DEFENSE MOBILITY FUELS

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CONFERENCE ON
COMPOSITION OF TRANSPORTATION SYNFUELS
PANEL ON
DEFENSE MOBILITY FUELS

Opening Remarks: LCDR L. A. Lukens
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SWRI/DOE

Text

Taken in the traditional sense of providing for the national defense, the central defense energy issue is basically one of guaranteeing adequate supplies of energy for U.S. interest both at home and abroad under both peacetime and wartime conditions. In addressing this issue, there are a number of aspects with which we must be concerned.

The DOD is basically in the transportation business and, as such, we must be concerned about our present and continued heavy reliance upon liquid petroleum products. DOD, the largest single U.S. energy user, accounts for about 2% of the national energy consumption through direct usage and another 2-3% indirectly through defense related industries. These percentages represent typical peacetime requirements. For a typical wartime scenario, DOD's portion of the national energy requirements would increase by a factor of about 3.

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Of the DOD's current total energy requirements, about 70% is in the form of liquid petroleum products or approximately 480,000 barrels per day. Unlike the civilian sector, wherein approximately 70% of the petroleum consumption is for gasoline and heating oil products, DOD is consiberably more dependent upon the middle distillate fuels, with approximately 79% of our liquid petroleum supplies being consumed by shipboard and aircraft systems.

Looking to the foreseeable future, we see little or no relief in this pattern of heavy DOD dependence upon petroleum fuels. As a matter of fact, our current projections indicate little or no significant decrease in DOD's future requirements for liquid hydrocarbon products. As is the case in the civilian transportation industry, we continue to design and build weapon systems under the a priori assumption that they will be fueled with petroleum-like products. Accordingly, these newly designed vehicles, as well as those currently in operation, will continue to be the mainstay of the DOD until the turn of the century. My point is simply this: unless our present design approaches as well as many of our currently operating systems are modified extensively, liquid hydrocarbons will continue to be the primary fuel for the DOD well into the 21st Century.

We must find alternatives - alternatives which are domestically controllable, technically feasible, and economically, environmentally, and socially acceptable.

For the near term, say for the next half century or so, these alternatives for liquid hydrocarbon transportation fuels will, for the most part, find their genesis in various fossil energy forms. The problem, of course, is that to make this a practical reality, we must convert the lower availability forms, such as coal, oil shale and tar sands, into the higher availability forms required of our present day systems, particularly as requried for the transportation industry and particularly as required by our mobile defense systems. For the production of transportation fuels, each of these fossil energy sources pose certain advantages and disadvantages.

While coal certainly offers one of the greatest potentials for relieving our ever growing dependence upon imported oil, the U.S. technology for producing middle distillate liquid fuels from coal is lagging that of other alternatives, particularly oil shale. Moreover, because of the high degree of costly hydrotreating required to bring coal liquids into the middle distillate fuels range, economic considerations will most likely direct liquid products derived from coal towards the gasoline, boiler heating oil, and petrochemical feedstock markets. Accordingly, further consideration of coal derived defense mobility fuels must necessarily await further advances in coal processing technologies leading to the commercial availability of the middle distillate fuels of primary interest to the military.

From a technical viewpoint, tar sands represent a potentially viable source of middle distillate range defense mobility fuels. However, the relatively small extent of the U.S. tar sand deposits and the lack of any significant national effort to develop these deposits precludes serious consideration of this alternative, at least for the immediate future.

Of the various fossil energy alternatives to petroleum, oil shale must be considered the most attractive near term source of defense mobility fuels. Within the U.S. several oil shale extraction technologies have been developed and tested in equipment ranging from one-tenth to one-fourth commercial size. Compared to other synthetic sources of liquid hydrocarbon fuels, oil shale appears to be more economically viable; however, not sufficiently viable to date to muster the required private investor interest to commercially develop this important resource.

With regard to the conversion of syncrudes into refined petroleum products, there is a need to improve the economics of refining syncrudes in order to bring the cost of synfuels into a more competitive status with the price of conventional fuels. To achieve this competitive economic status for a syncrude refining industry will obviously require some research effort directed towards the optimization of refining methods specifically tailored to syncrude processing requirements.

As with refining, the end-use testing of synfuels is not considered a major technical barrier to commercial development. Demonstrating the suitability of synfuels in various end-use systems is, nonetheless, of importance in establishing the overall economics of this growth industry. With respect to the DOD interest, however, it is essential that the suitability of synfuels for military use be fully assessed before the Armed Forces will be prepared to acquire and use these fuels at the time they become available in commercial quantities.

Defense Mobility Fuels Action Plan

In December 1977, the Deputy Secretary of Defense established a Task Force, chaired by the Deputy under Secretary of Defense (Research and Advanced Technology) to address and to make recommendations on the alternatives available to DOD to meet its future mobility fuel requirements. While the specific recommendations of this Task Force are currently under review, I can tell you that the Task Force is stressing the need to develop a comprehensive Defense Mobility Fuels Action Plan, the essential ingredients of which place heavy emphasis in the following areas:

- Cooperative efforts between DOD and DOE to assist in meeting DOD's mobility fuel needs through commercial development of domestic synthetic fuel sources.
- The development of technical and operational plans for DOD to accommodate a transition from the use of conventional to synthetic fuels in the post 1985 time frame.

- An accelerated DOD engine/fuel technology program to establish acceptable synthetic fuel specifications and to develop engine systems capable of burning a broad range of synthetic fuels.
- The development of the required industrial base to enable DOD to implement the capability to use synthetic fuels.

In general, this action plan is directed towards minimizing the potential loss of military effectiveness that would inevitably result from a disruption of energy supplied under foreign control. This objective can best be met by placing the DOD in the position of an informed customer for the fuels produced by the emerging commercial synfuel industry. The various synfuel programs now underway within the DOD, as well as those planned for the future, are specifically designed for this purpose.

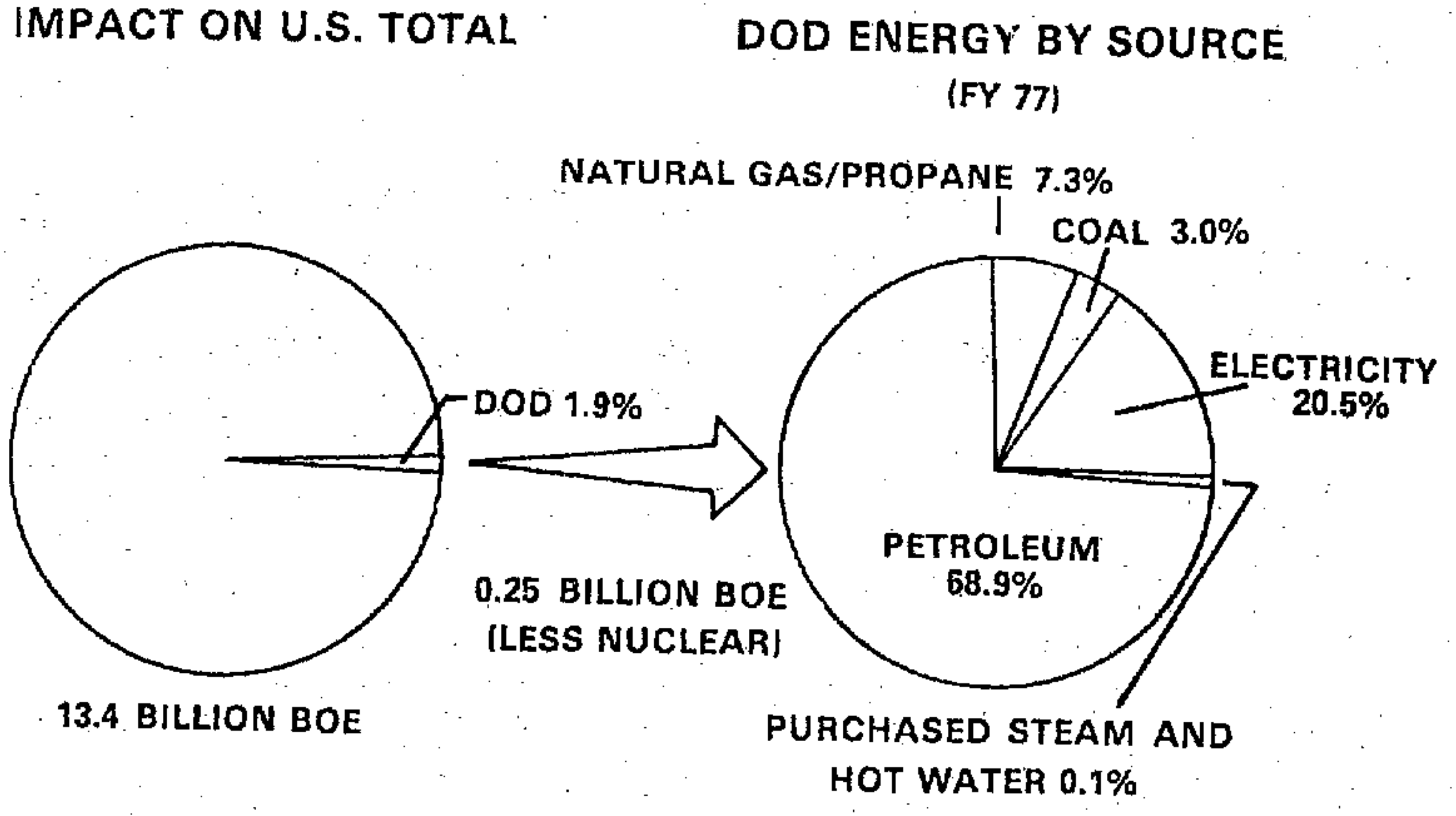
In summary our various R&D efforts are directed towards assessing the suitability of synthetic fuels for DOD use, with early emphasis on oil shale. Our final products from this R&D effort will be fuel procurement specifications and end use guidelines for the operating forces. If we do our job right, we will contribute towards ensuring that our energy supply lines remain full, providing energy to the Armed Forces in the right form, in the right place and in sufficient quantities to carry out our missions around the World.

SYNTHETIC
FUEL
RESEARCH AND
DEVELOPMENT
PROGRAMS

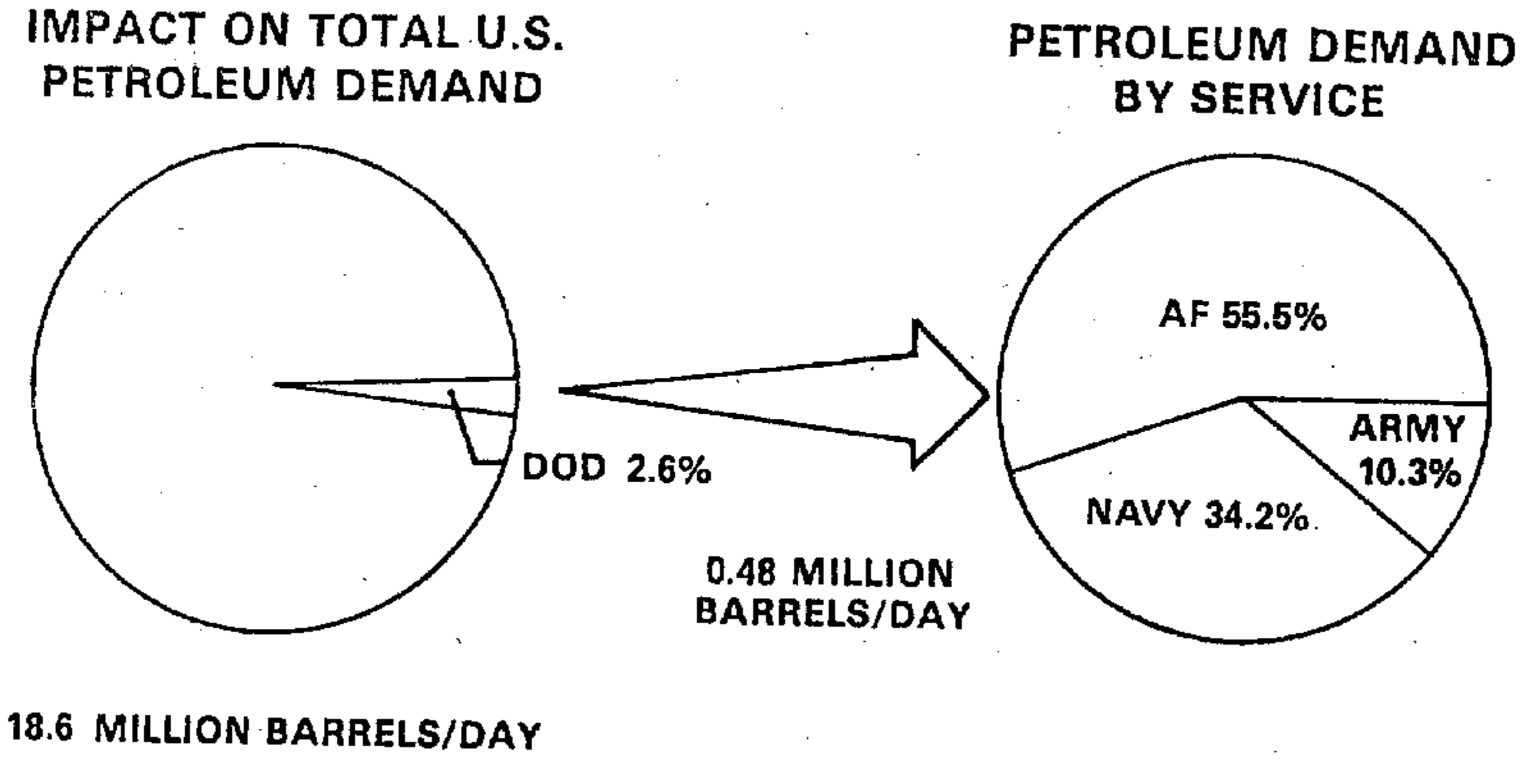
"IN FACT, THERE IS NO MORE SERIOUS THREAT TO THE LONG TERM SECURITY OF THE UNITED STATES AND TO ITS ALLIES THAN THAT WHICH STEMS FROM THE GROWING DEFICIENCY OF SECURE AND ASSURED ENERGY RESOURCES."

SECRETARY OF DEFENSE HAROLD BROWN.
TESTIMONY BEFORE THE HOUSE AD HOC
COMMITTEE ON ENERGY, MAY 4, 1977

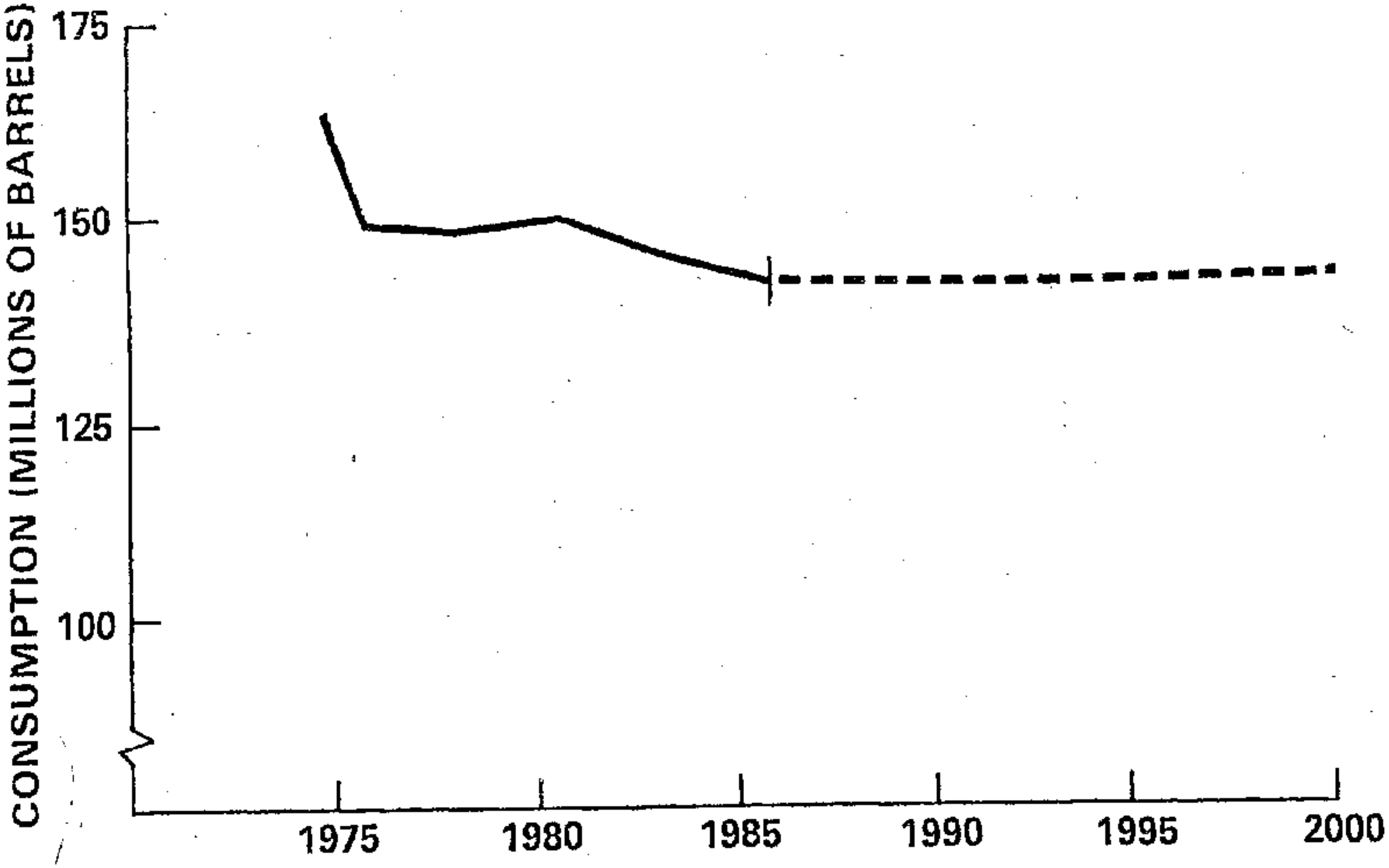
FY 77 DOD ENERGY DEMAND (EXCLUDING NUCLEAR)



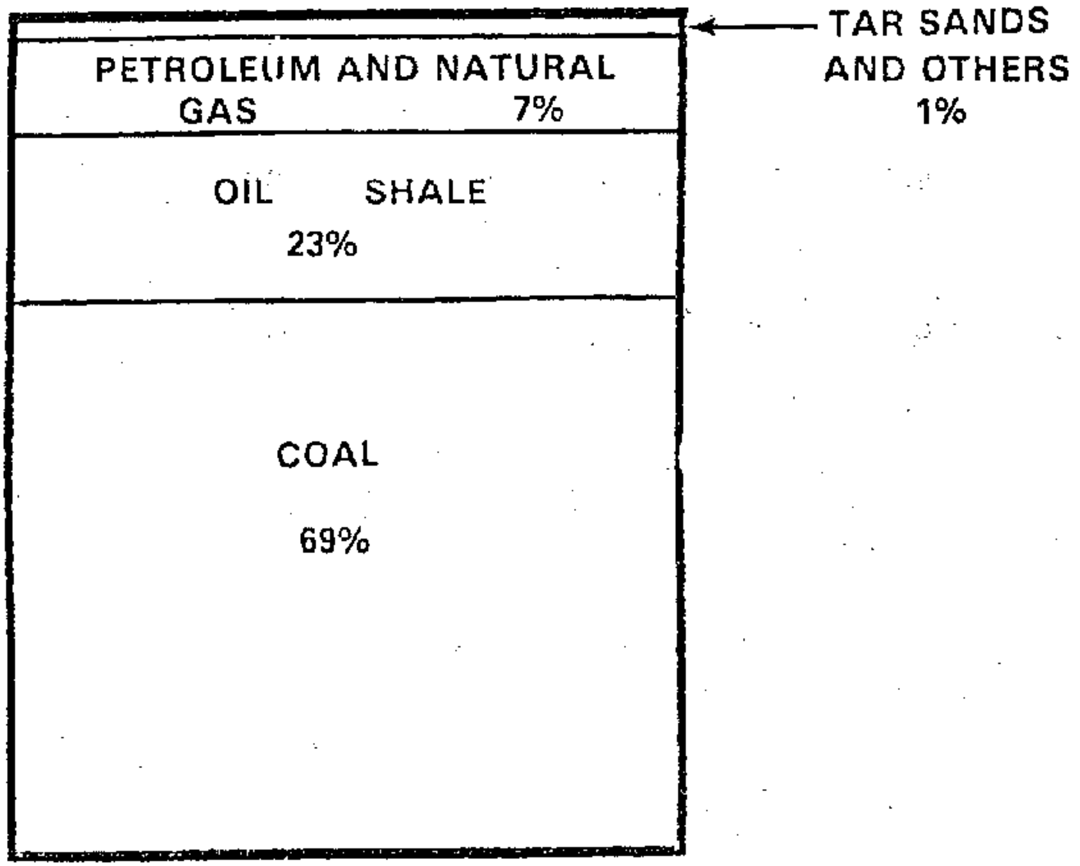
FY 77 DOD PETROLEUM ENERGY DEMAND



DEFENSE CONSUMPTION OF MOBILITY FUELS



U.S. RECOVERABLE FOSSIL FUEL RESOURCES



COMPARISON OF SYNTHETIC CRUDE OIL SOURCES

	HIGH QUALITY U.S. CRUDE	RAW SHALE OIL	ATHABASCA TAR SANDS BITUMEN	COAL-DERIVED CRUDE
HYDROGEN/ CARBON	1.70	1.64	1.50	1.25
SULFUR, % WEIGHT	0.2	0.8	4.6	0.2
NITROGEN, % WEIGHT	0.1	2.0	0.4	0.7
OXYGEN, % WEIGHT	< 0.1	1.40	0.94	1.62

NOTE: KEROSENE JET FUEL HAS A HYDROGEN/CARBON RATIO OF 1.81 TO 2.01

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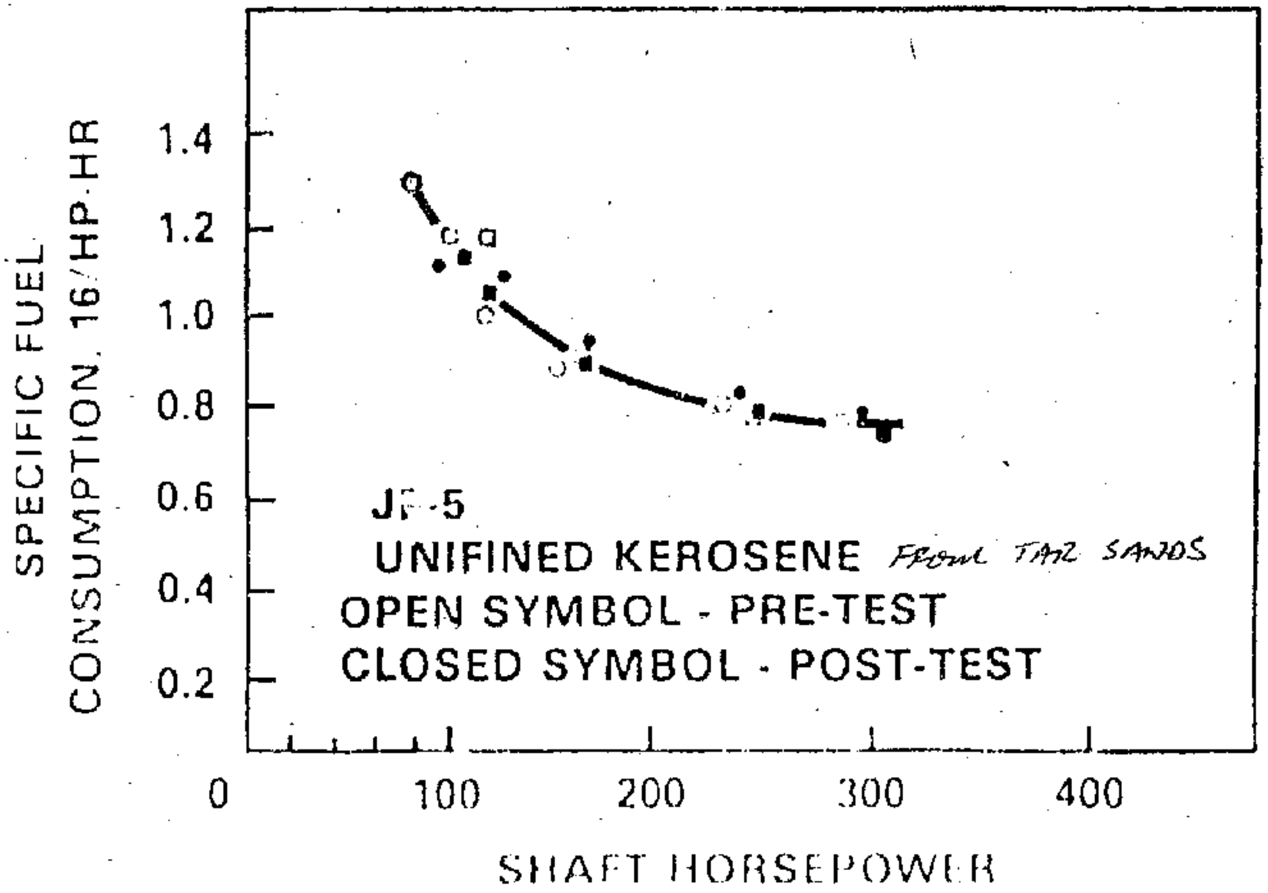
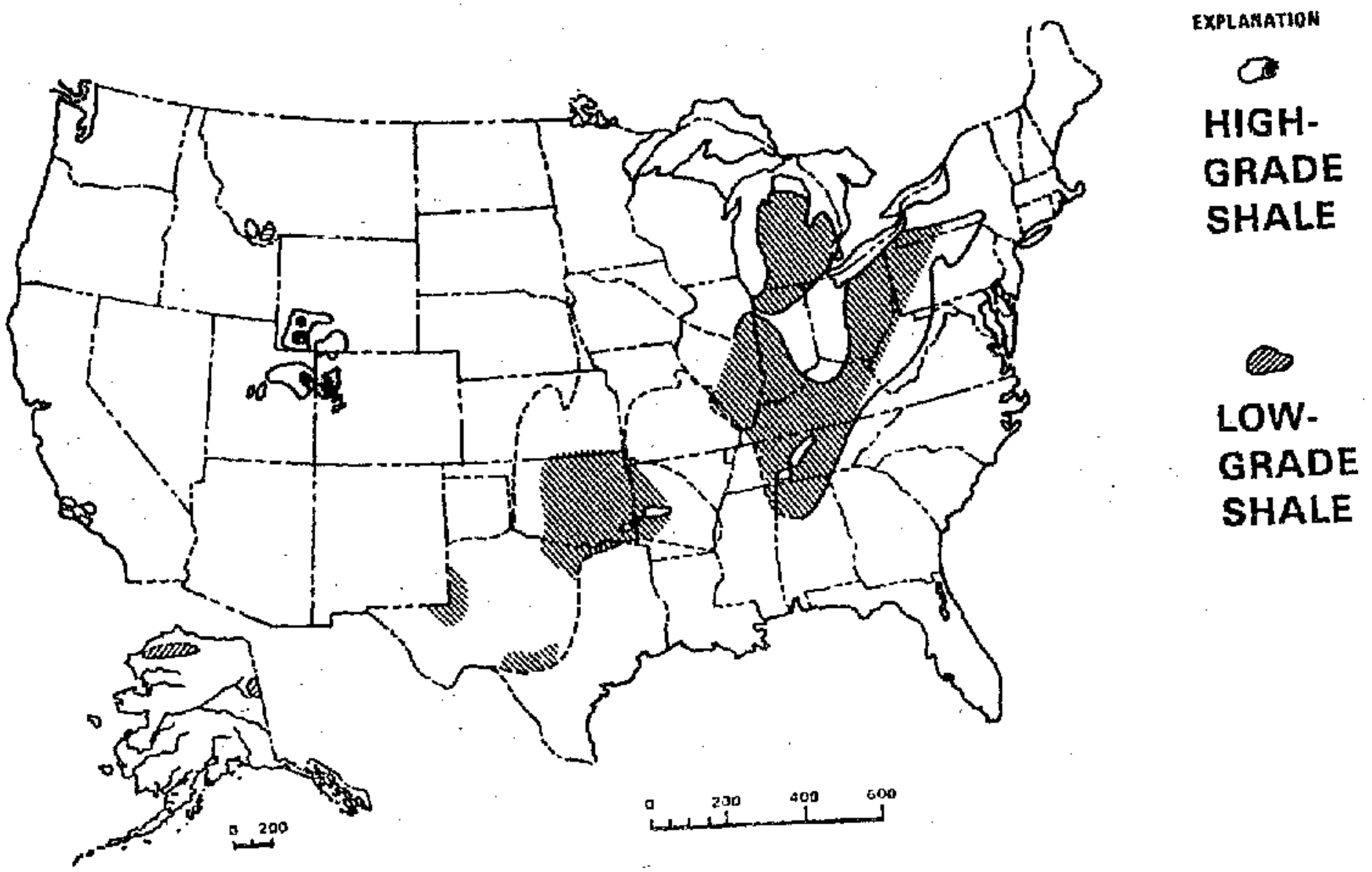
ENGINE PERFORMANCE RESULTS

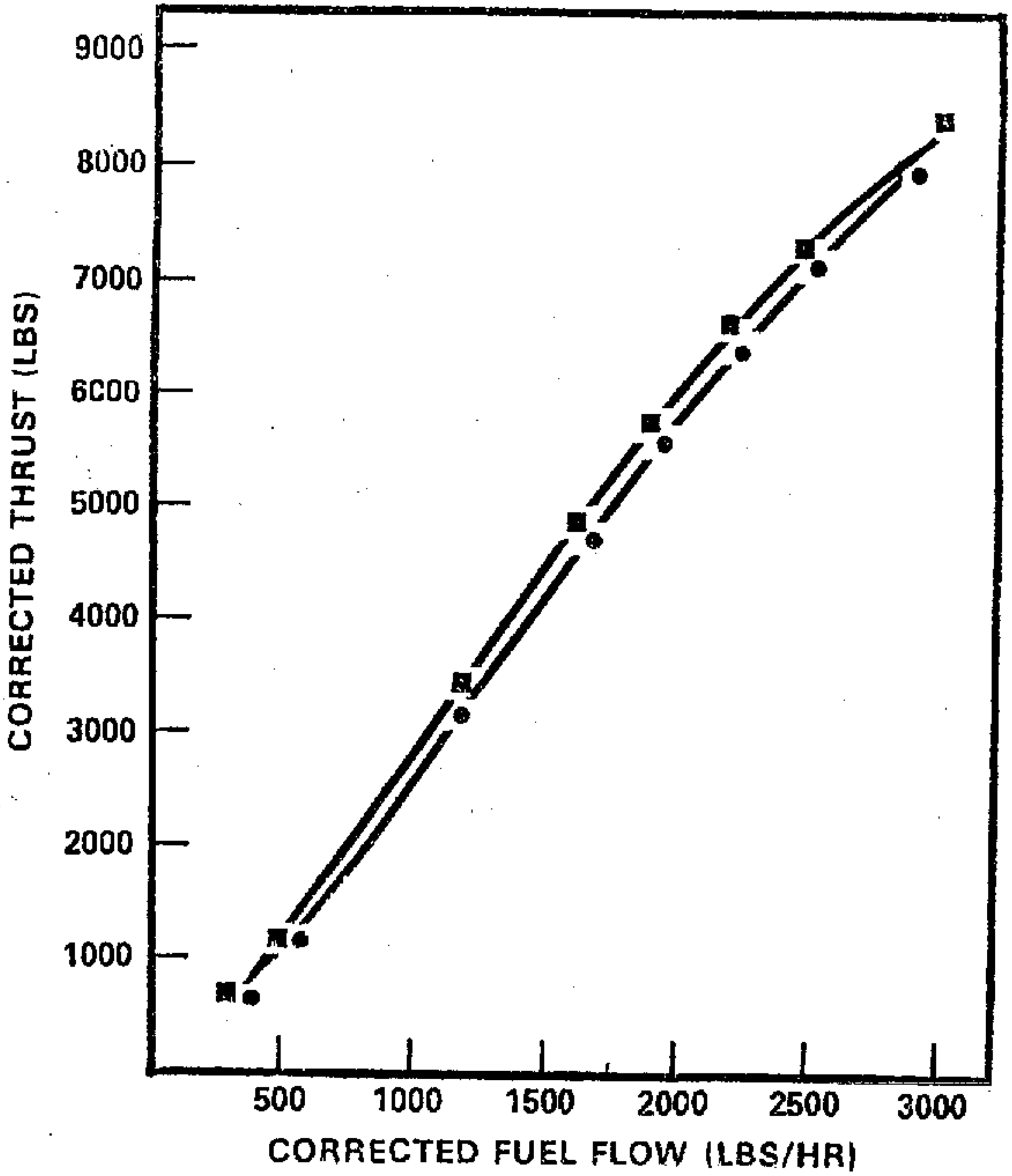


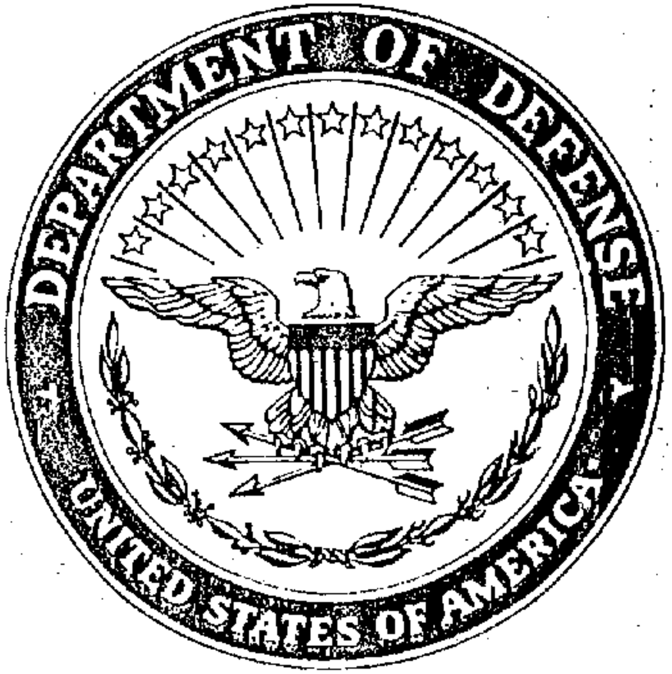
PRINCIPAL REPORTED OIL-SHALE DEPOSITS OF THE UNITED STATES



SHALE OIL PERFORMANCE CORRECTED TO STANDARD DAY CONDITIONS

LEGEND
- ● PETROLEUM JP-5
- ■ SHALE JP-5

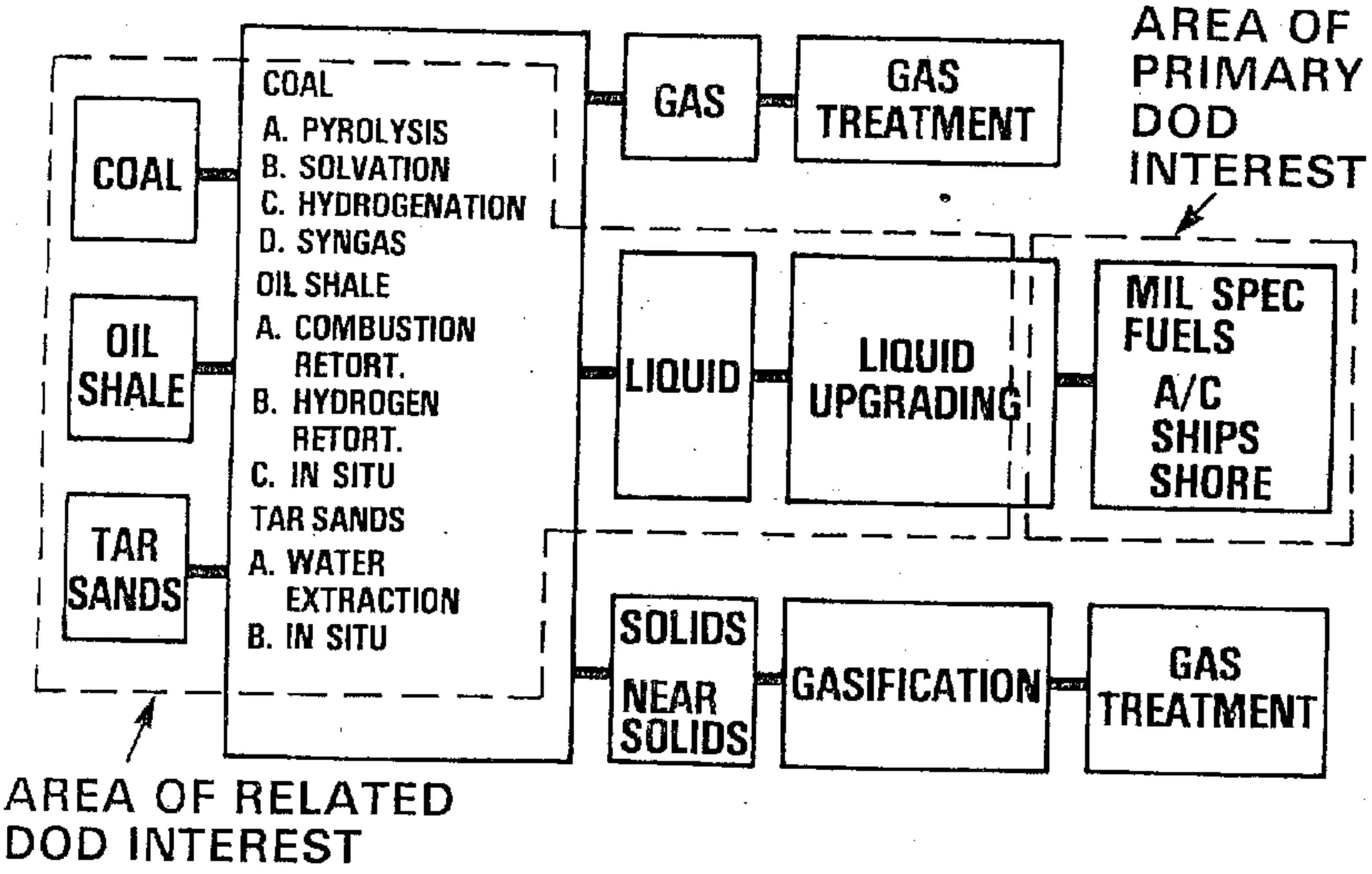




DEFENSE MOBILITY FUELS ACTION PLAN

DOD ENERGY R&D PROGRAM

SYNTHETIC FUEL PROGRAM



COAL

OIL SHALE

TAR SANDS

COAL
- A. PYROLYSIS
- B. SOLVATION
- C. HYDROGENATION
- D. SYNGAS

OIL SHALE
- A. COMBUSTION RETORT.
- B. HYDROGEN RETORT.
- C. IN SITU

TAR SANDS
- A. WATER EXTRACTION
- B. IN SITU

GAS

GAS TREATMENT

LIQUID

LIQUID UPGRADING

MIL SPEC FUELS
A/C
SHIPS
SHORE

SOLIDS
NEAR SOLIDS

GASIFICATION

GAS TREATMENT

AREA OF PRIMARY DOD INTEREST

AREA OF RELATED DOD INTEREST

FUELS RESEARCH & DEVELOPMENT FOR ARMY WEAPON SYSTEMS

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FUELS RESEARCH AND DEVELOPMENT FOR ARMY WEAPON SYSTEMS

The US Army inventory of mobile equipment encompasses a wide variety of powerplant systems which are fueled by three primary liquid hydrocarbon fuels; namely, automotive gasoline (MOGAS), jet turbine fuel (JP4, JP8, and JP5), and diesel fuel. A small portion of the aircraft fleet continues to use aviation gasoline for reciprocating piston engines, but this is in a gradual phase-out as these are being replaced by turbine-powered versions. These fuels and their applications are described by the following specifications:

FUEL	COMBAT/TACTICAL USE	NATO DESIGNATION	ADMINISTRATIVE OR NON-COMBAT USE
Automotive Gasoline	MIL-G-3056D	F-46	VV-G-1690B and ASTM D439
Jet Turbine Fuel	MIL-T-5624G, MIL-T-83133	F-40/F-44 F-34	ASTM D1655
Diesel Fuel	VV-F-800B	F-54	ASTM D975

The fuel requirements for this fleet of materiel and equipment obviously must encompass and ultimately satisfy a wide range of powerplant systems ranging from small two-cycle spark-ignition engines found in utility equipment and remote pilot vehicles to large two cycle and four cycle compression-ignition engines used in armored vehicles, self-propelled guns, and tactical support equipment. In addition, gas turbine powerplants, now being introduced into power generation equipment and the new main battle tank, are used in fixed/rotary wing aircraft.

In those instances where new powerplants are developed for specific weapon delivery systems, research programs are initiated early in the materiel acquisition cycle to insure their satisfactory operability on existing military fuels. Although some of these powerplants evolve from commercially-available systems, their configuration has been modified to fit the performance needs of the developing equipment which in turn may create fuel requirements exceeding those prevailing in the civilian sector.

Research on developing fuel requirements for new/modified powerplant system starts with fuel characterization, definition of fuel property compliance with the proper specification, and identification of fuel quality which may be relaxed to assist in overall refinery output efficiency. This is followed by laboratory component testing including combustor operation and single cylinder engine testing to identify any combustion performance problems, potential emissions generation, hardware incompatibility, engine lubricant interactions, and potential effects on engine life cycle goals.

Following this, full-scale engine dynamometer testing is performed to identify hardware acceptability and provide minimal assurance of no maintenance problems. During this portion of testing, long-term durability effects are defined. A follow-on to the full-scale dynamometer testing involves the fleet testing requirement where equipment operates under field conditions to validate the previously developed dynamometer data. For discussion purposes, one could assess the quantity of fuel and test hours on fuel wetted/affected components of major engine development and qualification programs. The T700-GE-700 (developed for the UH-60 and AH-64 aircraft) for instance, utilized approximately 70,000 test hours to develop and qualify its fuel control and related accessories. Combustor and related testing included approximately 1300 hours. Overall engine test hours were approximately 8,000. Total fuel consumed during the development program was approximately 800,000 gallons. This gives a good indication as to the time and fuel quantities required for new engine certification.

As was mentioned previously, US Army fuels are divided into Combat/Tactical versus Administrative/Non-Combat applications. The Combat/Tactical designation identifies requirements unique to the military which are not found in commercial fuels. These requirements therefore provide the basis for our R&D program in the integration of fuel property requirements to powerplant systems. These major requirements which are the pacing factors for our R&D program are:

- Commonality of Fuels - Increased emphasis within NATO standardization and interoperability has resulted in a requirement to reduce the number of fuels needed within the military supply system. This requested reduction in fuel types will concurrently improve the logistic posture in terms of the supply of fuels to combat areas. As part of this thrust, the ability of military engines to operate on a wide slate of fuels or have a multifuel capability is being pursued.

- Survivability - As a result of the recent Middle East confrontations, the survivability of armored vehicles against the fire threat surfaced as a critical need. In response to this, a DA program entitled Fire Survivability of Combat Vehicle (FIS-COV) was formerly established to reduce/eliminate this threat. On part of this program identifies development of a fire-safe fuel. This fuel, when fully developed, will eliminate the fire threat of diesel fuel when armored vehicles operate in hostile environments.

- Stability - Military operations have generated a requirement for fuels to possess long-term stability. This results from product storage for (1) emergency and stand-by use, (2) war reserve stocks, (3) intermittent operational use, and (4) depot rebuild processes. More recently, an additional requirement for storage of vehicles in Europe in a fully-fueled condition has tentatively surfaced as a means to improve operational readiness.

Other fuel requirements unique to the military and considered to be important are listed as follows:

- minimum operating temperature limitations to allow use regardless of environment.

- specific fuel additive restrictions and requirements (fuel system icing inhibitor, corrosion inhibitor, biocide, etc.).

- improved combustion efficiency to reduce fuel consumption (energy conservation) and to extend operating range capabilities.

- variable quality specification properties to allow maximum production while meeting minimal requirements.

FUELS RESEARCH AND DEVELOPMENT FOR ARMY MATERIEL

PRIMARY ARMY MOBILE FUELS

	COMBAT		ADMINISTRATIVE	
FUEL	MIL SPEC	NATO DESIGNATION	FED SPEC	INDUSTRY STD
Automotive Gasoline	MIL-G-3056D	F-46	VV-G-1690B	ASTM D439
Jet Turbine Fuel	MIL-T-5624G MIL-T-83133	F-40/F-44 F-34	MIL-T-5624G MIL-T-5624G	ASTM D1655 ASTM D1655
Diesel Fuel	VV-F-800B	F-54	VV-F-800B	ASTM D975

ENGINE SYSTEMS USED IN ARMY EQUIPMENT

SPARK-IGNITION

Two-Cycle	Air-Cooled	Normally-Aspirated
Two-Cycle	Liquid-Cooled	Normally-Aspirated (Marine Application)
Four-Cycle	Liquid-Cooled	Normally-Aspirated
Four-Cycle	Air-Cooled	Normally-Aspirated and Turbocharged (Marine and Aviation Applications)

COMPRESSION-IGNITION

Two-Cycle	Liquid-Cooled	Normally-Aspirated and Turbocharged
Four-Cycle Four-Cycle	Liquid-Cooled Air-Cooled	Normally-Aspirated, Turbocharged and Multifuel Turbocharged

GAS TURBINE

Gas Turbine	Turbo-Shaft	Aviation and Ground

REQUIREMENTS FOR ARMY FUELS

- Commonality of Fuels
    - NATO Standardization and Interoperability
    - Fuel Tolerance and Multifuel R&D
- Survivability
- Stability
- Ambient Temperature Limits
- Fuel Inhibitor Requirements
- Improved Combustion Efficiency
- Variable Quality Limits
- Emergency Fuel Applications

FUEL AND FUEL-RELATED R&D PROGRAMS

Fuel R&D

- Development of Fire-Safe Fuel System
- Evaluation of Alternate/Synthetic Fuels
- Development of Capability to Permit Use of High Sulfur Fuels
- Development of High-Energy Fuel
- Improvement of Combat Fuels Stability

Fuel-Related R&D

- Combustion Research on Gas Turbine Engines (Purdud Univ)
- Cetane Sensitivity for Diesel Engines (Teledyne-Continental)
- Integration of New Fuels (when available) Into Advanced Technology Demonstrator Rig and Full-Scale Engine Programs

PROPERTIES AND COMPOSITION OF JET SYNFUELS

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PROPERTIES AND COMPOSITION OF JET FUELS DERIVED FROM ALTERNATE ENERGY SOURCES

PART I. BACKGROUND AND N-ALKANE CONTENT

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INTRODUCTION

In the current climate of dwindling domestic production of petroleum, increased importing of petroleum, potential oil embargoes, and escalating prices, the Department of Defense has begun significant new fuels programs. These programs are evaluating the military potential of liquid transportation fluids derived from alternate fossil fuels—shale oil, tar sands and coal. Of major import to the U.S. Navy are fuels used primarily for aircraft propulsion, JP-5, and ship propulsion, Diesel Fuel Marine. The discussion in this paper will be limited to the former, jet fuel for naval aircraft. It should be noted, however, that JP-5 is sometimes used as a substitute ship propulsion fuel.

CRITICAL PROPERTIES OF JET FUEL

JP-5 must meet many stringent requirements if satisfactory performance in aircraft and fuel handling and storage systems is to be attained (1). In considering JP-5 derived from alternate fossil fuels, several critical properties stand out. With one or two exceptions, these key properties are affected more by the chemical characteristics of the fuel than by the physical properties. The important specification requirements may be primarily controlled by elemental composition, the amounts of each of the hydrocarbon classes—paraffin, naphthene, aromatic, olefin—or by specific chemical compounds. The critical properties are discussed briefly below.

A. Heat of Combustion—This property directly controls the range of a jet aircraft and it is desirable to maximize the value. Hydrocarbon fuels which are liquid at ambient temperatures have net heating values between 16,000 and 20,000 BTU/lb, and the minimum specification limit for JP-5 is 18,300 BTU/lb (1). Martell and Angello have shown that the heat of combustion for jet fuels increases linearly with hydrogen content (2). The amounts of nitrogen and oxygen in jet fuel are negligible with respect to heat of combustion, and the variation of sulfur in the allowable range of 0.0 to 0.4% would exert a maximum effect of 40 BTU/lb.

B. Freezing Point—Jet aircraft are exposed to low temperatures and the fuels must not interfere with flying operations by freezing and plugging filters. Commercial jet fuel (Jet A) has a specification requirement of -40°F maximum but that for military fuels is lower. JP-5 must freeze below -51°F because the Navy jets operate worldwide as well as at higher altitudes than commercial jets. U.S. Air Force bombers require an even lower freezing point, -72°F maximum, since long flights at high altitudes permit the fuel to reach lower temperatures. It has not been practical to make JP-5 from some petroleum crudes because the freezing point cannot be met along with the

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required flash point. Dimitroff, et al. (3) examined the influence of composition on freezing point of several types of fuels. They found the saturate fraction of a fuel usually exerted the greatest effect on freezing point but the aromatic fraction seemed to be important in some cases.

C. Flash Point—The Navy requires a high flash point for all fuels carried onboard ships except for a small amount of aviation gasoline which is carried on some aircraft carriers. The Avgas is stored in an armored box in the center of the carrier and air/fuel vapors are minimized in the storage tanks by using a water displacement system. JP-5, which is stored in the wing tanks (flush with the hull), has a minimum flash point of 140°F in order to reduce the hazard from this and other exposure situations. The flash point of a mixture such as a fuel is controlled by the quantity and volatility of the front ends (4). The flash point and other flammability properties of some alternate jet fuels is considered in another paper at this Symposium (5).

D. Combustion Properties—Jet engines give high combustion efficiencies (98-100%) for conversion of fuel to CO_2 and H_20. Other combustion characteristics can be deficient under such conditions, however. Flame radiation to the combustor walls can raise the temperature of the walls above desired levels (6,7). Soot deposition can also affect combustor wall temperatures. Smoke in the exhaust must be controlled both for military and environmental reasons.

The flame radiation, soot deposition, and smoke production may be closely related chemically. These three properties of a jet fuel are controlled by passing a simple wick burning test, the smoke point, or a slightly more complicated burner test, the luminometer number. The minimum smoke point for JP-5 is 19 mm, and the minimum luminometer number is 50.

A secondary control on combustion properties is obtained by limiting the aromatic content to 25% (1). Condensed polynuclear aromatics are significantly more detrimental to smoke point than monocyclics (8).

E. Thermal Oxidation Stability—Jet fuel cools several systems in a jet aircraft. In a subsonic plane, the major heat load comes from the engine lubricant but for aircraft flying faster than Mach 2.2, the structure must also be cooled. The ability of a fuel to withstand this thermal stress is the most critical fuel property for high-speed aircraft (9).

Degradation of the fuel is stimulated by the dissolved oxygen present in equilibrium with air (50-70 mg/1). Poor fuels form solids which coat heat exchanger surfaces and/or plug combustor nozzles. The Jet Fuel Thermal Oxidation Tester estimates these two properties by examining varnish formation on a heated metal tube and measuring the pressure drop through a filter. A satisfactory fuel passes a 2-1/2 hour test at 500°F.

Little research has been reported on the effect of chemical structure on thermal oxidation stability at 500°F, but Taylor has reported on tests in the 200°-400°F temperature range. He found that olefins, particularly multifunctional ones, increased deposit formation (10). At 275°F, 10 wt % indene in decane increased deposit formation 39-fold but some other aromatics decreased the deposit rate. Some sulfides and disulfides enhance deposit formation at concentration as low as 1000 ppm sulfur (11) and nitrogen compounds also participate in deposit formation (12).

F. Gum Formation—The low temperature stability of JP-5 is estimated by the Existent Gum Test. A maximum of 7.0 mg/100 ml gum is allowed in this test. Schwartz, et al. have found for gasoline that sulfur compounds are the most significant participants in gum formation but that nitrogen compounds, indanes, tetralins and olefins are also involved (13).

PROPERTIES OF ALTERNATE JET FUELS

Jet fuels made from oil shale, tar sands and coal were examined in this study. A brief outline of the processes involved in production of the fuels are listed in Table I. Further information on processing and fuel properties can be found in another paper in this symposium (14) and in the references cited in Table I.

Table II lists the properties of the fuels pertinent to this paper. The Laramie Energy Research Center in-situ shale fuels were not produced to meet the JP-5 specs but had a boiling range (350°-550°F) similar to JP-5. Since only limited amounts of the LERC samples were available, complete specification tests were not run. The discussion which follows compares, where possible, the alternate fuel properties with petroleum jet fuel properties taken from the literature. The effect of composition on properties is also described.

A. Heat of Combustion—The heat of combustion of alternate fuels is plotted in Figure 1 versus percent hydrogen. The graph shows data for the five COED, the tar sand, and the Paraho shale oil fuels. The line on this graph is curve D in Figure 3 of reference (2) and is based on 41 jet fuels derived from petroleum. The alternate fuel data fit the curve very well. The three COED fuels with high aromatic contents fall to the left. COED-1 and COED-5 fall slightly below the JP-5 requirement of 18,300 BTU/lb. Decreasing the aromatic content from about 25% to 5% (COED-1 to COED-3 or COED-2 to COED-4) increases the heat of combustion about 90 BTU/lb. The tar sands and Paraho shale fuels have higher heating values than the COED samples with similar aromatic contents. We feel this is due to a high naphthene content in the coal fuels, and expected consequence of hydrogenation of the highly aromatic syncrude obtained by coal pyrolysis (21).

B. Freezing Point/Flash Point—Most of the alternate fuel samples met the flash point requirement for JP-5. The flash point can be changed usually by the adjustment of the initial boiling point. The freezing point of several of the alternate jet fuels was too high, however. The freezing point/flash point relationships for the five COED (C-T to C-5), tar sands (TS), and Paraho shale oil (OS) are depicted in Figure 2. No consistent pattern is evident for these fuels.

For comparison, the properties of 29 petroleum-derived jet fuels are also shown on the graph. These latter fuels, which were part of the Coordinating Research Council (CRC)-Air Force (AF) fuel bank (22), did not meet all specifications in some cases. Examination of the CRC fuels is useful, however, to see the wide range in freezing points encountered for fuels with similar flash points. In Figure 2, the display is simplified by grouping the fuels by 10°F intervals for flash point. As an example, four petroleum-derived fuels had flash points between 161° and 170°F. The freezing points for these same fuels were -26°, -32°, and -76°F. One alternate fuel sample, COED-3 had a flash point in this range, and it had a freezing point of -58°F.

It is noteworthy that COED-2 and COED-4, both produced from Utah coal, had higher freezing points than the COED fuels made from Western Kentucky coal. This was the case even though COED's 1 through 4 had similar distillation ranges. The Paraho shale oil sample was far above the JP-5 fuel freezing point spec of -58°F. The LERC in-situ shale samples also had very high freezing points. -16°F for the multistep product and -15°F for the single step material. Flash points were not available for these two shale fuels.

C. Combustion Properties—The smoke points of several alternate jet fuels are displayed in Figure 3 as a function of aromatics content. In addition, this graph presents the smoke point vs. % of aromatic relationship for 29 CRC-AF petroleum-derived fuels (22). The general control of smoke point by aromatic content is apparent both for the petroleum-derived and the alternate fuels. Some fuels with low aromatic contents exhibit low smoke points, however, and do not fit the primary relationship. The four petroleum fuels which show this behavior possess high naphthene content, 80% or higher. COED-3and COED-4, which have been derived by severe hydrogenation (3000 psig to afford a low aromatic content) of a highly aromatic syncrude (21), should also contain high concentrations of naphthenes. Hence, the anomalous smoke point behavior shown, both by alternate and petroleum-derived jet fuels, can be explained on the basis that naphthenes influence this property if the aromatic content is low.

Smith (23) has suggested a formula for calculating the smoke point of kerosenes based on paraffin, naphthene, and aromatic content but it is not useful for the fuels discussed in this paper. The broad definition of aromatic and naphthene is not adequate for combustion considerations. For instance, one mole/1 of either butyl benzene or naphthalene would give about the same aromatic concentration by the specification test but the latter compound would have a much greater effect on the smoke point.

D. Stability—The thermal oxidation stability and gum-forming tendencies of the alternate fuels are listed in Table II. COED-1 and COED-5 fail the 500°F thermal stability test by slight amounts, but the Paraho shale oil material fails by 50°F. Further, this shale oil is the only fuel to fail the existent gum requirement of 7 mg/100 ml. The sulfur content of all of the alternate fuels is about the same and well below the 0.4% specification limit. Although jet fuel has no limit on nitrogen, the shale fuel is much higher in nitrogen than the other alternate and petroleum jet fuels.

Clay filtration of the shale jet fuel raised the breakpoint for thermal oxidation stability to 475°F but the existent gum remained high, 64 mg/100 ml, as did the nitrogen. Acid treatment (≈ 2 lb 98% H_2SO_4/bbl) reduced the basic nitrogen to zero, enabled the thermal stability requirement to be met but did not greatly improve the gum formation. Distillation to a 90% recovery gave a product which passed both thermal stability and gum (1.2 mg/100 ml) tests. Basic nitrogen remained high, however, These results do not delineate the role of nitrogen in fuel stability and additional work will be needed to clarify the stability behavior of shale fuels.

It is noteworthy that severe hydrogenation to reduce the aromatic content of coal liquids (COED-1 to 3 and COED-2 to 4) significantly improved the thermal oxidation stability (to >700°F).

E. *n*-Alkane Content—Since *n*-alkanes are likely to be related to the high freezing points of some of the alternate fuels, the concentration of these compounds was determined.

The saturate fractions were separated from the aromatics by pentane elation from activated silica gel (Davison Grade 923). Each saturate fraction was then analyzed by gas chromatography (GC) on a 300-ft Apiezon L capillary column at 140°C. A sample of 0.1 microliter was split 100:1 ahead of the column and the helium flowrate through the column was 1.0 cc/min. This column, when operated under the described conditions, had an efficiency of 184,000 theoretical plates for *n*-tetradecane. A known amount (5.0 wt %) of *n*-octane was added as an internal standard and the weight % of each *n*-alkane was calculated by comparing electronic integrator counts to the octane count. Identification of the *n*-alkane peaks was made on a Hewlett-Packard 5982 GC-MS system using a 100-ft OV-101 support-coated open tubular column—temperature programmed from 100° to 160°C and with a helium flowrate of 3 cc/min. Corroborating identification came from matching GC retention times for fuel components on the Apiezon L column with standards on the same column.

The *n*-alkanes were the major peaks in most of the saturate fractions. The *n*-alkanes from nonane to hexadecane were found in most of the alternate fuels. In addition, small amounts of *n*-heptadecane were found in the shale fuels. The *n*-alkane concentrations are listed in Table III. The sum of the *n*-alkanes in the fuels decreases in the order: Paraho shale, LERC shales, petroleum, tar sands, Utah COED's, W. Ky. COED's. This order holds for individual *n*-alkanes in the middle of the distillation range—C_{12}, C_{13}, and C_{14} but varies for smaller or larger compounds because of differences in initial boiling point or end point.

The total *n*-alkane concentration does not afford a significant relationship with freezing point. However, the freezing point does show some dependence on the amount of the larger hydrocarbons present in fuel samples. This is illustrated for *n*-hexadecane in Figure 4. The log (% C_{16}) vs. the reciprocal freeze point of the 11 fuels listed in Table II indicates a reasonable adherence to a solubility plot. This is remarkable in view of the different distillation ranges, the variation in aromatic/naphthene contents, and the neglect of other *n*-alkanes in this consideration. The Paraho jet fuel was treated with urea to remove *n*-alkanes (24). The percent of the *n*-alkanes removed by this process and the amount remaining in the fuel are shown in Table IV. Overall, 47% of the *n*-alkanes (17% of the total fuel) were removed. The percent removed increased with molecular weight. The removed material was 98% *n*-alkanes with the remainder being identified by GC-MS as mostly 2-methyl alkanes and 1-alkanes. The stripped sample with an *n*-C_{16} content of 0.17%, had a freezing point of -54°F which places it close to the curve in Figure 4.

DISCUSSION

Suitable jet fuels can be made from any of the alternate energy sources—oil shale, tar sands or coal. However, refining processes may have to be modified from those used with petroleum crude, and processing conditions may have to be more severe, particularly for oil shale and coal liquids. Since crudes from oil shale, tar sands and coal are closer in properties to the lower API gravity petroleum crudes, hydro-cracking and delayed coking will be used extensively in producing military fuels from these alternate sources.

The jet fuel properties which are of greatest concern with the new fuels are the freezing point, combustion properties, and stability, both thermal oxidative and storage. Additional understanding is required on the effect of composition on these properties. Development of such information will aid in selecting or modifying refining processes to produce suitable fuels at reasonable costs. Techniques to remove nitrogen from shale oil and to convert *n*-alkanes to lower freezing compounds are needed. Cheaper hydrogenation processes must be developed for economical conversion of coal liquids to jet fuels with satisfactory heats of combustion.

The high concentrations of *n*-alkanes found in the shale oil samples affords clues on the nature of the organic material in shale. This information indicates that oil shale contains many long, straight chain components. When thermally stressed, as in retorting or coking, such constituents would yield smaller fragments which would also have straight chains (25). The major products would be *n*-alkanes and 1-alkenes. Since the latter hydrogenate to the former, *n*-alkane concentration could be considerable. It is interesting that the three shale jet fuels studied in this work were high in *n*-alkanes. This is in spite of differences in production, refining, and hydrogenation processes.

Work will continue in relating composition to properties of the alternate jet fuels. This will include attention to non-specification properties and those properties which may be inherently different due to the origin of the base stock.

ACKNOWLEDGEMENT

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TABLE I

ALTERNATE FUEL SOURCES AND PROCESSES

Fuel Source*	Method of Production	Method of Refining	Hydrotreat	Reference
Shale-Paraho	Retort	Delayed Coking and Fractionation	Standard Pressure (Co-Mo)	15
Shale-LERC Multistep	In-Situ	Delayed Coking and Fractionation	1500 psig (Ni-Mo)	16,17
Shale-LERC Single Step	In-Situ	Fractionation after Hydrotreat	Total Oil 1500 psig (Ni-Mo)	18
Tar Sands-GCOS	Hot Water	Delayed Coking and Fractionation	Not Available	19,20
COED-1 FMC W.Ky. Coal	Pyrolysis	Fractionation	1500 psig (Ni-Mo)	21
COED-2 Utah Coal	Pyrolysis	Fractionation	1500 psig (Ni-Mo)	21
COED-3 W.Ky. Coal COED-4 Utah Coal	Pyrolysis	Fractionation	1st stage 1500 psig (Ni-Mo) 2nd stage 3000 psig (Pt)	21
COED-5 W.Ky. Coal	Pyrolysis	Fractionation	3000 psig (Ni-Mo)	21
Petroleum-A	Drilling	Not Available	Not Available	—
Petroleum-B	Drilling	Not Available	Not Available	—

* Paraho-Paraho Development Corp.; LERC-Laramie Energy Research Center; GCOS-Great Canadian Oil Sands, Ltd., FMC-Food Machinery and Chemical Co.

TABLE II

ALTERNATE FUEL PROPERTIES

Fuel	Thermal* Stability (°F)	Gum Existent (mg/100 ml)	Nitrogen (ppm)	Sulfur (wt. %)	Aromatics (percent)	Smoke Point (mm)	Viscosity at -30^{o}F (cks.)	Freezing Point (°F)	Heat of Combustion (BTU/lb)	Hydrogen (percent)
Shale-Paraho	450	81.7	680	0.05	26.0	22.0	frozen	-28	18,532	13.74
Shale-LERC Multistep	--	--	79	0.0001	23.7	--	--	-16	--	--
Shale-LERC Single Step	--	--	5	0.0005	21.3	--	--	-15	--	--
Tar Sands	Pass	1.2	--	0.01	19.3	20.0	12.85	-64	18,436	13.50
COED-1	495	0.0	40	0.05	24.8	17.0	23.69	-54	18,294	12.80
COED-2	510	0.1	42	0.04	24.1	17.0	22.94	-40	18,372	12.98
COED-3	>700	0.0	40	0.05	4.7	22.0	25.95	-58	18,383	13.34
COED-4	>700	0.1	43	0.03	6.1	22.0	23.03	-40	18,465	13.62
COED-5	485	0.1	37	0.03	24.1	18.0	9.04	<-70	18,282	12.81
Petroleum-A	Pass	<7	--	0.11	18.2	23.0	<16.5	-56	18,518	--
Petroleum-B	Pass	<7	--	<0.40	16.2	>19.0	<16.5	-59	--	--

*JFTOT Test, ASTM D3241, Pass indicates 500°F or higher

TABLE III

N-ALKANE CONTENT OF JET FUELS FROM ALTERNATE SOURCES

<u>WEIGHT PERCENT</u>

	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	Σ
Shale Paraho	0.90	3.28	7.46	7.12	6.66	5.14	3.32	2.45	0.3*	36.33
Shale-LERC Multistep	0.002	0.11	3.11	6.08	5.81	4.26	3.48	2.46	0.6*	25.31
Shale-LERC Single Step		0.05	3.00	5.66	5.36	3.91	3.17	2.58	0.8*	23.73
Tar Sands-2	0.26	0.54	1.48	2.59	2.43	1.32	0.73	0.15	—	9.50
Coed-1		0.08	1.18	0.73	0.66	0.56	0.46	0.2	—	3.90
Coed-2		0.04	1.08	1.50	1.51	1.27	1.08	0.66	—	7.14
Coed-3	0.01	0.11	0.99	0.68	0.70	0.55	0.42	0.27	—	3.73
Coed-4		0.06	1.42	1.49	1.53	1.28	1.01	0.66	—	7.45
Coed-5	0.02	0.63	2.33	1.23	0.76	0.38	0.11	(0.02)	—	5.48
Petroleum-A	0.20	1.72	3.63	3.88	3.49	2.13	0.81	0.14	—	16.00
Petroleum-B	0.29	1.97	3.85	3.38	3.13	1.82	0.72	0.05	—	15.71

*C_{17} peak broad, integration not accurate, not included in total

TABLE IV

RESULTS OF UREA STRIPPING OF PARAHO SHALE JET FUEL

N-Alkane	Concentration (Percent) Starting Material	Product	N-Alkane Concentrate	Percent ** Removed
Nonane	0.90	0.73	0.96	19
Decane	3.28	2.65	3.86	19
Undecane	7.46	5.43	11.54	27
Dodecane	7.12	4.66	16.50	35
Tridecane	6.66	3.33	19.13	50
Tetradecane	5.14	1.73	18.71	66
Pentadecane	3.32	0.67	15.16	80
Hexadecane	2.45	0.17	9.47	93
Heptadecane	0.3*	0.00	1.38	—
Total	36.33	19.37	98.0	

* Broad peak, integration not accurate, not included in total
** Based on comparison between product and starting material

NET HEAT OF COMBUSTION VS. PERCENT HYDROGEN

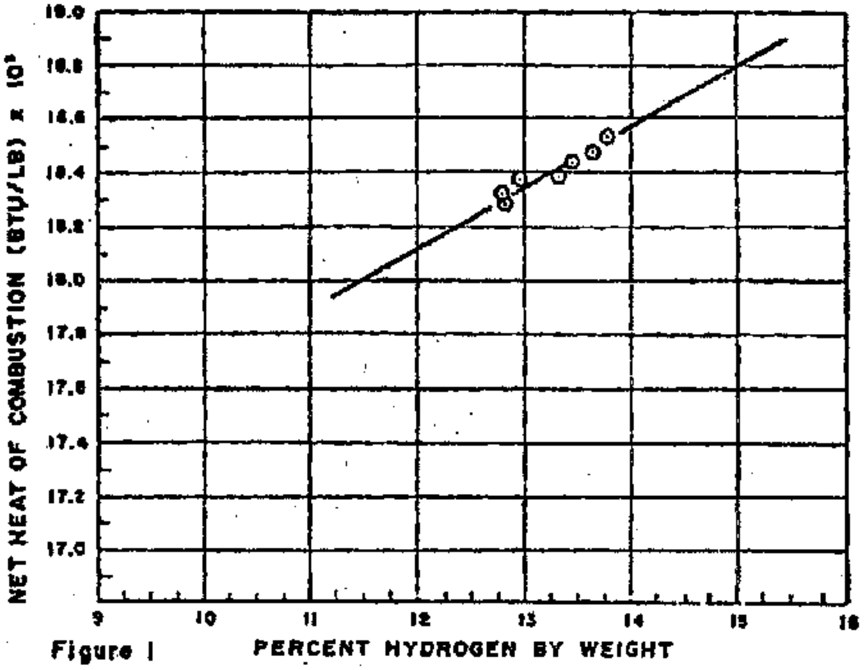

Figure 1

⊙JET FUELS FROM ALTERNATE ENERGY SOURCES

FREEZING POINT vs FLASH POINT

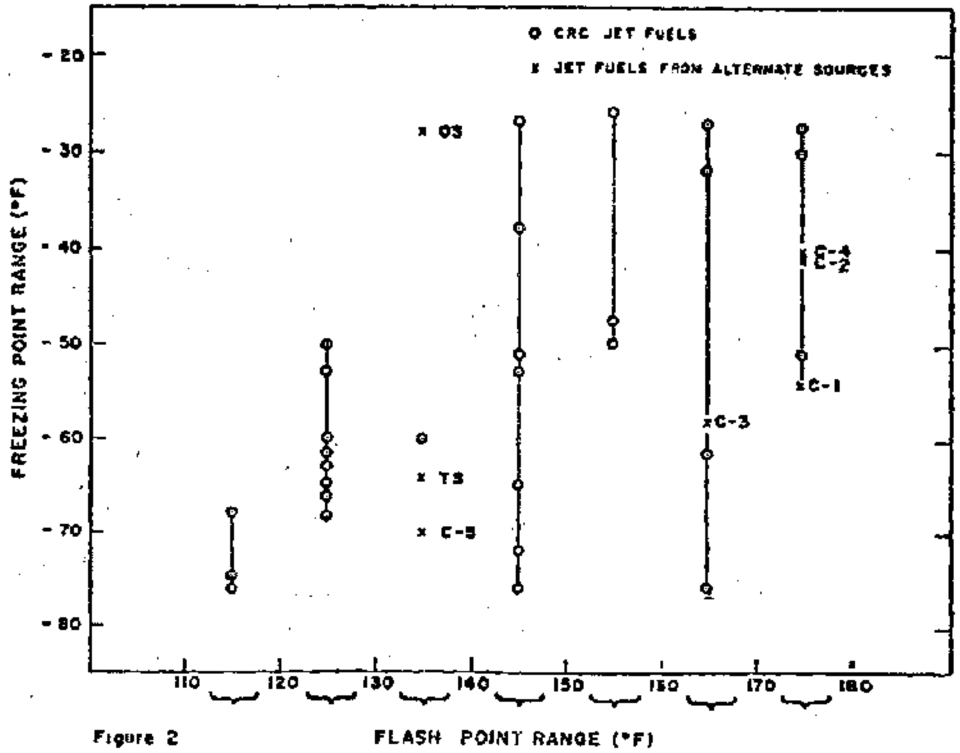

Figure 2

SMOKE POINT vs AROMATIC CONTENT

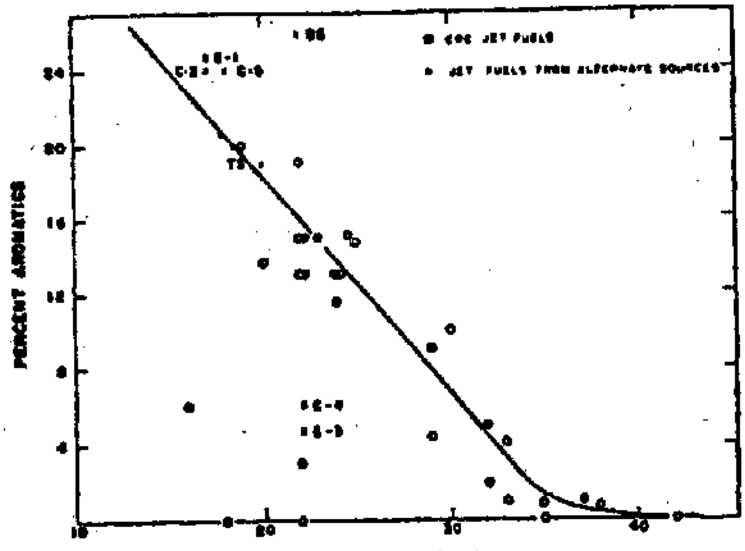

Figure 3 SMOKE POINT (mm)

EFFECT OF N-HEXADECANE ON FREEZING POINT

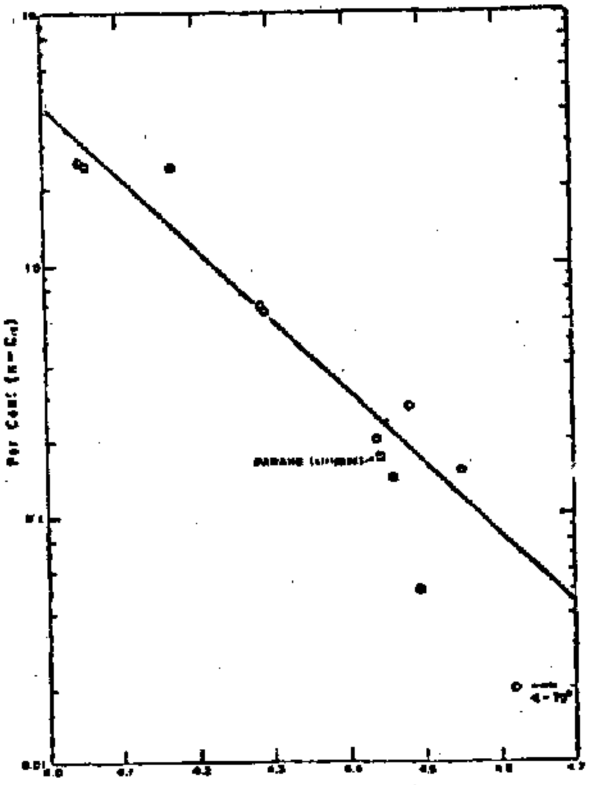

Figure 4 FREEZE POINT 1000/T (°K)

NAVAIR-NRL WORKSHOP

BASIC RESEARCH NEEDS FOR SYNTHETIC HYDROCARBON JET FUELS

JUNE 15 - 16, 1978

THERMAL OXIDATIVE STABILITY OF SYNTHETIC JET FUELS ( )*

Introduction: This presentation is part of the work conducted at the Naval Air Propulsion Center (NAPC) directed towards the study of the application of synthetic fuels for Navy aircraft use. The overall program objective is to establish the physical and chemical suitability of JP-5 derived from alternate (non-petroleum) sources for aircraft propulsion systems. The objective of this particular work is to establish a relationship between the organic nitrogen content and the thermal oxidation stability and storage stability of jet fuel derived from oil shale. The importance of this work is to obtain some knowledge of the effects of nitrogen on these properties since there is currently no specification requirement for the control of nitrogen in the JP-5 specification.

The fuel used in this study was derived from shale oil crude produced by the Paraho Process. The crude was refined in April 1975 by the Gary Western Refinery, Fruita, Colorado.

All of the thermal oxidation determinations made on the various fuels were performed with the Alcor Jet Fuel Thermal Oxidation Tester, coined the JFTOT. This is a standard ASTM test for evaluating fuel thermal oxidation behavior. The procedure is described by the ASTM D-3241 test outline. The criteria used for evaluating the deposition tendencies of a thermally stressed fuel are as follows:

(1) The deposit formed on the heated aluminum surface shall not exceed a spun deposit rating (TDR) of 17, as determined by the light reflectance device Alcor Mark 8A, tube deposit rater.

(2) The deposits formed in the bulk fuel that have not collected on the heated surface are trapped downstream by a filter at the fuel outlet of the preheater section. When a pressure drop of 25 millimeters is observed the fuel will be classified as thermally unacceptable. Once this pressure level has been reached, the JFTOT is put into a by-pass mode which essentially eliminates the fuel passage through the filter. The time to reach the by-pass mode is recorded.

The first determination made on the effects of fuel bound nitrogen on thermal oxidation stability was made by varying the acid extractable

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*(Numbers in parentheses refer to figures at end of the paper).

nitrogen concentration of the fuel, and then determining the breakpoint temperature in the JFTOT. The fuel samples were prepared as follows:

(1) A shale oil JP-5 containing 954 ppm total nitrogen was extracted by 0.1 N HCl. After neutralization with sodium bicarbonate and water washing the fuel contained 116 ppm total nitrogen, which could not be removed by acid extraction.

(2) The above fuel was then blended with the unextracted fuel containing the original 954 ppm nitrogen until the desired nitrogen concentration was reached. The basic nitrogen content was determined on each blend using the perchloric acid titration method. The non-basic nitrogen concentration was constant in all samples.

A breakpoint temperature determination on the fuels revealed that there was a relationship between the basic nitrogen content and the type of JFTOT failure observed. It was quite apparent that the basic nitrogen produced a greater difference in the breakpoint temperature using the pressure drop criterion than the deposit level on the heater tube. That is, a basic nitrogen concentration range of 7 to 838 ppm produced a 52°C difference in the breakpoint based upon filter drop, whereas, only a 10°C difference was observed with using the heater tube failure criteria (1).

In further pursuance of the effect of nitrogen, particularly the acid extractable type, work was continued with a petroleum derived fuel, which was essentially nitrogen free. The basic nitrogen that had been isolated was added into this fuel at various concentrations and a JFTOT determination was made at a constant test temperature of 260°C. This temperature is the current requirement for a fuel to pass according to the ASTM instructions and MIL-T-5624K for grades JP-4 and JP-5 fuel.

The results of the test showed that the fuel could probably tolerate a nitrogen concentration of the order of 100 ppm if the JFTOT thermal stability rating criteria were based solely on deposits forming on a heated surface. However, using the pressure drop criteria the nitrogen concentration must be less than 50 ppm (2) to obtain a pass rating for the fuel. With regards to the preheater section, responses to changes in nitrogen concentration were somewhat unusual and unexpected. The TDR increased as a function of the nitrogen content up to 300 ppm. The higher concentrations, 400 and 500 ppm nitrogen, produced TDR's equivalent to 50 and 100 ppm. A close inspection of the total TDR on the heater tube reveals that beyond 300 ppm the nitrogen compounds in the fuel are producing deposits in the bulk fuel at the cooler section of the JFTOT (3). This is also observed by the decrease in time for the filter section to be put into by-pass (2).

Since there had been a drastic shift in the TDR as a function of nitrogen content beyond the 300 ppm level an intermediate concentration of 348 ppm was investigated. A TDR of 13 was produced by this concentration of nitrogen which was in agreement with the previous trend. A complete breakpoint temperature analysis was run on the 348 ppm nitrogen fuel and was compared to undoped fuel. The nitrogen containing fuel produced a pressure drop failure at 254°C, and this failure was 25°C lower than the breakpoint temperature of the undoped fuel. This was only an approximation since the breakpoint temperature of the undoped fuel was greater than 279°C (4).

Attention was then shifted to identification of the nitrogen compounds in the acid extract. Some preliminary analytical work performed by NAPC and NRL showed the nitrogen compounds to be primarily substituted pyridines with alkyl substituents with two to nine carbons; quinolines with zero to four carbons and tetrahydroquinolines with two to four carbons. A thermal oxidation stability analysis was made on pure nitrogen compounds in a petroleum derived JP-5. The results showed that pyridine type compounds are innocuous at concentrations between 50 and 100 ppm. Pyridine compounds containing primary amine functional groups are deleterious to thermal oxidation stability. Pyrroles are also deleterious (5).

The next area of investigation was directed towards the evaluation of the storage stability of oil shale fuel containing low amounts of acid extractable nitrogen. The test employed was accelerated, subjecting fuels to 60° temperature for four weeks. The containers used in this test were 1.1 liter actinic glass jars. A one liter quantity of fuel was used. The containers were capped with aluminum foil to permit breathing during the storage period. Water was added at a concentration of 1.0 percent. The shale oil fuel samples were prepared by extraction with 1.10N HCl to remove the basic nitrogen, followed by silica gel percolation to remove the remaining nitrogen. The shale oil samples were then doped with the acid extracted nitrogen compounds to a concentration range of 8 to 125 ppm basic nitrogen. Some samples contained 25 ppm of an organic oxidation inhibitor, Dupont AO-22 (phenylene diamme), to determine if oxidation inhibition could be achieved during accelerated storage. A petroleum JP-5 with and without the inhibitor was incorporated in the study as a control . Thermal stability analyses of the samples before and after storage showed that small quantities of basic nitrogen, less than 20 ppm, caused the fuel to become unstable (6). However, the use of the inhibitor retarded this behavior (7). A high unacceptable level of peroxidation had also occurred during storage (8), however this was satisfactorily controlled by the inhibitor (9). There was some correlation observed between the peroxide content and the thermal oxidation stability of fuels containing low concentrations of nitrogen (10). This investigation also showed that a petroleum derived JP-5 with and without an oxidation inhibitor remained stable during this accelerated storage period.

RESULTS OF TEST NO. 1:

ORGANIC NITROGEN, PPM IN FUEL		JFTOT BREAKPOINT TEMPERATURES, °C AT	
ACID EXTRACTABLE N	TOTAL N(1)	HEATER TUBE	FILTER
7	123	(254)(2)	279
50	166	251	(241)
97	213	243	(232)
838	954	244	(227)

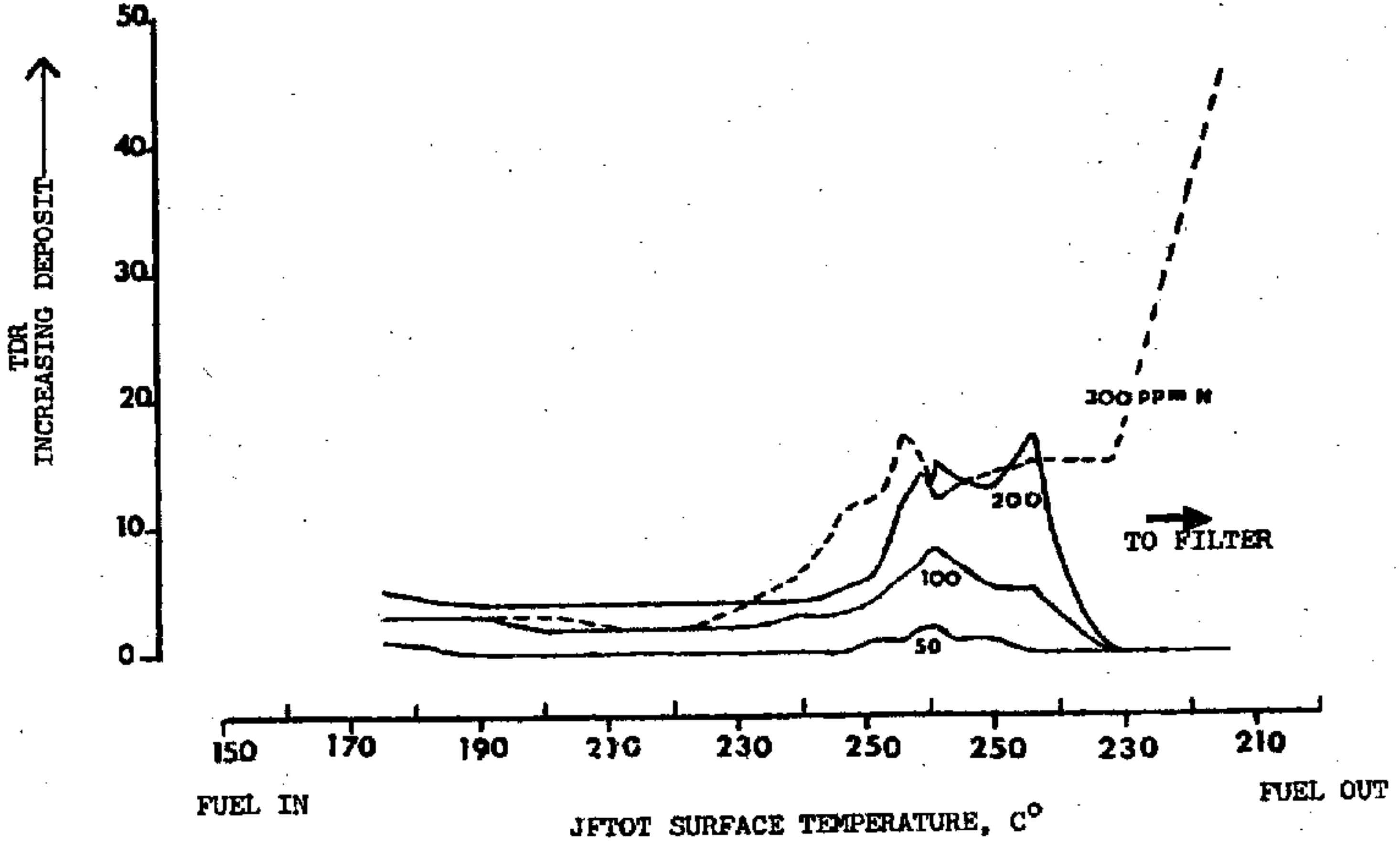
(1) NONEXTRACTABLE N CONSTANT 116 PPM.

(2) BRACKETED FIGURES INDICATE BREAKPOINT TEMPERATURE.

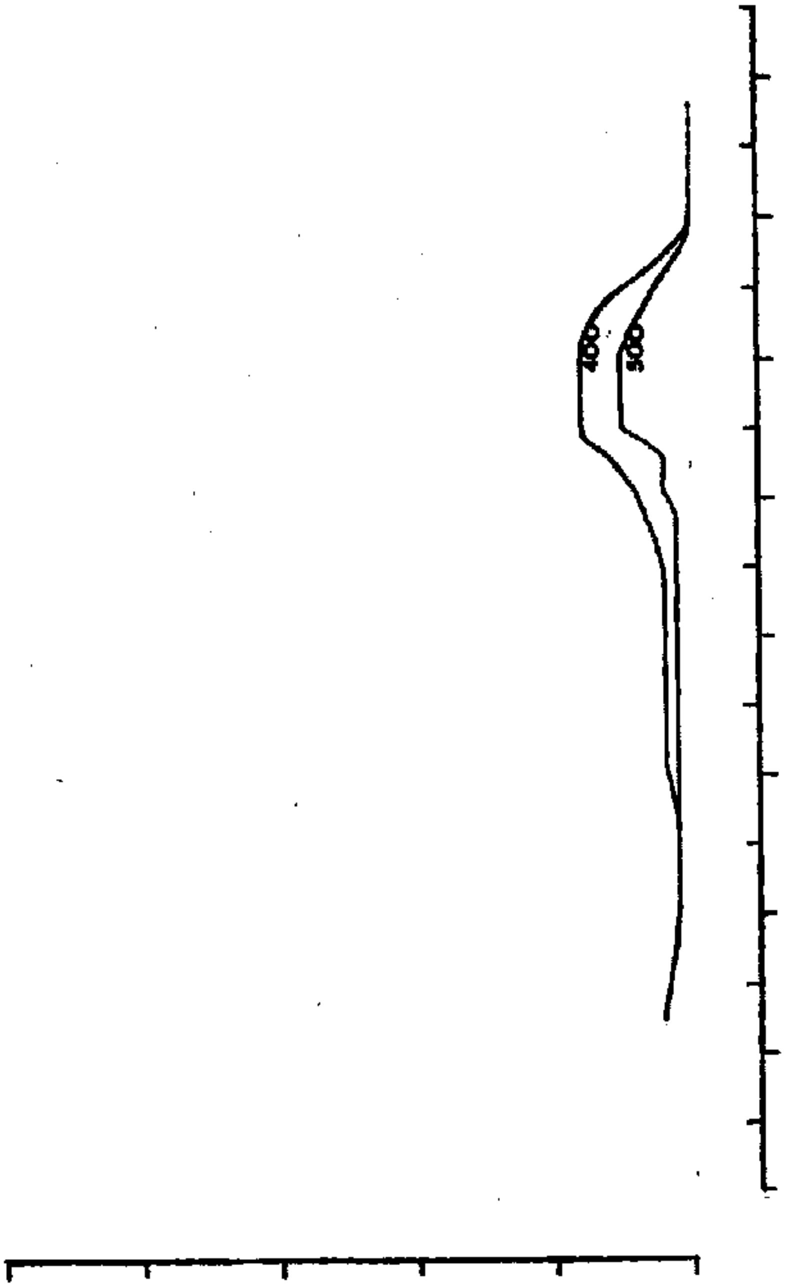
RESULTS OF TEST NO. 2:

NITROGEN CONCENTRATION, PPM	JFTOT RATING AT 260°C	
	MAXIMUM TDR	PRESSURE DROP
50	2	BYPASS 124 MINUTES
100	8	BYPASS 120 MINUTES
200	17	BYPASS 120 MINUTES
300	45	BYPASS 88 MINUTES
400	8	BYPASS 86 MINUTES
500	5	BYPASS 84 MINUTES

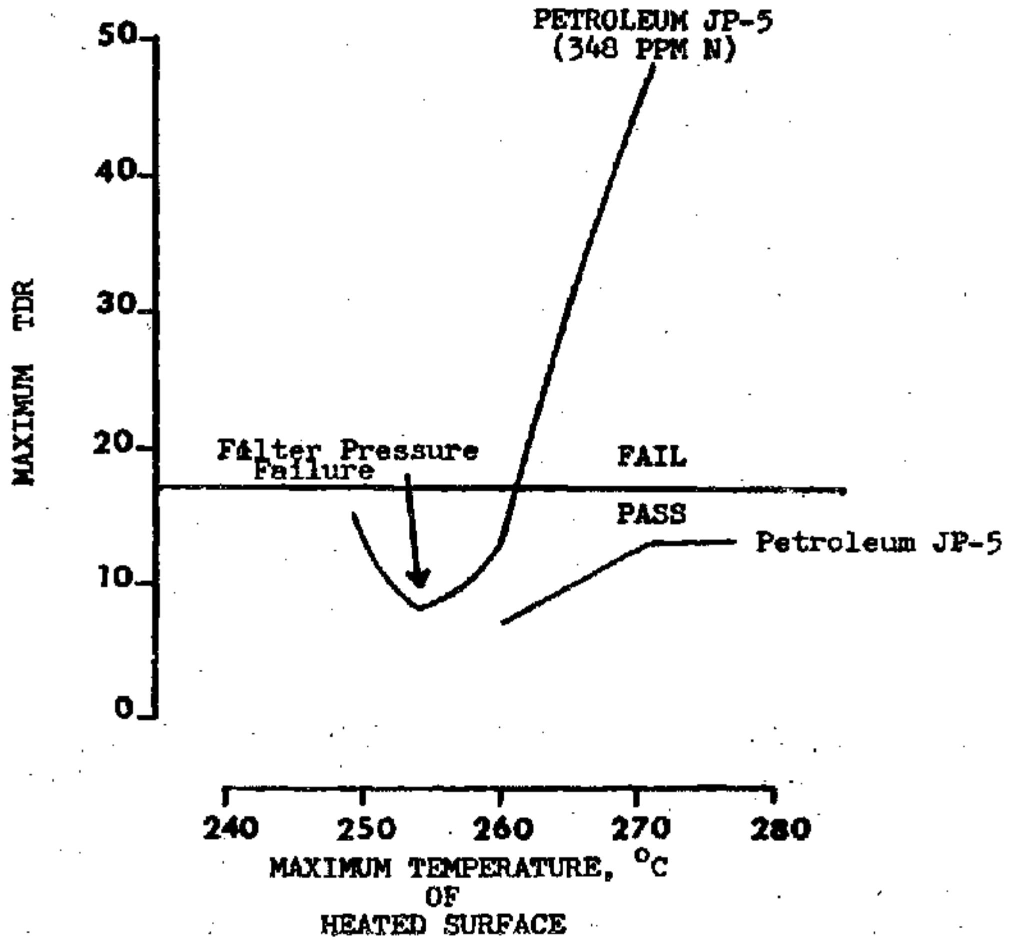
EFFECT OF ORGANIC NITROGEN CONCENTRATION ON FUEL THERMAL OXIDATION STABILITY



3A



EFFECT OF ORGANIC NITROGEN ON BREAKPOINT TEMPERATURE OF JP-5

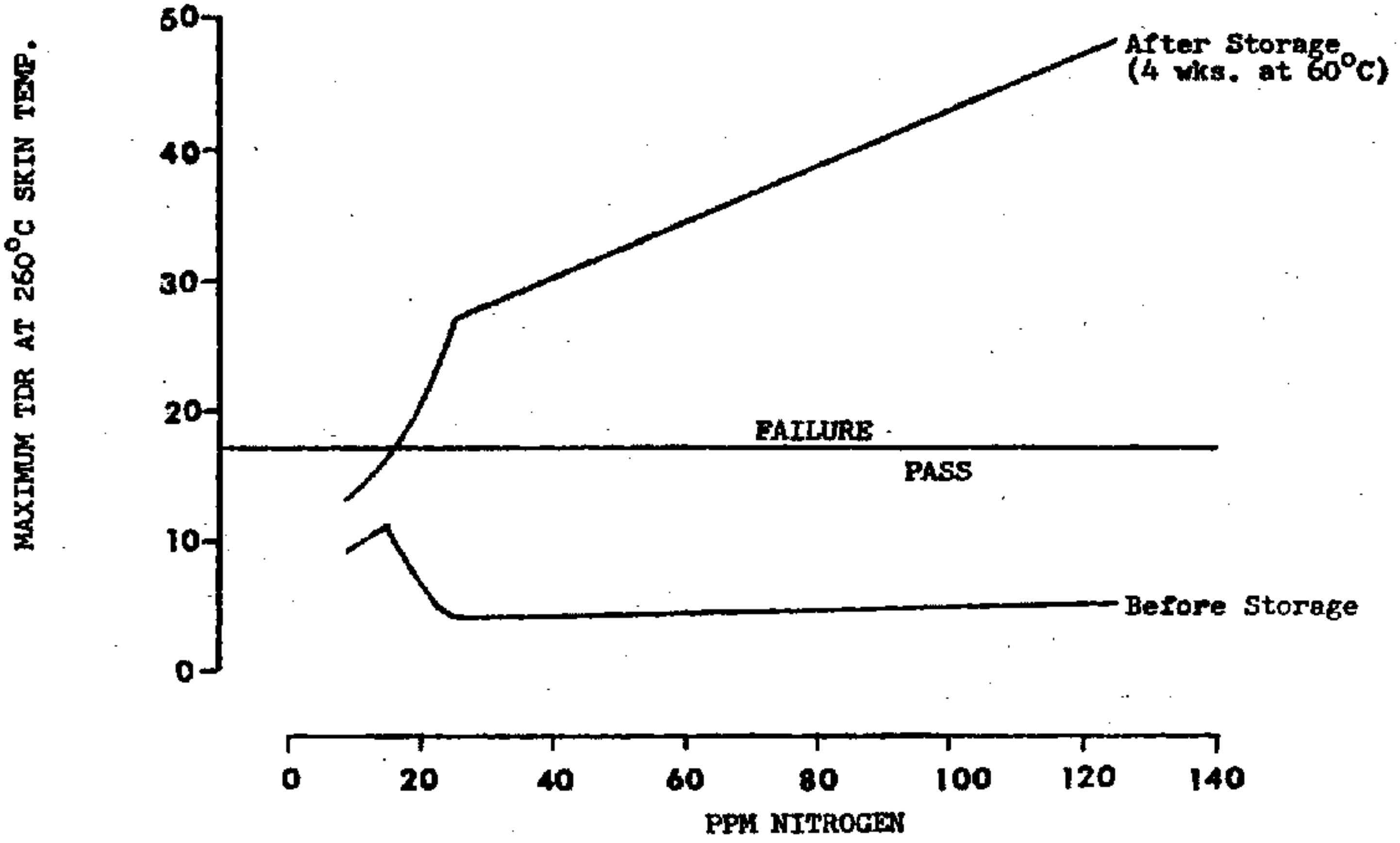


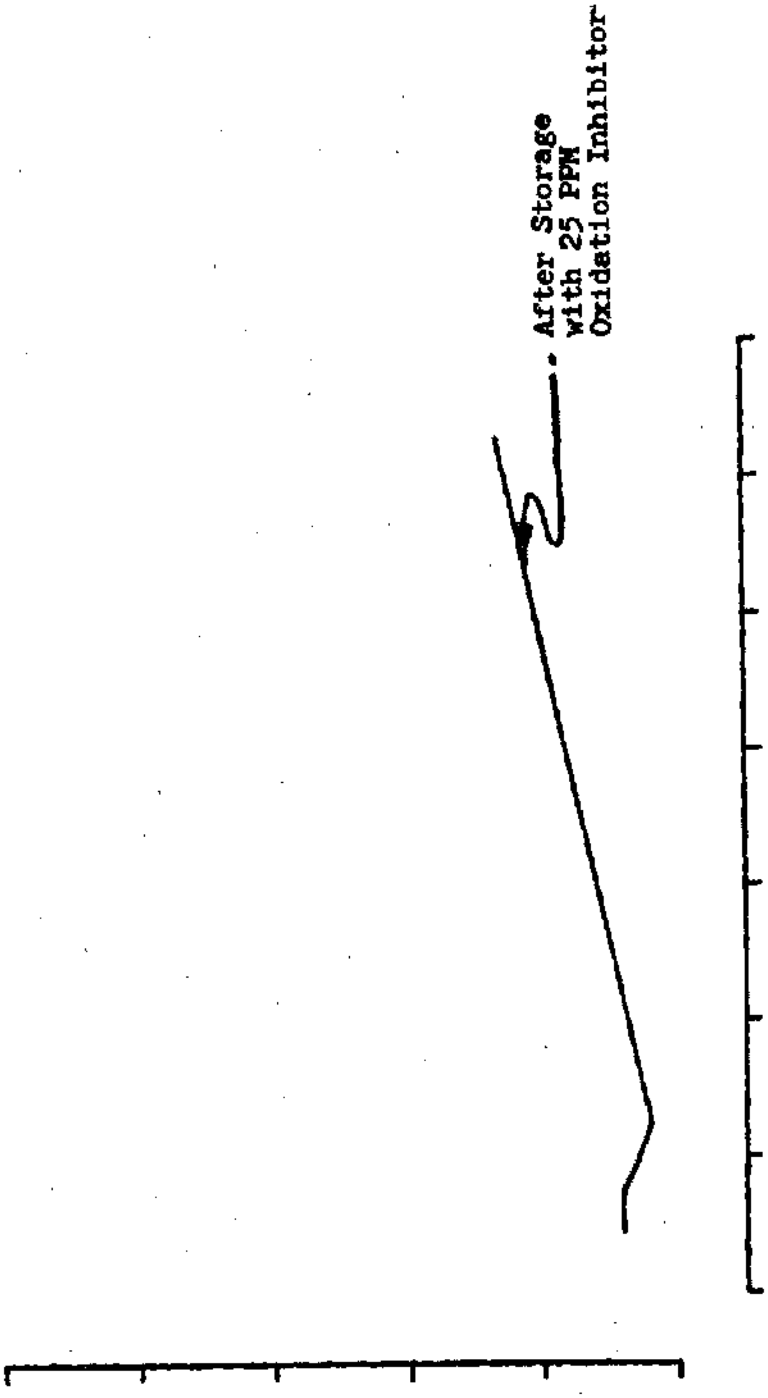
TEST NO. 3:

Compound Type	Concentration, ppm*	JFTOT Rating at 260°C	
		Maximum TDR	Pressure Drop, mm
4-t-butyl pyridine	28	6	8
4-t-butyl pyridine	56	1	20
2-t-butyl pyridine	49	10	1
5-ethyl-2-methyl pyridine	107	11	3
2,2-bipyridyl	42	5	0
2-amino-3-methyl pyridine	134	45	14
methyl 3-pyridyl ketone	78	14	10
4-benzyl pryidine	56	7	2
isopropyl quinoline	62	5	3
4-picoline	107	2	3
N,N-dimethyl aniline	82	6	5
Fractionated (160-175°C) Acid Extractable Nitrogen	116	7	0
Pyrrole	100	32	BYPASS
Acridine	70	4	0

*Determined by perchloric acid titration.

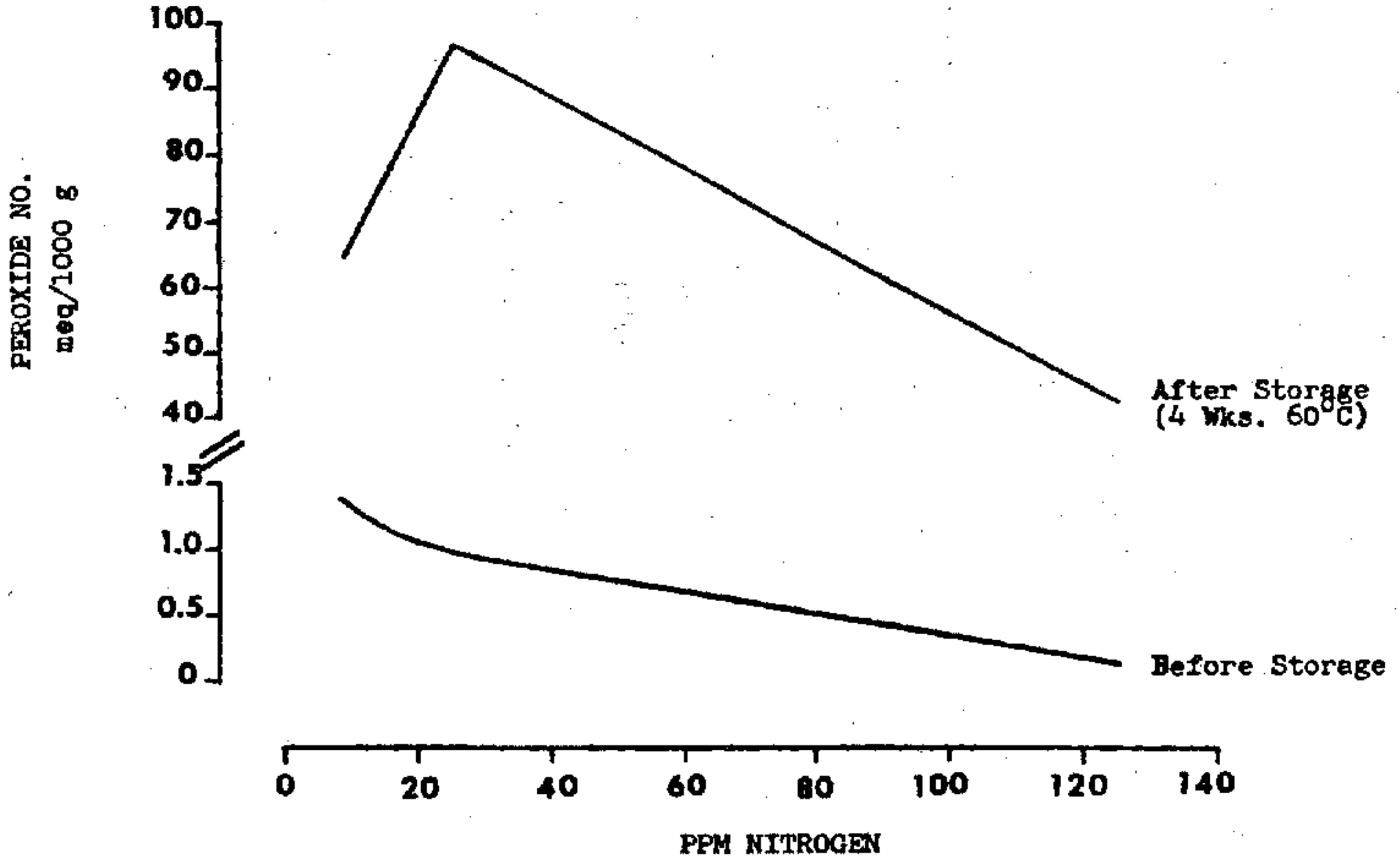
EFFECT OF ORGANIC NITROGEN ON FUEL THERMAL OXIDATION/STORAGE STABILITY

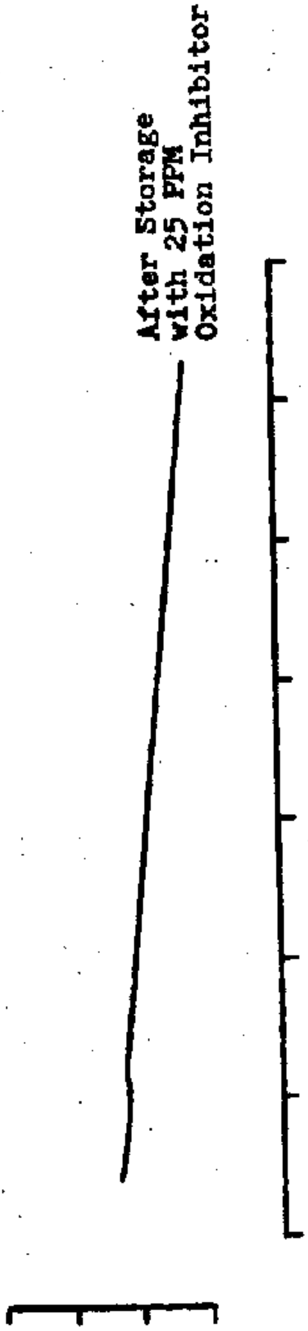




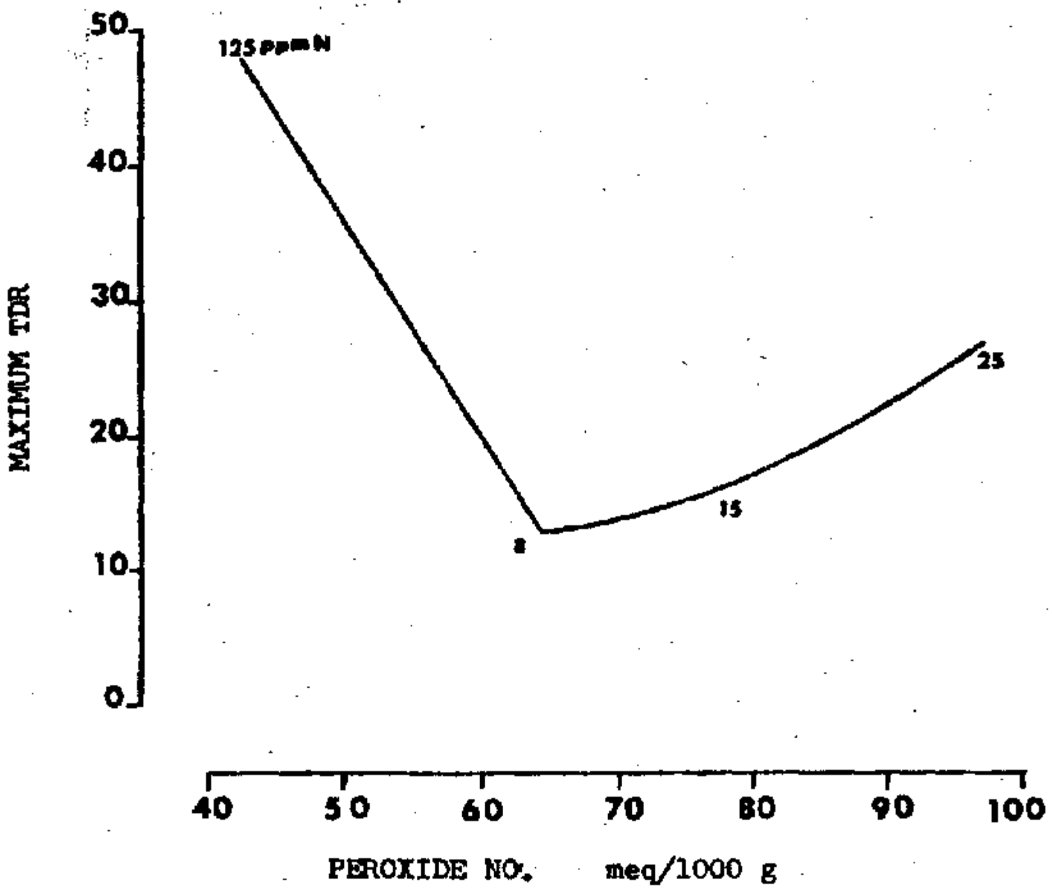
After Storage
with 25 PPM
Oxidation Inhibitor

EFFECT OF ORGANIC NITROGEN ON PEROXIDE FORMATION DURING ACCELERATED STORAGE




After Storage
with 25 PPM
Oxidation Inhibitor

RELATIONSHIP BETWEEN FUEL THERMAL OXIDATION STABILITY AND PEROXIDE CONTENT



USAF ALTERNATIVE FUEL PROGRAM

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Introduction

The Department of Defense consumes approximately 2.7 percent of the total U.S. demand for petroleum. The Air Force usage accounts for 57 percent of the DOD consumption with approximately 82 percent being consumed as jet fuel. The cost of this fuel to the Air Force has increased greatly since the 1973 oil embargo. The bill in 1973 was slightly over one-half billion dollars for 112 million barrels of JP-4, whereas, it is now approximately 1.6 billion dollars or about 6 percent of the Air Force annual budget for only 80 million barrels (Fig. 1).

At the present time, there is a great deal of emphasis by both the Department of Energy (DOE) and industry to develop the technology to produce hydrocarbon liquids from sources such as coal and oil shale which are available in huge quantities in this country. In addition, much research is being conducted to utilize heavy crudes (low pour point viscous oils) and residues (tar-like solids) which heretofore have been too costly to extract and process. Also, the North Slope crude, which is currently impacting the west coast refineries is more highly aromatic and heavier than conventional crudes and thus results in different refinery process economics for a conventional slate of products.

Each of these energy sources, while basically hydrocarbons, differ drastically as to compound types, mineral content, etc., and therefore each will have specific processing problems. Liquid hydrocarbons from coal, oil shale and tar sands will also be much more deficient in hydrogen than conventional crude. Hydrotreating (generic classification of processes involving hydrogen addition) is the most costly and evergy consuming operation in refining and is expected to become much more expensive in the future. Refining energy costs on coal liquids for example, could be relaxed by one-third if restrictions on aromatic content were relaxed. Refining costs are proportional to refinery energy costs. Therefore, a substantial cost saving on refined products such as a jet fuel would be achieved if the amount of hydrotreating in processing both petroleum and non-petroleum feedstocks is reduced.

The specification for JP-4, the standard Air Force jet fuel, was defined at a time when this product was both inexpensive and plentiful. While there have been refinements to the fuel specification to keep pace with engine development, JP-4 has basically maintained the critical properties first specified to insure availability and to fulfill aircraft operational requirements. A clear understanding of the relationships between fuel characteristics and aircraft system performance, engine durability, emissions, and survivability may result in dramatic cost reductions for a broadened specification fuel, but these reductions can only be realized with assurance that aircraft performance is not adversely affected.

In 1974, the Air Force Aero Propulsion Laboratory (AFAPL) at Wright-Patterson Air Force Base, Ohio, began a program to investigate the possibility of using jet fuel produced from domestic sources of liquid hydrocarbons other than petroleum. This program has been modified within the last year to concentrate on shale oil as a viable near term source of jet fuel. The DOD is currently determining the role it should play in stimulating the

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immediate development of synthetic fuels, particularly those derived from shale oil. An initiative to aggressively pursue shale oil as a source of jet fuel, fits well into the on-going Air Force program. The results of this effort together with other related findings and projections of future goals are discussed herein.

AVIATION TURBINE FUEL PROGRAM

Within the DOD, the AFAPL has prime responsibility for military aviation fuel. Under this charter the Laboratory initiated an extensive Aviation Turbine Fuel Technology Program early in 1974 to establish the properties of an aviation turbine fuel which will result in adequate fuel availability for the Air Force at an acceptable cost. This was not a major problem prior to the 1973 embargo in that JP-4 jet fuel was readily available worldwide at a very cheap cost. Two approaches are being pursued in this program: (1) relax specifications to reduce the level of processing required on conventional petroleum crudes and the lower quality crudes which are expected to be used in the near future, and (2) investigate the acceptability of fuel produced from alternate sources such as coal, oil shale and tar sands to meet the same relaxed specifications as for petroleum drived fuels. Figure 2 depicts the overall nature of the program. Fuel processing will be of primary importance to ascertain per-gallon fuel costs. The impact of reduced levels of refining on all aircraft system components must be determined. These include fuel system (pump, filters, heat exchangers, etc,) and airframe (fuel tank size and design, impact on range, etc.) considerations as well as turbine engine (mainburner augmentor degradation and emissions). It is anticipated that the optimum turbine fuel for Air Force use will be a compromise among these various considerations.

The primary emphasis on the program has been in the areas of fuel processing, fuel analysis and combustion effects. The fuel processing studies, to date, have centered around the refining of western shale oil. Because of its high hydrogen content and low residuum content, shale oil was considered an excellent candidate for a synthetic crude which could be refined into transportation fuels. Shale oil's paraffinic nature makes it ideal for the production of middle distillates such as diesel and aviation fuels.

Recently the Air Force initiated programs to develop new upgrading and refining procedures for the efficient and economic processing of whole crude shale oil into high yields of military transportation fuels while optimizing the yield of aviation fuel, Grade JP-4 or JP-8. Key to this effort, will be the upgrading step which converts the whole shale oil into a synthetic crude which would be suitable feed for most conventional refineries. Therefore, these programs will have considerable commercial impact. The upgrading and refining concepts to be pursued in this program have potentially lower costs for converting whole shale oil into a slate of products than state-of-the-art processing. The efforts include the application of novel approaches for improving the efficiency of hydrogen usage, selectively removing heteroatoms (especially nitrogen) and increasing yields of products.

Previously because of the unavailability of refined petroleum or synthetic fuels meeting a range of physical and chemical requirements as desired for various experimental efforts, a great deal of emphasis was placed on blending hydrocarbon components to simulate refined petroleum and synthetic fuels. Table 1 gives the mass spectrometer analysis of the initial boiling point to 568°F feed fraction for the synthetic liquids tested in the Exxon study (1). Table 2 gives an analysis of the blending components being tested in the Combustor Effects Tasks. These components when blended with base JP-4 and JP-8 fuels result in sample which have hydrocarbon compositions similar to hydroprocessed shale oils. Future availability of variable quality products from the various processing studies sponsored by the Government and industry will certainly enhance experimental results.

Primary emphasis in the experimental portion of the program revolves around a strong combustion technology effort necessary to establish the operating limits for future fuels derived from petroleum or shale oil or any other hydrocarbon source. The initial combustion efforts involved the quantification of the effects of fuel hydrogen and nitrogen content using a T56 single combustor modified to operate at conditions representative of a wide variety of engines in the inventory. Hydrogen content, representing various severity levels of hydroprocessing, was varied between 12.7 and 14.5 percent by weight by the addition of alkyl-benzenes to a base-line JP-4. Nitrogen content which could be as high as 2% in raw shale oil was varied between 0.1 and 1.0 percent by weight by the addition of pyridine. Results of the hydrogen variation effects on combustor liner temperature at low pressure cruise conditions are presented in Figure 3. These data, which are typical, show a significant increase in combustor liner temperature due to the more luminous radiative flame produced by the reduction of hydrogen content in the fuel. The effect of hydrogen content variations on smoke emissions for various combustor inlet temperatures is presented in Figure 4. It should be noted that the 756°K combustor inlet condition might be expected to result in a somewhat higher increase than the 644°K inlet. However, because of test facility limitations, a lower fuel/air ratio was required to maintain a 922°K exhaust temperature resulting in a lower absolute smoke emission. Figure 5 illustrates the effects of fuel bound nitrogen conversion on NOx production as a function of fuel bound nitrogen level and combustor inlet temperature (4). The shale oil processing program will establish the nitrogen levels possible with various types and levels of denitrogenation. Nitrogen compounds present a serious problem to the refiner since they are well known hydrotreating catalyst poisons. In addition many organic nitrogen compounds are detrimental to required thermal stability levels for most fuels. Therefore it is unlikely that shale oil derived fuels will ever have high levels of nitrogen. However, other portions of the overall Air Force program should provide guidance to this aspect.

Current combustor efforts in the Aviation Fuel Program have expanded into three contractual efforts, two initiated in 1977 and one in 1978, to investigate the effect of fuel property variations on three classes of combustors in the inventory. The General Electric Co. is assessing the effects of hydrogen content variation, volatility, aromatic type and end boiling point on the performance and durability of the low pressure can (J-79) and full annular type (F101) combustors. The 1978 program is addressing fuel parameter effects on high pressure can type combustors. These results as well as those from the Fuel/Engine/Airframe Optimization Study, initiated within the last year will provide guidance on the specific direction of the overall program in the future.

The Fuel/Engine/Airframe Optimization Study is determining the extent to which fuel properties can be varied without detrimental effects to an Air Force aircraft mission. Douglas Aircraft Co. (Long Beach, CA) is the prime contractor with subcontracts to Pratt & Whitney Aircraft Group and Union Oil Co. of CA, for imputs on engine operation and fuel processing costs, respectively. The shale oil processing efforts will have a large impact on this effort when the economic data are available. The second part of the program will be directed towards establishing fuel properties which will minimize aircraft life cycle costs. This will consist of a tradeoff between fuel physical and chemical characteristics and associated fuel cost savings coupled with improved potential availability and aircraft system costs associated with modifications required to utilize a broadened fuel specification. This tradeoff study will be the primary means of developing specific guidance to all experimental and developmental efforts planned to be initiated in 1979 and shown in Figure 6.

ADVANCED DEVELOPMENT PLAN FOR AVIATION FUEL

The Aviation Turbine Fuel Technology Program is structured so that an interim specification will be defined four years after the program initiation. This interim specification will be developed with strong imputs from the shale oil processing efforts. It is projected that it will be similar to JP-8 and will serve as a guide to the engine and aircraft manufacturers as well as to the fuel suppliers. The program is then expected to lead to a significant fuel specification change in approximately 15 years. Such a fuel might have characteristics such as those outlined in Table 3.

SUMMARY

The Air Force, the largest consumer of petroleum within the Department of Defense, has an ongoing program to define the specification requirements for a fuel which will maximize the availability and minimize the cost of turbine fuel in the future. This effort has been in progress for the past four years and certain highlights have been attained. These are outlined in Table 4. In December 1974, a formalized agreement with regard to Alternative Fuel Developments, was finalized between NASA's Lewis Research Center and AFAPL. NASA responsibility for commercial jet fuel development can be of importance to Air Force in a number of areas and vice versa. In January 1975, the AFAPL began to establish a combustion technology base in order to develop information concerning the effect of fuel quality on combustor performance and life. Later that year, in March, the Exxon study clearly identified western shale oil as the optimum domestic alternative to petroleum as a source for jet fuel.

The Office of Naval Research in April 1975 sponsored an effort which refined 10,000 barrels of jet fuel. Although the jet fuel was of poor quality as received, AFAPL technicians were able to produce acceptable fuel by an extensive (and expensive) clay adsorption process on approximately 2000 gallons. After clean-up the fuel was further tested and evaluated, additives were added, engine endurance tests were completed and the fuel was then certified for flight. On June 18, 1975, General James Stewart, the Commander of the Aeronautical Systems Division, flew a T-39 aircraft from Wright-Patterson Air Force Base to Fort Worth, Texas on the shale oil derived JP-4. This was significant in that it was the first flight of a jet powered aircraft on a fuel not produced from petroleum and it demonstrated that shale oil was a truly viable source of jet fuel even though the processing steps had not been optimized or were not economically attractive. In April 1976, a study was initiated with Bonner and Moore Associates Inc. to determine the effect of relaxing certain critical fuel requirements on improving availability of fuel from domestic petroleum. From a survey of domestic refineries it was determined that increases of about 28 percent could be realized by relaxing freeze point, aromatics, final boiling point and smoke point. In August 1977, AFAPL initiated an effort, with Douglas Aircraft Co. as the prime contractor, to determine the extent to which fuel properties can be varied without detrimental effects to the overall system. A key part of this effort will be the effects of fuel cost (and availability) on the final trade-off. With regard to refining of shale oil, the Chevron program, sponsored by DOE, early this year clearly demonstrated that large yields of middle distillate products including jet fuel could be economically produced from shale oil crude using available refinery technology. Using this excellent program as a comparison standard of state-of-the-art technology the Air Force has launched into the intensive shale oil-to-jet fuel processing study which should provide valuable information regarding the relationship between fuel quality and process economics so badly needed to perform meaningful trade-off assessments. This effort has just been initiated and should be completed in early 1981. DOE continues to investigate, in general, the processing of shale oil and these efforts will impact and provide guidance to the specific Air Force jet fuel problems. Although the Air Force charge in synthetic fuels development is restricted to aviation turbine fuels, the efforts since synthetic fuel availability is a highly complex and dependent variable in any future energy equation.

CONCLUSIONS

The Air Force conclusions concerning the future situation with regard to jet fuel are summarized on Table 5. Even with sizable increases in continental US reserves of petroleum, future availability of jet fuel is dependent on the development of a domestic synthetic fuel industry. Based on the chemistry of the crude shale oil and the nearness of commercialization of production operations, shale oil is the most promising domestic source of middle distillate feedstock. Anticipating the key role to be played by shale oil and the fact that the crude will be produced by industry, AFAPL has initiated an exploratory development and manufacturing technology program to determine the overall production and economic factors necessary to better assess the impact of shale oil on future Air Force systems. These data are required in order to provide the information necessary to include synthetic fuel as part of any future jet fuel specification developed by the Air Force. Concurrent with development of a shale oil industry, the Air Force must assure as smooth a transition as possible to the unqualified use of jet fuel from shale; this can only be done by establishing meaningful fuel specifications and performing the endurance tests, flight tests and perhaps larger service tests to answer all questions regarding full scale operations.

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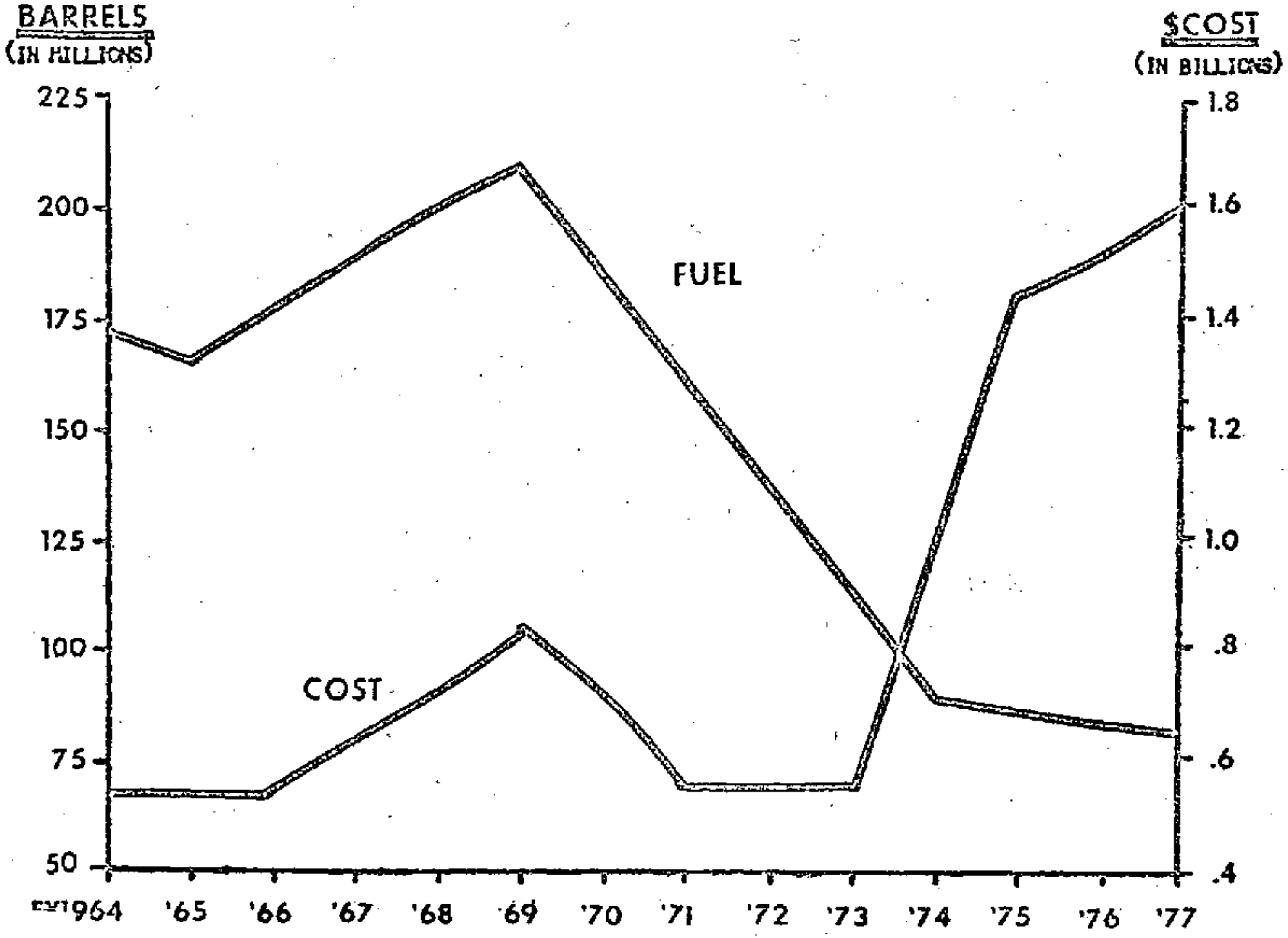

FIG. 1 - AIR FORCE AVIATION FUEL CONSUMPTION STATISTICS

USAF AVIATION TURBINE FUEL TECHNOLOGY PROGRAM

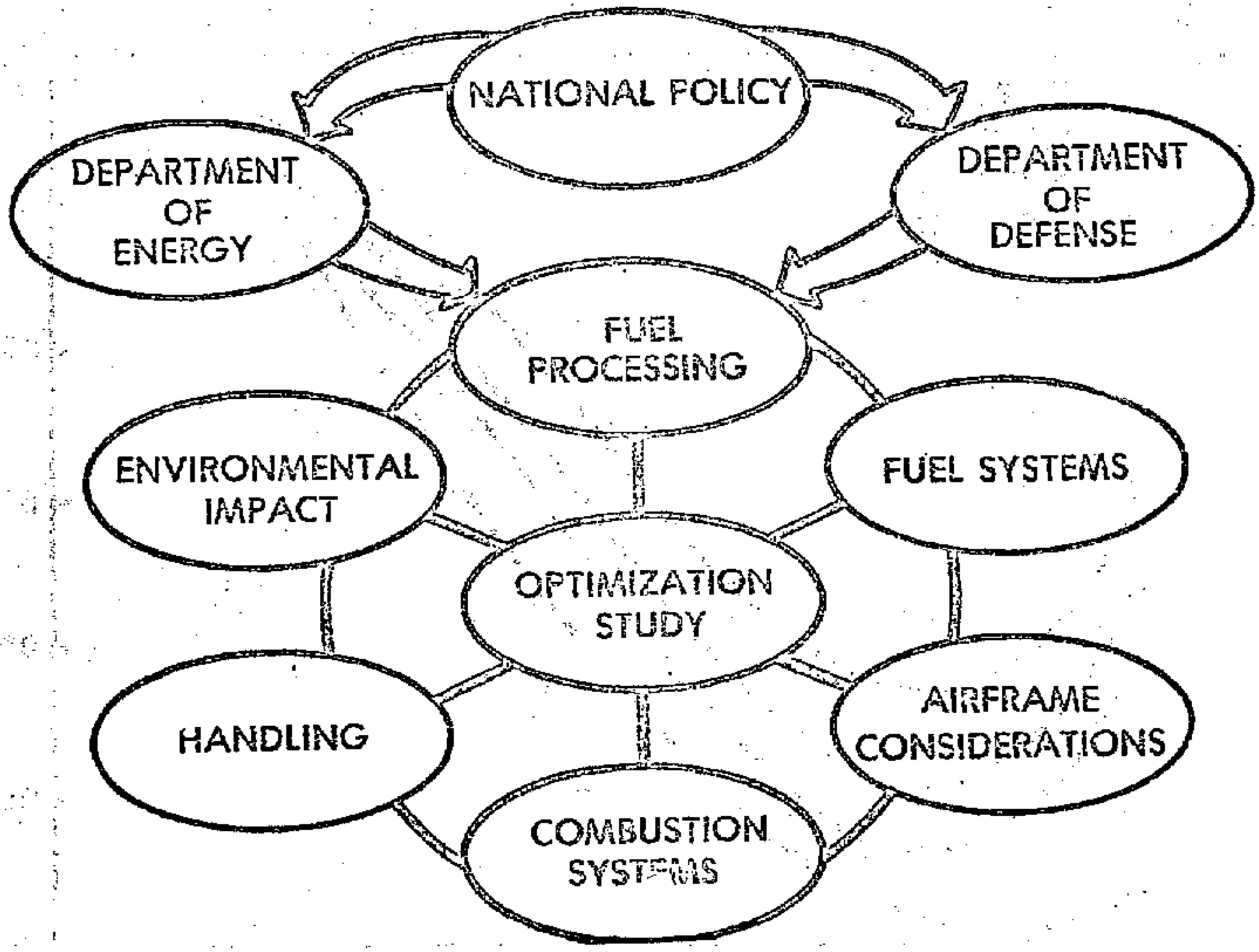

FIG. 2.—AIR FORCE AVIATION TURBINE FUEL TECHNOLOGY PROGRAM

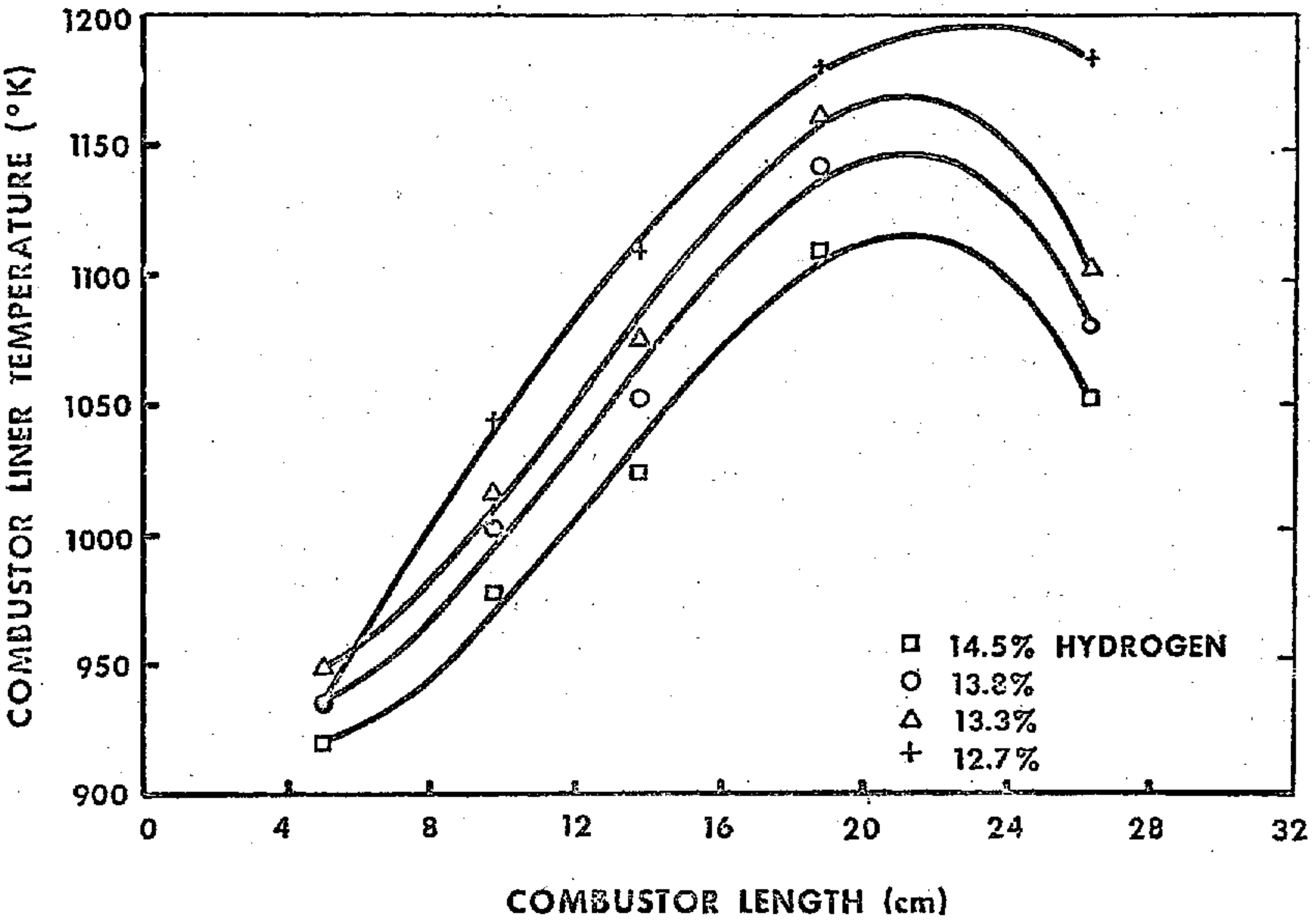

FIG. 3.- FUEL HYDROGEN CONTENT EFFECT ON COMBUSTOR LINER TEMPERATURE

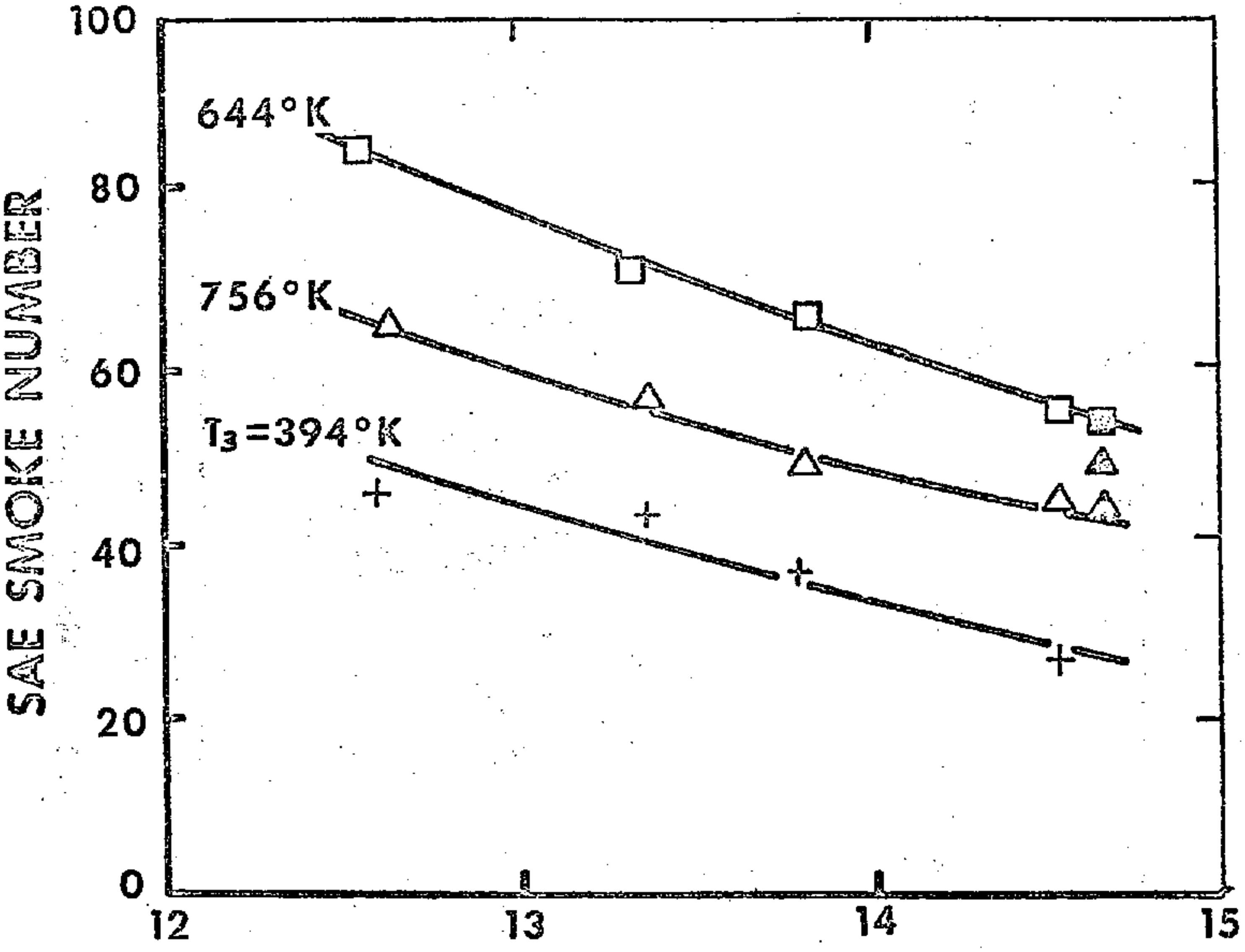

FIG. 4 - FUEL HYDROGEN CONTENT EFFECTS ON SMOKE EMISSIONS

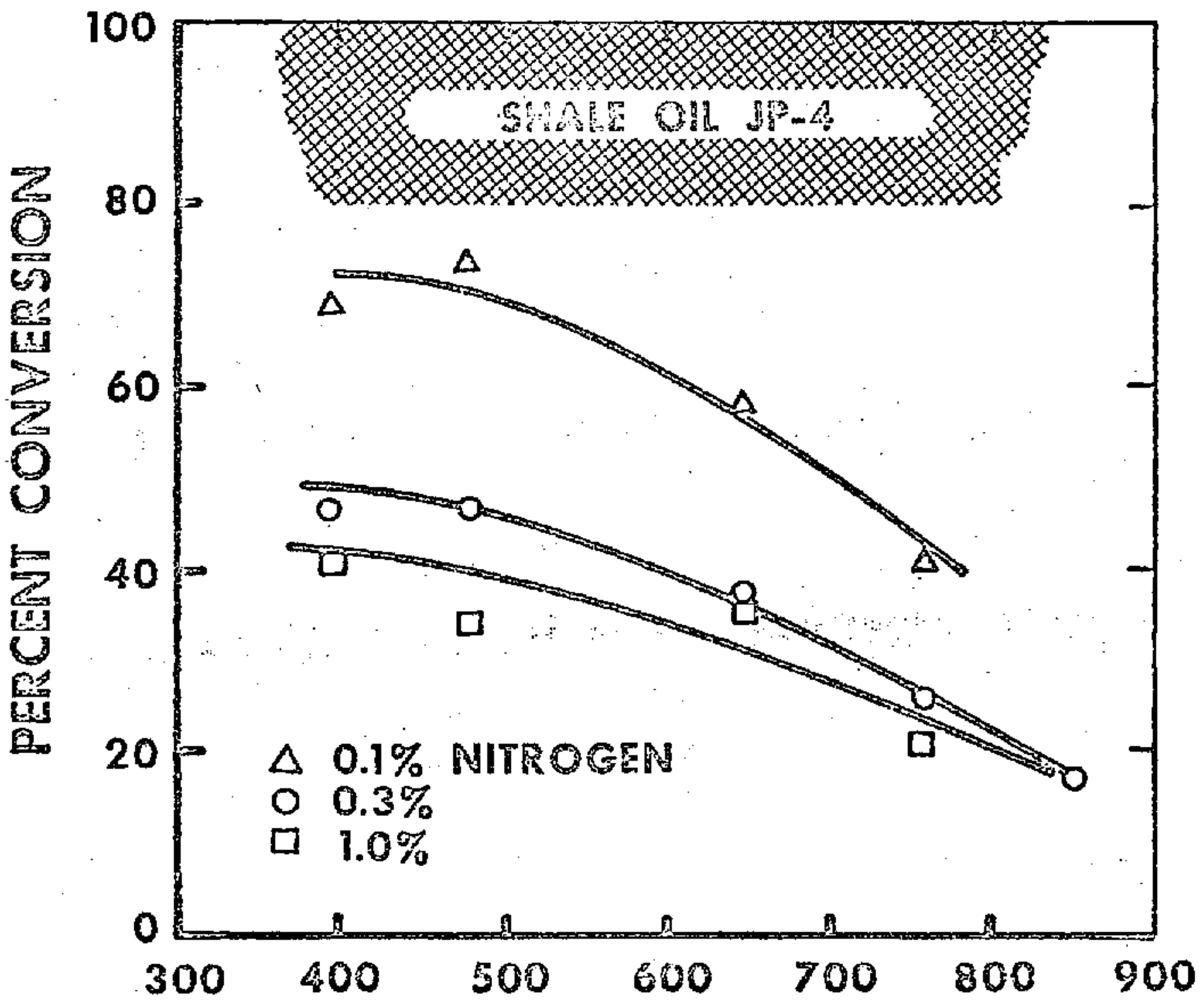

FIG. 5 - FUEL BOUND NITROGEN CONVERSION TO NOx

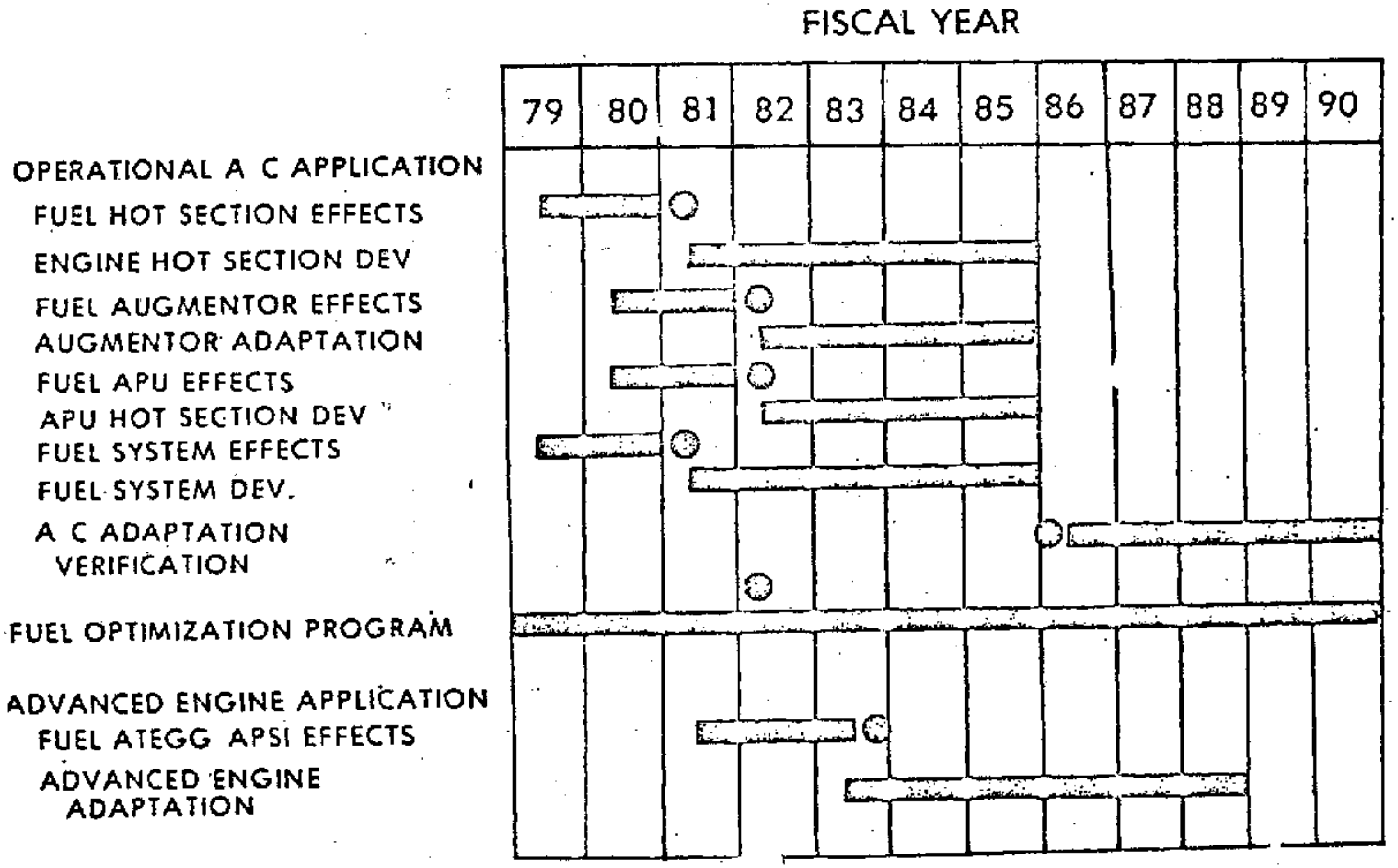

FIG. 6 - AIR FORCE AVIATION TURBINE FUEL TECHNOLOGY PROGRAM SCHEDULE

TABLE 1 - MASS SPECTROMETER ANALYSIS OF SYNCRUDES

INITIAL BOILING POINT TO 568°K FEED FRACTIONS

	Paraho	Tosco II	Garrett	Synthoil	H-Coal
Paraffins	33.2	25.8	35.9	0.5	1.4
Monocycloparaffins	4.6	28.3	5.9	38.8	43.4
Dicycloparaffins	11.3	9.3	10.5	8.5	8.3
Tricycloparaffins	10.3	6.4	8.4	0.0	1.6
Total Paraffins	59.4	69.8	60.7	47.8	54.7
Alkylbenzenes	18.4	17.0	16.5	21.2	24.2
Indans	11.6	7.9	10.7	21.4	17.2
Indenes	5.0	2.7	4.1	7.7	0.2
Naphthalenes	5.2	2.3	7.6	1.6	3.2
Total Aromatics	40.2	29.9	38.9	51.9	44.8

TABLE 2 - HYDROCARBON ANALYSIS OF BLEND MATERIALS-% (BY WT.)

	Xylene	2040 Solvent	Gulf Mineral Seal Oil
Paraffins			43.5
Cycloparaffins			30.2
Dicycloparaffins			9.9
Tricycloparaffins			4.6
Total Paraffins			88.2
Alklbenzenes	100.00	35.5	4.0
Indans/Tetrolins		6.8	4.8
Indenes		0.09	1.4
Naphthalene		18.6	0.9
Naphthalenes		39.0	0.14
Acenaphthylenes		–	0.44
Tricyclic Aromatics			
Total Aromatics	100.00	99.99	11.68

Table 3 - Future Fuel Specification

Final BP, Max. °F	600
Flash Pt., Min-Max, °F	90-130
Freeze Pt., Max, °F	-30
Net Heat of Combustion, Min, Btu/#	18,300
Aromatics, Vol.%, Max.	35
Nitrogen, Wt.%, Max.	0.005
Hydrogen, Wt.%, Min.	13.0

TABLE 4 - HIGHLIGHTS - AF ALTERNATIVE AVIATION FUEL PROGRAM

DEC 74	- FORMALIZED AGREEMENT WITH NASA	
JAN 75	- START ALTERNATIVE FUEL COMBUSTION R&D	(AFAPL)
MAR 75	- SHALE OIL IDENTIFIED AS OPTIMUM TECHNICAL ALTERNATIVE	(AFAPL/NASA)
APR 75	- 1100 BBL JET FUEL PRODUCED FROM SHALE OIL	(NAVMAT)
JUN 75	- SHALE FUEL UPGRADED AND FLOWN IN AIR FORCE T-39	(AFAPL/AFLC)
APR 76	- INITIATE RELAXED SPECIFICATION/AVAILABILITY TRADEOFF STUDY	(AFAPL/NAPC)
AUG 77	- RELAXED SPECIFICATION/SYSTEM TRADEOFF	(AFAPL)
JUN 78	- SHALE OIL IDENTIFIED AS ECONOMICALLY ATTRACTIVE SOURCE OF JET FUEL	(DOE)
JUL 78	- SHALE OIL VARIABLE QUALITY PROGRAM	(AFAPL)

TABLE 5 - PRELIMINARY CONCLUSIONS OF AIR FORCE'S AVIATION TURBINE FUEL PROGRAM

- FUTURE JET FUEL AVAILABILITY DEPENDENT ON SYNTHETIC FUELS
- SHALE OIL MOST VIABLE DOMESTIC ALTERNATIVE SOURCE OF JET FUEL
- VARIABLE QUALITY FUEL SAMPLES REQUIRED TO DETERMINE FACTORS AFFECTING ECONOMICS AND PERFORMANCE
- FUTURE MILITARY SPECIFICATIONS MUST BE FLEXIBLE ENOUGH TO INCLUDE SYNTHETIC FUELS
- ACCEPTANCE PROGRAM REQUIRED TO ASSURE SMOOTH TRANSITION TO SYNTHETIC FUELS