ADVANCED JET FUELS — JP-4 THROUGH JP-8 AND BEYOND

by
W. E. Harrison III,
WL/POSF, WPAFB, OH
H. C. Mongia
GE Aircraft Engines, Cincinnati, OH
and
S. P. Heneghan and D. R. Ballal
University of Dayton, Dayton, OH.

ABSTRACT

Jet fuel requirements have evolved over the years as a balance of the demands placed by advanced aircraft performance (technological need), fuel cost (economic factors), and fuel availability (strategic factors). In a modern aircraft, the jet fuel is the primary coolant for aircraft and engine subsystems and provides the propulsive energy for flight. To meet the evolving challenges, the U.S. Air Force, industry and academia have teamed to develop new and improved fuels that offer increased heat sink and thermal stability, properties that will enable improved aircraft design and decrease fuel system maintenance due to fuel fouling/coking. This paper describes the team effort to develop improved JP-8, named "JP-8+100", that offers a 55C (100F) improvement in thermal stability and a 50% increase in heat sink.

The government, industry, and academia team has made numerous advances in the development of JP-8+100 with a more complete understanding of the fundamental processes of deposition, new approaches to reducing fouling/coking, and new tests and models to assist the designers of aircraft and engine fuel systems. Some of the principal advances are: new quantitative research devices and fuel system simulators that provide thermal stability information that cannot be obtained using the standard JFTOT test; new techniques to measure oxygen consumption and fuel degradation pathways; a free radical theory to explain behaviors such as the inverse relationship between thermal and oxidative stability, advanced CFD models with coupled degradation chemistry, and a new thermal stability ranking scale for jet fuels. The insight obtained has been applied to the development of an additive package for JP-8 that shows thermal stability improvements equal to or greater than the stated goal and enables the development of even higher thermal stability fuels such as JP-900.

NOMENCLATURE

AFTS	Aviation Fuel Thermal Stability Test Unit
AH	Antioxidant molecule
ARSFSS	Advanced Reduced Scale Fuel System Simulator
ASTM	American Society for Testing and Materials
BHT	Butylated-hydroxy-toluene
CFDC	Computational Fluid Dynamics with Chemistry
CONUS	Continental United States
EDTST	Extended Duration Thermal Stability Test
NIFTER	Near Isothermal Flowing Test Rig
HLPS	Hot Liquid Process Simulator
ICOT	Isothermal Corrosion Oxidation Test
JFA5	DuPont proprietary jet fuel additive
JP	Jet Fuels
JP-TS	Jet Propellant - Thermally Stable
k	Rate constants
MCRT	Microcarbon Residue Test
QCM	Quartz Crystal Microbalance
RH	Fuel hydrocarbon molecule
R_i	Rate of radical formation
TAC	Total Accumulated Cycles
TS	Thermal Stability
X·	Free radicals (X= A, R, RO_2, RO, HO)
8Q405	Betz proprietary additive

INTRODUCTION

Current environmental and technological demands posed on the Air Force and the aircraft and engine manufacturers require the jet fuel to accomplish a variety of *non-combustion* related tasks. For example, the fuel is the primary coolant for aircraft hydraulic and environmental control subsystems and the primary

coolant for the engine. Future high performance, high thermal efficiency engines will not only produce *more* excess heat, but also will have less fuel available with which to manage and transfer that heat. The end result is that jet fuel is exposed to significantly higher temperatures for longer periods of time causing the fuel to degrade and foul aircraft and engine components. In 1990, an Aircraft Thermal Management Working Group of Wright Research and Development Center (WRDC) investigated the cooling requirements for current, next generation, and future aircraft (Harrison, 1990). Fig. 1 illustrate the maximum estimated heat loads and Fig. 2 provides the worst case temperatures, pressures, and residence times experienced by fuel in various engine and airframe components. The WRDC working group reached an alarming conclusion: "*aircraft development in the near future will suffer performance penalties as tremendous quantities of ram air or excess fuel will be required to meet the heat sink requirements.*" To resolve the problem, the WRDC working group recommended the development of high thermal stability fuels, such as (i) a high temperature thermally stable JP-8+100 fuel which provides a 50% improvement in heat sink capability over conventional JP-8 fuel, and (ii) a new fuel JP-900 that has a 482C (900F) thermal stability and could eliminate the need to recirculate fuel onboard an aircraft.
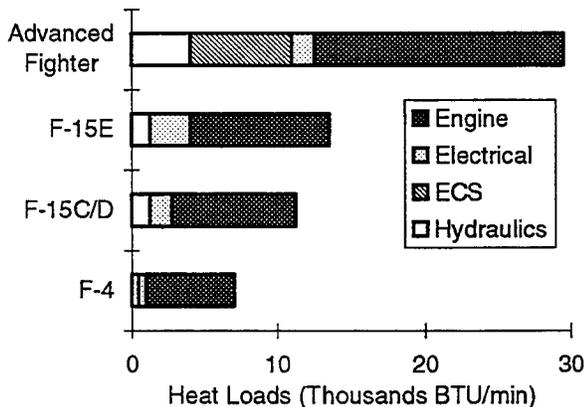

Fig. 1: Maximum estimated excess heat loads for various aircraft.

This paper reviews a brief history of jet fuel development; describes the challenges faced by the Air Force, industry and academia to develop the JP-8+100 thermally stable fuel; discusses recent findings and fundamental understanding of the fuel degradation process; and outlines the potential technological benefits of developing future generations of high heat sink fuels.

CONVENTIONAL JET FUELS

Martel (1987) described the history of military jet fuels, their development and detailed specifications. Today the three standard U.S. (NATO) military jet fuels are JP-4 (F-40), JP-5 (F-44) and JP-8 (F-34). The Air Force also uses two specialty fuels JPTS and JP-7. The commercial sector in the continental

U.S. (CONUS) uses Jet A and the international commercial airlines use Jet A-1. These fuels are briefly described below:
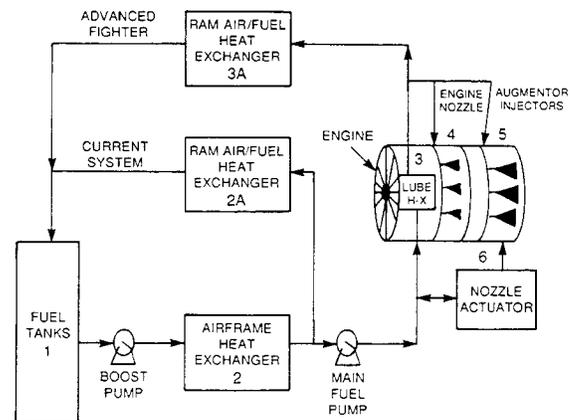
	1	2	2A	3	3A	4	5	6
T (F)	<160	<250	<250	300	<325	325+	500+	<350
P (psi)	<25	<80	<80	1200 to 2000	<80	<40#	<40#	1500 to 4000
Time	min to hrs	<15 sec	<2 sec	<3 sec	<2 sec	<2 sec*	min*	<20 min

*Time: <100 msec
#Pressure: 1200 - 2000 psi

Fig. 2: Worst case temperature, pressure, and residence time experienced by fuel in various airframe and engine components.

(i) JP-4: Since 1951 this gasoline/kerosene blend fuel has been the main fuel used by the military. Its high volatility allowed the fuel to be easily ignitable and allowed for refiners to produce large quantities of fuel. The fuel vapor pressure was restricted to 0.14 to 0.2 atm. to decrease fuel boil-off losses and to reduce vapor lock problems at high altitude. In addition the gasoline portion of the fuel allowed the fuel to have a very low freeze point.

(ii) JP-5: Since JP-4 was highly volatile and the Navy was concerned about fires on aircraft carriers, the Navy adopted the use of a high flashpoint kerosene fuel JP-5 (60C flash point). This fuel is used on all aircraft carriers and aircraft capable ships.

(iii) Jet A and Jet A-1: The commercial airlines recognized in the 1950's the advantages of kerosene fuels from a safety standpoint. Both fuels have a minimum flashpoint requirement of 37.7C. Jet A and Jet A-1 are similar. The only difference is in minimum freeze point temperature, with Jet A specification requiring -40C and the Jet A-1 specification

2

TABLE 1: SUMMARY OF THERMAL STABILITY TEST RIGS AND CONDITIONS

Test	Temperature Range (C)	Reference	Miscellaneous
Static Tests			
QCM	140	Zabarnick, 1994	Closed system - measure surface deposits
ICOT	180	Grinstead, 1994	Bubbling air - measures bulk deposits
MCRT	225	Grinstead, 1994	Distillation - measures residual deposits
Flowing Tests			
Gravimetric JFTOT	260	Beal et al., 1992	
	180-380	Marteney and Spadaccini, 1986	Constant heat flux system
Augmentor	up to 1000C	Edwards, 1992	Vaporization flow system - simulates afterburner and nozzle soak back
Phoenix	200-300	Heneghan et al., 1993b	Constant wall temperature with on-line dissolved O_2 measurement
NIFTER[†]	140-210	Jones et al., 1993	Isothermal flow system with on-line dissolved O_2 measurement
HLPS	335	Biddle et al., 1994	JFTOT flow System
Engineering Tests			
AFTS*	180-230	Dagget and Veninger, 1994	
		Chin and Lefebvre, 1992	Recirculating system
EDTST[‡]	160-200	Dieterle et al., 1994	Establishes fuel bulk and wetted wall temperatures
ARSFSS**		Morris and Binns, 1994	Configured to simulate F-22

[†] Near Isothermal Flowing Test Rig   * Aviation Fuel Thermal Stability Test Unit

[‡] Extended Duration Thermal Stability Test   ** Advanced Reduced Scale Fuel System Simulator

requiring -47C. Jet A is used in CONUS and Jet A-1 is used internationally.

(iv) JP-8: The Air Force began converting from JP-4 to JP-8 in 1979. JP-8 is Jet A-1 with a military additive package consisting of fuel system icing inhibitor (FSII), corrosion inhibitor/lubricity enhancer, and an antistatic additive. JP-8 fuel is used as a single fuel on the battlefield since it can be used in all ground mobile diesel equipment (HUMMERs, trucks, tanks etc.,) as well as in all aircraft.

(v) JP-7 and JP-TS: JP-7 is a highly refined kerosene consisting of primarily paraffins and cycloparaffins used in the SR-71 aircraft. It was specially formulated for high altitude, Mach 3+ operation. JPTS is a highly refined kerosene with at low freeze point used in the U-2 aircraft. JPTS is the only fuel that currently uses a thermal stability additive package, JFA-5, a proprietary package made by DuPont.

Jet Fuel Need: With the demands for improved performance engines and more capable aircraft, the Air Force realized the need for high thermal stability and high heat sink fuels. Since it is in the process of converting from JP-4 to JP-8 because of the improved safety of JP-8, all advanced fuel research has focused on a kerosene based fuel. As aircraft and engine improvements have been made, the fuel has become the primary heat sink for all the waste heat generated by aircraft and engine subsystems. Current aircraft can thermally stress the fuel to temperatures above its thermal stability causing the fuel to degrade and form varnishes, gums (oxidative instability products) and coke (thermal instability products). Fuel fouling/coking is an expensive maintenance burden. Fouling distorts nozzle spray pattern which can lead to damage in combustors and over temperature in the first stage turbine blades. Fouling in augmentors can effect lightoff and can cause a low frequency acoustic phenomenon called rumble. Other more subtle

problems found with fuel fouling include increased difficulty with cold starts, altitude relights, and fuel control anomalies.

With an increase in engine performance and higher heat loading, engine component design (pumps, valves, manifolds, filters, controls, heat exchangers, fuel nozzles, augmentor parts) has become more difficult. Operating temperatures in main burner nozzles, thrust vectoring fuel powered actuators, fuel controls and augmentor parts in many cases are above the thermal stability of the fuel and designs to reduce fuel temperatures are complex, heavy and costly. Improved stability fuels such as JP-8+100 offer significant benefits to the designer of these components.
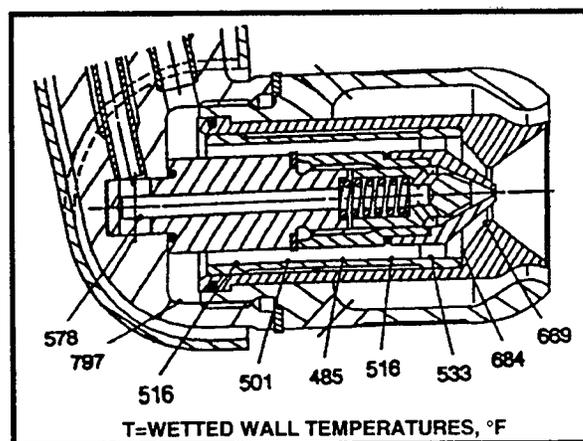

Fig 3: Typical fuel nozzle wall temperatures measured in an advanced engine. Data are for cruise condition (T_3 = 1260F, Fuel Inlet Temp. = 350F).

3

TABLE 2: SUMMARY OF ANALYTIC TESTS

| Compounds Detected	Detection Technique	Reference	Comments
Dissolved O_2	GC - Thermal Conductivity	Rubey et al., 1992	On-line in Phoenix rig and NIFTER 1 ppm sensitivity
Dissolved O_2	Headspace Pressure	Zabarnick, 1994	On-line in QCM
Antioxidants, phenols, peroxides	Cyclic Voltammetry	Kauffman, 1989, 1992, 1994	Off-line, fast, portable, minimal waste products
Phenols	Ultra Violet/Visible Spectroscopy	Murray, 1949	Off-line, very simple, shows good correlation to thermal stability
Polar heteroatom compounds	Solid Phase Extract/GC-AED	Grinstead et al., 1994	Off-line, quantitative, atom-sensitive
Polar heteroatom compounds	Solid Phase Extract/GC-MS	Schulz, 1992	Off-line, allows identification of compounds
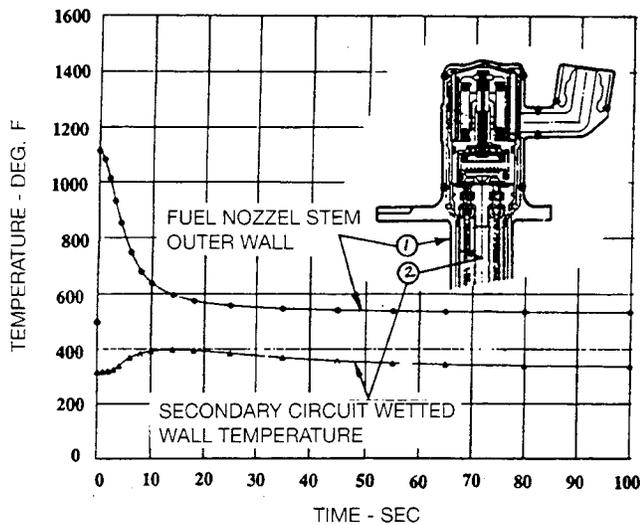
Fig. 4: Time variation of measured wall temperatures of an engine nozzle immediately following engine pull back.

Jet Fuel Operating Temperatures: Next generation high performance engines may operate for some applications at much higher fuel and combustor inlet temperatures. If for these advanced cycles, one uses current production technology fuel nozzles, for example the F404 nozzle shown in Fig. 3, at the fuel inlet temperature of 176C (350F) and the combustor inlet temperature of 682C (1260F) at the cruise condition, the predicted wetted wall temperature is 425C (797F) as compared to the desirable wetted wall limit of 204C (400F) with JP-8. The corresponding desirable maximum bulk fuel temperature of 163C (325F) is lower than the inlet fuel temperature for this particular advanced application. One must, therefore, develop aviation fuels with thermal stability characteristics better than that of JP-8. Fig. 4 shows the time variation of measured wall

temperature of an engine fuel nozzle of an advanced fighter engine immediately following the engine pull back. Outer wall transient temperatures as high as 538C (1000F) and steady state temperatures close to 288C (550F) are measured. For the secondary circuit, wetted wall temperature increases from 149C (300F) to 204C (400F), and then asymptotically reaches 176C
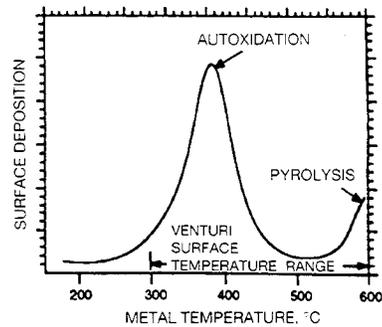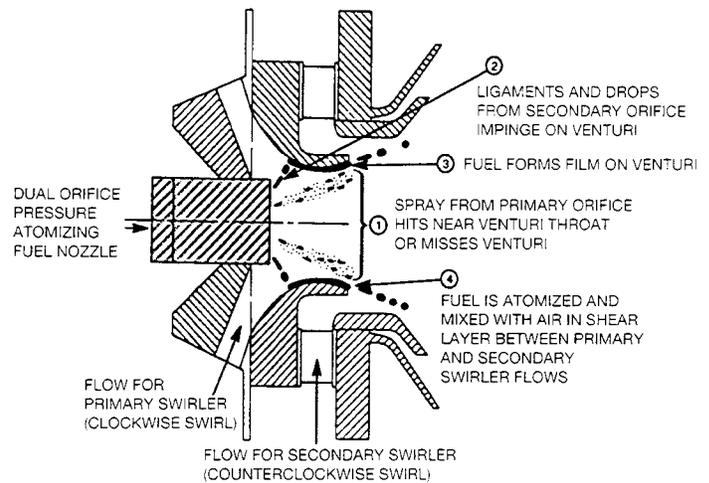

Fig. 5: Schematic of (a) production engine combustor swirl cup and (b) surface deposition vs. metal temperature relationship.

4

(350F). If the secondary fuel passage has no recirculation, coke barrier coating, and is not completely purged, the excessive stem wall temperature levels can lead to unacceptable soak back coking/sticking problems, especially if the engine is shut down 15 seconds after the fuel chop.

Fig. 5 shows a production engine combustor swirl cup, a fuel-air mixing device designed to decrease the sensitivity of the fuel injection system to fuel type. This device has worked free of carbon deposition as long as the fuel film temperature remains below or above certain critical metal temperatures. The carbon deposition tendency of a given swirl cup venturi surface can worsen or improve with the fuel switchover from JP-4 to JP-8. It is therefore important to understand the fundamentals of venturi carboning and how the operating temperature window changes as a function of engine operating conditions and the fuel properties. Further, a systematic analytical, component and engine system test plan must be proposed to quantify potential toxic effects, hot-section hardware durability, high temperature lubricity, and heat sink capability of high thermal stability jet fuels.

JP-8+100 Program: The U.S. Air Force initiated a "JP-8+100" program in 1989 with the cooperation of industry, private laboratories, and universities. In the past, jet fuel development took the path of best compromise solution to engine performance requirements (technological needs), fuel cost (economic factors), and fuel availability (strategic factors). These same factors guided the development of high thermal stability jet fuels. The main goal of this program was to increase the heat sink capacity of current JP-8 fuel by 50 percent (i.e., a 55C increase in fuel operating temperature from 163C to 218C) by developing additives blended with the fuel at a typical cost of $1 per 1000 gallons thereby alleviating the need for using expensive specialty fuels such as JP-7 and JPTS. To meet this goal, the following four major research tasks were identified and progress on each task is discussed.

1. Identify and develop new fuel thermal stability test techniques.
2. Develop a fundamental understanding of fuel thermal stability.
3. Develop global chemistry models and a thermal stability scale.
4. Identify effective thermal stability improving additive packages.

THERMAL STABILITY RESEARCH

Test Technique Development: Since 1973, the standard for evaluating thermal stability has been the jet fuel thermal oxidative tester (JFTOT) and the test procedure as described in the American Society of Testing and Materials (ASTM) D3241. This test is only adequate for determining a go/no-go fuel rating and therefore does not provide any quantitative information whatsoever. Also, it is of questionable value because JFTOT is based on a single high fuel operating temperature (260C) and fuel quality is measured by a simple visual observation.

These limitations of JFTOT in defining thermal stability led to the development of several advanced research instrumentation and quantitative test techniques within the last five years. These test techniques, which are summarized in Table 1, may be categorized into three classes; static tests, flowing tests, and large-scale engineering tests.

In all static and flowing tests, the residence time and temperatures are sufficient to ensure the complete autoxidation of the dissolved oxygen within the test zone. As discussed later, fuel oxidation characteristics are crucial to understanding test results and the thermal stability mechanism (Hazlett, 1991). Concurrently, *three* new analytic tests were developed to measure: (i) dissolved oxygen using gas chromatography (GC), (ii) antioxidants, peroxides, and phenols using cyclic voltammetry, and (iii) polar carbon, sulfur, and oxygen using solid phase extraction technique. These techniques are summarized in Table 2.

Fundamental Advances: During the last few years research into the development of JP-8+100 has resulted in several significant fundamental advances in the understanding of jet fuel oxidative and thermal stability. Two important advances are: (i) relationship between thermal and oxidative stability and (ii) understanding the free radical mechanism of oxidation. Each of these developments are discussed below.
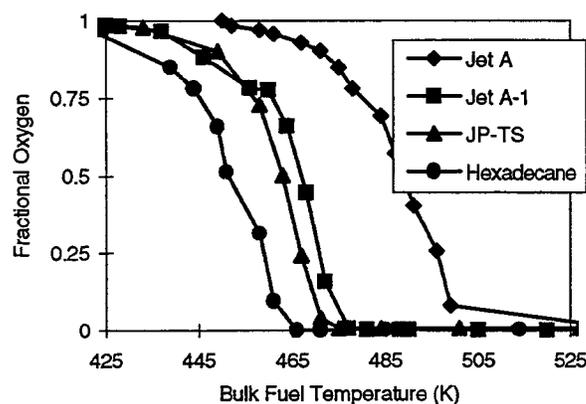

Fig. 6: Fractional oxygen remaining vs. output bulk fuel temperature at constant flow conditions in Phoenix rig.

1. Thermal and Oxidative Stability: Fig. 6 illustrates the oxidation behavior of four jet fuels as a function of bulk fuel temperature at a constant fuel flow in a Phoenix rig. These and other tests on both the Phoenix rig (Heneghan et al., 1993b) and the NIFTER (Jones et al., 1993) showed that a more thermally stable hydrotreated fuel such as JPTS oxidized at a lower temperature or in a shorter residence time than Jet A and Jet A-1 that have lower thermal stability. The trend towards oxidation at a lower threshold temperature continued for a pure hydrocarbon fuel such as hexadecane. This inverse relationship between the thermal stability, as defined by deposits, and oxidative stability, as defined by the production of oxidized

products has also been observed by Heneghan et al. (1993a) and Hardy et al. (1992). The general behavior is shown plotted in Fig. 7. Heneghan and Zabarnick (1994) showed that the observed inverse behavior was consistent with the known free radical autoxidation mechanisms if the free radical of a radical-trapping antioxidant is the precursor molecule to deposit formation. Next, this free radical mechanism is described.
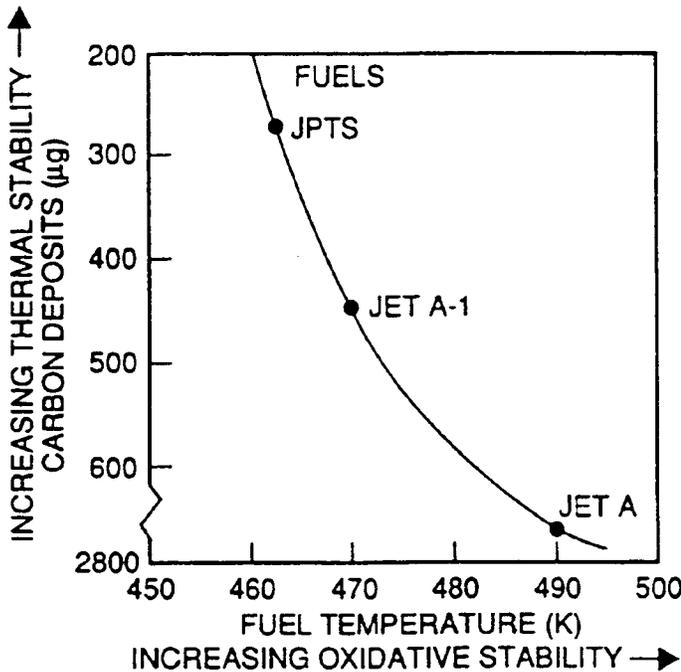

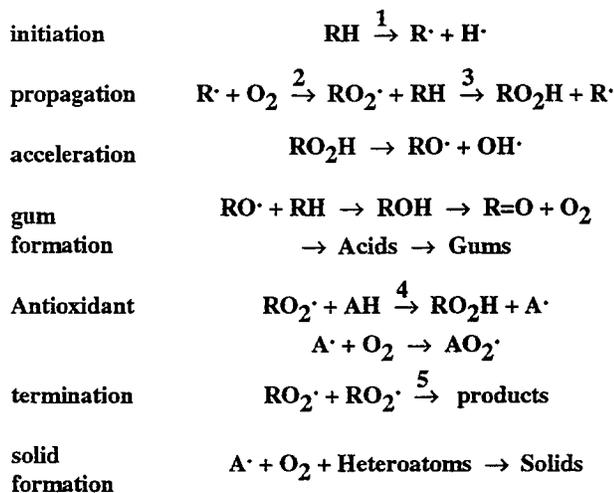**Fig. 7: Inverse relation between thermal stability and oxidative stability for various jet fuels.**

Fig. 8: Free radical autoxidation mechanism.

2. Autoxidation Mechanism: Fig. 8 illustrates the complete free radical mechanism for solid carbon and gum formation. In these reactions, AH is the antioxidant molecule, and the precursor to deposits is identified as $A^\bullet$. The rate of oxidation for this system (for sufficient oxygen) is given as:

$$-d(O_2)/dt = R_i + k_3[RO_2^\bullet][RH] \qquad (1)$$

where R_i is the rate of formation of $R^\bullet$, the subscripts refer to reactions shown in Fig. 8, and

$$[RO_2^\bullet] = \frac{k_4[AH] - \sqrt{k_4{}^2[AH]^2 + 8k_5R_i}}{-4k_5} \qquad (2)$$

This mechanism shows that the rate of oxygen consumption is independent of the oxygen concentration. It also reveals that at a low enough oxygen concentration, the rate-limiting step will switch from reaction (3) to reaction (2). At that time, the consumption of oxygen will be first order in oxygen. The increased lifetime of R due to the decreased oxygen is responsible for the appearance of methane in the Phoenix rig experiments only after a complete depletion of the oxygen occurs. The rate of oxidation vs. time at constant temperature was observed to increase proportionately to the amount of oxidation that had occurred up to that time. (i.e. $k_o(t) \propto ([O_2]_0 - [O_2]_t)$. Zabarnick (1993) demonstrated the proposed autoxidation/antioxidant mechanism and showed that the following peroxide decomposition reaction may account for the observed autoacceleration;

$$RO_2H \rightarrow RO^\bullet + HO^\bullet \qquad (3)$$

Global Reaction Mechanisms

1. Global Chemistry Model: Krazinski et al. (1992) developed a model of computational fluid dynamics with chemistry (CFDC) to predict jet fuel degradation. This CFDC model incorporates the process of jet fuel oxidation and deposition and requires a global reaction kinetics scheme to represent a series of elementary reaction steps. Typically the global reaction rate parameters are assumed to be in Arrhenius form with parameters A and E that are independent of time and temperature

Katta et al. (1993) used the Arrhenius assumption to predict the deposition profiles in an isothermal flowing system and observed that the activation energy changed with temperature. Heneghan (1994) studied the source of the global oxidation rate constant using the autoxidation peroxide decomposition mechanism and found that the global rate constants for oxidation were neither constant in time nor Arrhenius in form. Heneghan and Chin (1994) developed a new oxidation model, including autoacceleration, and incorporated this into a CFDC code. Fig. 9 shows that this model satisfactorily predicts the shape and amount of the deposition rate in the NIFTER flowing systems. Under high temperature high flow rate conditions typical of the real fuel systems, turbulent diffusion of the oxygen was found to be responsible for the increased oxygen consumption which results from a radially non-uniform temperature profile.
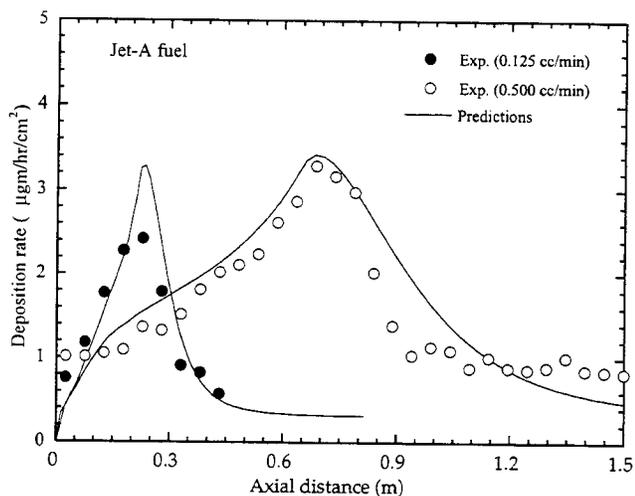
6

Fig. 9: Comparison of calculated vs. experimental deposit formation in NIFTER using global oxidation parameters.

2. Thermal Stability Scale: Heneghan and Kauffman (1994) performed a non-parametric statistical analysis of the thermal stability results for 12 fuels and 6 test techniques to develop an average thermal stability scale. This average thermal stability scale serves a dual purpose: (i) it represents a good test independent scale by which new analytic or physical tests can be evaluated, and (ii) the scale can be used to quantify improvement in jet fuels. Heneghan and Kauffman (1994) further showed that there were several quantitative analytic tests which reproduce the average scale as well as the individual thermal stability tests. These quantitative analytic tests overwhelmingly implicated phenols as the major "bad actors" in jet fuels. GC-MS identification of polar compounds in jet fuels showed that nearly all fuels contain alkylphenols (i.e. methyl-, dimethyl-, or methylethyl- phenols).

ADDITIVES TESTING

A prime goal of the "JP-8+100" development program was to find an additive or an additive combination that will improve the thermal stability of JP-8 fuel by 55C and/or closer to that of the JPTS fuel. Laboratory tests, while having significant advantages in assessing the development of an additive package, all have some inherent disadvantages. Static tests are simple to operate, typically yielding results in less than a day. This allows many additives to be tested. However, these tests are operated under accelerated test conditions (i.e. excess oxygen or temperature). Flowing tests more closely approach reality, but require significantly more time both in testing and turnaround thereby limiting the number of additives that can be evaluated. The large scale engineering rigs are the closest to reality in

temperature, flow conditions, oxygen level, and recirculation but require significant time to evaluate an additive and often produce conflicting results. To accommodate a large number of potential additives, a series of static and JFTOT type tests were used to screen additives. Only those which showed significant improvement in a variety of fuels and tests were used in the flowing and finally large scale engineering test rigs.

1. Static Tests: Many classes of additives were tested by Grinstead (1994), Biddle (1994), and Zabarnick and Grinstead (1994). These additive classes comprised antioxidants, detergents, dispersants, and metal deactivators. The QCM, ICOT, MCRT, HLPS, and JFTOT breakpoint tests were used for screening the additives. Eventually Anderson et al. (1994) identified a combination dispersant (Betz 8Q405), antioxidant (butylated-hydroxy-toluene, BHT) and metal deactivator as the most effective additive combination tested to date.

Fig. 10 shows deposit formation vs. test duration in a QCM for three different additive combinations and a neat JP-5 fuel sample. It can be readily observed that nearly an order of magnitude improvement in JP-5 fuel thermal stability is realized in this fuel by using the most effective additive package.
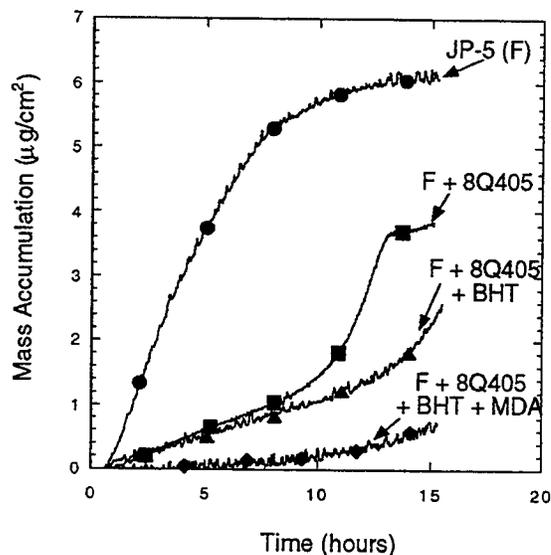

Fig. 10: Deposit formation vs. time in QCM for various additives.

2. Flowing Tests: Dieterle et al. (1994) used a large-scale engineering setup for extended duration tests (EDTST) which simulates the high heat flux and high fuel flow of practical aircraft fuel systems. Essentially, this test uses preheaters and main heaters to establish both the appropriate bulk fuel temperature (162C) and wetted wall temperature (204C) limitations for current JP fuels. The additized fuels are then tested to determine the thermal stability of jet fuels at 218C (bulk temperature) and 260C (wetted wall temperature) respectively. Fig. 11 shows the result. There has been a

significant decrease in deposits formed in the JP-8+100 fuel versus the base JP-8.

Morris and Binns (1994) are currently in the process of setting up the ARSFSS test facility to simulate the thermal stresses of an F-22 aircraft fuel system. This test facility comprises hydraulic and heating systems to simulate the wing tanks, engine nozzles, flow divider valves, actuators, and servos. The system is designed with recirculation of stressed jet fuels and will soon be used to further evaluate the most effective additive package.
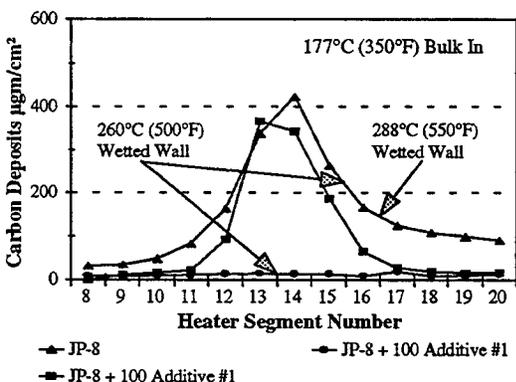

Fig. 11: EDTST showing improvement in thermal stability by addition of JP-8+100 additive package.

3. Engine and Flight Tests: Although extensive laboratory testing of JP-8+100 was conducted, the true validation of the fuel is obtained by testing in actual aircraft hardware. Initial combustion tests of JP-8+100 were conducted in a CFM-56 combustor rig at Wright Laboratory. These tests showed excellent combustion behavior through a wide range of fuel to air ratios. Also, the fuel was tested in a F100-PW-200 engine in a 50 hour, 224 TAC (total accumulated cycles) test. The engine was "dirty" with visible fouling typical of those found in the fleet. The JP-8+100 additive cleaned lightly fouled components, and improved overall engine performance by opening several small orifices such that the engine could operate at design conditions. Several other engines were tested (T63-A-700, F100-PW-200 (4000 TAC test), F100-PW-229 and in components of the F119-PW-100 engine) with similar improvements. Since these tests were successful, a flight test was conducted at Edwards AFB in September 1994. An F-16 with a F100-PW-220E engine was flown for 4.4 hours throughout the entire flight envelope and including engine restarts. This test found no problems, which cleared the fuel for use in other aircraft. Currently, a field demonstration at Kinsley Field, Oregon is being conducted to quantify long term benefits of JP-8+100.

ADVANCED JET FUELS - BEYOND JP-8

As stated earlier, the JP-900 fuel completely eliminates the need to recirculate fuel. Currently, there are two radically different designs for this fuel. The first is a totally new fuel produced from highly thermally stable hydrocarbons, principally saturated cyclic paraffins. A second, and a more cost-effective but an ambitious approach, is to build upon the experience gained in the "JP-8+100" program and develop an additive to extend the thermal stability of JP-8 to produce JP-900.

Edwards and Liberio (1994a) and Edwards and Zabarnick (1993) have studied the first approach in a flowing system. They have investigated several candidate compounds including Decalin, JP-10 (exotetrahydrodicyclopentadiene), methylcyclo-hexane, JP-7, and several normal paraffins. They found that the JFTOT breakpoint was a good indicator of fuel thermal stability at 480C. Edwards and Liberio (1994b) also studied the effects of oxidation versus pyrolysis. They report the interesting result that at high temperatures the surface depositions of decalin and JP-7 could be reduced by saturating with air or adding benzyl alcohol. This is in contrast to the lower temperature autoxidative regime where removal of oxygen results in decreased deposits for nearly all fuels. They further identified the temperature regime resulting in significant pyrolysis as the major indicator of fuel degradation.

Eser et al. (1992) have identified several compounds that exhibit significant stability in the temperature regime of JP-900. Recently, Eser et al. (1994) have identified activated graphite as a possible additive for JP-900. They propose that the activated graphite works in two ways to reduce deposits at 480C. First is the basic equipartitioning of deposits between test surface and the activated carbon surface. However, GC analysis showed that the presence of activated graphite also inhibited the decomposition of large chain hydrocarbons, probably through a hydrogen donor mechanism that has yet to be fully explained.

SUMMARY

This paper has discussed the development of a high thermally stability JP-8+100 fuel which provides a 50 percent improvement in the heat sink capability over conventional JP-8 fuel, and offers significant cost and safety advantages over JP-4 fuel. Some principle advances made towards achieving this goal are:

1. New test techniques were developed that are superior to the established go/no-go JFTOT type tests. Also, new analytical tests were discovered to follow oxygen consumption and carbon deposition, antioxidant, peroxide, phenols, polar carbon, and sulfur concentrations in static and flowing fuel systems.
2. A free radical theory of thermal and oxidative stability was developed. Also, a thermal stability scale was developed based upon statistical analyses.
3. Global reaction mechanisms were discovered and used in computer models to predict oxidation and deposition processes in jet fuels.
4. An additive package was developed for JP-8 fuel. Screening tests were used to select appropriate additive combinations and the EDTST has shown significant improvement in JP-8 fuels using one additive package.

Finally, some ideas on the development of an advanced JP-900 fuel have been presented including testing of possible compounds and additives.

REFERENCES

Anderson, S. D., Harrison III, W. E., and Roquemore, W. M., 1994a, "Development of TS Additive Package for JP-8," 5th International Conference on the Handling and Stability of Liquid Fuels, Rotterdam, the Netherlands.

Beal, E. J., Hardy, D. R., and Burnett, J. C., 1992, "Results and Evaluation of a Jet Fuel TS Flow Rig which Employs Direct Gravimetric Analysis of both Surface and Fuel Insoluble Deposits," *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels,* U.S. Department of Energy Washington D. C., Vol. 1, pp. 245-259.

Biddle T. B., Hamilton, E. H., and Edwards, W. H., 1994, "United Technologies Corporation R&D Status Reports to WL/POSF, Contract No. F-33615-90-C-2051," Wright Patterson Air Force Base, OH.

Chin, J. and Lefebvre, A. H., 1992, "Experimental Techniques for the Assessment of Fuel Thermal Stability," *J. Prop. Power,* Vol. 8, pp.3-4.

Chin, L. P., Katta, V. R., and Heneghan, S. P., 1994, "Numerical Modeling of Jet Fuel Autoxidation in Flowing Systems," *ACS Petroleum Chemistry Preprints,* Vol. 39, pp. 19-25.

Dagget, D. L. and Veninger, A., 1994, "The Development of an Aviation Fuel Thermal Stability Test Unit," 39th International Gas Turbine and Aeroengine Congress, The Hague, the Netherlands, Paper No. 94-GT-217.

Dieterle, G. L., Binns, K. E., and Williams, T. F., 1994, "System Evaluation of Improved Thermal Stability Jet Fuels", 5th International Conference on the Handling and Stability of Liquid Fuels, Rotterdam, the Netherlands.

Edwards, J. T., 1992, "Deposition During Vaporization of Jet Fuel in a Heated Tube," 30th Aerospace Sciences Meeting, Paper No. AIAA 92-0687, Reno, NV,

Edwards, J. T. and Liberio, P. D., 1994a, "The Thermal/Oxidative Stability of Fuels at 480C (900F)", *ACS Petroleum Division Preprints,* Vol. 39, pp. 86-91.

Edwards, J. T. and Liberio, P. D., 1994b, "The Relationship between Oxidation and Pyrolysis in Fuels Heated to 590C (1100F)", *ACS Petroleum Division Preprints,* Vol. 39, pp. 92-96.

Edwards, J. T. and Zabarnick, S. 1993, "Supercritical Fuel Deposition Mechanisms" *Ind. Eng. Chem. Res.,* pp. 3117-3121

Eser S., Song C., Copenhaver R., and Parzynski M., 1992, "Kinetics of Thermal Degradation and Solid Formation During High-Temperature Stressing of Jet Fuels and Related Compounds", *ACS Petroleum Division Preprints,* Vol. 37, pp. 493-504,

Eser, S., Gergova, K. M., Arumugam, R., Schobert, H. H., 1994, "Effect of High Surface Area Activated Carbon on the Thermal Stability of Jet Fuel", 5th International Conference on the Handling and Stability of Liquid Fuels, Rotterdam, the Netherlands.

Grinstead, R. R., 1994, "Evaluation of JP-8+100 Additives by Isothermal Corrosion Oxidation Test and Microcarbon Residue Test," University of Dayton Technical Report: Dayton, OH, UDR-TR-94-85.

Grinstead, R. R., Heneghan, S. P., Striebich, R. C., and Zabarnick, S., 1994, "Jet Fuel Thermal Stability and Analytic Test Data," University of Dayton Technical Report: Dayton, OH, UDR-TR-94-20.

Hardy, D. R., Beal, E. J., and Burnett, J. C., 1992, "The Effect of Temperature on Jet Fuel Thermal Stability using a Flow Device which Employs Direct Gravimetric Analysis of both Surface and Fuel Insoluble Deposits," *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels,* U.S. Department of Energy Washington D. C., Vol. 1, pp. 260-271.

Harrison III, W. E., 1990, "Aircraft Thermal Management: Report of the Joint WRDC/ASD Aircraft Thermal Management Working Group," WRDC-TR-90-2021, Wright Patterson AFB OH.

Hazlett, R. N., 1991 Thermal Oxidation Stability of Aviation Turbine Fuels, American Society for Testing and Materials, Philadelphia, PA.

Heneghan, S. P., 1993, "Analysis of Hetero-Atom Compounds in Jet Fuels," Ohio Valley Chromatography Symposium, Heuston Woods, OH.

Heneghan, S. P., 1994, "Determining and Understanding the Global Oxidation Parameters of Jet Fuels," *ACS Petroleum Division Preprints,* Vol. 39, pp. 14-18.

Heneghan S. P., and Kauffman R. E. "Analytic Tests and Their Relation to Jet Fuel Thermal Stability," 5th International Conference on the Handling and Stability of Liquid Fuels, Rotterdam, the Netherlands.

Heneghan, S. P. and Zabarnick, S., 1994, "Oxidation of Jet Fuels and the Formation of Deposits," *Fuel,* Vol. 73, pp. 35-43.

Heneghan, S. P., Locklear, S. L., Geiger, D. L., Anderson, S. D., and Schulz, W. D., 1993a, "Static Tests of Jet Fuel Thermal and Oxidative Stability," *AIAA Journal of Propulsion and Power,* Vol. 9, pp.5-9.

Heneghan, S. P., Williams, T. F., Martel, C. R., and Ballal, D. R., 1993b, "Studies of Jet Fuel Thermal Stability in A Flowing System," *Trans. ASME J. Eng. Gas Turb. Power,* Vol. 115, pp. 480-484.

Jones, E. G., Balster, W. J., and Post, M. E., 1993, "Degradation of a Jet-A Fuel in a Single Pass Heat Exchanger," International Gas Turbine and Aeroengine Congress and Exposition: Cincinnati, OH, Paper No. 93-GT-334 (Accepted for publication in *Trans. ASME Jour. Eng. Gas Turb. Power*).

Kauffman, R. E., 1989, "Development of a Remaining Useful Life of a Lubricant Evaluation Technique, Part III: Cyclic Voltammetric Methods", *Lubrication Engineering,* Vol. 45, pp. 709-716.

Kauffman, R. E., 1992, "New Techniques to Predict and Evaluate the Effectiveness of Antioxidants in Jet Fuels," *ACS Petroleum Division Preprints*, Vol. 37, pp. 412-417.

Kauffman, R. E., 1994, "New, Rapid Techniques for Determining the Hydroperoxide Content, Oxidation Stability, and Thermal Stability of Jet Fuels," 39th International Gas Turbine and Aeroengine Congress, The Hague, the Netherlands, Paper No. 94-GT-346.

Katta, V. R., Jones, E. G., and Roquemore, W. M., 1993, "Development of Global Chemistry Model for Jet-Fuel Thermal Stability Based on Observations from Static and Flowing Experiments," 81st AGARD Symposium on Fuels and Combustion Technology for Advanced Aircraft Engines, Collifero, Italy, AGARD-CP-536, Paper No. PEP-19.

Krazinski, J. L., Vanka, S. P., Pearce, J. A., and Roquemore, W. M., 1992, "A Computational Fluid Dynamics and Chemistry Model for Jet Fuel Thermal Stability," *J. Eng. Gas Turb. Power*, Vol. 114, pp. 104-110.

Martel, C. R., 1987, "Military Jet Fuels," AFWAL-TR-87-2062, Wright Patterson Air Force Base, OH.

Marteney, P. J. and Spadaccini, L. J., 1986, "Thermal Decomposition of Aircraft Fuel," *Trans. ASME J. Eng. Gas Turb. Power*, Vol.108, pp. 648-654.

Morris, R. W. And Binns, K. E., "Evaluation of Improved Thermal Stability Jet Fuels in an Advanced Reduced Scale Fuel System Simulator", Abstract to 5th International Conference on the Handling and Stability of Liquid Fuels, Rotterdam, the Netherlands, page 42.

Murray, M. J., 1949, "Total Phenols in Gasolines and in Cresylic Acids," *Anal. Chem.*, Vol. 21, pp. 941-945.

Rubey, W. A., Striebich, R. C., Anderson, S. A., Tissandier, M. D., and Tirey, D. A., 1992, "In-line Gas Chromatographic Measurement of Trace Oxygen and Other Dissolved Gases in Flowing High Pressure Thermally Stressed Jet Fuel," *ACS Petroleum Division Preprints*, Vol. 37, pp. 371-377.

Schulz, W. D., 1992, "Oxidation Products of a Surrogate JP-8 Fuel," *ACS Petroleum Division Preprints*, Vol. 37, pp. 383-392.

Zabarnick, S., 1993, "Chemical Kinetic Modeling of Jet Fuel Autoxidation and Antioxidant Chemistry," *Ind. Eng. Chem. Res.*, Vol. 115, pp. 1012-1017.

Zabarnick, S., 1994, "Studies of Jet Fuel Thermal Stability and Oxidation Using a Quartz Crystal Microbalance and Pressure Measurements," *Ind. Eng. Chem. Res.*, Vol. 33, pp. 1348-1354.

Zabarnick, S. and Grinstead, R. R., 1994, "Studies of Jet Fuel Additives Using the Quartz Crystal Microbalance and Pressure Monitoring at 140C," *Ind. Eng. Chem. Res.*, Vol. 33, pp. 2771-2777.

10