

FUELS RESEARCH - FUEL THERMAL STABILITY OVERVIEW

Stephen M. Cohen
National Aeronautics and Space Administration
Lewis Research Center

It has become apparent that the world supply of petroleum crude is a limited resource and that alternative fuels or crude supplies must be examined as a means of ensuring an adequate supply of aviation fuel for the next 50 years or more. Several changes that may be expected include refinery processing of higher boiling-point crude fractions to increase the yield of mid-distillate fuels, relaxing current jet fuel specifications to increase yield, and incorporating alternative crude sources such as shale oil or coal oil into refinery feedstocks. These approaches are not necessarily mutually exclusive and, in fact, would likely be used in combination to alleviate fuel availability problems.

One potentially detrimental effect that must be considered in any of these approaches concerns the chemical instability of the jet fuel product. The term instability refers to chemical alteration or degradation of the fuel that may occur as a result of thermal stress (thermal instability) or during long-term storage (storage instability). The problem manifests itself as sediment in storage tanks or filters, fouling of heat-exchanger surfaces, or undesirable deposits in fuel manifolds or combustor spray nozzles.

Thermal instability was first identified as a problem in aviation turbine engines in the 1950's, but the development of the SST in the 1960's focused much more attention on it. In the SST, the fuel serves as a heat sink for the wing surfaces, which are aerodynamically heated, and as a result the fuel is susceptible to thermal degradation.

In subsonic aircraft, aerodynamic heating is not a problem and fuel tank temperatures are much lower than those in supersonic aircraft. However, in the subsonic aircraft fuel system, high fuel temperatures are encountered in the lubricating-oil heat exchanger (where the fuel is used to cool the engine lubricant) and in the combustor fuel manifold and nozzles. Thermal instability can result in deposits fouling heat-exchanger surfaces, which can decrease heat transfer, and in deposits in spray nozzles causing nonuniformities in spray patterns, which could reduce hot-section-component durability. The current trend toward higher cycle-pressure-ratio engines with higher combustor inlet temperatures tends to aggravate stability problems, as do more sophisticated fuel injection systems with closer spray-nozzle tolerances and multiple injectors with lower pilot-fuel flow rates.

Much information has been obtained on the nature of the chemical processes associated with thermal instability. It is generally agreed that autoxidation, from oxygen in the fuel, is the primary mechanism in initiating deposit formation. The course of the reaction can be followed by moni-

toring the concentration of intermediates, such as the hydroperoxides. The chemistry of the reactions involved is usually free radical, and therefore any constituent that tends to form free radicals easily will probably be instrumental in degrading the fuel out of proportion to its concentration. Heterocompounds containing nitrogen, sulfur, or oxygen and trace metals, particularly copper, have been shown to be detrimental to stability. Although some aspects of the degradation process are understood, much information is still lacking. For example, beyond elemental analyses, little is known regarding the actual structure of the deposit. Also, the specific influence of the many possible nitrogen-containing compounds, singly or in combination, has only begun to be determined.

Shale and coal syncrudes are typically higher in one or more of the elements likely to promote deposition, and fuels derived from these feedstocks will probably exhibit degraded thermal stability without additional refinery processing. Future fuels derived from petroleum with potentially broadened properties may contain higher concentrations of olefins and aromatics, which can also degrade stability characteristics. Many of these factors will be significant in the use of broadened-property or synthetic fuels.

Several test methods have been developed for characterizing jet fuel thermal stability. Two test procedures currently in use for specifying aviation turbine fuels are the ASTM-CRC Fuel Coker and the Jet Fuel Thermal Oxidation Tester (JFTOT). Both of these methods pass the test fuel over a heated tube and then through a filter that traps any degradation products formed during the test. A qualitative assessment of the thermal stability of the fuel is provided by the extent of filter plugging as indicated by measuring the pressure drop across the test filter and by a visual evaluation of the amount of deposit on the heated tube. The simple pass-or-fail criterion provided by these tests is adequate for the present generation of relatively stable fuels, but a more quantitative measure of stability may be desirable in the future as fuels that may not have uniformly high quality become more common.

The objectives of NASA's thermal stability research are to determine the thermal stability characteristics of potential future fuels, to identify and examine the effects of these characteristics on aircraft fuel systems, and to evolve advanced fuel system technology and design guidelines for future fuels with lower thermal stability. Thermal stability considerations may affect fuel availability, total fuel-related systems cost, overall system energy consumption, engine performance and durability, and environmental considerations.

On November 1 and 2, 1978, Lewis hosted a workshop on jet fuel thermal stability in order to present a forum for discussing the various aspects of the thermal instability problem and to identify critical areas for focusing future efforts (ref. 1). Some of the conclusions of this workshop were as follows:

1. New laboratory techniques are not required, but improvements in existing test methods are needed.

2. End-use performance is not well correlated with laboratory test devices.
3. Trends in engine design indicate a more severe problem in the future.
4. There is a need for balance between concerns for thermal stability and emission controls, energy efficiency, durability, and cost.

The workshop also recommended the following areas for future work:

1. Perform more detailed characterization of deposits.
2. Examine effects of fuel composition.
3. Perform additional studies on the effects of metal surfaces, dissolved metals, additives, and interactions.
4. Obtain parametric data by using a generalized test apparatus that could relate laboratory screening tests to actual performance.
5. Study storage and aging effects.
6. Develop standard sampling and handling techniques.
7. Establish referee fuels.
8. Determine importance of non-free-radical reactions.
9. Conduct survey to determine stability at delivery point.

The first five recommendations for future work are presently being actively pursued under NASA sponsorship. A contractual effort on the chemistry of fuel deposits and precursors is presently in the planning stages. The results of two contracted activities are given in two papers, the first by Dr. Alexander Vranos of UTRC, on an experimental study of thermal stability, and the second by Dr. Stephen R. Daniel of the Colorado School of Mines, on the effects of nitrogen compounds on stability. In addition, Mr. C. J. Nowack of the Naval Air Propulsion Center will bring us up to date on part of the Navy's activities.

A number of research projects are being conducted here at Lewis. Mr. Edgar L. Wong is studying the chemistry of fuel thermal deposits by using a modified JFTOT and pure compounds. Dr. Albert C. Antoine is examining the effects of nitrogen compounds on thermal stability by doping jet fuels. Under the characterization of fuel thermal stability are two related efforts. The first is a parametric study over a wide range of conditions using a test facility capable of determining the effect of many variables. Besides evaluating future fuels this apparatus will (1) aid in relating laboratory-scale tests to full-scale experience, (2) help in determining the potential of accelerated testing, and (3) provide data on the mechanisms underlying the deposition process. The second part of the characterization effort is aimed at developing and improving techniques for examining the products of degradation so as to learn as much as possible from every sample and every test.

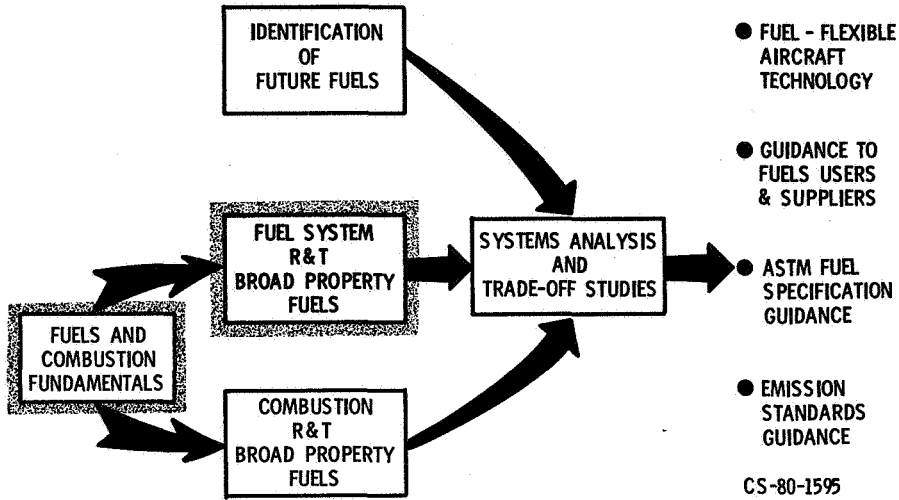
As a part of these efforts a special test section was designed and built for use with the standard JFTOT. In this apparatus deposits are formed on a flat specimen rather than on a tube. With this geometry a number of analytical tools can be used for deposit analyses. This apparatus will be used for making samples to aid in developing diagnostic techniques and also as a screening device for the parametric test facility.

Because of a crowded schedule there was not sufficient time at the symposium to present the work of all the organizations involved in thermal stability research. In addition to those organizations represented here, there is a considerable body of work being supported by the Naval Research Laboratory, the Air Force Aero Propulsion Laboratory, the Army Fuels and Lubricants Research Laboratory, and the DOE Bartlesville Energy Technology Center.

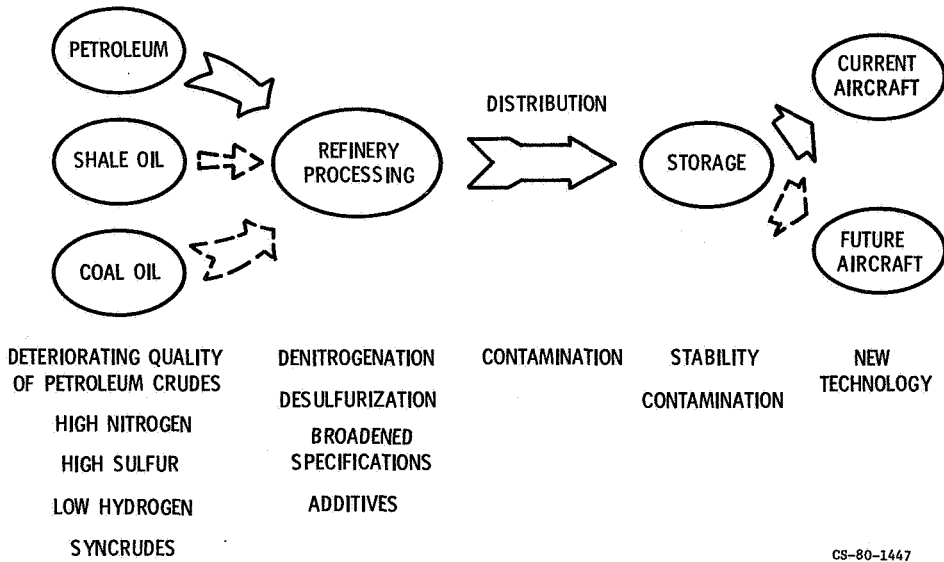
REFERENCE

1. Taylor, William F., ed.: Jet Fuel Thermal Stability. NASA TM-79231, 1979.

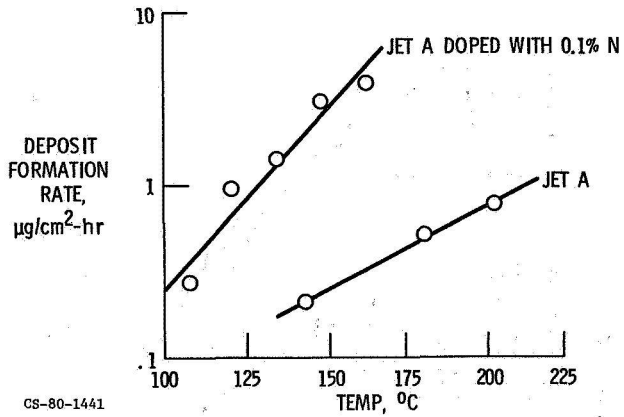
AIRCRAFT RESEARCH AND TECHNOLOGY FOR FUTURE FUELS



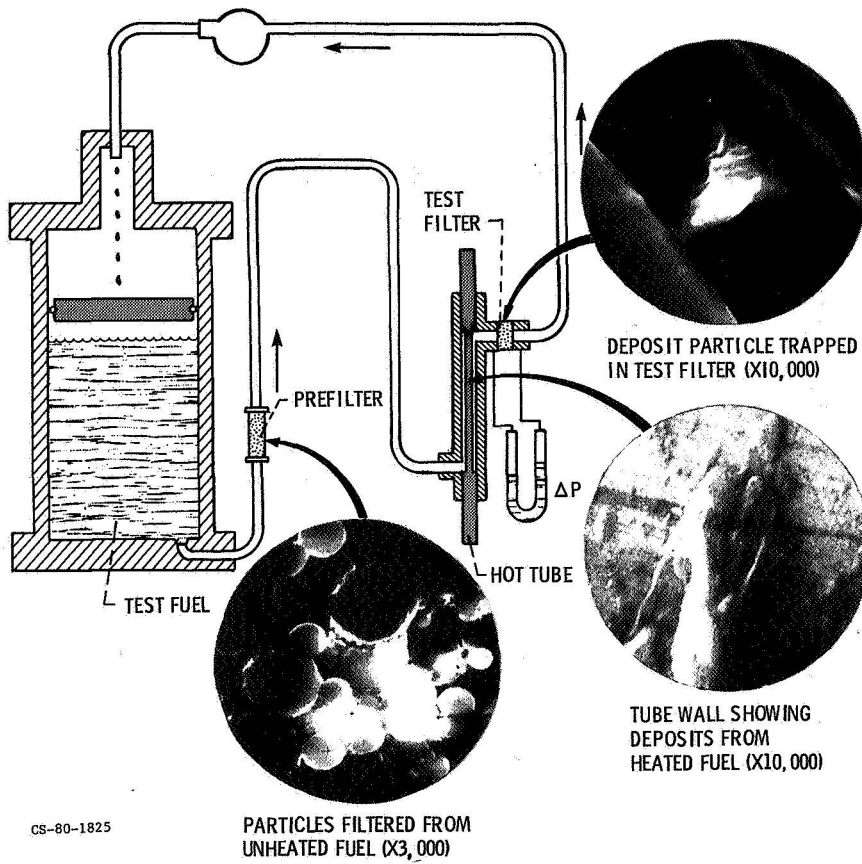
THERMAL STABILITY CONSIDERATIONS



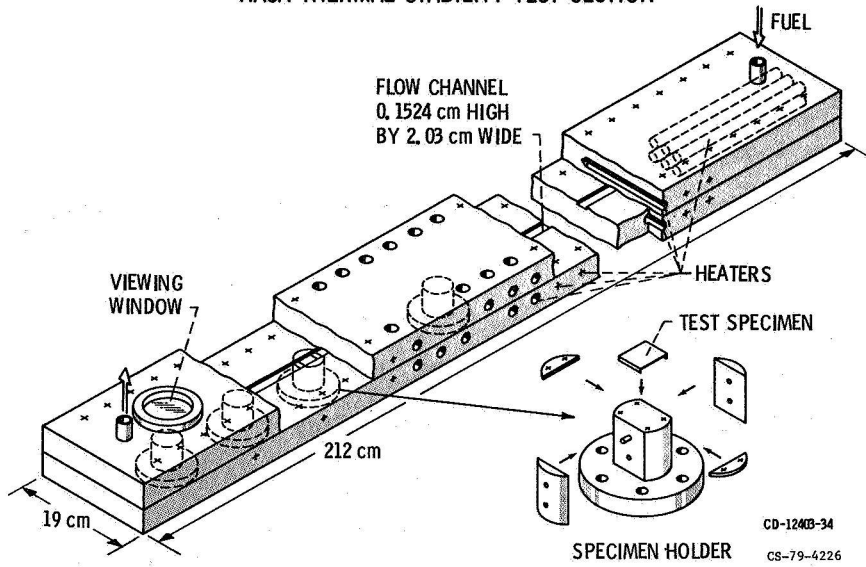
EFFECT OF FUEL NITROGEN CONTENT ON THERMAL STABILITY



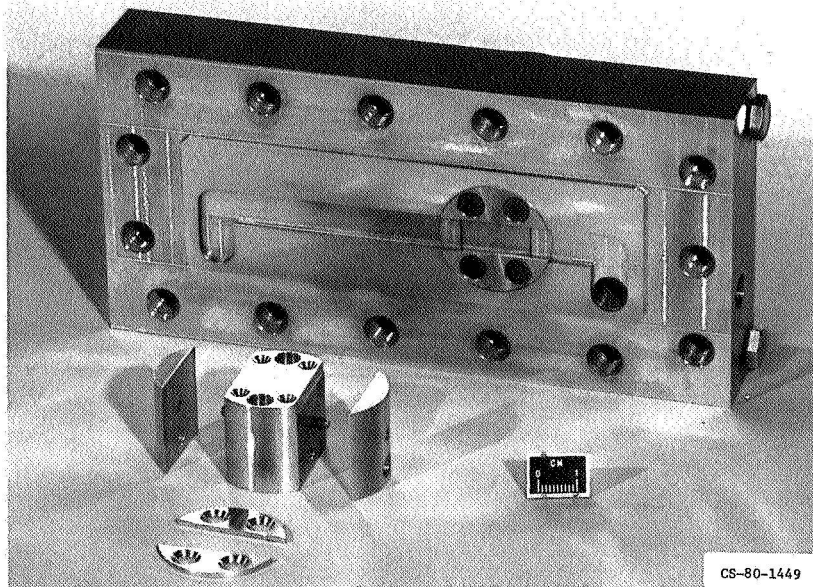
JET FUEL THERMAL OXIDATION TESTER (JFTOT) SCHEMATIC



NASA THERMAL STABILITY TEST SECTION



FLAT SAMPLE HOLDER FOR JFTOT



SOME ANALYTICAL TECHNIQUES FOR THERMAL STABILITY TESTS

TECHNIQUE	INFORMATION TO BE OBTAINED
GAS CHROMATOGRAPHY/ LIQUID CHROMATOGRAPHY	FUEL COMPOSITION, PRIOR TO AND FOLLOWING TEST
POLAROGRAPHIC SENSOR	MONITOR TOTAL DISSOLVED O ₂ IN FUEL
MICROBALANCE	WEIGHT OF DEPOSITS AND PARTICULATES
SCANNING ELECTRON MICROSCOPY	MORPHOLOGY OF DEPOSIT AND PARTICULATES
ATOMIC SPECTROSCOPY ELEMENTAL ANALYSIS	TRACE METALS IN FUEL COMPOSITION OF DEPOSITS AND PARTICULATES
ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)	COMPOSITION AND STRUCTURE OF DEPOSITS AND PARTICULATES
FOURIER TRANSFORM INFRARED (FT-IR)	STRUCTURE OF DEPOSITS AND PARTICULATES
PHOTOACOUSTIC SPECTROSCOPY (PAS)	DEPOSIT STRUCTURE, THERMAL DIFFUSIVITY, THICKNESS
WET METHODS (TITRATION)	MONITOR HYDROPEROXIDE FORMATION IN FUEL