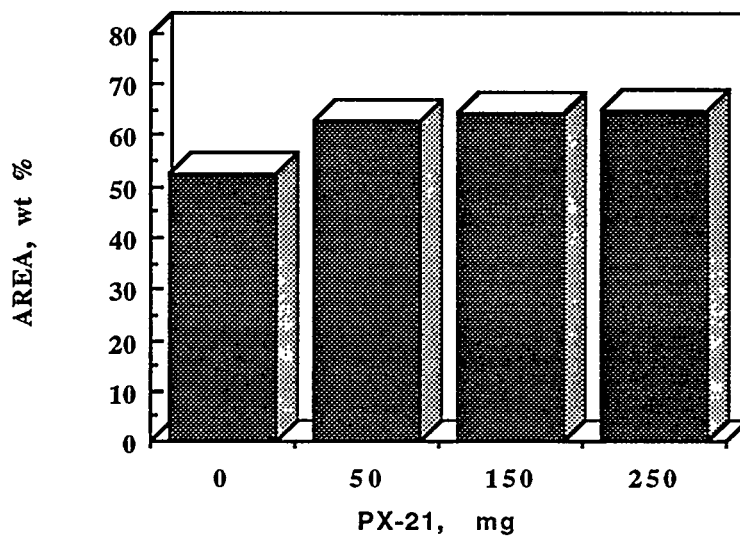


Figure 6. The Relative Concentration of Dodecane in the Liquids Obtained from Stressing with and without Added PX-21.

Table I. Yield of Liquid and Solid Products and Reactor Pressure after Thermal Stressing of JPTS with and without PX-21 at 425°C for 5 h.

Sample JPTS: 10 ml (PX-21: 50 mg)	Solid on reactor walls, mg, ± 10 mg	Liquid yield, ml ± 0.3 ml	Final gas pressure (cold), psi ± 100 psi	Increase of weight of solid, %
JPTS in N ₂	20	9.0	200	-
JPTS+PX-21 in N ₂	-	9.5	100	32
JPTS in air	30	8.2	200	-
JPTS+PX-21 in air	-	8.8	100	34

Table II. Yield of Liquid and Solid Products and Reactor Pressure after Thermal Stressing of JPTS with and without PX-21 at 450°C for 5 h.

Sample JPTS:10 ml PX-21:100 mg	Solid on reactor walls, mg ± 10 mg	Liquid yield, ml ± 0.3 ml	Final gas pressure (cold), psi ± 100 psi	Increase of weight of solid, %
JPTS in N ₂	60	5.1	550	-
JPTS+PX-21 in N ₂	-	5.5	300	35
JPTS in air	83	4.5	500	-
JPTS+PX-21 in air	-	5.0	300	50

Table III. Percent by Volume of Gases Obtained from Thermal Stressing Experiments of JPTS with and without PX-21 at 425°C for 5h in Nitrogen.

Compounds identified	JPTS stressed alone, %	JPTS stressed with 100 mg PX-21, %
methane	37.58	34.55
ethane+ethylene	34.06	34.73
propane	14.20	20.99
propylene	9.67	0.00
i-butane	0.94	1.07
butane	0.56	0.00
butene	1.67	8.66
pentane	1.14	0.00
pentene	0.10	0.00
hexane	0.08	0.00

Table IV. Surface Area of PX-21 Activated Carbon after Thermal Stressing with JPTS.

Stressing conditions	BET N ₂ surface area, m ² /g
unstressed JPTS	2090
425°C, 5h, in nitrogen	785
425°C, 5h, in air	630
450°C, 5h, in nitrogen	550
450°C, 5h, in air	320

Table V. Some Experimental Results from Stressing of Dodecane with 5 and 50% Decalin and 50, 150 and 250 mg PX-21 at 450°C for 1h.

	Dodecane + 5% Decalin				Dodecane + Decalin 50%			
	0 mg PX-21	50 mg PX-21	150 mg PX-21	250 mg PX-21	0 mg PX-21	50 mg PX-21	150 mg PX-21	250 mg PX-21
Color	yellow	yellow	yellowish	yellowish	yellowish	colorless	colorless	colorless
Liquid, ml	7.6	5.6	5.0	4.6	9.6	9.5	9.0	7.0
Deposit, mg	45	-	-	-	20	-	-	-
Increase of solid weight, %	-	75	75	80	-	55	65	70

Table VI. The Main Compounds Identified in the Liquids Obtained after Thermal Stressing of Dodecane+Decalin 50% Mixed with 50, 150 and 250 mg PX-21 at 450°C for 1h.

Compounds identified	Dodecane+ Decalin 50%	Dodecane+ Decalin 50% + 50 mg PX-21	Dodecane+ Decalin 50% + 150 mg PX-21	Dodecane+ Decalin 50% + 250 mg PX-21
n butane+butene	1.05	0.13	0.36	0.49
n pentane+pentene	1.51	0.48	0.83	1.27
n hexane	1.33	0.84	1.25	2.02
n heptane	1.27	1.04	1.17	1.54
n octane	1.41	1.26	1.26	1.58
n nonane	1.24	1.23	1.29	1.63
n decane	0.46	0.63	0.73	1.05
n undecane	0.56	0.53	0.51	0.31
n dodecane	28.68	35.11	35.39	36.50
cis decalin	20.78	20.11	18.14	14.17
trans decalin	30.96	29.35	29.55	27.78
naphthalene	0.09	0.70	1.17	1.99
tetralin	0.40	0.92	1.30	1.99

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DEVELOPMENT OF OXYGEN SCAVENGER ADDITIVES FOR JET FUELS

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Abstract

Our current research program is in response to the U. S. Air Force's FY93 New Initiative entitled "Advanced Fuel Composition and Use." The critical goal of this initiative is to develop aircraft fuels which can operate at supercritical conditions. This is a vital objective since future aircraft designs will transfer much higher heat loads into the fuel as compared with current heat loads. In this paper it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient in flight removal of a fuel's dissolved oxygen. It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. It is envisioned that a thermally activated reaction will occur, between the oxygen scavenging additive and dissolved oxygen, in a controlled and directed manner. Consequently formation of insoluble thermal degradation products will be limited. It is believed that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function in significantly higher temperature regimes. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future development of endothermic fuels.

1. Introduction

Currently, aircraft fuels have a practical temperature limit (325°F, 150°C) which cannot be exceeded without causing serious problems in the fuel system. If this temperature threshold is exceeded, the fuel chemically decomposes to form gums and solids which adversely affect the fuel system. Conventional wisdom posits

that these fuel deposits are the end result of a sequence of complex chemical reactions that are thermally promoted between oxygen dissolved in the fuel and certain "reactive" fuel molecules.¹ If this paradigm (i.e. conventional wisdom) is correct then efficient removal of oxygen from the fuel would limit the oxidative break down of the fuel. Consistent with this view is the general observation that purging a jet fuel of dissolved oxygen usually will result in a tremendous improvement in the thermal stability of that fuel.²

Recent studies have revealed that most of a fuel's dissolved oxygen is consumed by chemical reactions which initially produce peroxides at temperatures between 150-260°C.³ In addition, the following experimental observations provide very significant clues as to the nature of the chemical reactions between oxygen and trace fuel components at these temperatures:

(i) Jones et al. have recently reported how different concentrations of dissolved oxygen affect the formation of insolubles in jet fuels at 185°C. Of the two Jet A's examined, one was found to produce insolubles at a rate which exhibited a zero order dependency in oxygen, while the other fuel produced insolubles at a rate which exhibits a first order dependence in oxygen.^{4, 5}

(ii) Classical chain - breaking donor antioxidants (i.e. substituted phenols and phenylene diamines) usually do not inhibit deposit formation when a fuel is stressed at temperatures of 150-250°C.^{6,7}

Based upon observation (ii) it should be clear that the sub-critical oxidative stability of jet fuels is currently problematic. Consequently, it is imperative that this problem be rectified in order that future aircraft fuels possess adequate thermal stability to enable them to achieve supercritical conditions with minimal degradation within the fuel system. It is proposed herein that the efficient removal of dissolved oxygen from jet fuels during flight might provide the necessary improvement in sub-critical fuel stability. If this line of reasoning is correct, then the fundamental problem can be reduced to the problem of removal of a fuel's dissolved oxygen before it contributes to the thermal degradation of the fuel.

There are two fundamentally different approaches to the removal of dissolved oxygen from a jet fuel during flight. One approach would be to utilize a

technological solution (on board purging), while another approach would be to effect a chemical solution. We envision the chemical solution to entail adding a specifically designed fuel additive (concentration 200-400 ppm) to the jet fuel. Theoretically, this additive would chemically react (as the temperature of the fuel increases) with the dissolved oxygen and thus remove it, in an innocuous manner, from the fuel during flight. In this manner the jet engine would receive its fuel with minimal dissolved oxygen (hence the fuel will have high thermal stability), and there would not be any "unnecessary" (i.e. purging technology) payload added to the aircraft.

The focus of our research program is to explore the fundamental chemistry necessary to develop potential fuel additives (candidates) that will function as thermally activated oxygen scavengers. It is envisioned that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function as "JP-900" fuels. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future endothermic fuels. This is a vitally important objective since it is now clear that most of a jet fuels thermal oxidative degradation occurs at sub-critical temperatures, *Vide supra*. Therefore, all of our current efforts in additive development are directed at solving the sub-critical oxidation problem. It is anticipated that future work will examine the chemistry of all successfully developed sub-critical additive candidates under supercritical conditions.

In order to logically articulate an approach to the development of thermally activated oxygen scavengers the fundamental reactivity of molecular oxygen with organic molecules needs to be reviewed.

IA. The Reaction of Organic Molecules with Molecular Oxygen

Recently we have published an in depth "state of the art" discussion of the various (low temperature) reaction mechanisms potentially involved in the oxidative phase of the degradation of petroleum products.^{8,9} Consequently, only a brief summary of the pertinent details of autoxidation with respect to this proposal will be addressed.

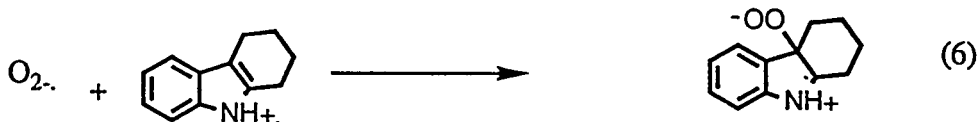
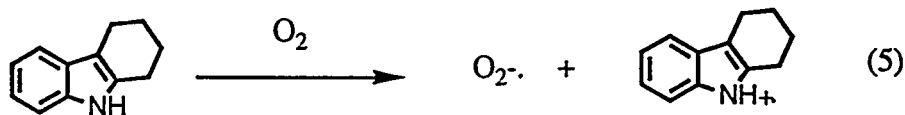
The most common type of reaction between organic molecules and molecular oxygen is a peroxy radical-chain oxidation. For this mechanism the observed initial rates of oxygen absorption are found to be (i) independent of oxygen concentration when the partial pressure of oxygen above the solution exceeds 100 torr (i.e. zero order in oxygen), (ii) one half order with respect to the initiator concentration, (iii) first order with respect to the concentration of RH, and (iv) inhibited in the presence of phenolic antioxidants.

We have recently proposed a second, less common type of reaction between electron rich (i.e. readily oxidizable) organic molecules and molecular oxygen as being important in the oxidative degradation of various fuels.^{8, 10} We have designated this reaction as electron transfer initiated oxygenation (ETIO), and define such a reaction as:

Any oxygenation reaction in which the rate limiting step involves an electron transfer from the substrate to molecular oxygen (or its reduction products).

The ETIO concept should be thought of as an entire family of oxidation mechanisms (not just one mechanism) in which the common feature is rate limiting electron transfer. The ETIO concept provides a rational explanation for the previously mentioned Jet A O₂ order dependency noted by Jones et al.⁴ Most currently used petroleum antioxidants are designed to suppress the classical peroxy radical-chain oxidation. Since the ETIO concept represents an alternative oxidation pathway it might provide a rational explanation for the oxidative degradation of fuel products in the presence of chain breaking antioxidants (hence, observation (ii) in the introduction can be rationalized).¹¹

Below is depicted the simplest possible description of an ETIO mechanism using tetrahydrocarbazole (THC) as a model substrate. In this mechanism reaction (5) is the rate limiting step with steps (6) and (7) being fast:



Invoking the standard steady state approximations and deriving the corresponding rate law yields: ⁸

$$-d[\text{THC}] / dt = k[\text{THC}][\text{O}_2]$$

Thus the rate law from the most simple depiction of an ETIO reaction is second order overall (first order in both $[\text{O}_2]$ and $[\text{THC}]$). Consequently, the presence of a first order dependency in oxygen, for an autoxidation, is consistent with the ETIO concept and inconsistent with the operation of the simplest depiction of a peroxy radical chain.

In addition, it is important to note that both mechanisms form the same initial oxidation product (RO_2H). Therefore the peroxy radical chain mechanism and the ETIO mechanism are linked by a common intermediate (an organic hydroperoxide). Therefore, an autoxidation in which an ETIO mechanism provides initiators (from hydroperoxide decomposition) for a peroxy radical chain, would be expected to exhibit a small fractional order dependency in oxygen, *Vide infra*.

The validity of the above mentioned idea that both ETIO and peroxy radical-chain oxidation can contribute to the oxidative degradation of various petroleum products is supported by an interpretation of recently published studies. It is important to realize that each mechanism can operate either independently or simultaneously. Fodor et. al ¹² have measured the rates of peroxide formation in jet fuels at temperatures from 43-120°C with oxygen partial pressures ranging

from 2-165 psi. The rate of peroxide formation was found to be independent of the oxygen partial pressure. In addition, Black et al.¹³ have recently reported that peroxide formation upon stressing several jet fuels(low pressure reactor (LPR) method, 100°C, 100 psi oxygen) could be significantly suppressed by use of phenolic antioxidants. Both of these reports are consistent with a peroxy radical chain mechanism for peroxide formation during simulated aging of the studied jet fuels.

Hardy et al.¹⁴ have stressed (LPR, 80°C, 25-100 psi O₂) straight run diesel fuels that contained 30% catalytic cracked LCO (light cycle oil) and measured insoluble formation as a function of oxygen partial pressure. For those fuels which were oxidatively reactive, the amount of insolubles produced were found to be a function of the oxygen partial pressure. Data presented for one diesel fuel/LCO blend indicates that initial insolubles formation for this fuel exhibits an approximate first order dependency in oxygen. However, the other reactive diesel fuel blends exhibited oxygen order dependencies of less than one. The one diesel/LCO blend in which insoluble formation was found to exhibit first order dependency in oxygen is consistent with the operation of a simple ETIO type pathway for deposit formation. In addition, Hardy et al.¹⁵ and Bernasconi et al.¹⁶ have shown that standard antioxidants (substituted phenols, and phenylene diamines) are generally not effective in limiting insoluble formation for oxidatively reactive diesel fuels. Thus, all of these observations are inconsistent with a simple peroxy radical-chain mechanism for the observed diesel/LCO blend oxidative degradation.

II. Experimental Section

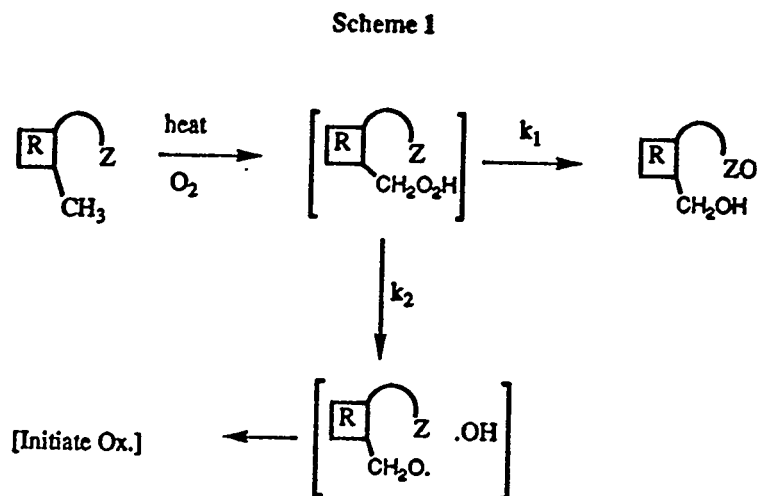
All experimental details have been previously described. 17a

III. Development of Oxygen Scavenger Additives

Contained in this section is a logical articulation of our approach to the development of oxygen scavenger additives. For clarity this section is divided into 2 parts; with part A developing and establishing the necessary presuppositions and the overall thinking. Presented in part B is our preliminary results to date.

IIIA. Conceptualization of Idea

The idea conceptualized in Scheme 1 is predicated upon the following observations concerning jet fuel degradation, as indicated by both peroxide and



insolubles formation:

- (i) insoluble formation increases with temperature and at $< 300^\circ\text{C}$, tends to involve reactions of trace indigenous heteroatom

containing molecules (S,N, and probably O) with dissolved oxygen.^{1, 17b,18}

(ii) most of the oxygen consumption by the bulk fuel and concomitant peroxide formation occurs at temperatures between 150-260°C.^{3,5}

(iii) under the pressure regimes typically found in current jet engines(or simulating devices), somewhere between 300-450°C a jet fuel experiences the physical transition from a liquid into a supercritical fluid. This phenomenon usually results in a sharp decrease in the rate of autoxidative deposit formation .²

(iv) at temperatures >400°C, most fuel insolubles tend to be produced by pyrolysis reactions.^{19,20}

If the above stated observations and interpretations are correct, and if it is possible to extrapolate aspects of low temperature chemistry (i.e. 50-100°C) into the temperature regime of 160-300°C, then in Scheme 1 is wedded a logical approach to significantly enhance sub-critical jet fuel stability. Inherent in the design of Scheme 1 is the presupposition that the *primordial* fuel degradation reactions reported in the introduction, (i-ii), are ETIO in nature (except the one jet A mentioned in (i)). Consequently, in the absence of oxygen the extent of these reactions will be greatly limited. The additives represented in Scheme 1 will be designed to undergo the ETIO reaction at a lower temperature than the fuel's indigenous ETIO "bad actors". Although this approach does not directly address supercritical fuel stability, it is believed that significant thermal stability improvement will be achieved for the following reasons:

(v) Taylor¹⁸ has reported in his 1974 study, at least for the two jet fuels examined, that reduction of the dissolved oxygen content from air-saturated values (~60ppm) to less than 15ppm, decreased deposit formation produced under supercritical conditions by greater than 50% (when compared to similar deposit levels produced without oxygen removal).

(vi) we envision the oxidized additives structurally containing both, a polar head group and a hydrocarbon tail which may enhance the "solubility capacity" of the supercritical fluid (i.e. the oxidized additive may be able to peptize insolubles).

In Scheme 1 is articulated a logical formulation of how an oxygen scavenger additive would perform its function. The sequence of events begins with the thermally promoted reaction between a portion of the additive molecule [R] and dissolved oxygen to form the initial REDOX product (i.e.. on a gross level, the additive is oxidized while oxygen is reduced to produce the "generic hydroperoxide" shown in Scheme 1. The actual details of these events are complex, and currently are speculative. However, we here postulate that the ideal additive will react with oxygen by ETIO, and not by a peroxy radical chain mechanism.⁸ Therefore we set the following experimental criteria for a successful additive candidate:

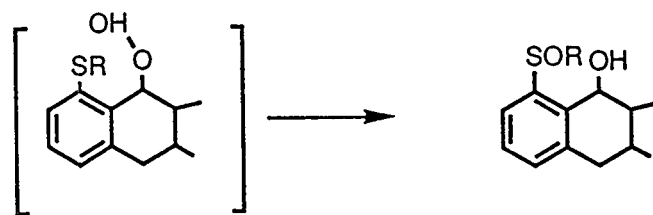
- a) a potential additive candidate must have a rate law that exhibits a first order dependency in both oxygen and the substrate.

- b) a potential additive candidate must exhibit a significant rate of oxygenation in the presence of a high concentration of a phenolic antioxidant.

As indicated in Scheme 1 the fate of the "generic hydroperoxide" is dependent on the relative magnitude of the rate constants k_1 and k_2 . Ideally a pendant nucleophile (Z) is appropriately poised for facile intramolecular hydroperoxide reduction (k_1) to produce the corresponding secondary REDOX product. In Scheme 1 it is assumed that all REDOX products are soluble in the liquid fuel. Competitive with the " k_1 " process is the thermally promoted homolysis of the weak O-O peroxide bond to produce the reactive hydroxyl and alkoxy radicals. The rate constant for this process is designated k_2 and to the extent that k_2 is competitive with k_1 , the fuel will be subjected to general autoxidative degradation (by these radicals initiating peroxy radical chains). To limit this scenario at least two criteria will be employed to maximize the " k_1 " process at the expense of the " k_2 " process:

- (vii) the molecular structure of the primary REDOX product needs to promote the facile intramolecular formation of the appropriate transition state for its rapid conversion into the secondary REDOX product. This can be accomplished by positioning the Z atom exactly five or six atoms removed from the terminal oxygen of the hydroperoxide (see Scheme 2).²¹

Scheme 2



(viii) for certain additive molecular designs, the molecular structure of the primary REDOX product will be so unstable, that spontaneous conversion into secondary REDOX products will occur (consequently the presence of a Z group is not necessary).

IIIB. Preliminary Data

In table 1 is compiled preliminary results of the initial screen of various potential additive candidates. The note worthy feature is that our first three additive candidates, fluorene, 2,5-dimethylpyrrole (DMP) and 1,2,5-trimethylpyrrole (TMP), were deemed as non viable additive candidates. This is based upon the candidates not meeting the previously discussed order and additive criteria. Most importantly, however, is that one compound, candidate 1, met our preliminary criteria.

In figure 1 is presented a more detailed analysis of the oxidation of candidate 1 in dodecane. In plot A is shown a GC analysis of the consumption of candidate 1 at 120°C. A linear plot with much scatter in the data is revealed. In plot B is shown an analogous plot at 150°C, the important features being the linearity of the consumption curve and the apparent lack of an induction period. Finally, in plot C is revealed a linear curve for the rate of formation of the oxidation product of candidate 1.

In table 2 is presented a preliminary initial rate study for the oxygenation of candidate 1 under different experimental conditions. Two experimental observations are pertinent: First, while candidate 1 is consumed most rapidly in the absence of BHT, in the presence of 1, 2, or 3 equivalents of BHT a significant rate of oxygenation is observed. Second, changing the solvent from nonpolar hydrocarbons (dodecane and decalin) to a more polar solvent (1,2,5-

trichlorobenzene) results in an increase in the rate of oxygenation for candidate 1. This result is consistent with a transition state for the oxygenation of candidate 1 being polar.

Conclusion

In this paper it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. Consequently, it is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited.

To date our data has identified one potential additive candidate which meets our preliminary specifications. Work is in progress to examine and tailor appropriate solubility characteristics for this additive candidate.

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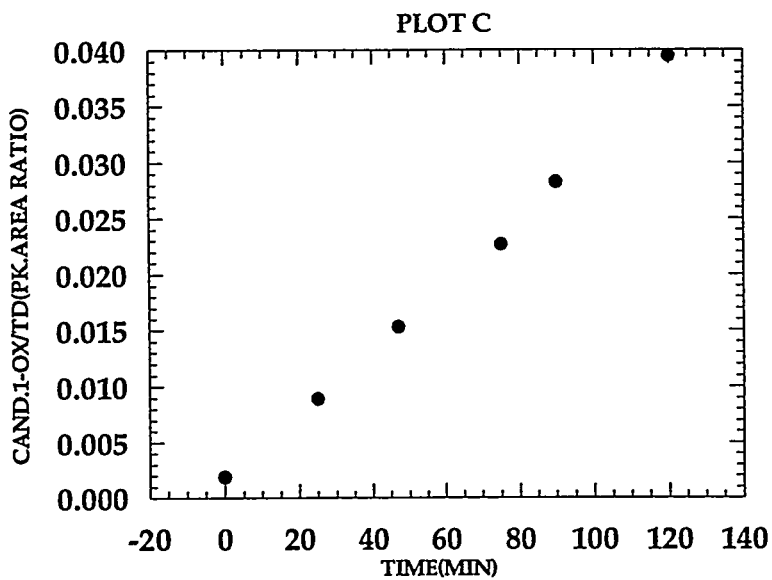
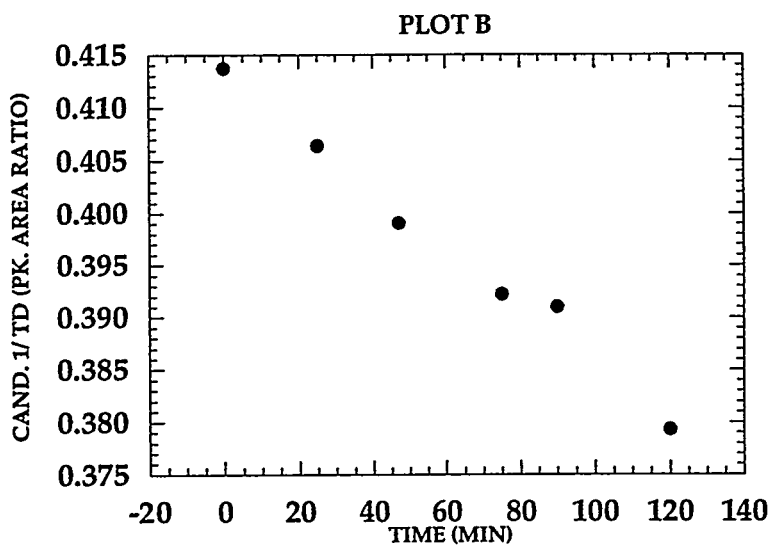
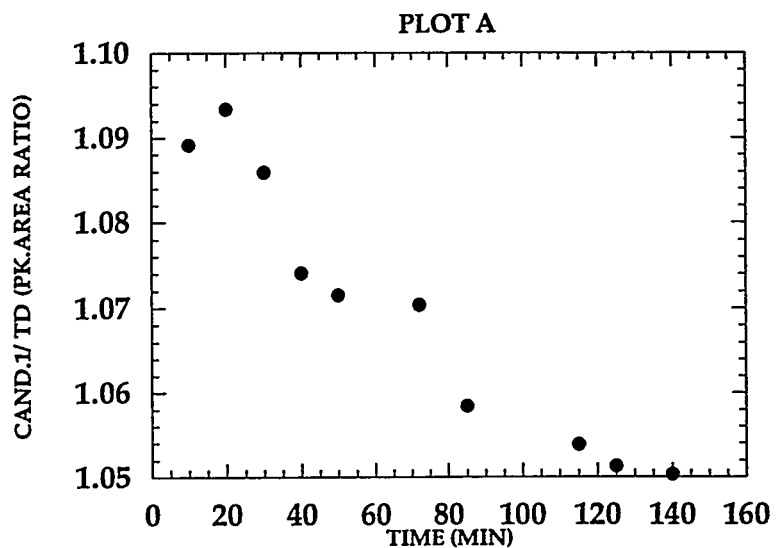


Figure 1. Change in substrate concentration as a function of time, in dodecane.

Table 1

Reaction Order Data for Additive Candidates

Substrate	Additive(s)	Solvent	Temp. °C	Subs. order	O ₂ order
fluorene	none	dodecane	165	not det.	0.8
fluorene	BHT	dodecane	165	no Rx.	no Rx.
DMP	amine	dodecane	120	1.1	0.8
DMP	amine/BHT	dodecane	120	not det.	approx. 0
TMP	none	dodecane	100	not det.	approx. 0
Candidate 1	BHT	dodecane	150	1.1	1.2
Candidate 1	BHT	decalin	150	1.0	1.3

Table 2

Initial Rate of Consumption for Candidate 1 at 150°C

Solvent	Additive (eqs.)	Int. rate of loss
dodecane	none	1.24×10^{-4}
dodecane	1 x BHT	1.36×10^{-5}
dodecane	2 x BHT	1.70×10^{-5}
dodecane	3 x BHT	1.57×10^{-5}
trichlorobenz.	1 x BHT	3.24×10^{-5}
decalin	1 x BHT	1.03×10^{-5}

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DEVELOPMENT OF THERMAL STABILITY ADDITIVE PACKAGES FOR JP-8

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Advanced military aircraft use fuel as the primary heat sink to cool engine and airframe components. As the fuel is thermally stressed, thermal oxidative reactions take place that result in the formation of deposits. These deposits degrade aircraft performance and ultimately lead to premature servicing of the affected components. The frequency of these incidents, coupled with the projected cooling requirements for future systems, demonstrates that current thermal stability limits are inadequate. In response to this situation, the United States Air Force (USAF) has embarked on a program to improve thermal stability using specially formulated additive packages. Results indicate that additives offer significant thermal stability improvement. This paper describes the USAF program to develop and deploy an improved JP-8 for fleet-wide use by 1998.

Introduction

Jet fuel is used as the primary heat sink in advanced military aircraft to cool engine and airframe components in addition to providing the propulsive energy for flight. The heat dissipated into the fuel causes thermal degradation leading to the formation of insoluble materials. These materials foul critical fuel system components affecting the efficient and safe operation of the aircraft. Thermal stability limits have been established to assure fuel quality and to control the severity and incidence of fouling problems. However, actual field experience indicates that fuel degradation and deposition is a current problem that adversely affects fleet operations and costs millions of dollars each year to correct. Heat loads in future systems are projected to increase placing even more emphasis on the fuel as the cooling medium.¹ The status quo for thermal stability is untenable if the operability and performance goals of advanced military aircraft are to be achieved and maintained.

The causes and effects of thermal instability have been studied and documented by many researchers over the years.² Thermal stability in this case refers to the tendency of a fuel to form bulk and surface deposits under thermal oxidative stress. In simple terms, heat promotes the autoxidation of the fuel via a free radical mechanism forming a variety of oxidized species. Subsequent reactions involving these intermediates results in the formation of soluble and insoluble products. Reactions between trace polar compounds (e.g. sulfur, nitrogen and oxygen containing molecules) and the oxidized intermediates produce the deleterious fuel system

deposits. Any technique that interferes with or inhibits these reactions or removes the polar contaminants from the fuel should benefit thermal stability.

The degree of improvement required over conventional JP-8 was based on heat load projections for advanced aircraft. The stability of conventional fuel restricts the maximum bulk temperature to 325°F (163°C) at the inlet to the main burner nozzle and to a wetted-wall temperature of 400°F (204°C) inside the nozzle passages. These limits were established based on field experience to minimize deposition and extend service life. Under certain flight conditions these temperatures are exceeded which increases deposition rates substantially. The enormous throughput of fuel magnifies the problem and results in considerable deposition. The primary concern with thermal stability in advanced aircraft is not related to large temperature increases, but the time-at-temperature and fuel recirculation after thermal stressing. More advanced concepts under development (Integrated High Performance Turbine Engine Technology Program) will subject the fuel to considerably higher temperatures, exacerbating any thermal stability problems. Based on the current state of affairs along with the knowledge of future requirements, the USAF set a goal of increasing thermal stability limits 100°F (56°C). This translates into allowing the bulk temperature to reach 425°F (218°C) and the wetted-wall temperature to reach 500°F (260°C), providing a 50% increase in available heat sink. The improved stability fuel is referred to as JP-8+100.

There are a variety of techniques that can be used to improve thermal stability. Some of the options include hydro-refining, clay filtration, removal of dissolved molecular oxygen, metal surface treatments and additives. Each technique has advantages and disadvantages related to cost, practicality and efficacy. After considering the available options and the ramifications associated with each, the USAF selected the additive approach to improve the thermal stability of JP-8.

Additive Development

Additives are used extensively in petroleum products to enhance a variety of properties including thermal stability. Motor gasoline, diesel fuel and lubricating oils all contain additives designed to improve performance. The tremendous demand for these products encouraged vigorous investment in additive development. The situation with jet fuel is very different. The comparatively low demand, high degree of specification and fungible nature detracts from the incentive to pursue costly additive development and approval efforts. As a result, very few additives are available specifically designed to enhance thermal stability. Metal deactivator additive (MDA) is the only such additive permitted in both civil and military fuels. JFA-5 is an additive package consisting of an antioxidant, a dispersant and MDA and is used exclusively in

JPTS, a highly refined kerosine used in the U-2/TR-1 aircraft. Testing was performed in a variety of fuels and the results showed that our thermal stability goals could not be achieved with MDA or JFA-5. Consequently, petroleum companies and additive manufacturers were contacted and requested to submit additive candidates for our evaluation. Most of the candidates submitted are used in products other than jet fuel, the remaining candidates are experimental. Over 200 additives have been submitted to date, with two showing particular promise. The additives discussed in this paper include an antioxidant, a metal deactivator, a dispersant and a detergent/dispersant. A description of these additives can be found in Table 1.

A great deal of effort was spent in determining how best to screen a large number of additives in a short period of time. The approach follows a hierarchical structure starting with simple screening tests and culminating in full-scale component and engine tests (Figure 1). The strategy is to use the screening tests to identify the promising additives quickly, reject the others and move forward with a small set of candidates. A variety of fuels are used to assure that additive performance is not restricted to a single fuel. The most promising additives are promoted for evaluation in more complex test devices that attempt to simulate some portion of the fuel system. If positive results are obtained here, material and additive compatibility, storage stability, specification conformance and combustion performance testing is initiated. The final step in the process is evaluation of JP-8+100 in the reduced scale fuel system simulator (RSFSS). The RSFSS is a 1/72 scale model of the F-22 fuel system and is designed to closely simulate all aspects of the fuel system. Successful testing in the RSFSS is followed by full-scale component and engine tests.

Screening Tests

Three different screening tests are used to perform the initial evaluations on every additive submitted for the JP-8+100 program. These tests are not designed to simulate any particular part of the fuel system or environment. The test temperature and/or the availability of dissolved oxygen is elevated to accelerate the deposition process. Dose levels used for the additives are based on the recommendations of the manufacturer. Packaging, reformulation and optimization is carried out only if the additive performs well in each screening test and in each reference fuel. The "optimized" additive or additive package is used for all subsequent testing.

Additive performance and acceptance is based on the ability of an additive to reduce deposition to a level similar to JPTS. Each test device establishes a thermal stability baseline with JPTS and all JP-8+100 formulations are then compared to that baseline to determine additive efficacy. The reference fuels used in the screening tests are listed in Table 2.

Hot Liquid Process Simulator (HLPS): The HLPS is a derivative of the well known Jet Fuel Thermal Oxidation Tester (JFTOT), ASTM D 3241, a device long in use as a jet fuel qualification test. The test conditions selected to evaluate additive performance are similar to those used to qualify JPTS. Tests are performed at 335°C for 5 hours at a flow rate of 3 mL/min. Series 316 stainless steel tubes are substituted for the conventional aluminum tubes to permit quantitation of the deposit by carbon burnoff using a LECO RC-412 Carbon Analyzer.

Test results obtained with the HLPS are shown in Figures 2, 3 and 4. Figure 2 shows the performance of the two most promising additive packages in our primary reference fuels. Significant reduction in surface carbon is obtained as well as elimination of any increase in differential pressure on the 17 μm stainless steel filter. Figure 3 shows the effect of combining the individual components of the additive package on surface deposition. In fuel 2926 and 2980, the addition of BHT reduces surface carbon, however, in fuel 2827 BHT increases deposits slightly. These results are consistent with other experiments that show fuel 2926 consumes oxygen quite rapidly, 2980 consumes oxygen at an intermediate rate, whereas fuel 2827 consumes oxygen slowly. Antioxidants are most effective in those fuels that oxidize readily and have little or no effect in fuels that oxidize slowly.³ The effect of MDA on surface carbon in the HLPS is quite predictable. In each case, the addition of MDA reduces surface carbon. Clark⁴ has attributed the beneficial results seen in the JFTOT or HLPS to a passivating action of the MDA on a clean metal surface. The short duration of the test exaggerates the benefits of MDA and can make poor quality fuels appear better than the best hydrotreated fuels. A complete metals assay has not been performed on these reference fuels to determine the presence and level of transition metals. The line superimposed over the plots indicates the deposit level for JPTS.

The potential of MDA to cause an increase in deposition rate at longer test times was evaluated in the HLPS using the additive package with and without MDA. Figure 4 shows the effect of MDA on surface deposition in tests performed up to 30 hours. The MDA did not cause any increase in surface carbon in these extended tests, however, other test devices are more suited to investigate this phenomenon. Indiscriminate use of MDA is not recommended as a panacea for thermal stability problems. When thermal stability is off-specification due to dissolved catalytic metals, the use of MDA is appropriate and advisable. Its use as a permanent part of any additive package for JP-8 is still to be determined.

Isothermal Corrosion/Oxidation Test (ICOT): The ICOT apparatus used for additive screening is described in ASTM D4871. In the ICOT, 100 mL of fuel is placed in a glass test tube and inserted into an aluminum block heater at 185°C. A water-cooled condenser (20°C) is fitted to the test tube and a glass blower tube inserted through the condenser into the fuel. Air is sparged into the fuel at 1.3 L/hr. The fuel is stressed for 5 hours, removed from the heater and allowed to stabilize overnight. The bulk insolubles are measured gravimetrically by filtering the

entire sample through a 1 μm glass fiber filter. Surface insolubles formed on the blower tube were evaluated visually.

The ICOT results for the reference fuels and the two additive packages are shown in Figure 5. In all three fuels, both additive packages reduce bulk insolubles to zero. The surface deposits on the blower tube were also dramatically reduced. The neat fuels formed a deposit band of 5 - 8 mm in width, the additized fuels were 1 mm or less. Figure 6 shows the results of adding MDA to 8Q405 and BHT. The positive response to MDA was unexpected because the entire system is composed of glass. Similar results have been obtained with other fuels even though dissolved catalytic metals were not present. Although we feel this is a very valuable screening tool, a caveat must be mentioned when using tests such as the ICOT to evaluate thermal stability or additive efficacy. Any test that is accelerated by the addition of excess oxygen may give misleading results. For example, hydrotreated fuels of high thermal stability oxidize readily producing copious amounts of insoluble material because autoxidation reactions are driven far beyond what would occur in actual aircraft systems. Any effect of an additive is quickly overwhelmed by the extent of oxidation.

Quartz Crystal Microbalance (QCM): The QCM apparatus has been described in detail previously and will only be discussed briefly here ^{5,6}. The fuel is stressed in a 100 mL Parr bomb reactor which has been modified with an rf feedthrough for the QCM. A pressure transducer is used to monitor the pressure decay in the reactor that results from oxygen reaction. The reactor is heated with a clamp-on band heater which is controlled by a PID temperature controller via a thermocouple immersed in the fuel. The reactor is filled with 60 mL of fuel leaving ~40 mL of headspace. The fuel and headspace are sparged with air for 1 hour at room temperature prior to each run. After sparging, the reactor is sealed at atmospheric pressure and the heater is turned on. A computer monitors the quartz crystal frequency, the crystal damping voltage, the temperature and the headspace pressure at 1 minute intervals. A typical run is 15 hours at a temperature of 140°C. QCM deposition data are only valid for the relatively constant ($\pm 0.3^\circ\text{C}$) period of the run after the ~45 minute heat-up time.

The change in the quartz crystal frequency with time at constant temperature is used to monitor deposition. The total mass accumulation after 15 hours for the reference fuels with and without the additives is plotted in Figure 7. In each case, the additive packages reduce surface deposits to levels similar to JPTS. The effect on deposition by adding BHT and MDA to 8Q405 is shown in Figure 8. These results demonstrate the effect of BHT on a fuel that oxidizes readily versus one that consumes oxygen slowly. Fuel 2926 benefits significantly when BHT is added to 8Q405 contrary to the effect in fuel 2827. The MDA adversely affects fuels 2827 and 2980 when added to the 8Q405 and BHT. The deposition curves for these runs show a positive change in slope towards the end of the 15 hour test. The explanation for this behavior is not

clear, but is likely related to the continued stressing of the fuel over the duration of the experiment.

Simulation Tests

The next step in the additive development process is testing in fuel system simulation test rigs. Only additives that have met the criteria established in the above screening tests are evaluated. These devices have been designed to simulate different parts of an aircraft fuel system.

Augmentor Fouling Simulator: Details of the augmentor simulator have been described previously and will only be discussed briefly here.⁷ This device consists of a tube heated to ~620°C in which fuel flowing at a low rate (1.5 mL/min) is vaporized at 1 atm. This low flow simulates leaking or residual fuel in the augmentor injection system. Periodically, a short surge of fuel at a much higher flow rate (3000 mL/min) is sent through the tube, simulating augmentor use. After the test period, the tube is sectioned and the deposition determined by carbon burnoff. The majority of deposit is located where the fuel changes phase from liquid to gas. This behavior is consistent with field observations.

Results of augmentor tests under both surge and non-surge conditions for the reference fuels and 8Q405 are shown in Figure 9. The quantity of deposits is consistently reduced under surge conditions. This is most likely due to a mechanical "scraping" of the deposit by the high fuel flow. 8Q405 adds to the deposit under non-surge conditions, but is seen to reduce deposits with the surge flow. The improvement may be related to a change in the physical characteristics of the deposit, e.g., the density, which facilitates removal under the high flow condition. The benefit of 8Q405 predominates at short test times (~7 hours) essentially extending the induction period. As the surface becomes coated, the deposition rate increases and parallels the neat fuel. The excellent performance of fuel 2926 in this test remains to be explained.

Extended Duration Thermal Stability Test (EDTST): The EDTST was designed to evaluate the most promising additive candidates under conditions that closely simulate the fuel system on advanced military aircraft. The test rig consists of a 60 gallon feed tank, a gear pump, two clam-shell heaters and a collection tank. The first heater or preheater is used to establish the desired bulk fuel temperature before entering the second heater. Bulk fuel temperatures selected are representative of the fuel temperatures encountered due to airframe and engine heat loads. The second heater is used to establish wetted-wall temperatures associated with main burner injection nozzles. Emphasis is placed on bulk fuel and wetted-wall temperatures because they are used to define limits for engine fuel system design.⁸

EDTST results for fuel 2980 with the two additive packages are shown in Figures 10 and 11. Section number refers to the relative distance along the stainless steel tube. A bulk fuel temperature of 177°C and a wetted-wall temperature of 260°C were used for these tests. These temperatures are considerably higher than the design limits imposed on current aircraft (163°C and 204°C). Both additive packages reduced surface deposits to levels slightly higher than JPTS. Analysis of the filterable deposits showed substantial reduction here as well. Full realization of the 218°C bulk temperature has not yet been demonstrated, however, even JPTS (our thermal stability benchmark) breaks down at this bulk temperature and forms deposits in the preheater.

Material and Additive Compatibility, Specification Conformance, Storage Stability and Combustion

Material and Additive Compatibility, Specification Conformance: The next phase of the program is to perform compatibility and specification conformance testing with the JP-8+100 additive candidates per ASTM D4054. A comprehensive material list has been prepared that includes over 150 metallic and non-metallic materials. Airframe materials are immersed in the test fuel and placed in an oven at 93°C for 28 days. Every seven days the fuel is exchanged with fresh fuel. Test fuels include JP-8, JP-8+100 and four times the maximum recommended concentration of the JP-8+100 additives. The procedure for evaluating the engine materials is similar, but the test temperature is raised to 163°C and 218°C. Testing is currently underway and preliminary results do not indicate any unusual problems with the JP-8+100 additives.

Additive compatibility testing has been completed with the JP-8+100 candidates and all approved military specification additives. The additives included corrosion inhibitors per QPL-25017 revision 17, fuel system icing inhibitor (diethylene glycol monomethyl ether), MDA and static dissipater additive. No evidence of incompatibility was noted following the guidelines in Procedure B of ASTM D4054.

Specification conformance of JP-8+100 was evaluated using Procedure A of ASTM D4054. All JP-8 (MIL-T-83133D) specification tests were run on the base JP-8 and the JP-8+100 candidates. Both JP-8+100 fuel candidates failed ASTM D3948, Standard Test Method for Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer. 8Q405 and MCP-147B both function as surfactants to prevent agglomeration and surface adhesion of insoluble materials. The effect of surfactants on coalescence is well known and the results were not unexpected. Several efforts have been initiated to further evaluate the extent and severity of the water shed problem. Another property affected by the addition of 8Q405 was electrical conductivity. At a concentration of 100 mg/L, 8Q405 increased conductivity an average of 140 pS/m in our three reference fuels. This effect on conductivity

must be taken into account in order to assure that current conductivity requirements for JP-8 (150 - 600 pS/m) are not exceeded.

Storage Stability: An accelerated storage stability test has been developed for use as a tool to predict the long-term storage characteristics of JP-8+100 formulations. The procedure is a modified version of the storage stability test developed by the Naval Research Laboratory and Naval Air Warfare Center.⁹ Four fuels which exhibit widely different thermal oxidative stabilities have been selected for testing. These fuels represent fast and slow oxidizers and high and low deposit producers. Briefly, 250 mL aliquots of each fuel is placed in 300 mL capacity Parr reactors. The reactors are pressurized with 50 psi air and placed in a convection oven at 100°C. One reactor is removed every 24 hours, cooled to room temperature in a water bath and depressurized. 200 mL of the stressed fuel is filtered through preweighed 0.8 µm filters and the particulates determined gravimetrically. The remaining 50 mL is analyzed for peroxides, phenols, conductivity and total acid number. Testing of the fuels has recently been initiated and results are unavailable at this time.

Combustion Characteristics: Combustion experiments were conducted with fuel 2980 and 2980 plus 8Q405/BHT/MDA to investigate the effects of the additive package on combustion performance. The concentration of the additive package was varied from normal concentration to 100 times normal strength to exaggerate any possible effects. Performance parameters investigated included combustion efficiency (emissions) and stability (lean blow-out).

The combustor used in these experiments was a single-cup General Electric CFM56 swirl-cup and dome configuration. The combustor was operated at atmospheric pressure with inlet air temperatures of 260°C. The air flow rates delivered to the dome varied from 2 - 6% dome pressure drop. Emissions data is presented in Figure 12 and was obtained with a water-cooled sampling probe. The plot shows the combustion efficiency as a function of equivalence ratio for the different additive concentrations in the fuel. The results indicate that even at 100 times the recommended additive concentration, no loss in combustion efficiency was apparent. Figure 13 shows lean blow-out data as a function of combustor loading. The additive package had no detrimental effect on combustor stability at any of the concentrations investigated.

A single stationary turbine blade was placed in the exhaust stream of the combustor to determine if the combustion products would attack the thermal barrier coating or the metal surface with the additives present. The blade was air-cooled to simulate temperatures in this area of the engine. A visual inspection of the blade did not reveal any coking or erosion of the surface. A more in-depth analysis of the blade will be performed using scanning electron microscopy.

Reduced Scale Fuel System Simulator (RSFSS)

Testing in the RSFSS is the last step in the additive evaluation process before full-scale component and engine tests are accomplished. The RSFSS was configured to accurately simulate the thermal management system in the F-22. Actual engine and airframe hardware was modified to scale and incorporated into the simulator to evaluate performance degradation due to fouling. A generic mission cycle was devised to closely simulate heat loads, fuel flows, time at temperature, transients and fuel recirculation at different flight points. A complete test consists of 75 missions at ~2.5 hours each. The 75 missions are run consecutively, consuming ~700 gallons of fuel.

At the end of the test, the burner feed arm is removed from the rig, sectioned and surface deposits measured by carbon burnoff. Figure 14 is a plot of burner feed arm deposition with fuel 2980 and 2980 plus 8Q405/BHT/MDA. At a wetted-wall temperature of ~218°C, significant deposition occurred with 2980. The JP-8+100 additives were able to reduce the surface deposits to near background levels.

The servo valves and the flow divider valve were calibrated before each test to establish baseline performance characteristics. Hysteresis increased significantly in each valve after fuel 2980 was run. The hysteresis check after JP-8+100 showed no deviation from the initial calibration. The valves were disassembled after each run to visually inspect for deposition. The internal components of the servo valves and the flow divider valve were coated with a brown stain or lacquer after fuel 2980 was run, but appeared clean after JP-8+100 was run.

Full-scale component and engine testing follows successful testing in the RSFSS. Plans are in place to run JP-8+100 in full-scale nozzle tests, combustor rigs, fuel control systems and in a variety of military engines. The benefits of JP-8+100 will be demonstrated in these tests and validated for fleet wide use by 1998.

Conclusions

The work presented in this paper demonstrates that additives are a viable approach to improving thermal stability. By combining the appropriate constituents into an additive "package", i.e., an antioxidant, a metal deactivator and a dispersant, fuels of varying quality can be significantly improved. The efficacy of the additives tested here is fuel dependent and it is doubtful that any additive or group of additives will be universally effective. The requisite improvement in thermal stability for advanced military aircraft can be realized by the judicious selection of additives.

The detergent and dispersant type additives facilitate water entrainment and interfere with efficient water separation. This problem was expected and plans are in place to investigate the scope and severity of the problem and remedy the situation.

The ability of any single bench-scale test to accurately predict in-service thermal stability has yet to be demonstrated. The approach of screening in accelerated tests and validation in simulators may eventually lead to the development of relationships between simple laboratory tests and fuel performance in the field. Testing to be completed in the next two years will validate this premise. At a minimum, the screening tests have the potential to become standardized techniques for the measurement of thermal stability.

Acknowledgments

The authors would like to acknowledge the contributions of the many people responsible for generating the data presented in this paper. Tedd Biddle and Bill Edwards of Pratt & Whitney, Becky Grinstead, Steve Zabarnick, Ed Binns, Gordon Dieterle and Jim Shardo of the University of Dayton Research Institute and Mike Burns of WL/POSC. The authors also acknowledge valuable discussions with Mel Roquemore of WL/POSC and Grant Jones of Systems Research Laboratory.

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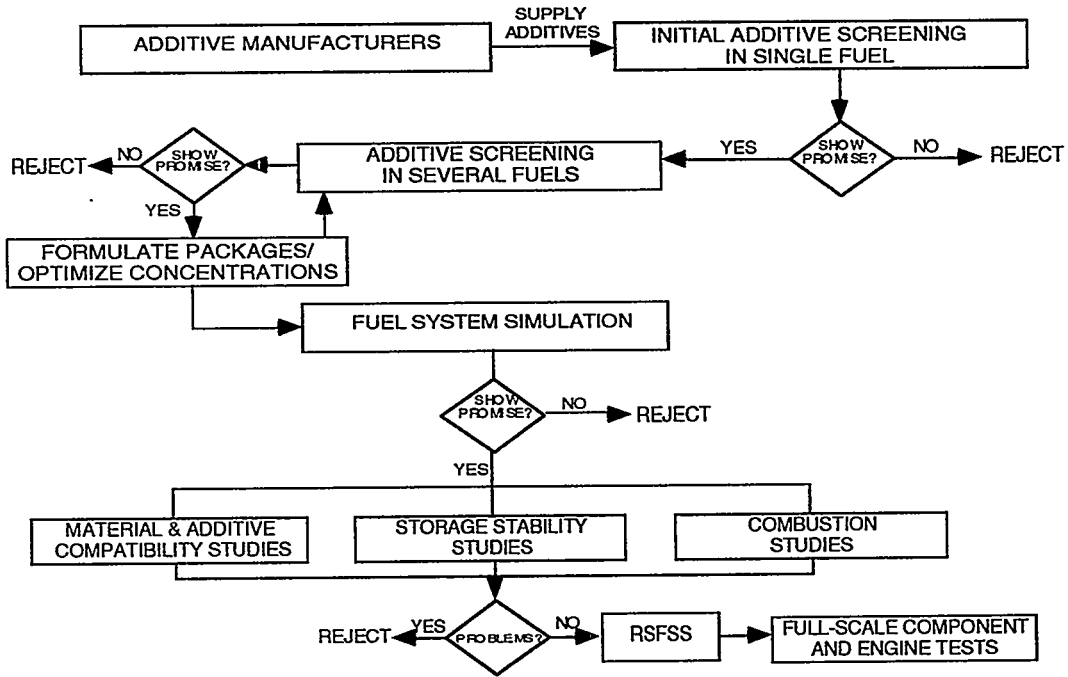


Figure 1. Additive Development Process

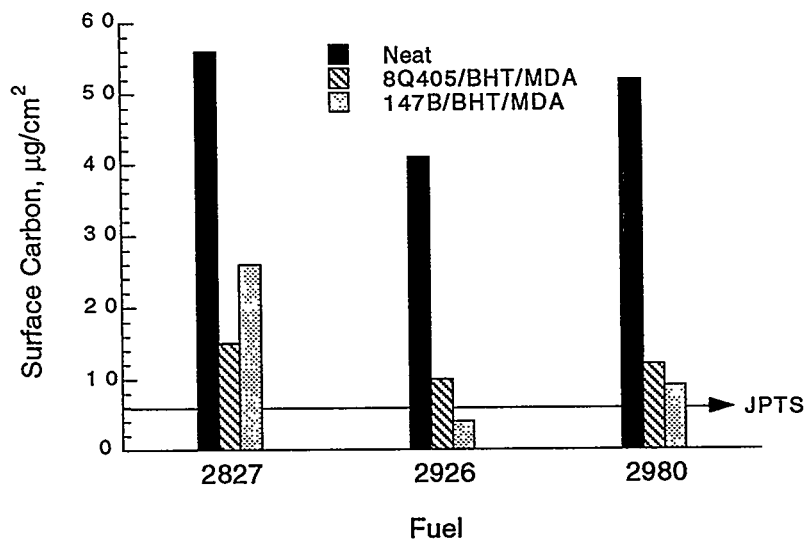


Figure 2. HLPS Results for JP-8+100 Candidates

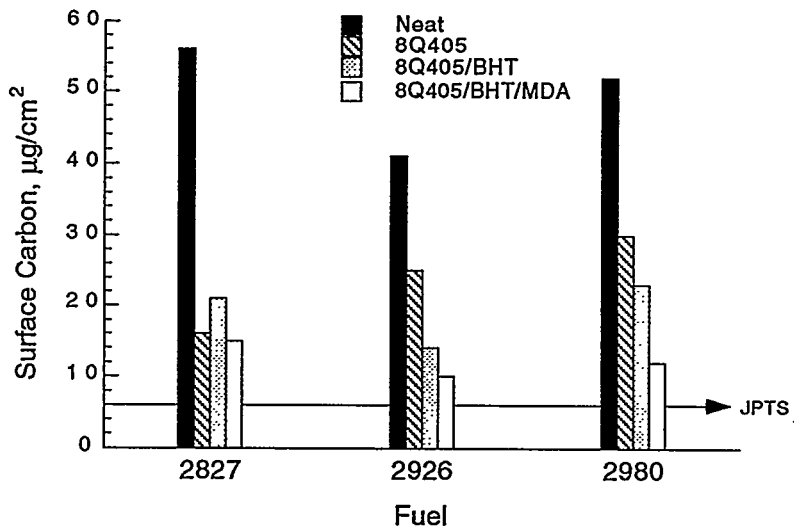


Figure 3. Effect of Individual Additives on Deposition

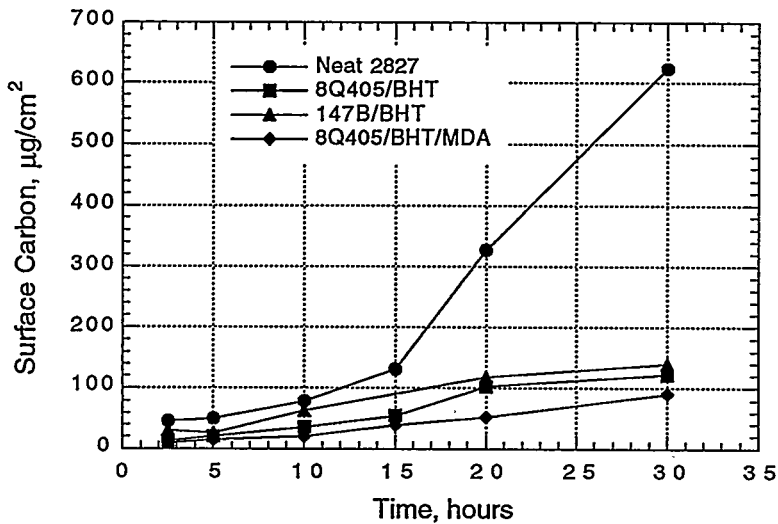


Figure 4. Extended Duration Testing in HLPS

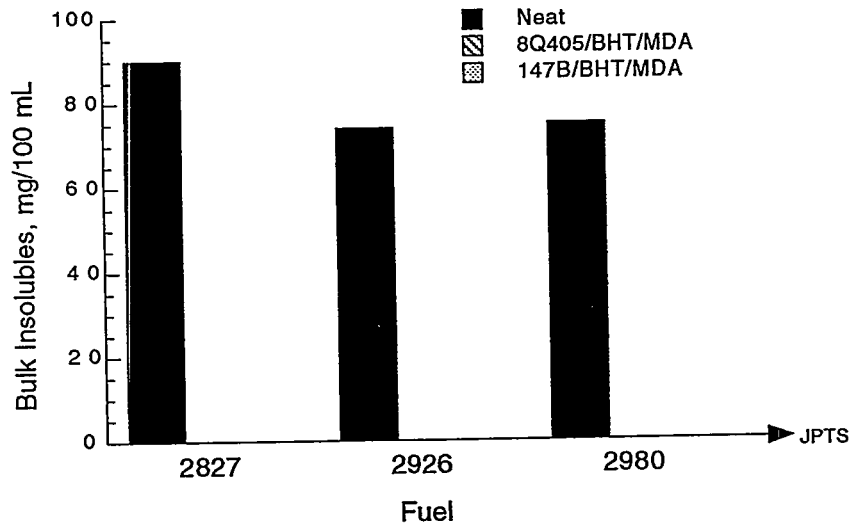


Figure 5. ICOT Results for JP-8+100 Candidates

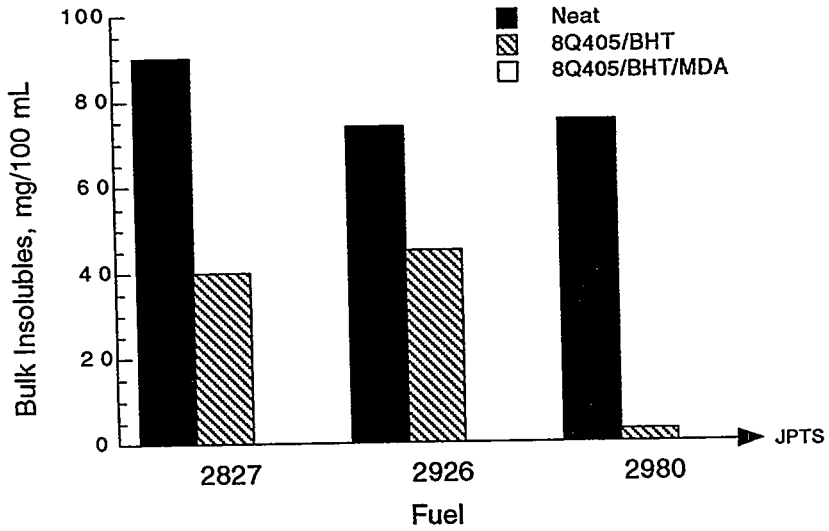


Figure 6. Effect of MDA on Bulk Insolubles

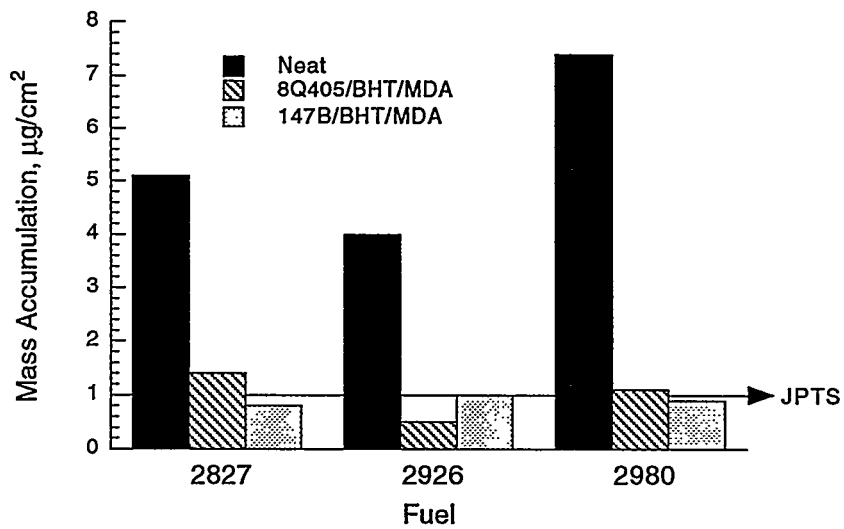


Figure 7. QCM Results for JP-8+100 Candidates

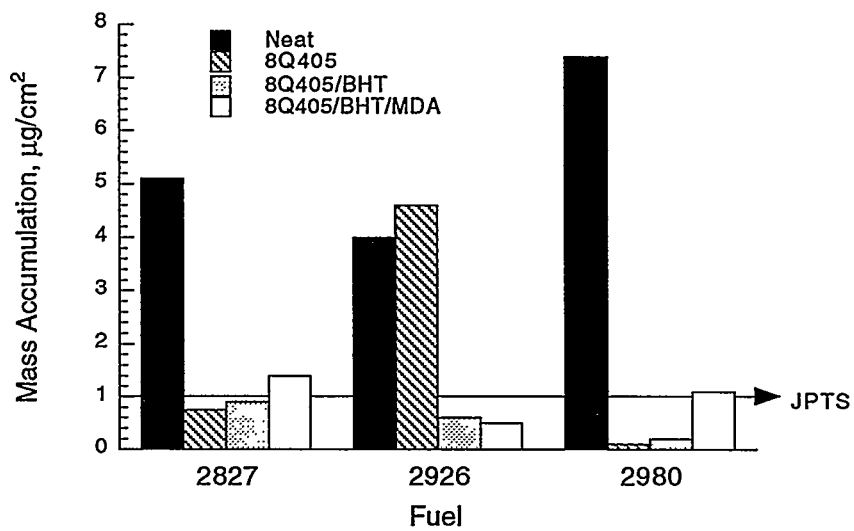


Figure 8. Effect of BHT and MDA on Mass Accumulation

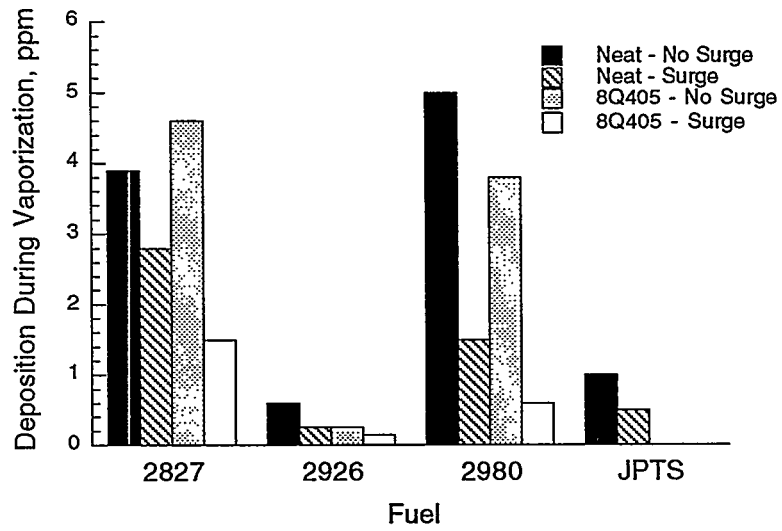


Figure 9. Augmentor Deposition Results for 7 Hour Tests

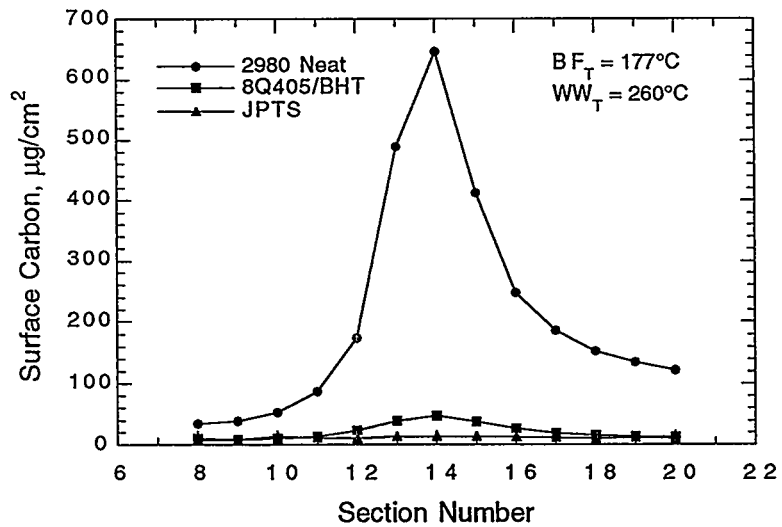


Figure 10. EDTST Results for Fuel 2980 and JPTS

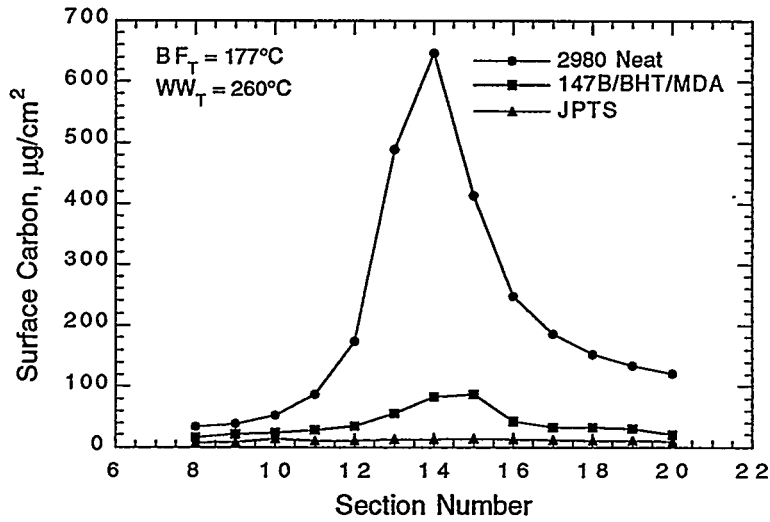


Figure 11. EDTST Results for Fuel 2980 and JPTS

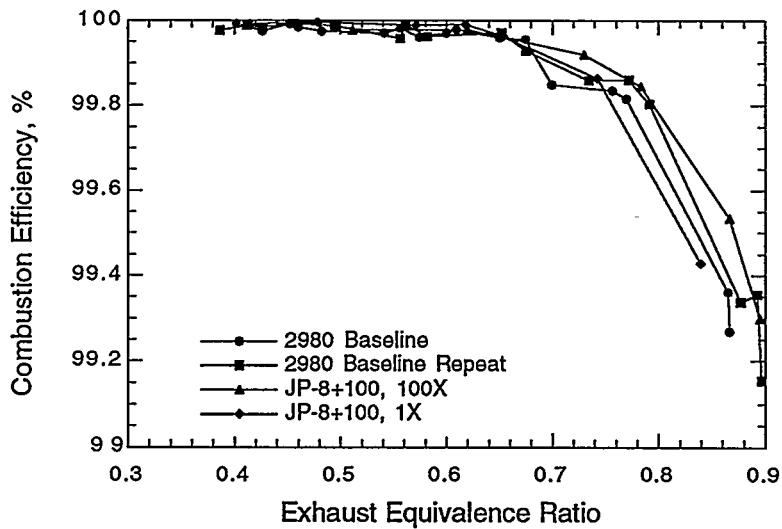


Figure 12. GE CFM56 Combustor Efficiency

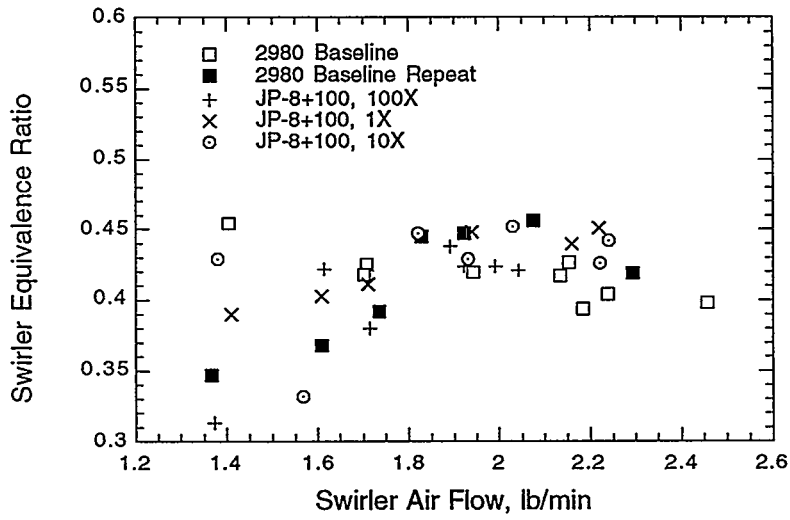


Figure 13. GE CFM56 Combustor Stability

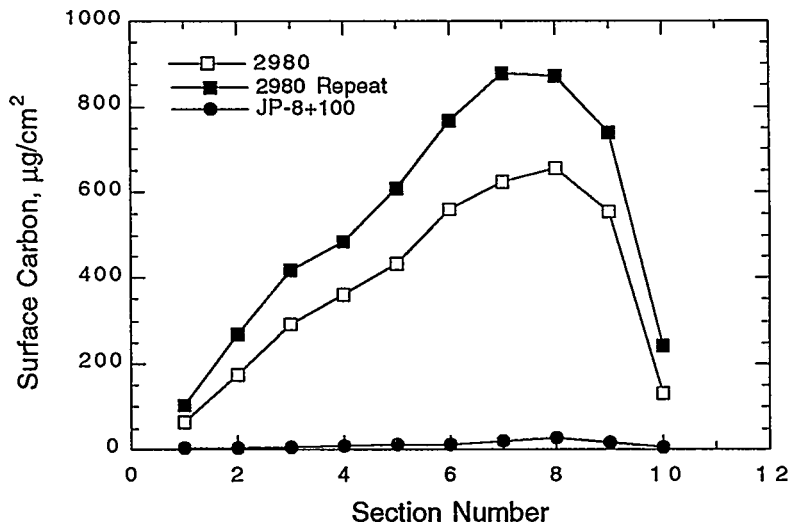


Figure 14. RSFSS Burner Feed Arm Deposition Results

Additive	Function	Formula	Concentration, mg/L
BHT	Antioxidant	2,6-Di-t-butyl-4-methylphenol	25
MDA	Metal Chelator	N,N'-Disalicylidene-1,2-propane diamine	10 (7.5 active)
8Q405	Dispersant	Proprietary	100
MCP-147B	Detergent/Dispersant	Proprietary	300

Table 1. Additive Descriptions

Fuel Code	Fuel Description	HLPS Breakpoint °C	HLPS Surface Carbon $\mu\text{g}/\text{cm}^2$	HLPS ΔP mm Hg/min	ICOT Insolubles mg/100 mL	QCM Surface Dep $\mu\text{g}/\text{cm}^2$
2799	JPTS	398	6	1/300	0	1.0
2827	Jet A St. Run	266	56	300/240	90	5.1
2926	Jet A H. Treat	288	41	70/300	74	4.0
2980	Jet A Merox	288	52	12/300	75	7.4

Table 2. Reference Fuels

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on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
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**STUDIES OF JET FUEL ADDITIVES USING THE QUARTZ CRYSTAL
MICROBALANCE AND PRESSURE MONITORING AT 140 C**

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The quartz crystal microbalance (QCM) and pressure monitoring are used for the evaluation of jet fuel additives for the improvement of jet fuel thermal stability. The mechanisms of additive behavior are determined by measuring the time dependent deposition with the QCM and oxidation by pressure measurements. Studies at various additive concentrations permits the determination of optimum additive concentrations. Additive packages made of mixtures of antioxidants, detergent/dispersants, and metal deactivators are shown to yield good improvements in thermal stability over a wide range of jet fuel types.

Introduction

Recent advances in jet aircraft and engine technology have placed an ever increasing heat load on the aircraft. The bulk of this excess heat is absorbed by the aircraft fuel, as jet fuel is used as the primary coolant for the numerous heat sources. This hot fuel reacts with dissolved oxygen to form oxidized products and deposits. The formation of deposits results in the fouling of fuel lines, valves, actuators, nozzles, and various other aircraft components with the potential to result in catastrophic failure. Jet fuel additives are added to fuel in small quantities to improve its oxidation and deposition characteristics.

In this paper we present results on the study of four classes of jet fuel additives: antioxidants, dispersants, detergents, and metal deactivators. Other additives used in jet fuels are: lubricity enhancers, static dissipaters, and corrosion inhibitors. Antioxidants interfere with the fuel autoxidation chain mechanism by intercepting peroxy radicals, which are the primary radicals responsible for continuing the chain.¹ These antioxidants molecules have an easily abstractable hydrogen atom which encourages reaction with peroxy radicals. Dispersants and detergents usually consist of molecules with a polar "head" attached to long non-polar hydrocarbon chain. In a non-polar fuel the hydrocarbon chain is attracted to the bulk fuel, and the polar head is attracted to any polar compounds or groups of compounds present in the fuel. Dispersants work by surrounding these polar compounds forming a micelle-like structure around the polar compound. Thus, the polar compounds present are not able to aggregate and form larger groups of polar compounds that would result in formation of insoluble deposits and gums.

Detergents act in a similar manner but the polar head actually binds to the surface while the hydrocarbon chain extends into the fuel. Detergents are able to remove polar species from surfaces. Metal deactivators are species that can bind to metal atoms that may be present as atomic or molecular species in the bulk fuel or by binding to metal surfaces. The interaction of these metal deactivator species with the bulk and/or surface metal atoms discourages the well known catalysis of chemical reactions by metals.

The present work is part of the Air Force JP-8 + 100 program, in which an additive package is being developed to extend the thermal stability of JP-8 jet fuel by 100 degrees F ("Thermal stability" refers to the deposit forming tendency of a fuel). This program involves the evaluation of proprietary and non-proprietary additives from many manufacturers. Table I lists the additives studied in this work, their additive classification (as stated by the manufacturer), and the type of compound, if known. In this work, a quartz crystal microbalance (QCM) is used for the real-time, *in situ* monitoring of the surface deposition. Also, a pressure transducer is used to monitor the pressure decay in the reactor that results from oxygen reaction. The combination of a very sensitive technique for monitoring deposition (QCM), along with a method for directly monitoring oxidation (pressure measurements) allows us to not only evaluate additives but also to study and classify additives based upon their deposition/oxidation characteristics.

Experimental

The experimental apparatus has been described in detail previously, and will only be discussed briefly here.^{2,3} The fuel is stressed in a 100 ml Parr bomb reactor which has been modified with an RF feedthrough for the quartz crystal microbalance. It is heated with a clamp-on band heater which is controlled by a PID temperature controller via a thermocouple which is immersed in the fuel. The reactor is filled with 60 ml of fuel and thus contains a \approx 40 ml headspace. The fuel and headspace are sparged with air for one hour at room temperature prior to each run. At the end of the sparge period the reactor is sealed at atmospheric pressure and the heater is turned on. At this point the computer data acquisition is initiated. The computer monitors the quartz crystal frequency, the crystal damping voltage, the temperature, and the headspace pressure at one minute intervals. A typical run is performed for 15 hours at a temperature of 140 °C. QCM deposition data is only valid during the relatively constant (\pm 0.3 °C) period of the run after the \approx 45 minute heat-up time. The Parr reactor is cleaned thoroughly between runs and a new quartz crystal is used for each run.

The change in the quartz crystal frequency in time at constant temperature is used to monitor the deposition. The quartz crystals used were 5 MHz, 2.54 cm diameter, 0.33 mm thick, AT-cut wafers. These crystals, obtained from Maxtek Inc., were manufactured with gold electrodes and overtone polished. The quartz crystal resonator is driven at 5 MHz by an oscillator

circuit that was developed at Sandia National Labs.³ This circuit tracks the impedance variations of the crystal in order to determine the resonant frequency of the device. The oscillator circuit also provides an amplitude output that indicates crystal damping. The reactor was also fitted with a Sensotec 0-50 psia absolute pressure transducer.

The theory that relates the measured frequency changes to surface mass has been presented in detail elsewhere,⁴ and will only be discussed briefly. When a crystal is excited at its resonant frequency it undergoes a shear deformation with displacement maxima at the crystal faces. Mass accumulation on the crystal surface moves synchronously with the surface, resulting in a decrease in the resonant frequency. Also, a thin layer of liquid can be entrained by the surface, also resulting in a decrease in the resonant frequency. The decrease in resonant frequency is described by

$$\Delta f_0 \approx -\frac{2f_0^2}{N(\mu_q \rho_q)^{1/2}} \left[\rho_s + \left(\frac{\rho \eta}{4\pi f_0} \right)^{1/2} \right] \quad 1)$$

where f_0 is the unperturbed resonant frequency, N is the harmonic number, μ_q is the quartz shear stiffness, ρ_q is the quartz mass density, ρ_s is the surface mass density (mass/area), and ρ and η are the liquid density and viscosity, respectively. Thus the frequency change is due to two terms: the first results from changes in surface mass density (the quantity we wish to measure), the second is due to changes in liquid properties (density and viscosity). If the liquid properties are constant, then changes in frequency can be used to determine surface mass accumulation. The liquid properties, density and viscosity, should remain relatively constant under conditions where temperature is held constant and the chemistry of the fuel is restricted to small extents of reaction. Under these conditions the surface deposition can be related to the frequency as

$$\rho_s = -\left(2.21 \times 10^5 \text{ g / (cm}^2\text{s)}\right) \frac{\Delta f}{f_0^2} \quad 2)$$

for the fundamental resonance. The surface deposition measurements reported here occur for fuel oxidation at constant temperature (± 0.4 C) and under limited oxygen conditions, where only a small fraction of the fuel molecules undergo chemical change.² Thus, the fuel density and viscosity remain constant during our measurements, and the above equation can be used to measure surface deposition.

Under conditions where the liquid properties are changing, the amplitude output of the oscillator circuit can be used to determine the motional resistance of the crystal.³ The motional resistance can then be related to these changes in liquid properties and thus the changes in liquid properties can be resolved from the surface mass accumulation. We have observed changes in crystal damping for some of the additives studied in this work, despite observing no changes in liquid fuel properties. No changes in crystal damping were observed for any of the neat

(unadditized) fuels during a run. The implications of these changes in crystal damping will be discussed below.

In general, the reproducibility of the mass deposition measurements on fuels is limited to $\pm 20\%$ for the QCM technique. This estimate of the precision of the technique was derived from multiple runs of the same fuel, performed for various fuels.

Results and Discussion

In Table II are listed the fuels studied here and their properties. We have chosen to perform additive testing using a wide variety of different fuels to insure that the additive evaluation is not biased by the study of a single fuel type. Thus this work involves the study of both hydrotreated and unhydrotreated fuels. In this paper we report on a representative sample of fuel types. The first fuel is a non-hydrotreated Jet A fuel that is a moderate to heavy depositor, called fuel F-2827. This fuel exhibits a relatively low JFTOT (Jet fuel thermal oxidation test) breakpoint and contains a measurable amount of sulfur. In Figure 1 are shown the deposition results from the QCM for fuel F-2827 at 140°C for 15 hours with varying concentrations of Betz SPEC-AID 8Q405. This additive is classified as a dispersant by the manufacturer (see Table I). The additive concentration was varied from 0 to 100 mg/l. The figure demonstrates that at all concentrations tested the additive significantly improves the thermal stability of this fuel at short times. At 10 mg/l SPEC-AID 8Q405 shows a large improvement in thermal stability until ≈ 7 hours, at which time the deposition rate increases. At long times the deposition begins to approach that of the unadditized fuel. Similar behavior is exhibited for the 25 mg/l run, except here the low deposition region is extended out to ≈ 9 hours. Also shown in the figure are runs with 50 and 100 mg/l of SPEC-AID 8Q405. These two runs exhibit low deposition during the entire 15 hour experiment. Within the experimental uncertainty the deposition at 50 and 100 mg/l are the same. We will show below that though SPEC-AID 8Q405 has limited antioxidant characteristics it works primarily as a dispersant. The concentration dependence demonstrated in Figure 1 implies that at low concentrations the dispersant capability of this additive is overwhelmed by the relatively high concentration of polar species and/or aggregate particles generated in this fuel. At 50 mg/l and above there exists a high enough concentration of the additive to disperse the polar species created by the autoxidation process over the entire 15 hour run time of the experiment. These results show how an additive concentration can be optimized for a given fuel and stressing conditions using the QCM. It is important to understand that this concentration dependence is only valid for the temperature, time, and oxygen availability conditions of this experiment. At higher temperatures, it is expected that the oxidation rate will increase, thus deposit rate increases will occur, shortening the time to the sudden deposition rate change in this fuel/additive combination. The final amount of deposition after oxygen

consumption is completed is mainly controlled by the oxygen availability in the system and thus should not be greatly effected by relatively small changes in temperature. With relatively large changes in temperature, mechanistic changes will occur in the autoxidation process, resulting in changes in both oxidation and deposition.¹

In Figure 2 are shown the deposition data for DuPont JFA-5 in fuel F-2827 over the concentration range 0 to 24 mg/l. The figure demonstrates that JFA-5 improves the thermal stability of F-2827 early in the run, but at all concentrations the deposition increases above that of the neat fuel later in the run. The 6 mg/l run shows improved deposition until 5 hours into the run, after which the deposition is $\approx 0.5 \mu\text{g}/\text{cm}^2$ above the neat fuel. The 12 mg/l run shows low deposition until ≈ 7 hours, after which the deposition is 1-2 $\mu\text{g}/\text{cm}^2$ above the neat fuel. In the 24 mg/l run, the deposition remains low for ≈ 8 hours, after which deposition is 2-3 $\mu\text{g}/\text{cm}^2$ above the neat fuel. It appears that JFA-5 actually decreases the fuel thermal stability for extended stressing times. An added complication in interpreting this data is the observation that for these runs with JFA-5 the crystal damping voltage did not remain constant during the course of the run. The damping voltage was observed to increase along with the apparent increase in deposition observed at long times. Changes in damping voltage are normally caused by changes in the fuel density and viscosity. These properties were measured after the completion of thermal stressing; under the conditions employed in this study no significant changes in viscosity and density were observed. As the liquid properties are not changing during the run, the change in damping voltage must be due to some other process that causes crystal damping. One possibility is the formation of a thin viscous film on the crystal electrode surface. The formation of such a film would result in a damping voltage change and an apparent increase in deposition due to the decrease in crystal frequency caused by the film formation. We have no other evidence to support this supposition, but at this time viscous film formation appears to be a reasonable hypothesis to explain the observations.

If the formation of viscous films result in anomalous increases in deposition for JFA-5, how do we evaluate this additive properly? As we have no data on the properties of this film, it is safer to assume that its formation is a negative characteristic of the additive. It is reasonable to expect that the formation of a viscous film would add to the fouling of fuel systems and therefore be a characteristic to be avoided in a potential additive. The formation of gums in fuels is detrimental to fuel systems, and a viscous film is likely to effect fuel negatively by a similar mechanism.

The effects of the addition of SPEC-AID 8Q405 and BHT in fuel F-2922 are shown in Figure 3. This fuel is hydrotreated and oxidizes quite rapidly as shown by the relatively rapid pressure decay observed for the unadditized fuel. BHT, which is an antioxidant, is added at 25 mg/l and causes a significant slowing of the oxidation. The unadditized fuel consumes oxygen

over the first seven hours, at which time the pressure decay levels as the oxygen present is completely consumed. The additized fuel continues to consume oxygen even up to the end of the 15 hour run. The additized fuel also appears to have a higher initial vapor pressure, perhaps due to the carrier oil in which the additive is dissolved. The effect of the additive on the fuel thermal stability is also shown in the figure. The additized fuel produces deposition to a smaller extent until nine hours, at which time the deposition increases above that of the unadditized fuel. The smaller deposition at short times appears to be due to the slower rate of oxidation that results from the presence of the antioxidant. But when the oxygen is consumed, the additive actually results in increased deposition. This effect has been observed for a wide variety of antioxidants in fuel F-2922. Apparently, the polar nature of the antioxidant molecules result in their causing increased deposition upon their being oxidized. It is well known that the presence of polar, easily oxidizable molecules has a detrimental effect on the thermal stability of fuels.⁵ We have found, as shown below, that the addition of a detergent/dispersant additive can prevent the antioxidant from causing a reduction in the thermal stability of the fuel. Thus one gets the positive effect of the antioxidant inhibition of the oxidation process without increased deposition.

Also shown in Figure 3 are results for the addition of 100 mg/l of SPEC-AID 8Q405 to F-2922. SPEC-AID 8Q405 is classified by the manufacturer as a dispersant. The figure shows that oxidation is slowed by the addition of this additive; this pressure decay is very similar to that observed for BHT. This additive also decreases the deposition significantly up to ten hours, when the deposition suddenly increases, leveling off at a mass accumulation similar to the unadditized fuel at 14 hours. Thus, although this additive displays antioxidant properties, it also shows a significant effect on the deposition, as also observed for fuel F-2827 in Figure 1. Apparently, the sudden increase in deposition observed at ten hours is also due to this dispersant additive being overwhelmed by the large production of polar species in this fuel. Note that Figure 1 shows that the sudden increases in deposition in fuel F-2827 containing SPEC-AID 8Q405 occurs at much lower concentrations than for F-2922. We have observed previously that F-2827 consumes oxygen much more slowly than F-2922;² thus the optimum concentration of a dispersant will be higher for the faster oxidizing fuel (F-2922), as seen here.

The effect due to the addition of both SPEC-AID 8Q405 and BHT to fuel F-2922 is also shown in Figure 3. The oxygen decay is very slow when the two additives are present; oxygen consumption is only partially complete at 15 hours. At these concentrations the antioxidant properties of these two additives appears to be enhanced by the presence of the other. The deposition measured is extremely low during the entire run, reaching only $0.2 \mu\text{g}/\text{cm}^2$ at the end of the run. In this hydrotreated fuel, a combination of antioxidant and detergent/dispersant appears to work quite well; the antioxidant slows the oxidation, while the dispersant keeps the polar compounds formed during oxidation in solution so that they cannot aggregate to form

larger depositing species. Note that the slowly oxidizing, non-hydrotreated fuel F-2827 does not require the presence of the antioxidant additive to achieve low deposition with the addition of SPEC-AID 8Q405 (Figure 1).

We have found two requirements for a fuel to be useful in evaluating antioxidants at 140 C for use in a thermal stability additive package. The fuel must oxidize relatively rapidly so that the oxidation is easily monitored, and the fuel must produce an easily measurable amount of deposits. Fuels that are slow oxidizers, such as F-2827, are not useful for evaluating antioxidants; such fuels tend to be heavy depositors. Fuels that oxidize rapidly, such as F-2747,² have a tendency to be very light depositors, making it difficult to evaluate their effect on thermal stability. A fuel such as F-2922 which oxidizes rapidly and produces an easily measured amount of deposits, as shown in Figure 3, is ideal for evaluation of antioxidants.

JPTS is a special purpose jet fuel developed for the U-2 aircraft. This fuel has excellent thermal stability characteristics and contains 12 mg/l of JFA-5 by specification. We have examined the oxidation and thermal stability of a JPTS fuel (F-2799) with and without JFA-5; the data are shown in Figure 4. JFA-5 is an additive package which consists of an antioxidant, a dispersant, and a metal deactivator. Figure 4 shows that the presence of the additive greatly delays the oxidation process. The unadditized fuel oxidizes very rapidly, reaching a minimum pressure in less than two hours. The additized fuel oxidizes very slowly over the first seven hours; oxidation then occurs rapidly, reaching a minimum pressure at 12 hours. The additized fuel produces deposits slowly during the first ten hours, at which time there is a sudden increase in the deposition rate. This sudden increase corresponds to the time of pressure decrease that results from the oxidation of this fuel. The unadditized fuel produces deposits during the early, rapid oxidation, and then deposits more slowly after two hours. It is possible that some of the deposition is missed in the unadditized fuel, as the oxidation process occurs rapidly and can occur during the 45 minute heat-up time, when the deposition process cannot be monitored. It is apparent from the large delay in the oxidation and deposition of the additized fuel that JFA-5 acts as an antioxidant under these conditions. Presumably, the species responsible for this delay is the antioxidant present in the JFA-5 package.

The effect of additives on fuel F-2963 is shown in Figure 6. This is a JP-5 fuel which has been doped with ≈ 50 ppb copper. The presence of copper in fuel is known to result in decreased thermal stability; the U.S. Navy uses copper fuel lines in its aircraft carriers, and therefore has problems with copper contamination of its fuels.⁶ Figure 6 shows that the neat fuel produces deposits quite heavily, leveling off at near $6 \mu\text{g}/\text{cm}^2$ at 12 hours. The pressure plot also shows that the neat fuel consumes oxygen over the first nine hours of the run. The addition of 100 mg/l of SPEC-AID 8Q405 results in much decreased deposition, although the deposition rate shows a rapid increase at 11 hours before leveling off at 13 hours. The addition of SPEC-AID 8Q405 also

slows the oxidation of the fuel. Also shown in the figure is the combination of SPEC-AID 8Q405 and BHT. This combination further decreases the oxidation rate and also decreases the final amount of deposits measured. No sudden change in deposition rate is observed with this additive combination. Also shown in the figure is the effect of adding SPEC-AID 8Q405, BHT, and 10 mg/l of MDA. MDA is a metal deactivator which is thought to improve the thermal stability characteristics of fuels which contain an excess of dissolved metal species. This three additive combination further decreases the deposition observed in this fuel (no pressure measurements are available for this additive combination).

We have tested the effectiveness of variety of additives and additive packages in a variety of different fuels. A comparison of four additive combinations in eight different fuels is shown in Figure 5. The mass accumulation plotted is the QCM measured final accumulation at the end of the 15 hour run at 140 C. The time chosen can affect the comparative results as some additized fuels show sudden increases in deposition following a period of relatively light deposition (e.g., see Figure 2). We have chosen the mass accumulation at 15 hours for comparison purposes as it represents a worst case for fuels which display sudden deposition increases. Thus this comparison will be biased against such additives. The horizontal line near $1 \mu\text{g}/\text{cm}^2$ represents the deposition of JPTS; a fuel with very good thermal stability characteristics and whose mass accumulation is a goal of the additive program. The neat fuels shown in the figure display deposition over the range 2.9 to $10 \mu\text{g}/\text{cm}^2$. The addition of SPEC-AID 8Q405 alone improves some fuels substantially (F-2980 and F-2827), some slightly (F-2985 and F-2963), and some not at all (F-2926 and F-2922). Fuels F-2926 and F-2922 are both fuels that oxidize readily (F-2922 is hydrotreated); it has been demonstrated in static tests with bubbling oxygen that these fuels produce copious deposits when given unlimited oxygen.⁷ Thus, an antioxidant, BHT, was added to these fuels in order to limit the rate of oxidation. The figure shows that the addition of BHT greatly improves the behavior of F-2922 and F-2926 but shows only small improvements for the other fuels, all of which are slower oxidizers. The addition of BHT does not significantly worsen the thermal stability of fuels F-2827 and F-2980 which were strongly improved by SPEC-AID 8Q405. Thus the combination of SPEC-AID 8Q405 and BHT, a dispersant and antioxidant, significantly improves four of the eight fuels (this additive combination also improves a variety of other similar fuels). The other four fuels (F-2936, F-2934, F-2985, and F-2963) show only partial improvements with this additive package. These four relatively heavily depositing fuels have proven to be very difficult to improve with additives. It was found that the addition of a second detergent, Mobil MCP-477, to the package produced significant improvements, as shown in the figure. The addition of MCP-477 brings both F-2936 and F-2963 below the $1 \mu\text{g}/\text{cm}^2$ goal, while F-2985 and F-2934 remain slightly above the goal. Unfortunately, it was found in flowing tests at higher temperatures that this three additive package generally increased deposition above

the neat fuel. This discrepancy between higher temperature flowing tests and the 140 °C QCM measurements only occurred for packages involving MCP-477. Apparently MCP-477 enhances deposition at higher temperatures; further work on the QCM at higher temperatures is being studied in order to determine the cause of this discrepancy. The fourth additive combination shown in the figure is for MDA, a metal deactivator, added to SPEC-AID 8Q405 and BHT. This gives surprisingly poor results for fuels F-2934 and F-2985, markedly increasing their deposition. The only fuel in which this package shows improvement over the SPEC-AID 8Q405 and BHT package is fuel F-2963. This result is not surprising considering that fuel F-2963 has been doped with 50 ppb of copper; a metal deactivator additive is designed to improve such a fuel. Other tests at higher temperatures have shown significant improvements for MDA;⁷ future QCM work at higher temperatures will attempt to study this behavior.

In the past, jet fuel additives have been evaluated in a wide variety of experimental devices. Various workers have used modified and unmodified versions of the JFTOT at various temperatures, see for example Morris et al.⁶ Flask oxidation tests have been performed to evaluate antioxidants, see for example Kendall and Mills.⁸ Also, relatively large scale single tube heat exchangers have been used to measure the effects of additives, see for example Clark.⁹ These various tests differ in the essential parameters for examining fuel thermal stability: temperature, stress duration, oxygen availability, and surface materials, among others. Most tests are conducted under accelerated conditions, where the temperature or oxygen availability are increased above real fuel systems conditions. The study of additives in this work was performed at 140 °C, a relatively low temperature compared with other thermal stability tests. The presence of an air headspace in our reactor yields a higher oxygen availability than a flowing test by a factor of ≈ 4 .² Also, the fact that our test is conducted in static mode at low temperatures dictates that the test time be relatively long (15 hours). Aircraft fuel systems consist of extremely complex pathways for fuel flow with various residence times at various temperatures; these temperatures and residence times vary with flight conditions, e.g. higher fuel system temperatures may occur at flight idle descent. In the laboratory, it is impossible to test additives under the exact conditions of an aircraft. These QCM tests address one set of conditions that the fuel may encounter— low temperature and moderate oxygen availability— as might occur in the fuel tank or fuel recirculation line. Higher temperature flowing tests may do a better job of simulating high temperature parts of the fuel system, such as the engine fuel nozzle. High oxygen availability tests, such as flask tests with bubbling oxygen, address a different regime. The Air Force JP-8 + 100 additive program is using a wide variety of tests in an attempt to simulate most conditions to which a fuel is subjected. A successful additive package must have the ability to prevent deposition over this wide range of conditions. Despite this wide range of conditions, the QCM has been used successfully to screen dozens of additives for study in high temperature

flowing tests such as the Phoenix Rig.¹⁰ On occasion additives have been found that perform quite differently in these two regimes. Thus, the limitations of a single device at a single temperature and oxygen availability must always be kept in mind.

Conclusions

We have demonstrated the usefulness of the QCM and pressure monitoring for the evaluation of jet fuel additives. The simultaneous measurement of time dependent deposition and oxidation also permits one to determine the mechanisms by which these additives operate. Additives that behave as antioxidants should delay or slow the onset of oxidation and thus oxygen removal. Detergent/dispersants will delay or prevent the formation of deposits. We have observed additives that exhibit both antioxidant and detergent/dispersant characteristics. These time dependent measurements allow us to readily determine the optimum concentration of additives. The antioxidants studied to date all appear to actually increase the deposit formation tendency of a fuel. We have found that an antioxidant in combination with a detergent/dispersant can yield the best characteristics of the two additive types for fuels which oxidize rapidly; the antioxidant delays the oxidation, while the detergent/dispersant prevents the formation of additional deposition due to the presence of the antioxidant. Slowly oxidizing fuels, which do not require the presence of an antioxidant, also show good improvement with this additive combination. Fuels with high metal concentrations also require the presence of a metal deactivator in addition to the antioxidant and detergent/dispersant, although the metal deactivator has a deleterious effect on some fuels.

Acknowledgments

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Table I. Properties of Additives Studied

Additive Name and Supplier	Additive Classification	Type of Compound	Concentration (mg/l)	Percent Active Ingredient
Betz SPEC-AID 8Q405	Dispersant	proprietary	100	proprietary
DuPont JFA-5	High Temperature Thermal Stability Package	Mixture of antioxidant, dispersant, and metal deactivator	12	proprietary
BHT	Antioxidant	2, 6 di-t-butyl-4-methylphenol	25	100 %
MDA	Metal Deactivator	N,N'-disalicylidene-1,2 propanediamine	10	73 to 75 %
Mobil MCP-477	Detergent	proprietary	300	100 %

Table II. Properties of Fuels Studied

Fuel Number and Designation	Hydrotreated?	JFTOT Breakpoint (°C)	Sulfur Mass %	Other Notes
F-2747 (Jet A-1)	Yes	332	<0.05	Light depositor
F-2827 (Jet A)	No	282	0.10	Heavy depositor
F-2922 (Jet A)	Yes	277	0.02	Fast oxidizer
F-2963 (JP-5)	Not known	232	0.04	High copper fuel
F-2799 (JPTS)	Yes	398	<0.05	High thermal stability
F-2926 (Jet A)	Not known	288	0.10	
F-2980 (Jet A)	No	288	0.10	Merox treated
F-2936 (JP-5)	Not known	277	0.10	
F-2934 (Jet A-1)	Not known	266	0.10	High acid number
F-2985 (JP-5)	Not known	266	not measured	High in nitrogen cmpds.

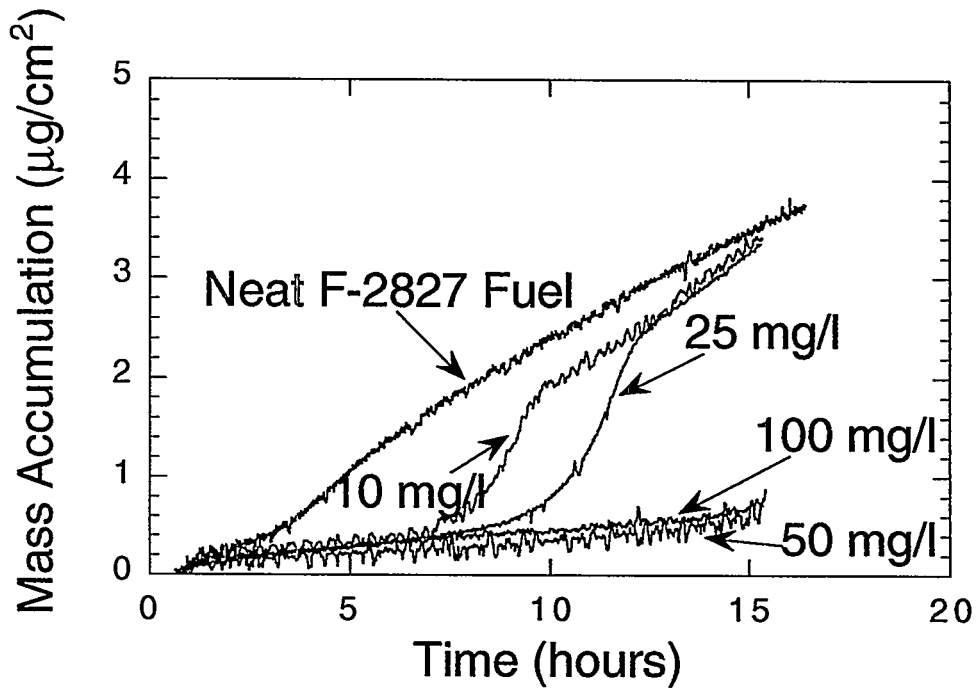


Figure 1. Plots of mass accumulation vs time for fuel F-2827 with varying concentrations of SPEC-AID 8Q405.

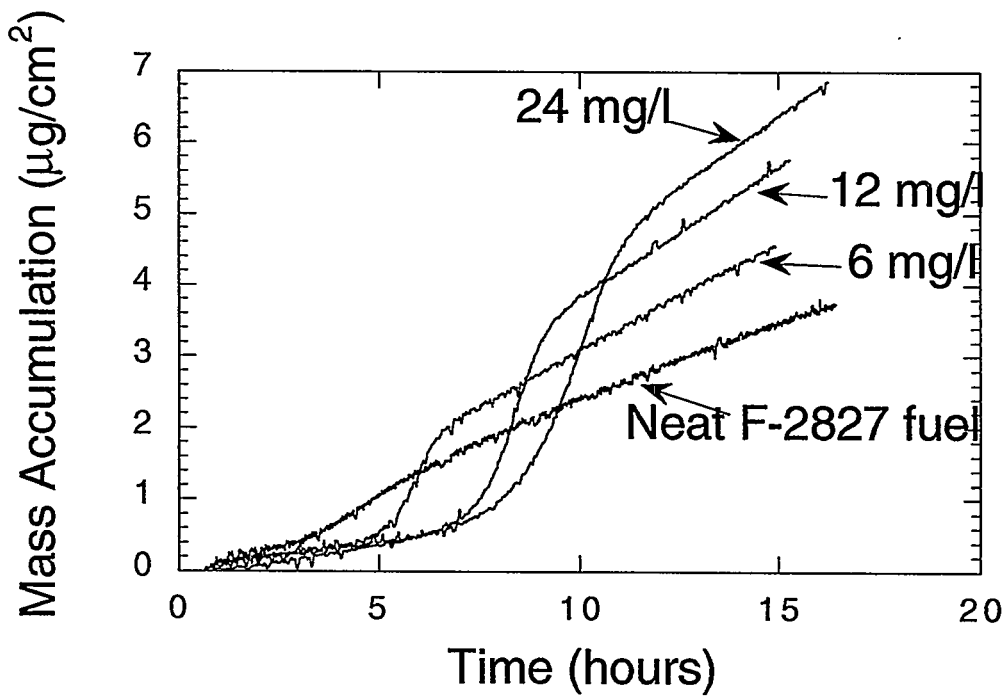


Figure 2. Plots of mass accumulation vs time for fuel F-2827 with varying concentrations of JFA-5.

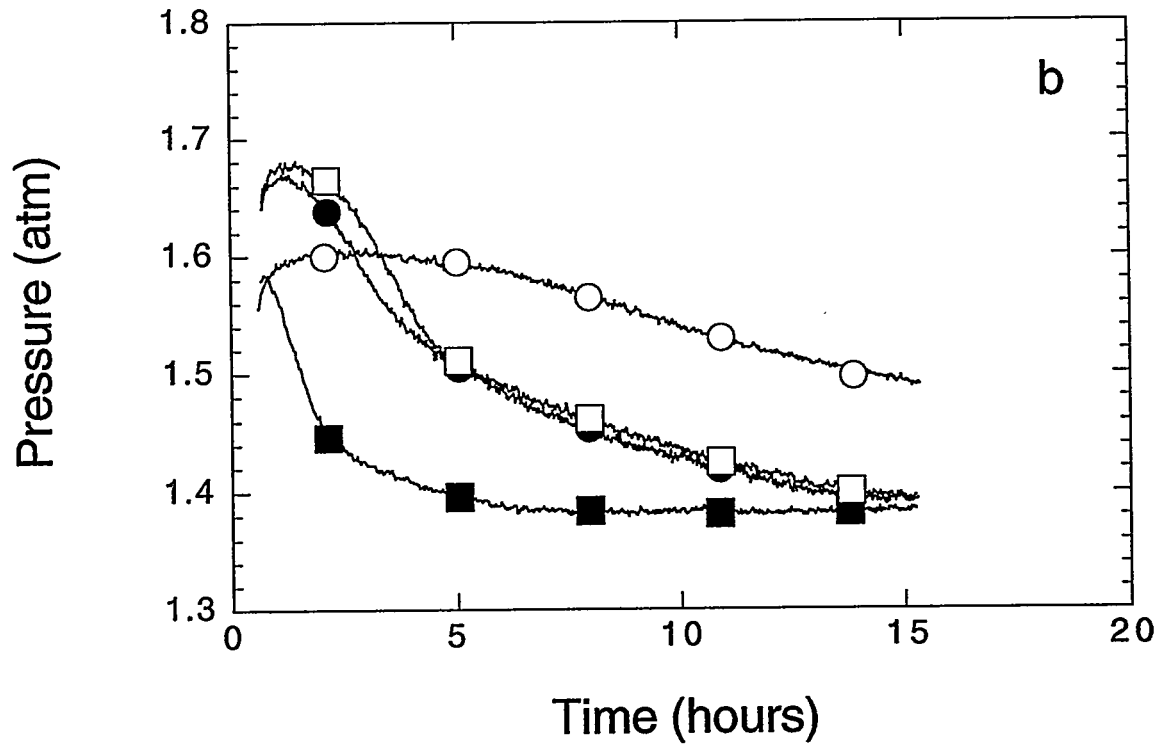
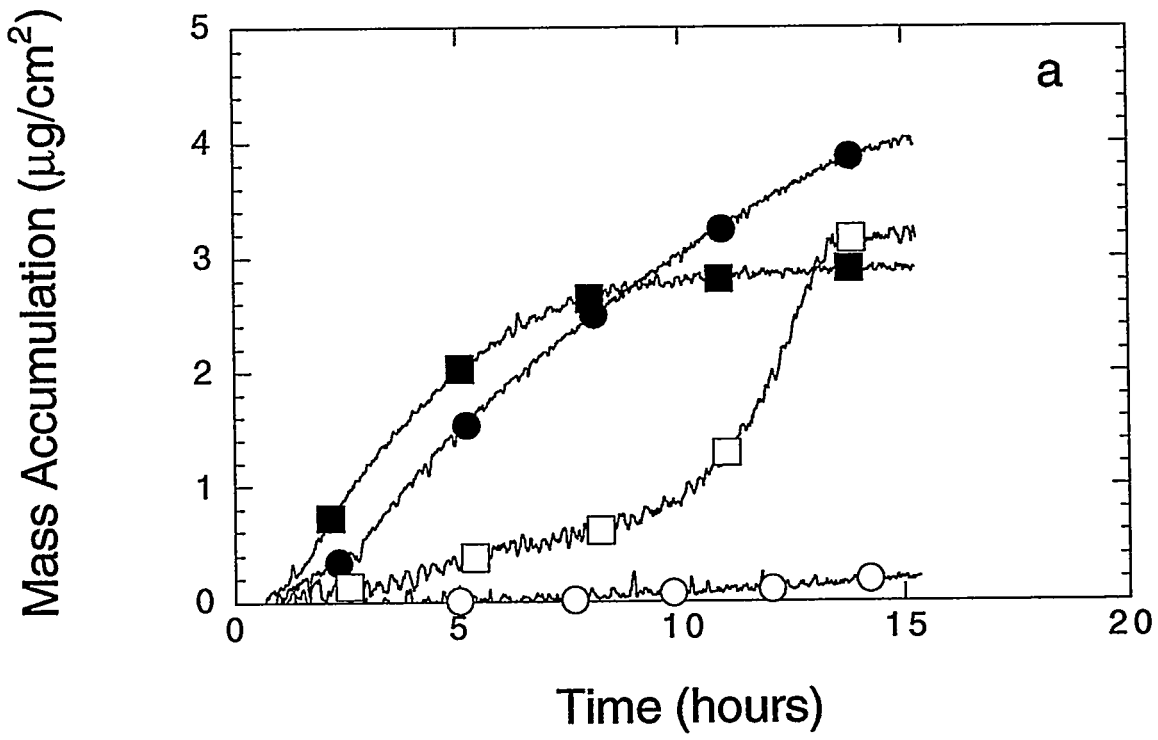


Figure 3. Plots of mass accumulation and pressure vs time for fuel F-2922: ■ neat fuel, ● with 25 mg/l BHT, □ with 100 mg/l SPEC-AID 8Q405, ○ with both SPEC-AID 8Q405 and BHT.

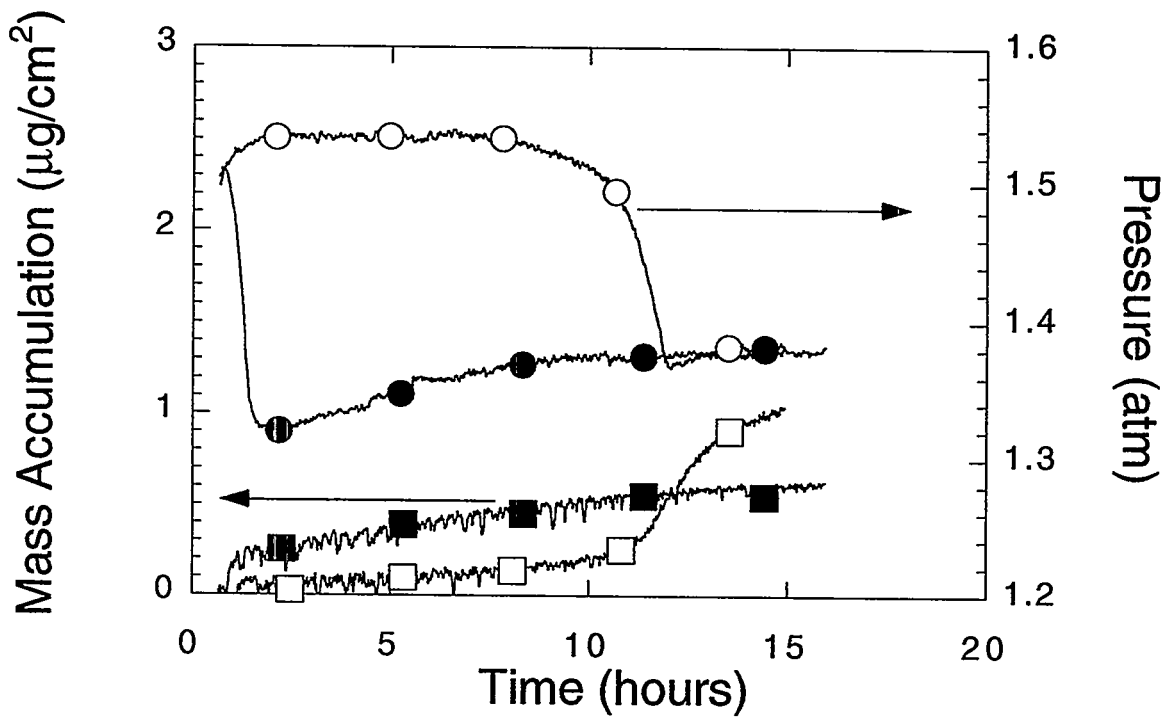


Figure 4. Plots of mass accumulation and pressure vs time for fuel F-2799 (JPTS): \square mass accumulation of fuel, \blacksquare mass accumulation of fuel without JFA-5, \circ pressure of fuel, \bullet pressure of fuel without JFA-5.

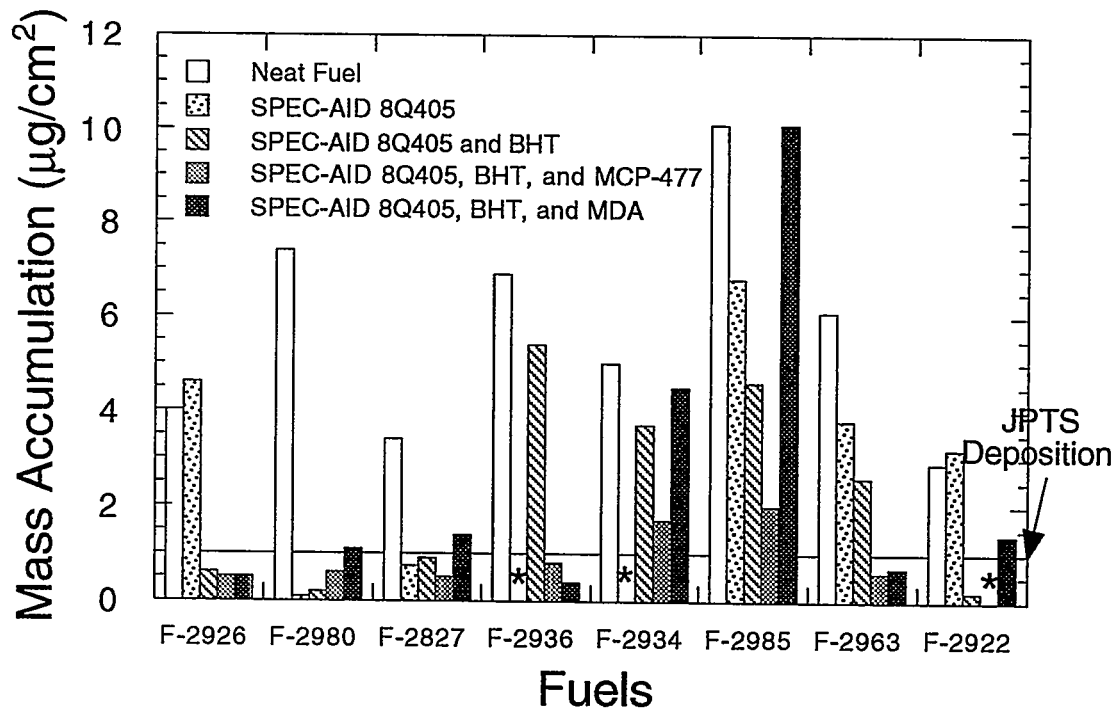


Figure 5. Comparison of mass accumulation for eight fuels with four additive packages.

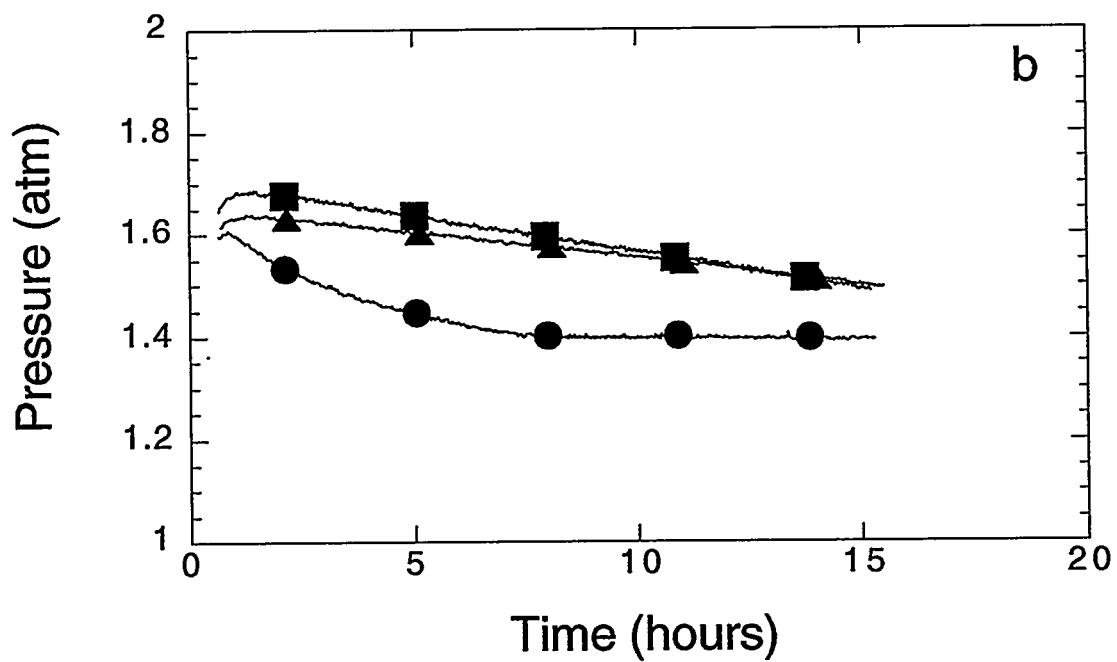
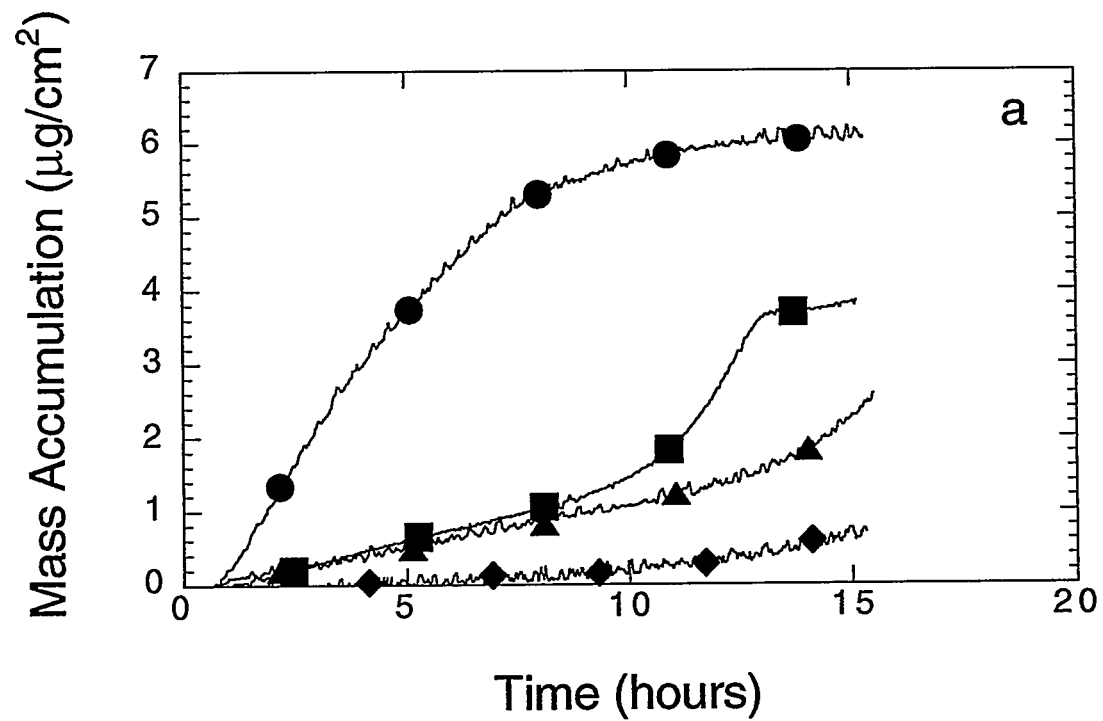
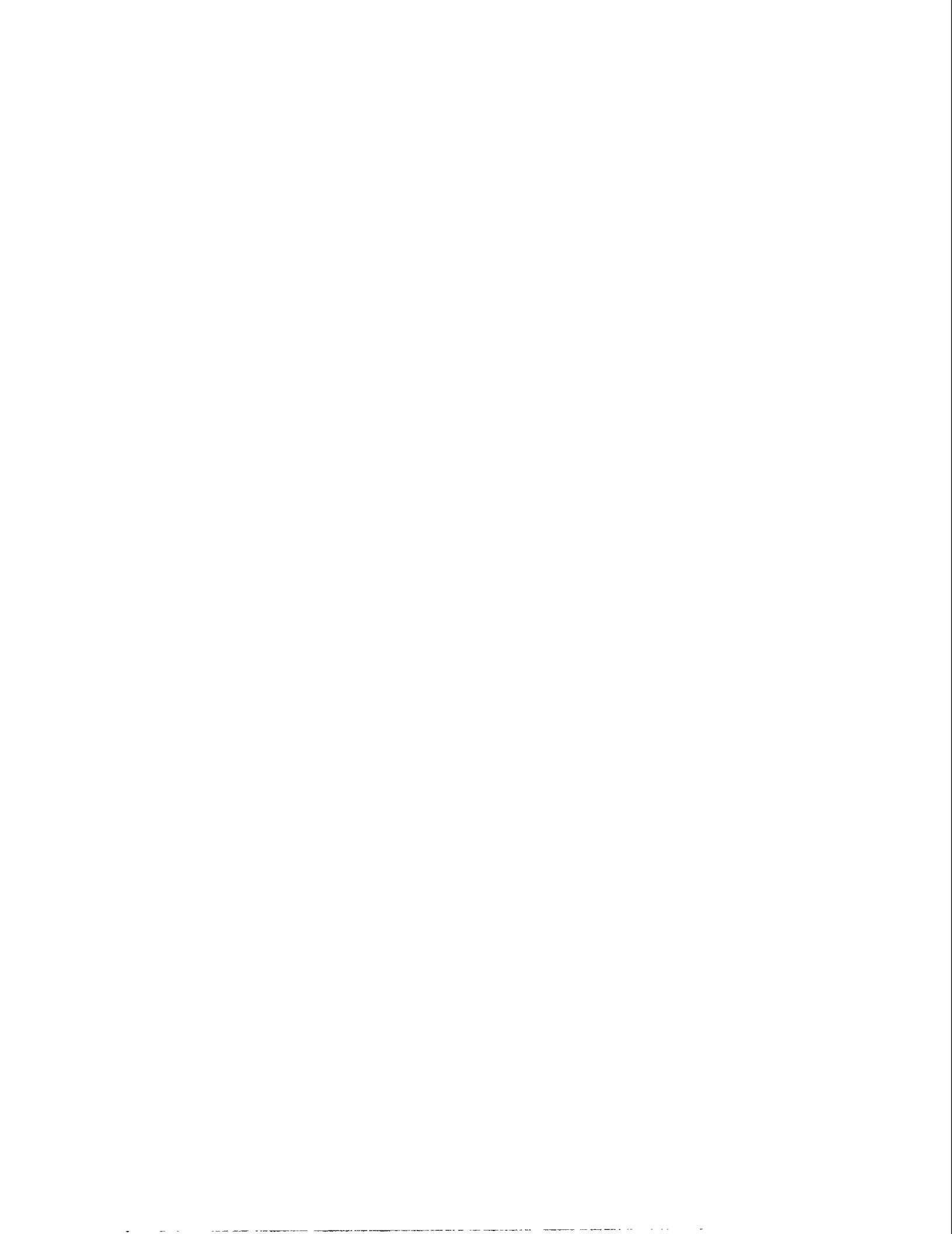


Figure 6. Plots of mass accumulation and pressure vs time for fuel F-2963: ● neat fuel, ■ with 100 mg/l SPEC-AID 8Q405, ▲ with 100 mg/l SPEC-AID 8Q405 and 25 mg/l BHT, ◆ with SPEC-AID 8Q405 and BHT and 10 mg/l MDA.



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EFFECT OF ADDITIVES ON THE FORMATION OF INSOLUBLES IN A JET FUEL

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ABSTRACT

Dynamic near-isothermal techniques have proven to be valuable in assessing the tendency of aviation fuels to form surface and bulk insolubles under thermal stress. These methods are applied in this study to the investigation of the neat Jet-A fuel POSF-2827 and changes introduced by a series of four candidate additives. In each case fuel is stressed while flowing through a heat exchanger under near-isothermal conditions at 185°C. The average surface deposition rate as a function of stress duration and the quantity of both surface and bulk insolubles have been determined after complete consumption of the dissolved oxygen. The additives, introduced individually, include a common antioxidant, a metal deactivator, a dispersant, and a combination detergent/dispersant. Of the four additives, only the dispersant-types are found to improve fuel thermal stability.

INTRODUCTION

Aviation fuels, when subjected to heat in the presence of oxygen, undergo degradation from autoxidation reactions.¹ Insoluble products formed in these reactions tend to foul heated surfaces, causing reduced efficiency and possible blockage in heat exchangers, hysteresis in servocontrols, and changes in nozzle geometry. Being the primary heat sink in modern aircraft, fuel will experience increased thermal stress as aircraft performance is enhanced.² Minor fuel constituents containing sulfur and nitrogen have been implicated as the primary cause of insoluble formation.

Methods of improving the stability of poorer quality fuels that are based on hetero-atom removal, such as clay- or hydro-treatment, do not always represent practical solutions because of the cost involved. The introduction of low-cost additives which may improve the thermal-oxidative stability is appealing. Additives such as antioxidants for slowing oxygen consumption, metal deactivators for chelating dissolved metals or passivating tubing walls, and dispersants for increasing solubility would appear to be the most promising from a thermal-stability standpoint.

Martel³ has summarized jet-fuel additives including, in addition to the above, corrosion inhibitors, lubricity improvers, icing inhibitors, static dissipators, and pipeline drag reducers.

Since each fuel has a different chemical composition, the behavior of an additive for reducing insolubles will be dependent upon the reaction kinetics within the fuel. No additive is expected to be universally effective. For example, the DuPont additive JFA-5 is specified for use in JPTS (thermally stable jet fuel) because it contains a mixture of a high-temperature antioxidant, a dispersant, and a metal deactivator.³ Similarly, to promote storage stability, hydrotreated fuels require the addition of low-temperature antioxidants to replace the natural antioxidants removed during processing.⁴

The approach in the current study was to 1) select a typical Jet-A fuel exceeding US Air Force requirements, 2) investigate its tendency to form insolubles at 185°C, and 3) individually add several candidate additives and investigate changes in the formation and quantity of insolubles. Deposition experiments were conducted over long test times to emphasize deposition on previously fouled surfaces.⁵ Several criteria were applied in assessing beneficial or possibly deleterious effects introduced by the additives. The additive producing the most improvement was then subjected to further testing at several other temperatures. The goal was to address some fundamentals of additive behavior in altering the thermal-oxidation stability. In future studies beneficial synergism among these additives will be investigated by studying combinations. The advantage of the isothermal approach employed in this study is the ability to focus on chemical effects without the additional complexities associated with fluid dynamics at higher flows and without the surface-temperature changes that can occur as deposits accumulate.

EXPERIMENTAL

The baseline fuel, POSF-2827, has a JFTOT breakpoint of 266°C and a sulfur level of 0.079% (w/w). The presence of sulfur probably accounts for interest in this fuel and makes it a good candidate for the study of insoluble formation. In seeking improvement in thermal stability through the introduction of additives, it is important to select a representative, average fuel that produces measurable insolubles rather than an excellent fuel in which improvements would be difficult to detect. POSF-2827 is a typical Jet-A fuel. Kendall and Mills⁶ addressed fuels of this type in which oxidation is inhibited by the presence of sulfur--but at the expense of increased insoluble formation.

The experiments were conducted using the Near-Isothermal Flowing Test Rig (NIFTR) which has been described previously.⁷ Figure 1 shows the heat exchanger which was operated in the double-pass mode to extend reaction time. Fuel, which is saturated initially with respect to air and which contains 64 ppm (w/w) of oxygen, is pumped at a pressure of 350 psi through 0.125-

in.-o.d., 0.085-in.-i.d. commercial stainless-steel (304) tubing clamped tightly in a 36-in. heated copper block. Two in-line Ag-membrane filters (0.45 and 0.2 μm) collect the non-adhering bulk insolubles.

Deposition rates were measured in 72-hr experiments that were run continuously at a fixed fuel-flow rate; reaction time or stress duration was determined from the flow rate, tube dimensions, and location along the tube axis. At the end of each test, the heated tube was cut into 2-in. sections, and the quantity of carbon in the deposits was determined from surface-carbon burnoff (LECO RC-412). Deposition rates were determined from the amount of carbon in each 2-in. segment and the stress time calculated to its midpoint. Each section provides one data point representing the rate averaged over the entire test time (i.e., ~ 72 hr). Rate is expressed in units of micrograms of carbon per unit stress time per unit volume of fuel passed through the system.⁷ Dissolved oxygen was measured in separate experiments using a 32-in. tube as a reaction cell and GC detection;⁸ stress duration was changed by varying the flow rate. In long-term (72-hr) tests, most deposition occurs on previously fouled surfaces; for this reason a passivated tube (Silcosteel⁹) was used to minimize catalytic wall effects during oxygen measurements. In dynamic isothermal experiments, stress duration differs from experimental test time. Stress duration is the reaction time at temperature, and the experimental test time (along with the fuel-flow rate) determines the total quantity of fuel passed through the system.

Photon-correlation spectroscopy was selected for sizing of sub-micron particles, based on the techniques outlined by O'Hern et al.¹⁰ Fuel was stressed within the NIFTR for selected times at 185°C, and particles in the effluent were sized after cooling to room temperature. The size measurements are viewed as an upper limit to the *in-situ* sizes.

The four selected additives are listed in Table 1. These include an antioxidant, a metal deactivator, a dispersant, and a combination detergent/dispersant. Concentrations of dispersants were based on manufacturers' suggestions, cost constraints, and previous tests in this laboratory.¹¹ Since the neat fuel does not contain measurable dissolved metals, MDA concentration was set at 2 mg/L for possible wall passivation.

RESULTS AND DISCUSSION

Oxygen Loss. The behavior of the dissolved oxygen as a function of stress duration at 185°C is shown in Fig. 2. Oxygen in the neat fuel is totally converted in about 20 min. The rate is constant down to 30% residual oxygen, indicating oxygen non-limited kinetics. Below 30% the rate becomes oxygen limited, as evidenced by tailing. Walling¹² has summarized the rate expressions for the disappearance of oxygen at high and low oxygen concentrations. Neither BHT nor MDA alters the oxygen consumption. The presence of certain types of sulfur compounds

causes hydroperoxide concentration to remain low and the kinetic chain length to approach unity. Chain-breaking antioxidants such as BHT (hindered phenol) are ineffective since a molecule of antioxidant is destroyed for every molecule of oxygen consumed.¹³ In the absence of dissolved metals and with inactive wall surfaces, a metal deactivator is similarly not expected to have a pronounced effect. Only one of the additives, MCP-147B, seems to perturb the oxygen consumption by increasing the reaction rate. At a concentration of 300 mg/L, this additive is directly participating in the reaction as a pro-oxidant or as an initiator.

Ideally, an additive should retard or certainly not increase the rate of autoxidation. In aircraft fuel lines, the fuel spends very little time at elevated temperature; therefore, oxygen conversion, in practice, is minimal. However, the very large fuel throughput offsets the conversion and leads to the observed fouling. In isothermal simulations only small amounts of fuel are used (~ 1.1 L); however, with 100% oxygen conversion, the extent of fouling per unit volume of fuel used is significant. In either case an additive such as MCP-147B that increases the autoxidation rate is of concern and its use should be decided based on further testing.

Dependence of Deposition Rate on Stress Duration. Figure 3 shows the deposition profiles at 185°C obtained at a flow rate of 0.25 mL/min. The 72-hr-average rate profiles for the additives BHT and MDA as well as the neat fuel appear to be the same within experimental reproducibility, displaying maxima around 9 min and completed deposition around 20 min which is consistent with the observed consumption of oxygen. The additives MCP-147B and 8Q405 cause significant changes in the deposition profiles. For stress times of less than 3 min, the former exhibits a reduced deposition rate but at longer times leads to a higher rate, maximizing around 6 min with no tailing. This additive appears to be promoting the deposition rate, as might be expected from the oxygen-loss data. The latter additive reduces the deposition rate for over 15 min of stressing and delays the maximum to around 12 min. The 8Q405 appears to behave as might be expected for an effective additive based upon a deposition-rate criterion, namely, reduced rate and delayed deposition. The MCP-147B displays undesirable behavior, based on a deposition-rate criterion.

Quantification of Insolubles. Other criteria for evaluating the additives on the basis of data from the same experiments are quantity of surface insolubles (integral under the rate profiles), bulk insolubles (carbon burnoff of the in-line filters), and finally the total insolubles (sum). In each case these quantities are expressed in terms of micrograms of insolubles per milliliter of fuel that is initially saturated with respect to air at room temperature. Insolubles are plotted in Fig. 4 for the neat fuel and each additive. Clearly, neither BHT nor MDA has a beneficial effect for POSF-2827 fuel under the test conditions; however, these additives do not reduce thermal stability. In contrast, both dispersants cause significant reduction in surface and

bulk insolubles. Using quantity of insolubles produced from POSF-2827 as a criterion, both MCP-147B and 8Q405 result in a 50% reduction and would be rated as effective additives.

Bulk insolubles are quantified only at the end of 24-min of stressing or complete oxygen conversion. Surface insolubles, on the other hand, can be evaluated after any selected stress time, t , at 185°C by integrating under the curves in Fig. 3 up to time t . Thus, the performance of each additive in reducing surface deposits can also be evaluated as a function of stress duration.

Selection of Most Effective Additive. Based on the above evaluation criteria, neither BHT nor MDA improves the thermal behavior of the fuel as tested. The detergent/dispersant MCP-147B, while reducing insolubles, showed less than desirable signs both in the oxygen experiments and in the deposition rate by initiating or promoting thermal degradation. The dispersant 8Q405 does not alter the oxygen reaction rate but reduces both the deposition rate and total quantity of insolubles. For these reasons 8Q405 was selected for further testing.

It should be noted that the current study is limited to a single fuel and four additives. Development of any additive package requires the consideration of a broad family of fuels and additive combinations. Both MCP-147B and 8Q405 have quite different proprietary structures and chemistry. We expect their behavior to be different in every fuel.

Other Tests with 8Q405 Additive. Figure 5 shows a comparison between the deposition using neat and additized fuel at 165, 185, 205, and 225°C. Significant reduction in deposition rates is observed at each temperature. Similar improvements in the quantity of insolubles would be expected (see Fig. 6). Note that the inverse temperature dependence of the total insolubles that has been reported in 6-hr tests¹⁴ is also reflected in the 72-hr experiments for both the neat and the additized fuel.

The fact that a dispersant-type additive shows the most promise in POSF-2827 fuel suggests that its role is to keep potential insolubles in solution, possibly by delaying agglomeration processes. The 8Q405 does not slow the autoxidation rate, but the subsequent chemical and physical steps leading to insolubles are delayed and the quantities are reduced. Insolubles that do come out of solution may be dispersed and kept small. Particles formed during the stressing of POSF-2827 fuel have been sized using photon-correlation spectroscopy. The measured diameter for the neat and 8Q405-doped fuel is shown in Fig. 7 as a function of stress duration at 185°C. The dispersant causes significant reduction in both particle size and number density (not shown), consistent with the earlier discussion.

CONCLUSIONS

The effect of four additives in improving the thermal stability of a particular Jet-A fuel has been evaluated in long-term (~ 70-hr) tests in which most of the deposition occurs on previously fouled surfaces. Neither the antioxidant (BHT) nor the metal deactivator exhibit beneficial effects. Some limited improvement was observed for a detergent/dispersant; however, indications of increased rates of oxygen consumption and deposition raise concerns as to its overall benefit. A dispersant additive 8Q405 exhibited significant reduction in deposition rates and quantity of insolubles over the temperature range 165 - 225°C. Improvement is explained in terms of particle-size reduction and decreased total insolubles caused by efficient dispersant activity.

Dynamic near-isothermal studies have provided details of oxidation and deposition kinetics for the Jet-A fuel, POSF-2827. These methods are currently being applied to evaluate the use of additives in other Jet-A and JP-8 aviation fuels.

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TABLE 1

ADDITIVES TESTED WITH POSF-2827 FUEL

CLASS	NAME	CHEMICAL NAME	MANUFACTUROR	CONCENTRATION (mg/L)
Antioxidant	BHT	2,6-di-tert-butyl-p-cresol	DuPont	25
Metal Deactivator	MDA	N,N'-disalicylidene-1,2-propanediamine	DuPont	2
Dispersant	8Q405	Proprietary	Betz	100
Detergent/Dispersant	MCP-147B	Proprietary	Mobil	300

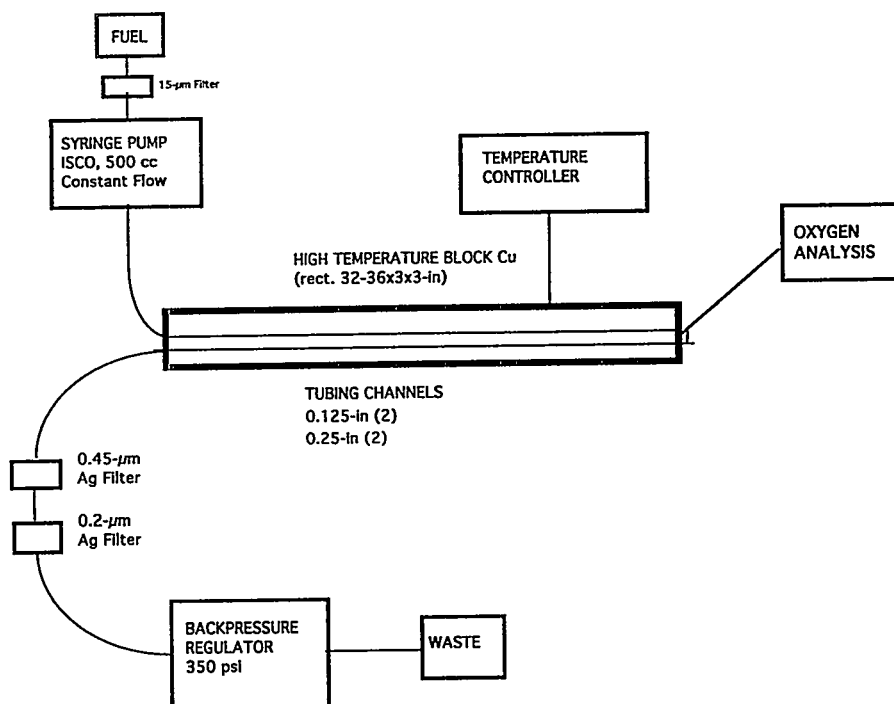


Figure 1. Schematic Diagram of Apparatus (NIFTR)

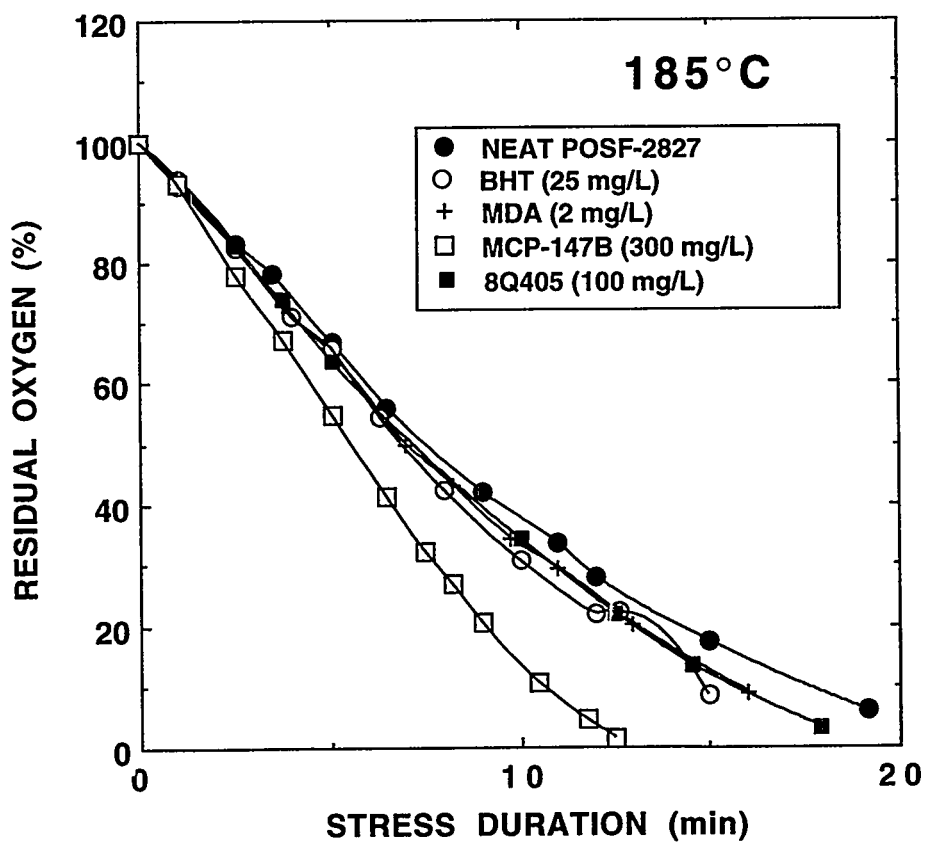


Figure 2. Consumption of Dissolved Oxygen at 185°C in Neat and Additized Fuel.

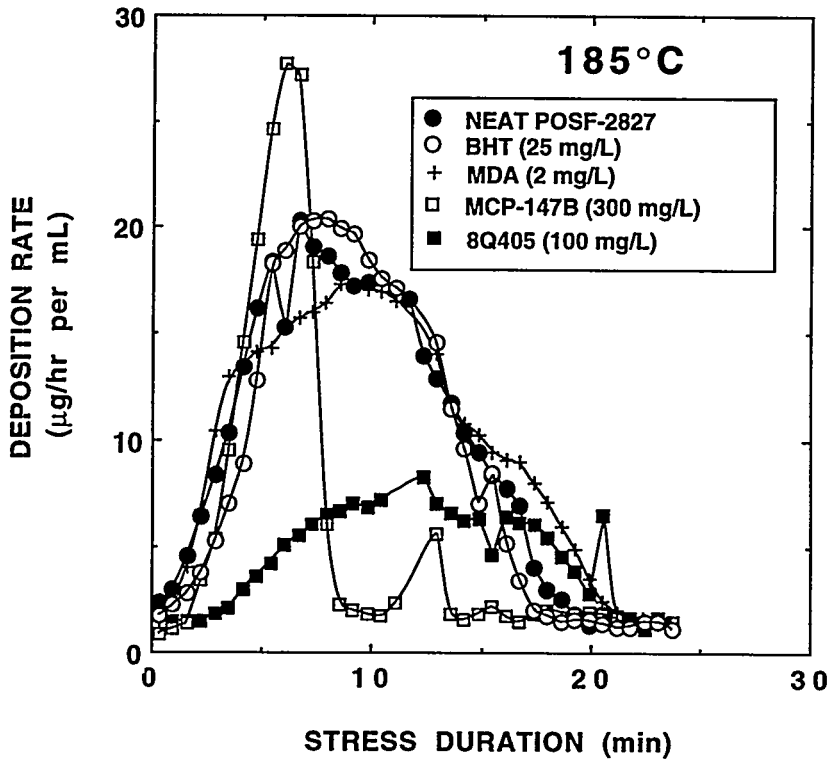


Figure 3. Surface Deposition Rates for Neat and Additized Fuel as a Function of Stress Duration at 185°C.

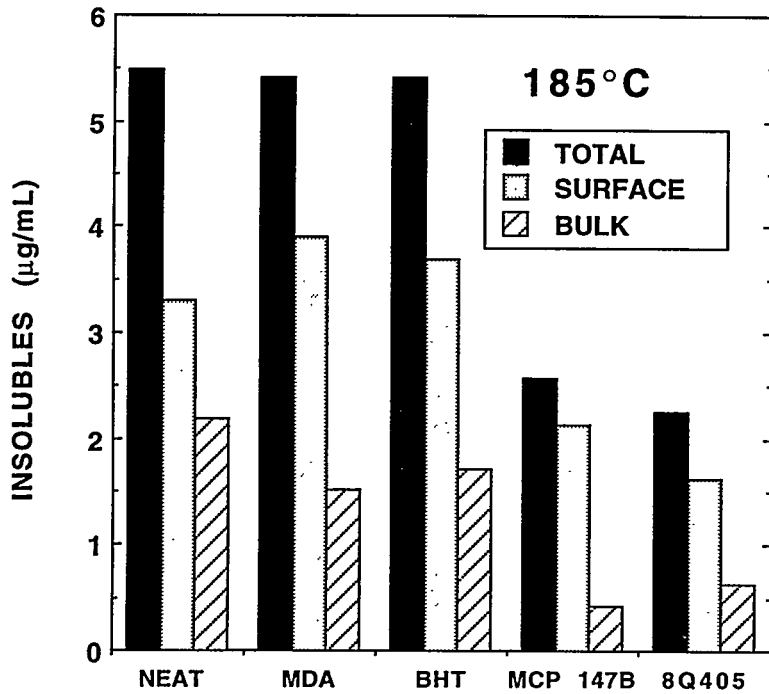


Figure 4. Bulk, Surface, and Total Insolubles Formed at 185°C.

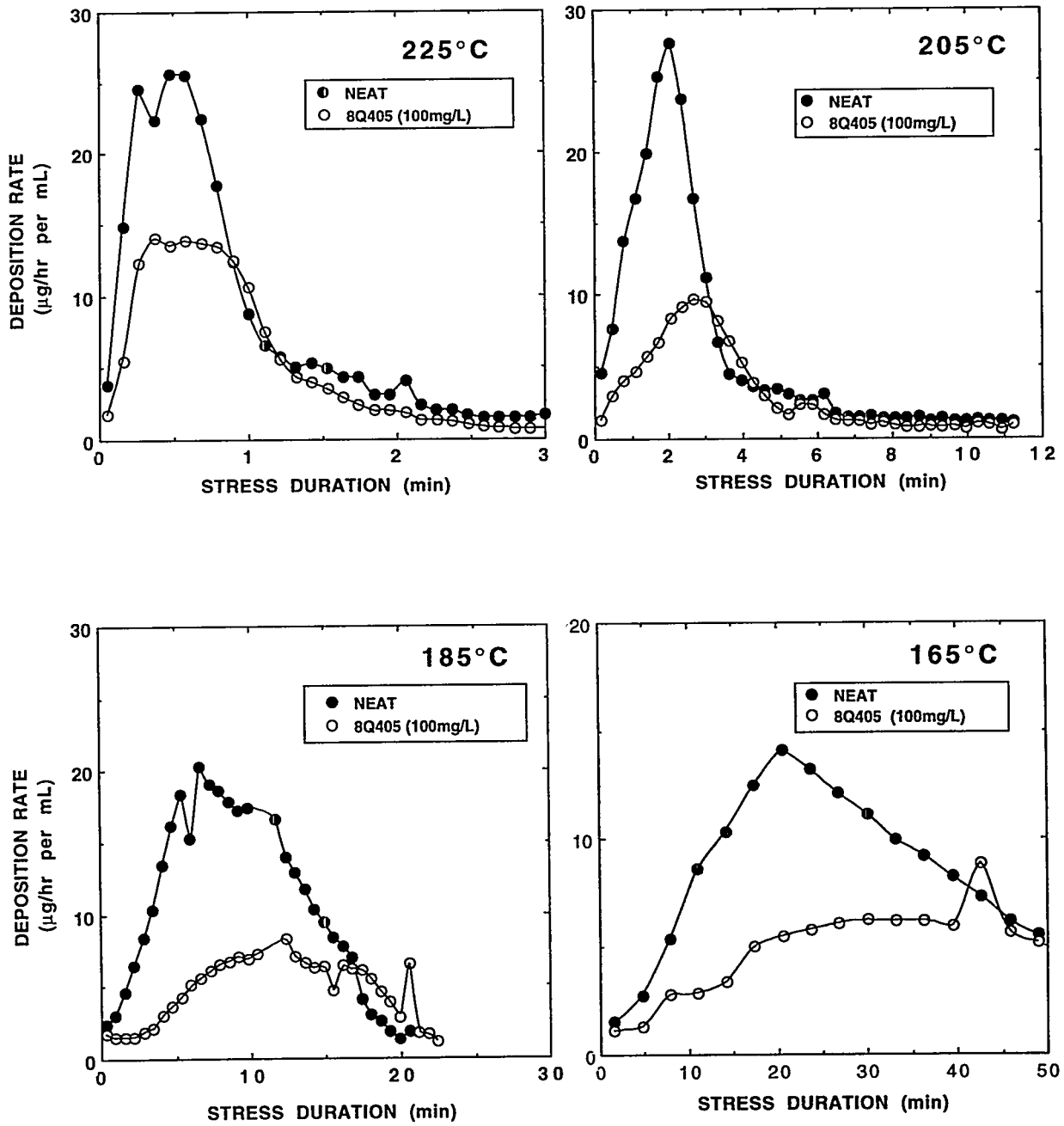


Figure 5. Deposition Rate. Stress Time Dependence at Series of Temperatures

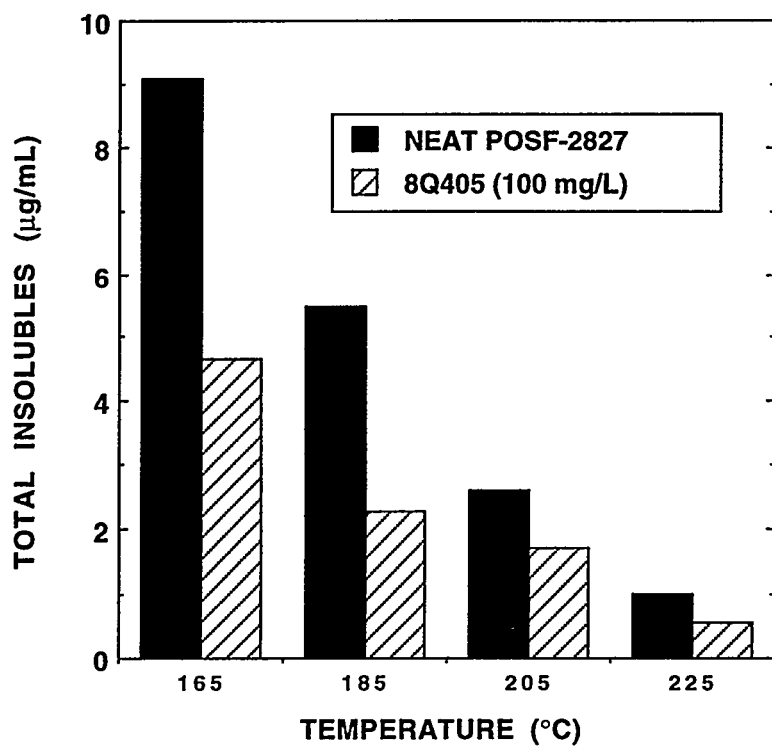


Figure 6. Total Insolubles as a Function of Temperature.

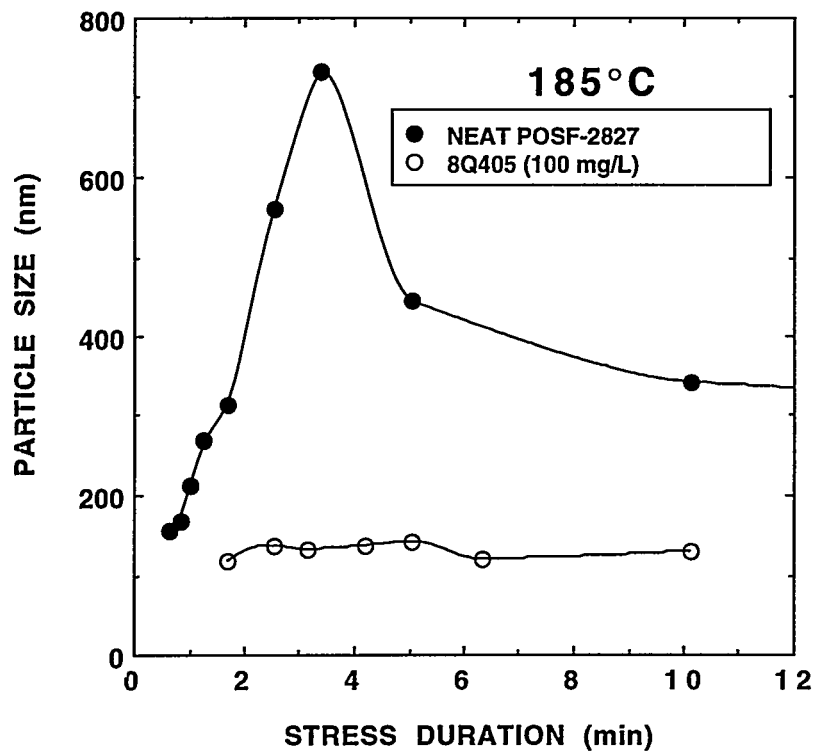


Figure 7. Particle Size of Insolubles as a Function of Stress Duration at 185°C.

