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FUELS CHARACTERIZATION STUDIES

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The major thrust of the Lewis Research Center fuels characterization research effort is not only to characterize fuels derived from petroleum and nonpetroleum sources, but also to evaluate the use of current analytical techniques in the characterization of broadened-properties fuels. The research involves modifying these techniques or developing methods superior to those presently employed. Included in the latter category are liquid chromatography, gas chromatography, and nuclear magnetic resonance spectroscopy. Another important related area, synfuel hydroprocessing research, involves the use of an in-house hydroprocessing facility to study the effects of processing variables on the characteristics of fuels derived from syncrudes and supplies samples for the analytical research program.

In comparison with a specification Jet A, the broadened-properties fuels exhibit characteristics that reflect some of the potential changes in future aircraft fuels. A number of these fuel property changes, listed in Table 1, could occur as a result of an increase in the amounts of cracked stock streams to be used in future jet fuel production or the introduction of syncrudes into the refineries. A workshop was held at Lewis in 1977 to consider potential changes in jet fuel characteristics, particularly in the areas of combustion quality, freezing point, thermal stability and materials compatibility (ref. 1). A petroleum-derived broadened-properties fuel which was proposed at this workshop has been procured and characterized to serve as a referee fuel for analytical characterization and experimental combustor work (ref. 2). This experimental referee broadened-specification (ERBS) fuel is of major importance to the analytical methods development program. The ERBS fuel requirements and blend results are given in Table 2.

One specific area of fuels characterization that is presently receiving increased attention is hydrocarbon group-type analysis. Generally, group-type determinations on fuels distilling below 589 K (600° F) are performed by the fluorescent indicator adsorption method (FIA-ASTM D1319) (ref. 3). This method is time consuming, limited in its range of applicability, and subject to a number of errors. Recently, high-performance liquid chromatographic (HPLC) methods have been developed that improve all aspects of group-type analysis (refs. 4 to 7). A Lewis study that compared two HPLC techniques with the FIA method for a number of petroleum, shale, and coal-derived fuels indicated that significant differences did exist in the group-type results found, especially for the synfuels (ref. 7). Selected data from this study are presented in Table 3. These findings stressed the need for further research in this area. Currently, in-house HPLC group-type methods development is being approached from several directions, including aromatic fraction standards development and the elimination of standards through removal or partial removal of the alkene and aromatic fractions or through the use of

whole fuel refractive index values. More sensitive methods for alkene determinations using an ultraviolet-visible detector are also being pursued. Preliminary studies involving chemical removal of the alkene and aromatic fractions has yielded results that agree well with those found by the FIA method but demonstrate superior precision. This HPLC technique requires as little as ten minutes to complete. Research is continuing to further standardize this method, to improve the overall precision and accuracy of the results, and to extend the range of its applicability.

In addition to its use in qualitative and quantitative analyses of fuels, gas chromatography (GC) has been applied to the determination of a number of fuel physical properties (refs. 8 to 10). Some of the more successful GC physical property determinations for petroleum-derived fuels are the distillation curve (simulated distillation), heat of combustion, hydrogen content, API gravity, viscosity, flash point, and (to a lesser extent) freezing point. In a Lewis study that examined the feasibility of applying the GC relationships derived for petroleum fuels to synfuels, it was found that the simulated-distillation, heat-of-combustion, and hydrogen-content results were reasonably accurate but that the results of the other bulk fuel properties were not (ref. 10). Shale-derived fuels tended to yield results that were higher than the actual physical property value; coal-derived fuels yielded low results. Further investigations are warranted to develop GC physical property relationships that would be applicable to synfuels. Current research is aimed at developing a GC method for the determination of total synfuel nitrogen as well as the boiling-point distribution of the nitrogen-containing compounds in synfuels, by combining simulated distillation data and data obtained using a thermionic detector. Much of this effort has been devoted to the characterization of this detector due to the continued controversy concerning its stability and effective lifetime. The results of the study indicate that the simulated distillation-thermionic detector combination is a viable technique that has the potential of being developed into a routine method for future synfuel analysis.

Efforts to obtain detailed information on fuel composition by hydrogen and carbon-13 nuclear magnetic resonance spectroscopy (H and C-13 NMR) have been increasing in recent years due to the sizable amounts and types of data that can be obtained. A complete H and C-13 NMR sample analysis provides information on such important quantities as hydrogen to carbon ratios, relative amounts of each hydrocarbon group type, and, of particular importance, a detailed constituent breakdown (refs. 11 to 13). Lewis has initiated a grant with the University of Utah Research Institute to study petroleum and shale-oil-derived fuels primarily using C-13 NMR techniques. One objective is to correlate C-13 NMR data with fuel physical properties and combustor test results using Jet A and several broadened-properties fuels. A second is to examine the applicability of C-13 NMR to the determination of the composition of shale-oil crudes and products obtained from various stages of processing. The final objective is to employ C-13 NMR as a tool for monitoring fuel thermal degradation reactants and products of low thermal stability turbine fuels. To achieve the degree of detail required in the studies, samples are separated into as many as 16 to 20 fractions prior to

analysis. The combustor data are to be obtained from ongoing in-house and contract work; the processed shale oil samples are being obtained from the Ashland Oil Extractracracking Process through an Air Force Wright Aeronautical Laboratories contract.

A laboratory-scale hydroprocessing facility provides Lewis with the capability to generate a number of the samples required for analytical methods development as well as to perform limited studies on the synthesis and characterization of aviation turbine fuels derived from nonpetroleum sources. The facility is diagramed in Figure 1. A recent study was conducted to determine the characteristics of TOSCO II-derived fuels obtained under medium-severity hydroprocessing conditions and Paraho-derived fuels obtained under low-, medium-, and high-severity conditions. The fractions of whole shale oil boiling below 343° C (650° F) were hydroprocessed, and final distillations of each product were performed to obtain a fuel in the Jet A boiling range and a broadened-properties fuel with a final boiling point of 327° C (620° F). All products and final distillates were characterized in detail to identify those properties of the fuels that did not meet present specifications. A pictorial summary of the nitrogen results obtained for the Paraho crude oil and products is shown in Figure 2. It was determined that with the exception of the freezing point, which was high, a specification Jet A fuel can be produced from these syncrudes by the combination of high-severity hydroprocessing and distillation. The broadened-properties fuel produced from the same hydroprocessed product exhibited characteristics that were within the specifications set for the ERBS fuel in all cases except the freezing point and hydrogen content, which were both high.

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POTENTIAL JET FUEL CHARACTERISTICS

CHARACTERISTIC		CURRENT JET A	FUTURE BROADENED-PROPERTIES FUELS
COMPOSITION:			
	AROMATICS, vol %	17-25	25-40
	HYDROGEN, wt %	13.5-14.0	12-13.5
	SULFUR, wt %	0.01-0.1	~0.3
	NITROGEN, ppm	<10	50-2000
VOLATILITY:			
	FLASH POINT, ^{o}C	38-66	38-66
	BOILING RANGE, ^{o}C	171-277	171-343
FLUIDITY:			
	FREEZING POINT, ^{o}C	-46 TO -40	-34 TO -18
	VISCOSITY, cs AT - 23^{o} C	~5	~12
HEAT OF COMBUSTION:			
	MJ/kg	42.80-43.26	41.87-42.80
THERMAL STABILITY:			
	BREAKPOINT TEMP, ^{o}C	≥260	?

Table 1

CS-80-1568

EXPERIMENTAL REFEREE BROADENED-SPECIFICATION (ERBS)

AVIATION TURBINE FUEL - REQUIREMENTS AND BLEND RESULTS

PROPERTY	REQUIREMENTS	BLEND RESULTS
COMPOSITION:		
HYDROGEN, wt %	12.8+0.2	12.86
AROMATICS, vol %	REPORT	35.0
SULFUR, MERCAPTAN, wt %	0.003 MAX	0.0005
SULFUR, TOTAL, wt %	0.3 MAX	0.085
NITROGEN, TOTAL, ppm	REPORT	54
NAPHTHALENES, vol %	REPORT	13.2
HYDROCARBON COMPOSITIONAL ANALYSIS	REPORT	
VOLATILITY:		
DISTILLATION TEMP, ^{0}C (^{0}F)		
INITIAL BOILING POINT	REPORT	162 (324)
10 %	204 (400) MAX	188 (370)
50 %	REPORT	215 (419)
90 %	260 (500) MIN	279 (534)
FINAL BOILING POINT	REPORT	328 (622)
RESIDUE %	REPORT	1.2
LOSS, %	REPORT	0.3
FLASHPOINT, ^{0}C (^{0}F)	38 (100) MIN	60 (140)
GRAVITY, API (15^{0} C)	REPORT	37.1
GRAVITY, SPECIFIC (15/15^{0} C)	REPORT	0.8381
FLUIDITY:		
FREEZING POINT, ^{0}C (^{0}F)	-23 (-10) MAX	-29 (-20)
VISCOSITY, AT -23^{0} C (-10^{0} F), cSt	12, MAX	7.2
NET HEAT OF COMBUSTION, KJ/Kg (Btu/lb)	REPORT	42 427 (18 275)
THERMAL STABILITY:		
JFTOT, BREAKPOINT - TEMP, ^{0}C (^{0}F) (TDR, 13; AND ΔP, 25 mm)	238 (460) MIN	255.5 (492)

CS-80-1572

Table 2

COMPARISON OF AROMATICS DETERMINATION BY FIA AND HPLC METHODS

CRUDE SOURCE AND FUEL BOILING RANGE	FIA		HPLC METHOD 1		HPLC METHOD 2	
	AROMATICS,* %	MAXIMUM DEVIATION, % AROMATICS	AROMATICS, %	DIFFERENCE (HPLC-FIA)	AROMATICS, %	DIFFERENCE (HPLC-FIA)
PETROLEUM 107^{0}-262^{0} C	21.2	0.4	17.6	-3.6	21.3	0.1
138^{0}-258^{0} C	17.4	0.3	13.4	-4.0	16.4	-1.0
SHALE 121^{0}-288^{0} C	15.7	2.5	21.3	5.6	20.8	5.1
COAL 121^{0}-288^{0} C	26.4	2.4	30.3	3.9	26.1	-0.3
COAL 121^{0}-343^{0} C	29.0	3.6	30.2	1.2	25.2	-3.8

*AVERAGE OF RESULTS FROM 3 LABORATORIES.

CS-80-1571

Table 3

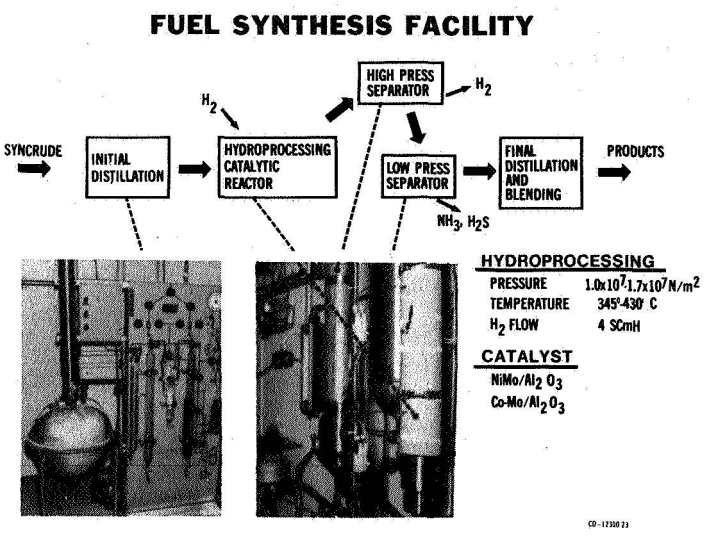
FUEL SYNTHESIS FACILITY
SYNCRUDE
INITIAL DISTILLATION
H_2
HYDROPROCESSING CATALYTIC REACTOR
HIGH PRESS SEPARATOR
H_2
LOW PRESS SEPARATOR
NH_3, H_2S
FINAL DISTILLATION AND BLENDING
PRODUCTS
HYDROPROCESSING
PRESSURE $1.0x10^7$-$1.7x10^7$ N/m^2
TEMPERATURE 345°-430° C
H_2 FLOW 4 SCmH
CATALYST
NiMo/Al_2O_3
Co-Mo/Al_2O_3

Figure 1

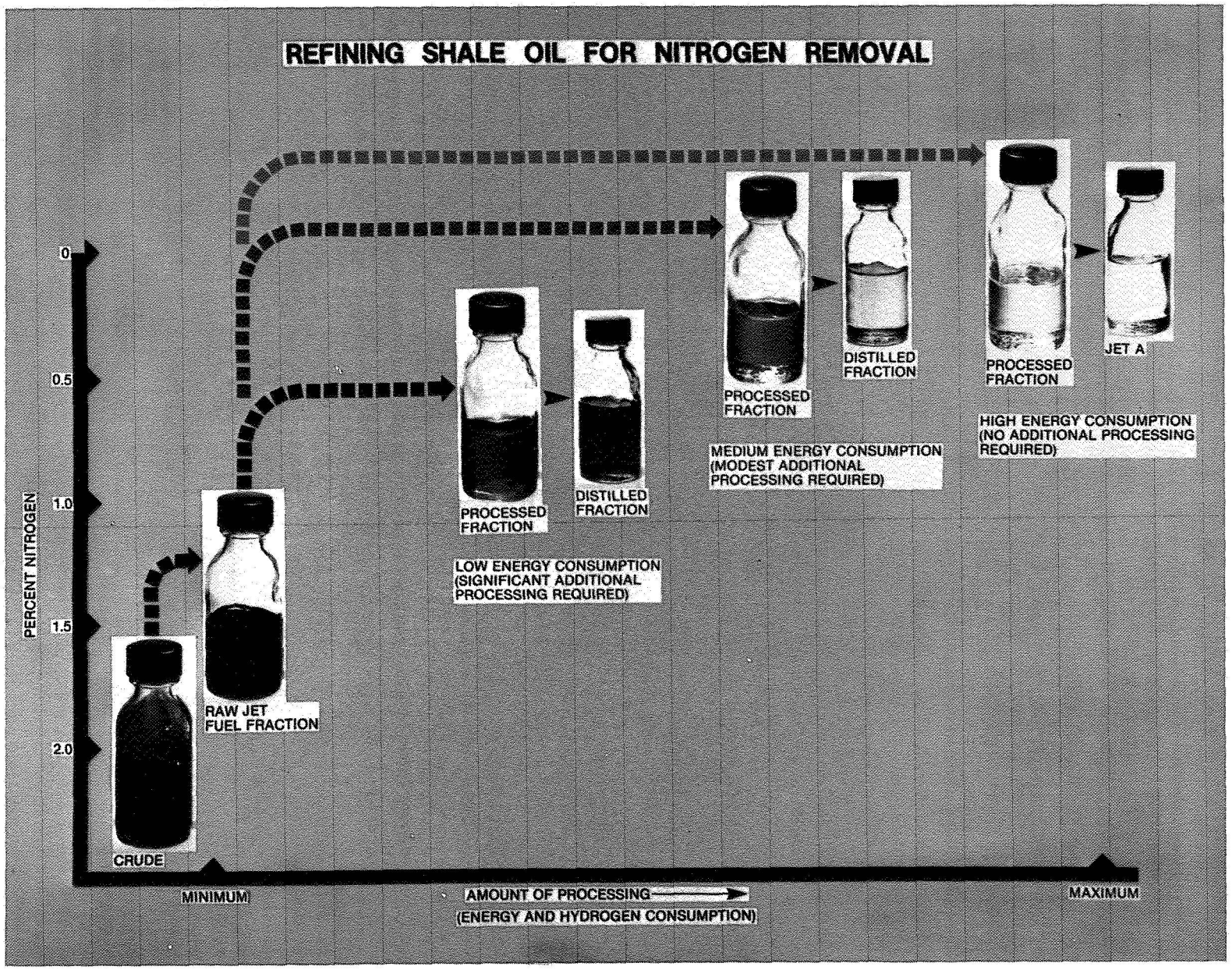
REFINING SHALE OIL FOR NITROGEN REMOVAL
PERCENT NITROGEN
0
0.5
1.0
1.5
2.0
CRUDE
RAW JET FUEL FRACTION
PROCESSED FRACTION
DISTILLED FRACTION
LOW ENERGY CONSUMPTION (SIGNIFICANT ADDITIONAL PROCESSING REQUIRED)
PROCESSED FRACTION
DISTILLED FRACTION
MEDIUM ENERGY CONSUMPTION (MODEST ADDITIONAL PROCESSING REQUIRED)
PROCESSED FRACTION
JET A
HIGH ENERGY CONSUMPTION (NO ADDITIONAL PROCESSING REQUIRED)
MINIMUM
AMOUNT OF PROCESSING
(ENERGY AND HYDROGEN CONSUMPTION)
MAXIMUM

Figure 2