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DIVISION OF PETROLEUM CHEMISTRY, INC.
American Chemical Society

Chicago, IL
August 20-25, 1995

Volume 40, No. 4
August 1995

Symposium on Coke Formation and Mitigation
Presented before The Division of Petroleum Chemistry, Inc.
210th National Meeting, American Chemical Society
Chicago, IL, August 20-25, 1995

Deposition from High Temperature Jet Fuels

Tim Edwards
USAF Wright Laboratory
WL/POSF Bldg 490
1790 Loop Rd N
Wright Patterson AFB, OH 45433-7103

Joseph V. Atria
Fuel Science Program
209 Academic Projects Building
Pennsylvania State University
University Park, PA 16802

INTRODUCTION

The fuel is the main coolant on board aircraft. The fuel is used to cool the avionics, the environmental control system, the hydraulic system, the lubricating oil, and other systems. Current aircraft typically stress the fuel to a maximum of ~160°C (325°F) prior to combustion. Some applications are being examined where the fuel would be heated to temperatures on the order of 540°C (1000°F) or higher. The thermal stability of the fuel, as characterized by surface and filter deposition, is a serious constraint on the operation of such aircraft. This paper discusses recent work at the Air Force Wright Laboratory on mitigating thermal stability problems, where a single-tube heat exchanger is used to assess thermal-oxidative and pyrolytic deposition from high temperature jet fuels.

Two types of deposition are found in situations where jet fuels are thermally stressed to high temperatures (~650°C/1200°F) in flowing systems— thermal-oxidative and pyrolytic. Four mitigation methods are evaluated for the two types of deposition: fuel processing, fuel deoxygenation, additives, and surface treatment. In general, thermal-oxidative deposition is most amenable to control by fuel processing, additives, and (of course) fuel deoxygenation. Pyrolytic deposition is much less amenable to control, although additives and surface treatments show positive results under some conditions.

EXPERIMENTAL

The apparatus consists primarily of a fuel tank, a pump, and a tube running through a furnace (2-4). The fuel is air- or nitrogen-sparged to assure saturation of the fuel (~70 ppm O_2 (w/w) in air saturated fuel (0.0018 molar)). The flow system is initially purged with nitrogen prior to fuel introduction to remove any air present. The fuel is pumped through the system with a SSI high pressure liquid chromatography pump. An initial 0.45 μm filter is used to remove any particulates present from fuel handling and to maintain a consistent filtration level between fuels. The test section consists of a 122 cm (48 inch) long, 3.2 mm (0.125 in.) OD, 1.4 mm (0.055 in.) ID 316 stainless steel tube passing through a Lindbergh laboratory furnace with a 91.5 cm (36 inch) actively heated zone. The furnace temperature was typically ~1050°C for these tests. The tube is rinsed with acetone prior to testing to remove any residual hydrocarbons. After exiting from the furnace, the products are cooled to room temperature and filtered before passing through a back pressure valve which regulates the system pressure. A 2 μm stainless steel filter is used upstream of the back-pressure valve. This filter is analyzed for deposition by carbon burnoff as are tube sections as described below. The filter deposits are not reported; in general, the filter deposits are of the same magnitude and follow the same trend as the pyrolytic deposits in the tube, except in cases where the heat exchanger (cooler) tube downstream of the hot section plugged. These cases will be pointed out in the text. After a test, the stainless steel test section is cut into 5 cm (2 in.) sections, washed with hexane, vacuum dried at ~120°C for 2 hours, and analyzed by carbon burnoff (Leco surface carbon analyzer) to measure carbon deposition. The deposition can be converted to ppm by dividing the carbon deposit weight (μg) by the total amount of fuel used in the test (g). The total amount of fuel is calculated as flow rate X test time X fuel density (typically ~0.8 g/cc for jet fuels).

Table 1.
Deposition Results. Conditions: 33mL/min. 7 hrs. 1000 psig BzOH and THQ Additives Added at 500 ppm, 8Q405 @ 100 mg/L Values in Parentheses are Estimated.

Test #	Fuel ID# / saturated with	Additives added at WPAFB	Max. wall T, °C	Fuel outlet T, °C	Vol. % crack -ing	Total thermal oxid. surf. dep., ppm	Max. surface pyrolytic dep., ppm
9/93-17	JP-7 2818/N_2	none	758	(663)	23	--	0.20
8/93-10	JP-7 2818/air	none	721	(625)	6	0.02	0.06
8/93-7	decalin/air	none	730	(655)	6	0.05	1.78
2/95-6	Jet A 2827/air	none	749	671	24	0.36	1.71
3/95-4	Jet A 2827/air	none	738	666	29	0.37	1.57
3/95-7	JPTS 2976/air	none	733	669	23	0.05	0.06
1/95-6	Jet A 3084/air	none	738	650	24	0.58	0.16
2/95-5	Jet A 3084/air	none	741	652	18	1.04	0.08
2/95-1	Jet A 3084/N_2	none	738	655	28	--	0.15
3/95-8	Jet A 3084/N_2	none	733	669	24	--	0.10
3/95-9	Jet A 3084/N_2	BzOH	733	664	24	--	0.10
2/95-15	Jet A 3084/air	BzOH	727	685	27	0.81	0.19
2/95-4	Jet A 3084/air	THQ	738	655	18	0.84	0.09
3/95-1	Jet A 3084/air	8Q405	730	677	28	0.09	1.18
2/95-16	Jet A 3084/air	BzOH/8Q405	727	677	24	0.12	1.21
3/95-2	Jet A 3084/air	THQ/8Q405	(744)	677	24	0.13	1.63
1/95-5	Jet A 2926/air	none	738	650	23	0.26	0.13
2/95-12	Jet A 2926/air	none	702	666	18	0.25	0.07
2/95-9	Jet A 2926/N_2	none	(733)	660	18	--	0.06
2/95-7	Jet A 2926/air	THQ	733	650	20	0.48	0.07
2/95-8	Jet A 2926/N_2	THQ	(733)	660	18	--	0.04
2/95-10	Jet A 2926/air	BzOH	708	660	18	0.33	0.08
2/95-11	Jet A 2926/air	BzOH/8Q405	738	663	18	0.09	3.26
3/95-5	Jet A 3119/air	none	727	671	29	0.97	0.20
3/95-6	Jet A 3119/air	JP-8 pkg	733	677	30	0.47	0.22

The tube wall temperature distribution is measured by K-type thermocouples spot-welded to the outside of the tube. The fuel temperature at the furnace outlet is measured by a thermocouple inserted into the flow. The design is different from earlier reports (4), so the fuel outlet temperatures are not comparable. Pressure is measured between the filter and the back pressure valve and also at the pump. The fuel cooler is mechanically cleaned and rinsed with acetone between tests. Typical test results are shown in Figure 1. The baseline conditions are: flow rate - 33 mL/min; pressure - 69 atm; and run duration - 7 hrs. This baseline was selected to yield similar thermal-oxidative and pyrolytic deposit thicknesses. The separation between oxidative and pyrolytic deposition is clear for the air-saturated fuels. The flow in the pyrolytic region of the tube is calculated to be turbulent (Re~15000 at a fuel temperature of ~ 650°C (1200°F)), with a fuel residence time in the tube of ~2 seconds. These quantities are calculated with temperature-dependent fuel properties.

A three-way valve downstream of the back pressure valve allows the product flow to be diverted to a sampling system where the liquid products are analyzed (off-line) at ambient conditions. Light gas formation (cracking) is calculated as the volume % of the liquid feed that has turned into gas (C_1-C_4), e.g., the amount of cracking is calculated by measuring the difference in fuel flow before and after heating, vol. % cracking = 100 X (vol. fuel fed - vol. fuel collected)/volume fuel fed. Fuel samples were first solid-phase-extracted (SPE) by pushing 10 mL of sample through a silica-gel (SiOH)-filled tube and then extracting the polar species in 1 mL of methanol. Solid phase extraction was conducted to both concentrate the polar additive species which are at part-per-million levels and extract them from the complex fuel mixture to help detect the additives by gas chromatography/mass spectrometry (GC/MS). GC/MS was conducted on a Hewlett Packard 5890 series GC/MS using a scanning ion method (SIMS), 1 μL injection, and a split of 50. Results were quantified by comparing peak integrated areas to calibration curves of the individual species (additives tetrahydroquinoline and benzyl alcohol and reaction products quinoline and benzaldehyde) which were prepared using the same GC/MS parameters.

RESULTS AND DISCUSSION

The four types of deposition mitigation are described below for both thermal-oxidative and pyrolytic deposition. The degree of thermal stress of the fuel is characterized by fuel outlet temperature, maximum wall temperature, and volume % of fuel cracked to gas. It was difficult to reproduce all three variables from test to test. The thermocouple wires were exposed to 1050°C, which lead to extensive oxidation and possible errors. The fuel outlet temperature was measured by a thermocouple inserted into the flow. This thermocouple was exposed to significant fouling and to the high furnace temperatures, which led to regular failures during disassembly and cleaning. The cracking measurement appeared to be the most consistent measure of thermal stress to the fuel. Thus, the comparisons in the following sections will generally be made between tests of similar extent of cracking. Results are listed in Table 1. Decalin is significantly more stable than jet fuels to gas formation under these conditions (4), and is compared to fuel tests with similar temperatures, rather than cracking levels.

Fuel Processing

Several fuels and pure hydrocarbons have been tested under similar conditions. The results are shown in Table 1. The increased thermal-oxidative stability (and cost!) for JP-7 and pure hydrocarbons is well known (1-3). JP-7 is a highly processed fuel similar in character to Exxsol D80, with anti-icing and lubricity additives. The thermal oxidative stability of the various jet fuels has been discussed in other papers (2,3). The pyrolytic deposition levels for the various fuels have not been measured before in a flowing test. Table 1 includes deposition data for JP-7 and decalin from (4). The results contrast with those found in batch reactors (5), where decalin was found to be more stable (in terms of solid formation) than paraffinic jet fuels like JP-7 and Jet A under pyrolytic conditions. Interestingly, the pyrolytic deposition from the various fuels is fairly similar, and is significantly less than that from decalin (air-saturated decalin ~1.5 ppm, N_2-saturated decalin ~10 ppm (4)). This may be due to some components of the fuels acting as hydrogen donors (see additive section below). A typical Jet A might contain 40% paraffins/isoparaffins, 40% naphthenes, and 20% aromatics.

The deposition behavior as a function of cracking level is shown in Figure 2. The Jet A fuels studied were generally similar in deposition level, with the exception of Jet A 2827, which showed at large 1.5 ppm deposition peak at about 90 cm along the tube. A similar plot could be made as a function of maximum wall temperature or fuel outlet temperature, although the scatter in the data is larger. It was originally planned to study the pyrolytic deposition as function of fuel residence time (flow rate) and temperature. However, lower flow rates produced extensive plugging of the heat exchanger (cooler) downstream of the hot section. Often, the 4.6 mm ID cooler tube plugged in two hours. Similar plugging was seen for cracking levels above 30%. In general, lower flow rates produced a higher surface deposition level for a given extent of cracking. For example, Jet A 3084 produced a pyrolytic surface deposition of 5 ppm at 27% cracking at a flow rate of 12 mL/min.

Fuel Deoxygenation

It is well known that deoxygenation of fuel essentially eliminates thermal-oxidative deposition (1,6). In earlier tests at WL, it was found that deoxygenation of fuel could dramatically affect pyrolytic deposition also (4). For decalin, it was found that fuel deoxygenation increased pyrolytic deposition by ~10X. Apparently, the fuel oxidation products were acting in a manner to minimize pyrolytic deposition (apparently by hydrogen donation—see below). The effect was smaller for multi-component (paraffinic) fuels such as JP-7, and Exxsol D80 (4). In the current tests with various Jet A fuels, it was found that fuel deoxygenation had a much smaller impact on pyrolytic deposition than was seen for decalin. The results are listed in Table 1 and can be seen in Figure 2. Interestingly, deoxygenated Jet A 2926 showed complete elimination of all deposition below pyrolysis, while deoxygenated Jet A 3084 showed deposition appearing at an intermediate position between the thermal-oxidative and pyrolytic deposition (as shown in Figure 1). Sub-pyrolytic deposition in deoxygenated fuels apparently driven by sulfur compounds was observed by Taylor (6).

Additives

Several additives have been found by Penn State researchers that reduce pyrolytic deposition in batch

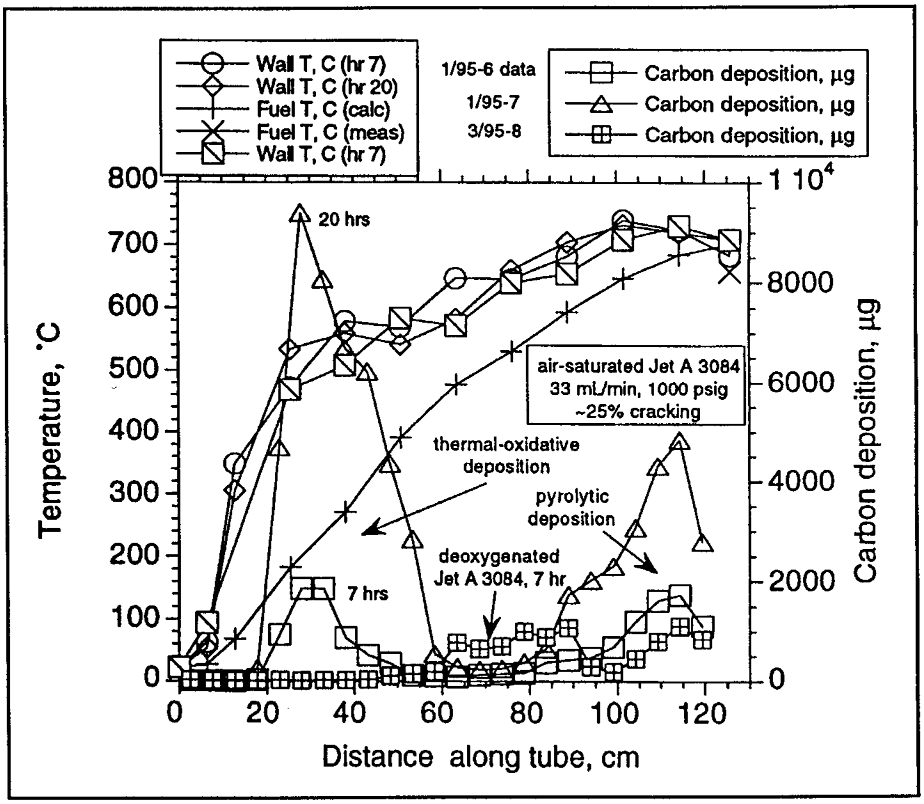

Figure 1. Typical test results. Air-saturated Jet A 3084, 33 mL/min., 7 hrs., 69 atm.

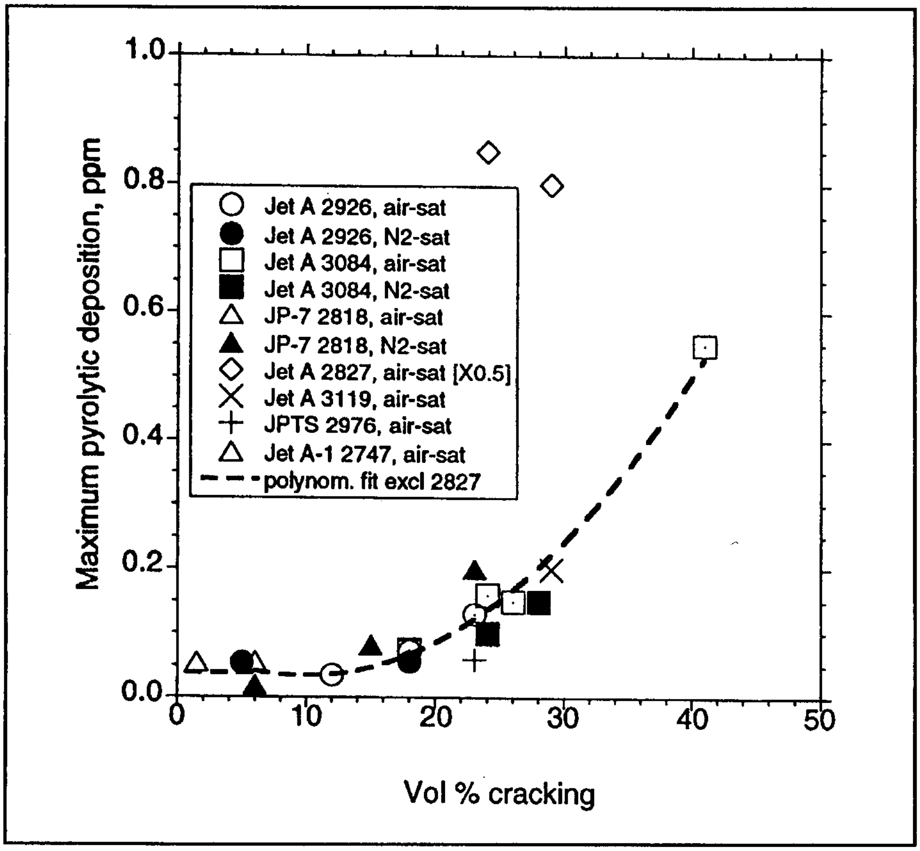

Figure 2. Maximum pyrolytic deposition as a function of cracking extent for various jet fuels.

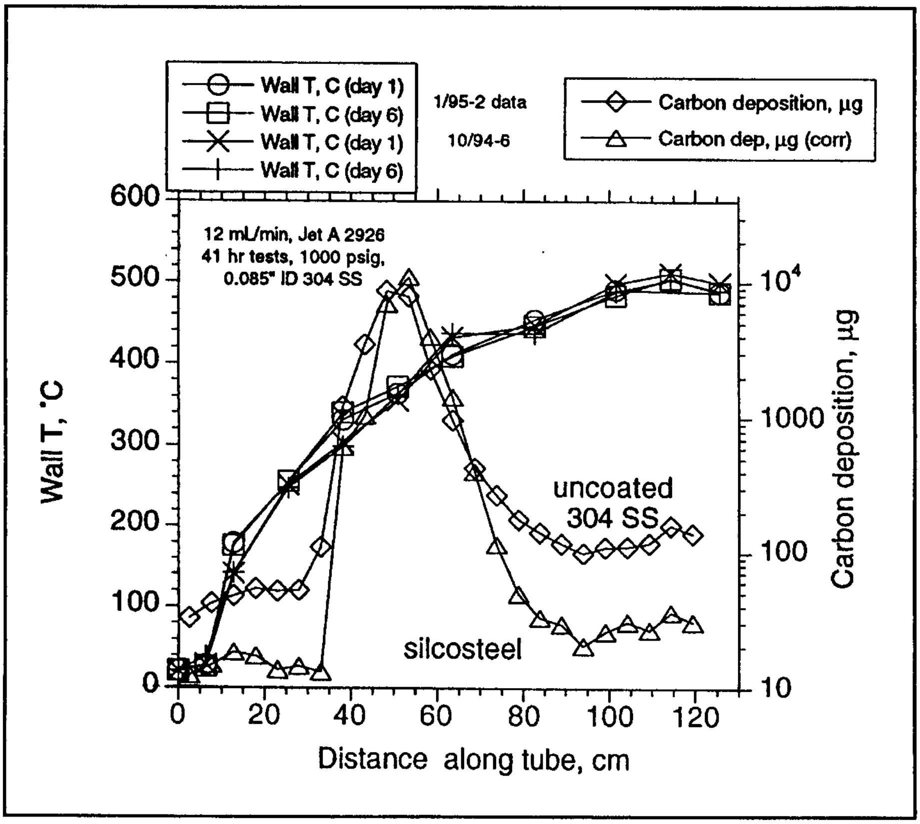

Figure 3. Deposition results with coated and uncoated tubes. 12 mL/min., 41 hrs., fuel outlet T~480°C (900°F), 2.2 mm (0.085") ID 304 SS tubing.

reactors (8,9), notable benzyl alcohol (BzOH), tetrahydroquinoline (THQ), and tetralin (THN). The additives apparently act as hydrogen donors, capping reactive radicals that might otherwise lead to solid formation. The additives were found to be effective in fuels at the 5% level. For comparison, Jet A 2926 in a batch reactor at 450°C for 4 hours yields ~25% gas and 2% solids (5). As shown in Figure 2, these flowing tests achieve 25% gas formation in ~2 seconds at ~650°C maximum fuel temperature. The resulting surface and filter depositions are on the order of 0.1 ppm. For reference, a pyrolytic deposition rate of 10 ppm will plug the tubes used in these tests in a matter of hours. In earlier tests of decalin and JP-7, it was found that 200 ppm benzyl alcohol dramatically reduced the pyrolytic deposition from deoxygenated decalin (4). A significant reduction in deposition from deoxygenated Exxsol D80 was also seen with benzyl alcohol and tetralin, although JP-7 was relatively unaffected. Note that typical jet fuel additives are added on the 100 ppm level, rather than the 1% (10000 ppm) level. Wright Laboratory is engaged in a program to develop dispersant/detergent-type additives to reduce thermal-oxidative deposition from jet fuels (7). One of the best candidates found thus far is a proprietary Betz dispersant, 8Q405. In earlier tests at somewhat lower temperatures (900-1000°F), it was found that 8Q405 at 100 mg/L significantly reduced the thermal-oxidative deposition rates from air-saturated jet fuels and did not affect the pyrolytic stability of the fuels (3, 7).

The deposition results for the various additives in Jet A fuels are shown in Table 1. It appears that THQ and BzOH at a concentration of 500 ppm produce small decreases (if any) in pyrolytic deposition under these conditions in Jet A fuels. Often, an increase in thermal oxidative deposition is seen. THQ and BzOH were tested for thermal-oxidative stability at 140°C in a batch reactor equipped with a quartz crystal microbalance

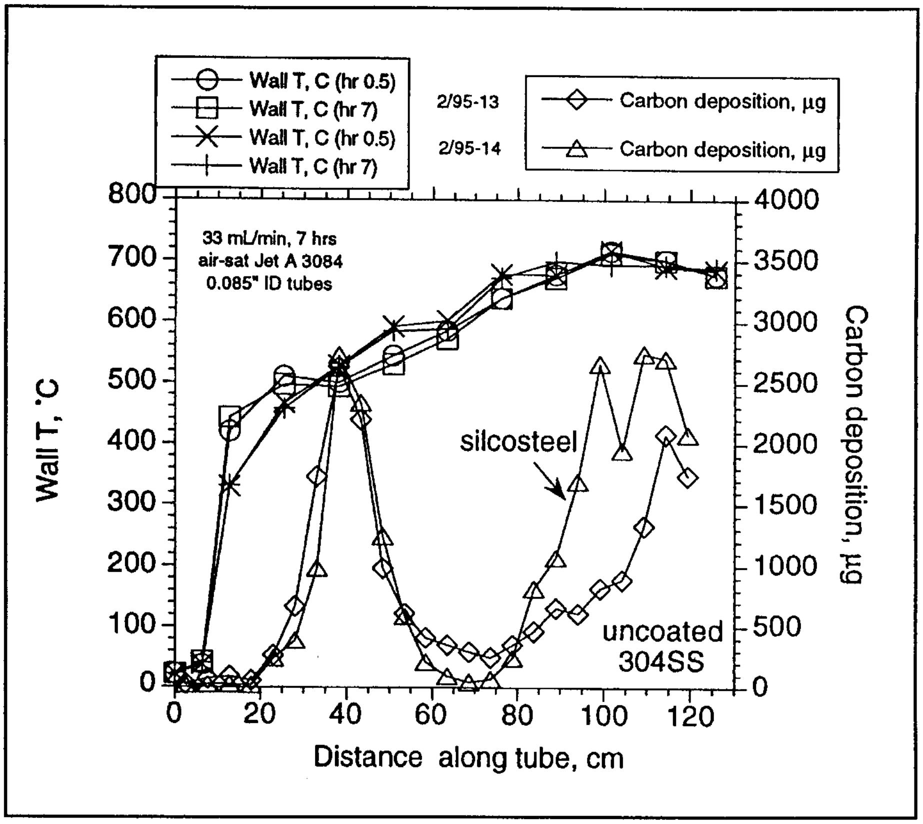

Figure 4. Deposition results with coated and uncoated tubes. 33mL/min., 7 hrs., fuel outlet T~650°C (1200°F), 2.2 mm (0.085") ID 304 SS tubing.

(QCM) (11). In the QCM, THQ was found to increase deposits, while BzOH reduced thermal-oxidative deposits. Thus, there appear to be some interactions between the THQ and BzOH and the thermal oxidation reactions in the fuels. The reduction in pyrolytic deposition with the THQ and BzOH is much smaller than that seen for decalin in earlier work (4). It is possible that the Jet A fuels have components (hydroaromatics) capable of hydrogen donation at the higher temperatures seen in the flow reactor tests, as compared to the batch reactor tests. Note also that the Betz 8Q405 shows thermal instability leading to higher pyrolytic deposition at the 650°C (1200°F) fuel temperatures of this work. The effectiveness of the 8Q405 additive in reducing the (lower temperature) thermal-oxidative deposition is apparent from the Table. The specification additive package for JP-8 (icing inhibitor, corrosion inhibitor, and static dissipator) reduced the thermal-oxidative deposition from Jet A 3119 and did not affect the pyrolytic deposition at 650 {C (1200 {F).

Fuel products were analyzed to determine the amount of additives remaining and converted to their hydrogen deficient species upon reaction with the fuel at high temperatures. After solid phase extraction, the only major peaks detected by GC/MS were of the additives and their byproducts. In the case of the Jet A 2926 doped with THQ under air-saturation conditions, results showed the stressed fuel contained equal amounts of THQ and quinoline. The THQ-to-quinoline ratio increased slightly to 1.5 to 1 in the nitrogen saturation experiment with the same fuel. In the benzyl alcohol treated fuels, less reaction was seen. In the case of Jet A 2926, the benzyl alcohol-to-benzaldehyde ratio was 12 to 1. This ratio decreased slightly to 11:1 in air-saturated Jet A 3084 and 10:1 in N_2-saturated Jet A 3084. When 100 mg/L of the thermal-oxidative stability additive 8Q405 was also added to Jet A 2926 doped with benzyl alcohol the benzyl alcohol:benzaldehyde ratio increased to 15:1. These results differ from batch reactor results done at Penn State, where THQ was found to remain in higher amounts than benzyl alcohol after stressing in dodecane 450°C. Again, however, these flow reactor tests are performed at much higher temperatures for much shorter residence times.

Surface Treatment

An inert, vapor-deposited coating was tested to examine the effect upon deposition. The coating tested was "Silcosteel", from Restek, Inc. This coating was also tested by Jones (10), who found that the coating was more inert than a bare stainless steel tube, which was found to catalyze dissolved-oxygen-consuming reactions. The activity of the Silcosteel-coated tubes for these reactions was similar to that of tube with a layer of deposit on the surface (fouled tubes). The Silcosteel tubes have been tested under a variety of conditions in this work. It was found that the coating increased the initial period before the onset of deposition (the induction time), but once a deposit layer was formed, the coated and uncoated tubes were, not surprisingly, very similar in deposition behavior. The coating apparently resists the initial deposition on the surface, but only for a relatively short time. For example, the results of two 41 hr tests at 12 mL/min are shown in Figure 3. In the area of heavy deposition, the two surfaces have very similar deposition; in areas of light deposition, the coated tube has noticeably less deposition. Note that the deposition scale is logarithmic. In Figure 4, the results of two tests at higher temperatures are shown. Again, the coating shows results very similar to the uncoated tubes in areas of heavy deposition.

CONCLUSIONS

Several Jet A fuels were heated to ~650°C in a single-tube heat exchanger to examine the impacts of fuel processing, deoxygenation, additives, and surface coatings on thermal-oxidative and pyrolytic surface deposition. It was found that fuel processing and deoxygenation could significantly reduce thermal-oxidative deposition, but had little effect on pyrolytic deposition from Jet A fuels. Additives developed from batch reactor studies to suppress pyrolytic deposition were relatively ineffective in Jet A fuels, in contrast to significant reductions seen in decalin and Exxsol D80 in earlier tests. An inert surface coating resisted the initial deposition layer on surfaces, but was ineffective in areas of heavy deposition.

ACKNOWLEDGMENTS

This work is supported by the Air Force Office of Scientific Research (AFOSR). Julian Tishkoff is the AFOSR Program Manager.

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Symposium on Coke Formation and Mitigation
Presented before the Division of Petroleum Chemistry, Inc.
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Fouling of Stainless Steel and Silcosteel Surfaces During Aviation-Fuel Autoxidation

E. Grant Jones and Walter J. Balster
Systems Research Laboratories, Inc.
A Division of Space Industries International, Inc.
2800 Indian Ripple Road
Dayton, OH 45440-3696

Wayne A. Rubey
University of Dayton Research Institute
Environmental Sciences Group
KL102, 300 College Park
Dayton, OH 45469-0132

INTRODUCTION

The fouling of surfaces from carbonaceous deposition in aircraft fuel lines is a serious problem which results in costly downtime for the cleaning or replacement of critical components. Most of the deposition occurs in hot sections such as heat exchangers; however, all regions experience some deposition. This problem is predicted to be more serious for future aircraft where greater heat loads will require dissipation by the fuel (1). Fouling arises mainly from insolubles which are formed in temperature-dependent autoxidation reactions involving minor fuel components and oxygen dissolved in the fuel. Some fuels containing heteroatoms such as sulfur or nitrogen have a propensity for fouling surfaces at elevated temperatures (2). Possible solutions to this problem that have been pursued include use of: 1) better quality fuels; 2) refining methods such as hydrotreatment to reduce heteroatom content; 3) engineering designs to reduce the temperature loads from hot components; 4) individual additives or fuel additive packages; consisting of antioxidants, dispersants, detergents, and metal deactivators, and, 5) surface-treated tubing that may delay the initial deposition processes or reduce the quantity of deposits. The goal of the current study was to investigate possible mitigation of initial surface fouling through the use of surface treatment. When deposits cover all of the fuel-exposed surfaces, any initial advantage of passivated tubing will be negated; however, depending on the temperature and total exposure time, initial reductions may significantly reduce maintenance.

Based on dynamic isothermal experiments, we have reported that the rate of autoxidation in the Jet-A fuel POSF-2827 depends on the nature of nearby surfaces (3). Cleaned stainless-steel (304) surfaces were found to accelerate autoxidation; whereas when the same surfaces were heavily fouled by deposits, the result was slower autoxidation. It was argued that active surface sites on the stainless steel were blocked as the surface became fouled. These findings suggested that the use of tubing with surfaces passivated, not by deposits but by prior surface treatment with inert coatings, might offer significant benefits by slowing autoxidation reactions and, thereby, reducing surface fouling.

Recent studies which were performed using inverse chromatographic procedures (4, 5) have shown interesting results with respect to adsorptive behavior. With the use of a variety of sulfur- and nitrogen-containing organic substances (chemical probes), it has been demonstrated (5) that coated and inerted tubing provides much higher transport efficiency than conventional stainless-steel tubing. This same inerting technology has been applied to passivation of gaseous sample-collection devices (6) where non-interacting surfaces are required.

Glass-lined tubing, for example, which has been used for many years by chromatographers to achieve improved transport of trace chemicals was a potential candidate for consideration; however, Silcosteel which is a more robust tubing with passivated inner walls has recently been marketed by Restek Corporation for use in chromatography to reduce surface adsorption. This tubing, made to the same dimensions as commercial stainless-steel tubing, has an inert silica-treated inner surface covered with a monolayer of a specific stain-

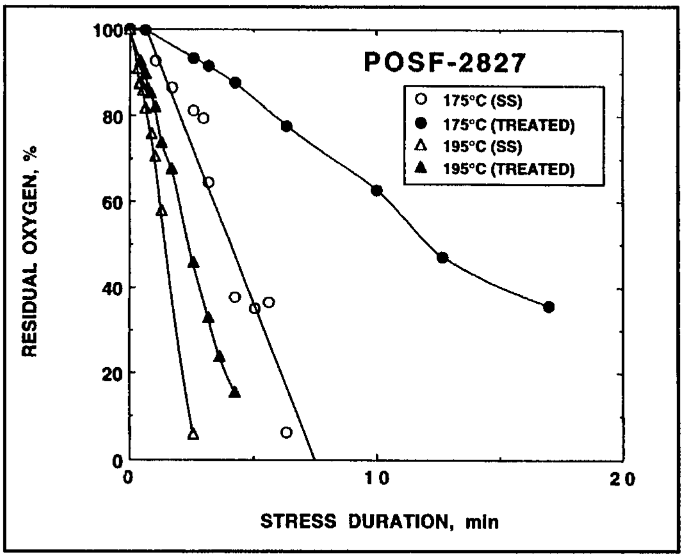

Figure 1. Plots of oxygen loss at 175°C and 185°C measured in stainless-steel and treated tubes.

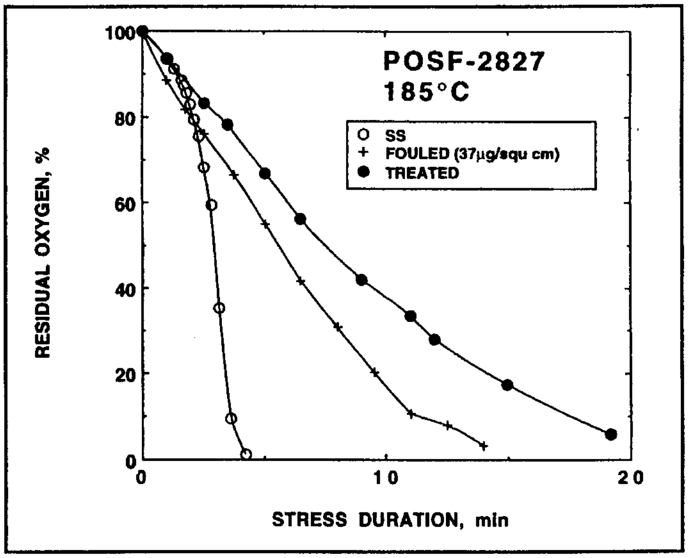

Figure 2. Plots of oxygen loss at 185°C measured in stainless-steel, fouled and treated tubes.

less-steel tubing with respect to surface fouling. Measurements of the rate of autoxidation, the rate of surface deposition, and the quantity of insolubles formed have been made during passage of POSF-2827 aviation fuel through each type of tubing clamped inside a single-pass heat exchanger. Results are reported for block temperatures of 155, 185, 255 and 300°C. Additives—in particular, dispersants—have been shown to reduce surface deposits in this fuel (7, 8). In order to investigate potential synergism from a combination of surface and fuel treatment, we have also compared deposition occurring at 185°C in each type of tubing for POSF-2827 fuel treated with the detergent 8Q405.

EXPERIMENTAL

A straight-run Jet-A fuel POSF-2827 which meets all aviation specifications was used for these tests. Experiments were conducted using Near-Isothermal Flowing Test Rig (NIFTR) single-pass heat exchanger. This rig has been described in detail elsewhere (9) and is reviewed here only briefly. Fuel (saturated with respect to air at room temperature) was pumped at a pressure of 2 MPa through 0.125-in O.D., 0.085-in I. D.. tubing tightly clamped in a 42-kg copper block maintained at reaction temperature. In-line filters (0.45- and 0.20-μm) capture bulk insolubles at the end of the heated section, and subsequent reaction occurred under isothermal conditions. Two separate experiments were conducted to monitor autoxidation using GC oxygen analysis (10) and surface deposition using carbon burnoff. In the first, oxygen dissolved in the fuel was monitored for fuel passage through a fixed-length (32-in) tube. Residence time time or reaction time was varied by changing the flow rate to provide profiles of residual dissolved oxygen (%) as a function of time. In the second, a fixed flow rate was used for test times ranging from 6 to 72 hr, after which the tubing was cut into 2-in. sections and the carbon measured using a LECO RC-412 surface-carbon analyzer. For isothermal reaction conditions, the distance along the heated tube could be converted to reaction time, and profiles of deposition rate as a function of stress duration could be obtained. Since the carbon measurements were made after completion of each test, the calculated deposition rate represents an average over the entire test time.

The two types of experiments (autoxidation and deposition) were conducted under identical conditions using stainless-steel (304) tubing and Silcosteel tubing, and results obtained for reaction occurring in each type of tubing were directly compared. In most cases reaction was taken to 100% conversion of dissolved oxygen, leading to an inherent normalization for quantification of insolubles. Finally, reaction in each type of tubing was studied using POSF-2827 fuel treated with the dispersant fuel additive 8Q405 (Betz Corp., 100 mg/L).

RESULTS AND DISCUSSION

Autoxidation

Figure 1 shows the dissolved oxygen measured in POSF-2827 fuel as a function of stress time at 175 and 195°C. The rate of autoxidation is significantly reduced (by a factor of two or three) when reaction occurs in the treated rather than the stainless-steel tubing. The explanation for this effect is as follows. The steel surface offers active sites to promote autoxidation. These sites are eliminated by the passivating effects afforded by the Silcosteel process. This observation is consistent with our earlier reports of reduced autoxidation rates measured in tubing that had previously been passivated by deposits (see, for example, Figure 2 which shows results at the intermediate temperature, 185°C, using 1) stainless-steel tubing, 2) Sil-

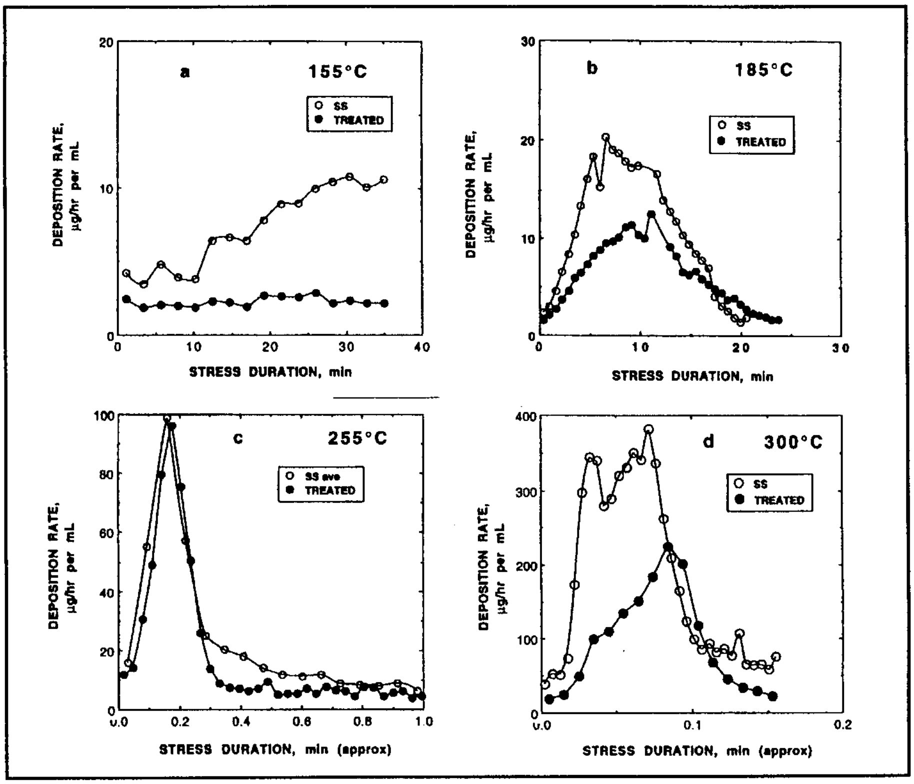

Figure 3. Deposition rate profiles; a) 155°C (48 hr, 0.07 mL/min), b) 185°C (72 hr, 0.25 mL/min), c) 225°C (18 hr, 2.5 mL/min), and d) 300°C (6 hr, 16 mL/min) for stainless-steel and treated tubes.

costeel-treated tubing, and 3) stainless-steel tubing fouled approximately uniformly by carbonaceous deposits (37 µg/cm^2) from the current fuel). The order of surface activity for autoxidation is SS > Deposit-Fouled > Silcosteel. Reduced autoxidation is achieved through the use of passivated tubes. The magnitude of this effect will be both temperature- and conversion-dependent. Based on autoxidation changes alone, we would expect reduced deposition rates and delays (stress duration) in overall deposition on the treated tubes.

Deposition

The results of a series of deposition experiments are given in Figure 3. The reaction conditions for the two types of tubing were identical. The reaction at 155°C and 185°C was isothermal as a result of the slow flow rate and low block temperatures. However, the high-temperature runs required faster flow rates, resulting in a significant departure from isothermal conditions. Thus, much of the deposition occurs at temperatures below the block setting, and stress times are approximate (upper limit). With the exception of the reaction occurring at 255°C, the deposition rates are significantly lower on the treated tubes. The location of the maximum occurs at longer stress times. The measured rates are averages over the entire test time which varies from 6 to 72 hrs. As the test time is extended and more deposits accrue, eventually the deposition-rate profiles for the different types of tubing should become equal, representing the profile for deposition on a heavily fouled tube. This test time may be short at higher temperatures because of more total fuel being passed through the system and reaction rates being faster, but evidently at 155°C the amount of deposition on the treated tube is barely detectable; thus, very long test-time averages will be necessary to achieve sufficient surface coverage to mask completely the original treated surface.

Quantification

The quantity of bulk insolubles (filter) and surface insolubles (integral under deposition profiles) and their sum are shown in histogram form (Figure 4). The quantity of surface deposits is significantly reduced on the treated tubes. One would not expect the quantity of bulk insolubles to be reduced by surface treatment unless the oxygen conversion were less in the treated tube. This may be the case at 155°C. The quantity of bulk insolubles measured at the two highest temperatures is unaffected by treated tubing. We have no explanation for the reduction at 185°C, except that slower autoxidation may produce smaller particles which are able to pass through the in-line filters.

Dispersant Additive

Figure 5 shows changes in reaction at 185°C introduced by the dispersant additive. In this 18-hr test, significant reductions in surface deposition rates and total surface carbon are observed. For reaction in steel tubes, compare the reduction in total surface carbon from 3.3 to 2.6 µg/mL using the additive. For reaction in treated tubes, compare the reduction in total surface carbon from 2.5 to 1.2 µg/mL using the additive. Reductions in surface and bulk insolubles have been reported with the use of 8Q405 in POSF-2827 fuel (7, 8), but synergism appears to be present in the combination of dispersant-treated fuel and treated tubes. The origin of this effect does not appear to be related to autoxidation; we have studied autoxidation in treated fuel and found no significant differences in the rates measured in steel and those measured in treated tubes. Rather, this effect may be related to solubility, particle size, and adherence of insolubles to different types of surfaces. For example, 8Q405 has

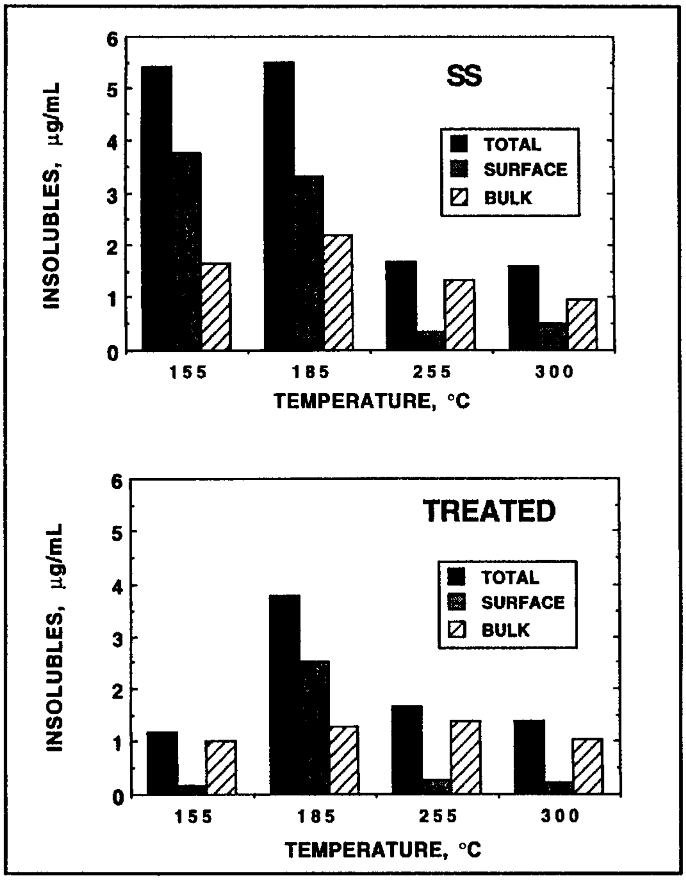

Figure 4. Insolubles formed in reaction in stainless-steel and treated tubes.

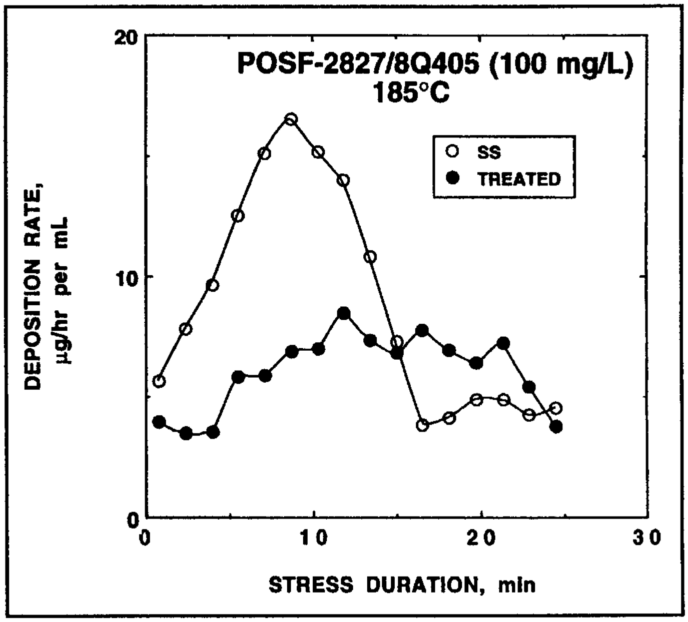

Figure 5. Deposition-rate profiles (185°C, additized fuel, 18 hr, 0.25 mL/min) for reaction in stainless-steel and treated tubes.

been found to reduce the diameter of bulk insolubles formed at 185°C (8).

The strength of adherence of insolubles to Silcosteel and stainless-steel surfaces is not clear from the current laminar flow tests. However, the improvement observed with the dispersant additive suggests that: 1) a combination detergent/dispersant fuel additive possessing better surface cleaning properties, and 2) periodic abrasive cleaning may offer additional improvement if the initial surface bonding to Silcosteel surfaces is weak. These areas are currently being studied.

CONCLUSIONS

The rates of autoxidation and deposition occurring during passage of aviation fuel through heated tubes are found to depend strongly on the nature of the surface layer. As compared to reaction in stainless-steel tubes, reaction in tubes treated with the Silcosteel process is characterized by a reduced rate of autoxidation which, in turn, causes a reduced deposition rate. Once a significant amount of surface deposit has accrued, the inner walls cannot be distinguished and rates will be comparable. Thus, advantages in the use of treated tubing will be most significant during the initial deposition processes. Depending on the surface temperature and region of the aviation fuel lines, periodic replacement with treated tubes may be cost effective. Servocontrols and nozzles which have tight tolerances and which are particularly sensitive to minimal surface fouling would be ideal candidates for surface treatment. The introduction of a fuel additive (dispersant) coupled with surface treatment has been shown to offer additional mitigation of surface fouling.

ACKNOWLEDGMENTS

This work was supported by Wright Laboratory, Aero Propulsion and Power Directorate, Wright-Patterson Air Force Base, OH, under USAF Contract Nos. F33615-90-C-2033 and F33615-92-C-2207. The authors would like to thank Mr. Tim Gootee for performing the surface-carbon analyses and Mrs. M. Whitaker for lending editorial assistance.

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