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JET FUEL THERMAL STABILITY

A Workshop held at
Lewis Research Center
Cleveland, Ohio
November 1-2, 1978

NASA

NASA Technical Memorandum 79231

JET FUEL THERMAL STABILITY

William F. Taylor, Editor
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Linden, New Jersey

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1979

FOREWORD

As the fuel availability problem becomes more acute, additional attention is being focused on broadened-specification and nonpetroleum-derived turbine fuels. These fuels, with a higher aromatic and heterocompound content, have a greater potential for forming deposits at elevated temperatures than current fuels. Due to higher compression ratios and staged fuel injection, newer engines will be operating with higher fuel temperatures and longer residence times to further complicate the problem.

In order to present a forum for discussion of the various aspects of the thermal stability problem and to identify critical areas for future research, the Lewis Research Center sponsored the Jet Fuel Thermal Stability Workshop. Dr. William F. Taylor of Exxon Research and Engineering Company was the workshop chairman.

This report, edited by Dr. Taylor, presents the conclusions and recommendations of each of four working groups. In addition, the figures from a number of presentations made during the introductory session are included, giving a synopsis of much of the work presently being conducted in this field.

Stephen M. Cohen
Workshop Organizer

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JET FUEL THERMAL STABILITY

INTRODUCTION

The Jet Fuel Thermal Stability Workshop was conceived and sponsored by the NASA Lewis Research Center as a means to bring together various workers involved in the different phases of the aircraft turbine fuel stability problem so as to share their results, conclusions and plans and to interchange ideas for the planning of future work.

This report summarizes the findings and conclusions of the workshop. Thirty eight participants met for two days. Included were representatives from universities; various segments of industry including petroleum refining, engine and airframe manufacturing, and airline transportation; and a number of branches of government including the Air Force, Navy and Department of Energy. A number of NASA personnel were in attendance as working group coordinators and observers. Participants are listed in Appendix D.

The workshop started with a plenary session during the first morning. Welcoming remarks were made by W. L. Stewart, Director of Aeronautics. The following presentations were then made:

1. Introductory Remarks: Changes and Their Challenges
   William F. Taylor - Exxon Research and Engineering Company

2. NASA Jet Fuel Thermal Stability Activities
   Gregory M. Reck - NASA Lewis Research Center

3. Air Force Aviation Turbine Fuel Thermal Oxidation Stability R&D
   Charles R. Martel - Air Force Aeropropulsion Laboratory

4. Some Chemical Aspects of Deposit Formation
   Robert N. Hazlett - Naval Research Laboratory

5. Refining Jet Fuel for Thermal Stability
   William G. Dukek - Exxon Research and Engineering Company

6. Fuel Thermal Stability/Engine Trends
   Allyn R. Marsh - Pratt & Whitney Aircraft Group

7. Thermal Stability Activities
   Maurice W. Shayeson - General Electric Company

8. Thermal Stability Efforts
   A. E. Peat - Rolls-Royce Limited

9. Airline Status Report
   Walter D. Sherwood - Trans World Airlines

The visual aid material which was employed in these presentations is attached in Appendix A.

After the plenary session, the participants were organized into four working groups as follows:

I. Basic Research
   Chairman: Robert N. Hazlett - Naval Research Laboratory

II. Laboratory Characterization Techniques
   Chairman: Charles R. Martel - Air Force Aeropropulsion Laboratory

III. Applied Research and Test Simulators
   Chairman: Royce Bradley - Air Force Aeropropulsion Laboratory

IV. Engine System Trends and Requirements
   Chairman: Walter D. Sherwood - Trans World Airlines

Working group participants first addressed the question as to what is the present state-of-the-art for their respective topics and proceeded from there to identify future trends and needs. To aid in focusing working group discussions, some representative questions were provided to members of each of the working groups prior to the meeting. These questions are shown in Appendix B. In addition, to aid in the state-of-the-art review, preliminary copies of the Coordinating Research Council's "CRC Literature Survey on the Thermal Oxidative Stability of Jet Fuel" were made available to workshop participants. This report was in preparation at the time and will be released when the study is completed.

Brief reports were prepared by each working group, and these reports were presented to all attendees for discussion at the final session of the workshop by the Working Group chairmen. The written report of individual working groups' conclusions and recommendations are attached as Appendix C. In addition, the proceedings of this final session were recorded on tape and subsequently transcribed. This transcription of the summary session was particularly useful to the editor in preparing this workshop report.

PROBLEM STATEMENT

As the U.S. and world's supply of recoverable petroleum is exhausted, major changes will undoubtedly take place which will impact in some, but yet undefined, way on the sources, refining methods, properties and use of jet fuel. In June 1977, NASA sponsored a workshop on "Jet Aircraft Hydrocarbon Fuels Technology" to discuss the implication of such changes for aircraft turbine fuels. Focusing on the 1990 to 2000 time period, it was felt that petroleum crudes would still furnish most of hydrocarbon fuel liquids, with a small but growing contribution from synthetics such as shale oil and coal liquids. It was felt that in addition to keen competition for petroleum per se there would also be sharp competition for the distillate fraction currently used for jet fuel production. This latter competition would probably be caused both by increased jet fuel use itself and by competition from other distillate uses such as for diesel fuel and petrochemical feedstocks. Thus, the high quality petroleum distillates used to make current specification jet fuels may not be readily available. Synthetics and/or heavier petroleum fractions can be used to manufacture current specification jet fuels but will probably require substantial boiling range conversion and hydrogenation, both of which will increase cost and energy consumption during fuel manufacture. This serious future situation indicates a need for all concerned parties to begin now to reexamine the tradeoffs between fuel composition and specifications and engine and aircraft design in order to try to determine if a more optimum combination exists for future aircraft.

One major problem area which must be addressed in order to use either broadened-specification petroleum derived fuels or fuels composed of, or containing, synthetic derived stocks is the question of fuel stability. Fuel stability broadly refers to deleterious fuel-derived sediments and/or deposits which form via chemical reactions either during prolonged storage at ambient conditions (generally referred to as fuel storage stability) or from exposure to higher temperatures while the fuel is being delivered from on-board storage to the combustion section of the engine (generally referred to as fuel thermal stability). The question of fuel stability is complex and depends not only on the chemical nature of the fuel but also on the environment to which the fuel is exposed.

SUMMARY OF WORKING GROUP CONCLUSIONS AND RECOMMENDATIONS

Significant additional research and development is needed to aid in coping with the fuel stability problems which would be associated with the potentially poorer quality fuels of the future such as broadened-specification petroleum derived fuels or fuels produced either wholly or in part from synthetic sources. This problem could well be aggravated by potential trends in engine design leading to more severe thermal stress on the fuel in the future. Although much is known about the thermal oxidative stability of current specification petroleum derived fuels, our present state of knowledge does not suggest easy solutions to this problem nor does it allow detailed predictions to be made about the effect on stability of future fuel related changes. Thus, the broad objective of research and development activities should be to expand our current knowledge with the aim of establishing a fuel stability technology base which can be used in the future, for example, to identify feasible ways to ensure adequate fuel stability and to help in the design of engines and airframe components from the stability viewpoint. Ideally such a technology base could also make an important contribution to an overall future jet fuel composition and use optimization. Some important considerations relative to this overall problem include (1) fuel availability, (2) total fuel related costs of the system, (3) overall system energy consumption, (4) engine performance and durability, and (5) environmental considerations including the influence of low emission combustion designs on fuel stability requirements.

BASIC RESEARCH

The detailed recommendations of the Basic Research Working Group are shown in Table 1. Basic research has an obvious major role to play. Extensive fundamental studies of a number of areas critical to dealing with the fuel stability problem need to be carried out. Some major areas where fundamental work should be focused include:

- Studies to determine if non-free radical reactions are important in deposit formation.
- Additional chemical and physical characterization of deposits and their dependence on fuel type and environmental factors such as solvent and metal surface effects. In addition, deposits should be characterized to see if they change in character with time and depth.
- Studies to elucidate fuel compositional effects such as those related to boiling range and heteroatom content.
- Further explore and investigate additive effects for a number of additive approaches including "peroxide decomposers", antioxidants and dispersants. Additive interactions should also be studied.
- Further investigate metal surface and dissolved metal effects.
- Studies to investigate storage and aging effects as the fuel passes from the refinery to the aircraft including the role of intermediate hydroperoxides.

LABORATORY CHARACTERIZATION TECHNIQUES

The detailed recommendations of the Laboratory Characterization Techniques Working Group (Group II) are shown in Table 2. The group concluded that the primary function of laboratory test techniques should be to measure and/or rank the stability of various fuels. They considered and rejected the need for drastically new laboratory techniques to measure the thermal oxidative stability of modified specification and/or synthetic derived jet fuels. Further improvements in existing test methods are needed, however. The existing techniques were reviewed and analyzed in detail and a number of specific recommendations made for further work to improve these techniques. Concern was also shown for important related problems such as sampling and it was recommended that standard techniques be developed to reduce data variability from this source. Similar concern was shown for the difficult problem of relating small scale laboratory test devices to actual use problem areas such as engine fuel nozzle plugging.

APPLIED RESEARCH AND TEST SIMULATORS

The detailed recommendations of the Applied Research and Test Simulator Working Group (Working Group III) are shown in Table 3. The group recommended two types of approaches be used for fuel system simulator studies of jet fuel stability. The first approach involves parametric studies in a general design type of simulator whose objective would be to provide parametric design data under near real world conditions. Such data could be used to predict fuel performance in a variety of aircraft systems. The second approach would involve systematic studies in a complex simulator constructed to reflect the specific conditions in a single, given aircraft system. Parametric simulator studies will be particularly useful in bridging the gap between small scale laboratory test device results and performance in actual fuel systems. They will also provide a predictive design variable data base for aircraft fuel system designers analogous to those routinely developed in the chemical and petroleum industry via pilot plant process variables studies whose results are used to establish commercial production unit process designs.

Traditional, specifically designed simulators would be used to demonstrate individual aircraft fuel system designs and to study specific flight parameters in more detail where needed.

ENGINE SYSTEM TRENDS AND REQUIREMENTS

The detailed recommendations of the Engine System Trends and Requirements Working Group (Group IV) are shown in Table 4. The group concluded (1) thermal stability is a problem today and (2) trends in engine design are potentially toward a more severe environment for the fuel. Thus, they emphasized the importance of having fuels available in the future with good thermal oxidative stability. In this regard, they expressed a need for balance between concerns for aircraft emission controls, energy efficiency, engine durability, and fuel cost. Shorter-term they recommended that the question of fuel thermal stability changes from the refinery to the actual airport delivery point be investigated.

TABLE 1

BASIC RESEARCH RECOMMENDATIONS

A. Deposits

1. Employ modern surface analysis techniques: ESCA, Auger, Pyrolysis GC, ESR, CIDNIP and study deposit vs. depth especially for actual engine parts but also JFTOT and other test devices.

2. Check deposit chemistry and morphology for possible changes with time due to temperature on the hot surface.

3. Compare filterable deposits and varnishes.

4. Investigate solubility effects on deposits - include effects of fluid temperature, fluid and deposit chemistry, and flow rate.

5. Study deposit morphology and chemistry as a function of parameters: temperature, pressure, oxygen concentration, aging and composition of fuel.

6. Employ photo-acoustic spectroscopy and/or attenuated multiple reflectance IR to analyze gum and especially solid thermal deposits.

7. Employ radioactive tagging of contaminants.

B. Metals

1. Compare 3 possible metal effects

   Dissolved metals

      vs. Metal surface
      vs. Non-metal surface

   Look for stoichiometric metal involvement by analysis of deposits.

2. Investigate metal effects with and without O_2 and peroxides.

3. Check the effects of nitrogen compounds on copper pickup (especially in light of synfuels).

C. Storage and Aging

1. Monitor thermal stability from refinery through supply system.

2. Aerobic aging - check peroxides and electron spin - initial and with time.

3. Anaerobic aging - do peroxides account for all the aging.

TABLE 1 (concluded)

D. Reactions

1. Test fuel and deposits with ESR and CIDNIP for free radical reactions.

2. Follow disulfide decomposition with ESR.

3. Follow fouling reaction mechanisms/precursors in liquid phase employing field ionization mass spectrometry and other techniques.

4. Analyze oxygen concentrations in liquid and vapor phase in storage and aircraft tanks and as a function of time through flight conditions.

5. Examine effects of prevaporized/premixed fuel on deposition.

6. Explore MW in dispersions and in adherent deposits by light scattering/Tyndall effect and/or gel permeation chromatography.

7. Test effect of bifunctional N, O, and S materials.

8. Study variations of thermal stability with boiling range of real fuels.

9. Analyze fuels for trace components and their effects on fouling, using "specific detector" gas chromatography.

E. Additives

1. Investigate "peroxide decomposers" for controlling deposition (as used in the polymer industry, such as:

   Ni diacetylacetonate
   and non-metallic equivalents)

2. Explore antioxidant and dispersant thermal stability effects in a variety of fuels.

3. Study inhibitor interactions in storage and fouling.

F. Miscellaneous

1. Investigate effects and mechanisms of various treatments - clay, H_2, separations - on thermal oxidation stability and composition of fuels.

2. Examine deposition as a function of reaction mechanism or deposition mechanism.

TABLE 2

LABORATORY CHARACTERIZATION TECHNIQUES RESEARCH RECOMMENDATIONS

I. Existing Laboratory Techniques

A. Jet Fuel Thermal Oxidation Tester (JFTOT)

a. Examine actual aircraft and engine fuel systems and determine the actual temperatures, pressures, flow rates, etc. of the engine fuel nozzles that are experiencing plugging problems. Use these data to select more realistic JFTOT test conditions (pressure, temperature, residence times, prefiltration, etc.).

b. Recommend that ASTM be asked to re-examine the need for and degree of in-line fuel prefiltration for the JFTOT.

c. Research is needed to identify and develop improved tube deposit rating techniques that correlate with fuel heat exchanger fouling and nozzle plugging.

d. Reference fuels such as pure hydrocarbons and concentrates containing reactive species should be investigated for use as calibration fluids.

e. Temperature control of the JFTOT test (Dutch weave metal) filter should be investigated.

B. ASTM-CRC Fuel Coker

Reference fuels are needed so that instrument performance could be checked periodically.

Information is needed as to the actual effects of trace elements in the fuel on thermal stability, as trace elements are believed to promote deposition. If this is of concern, the sample size and length of test required may need to be increased in order to obtain useful data when the trace elements are present in parts per billion quantities.

C. Research Fuel Coker

This instrument is a higher temperature version of the ASTM-CRC Fuel Coker. The test filter is the same for both units and the preheater tube is of stainless steel for the Research Fuel Coker. The users have not reported any operational problems. Also see JFTOT and ASTM-CRC Fuel Coker discussions above.

D. Monirex Fouling Monitor

Research needs include further evaluation of the hot wire method, and the differential fouling test method. Development of a reference fuel for better device precision and inter-device correlation would advance the state of the art.

E. Thermal Fouling Tester (TFT)

With the design of a new test section and an operating technique specifically tailored to discriminate and rank jet fuels, this device could possible equal or perhaps surpass the present JFTOT technique. In this technique, rating of a fuel sample would be strictly based on heat transfer characteristics of the deposits generated and expressed as a maximum delta T attained. Such a rating system would be highly desirable as it excludes the operator from having to make a rating judgment as is now the case with the JFTOT visual method.

F. Thornton Flask Test

The method provides (1) a portable and easily conducted procedure for field measurements, (2) field samples may be taken directly into the test unit, thereby reducing sample container/shipping problems, and (3) the procedure provides a measurement in 1 1/2 to 2 hours.

Further development is needed to (1) improve the repeatability and (2) provide correlation with specification techniques.

G. Oxygen Uptake Measurements

Measuring oxygen uptake alone in a typical jet fuel under well-controlled temperature conditions is relatively simple but it would be necessary to also measure oxygen products or sludge for a meaningful test. The technique does not lend itself to quality control as does a rig such as the JFTOT but is more useful for research studies into oxidation mechanism and system variables.

H. Thermal Precipitation

The thermal precipitation test is a specification requirement for MIL-T-38219 Grade JP-7 fuel. It is useful for fuels where cyclic heating and cooling in the system may leave deposits which affect engine components.

The thermal precipitation test is similar in principal to the Thornton Flask test described above.

II. Related Problems

A. Sample Containers

The results of poor sampling techniques and their effect on the thermal stability test results have been documented both in these sessions and in other technical meetings. It is this group's recommendation that both sampling and sample containers be seriously considered in order to maintain the validity and precision of the various thermal stability test methods. Areas to be considered would include: (1) Sampling location and method of drawing samples. (2) Types of sample containers and how the containers would be used in sampling. If using epoxy-coated containers, should the type of epoxy be specified and should the epoxy coating undergo a fuel exposure period before using. If unlined sample containers are to be used, how should they be treated or rinsed with fuel prior to sampling. Also, sample container seals must also be considered.

TABLE 2 (concluded)

This work will be valuable for other fuel tests where sampling is important.

B. Peroxide Formation Test for Thermal Stability of Jet Fuel

Peroxide formation has not been widely applied to jet fuel thermal stability testing and further investigations are required. The relative importance of peroxides and fuel components to final deposits has not been established and it is likely that this will vary markedly among various fuels. Peroxide formation is suitable for research studies of thermal stability and problems with specific fuels but is not recommended for general thermal stability testing of all jet fuels.

TABLE 3

APPLIED RESEARCH AND TEST SIMULATORS RECOMMENDATIONS

The need for a complete parametric study that will provide data under a variety of steady-state conditions is evident. The study would use a device consisting of an instrumented tube capable of being exposed to the entire range of engine conditions and designed to give quantitative data on the rate of formation and characteristics of fuel degradation products, particularly deposits formed under these conditions. The results from this effort could then be used by the designer to predict the performance of fuel in an aircraft, the results could also be used to evaluate small-scale test devices. The priority of the parameters to be included in a program of this type differ depending on whether emphasis is in the area of design or fuel studies. A list of these parameters and the order of importance to the two areas are:

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

During parametric testing, the heat flux used in preconditioning the fuel must be minimized to avoid unrealistic fuel deterioration in the preconditioner. It is not yet known whether simulator testing can be accelerated. The results of these parametric tests should indicate the possibility of accelerating future tests both on this test device and on small-scale devices. It is noted that by sufficiently reducing the pressure and/or increasing the temperature in the test device the effects of two-phase flow and supercritical conditions on thermal stability can be investigated. The fuel type can be varied to include fuels from alternative sources in addition to currently produced fuels.

TABLE 3 (concluded)

It must be realized that the results of the parametric program won't answer all questions regarding fuel performance in an aircraft engine; e.g. steady-state results may not be additive in a dynamic system. However, the parametric program should provide the best source of predictive data for design purposes. Final confirmation may require a test program using aircraft engine hardware for each specific aircraft of concern.

It is recognized that the design of supersonic aircraft fuel systems will require a fuel tank simulator (akin to that described above) in which flight parameters and their effect on thermal/oxidative stability can be systematically studied. Clearly the geometry will differ from the engine simulator, as will the selection and range of variables. The device should incorporate means of studying the effects of tank insulation, inerting and cleaning techniques. It is further recognized that the engine and aircraft tank simulations will likely be carried out independently until such time as a system design is laid down; at that point, integrated systems tests are indicated.

TABLE 4

ENGINE SYSTEM TRENDS AND REQUIREMENTS - RECOMMENDATIONS

1. NASA should sponsor or coordinate a survey of fuel thermal stability at airports. Precautions on sampling and transporting samples are mandatory.

2. In view of the concern over fuel thermal stability problems and in the national interest as well, NASA should determine the realistically practical limits of aircraft emission control with full consideration of all fuel property and cost objectives, energy conservation, engine durability, consumer costs for transportation and inflationary pressure.

3. It is recommended that the present thermal stability levels be retained for any proposed fuel specifications in the foreseeable future as long as it is cost effective.

APPENDIX A

FIGURES FROM INTRODUCTORY SESSION

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INTRODUCTORY REMARKS: CHANGES AND THEIR CHALLENGES

William F. Taylor

Exxon Research and Engineering Company

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CHANGES AND THEIR CHALLENGES

- IN THE FUTURE JET FUEL WILL NO LONGER NECESSARILY BE INEXPENSIVE, EASILY AVAILABLE, AND TIME INVARIANT IN COMPOSITION AND/OR PROPERTIES.

- THESE FUEL CHANGES WILL CREATE CHALLENGES FOR FUEL PRODUCERS, ENGINE AND AIRFRAME MANUFACTURERS AND USERS.

- THERMAL STABILITY WILL BE ONE OF THE MAJOR PROBLEM AREAS.

JET FUEL IN A TRANSITION PERIOD

- EVOLUTIONARY CHANGES, E.G. POORER QUALITY CRUDES
- BROADENED SPECIFICATIONS
- INTRODUCTION OF SYNTHETIC CRUDES, E.G. SHALE OIL

GROSS CHEMICAL PROCESS IN LIQUID PHASE DEPOSIT FORMATION

PARENT FUEL		SOLUBLE OXIDATION PRODUCTS		INSOLUBLE OXIDATION PRODUCTS
• JET FUEL HYDROCARBON, I.E., C_5 TO C_{15} PARAFFINS, NAPHTHENES AND AROMATICS • TRACE SULFUR AND NITROGEN CONTAINING COMPOUNDS • LOW LEVELS OF OLEFINS	$\xrightarrow{O_2}$	• INITIAL OXIDATION PRODUCTS • SOLUBLE IN JET FUEL • LOW OXYGEN CONTENT, I.E., 8 TO 12 • INCORPORATION OF SULFUR AND NITROGEN INTO PRODUCTS	$\xrightarrow{O_2}$	• EXTENDED OXIDATION PRODUCTS • INSOLUBLE IN JET FUEL • HIGHER OXYGEN CONTENT, I.E., 18 TO 25% • INCORPORATION OF SULFUR AND NITROGEN • MOLECULAR WEIGHT 200 TO 600

GROSS PHYSICAL PROCESS IN LIQUID PHASE DEPOSIT FORMATION

AGGLOMERATION IN LIQUID		COLLECTION ON SURFACES		FUSION ON SURFACES
AGGLOMERATION OF "INSOLUBLE" OXIDATION PRODUCT MOLECULES IN THE JET FUEL TO MICROSPHERICAL PARTICLES 500 TO 3,000 ANGSTROM UNITS IN SIZE (TYPICALLY 1,000 A IN SIZE).	→	MICROSPHERICAL PARTICLES SETTLE TO SURFACES FROM LIQUID OR COLLECT ON SURFACES AFTER IMPINGEMENT FROM MOVING FLUID. LOSS OF VOLATILE FUEL ALSO CAN LEAVE NON-VOLATILE PARTICLES ON SURFACES.	→	MICROSPHERICAL PARTICLES ON SURFACE UNDERGOES COLLESCENCE AND PLASTIC FLOW TO FORM VARNISH LIKE SUBSTRATE UPON WHICH ADDITIONAL PARTICLES COLLECT. FURTHER OXIDATION MAY TAKE PLACE TO FORM DARK, BRITTLE "COKE" LIKE DEPOSITS IN ENVIRONMENTS SUCH AS "EMPTY" WING TANKS.

AUTOXIDATIVE PRODUCTS ARE NUMEROUS

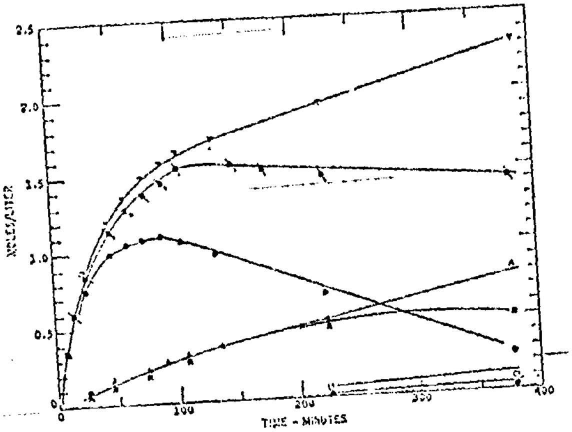
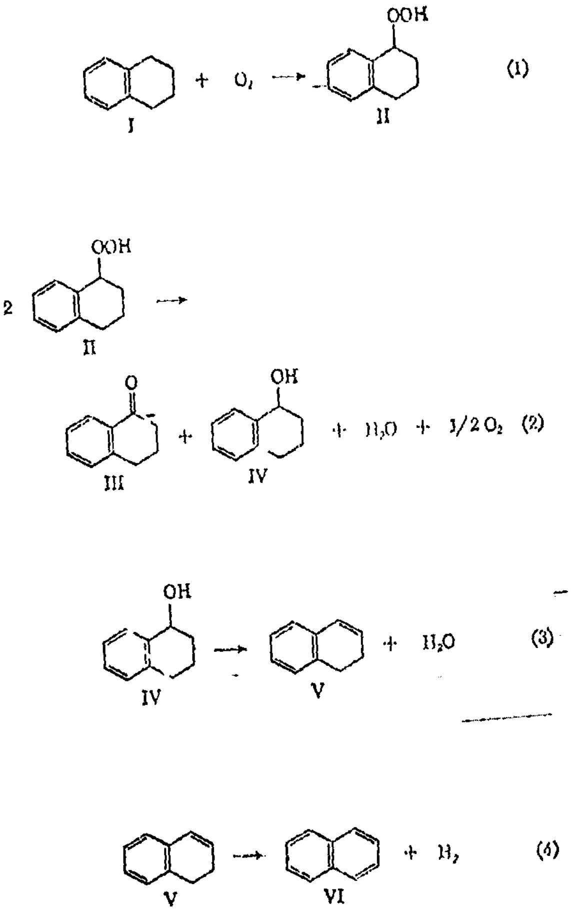


Figure 5. Reactants and liquid product changes during the catalyzed oxidation of tetralin at 115°. Other conditions: 4 ml of tetralin in 2 ml of chlorobenzene, 0.30 g of catalyst, and 1 atm pressure. ▼, tetralin consumed; ●, oxygen consumed (by volumetric change); ●, tetralin hydroperoxide (II) content; ▲, ketone (III) content; ■, alcohol (IV) content; O, 1,2-dihydronaphthalene content; Ø, naphthalene content.



SOURCE: W. F. TAYLOR, J. PHYS. CHEM. 79 2250 (1970).

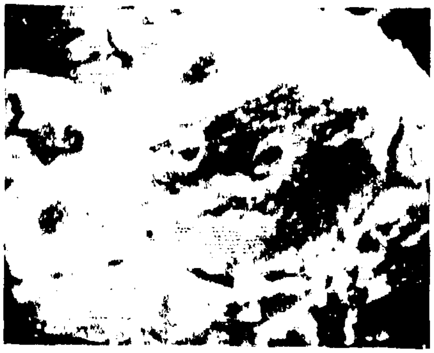
FUEL STABILITY REGIMES VARY WIDELY

- LOW TEMPERATURE, LIQUID PHASE, AUTOXIDATIVE REACTIONS
- INTERMEDIATE
- HIGH TEMPERATURE, VAPOR PHASE, PYROLYSIS REACTIONS

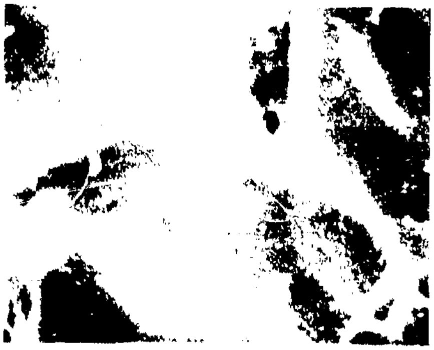
MORPHOLOGY OF DEPOSITS

77 PPM O_2 (AIR SATURATED)

6.4 PPM O_2



0.3 PPM O_2



SOURCE: FINAL REPORT "DEVELOPMENT OF HIGH STABILITY FUEL" CONTRACT N00140-74-C-0618, JANUARY 1975.

ALL SEM'S AT 10,000 X; SAME PURE COMPOUND JET FUEL; DEPOSIT LEVEL 25-29 μG C/CM 44 HRS.

FLOW FROM RESEARCH & DEVELOPMENT TO END USE

FUEL THERMAL STABILITY

BASIC RESEARCH → BENCH SCALE STUDIES → SIMULATIVE STUDIES → ENGINE AIRCRAFT USE

CHEMICAL AND PETROLEUM PROCESS DEVELOPMENT

LABORATORY STUDIES → BENCH SCALE STUDIES → LARGE PILOT PLANTS -- DEMONSTRATION UNITS → COMMERCIAL PLANT

WORKING GROUPS

- BASIC RESEARCH
- LABORATORY CHARACTERIZATION TECHNIQUES
- APPLIED RESEARCH AND TEST SIMULATORS
- ENGINE SYSTEM TRENDS AND REQUIREMENTS

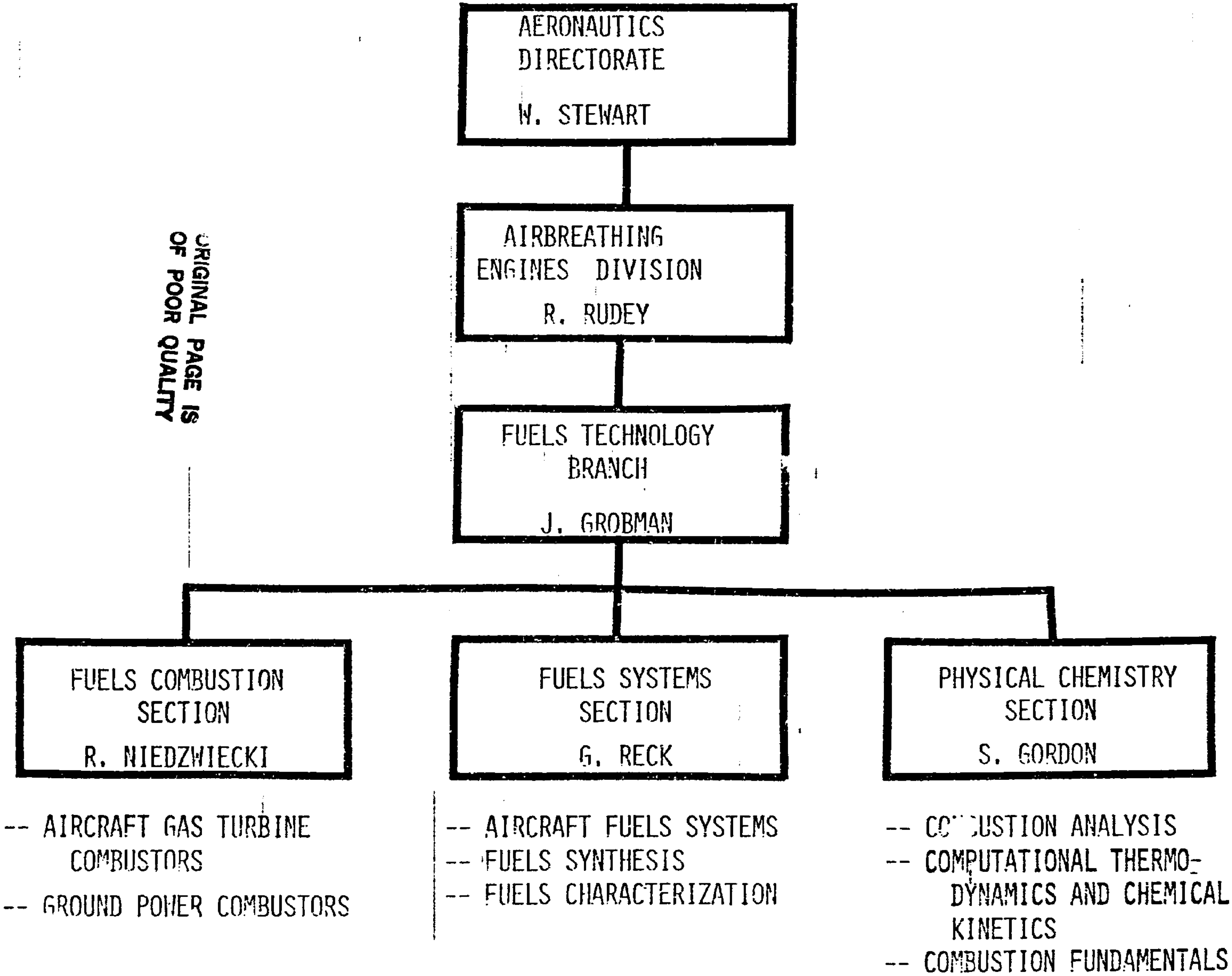
OBJECTIVES OF FUEL STABILITY WORKSHOP

- REVIEW THE STATUS OF THERMAL STABILITY RESEARCH
- DISCUSS CURRENT AND ANTICIPATED FUTURE PROBLEMS
- IDENTIFY RESEARCH NEEDS

NASA JET FUEL THERMAL STABILITY ACTIVITIES

Gregory M. Reck

NASA Lewis Research Center


AERONAUTICS DIRECTORATE
W. STEWART
AIRBREATHING ENGINES DIVISION
R. RUDEY
FUELS TECHNOLOGY BRANCH
J. GROBMAN
FUELS COMBUSTION SECTION
R. NIEDZWIECKI
FUELS SYSTEMS SECTION
G. RECK
PHYSICAL CHEMISTRY SECTION
S. GORDON
-- AIRCRAFT GAS TURBINE COMBUSTORS
-- GROUND POWER COMBUSTORS
-- AIRCRAFT FUELS SYSTEMS
-- FUELS SYNTHESIS
-- FUELS CHARACTERIZATION
-- COMPUTATIONAL THERMODYNAMICS AND CHEMICAL KINETICS
-- COMBUSTION FUNDAMENTALS

FUELS TECHNOLOGY BRANCH

FUEL THERMAL STABILITY ACTIVITIES

<u>OUTSIDE</u>

-- EXPERIMENTAL STUDY CONTRACT - UNITED TECHNOLOGIES RESEARCH CENTER

-- GRANT WITH COLORADO SCHOOL OF MINES - EFFECT OF NITROGEN COMPOUNDS ON STABILITY

-- FUEL DEGRADATION STUDY (PLANNED)

<u>IN-HOUSE</u>

-- THERMAL STABILITY STUDIES OF DOPED FUELS WITH JFTOT

-- STABILITY STUDY WITH SYSTEM SIMULATOR (PLANNED)

-- EFFECT OF HYDROPROCESSING SEVERITY ON STABILITY

-- MECHANISMS OF THERMAL DEGRADATION OF ALTERNATE FUELS (PLANNED)

EXPERIMENTAL STUDY OF TURBINE FUEL THERMAL STABILITY IN AN AIRCRAFT FUEL SYSTEM SIMULATOR

UNITED TECHNOLOGIES RESEARCH CENTER

OBJECTIVES

1. PROVIDE A MEANS OF OBSERVING THE EFFECTS OF FUEL THERMAL STABILITY ON THE SIMULATED FLIGHT BEHAVIOR OF AN AIRCRAFT FUEL SYSTEM

2. PROVIDE A MEANS OF ACCELERATING THE FUEL THERMAL BREAKDOWN FOR OBTAINING PARAMETRIC AND BREAKPOINT INFORMATION

3. ESTABLISHING CRITERIA FOR THE QUANTITATIVE ASSESSMENT OF FUEL THERMAL DEGRADATION

APPROACH

TASK I - DESIGN OF APPARATUS

TASK II - CONSTRUCTION OF APPARATUS & EVALUATION OF FUELS

TASK III - CALIBRATION AND BASELINE TESTS

TASK IV - COMPREHENSIVE TESTS OF FUEL THERMAL STABILITY

TASK V - REPORTS & RECORDS

UTRC - EXPERIMENTAL THERMAL STABILITY STUDY

FUEL SYSTEM SIMULATOR FEATURES:

-- INCLUDE SUPPLY TANK, PUMP, MANIFOLD, NOZZLE, HEATING SYSTEM, AND DISCHARGE TANK
-- SATURATED OR DEOXYGENATED TEST FUEL
-- INDEPENDENT HEATING OF FUEL SUPPLY AND MANIFOLD/NOZZLE
-- NOZZLE SPRAY CHARACTERISTICS WILL BE MONITORED

TEST FUELS:

1. JET A, BREAKPOINT TEMPERATURE $\geq$ 260°C
2. BROAD SPECIFICATION (SIMILAR TO ERBS, OR DIESEL 2), BREAKPOINT TEMPERATURE $\leq$ 240°C

PRELIMINARY TEST CONDITIONS:

1. FUEL SUPPLY TEMPERATURES - AMBIENT TO 150°C
2. MANIFOLD & NOZZLE WALL TEMPERATURES - 240 TO 400°C
3. FUEL FLOW - 10 TO 100 KG/HR
4. DEOXYGENATED AND AIR SATURATED FUEL

NASA GRANT - COLORADO SCHOOL OF MINES

PRINCIPAL INVESTIGATOR - DR. STEPHEN DANIEL

OBJECTIVE: DETERMINATION OF THE MECHANISM OF INFLUENCE OF ORGANIC NITROGEN COMPOUNDS ON FUEL INSTABILITY

APPROACH:

1. ISOLATION AND CHARACTERIZATION OF LEWIS-BASE COMPONENTS FROM SYNCRUDES
2. DETERMINATION OF THE EFFECT OF THIS EXTRACT ON THE STORAGE STABILITY OF PETROLEUM-DERIVED JET A
3. IDENTIFICATION OF INDIVIDUAL FUEL COMPONENTS UNDERGOING ALTERATION DURING THE AGING PROCESS
4. MODEL SYSTEM STUDIES

GRANT PROGRESS:

I. ISOLATION & CHARACTERIZATION OF LEWIS-BASED COMPONENTS FROM SYNCRUDES

-- LEWIS BASE EXTRACT HAS BEEN PREPARED FROM SYNCRUDES

-- GC WITH SELECTIVE NITROGEN DETECTOR (AFID) IS BEING USED FOR CHARACTERIZATION

-- GC/MS USED FOR DETAILED CHARACTERIZATION

II. STORAGE STABILITY EXPERIMENTS

-- JET A BASE FUEL HAS BEEN CHARACTERIZED

-- ACCELERATED AGING TESTS CONDUCTED AT 121°C

-- AGING MONITORED BY TWO "GUM" TESTS

<u>DISSOLVED GUM</u> - VACUUM EVAPORATION WITH IR HEATING OF FILTERED SAMPLE

<u>FILTERABLE GUM</u> - WEIGHT OF DEPOSIT ON GLASS COVER SLIP IMMERSED IN REACTION VESSEL

-- COMPARISON OF JET A WITH JET A SPIKED WITH EXTRACT TO 5 PPM N HAS SHOWN INCREASE IN FILTERABLE GUM IN SPIKED SAMPLE

GRANT PROGRESS:

III. ACTIVE COMPONENT IDENTIFICATION

-- GC ANALYSIS OF FILTERED, AGED JET A WITH UNAGED JET A SHOWS NO OBVIOUS QUALITATIVE DIFFERENCES

-- SCRUBBING JET A WITH H_2SO_4 SIGNIFICANTLY REDUCED FILTERABLE GUM

-- EVALUATING THE EFFECT OF A NUMBER OF NITROGEN COMPOUNDS ON AGING OF JET A, SINGLY AND IN COMBINATION WITH PEROXIDES.

IV. MODEL SYSTEM STUDIES

-- AGING STUDIES ARE BEING CONDUCTED WITH SIMPLE FUEL MODELS - BLENDS OF VARIOUS COMPONENTS IN DODECANE

-- COMPONENT CONCENTRATIONS DURING AGING ARE BEING MONITORED

EFFECT OF NITROGEN COMPOUNDS ON THE THERMAL STABILITY OF JET FUELS

LEWIS IN-HOUSE ACTIVITY

OBJECTIVE:

TO DETERMINE THE EFFECT OF CONCENTRATION OF VARIOUS TYPES OF NITROGEN CONTAINING COMPOUNDS ON THE THERMAL STABILITY OF AIRCRAFT TURBINE FUELS

APPROACH:

VARIOUS NITROGEN COMPOUNDS (INCLUDING CARBAZOLE, PYRIDINES, PYRROLE, INDOLE QUINDLINE) WILL BE ADDED TO JET A, SINGLY AND IN COMBINATION, AT SEVERAL CONCENTRATION LEVELS

JFTOT BREAKPOINT TEMPERATURES WILL BE CORRELATED WITH NITROGEN CONCENTRATION

AIR FORCE AVIATION TURBINE FUEL THERMAL OXIDATION STABILITY R&D

Charles R. Martel

Air Force Aeropropulsion Laboratory

PREVIOUS THERMAL STABILITY PROGRAMS

ADVANCED AIRCRAFT FUEL SYSTEM SIMULATOR TESTS

JFTOT TEST METHOD DEVELOPMENT -CRC/ASTM

JFTOT HEATED RESERVOIR PROGRAM - CRC

PRESSURE EFFECTS ON JFTOT TUBE DEPOSITS

JFTOT TUBE DEPOSIT RATING COMPARISON

COKER/JFTOT CORRELATION

MOGAS JFTOT TESTS

CURRENT AFAPL/SFF THERMAL STABILITY PROGRAMS

- JFTOT TEST FOR THERMALLY STABLE JET FUEL (JPTS)
- JFTOT TEST FOR LOW VOLATILITY TURBINE FUEL (JP-7)
- J-79 FUEL NOZZLE PLUGGING TESTS (GENERAL ELECTRIC)
- JP-8 SAMPLE CAN/FUEL DEGRADATION PROBLEM

JPTS THERMALLY STABLE JET FUEL

PRESENT SPEC TEST:

- ASTM/CRC COKER AT 450/550/6 TEST CONDITIONS

PROPOSED TEST:

- JFTOT TEST - 2 1/2 HOURS, 500 PSIG, TEST TEMPERATURE OF ABOUT 335°C (635°F). USE MARK 8A TUBE DEPOSIT RATER.

REF: AFAPL-TR-78- , "THERMAL OXIDATIVE STABILITY TEST METHODS FOR JPTS FUELS".

JP-7 LOW VOLATILITY TURBINE FUEL

PRESENT SPEC TESTS:

- THERMAL PRECIPITATION TEST PER APPENDIX B, MIL-T-38219A
- RESEARCH COKER TEST AT 500/600 PER APPENDIX A, MIL-T-38219A

PROPOSED TESTS:

- JFTOT TEST - 5 HOURS, 500 PSIG, TEST TEMPERATURE OF ABOUT 350 TO 370°C. USE MARK 8A TUBE DEPOSIT RATER.

ALCOR MARK 8A TUBE DEPOSIT RATER

- PROPOSED FOR USE WITH JP-7 AND JPTS FUELS.
- ANTICIPATED LIMITS:

MAX. ΔTDR = 12 (ΔTDR = MAXIMUM POST TEST RATING MINUS PRETEST RATING)

REF: AFAPL-TR-77-53, "DETERMINATION OF THE EFFECT OF PRETEST RATING OF JET FUEL THERMAL OXIDATION TESTER TUBES ON POST-TEST RATINGS USING THE TUBE DEPOSIT RATER", JUNE 1977.

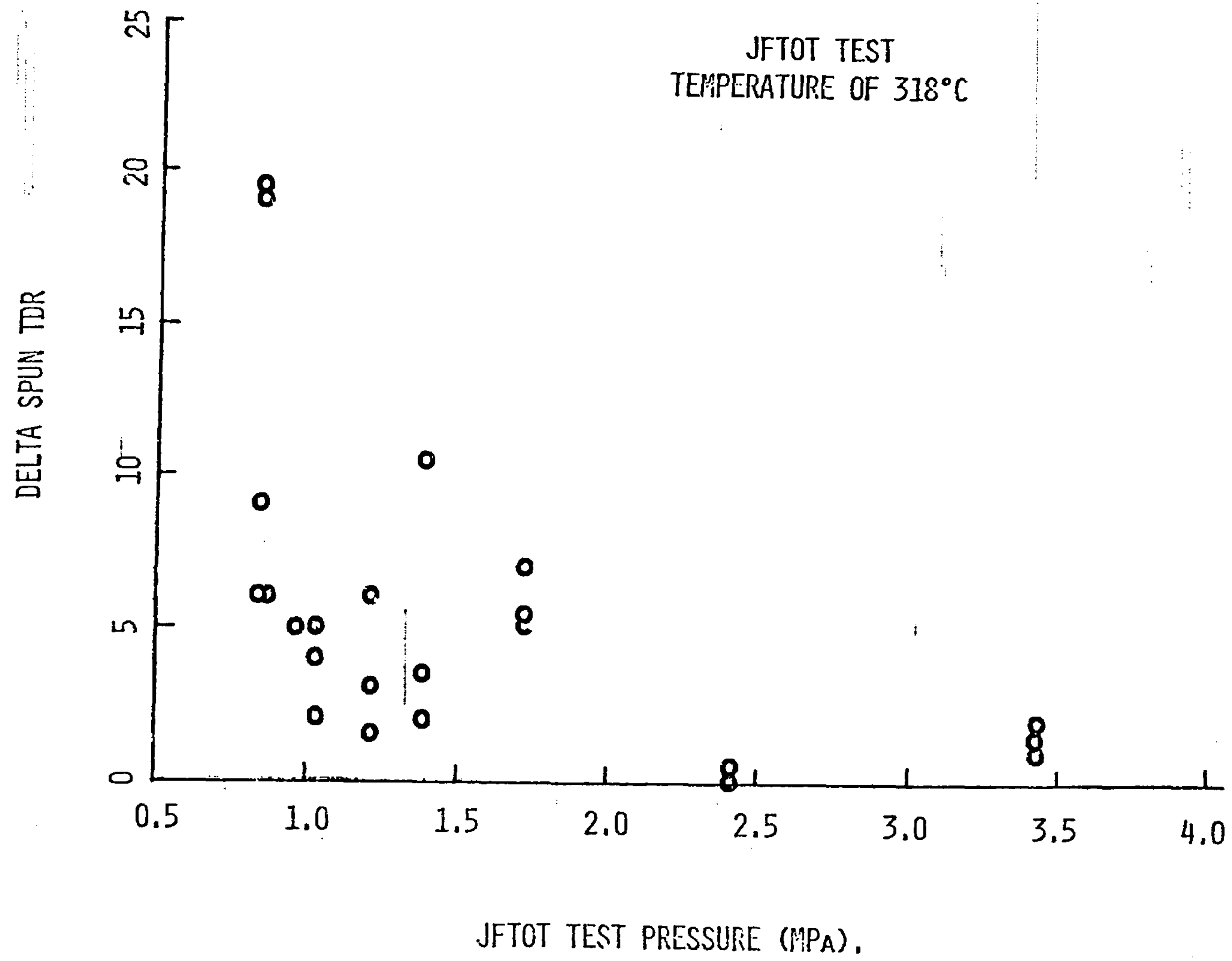
AFAPL-TR-75-49, "COMPARISON OF RATING TECHNIQUES FOR JFTOT HEATER TUBE DEPOSITS", OCTOBER 1975.

R & D NEEDS - IMPROVED QUALITY CONTROL TEST

- REEXAMINE PRACTICE OF FUEL PREFILTRATION
- RUN AT REALISTIC TEST TEMPERATURES. TRADE-OFF OF TEMPERATURE FOR TIME QUESTIONED.
- WHEN SHOULD HEATED RESERVOIR BE USED?
- DEPOSIT RATING METHODS QUESTIONED.
  - WHAT DOES COLOR OR OPTICAL REFLECTIVITY MEAN TO ENGINE?
  - HEAT TRANSFER MEASUREMENTS CAN BE MISLEADING. REQUIRES TOO LONG A TEST OR TOO HIGH A TEMPERATURE.
  - WHY DOES TEST PRESSURE AFFECT DEPOSITS?
- NEED STANDARD SAMPLE CANS MADE OF INERT MATERIALS QUESTION NEED FOR INERT ATMOSPHERE OVER SAMPLE.

R & D NEEDS - WHAT ARE EFFECTS OF SUPERCRITICAL OPERATION?

FUEL	CRITICAL TEMP °C (°F)	PRESSURE AT CRITICAL TEMP (PSIA)
JP-4	288 (550) TO 365 (690)	500 TO 400
JP-5	382 (720) TO 415 (780)	300 TO 280
JP-7	400 (760)	270
JP-8	370 (700) TO 405 (760)	350 TO 275



EFFECT OF TEST PRESSURE ON TUBE DEPOSITS

SAMPLE CAN PROBLEM

JFTOT BREAKPOINT DATA FOR JP-8

SAMPLE I.D. (NO. LABS)	AVE B.P. (°C)	B.P. RANGE	FAILURE MODE
AF LINED CANS (6)	295	270 TO 310	DEPOSIT (5), ΔP(1)
GE LINED CANS (1)	285		DEPOSIT (1)
GE UNLINED CANS (7)	<250	220 TO <230	ΔP (7)
GE GLASS BOTTLE (1)	300		DEPOSIT (1)

JFTOT BREAKPOINT DATA FOR JP-4

SAMPLE I.D. (NO. LABS)	AVE B.P. (°C)	B.P. RANGE	FAILURE MODE
AF LINED CANS (5)	262	<260 TO 265	DEPOSIT (3), ΔP(4)
GE LINED CANS (1)	265		DEPOSIT (1)
GE UNLINED CANS (7)	258	240 TO 265	DEPOSIT (5), ΔP(5)

R & D NEEDS - SIMPLE BUT SENSITIVE FUEL SYSTEM SIMULATOR

- SINGLE TUBE HEAT EXCHANGER:
  - USE TUBE FROM ACTUAL A/C FUEL-OIL HEAT EXCHANGER
  - SACRIFICE TUBE AFTER EACH TEST
  - MEASURE FUEL-SIDE HEAT TRANSFER
- NEED FUEL NOZZLE THAT SIMULATES COMBUSTOR CONDITIONS
- SMALL SIZE TO REDUCE FUEL NEEDS
- ACCURATELY SIMULATE TEMPERATURE, PRESSURES, REYNOLDS NUMBER
- AUTOMATED TO PERMIT CONTINUOUS OPERATION

SOME CHEMICAL ASPECTS OF DEPOSIT FORMATION

Robert N. Hazlett

Naval Research Laboratory

The NRL work is attempting to give a chemical rationale for the reactions which begin with that between dissolved oxygen and fuel molecules and end with the formation of solid varnishes and/or suspended particulate matter. The presentation will be divided into 3 parts: liquid phase reactions triggered by oxidation, the relationship between liquid phase reactions and deposit formation, and the characterization of deposits.

I. LIQUID PHASE CHEMISTRY

Figure 1 - The bulk of the NRL work has been done in a modified JFTOT which can be used at more extreme conditions than the standard JFTOT. Further, fuel samples can be directed to a gas chromatograph for real time determination of oxygen depletion and product formation.

Figure 2 - GC features include a helium ionization detector which has excellent sensitivity for low molecular weight gases.

Figure 3 - Considerable research has been conducted using n-dodecane, a pure hydrocarbon which is a major constituent of JP-5. Analytical considerations are greatly simplified by this choice.

The initial product from O_2/dodecane reaction is a hydroperoxide. This product is formed in a free radical reaction occurring between 400 and 500°F in the JFTOT flow system. Decomposition of the hydroperoxide at higher temperatures (550-750°F) forms alcohols and ketones. Carbon monoxide also forms during this regime.

Figure 4 - This Arrhenius plot depicts the production of scission products. The various sections of the curves can be related to hydroperoxide decomposition (600-750°F), minimum reactivity (750-900°F) and pyrolysis (above 900°F). The plots for CO and the n - alkanes exhibit similar slopes. n - Decane and hydrogen exhibit unique behavior.

Figure 5 - Olefins are also produced from thermal oxidative stress of n - dodecane. At lower temperature, paraffins predominate over the 1-olefins, but equal amounts were found at temperatures of 800°F and above. The distribution pattern with carbon number is noteworthy.

Figure 6 - The sum of all n - alkanes and 1-olefins is plotted in this graph. The dissolved oxygen concentration significantly affects product yield, particularly at lower temperatures (60 ppm is the amount of O_2 dissolved when n - dodecane is equilibrated with air at 1 atmosphere pressure).

Figure 7 - The 3 reaction regimes occurring in the n - dodecane/O_2 system are:

(a) liquid phase oxidation - 400 - 500°F

(b) hydroperoxide thermolysis - 550 - 750°F

(c) pyrolysis - 900°F and above

Regime (a) can be explained on the basis of well-established oxidation chemistry and will not be addressed in this talk. Regime (c) can be explained on the basis of the Rice-Kossiakoff mechanism as developed by Fabuss, Smith, and Satterfield and modified here for high pressure conditions.

Figure 8 - Regime (b) can be explained using an initial thermolysis of hydroperoxide. The alkoxy radicals formed react primarily to form alcohols in the reducing environment but also decompose to ketones. A third path affords cleavage to smaller fragments which include primary alkyl radicals. These radicals can participate in the chain propagation reactions shown in Fig. 7 to form similar products, small alkanes and olefins, found in the higher temperature pyrolysis regime. Termination via secondary alkyl radicals appears to be more important than beta-scission, however, at lower temperatures and the alkane yield exceeds olefin yield.

Figure 9 - Product formation from n - dodecane is similar for 3 metals used as heater tubes in the JFTOT. Thus these metals are not catalytic for the oxidation reactions examined.

Figure 10 - Some aromatics added to n - dodecane inhibit the oxidation step.

Figure 11 - Fluorene is the best inhibitor for the oxidation reaction. The inhibitory action may be related to the strength of the pertinent C-H bond.

Figure 12 - The aromatic compounds also affect the reactions initiated by hydroperoxide thermolysis, reducing the yield of hydrocarbons.

Figure 13 - In addition, fluorene reduces the olefin/paraffin ratio at 800°f and below.

II. RELATIONSHIP BETWEEN LIQUID PHASE CHEMISTRY AND DEPOSIT FORMATION

Figure 14 - The deposits formed during thermal oxidative stress in the modified JFTOT were evaluated using the Alcor Tube Rater. Since tubes (particularly stainless steel tubes) usually had an initial meter reading above zero, the difference between the after and before readings (ΔTDR) have been utilized in the plots. This figure for n - dodecane flowing over 316 s.s. indicates deposit formation coincides with hydroperoxide decomposition. In addition, the ΔTDR and CO values exhibit a remarkably similar rise as peroxide decays.

Figure 15 - The Arrhenius plot illustrates further the parallel behavior observed in the different portions of the graph:

550-750°F, 750-900°F, and above 900°F.

Figure 16 - For a complex hydrocarbon mixture (CRC fuel RAF-177), the pattern is somewhat different but relationships are still apparent. In this case, deposit forms during the oxidation phase and also as hydroperoxide decomposes. Deposit formation decreases some after all of the peroxide is reacted.

Figure 17 - An aluminum heater tube used with RAF-177 exhibits a different pattern although some deposit forms during hydroperoxide decomposition.

Figure 18 - The deposit maxima for 2 fluids with 3 metals are summarized and compared with hydroperoxide concentrations. Deposit formation for the stainless steels coincides with the temperatures of maximum ROOH concentration and/or ROOH depletion. Since the free radical concentration is relatively high at these temperatures, we propose that reactions forming solids are associated with free radical reactions. The inadequate evaluation of deposit quantitation may limit the application of these relationships to single fuel metal systems.

III. CHARACTERIZATION OF DEPOSITS

Figure 19 - NRL has also approached the fuel deposit mechanism from the deposit end by use of both qualitative and quantitative techniques. ESCA and Auger analyses have not been very informative. Ellipsometry is questionable as a quantiattive tool because a deposit which adsorbs light requires an absorption coefficient in the thickness calculation. Pyrolysis GC will be tried in the future. Elemental analysis is a marginal technique for the JFTOT tubes because of inadequate sample. However, this analysis has been useful when applied to deposits formed in other devices run for much longer times.

Figure 20 - Tomcat (F-14) heat exchanger tubes have been used at NAPTC in lube oil/fuel heat exchange tests. These 1/8 inch O.D. tubes have been cut into segments and cleaned to remove any lube deposit on the exterior. The resulting stainless steel specimens have been analyzed for the elemental composition of the organic fuel derived deposit on the interior.

Carbon, hydrogen, and nitrogen can be determined simultaneously on a segment but oxygen and sulfur require separate segments. An increasing trend is observed for all elements going from the cool end (fuel in) to the hot end. The data also indicates that with this experiment, more deposit is laid down on those segments to which fins had been welded. This latter phenomenon was observed in several tests.

Figure 21 - Atom ratios for the segments from 4 tests were calculated. The concentration of hetero atoms in the deposits is remarkable. The amount of nitrogen in the deposits, 1 atom or greater for each 10 carbon atoms in three of the tests, is surprising for these petroleum derived fuels. The amount of nitrogen in the total tube deposits, however, amounts to only 0.01 ppm of the total fuel flow.

The oxygen/carbon ratios are also very high, particularly for Tube B. The hydrogen/carbon ratios indicate the deposit tends toward an aromatic structure. Tube B again appears to be a maverick. Some absorption of water into the polar organic deposit seems likely for Tube B. Organic dibasic acids, i.e., phthalic acid, have an O/C atom ratio of 0.5. Consequently, oxygen contents of this magnitude may reflect a reasonable deposit composition.

Figure 22 - Deposits on heat exchanger tubes stressed in the AF simulator have also been examined at NRL. For these analyses the fuel derived varnish was removed from the steel tube. Atom ratios found for 7 different fuel tests fell

in a narrow range for H/C and N/C. The O/C ratio was relatively high except for AFFB-11 and -12, which are high stability JP-7. The low H/C values indicate a concentration of aromatic species in the deposit. The N/C and O/C values are generally lower than those found for the NAPTC heat exchanger deposits.

Figure 23 - Compounds in jet fuels which contain heteroatoms make a major contribution to deposit formation.

Further, these compounds appear to be highly aromatic. These two findings are also characteristic of gums formed from fuels during low temperature storage. The limited amount of dissolved oxygen available for reaction with a fuel in a flow system is insufficient to form the extensively oxidized products found in thermal deposits. Rather, the high oxygen content in deposits suggests that partially oxidized compounds in a fuel are easily attacked and further oxidized by dissolved oxygen as the fuel is thermally stressed.

JFTOT MODIFICATIONS

- 1000 PSI CAPABILITY
- 1000 °F CAPABILITY
- TEST SECTION - 5 INCH HEATED LENGTH
- STAINLESS STEEL TUBES - 316 AND 304
- SAMPLE TAKEOFF TO GC
  - BEFORE TEST SECTION
  - AFTER PUMP
- IMPROVED TEST SECTION SEALS
- T/C IN LIQUID AT TEST SECTION EXIT
- STRAIN GAUGE PRESSURE TRANSDUCER

Figure 1

GAS CHROMATOGRAPH FEATURES

- LIQUID SAMPLING - 10 MICROLITERS
- DUAL DETECTORS
  - ~~HELIUM~~ IONIZATION (O_2, N_2, H_2, CO, CH_4, C_2H_6)
  - FLAME IONIZATION (HYDROCARBONS)
- DUAL COLUMNS - SERIES OR PARALLEL
- COLUMN BACK FLUSH

Figure 2

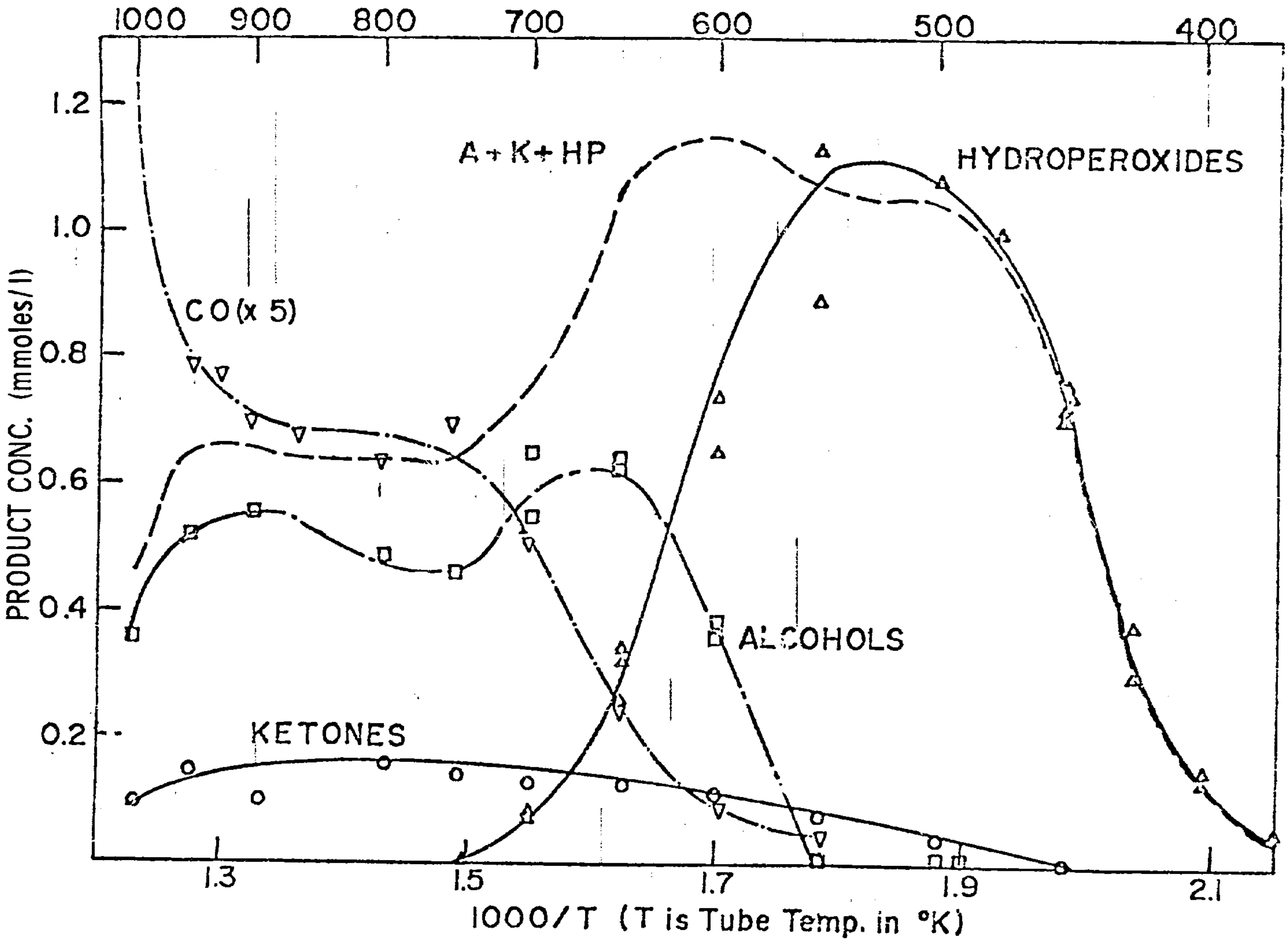
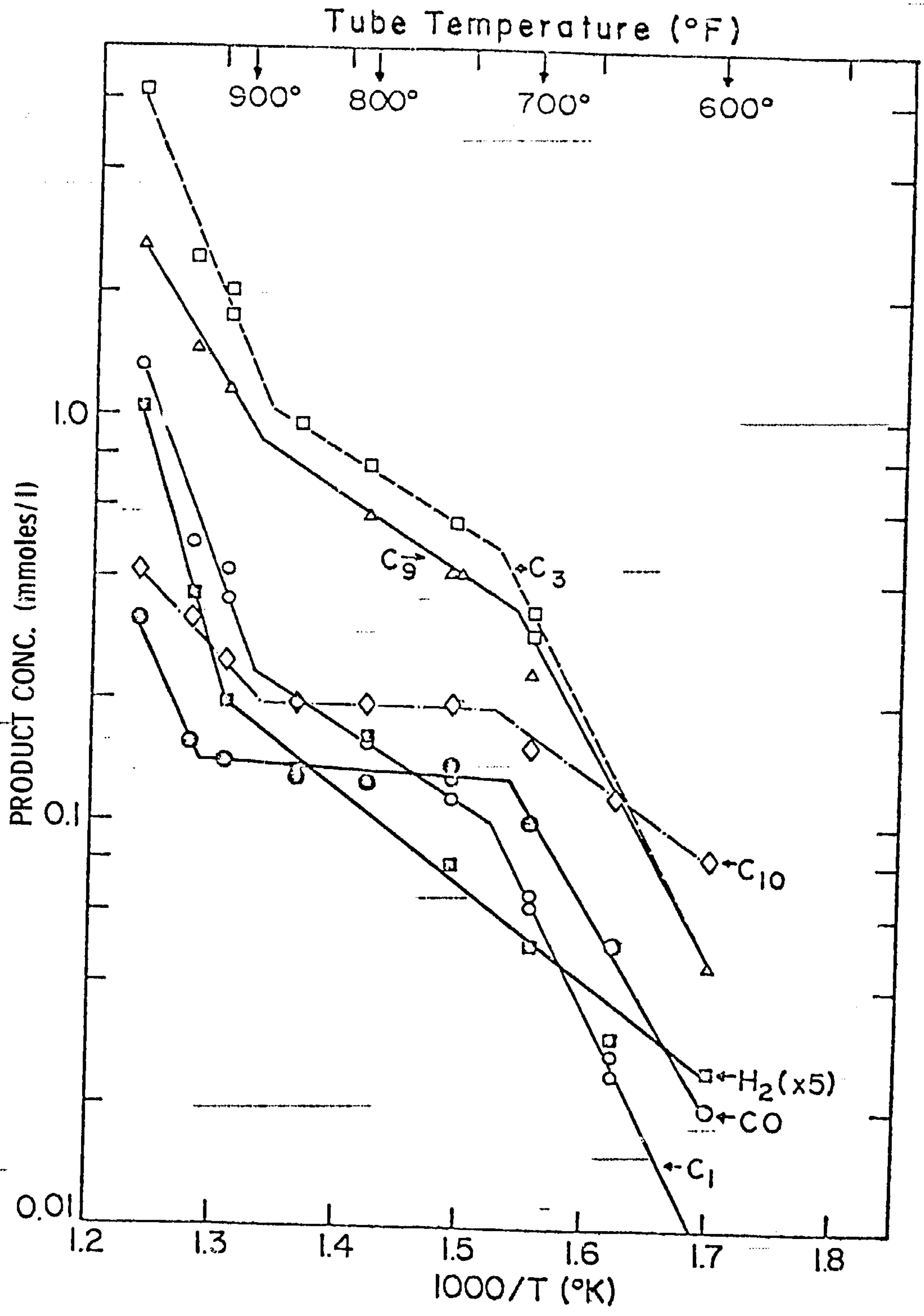

1000
900
800
700
600
500
400
1.2
1.0
0.8
0.6
0.4
0.2
PRODUCT CONC. (mmoles/l)
A+K+HP
HYDROPEROXIDES
CO(x 5)
ALCOHOLS
KETONES
1.3
1.5
1.7
1.9
2.1
1000/T (T is Tube Temp. in °K)

Figure 3



Tube Temperature (°F)
900°
800°
700°
600°
PRODUCT CONC. (mmoles/l)
1.0
0.1
0.01
C_9
C_3
C_{10}
H_2(x5)
CO
C_1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1000/T (°K)

Figure 4

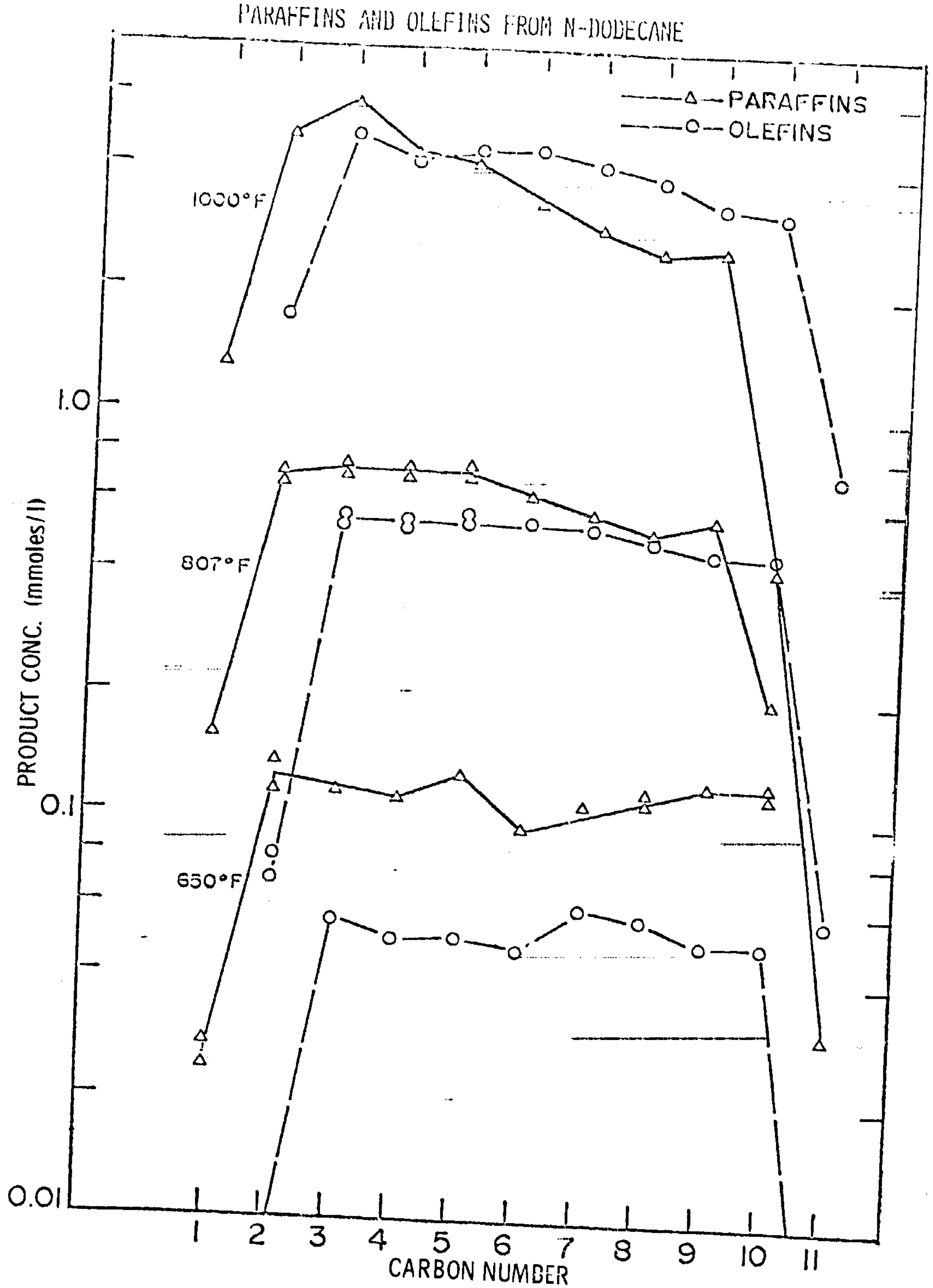

PARAFFINS AND OLEFINS FROM N-DODECANE
PARAFFINS
OLEFINS
1000°F
807°F
650°F
PRODUCT CONC. (mmoles/l)
1.0
0.1
0.01
1
2
3
4
5
6
7
8
9
10
11
CARBON NUMBER

Figure 5

EFFECT OF OXYGEN ON SMALL HYDROCARBON PRODUCTION FROM DODECANE

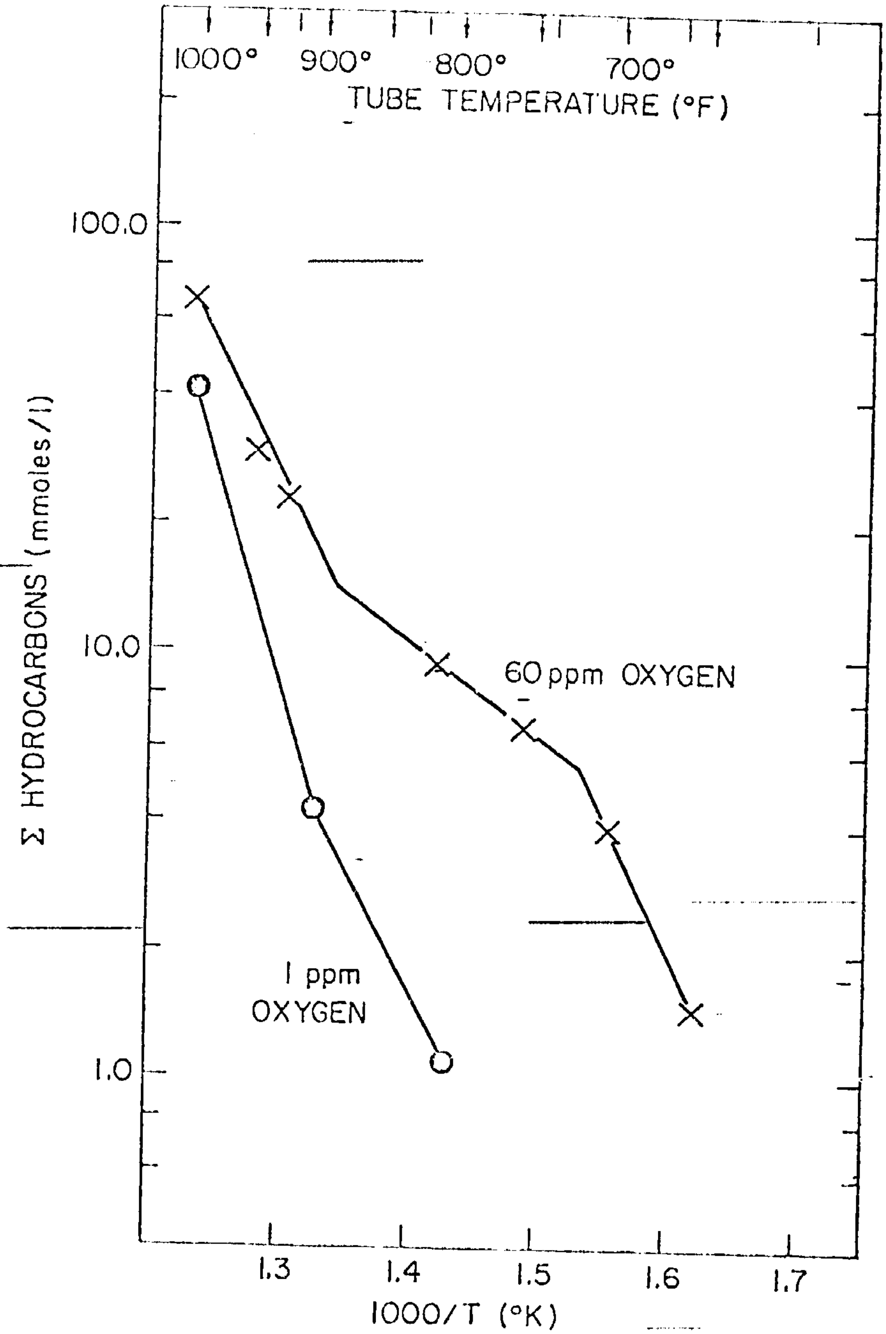


Figure 6

PYROLYSIS OF N-DODECANE
FABUSS-SMITH-SATTERFIELD MECHANISM

INITIATION $\quad R\text{-}H + X\cdot \longrightarrow R\cdot\ (sec) + XH$

PROPAGATION

$$\left\{\begin{array}{l} R\cdot\ (sec) \xrightarrow{\beta\text{-scission}} \text{1-OLEFIN} + R'\cdot\ (pri) \\ R'\cdot\ (pri) + R\text{-}H \xrightarrow[\text{transfer}]{\text{hydrogen}} R'\text{-}H \begin{pmatrix}\text{smaller} \\ \text{n-alkane}\end{pmatrix} + R\cdot\ (sec) \end{array}\right.$$

NET $\quad 2\,R\text{-}H + X\cdot \longrightarrow \text{1-OLEFIN} + R'\text{-}H + XH + R\cdot\ (sec)$

PREDICTIONS—EQUAL AMOUNTS OF INTERMEDIATE SIZE HYDROCARBONS

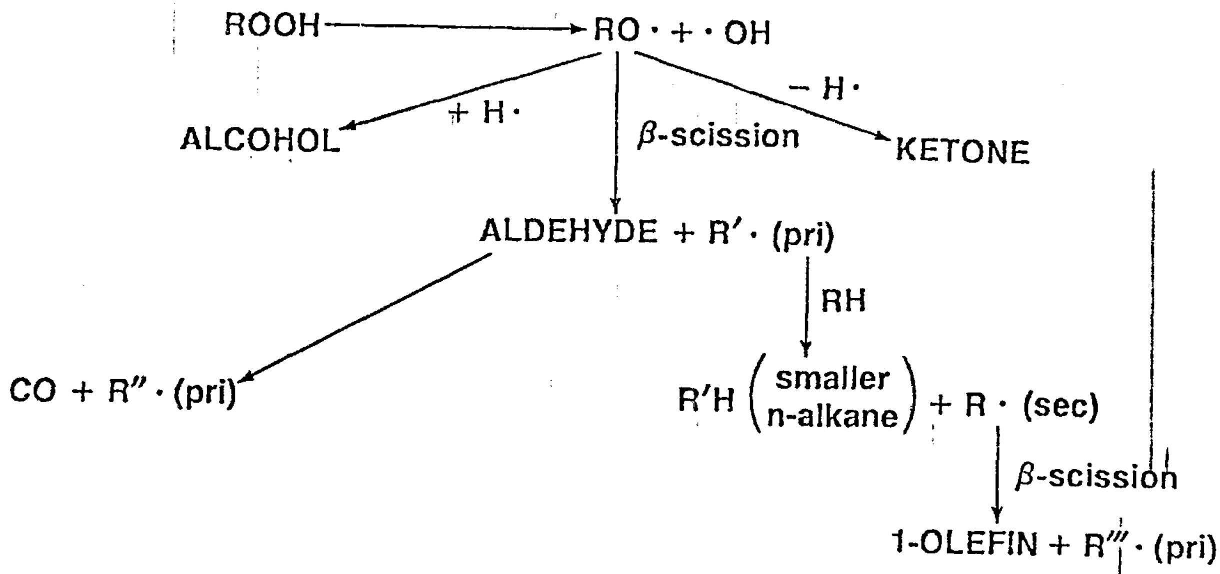
—LOW YIELDS OF METHANE, ETHYLENE, N-DECANE, N-UNDECANE, AND 1-UNDECENE

—SINGLE STEP PROCESS AND MINIMAL RADICAL ISOMERIZATION BECAUSE OF HIGH PRESSURE

Figure 7

NRL

HYDROPEROXIDE THERMOLYSIS



PREDICTIONS—EQUAL AMOUNTS OF INTERMEDIATE SIZE HYDROCARBONS
—LOW YIELDS OF METHANE, ETHYLENE, N-UNDECANE AND 1-UNDECENE
—N-DECANE FAVORED OVER OTHER N-ALKANES
—N-ALKANES FAVORED OVER 1-OLEFINS

Figure 8

NRL

EFFECT OF METALS ON PRODUCT FORMATION

MAX. TUBE TEMP—°F (°C)	METAL	PRODUCT (MMOL/L)		
		H_2	CO	C_2H_6
600 (316)	316 S.S.	0.005	0.020	0.046
	304 S.S.	0.010	0.020	0.040
	Al	0.005	0.023	0.062
800 (427)	316 S.S.	0.033	0.128	0.700
	304 S.S.	0.030	0.130	0.740
	Al	0.020	0.122	0.680

Figure 9

NRL

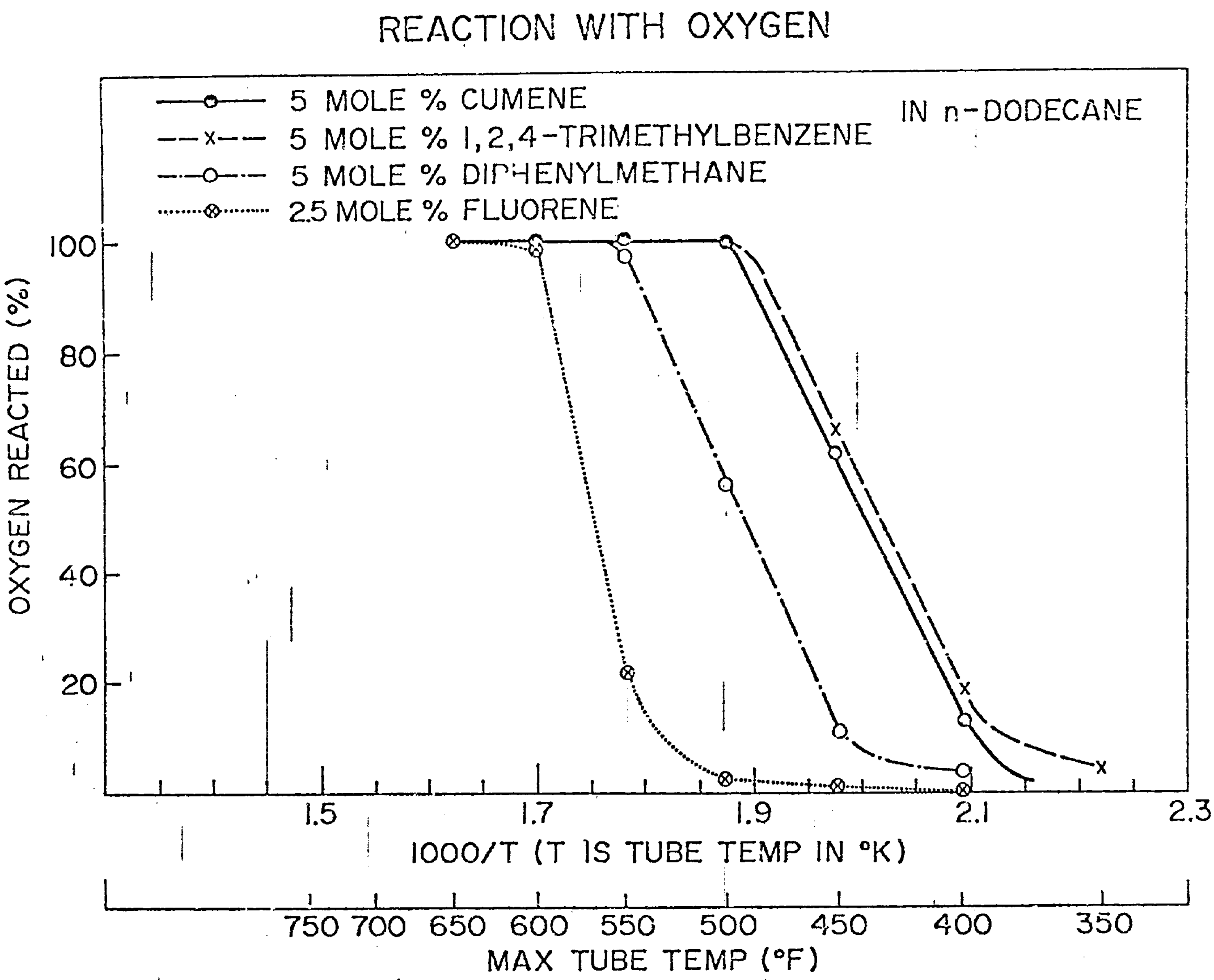

REACTION WITH OXYGEN
5 MOLE % CUMENE
5 MOLE % 1,2,4-TRIMETHYLBENZENE
5 MOLE % DIPHENYLMETHANE
2.5 MOLE % FLUORENE
IN n-DODECANE
OXYGEN REACTED (%)
100
80
60
40
20
1.5
1.7
1.9
2.1
2.3
1000/T (T IS TUBE TEMP IN °K)
750 700 650 600 550 500 450 400 350
MAX TUBE TEMP (°F)

Figure 10

REACTIVITY WITH DISSOLVED OXYGEN

ADDITIVE*	CONCENTRATION	TEMPERATURE**
NONE	5.0 MOLE %	437°F
CUMENE	"	434
INDANE	"	435
N-PROPYLBENZENE	"	436
CYCLOHEXYLBENZENE	"	437
1–ETHYL–2–METHYLBENZENE	"	440
1, 2, 4–TRIMETHYLBENZENE	"	440
2–METHYLNAPHTHALENE	"	457
TETRALIN	"	457
DIPHENYLMETHANE	"	494
INDENE	"	530
FLUORENE	1.0 MOLE %	532
FLUORENE	2.5 "	568

*DISSOLVED IN N-DODECANE

**TEMPERATURE AT WHICH 1/2 OF DISSOLVED OXYGEN (60 PARTS PER MILLION OR 1.8 MILLIMOLES/LITER) HAS REACTED IN THE NRL JFTOT; 5 INCH 316S.S. TUBE

Figure 11

TOTAL HYDROCARBON PRODUCTS FROM JFTOT*

SAMPLE	650°F	700°F	800°F	900°F
DODECANE	1.45	3.95	11.25	28.63
+ 1 MOLE % FLUORENE	0.50	1.18	2.21	30.55
+ 5 MOLE % DIPHENYLEMETHANE	–	1.73	4.07	–
+ 5 MOLE % 2-METHYL NAPHTHALENE	–	3.08	7.71	–
+ 5 MOLE % INDANE	–	1.12	2.63	–
+ 5 MOLE % TETRALIN	–	1.11	2.59	–

*MILLIMOLES/LITER
DISSOLVED OXYGEN CONTENT–1.8 MMOLES/L
316 S.S. TUBES (5 INCH)

Figure 12

EFFECT OF TEMPERATURE ON OLEFIN/PARAFFIN PRODUCT RATIO

TEMP. (°F)	RATIO OF OLEFIN TO PARAFFIN	
	DODECANE	+ 1 MOLE % FLUORENE
650	0.44	0.16
700	0.62	0.25
750	0.71	0.34
800	0.77	0.48
850	0.79	0.79
900	0.86	0.87

*316 S.S. TUBES (5 INCH)

Figure 13

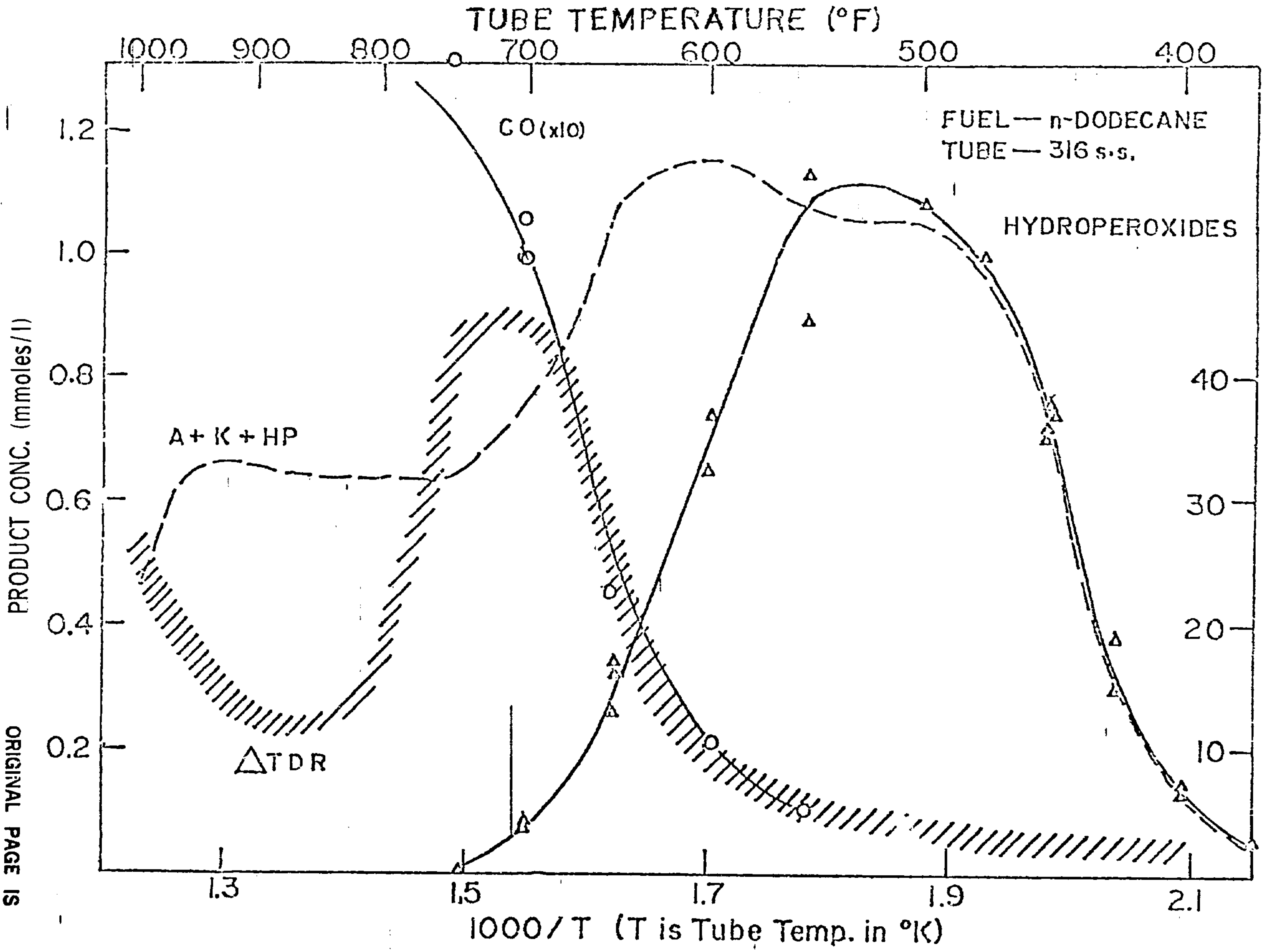


Figure 14

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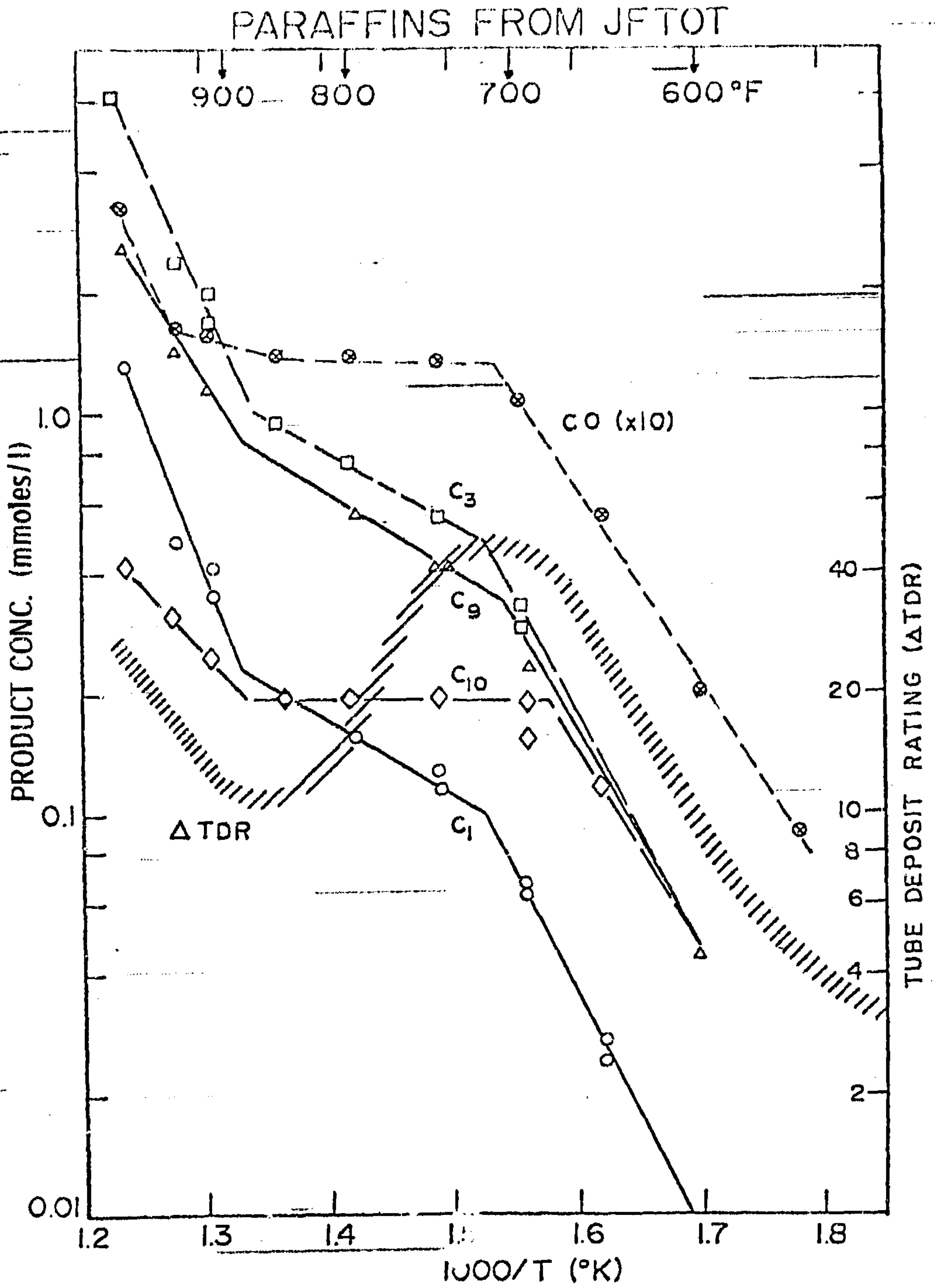


PARAFFINS FROM JFTOT
900
800
700
600°F
CO (x10)
C_3
C_9
C_{10}
C_1
ΔTDR
PRODUCT CONC. (mmoles/l)
1.0
0.1
0.01
TUBE DEPOSIT RATING (ΔTDR)
40
20
10
8
6
4
2
1.2
1.3
1.4
1.6
1.7
1.8
1000/T (°K)

Figure 15

OXYGENATED PRODUCTS AND TUBE DEPOSITS

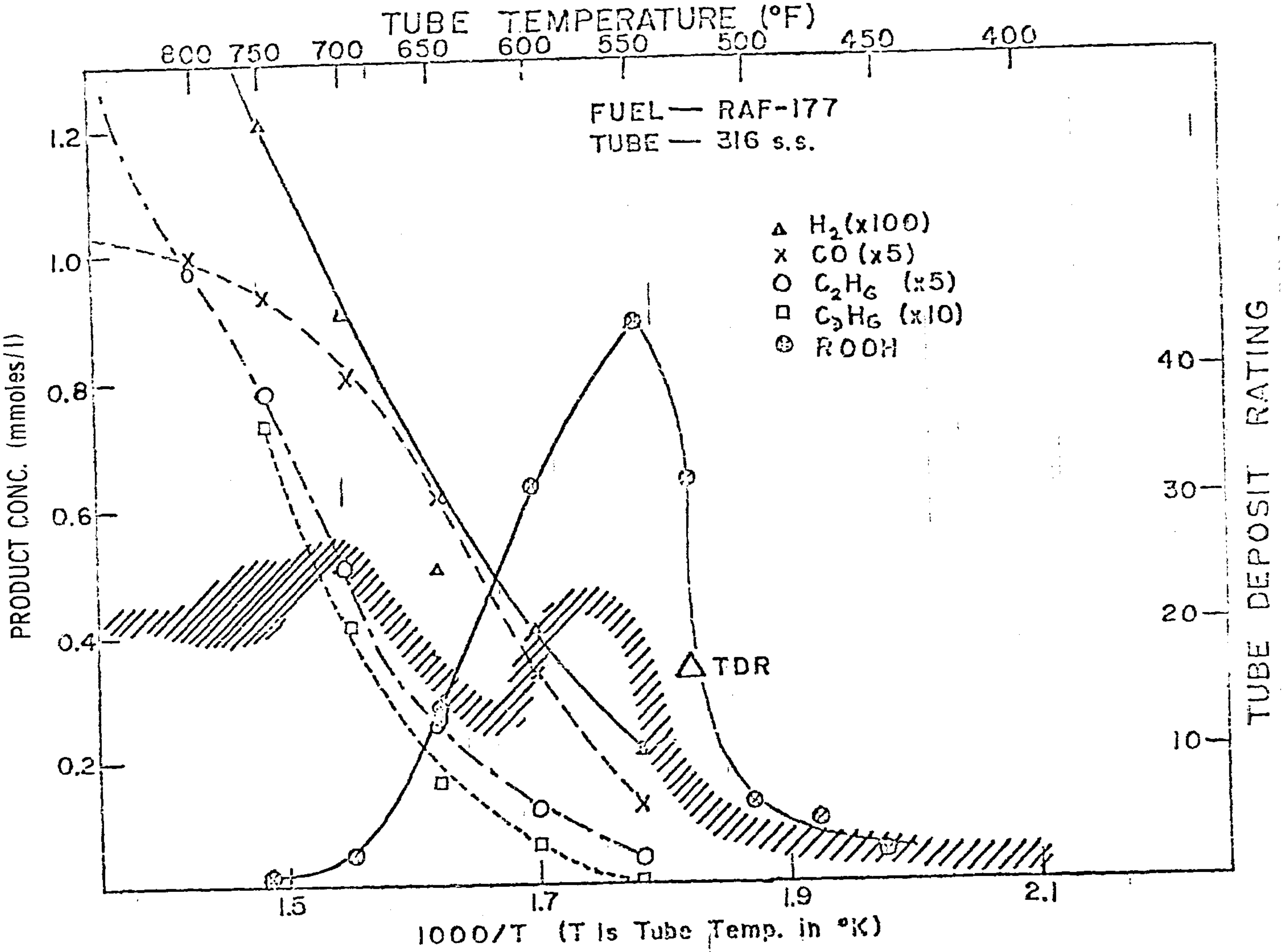
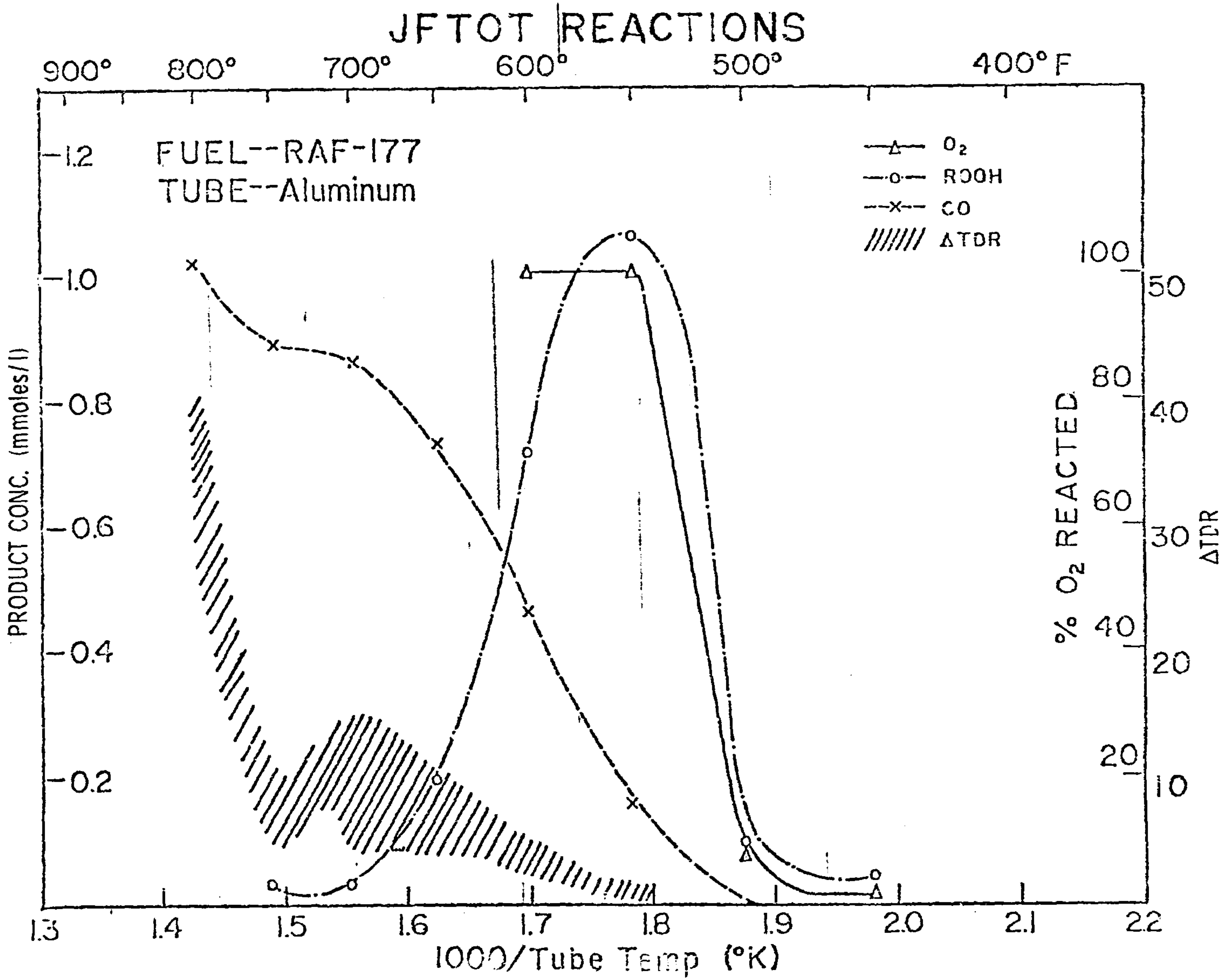


Figure 16



JFTOT REACTIONS
900°
800°
700°
600°
500°
400° F
FUEL--RAF-177
TUBE--Aluminum
O2
ROOH
CO
ΔTDR
PRODUCT CONC. (mmoles/l)
1.2
1.0
0.8
0.6
0.4
0.2
% O2 REACTED
100
80
60
40
20
50
40
30
20
10
ΔTDR
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
1000/Tube Temp (°K)

Figure 17

DEPOSIT MAXIMA FOR HEATER TUBES

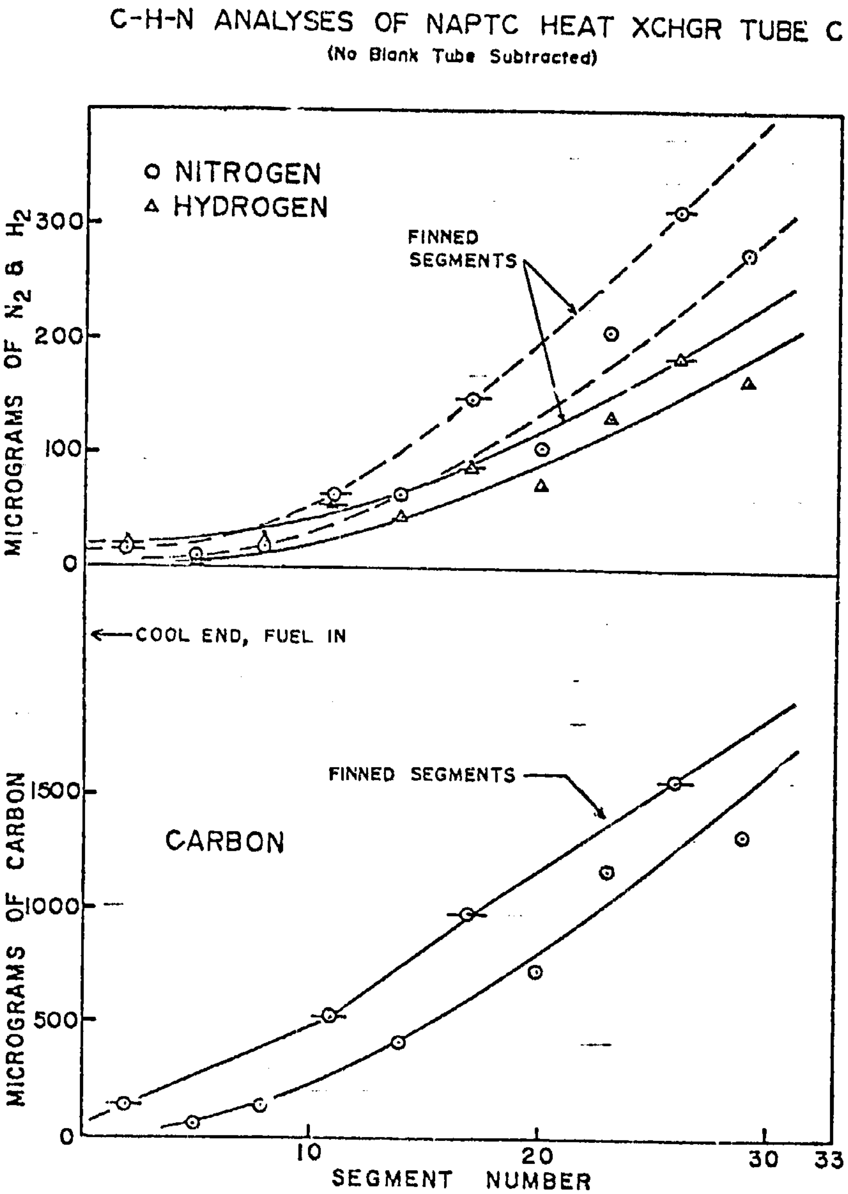
	N-DODECANE	RAF-177
ALUMINUM	700°F(?) > 800	700°F > 800
304 STAINLESS	700 > 900	560 710(?) 870
316 STAINLESS	720 1000	560 710
ROOH — MAXIMUM	500-525	550
DEPLETED	700	700

Figure 18

DEPOSIT EXAMINATION TECHNIQUES

METHOD	INFORMATION	COMMENTS
ESCA	ELEMENTS PRESENT CHEMICAL STRUCTURE	MARGINAL SENSITIVITY
AUGER	ELEMENTS PRESENT DEPOSIT THICKNESS	INTERPRETATION DIFFICULT
CARBON, HYDROGEN	ELEMENTAL COMPOSITION QUANTITATIVE ESTIMATE	MARGINAL SENSITIVITY
ELLIPSOMETRY	DEPOSIT THICKNESS	EXAMINE SMALL AREA
PYROLYSIS GC	CHEMICAL STRUCTURE	INCOMPLETE REACTION?

Figure 19



C-H-N ANALYSES OF NAPTC HEAT XCHGR TUBE C
(No Blank Tube Subtracted)
NITROGEN
HYDROGEN
FINNED SEGMENTS
MICROGRAMS OF N_2 & H_2
300
200
100
0
COOL END, FUEL IN
FINNED SEGMENTS
CARBON
MICROGRAMS OF CARBON
1500
1000
500
0
10
20
30
33
SEGMENT NUMBER

Figure 20

NAPTC HEAT EXCHANGER DEPOSITS

TUBE	FUEL TEMP °F—IN/OUT	ATOM RATIO H/C	N/C	O/C	S/C*
A	286/366	0.7–1.7	0.08–0.13	0.3–0.7	0.02–0.04
B	250/330	1.4–2.4	0.08–0.11	0.8–1.2	—
C	260/340	1.1–1.5	0.11–0.18	0.3–0.5	0.04–0.12
D	260/340	0.5–0.8	0.03–0.04	**	—

* LIMITED DATA FOR S/C
** DATA NOT RELIABLE

Figure 21

NRL

AIR FORCE HEAT EXCHANGER DEPOSITS

FUEL	FILM TEMP (°F-CALC.)	ATOM RATIO		
		H/C	N/C	O/C
AFFB-10	512	0.60	0.053	0.28
AFFB- 9	544	0.48	0.019	0.20
AFFB- 8	550	0.52	0.027	0.25
AFFB-16	554	0.53	0.017	0.23
AFFB-13	564	0.45	0.006	0.22
AFFB-11	665	0.57	0.005	0.22
AFFB-12	688	0.62	0.011	0.10

Figure 22

NRL

IMPLICATIONS FROM ELEMENTAL ANALYSIS OF JET FUEL THERMAL DEPOSITS

- HETEROATOMS CONCENTRATED IN DEPOSITS
- HIGH OXYGEN CONTENT DERIVED FROM OXYGEN COMPOUNDS IN STARTING FUEL
- LOW H/C RATIO INDICATES AROMATICS IN DEPOSITS
- OXIDATION REACTIONS TRIGGER INVOLVEMENT OF HETEROATOM COMPOUNDS

Figure 23

NRL

REFINING JET FUEL FOR THERMAL STABILITY

William G. Dukek

Exxon Research and Engineering Company

Routine testing of jet fuel for thermal stability evolved in the 50's when it had become evident that older tests such as Potential or Existent Gum did not predict the tendency of fuels in the high temperature environment of the engine fuel system to produce deposits. Refiners equipped themselves with the CRC ERDCO Fuel Coker subsequently standardized as ASTM D1660 to test fuels for thermal stability. In the early 70's, the scaled-down version of the Fuel Coker, the Alcor Jet Fuel Thermal Oxidation Test (JFTOT) was developed by CRC and standardized as ASTM D3241. Many, but not all, refiners replaced Fuel Cokers with JFTOT's because the latter was a shorter test that used less fuel and less manpower. Moreover, it appeared to exhibit better test precision. Specifications for U.S. commercial fuel offer the refiner the choice of either test method. Abroad most specifications have dropped the Fuel Coker and refiners have generally installed JFTOT testers.

The most significant fact to note about the thermal stability test is that the refiner does <u>not</u> tailor his processing steps to meet it (<u>VG-1</u>). His experience tells him that if he meets other critical specification requirements as dictated by the type of crude he will usually meet the pass/fail criteria of the thermal stability test. Knowing that deposits in the stability test result from traces of reactive species that occur either naturally or in basic processes such as distillation or cracking, the refiner does not make a stability rating in his crude assay cuts but instead checks refinery fuel blends prior to shipment. If one fails the test -- which is seldom -- he does not reprocess but ships the product as No. 1 fuel oil or blends it into other fuel oils. His finishing processes for jet fuel components are dictated by the needs to improve odor (i.e., remove mercaptans), to lower total sulfur (sour crude), to reduce acidity, to upgrade color or color stability (for dual purpose jet fuel/kerosene) or to remove or react aromatics and olefins (for smoke point improvement).

Refining experience with finishing processes has supported the findings of researchers in the field of oxidation stability. The marginal processes in terms of thermal stability convert thiols (mercaptans) to disulfides rather than remove them (<u>VG-2</u>). For this reason, among others, the worst of these processes -- doctor sweetening -- has largely disappeared. Instead there remain conversion processes such as air sweetening (which uses antioxidant as a catalyst), MEROX (which uses a fixed bed cobalt catalyst) and copper sweetening (which uses cupric chloride solution). Processes which actually <u>remove</u> mercaptans from the fuel tend to upgrade thermal stability. Chemical treating methods involve caustic washing usually followed by water washing and clay filtration. Mercapfining is a trade name for a mild catalytic hydrotreating step that only removes thiols leaving other sulfur compounds untouched. Operated at a somewhat higher temperature and pressure, the catalytic process is called Hydrotreating and, in fact, will remove sulfides as well as thiols.

The most severe of these finishing processes involves removal of aromatics as well as sulfur compounds and results in the greatest improvement in thermal stability. Acid treating is still employed by some refiners for this purpose. However, refiners are more apt to use extraction processes to remove aromatics. Sulfur dioxide is the usual extraction media. Alternatively, the aromatics can be hydrogenated to naphthenes by higher pressure hydrogenation.

Typical processing sequences carried out on Jet A fuel at four different refineries show application of various finishing methods on blend components (VG-3). Refinery A typically processes sour crude and employs both hydrotreating and extraction to meet mercaptan and smoke point levels. Refinery B usually processes sweet crudes and uses chemical treating methods to meet acidity. Refinery C processes Alaskan Crude and must defulfurize; aromatics are usually critical. Refinery D is usually mercaptan limited and uses both chemical and hydrogen methods. In no case is thermal stability the limiting property.

The only examples of refinery processing dictated by thermal stability derive from special purpose military fuels (VG-4). JP-4 is usually mercaptan limited and processed by both chemical and hydrogen methods. JP-7, on the other hand, requires considerable additional processing such as aromatics extraction to meet the Luminometer Rating. In so doing, thermal stability is upgraded from a 260°C JFTOT breakpoint to an estimated 370°C JFTOT breakpoint (JP-7 requires a Research Coker Thermal Stability Test). One special fuel called Thermally Stable Kerosene is manufactured to an estimated 320°C JFTOT breakpoint (the specification requires a D 1660 Fuel Coker Test) by blending a highly processed component with a conventionally processed fraction. It turns out to be the only product that is specifically limited by its thermal stability requirement.

THERMAL STABILITY IS THE BY PRODUCT OF TYPICAL REFINERY JET FUEL PROCESSING

- STABILITY RATING IS NOT A BASIC ASSAY TEST
- OXIDATION INSTABILITY RESULTS FROM REACTIVE SPECIES
  - MERCAPTANS (SOUR CRUDES)
  - DIOLEFINS AND OLEFINIC AROMATICS
  - N, S, OR O COMPOUNDS
- PROCESSING IS CARRIED OUT FOR SPECIFIC REASONS
  - ODOR IMPROVEMENT (MERCAPTANS)
  - SULFUR REDUCTION
  - REDUCE ORGANIC ACIDITY
  - REMOVE COLOR BODIES
  - SATURATE OLEFINS (GUM)
  - AROMATIC REMOVAL
- MOST PROCESSING UPGRADES OXIDATION STABILITY

  EXCEPTION: MERCAPTAN COVERSION TO DISULFIDES
- BLENDS THAT FAIL JFTOT OR COKER TS TESTS ARE SOLD AS NO. 1 FUEL OIL

COMPARISON OF REFINERY FINISHING PROCESSES FOR JET FUEL

(LISTED ORDER CORRESPONDS TO INCREASING STABILITY IMPROVEMENT)

PROCESS	PRINCIPLE	ADVANTAGE	DISADVANTAGE
MERCAPTAN CONVERSION ($RSH \rightarrow RSSR$)			
1. AIR SWEETENING	O_2 AND NaOH	• LOW	• CONTROL • EFFLUENTS • NO S REDUCTION
2. MEROX	OXIDATION WITH CO CATALYST	• LOW COST • NEW-SIMPLE	
3. COPPER SWEETENING	OXIDATION WITH LIQUID $CuCl_2$	• LOW COST	• Cu CARRYOVER
MERCAPTAN REMOVAL			
4. CAUSTIC WASH	$RSH \rightarrow Na\ SR\downarrow$	• LOW COST	• EFFLUENT
5. MERCAPFINING	$RSH + H_2 \rightarrow H_2S\uparrow$ (CATALYST)	• LOW TEMP AND PRESS.	• HIGH CAPITAL COST
6. HYDROTREATING	$RSH + RSR + H_2 \rightarrow H_2S\uparrow$ (CATALYST)	• MOD. TEMP. AND PRESS.	• EXPENSIVE • H_2 SUPPLY
AROMATICS REMOVAL			
7. ACID TREATING	 $+ H_2SO_4 \rightarrow$ SLUDGE	REMOVE MOST REACTIVE SPECIES AND COLOR BODIES	• EXPENSIVE • EFFLUENTS • SLUDGE
8. EXTRACTION	 $+ SO_2 \rightarrow$ EXTRACT	REMOVES AROMATICS AND S CPDS	• EXPENSIVE • REGENERATION
9. HYDROGENATION	 $+ H_2 \rightarrow$  (CATALYST)	HIGH TEMP AND PRESS.	• EXPENSIVE • H_2 MFG ROAD

TYPICAL REFINERY PROCESSING FOR JET A FUEL

REFINERY CRUDE SOURCES STREAMS	A DOM SOUR/IMP 1	A DOM SOUR/IMP 2	A DOM SOUR/IMP 3	A DOM SOUR/IMP 4	B DOM SWT/IMP 1	B DOM SWT/IMP 2	B DOM SWT/IMP 3	C N. SLOPE 1	D DOM/IMP 1	D DOM/IMP 2
JET FUEL FINISHING										
PS		X							X	
CW-WW-CF					X	X		X		X (MF)
HT-CW-CF	X	X	X							
AT-CF							X			
EX-CF				X						
LIMITING PROPERTIES	AROMATICS RSH				ACIDITY AROMATICS			SULFUR AROMATICS	RSH	

CW = CAUSTIC WASH
WW = WATER WASH
CF = CLAY FILTRATION
MF = MERCAPFINING
HT = HYDROTREATING

AT = ACID TREATING
EX = AROMATICS EXTRACTION
PS = PARAFFIN SEPARATION

PROCESSING OF MILITARY JET FUELS

FUEL GRADE	JP-4		JP-7	KEROSENE	
MIL SPEC	5624K		38219	25524B	
THERMAL STABILITY REQUIREMENT AS JFTOT BREAKPOINT, °C	260		(370)	(320)	
PROCESSING	1	2	1	1	2
CW-WW-CF	X				
EX			X	X	
HT		X	X	X	X
RD			X	X	
AD			X	X	
LIMITING PROPERTY	RSH		LN	$\boxed{\text{TS}}$	

CW-WW-CF = CAUSTIC/WATER WASH - CLAY FILTER
EX = AROMATICS EXTRACTION
HT = HYDROTREATING
RD = REDISTILLATION
AD = ADDITIVES

FUEL THERMAL STABILITY/ENGINE TRENDS

Allyn R. Marsh

Pratt & Whitney Aircraft Group

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FUEL THERMAL STABILITY AFFECTS MAINTENANCE COSTS

Fact

The aviation gas turbine "Hot Section" is:

- Costly to manufacture
- Costly to maintain
- Vulnerable to premature deterioration due to inadequacies in jet fuel thermal stability

Inadequate thermal stability causes engine fuel system fouling/coking which disrupts normal fuel distribution and engine hot section temperature profiles.

Conclusion

Thermal stability is the most important jet fuel property considering impact on engine maintenance cost.

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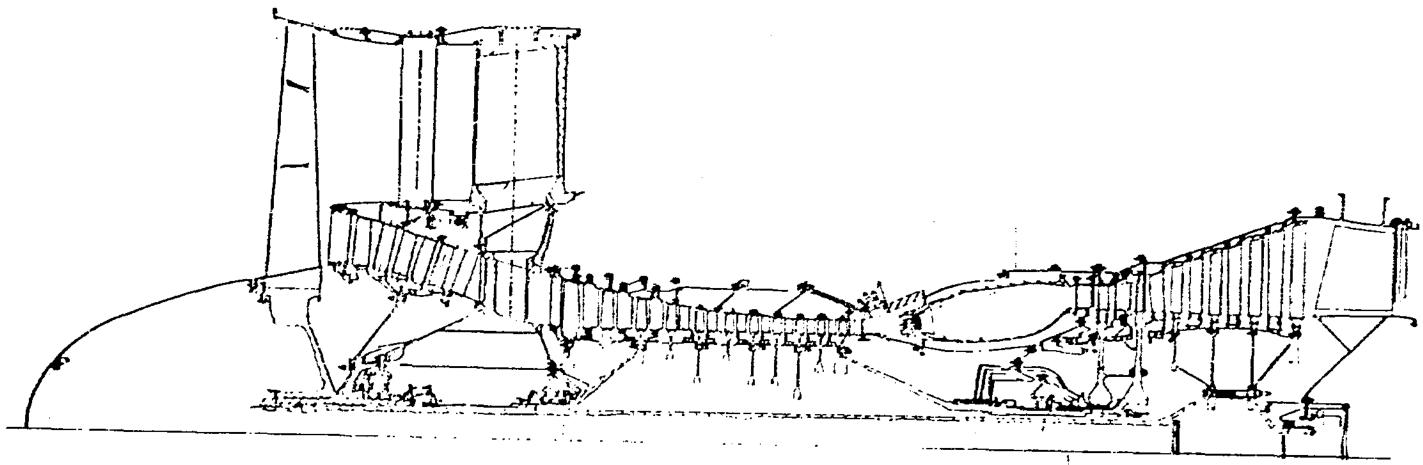
AVIATION TURBINE ENGINE



HOT SECTION PARTS SUBJECT TO FUEL PROPERTY EFFECTS

- Fuel nozzles and supports
- Burners and transition ducts
- Turbine foils, seals and disks

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EVOLUTION/TREND IN AVIATION
TURBINE ENGINE DESIGN AND PERFORMANCE

(Compared at altitude max. cruise conditions)

Engine model	Time	Fan to core by pass ratio	Core compression ratio	Relative fuel consumption	Compressor discharge temperature
JT4-11	(1958)	0/1	12.5/1	1.000	555°F
JT3D-7		1.38/1	14.8/1	0.848	568°F
JT8D-9		0.95/1	17.4/1	0.856	668°F
JT8D-17	20 years	0.99/1	17.7/1	0.888	688°F
JT9D-7A		5.13/1	24.7/1	0.706	771°F
JT9D-7F		4.99/1	25.6/1	0.693	784°F
JT9D-70A	(1978)	4.65/1	27.6/1	0.698	811°F
JT10D	12 years	6.15/1	30.9/1	0.642	848°F
E^3	(1990)	6.55/1	38.6/1	0.586	898°F

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TREND IN HOT SECTION TO TOTAL ENGINE MANUFACTURING COST

	Burner, trans. duct, fuel nozzles & supports	High & low pressure turbine w/o cases and shafts	Total-Hot Section
JT3D-7	5.8%	15.4%	21.2%
JT8D-9	3.7%	17.6%	21.3%
JT8D-17	4.3%	20.8%	25.1%
JT9D-7	2.5%	23.9%	26.4%
JT9D-7F	2.6%	27.0%	29.6%
JT9D-70	2.9%	28.9%	31.8%

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TREND IN HOT SECTION MAINTENANCE COST

(Shown as % of total engine maintenance material cost)

Engine model	Burner section	High & low turbine section	Total-Hot section
JT3D	1.2%	13.5%	14.7%
JT8D-7,-9	1.2%	19.8%	21.0%
JT8D-17	1.1%	26.3%	27.4%
JT9D	3.4%	46.6%	50.0%

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P&WA COMMERCIAL ENGINE EXPERIENCE BASE

	Operating engines *1	Years of experience *2	Engine hours per year *3
JT4	600	20	2,200,000
FT4(Industrial)	1,070	15	6,300,000 hrs (total-all years)
JT3D	4,200	17	15,000,000
JT8D	7,750	14	17,000,000
JT9D	1,300	8	4,800,000
Totals	14,920		39,000,000

*1 Installed active engines - excludes military

*2 Commercial & Industrial

*3 Commercial engine hours-current annual rate excluding industrial

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FACTORS INFLUENCING AVIATION TURBINE ENGINE HOT SECTION LIFE

- Design maturity
- Engine maintenance/engine condition/component efficiencies
- Engine operational variables
- Fuel thermal stability
  - Actual stability level at airport
  - Specification pass-fail test level at refinery

Abnormal or unfavorable variations in temperature level and/or pattern is a principal common denominator to all factors influencing hot section life

J20003-8
R783010

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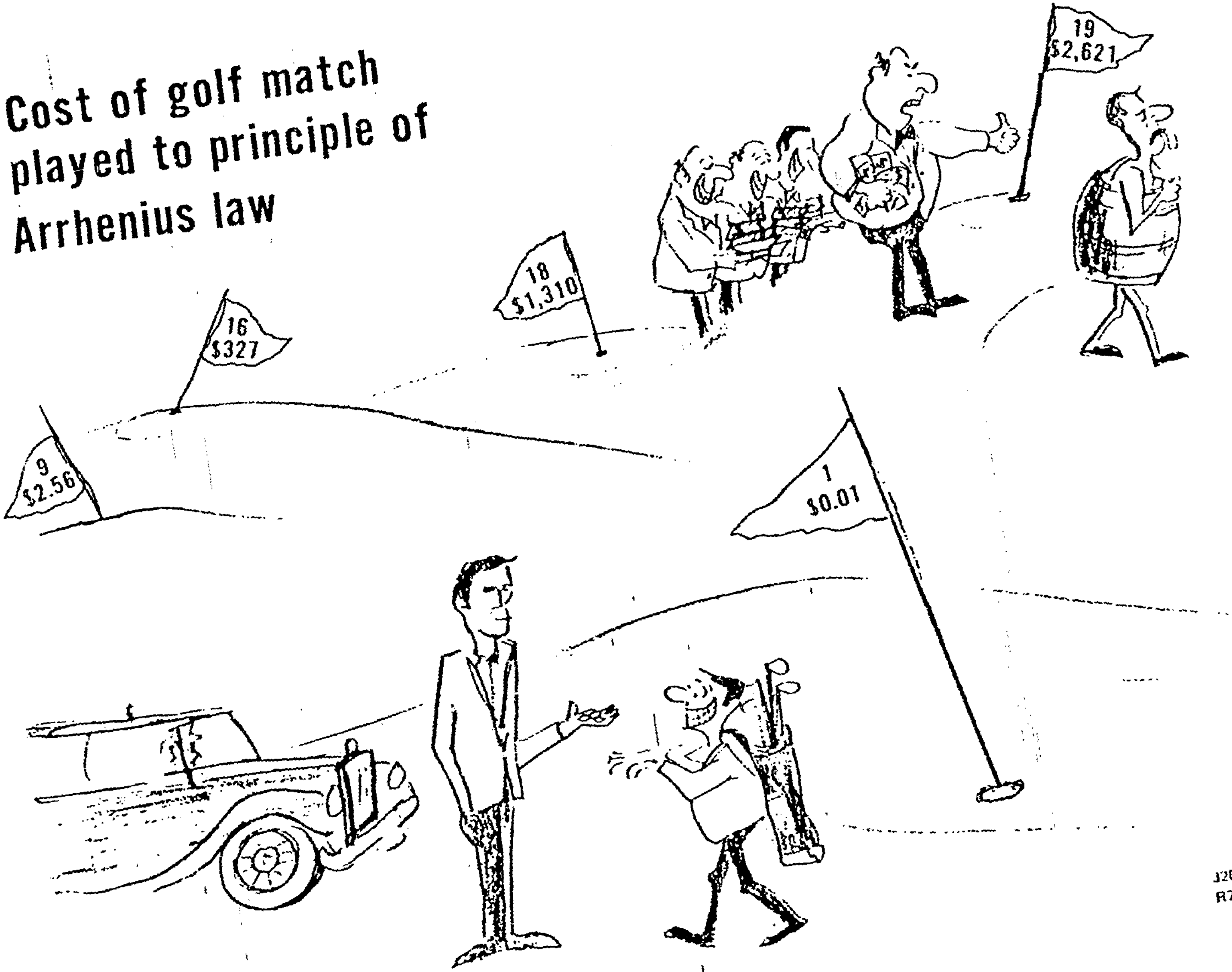
Cost of golf match played to principle of Arrhenius law



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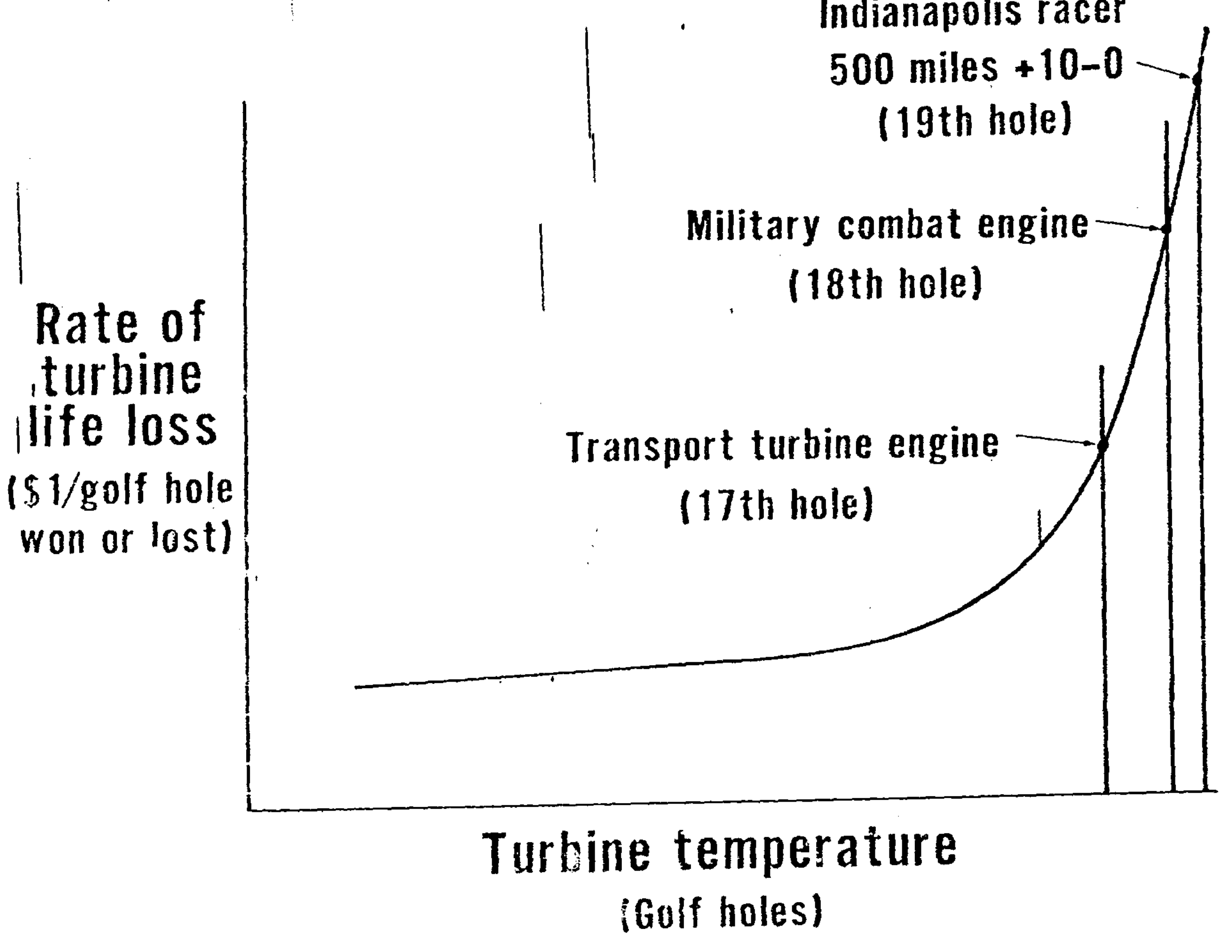
R7830

EFFECT OF TEMPERATURE ON TURBINE LIFE

(Principle of Arrhenius law applied to turbine life)



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HOT SECTION COMPONENTS ARE SUBJECT TO FOUR MODES OF THERMAL DETERIORATION

- Creep/stress rupture
- Low cycle fatigue
- Oxidation
- Corrision

All modes are destructive, subject to the principles of Arrhenius law, and tend to accelerate by self generating mechanisms

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AVIATION TURBINE ENGINE TRENDS VERSUS AVIATION FUEL TRENDS

Engine trends

- By pass ratio — Increasing
- Compression ratio — Increasing
- Fuel efficiency — Increasing
- Severity of fuel thermal enviornment in hot section — Increasing
- Cost of hot section — Increasing
- Maintenance cost of hot section — Increasing
- Allowable exhaust emissions — Decreasing

Fuel trends

- Cost — Increasing
- Combustion quality — Decreasing
- Thermal stability — Decreasing

Conclusions

- Fuel quality trends are not fully compatable with engine trends and user expectations
- Adequate fuel thermal stability is vital to the attainment of engine design, performance and cost objectives and to user expectations

J20003–10
781810

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2 OF 2

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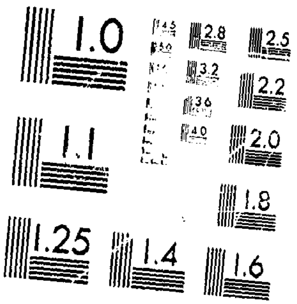


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

THERMAL STABILITY ACTIVITIES

Maurice W. Shayeson

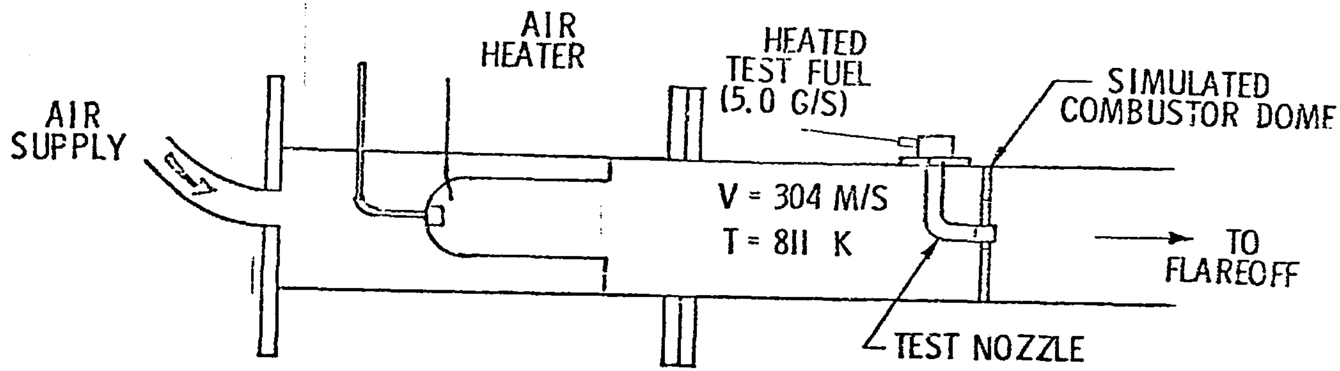
General Electric Company

C-2

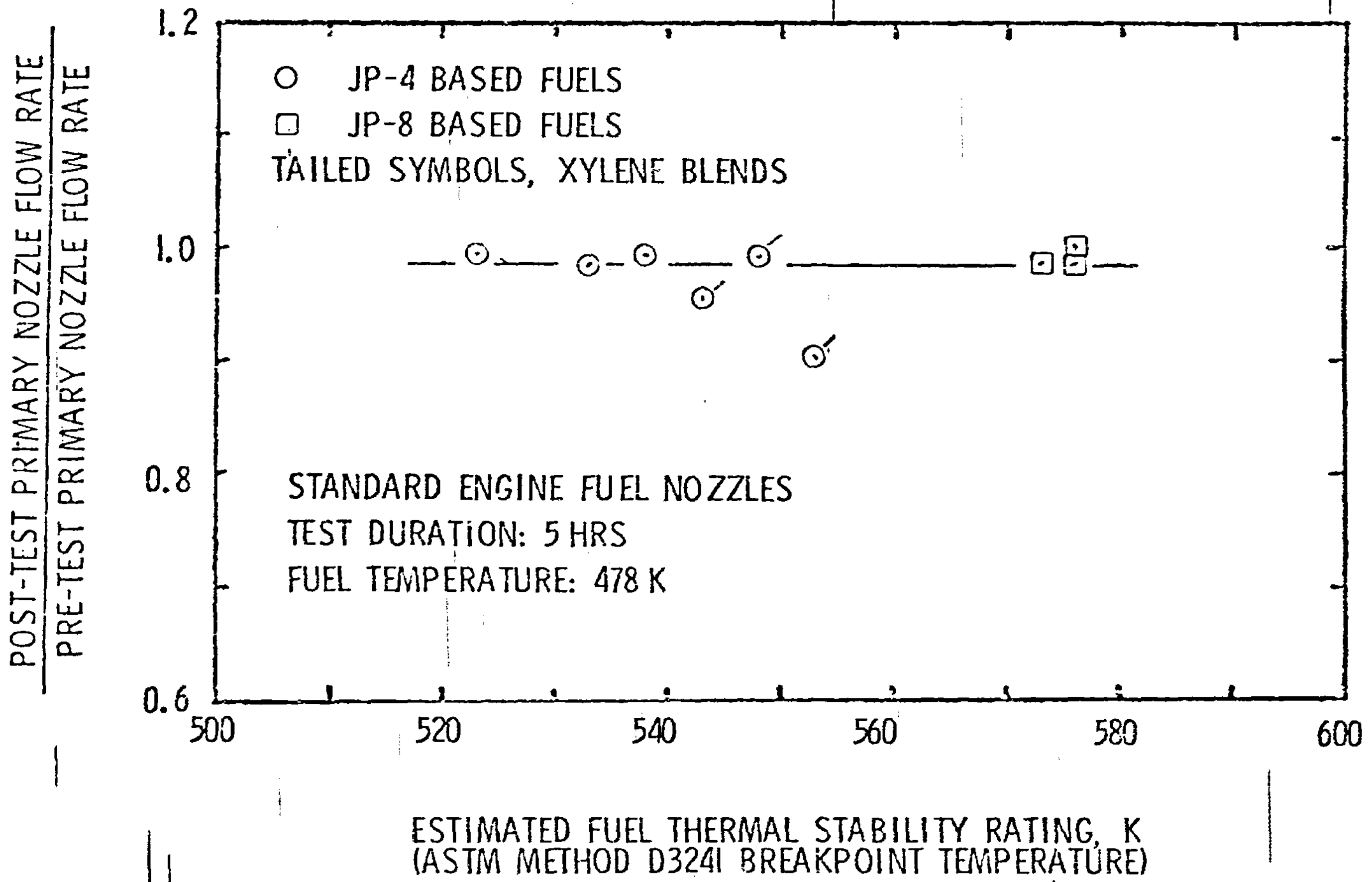
THERMAL STABILITY RATINGS OF TEST FUELS

FUEL NUMBER	COMPOSITION	JFTOT BREAKPOINT, °C
1	JP-4	260 ± 15
2	JP-8	303 ± 28
3	JP-8 + WHITE OIL	303 ± 8
4	JP-8 + NAPHTHALENES	280 ± 20
5	JP-8 + XYLENE	285 ± 25
6	JP-8 + MORE XYLENE	275 ± 35
7	JP-8 + LESS NAPHTHALENES	300
8	JP-4 + NAPHTHALENES	265 ± 15
9	JP-4 + LESS NAPHTHALENES	250 ± 10
10	JP-4 + XYLENE	280
11	JP-4 + LESS XYLENE	275 ± 5
12	JP-4 + XYLENE AND WHITE OIL	270

FUEL NOZZLE FOULING TEST SETUP



EFFECT OF FUEL THERMAL STABILITY RATING ON J79 FUEL NOZZLE FOULING TENDENCY



JP-4 SAMPLES FROM GE

	BREAKPOINT	FAILURE MODE
TEXACO	265 °C	TUBE
EXXON	250 °C	TUBE & ΔP
ALCOR	240 °C	ΔP
DUPONT	< 260 °C, 260 °C	ΔP, ΔP
NRL	260 °C	TUBE & ΔP
ASHLAND	265 °C	TUBE & ΔP
W-PAFB (UNLINED SAMPLE CONTAINER)	260 °C	TUBE
W-PAFB (LINED SAMPLE CONTAINER)	265 °C	TUBE

JP-4 SAMPLES FROM W-PAFB

	BREAKPOINT	FAILURE MODE
TEXACO	265 °C	TUBE
EXXON	NO SAMPLE	--
ALCOR	260 °C	ΔP
DUPONT	265 °C	TUBE & ΔP
NRL	< 260 °C, 265 °C	TUBE, ΔP
ASHLAND	260 °C	ΔP

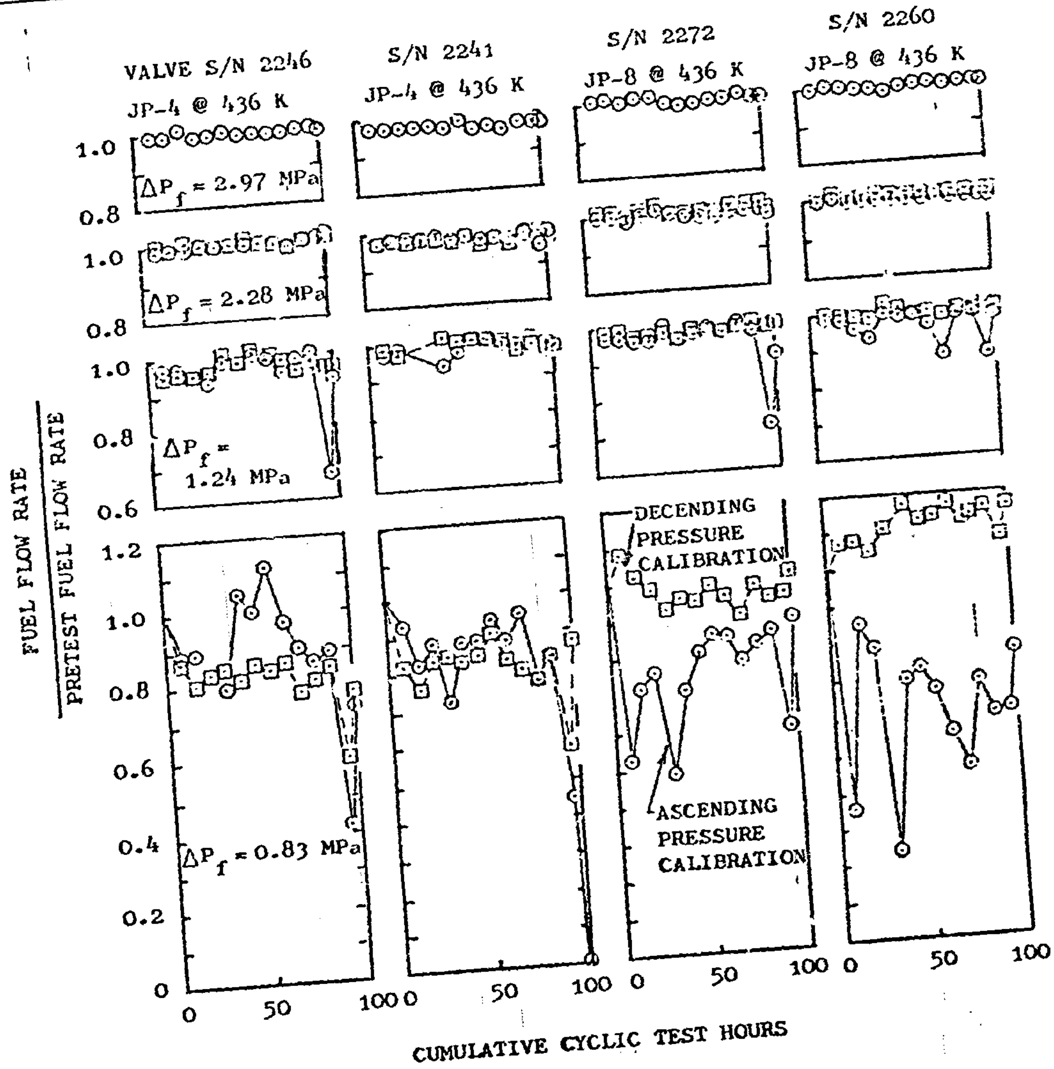
JP-8 SAMPLES FROM GE

	BREAKPOINT	FAILURE MODE
TEXACO	<260 °C	ΔP
EXXON	<260 °C	ΔP
ALCOR	220 °C	ΔP
DUPONT	<260 °C	ΔP
NRL	230 °C	ΔP
ASHLAND	250 °C	ΔP
W-PAFB (UNLINED SAMPLE CONTAINER)	<280 °C	ΔP
W-PAFB (LINED SAMPLE CONTAINER)	>280 °C, <290 °C	TUBE

JP-8 SAMPLES FROM W-PAFB

	BREAKPOINT	FAILURE MODE
TEXACO	$<310\ ^\circ C$	TUBE
EXXON	NO SAMPLE	--
ALCOR	$290\ ^\circ C$	TUBE
DUPONT	$300\ ^\circ C$	ΔP
NRL	$>270\ ^\circ C, <285\ ^\circ C$	TUBE
ASHLAND	$295\ ^\circ C$	TUBE
W-PAFB (LINED SAMPLE CONTAINER)	$300\ ^\circ C$, $310\ ^\circ C$	TUBE

F101 FUEL NOZZLE METERING VALVE GUMMING TEST RESULTS, HOT FUEL CYCLIC TEST RIG



THERMAL STABILITY EFFORTS

A. E. Peat

Rolls-Royce Limited

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Date OCT 78 | Chart No. 1

THERMAL STABILITY — TYPICAL ENGINE DATA

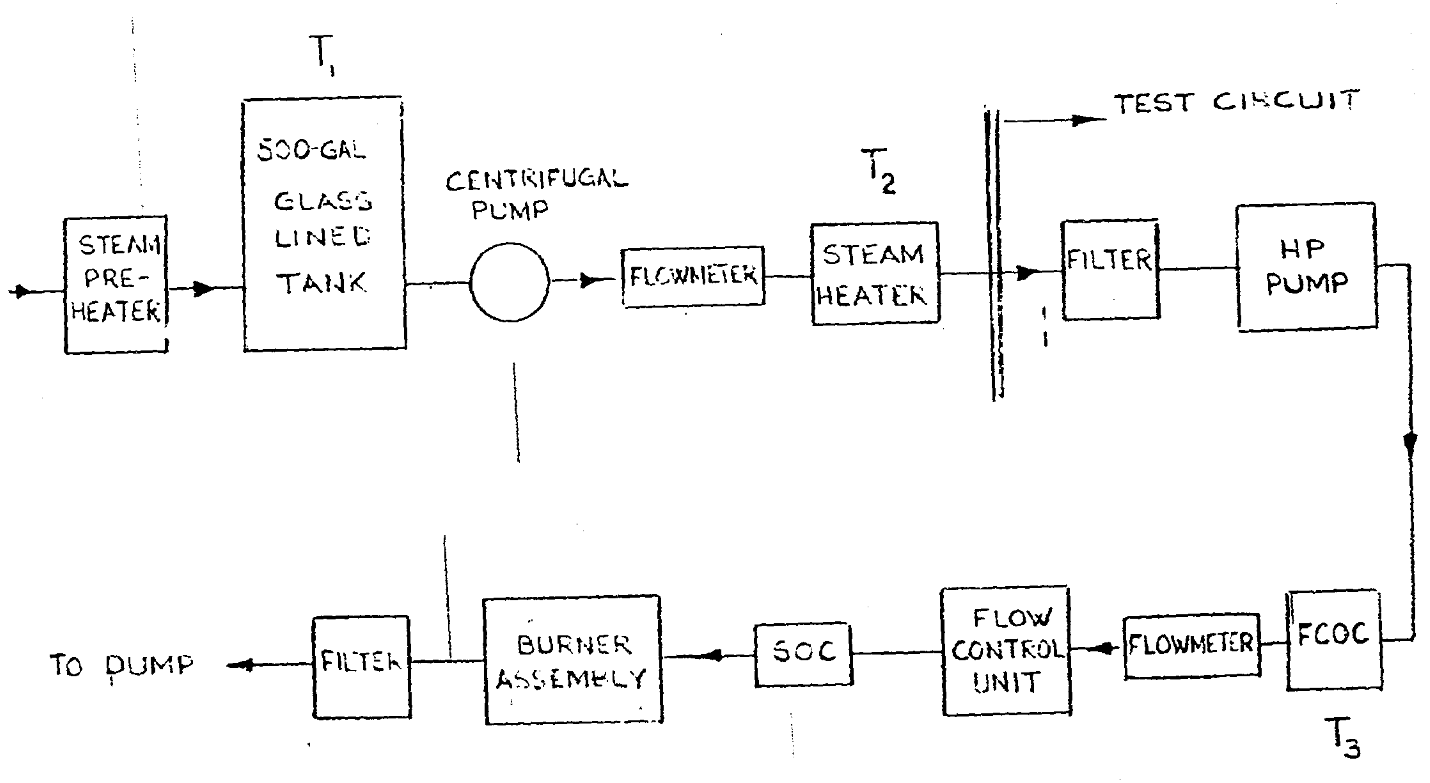
COMPRESSOR D TEMP.	°K	(°C)	FUEL FLOWS ft/sec
AVON	590	(317)	2—3 IDLE
↓			4—35 T.O.
211-22	880	(607)	

ONSET OF DEPOSITS Ex AVTUR Approx 775 °K ± 25°
(502)

HIGH FUEL TEMPERATURE RESEARCH
TEST CIRCUIT

Date

Chart No. 2



Date

Chart No. 3

HIGH FUEL TEMPERATURE RESEARCH

TEST TEMPERATURE LEVELS AND FUEL DATA

TEST N°	DURATION HOURS	FUEL TEMPERATURE °C			KEROSINE TREATMENT	FUEL SG 15/15°C	THERMAL STABILITY ΔP INCHES Hg	COKER THRESHOLD °C	JFTOT THRESHOLD °C
		SUPPLY TANK	HP PUMP IN	FFR & BURNER					
		T_1	T_2	T_3					
1	100	75	110	130	ACID	0·791	0·15 to 0·3		
2	100	75	130	150	ACID	0·790	0·15 to 0·2	190	
3	100	100	140	175	MEROX	0·794	0·05 to 0·2	205/175	275/290
4	5	110	170	200	MEROX	0·792	0·05 to 0·1	175	270

HIGH FUEL TEMPERATURE RESEARCH
NOMINAL TEST CYCLE CONDITIONS

Date

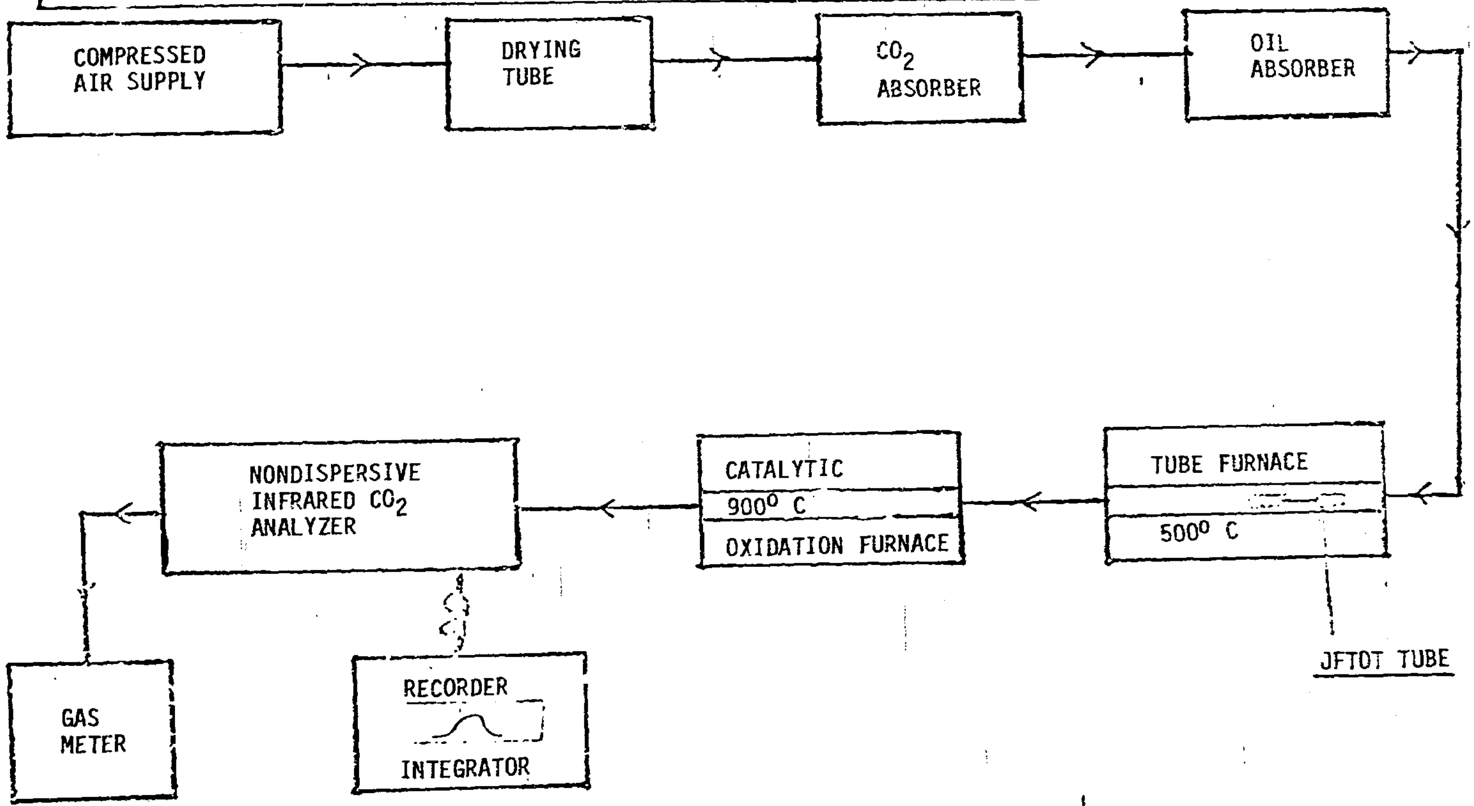
Chart No. 4

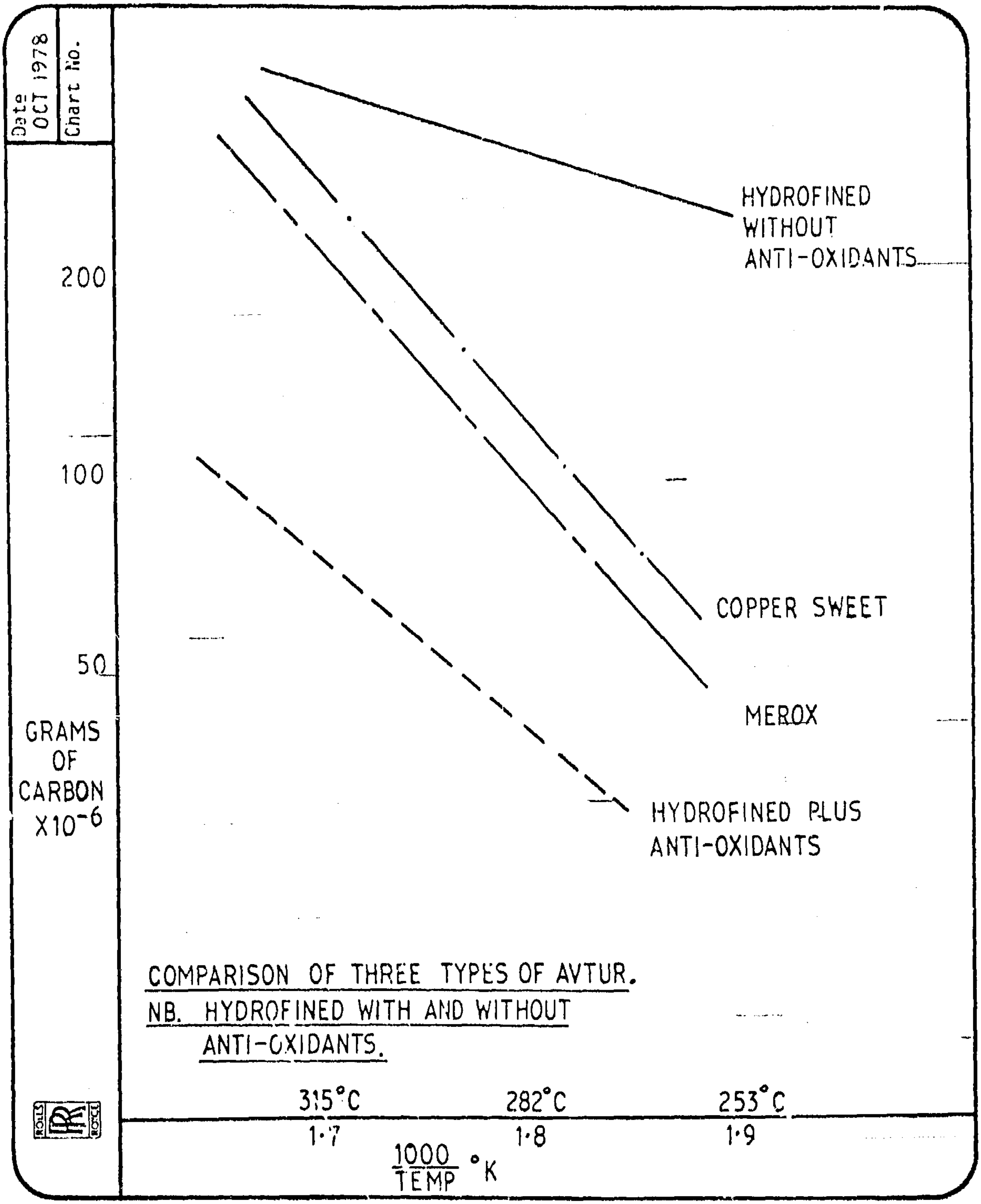
DURATION	ENGINE CONDITION	% RPM	FUEL FLOW/ GPH	HP PUMP PRESSURE PSIG INLET	HP PUMP PRESSURE PSIG DELIVERY	MAIN BURNER INLET PRESSURE PSIG
5 MINS	IDLE	60	110	90	300	30
5 MINS	MAX.	100	400	80	570	290
2 HR 30 MINS	CRUISE	95	400	80	570	300
5 MINS	IDLE	60	110	90	300	30
15 MINS	STATIC	0				

SCHEMATIC DIAGRAM OF COMBUSTION APPARATUS

Date

Chart No. 12





Date OCT 1978
Chart No.
200
100
50
GRAMS OF CARBON X10-6
HYDROFINED WITHOUT ANTI-OXIDANTS
COPPER SWEET
MEROX
HYDROFINED PLUS ANTI-OXIDANTS
COMPARISON OF THREE TYPES OF AVTUR.
NB. HYDROFINED WITH AND WITHOUT ANTI-OXIDANTS.
315°C
282°C
253°C
1·7
1·8
1·9
1000/TEMP °K

Date Oct 78
Chart No. 14

FUEL DEGRADATION — BURNER ARM

BURNER	Av. Wt. per. BORE mgm	CARBONACEOUS %	TYPICAL SPEC. ANALYSIS MAJOR ELEMENTS
SPRAY (100 hrs)	1·0	50 – 90	Fe, Ni, Cr, Al, Si
AIR BLAST (2000 hrs av.)	20·0	60 – 85	Na, Pb, Fe, Ag, Si
(513 hrs)	16·0	85	Cu, Fe

AIRLINE STATUS REPORT

Walter D. Sherwood

Trans World Airlines

Many of us recall the birth of the subject of turbine fuel thermal stability - back in the mid 1950's. The earliest problems that I personally can recollect related to the P&W J-57 engine which was the predecessor to the JT3 and JT4 series engines used on 707/DC8 aircraft at the onset of US Commercial Airline jet service. Because of the seriousness of the problem, a shotgun approach was taken by the engine manufacturer. Along with redesign of the fuel manifold and nozzle arrangement, pressure was brought to bear on the industry to develop a test to classify fuel as to its tendency to decompose and form gum deposits under heat conditions. As you all know, the "Erdco Coker" was conceived as an early answer to the determination of fuel thermal stability. I relate this history only to set the stage for the "history repeats itself" message I'm trying to convey.

Over the years since the mid 1950's, the coker test became more sophisticated and engine fuel system designs were made less critical of fuel thermal stability characteristics. Today, the somewhat controversial JFTOT tester is being used more widely as a more sophisticated device to determine the elusive thermal stability precipice for turbine fuels. At the same time, pressures for more efficient engine coupled with over concern about aircraft engine contributions to air pollution are driving the industry toward the return of the thermal stability problems of 20 to 25 years ago. Witness the JT8D "low smoke" combustor designed to improve the esthetics of 727/737/DC9 airport operations. Although I speak only of TWA experience, I have confidence that TWA's problems are common with all JT8D operators experience.

The JT8D "low smoke" combustor has accomplished the goal of decreasing visible smoke at the expense of increased maintenance cost. Uneven flow patterns of JT8D fuel nozzles are the direct result of fuel decomposition causing nozzle clogging which in turn results in downstream hot section damage and deterioration ~~of~~ engine reliability and performance. The fuel decomposition I refer to is the direct result of the increased heat input to fuel in the fuel nozzles of the "low smoke" combustor as compared to earlier JT8 combustor designs.

As a means of combating this JT8D problem, TWA has developed an "in-situ" flushing procedure for JT8D fuel manifolds and nozzles. A concentrated solution of detergent and water is injected into the primary and secondary fuel manifold connections at the P&D valve. This solution is allowed to soak in the system for 30 minutes and then a large quantity of detergent under high pressure is pulsated through the system followed by a purge of high pressure air. TWA experience with this procedure shows that high time nozzles (2000 to 2600 hours of service) are restored to within 90% of new nozzle flow rates. TWA is presently flushing JT8D nozzles every 1000 hours as this best fits its maintenance program and prevents excessive deposit build-up. TWA estimates that this flushing procedure results in over $1 per engine flight hour savings in hot section maintenance costs.

Although the JT8 engine is not a "new technology" design, it will be around for many years to come and at a high population density. Looking at the newer technology designs leads one to the conclusion that thermal stability and its characterization will be of increased concern in the next decade and beyond. Wtih the emphasis on fuel efficiency and ecology, future engine designs could increase thermal stress on fuel and the need for a better definition of thermal break points.

Although engine maintenance is a very important cost area in commercial airline operation, the increased cost of fuel today over its cost in 1973 makes fuel the dominant portion of direct operating cost. (35-40% of direct). It may come as a shock to those whose life has been devoted to reducing engine maintenance cost to learn that fuel consumption has become more important (2½ to 3 times) than engine maintenance cost. However, to reassure the power plant engineering fraternity, there is a strong bond between fuel consumption and engine maintenance. As Al Marsh pointed out earlier, engine cold section condition can contribute to the health of the hot section and therefore the end result - fuel consumption.

Maintenance of satisfactory fuel nozzle flow rate and spray pattern will minimize turbine distress which greatly influences average specific fuel consumption (pounds of fuel per pound of thrust). Because of the increasing importance of fuel consumption to the direct operating cost picture, increased maintenance effort on engines susceptible to fuel thermal stability problems must be thoroughly evaluated. Such increased maintenance effort is a "band-aid" approach and design improvement efforts are mandated for the long term solution to the airline cost squeeze problem.

In summary, airlines today are faced with the return of thermal stability problems of the past!

APPENDIX B

ADVANCE QUESTIONS

GROUP I. BASIC RESEARCH

1. More information is needed on the effect of trace elements and compounds on the decomposition of liquid fuels.

   a) What is rate and mechanism of heterogeneous decomposition of liquid fuels by trace Cu or other elements that might be picked up in fuel lines?

   b) Are there any foreign materials that could act the opposite way, as stabilizers for liquid fuels?

   c) What are heterogeneous catalytic effects on autoxidation reactions of fuels?

   d) What is the effect of temperature and pressure on all these surfaces or heterogeneous reactions?

2. Phenol is a known antioxidant

   a) What is effect of phenol on the stability of various liquid fuels and the kinetics and mechanism of the reactions?

   b) Would any products of the reaction cause problems in combustion such as increased emissions?

   c) Is phenol stable in the gas phase: What is kinetics and mechanism of phenol-fuel gas phase reaction?

3. What is the kinetics and mechanism of decomposition of certain organic sulfides, phosphides and aliphatic amines which are known inhibitors of oxidation reactions? Study both in liquid and gas phase.

4. Most organic sulfur and nitrogen compounds accelerate fuel decomposition. But some, like certain amines, diphnyl sulfide and dibenzothiophene do not accelerate fuel decomposition. What is key difference in reaction mechanisms that accounts for this effect?

5. What is mechanism of liquid fuel oxidation by dissolved peroxides? Explanation of observed alcohol and ketone concentration profiles would help understanding of peroxide effects. How important is peroxide reactions in the fuel stability problem.

6. How does mechanism of decomposition of deoxygenated fuels differ from that of O_2 containing liquid fuel in the presence of various organic

nitrogen and sulfur compounds? Usually deoxygenation helps fuel stability but not always. Mechanism of these reactions needs to be better understood.

7. Are there synergistic effects when certain organic sulfur, nitrogen and oxygen compounds (peroxides) are present together in an olefin fuel? Some inpurities may be harmless alone but bad when present together. We need to study the mechanisms of such interactions probably both in liquid and gas phases.

8. Is the gas phase pyrolysis of hydrocarbons catalyzed by copper or other trace liquid or solid impurities? Is pyrolysis of olefins and aromatic hydrocarbon mostly homogeneous or heterogeneous?

9. What is mechanism and rate of gas phase pyrolysis and oxidation of various hydrocarbons in the presence of various organic nitrogen and sulfur compounds?

10. What is the stability in the gas phase of the 2 compounds diphenyl sulfide and dibenzothiophene which do not promote hydrocarbon liquid phase decomposition? How are their liquid or gas phase thermal decompositions different from that of other compounds that promote decomposition of the hydrocarbon? (Combine with #4).

11. Propylene is a well known inhibitor of gas phase free radical chain reactions. What effect would it have on rate and mechanism of pyrolysis of a paraffin or aromatic hydrocarbon with and without the presence of various organic nitrogen and sulfur compounds that promote free radical decomposition? It might be interesting to find out also what effect propylene has on the oxidation of paraffins. Usually olefins are quite susceptible to oxidation, but a study of this system might give some useful mechanism information.

12. What are typical quantities of oxygen dissolved in fuel and what factors control this?

13. What are the actual molecules which are the building blocks of deposits? How can the structure and properties of these molecules be characterized?

14. How do physical processes interact with chemical kinetic processes? What is the role of solvent effects in liquid phase systems, volatility effects in vapor phase systems and fluid mechanics effects in general?

15. How do microspherical deposit particles form from individual compounds? How can these particles be more clearly characterized?

16. What is the mechanism of microspherical deposit particles collection and agglomeration on surfaces and in pores of filters?

17. How should the effects of fuel composition on sediment and deposit formation be elucidated? How can mechanistic kinetics studies and basic research studies on the effect of fuel composition on deposit formation be integrated?

GROUP II. LABORATORY CHARACTERIZATION TECHNIQUES

1. In the evaluation of deposits on JFTOT tubes

   a) Should it be done by combustion?

   b) Should non-carbon deposits be determined?

   c) Is the TDR value of 13 acceptable for breakpoint temperature determination?

   d) Are color(ful) deposits indicative of incipient failure?

2. What are the needs for establishing reproducibility and precision criteria in the JFTOT test?

3. To what extent should the deposit profile be considered? How should the problem of the "solvent effect" be addressed?

4. What are the needs for uniformity of handling of fuel particularly in regard to filtration? Is the 0.45 μ filter realistic when considering engine conditions?

5. What is the status of potential JFTOT replacement instruments or methods?

6. Should there be a peroxide formation test?

7. What has been the experience with the heated reservoir modification of the JFTOT tester?

8. Should there be an evaluation of the fuel just prior to injection into the aircraft? If so, how should this be done?

9. There seems to be an ongoing effort in ASTM to correlate JFTOT data with CRC Coker data. Is it really important to consider this?

GROUP III. APPLIED RESEARCH AND TEST SIMULATORS

1. What simulators are being or have been used? What are the results? Are the reports available?

2. What problems have been observed in practice?

3. What are the major causes of thermal stability problems?

   dissolved O_2
   trace compounds of S, N_2, O_2, or metals
   hydrocarbon composition & amount
   metal surfaces
   additives
   interactions
   storage time
   other

4. Where would a thermal stability problem initially manifest itself, in the injection nozzles, in the manifold, or on heat transfer surfaces?

5. What area of an engine system would be the first to be adversely affected by a stability problem?

6. Should a simulation attempt to simulate that portion of the engine that shows the first sign of the problem or the most critical area? Can both be done?

7. What scale of testing would be meaningful and would allow extrapolation to a real engine?

8. What is a realistic and practical temperature and pressure profile, and cycle, for a simulator?

9. How should stability be determined in a simulator?

   spray characteristics
   ΔP
   change in heat transfer coefficient
   amount of deposits
   composition of deposits
   amount of carbon in deposits
   other

10. Is it necessary or desirable to fully identify deposits?

11. Are all the parameters scalable?

12. Can the tests be accelerated?

13. Would any trends or projections of future fuels or fuel systems change any of the above?

14. How would an SST simulator differ from one designed for subsonic flight?

GROUP IV. ENGINE SYSTEM TRENDS AND REQUIREMENTS

1. Are there any problems, borderline situations, or sensitive areas with respect to thermal stability for present specification fuels? Is there adequate statistical overhaul data to pinpoint these problems?

2. What will be the trends in the near future with respect to thermal stability requirements? Will the low emission combustor designs make increased demands on thermal stability and, if so, in what respects?

3. How well do the present specifications, such as JFTOT, relate to actual fuel degradation behavior in engines? Is there a predictable relationship between JFTOT and actual thermal breakdown in the field?

4. What trade offs are there between stringent requirements for fuel thermal stability, and engine time between overhaul? How low a thermal stability fuel can be tolerated? Can reduction in engine efficiency with operating life be linked in some respects to fuel deposits?

5. What are the effects of fuel degradation or fuel nozzle performance? Can nozzle designs be made less sensitive to fuel deposits?

6. What effects may fuel degradation have on heat exchange surfaces in the engine system?

7. Are these critical areas with respect to thermal stability in the fuel system, outside the engine? Will fuel heating systems, such as for use of high-freezing-point fuels add more thermal stability stresses to the system?

8. Is the fuel delivered to the user the same, in terms of thermal stability, as that specified at the refinery? Does storage instability contribute to thermal instability? Would point of delivery, quick tests, be of benefit?

9. What is the feasibility of using fuel purging, fuel cooling, or insulation to minimize fuel temperatures?

APPENDIX C

WORKING GROUP REPORTS

GROUP I. BASIC RESEARCH
Chairman: Robert N. Hazlett

PART I

WHAT DO WE KNOW ABOUT THE BASIC CHEMISTRY AND PHYSICS OF THERMAL OXIDATION STABILITY?

A. Mechanisms of Deposit Formation

1. Oxidation is the trigger

2. Chemistry is largely free radical but condensation reactions may also be important (e.g., aldehyde condensations)

3. Reaction is temp. dependent - start ∿ 200°F

4. Metals influence deposit formation

   a) heterogeneous (surfaces) } different
   b) homogeneous (dissolved) } mechanisms

   Copper is most deleterious metal - effect may depend on fuel composition

5. Solvent effects important but still poorly understood

6. Deposits form in both liquid and vapor phases - in wing tanks worst situation exists when both phases are present

B. Characteristics of Deposits

1. Most are microspherical but other morphologies are observed (plates, rods)

2. Temp. and dissolved O_2 influence morphology

3. Other characteristics include

   a) H/C ratio is lower than original fuel
   b) Oxygen level is greatly enhanced in desposits
   c) Other heteroatoms are concentrated

C. Effects of Fuel Compositions

1. Hydrocarbon types

   a) benzene derivatives less deleterious than napthalene
   b) some olefins deleterious
   c) acetylenes greatly promote instability

2. Oxygen and nitrogen containing species can be deleterious - also sulfides - aldehydes

3. Interactions between fuel components are important

4. Dissolved O_2 content critical - is typically 50-75 ppm in air saturated fuels at sea level.

D. Effects of Storage and Handling on Thermal Stability

1. Handling and sampling may be more important than composition effects

2. Storage effects variable - some fuels show improved stability - others worsen

3. Erratic storage effects may be related to peroxide content of fuels - these decompose on standing

4. Recommended storage procedures

   a) Deoxygenate fuel before storage
   b) Avoid light
   c) Keep metals out
   d) Preferred containers - Pyrex glass or Epoxy-lined metal cans
   e) Decompose peroxides prior to storage via heat or by chemical reduction

E. Use of Additives

1. No "universal" additives - effectiveness depends on fuel composition

2. Anti-oxidants useful in enhancing storage stability - probably not thermal oxidation stability

3. Other potentially useful additives:

   a) Metal deactivators - especially for copper
   b) Dispersants - keep deposits dispersed - but tend to disperse H_2O as well
   c) Metal passivators

4. Lubricity additives may adversely affect thermal stability

5. Additives can interact in as yet unknown ways - have to be aware of possible problems

6. Market for additives not developed - inhibits research

7. Future developments - e.g., synfuels may require additives - trade-offs between hydrogenation costs and additive usage will be needed

PART II

WHAT SHOULD WE KNOW TO ADEQUATELY DEFINE AND/OR RESOLVE THE PROBLEM?

A. Deposits

1. Using ESR on solids formed from fuels, can one see evidence for radical reaction pathways?

2. We need more detailed information on gum deposits, preferably from actual engines or storage tanks.

3. What happens to deposits on JFTOT tubes or actual engine parts as it remains on the hot surface? Does it pyrolyze? Do the earliest deposits differ greatly from later adherent materials? How does the composi~~ti~~on change with depth for deposits on both real-life engine parts and JFTOT tubes?

4. How does a microspherical deposit particle form? Is it via a second liquid phase which forms a sphere due to surface tension?

5. What is the molecular weight distribution of soluble, insoluble, and adherent gums and deposits?

6. What is the difference between surface varnishes (adherent gums) and filterable deposits?

B. Metals

1. What is the importance of dissolved metals versus surfaces? (e.g. would inert surface show similar effects?)

2. What happens to the rate of deposition after surfaces become coated, thus probably eliminating exposed metallic surface effects?

3. How do dissolved metals catalyze fuel deterioration? Is it non-radical chemistry?

C. Storage and Aging

1. When obtaining fuel samples for testing, where in the fuel stream does one sample? - At the refinery, from a tank car, from a fuel tank in a vehicle? What containers do we use for samples?

2. If one removed all dissolved oxygen and peroxides, would there be any storage stability problems?

3. The thermal stability has been observed to improve, degrade, or remain constant after storage of various fuels - why? What is happening? What is the difference between the fuels that improve and those that degrade?

D. Reactions

1. Aside from free radicals, what reactions are taking place and what is their relative significance? (e.g., condensation of ketones and aldehydes)

2. Is it possible to stop the initial oxidation reaction?

3. What happens to di-olefins? Are they found in jet fuels?

4. What is the significance of bi-functional compounds, as well as hetero-atom compounds where neighboring carbon atoms tend to be more reactive?

5. What are the mechanisms of diphenyl sulfide, diphenyl disulfide, and dibenzothiophene reactions in a clean system?

E. Additives

1. Could dispersants decrease the severity of problems from gum formation? Can dispersants play a useful role in stabilizing fuel and what are their effects on other properties?

2. Is the need for different additives for different fuels because of trace contaminants or fuel hydrocarbon composition? or both?

3. How is additive performance affected by boiling range of fuels?

4. Are there any peroxide decomposers, radical scavengers, or combination of both, which are both effective and reasonably priced? (must be non-metallic)

F. Miscellaneous

1. Why does pre-treatment (clay, H_2, chemical separations) improve stability of some fuels and not others?

2. How much oxygen is dissolved in fuel at various stages during flight?

3. What is the relationship between thermal stability and boiling range of fuels?

4. Will pre-vaporization pose any new thermal stability problems?

5. Solubility effects are unknown, but too complex for immediate attack. This may become a critical area when synfuels begin to be blended in.

PART III

WHAT EXPERIMENTS WILL GIVE THE INFORMATION WE NEED?

A. Deposits

1. Employ modern surface analysis techniques: ESCA, Auger, Pyrolisis GC, ESR, CIDNIP and study deposit vs. depth especially for actual engine parts but also JFTOT and other test devices.

2. Check deposit chemistry and morphology for possible changes with time due to temperature on the hot surface.

3. Compare filterable desposits and varnishes.

4. Investigate solubility effects on deposits - include effects of fluid temperature, fluid and deposit chemistry, and flow rate.

5. Study deposit morphology and chemistry as a function of parameters: T, P, O_2, aging and composition of fuel.

6. Employ photo-acoustic spectroscopy and/or attenuated multiple reflectance IR to analyze gum and especially solid thermal deposits.

7. Employ radioactive tagging of contaminants.

B. Metals

1. Compare 3 possible metal effects

   Dissolved metals

   vs. Metal surface
   vs. Non-metal surface

   Look for stoichiometric metal involvement by analysis of deposits.

2. Investigate metal effects with and without O_2 and peroxides.

3. Check the effects of nitrogen compounds on copper pickup (especially in light of synfuels)

C. Storage and Aging

1. Monitor thermal stability from refinery through supply system

2. Aerobic aging - check peroxides and electron spin - initial and with time

3. Anaerobic aging - do peroxides account for all the aging

D. Reactions

1. Test fuel and deposits with ESR and CIDNIP for free radical reactions.

2. Follow disulfide decomposition with ESR.

3. Follow fouling reaction mechanisms/precursors in liquid phase employing field ionization mass spectrometry and other techniques.

4. Analyze oxygen concentrations in liquid and vapor phase in storage and aircraft tanks and as a function of time through flight conditions.

5. Examine effects of prevaporized/premixed fuel on deposition.

6. Explore MW in dispersions and in adherent deposits by light scattering/Tyndall effect and/or gel permeation chromatography.

7. Test effect of bifunctional N, O, and S materials.

8. Study variations of thermal stability with boiling range of real fuels.

9. Analyze fuels for trace components and their effects on fouling, using "specific detector" gas chromatography.

E. Additives

1. Investigate "peroxide decomposers" for controlling deposition (as used in the polymer industry, such as:

   Ni diacetylacetonate
   and non-metallic equivalents)

2. Explore antioxidant and dispersant thermal stability effects in a variety of fuels.

3. Study inhibitor interactions in storage and fouling.

F. Miscellaneous

1. Investigate effects and mechanisms of various treatments - clay, H_2, separations - on thermal oxidation stability and composition of fuels.

2. Examine deposition as a function of reaction mechanism or deposition mechanism.

GROUP II. LABORATORY CHARACTERIZATION TECHNIQUES
Chairman: Charles R. Martel

I. OBJECTIVE

To determine the status of existing laboratory techniques suitable for determining the thermal oxidative stability of aviation turbine fuels; to define the problems and shortcomings of these techniques; and to identify recommended research and possible improvements in these techniques.

II. EXISTING LABORATORY TECHNIQUES

The laboratory techniques available for characterizing the thermal oxidative stability of fuels are listed and discussed below.

A. JET FUEL THERMAL OXIDATION TESTER (JFTOT)

The JFTOT is a relatively new test method now in use for aviation turbine fuel quality control per ASTM D3241. The test fuel is flowed past a polished aluminum heater tube and then through a 17 micron filter. Plugging of the filter or the formation of deposits on the heater tube darker than a light tan are the test criteria used to characterize fuel thermal stability. Test temperature, test time and test pressure are variable.

1. Status - The JFTOT is widely used as the quality control check for aviation turbine fuels. Normal pass/fail operating conditions are 260°C heater tube temperature, 500 psig operating pressure and a 2 1/2 hour test time. For commercial fuels a waiver to 245°C heater tube temperature is available.

Work is underway by the AF to select suitable JFTOT test parameters for speciality jet fuels JPTS and JP7.

2. Problems -

a. Choice of test parameters - The choice of JFTOT test parameters has been based largely on the older ASTM-CRC Fuel Coker, as the JFTOT is basically a minaturized coker. A better understanding of the deposit-formation conditions in actual aircraft engines would likely improve JFTOT accuracy (i.e., the ability of the JFTOT to predict the deposit forming tendencies of fuels). Specific parameters of concern include:

(1) Test pressure selection - Presently the JFTOT is operated above the critical pressure of typical jet fuels. The quantity of heater tube deposits can be increased by operating the JFTOT at a lower pressure near the boiling point of the fuel. Also, deposits appear to differ significantly between single and two-phase flow. The ideal or most realistic test pressure has not been established.

(2) Fuel prefiltration - Currently the fuel to be tested in the JFTOT is filtered through Whatman filter paper of 17 micron nominal pore size. Within the JFTOT a 0.45 micron filter is used immediately prior to the heater tube to improve test precision. This high degree of filtration is unrealistic as compared to actual aircraft fuel systems. The degree of prefiltration is known to affect the amount of deposits formed with some fuels.

(3) Test filter temperature - In the JFTOT the temperature of the test filter is not directly controlled. The test filter in the JFTOT, being downstream of the heater tube, is supposed to simulate engine fuel nozzles. By not controlling the temperature of the test filter the accuracy of the simulation undoubtedly suffers, but the effect of this factor on the accuracy of the JFTOT is unknown.

b. JFTOT Calibration - There are no absolute standards that can be used to calibrate the performance of the JFTOT (or of any other thermal stability test device.) The use of standard reference fuels has been proposed ~~to~~ improve the precision of the JFTOT.

c. Tube deposit rating - Currently, deposits are rated by visually comparing deposit color to color standards. This method is highly subjective, has poor precision, and is of unknown accuracy (i.e., the deposit color may not correlate with heat exchanger fouling and engine fuel nozzle plugging). The Alcor Mark 8A Tube Deposit Rater (TDR), an optical reflectance device having improved precision but not necessarily improved accuracy, is available but is not in widespread use. Research has been done on various alternative deposit rating methods including beta ray backscatter, deposit combustion with subsequent measurements of the carbon dioxide formed, Auger spectroscopy, and ellipsometry. None of these alternatives has been developed to a point suitable for laboratory use.

3. Opportunities:

a. Deposit Profile - The heater tube deposit profile vs. tube length and test temperature may provide useful information such as the prediction of the breakpoint of the fuel, unusual solvent characteristics of the fuel, two-phase flow, etc. Deposit colors may indicate the presence of undesirable trace metals such as copper.

b. Since additives are known to reduce deposit formation or modify their character, their effects on JFTOT ratings should be more widely investigated.

c. Heated reservior - The heated reservoir now available provides a significant increase in time for free oxidation reactions at a controlled temperature ahead of the test section. It may prove to be highly useful for determining thermal oxidation stability problems with certain types of fuels. It has the possibility of turning the JFTOT into a miniature fuel system simulator suitable for research programs.

d. Metal Catalysts - By using heater tubes of varying composition the effects of different metals on deposit formation can be determined.

e. Long Term Tests - By using a larger reservoir or an external source of test fuel, extended JFTOT tests can be run for ten's to hundred's of hours to examine deposit formation vs. time and test temperature.

4. Recommended Research:

a. Examine actual aircraft and engine fuel systems and determine the actual temperatures, pressures, flow rates, etc. of the engine fuel nozzles that are experiencing plugging problems. Use these data to select more realistic JFTOT test conditions (pressure, temperature, residence times, prefiltration, etc.).

b. Recommend that ASTM be asked to re-examine the need for and degree of in-line fuel prefiltration for the JFTOT.

c. Research is needed to identify and develop improved tube deposit rating techniques that correlate with fuel heat exchanger fouling and nozzle plugging.

d. Reference fuels such as pure hydrocarbons and concentrates containing reactive species should be investigated ~~for~~ use as calibration fluids.

e. Temperature control of the ~~JFTOT~~ test (Dutch weave metal) filter should be investigated.

II.B. ASTM-CRC Fuel Coker
ANSI/ASTM D 1660

1. Status:

These instruments have been used successfully for over twenty years to furnish thermal stability characteristics of aviation turbine fuels. Many laboratories outside of Eastern Europe and Western Asia have one or more units. The fuel coker is still in production to meet a continuing world-wide demand. The manufacturer of the coker, Erdco Engineering Corporation, will continue to furnish the components required for test and maintenance.

The allowed manufacturing tolerances for the test filter and inner tube are being tightened, and the fuel pump capacity will be increased to provide greater bypass and to further reduce the possibility of pulsations in fuel flow. These charges have yet to be evaluated by ASTM, but are hoped to improve test precision.

The instrument cabinet is being redesigned to utilize lower cost enclosures to reduce the need for higher prices with declining instrument shipments.

Usage of the ASTM/CRC Fuel Coker declined for five years based on shipments of test filters and inner tubes. During the last two years, demand has increased with an even more marked growth during the last year. This has caused inventory outages which are being corrected.

2. Problems: (attributed to users)

1. Sample size limits ease of shipment
2. Intermittent pump effects
3. Precision of filter
4. Repeatability of test results
5. Visual rating of tube deposits (See II.A.2.C., above).

3. Opportunities:

Work is underway to tighten test component tolerances and to reduce the pump effects to improve precision.

4. Research Needs:

Reference fuels are needed so that instrument performance could be checked periodically (See II.A.4.d., above).

Information is needed as to the actual effects of trace elements in the fuel on thermal stability, as trace elements are believed to promote deposition. If this is of concern, the sample size and length of test required may need to be increased in order to obtain useful data when the trace elements are present in parts per billion quantities.

II.C Research Fuel Coker

1. Status:

Approximately fifteen of these instruments are available worldwide. Due to their ability to test at higher temperatures, improvements in the thermal stability of fuels such as JP7 have been obtained.

2. Problems:

This instrument is a higher temperature version of the ASTM-CRC Fuel Coker. The test filter is the same for both units and the preheater tube is of stainless steel for the Research Fuel Coker. The users have not reported any operational problems. Also see JFTOT and ASTM-CRC Fuel Coker discussions above.

II.D. Monirex Fouling Monitor

1. Status:

Monirex jet fuel testing has been done on a differential hot wire device using two different fuel samples which are, in every way possible, subjected to the same test conditions. Hot wire sensors are used to collect foulant deposits. Results are based on the difference in the rates of change of the heat transfer coefficient for the two fuels. The Monirex Fouling Monitor is presently in product development. Delivery and costs are not available at this time. The original Monirex device using a single hot wire has been used for refinery fouling tests and is also in product development.

2. Problems:

The Monirex hot wire Fouling Monitor is still in development.

3. Opportunities:

The problem of interpreting JFTOT and coker tube deposit data can be eliminated, as the Monirex unit outputs heat transfer data about the deposit fouled wire surface.

The Monirex device capability to test at one specific wire temperature provides an opportunity to evaluate in greater detail the mechanisms of fouling.

4. Research Needs:

Research needs include further evaluation of the hot wire method, and the differential fouling test method. Development of a referance fuel for better device precision and inter-device correlation would advance the state-of-the art.

II.E. Thermal Fouling Tester (TFT)

1. Status:

The TFT, a derivative of the JFTOT, is presently in wide use as a laboratory device to evaluate the effectiveness of antifoulant additives in refinery feedstock.

In its basic function the TFT maintains a preset fluid discharge temperature, and the rise in heater tube temperature is indicative of fouling or deposit build-up on the heater tube.

2. Problems:

From recent CRC work it was established that in its present configuration, the TFT is not too well suited for establishing thermal stability characteristics of turbine fuels.

3. Opportunities:

With the design of a new test section and an operating technique specifically tailored to discriminate and rank jet fuels, this device could possible equal or perhaps surpass the present JFTOT technique. In this technique, rating of a fuel sample would be strictly based on heat transfer characteristics of the deposits generated and expressed as a maximum delta T attained. Such a rating system would be highly desirable as it excludes the operator from having to make a rating judgment as is now the case with the JFTOT visual method.

Disadvantages of the TFT would in all probability be an increased test time in order to generate a significant delta T.

II.F. Thornton Flask Test

1. Status:

This portable test device is used for rapid field measurements of the thermal stability of aviation turbine fuels. The procedure uses a 150 ml sample in a 250 ml Pyrex flask (which is open to the atmosphere) immersed in a 150°C controlled temperature bath for 60 minutes. Fuel degradation is assessed by either measurement of the reduction in light transmission using a spectrophotometer or more simply by assessing the extent of color change using available standards.

2. Problems:

A rough correlation has been established with a 1/2 scale simulator and laboratory test methods. However, the repeatability of this test is in the order of $\pm$ 10% when used for field measurements.

3. Opportunities:

The method provides (1) a portable and easily conducted procedure for field measurements, (2) field samples may be taken directly into the test unit, thereby reducing sample container/shipping problems, and (3) the procedure provides a measurement in 1-1/2 to 2 hours.

4. Research Needs:

Further development is needed to (1) improve the repeatability and (2) provide correlation with specification techniques.

II.G. Oxygen Uptake Measurements:

Oxidation mechanisms of liquid hydrocarbons are usually studied by researchers in laboratory glassware. Typically oxygen is bubbled into a pure hydrocarbon such as tetralin dissolved in a solvent. The mixture is well-stirred and held at a specific temperature. The amount of oxygen absorbed is measured as a function of time, and frequent samples of liquid (and gaseous) products are taken to measure hydroperoxides, complex intermediates, acids, ketones, etc. Frequently metal salts are introduced to catalyze oxidation, and sludge products are measured by filtration and weighing. Many variations of this technique are employed - air for oxygen, reflux, metal strips, highly sophisticated techniques to measure oxidation intermediates, etc.

Measuring oxygen uptake alone in a typical jet fuel under well-controlled temperature conditions is relatively simple but it would be necessary to also measure oxygen products or sludge for a meaningful test. The technique does not lend itself to quality control as does a rig such as the JFTOT but is more useful for research studies into oxidation mechansim and system variables.

II.H. Thermal Precipitation:

The thermal precipitation test consists of heating the fuel to 300°F for two hours. After cooling, the fuel is filtered through a 0.45 micron Millipore filter and the color compared to a standard color chart.

The test was developed after sluggish response and sticking was observed in close tolerance parts subjected to hot JP-7 fuel. Research coker tests of the JP-7 fuel did not identify this aspect of thermal instability.

The thermal precipitation test is a specification requirement for MIL-T-38219 Grade JP-7 fuel. It is useful for fuels where cyclic heating and cooling in the system may leave deposits which affect engine components.

The thermal precipitation test is similar in principal to the Thornton Flask test described above.

III. RELATED PROBLEMS AND RESEARCH NEEDS

A. SAMPLE CONTAINERS

The importance of sampling procedures and sample containers was discussed during the Plenary Session. The Coordinating Research Council has a small program underway to investigate this problem. Suppliers and consumers are to submit their sampling techniques which will be compiled and evaluated by the Thermal Stability Group of the Coordinating Research Council.

The results of poor sampling techniques and their effect on the thermal stability test results have been documented both in these sessions and in other technical meetings. It is this group's recommendation that both sampling and sample containers be seriously considered in order to maintain the validity and precision of the various thermal stability test methods. Areas to be considered would include: (1) Sampling location and method of drawing samples. (2) Types of sample containers and how the containers would be used in sampling. If using epoxy-coated containers, should the type of epoxy be specified and should the epoxy coating undergo a fuel exposure period before using. If unlined sample contners are to be used, how should they be treated or rinsed with fuel prior to sampling. Also, sample container seals must also be considered.

This work will be valuable for other fuel tests where sampling is important.

III.B. PEROXIDE FORMATION TEST FOR THERMAL STABILITY OF JET FUEL

Peroxide formation has been proposed as a test to assess thermal stability based on an autoxidation mechanism for deposit formation. (See CRC Literature Survey - Jet Fuel Thermal Oxidation Stability, Chapter IV). Peroxide compounds are found in the propagation steps and in the termination step products.

Peroxide formation has not been widely applied to jet fuel thermal stability testing and further investigations are required. The relative importance of peroxides and fuel components to final deposits has not been established and it is likely that this will vary markedly among various fuels. Peroxide formation is suitable for research studies of thermal stability and problems with specific fuels but is not recommended for general thermal stability testing of all jet fuels.

IV. GENERAL COMMENTS

A. FUEL THERMAL OXIDATION TESTS

All of the existing laboratory techniques discussed in Section II, above, are fuel oxidation tests. Oxidation tests, being rate and time dependent, are non-equilibrium tests, and by their nature have poorer precision than equilibrium tests such as gravity. Tightening mechanical test variables such as temperature, flow rate, and pressure can afford only limited benefits, and a point is soon reached where little or no further improvement in test precision will be realized.

B. RELATION OF SMALL SCALE TESTS TO FIELD PROBLEMS

The Applied Research and Test Simulator Group and the Engine System Trends and Requirements Group both reported that engine fuel nozzle plugging was the most critical thermal stability problem in today's and tomorrow's engines. Engine fuel nozzle types in current use include the pressure atomizing type, the pressure atomizing air assist type, the slinger type, and the airblast atomizing type. The various types of engine fuel nozzles differ significantly in their susceptability to deposits and to the nature of the deposits. For example, the hard lacquer type of deposit may cause malfunction of nozzle valves that switch fuel flow from the primary to the secondary nozzles, while the formation of thick, flaky deposits can result in the sudden blockage of small orifices.

Existing small scale tests do not attempt to differentiate among deposit types. Furthermore, to obtain sufficient deposits for detection the test is significantly increased in severity to obtain test results in a matter of a few hours with a small quantity of test fuel. The test condition used with the JFTOT, Cokers, Monirex, and the Thermal Fouling Test are selected to obtain detectable deposits in a matter of a few hours. These test conditions differ significantly from the actual engine nozzle conditions that may result in deposits after several hundred or several thousand hours of operation.

GROUP III. APPLIED RESEARCH AND TEST SIMULATORS
Chairman: Royce Bradley

1. Several simulators are in use or have been in use to evaluate fuel thermal stability. Two simulators, Shell-Thornton's half-scale rig and the USAF's advanced aircraft fuel system simulator are both large scale rigs and involve complete fuel systems. Other simulators such as the USN's single tube heat exchanger and General Electric's and Pratt & Whitney's nozzle simulators only consider one portion of a fuel system. At least two additional simulators are planned, one by United Technology Research Center (UTRC) and the other by Rolls-Royce. Both of the proposed simulators are primarily concerned with thermal stability in the engine fuel system. Both programs are parametric efforts with the UTRC program being somewhat more limited in scope than the Rolls-Royce program.

2. Reports are or will be available delineating the results obtained on each of the simulators. Published reports are listed in the thermal stability literature survey that will be published by the Coordinating Research Council.

3. Problems experienced in operation are initially encountered in the nozzle area; i.e., nozzle plugging due to deposits in the discharge orifice and other small passages or gum formation between moving components. These problems are equally likely in both subsonic and supersonic aircraft. Long residence time in certain locations (e.g., divider valves) and high heat flux are the primary contributors to the problems. Performance degradation problems are also experienced in heat exchangers, however, the effects are much different than in nozzles. Heat exchanger performance degradation is gradual and can often be delayed by oversizing the heat exchanger. In contrast, deposit flaking may cause plugging of individual fuel nozzles and subsequent performance problems; design changes to reduce this problem are much more difficult.

4. It is difficult and expensive using aircraft type hardware, to design a simulator that will provide the necessary conditions found in a given aircraft engine. It is even more difficult to design a simulator that will generate data relating to fuel performance in a variety of different aircraft. This latter difficulty is due to the tremendous variation in aircraft environmental conditions and hardware.

5. The need for a complete parametric study that will provide data under a variety of steady-state conditions is evident. The study would use a device consisting of an instrumented tube capable of being exposed to the entire range of engine conditions and designed to give quantitative data on the rate of formation and characteristics of fuel degradation products, particularly deposits formed under these conditions. The results from this effort could then be used by the designer to predict the performance of fuel in an aircraft, the results could also be used to evaluate small-scale test devices. The priority of the parameters to be included in a program of this type differ depending on whether emphasis is in the area of design or fuel studies. A list of these parameters and the order of importance to the two areas are:

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

During parametric testing, the heat flux used in preconditioning the fuel must be minimized to avoid unrealistic fuel deterioration in the preconditioner. It is not yet known whether simulator testing can be accelerated. The results of these parametric tests should indicate the possibility of accelerating future tests both on this test device and on small-scale devices. It is noted that by sufficiently reducing the pressure and/or increasing the temperature in the test device the effects of two-phase flow and supercritical conditions on thermal stability can be investigated. The fuel type can be varied to include fuels from alternative sources in addition to currently produced fuels.

6. It must be realized that the results of the parametric program won't answer all questions regarding fuel performance in an aircraft engine; e.g., steady-state results may not be additive in a dynamic system. However, the parametric program should provide the best source of predictive data for design purposes. Final confirmation may require a test program using aircraft engine hardware for each specific aircraft of concern.

7. It is recognized that the design of supersonic aircraft fuel systems will require a fuel tank simulator (akin to that described above) in which flight parameters and their effect on thermal/oxidative stability can be systematically studied. Clearly the geometry will differ from the engine simulator, as will the selection and range of variables. The device should incorporate means of studying the effects of tank insulation, inerting and cleaning techniques. It is further recognized that the engine and aircraft tank simulations will likely be carried out independently until such time as a system design is laid down; at that point, integrated systems tests are indicated.

GROUP IV. ENGINE SYSTEM TRENDS AND REQUIREMENTS
Chairman: Walter D. Sherwood

INTRODUCTION:

This group took note of the importance of fuel efficiency, engine durability, and emissions. Some reasonable balance is necessary because gains in some areas cause degradations in others. The group examined the impact of fuel properties, particularly thermal stability.

SUMMARY OF CONCLUSIONS:

1. ~~There are~~ problems and sensitive areas in engine fuel systems with respect to deposits with today's fuel. The relative influence of factors (i.e. fuel system design, operational procedures or thermal stability per se) cannot be defined.

2. Trends in engine design are toward a potentially more severe environment for fuel, however today's thermal stability levels will be the target for new engine designs. Low emission combustor designs could make increased demands on thermal stability and therefore care must be exercised to ensure that nozzle and manifolding design caters to the problem. Recognition of the practical limits of emission control must be achieved by all regulatory agencies acting in concert.

3. Relationship between ~~thermal~~ stability test methods and actual fuel degradation behavior in engines is unknown. The predictable relationship between JFTOT and actual behavior in the field is only directional in nature.

4. Fuel cost at today's prices is several times the total engine maintenance cost in the direct operating cost picture.

5. The effect of fuel degradation on fuel nozzle performance is to accelerate turbine performance degradation and increase fuel consumption and engine maintenance. Fuel system/nozzle design or redesign to achieve less sensitivity to fuel deposits is possible in some cases.
6. For subsonic commercial engine operations, fuel degradation effects on heat exchangers (fuel/oil-coolers) has not been a significant problem to date and does not appear to be a future design problem with fuels meeting present specifications. For potential supersonic commercial applications, research on effects of fuel with various thermal stability levels should be conducted for heat exchanger system designs.
7. With today's commercial aircraft designs, there are no areas outside the engine considered critical from a thermal stability standpoint. Properly designed fuel heating systems will not add more thermal stability stresses to the fuel on subsonic commercial aircraft.
8. Thermal stability at airport delivery points is a potential question to be resolved (see recommendations). Storage instability contribution is not of concern in commercial operations due to the relatively short time between production and consumption of the fuels involved. Point of delivery, quick tests for thermal stability are not considered of sufficient benefit to merit development at this time.
9. Need for purging, cooling or insulation is highly dependent on application of the engine. Feasibility of any of the foregoing is completely design sensitive.

RECOMMENDATIONS:

1. NASA should sponsor or coordinate a survey of fuel thermal stability at airports. Precautions on sampling and transporting samples are mandatory.

2. In view of the concern over fuel thermal stability problems and in the national interest as well, NASA should determine the realistically practical limits of aircraft emission control with full consideration of all fuel property and cost objectives, energy conservation, engine durability, consumer costs for transportation and inflationary pressure.

3. It is recommended that the present thermal stability levels be retained for any proposed fuel specifications in the foreseeable future as long as it is cost effective.

APPENDIX D

WORKSHOP PARTICIPANTS

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