

Thermal
Oxidation
Stability of

Aviation
Turbine Fuels

Robert N. Hazlett



Monograph 1

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ASTM Publication Code Number (PCN)
31-001092-12



ASTM
1916 Race St.
Philadelphia, PA 19103

Library of Congress Cataloging in Publication Data

Hazlett, Robert N.

Thermal oxidation stability of aviation turbine fuels/Robert N.

Hazlett.

(Monograph: 1)

Includes bibliographical references and index.

ISBN 0-8031-1248-3

1. Airplanes—Fuel. 2. Fuel—Oxidation. 3. Fuel—Thermal properties. I. Title. II. Series: Monograph (American Society for Testing and Materials); 1.

TL704.7.H39 1991

629.134'351—dc20

91-36246

CIP

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Dedication

I dedicate this book to my wife, Margaret, who patiently encouraged me throughout and accepted my long hours at the word processor. I also recognize those who have been positive influences in my professional career: Max Barber, my high school science teacher; Dr. Ruth Thompson, my college chemistry professor; Dr. William McEwen, my thesis advisor for my Ph.D. research; and Dr. Homer Carhart, my long-time mentor and friend at the Naval Research Laboratory.

Acknowledgments

The author thanks the following individuals for furnishing copies of figures or tables used in the monograph.

Royce P. Bradley, Wright-Patterson AFB: Figure 1 of Chapter III.

Richard H. Clark, Shell Thornton Research Centre: Figures 6 and 7 of Chapter IV; Figure 6 of Chapter V; Figure 4 of Chapter VI; Figure 1 of Chapter VIII; Figures 2 and 3 of Chapter IX.

T. F. Lyon of General Electric Co.: Figure 2 of Chapter I.

Robert E. Morris of the Naval Research Laboratory: Figure 1 of Chapter IX.

E. M. Nesvig of Erdco Engineering: Figure 1 of Chapter II.

C. J. Nowack of the Naval Air Propulsion Center: Figure 3 of Chapter I; Figures 3 and 4 of Chapter III; Figure 4 of Chapter IV; Table 1 and Figures 3, 7, and 8 of Chapter V.

John E. Schmidt of Boeing Co.: Table 2 and Figure 4 of Chapter I; Figure 3 of Chapter X.

William F. Taylor of Exxon Research and Engineering: Figure 2 of Chapter VI; Figure 3 of Chapter VII.

George R. Wilson of Alcor, Inc.: Figure 2 of Chapter II.

The author thanks Richard H. Clark of Shell Thornton Research Centre, Pierre J. Marteny of United Technologies Research Center, and C. J. Nowack for providing many important documents and papers used in writing the monograph.

The author also thanks the reviewers, whose suggestions significantly improved the readability and technical quality of the monograph. He also thanks his wife Margaret who diligently proofed the text.

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Glossary of Terms, Acronyms, Symbols, and Standards

A	area
AAFSS	advanced aircraft fuel system simulator (United States Air Force)
AFAPL	Air Force Aero Propulsion Laboratory (U.S.)
AFDTA	aircraft fuel deposit test apparatus (single tube rig built by United Technologies Research Center)
AFFB	USAF fuel bank sample
AF-SIM	see AAFSS
AKU	advanced kinetic unit (single tube rig built by Esso Research and Development Co.)
AN-2	hindered phenol antioxidant (Ethyl Corp.)
AO	antioxidant
ARCO	Atlantic-Richfield Co.
ASTM D 1655	Specification for Aviation Turbine Fuels (U.S.)
ASTM D 1660	Test Method for Thermal Stability of Aviation Turbine Fuels (uses ASTM-CRC fuel coker)
ASTM D 2276	Test Methods for Particulate Contaminant in Aviation Turbine Fuels
ASTM D 3241	Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)
at%	Atomic percent
AVTUR	kerosene-type <i>aviation turbine fuel</i> (U.K.)
B-52	U.S. Air Force jet bomber
BP	British Petroleum, Ltd.
BuMines	Bureau of Mines (U.S.)
C	carbon (chemical element)
CFDC	computational fluid dynamics and chemistry (physicochemical model for predicting flow and deposit phenomena)
CFR	Cooperative Fuel Research (organization that became the CRC)
CI	corrosion inhibitor (also used as lubricity improvers)
COED	char oil energy development: a coal liquefaction process developed by FMC Corp., Princeton, NJ
Coker	ASTM coker used in specification testing for thermal stability
CRC	Coordinating Research Council (U.S.)
DFM	diesel fuel marine (U.S. Navy fuel for ships)
DMD	deposit measuring device (dielectric method developed by Southwest Research Institute)
DOD	Department of Defense (U.S.)
DOE	Department of Energy (U.S.)
DTS-1	USSR flow rig for thermal stability studies
E_{act}	energy of activation for chemical or physical process
EDS	Exxon donor solvent coal liquefaction process
F-14	U.S. Navy fighter aircraft
FCA	fuel coking apparatus (UTRC)

FDTA	fuel deposit test apparatus (UTRC multitube rig)
FIMS	field ionization mass spectrometry
FOA-3	fuel oil additive No. 3 (duPont)
FOA-310	fuel oil additive No. 310 (duPont)
FSII	fuel system icing inhibitor
GE	General Electric Co.
GE-4-SIM	General Electric fuel system simulator
GE-NZ	General Electric fuel nozzle test facility
GOST-9144	thermal stability test methods used in USSR
GOST-11802	aviation turbine fuel specifications
GOST-17751	
H	hydrogen (chemical element)
<i>h</i>	heat transfer coefficient
H-COAL	a coal liquefaction process developed by Hydrocarbon Research, Inc.
Hitec 515	corrosion inhibitor (Ethyl Corporation)
HR/MS	high resolution mass spectrometry
HTU	heat transfer unit (built by Esso Research and Development for CRC SST program)
HX	heat exchanger
ID	inside diameter
IFAR	injector feed-arm rig (Shell Thornton)
in. Hg	inches of mercury (measure of pressure)
IONOL	hindered phenol antioxidant (Shell Chemical Co.)
IP 323	Institute of Petroleum (U.K.) designation for Thermal Stability Test Method by JFTOT
IR	chemical analysis by infrared
Jet A	designation for commercial aviation turbine fuel refined to ASTM D 1655 specification (kerosene type)
Jet A-1	designation for low freeze point commercial aviation turbine fuel refined to ASTM D 1655 specification (kerosene type)
Jet B	designation for commercial aviation turbine fuel refined to ASTM D 1655 specification (wide-cut type)
JFA-5	thermal stability additive composed of polymers, organic amines, and amides (duPont)
JFTOT	jet fuel thermal oxidation tester (manufactured by Alcor, Inc. and used in many jet fuel specifications)
JP-4	U.S. military jet fuel (wide-cut type); specification MIL-T-5624M
JP-5	U.S. military jet fuel (high flash point kerosene type); specification MIL-T-5624M
JP-7	USAF special jet fuel for high-speed aircraft (low volatility); specification MIL-T-38219B
JP-8	U.S. military jet fuel (kerosene type); specification MIL-T-83133B
JPTS	USAF special jet fuel with high thermal stability; specification MIL-T-25524C
kCal/mol	kilocalories/mole (measure of energy in a chemical or physical process)
kJ/mol	kilojoules/mole (measure of energy in a chemical or physical process)
Lube	lubricant
MDA	metal deactivator additive
MEC	main engine fuel control
MHR	mini heated reservoir (used as a preheat device with JFTOT)

MINEX	miniature heat exchanger rig developed by General Electric Co.
MS	mass spectrometry
N	nitrogen (chemical element)
NAA	North American Aviation Co.
NASA	National Aeronautics and Space Administration (U.S.)
NAPC	Naval Air Propulsion Center (U.S.)
NIPER	National Institute for Petroleum and Energy Research (U.S.)
NRL	Naval Research Laboratory (U.S.)
O	oxygen (chemical element)
OD	outside diameter
PDA	phenylene diamine antioxidant
ppb	parts per billion
ppm	parts per million
PRC	Petroleum Research Centre, Baghdad, Iraq
psia	pounds per square inch absolute (measure of pressure)
psig	pounds per square inch gauge (measure of pressure)
<i>q</i>	quantity of heat
RAF	reference aviation fuel from CRC fuel bank
RFT	rectangular flow tester (UTRC)
RP-1, RP-2, and RP-3	grades of aviation turbine fuel (Peoples Republic of China)
S	sulfur (chemical element)
SIMS	secondary ion mass spectrometry
SR-71	high-speed reconnaissance aircraft (USAF)
SS	stainless steel
SST	supersonic transport
STHTR	single tube heat transfer rig (Shell Thornton)
SY2226	thermal stability test method used in People's Republic of China
T-1, TS-1, T-2 and RT	grades of aviation turbine fuel (USSR)
TDR	tube deposit rater (used by some organizations to rate deposits on JFTOT heater tubes)
TOSCO	company active in developing oil shale as a source of hydrocarbon fuels
TOPANOL	hindered phenol antioxidant (ICI, Ltd.)
USAF	United States Air Force
UTRC	United Technologies Research Center
XPS	X-ray photoelectron spectroscopy (used to analyze surfaces and deposits)

CHAPTER I

Introduction

In the formative years of gas turbine engine development, it was thought that the engine could run on most liquid fuels. It was soon realized, however, that much better performance could be obtained if fuel properties were restricted. The number of properties specified increased over the years, and today's aviation gas turbine fuels must meet a long list of requirements. In fact, our current jet engine fuels have the most extensive specifications of all hydrocarbon-based fuels.

For instance, it was determined that the starting of a gas turbine engine, either on the ground in cold weather or in the air after a flameout, was controlled by properties such as vapor pressure, distillation range, and viscosity. High levels of aromatic hydrocarbons decreased combustor life and increased smoke in the aircraft exhaust. Other important properties which required specification limits were corrosion, materials compatibility, water separation, freeze point, heat of combustion, safety, electrical conductivity, and stability.

Stability relates to the fuel's resistance to change in properties which would degrade the performance of the aircraft or the fuel-handling system on the ground. Most physical properties and the bulk chemical composition of aviation turbine fuel do not experience any significant changes during storage or use. Properties which are sensitive to trace amounts of chemical components, however, undergo changes which are important to aircraft operation. This can occur due to depletion of an additive through chemical reaction or through absorption onto a pipeline or other fuel-handling component. Desorption of surfactants or polar compounds can also drastically alter properties and cause a fuel to fail a specification. Properties which are particularly subject to this type of behavior are electrical conductivity, water separation, and stability.

The term *stability* is normally reserved for use in the context of a small chemical change in the fuel. This may occur at ambient temperatures, in which case it is designated as storage stability. Chemical changes associated with storage stability are formation of hydroperoxides, insoluble sediments, and gums.

A second type of instability relates to fuel degradation at elevated temperatures in an aircraft fuel system and engine. A poor fuel will form insoluble materials under the thermal stress in a jet engine, and these materials will coat surfaces and/or plug filters. This type of stability is called *thermal oxidation stability* if oxidation is involved and *thermal stability* if dissolved oxygen is absent from the fuel. Thermal oxidation/thermal stability of jet fuel is the subject of this monograph. Although the term *thermal stability* is appropriately used only for instability occurring in the absence of oxygen, it will be used interchangeably with *thermal oxidation stability* throughout this monograph. The context will make clear whether oxidation is involved or whether pyrolysis is the chemical phenomenon being addressed.

Previous Reviews of Thermal Oxidation Stability

The concern about thermal oxidation stability of aviation turbine fuel surfaced in the early 1950s. Substantial work was done on the subject in the next decade, and an extensive review was completed by the Bureau of Mines in 1962 [1]. This review emphasized fuel composition,

stability additives, and test methods. Approximately 100 reports or articles were reviewed and abstracts presented. Summarizing statements were presented on the major topics, conclusions were made, and recommendations were submitted.

A second major review of thermal stability was published in 1979 by the Coordinating Research Council (CRC) [2]. This work by multiple authors divided the subject into seven topics followed by a summary chapter. Over 200 references were listed, and abstracts were included for over 150 of the publications. The topics addressed in the CRC report were:

1. The importance of thermal oxidation stability.
2. Test devices and methods.
3. Fuel system simulators.
4. The chemistry of deposit formation.
5. The effect of deoxygenation on deposit formation.
6. Catalysis and the effects of metals.
7. The role of additives in deposit formation.

Substantial research has been conducted in thermal stability since the publication of the CRC report. This monograph will concentrate on the newer work but will include information from earlier studies where needed to give a comprehensive picture of the overall subject of thermal oxidation stability. The monograph is not an exhaustive review of all previous research, but the hope is that all significant aspects will be addressed in an adequate manner. Conflicting concepts and ideas are presented if such positions are supported by the literature. The author has presented his opinion on controversial topics in those cases where a reasonable explanation seems possible.

Early Experiences

The first occurrence of thermal oxidation instability came in the J-57 engine, the first U.S. jet engine with a high pressure ratio. Consequently, the fuel was exposed to high temperatures as it flowed through the manifold located in the compressor discharge region of the engine. The J-57 utilized a dual fuel feed system with primary and secondary flows [3]. Under cruise conditions, the engine operated mainly on the primary flow, and very little of the flow was delivered by the secondary manifold. Because of this low rate of flow in the secondary manifold, the fuel was subjected to high temperatures for prolonged periods of time. Under these conditions, the fuel could form insoluble materials, which deposited in the manifold and combustor nozzles. Nozzle flow became abnormal, heat release in the combustor became erratic, and the turbine section sustained severe mechanical distortion. The problem in the J-57 was alleviated by manifold redesign. This instability behavior was observed in tests of other engines and was reported to be more severe under simulated altitude conditions and in engines which employed fuel as a heat sink [4].

The fuel instability problems with the J-57 were encountered in military aircraft. A serious experience with commercial aircraft occurred in the 1960s [5]. This difficulty related to the erosion of the first stage turbine blades and air seals on JT3D/MC-6 and MC-7 engines. Costs for the replacement of the affected blades exceeded \$1,500,000 per year. This again resulted from deposition of fuel-generated insolubles in the combustor nozzles and accompanying distortion of the spray patterns. Copper contamination derived from a copper sweetening process in the refinery was responsible for the poor fuel quality.

Subsequent experience with aviation turbine engines demonstrated that other components of the aircraft fuel system, in addition to the nozzles, could be negatively impacted by poor fuel stability. The CRC review [2] summarized the problems as follows:

a. Fuel/Oil Heat Exchanger

In the heat exchanger, hot lubricating oil and hydraulic fluid are cooled by the fuel flowing to the engine. To reduce weight and volume, the tubes are designed to have very high heat transfer coefficients. For this reason, fuel-derived deposits having very little thickness can have a significant, adverse effect on heat transfer performance.

b. Fuel Metering Control

In the fuel control, which is generally downstream of the heat exchanger, heated fuel passes through many close-clearance valves and actuators in the servo system. Flow in this system is quite low, sometimes resulting in long residence time at high temperature. Fuel-derived deposits can form on sliding surfaces and cause malfunctions of the fuel metering system.

c. Fuel Injection Nozzles

In the fuel injection nozzles, heated fuel passes through the close-fitting, flow-divider valves and small passages in the spin chambers and metering orifices. Additional heat enters the fuel from the hot compressor case and the compressor discharge air stream in which the nozzle is located. Fuel-derived deposits having very little thickness can adversely affect the operation of the flow-divider valves. On other interior hot surfaces of the nozzle, particularly where fuel residence time is relatively long, deposits can become quite thick. Eventually some of these can flake off and block downstream passages.

As indicated with the J-57 problem, hardware modifications can resolve or improve a fuel stability problem but fuel quality is also critical to assure efficient operation of the aircraft fuel system.

Flight Tests

The ultimate proof of the relevance of thermal oxidation stability can come only from aircraft operations. This is costly and difficult, however, because instability problems develop over long time periods—hundreds and thousands of hours. Large quantities of fuel are required to conduct these long-term tests. Furthermore, each fuel must be isolated and its quality ensured (stability unchanged) throughout the test program, which could take several months. Exposure to high storage temperatures must be prevented, and contamination throughout the entire fuel-handling system must be controlled and monitored.

In spite of these difficulties, flight tests were conducted in the 1950s to evaluate the role of thermal oxidation instability in aircraft problems. The U.S. Air Force operated an F100C aircraft, powered by a J-57 engine, in a massive program—212 flights [3]. Five jet fuels of varying thermal stability were utilized, each fueling the aircraft for 100 h. Distinct differences were found in the performance of the five fuels. The worst fuel had been identified as a poor fuel on the basis of problems in B-52 operation [6]. Heavy deposits accumulated in less than 100 h, requiring premature engine overhauls at ten times the normal rate.

Extensive laboratory testing was conducted simultaneously with the flight tests [7]. This testing involved the development of the CRC coker and its use to evaluate the thermal oxidation stability of the five fuels in the flight program. It was observed that both the preheater deposits and filter pressure drop in the coker test must be included in correlating flight/laboratory data. A very useful comparison, Fig. 1, was developed involving the percent decrease in engine fuel flow and a coker rating that was the sum of the preheater deposit rating and the square root of the filter pressure drop.

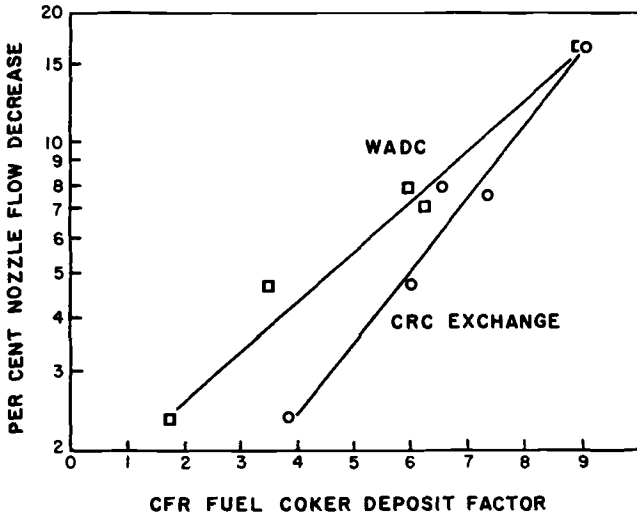


FIG. 1—Coker results related to flight tests. Reprinted with the permission of the Society of Automotive Engineers, Inc., 1959.

The U.S. Navy also reported flight experience on the J-57 engine in fighter aircraft [6,7]. Six engines in the program were inspected for nozzle and fuel manifold fouling after 50 to 135 h of operation. Deposition was minor in all of the engines, and no significant change in fuel system appearance was noted due to the variation of engine operating time. The fuel used in the Navy flight tests passed the coker test with a No. 1 maximum preheater rating and 17-kPa (5 in. of Hg) filter pressure drop after 300 min for conditions of 149°C (300°F) preheater and 260°C (500°F) filter. This indicates that the fuel was excellent since the filter was held at a temperature 56°C (100°F) higher than for standard coker specifications.

These flight tests demonstrated that fuel quality is critical for satisfactory operation of aviation turbine engines. Further, this body of information showed that laboratory testing could produce results which were very useful in defining thermal stability of fuels in jet engines.

Recent Problems with Thermal Stability

Recent concerns about thermal oxidation stability have arisen in Brazil, the United States, and China, but the published information on these problems is limited. The difficulty in the aircraft operating in the People's Republic of China involved a deposit in a fuel system filter [8]. No reports have been published on this problem.

The problems in Brazil and the United States involved CF6-80A engines. In addition, the Brazilian difficulty was found on CF6-50E engines. In both engines, brownish black coatings formed on the interior surfaces of the main engine control (MEC). The deposits caused unstable engine speed, throttle stagger, hot starts, engine stall, and high exhaust gas temperature during start [8,9]. Severe contamination was observed in 3000 h of flight time in some situations, although similar aircraft operating in other environments normally attain 18 000 h of MEC operation with no difficulty. A contaminated MEC must undergo a costly complete teardown. Forty CF6-80A MECs required cleaning in 1984 and twenty-two in 1985.

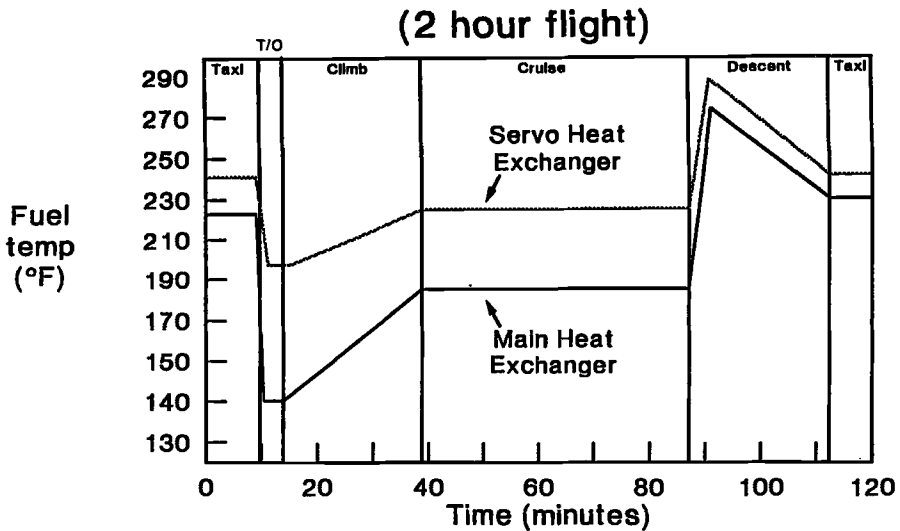


FIG. 2—Fuel temperature versus flight time for engine heat exchangers.

Multiple factors were entwined in this thermal stability problem: (a) engine design, (b) fuel specifications, (c) refinery processes, and (d) fuel chemistry. The CF6-80A and CF6-50E engines include heat exchangers to prevent icing in the MEC servo lines [10]. The resulting increase in the temperature of the fuel, which has a long residence time in the MEC, is shown in Fig. 2. The servo heater, which was on at all times, elevated the temperature 25°C (45°F). The MEC has been redesigned to bypass the heater when icing is unlikely.

In Brazil, aviation turbine fuel was purchased to the ASTM D 1660 method (ASTM Test Method for Thermal Stability of Aviation Turbine Fuels) at the 149/204°C (300/400°F) specification parameters (D 1660 will be described in Chapter II). The fuels obtained from some refineries under this specification were found to be marginal on the D 3241 JFTOT (ASTM Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels—JFTOT Procedure) test run at 260°C (see Chapter II for description). The Brazilian jet fuel specification has been changed, and the JFTOT procedure has replaced the ASTM Coker for the estimation of thermal stability. Both methods are permitted in the U.S. Jet A specification, ASTM Specification for Aviation Turbine Fuels (D 1655), but the JFTOT is the technique most widely used for jet fuel purchase in the United States.

The Brazilian fuel in question was refined by processes which included the Bender process (lead plumbite) to convert mercaptans to disulfides. Fuels produced with this process have poorer stability than those sweetened by other processes or those hydrotreated to lower sulfur content. The use of the Bender process has been discontinued at the pertinent refinery in Brazil.

Several deposits from the contaminated MECs were subjected to various analyses. In general, inorganic elements were a major part of these solids. Copper and sulfur were predominant in many of the deposits, but aluminum and sulfur were major components in a deposit from another aircraft. The chemistry will be discussed in Chapter VI.

The ASTM task force [8] found that the information on the MEC contamination was not

adequate to precisely define the cause of the difficulty. However, the measures taken with respect to engine redesign, fuel specifications, and refinery processing appear to have resolved the problem. Thus, both hardware and fuel quality may have been factors in unsatisfactory operation of the MECs.

These recent thermal stability problems suggest that current engine designs are moving in the direction to stress jet fuel to higher temperatures. It would appear that current specifications, which have served well over the years to insure satisfactory fuel, furnish little margin of quality for these increased temperatures.

Fuel Quality and Component Testing

The evaluation of fuels in flight tests were discussed earlier. These operations demonstrated that fuel quality can definitely reduce the time between overhaul. Although these expensive flight tests have been limited, many engineering tests at a much smaller scale have been conducted on components or closely related equipment of aircraft. The components used for thermal stability are usually injector nozzles, oil/fuel heat exchanger tubes, and burner feed arms.

Injector Nozzle Testing

A study on fuels of varying thermal stability was reported by Gleason et al. [11]. To explore deposit formation in the flow divider valve of an F101 fuel nozzle, the fuels were tested in a high-velocity hot gas stream at higher than normal temperatures for time periods up to 100 h. Periodic calibration throughout the test established the flow rates at various pressures. The flow/pressure patterns were defined for primary and secondary lines of the divider valve. Deposition in the flow divider valve would make its operation sluggish, and a higher pressure would be required to institute flow in the secondary orifice. Thus, the pressure hysteresis for secondary flow in the flow divider valve was quantitated. Different times to reach an increase (10%, for instance) in hysteresis were found for different fuels fed to the nozzle at the same fuel temperature.

This hot gas system was utilized in testing injector nozzles from many other engines [12–14] (see Fig. 3 of Chapter III for a block diagram of the test apparatus). The pressure hysteresis was defined for the flow divider valve of each nozzle where applicable. In addition, the reduction of flow due to restrictions in the nozzle produced by deposits was measured in the primary orifice and in the secondary orifice if applicable. A linear relationship was observed for the log of a specific increase in hysteresis versus fuel temperature, as were similar relationships for reduction in primary and secondary flow. Fuels of varying quality could be put into a unified relationship by plotting the log of time for a specific change in flow behavior versus the weighted temperature parameter shown below. This parameter includes two temperatures, the fuel temperature at the nozzle and the fuel breakpoint temperature (i.e., the temperature at which the fuel fails ASTM D 1655 thermal stability specification) as determined in the jet fuel thermal oxidation tester (JFTOT).

$$\text{Weighted Temperature parameter} = (C_0 + C_1 \times T_{BP} - T_F), \text{ } ^\circ\text{F}$$

where

- C_0 and C_1 = empirical coefficients,
- T_{BP} = JFTOT breakpoint in $^\circ\text{F}$, and
- T_F = fuel temperature at nozzle in $^\circ\text{F}$.

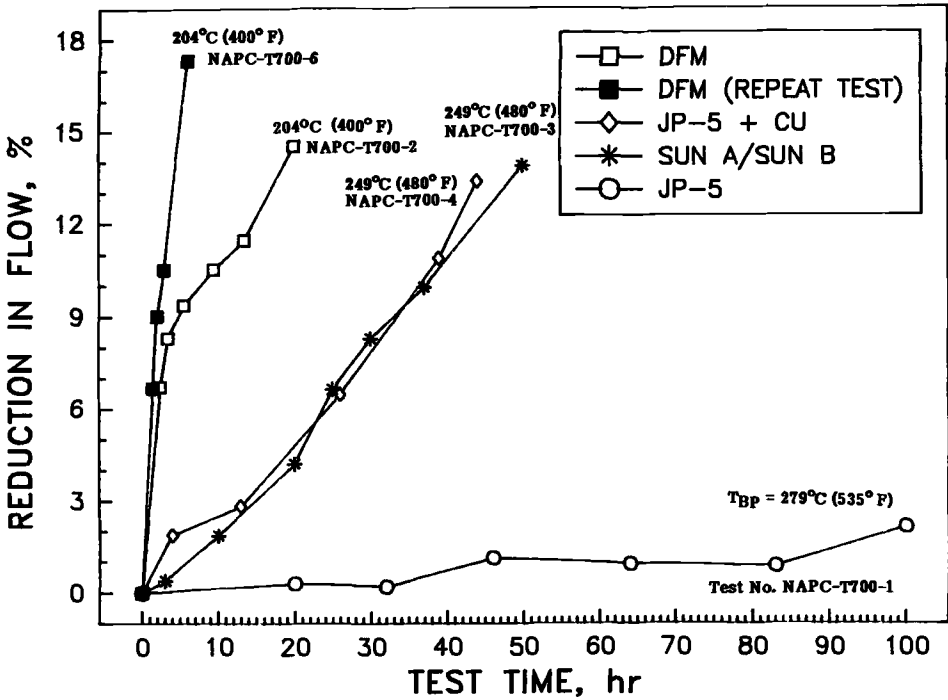


FIG. 3—T700 engine fuel-nozzle flow characteristics using four different fuels under similar test conditions, 200°C (393°F) fuel-in temperature, 374°C (705°F) filter cavity temperature, 20.4-kg/h (45-lb/h) fuel flow.

Each nozzle exhibited its own characteristic pattern, but the equation above involving the JFTOT breakpoint could be applied. The coefficients for each nozzle were different, however (see Table 1 of Chapter V for specific results). In addition, the coefficients for the hysteresis increase, for the primary flow reduction, and for the secondary flow reduction of a specific injector were different, sometimes markedly so. As expected, nozzles with larger orifices exhibited minor effects compared to those with narrow ones. The latter nozzles are less tolerant to fuel with a lower thermal stability. Thus, some engines, on the basis of the injector design, should show definite degradation in performance before other more tolerant engines burning the same fuel at similar thermal stress conditions. Further, these injector tests confirm that the operation of the engine varies with the fuel burned and that the quality of the fuel with respect to thermal stability is critical.

This latter point was dramatically demonstrated in a program to evaluate emergency fuels for Naval aircraft [15]. In these injector tests, a diesel fuel, a copper-contaminated JP-5, and a high aromatic fuel blend were compared to specification quality JP-5 in the hot gas system. The T700 engine nozzle used for this comparison was run at 2.27 kg (5 lb) per h with a fuel-in temperature of 200°C (392°F). The rapid reduction in flow for the diesel fuel is shown in Fig. 3. The high aromatic blend and the copper-doped fuel exhibited intermediate but similar flow reductions, but the JP-5 showed only a modest 2% reduction in 100 h.

TABLE 1—*Evolution/trend in aviation turbine engine design and performance (compared at altitude max cruise conditions).*

Engine Model	Time	Core Compression Ratio	Relative Fuel Consumption	Compressor Discharge Temperature, °C (°F)
JT4-11	(1958)	12.5/1	1.000	291 (555)
JT3D-7	↑ 20 years	14.8/1	0.848	298 (568)
JT8D-9		17.4/1	0.856	353 (668)
JT8D-17	↓	17.7/1	0.888	364 (688)
JT9D-7A		24.7/1	0.706	411 (771)
JT9D-7F	↓ (1978)	25.6/1	0.693	418 (784)
JT9D-70A		27.6/1	0.698	433 (811)
JT10D	↑ 12 years	30.9/1	0.642	453 (848)
E ³	↓ (1990)	38.6/1	0.586	481 (898)

Heat Exchanger Testing

Many research studies have shown that the quality of a fuel affects the degradation of heat transfer in a single tube derived from an aircraft engine or patterned after a tube from an engine. Shell (Thornton Research Centre) found that each of eleven Jet A-1 fuels tested gave an Arrhenius relationship versus fuel outlet temperature [16]. Large differences in slope and intercept were observed for fuels of various qualities, however, with fuels giving equivalent fouling rates at temperatures varying from 120 to 210°C.

The Naval Air Propulsion Center likewise found with copper-doped JP-5 that heat transfer deterioration varied with the quality of the fuel [17]. The deposition rate of insolubles on the inside of the F-14 heat exchanger tube also increased as the thermal stability of the fuel decreased.

The Air Force observed significant heat transfer variations in heated manifold studies in their fuel system simulator. The better quality fuels, particularly JP-7 fuels with much higher thermal stability, exhibited lower fouling rates [18–20].

The component test results confirm those of the flight tests that the thermal stability quality of a jet fuel is important to the operation of modern aircraft.

Stress Conditions in Aviation Turbine Engines

A jet aircraft has many sources of heat and most of these dump heat into the jet fuel [21]. Some of these sources, such as fuel pumps, warm the fuel as a consequence of working on the fluid. In other cases, the fuel must pass through a heated region such as the compressor discharge on the way to the combustor. Other systems require cooling, and the fuel, having a reasonable heat capacity, serves as a coolant. These latter heat sources include lubricating, hydraulic, electrical, and environmental systems. Higher speed aircraft dump greater amounts of heat in the fuel, thus increasing the thermal stress on the fuel. An aircraft operating in the descent mode puts more stress on the fuel since the heat sources are still at high temperatures, but the fuel flow rate is lower than in takeoff or cruise modes. Thus, a smaller quantity of fuel is absorbing about the same amount of heat.

Modern engines are significantly more fuel efficient than those produced in the 1950s [22]. This is shown in Table 1 for data on Pratt and Whitney engines. The relative fuel consumption had dropped from 1.000 to 0.698 in 1978 with a further projected drop to 0.586

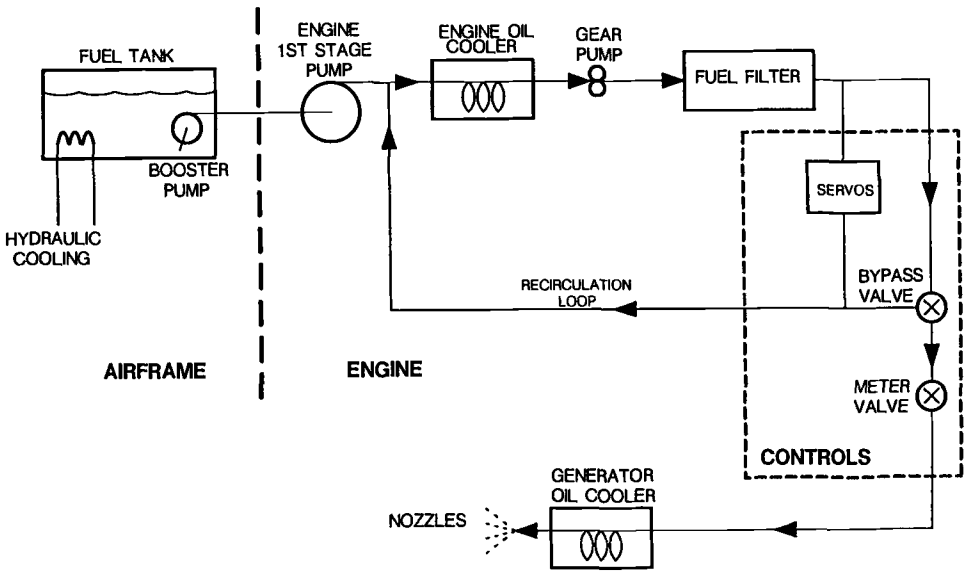


FIG. 4—Generic subsonic airplane fuel system.

in 1990. This comes about from a significant increase in the compression ratio, which affords a more favorable thermal cycle. As shown in the table, this results in much higher compressor discharge temperatures. Therefore the fuel, which is exposed to this higher temperature but at a lower flow rate, is stressed more severely in engines of recent design.

An Air Force report states that the primary jet fuels—JP-4, JP-5, Jet A, Jet A-1, and Jet B—can be used at a maximum temperature delivered to the combustor of 163°C (325°F) [21]. This report also details temperatures and heat loads throughout the fuel systems of selected military aircraft, both subsonic and supersonic.

Fuel and wall temperatures in a TF30 engine were measured by Marteny and Spadaccini [23]. During altitude cruise, the nozzle wall temperature ran from 260 to 316°C (500 to 600°F), and the temperature of the fuel entering the nozzle was 154 to 191°C (310 to 375°F). The temperatures in the afterburner (A/B) were less than these values during maximum power operation, but the fuel approached 427°C (800°F) following A/B shutdown.

Boeing Co. presented an overview of the thermal environment of a generic subsonic commercial airplane fuel system [24]. The components and fuel flow for this system are depicted in Fig. 4. Many characteristics of this system are tabulated in Table 2 for the flight idle (descent) mode, the regime putting the most stress on the fuel. Included are fuel flow rates, fuel residence times, fuel temperatures, and heat loads for the various components. In addition, the table lists the materials to which the fuel is exposed at the temperatures throughout the fuel system. Note the great variety of materials used at elevated temperatures—metals (aluminum, stainless steel, bronze, and nickel), glass, polymers (epoxy), and rubbers (silicone and fluorocarbon). The maximum temperature, with the exception of the fuel nozzles, is 160°C (320°F), very close to that recommended by Ref 21. The fuel temperature in the combustor nozzles can attain 204°C (400°F) in the descent mode, but the residence time is less than 1 s. Fuel temperatures in the cruise mode for this subsonic aircraft are 11 to 56°C (20 to 100°F) lower than those shown in the table for the descent mode and

TABLE 2.—Current commercial aircraft fuel environment, flight idle (descent) conditions.^a

Fuel System Component	Fuel Flow, lb/min (% pump)	Single Pass			Heat Load, Btu/lb	Pressure, psia	Surface Temperature, °F	Surface Material
		Fuel Temperature, °F	Residence Time, s	Fuel Temperature, °F				
Fuel tank	...	-40 to +120	5×10^3 to 5×10^4	...	2.5-3.5	-50 to +130	Al, epoxy, SR, ZnCr (ASTM D4054)	
Tank boost pump	8-15 (2.5-5%)	123-128	15-30	2-4	25-35	Fuel	Al, SS, carbon	
Engine 1st stage pump	8-15 (2.5-5%)	127-150	13-32	2-13	75-100	Fuel	Al, SS, carbon	
Engine oil cooler	200-350 (100%)	245-320	0.7-1.4 ^c	0.1-1.5	75-400	200-320	Al, SS	
Engine gear pump	200-350 (100%)	245-320	0.5-0.6	0.6-1.2	350-400	Fuel	Al, SS, bronze	
Fuel filter	200-350 (100%)	245-320	0.5-1.0	...	75-400	Fuel	Al, epoxy, glass	
Main engine control	200-350 (100%)	245-320	1.1-5.0	...	350-400	Fuel	Al, SS, Ni, silicone, FC	
Control servos	1-30 (0.3-10%)	245-320	1.0-20	...	350-400	Fuel	Al, SS, Ni, silicone, FC	
Bypass recirculation	180-325 (95-97.5%)	245-320	...	1.0-1.5	75-100	Fuel	Al, SS	
Generator oil cooler	8-15 (2.5-5%)	245-320	10-15	...	40-100	~320	SS, Ni	
Fuel nozzles	8-15 (2.5-5%)	~300-400	0.15-0.8	40-50	40-100	450-550	SS, Ni	

NOTE: Al = aluminum; SS = stainless steel; Ni = nickel alloy; SR = silicone rubber; FC = fluorocarbon; ZnCr = zinc chromates.

^aRevised table by John Schmidt, April 1991.

^bBased on maximum tank temperature of 120°F.

^c8 to 12 s for cooler outside of recirculation loop.

the residence times are shorter, much shorter in components such as the generator oil cooler and the fuel nozzles.

The wide range of stress conditions and the variety of materials characteristic of a modern aircraft fuel system highlight the problem of defining a specification test or designing a research device which will give a meaningful and relevant measurement of the thermal stability of a fuel. These data afford a useful starting point, however.

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CHAPTER II

Specification Methods and Limits

The importance of thermal oxidation led to the realization that fuels must be qualified in order to meet the thermal requirements for use in jet aircraft. This property is controlled by the composition of the fuel, including fuel additives and contaminants, and by the exposure conditions in an aircraft fuel system.

The composition of fuels is very complex since a typical jet fuel, be it a commercial or military one, contains several hundred hydrocarbons. In addition, trace amounts of many other organic and inorganic compounds may be present. These trace components, which contain sulfur, nitrogen, oxygen, and metals, exert very significant control over thermal oxidation stability. Furthermore, fuels are not only chemically complex, they differ greatly in composition as a result of variations in crude sources and refining processes. Thus, a straightforward chemical specification test is not a realistic approach to define thermal oxidation stability.

The thermal and flow conditions that fuels encounter vary with the aircraft and engine design and with the flight conditions. Fuels are also utilized in aircraft with differing fuel system designs. Therefore, a specification test cannot qualify a fuel for the many environments to which it may be exposed. In essence, a stability test must assure that the fuel performs acceptably at the most extreme thermal conditions to which it is applied.

Additional limitations on a thermal oxidation stability test include test time and fuel volume. Aircraft/engine effects related to stability exert problems in the time frame of hundreds of hours. A specification test, however, should be completed rapidly—not over a day maximum. Compensation for this time differential is two-fold: (1) increase the temperature of the test method to increase the rates of the chemical reactions; and (2) utilize sensitive techniques to estimate the amount of fuel-insoluble products. Similar considerations apply to the fuel volume situation; a test uses a few litres at most, whereas a large commercial aircraft will burn thousands of litres an hour.

In consequence of these chemical, thermal stress, and testing considerations, specification tests involve compromises, contain subjective and empirical evaluations, and are usually based on pass/fail criteria. Nevertheless, the specification test methods which are used have assured, with rare exceptions, fuels with acceptable thermal oxidation stability.

Two types of thermal stability tests (Table 1) are cited in various specifications [1] for aircraft turbine fuels. These are based on dynamic devices involving fuel flow through heated metal components and static fuel stress devices. The flow devices have predominated in specifications over the years, and the static tests have afforded supplementary quality control in a limited number of specifications. The exceptions to this statement are the USSR turbine fuel specifications, which utilize only a static test for civil aircraft fuel. The USSR also relies primarily on static thermal stress tests for military jet fuel.

The dynamic thermal oxidation testers expose fuel to high temperatures for less than 1 min and are useful for aircraft with modest ram heating (<2.2 Mach No.) and no bypass

TABLE 1—*Specification methods for thermal oxidation stability.*

Method Name	Number	Operational Principle
CRC Coker	ASTM D 1660	Fuel flow through heated components
JFTOT	ASTM D 3241 IP 323 ISO 6249	Fuel flow through heated components
Dynamic Test	USSR 17751	Fuel flow through heated components
Dynamic Thermal Stability	PRC (China) SY2226	Fuel flow through heated components
Research Coker	None	Preheated fuel pumped through heated components
Thermal Precipitation Rating	App. B of U.S. MIL-T-38219B	Static heating with collection of residue on filter for color comparison
Static Test	USSR 9144	Static heating with collection of residue for gravimetric measurement
Static Test	USSR 11802	Static heating with collection of residue, soluble gum, and insoluble gum for gravimetric measurement

fuel flow. The static tests typically heat the fuel for several hours and thus apply to aircraft in which the fuel attains an elevated temperature in tankage either by virtue of high Mach No. flight or by fuel recycle through heat exchange equipment or pumps. The research coker attempts to meet both regimes, combining a heated reservoir in which the fuel is preheated for several hours with a flow section exposing the fuel to higher temperatures for a short time.

CRC/ASTM Coker

This device was developed in the 1950s in the United States when the problem of fuel instability in aircraft fuel systems was first recognized [2]. Chemical tests and traditional static stability tests had been found to have little relevance to the high temperature problem. An apparatus was sought which would have some thermal stress conditions similar to fuel exposure during flight. A joint military/industry group under the jurisdiction of the Coordinating Research Council developed the coker [3], conducted cooperative testing, and compared the capability of this flow device with flight experience. On the basis of these efforts in the CRC, the CRC coker was accepted as a tentative standard in 1959 by ASTM. It was accepted as a full standard, D 1660, a short time later. D 1660 has been in military and civil specifications since then but has been almost completely replaced by the jet fuel thermal oxidation tester (JFTOT) in recent years. The CRC/ASTM coker, as well as spare parts, can no longer be purchased. The coker is an alternate method to the JFTOT in some specifications.

The coker (Fig. 1) combines two stress sections, a preheater tube with fuel flow followed by a filter housing heated to a higher temperature. The aluminum preheater tube is heated internally with an electric-powered cartridge heater. The electric power is controlled to attain a desired fuel-out temperature as the fuel flows between an outer and inner tube. The inner tube is rated visually at the end of a test for discoloration resulting from insoluble deposits plating onto the metal surface. The test is conducted in a region of laminar flow, and the length of tube exposed to fuel is 330 mm (13 in.). Attaining a specific fuel-out

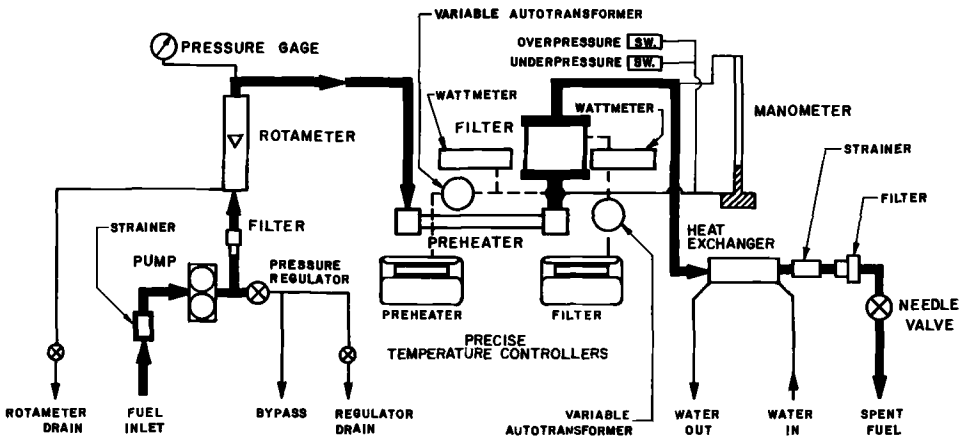


FIG. 1—Schematic diagram of CRC/ASTM fuel coker.

temperature requires a higher preheater tube metal temperature. Dukek [4] estimated that a bulk fuel outlet temperature normally used in specifications, 149°C (300°F), requires a maximum preheater skin temperature of 193°C (380°F).

The filter, located immediately downstream of the preheater, is in a separate metal housing with its own heating unit. This section represents the combustor nozzles or fine orifices in fuel control devices where insoluble products may lodge. A thermocouple measures the temperature of the housing, which, with its much larger mass, keeps the filter near the desired temperature. The pressure difference across the nominal 25- μm precision stainless steel filter is measured with a mercury manometer. The ΔP is measured periodically or until a maximum of 88 kPa (26 in. Hg) is reached.

Thus, a fuel is rated on two criteria in ASTM D 1660: (1) discoloration of the preheater tube and (2) pressure buildup across the filter. The fuel flow is normally set at 2.7 kg (6 lb) per hour, but the temperatures can be set at various values with an upper limit established by the volatility of the fuel. This limit for the preheater fuel-out temperature is 177°C (350°F) for JP-4 (Jet B) fuels and 232°C (450°F) for JP-5 fuels [3].

Specification parameters for commercial jet fuel and most military fuels is 5-h test time at settings of 149°C (300°F) for the preheater fuel-out temperature and 205°C (400°F) for the filter temperature.

In the application of this test in specifications, it is used on a pass/fail basis. Tube deposits are rated on a scale of zero to four by comparison with an ASTM color standard (available from ASTM headquarters as Adjunct No. 12-416600-00). The scale is as follows:

Deposit Code	Appearance
0	No visible deposits
1	Haze or dulling, no color
2	Barely visible discoloration
3	Light tan
4	Heavier than Code 3

The ASTM Aviation Turbine Fuel Specification D 1655 and most other jet fuel specifications that use this test require a passing fuel to have a rating less than Code 3 for the

preheater. The filter pressure drop rating for a satisfactory fuel must be no greater than 10 kPa (3 in. Hg). If the fuel fails either of these criteria, it is unacceptable. Fuels usually fail to pass the test on the basis of deposition on the preheater tube rather than on pressure drop.

The CRC Coker is allowed as an alternate in the Specification for Thermally Stable Kerosene (JPTS), U.S. MIL-T-25524c, Amendment 2. This specification requires testing at a preheater fuel-out temperature of 232°C with the filter temperature set at 288°C. A maximum tube rating of <Code 3 and a maximum pressure differential of 3.3 kPa (25 mm Hg) are limits in this specification.

Smith compared the ASTM Coker breakpoint temperature of several fuels with a failure temperature for the same fuels determined on the basis of heat transfer deterioration in the Shell Research single tube heat transfer rig (STHTR) [5]. The author found good correspondence, not only in the ranking of the fuels, but also between the two temperatures. This study validated the relevance of the coker to heat transfer measurements in engineering scale equipment.

The CRC Coker can be used as a research tool also, in which case the code ratings and pressure drop would be determined as a function of the preheater and filter temperatures.

Precision statements for the coker were defined in cooperative tests under ASTM cognizance. The repeatability and reproducibility are both poor. For instance, in the critical Code 2 to 3 range for preheater deposits, the allowable repeatability difference is two code numbers and the allowable reproducibility difference is 2.5 units. For pressure drop comparison, very substantial differences are allowed for repeatability, and, of course, those for reproducibility are even greater.

Jet Fuel Thermal Oxidation Tester

The CRC/ASTM Coker had several drawbacks. Each test required a large amount of sample, 19 L, and only one test could be completed in an 8-h day. The possibility of picking up wear debris in the fuel could not be eliminated since the pump was located ahead of the heated test section. Further, the test controls fuel temperature rather than metal temperature, a more important criterion in an aircraft fuel system. The precision of the test was also poor.

With these problems in mind, the CRC [6] evaluated several alternate techniques in a search for an improved method of rating aviation turbine fuel thermal stability. The jet fuel thermal oxidation tester (JFTOT) was selected as a replacement for the coker. The test parameters of the two devices are compared in Table 2, and Fig. 2 presents a diagram of the JFTOT apparatus.

The JFTOT was designed to and did overcome some of the serious shortcomings of the coker. The volume of fuel sample was drastically reduced, and the test time was cut in half. Pump debris was eliminated by placing a flow-defining gear pump beyond the test section. The test section was pressurized with nitrogen. System pressure was increased to allow fuel stress at higher temperatures. A floating piston in the fuel reservoir separated fresh fuel from spent fuel.

The heater tube is heated by resistance heating as an arm of an electrical circuit with temperature control by a thermocouple positioned at the point of maximum temperature (this position is 38.7 mm from the fuel inlet for the standard aluminum heater tube). The temperature profile is very sharp, rising from ambient at the fuel inlet (position 0.0 mm) to the control temperature at 38.7 mm. The filter in the JFTOT is located in the exit of the heater tube housing and is heated only by the hot fuel leaving the housing. Consequently, the filter is at a substantially lower temperature than the heater, the reverse of the coker

TABLE 2—Comparison of CRC Coker with JFTOT.

Parameter	CRC Coker	JFTOT
Fuel volume	19 L (5 gal)	0.6 L (0.16 gal)
Fuel flow rate	60 mL/min (6 lb/h)	3 mL/min
Test time	5 h	2.5 h
Temperature control	Fuel-out	Heater tube
Heating method	Cartridge heaters in preheater tube and filter housing	Electrical resistance heating of tube; filter unheated
Pump location	Before test section	After test section
System pressure	1.0 MPa (150 psig)	3.45 MPa (500 psig)
Length of heater tube	330 mm (13 in.)	60 mm (2.375 in.)
Fuel residence time in heater tube	10 s	13 s
Filter	25 μ m stainless steel	17 μ m stainless steel
Flow regime	Laminar	Laminar
Rating criteria	1. Tube deposits 2. Filter pressure drop	1. Tube deposits 2. Filter pressure drop

environment in which the filter is heated separately to a higher temperature than the preheater tube. This is probably a factor in the lower severity of the delta P measurement for the JFTOT versus the coker.

The same two rating criteria are used in specifications for fuels tested in the JFTOT and the coker. Heater tubes are rated using the same color standards mentioned under the description of the coker and with the same limit, less than a Code 3. The pressure drop limit for the filter is 3.3 kPa (25 mm Hg) for the JFTOT, much lower than the Coker limit. Further, it should be noted that the flow rate through the filter as well as the porosity, cross-sectional area, and temperature are much different.

The JFTOT was accepted as ASTM Standard Method D 3241 in 1973. It has almost completely replaced the CRC Coker as the aviation turbine fuel thermal oxidation stability method cited in specifications [1]. However, a number of specifications allow Method D 1660 as an alternate test to D 3241.

The test conditions spelled out for the JFTOT in most commercial and military specifications [1] require a heater tube control temperature of 260°C. ASTM D 1655, however, allows retesting at 245°C if a fuel fails at 260°C.

The JFTOT conditions are changed from the ASTM D 1655 parameters for two military fuels, JP-7 (MIL-T-38219B) and Thermally Stable Kerosene (JPTS)(MIL-T-25524C.Amd. 2). The heater tube control temperature is set at 355°C for JP-7 and 335°C for JPTS. The system pressure is kept at 3.45 MPa, the same value used in the D 1655 specification. The filter pressure differential for a satisfactory fuel is 3.3 kPa (25 mm Hg) maximum for these fuels, but the deposits on the heater tube are rated by the tube deposit rater (TDR) (see below) rather than the ASTM color standard. A maximum TDR of 12 is allowed for this measurement.

The U.S. Air Force examined the rating relationships between the ASTM Coker and the JFTOT [7]. Correlation between the two instruments could not be determined for JP-4 since most samples of this fuel boil at their breakpoint temperatures in the ASTM Coker. The best approximations of a valid range of JFTOT temperatures equivalent to the 149°C (300°F) Coker specification temperature for kerosene fuels was 228 to 262°C (442 to 504°F) for visual comparison. The comparable range using a spun 18 TDR rating for the JFTOT was 210 to 257°C (410 to 495°F).

In a similar study, the Naval Air Propulsion Test Center compared the breakpoint of

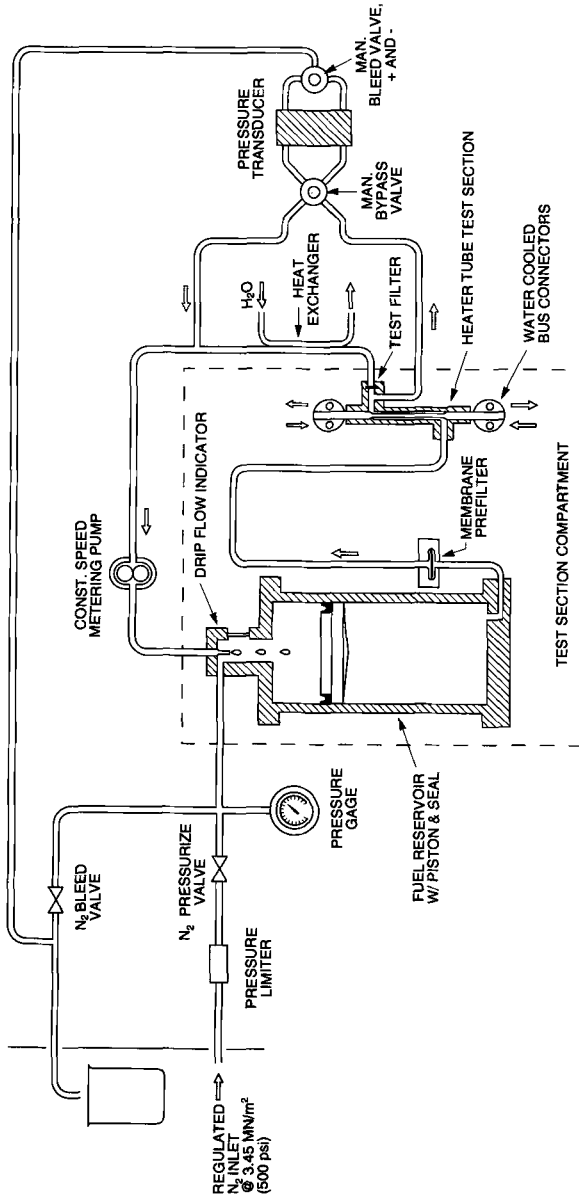


FIG. 2—Schematic diagram of the jet fuel thermal oxidation tester.

fuels with the coker and JFTOT [8]. The conclusion was reached that the JFTOT result will be 110°C (200°F) higher than the coker. The authors concluded that this relationship is not unrealistic since the JFTOT measures maximum heat exchanger metal temperature, whereas the coker measures the fuel temperature leaving the heat exchanger.

Kendall and Earls demonstrated that the breakpoint by the JFTOT afforded a reasonable relationship with deterioration of the heat transfer coefficient [9]. The latter measurement was conducted on the Shell Research single tube heat transfer rig at 225°C.

The subjective nature of the visual rating of tubes led to attempts to make the rating of deposits more objective. The most widely used instrument is a light reflectance meter which observes a reduced amount of light from a tube covered with a deposit. This tube deposit rater may be operated in a spun mode which gives an average reading around the circumference at a particular position or in the stationary mode looking for the maximum spot reading. Meter readings are made along the length of the tube to establish the maximum deposit rating. The United Kingdom Ministry of Defense allows this rating device as a secondary measurement method, but the method has been opposed by portions of industry.

A significant difficulty with respect to the TDR is how to rate the "peacock" or "abnormal" colors which give low light reflectance by the TDR and are rated as a fail by the visual method. Martel and Bradley have demonstrated with the combined use of Auger electron spectroscopy and an ion gun sputtering technique that the "peacock" deposits are very thick [10]. In fact, they correspond to a Code 3 or greater visual rating and are definite "fails" in a JFTOT test.

Recent measurements of deposit thickness by optical interference techniques have supported the viewpoint that "peacock" deposits are thick, of the order of one fourth to one half the wavelength of the incident light [11]. Continuing studies with optical interference as well as with dielectric strength measurements offer promise for development of a less arbitrary, more objective technique to quantitatively determine the amount of deposit on a tube.

The JFTOT is used as a pass/fail rating instrument for specification purposes. Consequently, no generally accepted method for determining precision is available.

In a recent critique, Datschefski has summarized the problems with the JFTOT [12]. He discussed heater tube metallurgy and particularly pointed out the inhibition of deposit formation on aluminum due to magnesium migration to the surface. The problem with rating tube deposits was also examined, and the author made a proposal to utilize carbon burnoff as a means of rating deposits. In addition, the author observed that the fuel is not preheated in the JFTOT and that the very low flow velocity affords laminar flow. This is in contrast to aircraft fuel systems in which the flow is turbulent in most of the components and tank fuel temperatures may reach 100°C. The author suggested several features which should be considered to overcome the aforementioned difficulties.

Research Coker

Shortly after the CRC Coker was developed but a number of years before work on the JFTOT began, it was anticipated that a device would be needed to qualify fuels for higher temperature operation. Efforts went into modifying the CRC Coker so that the fuel could be stressed in an environment representing heating in aircraft tanks during supersonic flight. The preheater and filter sections of the CRC Coker, with temperature capability increased to 400°C (752°F), were retained in the experimental device, which was named the research coker [2]. A heated reservoir was added to increase the time and degree of thermal exposure, and the system pressure was boosted to 1.7 MPa (250 psig) to handle increased fuel vapor pressures.

TABLE 3—USSR static test method limits (mg/100 mL).

Fuel	Gost 9144-79	Gost 11802-66
T-1 kerosene	Residue, 18 max	...
TS-1 kerosene regular	Residue, 10 max	...
TS-1 kerosene premium	Residue, 8 max	...
T-2 wide cut	Residue, 10 max	...
Thermally stable	...	Residue, 6.0 max Soluble gum, report Insoluble gum, nil
RT kerosene	...	Residue, 6.0 max Soluble gum, 30.0 max Insoluble gum, 3.0 max

This device was not widely used or tested and has never been adopted by a society or industry. Poor reproducibility between instruments was a factor in limiting its usefulness [13]. It was used by the U.S. Air Force to purchase JP-7, a low volatility kerosene used in high-speed aircraft (MIL-T-38219B). For this specification, the temperatures were set at 149°C (300°F) for the reservoir, 260°C (500°F) for the preheater out, and 316°C (600°F) for the filter. The test was run for 5 h at a flow rate of 2.7 kg (6 lb) per hour.

JP-7 thermal stability is now defined using the JFTOT at 355°C heater tube control temperature.

Other Dynamic Testers

The USSR and People's Republic of China use dynamic tests in some aviation turbine specifications. These tests are thought to be similar to the CRC/ASTM Coker. For instance, the USSR requires Gost Test 17751-79 for Specification RT Kerosene, No. 16564-71 [1]. This is a 5-h test run at 150 and 180°C, conditions similar to the D 1660 temperatures of 149 and 205°C. The tube rating criteria is 2.0 maximum (may be a different scale than ASTM color standard). The specification for filter pressure differential is set at a maximum of 10 kPa (0.1 atm or 76 mm Hg).

Less is known about the People's Republic of China dynamic test, SY2226. It is required for kerosene RP-1, RP-2, and RP-3 grades of aviation turbine fuel. Fuel must be tested periodically, but test conditions are not available. The pass criteria for RP-3 are the same as ASTM D 1655, 10 kPa (76 mm Hg) maximum for pressure drop and <Code 3 for tube color.

Static Testers

Static test methods are used as a supplementary check on thermal oxidation stability of JP-7 and as primary evaluation criteria for most aviation turbine fuels utilized in the USSR. The two types of tests are significantly different [14].

In the thermal precipitation rating applied to JP-7, 11.4 L of fuel are heated for 2 h at 149°C to simulate aircraft wing tank heating at supersonic flight conditions. Exposure in the heated reservoir totals 4.5 h when warmup and cooling times are included. Insoluble material formed during the stress is collected after the cooling period on a 0.45- μ m membrane filter. The color of the filter is rated against color standards in Appendix 3 of ASTM Method D 2276. A maximum rating of B-2 is allowed for an acceptable JP-7.

Two static tests are called for in USSR jet fuel specifications. Test parameters, which are

similar for both tests, stress 50 mL of fuel in sealed glass containers at 150°C in the presence of copper. Gost Method 9144-79 conducts the test for 4 h with a fuel/air ratio of 1/1.3, and Gost Method 11802-66 performs the test for 5 h with a fuel/air ratio of 1/3.5. Gost 9144-79 estimates the stability of the fuel on the basis of the amount of filterable insolubles. Gost 11802-66 uses this measurement as well as an estimate of the soluble gum and insoluble gum. Test limits for the various USSR fuels are different as indicated in Table 3 [1].

The presence of the copper in these tests makes the USSR static tests very severe. The reason for the copper exposure is not known. One can speculate that the USSR aircraft or fuel-handling system contain copper alloy components. In lieu of this possibility, it would seem that the copper is included to sharply reduce the length of the test.

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CHAPTER III

Simulators and Large-Scale Rigs

The specification devices discussed in Chapter II provide limited details on thermal oxidation with respect to aircraft design and operation. Much additional information is needed to design an aircraft system, select materials, and define thermal limitations. The specification testers are inadequate because they (a) operate at elevated temperatures to reduce test time, (b) minimize fuel consumption by reducing flow rate and test time, and (c) incorporate only one or two simple, generic parts in the stress portion of the device.

A NASA workshop [1] recommended a priority list for parameters of importance in building large-scale thermal stability testers. The results from use of such a rig could aid in the design of aircraft fuel systems and in defining the requirements for fuel quality. The priority list is shown in Table 1.

It is noteworthy that the workshop participants gave the same four parameters the highest priority both for fuel system design and for fuel requirements.

This chapter will present a description and the characteristics of several large rigs but will defer discussion of experimental test results with these devices to later chapters. *Fuel system simulators* are large-scale rigs which incorporate many components into a test system and use substantial amounts of fuel. Also included in this chapter are rigs which stress fuel in a limited number of components, frequently only one. This group of devices is based on engine-qualified equipment such as combustor nozzles, afterburner spraybars, and heat exchanger tubes. These latter testers are less complicated than the simulators, utilize smaller quantities of fuel, but are frequently operated for long periods of time, up to 100 h or longer. Test equipment designed to evaluate the stress in aircraft fuel tanks will also be treated in this chapter.

Chapter IV, which follows, will consider research devices other than those used in the specification methods discussed in Chapter II and the rigs described in this chapter. The devices dealt with in Chapter IV typically use volumes of fuel and stress times intermediate between those in Chapters II and III. The Chapter IV devices are frequently used for research in fuel chemistry, additive evaluation, fuel surveys, and temperature effects.

Fuel System Simulators

Three large-scale rigs are reported in the literature. All of these were designed for the purpose of addressing the thermal stability problems associated with supersonic transports. Chapter III of Ref 2 describes these devices, discusses some of the experimental results, and presents additional references.

GEA Fuel System Simulator

This simulator consisted of a 590-L (156-gal) heated tank with altitude control, boost pump, high pressure pump, fuel/oil/hydraulic heat exchanger, controls and accessories package, manifold drain valve, and nozzle [3]. Major emphasis was placed on heat exchanger

TABLE 1—Priority list for parameters of importance in building large-scale thermal stability testers.

Parameter	Design	Fuel
Wall temperature	1	1
Inlet temperature	2	2
Velocity (Reynolds number)	3	3
Residence time	4	4
Pressure	5	...
Surface/volume ratio	6	...
Materials	7	...
Surface finish	8	...
Cleaning	9	...
Dissolved oxygen	10	...
Fuel type	...	5
Contamination	...	6
Additives	...	7

performance. Operation of the fuel tank at reduced pressure afforded a significant reduction in the dissolved oxygen content of the fuel. The simulated heat exchanger consisted of eight tubes from an aircraft heat exchanger (the engine contained 341 tubes) which were heated electrically to achieve the desired metal temperature profile. Effects of hot fuel on close-clearance valves and a single combustor nozzle were examined. From the results obtained, estimates were made of the life expectancy of the various system components as limited by fuel-formed insolubles.

Advanced Aircraft Fuel System Simulator

This apparatus was built by North American Aviation, Inc. under the supervision of the Coordinating Research Council as a part of the United States SST program in the 1960s [4]. After this SST effort was concluded, the original rig was modified by North American for U.S. Air Force needs [5]. The Air Force then conducted extensive parameter and fuel testing related to their advanced aircraft.

The USAF simulator was not designed to simulate a specific aircraft but utilized conditions representative of those anticipated in high-speed aircraft. Airframe and engine components were both incorporated into this large-scale rig. A schematic of the simulator is shown in Fig. 1. Fuel was stored in five epoxy-lined underground 95 000-L (25 000-gal) storage tanks. Fuel was pumped from a storage tank into the 1500-L (400-gal) simulated fuselage tank or the 380-L (100-gal) simulated wing tank. Both tanks included simulated aerodynamic heating and cooling. Altitude simulation was provided. Fuel was pumped from the tanks through an airframe filter and heat exchanger. A high-pressure, variable-speed pump then pumped the fuel through an engine filter, heat exchanger, manifold, and nozzle. The two heat exchangers, airframe and engine, transferred heat from oil to the test fuel.

The number of tubes in the heat exchangers was determined by the flow rate required for one nozzle. The manifold consisted of a 305-cm (120-in.)-long smooth-bore Type 321 stainless steel tube that was heated by passing electric current directly through the tube. The tube had a 0.071-cm (0.028-in.) wall thickness and an outside diameter of 0.794 cm (0.3125 in.). Additional heat was supplied to the nozzle by replacing the sprayhead with a block of steel containing cartridge heaters.

The AF simulator was operated in two modes—steady state and cyclic. The second mode simulated flight profiles. Typical flow rates in the cyclic mode [6] were 22 L (5.8 gal) per

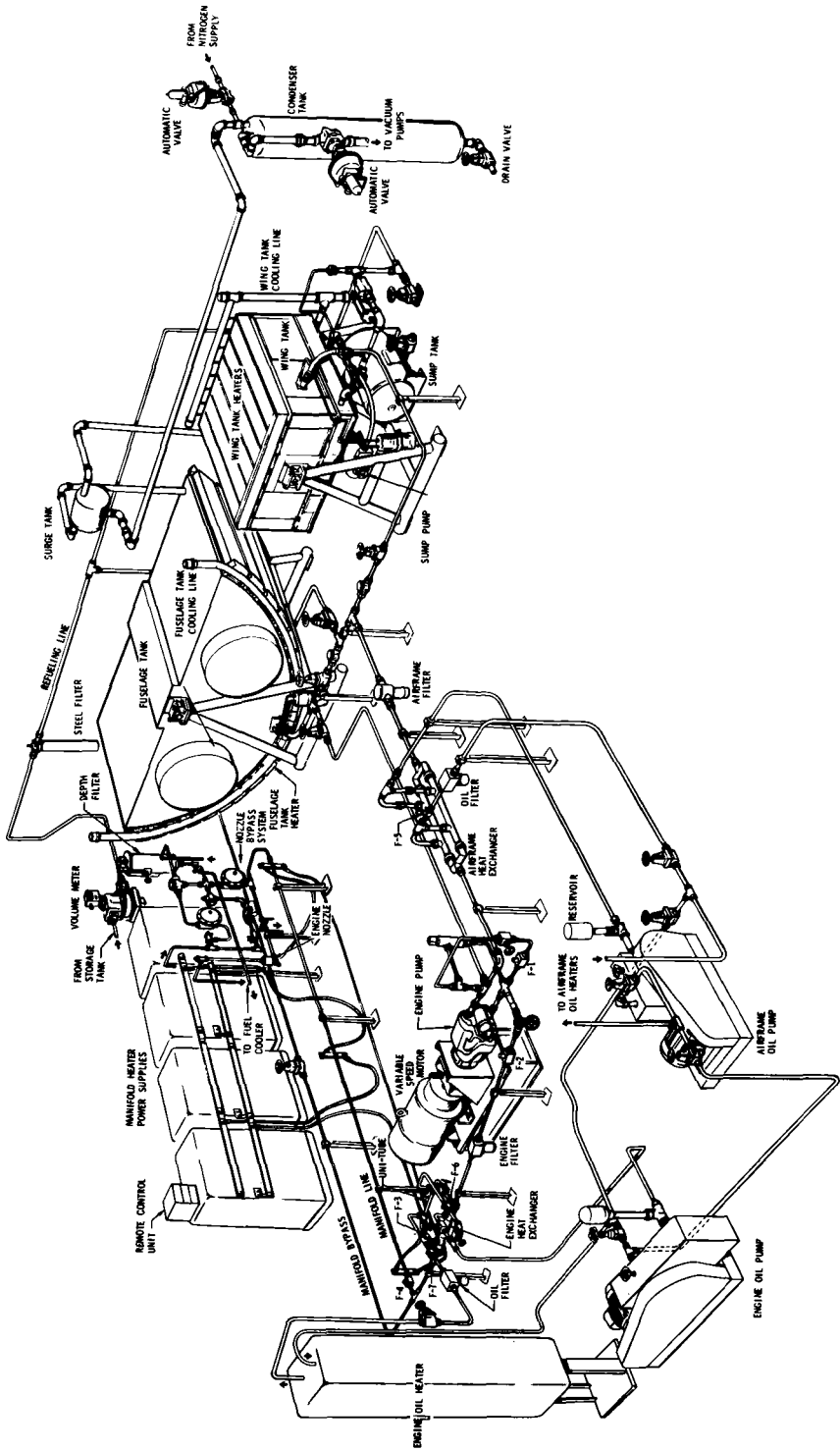


FIG. 1—Schematic of the U.S. Air Force advanced aircraft fuel system simulator.

min in climb/acceleration, 10 L (2.7 gal) per min during cruise, and 2.7 L (0.7 gal) per min during descent. Nine different fuels were evaluated in the extensive AF program which totaled up to 500 h of operation on some fuels. The tanks were examined for deposits, and other components were observed for performance degradation. Deterioration of heat transfer in the manifold due to deposition was determined using ten thermocouples attached to the tube. Changes in pressure drop through the nozzle were also measured. The manifold and nozzle were the components which most frequently exhibited difficulties due to poor fuel quality.

Half-Engine-Scale Fuel System Rig

The Concorde supersonic transport (SST) program in England and France faced the question: "Will a Mach 2.2 aircraft require a jet fuel of better thermal stability than an aircraft flying at subsonic speeds?" To supply some of the answers, a fuel system simulator was constructed at Shell's Thornton Research Centre in the 1960s [7]. This rig was designed on a somewhat more simple basis than the USAF apparatus and operated only at steady-state conditions and hence at a constant fuel flow rate and at a constant temperature during any one run.

A diagram of the Thornton rig is shown in Fig. 2. Fuel was taken directly from a refinery and pumped at 1900 L (500 gal) per h to a steam-heated heat exchanger and a heated glass-lined 1900-L (500-gal) conical vessel. In this vessel, the fuel was maintained at a selected temperature between 80 and 100°C for 1 h, simulating the bulk heating it would receive in the aircraft fuel tanks. Fuel was extracted from the holding vessel by a boost pump and delivered through three aircraft oil coolers in series. The first two coolers simulated the hydraulic and other auxiliary coolers in the aircraft. The flows through the third cooler, from a Pegasus engine, were arranged to reproduce velocities and temperatures expected in the Olympus 593 engine oil cooler. All three heat exchangers were supplied with hot oil as the heating agent. The test filter following the oil coolers was a stainless steel wire gauze with 17- μm porosity. The filtered fuel passed through to a full-scale engine pump operated to give the correct pressure level at the nozzles. Spent fuel from the nozzles was collected and cooled.

The engine oil cooler, the third in line, was operated at temperatures of 140 to 180°C. Plain or partially dimpled tubes were used in this test cooler. The cooler was instrumented so that the heat transfer coefficient could be determined throughout the 90-h runs. The test filter following the third cooler was maintained at the same temperature as the cooler. Increases in pressure across the test filter and oil cooler were monitored. The pressure increase was usually much greater through the filter than through the cooler. A third criteria of fuel performance used in the half-scale rig was the amount of deposit in the heat exchanger tubes.

Engine Component Rigs

Engine Nozzle Testers

Degradation of combustor nozzle performance is the most widespread problem associated with thermal stability. This has been addressed experimentally by utilizing a single, engine-qualified nozzle in a stress environment. The General Electric Co. (GE), under contract to USAF [8], tested J79 nozzles for 5 h. Minimal effects were observed for this short time period with any of 13 fuel samples. In later GE work [9-11] for the AF, stress tests were extended to 100 h and expanded to nozzles qualified for five additional engines.

This work was continued on U.S. Navy contracts with Southwest Research Institute (SwRI)

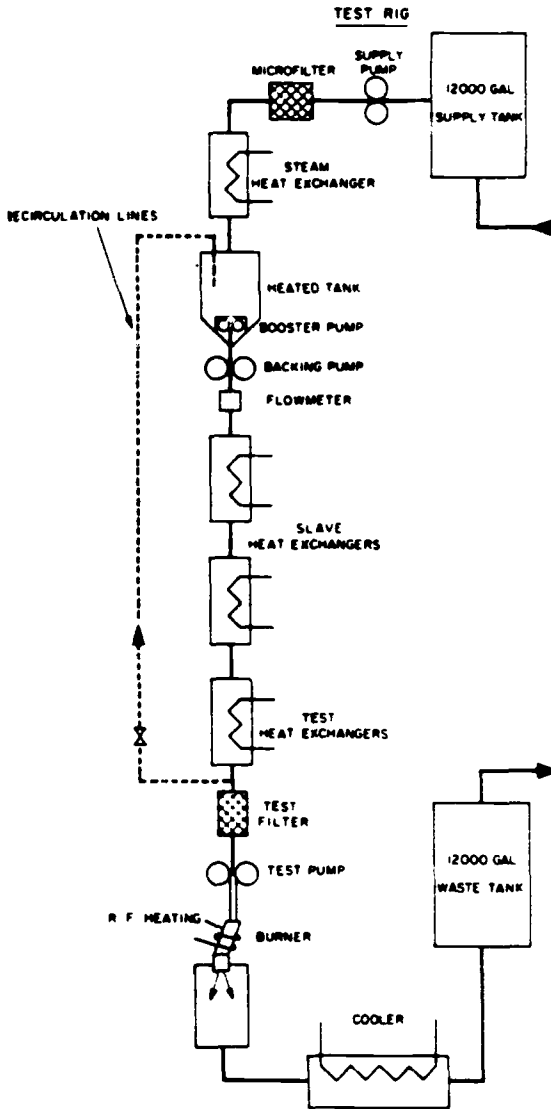


FIG. 2—Schematic of Shell-Thornton half-engine-scale fuel system rig. Reprinted with permission of the Society of Automotive Engineers, Inc. Originally published 1968.

[12–14]. GE did the nozzle testing on subcontract to SwRI. In addition, GE conducted a study of T700 and F404 nozzles for the Naval Air Propulsion Center [15]. In total, nozzles qualified on eleven different engines have been tested for extended time periods. Many of these programs observed degradation of nozzle performance with some jet fuels.

A nozzle test facility is shown in Fig. 3. Fuel is pumped into the facility, filtered, and heated by an oil/fuel heat exchanger. The heating oil was Therminol 55, a synthetic hydrocarbon mixture suitable for use from -20 to 316°C (0 to 600°F). The heated fuel transits

into the test section, where it is stressed at simulated engine conditions. The nozzle is immersed in a gas flow heated to the desired temperature by a natural gas burner. The fuel discharged from the nozzles is collected via tubes welded to the nozzle tips. This makes it impossible to observe the spray angle or quality, but avoids the necessity of burning the fuel or collecting a mist. The discharged fuel is cooled and collected in a storage tank.

Temperatures and pressures are monitored electronically at various points in the facility while fuel mass flow rate is measured directly. Nozzle temperature, fuel temperature, and fuel mass flow rate are accurately controlled. Thermocouples are attached to the nozzles at points considered significant for the formation of fuel deposits, such points also being suitable for installed engines in the event that flight tests would be considered for later correlation purposes. A flow cycle of 30 min is frequently used. As an example, the T700 nozzle is run for 29 min at steady-state flow of 20 kg (45 lb) per h, followed by 30 s at a 10% increase in flow, and finally by 30 s at 30% under steady-state flow.

Fuel nozzle fouling is defined by either a decrease in flow rate for a given fluid pressure drop, or, for atomizers having internal flow-divider valves, an increase in pressure hysteresis for secondary fuel flow. Criteria normally used in the GE work for a significant degradation in nozzle performance are as follows:

1. A 10% reduction in primary orifice flow.
2. A 5% reduction in secondary orifice flow, where applicable.
3. A 10% increase in hysteresis of the flow divider valve operation.

The temperature conditions in this test depend upon the particular nozzle, the stress characteristic of a specific engine, the fuel under test, and the flow cycle. Tests have been conducted at fuel temperatures into the test section between 130 and 230°C and at nozzle metal temperatures between 260 and 523°C. This compares with the recommended maximum fuel stress temperature of 163°C (325°F). Thus, the nozzle testing can be relatively severe.

Afterburner Spraybar Tests

Some military aircraft use afterburners to attain rapid acceleration in specific flight operations. The fuel flow may be intermittent, with periods of no flow. The stagnant fuel in the spraybars vaporizes after the flow is turned off but heavy ends are exposed to the high temperatures of the turbine exhaust. Deposition is of concern in such a situation, particularly with emergency fuels having higher end points than JP-4, JP-5, or JP-8.

Test facilities for afterburners are similar to those used for main combustor nozzles [16]. General Electric's experimental spraybar setup is much like that shown in Fig. 3 for nozzle testing. The fuel is preheated with steam rather than an oil/fuel heat exchanger since lower fuel inlet temperatures are required. Standard aircraft spraybars are placed in the test section and are heated by a hot gas flow. The effluent fuel from the spraybar is burned as opposed to collection of the liquid spray practiced with the nozzle test facility.

GE operated the spraybar apparatus with a fuel inlet temperature of 94°C and with the spraybar immersed in the hot gas flow at temperatures of 677 to 885°C. Note that the fuel temperatures are substantially below and that the temperatures of the hot gas in contact with the exterior of the test section are much higher than those used in the nozzle tests. Cyclic fuel flow is the standard mode of operation—7 s on, 23 s off. The flow rate is set at 93 kg (206 lb) per h for the J79 and 122 kg (269 lb) per h for the J85. The test protocol utilizes 4500 cycles. Flow calibrations on the test spraybars are conducted at 3 to 12-h intervals to define reductions in flow rate or increases in flow hysteresis.

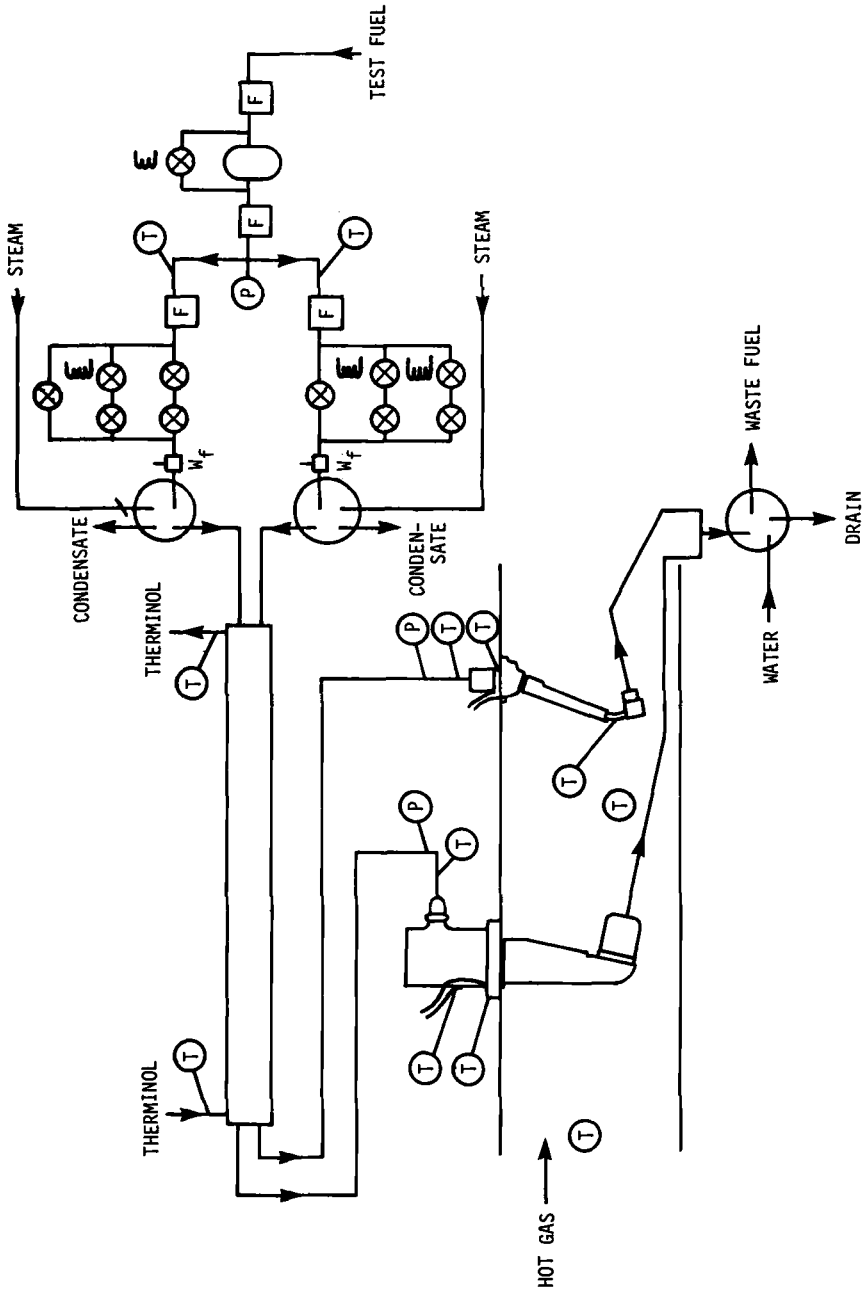


FIG. 3—Schematic of F404/T700 fuel nozzle fouling test rig (GE).

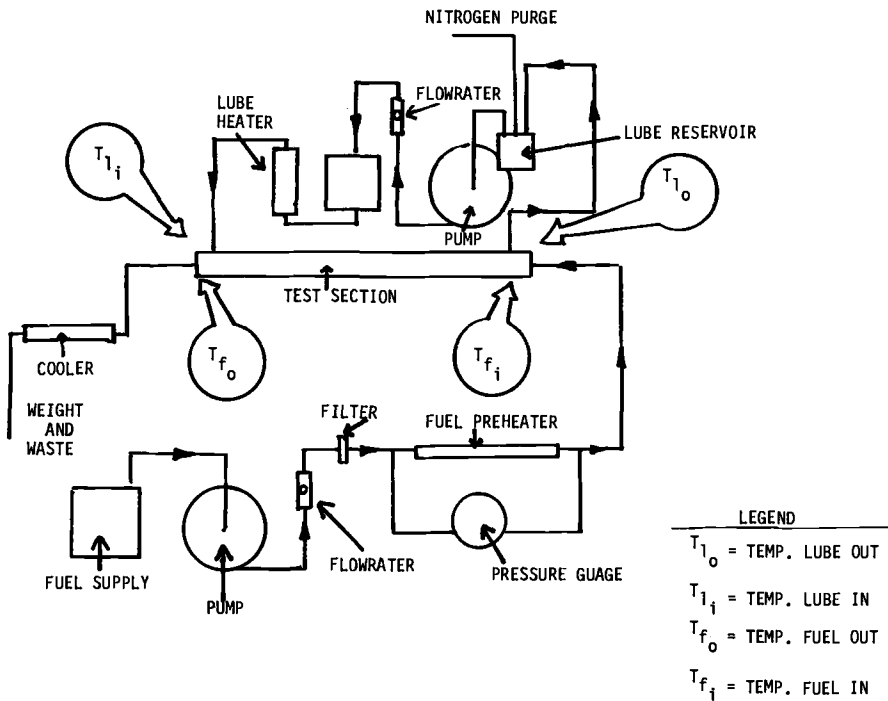


FIG. 4—Schematic of Naval Air Propulsion Center single tube heat exchanger rig.

Single Tube Heat Exchanger

Many thermal stability testers have been constructed and operated to measure the changes in heat transfer as fuel passes through a stressed test section. Most of these devices use simple tubes and will be examined in the next chapter. One setup, which utilized an engine qualified heat exchanger tube, will be described in this chapter.

This single tube heat exchanger was assembled and operated at the Naval Air Propulsion Center [17]. As seen in Fig. 4, fuel was pumped through the assembly consisting of a fuel preheater and a single aircraft heat exchanger (HX) tube from an F401 engine [18]. After exiting the preheater, the fuel was heated by a counterflow of hot engine lubricating oil moving through a surrounding annulus. Flows of both fluids were metered and the temperatures were maintained at prescribed values. The heat exchanger tube, typical of engine heat exchangers, had several depressions on the interior to insure turbulent flow of the fuel. Semicircular baffles were attached evenly along the outside of the tube to prevent distortion during thermal stress and to produce lube oil turbulence for even heating of the tube. The fuel flow was once-through while the lubricating oil was recirculated. The lube was inerted by sparging with nitrogen to prevent deposition on the oil side of the tube.

The heat exchange effectiveness coefficient was calculated from the fuel and lube temperatures and plotted as a function of time. The deterioration of heat transfer is a measure of deposit formation. The fuel in and out temperatures were maintained constant. Thus, the lube in temperature had to be increased as deposit on the fuel side built up insulation to heat transfer. This rig was operated at fuel and lube flows of 1.63 to 10.83 L/h (0.43 and

2.86 gal/h). Test conditions for fuel were in the range of 124 to 136°C and 170 to 188°C for the inlet and outlet temperatures, respectively. Lube initial temperatures were 178 to 210°C for the inlet and 171 to 199°C at the outlet. Typical tests were conducted for several hundred hours.

Some difficulty was experienced with temperature control. However, by averaging the data over 12-h periods, the data could be smoothed. A criteria for degradation used in this work was a 1% decrease in effectiveness coefficient. This point was reached beyond 100 h for a good fuel with a fuel-out temperature of 170°C, but fuel contaminated with copper exhibited much more rapid decay.

Fuel Tank Simulator

During the U.S. SST program, concern arose about deposition of fuel-insoluble products in the aircraft fuel tanks. This problem comes about from the following circumstances: certain tanks are used first during a flight; these tanks become quite hot due to aerodynamic heating; much of the fuel remaining in the tank evaporates at the low atmospheric pressure of the cruise portion of the flight (7.1 kPa/0.07 atm at 18 000 m/60 000 ft); the less volatile portion of the fuel is severely stressed during the rest of the flight; reactions forming deposits may occur.

Boeing Co. built and operated a fuel tank simulator to evaluate this potential problem [19]. A 132-L (35-gal) simulator was built (50-cm/20-in. cube) which could be heated on upper and lower surfaces by steam and be operated at reduced pressures. Tanks tested were made of aluminum, aluminum-coated Teflon, stainless steel, and titanium. In addition, panels of these materials and others were installed in the tanks for some tests. Insulated panels were included in the test program. Tests were conducted by putting 104 L (27.5 gal) of Jet A into the tank. Most of the fuel was removed after a soaking period. The tank simulator was then exposed to the temperature, pressure, and fuel management protocol desired for a particular flight profile. One test comprised on the order of 40 to 60 simulated flights. The tanks were then examined visually and by measuring emissivity. The deposit thickness was estimated in some tests by the beta backscatter technique.

The test temperatures chosen were representative of skin temperatures at Mach numbers of 2.5 to 3.0 (200 to 260°C). Simulated flights of 2 and 3 h were conducted. For an uninsulated tank, the fuel temperature was close to the tank surface temperature for most of the flight. However, the fuel temperature was near the peak temperature for only 10 min if the tank had insulation. Tank pressures were held at 7.1 kPa (0.07 atm) (open vent) or 35 kPa (0.34 atm) (pressurized tank).

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CHAPTER IV

Research Tests and Devices

Many devices have been constructed and used to examine various parameters of thermal oxidation stability. Tools for defining fuel quality for specification purposes have been discussed in Chapter II, and simulators and large-scale devices have been described in Chapter III. The devices dealt with in this chapter have been used in many extensive research programs. Although the distinction is somewhat arbitrary, the devices described in this chapter are generally less complicated and smaller than those presented in Chapter III. In consequence, it has been possible to conduct research programs requiring extensive changes in experimental conditions with modest amounts of fuel and within reasonable time frames.

The presentation in this chapter will divide the devices into the following categories:

1. Single tube testers.
2. Multiple tube testers.
3. JFTOT modifications.
4. ASTM coker modifications.
5. Static testers.
6. Other devices.

General descriptions will be given for each category, but the data obtained using these devices will be presented in later chapters. Detailed descriptions of representative devices will be given followed by brief references to other similar apparatuses.

Single Tube Testers

Single tube devices utilize tubes of various lengths, diameters, wall thicknesses, and materials. Tubes are frequently heated electrically, but hot oil or fluidized beds may be the source of heat input to the fuel. The vast majority of devices pass the fuel through the interior of the tube in contrast to the JFTOT specification device, which flows fuel on the outside of an electrically heated tube.

Fuel performance may be gauged by observing changes in heat transfer, by following changes in pressure through an associated filter, or by measuring the amount of deposit in the tube at the end of an experiment. The latter may be estimated by direct weighing or by combusting the deposit to carbon dioxide, which is determined quantitatively with a suitable detector. Observing heat transfer changes or filter plugging are physically more relevant to engine thermal stability problems and also have the advantage of giving data throughout a test. These properties usually require elevated temperature or long-term tests to achieve observable changes, however. Hence, the estimation of the quantity of deposit at the conclusion of a test is more widely used as a measure of fuel degradation. This technique affords only one point per run but allows shorter runs since methods to determine the amount of deposit are more sensitive than those of heat transfer and filter pressure changes. Kendall et al. [1] compared the increase in tube wall temperature with the amount of deposit by carbon burnoff at the end of tests of various lengths. These authors found an empirical

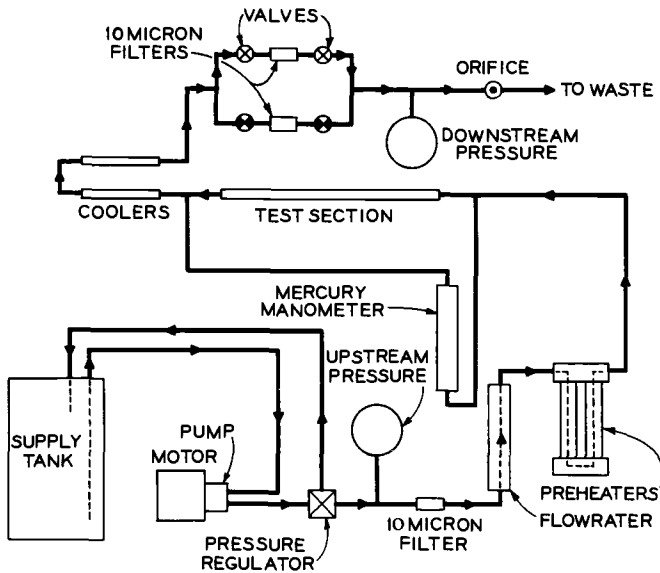


FIG. 1—Flow diagram of Minex rig (GE).

exponential relationship between the two properties. They utilized this correlation to estimate the amount of deposit formed at different test times. Thus they generated a picture of the buildup of carbon as a function of time throughout the test.

TeVelde et al., on the other hand, found a linear log-log relationship between measured deposit loading and a calculated deposit resistance derived from heat transfer parameters [2]. This relationship is more reasonable on a physical basis since the change in heat transfer would be expected to be a direct function of the thickness, and hence the mass, of deposit on the surface.

Minex Heat Transfer Rig

The Minex rig was developed by the General Electric Company to reproduce, in a miniature heat exchanger, the pertinent conditions that exist in full-scale heat exchangers constructed for SST aircraft [3-4]. Assessment of the thermal stability of a fuel by the Minex depended entirely upon precise functional measurements. At each temperature condition, sufficient data were obtained to determine whether the heat transfer coefficient was constant with respect to time or dropping due to progressive formation of tube wall deposits. Figure 1 presents a schematic drawing of the essential components of the Minex device. The basic test element was a small-bore, electrically heated steel tube. Fuel flow rate was approximately 7.6 L (2 gal) per h. Precise instrumentation was provided to measure temperatures and flow. Fuel was brought up to the desired test element inlet temperature by means of a three-element preheater.

A Minex test on a fuel consisted of a series of runs, each run conducted at constant conditions. Data were taken at intervals of about 90 min. A trend in heat transfer coefficient was established for a particular fuel-out temperature. This required 8 to 25 h. The fuel-out temperature was raised in 14°C (25°F) steps to establish a curve of loss rate versus temperature. Values of the heat transfer coefficient were calculated from the heat absorbed, the

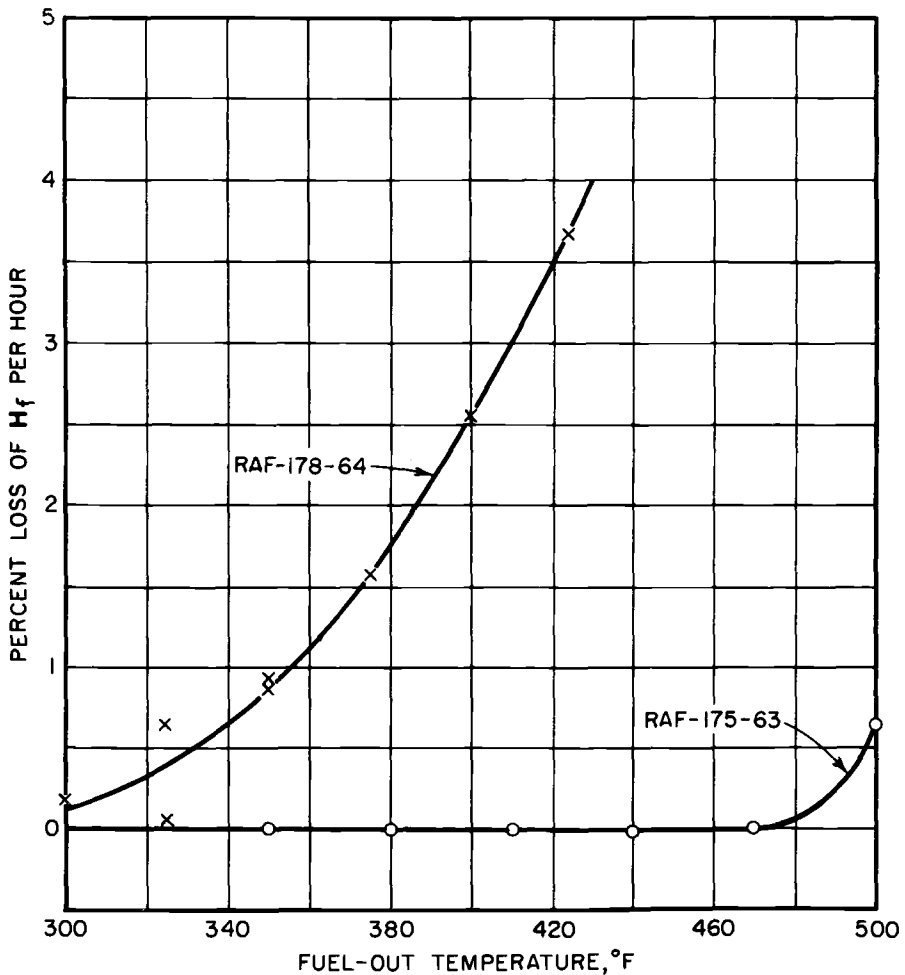


FIG. 2—Typical decay rates of heat transfer coefficients in the Minex rig.

tube inside area, and the temperature difference between fuel and metal at tube midpoint. Data were corrected to a common temperature level by using the Colburn equation for flow in tubes. A useful form of the data was a plot of the percent loss in heat transfer coefficient per hour versus fuel-out temperature. A comparison of two fuels tested in the CRC SST program is shown in Fig. 2 [5].

The Minex system was refined and modified several times, ultimately evolving to the Minex III [6]. The revised version used an electrically heated 1.45-m (57.1-in.)-long Type 321 stainless tube with a 0.56-mm (0.022-in.) ID and 1.07-mm (0.042-in.) OD. The measuring section comprised 0.40 m (15.7 in.) of the total length. Fuel flow rate was approximately 0.95 L (0.25 gal) per h. Initial work with volatile fuels produced unacceptable data, but this was rectified by increasing the pressure on the fuel from 3.1 to 4.8 MPa (450 to 700 psi). The Minex III was normally run in the program mode in which the maximum metal temperature was increased 0.55°C (1°F) per min. Reference sensors were incorporated into the

device to compensate for the increase in ΔT resulting from the temperature program. This avoided confusion between a temperature change due to deposits and the programmed temperature rise. Temperature differences of 0.3 to 0.8°C (0.5 to 1.5°F) were taken as endpoints to a fuel test. These modest changes were considered necessary to avoid buildup of excessive deposits, which were found to be very difficult to remove from the interior of the small tube. Tests with Minex III were much shorter than those with the original Minex. The Minex saw limited use since it was very difficult to remove the deposit from the tube after test. Reuse of the precision tubes was considered mandatory because of the cost.

Advanced Kinetic Unit

The Exxon R&E Company developed the advanced kinetic unit on contract to the U.S. Navy [7]. The molecular oxygen content of the fuel was adjusted in a treatment vessel by sparging with helium (Fig. 3). The sparged fuel passed through an oxygen sensor and then to a fuel delivery cylinder. The treated fuel was separated from the nitrogen drive gas by use of two individual pistons which were separated by a small water layer. The fuel was forced from this vessel into the test section with high-pressure nitrogen. The test section comprised a 1.21-m (48-in.)-long, 6.35-mm (0.25-in.) OD, 2.11-mm (0.083-in.) wall Type 304 stainless steel tube. The tube was heated externally by four separately controlled heating units. Thermocouples held against the outside wall of the test section controlled and monitored the rising temperature throughout the length of the tube. The stressed fuel passed through a cooler and then into a high-pressure reservoir where it was kept under nitrogen pressure at 6.9 MPa (1000 psig).

The rate of deposit formation was measured after a 4-h run. The reactor tube was cut into 16 sections, each 76 mm (3 in.) long. Carbon burnoff defined the amount of deposit on each section. Tests were conducted over the range of metal temperatures from 150 to 538°C.

Aircraft Fuel Deposit Test Apparatus

United Technologies Research Center designed, constructed, and used a resistance-heated tube apparatus which could be operated continuously at fuel flow rates up to 91 kg (200 lb) per h and pressures up to 6.9 MPa (1000 psig) [8]. As seen in Fig. 4, fuel was pumped from a 1040-L (275-gal) reservoir—which was equipped with air sparging capability—through appropriate filters, flowmeter, and a high-pressure-drop orifice into the test section. The Type 316 stainless steel tube was 2.4 m long, 3.17-mm OD, and 0.50-mm wall thickness. Thirty-three thermocouples distributed along the tube measured the outside wall temperature, and fuel pressure and temperature were measured at five points along the tube. From the test section, the fuel passed through a cooler, a back-pressure regulator, and then into a fuel dump.

A data reduction program was used to calculate heat transfer coefficients at each wall temperature measurement location. After the completion of a run, the test section was carefully sectioned into 51-mm-long specimens which were heated in a vacuum at 122°C for 16 h to remove fuel. The specimens were then subjected to carbon burnoff to estimate the amount of deposit laid down during the experiment. Flow was normally turbulent, and run time was in the range of 1 to 20 h.

Single-Tube Heat-Transfer Rig

The Thornton Research Centre of Shell Research developed a single-tube heat exchanger rig which that laboratory has used extensively over a period of many years [9]. This apparatus

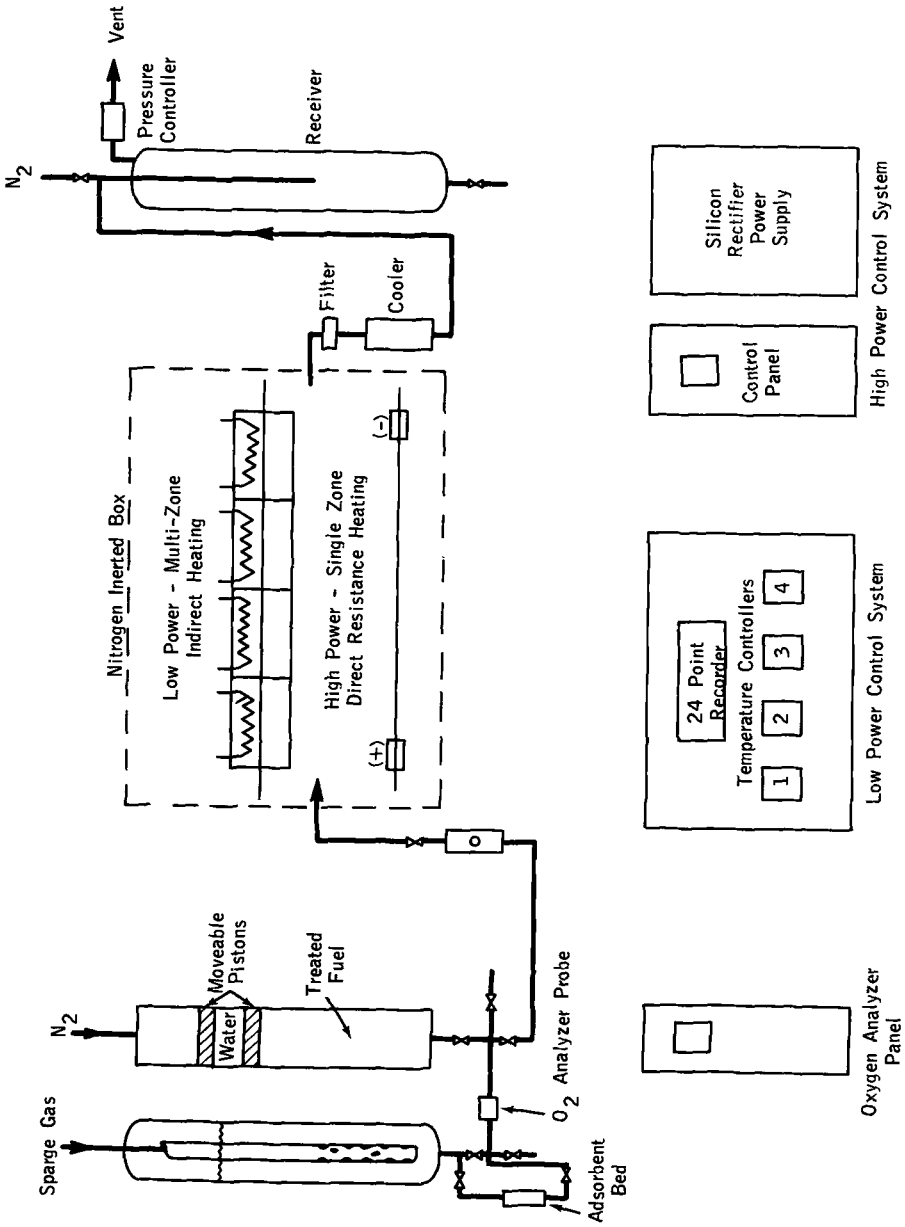


FIG. 3—Schematic of Esso advanced kinetic unit.

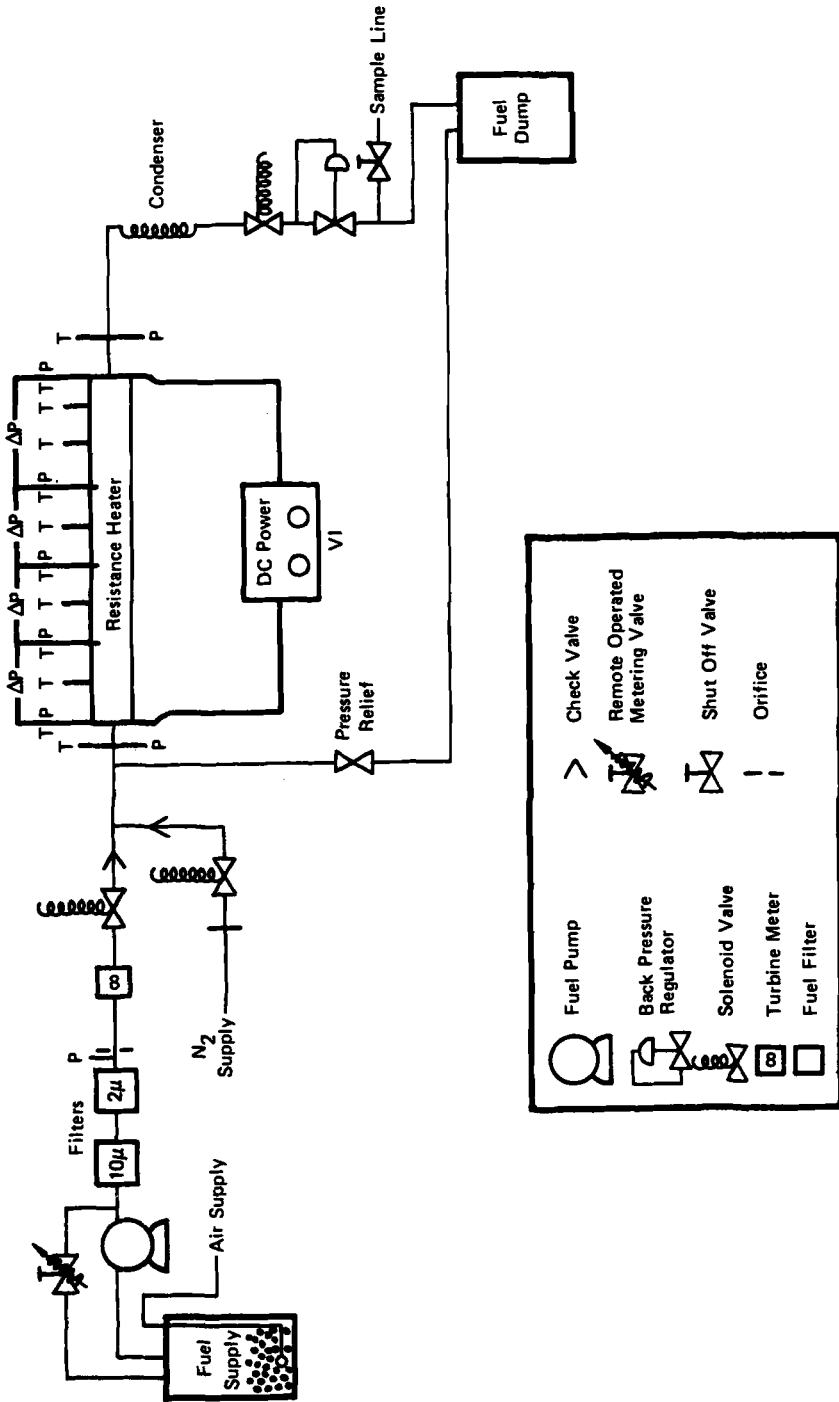


FIG. 4—Schematic of aircraft fuel deposit test apparatus (UTRC).

was originally used on the Concorde SST program but has been applied more recently to other topics including subsonic fuel problems. This rig was instrumented so that small changes in heat transfer coefficient could be measured accurately. The device comprised three heated regions, a 20-L glass vessel heated by a surrounding mantle, an electrically heated preheater, and an electrically heated test section. The stainless steel tubes in the latter had the following dimensions: length—0.198 to 0.273 m (7.6875 to 10.25 in.) and ID—2.13 to 2.79 mm (0.084 to 0.110 in.). Other dimensions have been used in later research as well as dimpled tubes to encourage turbulent flow in the test section. A test filter with a nominal pore size of 18 μm was located beyond the test section to trap solid decomposition products as evidenced by an increase in pressure drop. The heat transfer coefficient, h , is derived from measurements of heat input to the fuel, q , the internal area of the tube surface, A , and the logarithmic mean temperature difference.

The Thornton single tube rig has been applied to many studies and has been operated at a variety of test conditions. For instance, temperatures of the fuel in the heated flask have covered the range 70 to 125°C, fuel temperature at the test section outlet has covered the range 150 to 242.5°C, and Reynolds number in the test heat exchanger has varied from 3000 to 8100. Typical flow rates have been 1.89 and 3.78 g/s. Typical test times were 24 h, but runs extending to several hundred hours were also conducted.

Other Single Tube Rigs

Several other devices will be briefly described below. They have common components such as a fuel reservoir, a pump, and a heated tube.

Shell Development Company built an apparatus in the 1950s to examine filter clogging from thermally stressed fuel [10]. Heating was via circulating hot oil. Fuel outlet temperature was maintained at 149°C (300°F). Flow was laminar through a 0.69-m (27-in.)-long, 9.53-mm (0.375-in.) OD galvanized pipe. System pressure was 345 kPa (50 psig), much lower than that in an aircraft system. The increase in pressure through a nominal 2- μm filter was measured with time as the hot fuel exited the heated tube. Typical test times were 1 to 4 h.

A later Shell Development Company apparatus had significantly greater capability [11]. Tests of up to 100 h were conducted with flow rates affording both laminar and turbulent flow. Test pressures were either 3.45 or 6.9 MPa (500 or 1000 psia), and fuel temperatures were varied from 212 to 538°C (100 to 1000°F) in keeping with the application of the device to the SST program. Resistance heating was applied to 0.61-m (2-ft)-long tubes of various materials. Nominal tube ODs of 3.18 and 4.76 mm (0.125 and 0.188 in.) were used. A series of thermocouples afforded data from which heat transfer information could be derived. In addition, pressure drop was measured through the tube as well as through a sintered stainless steel filter downstream of the heated tube. Deposit formation was determined by carbon burnoff.

Engineers at the NASA Lewis Research Center built and operated a single tube apparatus that forced the fuel through the heated test section with gas pressure [12]. Fuel, either aerated or deoxygenated, was fed through a resistance-heated tube and then via a sintered metal filter before entering a cooler and waste tank. Nichrome V tubing of 3.96 or 4.76 mm OD was used, both with a wall thickness of 0.508 mm. Several thermocouples were equally spaced along the length of the heated tube, which was 1.37 m long. Tests were typically run at 1.37 kg/h for approximately 20 h at a fuel temperature at the tube outlet of 371°C (700°F). System pressure, which was established with nitrogen gas at the waste tank, ranged from 17 to 4240 kPa (2.5 to 615 psia). The thermocouple measurements gave some indication of

changes in heat transfer, but the main data derived with this rig came from carbon burnoff of segments cut from the heated tube at the conclusion of an experiment.

Vranos et al. at UTRC assembled a device, named the *fuel coking apparatus*, which contained an isothermal test section in order to afford easier interpretation of the data [13]. This was accomplished by raising the fuel temperature in a resistively heated stainless steel tube just ahead of the test section, which was encased in a massive temperature-regulated copper block. The Type 304 stainless steel test section within the block was either 1.80 or 4.78-mm (0.071 or 0.188-in.) ID and 0.69 m (27 in.) in length. Several thin strips weighing about 1 g each were inserted into the test section tube. Therefore, weighing on a sensitive balance was a feasible means of determining the amount of deposit formed during a stress test. Fuel flow, which was always in the turbulent region, could be varied between 4.1 and 13.2 kg (9 and 29 lb) per h, thus affording a range of velocities and residence times.

Russian literature also reports the use of tube testers for defining deposition aspects of heated jet fuels. Kafengauz and Gladkikh [14] describe a device for heating a fuel flowing at 3.75, 15, or 30 m/s through a stainless steel tube whose wall temperature was varied from 202 to 902°C. Fuel was recirculated between 1000 and 10 000 times. An increase in wall temperature as a function of its initial value was the criteria used to demonstrate the formation of carbonaceous deposits.

Aliev et al. applied a flow apparatus to the examination of various USSR jet fuels [15]. This device, the DTS-1 unit, measures the time for plugging of a test filter or the delta P at the end of a 4 or 5-h test time. This Russian apparatus may be similar to the ASTM coker, but details of the instrument are limited.

Multiple Tube Testers

Several useful devices have incorporated more than one tube into the fuel stress equipment. Some units have tubes in series with thermal stress increasing as the fuel passes from the inlet to the outlet of the apparatus. Other rigs incorporate tubes in parallel, mainly to increase the rate of data production. Three devices will be described below.

Heat Transfer Unit

As part of the U.S. SST program, Esso research assembled a sophisticated heat transfer unit (HTU) which consisted of a preheater coil and eight electrically heated heat transfer test stages [3,16]. The unit (Fig. 5) was fed from a 95-L (25-gal) stainless steel preconditioning tank in which the temperature is controlled and the oxygen content of the fuel is stabilized. Each heat transfer stage consisted of a stainless steel tube containing an inner electrically heated Inconel tube equipped with thermocouples to measure skin temperatures. Thus, the fuel flowed through the 1.07-mm annulus between the heated Inconel heater and the outer and cooler stainless steel tube. Each stage was 1.01 m in length with ODs of 7.9 mm. The stainless tubes were cleaned with solvent and extensive wire brushing between experiments. The Inconel heaters were cleaned with emery paper and polished with crocus cloth before each test. The heat transfer stages were connected in series with provisions for bypassing any of the stages. The heat input to each stage was separately controlled so that the temperature level of each succeeding stage was about 19°C higher than the previous stage. A metal-to-fuel temperature differential of about 28°C was maintained in each stage.

Fuel flow at 1.13 L/min was in the turbulent range comparable to that in aircraft heat exchangers. A typical 100-h run required 6800 L of fuel. Final outlet temperature of the fuel was 370°C. Metal surface and fuel temperatures were measured across each stage. These data along with fuel flow rate information provided the data necessary for calculating fuel

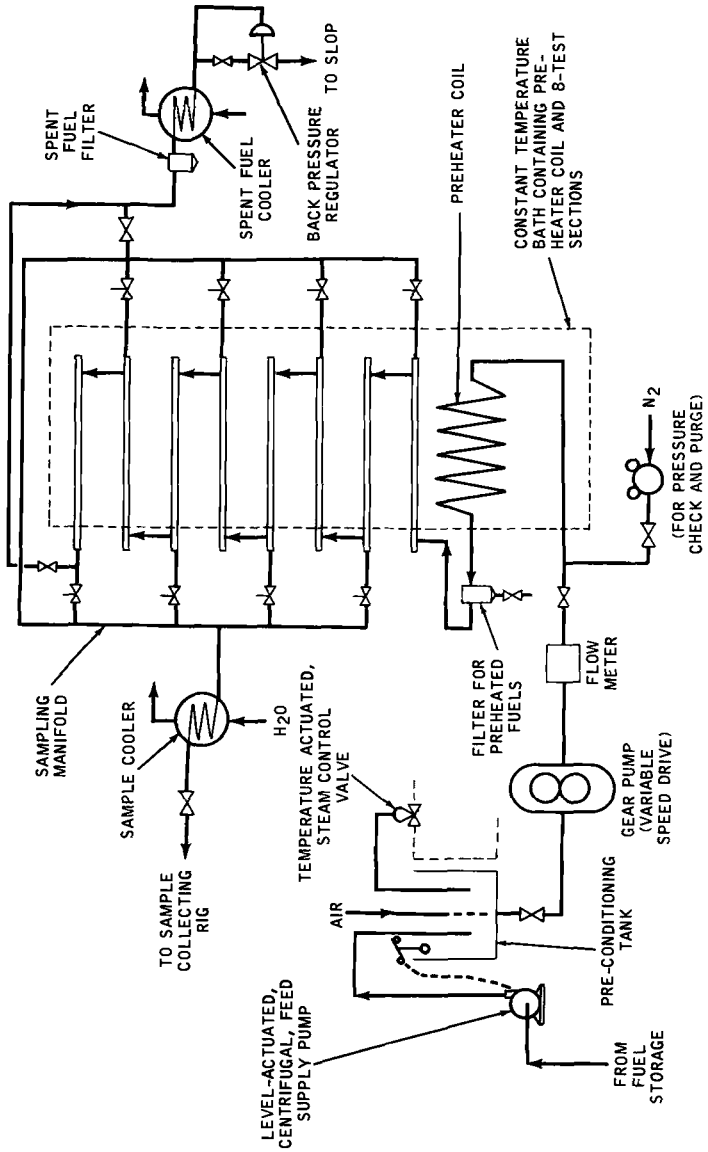


FIG. 5—Flow diagram of the Esso heat transfer unit.

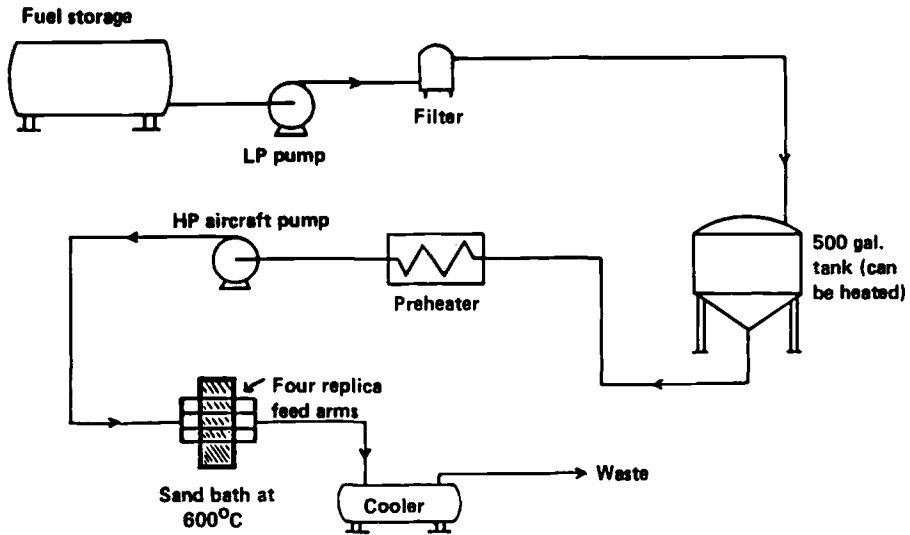


FIG. 6—Flow diagram of Shell-Thornton injector-feed-arm rig.

side heat transfer coefficients. Samples could be collected at the exit from each heat transfer stage for later analysis for oxygen content, peroxide number, and light transmission. At the end of a test, the Inconel heaters were rated visually for deposits.

Injector Feed-Arm Rig

The Thornton Research Centre of Shell Research, in conjunction with Rolls Royce PLC, developed the IFAR apparatus to measure deposit deposition quantitatively at well-characterized temperatures. The apparatus, first used by Peat [17], included four model feed arms mounted in parallel in a heated fluidized bed [1]. Fuel is fed from a large tank through two series-mounted high-performance aviation oil coolers as shown in Fig. 6. A high-pressure piston pump directs the divided flow to the feed arms. The latter, which simulated the burner tubes leading to the nozzles of a large gas turbine, has a 100-mm heated zone and a total length of 349 mm. The tube OD and ID are 11.12 and 4.76 mm, respectively. Thermocouples for control and monitoring are imbedded in the tubes. Other thermocouples measure temperatures in the sand bath and in the fuel into and out of the steel tubes. Fuel flows are maintained in the turbulent region, and the pressure is typically selected to prevent fuel boiling.

The IFAR is usually operated to reflect a severe condition; for instance, a 165°C bulk fuel inlet temperature and a 300°C inner wall temperature. Fouling is monitored indirectly during a test via the rise in the tube inner wall temperature resulting from the deposit's insulating effect on heat transfer. The main evaluation procedure, however, involves carbon burnoff of the deposit at the completion of an experiment which might run up to 100 h.

Fuel Deposit Test Apparatus

United Technologies Research Center designed and built a rig which incorporated many features for studying thermal oxidation stability [18]. It combines three tubes in parallel in

a first stage with increasing temperature followed by a second stage with a second set of three parallel tubes operated at isothermal conditions. In between the two sets of tubes and following the second set are stainless steel wafers which afford a measure of deposition. A filter (15 μm) downstream from each stress line plugged early in many runs and was removed for many tests. The resistance-heated tube sections provide information on the deposit formation that occurs when the temperature differential between the surface and fuel is large (approximately 100 K), whereas the isothermal tubes and metal wafer specimens yield data for the condition when the surface and fuel temperatures are equal. The apparatus was designed so that all components directly in contact with the fuel were constructed from either stainless steel, steel, plastic, or aluminum.

All of the tubes are fabricated from 2.20-mm ID by 3.20-mm OD, Type 316 stainless steel tubing. The heated tubes and the isothermal tubes are 0.91 and 0.30 m long, respectively. Multiple thermocouples monitor the temperature on both sets of tubes. Fuel temperatures are measured at inlet and outlet flows, usually in instrumentation plenums which contain the 6.40-mm-long by 3.20-mm-wide by 0.05-mm-thick stainless steel wafers. The device has the capability to operate at pressures up to 3.4 MPa, temperatures to 500 K, and fuel flow rates to 14 kg/h per tube. Test times vary from a few to several hundred hours. The use of the three stress lines in parallel allows replacement of one or more tubes at selected times. Thus, data for several test-time periods can be obtained in one experiment on a fuel. The deposition rate on the heated and isothermal tubes is defined by sectioning the tubes at the end of a run, drying the sections in a vacuum oven at 370 K, combusting the deposit in the presence of oxygen, and measuring the amount of carbon dioxide as an estimate of the amount of deposit. The stainless steel wafers are weighed directly to define any weight gain due to deposit lay down during the test. The minimum amount of deposit that can be accurately determined by carbon burnoff from a tube section is 200 μg , and the weighing procedure used with the wafer specimens is accurate to 10 μg .

JFTOT Modifications

The jet fuel thermal oxidation tester has been used in a large number of research programs. This has involved using the standard JFTOT in a nonspecification mode as well as changing some parts of the standard apparatus. Evaluation of the result of a JFTOT test by other than visual ratings has been widely practiced also.

A common nonspecification use of the JFTOT is to define the breakpoint of a fuel [19]. In this procedure, the fuel is tested at several temperatures. The temperature at which the tube or pressure readings exceeds a specific criteria level is defined as the breakpoint. Normally, the criteria for the ASTM D 1655 specification—a tube deposit rating less than Code 3 and a delta P limit for the filter of 25 mm—are used as limits in regard to breakpoint.

Thornton Research Centre raised the test temperature of the JFTOT to 350°C [20]. The deposit is then combusted and the amount of carbon dioxide measured to estimate the deposit quantity and, hence, the fuel quality. The higher temperature was required to obtain enough deposit in a 2.5-h test to give reliable data. The aluminum tubes are pretreated by combustion at 460°C to remove organic material adsorbed in the aluminum oxide coating. This is followed by polishing with an aqueous diamond paste to remove magnesium oxide (MgO) which migrates to the surface during the 460°C exposure. The MgO must be removed since it inhibits deposit lay down on the JFTOT tube [21]. The Thornton group has also used other tube materials in the JFTOT, comparing deposit formation on aluminum and stainless tubes at 350°C [22]. In addition, Shell Research has used the JFTOT to examine effects of flow rate over the range of 1 to 11 mL/min and to evaluate test duration, both at 350°C.

The Naval Research Laboratory has used carbon burnoff with stainless steel tubes in the JFTOT as a means of quantifying the amount of deposit. Further, these workers compared carbon burnoff results with the readings from the Alcor tube deposit rater with an optical interference method and with a dielectric technique [23]. The TDR compared poorly with the other measurements, but carbon burnoff, interference, and dielectric measurements correlated well with each other.

Scientists at BP Research Centre replaced the JFTOT test filter with a 0.45- μm Millipore membrane. They were able to weigh these filters directly to define the amount of particulate matter exiting the hot section. Effects of soluble copper and metal deactivator additive on particulate formation were defined with this technique [24].

Hazlett, Hall, and Matson extensively modified the JFTOT to increase its value as a research tool [25]. They replaced the 60-mm heater tubes with longer ones which had a heated length of 127 mm. The purpose of the longer tubes was to moderate the sharp temperature rise of the standard tube, thus allowing a better definition along the tube. Tubes of various materials were used with most studies using stainless steel tubes, Type 304 or 316. This JFTOT also had upgraded pressure and temperature capability, 7 MPa and 540°C, respectively. The seal at the hot end of the tube was modified for these more extreme conditions. This modified JFTOT was fitted with a sample takeoff valve, which directed the sample directly to a gas chromatograph for chemical studies.

A laboratory technique incorporating a bulk heating step ahead of the JFTOT was developed by the CRC JFTOT Evaluation Panel. Several approaches were tested before settling on the mini-heated reservoir (MHR) [26]. The 230-mL reservoir, which was heated with a 600-W cartridge heater, was located between the JFTOT reservoir and the heater tube test section. The MHR was provided with stirring and temperature control. This modified JFTOT has not been used in any research programs or in specification development. Interest in this or similar apparatus was renewed at the time of difficulty with main engine controls of aircraft operating in Brazil. In that problem, fuel had a period of stress at intermediate temperatures, a condition for which the MHR-modified JFTOT was designed.

The standard JFTOT has been used with a glass outer tube housing by the Naval Air Propulsion Center and others. This allows observation of deposit formation during a test.

Datschefski presented an evaluation of the JFTOT as a research tool for thermal stability [27]. He recommended that stainless steel tubes replace the aluminum ones, that a quantitative measurement of the amount of deposit be used (carbon burnoff, for instance), that preheat of fuel be included to better simulate stress conditions in modern, more efficient engines, and that a capillary tube heater be designed that would operate in the turbulent flow regime.

ASTM Coker Modifications

Several modifications of the ASTM D 1660 Coker were developed over the years, mostly in the 1960s. Most of these have been described in several reviews [28–31]. In the following discussion we will emphasize the high-temperature research coker, the modified fuel coker, and the gas drive fuel coker.

CRC High-Temperature Research Fuel Coker

The standard ASTM Coker has a fuel-out temperature limitation of 232°C (450°F). This is inadequate for supersonic aircraft fuel systems. Further, aerodynamic heating raises the fuel temperature in the aircraft tanks where it can cook for extended periods of time. To address this fuel stress environment, the research coker was designed for evaluating fuel

thermal stability at high temperatures, incorporating the concept of tank heating into its simulation [32]. A 38-L (10-gal) stainless steel reservoir added ahead of the ASTM Coker preheater could be heated to 149°C (300°F). The apparatus was designed to permit a fuel-out temperature at the preheater of 398°C (750°F) and a system pressure of 1.7 MPa (250 psi) rather than the 1.03-MPa (150-psi) value for the standard coker. Pump wear and even failure were a problem with this device, probably due to the high temperature and pressure the pump endured in its location between the heated storage vessel and the preheater. Preheater tubes were frequently difficult to rate due to debris from the pump adhering to the tube. The research coker was used by the USAF to purchase JP-7, a low-volatility kerosene used in high-speed military aircraft.

Modified Fuel Coker

The research coker was not widely accepted or used because of its limited application. Projections for future fuel requirements stimulated development of alternate cokers, however, which could exceed the thermal stress capabilities of the standard ASTM Coker. The design of the modified coker was in response to this perceived need [33]. The modified coker was designed on the foundation of the ASTM Coker. The two significant changes were (a) provision to prestress the fuel by heating in a reservoir before introducing it into the test section, and (b) upgrading the test section to reach preheater fuel outlet temperatures up to 426°C (800°F). The annulus between the preheater tube and the surrounding holder was reduced from 0.76 to 0.38 mm. Reduction of the flow rate from 2.7 to 1.1 kg (6 to 2.5 lb) per h afforded the same residence time as in the research coker. Prefiltered fuel was introduced into the reservoir, where it was heated to the desired temperature, usually 93 to 149°C (200 to 300°F), for 4 h. The fuel was then aerated and tested in the modified coker 16 to 24 h after completion of the prestressing step. Heat was applied to produce the desired preheater outlet fuel temperature and filter surface temperature. The thermal instability of the fuel was based on the increase in pressure drop across a precision-sintered stainless steel filter after 5 h and visual ratings of the deposit condition on the preheater surface.

Pump wear problems and other precision difficulties with the modified coker restricted interest in widespread use of this device. In addition, the Concorde SST thermal stability fuel requirement was satisfied with a specification based on the standard ASTM Coker. Only a limited number of military aircraft required higher thermal stability fuel, and this was initially met by testing with the research coker.

Gas Drive Fuel Coker

To eliminate the problems of pump wear, preheater tube heat losses, and large sample volumes posed by the ASTM Coker, the gas-drive coker was designed [34]. The basic equipment layout was the same for both devices with the following exceptions: the ASTM Coker fuel pumping system was replaced by a gas drive system maintained at 1.45 MPa (210 psi), the preheater section was replaced with a more efficient model, and the temperature controller was changed to increase the operating range to 426°C (800°F). The fuel flow rate of 1.13 kg (2.5 lb) per h gave a residence time of 14 to 15 s in the preheater section, similar to the 10 s of the ASTM Coker.

The participants in this CRC cooperative development felt that the gas drive fuel coker had good precision and offered an improved tester for high-temperature stress. However, it used large amounts of fuel and required long test times. These undesirable features were overcome by the JFTOT, which was under development in the same time frame, and the gas drive coker did not move into jet fuel testing or specification efforts.

Other Coker Modifications

A micro fuel coker was developed by Alcor, Inc. as part of the effort to reduce sample size and test time. As the name implies, these objectives were met and this device was an immediate forerunner to the Alcor JFTOT which became the tester for specification use [29]. A slightly modified version of the Alcor microcoker was used in an extensive experimental program at the Bureau of Mines [35]. The small sample requirement was particularly important for this study, which incorporated radiotracer additives into fuel samples.

Smith modified the ASTM Coker to allow the study of effects of metals on thermal oxidation stability [36]. He did this in two ways. In one, he exposed the fuel to various metals for periods of time up to 360 min by adding a heated reservoir ahead of the coker. The metal specimens were mounted on paddles that stirred the fuel which could be heated to 150°C (302°F). This fuel was then tested in the ASTM Coker. In another scheme, preheater tubes were made from various metals or metal foil specimens were inserted in the normal aluminum tubes. Smith also used the research coker by adding stirring paddles from various metals to the stainless steel heated tank of this device. The exposure time and maximum temperature in this latter apparatus was the same as that in the modified ASTM Coker.

Static Testers

Many attempts have been made over the years to utilize simple testers to define thermal stability. In addition, simple apparatuses have been designed to study some aspect of the oxidation chemistry which is involved in thermal stability. Most such efforts have utilized static tests, ones in which the fuel is heated or reacted as a batch. The thermal precipitation method is included in the JP-7 specification and was described in Chapter II, Specification Methods and Limits. USSR static test methods used in specifications were also discussed in Chapter II.

Johnston and Anderson reviewed static thermal stability tests which had been proposed prior to 1964 [30]. Each of these saw limited use, and the Johnston/Anderson reference should be utilized to gain further information about any of these methods. One static method of that era, the Phillips 5-mL bomb, did develop widespread interest and will be included in the more detailed discussions below.

Phillips 5-mL Bomb

A simple approach to measuring thermal stability involving a very small sample was the Phillips Petroleum Co. 5-mL bomb technique [37]. A 5-mL sample of an air-saturated jet fuel was heated in a stainless steel bomb pressurized with air to 345 kPa (50 psig) at a preselected temperature. The test was started with the fuel at 32°C (90°F) and was terminated by rapid quenching in ice water exactly 20 min after the heater was turned on. Repeat tests on separate samples of the same fuel stressed the fuel to different temperatures. The light transmittance of the stressed samples at 350 m μ m wave length were compared to that of the unstressed fuel. The loss in transmittance was plotted against the fuel stress temperature. The failure point for the fuel was defined as the maximum temperature to which the fuel could be heated before the transmittance dropped 25%. Other percent changes were examined, but the 25% value afforded a better correlation with coker data.

The test is based on the theory that thermal stresses generate micelles in the fuel and that deposits are ultimately formed by agglomeration of these particles [38]. This thesis has never been verified, however, and it seems improbable that development of color could be a reliable estimate of thermal instability. Although comparisons of data for the 5-mL bomb

and various cokers showed general trends, the correlations were poor [29]. In particular, fuels with additives gave unacceptable relationships.

Flask Oxidation Test

A recently developed static test has been used extensively by the Thornton Research Centre [20,39]. This equipment requires 400 mL of sample and is used to probe the oxidation mechanism rather than the combined processes of oxidation and deposition. As shown in Fig. 7, air passes through a sintered disk at the bottom of the flask into the fuel sample. The flow of air at 80 mL/min replenishes the oxygen supply and stirs the fuel. A heated oil bath surrounding the flask brings the fuel to the desired temperature (145 to 190°C) within 15 min. By measuring the reduction in oxygen partial pressure of the effluent air, the fuel's oxidation rate can be measured. A sensitive oxygen analyzer resolves concentrations as small as 0.01 vol%, and repeatability of the rate of oxidation was plus or minus 10%. Glassware must be cleaned rigorously to remove residual organics and metals. This apparatus has been very useful in studying the effects of additives and metals on the oxidation process as well as defining differences between fuels.

Other Static Testers

Amos and Knight used a flask test to examine the effects of nitrogen and sulfur compounds (and their interactions) on hydrotreated AVTUR [40]. An 850-mL sample was heated at 150°C for 4 h. After cooling to ambient, the sample was filtered through a 0.1- μ m membrane filter to determine the amount of insoluble material formed during the test.

Martene et al. used 4.5-mL sealed stainless steel tubes to stress fuels at 330°C for 2.5 h [41]. Deposits were collected on preweighed Type 316 stainless steel strips inserted into the tube. The deposits were found to be unevenly distributed on the strips. The flat strips afforded ready analysis for elemental composition by techniques such as Auger electron spectroscopy.

Other Devices

Additional testers which do not readily fit into the categories previously discussed will be grouped in this miscellaneous section.

Exxon Wing Tank Testers

SST aircraft dump more and more heat into the fuel as the aircraft speed increases. The ram heating effect transfers heat into the fuel wing tanks. Fuel vaporization increases as the temperature rises and the extent of vapor in contact with the hot wing surfaces increases as fuel is used during flight. Exxon constructed two laboratory devices to examine the effects of this stress environment [42]. A so-called phase study unit vaporized jet fuel flowing at 50 mL/h as it entered a heated 0.74-m-long (5.7-mm) ID glass reactor. An internal independently heated glass probe was examined at the end of a test for evidence of deposit formation. The fuel was operated in an air-saturated mode and in a deoxygenated mode. Observations were qualitative only.

In the second unit, two-phase flow was established through a 3.8-cm-diameter, 100-cm-long glass tubular reactor. Fuel at 125 mL/h flowed down a slight incline through the five independently heated zones of the reactor. The temperature of the zones increased as the fuel moved downstream. Gas, either air or air/nitrogen mixtures, flowed at 5 L/min. Carefully

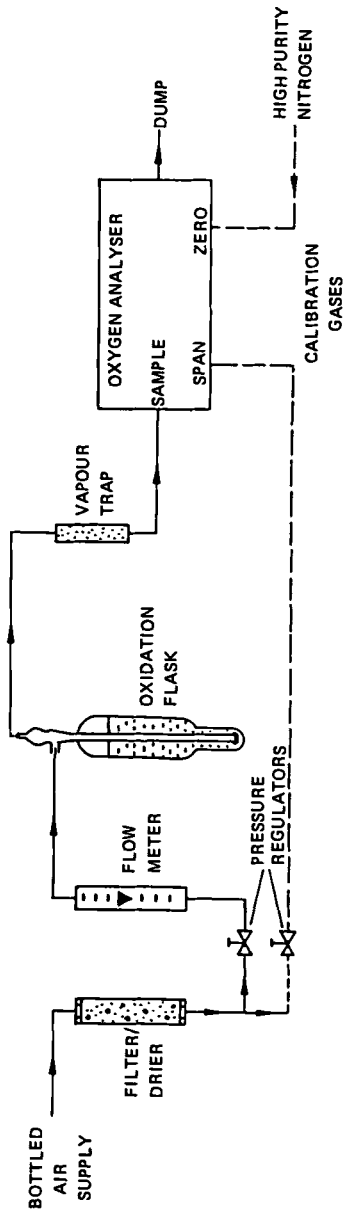


FIG. 7—Schematic diagram of the Shell-Thornton flask oxidation test.

weighed strips of various materials, 1.0 cm by 10 cm, were positioned in the center section of each zone. Liquid residence time was 14 s per strip. Apparatus operation was conducted at temperatures up to 260°C (500°F) and at pressures down to 20 kPa (3 psia) to simulate the environment at high speed and high altitude. The rating of the experiment was made at the end of a 4-h run by weighing the fuel-free metal specimens.

UTRC Rectangular Flow Tester

United Technologies Research Center built an apparatus which combined the capability of defining deposition rate as well as examining the character of the deposit [43]. This device had a flow passage 0.28 cm high by 3.2 cm wide by 61 cm long which was formed between the cover and base plate of the assembly. Four specimen mounts were attached along the length of the cover. These held stainless steel discs which were used in the determination of coking rates and chemical characteristics. Direct weighing was an acceptable measurement of deposit mass on the 0.7-g discs, and the flat discs afforded chemical analysis by infrared or other techniques. The test assembly, heated by buried 1500-W heaters, was constructed from copper-beryllium alloy but was plated with gold or nickel to minimize catalytic effects. A control thermocouple was mounted at the midpoint of the base and the cover. A spray nozzle on the downstream end of the tester allowed observations on spray character.

The fuel was preheated up to 422 K (300°C) for some tests. Flow rates of 9.5 to 95 L (2.5 to 25 gal) per/h afforded laminar or turbulent flow. Tests were run at temperatures of 422 to 672 K (300 to 750°F) and pressures of 0.69 to 2.07 MPa (100 to 300 psig).

Advanced Fuel Research Mini-Reactor

The Advanced Fuel Research Co. built a small reactor which was designed primarily to examine the chemistry occurring in thermal oxidation stability [44]. The fuel passed at 0.5 mL/min through a 1.8-mm (0.07-in.) ID glass-lined stainless steel tube which was heated electrically. A 0.2-mm (0.008-in.)-diameter stainless steel wire was located centrally inside the tube to collect deposits. A filter downstream of the stress section collected any particulate matter. On-line Fourier transfer infrared cells allowed direct observation of absorption peaks pertinent to thermal oxidation stability. Deposit collection was a weak part of this apparatus since the deposit measuring wire was a small fraction of the surface exposed to the fuel and the input of heat was via the tube rather than the wire.

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CHAPTER V

Physical Effects on Thermal Stability

Physical factors play a major role in the phenomena involved in the formation and deposition of fuel-insoluble material. Temperature is the most important of these factors and will be dealt with in some depth. Other physical parameters to be discussed include system pressure, flow regime, heat transfer, deposit morphology and physical characteristics, and surface roughness of the test section. In addition, some recent efforts in modeling the overall process of thermal oxidation stability will be addressed in this chapter although the models include chemical as well as physical effects. The variety of equipment used in thermal stability work and the multiplicity of goals behind this type of research may explain the different results and conclusions reached by different investigators. If a reasonable explanation can resolve a difference in results, this will be presented.

Temperature

At fuel temperatures from ambient up to about 100°C (212°F), jet fuel of specification quality will exhibit no problems due to insolubles formation. Near or above this temperature, deposition begins and becomes progressively worse up to a somewhat higher temperature, at which point the deposition decreases sharply. This reduction at higher temperatures (325 to 400°C) will be presented in some of the research results which follow and will be examined for explanations.

Temperature effects have been studied in many different devices, both static and dynamic. The emphasis in this chapter will be on dynamic since such devices mimic movement of fuel through an aircraft fuel system and limit the amount of oxygen to which the fuel is exposed.

Tests in the CRC/NAA Simulator

In the U.S. SST program, this simulator was operated at two stress conditions, 2.5 and 3.0 Mach. For 2.5 Mach, the maximum fuel temperature into the combustor nozzle was 120°C (250°F) during cruise and 205°C (400°F) during descent, the most severe stress during flight. The corresponding conditions for 3.0 Mach were about 145°C (295°F) for cruise and 260°C (500°F) for descent. The consequences of the temperature differences for the two Mach number regimes are shown in Fig. 1 [1-2].

The pressure drop through the engine nozzle demonstrated no increase for the 2.5 Mach case after 42 simulated flight cycles, but a definite increase was observed for the higher flight speed. The increase was particularly noteworthy for the climb portion of the flight as deposition began to exert an effect at about the tenth cycle of the test program.

Tests in the AF-SIM

The USAF tested nine jet fuels in their simulator. The results for seven of the fuels are depicted in Fig. 2 [3]. Data plotted are for the rate of change of deposit thermal resistance versus a calculated temperature at the fuel/manifold interface. The dramatic effect of tem-

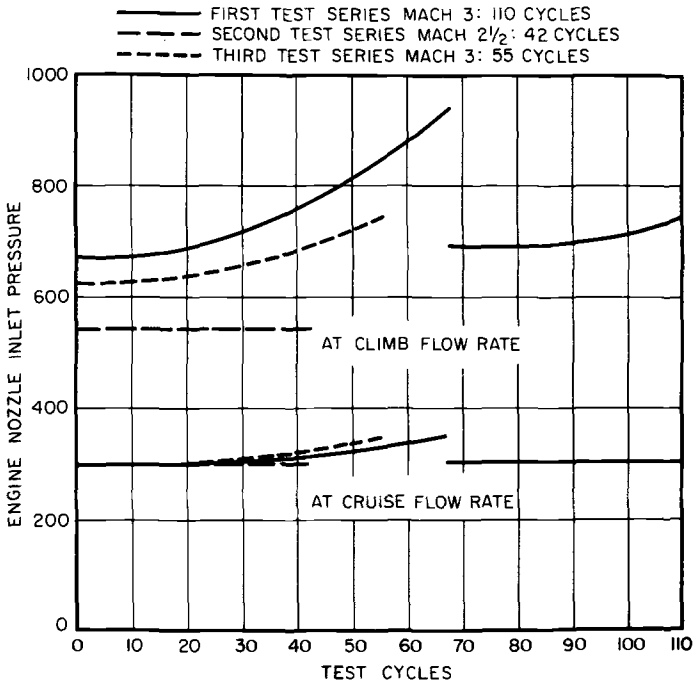


FIG. 1—Pressure drop across engine nozzles in large-scale test rig (psig).

perature as well as the large variation in fuel behavior is illustrated in this figure. Note that these comparisons are for the steady-state mode of operation. Fuels AFFB-11 and -12, which were JP-7's, exhibited exceptional behavior, much lower changes in thermal resistance even at 370°C (700°F) film temperatures. The fuel breakpoints as determined by the JFTOT rated the seven fuels in the same order as this manifold test. Further, this simulator data are interesting in that the deposition, as evidenced by the thermal resistance changes, undergoes a sharp reversal for the three fuels which were tested above 316°C (600°F). The reduction was observed in the temperature range 330 to 385°C.

Tests in the GE-NZ Apparatus

Some discussion of this equipment and its use were presented in Chapters I and III. Representative data from hysteresis in fuel flow in an F404 nozzle is shown in Fig. 3 [4]. The "weighted temperature parameter" for the abscissa was defined in Chapter I and involves the breakpoint temperature by the JFTOT and the measured fuel temperature entering the nozzle. By this treatment of the data, fuels of varying quality can be put into a unified relationship. This is the case for the three fuels used for the data in this figure; breakpoints were 221, 226, and 243°C, respectively. The correlation coefficient of 0.98 demonstrates the usefulness of this type of testing. Unfortunately, each engine nozzle has its own characteristics and must be tested separately to define the coefficients for the "weighted temperature parameter." Further, different coefficients are required for valve hysteresis, primary flow reduction, and secondary flow reduction where applicable. A summary of C_0 and C_1 values for three flow characteristics and ten jet engines are listed in Table 1 [5].

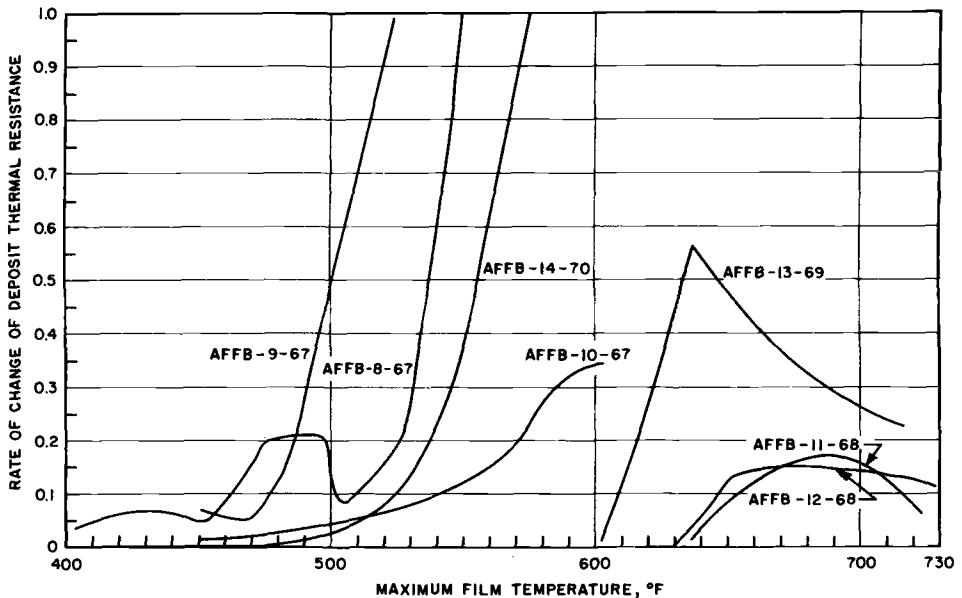


FIG. 2—Comparison of steady-state deposit rates in advanced aircraft fuel system simulator.

While all of the atomizers showed a reduction in fouling life with increasing fuel temperature, several—T53, T76, TF30, and T700—with small or negative C_1 values showed little correlation between fouling life and JFTOT breakpoint temperature. This finding may be related to the features of these nozzles. The T76 and T700 are single-orifice nozzles, and the flow-divider valves for the TF30 and T53 are in a separate location outside the engine casing. Reference 5 has utilized this information to predict fouling lives for the nozzles of various engines as a function of fuel inlet temperature to the nozzle, assuming a fuel breakpoint of 260°C (500°F). In addition, the analyses evaluated the effect on nozzle life of using emergency fuels, i.e. diesel, for military operations.

Tests with the Esso HTU

The U.S. SST program, operating through the Coordinating Research Council, conducted research with the heat transfer unit built at Esso. This apparatus provided an extensive variety of data, both physical and chemical [2,6], over 100 h of operation. The changes observed for these properties as a function of heater tube skin temperature as fuel flowed through this eight-stage reactor are shown for one fuel, RAF-179-64, in Fig. 4. Although chemical reactions occurred at temperatures below 260°C (500°F), changes in heat transfer coefficient and evidences of deposition were observed only at temperatures somewhat in excess of 260°C. When these two properties began to change, they underwent rapid changes with respect to temperature. The initial changes were a decrease in heat transfer coefficient and increase in tube deposit rating. Both of these properties experienced sharp reversals in behavior, however, at higher temperatures—about 300 to 330°C—the heat transfer improving and the deposition rate decreasing. Three other fuels were run on the HTU, one responding to temperature similarly to RAF-179-64, one deteriorating at a lower temperature, and the third exhibiting more resistance to stress.

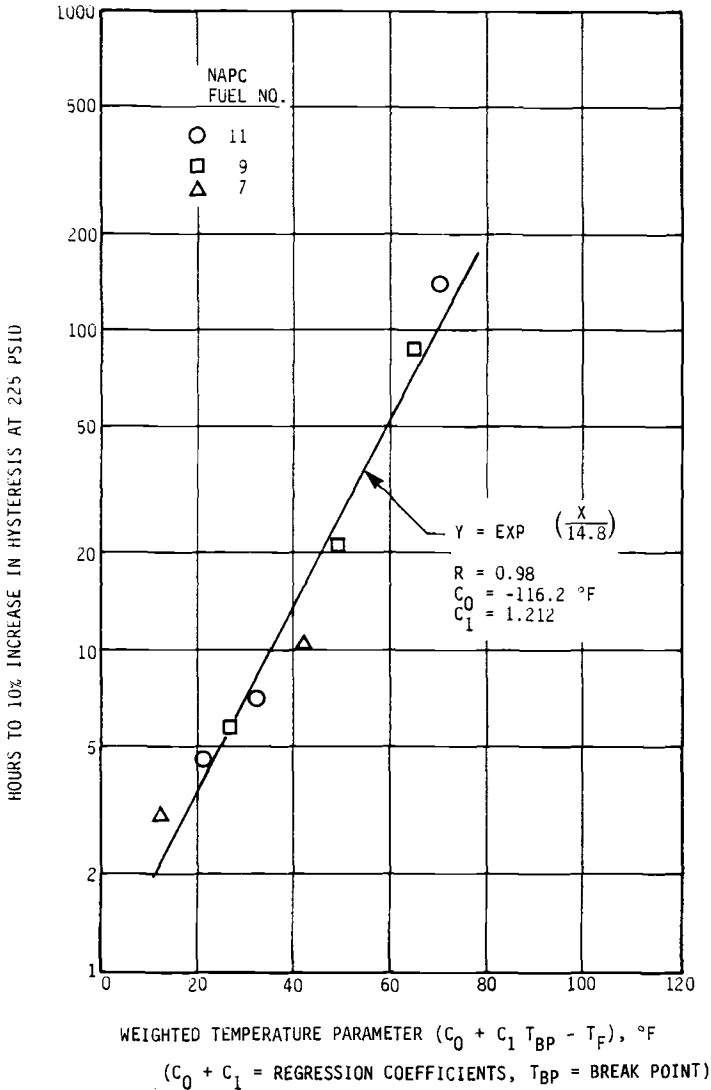


FIG. 3—Correlation of F404 fuel nozzle fouling test results.

Tests in the Exxon AKU

The Exxon advanced kinetic unit (AKU) was used to study deoxygenation situations for thermal stability of jet fuel over a wide range of temperatures. It was initially tested with air-saturated fuels, however, and a typical plot for deposit formation rate versus heater tube wall temperature is shown in Fig. 5 for a JP-5 [7-8]. Only small amounts of deposit formed, as determined by carbon burnoff after a 4-h test for temperatures below 260°C (500°F) but deposition accelerated markedly above this temperature, attaining a peak at 400°C (752°F). The sharp decline which followed led to a gradual second rise as the wall temperature reached 540°C.

TABLE 1—Summary of nozzle-fouling regression results.

Engine Nozzle	Fouling Test Type	Flow Divider Tested	Regression Results, °F	
			C ₀	C ₁
T56	Valve hysteresis	Yes	127.5	0.655
	Total flow	Yes	140.5	0.647
T58	Primary	No	327.5	0.313
	Secondary	No	293.7	0.356
T53	Total flow	No	687.4	-0.401
T76	Total flow	No	512.2	0.050
TF30	Primary	No	501.7	-0.114
F404	Valve hysteresis	Yes	-116.2	1.212
	Total flow	Yes	154.4	0.685
T700	Flow	No	478.3	-0.068
J79-17A	Primary	Yes	386.7	0.186
	Secondary	Yes	352.3	0.225
J79-17C	Valve hysteresis	Yes	356.5	0.262
	Primary	Yes	373.0	0.782
	Secondary	Yes	223.6	1.226
J85-21	Valve hysteresis	Yes	245.8	0.434
	Secondary	Yes	91.4	0.757
	Valve hysteresis	Yes	386.8	0.161

Tests with the Shell STHTR

The Shell group has measured the temperature response of a large number of fuels in their single tube heat transfer rig. The data for eleven of the fuels are reported in a recent reference [9]. An Arrhenius plot for three of these fuels illustrates the variation of response to fuel outlet temperature (Fig. 6). A linear Arrhenius response was evident for the deterioration in heat transfer coefficient.

Energy of Activation Considerations

Many studies have found a linear change in the log of some fuel property versus the reciprocal of some system temperature. Properties measured include pressure drop, heat transfer, nozzle flow, and coking or deposition rate. Temperatures evaluated are fuel temperature at some particular point in the system or the temperature of a metal surface to which the fuel is exposed. The temperature/property data, when presented in an Arrhenius graph, may afford useful information about the chemistry or physics of the stress system. The slope of the plot can be converted to an "apparent energy of activation," E_{act} . Table 2 lists E_{act} data derived from some of the tests discussed in the earlier sections of this chapter as well as from other representative documents.

The table indicates that a wide range of "apparent E_{act} " can be found in the different experimental apparatuses. There is no obvious pattern of parameters measured versus E_{act} . In fact, the same organization using different devices finds widely varying activation energies. For instance, Exxon has found variations from 21 to 188 kJ/mol and UTRC has found the wide range of 42 to 167 kJ/mol. The latter organization found this wide range using one device, the aircraft fuel deposit test apparatus. Marteney and Spaddaccini found a low and a high E_{act} for the same fuel, depending on the temperature [14]. The low E_{act} (42 kJ/mol) was found for temperatures up to 260°C for a JP-5, but the higher value (167 kJ/mol) was measured above this temperature up to about 350°C. These authors suggest that the low

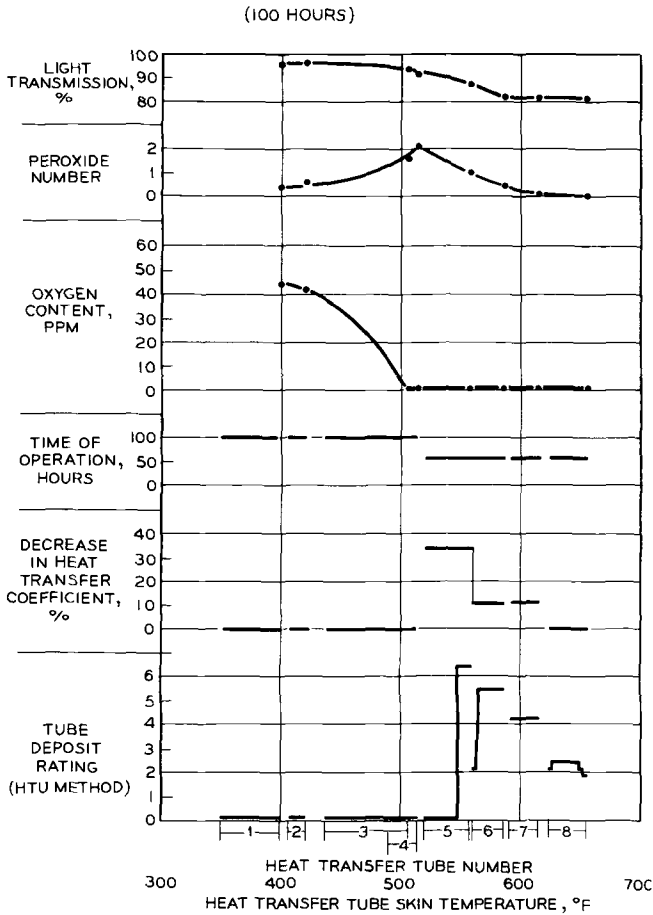


FIG. 4—Heat transfer unit data on reference fuel RAF-179-64 in HTU.

value may be associated with a heterogeneous reaction (catalyzed or wall-influenced) which typically have E_{act} 's of 21 to 63 kJ/mol [17]. Further, Marteny and Spadaccini suggest that the higher values relate to homogeneous liquid phase reactions which characteristically have activation energies of 105 to 210 kJ/mol. It is noteworthy that the E_{act} for an important fuel and hydrocarbon reaction—hydroperoxide decomposition (125 to 150 kJ/mol)—is within this range. Shell Thornton found an E_{act} of 68 kJ/mol for the rate of initiation of radicals from *tert*-butyl peroxide in Jet A-1 [18]. This experiment was performed in Shell's flask oxidation apparatus.

Thus, we find that the use of activation energies must be used with caution. Marteny and Spadaccini state that the deposition response to temperature does not necessarily denote relative deposition rate or a specific reaction path. In actuality, this reaction is probably not an encompassing one-step or "global" reaction but a set of reactions, both parallel and series, which would require a very detailed study to decouple or isolate.

Fuels exhibit a range of responses to temperature when tested in the same apparatus [9]. Further, the variety of devices and the variation in stress environment used to estimate

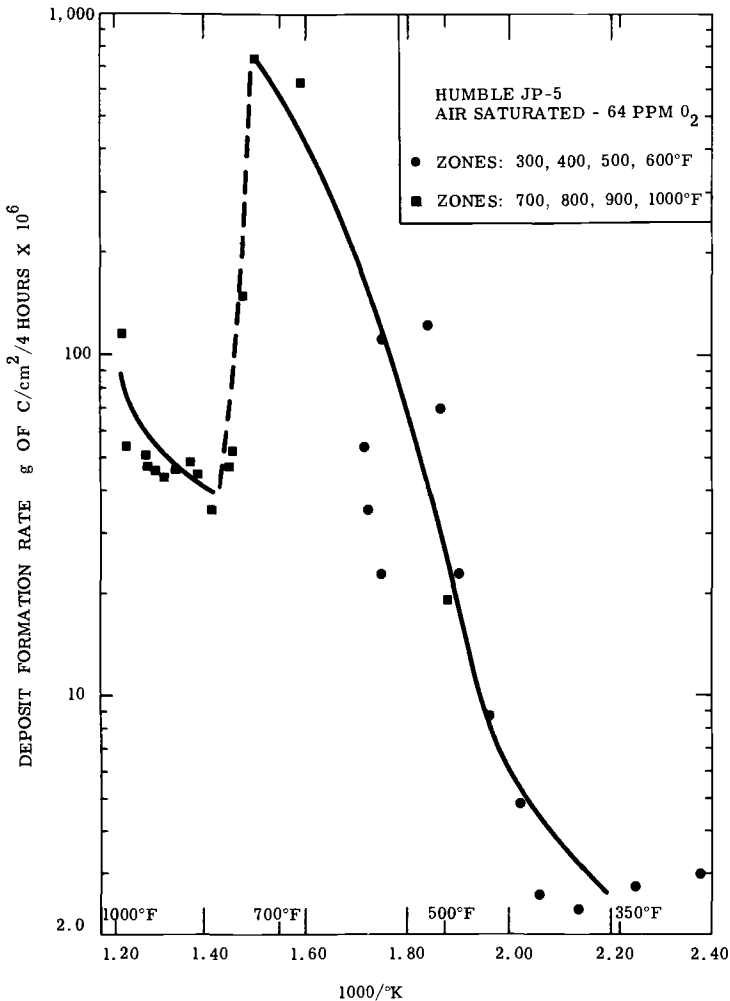


FIG. 5—Arrhenius plot for fuel deposition in AKU.

thermal instability amplify the problem of comparing results of tests. Consequently, a worker in this field needs to design his research equipment to closely parallel the stress conditions for the part of the aircraft in which he is interested. Operation of the equipment should be in a manner closely relevant to the requirements of the system for which he is testing. Finally, comparison of the thermal stability quality of a set of fuels is valid only over a limited temperature range and extrapolation outside that range is of questionable value.

Deposition Rate Dropoff at Higher Temperature

At higher temperatures the deposition/temperature pattern changes, showing a plateau with temperature or even exhibiting a sharp decrease. This has been observed with simulators (Fig. 2) and research devices (Figs. 4 and 5). Other workers have also reported this type

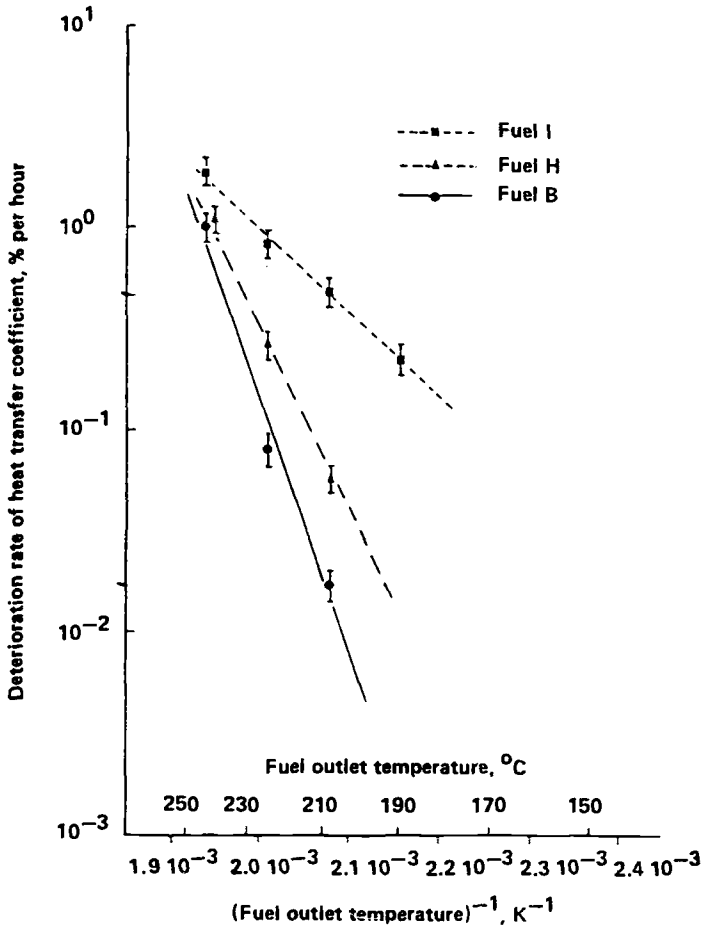


FIG. 6—Arrhenius plots of heat transfer coefficient deterioration in STHTR.

of behavior, Hazlett in a modified JFTOT [19] and Marteny and Spadaccini in a single-tube heated tube rig [14]. Taylor explained this by suggesting that the sharp dropoff coincided with the critical point of the fuels in his study [7]. The calculated critical point for his fuel was 410°C. Hazlett proposed, based on research to be discussed in Chapter VI, that the sharp decrease was due to a chemical factor. Namely, the fuel hydroperoxides which had formed by reaction between the dissolved oxygen and the fuel components were completely decomposed at 380 to 400°C [19]. This latter viewpoint has been accepted by other researchers [14].

Pressure

Several studies have examined the effect of system pressure in the fuel stress device. An early study by Watt et al. at NASA examined the effect of pressure for three air-saturated fuels and for the same fuels when deoxygenated [20]. These workers utilized their single

TABLE 2—"Apparent energies of activation" from thermal stability studies.

Test Device	Property Measured	Temperature Measured	E_{act} , kJ/mol	Reference
Exxon: 2-phase	Deposition by weight	Fuel	42	[10]
Exxon: AKU	Deposition by burnoff	Heater tube	21 to 188	[7]
NAPC: JFTOT	Deposition by optical interference	Heater tube	84 to 121	[11]
PRC: JFTOT	TDR: optical reflectance	Heater tube	51 to 165	[12]
UTRC: RFT	Deposition by weight	Metal wall	38 to 42	[13]
UTRC: AFDTA	Deposition by burnoff	Heater tube	167 (Range 1) 42 (Range 2)	[14]
UTRC: FCA	Deposition by weight	Fuel	42	[15]
SHELL: STHTR	Heat transfer	Fuel	120	[16]
SHELL: JFTOT	Deposition by burnoff	Heater tube	9 to 86	[16]

tube apparatus with a fuel-out temperature of 371°C (700°F), measuring the amount of deposit by carbon burnoff. The pressure range for air-saturated tests was 1.14 to 4.24 MPa (165 to 615 psia), but one deoxygenated fuel was tested down to 17 kPa (2.5 psia). Two of the air-saturated fuels showed moderate decreases in deposit quantity as the pressure increased but the third doubled in deposit amount in going from 1.14 to 2.17 MPa (165 to 315 psia). The deoxygenated fuel tested at 17 kPa (2.5 psia) showed a sharp rise in deposits at 138 kPa (20 psia) but then a sharper decline at higher pressures. The other two deoxygenated fuels exhibited opposite behavior, one increasing in deposit amount with pressure rise and the other decreasing. These differences were greater than could be accounted for by experimental error.

The USAF tested a JP-5 in their simulator with a fuel-out temperature of 327°C (620°F) and initial manifold temperatures up to 454°C (850°F). Under these conditions they found erratic results on deposit buildup and on heat transfer [21]. The problem was related to fluctuations in system pressure, and it was found that the wall temperature and heat transfer to the fuel could be modified significantly by varying the system pressure in the range of 2.38 to 4.24 MPa (330 to 600 psig). The authors suggested that the fuel in the hot portions of the tube was above the bubble point, which was estimated to be 404°C (760°F) and 2.14 MPa (310 psia). Therefore, the fuel was in a partially vaporized state in portions of the manifold, and changes in pressure induced turbulence along with improved heat transfer.

Bradley and Martel continued the USAF examination of pressure effects by varying the test pressure in the JFTOT [22]. They initially found that the breakpoints for two JP-4's were increased by raising the pressure from 2.52 to 2.86 MPa (350 to 400 psig). It was observed that the boiling points of these fuels at these pressures were very close to the breakpoint temperatures. Thus, deposition was occurring at temperatures corresponding to the bubble point: the partial phase change from liquid to vapor apparently dropped degradation particles or high molecular weight polar components out of the fluid onto the heater tube. Observations through a glass test housing for the JFTOT heater tube indicated that deposits form primarily at and downstream of a bubble site. Bradley and Martel concluded that many wide-range jet fuels, such as JP-4 and Jet B, with their greater volatility would be boiling during specification testing with either the JFTOT or the ASTM coker. Kerosene type jet fuels were not affected by lower pressures, however. These researchers recommended that the system pressure for specification testing in the JFTOT be raised from 2.86 MPa (400 psig) to 3.55 MPa (500 psig), an action that was taken by ASTM in 1974.

In a later report, Bradley and Martell examined the effect of pressure on JPTS, thermally stable jet fuel [23]. They found for this fuel of volatility similar to JP-5 that the visual or TDR values decreased as the pressure increased for a set temperature of 316°C (600°F). The data exhibited a great deal of scatter, especially at test pressures below the estimated fuel bubble point of 1.14 MPa (150 psig). A test pressure of 3.55 MPa (500 psig) was thought to be adequate for a specification test temperature of 335°C (635°F) for JPTS. This assures that the fuel is not boiling and makes the test more relevant to aircraft fuel systems.

Taylor used the Exxon advanced kinetic unit to define the effect of pressure on the deposition rate as measured by carbon burnoff. He looked at deoxygenated [7] and air-saturated fuels [8]. One deoxygenated JP-5 fuel gave the same deposit amount at 1.83 MPa (250 psig) as at 7.0 MPa (1000 psig). A second JP-5 fuel gave 30% less deposit at the higher pressure. The two fuels had similar volatility characteristics and both were at supercritical conditions over part of the heated tube which was controlled at temperatures rising up to 538°C (1000°F). An air-saturated JP-5 was run at a lower temperature, 149 to 316°C (300 to 600°F), well below the critical region. The deposit production, however, was 40% lower at 7.0 MPa than at 1.8 MPa.

Marteny and Spadaccini studied the deposition rate for a JP-5 at three pressures in the aircraft fuel deposit test apparatus [14]. The three pressures, 1.8, 2.9, and 5.6 MPa (250, 400, and 800 psig), were applied to a heater tube with temperatures controlled at 170 to 400°C (338 to 752°F). Carbon burnoff data for all three pressures fell on the same curve over the entire temperature range.

Although the data on pressure cited above are not in complete agreement, some general observations can be made. First, the system pressure should exceed that needed to prevent bubble formation since the phase change from liquid to vapor gives anomalous deposition patterns. This suggestion cannot be met, however, at high temperatures above the critical point. A second recommendation is that higher pressures be used, if possible, since most of the data found no change or less deposition as the pressure increased. For specification testing in the JFTOT, the currently used pressure of 3.45 MPa appears to be adequate. Research devices should consider higher pressures, however. For supercritical applications, a high pressure (greater than 4.2 MPa—600 psig) would seem to be reasonable. Fluids at supercritical conditions have unusual and high solubilities, thus possibly minimizing deposition on fuel system surfaces. Additional studies are needed to tie down the effects of pressure, and future devices should be tested initially at a variety of pressures before establishing fuel system conditions for a research program.

Flow Velocity and Test Duration

Two organizations, Shell Thornton Research Centre and United Technologies Research Center, have evaluated the effect of flow velocity on heat transfer and deposition rates. The latter organization has also examined the role of test duration in tests running up to 700 h. The two topics and the work of these two research centers will be discussed separately.

Flow Velocity Studies by Shell

Smith tested the effect of mass flows of 9.1, 13.6, and 18.1 kg (20, 30, and 40 lb) per h through the Thornton single tube heat exchanger [24]. Reynolds numbers were in the range of 4500 to 10 000. At any given time, Smith found that the higher the fuel flow rate, the greater the decrease in heat transfer. The quantity of deposit was not reported in this paper. Smith discussed residence time, the mass of potentially unstable species, turbulence, surface

temperature, laminar sublayer thickness, and deposit roughness as factors in this experimental behavior.

Peat of Rolls-Royce reported on tests in Shell's injector feed-arm rig at flow velocities of 1.06 to 5.72 m/s [25]. Flow conditions were in the turbulent regime. Total quantities of deposits on the feed arm were estimated by combustion to carbon dioxide. The amount of deposit decreased sharply with increased flow velocity between 1 and 2 m/s but stayed about the same above the latter value up to 6 m/s. A linear relationship was found for Log (carbon) versus metal wall temperature divided by the fuel flow velocity, the carbon decreasing as this quotient decreased. Later work with the same apparatus found no difference in deposition rate over a two-fold change in flow rate. Reynolds numbers were 10 000 and 20 000 [26].

More recent Shell studies have varied the flow rate of fuel passing through the JFTOT in the range of 1 to 11 mL/min. The flow regime for the JFTOT studies was laminar as opposed to the turbulent regime for other Shell experiments. Deposit quantity was determined by combustion of stressed heater tubes for a 2.5-h test at 350°C [16,27]. Some fuels exhibited sharp maxima in deposit amount, the peak coming at a flow rate of 7 to 8 mL/min. Enhancements up to five-fold were observed for some fuels, but other fuels gave a flat response for deposition versus flow rate in the JFTOT. Clark and Thomas suggested that the difference in behavior was due to the relative importance of chemical and physical factors in the laminar flow regime characteristic of the JFTOT. Fuels which had a low chemical reaction rate in the stagnant layer adjacent to the test section surface exhibited little effect of flow rate on deposition rate. For fuels giving higher chemical reaction rates, physical factors (diffusion) limit the availability of reactants in the stagnant layer. An increase in flow rate serves to replenish reactant concentration and, thus, to increase reaction and deposition rates within the stagnant layer. The authors warn, however, that the JFTOT response to flow rate in the laminar regime gives no prediction to the response in a research device operating in the turbulent regime.

Flow Velocity Studies by UTRC

UTRC has examined the effect of flow rate in several devices. In their rectangular flow tester, Vranos and Marteney found a modest decrease in deposition rate by increasing the flow rate from 2.14 to 6.85×10^{-3} kg/s, but the activation energy was similar for the two flows [13].

In the fuel coking apparatus, Vranos et al. observed that the coking rate as determined by weight increase in specimens located in the isothermal test section rose as the Reynolds number increased [15]. The rate increased about three-fold for a ten-fold increase in R_E . No obvious dependence upon flow regime (laminar or turbulent) was observed, although the dependence on R_E indicated that diffusion is an important step in the formation of surface deposits.

Other UTRC testing [17] has been done in a single-tube heat exchanger (AFDTA) operated at flow velocities from 0.21 to 14.9 m/s (0.7 to 49 ft/s), equivalent to a Reynolds number range of 400 to 21 000. Figure 7 illustrates the behavior for three flow rates of greatly different magnitude. The deposition rates for JP-5 were quite comparable over the temperature range tested even though the R_E varied from laminar (400) to well into the turbulent range (21 000). Some nonspecification fuels gave patterns similar to JP-5 for the effect of flow velocity but others produced significantly lower deposition rates at lower Reynolds numbers.

The fuel deposit test apparatus, a heated multiple-tube device, has also been used by UTRC in fuel velocity studies. One of these studies used two low Reynolds numbers, 70

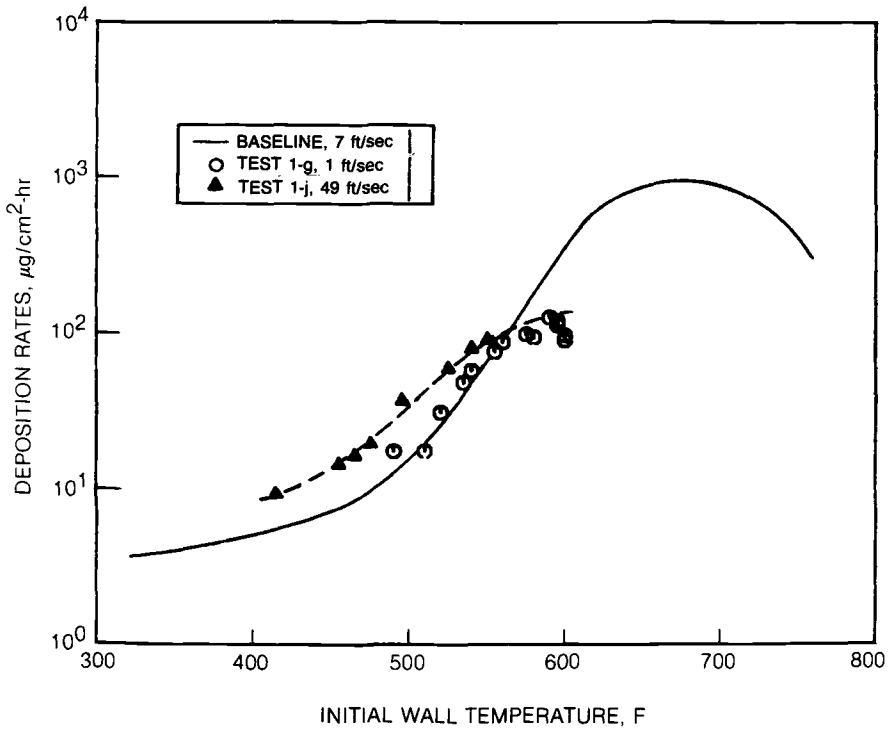


FIG. 7—Effect of flow velocity on deposition rates in JP-5 fuel for tests in AFDTA.

(0.07 m/s) and 920 (1.3 m/s) for the heater tube inlet conditions [28]. The deposition rates were similar for the two flow velocities, but the density of the deposit was estimated to be only 0.08 g/cm³ for the low-velocity test versus 0.8 g/cm³ for the 1.3 m/s test. Using this same apparatus at flow velocities of 0.076 and 0.30 m/s, Marteney observed a definite effect of flow velocity [29]. At wall temperatures below 260°C (500°F), the deposition rate was about ten times greater at the lower flow velocity where the longer residence time allows oxidation to proceed to a greater extent. The rate for the higher velocity catches up at temperatures approaching 316°C (600°F), and the maximum rate over the temperature test range is the same for both velocities.

We see several discrepancies trying to fit all of the data on flow velocity into an overall pattern. The preponderance of evidence indicates that the rate of deposition is greater at low Reynolds numbers. Marteney, in summarizing the UTRC studies at fuel velocities between 0.076 and 15 m/s (0.25 and 49 ft/s), states that the dependence of deposition rate on fuel velocity is weak for velocities above 0.3 m/s and strong for lower velocities [29]. This would appear to be a reasonable guide. Comparison between various data is difficult since chemical and physical parameters vary from fuel to fuel, since fuel temperatures versus metal wall temperatures vary from rig to rig, and since different techniques are used to estimate the fuel deterioration. Future velocity studies should emphasize conditions which approximate those in aircraft fuel systems. These are sometimes in the laminar regime as Marteney has tabulated for the TF-30 nozzle [29].

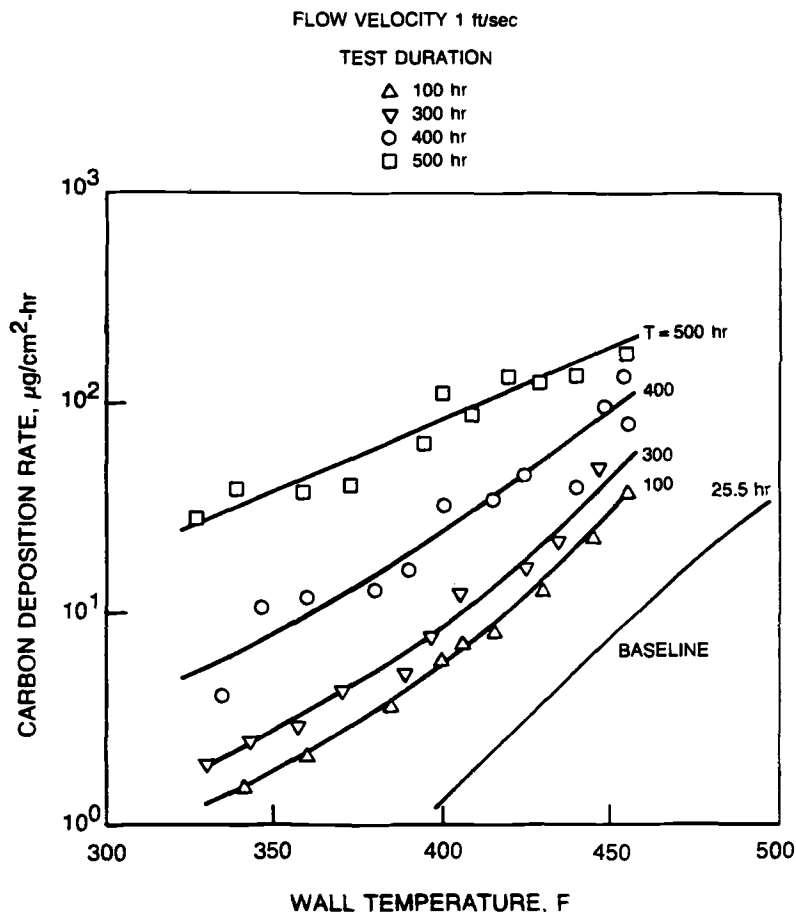


FIG. 8—Deposit formation in extended duration tests in the FDTA.

Test Duration Influence on Deposition Rate

In long duration studies at UTRC, the rate of deposit buildup on heated specimens was observed to increase with time. This was observed with the multi-tube rig, FDTA [28,29], and the single-tube rig, AFDTA [17]. The most dramatic effect of test time was done on the FDTA rig in tests up to 500 h with a JP-5 [29], but similar data was developed for a Jet A fuel [28]. Figure 8 demonstrates the case for JP-5 at a flow velocity of 0.3 m/s (1.0 ft/s). The deposition rate for a 500-h test was approximately eight times as great as that for a 100-h test. If the wall material significantly stimulates reactions, long duration tests should show a decrease in deposition rates as the wall is covered by deposit. If the deposition rate increases with time, as UTRC data indicate, an interaction with an existing deposit may be suspected. We suggest that the deposit is very porous and that the surface area increases as the total amount of deposit increases. The deposit must have modest catalytic activity for stimulating additional deposit formation.

Clark and Stevenson state that the time-dependence for deposition comprises three distinct

phases in the IFAR [30]. During the induction period, Phase 1, deposition is slow on the clean surface. Phase 2 comprises a period of near-constant deposition rate on the lacquered surface. The deposition rate may reduce in the third phase due to the insulating effect of the accumulated deposit. These authors estimated that the deposition rate was about four-fold greater on the lacquered surface than on the clean metal surface.

The long tests at UTRC formed large amounts of deposit in the heated tubes; in fact, substantial reductions in cross-sectional areas were found. The deposit accumulations were far in excess of what can be permitted in aircraft fuel systems, and Marteney [31] suggests that caution must be used in interpreting data from long duration tests, even those at low temperatures.

Clark and Thomas observed an acceleration in deposition rate in JFTOT studies comparing aluminum and stainless steel tubes. They found that the rate was proportional to time raised to the 1.7 power for both metals [16]. The authors suggested two possibilities to explain this phenomenon: (a) the deposit is more active than the metal in stimulating deposition, or (b) the rougher surface of the deposit alters mass transfer effects. A metal deactivator reduced the acceleration for both metals.

Kamin [11] also found that the deposition rate increased for longer durations. With the fiber optic modified JFTOT, he found that the first 0.14- μm layer of deposit took three times as long to form as the sixth 0.14- μm layer. This phenomenon of increasing deposition rates was observed consistently for each of six fuels tested. The tests ranged from 2.5 to 96 h in duration.

Heat Transfer Considerations

Jet aircraft contain several heat exchangers to cool important equipment or fluids. The fuel absorbs heat in these exchangers and is heated as a consequence. Any deposition on the heat exchanger surfaces from unstable fuel degrades the cooling desired. Thus, one important aspect of thermal stability is concerned with the effect of fuel quality on heat transfer and changes in heat transfer. Workers at NASA measured the rate of deposit formation in their single-tube rig by combustion to carbon dioxide [20]. Conversion of this amount to a thickness and the assumption of a value for the thermal conductivity of the deposit allowed them to calculate a decay in local wall-to-fluid heat transfer coefficient. Coefficient decreases for a 371°C (700°F) fuel-out temperature were substantial. In less than 1000 h, both for an air-saturated Jet A and even for Jet A sparged with nitrogen, the coefficient decreased at least 40%.

In a CRC program, four jet fuels were stressed for 100 h in the Esso heat transfer unit [6]. Deposition coincided with heat transfer coefficient deterioration for all fuels. However, neither oxygen content, peroxide number, pressure drop, or light transmission value consistently confirmed the initiation of heat transfer degradation.

Smith at Thornton Research Centre [24] presented the effect of test time on the heat-transfer coefficient for AVTUR at different conditions. Figure 9 depicts the linear behavior for decay in heat transfer coefficient versus hours of operation in the Shell STHTR. The decay rate is a function of the device temperature parameters; very little change for a fuel-out temperature of 150°C but a progressively greater drop with time as the apparatus was operated at temperatures up to 207.5°C. Smith observed that the heat transfer coefficient sometimes rose in the early stages of a test. This was then followed by a reversal and the expected decrease occurred. The explanation for this behavior is that the deposit surface is rougher than the smooth heater tube as installed. This deposit roughness encourages turbulence and, under certain conditions, can improve heat transfer. However, as the deposit with its lower thermal conductivity becomes thicker, the insulating property of the deposit

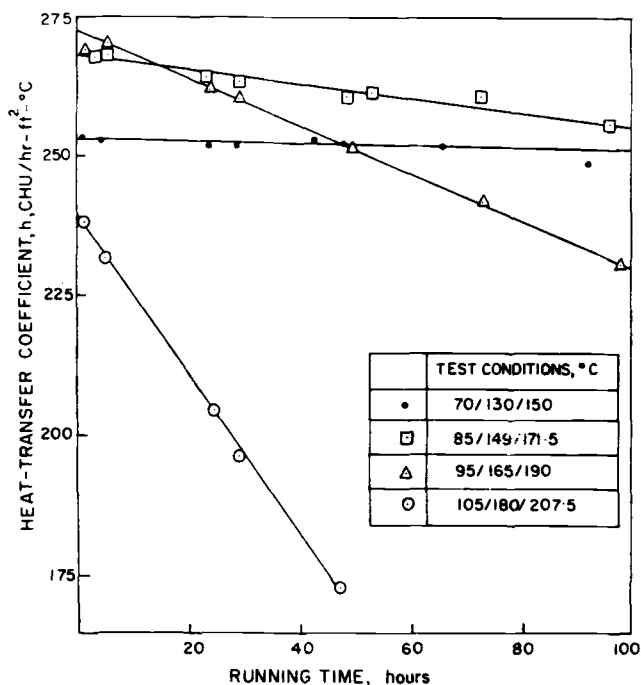


FIG. 9—Changes in heat transfer coefficient at four different temperature conditions. Fuel: AVTUR. Reprinted with permission from *Industrial Engineering Chemistry Process Design and Development*; Copyright 1969 by the American Chemical Society.

predominates and the coefficient decreases. Smith tested this hypothesis by using dimpled tubes. The dimples encouraged turbulence as expected, and the initial improvement in heat transfer was not observed with these heater tubes. In his elegant treatment, Smith related the deposit thickness for reversal in coefficient to the laminar sublayer along the tube surface. He calculated the sublayer to be 0.086 mm (0.0034 in.) and experimentally confirmed with microscope studies a deposit roughness of similar magnitude, 0.051 mm (0.002 in.).

Work at Shell Development Co. [32] also reported the improvement of heat transfer in the first few hours of operation of their single-tube heat exchanger apparatus. This was evaluated by a reduction in heater-tube wall temperature which reversed later and climbed to a level higher than the starting value. This behavior was found on deoxygenated as well as air-saturated fuels. The system temperature was substantially higher than in Smith's work.

Delfosse measured the fuel and lubricant temperatures in the NAPC single-tube heat exchanger. This uses a single tube from an F-14 aircraft heat exchanger and has built-in restrictions to encourage turbulence [33]. The temperatures were converted to a calculated heat exchange effectiveness factor. Although the data exhibited considerable short-term scatter, it could be smoothed by averaging over longer periods of time, such as 12 to 30 h. Generally, the effectiveness factor showed a linear decay with test time except for one fuel which produced an increase during the first 200 h of operation. The tubes were analyzed for deposit quantity after the experiments. It was found that there was a reasonable linear relationship between the amount of deposit and the time to a 1% decrease in the effectiveness factor.

For the Shell injector feed-arm rig, Kendall et al. measured the tube inner wall temperature during a test and the accumulated weight of deposit at the end of a test [26]. The two measurements were related by an equation showing that the amount of deposit was proportional to the increase in wall temperature raised to a power. The exponent was between two and three, depending on the test fuel and conditions. The deposit amount derived from this equation when plotted versus time exhibited an initial induction period for deposition. This was followed by a linear growth in deposit quantity over the midrange of an 80-h test and then a slight dropoff towards the end of the test. A thermal resistance calculated from a temperature ratio afforded a linear plot versus the amount of deposit.

TeVelde et al. at UTRC estimated the carbon loading as well as the thermal resistance at the end of a series of runs [34]. The thermal resistance was calculated using a deposit density of 1 g/cm^3 and a thermal conductivity of 0.21 W/m-K . The carbon amount and thermal resistance afforded an excellent linear relationship on a log-log plot.

The above data indicate that deposit quantity and heat transfer characteristics are related in a reasonable manner and that either one can be used to evaluate fuel performance.

Deposit Morphology and Physical Characteristics

The classic work on deposit morphology was published by Schirmer in 1970 [35]. He used the scanning electron microscope to examine the microstructure of deposits at magnifications up to $\times 20\,000$. Schirmer took 432 micrographs of 98 different specimens. The samples were taken from eleven different fuel system simulators or test rigs. Seven of the rigs were operated at more than one test condition and six were used with more than one fuel. The deposits from these various devices were found to be remarkably consistent in form, being built of soft particles that are spherical in shape. The particle size centered around $0.10 \text{ }\mu\text{m}$. The microspheres accumulate on deposit surfaces in randomly packed structures which become more closely packed in the substrate of the deposit and undergo fusion on heated surfaces. Fissures, which penetrated into the substrate, were observed in many of the samples. The morphology of the structures exhibited no trend with temperature or type of test. The spherical shape is not unique to these liquid-based systems; gas phase reactions such as carbon black production and soot formation in combustion engines produce microspheres.

Schirmer proposed that the particles he observed could be micelles composed of soluble polar fuel components which lose solubility as a consequence of oxidation. Some of these oxidized molecules react with active hydrocarbons or heteroaromatic species to form dipolar molecules. These latter structures comprise the skin of the micelle which surrounds other highly polar oxidized components. A $0.10\text{-}\mu\text{m}$ microsphere would have a nominal molecular weight of 300 million, but this would not be evident in most measurement techniques in which case the micelle would break down into its fragments.

The micellar theory has appeal, but support for its importance in thermal instability has not been forthcoming. A $0.01\text{-}\mu\text{m}$ micelle is huge. For instance, Glasstone indicates that the ionic micelles of a soap solution even at moderate concentration have a diameter of only 0.004 to $0.005 \text{ }\mu\text{m}$ [36]. In a jet fuel, less than 1 ppm of the fuel molecules form insoluble deposits, and this low concentration factor for active species argues against micelle formation in the thermal stability environment.

Other investigators have examined particles formed in stress tests. Johnson et al. stressed JP-4 and looked at the particles in the stressed fuel by electron microscopy [37]. They found elongated particles $0.2 \text{ }\mu\text{m}$ in length in one fuel and $1\text{-}\mu\text{m}$ spherical particles in another. Vranos used scanning and transmission electron microscopy to look at his deposits [15]. Surface deposits were not uniform, and patches of fresh surfaces were evident, particularly for deposits laid down at lower temperatures. Deposits consisted of coiled, chain-like clusters

TABLE 3—*Thermal conductivity data for deposits.*

Organization	English Units, Btu/h-ft-°F	Metric Units, W/m-°C	How Determined	Reference
NASA	0.07	0.121	Estimate	[20]
USAF	0.05–0.09	0.087–0.16	From temperature and thickness	[3]
Shell	0.022–0.11	0.038–0.19	From temperature and thickness	[38]
UTRC	0.12	0.21	From temperature and thickness	[34]
Shell	0.10	0.17	From temperature and thickness	[26]

of 0.0015- μ m-diameter particles. Marteney used low-power optical microscopy to look at deposits from the UTRC fuel deposit test apparatus [29]. The deposits appeared to be relatively uniform and nearly insensitive to the parameters of fuel velocity and local wall temperature. He did find fissures which were more pronounced with increasing thickness and test duration. He suggested that the fissures may accelerate deposit growth by providing regions where fuel can be trapped away from the flow and undergo reactions leading to formation of more solids.

Two physical properties of deposits from thermal stability tests, thermal conductivity and density, have been measured by several investigators. The thermal conductivity data are listed in Table 3.

Several investigators pointed out that the thermal conductivity of deposits varied at different locations on a heated tube and that a universal number could not be used. This seems to be evident in the data tabulated in Table 3.

Density data for deposits is listed in Table 4. The data listed exhibit a large range of values for density. The greatest spread is for the 0.08 to 0.8 g/cm³ values of UTRC in Ref 29. The authors found the low value for tests at low flow velocity (0.07 m/s) and the higher density at a much higher flow velocity (1.3 m/s). The low-density deposit would be extremely porous. There is little to choose among the other values in the table.

Surface Finish of Heater Tubes

The USAF observed in their simulator that deposits began to form at different times at the beginning of fuel tests even when all conditions were identical. Photomicrographs of the interior of manifold tubes revealed that the surface finish of the tube interiors varied [3]. Deposition, as indicated by the thermal resistance, was delayed for tubes with a smooth finish. However, once deposits were formed the rate of deposition was the same. The rate

TABLE 4—*Density data for thermal stability deposits.*

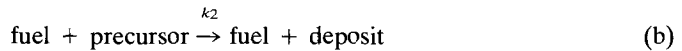
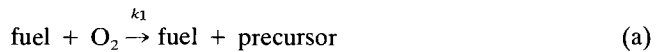
Organization	Density, g/cm ³	How Determined	Reference
UTRC	1.0	Estimated	[34]
Shell	1.45	Measured versus water	[26]
UTRC	0.08–0.80	Photomicrographs and deposit amount	[28]
UTRC	0.9	Photomicrographs and deposit amount	[29]

for a smooth tube lagged on the order of 5 h compared to a rough one. This behavior may be related to the encouragement of turbulence by the rough surface or it may be due to increased metal surface area which stimulates greater deposition.

This finding should be considered for its relevance to short-term testing, particularly for JFTOT specification tests which are 2.5 h.

Modelling of Thermal Stability Processes

Recent years have seen the beginning of efforts to combine the multiple chemical and physical processes involved in thermal oxidation stability into an overall scheme that can predict deposition rates. The first attempt was by Giovanetti and Szetela at UTRC [39]. They proposed a two-step global kinetic mechanism as follows:



Using experimental data from their own work and from Hazlett [19], these workers estimated preexponential constants and activation energies for Reactions (a) and (b). The model was partially successful in addressing different test times, temperature values, and fuel temperature-time history for the Jet A from which the input data were obtained.

Deshpande et al. expanded the UTRC model to include a third step involving a competing reaction path for precursor depletion which did not yield deposit [40]. Mass transfer considerations for the movement of precursor from bulk fluid to the wall were also included in the treatment. The authors applied their treatment to the Giovanetti-Szetela data [39]. By assuming certain activation energies, Deshpande et al. were able to obtain useful predictions which were slightly improved over the predictions from the UTRC model. From an analysis of results from variation of the diffusivity and preexponential factors, it was concluded that the process is mass transfer limited.

Roquemore et al. are applying computational fluid dynamics and chemistry (CFDC) to fouling processes in aircraft fuel system components [41]. CFDC models can provide insight into the coupling of chemistry, fluid mechanics, and heat transfer processes. The initial application assumed that deposit precursors are formed in the bulk fuel and transported by convection and diffusion to the heated wall. It was further assumed that every precursor coming in contact with the wall sticks and forms deposit. The chemistry was modeled by a single global expression of the Arrhenius type. Data from Marteney and Spadaccini [14] were used to calibrate the model. The treatment was encouraging but not completely successful. The authors suggest that two global rate equations may be necessary to cover low and high temperature ranges. The CFDC models contain parameters that cannot be calculated from first principles, and these parameters must be established for each fuel. In addition, extensive detailed chemical information is needed to tie in to the model results.

The computational models were developed further at Argonne National Laboratory [42]. Krazinski and Vanka used two global reactions to describe the chemistry processes in the UTRC aircraft fuel deposit test apparatus [17]. One reaction dealt with a low-temperature regime with a low E_{act} of 33 kJ/mol (8 kcal/mol), and the second dealt with a higher temperature (above 260°C) regime with an E_{act} of 167 kJ/mol (40 kcal/mol). The model was good up to the temperature where deposition rate declined. The authors proposed that the low-temperature reaction occurred on the wall and that the high-temperature reaction was a bulk-phase, homogeneous reaction. These suggestions have some merit. The low-tem-

perature one may be the initiation of the fuel oxidation scheme which produces hydroperoxide. The initiation step of autoxidation, the reaction of molecular oxygen with a fuel molecule, is not well understood but is considered to be subject to metal catalysis. The higher temperature reaction is probably the decomposition of hydroperoxides which have an energy of activation of about 147 kJ/mol (35 kcal/mol). The depletion of hydroperoxides explains the dropoff in deposition rate [19], a behavior with which the two global model did not cope.

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CHAPTER VI

Chemical Aspects of Thermal Stability

General Background

From the initial observation that thermal oxidation stability of aviation turbine fuels could induce problems in the fuel system, it was realized that the difficulties varied from fuel to fuel. For instance, flight performance in the F100C aircraft operating at the same test conditions varied considerably for five different fuels [1]. After 100-h tests, the decrease in fuel flow into the combustor varied from 2.44 to 18.44%, a 7.5-fold range in behavior. Figure 6 of Chapter V also illustrates the wide response of jet fuels to thermal oxidative stress [2]. In this figure, the deterioration in heat transfer coefficient for three Jet A-1 fuels is shown as a function of fuel outlet temperature from the Shell Research STHTR. At a low fuel-out temperature (210°C), one fuel effects a 25 times greater change in heat transfer than another fuel, but at a fuel-out temperature of 240°C the three fuels exhibit a similar effect on heat transfer.

These and other illustrations demonstrate that the composition of the fuel is critical in defining thermal stability effects. This chapter will address the composition and the associated chemistry that controls the reactions involved in fuel system deposit formation. Particular aspects of fuel chemistry—dissolved oxygen concentration, metal surface composition, metal ion concentration, and fuel additives—will be described in subsequent chapters.

Soon after the problem of jet fuel thermal oxidation was recognized in the 1950s, efforts were begun to understand the chemistry involved in this type of fuel degradation. The fuel chemistry studies carried out prior to 1962 were reviewed by Nixon [3] and Schwartz and Eccleston [4]. The level of knowledge in 1962 is indicated by a quote from the latter reference: “The effect of composition can be summarized by saying that the overall stability of a jet fuel depends upon the fuel composition; the gross hydrocarbon makeup is a minor factor and the minor trace components and contaminants are of major importance. Other components of the fuel, such as sulfur compounds, nitrogen compounds, oxidation products or intermediates, and trace contaminants, such as metals, have an important effect on deposit formation.” This statement is qualitatively accurate many years later, although a substantial amount of research has brought about a great increase in knowledge about the chemical composition and chemical reactions relevant to thermal stability. This chapter will summarize the important research which has afforded an improved understanding of this subject.

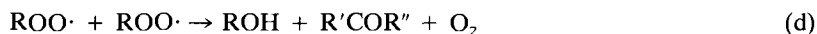
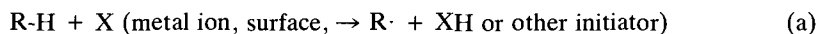
Autoxidation

Although jet fuels exhibit degradation in the absence of oxygen, degradation is usually more severe or occurs at a much lower temperature if a fuel is saturated with air [5]. The fuel/oxygen reaction, which involves free radical chains, is termed autoxidation. Although the trace and minor components of jet fuels have a strong influence on stability, 98% or

more of a specification quality fuel is composed of hydrocarbons. Thus, we will first examine hydrocarbon reactions to define a base for fuel instability chemistry.

Paraffin Oxidation

Autoxidation of paraffinic hydrocarbons is fairly well understood and involves three sequential reactions—initiation, propagation, and termination [6–9].



The initiation step, Reaction a, forms an alkyl-free radical, in most cases with the aid of a surface. The propagation Steps (b) and (c) carry the chain to a stable product, a hydroperoxide. A single initiation reaction can afford many hydroperoxide molecules, depending on the chain length of the propagation steps. Reaction (b) is relatively fast, and Reaction (c) is normally rate controlling. At low oxygen concentrations (1 to 20 ppm), however, Reaction (b) may be rate controlling. Termination reaction rates also depend on oxygen concentration, with Reaction (d) predominating at high oxygen concentrations and Reaction (f) at low concentrations. Reaction (d) forms an alcohol and a ketone as major products. The rates of the reactions in autoxidation are dependent upon temperature, hydrocarbon structure, and oxygen concentration. Catalysts and free radical initiators can also materially alter rates, particularly that for Step (a).

The presence of inhibitors also affects the rate of oxidation. Oxidation proceeds at a low but constant rate with added synthetic free-radical inhibitors. In fuels, natural inhibitors (i.e., sulfur compounds) exert similar control over oxidation rate.

If sufficient oxygen is present, the hydroperoxide concentration in uninhibited paraffin oxidation will reach a limiting concentration. Hydroperoxide decomposition ensues and additional reactions result from the free radicals formed. Alcohols and ketones are the major products in the initial stages of this process, but further reaction due to more extensive oxidation yields products such as acids, esters, hydroxy ketones, and other difunctional compounds.

If the oxygen supply is limited and the temperature increases, a situation characteristic of jet fuel flowing through an aircraft fuel system, hydroperoxide only reaches a low concentration. As it decomposes under the stimulus of the rising temperature, the products are alcohols, ketones, and small hydrocarbons. The autoxidation and hydroperoxide decomposition schemes described above occur with air-saturated *n*-dodecane flowing through a modified JFTOT [10]. The oxygenated products for this hydrocarbon, which is one of the most abundant components in jet fuel, are depicted in Fig. 1 as a function of heater tube temperature. The hydroperoxides form above 205°C (400°F) as the dissolved oxygen is used up. Under the flow conditions in the JFTOT, the hydroperoxides are stable in a narrow temperature range up to about 300°C (572°F). Above this temperature, the hydroperoxides

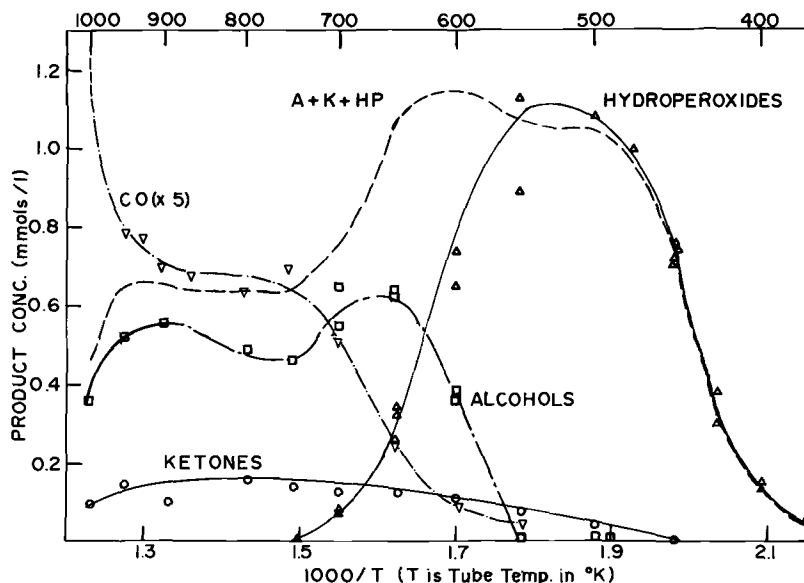


FIG. 1—Oxygenated species formed by reaction between *n*-dodecane and air; A + K + HP = alcohols + ketones + hydroperoxides; CO = carbon monoxide (modified JFTOT).

decompose to C_{12} alcohols and ketones, the former predominating in the reducing environment after oxygen is depleted. This work by Hazlett, Hall, and Matson has been supported and extended by other investigators [11]. Similar behavior has been observed for jet fuels, but the fuel hydroperoxides attain lower concentrations [12]. Experiments in a static tester support the fuel autoxidation mechanism discussed above [13].

Flask Oxidation Studies

Autoxidation phenomena related to thermal oxidation stability have been examined in a number of laboratories. Extensive efforts have been reported by the Thornton Research Centre, who measured the uptake of oxygen from air bubbling through fuel in a flask at 145 to 190°C [2]. By adding a radical initiator or radical scavenger to an oxidizing fuel, aspects of the autoxidation such as radical initiation rate could be determined. The radical initiation rate gave a fairly good relationship with the heat transfer coefficient deterioration rate for a set of fuels run in the STHTR. All of the fuels contained natural (sulfur concentration 0.03% or higher) or synthetic antioxidants.

The theoretical rationale for the Thornton flask oxidation work was presented in a later paper [14] where it was observed that the radical initiation rates could be estimated for hydrotreated fuels if the antioxidant dope rate was known. The oxidation and radical initiation rates were determined for fuels doped with model sulfur compounds, neutral polar extracts, and various acid extracts [15]. *n*-Hexyl sulfide afforded a minimum effect but phenyl disulfide exerted an 85% reduction in the radical initiation rate. Neutral polar extracts also inhibited the oxidation rate after an initial brief pro-oxidant effect. Phenols and strong acids from the extracts boosted the oxidation rate significantly when first added, but the rate then decayed and approached the base rate after about 60 min. Weak acids produced only a

minor effect. Nitrogen compounds exhibited mixed behavior in the Thornton experiments [16]. Quinoline and substituted pyridines acted as pro-oxidants, but 2,5-dimethylpyrrole depressed the oxidation rate, even at 3 ppm. Addition of model acids generally supported the findings with acid extracts, but a substituted phenol was a mild antioxidant. The increase in oxidation rate effected by metal ions (Cu and Fe) has also been demonstrated in flask oxidation tests as has the reduction in rate due to metal deactivator complexing Cu ion [2,14].

Autoxidation studies in a closed container at a lower temperature were conducted by Mayo et al. [17]. The oxidation rate was monitored by analysis of the atmosphere above the fuel for oxygen concentration. The long runs produced large amounts of soluble gums which were isolated and then analyzed by several techniques including FIMS. This latter technique showed that the gums contained significant amounts of oxidized dimers and trimers.

Batch studies at the Naval Research Laboratory emphasized product formation for autoxidation of *n*-dodecane, a major hydrocarbon component in jet fuels [18–19]. Experiments were conducted at 150 to 200°C for periods of a few hours, and the oxidation rate was estimated by analysis for oxygen content in the gas flowing through the heated fuel. Major products were alcohols and ketones, but other significant products were acids, esters, hydroperoxides, cyclic ethers, small paraffins, and olefins. An internal reference technique was used to define the oxidation rate of the C-12 alcohols and ketones relative to the starting material. The alcohols oxidized 5.2 times as fast as *n*-dodecane, and the predominant products were the corresponding C-12 ketones. The ketones were shown to be relatively stable, oxidizing only 1.3 times as fast as *n*-dodecane. The ketones and alcohols are not significant precursors to acids. Rather, the evidence is that acids come from hydroperoxide decomposition via alkoxy radicals, Reaction g. This is supported by the presence of the



smaller *n*-alkanes in the oxidation product mixtures. The aldehydes formed in Reaction (g) can oxidize readily to acids and esters by formation of the intermediate peracids.

Hydrocarbon Structure and Deposition

Ninety-eight percent or more of a jet fuel is composed of hydrocarbons. Aliphatic and naphthenic molecules predominate. Many specifications allow up to five vol% olefins, but typical values are in the 1 to 3% range. Aromatic hydrocarbon concentrations are limited to 20 vol% (25% if supplier notifies purchaser) in many commercial operations (e.g., ASTM D 1655) and 25% in military equipment (e.g., MIL-T-5624N). These aromatic levels are approached in jet fuels produced in some areas of the United States. Some specifications have a limit of 3 vol% for naphthalenes, but this level is rarely approached. Because of the distillation end point for jet fuels, only traces of naphthalenes with substituents comprising more than two carbons are found.

Deposition studies from a number of programs involving pure hydrocarbons have been published. Work has involved three types: a single pure hydrocarbon, mixtures of pure hydrocarbons, and pure hydrocarbons added to fuels. In the Esso two-phase flow reactor operated at 21-kPa (3-psia) pressure and temperatures below 232°C (450°F), Taylor found that the deposit formation for *n*-alkanes decreased moderately as the molecular size increased [20]. Branched alkanes increased formation relative to *n*-alkanes. Olefins at a 10 wt% concentration, well above that allowed in specifications, in *n*-decane increased deposit formation 3 to 35 fold compared to 100% *n*-decane. Only diolefins and indene exhibited large

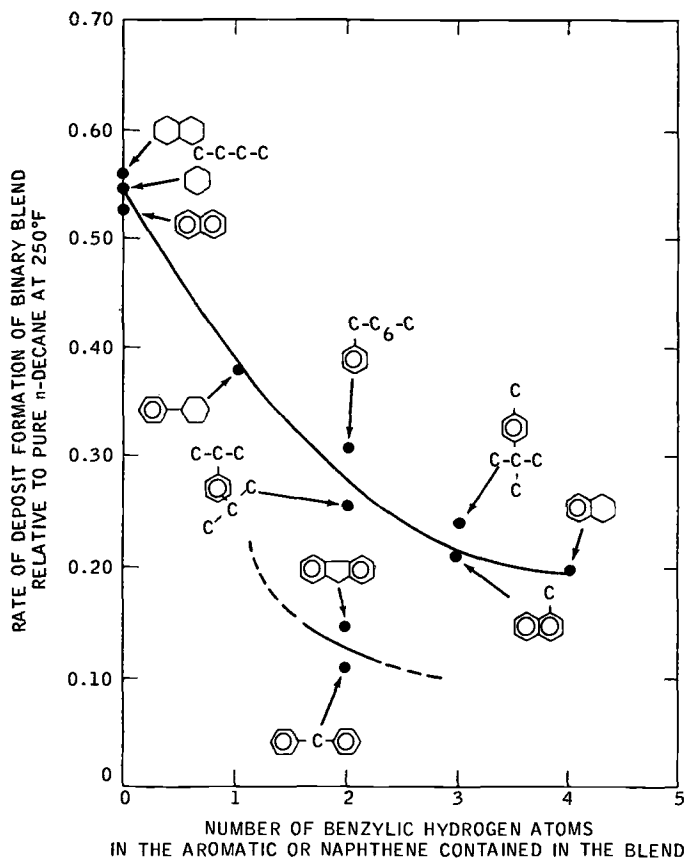


FIG. 2—Relative rate for deposit formation at 121°C (250°F) for various 10/90 aromatic or naphthene in *n*-decane binary blends compared to pure *n*-decane. Upper curve: hydrogen attached to carbon atom alpha to a single π electron system. Lower curve: hydrogen attached to carbon atom between two separate π electron systems. Reprinted with permission from Industrial and Engineering Chemistry Product Research and Development; Copyright 1969 by the American Chemical Society.

effects. Cycloalkanes exerted a modest inhibition on the deposit formation rate of decane, but many aromatics significantly reduced deposits, particularly at lower temperatures (Fig. 2). Fluorene and diphenylmethane, the most effective aromatic inhibitors, reduced decane deposition almost ten-fold at a 10 wt% concentration. The number of benzylic hydrogens in the structure showed a correlation with the reduction in deposition.

The high deposit level found for indene seems related to its ready formation of a 1:1 copolymer with oxygen [21]. Testing entirely in the liquid phase and at somewhat higher temperatures than Taylor, Hazlett also observed that 5 mol% indene significantly increased the rate of deposition in the alkane, *n*-dodecane, stressed in a modified JFTOT [22]. This is in spite of the fact that the depletion of dissolved oxygen was slowed down by indene.

Hazlett found no significant inhibition of deposit formation for fluorene or for a variety of other aromatic hydrocarbons over the temperature range 260 to 430°C (500 to 806°F). In fact, cumene, *n*-propylbenzene, triphenylmethane, and cyclohexylbenzene at the 5 mol% level in *n*-dodecane exhibited modest increases in deposits above 400°C (752°F). Several

TABLE 1—Reactivity with dissolved oxygen.

Additive ^a	Concentration	Temperature, ^b °C
None	...	225
Cumene	5.0 mol%	223
Indane	5.0	224
<i>n</i> -Propylbenzene	5.0	224
Cyclohexylbenzene	5.0	225
1-Ethyl-2-Methylbenzene	5.0	226
1,2,4-Trimethylbenzene	5.0	226
2-Methylnaphthalene	5.0	236
Tetralin	5.0	236
Diphenylmethane	5.0	256
Triphenylmethane	2.5	256
Indene	5.0	276
Fluorene	1.0	277
Fluorene	2.5	297

^aDissolved in *n*-dodecane.

^bTemperature at which one half of dissolved oxygen (60 ppm or 1.8 mM/L) has reacted in the JFTOT; 5-in. 316 SS tube.

aromatics did alter the oxidation chemistry patterns in *n*-dodecane. Table 1 lists temperature oxidation data for aromatics in *n*-dodecane at 5 mol% or less [22]. The simple one-ring benzenes had no effect on oxygen depletion. The multi-ring aromatics, however, did reduce the oxidation rate. Fluorene, the most effective, raised the temperature for 50% depletion of dissolved oxygen from 225 to 297°C at a concentration of 2.5 mol%. This oxidation behavior ties in with Taylor's observations on deposition rates at similar temperatures.

The aromatics active in reducing oxidation rate also exerted effects on the product distribution and yield from hydroperoxide decomposition and hydrocarbon pyrolysis [23]. This latter effect diminished at higher temperatures. The active aromatics, which have bond strengths of 343 kJ/mol (82 kcal/mol) or less for their weakest C-H bond [24], appear to behave as antioxidants. Thus, the free radicals from active aromatics formed by hydrogen abstraction are relatively stable at the temperatures of these experiments. Reaction of oxygen with such radicals is significantly slower than with alkyl radicals. Consequently, the overall rate of oxidation is reduced. This reduction in oxidation rate may afford a reduced deposition rate but, unfortunately, it does not guarantee it.

Hazlett tied the chemical reactions to the deposition behavior of *n*-dodecane flowing through a modified JFTOT with a Type 316 SS heater tube [22]. Figure 3 shows an Arrhenius plot for products of the breakdown of hydroperoxide as well as an estimate of the deposition rate. The latter used the Alcor tube deposit rater, a light reflectance meter. Although such ratings cannot be considered absolute, they are useful on a relative basis for each specific fuel/metal combination. Over the temperature range 300 to 375°C, the TDR readings exhibit the same slope as those for formation of soluble products, carbon monoxide, and the *n*-alkanes smaller than the starting material. By comparison with Fig. 1, it is seen that the hydroperoxide concentration is falling in this temperature range, and it was concluded that the deposits and soluble products were all derived as a result of hydroperoxide decomposition. The deposit rating decreased above 400°C. Again, this behavior was similar to that of the other products, which also exhibited a sharp change in slope at the same temperature. Since hydroperoxide was depleted at this temperature, the tie-in between hydroperoxide decomposition and deposit formation was reinforced for this pure hydrocarbon. At somewhat higher temperatures (above 475°C), the deposition rate and soluble product concentration

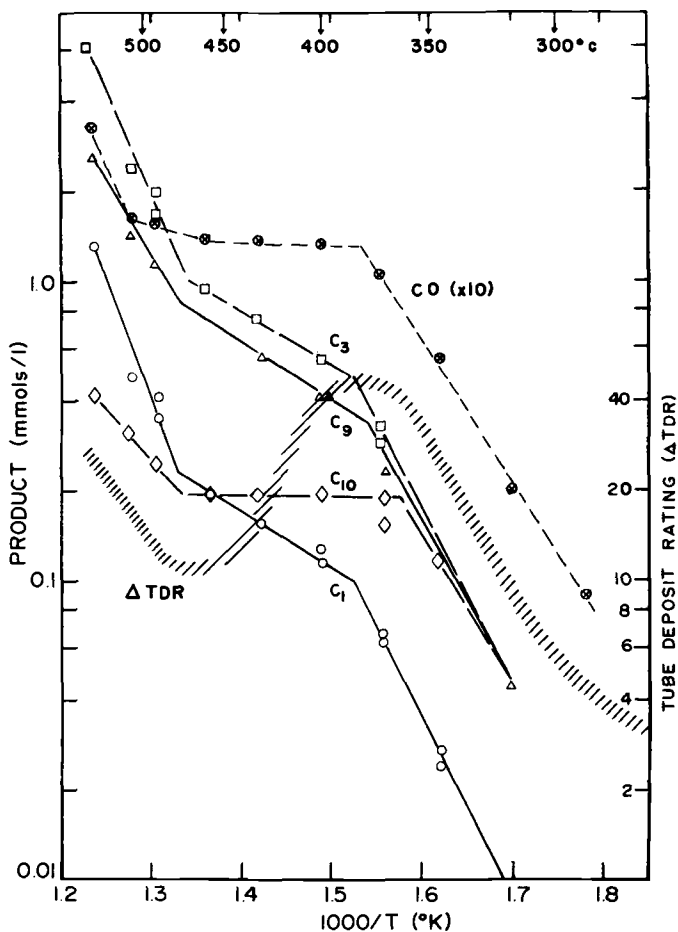


FIG. 3—Comparison of heater tube deposits with other Reaction products: C_1 = methane, C_3 = propane, C_9 = n-nonane, C_{10} = n-decane; CO = carbon monoxide (modified JFTOT).

rose again. This high temperature regime, which is relevant only to very high-speed aircraft, involves thermal pyrolysis of the hydrocarbon as well as oxidation products.

Although hydroperoxides are precursors to deposits, the reactions forming deposits are relatively minor in the overall scheme. For instance, the maximum hydroperoxide concentration found for *n*-dodecane was about 200 mg/L, whereas the typical deposit from a liter of fuel is 0.01 to 0.1 mg. Thus, the specific reactions that form deposits are definitely side branches to the primary chemical sequence. Nevertheless, it appears that dodecoxy free radicals are key intermediates in deposit formation for *n*-dodecane.

The Bureau of Mines performed two studies in which pure compounds were added to several jet fuels. In both cases, the compounds added were radioactively tagged and the percent of the specific compound in the deposit was estimated by measuring the radioactivity. No estimate of the total deposit was reported. In the first study the fuels were stressed at temperatures up to 205°C (400°F) in a 5-mL bomb [25]. All hydrocarbons added—

n-undecane, 1-dodecene, and five aromatics—gave about the same amount of radioactivity in deposits from freshly prepared samples. The radioactivity level in the deposits increased two- to three-fold after 26 weeks storage at 54°C (130°F). Even stable hydrocarbons such as diphenyl and *n*-undecane were detected in the deposits. Physical absorption or entrapment in the deposit pores may be a factor in these experimental findings.

In the second BuMines program, a similar study was carried out using a microfuel coker [26]. Again, the amount of radioactivity in the deposits for freshly prepared samples was approximately the same, irrespective of added tracer. After 52 weeks storage at 54°C (130°F), however, certain hydrocarbons gave dramatic increases in the radioactivity found in the deposits. Indenes showed the greatest increases, but indanes also had significant increases. Tetralin also exhibited an increase, particularly with one of the five fuels. It is noteworthy that the radioactivity increases were observed only with two fuels. Thus, the fuel/hydrocarbon blend must be critical to deposit formation. In this same study, nonradioactive blends containing 1% of either 1-methyl- or 1-ethylindene decreased the thermal stability of a fuel. On the other hand, 2-methylnaphthalene and 1-ethylindane did not change the fuel breakpoint.

Bol'shakov observed that either tetralin or acenaphthene drastically increased sediment formation in a variety of fuels oxidized at 200°C with air blowing [27]. Bushueva, using the same oxidation arrangement, reported similar findings [28]. In addition, he found that alkylbenzenes formed little sediment but that naphthalenes sharply increased sediment formation.

Datschefski reported that the olefin content of Jet A-1 fuel could be increased from 1 to 2% up to 8 to 10% without significantly altering the JFTOT breakpoint [29]. Lusebrink and Nixon found that monoaromatics as a class were stable in a tube heater with following filter to measure pressure buildup [30]. Aromatic olefins such as styrene and indene, however, stimulated the production of insoluble gum which plugged the filter.

Involvement of Compounds Containing Hetero Atoms in Deposit Formation

Sulfur, nitrogen, and oxygen compounds are found in petroleum. Sulfur, the most abundant of these elements in jet fuels, is limited to 0.3% in most commercial specifications, but up to 0.4% is permitted in some military specifications. These limits are in place to minimize turbine blade corrosion. The amounts of nitrogen and oxygen compounds are not limited, but both are assumed to be low in petroleum-derived jet fuels. Analyses for nitrogen and oxygen are done only rarely. Sulfur, nitrogen, and oxygen compounds will be addressed in separate sections as will acids and polar fractions. Interactive effects will be treated in addition.

Sulfur Compounds

A major study on the role of sulfur in thermal oxidation stability was made by Taylor and Wallace [31]. In this study, pure sulfur compounds were added at the 1000 ppm S level to a sulfur-free jet fuel. Experiments were conducted in the Esso wing tank tester at temperatures between 93 and 232°C (200 to 450°F). This glass reactor, operated at 21 kPa (3 psia), stressed fuel in two-phase flow, and deposit amounts were determined by weighing titanium strips. Of twelve sulfur compounds examined, two—diphenyl sulfide and dibenzothiophene—produced slight effects. Disulfides, thiols, and other sulfides exhibited significant increases, in some cases up to 20-fold. This effect increased as the temperature was raised. Deposit formation appeared to increase proportional to the square root of the sulfur concentration.

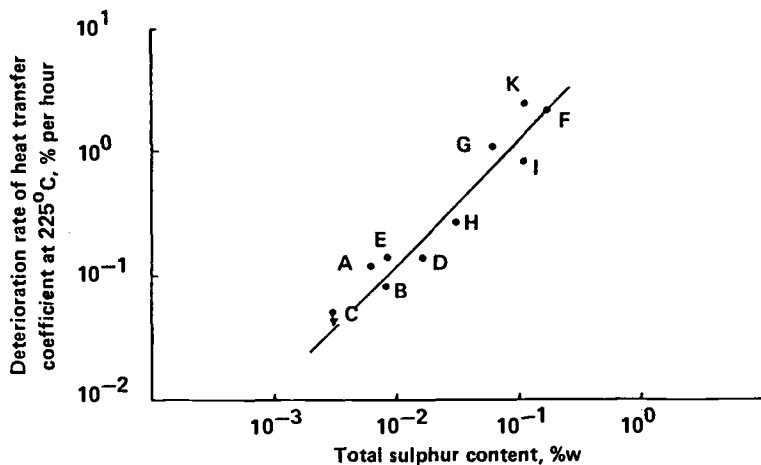


FIG. 4—Effect of sulfur compounds on fuel heat transfer behavior in STHTR.

In static fuel tests at 100 to 300°C, Davydov and Bol'shakov found that sediment formation followed mercaptan content [32]. Whisman et al. observed that *n*-butyl sulfide (0.3%) exerted little effect on the breakpoint of five fuels in a microfuel coker [26].

Shuler, Krynitsky, and Carhart followed particulate matter formation by light scattering in tests involving phenyl disulfide [33]. Decane containing this sulfide (0.18% S), when stressed in a bomb, demonstrated distinctly increased amounts of particulates compared to a sulfur-free hydrocarbon mixture. The effect of phenyl disulfide could be enhanced or diminished by specific hydrocarbons. Thus, cumene increased particulates but decalin and dodecene decreased particulates. Further tests with butyl disulfide demonstrated that butyl mercaptan formed as the disulfide decreased. In addition, definite involvement of dodecene and cumene with the disulfide was found.

Mills and Kendall tested a group of ten Jet A-1 fuels, representative of a range of feedstocks and refinery processes, in the Thornton STHTR [2]. The log-log plot in Fig. 4 shows the good correlation between the decay in the heat transfer coefficient and the total sulfur. This is a remarkable relationship in view of the probable variation in types of sulfur compounds in this series of jet fuels. Further work at Thornton examined the effects of sulfur compound class on the deposition rate in JFTOT tests at 350°C [15-16]. All sulfur compounds, which were added at the 0.1% S level, increased the amount of carbon found by combustion of the deposits. Thiophenes and an alkyl sulfide produced a modest increase in deposits, but all disulfides exerted a much more substantial increase.

Other researchers have used the JFTOT in sulfur compound studies. Amos and Knight found little effect on TDR or visual ratings for an alkyl disulfide at the 0.1% S level in AVTUR run at 290°C [34]. On the other hand, Savaya, Mohammed, and Abbas, operating the JFTOT at 296°C with hydrotreated kerosene, measured increases in TDR at 1000 ppm S for several sulfur compounds [35]. Alkyl sulfides, alkyl disulfides, thiophenes, and thiophenol increased TDR readings at this sulfur concentration. Reversals with concentration were observed for most compounds so that the ratings were substantially lower at 2000 or 3000 ppm than at 1000 ppm. It would be useful to rate these deposits by other techniques such as carbon burnoff or optical interference to confirm these reversals with concentration.

The JFTOT has also been used to explore the chemistry of sulfur compound oxidation

in a model hydrocarbon, *n*-dodecane [36]. No deposit measurements were reported in this study, which covered the temperature range of 100 to 340°C. *n*-Hexyl disulfide, at 0.2 or 0.4% S, did not modify the oxygen depletion rate but did effect a lower hydroperoxide concentration. A test with 0.4% S gave a lower ROOH level than a 0.2% S test. This demonstrates that the initiation and propagation steps for hydrocarbon oxidation are occurring but that the hydroperoxide is reacting with the disulfide to form a thiol sulfinate, R-S(O)-S-R. Thiophenol demonstrated a greater effect on the chemistry. Comparable oxygen depletion required a 30°C higher temperature for this compound at a sulfur concentration of only 0.03% and 10°C higher for a substantially lower concentration, 0.005%. Hydroperoxide was not observed at the 0.03% S concentration. The S-H bond of thiophenol is weak, 330 kJ/mol (79 kcal/mol), and the proton is subject to abstraction by alkoxy or peroxy radicals. This is demonstrated by the fact that phenyl disulfide, the dimer of the thiyl radical, was a predominant product in this experiment.

Nitrogen Compounds

Taylor studied the effects of nitrogen compounds on deposition in a wing tank simulator [37] as he had for hydrocarbon and sulfur compound classes. He found that indole, 2-ethylpyridine, and 2,5-dimethylpyrrole increased deposit formation rates four to ten fold when added at the 1000-ppm nitrogen level. This effect, which was tested in the 93 to 149°C (200 to 300°F) range, was more pronounced at higher temperatures. Other tests with the substituted pyrrole demonstrated that this compound increased deposits even at the 10-ppm N level.

Antoine determined the JFTOT breakpoints for a Jet A with and without added nitrogen compounds [38]. At doping levels of 0.01 to 0.1%, pyrrole dropped the breakpoint about 40°C and indole effected a 20°C decrease. In other work with the JFTOT, Reynolds reported the breakpoints for shale-derived liquids which had been produced by various retorting processes and refined to different degrees of severity [39]. Figure 5 depicts the effect of nitrogen concentration on breakpoint. A general trend is obvious: the breakpoint decreases as nitrogen increases, and almost all samples with more than 0.01% N failed the specification limit of 260°C (500°F). The nitrogen level is not a reliable predictor of thermal stability, however, since fuels with identical amounts of nitrogen exhibited breakpoints up to 100°C apart.

The U.S. Navy also used the JFTOT to examine the nitrogen question, particularly in relationship to the production of jet fuels from shale oil [40]. Using a TDR criterion of 17 maximum, the heater tube breakpoint was improved only 10°C by reducing the total nitrogen content in steps from 954 to 123 ppm, but the filter breakpoint was raised from 232 to 279°C. Nonbasic nitrogen compounds comprised 116 ppm in all of the samples, the remainder being organic bases such as substituted pyridines, tetrahydroquinolines, and quinolines. Addition of 50 ppm of 5-ethyl-2-methylpyridine to a nitrogen-free shale jet fuel did not cause failure on the JFTOT test at 260°C (TDR 4). Doping with 50 ppm of 2,5-dimethylpyrrole gave a TDR of 25 and severe filter plugging at the same temperature. A petroleum-derived jet fuel passed the JFTOT at 260°C when doped with alkyl-substituted pyridines or N,N-dimethylaniline at nitrogen concentrations in the range of 50 to 100 ppm. As others have found, however, pyrrole at 100 ppm gave failures on both TDR (32 max reading) and filter pressure drop and a diamine, 2-amino-3-methylpyridine, also caused a failure on TDR (45 max reading).

The Thornton Research Centre doped a petroleum-derived fuel with several nitrogen compounds at the 40-ppm N level, defining the performance at 350°C by carbon burnoff [16]. Quinoline and substituted pyridines produced similar and modest increases in depo-

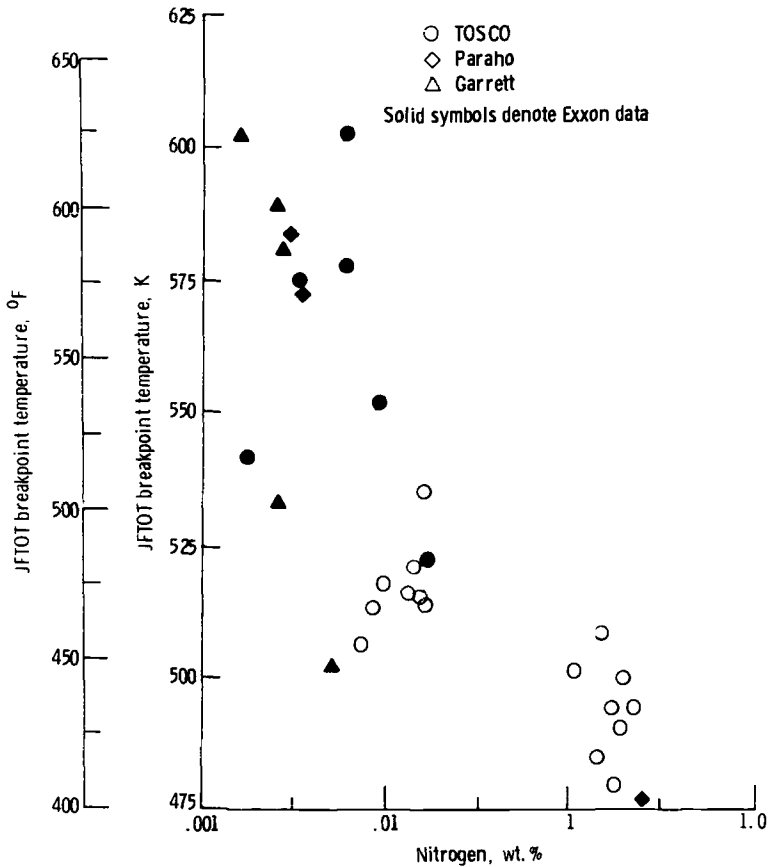


FIG. 5—Variation of JFTOT breakpoint temperature with nitrogen level after hydrotreatment.

sition. Indole and 2,5-dimethylpyrrole gave substantially more deposit, the former more than four times that of any of the pyridines. Additional JFTOT studies at the Royal Aircraft Establishment tested the effect of several nitrogen compounds on AVTUR 50 thermal stability [34]. Indole, quinoline, 2,4,6-trimethylpyridine, and 2-methylindole, all at 100-ppm N level, degraded the quality of the TDR and visual tube ratings. 2,5-Dimethylpyrrole exerted a marked effect, particularly on filter plugging, at concentrations of 1 ppm. Pre-heating the sample containing 2-methylindole at 150°C for 4 h markedly increased the filter pressure drop. Amos and Knight also looked at the effects of nitrogen compounds in AVTUR 50 which had been depolarized. The behavior was less pronounced than in untreated AVTUR 50, and higher heater tube temperatures were required to see changes due to the nitrogen compounds. The amount of deposit found by Amos and Knight in static tests for 4 h at 150°C did not afford data in agreement with the JFTOT tests.

Other thermal stability tests in static devices by Englin et al. indicated that removal of trace amounts (<1 ppm) of nitrogen bases from jet fuels decreased residue formation [41]. In other static tests, Bagnetto [42] observed that pyrrole at the 1000-ppm N level dropped the threshold temperature for the 5-mL bomb test from 254°C (489°F) to 223°C (433°F).

Oxygen Compounds, Acids, and Polar Fractions

Little research emphasis has been given to these components of jet fuels with respect to thermal stability. Lusebrink and Nixon, using a chromatographic technique to isolate gums, stated that a polar fraction high in oxygen and nitrogen was very deleterious [30]. This fraction consisted of nitrogen bases, phenols, and "neutral" components. The "neutral" fraction consisted largely of aromatic hydrocarbons, thiophenes, and a polymeric material rich in oxygen and nitrogen.

Mayo, Stavinoha, and Lee isolated polar gums from an oxidized JP-8. Fractions of this material were then added to an unoxidized fuel and tested in the JFTOT [43]. Monomeric oxidation products had a minor effect on filter pressure, on visual or TDR readings, and on a measurement of deposit volume based on dielectric measurements. A second fraction composed of polymeric and bifunctional monomeric components degraded the thermal stability of the fuel. In particular, filter pressure and the dielectric measurements showed dramatic effects. The latter increased 20 to 40 fold.

Turner et al. stressed two hydrotreated jet fuels at 60°C and followed the increases in hydroperoxides, acids, and gums [44]. The thermal stability was also determined in the JFTOT at 282°C maximum temperature. Visual and TDR ratings were made on the tubes. No correlation was found between acid number or gum content. The hydroperoxide level exerted some effect on TDR readings. Samples with peroxide numbers less than 150 ppm exhibited TDR patterns very similar to that of fuel which had not been subject to the 60°C stress. Samples with peroxide numbers above 450 ppm significantly increased total TDR readings and decreased the breakpoint temperatures up to 40°C. Even a peroxide level of 150 ppm would be unacceptable in practice since elastomers in aircraft fuel systems are attacked at concentrations as low as a peroxide number of 8 ppm.

Kendall, Clark, and Stevenson extracted polar materials from sweetened Jet A-1 fuels and fractionated the extract into phenols, weak acids, strong acids, and neutral polars [15]. The latter was high in sulfur, indicating a substantial portion of sulfur compounds in this fraction. The quantity of the extracts were neutral polar, 1300 mg/L; weak acids, 183 mg/L; phenols, 75 mg/L; and strong acids, 5 mg/L. The fractions were put separately and together into another fuel which was then tested in the JFTOT at 350°C and the amount of deposition determined by carbon burnoff. The additions were made to give the same concentration in the test fuel (except for weak acids) as in the original, unextracted fuel. The weak acid fraction, doped at 10% of its original concentration, was innocuous. Of the others, the order of decreasing effect was neutral polars, phenols, and strong acids. However, the order of effect on deposition on a unit weight basis was strong acids—most effective, phenols—next, and neutral polars—least effective. The combined extracts had a greater effect than the sum of the fractions, indicating positive interaction between the various classes. Acid extracts from a group of five fuels, when doped into a jet fuel with excellent stability, produced a wide range of deposition amounts, indicating that the specific nature of the acids exerts a major control over deposition behavior.

In further work at Thornton, Clark and Smith defined the deposition behavior of model acids doped into a Jet A-1 fuel at 100 mg/L [16]. Alkyl-substituted phenols exhibited a minor increase in deposition, and carboxylic acids were moderately prodeposition. Strong acids, ethane and *p*-toluene sulfonic acids, were strongly prodeposition. In spite of these differences in acid effects, Clark and Smith found a correlation between the total acid content (as determined by ion exchange chromatography) and the deterioration of the heat transfer coefficient measured in the STHTR. The relationship was developed on a log-log basis and must be used with caution.

Oleic and dilinoleic acids made distinct contributions to deposits in the radioactive tracer tests conducted by the Bureau of Mines [26].

Interactions Between Classes of Compounds

Datschefski defined the JFTOT breakpoints for blends of fuels containing high and low levels of olefins (5 and 10%), nitrogen (2 and 40 ppm), and sulfur in hydrofined and sweetened fuels [29]. The high-olefin, low-S, low-N mixture in the hydrofined fuel did not degrade the 290°C breakpoint of the hydrofined fuel but dropped that of the sweetened fuel from 275 to 260°C. All of the other combinations degraded thermal stability with the low-olefin, high-N, high-S blend exerting the greatest effect, a 60°C decrease in breakpoint in the sweetened fuel.

Amos and Knight found little interaction between model nitrogen and sulfur compounds in JFTOT studies [34]. In 4-h flask tests at 150°C, however, organic bases such as quinolines and pyridines gave significant amounts of insoluble material when stressed with sulfur compounds in a depolarized AVTUR 50 fuel. The increases were observed for di-*n*-octyl sulfide and di-isobutyl disulfide but not for thianaphthene (benzothiophene). Analysis of these solids supported the proposal that they were salts of the base with sulfuric acid. This would require extensive oxidation of the sulfide/disulfide to form sulfuric acid. Of four pyrrole/indole compounds tested, only 1,2,5-trimethylpyrrole rivalled the organic bases in the quantity of solids formed in the flask test.

Enhanced deposition was found by Shell's Thornton group for blends of the total acid extract from a jet fuel and several model sulfur compounds comprising sulfides, disulfides, and benzothiophene [15]. Of the sulfur compounds tested, only 2-ethyl thiophene showed a negative interaction with the acid extract in these JFTOT experiments. Total acid extracts from several other jet fuels exhibited varied behavior with *n*-hexyl sulfide; some interacted positively to increase deposition, but one had a decided negative interaction, and another did not demonstrate any interaction.

Clark and Smith at Thornton looked at interactions between three compound classes:

1. Acids and nitrogen compounds.
2. Nitrogen compounds and sulfur compounds.
3. Acids and sulfur compounds.

Hexanoic acid, at 100 ppm, enhanced deposition with all nitrogen compounds tested in 350°C JFTOT tests [16]. The interaction was modest for quinoline and alkyl-substituted pyridines but somewhat more for indole and 2,5-dimethyl pyrrole.

Phenyl disulfide was the sulfur compound used in the N/S interactions. With the exception of 2,4,6-trimethyl pyridine, which gave a modest enhancement, all nitrogen compounds produced negative interactions with the disulfide.

The model acids were also tested with phenyl disulfide. Phenols and carboxylic acids enhanced deposition in the JFTOT in blends with the disulfide. The strong acids decreased deposition, however. The authors suggested that some of these interaction results must be treated cautiously, however, since the 2,5-dimethyl pyrrole/phenyl disulfide blend exhibited severe filter blockage even though deposition on the heater tube was slight. Further, the strong acid/phenyl disulfide blend formed insolubles in the reservoir which were caught by the prefilter before exposure to the heated section.

Mushrush et al. studied the reactions of thiophenol with aromatic olefins [45–46]. Oxidations were conducted in sealed glass tubes at 120°C using either oxygen or *t*-butyl hydro-

peroxide as the oxidizer. A minor product was phenyl disulfide formed by dimerization of the thiyl radical resulting from oxidation of thiophenol. The bulk of the thiyl radicals added to the double bond of the olefin, styrene or indene, to give a condensation product. Further oxidation at the sulfur position to form a sulfoxide was observed with styrene. A small amount of styrene dimer and polymer were formed. Other products from indene reaction included phenylthiyl indanols and indanones. Molecular weight was increased in many of the reactions studied.

The problem with aircraft operating out of Brazil in the mid-1980s illustrates the intricacies and importance of fuel interactions in thermal stability [47–48]. The refinery at Rio de Janeiro used the Bender process to convert mercaptans to disulfides. The mercaptan level, although within the fuel specification, was higher than normal for a sweetened fuel. Analysis of the deposit from the jet engine control by Shell found high copper and high sulfur, 27 and 14%, respectively. In another sample, Exxon found high sulfur and aluminum. In fact, additional analytical chemistry evidence on the Exxon specimen suggested that the Al and S were combined in the inorganic compound, aluminum sulfate. Evidence for oxidation of a small but significant fraction of a thiol to a sulfonic acid at lower temperatures (ambient to 80°C) has been presented by Hazlett [49]. Much smaller conversions have been observed for the oxidation of disulfides to sulfonic acids [50]. Amos and Knight found salts of sulfuric acid and organic bases in the insolubles formed during flask oxidations at 150°C [34]. These results occurred with AVTUR 50 doped with model sulfur and nitrogen compounds. Presumably, alkyl sulfides or disulfides were oxidized to sulfuric acid. Although the model studies described were done with much higher oxygen availability, fuel from the Bender process may have contained thiols or disulfides which oxidized easily and extensively. The fuel from the Rio de Janeiro refinery, even though passing the JFTOT specification, was found to degrade heat transfer in the Shell STHTR somewhat worse than any other sweetened jet fuel that Shell had tested [47]. The Thornton Research Centre did consider that the fouling in the STHTR was consistent with a function of the total acid content and sulfur content which had been used successfully with other fuels. Use of the Bender process has been discontinued for refining jet fuel at the Rio refinery.

Characteristics of Deposits

Deposits formed by thermal degradation in jet engines and in laboratory rigs are largely insoluble in all common organic solvents, both polar and nonpolar. Chemically and physically, the residues from jet fuel appear to be closely related to the insoluble residues precipitated from furnace oils upon long periods of storage at ambient temperatures [51]. In jet fuels some change in physical properties, such as decreased solubility, is probably caused by the high temperature at which these residues are formed. The chemical nature of deposits will be considered in two parts: elemental composition and chemical structure.

Elemental Composition of Fuel System Deposits

A number of scientists have analyzed deposits from engines and reported their findings. Several representative sets of data are listed in Table 2.

The most notable of the observations from these findings is the high concentrations of the hetero atoms—oxygen, nitrogen, and sulfur. The oxygen amount is the highest of the elements with the exception of carbon. In fact, the atom ratio for O/C was greater than 0.2 for all samples in the table and exceeded 0.3 for three of the samples. The high sulfur and nitrogen are noteworthy in view of the low amounts of these elements in jet fuel. The H/C ratio for most samples is substantially less than that of the fuels and indicates that

TABLE 2—Engine system deposits.

Element, wt%	Engine Filter, Ref 51	Nozzle Screen, Ref 52	Engine Nozzle, Ref 1	CF6-50A Nozzle, Ref 53	TF-30 Manifold, Ref 53
Carbon	31.6	49–55	54.4	50.3	56.4
Hydrogen	4.0	6.5–8.5	8.6	2.4	3.1
Nitrogen	4.6	2–5	4.5	0.6	1.4
Sulfur	5.3	7–8.5	3.7
Oxygen	14.8	15–20	15.2	20.5	26.5
Ash	34.4	7.5–18	14.7	20.9	5.6
Total	94.7	...	101.1	94.7	93.0

aromatic or heteroaromatic compounds are significantly involved in deposit formation. The high ash contents can be ascribed to metal debris, such as pump wear, from the aircraft fuel system. Removal of underlying metal when the samples of deposits were scraped from the fuel system components is a second source of ash. Rogers reported that the ash contained large amounts of lead and iron but much lower amounts of copper [1].

Hazell et al. used Auger electron spectroscopy in combination with argon ion bombardment to estimate deposit depth and composition on JFTOT tubes [54]. Carbon was the predominant element found, but oxygen and sulfur levels were much lower—oxygen, 3%; sulfur, 0.4%—than those reported in the preceding paragraphs. Hazell's deposits were produced on aluminum tubes at accelerated conditions, 360°C.

Considerable analytical information has been reported for other devices and test environments [55]. The most extensive analyses were conducted by the Naval Research Laboratory [53]. In this work, Hazlett and Hall estimated the elemental composition of deposits from the Naval Air Propulsion Center single-tube heat exchange tests [56] and the U.S. Air Force AAFSS [57]. The NAPC tubes, which were stressed at fuel-out temperatures of 165 to 185°C (329 to 365°F), were sectioned and alternate segments analyzed for C-H-N, O, and S. Thus, the data were semiquantitative, but elemental ratios could be estimated. Carbon, as expected, was the major element found, but large amounts of oxygen and lesser amounts of nitrogen and sulfur were also present in these deposits. Most of the H/C atom ratios fell within the range of 0.4 to 1.7 and O/C within the range of 0.2 to 0.7. The higher ratios for H/C and O/C are thought to be due to water absorption on the organic deposit, which was thought to be highly polar. N/C atom ratios varied from 0.03 to 0.18 and S/C ratios from 0.02 to 0.10, indicating that both nitrogen and sulfur were present at the level of a few percent of the total deposit.

Examination of the USAF AAFSS deposits was accomplished by removing the material from the manifold, which had been cut in half the full length. Thus, a material balance could be obtained as shown in Table 3. The sum of C,H,N,O,S, and ash gave a good material balance (94 to 97%) except in three cases. Ash was due to metal particles from the tube wall. Duplicate analyses gave elemental totals within 3% of each other. The manifold temperature and corresponding percentage compositions and elemental ratios of the deposits are given in Table 3. These results are generally similar to the engine deposit results in Table 2 allowing for the higher ash content in the engine deposits.

The H/C atom ratios were uniformly low, 0.43 to 0.62, indicating a highly aromatic and/or heteroaromatic composition. The O/C ratios, which averaged about 0.20, support the viewpoint that oxidation is a key aspect of jet fuel instability. Two fuels, AFFB-11 and -12, gave especially low percentages and ratios for O, S, and N. These two fuels were JP-7's,

TABLE 3—U.S. Air Force simulator deposits.

AFFB Fuel	Fuel Type	Film Temperature, °F-Calculated	Atom Ratio			
			H/C	N/C	O/C	S/C
10	aged JP-7	512	0.60	0.053	0.28	0.01
9	JP-5	544	0.43	0.019	0.22	0.06
8	Jet A-1	550	0.52	0.027	0.25	0.01
16	JP-4	554	0.53	0.017	0.23	0.01
13	Jet A	564	0.45	0.006	0.22	...
11	JP-7	665	0.57	0.005	0.09	0.001
12	JP-7	688	0.62	0.011	0.10	0.003

AFFB Fuel	% Found						
	C	H	N	O	S	Ash	Total
10	57.6	2.8	3.3	17.6	1.5	0.0	82.8
9	61.0	2.4	1.3	15.9	8.3	0.1	89.0
8	65.6	2.9	2.1	21.4	1.6	2.8	96.4
16	68.1	3.1	1.3	20.9	1.0	0.3	94.7
13	69.3	2.6	0.5	20.4	...	0.3	93.8
11	73.6	3.5	0.4	8.4	0.3	1.7	87.9
12	79.9	4.2	1.0	10.8	0.7	0.2	96.8

which had higher stability and consequently were stressed at much higher temperatures. At this temperature, instability should be less oxidative and more pyrolytic. The hetero atoms would be less important for that type of environment. A second factor with respect to the JP-7's is the fact that these fuels contain less polar material.

The hetero elements become enormously concentrated in fuel deposits. Oxygen content of deposits varied from 16 to 21% (except the JP-7's). The amount of dissolved oxygen in a fuel at saturation is about 60 ppm. Thus, the concentration factor for oxygen can be 3000 or more. However, oxygenated organic compounds may also be present in the fuel and prevent a useful estimate of total oxygen availability in the fuels. The nitrogen and sulfur content of the AF simulator deposits is compared with the nitrogen and sulfur concentrations in the fuels in Table 4. The enhancement factor for nitrogen is tremendous, greater than 10 000/1 for all seven fuels. The sulfur enhancement factor is much lower but still substantial, 54 or greater in all cases.

Chemical Structure Information on Deposits

Infrared and mass spectrometric techniques have been invoked to examine deposits for structural information. Nixon detected the presence of carbonyl and aldehyde groups by IR and suggested that strong acids may also be present [3].

The low solubility of the deposits in useful solvents and the fact that deposits are normally formed on curved tubes create experimental difficulties. Vranos et al. partially solved this problem by using the UTRC fuel coking apparatus which incorporated flat specimens in the fuel flow [58]. Thus, reflectance IR could be applied to deposit characterization. Vranos found bands in his IR spectra of these specimens which were assigned to aliphatic and aromatic C-H bonds, carbon-oxygen single and double bonds, and hydroxyl bonds. The possible presence of anhydrides or imides was also proposed.

Serio et al. formed deposits and insoluble gums in a heated capillary tube at 450°C [59].

TABLE 4—Nitrogen and sulfur concentration in jet fuel deposits.

Fuel Sample	Nitrogen			Sulfur		
	In Fuel ^a	In Deposit ^a	Concentration Factor	In Fuel ^a	In Deposit ^a	Concentration Factor
AFFB- 8	0.000063	2.1	33,000	0.019	1.6	82
AFFB- 9	0.000089	1.2	13,000	0.066	8.0	120
AFFB-10	<0.00001	3.0	>300,000	0.014	1.2	88
AFFB-11	<0.00001	0.4	>40,000	0.0003	0.24	970
AFFB-12	0.000042	0.95	23,000	0.0003	0.74	2500
AFFB-13	<0.00001	0.5	>50,000	0.014
AFFB-16	0.00014	1.3	10,000	0.019	1.0	54

^aPercent by weight.

The portion of the insoluble product from a JP-5 fuel which was soluble in acetone appeared to be mostly aliphatic in character by Fourier transfer IR. Some carbon-oxygen single and double bonds were also detected in the spectra.

Serio et al. also applied FIMS to their deposits and insoluble gums [59]. Long chain alkanes predominated the spectra with minor amounts of aromatics. The large alkanes might be dimers formed from chain termination in the oxidation process. Dimers might be predicted for a pyrolysis regime which this testing environment approached—450°C. Another explanation is that only a small portion of the insolubles dissolved in acetone, in keeping with many observations that thermal stability deposits are poorly soluble in most solvents. Thus, the major portion of the material from the Serio work may not be represented by these results.

Malhotra and St. John scraped the deposits from a JFTOT heater tube and subjected them to FIMS analysis [60]. These deposits for an experimental jet fuel, JP-8X, lacked the alkyl-substituted indole peaks which are characteristic of deposits formed in diesel fuels in storage. Instead, the major peaks appeared to be hydrocarbon in nature. Only 30% of the deposit was volatilized under the pyrolysis/MS conditions, which had a maximum temperature of 500°C.

NIPER examined JFTOT tube deposits and filter-collected insolubles with HR/MS coupled to a temperature-programmed inlet probe [61]. On the average, the tube deposits and filter sediments appear to have similar composition. Results for a representative fuel are as follows:

1. *Tube deposit*—naphthalenes; phenols; other aromatics with one oxygen; aromatics with one nitrogen; traces of aromatics with two oxygens; traces of aromatics with nitrogen plus oxygen; traces of aromatics with one sulfur.
2. *Filter sediment*—olefins or cycloalkanes; aromatic hydrocarbons; phenols; benzothiophenes; dibenzothiophenes; compounds with alkylamine groups; pyrroles; pyridines (or anilines); indoles; other aromatics with one nitrogen.

The most abundant types on the heater tube included naphthalenes and phenols, with the latter appearing in the spectra at probe temperatures above 300°C. In contrast, naphthalenes appeared at temperatures below 150°C and again at temperatures above 300°C. These observations show that the naphthalenes were released by two mechanisms: (a) they were desorbed from the surface or released from polymeric cages at low temperatures and (b) they were produced by pyrolysis at high temperatures. All of the phenols came by the latter process. Indoles were the most abundant components found on the filter at probe temperatures above 300°C.

Effects of Storage at Low Temperatures

All fuels are stored at ambient conditions for various periods of time. Military organizations maintain reserves at strategic sites, frequently for several years. It is important to know if the quality of the fuel, including the thermal oxidation stability, has deteriorated during the storage period. Since both storage and thermal stability involve oxidation of organic molecules, the two types of stability may influence the other.

Several studies have addressed the effect of aging on thermal stability. These programs have aged fuels at ambient conditions, including several years in the desert, and under accelerated conditions up to 83°C. In reviewing early work, Schwartz and Eccleston [4] found that the thermal stability of some fuels improved after storage but others had poorer thermal stability.

Bagnetto [42] found a decrease in threshold failure temperature for only one of five fuels stored for six days at 83°C (180°F). The other four samples exhibited no degradation after 36 days at 83°C. Nixon [3] observed both degradation and improvement with storage but the former was the more common behavior. Seregin et al. [62] found degradation of jet fuel in a hot pumping test after storage at ambient conditions. The filter plugging test exhibited a shorter induction period for fuel stored in warm climates than for fuel stored in a moderate climate. In other tests at ambient conditions, Sablina et al. [63] reported that the thermal stability of five fuels, as estimated by a static test, changed little over a four-year period. A filter plugging test at 150 to 180°C indicated, however, that all fuels had degraded drastically within two to three years. In contrast to these findings, Whisman et al. [26] found no significant change in the microcoker breakpoint of five fuels after 52 weeks storage at 55°C.

Nowack et al. observed that a depolarized shale-derived jet fuel degraded slightly for a 260°C JFTOT test after four-week storage at 60°C [40]. The same fuel doped with extracted nitrogen bases at the 125-ppm N level failed badly after the storage period although passing easily when fresh. A similar behavior was exhibited by 5-ethyl-2-methylpyridine at a 50-ppm N concentration. Addition of 2,5-dimethylpyrrole at 50-ppm N caused failure of the fresh blend, and the aged blend had similar performance.

Refining Techniques to Improve Thermal Stability

Several processes which remove polar compounds have been found effective in improving thermal oxidative stability of many fuels. Schwartz and Eccleston reported that sulfur dioxide (SO₂) extraction, acid treating, and absorption methods improve the thermal stability of jet fuels [4]. Nixon reported similar findings but stated that the same treatment on different base stocks is often not equivalent in effectiveness [3]. Chertkov and Kolobova also saw improvement of jet fuel thermal stability after a percolation process [64]. Nixon's statement on the importance of base stock is supported by BuMines studies [26]. These workers depolarized five aircraft turbine fuels by percolation through silicagel. Two fuels, those with the lowest breakpoints, improved about 35°C in stability. Two other fuels exhibited 20 and 35°C drops in breakpoint, respectively, and the fifth fuel was improved only slightly. The latter three were high-quality fuels, having breakpoints above 330°C prior to the treatment.

Although several refining techniques improve thermal stability, most have drawbacks. Extraction methods with sulfuric acid, caustic, or SO₂ have waste disposal problems. Use of absorption methods with agents such as silicagel or alumina are expensive. Clay absorption, although cheaper, requires large quantities of material and is usually not cost effective.

Hydrotreatment has been found by several operators to be the refining technique to give the most improvement in thermal stability. This treatment removes or reduces several species which decrease thermal stability. For instance, trace metals, sulfur compounds, nitrogen compounds, acids, oxygen compounds, and olefins are significantly reduced in concentration. The extent depends on the species and the severity of hydrotreatment. The removal of polar species by hydrotreatment alters properties other than stability, however, and additives may be needed to attain acceptable fuel quality. For instance, corrosion inhibitors are needed to improve lubricity and antioxidants are required to control peroxidation [44].

Lander and Martel found that mild hydrogenation of Jet A-1 with a commercial catalyst at 3.55 MPa (500 psig) was almost as effective as a more severe processing with a noble metal catalyst [65]. This is illustrated in Table 5, which compares an untreated product with one that was desulfurized (mild hydrotreat) and another that drastically reduced aromatics (severe hydrotreat). The desulfurized sample had a JFTOT breakpoint 68°C (123°F) higher than the base fuel. Clay treatment of this material gave another 8 to 11°C (15 to 20°F)

TABLE 5—Hydrogenation and JFTOT breakpoint.

Processing Conditions	Baseline Jet A-1	Desulfurized Jet A-1	Desulfurized and Hydrogenated Jet A-1
Temperature °C (°F)	...	327 (620)	296 (565)
Pressure, MPa (psig)	...	3.55 (500)	3.55 (500)
Catalyst	...	Commercial	Noble metal
PRODUCT PROPERTIES			
Aromatics	12.0 vol%	11.7 vol%	Trace
Olefins	1.5 vol%	0.9 vol%	Trace
Total sulfur, wt%	0.036	Less than 0.001	Less than 0.001
Breakpoint, °C (°F)	286 (547)	354 (670)	>371 (>700)

improvement in breakpoint. Severe hydrogenation of the desulfurized fuel gave at least a 17°C (30°F) further increase in the JFTOT breakpoint, but the temperature limitation of the JFTOT prevented a precise definition. Thus, removal of almost all of the aromatics and olefins did not afford greatly improved performance compared to removal of polars as evidenced by total sulfur concentrations.

Kendall, Clark, and Wolveridge reported on the behavior of an extensive group of Jet A-1 fuels tested in the STHTR [66]. Sweetened fuels exhibited a broad pattern in a plot of stress temperature versus loss in heat transfer. On the other hand, hydrotreated fuels fell in a narrow band and exhibited 10 to 100-fold lower fouling rates than most sweetened fuels.

Datschefski found that small amounts of cracked product rendered a good quality jet fuel unacceptable [29]. One percent of a light catalytically cracked cycle oil dropped the JFTOT breakpoint of various base fuels 5 to 25°C, and up to a 35°C decrease was found for a 5% addition. Thermally cracked gas oil was less detrimental but still gave JFTOT decreases of 5 to 25°C at the 5% concentration. Datschefski concluded that there was little scope for any major increase in fuel supply through use of nonhydrotreated cracked fractions.

Speck ran a 90/10 blend of JP-5 and DFM in the JFTOT and the NAPC single-tube heat exchanger [67]. The JFTOT breakpoint decreased from 274 to 243°C. The heat transfer test confirmed the detrimental effect of 10% diesel fuel. The heat transfer effectiveness decreased 1% in only 37 h as opposed to 158 h for the JP-5. This again points up the difficulty of extending the availability of jet fuel by addition of heavier components.

Chemical Mechanisms in Deposit Formation

Extensive work on the chemistry of thermal stability has been described in the foregoing parts of this chapter. No detailed schemes have been published, however, which bring together the many facets discussed. Certainly the very low levels of conversion of fuel to insolubles slows the rate at which understanding of this subject develops. For instance, the amount of carbon deposited in the NAPC heat exchanger tests was 8 to 24 parts per billion (ppb wt/vol) even for the fuels with breakpoints as low as 213°C (416°F) [56]. Other tests have yielded similar results. Further, somewhat less than 1% of the dissolved oxygen in an air-saturated fuel ends up in the insolubles although oxidation reactions stimulate deposit formation.

Any mechanisms proposed for deposit formation must address three key facts:

1. Dissolved oxygen reacts with fuel components and sets up a sequence of reactions which leads to deposit formation.

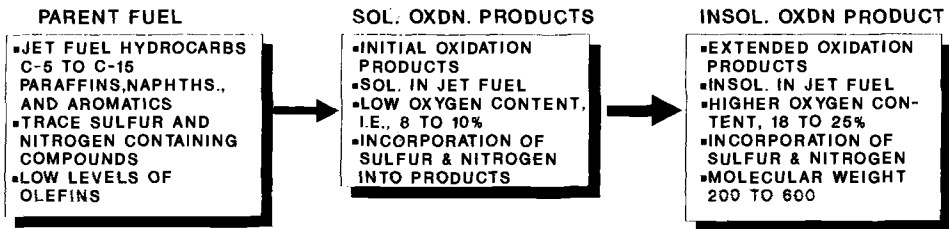
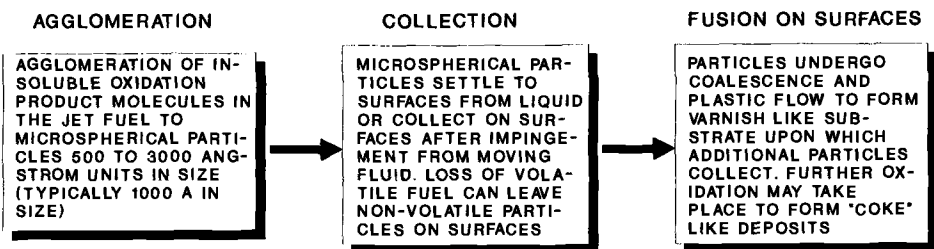
GROSS CHEMICAL PROCESSES**GROSS PHYSICAL PROCESSES**

FIG. 6—Chemical and physical processes in thermal stability deposition.

2. Compounds containing oxygen, sulfur, nitrogen, and metals are major participants in deposit formation.
3. A minuscule portion of the fuel, less than 0.1 ppm, ends up as detrimental, insoluble material.

Clark and Smith proposed a simplified two-step working scheme [16] which recognized these three key facts. In the first step, fuel hydrocarbons and oxygen react under catalysis of metals to form oxidized, but soluble, intermediates. The intermediates then combine with minor constituents, primarily sulfur and nitrogen compounds, to form insolubles.

Taylor has put more meat on his proposed mechanism [68–69]. In his first step, fuel components, including olefins and nitrogen and sulfur compounds, react with dissolved oxygen to form oxidation products (Fig. 6). These oxidation products, which are soluble in jet fuel, contain N, S, and 8 to 10% oxygen—approximately one oxygen per molecule of oxidized fuel molecule. Hydroperoxides are among the oxygenated compounds. Upon further oxidation, the oxygen content increases to 18 to 25% and the product becomes insoluble. Molecular weight is 200 to 600, and N and S are present. Subsequent to the two-step chemical processes, physical processes begin with agglomeration of insolubles in the liquid phase, attachment of the agglomerates to surfaces, and fusion of microspherical particles to form a varnish.

The Clark/Smith and Taylor chemical schemes differ in that Taylor proposes oxidation in both chemical steps as opposed to only the first step in the other scheme. No direct experimental evidence is available to distinguish between the two schemes. The scheme involving oxidation in both steps has the merit of increasing the oxygen content in the products and thus tying in better with the findings of high oxygen contents by elemental analysis.

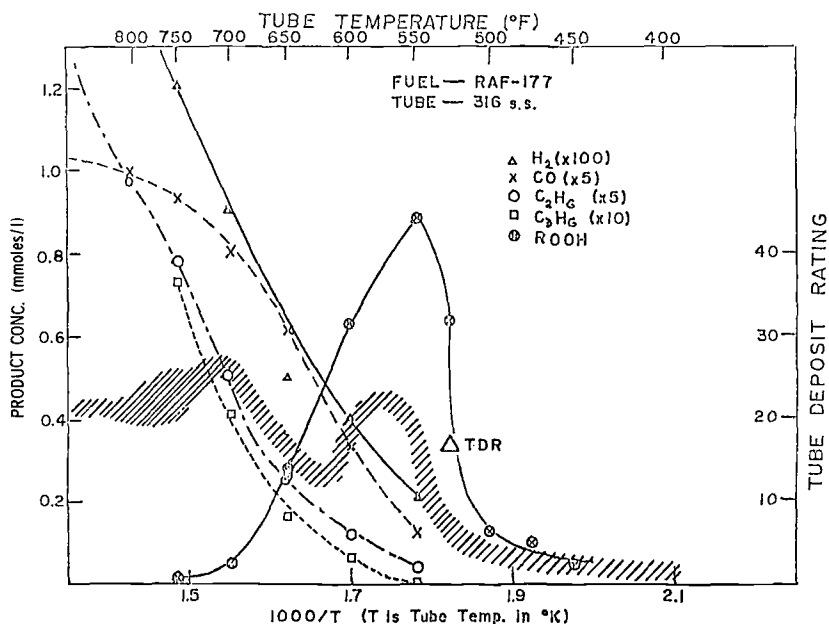


FIG. 7—Oxygenated products and tube deposits for a reference fuel tested in a modified JFTOT.

JFTOT studies with accompanying analyses for dissolved oxygen, hydroperoxides, and other soluble oxidation compounds suggest that deposit formation occurs at temperature regimes characterized by high free radical concentrations. This is shown in Fig. 3 for a stress of a pure hydrocarbon. During the decomposition of hydroperoxide, a thermal regime where the free radical concentration is high, the TDR reading is increasing abruptly and then falls when hydroperoxide is depleted. A jet fuel responds somewhat differently [23]. Figure 7 shows that the deposit rating rises sharply as the hydroperoxide concentration increases. The ROOH rise for the fuel is much sharper than for the pure hydrocarbon, suggesting that the fuel has natural inhibitors limiting peroxidation. Also, the peroxide formation for the fuel is delayed temperature-wise, which would support the view that this fuel contains natural inhibitors that effect an induction period. It is proposed that the free radical concentration for the fuel is high during the formation process for ROOH as well as during the decomposition step. Thus, the fuel exhibits two TDR maxima associated with peroxidation phenomena, one during buildup and the other during decay.

Compounds containing hetero atoms are more easily oxidized than most hydrocarbons found in jet fuels. Oxidation of sulfur compounds, probably by peroxides rather than directly by dissolved oxygen, can form a variety of products [70]. Most of the products add oxygen to the molecule. For instance, thiols are readily converted in part to sulfonic acids [71].

One theory proposes that the incorporation of N and S compounds into fuel molecules, along with further oxidation, develops polarity. As a consequence, their solubility in the nonpolar fuel decreases and solids form. The high concentrations of O, S, and N found in stress-formed deposits support this theory in contrast to a second theory which suggests that polymerization of olefins or pyrroles creates high-molecular-weight, insoluble products. Molecular weight determinations of deposit precursors also indicate polymerization is lim-

ited. Dimerization seems probable, however, since molecular weights of 340 to 414 were found [72].

The sediment formed in other distillate fuels under storage conditions appears to have characteristics similar to the thermally formed jet fuel deposits. For instance, Sauer et al. report high concentrations of oxygen, nitrogen, and sulfur in heating oil sediments which had a molecular weight of 500 [73]. Much of the oxygen was present as esters with lesser amounts as acids. These authors proposed a mechanism for sediment formation involving oxidation and condensation of hydrocarbons as well as nitrogen and sulfur compounds. Thiols were involved as catalysts for oxidation processes and, after oxidation to sulfonic acids, as catalysts for rearrangements and condensations. Esters were a major intermediate formed by reactions between two major oxidation products, hydroperoxides and aldehydes.

This latter sequence of reactions has some appeal since it incorporates a good amount of oxygen into the deposits. With respect to jet fuel deposits, however, thiols may be a minor participant since the mercaptan limit in most jet fuel specifications is 0.003% or lower [74]. Other sulfur compounds which form thiyl radicals under thermal stress can stimulate particulate formation. Taylor has shown this can occur even in the absence of dissolved oxygen, indicating that sulfonic acids are not essential for deposit formation from some fuels [5,75]. Some model studies by Shuler et al. suggest that thiyl radicals interact differently with various hydrocarbons and that the presence of dissolved oxygen alters the sulfur product obtained [33].

Summary

Because of the variety of crude sources, the differences in refining processes to produce jet fuels, and the different stress environments to which jet fuel is exposed, it is reasonable to state that deposits form by more than one mechanism. Thus, the definition of a universal process for insolubles formation is not likely. Further complicating our understanding is the small fraction (less than 0.1 ppm) of fuel which is converted into deposits or filterable solids. Examination of the fuel by advanced separation and chemical analysis techniques has exhibited limited success since the key, oxidation-sensitive compounds are present in very low concentrations and masked by the many hydrocarbon components in the fuel. In addition, extraction processes to enhance concentration of active species tends to chemically change the pertinent compounds.

Free-radical chemistry is important in solids formation in thermal stability. This involves autoxidation by dissolved oxygen to produce hydroperoxides and other oxidized products in low-temperature regimes. Pyrolysis, a second type of free-radical chemistry, becomes important at substantially higher temperatures if oxygen is absent or is depleted by reaction at lower temperatures.

Sulfur, nitrogen, and oxygen are found in large concentrations in deposits compared to their presence in unstressed fuel. Some of these compounds are more readily oxidized than fuel hydrocarbons and may be instrumental in increasing polarity and reducing solubility in the nonpolar jet fuel. The sulfur compounds of most concern are mercaptans/thiols and others, such as disulfides, which can form thiyl radicals and/or undergo reactions to incorporate oxygen into the molecule.

The literature is contradictory on the effect of nitrogen compound structure, but the total nitrogen concentration is not controlling. Fortunately, total nitrogen content in jet fuels from most crudes is low, a few ppm at most. Indoles, and possibly pyridines, encourage deposit formation under some test conditions. Pyrroles are not a major fraction of the nitrogen compounds in jet fuels, although many tests have demonstrated their detrimental effects.

Among oxygen compounds, hydroperoxides, as stated above, play a crucial role in deposition. Decomposition products of hydroperoxides, other than alcohols and ketones, appear to be important in the path to highly polar oxidation products which have limited solubility. Total acid concentration (sum of phenols, weak acids, and strong acids) has been related to heat transfer deterioration in one set of tests. Strong acids stimulate solids formation.

Hydrocarbons probably exert only a minor effect on deposition. Although effects have been noted for large mostly multi-ring aromatics, these would be present in very low concentrations in jet fuels because of their distillation range. Further, these effects were observed in a low-temperature two-phase flow apparatus where extensive oxidation could occur. Olefins conjugated to an aromatic ring, such as styrene and indene, can be very active in deposition. Again, these types of hydrocarbons are minor components in jet fuels.

Some contradictory results have been reported in the literature, particularly for model systems. Some observations can be made to understand these differences. First, many studies have used subjective estimates of thermal instability. This is particularly true of tests with the JFTOT and ASTM Coker. A second observation is that widely different experimental conditions have been used in various experiments. For instance, temperature, test time, metal exposure, availability of oxygen, and extent of oxidation have covered a wide range of conditions. In general, future programs should insure the following guidelines:

1. Make quantitative measurements of solids formation, heat transfer, and/or filter plugging.
2. Focus experimental conditions on a test environment relevant to an aircraft fuel system.
3. Limit the acceleration of reaction rates due to elevated temperatures.
4. Utilize complimentary experimental techniques to gain information on various aspects of thermal stability.

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CHAPTER VII

Reduction of Deposit Formation by Removal of Dissolved Oxygen

In previous chapters of this book, we developed the information that the dissolved oxygen in the fuel institutes reactions which lead to deposit formation. Specifically in Chapter VI, we showed that the dissolved oxygen forms fuel hydroperoxides which are intimately involved in deposit formation. The removal of oxygen has been proposed as a method to improve the thermal stability of a fuel. In particular, this would enable the fuel to stand a more severe stress (higher temperature and/or longer stress time) without forming an unacceptable amount of deposit.

Several investigators have examined the role of dissolved oxygen by reducing the oxygen concentration in fuel subjected to a thermal environment. This chapter will review the work on oxygen effects. Taylor presented an excellent review of the subject of thermal stability and deoxygenation in the Coordinating Research Council literature survey of 1979 [1]. Only limited research has been reported on deoxygenation since that report was published.

Evidence for the involvement of oxygen in fuel chemistry was presented by Shell Development Co. in a heat transfer rig operating at a severe fuel-out temperature of 516°C (961°F) [2]. These workers found an increase in gas yield for an air-saturated Jet A fuel versus the same fuel sparged with nitrogen gas even though the high temperature would bring the fuel into the pyrolysis regime. Hazlett et al. also observed an effect of dissolved oxygen on cracking product yield for a pure *n*-alkane [3]. At a heater tube temperature maximum of 427°C (800°F), the yield of smaller hydrocarbons—alkanes plus alkenes—for the low oxygen concentration (1.3 ppm) experiment was only 10% of the air-saturated (60 ppm) case. The differential was greater at lower temperatures and less at higher temperatures. The cracking yield for the low oxygen case at 538°C (1000°F) was 60% of the high oxygen test. Thus oxygen, which significantly increases the extent of reaction at lower temperatures, exerts some effect even at 538°C (1000°F), far above the temperature at which hydroperoxides have disappeared. Carbon monoxide is distinctly different from the other products, as expected, in that it is a very minor product for all low oxygen experiments.

Deposition in Fuels with Low Oxygen Content

Shell Development Studies

Shell experiments were among the earliest ones on reduced oxygen concentrations. Control of the oxygen level at sub-ppm levels markedly improved thermal stability and decreased heat exchanger fouling [4].

Later work with a Jet A [2] in the Shell Development 0.619-m (2-ft)-long, “Hastelloy C” single tube heat exchanger measured several parameters. The deposition was uniformly low throughout the tube after 100 h for the low oxygen experiment. The amount of deposition

for the air-saturated fuel was similar for the first 0.3 m (1 ft) of the tube but up to six times as much for the outlet portion of the tube. The estimate for deposit thickness in the deoxygenated case was less than 0.025 mm (0.001 in.), but the deposit filled the 1.6-mm (0.0625-in.) I.D. tube when the Jet A was saturated with air. The effect of the deposit was to increase the maximum inside tube temperature to 877°C (1610°F) versus 721°C (1330°F) for the aerated/deaerated comparisons. The deposit was porous and flow was still possible, although the pressure drop through the tube rose from an initial value of 152 kPa (7 psig) to over 1482 kPa (200 psig) at the end of the 100-h test.

NASA Studies

Watt, Evans, and Hibbard tested three Jet A fuels for the effects of deoxygenation. The tests compared air-saturated fuel at 45 ppm of oxygen with nitrogen-sparged fuel at 0.3 ppm of oxygen [5]. The NASA single tube rig, with a 3.96 or 4.76-mm (0.156 or 0.188-in.) O.D. "Nichrome V" heater tube, was used and deposition was estimated by carbon burnoff. Wall thickness was 0.508 mm (0.02 in.) for tubes of both O.D. Fuel-out temperature was held constant at 371°C (700°F), and pressure was varied between 1.14 MPa (165 psia) and 4.24 MPa (615 psia) for the comparisons. The fuels varied in performance, but the air-saturated tests always gave more deposit than the corresponding deaerated test. Oxygen increased the amounts of deposits from about three- to ten-fold. The metal temperature for incipient deposit formation increased by 103 to 200°C (185 to 360°F) with the removal of oxygen from the fuel.

The range of deposit quantities for 20-h tests with a fuel flow of 27.2 kg (60 lb) varied from 0.05 to 2.5 ppm of the total fuel with the lower values characteristic of the deaerated regime. Using some assumptions, the authors calculated the time for 50% blockage of their 3.96-mm (0.156-in.) O.D. heater tube (2.95-mm/0.116-in. I.D.). They found a 400-h time for the 2.5-ppm deposit rate and a 16 000-h time for the 0.05-ppm rate. Clearly, the 400-h time would be unsatisfactory since it would require frequent heat exchanger overhaul. Thus fuel temperatures of 371°C (700°F) and above would not be acceptable for aerated fuels. The value of deoxygenation is supported by this study.

These workers found two maxima in deposition amount versus the heater tube temperature for two of the fuels when aerated but a single maximum for low oxygen tests on the same fuels. Further, the high temperature maximum for the aerated fuel corresponded to the single maximum for the low oxygen sample. The authors suggested that two mechanisms are contributing to deposit formation. One is an oxidative process which occurs in the low temperature region of the stress, and the second is a higher temperature process that is much less influenced by dissolved oxygen and may involve pyrolysis. Removal of oxygen reduces deposition at low temperatures and allows the fuel to be stressed to a higher temperature before unacceptable degradation occurs. This dual mechanism fits in with the discussion in Chapter VI.

Aero Propulsion Laboratory Studies

Other studies on deoxygenation have used very low oxygen concentrations in the fuel. Bradley, Bankhead, and Bucher at AFAPL looked at intermediate dissolved oxygen levels in Air Force Fuel Bank fuel AFFB-14-70 [6]. The AAFSS was operated with manifold fuel inlet and outlet temperatures of 93°C (200°F) and 238°C (460°F), respectively. Test times varied from 37 to 106 h. A JFTOT was run in parallel to the simulator manifold using the same fuel. The JFTOT was run at various temperatures to obtain a breakpoint for both 2.5 and 5-h tests.

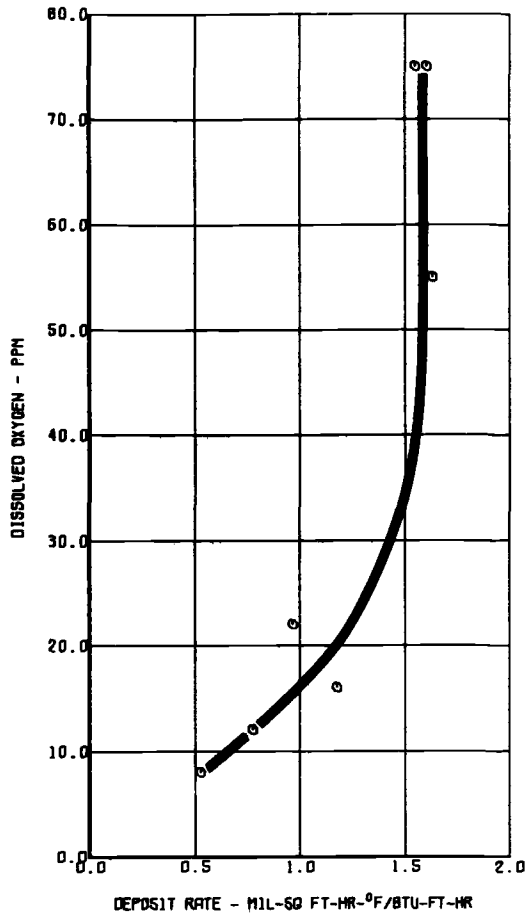


FIG. 1—Effect of dissolved oxygen on deposition rate in the advanced aircraft fuel system simulator.

Figure 1 illustrates the response in overall deposit thermal resistance in response to a decrease in dissolved oxygen concentration. Very little change in deposit resistance was found until the oxygen concentration was reduced below 30 ppm. At 8 ppm, the resistance rate of change was about one third the rate for the air-saturated test.

The corollary JFTOT tests supported the results on the simulator. Slight improvement in breakpoint was found by reducing the oxygen level from 75 to 35 ppm, but more significant improvement was noted below this latter concentration. The breakpoint for fuel AFFB-14-70 increased from 291°C (555°F) to 366°C (690°F) for the 2.5-h JFTOT test in going from 75 to 13-ppm oxygen.

Exxon Studies

The earliest Esso work was performed in their two-phase apparatus, which addresses the wing tank environment [7]. In this rig the oxygen concentration in the vapor phase was decreased from 21.3 kPa (160 mm Hg) partial pressure to 2.13 kPa (16 mm Hg). This

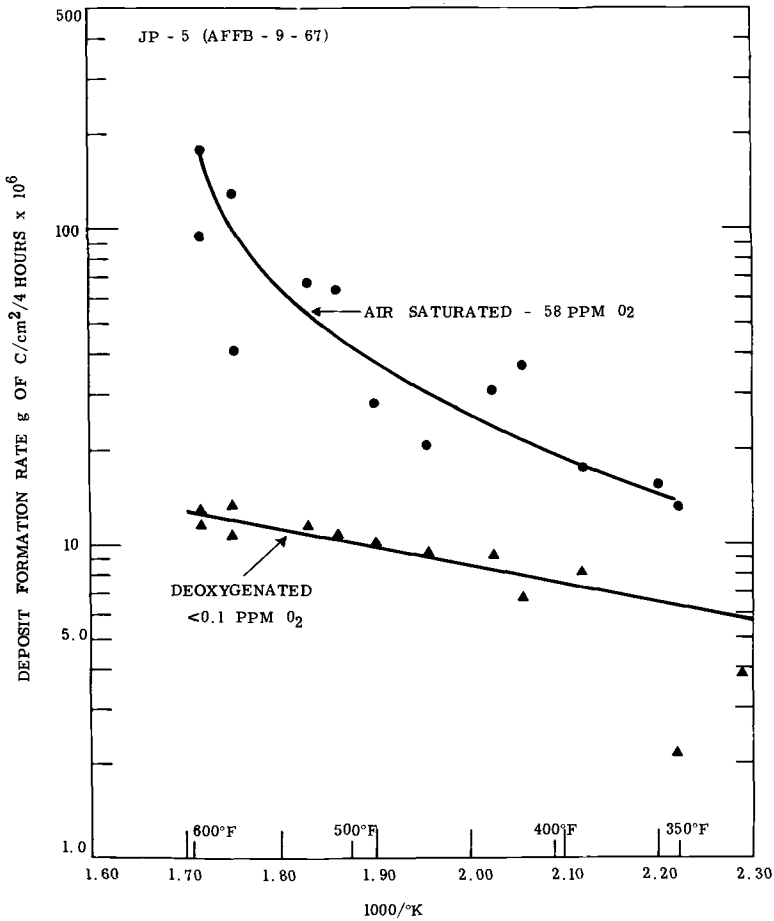


FIG. 2—Arrhenius plot for deposition in AKU: air-saturated versus deoxygenated fuel.

afforded a 40% reduction in deposition. The availability of oxygen is much greater in the two-phase apparatus, which may explain the modest effect of reduced oxygen concentration in this test.

The bulk of the extensive Exxon studies have been accomplished in their advanced kinetic unit, which stresses the fuel in a heated tube comprising four heated zones maintained at 7.0 MPa (1000 psig) pressure [8]. The tube is sectioned at the completion of the test and the deposit estimated by carbon burnoff. A typical comparison of a deoxygenated versus an air-saturated fuel is shown in Fig. 2 [9]. The effect of low oxygen is very dramatic, particularly at the higher temperature where the deposition rate was about 10% of the air-saturated rate. Most other jet fuels studied by Exxon displayed large reductions in deposition similar to this fuel. The behavior for six fuels with respect to total carbonaceous deposits is presented in Table 1 [8] for the temperature range 149 to 316°C (300 to 600°F). The fuel for Fig. 2 corresponds to Fuel B in Table 1.

Fuel C, the JP-7, exhibited a very low deposit level in the air-saturated state. Nevertheless,

TABLE 1—*The effect of deoxygenation on deposit formation.*^a

Fuel	Fuel Description	Oxygen Content, ppm	Micrograms of Carbon
A	JP-5 (fresh)	64	2 404
		0.1	315
B	JP-5 (4-year storage)	58	3 992
		0.1	655
C	JP-7	75	373
		0.7	257
D	Low aromatic, thermally stable	74	4 613
		0.1	882
E	30% JP-5/70% thermally stable	69	2 872
		0.3	589
F	Doctor sweetened	57	8 157
		1.4	37 265

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it benefitted from the removal of dissolved oxygen. Four fuels—A, B, D, and E—when stripped of oxygen yielded at least an 80% reduction in deposition in this Exxon rig.

The sixth fuel, F, behaved entirely differently from the others. It was the poorest fuel in the air-saturated test but was even worse when deoxygenated. Taylor considered several possibilities for the unusual behavior of this fuel and proposed that the disulfides (0.067 wt%) produced by the sweetening process were instrumental in stimulating high deposition rates [9]. The S-S bond is weak and behaves somewhat like the O-O bond in peroxides. The resulting thiyl radical, RS·, can institute free radical reactions which could lead to polymerization and insoluble deposits. The deposition rate with deoxygenated Fuel F was highest at low heater tube temperatures (less than 200°C), a finding which lends support to the rupture of the weak S-S bond.

The deaeration studies were extended to higher temperatures for Fuels A and B. Generally, the deposition rate increased with increasing temperature. Deaerated Fuel A attained a deposit rate of 100 ($\mu\text{g}/\text{cm}^2$)/4 h at about 593°C versus 288°C for air-saturated Fuel A. The corresponding data for Fuel B were 427°C versus 299°C.

Taylor conducted tests on Fuels A and B in the high temperature regime at intermediate oxygen concentrations. Fuel A, the fresh JP-5, produced less deposit as the oxygen decreased but reached the ultimate benefit only below 1.6 ppm of dissolved oxygen. Fuel B, on the other hand, exhibited no additional benefit in deposit reduction below 14.6 ppm. The latter fuel may have contained oxidized components formed during its four-year storage that might have contributed to deposit formation by pyrolysis at these elevated temperatures.

UTRC Studies

Vranos and Marteny used the UTRC rectangular cross-section rig to examine coking rate as related to deoxygenation [10]. They found a distinct reduction in deposition at low oxygen. For instance, at a test temperature of 260°C (500°F) the air-saturated sample produced about five times as much deposit as the nitrogen-sparged fuel. The coking rate for the deoxygenated fuel was low and about the same at 260 and 330°C (500 and 625°F).

Fuel Composition and Deoxygenation

Taylor and Frankenfeld at Exxon conducted extensive experiments in their four-zone apparatus to examine the effect of composition on deposition in deoxygenated jet fuel. A variety of hydrocarbons, sulfur compounds, nitrogen compounds, oxygen compounds, dissolved metals, and fuel additives were added to JP-5 in studies to define high stability fuel. These tests were conducted to a maximum temperature of 538°C (1000°F) with the exception of the hydrocarbon studies, which had a top temperature of 594°C (1100°F). Total carbonaceous material as determined by carbon burnoff was the criteria on performance. System pressure was 7.0 MPa (69 atm).

Hydrocarbon Effects

A blend of 25% *n*-dodecane, 25% 2,2,4- or 2,2,5-trimethylpentane, 30% isopropylcyclohexane, and 20% *sec*-butylbenzene was used as a base for defining hydrocarbon effects. This blend gave a total deposit amount comparable to Fuel A in the high temperature regime [11]. Either naphthalene or decalin decreased deposition when added at 5% to this blend. Presence of both in the same blend, however, reversed the reduction, but the total carbonaceous material was still less than the four-component blend [12]. Either tetralin or indane added at a 5% concentration reduced deposition about 50%, and the deposit quantity was reduced even further when both were present at 5% [11].

Some olefins at the 2% level in the model hydrocarbon blend increased deposition [11–12]. Deleterious olefins included alpha-methylstyrene, indene, and 1,8-nonadiene. An acetylene, 1-decyne, was the most active compound studied. Other olefins, including some dienes and divinylbenzene, lowered the deposition rate. In general, olefins which were undesirable produced high deposit formation rates at temperatures below 371°C (700°F). Significant quantities of the active olefins would not be found in jet fuels. Such compounds might be found in refinery stocks produced by cracking. However, they would be converted to acceptable hydrocarbons by hydrotreatment, which is universally used to finish jet fuels containing cracked stock.

Sulfur Compounds

Taylor examined the role of sulfur compounds in deposit formation for a JP-5 [9,13]. Compounds were added in amounts to give a sulfur concentration in the fuel of 3000 ppm, the specification maximum for most civilian jet fuels but less than the 4000 ppm permitted in many military fuels. Dissolved oxygen concentration was between 0.1 and 0.9 ppm for the sulfur compound work. The effects of two sulfides are depicted in Fig. 3. Both sulfides enhance deposition throughout the temperature range with maxima coming in the 427 to 482°C (800 to 900°F) range, but the phenyl benzyl sulfide exerts a much more significant effect. Polysulfides, disulfides, thiol, and other sulfides increased deposition, several dramatically. On the other hand, benzothiophene and dibenzothiophene did not contribute to the formation of deposits. A comparison of results for these Exxon studies are presented in Table 2.

The influence of sulfur concentration was examined with phenyl benzyl sulfide and tertiary dodecyl disulfide. Increasing the level from 300 to 3000 ppm approximately doubled the amount of deposits with both compounds [13].

Taylor suggested that the sulfur compounds react differently in the presence of oxygen and in a deoxygenated situation. In the latter case, the sensitive sulfur compounds pyrolyze to give thiol radicals which participate in deposit-producing free radical reactions. The heteroaromatic sulfur compounds do not readily pyrolyze because of the strength of the

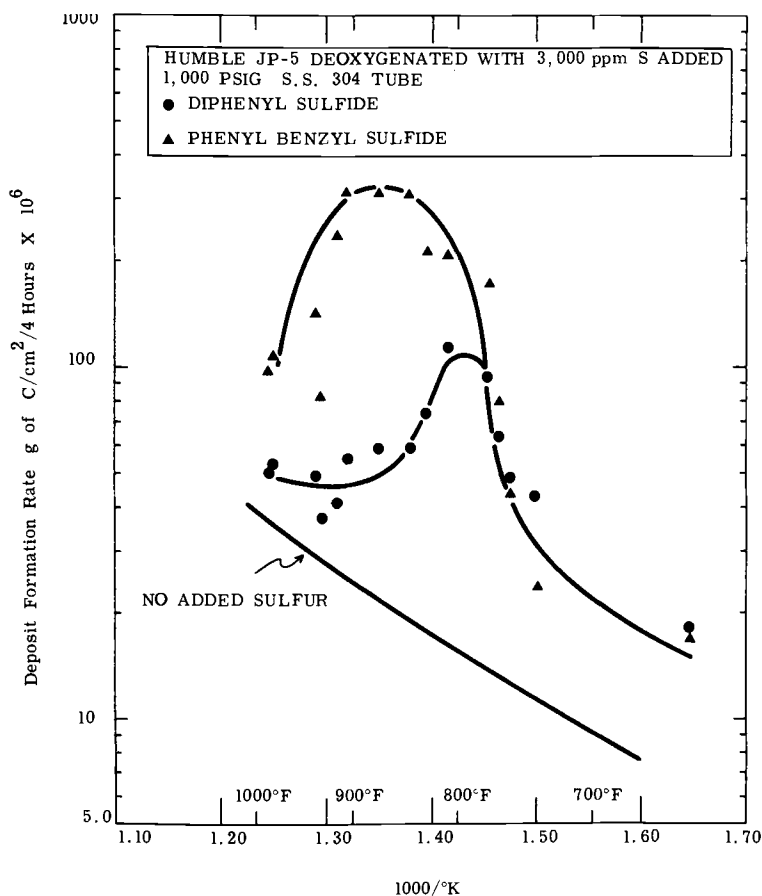


FIG. 3—Arrhenius plot for deposition from deoxygenated JP-5 with and without added organic sulfides (AKU).

aryl C-S bonds. The behavior of the doctor-sweetened fuel (F in Table 1) in a deoxygenated test seems to be in line with the findings for model sulfur compounds added to a fresh, stable, deoxygenated jet fuel. Some caution is necessary, however, since the temperature regimes for the doctor-sweetened test were 177 to 316°C versus 371 to 538°C for the model studies. Further, the doctor-sweetened fuel exhibited high deposition rates at temperatures below about 230°C, whereas the sulfide and disulfide compounds produced the highest rates above 400°C.

Nitrogen Compounds

Taylor and Frankenfeld doped a stable JP-5 with nitrogen compounds at the 100-ppm nitrogen level. A wide variety of structures represented all classes that might be present in jet fuels. These included a substituted pyrrole, indole, carbazole, a pyridine, quinolines, 2,6-dimethylaniline, and an amide, as well as several alkyl or cycloalkyl amines [14]. The effects of the nitrogen compounds were modest; some slightly decreased while others slightly increased deposition. This behavior demonstrates the difference between air-saturated and

TABLE 2—Sulfur compounds and deposit formation in a deoxygenated jet fuel.^a

Added Sulfur Compound	Micrograms of Carbon
Base fuel	1 485
Ditertiary nonyl polysulfide	7 450
Ditertiary dodecyl disulfide	7 295
Dibenzyl disulfide	6 691
Ditertiary butyl disulfide	10 659
Di- <i>n</i> -hexyl sulfide	5 739
Phenyl- <i>n</i> -propyl sulfide	3 020
Diphenyl sulfide	4 503
Phenyl benzyl sulfide	12 253
Phenyl methyl sulfide	2 190
Thiocyclohexane	2 788
1-Decanethiol	3 909
Benzothiophene	1 351
Dibenzothiophene	981

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deoxygenated chemistry since some nitrogen compounds were very active in promoting deposition when dissolved oxygen was present (see Chapter VI).

Oxygen Compounds

A variety of organic oxygen-containing compounds were studied for their effects on deposition from a deoxygenated JP-5. Significant increases were found for specific compounds, particularly hydroperoxides and peroxides [11–12,14]. The concentration was set at 100-ppm oxygen for these experiments. The compounds containing the O-O bond exhibited large increases in deposits with the total amount for *t*-butyl hydroperoxide being five times more than the base fuel. With this class of compounds, the major effects were found below 400°C (752°F). In fact, *t*-butyl hydroperoxide exhibited a 100 times greater deposit rate than the base fuel at 316°C (600°F). The peak rate for the peroxides was at about 371°C (700°F), the same temperature at which the air-saturated base fuel exhibited a maxima. This observation ties in with the mechanism of hydroperoxide formation and decomposition which was presented in Chapter VI.

The other oxygen compounds examined did not fall into a clear pattern. Although most compounds gave little or no change in deposit amount, most classes had one member that exerted a definite increase. For instance, decanoic acid doubled the deposit quantity but four other carboxylic acids were not very active in stimulating deposit formation. 2,6-Dimethylphenol, *n*-dodecyl alcohol, 5-nonanone, and methyl benzoate gave 40 to 70% increases, but other members in these classes were inactive. The compounds containing carbonyl or carboxyl functions exhibited rate maxima at 438 to 482°C (820 to 900°F). This behavior may be related to temperatures at which acids decarboxylate and ketones and esters decarbonylate. Free radicals would form in this environment and deposition could be stimulated.

Metal Effects

Studies at Exxon on deoxygenation, conducted on only one fuel, examined two aspects of phenomena due to metals—dissolved metals and metal surfaces. The data for dissolved metals are given in Table 3 [15]. Copper increased deposition but not as much as in an air-

TABLE 3—*Dissolved metal effects in deoxygenated JP-5.*

Metal	Concentration, ppb	Total Carbonaceous Deposit, μg carbon
None	...	2263
Copper	100	2963
	200	4763
Iron	10	4240
	100	5853
Vanadium	100	1118

saturated fuel (see Chapter VIII). Iron was considerably more active than copper with 10 ppb forming more deposit than 100 ppb of copper. Vanadium reduced deposition at a concentration of 100 ppb.

The Exxon advanced kinetic unit was operated with tubes constructed from different metals [16]. Using Type 304 SS as the base, only one material—titanium/3% aluminum/2.5% vanadium—gave comparable amounts of deposits. Pure titanium, Inconel 600, and 70/30 copper/nickel increased deposition by up to 2.6-fold. The titanium was the worst metal for this comparison, which extended to 538°C (1000°F). An aluminum alloy, 6061, could not be tested at high temperatures because of decreasing tensile strength. Therefore, it was compared with Type 304 SS at a temperature up to 316°C (600°F). Under that regime, aluminum was five times as active in deposit formation. The behavior of these metals is very different with a deoxygenated fuel as opposed to an air-saturated fuel, the results for which will be presented in Chapter VIII.

Fuel Additives

Exxon examined three antioxidants, a corrosion inhibitor, and an anti-icing additive with regard to thermal stability behavior in the advanced kinetic unit. A phenylenediamine AO, a hindered phenol AO, and the corrosion inhibitor, Hitec-515, exerted very little effect for these deoxygenated experiments. A second hindered phenol, 2,6-di-*t*-butyl phenol, increased deposition almost six-fold, although it was structurally very close to 2,6-di-*t*-butyl-4-methylphenol, which did not affect deposition. 2-Methoxyethanol, the anti-icing additive, increased deposition almost four-fold.

Interactions Between Added Compounds

Interactions between many of the compounds studied in the previous sections were investigated by Exxon [14,16]. Classes of compounds used in this phase of the work included olefins (alpha-methylstyrene), sulfur compounds (dibenzothiophene and phenyl-*n*-propylsulfide), nitrogen compounds (2,5-dimethylpyrrole, 2,6-dimethylaniline, and 2,4,6-trimethylpyridine), a furan (dibenzofuran), an acid (decanoic acid), a phenol (2,4,6-trimethylphenol), an alcohol (*n*-dodecyl alcohol), a ketone (5-nonanone), and an ester (methyl benzoate). All combinations were not tested, but 21 pair combinations were run in the advanced kinetic unit. Positive interactions were observed only if 2,5-dimethylpyrrole was one of the pair of added components. The interaction was moderate for the pyrrole/phenol and pyrrole/olefin pairs but strong for the pyrrole/thiophene and pyrrole/acid pairs. Strong negative interactions were found for the olefin combination with the ketone and for decanoic acid combined with the pyridine, the phenol, the ketone, or the furan. The findings highlight the complex chemistry involved in thermal stability in a deoxygenated environment.

General Comments

Deposit Characterization

Exxon performed chemical and physical examination of deposits formed in the AKU. The chemical analyses involved elemental analysis. Deoxygenated Fuel B (see Table 1) was stressed to 427°C (800°F) in one test and to 482°C (900°F) in a second. The deposit from the lower temperature test was found to have about 6% oxygen, but no oxygen was found for the high-temperature experiment [8–9]. Neither sulfur nor nitrogen was detected in the deposit formed at either temperature. These findings contrast sharply with the analyses for air-saturated fuel deposits presented in Tables 2 and 3 of Chapter VI. The lower oxygen levels for the deoxygenated tests would be expected since dissolved oxygen is not present to trigger hydroperoxide formation and stimulate free radical reactions. The absence of sulfur is unexpected in view of the strong effects of compounds containing this element in stimulating deposit production in deoxygenated fuels.

Scanning electron microscopy was used to examine the morphology of deposits formed with different amounts of dissolved oxygen [11]. Using an air-saturated model fuel blend, the deposits contained mostly spherical particles of about 0.2- μm (2000- Å) diameter, similar to Schirmer's findings discussed in Chapter V [17]. As dissolved oxygen content is reduced, the number of spherical particles decreases and the deposit takes on the character of a fused, amorphous varnish. Thus the presence of oxygen is important, not only for its influence on the chemistry of deposit formation, but also for physical factors.

Applications and Precautions for Using Deoxygenation

The removal of dissolved oxygen greatly reduces the rate of deposition and also increases the breakpoint of a jet fuel. This capability could find use in high-speed aircraft in the 3 to 5 Mach number regime. This regime stresses the fuel to much higher temperatures than the commercial operation of the Concorde at Mach 2.2. Use of thermally stable jet fuel is more likely to be a preferred approach at Mach 3 to Mach 4, but deoxygenation would be of significant benefit at Mach 4 to Mach 5. A combination of deoxygenation with thermally stable fuel might be required in the Mach 5 regime.

The use of deoxygenated fuels in jet aircraft will be physically difficult. Sparging a large volume of fuel with inert gas will be time consuming, and it will be difficult to reach and maintain low oxygen concentrations. Since fuels respond differently to dissolved oxygen concentration, a very low (less than 1 ppm) level should be the goal to obtain across-the-board benefits. Sparging must be carried out in a system which traps fuel vapors in order to protect the environment from pollution.

Aircraft fuel tanks are normally kept at the ambient pressure. This encourages breathing between the tank vapor space and the outside atmosphere. To minimize interchange of outside air with the deoxygenated (nitrogen) tank environment, a positive pressure would be required inside the tank. The pressure differential should be small to reduce structural requirements. Inert gas feed would be needed to maintain the desired differential versus the outside pressure as aircraft altitude changes.

Refining practices will be required to reduce or eliminate the amounts of active chemical species which stimulate deposition in deoxygenated fuels. Mild hydrotreat can eliminate most active olefins, but more severe hydrogenation may be required to control sulfides. Hydrogenation should also be used to eliminate thiols and mercaptans so that sweetening processes which produce disulfide will not be needed. Specification limits on total sulfur, mercaptans, and acids might have to be tightened, although they are very low in some current specifications.

The prevention of hydroperoxides during storage must be assured to guarantee the full benefit from deoxygenation. The above-mentioned benefits of hydrogenation have a competing negative effect; namely, natural oxidation inhibitors are removed and hydroperoxides form readily in storage. Solutions to this problem include use of the fuel shortly after production, one to two months. This is not always feasible, however. A second approach, keeping the fuel deoxygenated throughout its transport and storage, is logistically difficult. The most reasonable suggestion is to apply an antioxidant which can prevent peroxidation in storage and which is innocuous to deposition in a high-temperature stress. The selection of such an antioxidant must be done with care since Exxon found that hindered phenols of similar chemical structure behave very differently in a high-temperature deoxygenation test.

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CHAPTER VIII

Metal Effects on Thermal Stability

The effects of trace organic components on the thermal stability of fuels have been demonstrated in previous chapters. This chapter will deal with materials which exert effects at much lower concentrations, parts per billion (ppb) rather than parts per million (ppm). Metals dissolved in jet fuel are effective at these low concentrations because they are acting as catalysts for one or more of the chemical reactions involved in the sequence of insolubles formation. Metals are a fact of life for jet fuels, however, since refinery equipment, transportation equipment, storage tanks, and aircraft fuel systems are constructed from metals. In many cases the metals are chosen for these uses on the basis of material properties and economy rather than possible degradation of thermal oxidation stability or other important fuel properties.

Droegemueller examined the effect of preheater tube material on thermal stability behavior in the ASTM Coker instrument [1]. He observed that aluminum tubes afforded the lowest tube rating, with stainless steel being somewhat more reactive. Preheater tubes made from copper, copper-containing alloys, and silver dramatically increased deposit formation.

Copper contamination was indicted as the culprit in commercial operations in the 1960s [2]. Copper was derived from a refinery copper-sweetening process. The copper-generated solids deposited in the combustor nozzles and effected a distorted spray pattern in the engine.

An excellent review of the role of dissolved metals and metal surfaces in jet fuel thermal stability was presented by Nowack in Chapter VI of the Coordinating Research Council literature survey [3]. That review covered information prior to 1979.

This book builds on the earlier review and also discusses more recent work. Topics addressed are: (a) dissolved metal effects; (b) sources of dissolved metals; (c) effects of materials of construction; and (d) the mechanism of action.

Dissolved Metal Effects

The effects of copper contamination on aircraft problems were described above. Most of the indications on problems from metals have been demonstrated in engineering or research tests. These will be considered under several topics below.

Tests in Engine Components

Tests with JP-5, with and without copper contamination, were conducted by Southwest Research Institute in a T700 engine nozzle on a contract from the Naval Air Propulsion Center [4]. A comparison between NAPC Test 1 and Test 4 in Fig. 3 of Chapter I shows the effect of copper contamination on nozzle flow rate. The unadulterated JP-5 (Test 1) exhibited a 2% reduction in flow after 100 h of operation. The same fuel with 350 ppb of copper gave a 10% reduction in only 38 h. This large effect was produced by copper which was taken into the fuel by exposure to copper cuttings, so-called natural dissolved copper.

TABLE 1—*Effects of metal concentration on thermal stability.*

Fuel	Breakpoint Temperature Before Metal Addition		Metal Concentration for 260°C Failure, ppb		
	°C	°F	Copper	Iron	Zinc
A	271	520	74	136	...
B	268	515	99	165	...
C	282	540	105	154	250
D	279	535	89	151	200
E	282	540	50	145	250
F	296	565	100	152	420

The fuel lost much of the dissolved copper after passage through this fuel rig. In some tests, substantial amounts of copper were found in the deposit formed on the nozzle spin plate and throat.

JP-5 was also the fuel used in Naval Air Propulsion Center tests on single heat exchanger tubes from the F-14 jet fighter plane [5]. The fuel was doped to different levels of copper, but no tests with undoped JP-5 were run as a control. Two tests compared two levels of copper, 50 and 250 ppb, obtained by doping with an organic copper complex. The lower concentration required 107 h to produce a 1% loss in heat transfer effectiveness, but the higher level produced the same loss in 73 h. A 1% loss was exhibited in only 29 h for the same fuel containing 250 ppb of natural copper. JFTOT breakpoints on the three copper-containing samples gave the same trend as the heat transfer tests.

Rig Tests

Shell's Thornton Research Centre examined the role of copper at 10, 30, and 50 ppb with respect to heat transfer in the single tube heat transfer rig. The deterioration rate of the heat transfer coefficient was 0.26% for the control fuel and 1.13, 2.74, and 5.90% for the 10, 30, and 50-ppb copper-containing samples [6]. JFTOT results on breakpoint and carbon burnoff were in partial agreement with the heat transfer findings.

United Technologies Research Center (UTRC) operated its fuel deposit test apparatus at a wall temperature of 316°C (600°F) in testing effects of copper on carbon deposition [7]. At a concentration of 300 ppb, copper exerted an eight-fold increase in deposition rate compared to the control fuel. Fuel containing 100 ppb of copper gave slightly higher amounts of deposit, but the maximum deposition rate came at a lower temperature. A sample with 50 ppb copper formed less deposit than the control and also had a maximum at a lower temperature.

Experiments in the JFTOT

The influence of copper on thermal stability is amply demonstrated above. However, quantitative effects obviously varied significantly. Part of the variation can be ascribed to the fact that different rigs and different experimental conditions were utilized. Chemical factors are also important; this has been illustrated in tests with the JFTOT.

Nowack and Grabel found that JP-5 fuels responded differently to the amount and type of metal contamination [3,8]. Table 1 lists the JFTOT breakpoints for six fuels and also the amount of metal—copper, iron, or zinc—required in each fuel to cause failure at 260°C (500°F). The concentrations at failure were independent of the original stability of the fuels.

The lowest threshold levels that were observed to fail a fuel were 50 ppb of copper, 136 ppb of iron, and 200 ppb of zinc. Some fuels exhibited a high tolerance to a single dissolved metal. For example, one fuel required the presence of more than 105 ppb of copper before the 260°C criteria was reached. Another fuel failed at 165 ppb of iron, and a third failed at 420 ppb of zinc.

Datschefski added copper naphthenate to a Jet A-1, and the fuel passed the JFTOT at 260°C with copper concentrations of either 50 or 150 ppb [9]. The fuel failed at both concentrations, however, when the copper was natural. The failure was from very high filter pressure drops.

Morris and Turner looked at the effects of three copper compounds [10]. One was a salt of an organic acid, copper (II) cyclohexanecarboxylate, and the other two were chelate compounds, copper (II) benzoylacetonate and copper (II) ethyl acetoacetate. At a high concentration of 1600 ppb of Cu, the three compounds produced similar amounts of deposits. Significant deposition was found at temperatures as low as 200°C. All of these copper compounds also accelerated oxygen depletion and hydroperoxide formation at low temperatures. The maximum ROOH concentration was lower when copper was present and also occurred at a lower temperature. The oxygen depletion effect was observed even at very low levels, 1.6 ppb Cu.

Morris and Schreifels added a soluble organic magnesium compound to Jet A at a concentration of 50 ppm and tested the resulting sample in the JFTOT [11]. Depletion of dissolved oxygen was more rapid (similar to Cu), but hydroperoxide levels were similar to that of the undoped Jet A. A white deposit formed on the heater tube, which was run at a temperature maximum of 280°C. The white deposit was shown by photoelectron spectroscopy to be magnesium, demonstrating that the magnesium compound was thermally unstable above about 250°C.

Four coal-derived jet fuels were compared with a petroleum-derived JP-5 with regard to natural pickup of copper from strips and with regard to effect on JFTOT breakpoint temperature at the 200 ppb Cu level [12]. The two fuels with high aromatic contents (24 to 25%) solubilized copper three to four times faster than the low aromatic ones (5 to 6%). This effect may be related to the acid content, which also showed a large difference between the high and low aromatic fuels. The deterioration in breakpoint varied from 47 to 70°C. This compares to a drop of 82°C for a reference petroleum-derived fuel with the same amount of dissolved copper, 200 ppb. Failure was usually by filter pressure drop parameter.

Tests in Cokers

The ASTM Coker was the test device used by Shertzer to define the effects of copper and zinc on JP-5 thermal stability [13]. Naphthenate salts were added to attain the desired concentration of dissolved metal. Failures were observed for 500 ppb zinc and 100 ppb copper at 149/204°C (300/400°F) preheater/filter conditions. In one base fuel, failure for 50 ppb was found at 135/190°C (275/375°F) conditions and for 100 ppb at 121/177°C (250/350°F) temperature settings. For a clay-treated JP-5, 200 ppb Cu decreased the coker breakpoint from 218°C (425°F) to 149°C (300°F), but 50 ppb Cu dropped the breakpoint only 14°C (25°F).

Schenk, Johnston, and Monita used the gas-drive coker to study the role of lead, zinc, iron, and copper on the breakpoint of JP-7 fuels [14]. The metals effected fuel degradation at much lower concentrations than those listed for JP-5 fuels in Table 1. Added metals, as naphthenic acid salts, at concentrations as low as 15 ppb Cu, 25 ppb Fe, 100 ppb Zn, and 100 to 250 ppb Pb decreased the failure temperature 42°C (75°F). Again, different JP-7 samples responded to metal dopants to different extents. Difficulties were encountered in

maintaining the metals, particularly copper and lead, in the dissolved state. Tube ratings were difficult because deposits from the metal-containing fuels were colored and subject to misinterpretation. Fuel to which more than one metal was added exhibited strong effects on thermal stability. Copper and iron were essentially additive in their effect such that 10 ppb Cu plus 10 ppb Fe decreased the breakpoint about 42°C (75°F). Zinc was much more active in the presence of the other metals than by itself. For instance, the 42°C (75°F) decrease in breakpoint was found for 10 ppb of zinc in combination with 10 ppb of either Cu or Fe. Solubility, chemical analysis, and tube-rating problems plus variations in responsiveness of fuels prevented precise evaluation of effects of combined metals.

Flask Oxidation Studies

Kendall and Mills examined the effects of dissolved copper and iron on the oxidation rate of aviation kerosenes at 145°C [15]. They observed that 40 ppb of copper naphthenate boosted the oxygen use rate 5.3 times and that the iron salt exerted a 2.5-fold increase at 20 ppb. In a second fuel, the copper effect was more dramatic, but the iron was innocuous at 25 ppb. Iron, however, reduced the effect of copper when both were added to this latter fuel. These findings highlight the difficulty of defining the effects of metal addition to a fuel that contains other metals.

Sources of Dissolved Metals

JP-4 Fuels

Metal contents of JP-4 fuels were determined by the U.S. Air Force in a thermal stability survey [16]. With the exception of one fuel, the copper concentration was estimated to be 17 ppb or less. Iron was usually less than 50 ppb and zinc less than 75 ppb. Lead levels above 200 were common with a level of 540 ppb found in one fuel. All 19 fuels in the survey passed the ASTM Coker test at 163°C (325°F) or higher, even the samples with high copper and lead. The high copper fuel had been processed with a copper-sweetening step.

JP-5 Fuels

Shertzer reported that JP-5's carried on U.S. Navy aircraft carriers had high levels of copper, up to 1200 ppb [13]. The thermal stability properties of carrier fuels, as measured by the ASTM Coker, were degraded significantly. The source of the copper was the jet fuel pipelines on the carrier. These are constructed from copper/nickel alloys, either 90/10 or 70/30, in order to reduce seawater corrosion in the marine environment. This copper problem was resolved with an additive in the short term and with a reduction in the fuel acid specification in the long term.

A more recent extensive survey of JP-5 fuels as received on U.S. Navy aircraft carriers from replenishment ships and as dispensed into aircraft was conducted by Southwest Research Institute [17]. Ninety samples were subjected to JFTOT testing and trace metal analysis. An additional 111 samples were analyzed for trace metals only. The copper level ranged between 0 and 838 ppb with the received samples averaging less than the dispensed ones. The copper concentration for 73 samples of the 201 total exceeded 50 ppb. Forty of the ninety samples tested in the JFTOT failed at the 260°C tube temperature. Failure was always by filter pressure drop, sometimes accompanied by visual code failure. JFTOT failure always occurred when copper exceeded 50 ppb, and several samples with 25 to 50 ppb Cu also failed. The proportion of fuels failing the JFTOT was lower for the samples received

from the replenishment ships than for the fuels dispensed to aircraft. This would be consistent with the longer storage times for the latter samples and longer exposure to the copper-containing pipes in the aircraft carrier. The maximum zinc concentration found in any of the samples was 30 ppb, but the great majority were at the detection limit (4 ppb) or below. Iron maximum was 16 ppb, but again most samples were at or below the detection limit of 5 ppb. Nickel was found at 170 ppb for one sample; otherwise, no fuel had more than 52 ppb of this element. Copper and nickel concentrations were not related in any way, although they are probably both in the fuel from corrosion of the copper/nickel pipe.

Factors in Metal Solubility

Grabel and Nowack studied chemical factors related to solution of metals into fuels [8]. Iron was exposed to fuel under different conditions and in different forms but did not dissolve. Polished, acid cleaned, and rusted forms were tried as were temperatures up to 93°C (200°F) and storage times in the presence of tap or seawater up to 30 days. Copper and zinc readily migrated into the fuel. The dissolution for copper was shown to be strongly influenced by the content of organic acids in the fuel. For instance, removal of 80% of the acid reduced the rate for copper migration by 60%, but other polar compounds appeared to have some capability to dissolve copper. Added acids increased the rate of solution of copper. The rate was many times greater if oxygen was available and if the fuel was saturated with water. In practice, these latter conditions would be normal.

Removal of Metals

The U.S. Navy, with their severe copper contamination problem on aircraft carriers, examined techniques to reduce or eliminate this element in jet fuel. Clay filtration was tested by Shertzer [13]. Approximately 40 000 gal of fuel was passed through 63.5 kg (140 lb) of clay. The copper concentration was reduced from 71 ppb at the inlet to 22 ppb coming out of the clay, a 69% reduction. Calculations showed that clay filtration units five to ten times the size of shipboard filter/separators would be needed to afford adequate copper removal at the aircraft. This was considered unacceptable because of the space limitations on carriers. Ion-exchange cleanup was also considered but dismissed on similar grounds.

The U.S. Air Force considered clay filtration for JP-7 and JPTS, fuels which have high thermal stability requirements and are very sensitive to trace contaminants such as metals [18]. A drum of JP-7 doped with metal naphthenates was filtered through a single 6.8-kg (15-lb) attapulugus clay cartridge. In a single pass, Cu dropped from 44 to 2 ppb, Zn from 206 to 15 ppb, Pb from 222 to less than 3 ppb, and Fe from 91 to 19 ppb. Lead present as tetraethyl lead, however, was not removed. This is expected since the clay removes only polar compounds. Other tests demonstrated that a single clay cartridge was effective after filtration of 437 gal of JP-7, removing about 80% of the added copper throughout the test. This was in spite of the presence of 0.1% fuel system icing inhibitor and 200 ppm of PWA-536 lubricity improver, two highly polar additives which would compete with the metal salts for absorption sites on the clay.

Calculations on the capability of clay processing of JP-7 indicated that 75 000 to 95 000 L (20 to 25 000 gal) of fuel could be filtered in a portable field unit comprised of 48 cartridges in 60 to 80 min. A flow rate of 22.7 L (6 gal) per min per cartridge could be utilized. The cost for cartridges at an assumed price of \$4 each would add about a cent per gal to the fuel cost.

Effects from Exposure to Metallic Materials

Jet fuel encounters metals throughout its history. Much of this exposure is at low temperature before it reaches an aircraft, but the exposure in the aircraft is partially at elevated temperatures. The former situation is important since the exposure can be for a long time, while the latter is important since high-temperature reactions have much higher rates.

Smith studied both environments [19]. In one set of experiments he exposed aviation kerosene to various metals and alloys at temperatures of 115 to 150°C for 360 min. The fuel was then run through the ASTM Coker or the high-temperature coker. In the second set he operated the ASTM Coker with the preheater tubes covered with an appropriate foil or made from different metals or alloys. The results were consistent for the two different experimental arrangements. Copper and its alloys exerted moderate to great reductions in breakpoints. In fact, tubes wrapped with foil made from copper and its alloys decreased breakpoints about 69°C (125°F) compared to standard aluminum tubes.

Beryllium metal exhibited a moderate effect in Smith's 360-min tests. Of the other metals, only lead and tungsten produced any changes in the 360-min test, and the effects were slight for these metals. A tungsten alloy also gave a slightly harmful effect. Tubes with nickel, silver, or zinc surfaces produced about 14°C (25°F) reductions in breakpoints, and only slight changes were observed for any of the alloy tube materials other than the copper-containing ones.

Faith, Ackerman, and Henderson ran the JFTOT with heater tubes fabricated from 14 different metals or alloys [20]. The Jet-A fuel outlet temperature was controlled at 210°C (410°F), and the tubes were rated with a beta-ray backscatter instrument. Two rating criteria were reported, maximum deposit and total mass of deposit.

Aluminum 6061, Nickel 200, and Type 446 stainless steel (SS) exhibited the lowest deposit amounts. Type 316 SS, Inconel 600, aluminized nickel and Monel 400 were next in performance, producing two to six times more deposit than the best materials. Next came nickel and aluminized Type 304 stainless. Cartridge brass, L-605 (Haynes 25), 1015 steel, and Type 304 SS formed much greater amounts of deposit. Hastelloy C gave a small total mass of deposit, but it was concentrated in a narrow band, thus giving a thick deposit in a localized area. The heavy deposit on cartridge brass was expected since it contains 70% copper. Monel 400, the only other material in this test comparison with significant amounts of copper (32%), was intermediate in performance. The result for Type 304 SS was surprising in view of the good results with other stainless steels, Types 446 and 316. Type 304 gave the thickest deposit and also the most total mass.

Taylor reported that aluminum, Type 304 SS, and pure titanium gave equivalent deposition rates in Esso's two-phase flow apparatus with air-saturated fuel [21]. In these tests at low temperatures, two titanium alloys made several times as much deposit as aluminum, and copper surfaces were the worst material in this Esso comparison. Chapter VII reported a different order of performance for deoxygenated fuel in the Exxon advanced kinetic unit.

Cadmium plating stimulated deposition in fuel blends containing labelled oleic acid [22]. The interaction between the cadmium and oleic acid was much more pronounced after 52 weeks storage at 54°C (130°F). These tests were conducted in a microfuel coker.

Kendall and Mills at Shell Thornton compared aluminum and stainless steel tubes in the JFTOT operated with a maximum temperature of 350°C [6]. The deposit total was determined by carbon burnoff. On the average, stainless steel gave almost twice as much deposit as aluminum. The six fuels tested included hydrotreated, hydrocracked, and Merox-treated fuels plus blends of these three.

In follow-on work at Thornton by Clark and Thomas, the aluminum/SS comparison was continued in tests of various duration in the JFTOT [23] The passivating characteristics of

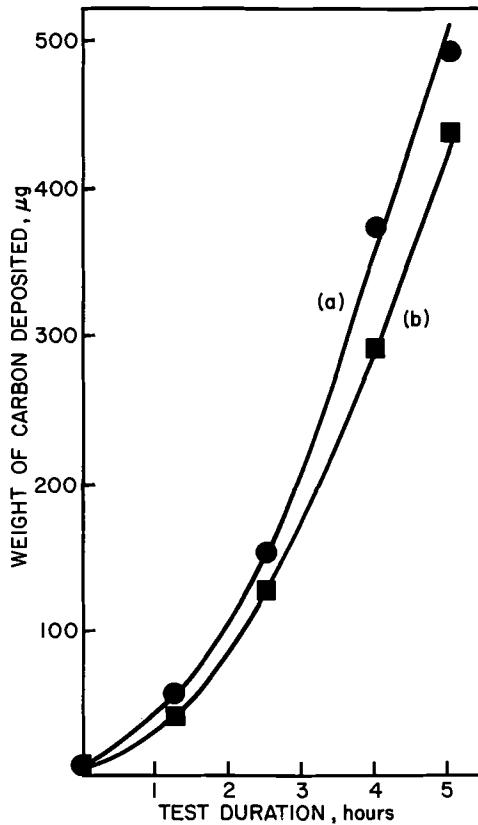


FIG. 1—The effect of test duration on carbon deposition in the TOFT (JFTOT) using Fuel A on two different metallurgies: (a) stainless steel; (b) aluminum. Reprinted with permission of the Society of Automotive Engineers, Inc., copyright 1988.

enhanced MgO concentrations on the surface of the aluminum tube were considered in this case. The comparison is presented in Fig. 1 for amounts of deposit at 350°C versus test duration. The stainless exhibits about 50% more deposit at short times, but this value is reduced to about 13% for a 5-h test. The authors suggested that deposit covers the surface as the test proceeds and fuel exposure to any catalytic activity of the metal surface decreases. Hence, after a period of time, any activity of the metal would be limited to the cooler portions of the tube where chemical reactions are slow and deposit is not normally formed. Interaction between the liquid and solid surface is then controlled by the organic fuel deposit, and metallurgy of the underlying metal should be of minor importance.

Workers at British Petroleum, operating the JFTOT at temperatures above the normal specification setting, observed lower deposition rates than expected [24]. Examination of the heater tube by Auger electron spectroscopy showed that magnesium, which is typically present at 1 at% in 6061 aluminum, had become enriched on the surface. In fact, at 365°C, magnesium attained a 10 at% concentration in only 45 min of test time. Further studies showed that an equilibrium concentration of 20% Mg could be attained at much lower temperatures if adequate time was used. Also, the studies indicated that the deposit thickness

is inversely related to the magnesium content of the surface. This latter theory was confirmed by a 365°C test with a magnesium-coated tube. No deposit formed with a copper-sweetened fuel after 20 min. Longer tests are needed to insure that magnesium maintains the inhibition. Gold, which is an inactive metal in many surface reactions, was also tried as a heater tube coating. This metal did not exhibit the inhibition observed with magnesium, however.

The observations on magnesium inhibition on deposition led to the addition of a note to ASTM Method D 3241-88a (JFTOT). This note states: "Heater tubes should not be reused. Tests indicate that magnesium migrates to the heater tube surface under normal conditions. The enriched magnesium surface may reduce adhesion of deposits to re-used heater tubes."

Morris at the Naval Research Laboratory tested the Mg migration rate over a wider temperature range [25]. The Mg concentration on the surface of the aluminum tube after a 2.5-h test with deoxygenated dodecane was almost linear with respect to temperature. Further, the NRL and BP data matched very closely. The Mg concentration was enhanced to 5% even at 150°C and was 8 to 10% at 260°C, the temperature used with the JFTOT specification test.

Stavinoha, Naegli, and McInnis measured deposit thicknesses on stainless steel JFTOT tubes as well as tubes coated with various metals by a vacuum deposition procedure [26]. Surfaces compared were Types 304 and 316 stainless steel (SS), aluminum, copper, magnesium, and gold. Thicknesses were measured by two techniques, dielectric strength (DMD) and Auger milling. Thick deposits, 1 to 3 μm , were formed by operating at 300 to 380°C since the DMD does not work well on thin deposits. All surfaces gave similar deposit thicknesses and total volume by DMD, within a range of about 2.5. Surprisingly, by DMD measurements copper gave the least amount of apparent deposit and magnesium was similar to aluminum. By Auger milling, the decreasing order of deposition was different: copper, magnesium = 316 SS, gold, aluminum. The authors suggested that the DMD may not be reliable for deposits which incorporate metals into their matrix as we know that copper does. The heavy deposits found for magnesium contrasts with the BP findings, but this could be due to the quality of the fuel used (JFTOT breakpoint 254°C) and the severity of the tests. The similarity of deposit amounts for all surfaces indicates that the coverage is extensive and that the underlying surface has only a slight effect on the deposition reactions.

We thus conclude that results of tests on aluminum tubes may be open to question as Clark and Thomas have suggested [23]. Stainless steel is preferred to aluminum in the respect that it does not form a passivating or inhibiting surface during heating. Stainless steel heater tubes have several other advantages including the one that this material is used in the hotter parts of aircraft fuel systems and is, therefore, more relevant to practice.

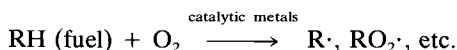
Surface roughness was important in deposition in the manifold of the U.S. Air Force simulator [27]. A stainless steel tube with a significantly smoother surface, as indicated by a microphotograph, exhibited a much lower rate of deposition during the first period of testing. After about 30 h, however, the rates were parallel. Once the surface is covered with organic deposit, the rate of further deposition appears to be independent of the underlying metal surface.

Mechanisms of Metal Action

We have seen that several metals alter the amount of deposit, usually increasing the total deposit. Very little research has been reported on the mechanisms of involvement. The bulk of the efforts have addressed the action of copper since it is the most active metal under most stability conditions.

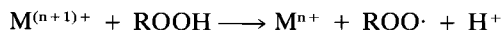
Copper and other active metals stimulate fuel instability at very low concentrations. This fact suggests that these metals are exerting catalytic functions. Uri discussed several pos-

sibilities for free-radical formation from transition metal/oxygen reactions as well as direct reaction between a metal ion and an organic molecule [28]. Clark suggests that metals catalytically increase the rate of initiation of free radicals as follows [29]



Catalytic activity of copper in the initiation stage of oxidation is supported by several findings. Kendall and Mills found a significant increase in oxidation rate in flask tests at 160° [15]. The increase was about 5 times at 5 ppb Cu and about 15 times at 25 ppb. Morris and Turner observed a shift in dissolved oxygen usage to lower temperatures in JFTOT tests with copper added [10]. Oxygen was depleted at 260°C in the presence of 132 ppb Cu versus 280°C for an undoped Jet A. The hydroperoxide formation curve was also shifted 20°C to lower temperatures by the copper. Some effect on this behavior was noticed at very low concentrations, 1.32 ppb. Marteney also found that copper at 100 ppb increased the rate of oxygen usage in the fuel deposit test apparatus [7]. Thus, we see good evidence that copper can increase the rate of free-radical initiation by acting as a catalyst.

Walling proposed that dissolved metal ions with multiple valence states can catalytically decompose hydroperoxides according to the following two-step redox scheme [30]



A free radical is produced in each step, and both radicals can institute oxidation chains which lead to further reaction and possible deposition. Thus, although autoxidation rates are accelerated, hydroperoxide concentrations are commonly reduced by the presence of multivalent metal salts. Research described in the next paragraph lends credence to the metal's role in hydroperoxide decomposition in the thermal oxidation stability environment.

In the JFTOT, Morris and Turner observed that the hydroperoxide level was lower when an organic copper compound was present even though the copper also instituted oxygen/fuel reactions at lower temperatures [10]. Nowack also found that the hydroperoxide level attained in a JFTOT test was sharply reduced in the presence of added copper [31]. Nowack's work also indicated that dissolved zinc reduced and that dissolved iron almost completely suppressed hydroperoxide formation.

In JFTOT tests with fuels containing soluble copper, the copper deposited on the heater tube and also formed copper-containing particulate matter which exited the apparatus [31]. Most of the copper plated out or became insoluble by 260°C, but incipient loss was evident at 200°C. Iron showed similar patterns at somewhat lower temperatures, incipient depletion at 150°C, and extensive depletion at 245°C. Soluble zinc appeared to deplete partially at room temperature with the remainder dissipating at about 290°C. Copper was found on SS heater tubes primarily at 200 to 250°C in JFTOT tests reported by Morris and Turner [10]. Copper was in the +2 valence state, comprising 10% on the outer surface of the deposit. The copper attained 60% concentration further into the deposit. In further JFTOT tests, workers at BP noted that dissolved copper was incorporated into the tube deposits and was also present in filterable solids exiting the instrument [32].

Workers at Shell [15] and BP [32] suggest that iron has a different pattern of action than copper, but specific details remain to be developed.

Some information has been developed which shows that copper is catalytically active in at least two roles in thermal oxidation stability: (a) increases the rate of initiation in the

hydrocarbon free-radical autoxidation mechanism; and (b) increases free-radical concentrations by decomposition of hydroperoxides. The role of other metals has not been defined to the same extent as copper, but they probably perform some of the same functions in degrading the thermal oxidation stability of jet fuels.

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CHAPTER IX

Additive Effects on Thermal Oxidation Stability

One of the first proposals to improve the thermal oxidation stability of aviation turbine fuels was the use of additives [1-4]. Initial work focused on antioxidants which had demonstrated useful performance for storage stability of other petroleum products—gasoline, diesel fuel, and heating oils. Modest, if any, benefits were found for the conventional hindered phenols and amines. Another class of additives, dispersants, exerted significant improvement in filter tests in the ASTM Coker or similar devices. Filtration times were extended from 200 to 800% for some additive/fuel combinations. Some fuels did not respond to dispersants, however. Further, dispersants interfere with separation of water from fuels. These initial results encouraged scientists to follow the promising leads, and research on defining the role of additives continues to the present.

The emphasis in additive studies has been on improvement of thermal stability. Another important concern, however, has dealt with the potential deterioration of stability from additives put in the fuel to improve some other property. Also of concern is the potential deterioration of other desirable fuel properties due to additives which benefit thermal stability. All aspects will be included in the discussion in this chapter.

Previous Reviews and Surveys of Additives

Schwartz and Eccleston included a review of additives in their survey of thermal stability literature [5]. They considered four types of additives—antioxidants (AO), dispersants, metal deactivators (MDA), and corrosion inhibitors (CI). They summarized their viewpoint as follows:

The use of additives to improve thermal stability of jet fuels appears to parallel experience with other fuels. There are no additives that are universally effective in all fuels and some fuels may respond poorly to additive treatment. . . . The improvement effected by additives investigated to date was usually small. Thus, additives may find their largest usage in upgrading marginal fuels where only a slight improvement will make the fuel acceptable. Dispersants and antioxidants appear to be the most effective additives for improving thermal stability of jet fuels.

Southwest Research Institute examined the literature through 1963 with the aim of evaluating additives for both storage and thermal stability [6]. This review was followed with an experimental program on storage/thermal stability behavior in high-stability JP-6 jet fuels [7]. Fifty-two proprietary additives were screened initially for adverse affects on other properties. Many were eliminated for further testing on the basis of water separation problems. Nineteen of these additives were included in the stability phase of the studies. Four additives were considered promising from the results of the combined storage (54°C/130°F, 8 to 16 weeks)/thermal stability (helium drive coker) tests. The tests were conducted with additive concentrations substantially above that of normal practice. Only two of the additives were

identified as far as function. One was a metal deactivator, and a second was a combined antioxidant/metal deactivator.

General Electric Co. surveyed the effects of 17 different additives in the Minex rig operated to give a finite fouling factor for the base fuel [8]. The six different classes of additives included in the testing were put in the fuel at the maximum concentrations permitted by a fuel specification or other document. The results can be summarized as follows:

1. Antioxidant, amine type	Detrimental
2. Antioxidant, phenol type	No significant effect
3. Metal deactivator	Beneficial
4. Antistatic additive	Beneficial
5. Corrosion inhibitors	Beneficial (two products)
	No significant effect (one product)
6. Anti-icing additive	Detrimental
7. Microbiocide	No significant effect

The most recent and most extensive review of the thermal stability additive literature was by Henry for the CRC literature survey of 1979 [9]. A synopsis of additive results from this report are presented below.

Antioxidants

Para-phenylenediamine antioxidants often decrease the thermal stability of jet fuels. Hindered phenol antioxidants are not normally detrimental and are beneficial in some fuels. The improvement compared to a base fuel is usually associated with long-term storage. This behavior in storage is related to the prevention of the buildup in storage of hydroperoxides. These oxidation products, which were discussed in Chapter VI, are known to degrade the thermal stability of jet fuels.

Metal Deactivator

This class of compounds is designed to chelate and thus inactivate metal ions dissolved in fuel. The most widely approved MDA is *N,N'*-disalicylidine-1,2-propanediamine, which can be added according to most specifications up to a maximum concentration of 5.7 mg/L. This MDA has demonstrated effectiveness in increasing the threshold concentration at which various dissolved metals affect thermal stability. Benefits were not universal, however, probably because of the uncertainty in dissolved metal contents of tested fuels. A closely related compound, *N,N'*-disalicylidine-1,2-ethanediamine, forms a chelate with copper which has a very low solubility in jet fuel [10]. Deposition of this chelate in fuel systems caused filter plugging and the ethane compound is no longer permitted in jet fuel. Recent research with MDA will be described below.

Metal Passivators

U.S. Navy work with benzotriazole has shown that copper pickup can be inhibited by this additive [11]. Thus, benzotriazole at 5 ppm can prevent deterioration in fuel thermal stability due to dissolution of copper from copper/nickel pipe on aircraft carriers. A J-57-P-8B engine operated satisfactorily for 92 h on JP-5 containing 40 ppm benzotriazole and no copper [12]. The engine also performed satisfactorily on fuel containing 0.4 and 1.2 mg/L of copper/benzotriazole complex. In this test, a gelatinous precipitate of the material collected on the fuel nozzle screens, but the fuel nozzle performance was not affected.

Corrosion Inhibitors/Lubricity Additives

High-molecular-weight fatty acids have a long history of use as corrosion inhibitors in fuel transfer and storage systems. More recently, some of the approved corrosion inhibitors have been used successfully to improve the fuel lubricity, usually for hydrotreated jet fuels.

Many tests have indicated that several of these materials do not degrade thermal stability. However, corrosion inhibitors containing phosphorus reduced thermal stability of jet fuels with high breakpoints on the JFTOT test [13]. Nevertheless, these phosphorus-containing inhibitors did not lower the breakpoint below 260°C, the specification limit.

Fluorocarbon lubricity additives reduced the fuel breakpoint in some tests on high-stability fuels but produced slight improvement or no change with other fuels [9]. In all cases, the fuels would still be suitable for high-speed aircraft.

Dispersants

Dispersants prevent agglomeration of insoluble particulates formed by instability reactions. The mode of action keeps the particles so small that they are not trapped by filters, neither do they adhere to fuel controls or heat exchanger surfaces. These materials have significant surface activity, however, and degrade the fuel/water separation characteristics.

JFA-5, an ashless dispersant composed of polymers, organic amines, and amides, has demonstrated effectiveness in improving thermal stability of high temperature jet fuels [10]. In fact, it is a required additive at 9 to 12 mg/L in a U.S. Air Force specialty fuel, MIL-T-25524B, thermally stable jet fuel (JPTS). This fuel is required to pass a JFTOT test at 335°C.

Other Jet Fuel Additives

Several other additives may be put into jet fuels. These include fuel system icing inhibitor, antistatic additives, microbiocides, and pipeline drag reducer additives. Fuel specifications vary considerably in their requirements, and none of these are found in all products. However, in addition to required usage, optional use is permitted in some specifications. The effects of these additives on thermal stability have not been well defined, but all but the pipeline drag reducer have some basis for use in aviation turbine fuels. The pipeline drag reducer is not currently approved for use by any specification, but it may be used in the future.

Recent Additive Studies

Several additive studies for jet fuel thermal stability applications have been completed since the CRC literature survey of 1979 [9]. The emphasis in the past decade has been on the chemistry of metal deactivator, but a few studies have examined antioxidants and other additives. In his 1987 review of military jet fuels, Martel summarized the use of all jet fuel additives [10]. The status of additives with respect to thermal stability at that date was similar to that presented in the earlier sections of this chapter.

Studies on Combinations of Additives

The U.S. Air Force conducted an extensive additive evaluation program on a shale-derived JP-4 [14]. Included in the test protocol were nine antioxidants, four corrosion inhibitors, fuel system icing inhibitor, conductivity additive, metal deactivator, and a thermal stability additive—JFA-5. Samples containing two to five additives of different classes were included

in the testing. One set of experiments held the fuel/additive blends at 21 to 27°C (70 to 80°F) for 15 months with samples tested at 0, 3, 9, and 15 months. Control samples containing FSII and antistatic additives, used as the baseline fuel, maintained a 310°C pass on the JFTOT throughout the test sequence. The thermal stability of some additive blends decreased, but all samples for all storage times passed at 290°C. Most decreases were associated with the presence of the antioxidant, N,N'-diisopropyl-*p*-phenylenediamine, at 24 mg/L. This antioxidant is no longer allowed in U.S. military jet fuels. MDA and JFA-5 improved the JFTOT breakpoint of the shale JP-4, but no quantitative information was developed.

A second set of tests stressed the shale-derived fuel at 43°C (110°F) for 15 months before defining the thermal stability with the JFTOT. This moderately accelerated test at 15 months affords the equivalent of five years storage at ambient temperatures. The control fuel for this set, which contained FSII, antistatic additives, and a corrosion inhibitor, had a JFTOT breakpoint of 320°C. The control fuel passed at this temperature after three and nine months storage but failed by preheater rating even at 300°C after 15 months storage. It did pass at 280°C, however, well above the specification value of 260°C for most military and commercial jet fuels. The deterioration at 15 months coincided with a high hydroperoxide level which was only 2.3 ppm at nine months but had increased to more than 500 ppm at 15 months. This set of 43°C (110°F) samples was designed to test antioxidants, and all nine were successful in keeping the peroxide concentration below 7 ppm throughout the 43°C, 15-month test. This seemed to benefit the thermal stability also as all samples containing AO's passed the JFTOT at 300°C. The phenylenediamine AO consistently dropped the breakpoint below 320°C, but it still passed at 300°C.

Antioxidants and/or Stabilizers

Nowack et al. included antioxidants in a study of shale-derived jet fuel stability [15]. The fuel was tested with and without added nitrogen-rich extracts or specific heteroaromatic nitrogen compounds. A phenylenediamine AO significantly reduced maximum TDR readings (10 down to 2 without added nitrogen compounds and 48 down to 13 with added nitrogen) at 260°C for samples stored at 60°C for four weeks. This appeared to be related to the additive's ability to control hydroperoxide formation. A hindered phenol, 2,6-di-*tert*-butyl-4-methylphenol, also gave control on peroxides and TDR readings with the exception of a fuel to which a substituted pyrrole had been added.

In flask oxidation studies, Kendall and Mills observed a 30 to 40% reduction in rate of fuel oxidation after addition of 50 mg/L of AN-2, 4,4'-methylene-bis(2,6-di-*tert*-butyl)phenol [16].

Morris, Hazlett, and McIlvaine examined several additives with respect to dissolved oxygen depletion, hydroperoxide formation, and deposition tendencies [17-18]. Additives included were traditional antioxidants—a hindered phenol (Ionol) and a diamine (N,N'-di-*sec*-butyl-*p*-phenylenediamine), a fuel oil stabilizer (FOA-3) which is a *tert*-aliphatic amine, the traditional metal deactivator (MDA), and a fuel oil additive (FOA-310) which is a blend of MDA with the *tert*-aliphatic amine of FOA-3. Tests were run with Jet A fuel in the JFTOT at 200 to 310°C with deposit estimation by carbon burnoff.

The temperature profile for oxygen depletion was unaffected by Ionol and FOA-3. On the other hand, the diamine (PDA), the MDA, and FOA-310 inhibited oxygen depletion at intermediate temperatures, 240 to 270°C. Oxygen reaction was virtually complete for all additives at 280°C, however. Ionol and FOA-310 attained hydroperoxide concentrations similar to the undoped jet fuel, although the maximum was shifted 10 and 20°C higher, respectively. The other three additives limited the hydroperoxide formation at all temper-

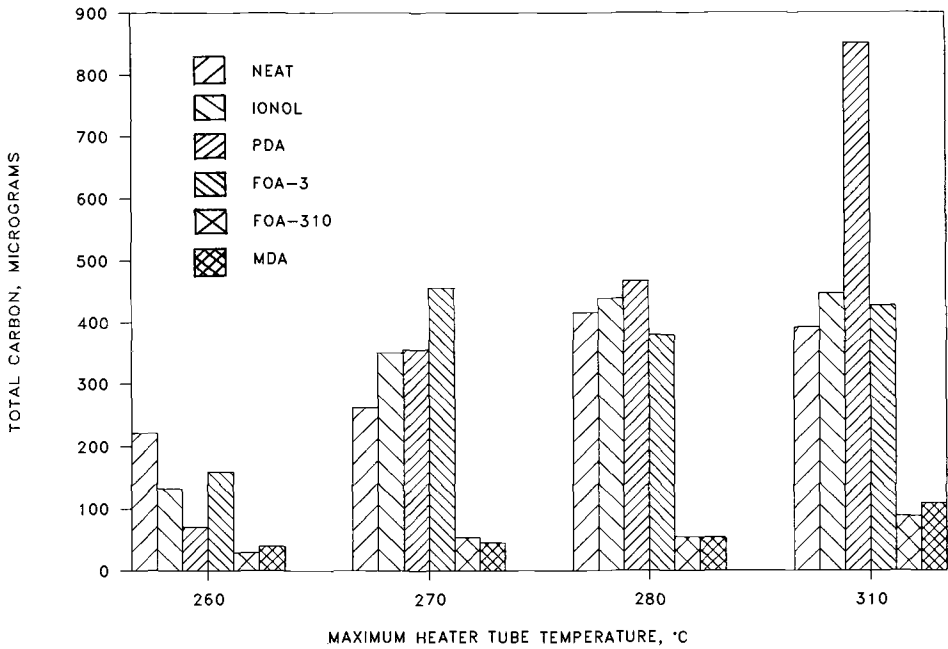


FIG. 1—Influences of additives on JFTOT heater tube deposition as determined by combustion.

atures. The PDA was the most effective in this function, allowing only one seventh the amount developed by the undoped fuel.

JFTOT heater tube deposits from these additive tests are presented in Fig. 1. The total carbon of the deposits was reduced by all additives at 260°C with FOA-310 and MDA exhibiting the greatest reduction. These two additives maintained the beneficial performance at 270, 280, and 310°C also, effecting 75% or higher reductions at these higher temperatures. Ionol and FOA-3 exhibited minor effects on deposit amounts at the higher temperatures. PDA doubled deposit amount at 310°C compared to the neat Jet A base fuel. Filterable insolubles were estimated by increases in the pressure drop. MDA and FOA-310 were very effective in suppressing filterable insolubles. At higher temperatures, the Ionol had no significant effect while the FOA-3 tended to increase filterable insolubles somewhat. The most rapid filter plugging occurred with PDA, with dramatic increases even at 270°C.

An overall summary of additive influences in this study are given in Table 1. MDA afforded significant reductions in heater tube deposits and filterable solids as well as some control over the rate of oxidation and hydroperoxide formation. FOA-310 acted identically with MDA with the exception of less effect on hydroperoxide concentration. The similarity of these two additives can be attributed to the metal deactivator, alone in MDA but in a mixture with a tertiary amine in FOA-310. Since the copper content of the fuel was found to be less than 1 ppb, the improvements in thermal stability were not a consequence of copper complexation by the MDA. The tertiary amine, as a single functional additive in FOA-3, exhibited limited activity except in reducing hydroperoxide concentration. This latter may result from the interaction of the hydroperoxide and FOA-3 to form an amine oxide. Considerably more research on MDA will be discussed in the next section.

The effect of antioxidant behavior on the thermal stability of various distillate fractions was examined by H-Sulaymon, Mohammed, and M-Al-Rawi [19]. Topanol (2,6-di-*t*-butyl-4-methylphenol) decreased TDR readings for JFTOT runs at temperatures of 243 to 300°C.

TABLE 1—Summary of additive effects on fuel properties after JFTOT stressing.

Additive	Heater Tube Deposits	Filterable Insolubles	Peroxidation	Oxygen Consumption
IONOL	0	0	0	0
PDA	+	++	--	--
FOA-3	-	+	-	0
FOA-310	--	--	0	-
MDA	--	--	-	-

NOTE: 0 = Minimal effect; +/- = significant increase/decrease; + + / - - = large increase/decrease.

The decreases were modest except for a 100 to 150°C distillation cut. Ninety ppm of the additive was needed before much effect was evident for the higher distillation cuts.

Metal Deactivator

Recent years have witnessed intensive research into the activity of metal deactivator and its mechanism of action. This research continues in a very active state. An example of the benefit afforded by MDA is illustrated in Fig. 2 for Shell Thornton's work with their injector feed arm rig [20]. The low concentration of 0.6 mg/L of MDA used in this test reduced carbon deposition in a 70-h test by 14-fold for Fuel A but only twofold for a second fuel. The dissolved metals content was not specified for these fuels, and the effectiveness of MDA may have been due to its chelating effect.

Metal deactivators were designed to counteract the effects exerted by metals dissolved in fuel. They exert this effect by forming a chelate with the metal ion which binds the ion strongly and reduces its ability to act independently. Some examples of that use will be given below. MDA exhibits beneficial effects beyond this function, however, and the current research, which examines other possible roles in thermal stability, will also be discussed.

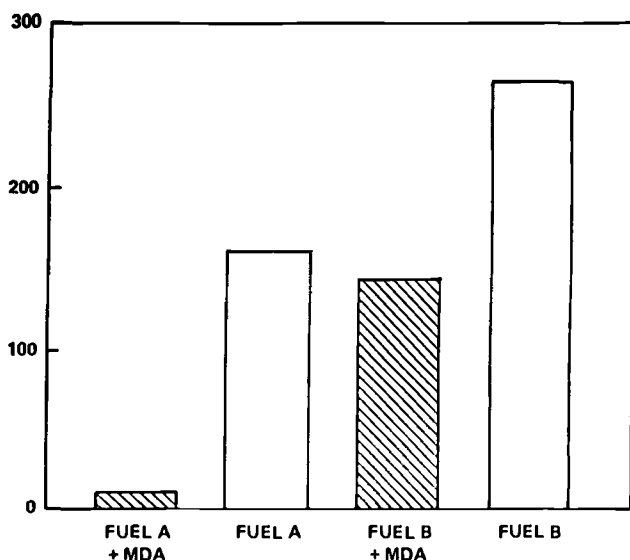


FIG. 2—Fuel deposition in the injector-feed-arm rig. MDA is the metal deactivator additive.

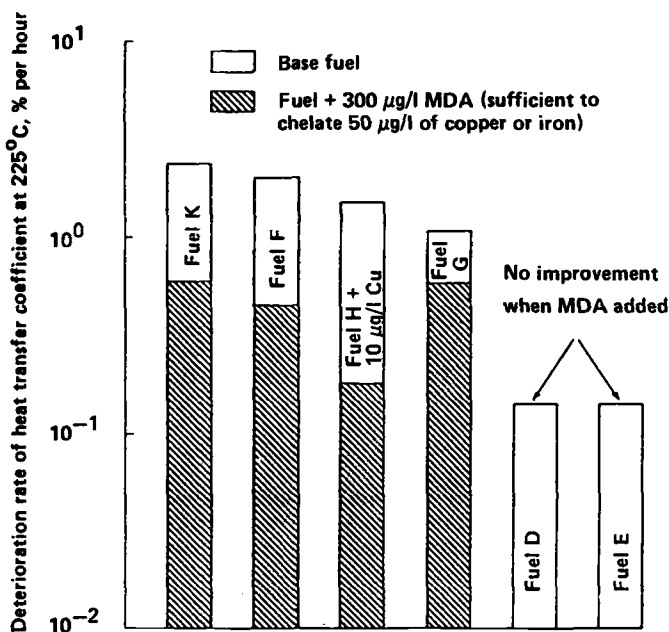


FIG. 3—The ability of MDA to improve fuel stability. MDA is the metal deactivator additive.

Workers at BP Research Centre doped a Merox-treated kerosene with dissolved copper or iron [21]. Copper at 83 ppb caused JFTOT failure at 260°C, but this was reversed with only 0.57 ppm of MDA. Iron at 78 ppb also failed at 260°C but easily passed with 5.7 ppm of MDA.

Morris and Turner looked at copper and Cu/MDA effects on Jet A behavior in the JFTOT with TDR readout [22]. An equimolar quantity of MDA (5.8 mg/L) with Cu (1.32 mg/L) produced reductions in tube deposition in regions of the tube above 250°C to levels similar to those formed from the fuel containing only MDA. At lower temperatures, however, deposition stimulated by the presence of copper was not reduced by MDA. Substantial signals for copper were found on the JFTOT heater tube by X-ray photoelectron spectroscopy at similar temperatures, 200 to 250°C. The location of copper on the tube was the same for the 1:1/Cu:MDA as for the fuel with only Cu added. With respect to liquid phase oxidation phenomena, MDA partially counteracted the effect of soluble Cu. The depletion of dissolved oxygen was not as rapid and the peak in hydroperoxide concentration was not as depressed as observed for copper containing Jet A.

Figure 3 depicts work performed in the STHTR [23]. These tests measured the deterioration of the heat transfer coefficient for periods of time up to 50 h. The fuels responding to MDA contained 10 to 20 ppb of copper and/or iron. Fuels D and E, which had very low levels of dissolved metals, exhibited no improvement. Shell has also demonstrated in the flask oxidation test that MDA reduces the effect of dissolved Cu on the fuel oxidation and initiation rates [23,24]. The behavior followed a 1:1 mole ratio demonstrating a unity chelation relationship between Cu and MDA. The MDA exhibited no benefit in the oxidation test when added in excess of a 1:1 ratio, indicating that this additive has no antioxidant function.

In tests in some devices, MDA produced a pronounced reduction in deposit formation

TABLE 2—Heater tube deposits attained with MDA addition (micrograms carbon on SS tubes).

MDA, mg/L	Maximum Heater Tube Temperature, °C		
	260	280	310
0	96.7	370.6	618.6
1.5	51.1	66.0	107.3
2.9	<10	50.8	97.2
5.8	<10	79.2	112.6
11.6	10.3	47.2	92.0

for fuels containing very low levels of dissolved metals. Work at the Naval Research Laboratory, for instance, observed reductions with only 1.5 mg/L of MDA in a Jet A with 4 ppb of Cu [22]. Table 2 shows data in the JFTOT at 260, 280, and 310°C for various concentrations of MDA. Reductions of 75 to 90% were the norm for all three temperatures. Most of the benefit was attained with 1.5 to 2.9 mg/L of MDA.

The Shell Thornton group compared the behavior of MDA in several types of tests with fuels of low dissolved metal contents [24]. The JFTOT operated at 350°C and with carbon burnoff gave a 74% reduction in deposition for 10 mg/L of MDA with aluminum tubes. The STHTR, operated with a fuel-out temperature of 225°C, afforded a much smaller reduction in deposition, 40%. Flask oxidation found only an 8% decrease in oxidation rate for the same fuel/additive blend.

Clark suggested that the variations in response to MDA could be reconciled on the basis that this additive acted in two modes [24]. The first, a metal chelation mode, operates in the JFTOT, STHTR, and flask oxidation devices when dissolved metal is present. The second, a metal passivation mode, is active at all MDA concentrations in the JFTOT, is operative only at higher concentrations in the STHTR, and is not involved in the flask test. Experiments in the injector feed arm rig supported this thesis. Fuel without additive had a 10-h induction period during which deposition was very low. The rate accelerated then and attained a uniform rate after about 40 h. The same fuel with 5.7 ppm MDA had a much longer induction period, about 30 h. The rate then increased and exhibited a slope similar to the undoped fuel. This increase in induction period was attributed to passivation of the clean heater tube surface by the MDA. The theory proposed that MDA was no longer active when the fuel deposit covered the surface and blocked access of MDA to the metal.

More recent studies by Clark and Stevenson used the mini-IFAR to evaluate MDA behavior [25]. The test fuel contained dissolved metals and was tested with different levels of MDA. The induction periods and deposition rates were consistent with the previous Shell Research studies and seemed to support the double role of MDA, chelation and passivation.

Several sophisticated surface analysis techniques have been applied to the definition of the metal deactivator role in thermal stability. Laser ionization mass analysis was used by workers at the BP Research Centre to look for absorbed MDA on aluminum and stainless steel substrates, including JFTOT tubes [21]. Characteristic peaks for MDA at 119 and 146 atomic mass units were observed by dipping a JFTOT tube into fuel containing MDA. Variation in contact time did not appear to alter the level of coating, but the extent of coverage was not quantifiable with this technique.

Workers at the Naval Research Laboratory utilized X-ray photoelectron spectroscopy (XPS) to address the MDA role [26]. Working with highly polished copper, aluminum and Type 304 SS coupons and with aluminum and stainless steel JFTOT tubes, the objective was to look for the element nitrogen which comprises 10% of the mass of MDA. Carbon and oxygen, other elements in MDA, are not reliable gauges at low absorption levels because

they are pervasive contaminants, even in the high vacuum required in XPS analysis. For exposures to *n*-dodecane containing 5.8 mg/L of MDA, the nitrogen signal in all XPS analyses was below or at the detection limit of 1 to 2%. Using the 2% limit, the maximum coverage of the metal surface by MDA would be on the order of 20% as estimated by this semi-quantitative technique. Complementary experiments with secondary ion mass spectrometry (SIMS) did detect ions characteristic of MDA, but the coverage was only partial. A stronger signal was obtained at 52 mass units higher than the MDA peaks, suggesting that most of the MDA was bound to chromium on the SS specimen.

SIMS was also used by Clark, Delargy, and Heins [27]. These workers varied the MDA concentration and the temperature of metal exposure in their absorption studies. Coverage on JFTOT tube surfaces was slightly above the noise level when exposed to a jet fuel containing 5.7 mg/L of MDA at ambient temperature. Coverage went up as the MDA concentration was increased and attained about 50% relative coverage at 57 000 mg/L. Raising the exposure temperature to 140°C exerted little effect, but the coverage produced in a standard JFTOT test at 260°C increased significantly for a 5.7 mg/L sample.

The studies with metal deactivator confirm its role with respect to its chelating function. In addition, much information shows that it can cause or extend induction periods for deposition. This behavior does not appear to be due to free-radical autoxidation chemistry, but considerable evidence points to a metal passivating role. Absorption of MDA onto metal surfaces has been demonstrated, but the coverage is only partial. Thus, the passivating theory is not fully proven. Further, Schreifels et al. showed that a multilayer of deposit forms on stainless steel at 260°C in 1 h, even with the highly stable compound *n*-dodecane [26]. This coating of organic material should prevent any continuing access of MDA to the metal surface and thus nullify any passivating behavior and terminate any induction period.

Conclusions on Additives

Additives which are beneficial to thermal stability under some circumstances are antioxidants, dispersants, metal deactivators, and passivators. The antioxidants can be useful in preventing hydroperoxide buildup in long-term storage since hydroperoxides degrade thermal stability. AOs are of limited benefit for fuels used shortly after production and for nonhydrotreated fuels which have natural inhibitors. The hindered phenols are acceptable AOs, but several studies have shown that phenylenediamines degrade thermal stability.

Dispersants have demonstrated the ability to improve thermal stability of jet fuels and to allow fuels to be stressed at higher temperatures. These additives, however, degrade water/fuel (W/F) separation and should be limited to use in special applications unless new dispersants can overcome the W/F separation problem.

Metal deactivators have a definite function for fuels containing dissolved metals or for fuels which will be exposed to copper or copper-containing alloys during service. Use in a potential passivating role is open to question. It has been suggested that a fuel free of metals, but containing MDA, may give erroneously good results in short-term tests such as a JFTOT specification test [24]. Performance in an engine over hundreds of hours, however, would be unsatisfactory after the initial induction period with a low deposition rate. Future research should resolve this uncertainty.

A metal passivator such as benzotriazole can prevent dissolved metals buildup in jet fuels; it acts by blocking access of the fuel to a metal surface. It may be needed in situations where significant exposure to copper or its alloys occurs.

Of the additives allowed in jet fuels to modify properties other than thermal stability, no significant effects have been defined which degrade thermal stability.

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CHAPTER X

High Temperature Requirements

A modern jet aircraft has many cooling requirements—lubricant, engine avionics, engine hydraulics, fuel nozzles, airframe environmental control, and hot sections. For a subsonic or low supersonic vehicle, the air can provide a substantial portion of the cooling [1]. However, at higher velocities the cooling loads become greater and the ram air temperature rises rapidly. The fuel is utilized to make up the difference and is the primary heat sink above Mach 3. Air can still make a contribution for cooling the engine's hot sections in the Mach 3 to 4 range, but this capability diminishes and is not important above Mach 4.

Exterior Surface Temperatures

The impact of higher aircraft velocities is illustrated in Fig. 1 for three proposed supersonic aircraft flying at different Mach numbers [2]. The rapid rise in stagnation (radiation equilibrium surface) temperatures is dramatic for each step in Mach number. The leading edges and other critical exterior surfaces become very hot at Mach 3.2 and above. The fuel, a major fraction of the takeoff weight, is used to cool these structural elements and the airframe. This adds to the thermal stress imposed on the fuel by the other cooling requirements. Consequently, the thermal stability of the jet fuel for high-speed velocities must be improved, at least for the higher Mach numbers.

Fuel Temperatures in Commercial Transports

Chapter I presented information on temperatures for fuel at various stages in an aircraft fuel system and engine. The emphasis in that chapter was primarily on subsonic and low supersonic aircraft. A temperature of 163°C (325°F) for the fuel entering the combustor nozzles is representative of the data for this flight regime. We turn now to fuel temperatures in higher velocity vehicles for commercial service.

The only supersonic transport in the so-called western world which has been operational is the British/French Concorde. This aircraft has had almost two decades of successful service from an engineering standpoint. The Concorde's cruise velocity is Mach 2.2 [3]. Initial calculations indicated that the fuel in the aircraft storage tanks would attain a temperature of 85°C (185°F). The peak temperature into the combustor nozzles was predicted to be 200°C (392°F). Later evaluations reduced these temperatures to 80°C (176°F) in the tanks and 150°C (302°F) entering the nozzles. Additional stress in the nozzles, which were immersed in 593°C (1100°F) compressor air, raised the fuel temperature further, but this latter exposure was limited to 1 or 2 s. Thus, the thermal stress on the fuel used in the Concorde is similar to that of subsonic jet aircraft. In fact, the Concorde does not require a special fuel but is fueled with the same jet fuel used in standard commercial operations. The Mach 2.2 environment imposes only minor demands on the fuel beyond those associated with subsonic aircraft.

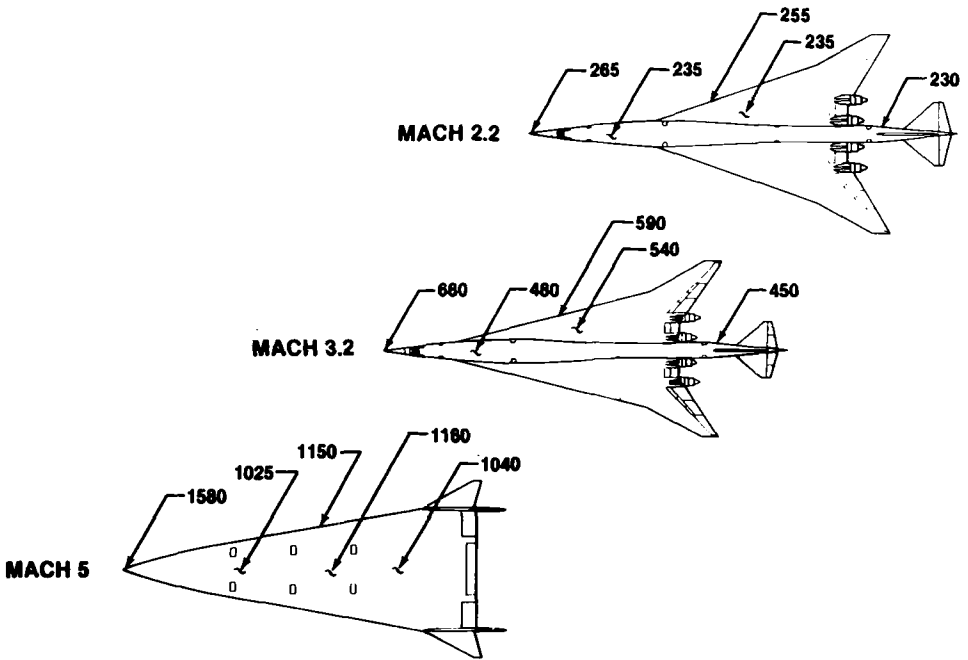


FIG. 1—Radiation equilibrium surface temperature in °F for aircraft designed to fly at different Mach numbers.

Dukek reviewed the U.S. supersonic transport program with emphasis on the fuel and lubricant requirements [4]. He predicted that the American project would require a super-refined jet fuel in order to satisfy the higher heat loads imposed on the fuel at the Mach 3 flight conditions.

The fuel temperatures calculated for the proposed U.S. SST vehicle are shown in Fig. 2. Data for Mach 2.5 and 3.0 are presented for a 3500-nautical-mile flight [5]. The calculated temperatures increased as the fuel passed out of the fuselage tank, through the airframe heat exchanger (Curve 2), the engine fuel pump (Curve 3), the engine heat exchanger (Curve 4), and into the combustor nozzles (Curve 5). The most severe fuel exposure came during the deceleration phase when the fuel flow was reduced significantly but the airspeed was still high. Thus, a small amount of fuel absorbed much heat, and the peak temperature for the fuel into the nozzle attained a temperature of 260°C (500°F) for the Mach 3 flight profile. This was 56°C (100°F) hotter than the temperature calculated for the Mach 2.5 velocity and about 111°C (200°F) hotter than the peak temperature for the Concorde at Mach 2.2.

Schmidt and Ohm compared the thermal environment for fuel in a subsonic and supersonic environment [6]. They presented the fuel system shown in Fig. 3 as representative for the supersonic vehicle. Compare this figure with Fig. 4 of Chapter I to note differences between their generic subsonic fuel system and the supersonic aircraft. Two major differences in equipment can be noted: (a) airframe cooling is included in the high-speed vehicle and (b) recirculation returns the fuel to the fuel tank rather than the engine oil cooler inlet. This latter feature should keep the average temperature of the fuel at a lower value.

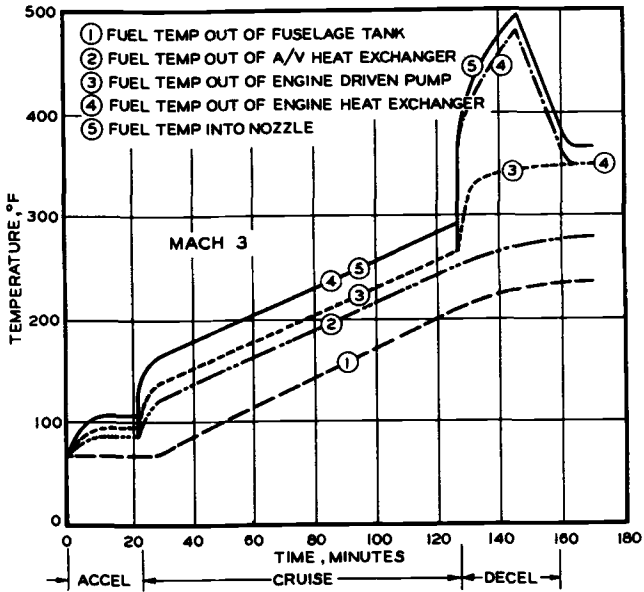
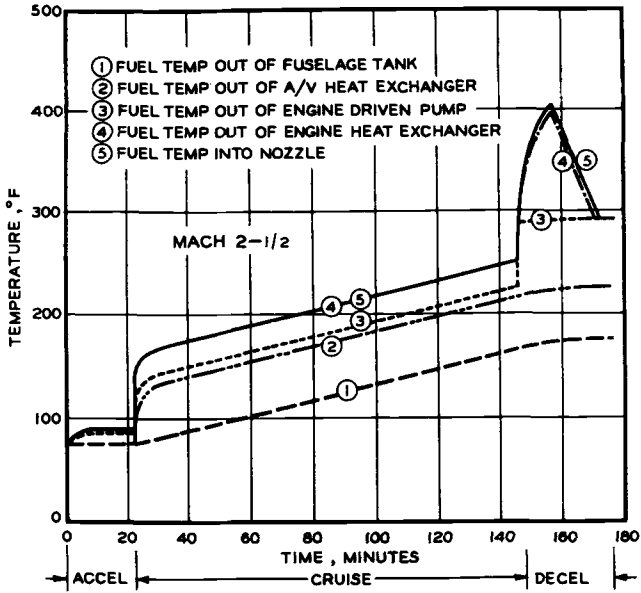


FIG. 2—Representative aircraft fuel system temperatures for supersonic aircraft designed to fly at Mach 2.5 and 3.0.

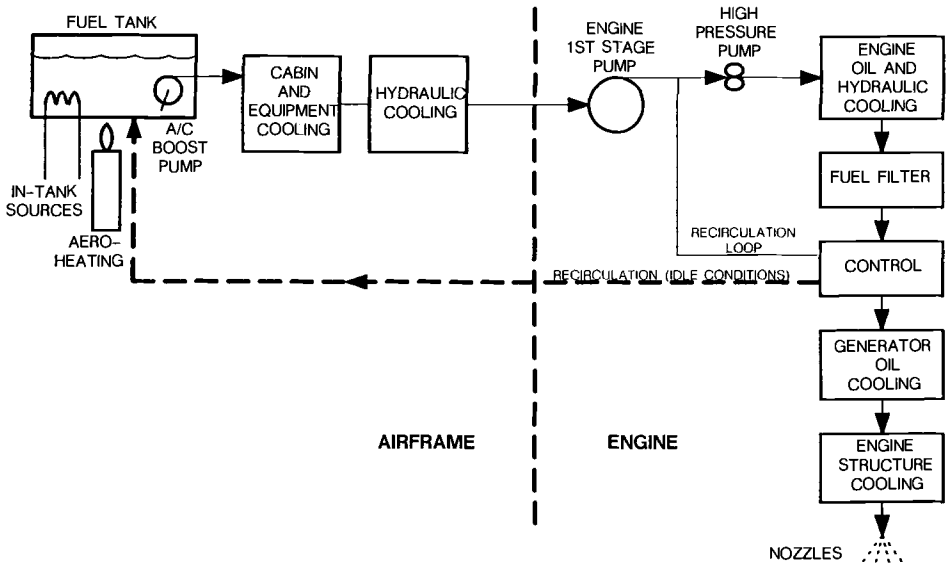


FIG. 3—Possible fuel system for high-speed aircraft. (Revised diagram by John Schmidt, 4/16/91.)

Schmidt and Ohm delineated differences in the thermal environment of a supersonic vehicle which would impact on thermal stability. These can be summarized as follows:

1. Fuel temperature in tank would plateau at about 93°C (200°F) at Mach 3 and above.
2. Heat loads are higher from airframe and engine.
3. Different materials of construction in contact with fuel:
 - a. Tanks (SS, titanium, composites).
 - b. Components (greater use of high temperature nickel alloys and steel).
4. Closed vent system and fuel tank inerting above $M = 2.5$ to 3.
5. Recirculation to fuel tanks for engine idle conditions.

Those features which raise the temperature would require a higher stability fuel. The effects of materials of construction are not well defined, but the information presented in Chapter VIII can give some very useful guidance. Recirculation to the tanks can increase exposure of a warm fuel to oxygen and hence might encourage hydroperoxide formation, a detrimental feature. However, inerting the tank ullage and maintaining the tanks at a reduced pressure consistent with the pressures at high altitude could definitely limit the oxygen exposure. Such measures would limit the consequent hydroperoxide formation and aid in minimizing deposit formation.

Fuel Temperatures in Military Aircraft

In a U.S. Air Force program conducted by the General Electric Co., temperatures in aircraft and engine components were measured during typical flights [7]. Subsonic and supersonic aircraft were examined flying in various environments. As an example, the XB-70A was put through a 130-min exercise at a 21-km (70 000-ft) altitude with 32 min at Mach 3. The peak temperature of 135°C (275°F) going into the combustor nozzle came as decel-

TABLE 1—Fuel temperature at combustor nozzle inlet.

Flight Operation	Temperature at Nozzle Inlet			
	Mach 3 +		Mach 4 +	
	°C	°F	°C	°F
Baseline	163	325	268	515
Transient	260	500	427	800
Transient with recirculation to aircraft tanks	204	400	316	600

eration and descent began. This modest temperature was due to the short time at Mach 3, recirculation of fuel at low demand, and the incorporation of a water boiler in the aircraft fuel coolant loop.

The SR-71 reconnaissance aircraft flies at Mach 3+ for extended periods [8]. The thermal stress on the fuel is somewhat more than that for the XB-70A. This is evidenced by the fact that JP-7, a fuel with higher stability than other military jet fuels, is required for the SR-71.

Pratt & Whitney Aircraft defined the thermal environment for engines for two proposed high-speed aircraft, a Mach 3+ interceptor and a Mach 4+ interceptor [9]. The engine for the Mach 3 airplane was an afterburning turbojet, and a turboramjet was chosen for the higher velocity vehicle. Calculated temperatures for fuel entering the combustor nozzles are shown in Table 1. The baseline case was developed on an aircraft-to-engine interface temperature of about 132°C (270°F). The transient operation with the greatest effect on fuel temperature was a sharp reduction of fuel demand while the interceptor was flying at high velocities. The transient condition was calculated for a low fuel recirculation rate, whereas the last entry in the table was based on a two to threefold increase in recirculation flow.

The Mach 3+ baseline case for this study gave a much lower peak temperature than that shown in Fig. 2 for the SST Mach 3 condition. This is in spite of the same aircraft/engine interface temperature. A part of the difference between the two cases is due to fuel recirculation with the Mach 3+ interceptor. Other factors in this difference can be ascribed to advanced technology available in 1973 versus 1965, use of insulated lines and components, emphasis on low heat generation designs and selection of components with reduced heat output.

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CHAPTER XI

Research and Development Goals for Future Aircraft Fuels

The vast network of international airlines and routes has developed as jet engines have been designed, upgraded, and perfected. Along with this remarkable improvement in power plants has been an accompanying growth in the use of petroleum and, in particular, the use of aviation turbine fuel. As we look to the future, what fuels will be important to the aviation industry? Further, what problems can we foresee with respect to thermal stability in the coming years?

We will address these questions in this chapter from two aspects:

1. Consider fuels to meet the high temperature requirements presented in Chapter X.
2. Consider fuels to supplement or replace the petroleum-derived ones which have been the backbone of the transportation industry throughout this century.

Fuels for High-Temperature Applications

High-temperature stress of jet fuels can come from two types of applications: in high-speed vehicles or in vehicles utilizing engines operating at very hot conditions such as stoichiometric combustion conditions. The Concorde aircraft has operated many years as the highest speed commercial passenger transport, cruising at Mach 2.2. Many military aircraft fly at supersonic velocities with the SR-71 operating at Mach 3+. The Concorde successfully uses Jet A-1, the fuel utilized by subsonic commercial transports, but the SR-71 requires JP-7, a fuel with thermal stability quality much higher than the widely used commercial and military jet fuels [1].

Interest has accelerated recently in high-speed vehicles. Fuels for these vehicles were the subject of a workshop in 1988 [2]. Spadaccini and Marteney presented an outline of potential fuels for various flight regimes [3]. Current jet fuels in wide use would be the fuel of choice up to Mach 2.5; JP-7, or similar high-stability fuel, has application to about Mach 4+; and unconventional fuels might be useful at higher Mach numbers. For instance, liquid methane has potential in the Mach 4 to 6 range and endothermic fuels in the 4 to 7 range. At even higher speeds, liquid hydrogen is the only fuel that could be used for an aircraft designed for multiple flights.

Thermal stability, defined as the resistance to formation of undesirable carbonaceous solids in the fuel system, is of concern for the current jet fuels, JP-7, and the endothermic fuels. The cryogenic fuels, methane and hydrogen, are very resistant to solids formation and will not be addressed further in the context of thermal stability.

JP Fuels and High-Temperature Applications

Lee and Niedzwiecki examined several JP fuels and thermal stability concepts for economic impact on supersonic transports [4]. They considered clay filtration, deoxygenation, desul-

furization, and hydrogenation as means of upgrading current JP fuels for high-temperature applications. No estimate was given by these authors on the effects of these treatments on improving thermal stability, but all have been identified in other research to be useful.

Gray and Shayeson concluded that aircraft and engine systems can be designed to operate in the Mach 3 range using JP-4, JP-5, and Jet A [5]. Bucknell, on the other hand, suggested that hydrotreated JP-5 would be required for a Mach 3+ interceptor [6]. This was based on the hydrotreated JP-5 passing an ASTM Coker test at 204/260°C (400/500°F). For a Mach 4+ interceptor, Bucknell found that JP-7 was necessary based on passing a research coker test operated at 149/260/316°C (300/500/600°F).

Examples of the improvement of thermal stability by various processes are given below. Clay treatment improved the JFTOT breakpoint of a JP-7 and two JPTS fuels by 31 to 67°C (55 to 120°F) [7].

The effects of deoxygenation on improving thermal stability were demonstrated in Chapter VII. As an example, Taylor found that deaerated fuel A attained the same deposition rate at about 593°C versus 288°C for the air-saturated liquid [8]. Fuel B exhibited a corresponding increase from 299 to 427°C. Deoxygenation, however, was not universally effective as was demonstrated with a fuel with a high disulfide content.

Lander and Martel observed a 68°C (123°F) increase in JFTOT breakpoint for a jet fuel desulfurized by mild hydrotreatment [9] with an additional boost of at least 17°C in breakpoint by a much more severe hydrogenation which converted aromatics to naphthenic hydrocarbons.

Selected additives have demonstrated effectiveness in improving thermal oxidation stability. One of these, JFA-5, is required in thermally stable kerosene, MIL-T-25524C-Amd.2 (7 Feb. 1985). This additive typically gives a 20 to 40°C improvement in JFTOT breakpoint [10], but unfortunately degrades water separation properties. Metal deactivator exhibits deposit reduction in short tests such as the standard 2.5-h JFTOT, but effectiveness is lost after an induction period in longer term tests (see Chapter IX). Standard antioxidants are ineffective in improving thermal stability at conditions typical of subsonic flight and would be of questionable value in high temperature applications. The hindered phenols might be needed to prevent hydroperoxide formation in hydrotreated JP fuels put into long-term storage.

In summary, several methods have demonstrated capability to improve stability of kerosene fractions for use to Mach 4+. Theoretically, the limit for use of kerosenes will not be determined on the basis of thermal stability but on their heat sink capacity. The techniques or processes chosen to attain a suitable thermal stability will depend upon economics, logistics, and safety [4]. Hydrogenation and additive treatment are attractive since they could be accomplished at a refinery. Hydrogenation is costly, however, and hydrogen may be in short supply in the future as the refining industry, in response to environmental concerns, reduces reforming for gasoline production. Additive treatment is inexpensive, but new ideas on additive functions at high temperatures will be required before this option is seriously considered. Deoxygenation, while very effective for low sulfur fuels, would have to be very efficient. Sparging would be required to remove dissolved oxygen to a very low level prior to introduction into the aircraft. Further, a low oxygen atmosphere would have to be maintained in the aircraft tanks, particularly for any vehicle using recirculation of hot fuel. Clay treatment would probably need to be performed at the airport, an inconvenient site, for a final tuneup of the fuel. Disposal of the used clay would be an environmental concern.

Endothermic Fuels

These liquids possess much larger heat sink capacities than JP fuels since they absorb heat of vaporization and heat of reaction in addition to sensible heat. Thus, endothermic fuels

have the potential to be the fuel of choice for high velocity craft flying in the Mach 4 to 7 range. Thermal stability is an ambiguous term for endothermic fuels. The purpose of this type of fuel is to change and thus serve as a coolant by absorbing the chemical heat of reaction. This is a desired and designed instability. An undesirable side product, solids, can also result from the pyrolysis. Deposition of these solids on a decomposition catalyst or in a fuel nozzle will degrade performance of an engine.

Many different hydrocarbons and mixtures have been tested as endothermic fuels. Alicyclic hydrocarbons have received the most attention in these studies with methylcyclohexane and decalin rating as top candidates. The former, although much more expensive than JP fuels, has been favored because of its clean reaction to toluene and hydrogen.

The U.S. Air Force sponsored major efforts in endothermic fuels in the 1960s and early 1970s. The Monsanto Co. studied the decomposition of *n*-hexadecane and observed up to 97% decomposition at 704°C (1300°F) [11]. Carbon deposition was less than 1%. In a later, more comprehensive program, Monsanto pyrolyzed 13 alicyclic and 2 aliphatic hydrocarbons in static and dynamic reactors [12]. Some of the compounds could be subjected to 90% conversion before particulate matter was observed. The authors suggested that the solids were formed as the end product of a series of consecutive reactions. Olefins, dienes, and polyolefins were proposed as important intermediates.

Shell Development Co. conducted other major U.S. Air Force programs on endothermic and vaporizing fuels. In one major study, over 200 dehydrogenation catalysts were tested for activity with methylcyclohexane [13]. Several exhibited activity superior to a platinum/alumina catalyst. This document listed 357 literature references. Additional work by Shell on this contract examined a wall-coated catalyst in order to minimize pressure drop [14]. Volume II of this document contained a bibliography of 1502 references on fuels, aircraft, engines, thermal reactions, catalytic reactions, stability, heat transfer, and combustion. Shell Development continued the production and testing of granular and wall-coated catalysts on a later U.S. Air Force contract (F33615-70-C1038) [15].

Endothermic fuels have experienced a renaissance in the past few years for civilian and military applications [2,4]. Two recent research programs have examined the noncatalytic decomposition of pure hydrocarbons. Moler and Steward decomposed three aliphatic hydrocarbons (*n*-dodecane, 2-methylundecane, and *n*-octane) and one alicyclic hydrocarbon, bicyclohexyl, over the temperature range of 650 to 800°C [16]. They developed first order rate constants from their experimental results. Taylor and Rubey reacted methylcyclohexane, toluene, *trans*-decalin, and naphthalene at temperatures up to 1050°C for 0.5 to 5-s time periods [17]. A similar study has detailed the temperature/time response of JP-8 to a pyrolysis environment [18].

The U.S. Air Force has reported recent catalytic decomposition studies with methylcyclohexane [19]. A packed bed reactor gave 95+ percent conversion of the starting hydrocarbon with 100% selectivity to toluene and hydrogen products. Good operation was attained in the temperature range of 449 to 538°C (840 to 1000°F) and pressure range of 0 to 6.9 MPa (0 to 1000 psi). Catalyst life was greater than 100 h. Results with a coated-surface catalyst were even more impressive. The conversion, selectivity, temperature range, and pressure range were the same, but the catalyst life estimate was >500 h and the catalyst volume was significantly reduced. All of these findings were substantially better than those from earlier catalytic studies.

Petroleum Supplements and Replacements

Crude oil reserves are limited, and eventually other sources of liquid fuels will need to be developed for transportation purposes. In addition, major, although temporary, upsets

in petroleum availability in the mid 1970s, the late 1970s/early 1980s, and in 1990 stimulated interest in alternative fuels. In response to these concerns, production of aviation turbine fuel, among other transportation fuels, from other sources has been investigated. The most extensive programs have dealt with shale-derived fuels, but a number of efforts have started with coal and some work has been accomplished with tar sands. Biomass has received little attention as a source of jet fuels. Very heavy crudes and bitumens will also be utilized as sources of transportation fuels. All of these resources require more extensive refining than is typical of current refineries.

This section will deal with the thermal stability data that has been generated on nonpetroleum-derived aviation fuels. Many of the samples available were produced in small reactors, but three of the shale operations have been carried out in refinery scale equipment. The treatment of the literature on these fuels will be representative rather than comprehensive.

Shale-Derived Fuels

A batch of 17 500 gal of kerosene, produced from Paraho shale oil for the U.S. Navy, gave a very low JFTOT breakpoint, 232°C [20]. This fuel, which was produced by delayed coking, fractionation, and mild hydrotreatment, contained 976 ppm of organic nitrogen [21]. Removal of the acid-extractable nitrogen, which accounted for 88% of the nitrogen, improved the JFTOT breakpoint to 254°C, still unsatisfactory.

A second DOD/DOE project converted 100 000 barrels of Paraho shale oil into a spectrum of DOD fuels at the Toledo, Ohio refinery of the Standard Oil Co. (Ohio). Processing of the crude to JP-5 fuel comprised moderate hydrotreating, fractionation, acid treatment, and clay finishing. The finished product contained one ppm of nitrogen and passed the JFTOT at 280°C (536°F) [22]. It initially failed at 300°C (572°F), but still passed at 288°C (550°F) after 25 weeks of ambient storage. In fact, this product passed at 266°C (510°F) at the end of two years of storage.

In another major program, JP-4 was produced from shale crude oil at the Caribou Four Corners Refinery using combined feedstock from Occidental and Geokinetics. Process steps included distillation, hydrotreating, hydrocracking, and product fractionation. The product used in the first series of tests had a JFTOT breakpoint of 310°C, and this level of stability was maintained throughout 15 months of ambient storage [23]. A second series of samples was stored at 43°C (110°F) for 15 months. The control sample maintained its 320°C JFTOT breakpoint for nine months but deteriorated after that, failing the test criteria at 300°C but passing at 280°C at the end of the 15-month period. The failure of the control sample was due to hydroperoxide buildup in the last six months of the experiment. Some of the fuels with added hindered phenol antioxidants prevented the hydroperoxide buildup and also the deterioration in JFTOT breakpoint throughout the entire 15-month storage period.

ARCO treated Tosco shale oil to low (10.4 MPa/1500 psi) and high (13.9-MPa/2000-psi) severity hydrogenation in a pilot study. Various boiling fractions from this work were subjected to JFTOT testing by NASA [24]. A rating criteria of 13 maximum (spun) on the TDR was set as the pass/fail mark. Although the high severity samples had higher breakpoints than the low severity fuels, only one of eight passed at 260°C (500°F). All of the low severity samples had >1100 ppm of nitrogen with breakpoints between 204 and 232°C (400 and 450°F). The high severity ones had <170 ppm of nitrogen and breakpoints between 232 and

TABLE 1—*Thermal stability of coal-derived distillates.*

Crude Source	Hydrogenation Severity	Aromatics % by D 1319	Hydrogen, %	Breakpoint, °C	Reference
H-Coal	Low	29.7	12.73	237	[24]
H-Coal	Low	33.8	12.47	236	[24]
H-Coal	Low	30.9	12.64	235	[24]
H-Coal	Low	26.3	12.79	243	[24]
H-Coal	High	5.9	13.56	252	[24]
H-Coal	High	6.7	13.26	288	[24]
H-Coal	High	5.8	13.31	288	[24]
H-Coal	High	5.5	13.73	310	[24]
COED	Low	22.4	13.07	263	[24]
COED	Low	28.5	12.88	263	[24]
COED	Low	25.2	12.96	268	[24]
COED	Low	20.1	13.24	275	[24]
COED	High	9.3	13.6	268	[24]
COED	High	11.6	13.44	244	[24]
COED	High	7.2	13.63	280	[24]
COED	High	5.4	13.69	316	[24]
COED	Low-Ky Coal	24.8	12.85	257	[25]
COED	Low-Utah	24.1	12.98	263	[25]
COED	High-Ky	4.7	13.34	>371	[25]
COED	High-Utah	6.1	13.62	>368	[25]
COED	Low-Ky	24.1	12.81	252	[25]
EDS	Low	45.5	11.9	236	[26]
EDS	Medium	21.6	12.7	281	[26]
EDS	High	10.2	13.1	295	[26]
EDS	Low	39.6	...	Fail ^a	[27]
EDS	Medium	20.7	...	Pass ^a	[27]
EDS	High	10.4	...	Pass ^a	[27]

^aD 3241 test at 260°C.

260°C (450 and 500°F). A trend between stability and nitrogen concentration was evident, but there was much scatter in the data.

Coal-Derived Fuels

Results of JFTOT tests are listed in Table 1 for fuels derived from various coals and by various processes. The main variable is the extent of hydrogenation.

Only two of the twelve samples from various pilot plant facilities failed the JFTOT at 260°C if severe hydrogenation was used in the refining process [24–27]. Both samples produced with a medium degree of hydrotreatment passed at the standard specification temperature. On the other hand, 8 of 13 products from low severity processing failed the specification test. Thus, it can be observed that severity of hydrogenation controls the aromatic and hydrogen contents, but these changes do not automatically afford a product with satisfactory thermal stability. Clay treatment of a COED (low-severity, Kentucky coal) product with a 252°C breakpoint improved the breakpoint to 282°C [28]. Four of the COED products—high and low Kentucky, and high and low Utah—were exposed to copper specimens until they attained a concentration of 200 ppb Cu. All four samples decreased sharply in breakpoint, at least 47°C. However, both high severity products still met the 260°C specification criteria after the exposure to copper.

Fuels Derived from Tar Sands and Heavy Oils

A middle distillate produced by Great Canadian Oil Sands, Ltd. from Athabasca tar sands met all specification requirements for JP-5 [29]. This material, which was produced by delayed coking, fractionation, and hydrogenation, passed the 260°C ASTM D 3241 thermal stability test and performed well in a 55-h engine test.

The U.S. Air Force supported efforts by Sun Refining and Marketing Co. to explore the potential for jet fuel production from domestic tar sands and heavy oils [30–31]. In Phase II of the program, laboratory size quantities of naphtha and kerosene were prepared from two tar sands and from two U.S. heavy oils. All eight samples passed the 260°C JFTOT with visual tube reading of zero and pressure differential of 0.013 kPa (1 mm Hg) or less. Phase III of the Sun effort used San Ardo heavy oil to make larger samples of JP-4 and JP-8. The process included hydrovisbreaking, hydrotreating, and hydrocracking. Both jet fuels gave zero readings for preheater tube readings and for delta pressure values.

Fuels from Biomass

Biomass is attractive from an environmental standpoint since it basically involves recycling of organic matter. Little work has been reported on jet fuel production from biomass, however. Alcohols, particularly those with low molecular weight, would be of questionable interest because of their low heat of combustion. This property controls aircraft range and should be maintained close to that of current JP fuels. Terpene hydrocarbons might have some appeal, however. One of these passed the JFTOT at 260°C [32].

General Observations

Substitutes for petroleum-derived JP fuels have been made and tested. One of the main concerns about these substitutes has been thermal stability. Certainly, products of adequate quality can be made from any of the fossil fuel resources—oil shale, coal, and tar sands. In fact, kerosene derived from tar sands is blended into Canadian petroleum products with no resulting difficulties. However, the cost of producing specification grade fuels from oil shale and coal is significantly higher than from petroleum. Thus, it will be some years before they will be utilized. The boom part of the boom-or-bust cycles since the early 1970s will have to be sustained for several years before shale and coal contribute in any measure to the transportation fuel pool.

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CHAPTER XII

Summary of Thermal Stability

We have seen in the previous chapters that thermal oxidation stability of jet fuels has a history stretching back 35 years. In fact, this fuel property demonstrated its importance soon after jet engines were installed on a significant scale as aircraft power plants. This chapter will highlight that history and make some recommendations to guide future programs in thermal stability.

Problems

Three serious problems with jet fuel thermal stability have been described in the literature. The first came in the 1950s when the J57 engine demonstrated combustor nozzle fouling in aircraft operations. Hardware modifications relieved the problem. This problem also sparked the development of the ASTM D 1660 Coker instrument which enabled the industry to define and monitor the thermal stability of aviation turbine fuel.

A second recorded aircraft problem was associated with nozzle fouling also. Distortion of the fuel spray patterns resulted in erosion of turbine blades and air seals. This 1960s problem was traced to copper contamination derived from a copper-sweetening process used at the refinery.

A more recent difficulty in the 1980s developed with CF6-80A and CF6-50E engines. Most of the problem was associated with aircraft operations in Brazil and involved deposition on interior surfaces of the main engine control. Multiple factors were entwined in this thermal stability problem: (a) engine design; (b) fuel specifications; (c) refinery processes; and (d) fuel chemistry. One major factor was the use of a servoheater in the main engine control, which elevated the temperature of the fuel as it flowed slowly through the control. A second significant factor was the use of the Bender process (converts mercaptans to disulfides) in production of the fuel. Both of these factors have been addressed, and this particular problem has been alleviated.

Many other engineering and laboratory programs have shown that fuel thermal stability is important in assuring the reliable operation of engines, fuel systems, and aircraft.

Devices to Examine Thermal Stability

Many rigs and apparatuses have been built, tested, and utilized to study thermal oxidation stability. All of these devices incorporate compromises into the design or operation. Reasons for this are the difficulty of completely simulating the exposure a fuel undergoes in an aircraft and the time and cost required to conduct long-term tests at realistic conditions. Thus, increased temperature is traded off for decreased test time. Laminar replaces turbulent flow to save on fuel quantity requirements in tests. A simple heater tube substitutes for a multicomponent, complex airframe/engine fuel system. Fuel is rated on the basis of an empirical pass/fail criteria rather than a numerical rating. This latter point was emphasized by Shayeson in a recent presentation [1]. He quoted Lord Kelvin to support his call for quantitative measurements of fuel properties:

When you measure what you are speaking about, and express it in numbers, you know something about it: but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind: it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of SCIENCE.

This is a pertinent comment with respect to measurements of thermal oxidation stability of aviation turbine fuels.

Specification Devices

Two dynamic testers, the ASTM D 1660 Coker and the ASTM D 3241 JFTOT, have experienced widespread use in thermal stability testing. The coker served well in the early part of the jet age but was replaced by the JFTOT for reasons of reduced sample size, reduction of problems from pump wear, better test parameter control, and shorter test time. Each device, in its time frame, has protected the user of jet fuel and given adequate quality product somewhat >95% of the time. Both tests utilize simple aluminum heater tubes to detect adhering deposits plus filters to trap suspended particles. Laminar flow is characteristic of these specification testers. Since the tests are accelerated by elevating the temperature and drastically limiting the test time, a very small amount of deposit forms on the heater tube. This requires a very sensitive means of rating the deposit—the best thus far is the human eye. As a consequence, these instruments afford only a pass/fail rating. Recently, some promising techniques have been advanced to enable a numerical rating to be obtained from a JFTOT test, but they require further development.

Recent evaluations have criticized the qualitative nature of the JFTOT test and also the deposit inhibiting character of the aluminum tubes [2]. Magnesium, which reduces the deposition rate, migrates to the surface of aluminum tubes during a test.

Promising proposals to improve the JFTOT have been made [2,3]. These include: (a) replacement of aluminum tubes with stainless steel to eliminate the problem from magnesium migration and to mimic the hotter components in engines which are constructed from stainless steel; (b) carbon burnoff to afford a quantitative measurement of deposit amount; (c) fuel preheat to simulate fuel temperature rise in tanks due to aerodynamic heating or due to recirculation from engine heat exchangers; and (d) design of a stress section affording turbulent flow. All of these suggestions should be investigated, but the problem of temperature acceleration remains. As a result of variation in energies of activation for deposition [4], fuels respond in different patterns to an increase in temperature. We await an idea which would surmount this temperature/time behavior. Possibly a supersensitive technique to measure minute amounts of deposit would allow tests at temperatures consistent with those in an engine. Another suggestion for any future tester would be to design the apparatus so that the fuel is actively absorbing heat from a hot, heated component. This arrangement is typical of many portions of the aircraft fuel system which have been problem areas as well as characteristic of the coker and the JFTOT.

Simulators

Simulators are used to design aircraft systems, select materials, compare fuels, and define fuel thermal limitations. They may simulate a complete airframe/engine fuel system or a single aircraft component. Tests are conducted at temperatures close to or slightly higher than those expected in practice and test times are frequently 100 or more hours. Turbulent flow is characteristic of most of the components in a simulator.

The most ambitious simulator was the CRC/NAA/USAF rig which incorporated all com-

ponents of an aircraft from the tank through the manifold to the nozzle [5]. The wing tank and engine manifold and nozzle were the main areas of distress resulting from long-term tests on seven different fuels. The wing tank was operated very hot and should not be of concern for applications below Mach 2.5. The problems in the manifold/nozzle, the components where the fuel reaches the highest temperature, point out that this component should be emphasized in defining fuel response to temperature. This finding reinforces the experience with aircraft operations over a 35-year period, namely two of the three reported operational problems have been due to nozzle fouling. The conclusion is that nozzle testing should be addressed to a greater extent in the future as opposed to the emphasis on heat exchanger testing in previous programs. It may also be in order to define a test which simulates the conditions in a main engine control with fuel at a low flow rate since the problem in Brazil was concentrated in this component.

Research Devices

A great variety of rigs have been applied to research programs on thermal oxidation stability. The vast majority of these testers have utilized heated tubes as the fuel stress section. Heating has been via hot fluidized bed, hot oil, or electrical resistance. Rating criteria used have been heat transfer changes and deposit mass (directly or carbon burnoff). Many devices incorporate filters into the system and measure an increase of pressure with time. Ranking of fuels by various rigs frequently exhibits inconsistencies. This should not be surprising since each device operates on a characteristic set of parameters. Further, fuels sometimes pick up trace amounts of contaminants during shipping or storage which degrade thermal stability.

Processes in Thermal Stability

Physical Processes

At fuel temperatures from ambient up to about 100°C, jet fuel of specification quality will exhibit no problems due to insolubles formation. Near or above this temperature, deposition begins and becomes progressively worse up to a somewhat higher temperature at which point the deposition decreases sharply. This reduction at 325 to 400°C is due to depletion of hydroperoxide, which triggers deposition.

Temperature effects have been studied in many different pieces of equipment and all find increases in deposits as temperature rises. The rates of increase, however, as represented by E_{act} are widely different. The fact that both physical (low E_{act}) and chemical (high E_{act}) processes are involved explains some of the differences. The overall deposition process probably involves a series of parallel reactions which will require a very detailed study to decouple or isolate.

Although the data on pressure effects are not in complete agreement, some general observations can be made. First, the system pressure for most applications should be in excess of that needed to prevent boiling since the phase change from liquid to vapor gives anomalous deposition patterns. Second, higher pressures should be used, if possible, since most of the data found no change or less deposition as the pressure increased. For specification testing in the JFTOT, the currently used pressure of 3.45 MPa appears to be adequate.

The effect of fuel flow velocity in most studies indicates that the deposition rate is greater at low velocities. The dependence is weak above a velocity of 0.3 m/s and strong for lower velocities. Future studies should emphasize flow rates approximating those in the fuel system component which a rig is simulating.

Several studies suggest that there is a reasonable correlation between heat transfer characteristics and deposit amount as measured directly or by carbon burnoff. Thus, either technique can be used to evaluate fuel thermal stability.

The surface of a heater tube has a significant effect on deposition rate as indicated by the following observations:

1. A smooth surface delays deposition compared to a rough surface.
2. Magnesium migration to the surface of an aluminum heater tube inhibits deposit formation.
3. Stainless steel tubes form more deposit than aluminum tubes.
4. Metal deactivator additive induces an induction period in deposition.
5. In long-term tests, the rate of deposition accelerates with time.

If the wall material significantly influences reactions, long-duration tests should show a decrease in deposition rates as the wall is covered by deposit. If the deposition rate increases with time as the organic deposit coats the heater tube, an interaction with existing deposit is suspected. The latter fits the experimental data better. This suggests three explanations: the deposit is more active than the metal in stimulating deposition, the rougher surface of the deposit alters mass transfer effects, or the deposit is porous with substantially more surface area than the underlying metal. The increased area of the porous deposit would speed up the apparent rate of deposition of a reaction occurring on a surface.

Chemical Processes

Oxidation of fuel components is a key process in the formation of deposits in thermally stressed jet fuels. Removal of dissolved oxygen makes all fuels, except some containing sulfur, much more stable. In fact, this procedure increased breakpoints for JP fuels from 75 to 300°C. Hydroperoxides are the key intermediates in the autoxidation scheme which produces insolubles. The role of hydroperoxides appears to be related to the high free-radical concentrations which are associated with the formation and decomposition steps for these compounds.

Compounds containing oxygen, sulfur, nitrogen, and metals are major participants in deposit formation. Elemental analysis of deposits formed in aircraft fuel systems and in many test rigs finds >10% oxygen, 0.5 to 5% nitrogen, and 1 to 8% sulfur. This is in spite of the low concentrations of sulfur and very low levels of nitrogen in the fuels. The oxygen may be derived from oxygen compounds naturally present in the fuel or from compounds formed in the autoxidation process. Metals, particularly copper, stimulate deposit formation at very low concentrations. Fifteen ppb of copper and 25 ppb of iron decreased the breakpoints of JP-7 fuels 40°C in gas-drive coker tests. For JP-5 fuels, more dissolved metal was required to fail the JFTOT at 260°C, 50 to 105 ppb of copper and 136 to 165 ppb of iron. The metals probably act as catalysts for initiation of autoxidation and/or for decomposition of hydroperoxides.

The extent of conversion of jet fuel into harmful insolubles in an aircraft fuel system is very small, <0.1 ppm. This fact makes the tracking of susceptible molecules very difficult even with the sophisticated analytical instruments available today. Further complicating this analytical problem is the probability that more than one sequence of reactions is forming insolubles. Thus, our present knowledge cannot take us much beyond a simplified reaction scheme—autoxidation forms soluble oxidation products, further oxidation increases the oxygen content and the polar product becomes insoluble, insoluble compounds agglomerate into microspherical particles, and particles attach to surfaces or plug filters.

Various refining techniques have been tested for improving thermal stability. Those which

are successful remove polar compounds. This supports the theory that S-, N-, and O-compounds are key players in forming insolubles. Hydrotreating is the most successful refinery process.

Two types of additives are of concern, those which benefit thermal stability behavior and those added to improve other fuel properties. Antioxidants, metal deactivators, dispersants, and passivators have some merit in improving thermal stability, but they should be used with caution. Metal deactivators may give false pass results in specification tests, and dispersants degrade water separation from fuel. Antioxidants seem to be of value only for the situation of long-term storage of hydrotreated jet fuel. Additive chemistry with respect to thermal stability is a useful area for study.

Of the additives allowed in jet fuels to modify properties other than thermal stability, no significant effects have been defined which degrade thermal stability with the possible exception of fuel system icing inhibitor.

Future Fuels

High Temperature Applications

Several methods have demonstrated capability to improve stability of kerosene fractions for use to Mach 4+. Theoretically, the limit for use of JP fuels will be determined on the basis of their heat sink capacity rather than thermal stability. Hydrogenation is the most attractive process for across-the-board application to thermal stability improvement. Deoxygenation could be a very useful technique. Ultimately, factors such as economics, logistics, and safety will exert significant influence in defining thermal stability requirements and choosing methods of improving thermal stability.

Recent work by the U.S. Air Force has demonstrated the promise of endothermic fuels for Mach 4 to 7 applications. The material with the best properties for endothermic uses is methylcyclohexane.

Petroleum Supplements and Replacements

Crude oil reserves are limited, and eventually other sources of liquid fuels will be needed for transportation purposes. Substitutes for petroleum-derived JP fuels have been produced from other fossil fuel sources such as oil shale, coal, and tar sands. Products of adequate quality can be made from any of these sources. The costs are significantly higher than from petroleum, however, and it will be some years before they are utilized. Continued research should be conducted to assure that suitable fuel properties can be obtained from these alternative resources at reasonable cost.

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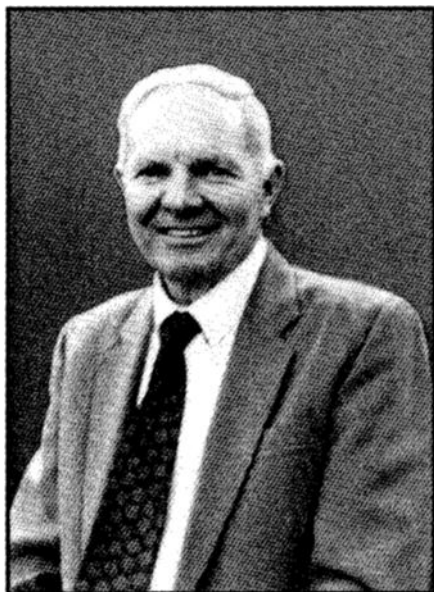
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About the Author

Currently retired from the Naval Research Laboratory, Dr. Robert N. Hazlett served there for 36 years. Most of Dr. Hazlett's career was spent in research on liquid fuels—rocket, jet, and diesel. His research on hydrocarbon fuels has dealt with properties, composition, availability, and stability of jet and diesel fuels. Hazlett's work in these areas has been widely published and referenced by others in the field.

The author holds a B.S. degree in chemistry from Sterling College, Kansas and a Ph.D. in organic chemistry from the University of

Kansas. Three Naval Research Laboratory publication awards, the Applied Science Award from the NRL Chapter of Sigma Xi, an Honorary D.Sc. from Sterling College, and the Black Bear Award to an outstanding alumnus of Sterling High School have been bestowed on this distinguished author.

Dr. Hazlett is an active member of ASTM's Committee D-2 on Petroleum Products and Lubricants, the American Chemical Society, the Coordinating Research Council, Sigma Xi, and the International Association for Stability and Handling of Liquid Fuels. The author spent one year (1984-1985) as an exchange scientist at the Materials Research Laboratory, Melbourne, Australia.

ISBN 0-8031-1248-3