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NASA CR-165165

(NASA-CR-165165)EXPERIMENTAL STUDY OF THEN81-12255STABILITY OF AIRCRAFT FUELS AT ELEVATEDTEMPERATURES (United Technologies Corp.)Unclass31 p HC A03/MF A01CSCL 21DUnclassG3/2829383C3/28

NASA CONTRACTOR REPORT

NASA

EXPERIMENTAL STUDY OF THE STABILITY OF AIRCRAFT FUELS AT ELEVATED TEMPERATURES.

By Alexander Vranos Pierre J. Marteney



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Prepared by UNITED TECHNOLOGIES RESEARCH CENTER East Hartford, CT 06108

For NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, LEWIS RESEARCH CENTER CLEVELAND, OHIO DECEMBER 1980 ERRATA SHEET FOR REPORT NASA CR-165165

(a) For reports missing Page 7, insert Page 7 (enclosed).

(b) Substitute Fig. 4 (enclosed) for Fig. 4.

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1. Report No. CR-165165	3, Recipient's Catalog No.		
4. Title and Subtitle		5. Report Date	
EXPERIMENTAL STUDY OF THE STA	BILITY OF AIRCRAFT FUELS		
AT ELEVATED TEMPERATURES	6. Performing Organization Code		
7. Author(s)	8. Performing Organization Report No. R80-954440-17		
		10. Work Unit No.	
9. Performing Organization Name and Addre	SS Contraction of the second		
United Technologies Research East Hartford, Conn. 06108	Center	11, Contract or Grant No, NAS3-21593	
		13 Type of Benort and Period Covered	
2. Sponsoring Agency Name and Address		Contractor Report	
National Aeronautics and Space Washington, DC 20546	14. Sponsoring Agency Code		
Project Manager, Stephen M. (NASA Lewis Research Center, (ohen, Cleveland, Ohio 44135		
6. Abstract		<u></u>	
	ABSTRACT		
An experimental study of aircraft gas turbine fuel sys Jet A is an aircraft gas turb the properties of future turb tion), which, under NASA spon	E fuel stability was conducted in stem. Two fuels were tested: Je- bine fuel currently in wide use. bine fuels, particularly ERBS (Ex- sorship, was considered as a poss	an apparatus which simulated an t A and Number 2 Home Heating oil. No. 2 HH was selected to represent perimental Reference Broad Specifica- ible next-generation fuel.	
Tests were conducted wi (including preheating and de and 672K (300 F and 750 F) a was determined at four equal were collected for infrared	th varying fuel flow rates, delive oxygenation). Simulator wall tem t fuel flows of 0.022 to 0.22 Kg/ ly-spaced locations along the len analysis.	ery pressures and fuel pretreatments peratures were varied between 422K sec (2.5 to 25 gal/hr). Coking rate gth of the simulator. Fuel samples	
The dependence of cokin activation energy of 9 to 10 surface temperature affect t	g rate in Jet A may be correlated kcal/mole, although the results he rate of decomposition. As a	with surface temperature via an indicate that both bulk fluid and consequence, flow rate, which contro	

The coking rate data for No. 2 HH oil are very highly temperature dependent above approximately 533K (500 F). This suggests that bulk phase reactions can become controlling in the formation of coke.

position reactions are initiated on the surface and continue in the bulk fluid.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Fuels, Turbine Thermal stability	Unclassified-Unlimited
Coking	
19. Security Classif. (of this report) 20. Security Classif. (Unclassified Unclassified Unclassified	of this page) 21. No. of Pages 22. Price* \$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22161

ABSTRACT (Cont'd)

The infrared spectra of as-received fuels are similar; differences in fuels are accentuated in deposit spectra, with a greater fraction of aromatics and oxygenerates found in No. 2 HH oil. Deoxygentation of fuel strongly limits coking rate and eleminates the oxygenate peaks in the deposit spectra. Preheating and holding of either fuel does not lead to increased deposition, suggesting that deposit precursors are removed during storage.

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Report CR-165165

Experimental Study of the Stability of Aircraft Fuels at Elevated Temperatures

Contractor Report

Alexander Vranos and Pierre J. Marteney

United Technologies Reserach Center East Hartford, CT 06108

Work Performed For

NASA-Lewis Research Center Cleveland, Ohio 44135

Under Contract NAS3-21593

Stephen Cohen, Project Manager

Experimental Study of the Stability of Aircraft Fuels at Elevated Temperatures

INTRODUCTION

The diminishing supply of petroleum in the form of crude oil has brought about concern for the future source of distillate fuels such as those used in gas turbines, and particularly those suitable for aircraft gas turbines. Many factors are involved in the specification of an aircraft turbine fuel, and any proposed departure from current specification must be preceded by a thorough study of the impact caused by change.

New blends of turbine fuels might come from revised refinery techniques using crude oil, or might result from mixing of fractions from a variety of sources, including crude oil, shale-oil or coal-derived liquids. An estimate of a possible next-generation jet fuel was compiled under NASA sponsorship, and was given the name ERBS (Experimental Referee Broad Specification Fuel). Studies relating to the adoption of new fuels blends have been conducted both by NASA (Ref. 1) and by other organizations, principally under NASA sponsorship. These studies have focussed on the effect of future fuels on combustor life and engine performance. However, a second area of concern is the stability of fuel at the elevated temperatures found in manifolds and nozzles. While these are both of concern in current engines using Jet A or JP-series fuels, the problems may be magnified with future fuels because the stability of future fuels is expected to be lower.

Hydrocarbon turbine fuels share the characteristic of forming deposits at elevated temperatures. In future engines, thermal stability problems may increase because of staged fuel injection and higher fuel temperatures expected with higher compression rations. In addition to problems identified with fuel heating in manifolds and nozzles, the stability of current and alternate fuels must also be considered in future combustor designs. An important consideration in advanced engines is the reduction of pollutants. Two concepts are particularly attractive from the emissions standpoint. These are the vaporizing combustor and the catalytic combus-In both cases, elimination of fuel droplets by prevaporization of fuel elimitor. nates variations in stoichiometry and permits tailoring of fuel-air rations for maximum benefit. Performance could be reduced, however, if fuel decomposes on hot surfaces prior to combustion. Since future (alternate) fuels may have inherentlypooror thermal stability because of increased levels of certain aromatic and heterocompounds, this carries the penalty of greater susceptibility to coking and thermal decomposition. Taken together, the use of alternate fuels and substantially-modified fuel and combustion systems, including the use of wing tank heaters, will certainly lead to accelerated fouling of fuel system surfaces and will present a major

problem unless the effects of thermal stress are understood and fuel system temperatures are carefully controlled.

Some studies which have been conducted on the thermal stability of fuels under Navy and Air Force sponsorship have attempted to provide quantitative information on the effect of operating variables and composition on deposit formation. Because of the large number of interactions which can occur, many tests are needed to isolate individual effects. Therefore, a significant data base, useful for design purposes, is lacking. However, using the existing data and the detailed chemical studies of Bolshakov (Ref. 2) it is possible to postulate mechanisms for deposit formation and to understand why alternate fuels could be especially troublesome. It appears that jet fuels with increased levels of certain aromatic and heterocompound content may, for a number of reasons, undergo accelerated thermal decomposition. First, some aromatic and heterocompounds readily initiate or participate in free-radical chain reactions, accelerating the homogeneous chain decomposition of the fuel and the formation of insolubles through secondary reactions. For example, acenapthene, a naturally-occurring constituent of petroleum, found in abundance in diesel fuel (Ref. 3), and likely to be found at a significant level in ERBS fuel, is particularly harmful because of its ability to initiate freeradical reactions (Ref. 2). Secondly, high molecular weight, resonance-stabilized radicals are easily formed from many substituted, condensed-ring molecules. Since these stable radicals do not pyrolyze to any significant extent, they exist at high concentrations and undergo appreciable absorption on surfaces where they subsequently undergo dimerization or polymerization (Ref. 4). Substituted napthalenes, also likely to be found at increased levels in ERBS fuels, behave similarly. In addition, some polar aromatic compounds may undergo homogeneous condensation reactions or may combine with oxidation products, in both cases forming high molecular weight insoluble products.

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The results of recent studies conducted at UTRC using Jet A fuel provided important background for this program. The UTRC studies provided information on the effect of mass transfer and, at the same time, overcame one of the chief drawbacks of many past fuel stability experiments, namely, the presence of large spatial temperature gradients. These results were used in developing the expeirmental program.

The purpose of this program was to design, fabricate, and test a fuel system simulator which was used to evaluate the effect of operating variables on the thermal stability of two turbine fuels, and to conduct parametric studies with the same fuels. The simulator was scaled to be a reasonable representation of a present-day commercial aircraft fuel system.

EXPERIMENTAL SYSTEM

Test Apparatus

The design of the experimental system was based, in part, on previous programs conducted at UTRC. Studies of the stability of hydrocarbon fuels at UTRC have been conducted from both fundamental and applied standpoints. The approach taken in this program reflected the experience, background and insight gained in previous research.

The fuel system simulator built for this program contains many of the design features of the previous programs, including the fuel supply system, the method of heating, and the system controls. A schematic drawing of the system is shown in Fig. 1. The simulator consisted of a fuel supply system, nozzle/nozzle support assembly, and spray chamber. The fuel supply system included a large reservoir for fuel storage, a smaller tank for preliminary heating of fuel, and associated pumps. Fuel was drawn from the 4000 gallon tank by gear pump with delivery pressure of 6.80×10^5 Pa (100 psig), boosted to 4.08×10^6 Pa (600 psig) in a second gear pump, and delivered through a turbine flow meter to the rig at pressures of 6.80 x 10⁵ to 2.04 x 10⁶ Pa (100 to 300 psig). Tests were also conducted with fuel preheated to 422 K (300 F) and held at that temperature for periods of 1 hour or greater to simulate in-flight fuel tank heating. A fuel heating loop, including a steam heater and insulated storage tank, was located between the pumps and the test assembly. All plumbing lines and fittings were stainless steel. For selected experiments, the fuel was deoxygenated by sparging the smaller tank with nitrogen for 16 hours prior to test. Partial pressure of oxygen in the fuel was monitored with a Beckman "Field Lab" polarographic analyzer. The minimum detectable level for this analyzer is estimated to be approximately 0.5 ppm.

The test assembly, Fig. 2, was fabricated from copper-beryllium alloy. All surfaces were plated with gold and nickel to minimize catalytic effects on the walls. A photograph of the components of the test channel is given in Fig. 3; the four insert and mount assemblies are shown in stages of assembly.

A passage of 0.0028 m (0.11") x 0.032 m (1.25") x 0.61 m (24") was formed between the cover and base plates of the test assembly. Four specimen mounts were attached along the length of the cover. These held stainless steel discs which were used in determination of coking rates and characterization of deposits. Each disc weighed approximately 0.7 g. A maximum deposit weight of 2000 microgram was produced; typical weights were in the range of 100 to 200 μ g. Samples after test were rinsed in a mixture of hexane and benzene, then heated in vacuum to remove residual fuel. Preliminary tests were conducted to assure that neither the solution nor heating treatment removed deposits. In addition to furnishing the rate of coking, the test discs yielded information on the nature of deposits. A limited number of discs was examined by reflection, using Fourier Transform Infrared Spectroscopy (FTIR). This technique permits broad wavelength, high-resolution infrared spectroscopy, leaving the sample undisturbed. Major chemical classes such as aliphatics, aromatics, or alcohols and ketones are readily identified. Correlation of these groups with fuel type or treatment adds to an understanding of coking processes.

Each of the two main assemblies was heated by four 1500 watt Chromalox heaters. An independent power supply, regulated by a proportional unit, controlled each set of four heaters. A control thermocouple was mounted at the midpoint of each assembly. Seven thermocouples were placed along the length of each channel to determine uniformity of temperature. One thermocouple was positioned to touch the back face of each specimen disc.

Commercially available, pressure-atomizing nozzles (Hago type S-S, 60°) were used. An assortment of sizes was obtained. These nozzles are rated for No. 2 Home Heating Oil at 6.80 x 10^5 Pa (100 psig) and 294 K (70 F); under the conditions of this program, flows departed significantly from the ratings. The desired flows were obtained by varying the nozzle size. Factory-rated nozzles of 2.29 x 10^{-3} to 2.22 x 10^{-2} Kg/sec (2.5 to 25 gph) were used; true flows were determined using a calibrated turbine meter.

The nozzle spray was confined in a cylindrical chamber fitted with two 0.076 m (3") diameter optical windows for viewing. A small purge of nitrogen gas kept the windows free of overspray. Although the nozzles are designed for No. 2 fuel, it was observed that the spray pattern at 2.04 x 10^5 Pa (300 psig) was more uniform with Jet A. The spray of No. 2 fuel tended to be heavier on the axis. No change in spray pattern was observed over the course of any run, nor was plugging observed, even in an extended run of 10 hr using No. 2 fuel at 561 K (500 F).

Selection of Fuels

The underlying philosophy of NASA in determining the stability of aircraft fuels has been to make comparisons between current and projected fuels. Accordingly, the baseline tests were conducted with Jet A fuel, which is now in use.

The comparison of a possible fuel of the future was summarized by representatives of the producers and users of aircraft turbine fuels in a NASA workshop (Ref. 1). The fuel was given the name ERBS (Experimental Reference Broad-Specification Fuel). Significant changes between Jet A and ERBS occur because of probable changes in availability and refining demands of crude oils. Nominal specifications of the two fuels are given in Table I.

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The most substantial differences between Jet A and ERBS are the increased aromatic and napthalene contents. The accompanying change in breakpoint temperature was estimated to be approximately 22 K (40 F) (Ref. 5).

Since ERBS was not commercially available, several approaches to obtaining a test fuel were considered. An important consideration was that a similar fuel could readily be obtained by other establishments which might perform related tests. Specialty-batch production or local blending were ruled impractical, and a purchase of a substitute ERBS was recommended.

Two readily-available fuels were considered: No. 2 Home Heating oil (#2 HH) and Diesel Fuel No. 2. Extensive tabulations of composition of these two fuels were not available. However, limited data indicated that #2 HH would have approximately 30-35 percent aromatics, while No. 2 Diesel might have approximately 25-30 percent aromatics. The higher level of aromatics in #2 HH weighed in favor of its suggestion as the "representative" ERBS. Complete analysis of each fuel sample was conducted; the results are shown in Table A.

The Jet A met all ASTM specifications, with the exception of aromatics. However, a waiver to 25 percent is in effect, and the observed 21.7 percent meets current requirements. The #2 HH, on balance, furnished a good representation of ERBS, falling near or within most specifications, except for lower aromatics and higher naphthalenes. This combination, however, probably led to the lower thermal stability. An interpolated value of 473 K (391 F) may be compared to the specification of 511 K (460 F).

Fuels were used without further preparation, except for filtering at various stages through successive filters as small as 5 micron. After initial purging of the supply lines, filters remained clear. In addition to samples of as-received fuel, samples were also collected at the outlet of the test section for estimate of the effect of stress on fuel composition. Analysis was conducted on the fresh and stressed samples using infrared spectroscopy. These results are discussed in a later section.

Experimental Procedure

Fresh sample discs were inserted into the test channel for each run. Each disc was assigned a number which was engraved on the disc; the engraved side faced away from the fuel flow. Discs were sealed within the holder to prevent intrusion of fuel into the back-side region. Only negligible deposition occurred on the back side. In instances of extremely-large deposition on the working surface, in which case a thick, black deposit was evident, only trace deposition could be seen on the closed side; the depositions estimated to be less than 5 percent. A pressure check at 300 psig was conducted at the start of each run. After checkout and stabilization of flow rate, heating was started. Depending on flow and desired test section temperature, heating required approximately 10 to 30 minutes. A complete print-out of run parameters was obtained every 5 minutes; special prints of individual points were taken on demand.

Time at run temperature was determined from control system print-outs. A correction for the effect of deposition during heating and cooling was considered. However, the very steep change in deposition rate with temperature and short times spent in cooling and heating amke this a negligible effect.

Fuel flow was continued after cessation of heating until rig temperature was below approximately 367 K (200 F), at which time the channel was disassembled and samples were removed. Discs were washed in a 1/1 mixture of benzene and hexane to remove residual fuel, dried in a special vacuum oven and weighed on a microbalance. Selected specimens were examined using infrared spectroscopy to determine gross composition and the relationship of deposits to fuel composition. The range of test variables is given in Table II.

The specific run conditions and results are summarized in Table III. The column headed "Variation" denotes runs in which special conditions were applied. Unless otherwise stated, test presusre was 2.04 x 10^6 Pa (300 psig). Rates R₁ to R₄ relate to positions along the channel in the flow direction; \overline{R} is the arithmetic average of data for each run.

RESULTS

Thermal stability tests were conducted in the fuel system simulator with Jet A and No. 2 Home Heating Oil (No. 2 HH) at temperatures of 422 to 672 K (300 to 750 F). Other parameters varied during tests included flow rates, system pressure, and pre-treatment of the fuel by heating or deoxygenation.

Tests Using Jet A

Axial variations of coking rate for Jet A fuel are shown in Fig. 4 as a function of surface temperature and flow rate. Wall temperatures and flow rates covered the ranges 750-500 F (672-533 K) and 25 - 2.5 gal/hr (2.14 x 10^{-2} - 2.14 x 10^{-3} kg/sec), respectively. Inlet fuel temperature was 294 K (70 F). It is evident in Fig. 4 that the coking rate distributions are sensitive to both flow rate and temperature. At the lowest temperature (533 K) and flow rate (2.14 x 10^{-3} kg/sec), curve (a), a maximum in coking rate, is observed. A maximum rate is attributed to the opposing effect of rising bulk fluid temperature, which tends to increase the coking rate, and depletion of liquid phase deposit precursors. At this low flow rate, there is sufficient heating of the fuel so that coking is observed at the first disc position and the maximum occurs at the second disc position. At increased temperature (589 K), curve (b), similar behavior is observed, except that average coking rate increases. Because the flow is also higher (6.78 x 10^{-3} kg/sec), the maximum rate occurs further downstream. This is similarly a bulk heating effect, i.e., the bulk fluid temperature is lower at any axial position at increased flow rate. An appreciable increase in wall temperature results in a corresponding increase in coking rate, curve (c). At a flow rate of 2.14 x 10^{-3} kg/sec, (the same as for curve (a)), the maximum coking rate occurs prior to the first disc position because of the higher temperature. A comparison of curves (a) and (c) indicates that the maximum rate at the higher temperature is at least four times greater than at the lower temperature and that the average rate is also increased by about the same factor. The temperature dependence of coking rate is discussed further in subsequent paragraphs.

The effect of fuel deoxygenation is also shown in Fig. 4. It is seen that deoxygenation produces very low coking rate with relatively flat distributions. At the same rate, the deoxygenated fuel at 603 K exhibits a rate approximately one third that of an air-saturated fuel at 533 K.

The dependence of maximum coking rate on surface temperature is given in an Arrhenius plot of Fig. 5. Curves are shown for flows of 2.14×10^{-3} and 6.85×10^{-3} kg/sec (2.5 and 8.0 gal/hr). The overall activation energy at 2.14×10^{-3} kg/sec is 9 kcal/mol, in reasonable agreement with previous work (Ref. 6). The point at 672 K has not been used in placing the curve, since the maximum rate would

have occurred prior to the first sampling location as shown above. As would be expected, the indicated point lies below the curve. At higher flow rate, the coking rate is lower at the same wall temperature, yet the dependence on temperature (activation energy) is approximately the same. In both cases, the magnitude of the activation energy suggests a surface-catalyzed process. Taken together, the two curves of Fig. 5 suggest that an Arrhenius expression is reasonable for the description of coking rate over the range of temperature indicated. However, it is evident that both bulk fluid temperature and surface temperature influence the coking rate, and fuel decomposition is not entirely a surface-dominated phenomenon. At the least, the surface should accelerate the initiation of the fuel decomposition. It may be that free radical reactions initiated at the surface propagate into the fluid at a rate determined by fluid temperature. Lower rates at increased flow are therefore attributed to lower bulk fluid temperatures, as discussed previously. The net effect is that increased fluid and wall temperature both accelerate the formation of deposits. It appears that the effect of preheating the fuel to 422 K (300 F) for 1 hour, as indicated by a single point, is to lower the coking rate. No conclusive explanation for this result is available, but it is possible that because of the very long holding time, deposit precursors are removed in the fule system prior to exposure to the hotter reaction surface. The results in Fig. 5 may also be compared with the results of previous "isothermal" tests conducted at UTRC, Ref. 6, where the fuel was rapidly heated prior to the working section, and coking was measured at conditions of equal wall and fluid temperatures. The UTRC results lie well below the present resutls, although the temperature dependence is nearly the same. Because of the bulk fluid heating effect which occurs in the present experiments, and a significant difference in surface to volume ration, the two experiments are not directly comparable. For these reasons, the coking rates should not be equal. However, the agreement in activation energies (slope of curves) is encouraging.

The effect of pressure on coking rate for both Jet A and No. 2 Heating Oil is shown in Fig. 6. In both cases, coking rate increases with pressure. For the test temperature of 533 K (500 F), the applied pressure exceeds the vapor pressure; therefore, the results are not attributable to phase change. A possible explanation is that dissolved oxygen comes out of solution at lower pressures, thereby lowering the rate of liquid-phase fuel-oxygen reations. Additional experiments would be required to explain the effect of pressure on coking rate.

Tests Using No. 2 Home Heating Oil

Axial variations of coking rate for No. 2 HH oil are shown in Fig. 7 as a function of surface temperature and flow rate, which varied over the ranges 603-533 K (625-500F) and 16.0 x 10^{-3} - 2.22 x 10^{-3} kg/sec (18-2.5 gals/hr), respectively. Inlet fuel temperature was 294 K (70 F). As with Jet A, fuel coking rate distributions are sensitive to flow rate and temperature. At the highest surface temperature, 603 K (625 K), and a flow rate of 2.22 x 10^{-3} kg/sec (2.5 gal/hr), a maximum occurs at the second disc, as shown by curve (a). Depletion of reactants forces a rapid drop-off in coking rate beyond this point. At the same surface temperatures but at a higher flow rate, 7.11×10^{-3} kg/sec, curve (b), the maximum coking rate is reduced and the maximum point is shifted downstream. In this sense, the behavior parallels that observed with Jet A fuel. At a lower temperature, 533 K (500 F), the effect of flow is reversed, and increased flow leads to increased coking rate. This may result from more rapid heating of the flue, induced by a transition from laminar to turbulent flow, or from a change in mechanism. In the latter case, surface reactions would be more important than bulk phase reactions in both the initiation of fuel decomposition and the formation of coke, and coking would be augmented by higher mass transport rates. Certainly, more data are required to specify the controlling factors. The effect of flow rate is summarized in Fig. 8.

The temperature dependence of coking rate of No. 2 HH oil is shown in Fig. 9. The data for Jet A at a flow of 2.14×10^{-3} kg/sec are included for comparison. No simple Arrhenius function is observed, and a sharp increase in temperature dependence is indicated above 533 K. Data at 533 K refer to only one flow rate so that a better comparison is made with the Jet A data. There appears to be no effect of fuel preheating at 533 K (500 F). On the basis of the results shown in Figs. 8 and 9, it is suggested that there may be two regimes of coke formation, a low-temperature, mass-transport-controlled regime of low activation energy, where coke formation occurs primarily by surface reactions, and a high-temperature, bulk-reaction-dominated regime of higher activation energy. In the high-temperature regime, increased flow reduces coking rate. Possibly, the morphology and chemical structure of cokes formed over a wide range of conditions could provide further insights into the nature of the coke formation process. This is suggested for future work.

CONCLUSIONS

An experimental study of thermal stability of Jet A and No. 2 Home Heating fuels in a fuel system simulator incorporated variations in temperature, flow rate, pressure, and fuel pretreatment. The conclusions which may be drawn from the results are:

1. The coking rate is largely determined by the temperature attained by the fuel; surface temperature is also important. An Arrhenius expression of coking rate, i.e., coking rate rising exponentially with surface temperature, satisfactorily fits the experimental data for Jet A. A simple Arrhenius expression does not hold for No. 2 Home Heating oil, suggesting that a more complex mechanism is responsible.

2. Flow rate determines the maximum temperature of the fuel and the point of maximum deposition. Increased flow rate may lead to lower deposition by reducing, residence time in the temperature range where bulk fluid reactions are important. On the basis of the results of this program, it may be expected that, for some fuels, an increase in flow rate can lead to an increase in coking rate.

3. Reduction in system pressure may permit dissolved oxygen to leave the liquid and reduce the rate of liquid-phase reactions between fuel and oxygen.

4. Preheating the fuel does not necessarily increase the rate of deposition. Although the temperature attained by the fuel in the simulator is increased by preheating, the storage of the heated fuel may permit depletion of deposition of precursors and products. It appears that this would be a function of storage time.

5. Deoxygenation, by severely diminishing the oxygen essential for formation of hydroperoxides or other precursors of coke formation, strongly limits the overall coking rate.

REFERENCES

1. Taylor, W. F., ed.: Jet Fuel Thermal Stability. (Symposium held at NASA LeRC, November 1-2, 1978), NASA TM 78231, 1979.

1

- 2. Bolshakov, G. F.: The Physico-Chemical Principle of the Formation of Deposits in Jet Fuels. NTIS AD 781164, U. S. Department of Commerce, 1974. (Translated from Russian by Foreign Technology Division, USAF.)
- 3. Kearns, G. L., et al.: Analytical Chemistry, Vol. 31, No. 10, p. 1646. October 1959.
- 4. Rakowsky, F. W. and G. H. Meguerian: Combustion and Flame, Vol. 10, p. 182, 1966.
- 5. Lohmann, R. P., E. J. Szetela, and A. Vranos: Analytical Evaluation of the Impact of Broad Specification Fuels on High Bypass Ratio Turbofan Engine Combustors. NASA CR 159454, 1978.
- 6. Vranos, A., P. J. Marteney and B. A. Knight: Determination of Coking Rate in Jet A Fuel. Presented at Annual Conference on Fouling of Heat Transfer Surfaces. Troy, NY, August 1979.

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TABLE I

FUEL PROPERTIES

				······································
	<u>Jet A</u>	ERBS	<u>Jet A</u>	No. 2 HH
	(ASTM D-1655 or nominal)	(Specification or nominal)	(Analysis)	(Analysis)
Specific Gravity	0.7753-0.8398	0.8438-0.8448	0.8128	0.8478
Viscosity, 80 F, CS			1.79	3.36
Sulfur, % Wt.	0.3	0.3	0.06	0.23
Aromatics, % Vol.	20(1)	35	21.7	30.4
Olefins, % Vol.	0.3	0.3	0.3	0.3
Napthalenes, % Vol.	3.0	7.5	2.0	12.3
Hydrogen, % Wt.	13.7	13.0	13.75	12.9
Nitrogen, ppmw			20	120
Oxygen, ppmw			1200	300
H/C Ratio			1.91	1.78 (2)
Breakpoint Temperature K (F)	533 (500)	511 (460)	528 (491)	473 (392)

ORIGINAL PAGE IS

(1) Temporary waiver to 25%

(2) Contract specification 513 K or less

TABLE II

TEST VARIABLES

Deoxygenated Fuel	sparged with nitrogen 16 hours
rieneated ruei	stored 1 hour before use
Probested Fuel	bested to $300 \text{ F} (322 \text{ K})$
	outlet - 6,000 to 34,290
Reynolds Numbers	inlet - 800 to 27,000
	(6.9 x 10 ⁵ to 2.07 x 10 ⁶ Pa)
Test Pressure	100 to 300 psig
Test Temperature	300 to 750 F (422 to 672 K)
	$(2.14 \times 10^{-3} \text{ to } 22.2 \times 10^{-3} \text{ kg/sec})$
Fuel Flow Rate	2.5 to 25 gal/hr

TABLE III

TEST CONDITIONS AND RESULTS

' Cobine Rate un/om2-br											
Run		Fuel		Temperature	Flow	Variation [*]	R1	Ro	R ₃	R _A	R
-				(Dag. F)	(gal/hr)					••	
1		٨		500	2.5		18.27	34.79	22.61	11.90	21.89
5		#9		300	2.5			3.44	3.36		3,40
. 7		#2		500	2.5		12.36	19.79	15.02	14.78	15.47
Ă		#9		300	2.5		14.46	21.19	17.36	4.79	14.46
5		∦2		500	2.5		23.69	48.55	26.21		32.82
5		#2		525	4.0	This local system	25.38	25.23	25.23	21.58	24.36
7		#2		500	5.0		19.00	23.00	21.75	13.13	19,22
8		A .		400	8.0		4.05	1.94	1.86	2.59	2.61
9		A		400	8.0	100 VII 100	4.94	2.06	2.47	2,06	2.88
10		A		600	8.0		16.00	15.00	28.33	12.00	17.83
11		A .		594	8.0		19.67	35,38	56.38	36.70	37.03
12		#2		625	2.5		71.23	323.57	97.44	22.34	128.65
13		112		625	8.0	Test , was have	27.58	42.51	70.59	48.83	47.38
14		#2		500	2.5	100 psig	10.85	11.99	12,61	7.35	10.70
15		A		500	2.5	200 psig	6,16	13.45	10.85	3.90	8.59
16		A ·		500	2.5	100 psig	3.31	6.10	3.83	5.84	4.77
17		Δ		750	2.5		141.40	72.80	37.80	42.00	73.50
18		A		500	8.0	Hented	6.31	7.00	6.90	7.39	6.90
19		#2		500	8.0	Heated	6.73	19.05	20.56		15.45
20		#2		625	9.0	Heated	22.45	172,10	44.05		79.53
21		110		625	2.5	De Or	71 65	67.19	48.94	66.90	58.67
22		#2		625	2.5	De Ox	55.76	138.31	56.00	42.00	73.01
22		#2		625	8.0	De Ox	21.50	50.00	26.50	32 50	12.61
22		<i>к</i> н		625	0.0	De Or	8 53	3.94	5.03	6 34	5 06
44 96		. A .		500	95.0	De Ox	1 45	2,24	A 60	5 57	1.50
26		112		560	20.0	200 psig	7.56	14.91	27.30	21.84	17.90
27		#2		500	2.5		14.99	14.63	10.45	6.80	11.71
28		112		500	18.0		12.19	18.29	22.58	27.32	20.10
20		* -		625	8.0		11.79	46.73	46.73	51.48	39.18
<i>~</i>		<i></i>		weeker .							

*Normal run at 300 psig, fuel as-received

 ${}^{\circ}$ Fuel preheated to 422 K (300°F) for 1 hour

Conversion to SI Units

Deg. F	Deg. K	gal/hr	Kg/sec (No.	<u>2 HH)</u>	Kg/sec (Jet A)
300	422	2.5	0.0022		0.0021
400	477	4.0	0.0036		0.0034
500	533	5.0	0.0044		0.0042
594	585	8.0	0.0071		0.0068
625	603	9.0	0.0080		0.0076
750	672	25.0	0.0220		0.0211





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Figure 2. — Schematic Drawing of Fuel System Simulator

SEE FIG. 2 FOR DIMENSIONS



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Figure 3. — Photograph of Simulator Parts

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SYMBOL TEMPERATURE FLOW 672K (750F) 2.14 × 10⁻³ Kg/sec (2.5 gal/hr) 533K (500F) 2.14 × 10⁻³ Kg/sec (2.5 gal/hr) 589K (600F) 6.78 × 10⁻³ Kg/sec (8 gal/hr) 533K (500F) 2.14 × 10⁻² Kg/sec (25 gal/hr) DEOXYGENATED Δ 603K (625F) 2.14 × 10⁻³ Kg/sec (2.5 gal/hr) DEOXYGENATED 0 PRESSURE 2.07 \times 10 + 6 Pa (300 psig) 150 140 130 120 110 3 100 COKING RATE — µg/cm²-hr COKING RATE — Kg/m²-sec $\times 10^7$ 90 80 C 2 70 60 50 40 30 20 10 0 **L**

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SAMPLE POSITION

3

4

Figure 4. — Coking Rate of Jet A vs Sample Location

2



Figure 5. — Arrhenius Plot of Coking Rate in Jet A





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PRESSURE: 2.07 × 10⁶ Pa





Figure 7. — Coking Rate of No. 2 Home Heating Oil vs Sample Position





1



Figure 9. — Arrhenius Plot of Coking Rate in No. 2 Home Heating Oil

APPENDIX

CHARACTERIZATION OF DEPOSITS

Deposits on specimen plates were examined by infrared absorption spectroscopy to determine relationships between the original fuel and deposits. The type of deposit found on the test channel and one particular disc after test are shown in Figs. A-1 and A-2, respectively. A very heavy deposit shown in Fig. A-2 was formed during the most severe stressing of the No. 2 Home Heating oil.

As-received fuels tended to appear nearly the same in the IR spectra. On the other hand, the formation of deposits strongly accentuates differences in fuels or the effect of treatment of fuels. Typical comparison spectra are shown in Figs. A-3 and A-4, which compare fuel spectra and deposit spectra from an as-received fuel and a deoxygenated fuel. Peaks near 2800 wave numbers (cm^{-1}) represent alkyl groups. Peaks between 800 and 2000 $\rm cm^{-1}$ represent a combination of aromatic and oxygencontaining groups. In Jet A, Fig. A-3, neat fuel yields deposits containing peaks in both alkyl and aromatic regions. The contribution of oxygen-containing groups appears predominantly at 1725 cm⁻¹, indicating the carbon-oxygen double bond. Satellite peaks at 1770 and 1840 $\rm cm^{-1}$ have been noted previously (Ref. 6) and offer the intriguing possibility of imides or anhydrides. A peak at 3200 cm^{-1} , associated with the hydroxyl group of alcohols, is not present. A concentration of alkyl benzenes in the deposits is indicated by a strong peak near 1600 cm⁻¹. Deoxygenation of fuel leads to deposits almost entirely lacking in the aromatic/oxygenate region, while alkyls are less strongly affected. It should be noted that the deposit from the deoxygenated fuel was thinner, and overall sensitivity would be lower.

In No. 2 Home Heating oil, Fig. A-4, the same general pattern is evident. Neat fuel yields significant peaks near 1600 cm⁻¹ and 800 cm⁻¹, solely due to aromatics, and a mixed contribution from aromatics and oxygenates in the region 1000 to 1600 cm⁻¹. A strong absorption due to -OH is found in the region 3200 cm⁻¹, and due to C-0 in the vicinity of 1200 cm⁻¹. The same combination of peaks at 1725, 1770 and 1840 cm⁻¹ is found as in the jet fuel deposit. Deoxygenation reduces all peaks except those near 800 cm⁻¹, which are attributed to aromatics.

The IR spectra of deposits therefore reveal several important clues to deposit formation. First, the variation in aromatic content of fuels is more strongly reflected in the deposit spectra than in the fuel spectra. Second, deposit formation has strong sensitivity to a mechanism involving oxygen, although the mechanism may be slightly different for alkyl and aromatic constituents in the fuel.



Figure A-1. — Test Channel After Test

TEST NO. 20 NO. 2 HH OIL, PREHEATED TEMPERATURE --- 625 F FUEL FLOW --- 9 gal/hr POSITION NO. 2



FUEL FLOW





Figure A-3. — Comparison of Deposit Spectra From Neat and Deoxygenated Jet A Fuel With As-Received Sample

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Figure A-4. — Comparison of Deposit Spectra From Neat and Deoxygenated No. 2 Home Heating Oil With As-Received Sample