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SYNCRUDE STABILITY STUDY

Final Report for June 9, 1980—March 31, 1983

May 1984

Date Published

Work Performed Under Contract No. AC19-80BC10188

Southwest Research Institute
San Antonio, Texas

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SYNCRUDE STABILITY STUDY
FINAL REPORT
For The Period
June 9, 1980 - March 31, 1983

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FOREWORD

The work reported here was conducted at the U.S. Army Fuels and Lubricants Research Laboratory at Southwest Research Institute for the Department of Energy under Contract DE-AC19-80BC10188. The program was monitored by Dr. Dennis W. Brinkman of the Bartlesville Energy Technology Center.

The work was conducted over a three-year period from June 9, 1980 through May 30, 1983. The principal investigator was Mr. John N. Bowden assisted by Dr. George H. Lee II. Dr. Brinkman provided gas chromatographic analyses for numerous samples used in the program and Dr. Dennis H. Finseth analyzed the same samples by ^1H NMR and low resolution mass spectrometry. This Final Report contains the results of the work for the entire program.

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ABSTRACT

This program was initiated to investigate the storage stability of syncrudes derived from coal and oil shale, and upgraded syncrudes, by procedures utilized for petroleum-derived fuels. Initially, the syncrudes were placed in storage at 43°C. After 4, 8, 16 and 24 weeks, aliquots were removed from storage for analysis of filterable precipitates, adherent gum, and soluble gum. Due to the high viscosity and boiling range of many of the syncrudes, special techniques were utilized to filter some of these samples for their measurements, which included heat and pressure. Investigation of other techniques for development of a test protocol that would successfully differentiate between various degrees of storage stability of syncrudes became a second objective of this program. To this end, solvent separations, accelerated stability tests at 80°C, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were investigated. Results of this work indicate that for the particular samples studied, the shale syncrudes are more stable than coal-derived syncrudes, and hydrotreatment of the shale syncrudes for upgrading tends to improve their stability. Thermal analysis by SC and/or TGA appears to show promise in evaluating syncrude stability, although finalized standard procedures still need to be developed.

EXECUTIVE SUMMARY

The technology for producing liquid fuels from alternative sources other than petroleum has continued to develop during the past few years, and several demonstration processes have generated numerous samples of unrefined coal liquids and shale oils. A significant characteristic of many of these liquids is their apparent instability in storage. It has been anticipated that many of these syncrudes may be used without or with minimal upgrading as fuels; therefore, an investigation into the storage characteristics of these materials was initiated. The storage characteristics of finished liquid fuels derived from coal, shale, and tar sands were the subject of earlier investigations.

During the initial year of the work reported here, available samples of coal- and shale-derived syncrudes were stored at 43°C for 24 weeks, and the characteristics during storage were monitored by procedures established for petroleum-based fuels: i.e., measurement of insoluble precipitates, adherent gum, and soluble gum in aliquots stored for 4, 8, 12, 16, and 24 weeks. During the tests, it was learned that, for many of the syncrudes investigated, these techniques were not satisfactory. Those materials with high viscosity and high boiling range were difficult to filter by the standard procedure to obtain the insoluble precipitate measurement. Adherent gum could be obtained with no problem; however, soluble or existent gum could not be measured due to the high boiling range of some of the syncrudes. The liquid portion would not evaporate at the gum test temperatures, giving a false indication of very high soluble gum values.

Employing the procedure referred to above, six samples of coal-derived syncrudes and eight samples of crude and hydrotreated shale oils were stored at 43°C for 24 weeks. The coal-derived liquids were described as two naphthas, a middle distillate, a heavy distillate, an atmospheric overhead, and a vacuum overhead. The shale oils included three crudes derived by three re-torting processes: above ground, modified in-situ, and in-situ. The other five shale oils represented varying levels of hydrotreating severity of two of the shale crude oils. When adequate quantities of samples were available, unfiltered and prefiltered aliquots were stored at 43°C.

At the end of the 24-week storage period, viscosity measurements were made in addition to the insoluble precipitate, adherent gum and, when possible, soluble gum determinations. Samples of the unaged and 24-week aged syncrudes were forwarded to the Bartlesville Energy Technology Center for simulated distillations which measured hydrocarbon, nitrogen, and sulfur distribution and to the Pittsburgh Energy Technology Center for nuclear magnetic resonance and mass spectrometry analyses. Elemental analyses also were performed on the unaged and aged (24 weeks, filtered and unfiltered) samples, and on soluble gums from the aged samples.

Storage tests and subsequent analyses of the coal-derived syncrude show that these liquids are generally unstable under these conditions. The level of oxidation products measured as gums varied considerably from sample to sample. Elemental analyses of the unaged, aged, and gum samples indicated that the lighter liquids, naphthas, and atmospheric distillates produce soluble gums high in heteroatom content, while the heavy and vacuum distillates gave gums with elemental analyses very similar to the unaged

liquid. This effect may be due to polymerization of the heavier liquids and/or the low volatility of these materials. A viscosity increase was observed for the heavy distillate during 24 weeks of aging at 43°C but not for the other coal liquids. Measuring of toluene-insoluble matter during the storage tests of the heavy distillate and vacuum overhead showed essentially no change over the 24-week period. Prefiltration of stored samples gave inconsistent results. In some syncrudes, the filtered aliquots produced more insoluble gum and soluble gum than the unfiltered aliquots while the reverse was true with other syncrudes.

The 43°C, 24-week storage test conducted with shale oils and hydrotreated shale oils appeared to indicate that the shale-derived liquids tested here are more stable than the coal liquids examined. Changes in gum levels for the hydrotreated samples and in heptane-insoluble material in the shale oil crudes during 24 weeks at 43°C were not large. Filtration prior to storage appeared to improve the stability of the hydrotreated modified in-situ shale oil samples proportionally to severity of hydrotreatment, but showed little effect on the above ground retorting process. Elemental analyses and viscosity measurements of aged shale oil samples were not significantly different from the unaged samples.

The hydrocarbon, sulfur, and nitrogen distribution analyses performed at the Bartlesville Energy Technology Center on aged and unaged samples showed very little changes in the bulk composition of these liquids during the storage tests. The ¹H-NMR and mass spectrometry analyses performed on the same samples at the Pittsburgh Energy Technology Center also showed virtually no change in the composition of the materials while aging under these conditions.

Three special blends of petroleum-derived fuels referred to as experimental referee broadened-specification (ERBS) fuels were evaluated for their storage stability characteristics at 43°C for 24 weeks. The three fuels differed in hydrogen content: one contained a nominal 12.8 wt% hydrogen, the second 12.3 wt%, and the third 11.8 wt%. These fuels were very stable at 43°C for 24 weeks as indicated by very little increase in gums formed during the storage period. Boiling point distributions by gas chromatography of the ERBS fuels prior to and after storage showed a loss of low-boiling fractions which was attributed to the vacuum filtration step used to determine the precipitates formed during storage.

In view of the difficulty in measuring the level of oxidation products formed during the aging of many of these syncrudes, the second phase of this work was devoted to investigating potential procedures for evaluating the stability characteristics of these materials and/or level of degradation during storage.

Earlier in this summary, a procedure for measuring hot toluene and n-heptane insolubles was mentioned. The same basic procedure with these and other solvents, i.e. cyclohexane, methyl-iso-butyl ketone and n-decane, was used to measure "solvent" insolubles produced during the 24-week, 43°C storage of the shale crude oils. Only small increases in "solvent" insolubles occurred during the storage period, and unfiltered samples generally produced more insolubles than the filtered ones. n-Heptane and n-decane are the best solvents for this procedure since more insolubles are measured. The polar

solvents tend to solubilize some of the filterable insolubles produced during the storage period.

Samples of intermediate streams from the refining of shale oil produced by the Occidental retorting process (modified in situ) became available for evaluation in this program. The refining process was Ashland Oil Company's Extractacracking® process and the streams supplied, in addition to the crude shale oil, were designated: hydrotreated oxy shale crude, crude shale hydrotreater (CSHT) recycle, Fluid Catalytic Cracker (FCC) tower overhead, raffinate, and JP-8 off-spec from guard case hydrotreater (GCHT). To accelerate the aging process and generate gum in a shorter period than 24 weeks as used in the first phase, these streams and crude were aged at 80°C for 3, 7, and 14 days. Under these conditions, the crude shale produced a moderate increase in insolubles after 14 days. The JP-8 off-spec GCHT generated moderate to severe increase, and the FCC tower overhead and raffinate generated a very large increase in insolubles during the aging period. The whole hydrotreated crude and CSHT recycle generated essentially no insolubles. The more stable process streams were hydrotreated, while the least stable streams were subjected to temperatures above 600°F during the processing. Hot heptane insoluble measurements gave results in the same order except that the crude shale oil yielded hot heptane insolubles at a higher level than those determined by filtering the aged sample after 14 days.

Thermal analysis by differential scanning calorimetry (DSC) and/or thermogravimetric analysis (TGA) appeared to show promise for evaluation of the stability of stored and aged fuels and gum deposits. Therefore, samples of unaged and aged coal-, shale- and petroleum-derived syncrudes and fuels were analyzed by these techniques. It was found that residues shown to be gums could be measured in heavy syncrudes using the TGA and DSC procedures. Naphthas and middle distillates derived from coal were found to be excessively volatile for analysis by these techniques.

INTRODUCTION

The continued emphasis on the development of technology for producing liquid fuels from alternative sources other than petroleum has produced several processes for liquefying coal and extracting oil from shale. The investigation of the properties of these materials and the effect of finished synfuels on engines that may eventually burn these fuels are important to the development of processes to refine the syncrudes. Some syncrudes may be used with little or no upgrading in an attempt to maximize energy efficiency. Furthermore, process reliability for these lower quality feedstocks may be a problem, so that system shutdown with syncrude in the lines may be a fairly common occurrence. One important characteristic of these alternative crudes is their decreased storage stability. Therefore, this project addresses the storage characteristics of syncrudes.

Stability and other properties of fuels and crudes derived from sources other than petroleum have been investigated by several workers (1-6).^{*} Techniques for investigating the storage characteristics of petroleum-based fuels have been modified and employed in the present and other work reported in the literature (7-8).

During the first year of work, available syncrudes derived from coal and shale were investigated for their stability using established storage tests applicable to petroleum fuels. It was learned that monitoring any suspected deterioration of the stored syncrudes at 43°C by procedures for petroleum fuels was not satisfactory. The second part of this project, which covered a period of 22 months, emphasized the development of techniques to determine the stability of coal and shale liquid syncrudes.

OBJECTIVE

The objective of this program was to investigate the storage characteristics of synthetic crudes derived from coal and from oil shale, and to develop a test protocol which would successfully differentiate between various degrees of storage stability for shale and coal syncrudes.

APPROACH

During the first phase of this project, samples of coal-derived liquids produced by different processes in pilot or demonstration plants were obtained by the Pittsburgh Energy Technology Center (PETC) and submitted for storage tests at 43°C lasting 24 weeks. Samples of shale-derived crudes and hydro-treated shale liquids obtained by the Laramie Energy Technology Center were also submitted for storage tests. Following the tests, samples of unaged and aged syncrudes were sent to the Bartlesville Energy Technology Center (BETC) for hydrocarbon, nitrogen and sulfur distribution analysis by gas chromatography, and to Pittsburgh Energy Technology Center for low-resolution mass spectrometry and nuclear magnetic resonance analyses.

^{*}Underscored numbers in parentheses refer to the references listed at the end of this report.

The second phase consisted of investigating techniques that would adequately monitor the degree of deterioration during storage of coal-derived and shale oil syncrudes. Techniques considered for this project included centrifugation, dewaxing prior to filtration, solvent separations, and thermal analyses. Centrifugation and dewaxing prior to filtration did not develop into feasible approaches and were not investigated further.

SYNCRUDE DESCRIPTIONS AND PROPERTIES

Six samples of coal-derived liquids described as two naphthas, a heavy distillate, a middle distillate, a vacuum still overhead product, and an atmospheric still overhead product were evaluated. The naphthas, middle distillate, and the heavy distillate were produced by the solvent-refined coal (SRC-II) process, while the last two materials were described as being produced by the H-coal process from Kentucky No. 11 coal.

Initial evaluation of these materials consisted of measuring specific gravity, kinematic viscosity at 40°C, pour point, distillation, elemental analysis, and existent or soluble gum. The data obtained are shown in Table 1. It should be noted that these materials had strong unpleasant odors, especially those identified as naphthas. All samples had a high concentration of nitrogen- and oxygen-containing compounds. The naphtha identified as PETC ID No. 1785 (AL-9490) had distillation characteristics comparable to a petroleum naphtha, although the soluble gum value of 9.3 mg/100 mL was relatively high. The second naphtha, PETC ID No. 9125 (AL-9493), appeared to be much less stable than the first one, based on distillation and soluble gum results. The distillation left a solid residue, which is not normally encountered, and the soluble gum was very high. The middle distillate, No. 1786 (AL-9492), had distillation results that approach that of a petroleum-derived middle distillate, and the soluble gum was relatively high. The heavy distillate could not be completely distilled by the ASTM D 86 procedure, since the material has many high boiling components which boil above the limit of the thermometer specified for this test (404°C).

The sample described as atmospheric still overhead, LO-1928 (AL-9792) could possibly be classified as a middle distillate. Distillations of this sample and the vacuum still overhead were performed by gas chromatography rather than by ASTM Method D 86.

Eight samples of shale syncrudes were received for storage studies. Three of these were identified as shale crudes retorted by different processes: the Paraho above ground retort, the Occidental modified in-situ, and the Geokinetics in-situ. The other five samples were upgraded crudes hydrotreated under varying conditions. Table 2 identifies and describes these materials. The properties determined for the shale-derived samples are shown in Table 3. The results of hydrotreatment of the crude shale oil are apparent in many of the properties shown in Table 3. The changes in several properties of the Occidental and Paraho crudes are depicted graphically in Figures 1-6. Figure 1 shows decreases in specific gravity and viscosity and an increase in pour point as the hydrotreatment severity of the Occidental crude shale oil is increased. Figure 2 shows a decrease in boiling point distribution as the severity increases. Figure 3 indicates that hydrotreatment increases hydrogen content, as would be expected, and decreases sulfur, nitrogen, and

TABLE 1. PROPERTIES OF COAL SYNCRUDES FROM PETC*

AL No.	9490	9491	9492	9493	9792	9793
Description	<u>Naphtha</u>	<u>Heavy Distillate</u>	<u>Middle Distillate</u>	<u>Naphtha</u>	<u>Atmospheric Still Overhead</u>	<u>Vacuum Still Overhead</u>
PETC ID No.	1785	1787	1786	9125	LO-1928	LO-1930
Property						
Specific Gravity 16°/16°C	0.7753	1.1020	0.9321	0.7870	0.8628	1.0443
Viscosity at 40°C	0.60	155.4	2.44	0.65	1.09	23.96
Pour Point, °C	below -70	-1	-50	below -60	-72	-18
Distillation**, °C						
IBP	53	324	186	50	4	206
10% recovered	83	334	204	85	89	274
20% recovered	92	341	213	96	117	298
50% recovered	110	365	238	120	188	357
90% recovered	143	---	273	157	238	438
End Point	169	---	301	173	318	485
% Recovered	98	---	99.0	97	---	---
% Residue	0.8	---	0.5	solid	---	---
% Loss	1.2	---	0.5	---	---	---
Carbon, wt%	85.00	89.72	85.35	84.19	85.56	89.81
Hydrogen, wt%	13.18	7.00	9.11	12.95	11.53	8.34
Sulfur, wt%	0.3	0.6	0.3	0.6	0.31	0.20
Nitrogen, wt%	0.40	1.23	0.94	0.51	0.64	0.72
Oxygen, wt%	2.14	1.80	4.82	3.18	3.64	1.62
Soluble Gum, mg/100 ml	9.3	20,514	17.9	406	13.0	12,340

* Pittsburgh Energy Technology Center.

** Distillation for first four samples is by ASTM D 86, for other two by D 2887.

TABLE 2. DESCRIPTION OF SHALE CRUDES RECEIVED FROM LETC*

REF-79-112, AL-9704-F: Paraho crude shale produced in the direct fired mode, shipped from Rifle, CO on September 4, 1979.

REF-79-150, AL-9706-F: Occidental crude shale oil produced by their modified in-situ process, received in Laramie on December 4, 1979 from Rifle CO.

REF-80-65, AL-9705-F: Geokinetics crude shale oil produced by their in-situ process and received in Laramie, June 4, 1980.

REF-79-148**, AL-9702-F: Hydrotreated Occidental crude shale oil received in Laramie, March, 1979 but identical to REF-79-150. Treated at 650-675°F, 1500 psig H₂, and contains approximately 0.6 wt% N.

REF-80-30**, AL-9699-F: Hydrotreated Occidental crude shale oil received in Laramie, March, 1979 but identical to REF-79-150. Treated at 775°F, 1500 psig H₂, and contains approximately 0.2 wt% N.

REF-80-33**, AL-9700-F: Hydrotreated Occidental crude shale oil received in Laramie, March, 1979 but identical to REF-79-150. Treated at 750°F, 1500 psig H₂, and contains approximately 0.4 wt% N.

REF-80-60, AL-9703-F: Produced from Paraho crude shale oil REF-79-112, hydrotreated at 650°F, 1500 psig H₂, and contains approximately 1.5 wt% N.

REF-80-68, AL-9701-F: Produced from Paraho crude oil REF-79-112, hydro-treated at 700°F, 1500 psig H₂ and contains approximately 1.0 wt% N.

*LETC - Laramie Energy Technology Center.

** Samples identical to REF-79-150 prior to hydrotreatment.

TABLE 3. PROPERTIES OF SHALE OIL RECEIVED FROM LETC

AL- No.	9706	9702	9700	9699	9704	9703	9701	9705
LETC No. (REF-)	79-150	79-148	80-33	80-30	79-112	80-60	80-68	80-65
Description	Occ.	HT Occ.* at 650°F	HT Occ.* at 750°F	HT Occ.* at 775°F	Paraho	HT Par.** at 650°F	HT Par.** at 700°F	Geokinetics
<u>Property</u>								
Specific Gravity, 16°C/16°C	0.9131	0.8728	0.8625	0.8479	0.9258	0.8955	0.8202	0.8979
Viscosity, cSt, at 40°C	35.63	10.94	7.48	4.69	40.84	20.41	15.52	13.19
Pour Point, °C	-3	2	11	22	28	28	23	23
GC Sim. Dist., °C								
Initial Boiling Point	104	79	64	43	127	31	74	120
1 wt% off	152	135	113	82	173	132	120	162
10 wt% off	240	233	218	192	244	224	214	228
50 wt% off	415	351	336	318	371	394	383	347
90 wt% off	532	478	459	443	500	522	518	482
99 wt% off	565	552	518	513	556	562	562	556
End Point	567	560	523	520	563	565	565	563
Carbon, wt%	84.29	85.60	86.10	86.11	84.88	84.83	85.40	84.51
Hydrogen, wt%	11.28	12.90	13.09	13.34	11.87	12.32	12.58	12.08
Sulfur, wt%	0.65	0.08	0.06	0.02	0.63	0.21	0.14	0.57
Nitrogen, wt%	1.53	0.82	0.55	0.26	2.11	1.64	1.42	1.72
Oxygen, wt%	1.46	0.65	0.40	0.76	1.42	0.88	0.60	1.35

*HT Occ - Hydrotreated Occidental shale oil.

**HT Par - Hydrotreated Paraho shale oil.

***Nitrogen values were determined on samples as received; those shown in Table 2 were reported by LETC as approximate values.

FIGURE 1. EFFECT OF HYDROTREATMENT ON SPECIFIC GRAVITY, VISCOSITY AND POUR POINT OF OCCIDENTAL SHALE CRUDE

FIGURE 2. EFFECT OF HYDROTREATMENT ON GC SIMULATED DISTILLATION OF OCCIDENTAL SHALE CRUDE

FIGURE 3. EFFECT OF HYDROTREATMENT ON ELEMENTAL COMPOSITION OF OCCIDENTAL SIALE CRUDE

oxygen content. An exception is the value for weight percent oxygen of the Occidental crude hydrotreated at 775°F which is higher than anticipated. Unfortunately, this sample was consumed in other analyses and tests; therefore, the value could not be confirmed. There are three possible explanations for this high value: The first is that the reported value is in error; the second is that a very tight emulsion with water was formed during retorting; and the third is the possibility of peroxide formation at the high hydrotreating temperature. The most plausible explanation is that there was an error in reporting the value since aliquots of the material stored at 43°C for 12 and 16 weeks had much lower oxygen values. A reduction in oxygen content of this magnitude did not occur in other stored hydrotreated shale samples. Figure 4 shows a decrease in specific gravity and viscosity, and virtually no change in pour point of the Paraho crude shale oil with increased hydrotreatment severity. Figure 5 shows random changes in boiling point distribution as the hydrotreatment severity increases. Figure 6 depicts an increase in hydrogen content and decrease in heteroatom content as severity of hydrotreatment of the Paraho crude shale oil is increased. Hydrotreated samples of Geokinetics shale crude were not provided; therefore, this type of data is not available for this report. The effects of hydrotreatment on the Geokinetics shale crude would be expected to be similar to those observed for the other shale crudes.

FIGURE 4. EFFECT OF HYDROTREATMENT ON SPECIFIC GRAVITY
VISCOSITY AND POUR POINT OF PARAHO SHALE CRUDE

FIGURE 5. EFFECT OF HYDROTREATMENT ON GC SIMULATED DISTILLATION OF PARAHO SHALE CRUDE

FIGURE 6. EFFECT OF HYDROTREATMENT ON ELEMENTAL COMPOSITION OF PARAHO SHALE CRUDE

STORAGE TEST PROCEDURES AT SOUTHWEST RESEARCH INSTITUTE

The storage tests were conducted at 43°C for periods up to 24 weeks. Sufficient 300 mL aliquots of each test sample were placed in 500 mL borosilicate glass bottles, wrapped in a black plastic film to prevent introduction of light, capped, and placed in storage. Every four weeks, the bottles were removed from hot storage, placed in a cold (2°C to 5°C) room overnight, uncapped for five minutes, capped, and returned to hot storage. This procedure was followed to insure adequate supply of air in each bottle. At periods of 2, 4, 8, 12, 16, and 24 weeks, single or pairs of bottles, depending on original sample size, were removed from storage and measured for precipitate, adherent gum, and soluble gum evaluations. These measurements were for the purpose of following the progress of the storage test and were conducted as follows:

The entire contents of each bottle were filtered through a preweighed Whatman glass-fiber filter 4.25 cm in diameter, 1.5 μ m pore size, supported in a Gooch crucible. This step varied depending on viscosity of liquid. The filtrate was set aside for other analysis. Heptane was used to rinse the bottle, and the rinsings were filtered through the same filter. The weight increase on the filter, after drying for 30 minutes at 110°C, was reported as precipitate. The bottle was then rinsed with two 50 mL portions of triple solvent consisting of equal volumes of toluene, acetone, and methanol (TAM). The rinsings were collected, evaporated to dryness in a preweighed beaker, and the residue reported as adherent gum. The sample filtrate was then analyzed for soluble gum by ASTM method D381. At the end of 24 weeks, or sooner for some samples, the residues and gums were further analyzed for elemental composition when sufficient size samples were available. The carbon and hydrogen analyses were conducted by burning the sample in a closed system and fixing the products of combustion in an absorption train. Nitrogen was determined by chemiluminescence, sulfur by x-ray fluorescence, and oxygen by neutron activation analysis. Also, the filtrate remaining after a portion was used for soluble gum measurement, was analyzed for elemental composition, and samples were forwarded to BETC and PETC for GC, low-resolution mass spectrometry, and NMR analyses.

When sufficient quantities of samples were available and the characteristics of the materials permitted, prefiltered and unfiltered samples were stored at 43°C. This procedure was intended to identify differences in storage characteristics that could be attributed to prefiltration of the samples. Prefiltration of the coal- and shale-derived liquids varied considerably in difficulty, depending on viscosity and pour point characteristics. The coal liquids described as naphtha could be filtered with a Buchner funnel, supporting a coarse filter paper, and water aspiration. The coal, heavy distillates, shale crude oils, and shale-hydrotreated crude oils were filtered using heat and pressure. A stainless steel cylinder with a capacity of approximately 1 gallon was used as a reservoir for the liquid. A filter made of fluorocarbon fibers held in a stainless steel filter holder was used. The entire system was heated with heating tape so that the liquid was

maintained at 38° to 43°C while filtering and pressurized to a range of 69 to 276 kPa.

Filtration of the samples following the prescribed storage periods also varied, depending on viscosity and pour point characteristics of the liquids. The coal-derived naphthas and distillates were filtered with suction as described above.

Prior to the adoption of the pressurized and heated filtering system described above, the heavy distillates from coal-derived liquids, and the shale crude samples after each storage period were analyzed for n-heptane or toluene insolubles. The procedure used was UOP Method 614-68 "Heptane Insoluble Matter in Petroleum Oils Using a Membrane Filter" (8). This procedure permitted easier handling of the viscous and waxy samples.

Kinematic viscosity at 40°C was determined on final storage samples and compared to the viscosity of the unaged sample.

RESULTS OF 43°C STORAGE TESTS

The storage test results for the coal-derived liquid syncrudes received from PETC are shown in Table 4. One naphtha (AL-9490) and the middle and heavy distillates (AL-9492 and AL-9491 respectively) were available in 3-gallon quantities each. The other coal-derived syncrudes were received in 1 gallon or smaller quantities; therefore, these samples had only single bottles containing 300 mL for each storage period. Sample AL-9493, PETC ID No. 9125, filtered sample, had only two aliquots of 300 mL in storage and was terminated after only 4 weeks. After 24 weeks, the unfiltered naphtha, AL-9493, generated considerably more precipitate, adherent, and soluble gum than both the filtered and unfiltered aliquots of the other naphtha sample, AL-9490. After 4 weeks of storage, the gum values for AL-9493 increased dramatically over the original sample. Beyond 4 weeks, the additional increases in total gum levels were comparatively small.

The storage of the unfiltered and filtered middle distillate samples (AL-9492) gave some interesting results.

- Filtration of this sample seemed to reduce the formation of precipitate, adherent, and soluble gums.
- The soluble gum for the unfiltered sample showed a dramatic increase after 2 weeks and again after 8 weeks. At 24 weeks, this value tripled. The precipitate and adherent gum values showed some increase over the 24-week period but not as dramatic as the increase in soluble gum values.
- The filtered middle distillate showed increases in soluble gum after 24 weeks, but much less than the unfiltered material. Precipitate and adherent gum increase during the storage period were slight.

The unfiltered sample AL-9792, atmospheric still overhead, had higher levels of insoluble precipitate, adherent gum, and soluble gum than the filtered sample throughout the test. Sample AL-9793, vacuum still overhead, showed

TABLE 4. STORAGE TESTS OF COAL LIQUIDS AT 43°C - mg/100mL
(Results are average of two samples except where noted)

Code	Description	Initial Existent Gum	2 Weeks			4 Weeks		
			Insoluble Precipitate	Adherent Gum	Soluble Gum	Insoluble Precipitate	Adherent Gum	Soluble Gum
AL-9490	Naphtha - Unfiltered PETC ID# 1785	9.3	0.3	0.6	62.3	0.3	0.5	183
	Filtered	---	0.4	0.5	139	0.3	0.2	164
AL-9493	Naphtha - Unfiltered(1) PETC ID# 9125	406	3.3	35.2	332	1.5	26.1	813
	Filtered(1)	---	3.7	34.9	676	2.6	29.0	1277
AL-9492	Middle Dist. Unfiltered PETC ID# 1786	17.9	0.4	0.1	133	0.3	0.1	123
	Filtered	---	0.2	0.1	58.5	0.1	0.3	78
AL-9491	Heavy Dist. Unfiltered PETC ID# 1707	30,514	---	---	13,794	---	---	14,131
AL-9792	Atm. Overhead - Unfiltered(1) PETC ID# L01928	13	5.4	0.6	142	5.7	0.5	307
	Filtered(1)	---	0.5	0.4	118	0.2	0.4	270
AL-9793	Vac. Overhead - Unfiltered(1) PETC ID# L01930	13,340	9.4	49.0	13,923	13.7	34.5	13,828
	Filtered(1)	---	81.5	21.0	19,673	13.1	75.6	13,232
Code	Description		8 Weeks			12 Weeks		
			Insoluble Precipitate	Adherent Gum	Soluble Gum	Insoluble Precipitate	Adherent Gum	Soluble Gum
AL-9490	Naphtha - Unfiltered PETC ID# 1785	0.4	1.2	186	0.2	0.6	179	
	Filtered	0.2(1)	0.3(1)	177(1)	0.4	0.7	270	
AL-9493	Naphtha - Unfiltered(1) PETC ID# 9125	1.4	72.8	811	1.7	31	968	
AL-9492	Middle Dist. Unfiltered PETC ID# 1786	1.3	0.4	282	3.6	0.7	241	
	Filtered	0.4	0.2	92	0.3	0.4	139	
AL-9792	Atm. Overhead - Unfiltered(1) PETC ID# L01928	6.8	1.0	429	5.4	17.6	618	
	Filtered(1)	0.9	0.8	351	3.6	3.7	546	
AL-9793	Vac. Overhead Unfiltered(1) PETC ID# L01930	17.0	1,875	22,521	11.5	81.4	27,285	
	Filtered(1)	25.0	129	17,046	12.8	110	17,943	
Code	Description		16 Weeks			24 Weeks		
			Insoluble Precipitate	Adherent Gum	Soluble Gum	Insoluble Precipitate	Adherent Gum	Soluble Gum
AL-9490	Naphtha - Unfiltered PETC ID# 1785	---	---	---	0.1	0.5	165	
	Filtered	---	---	---	0.1	0.2	173	
AL-9493	Naphtha - Unfiltered(1) PETC ID# 9125	---	---	---	7.3	38.5	891	
AL-9492	Middle Dist. Unfiltered PETC ID# 1786	---	---	---	1.8	1.1	948	
	Filtered	---	---	---	0.3	0.9	151	
AL-9792	Atm. Overhead Unfiltered(1) PETC ID# L01928	7.1	17.7	969	7.8	14.8	649	
	Filtered(1)	2.8	11.4	9.4	0.4	0.8	389	
AL-9793	Vac. Overhead Unfiltered(1) PETC ID# L01930	43.1	117	12,984	21.4	549	26,770	
	Filtered(1)	23.4	89.4	24,372	161	814	7,126	

(1) Single sample bottle results.

substantial increases in precipitate, adherent, and soluble gums over the 24-week period.

Only unfiltered aliquots of the heavy distillate sample (AL-9491) were placed in storage at the beginning of this program because this highly viscous material could not be filtered readily. Only soluble gum measurements were made at 2 and 4 weeks. These were so high that their significance was in doubt, therefore, further soluble gum measurements were not made. Later, the heated and pressurized filtering system was utilized to filter a portion of the heavy distillate and aliquots were placed in storage at 43°C. Hot toluene insoluble measurements were made on both the unfiltered and filtered samples after 2, 4, 8, 12, and 24 weeks of storage, and the results are shown in Table 5. Initially the UOP procedure for heptane-insoluble matter was attempted, but it was found that the heavy distillate AL-9491 due to its high aromaticity, was not soluble in heptane. The data in Table 5 show no consistent change in toluene-insoluble matter as the storage test progressed for both samples. The unfiltered sample contained more insoluble matter than the filtered one and changed very little with aging.

TABLE 5. STORAGE OF COAL LIQUIDS, 43°C -
TOLUENE-INSOLUBLE MATTER - WT%

Code AL No.	Description	Unaged	2 Weeks	4 Weeks	8 Weeks	12 Weeks	24 Weeks
9491	PETC No. 1787 unfiltered	0.71	0.61	0.66	0.65	0.83	0.72
9491	PETC No. 1787 filtered	0.36	0.44	0.52	0.46	0.54	0.59

Table 6 gives elemental analyses data for coal-derived unaged and aged liquids and for soluble gums produced during the storage period. No significant differences are noted between the analyses of unaged samples and the aged filtered or unfiltered samples except for oxygen content in several samples. A noticeable decrease in oxygen content of the stored naphthas (AL-9490 and AL-9493) and of the atmospheric overhead (AL-9792) was observed. Increases in sulfur measured by x-ray fluorescence, nitrogen by chemiluminescence, and oxygen by neutron activation were noted in the soluble gum residues from the naphthas, middle distillate, and the atmospheric overhead. The heavy distillate and atmospheric overhead showed little change in the elemental composition of the soluble gum produced during storage. Table 7 shows kinematic viscosities of the coal liquids measured at 40°C on unaged and aged samples. The heavy distillate, AL-9491, unfiltered and filtered showed a significant increases in viscosity in 24 weeks of 43°C storage, while the others showed very little change.

Twenty-four week 43°C storage test data for five samples of hydrotreated shale crudes are shown in Table 8. Insoluble precipitate, and adherent gum

TABLE 6. ELEMENTAL ANALYSES OF COAL-DERIVED LIQUIDS AND GUMS

Code No. AL- /Petc No.	wt%	Unaged	Aged-24 Weeks			
			Unfiltered Syncrude	Soluble Gum	Filtered Syncrude	Soluble Gum
9490/1785 (naphtha)	C	85.00	84.59	67.28	85.01	67.96
	H	13.18	12.88	7.49	12.87	7.64
	N	0.40	0.27	4.08	0.29	4.61
	S	0.28	0.25	3.30	0.25	3.18
	O	2.14	1.30	*	1.32	*
9491/1787 (heavy distillate)	C	89.72	89.43	88.63**	89.70	ND
	H	7.00	6.88	6.04	6.95	ND
	N	1.23	1.35	2.80	1.14	ND
	S	0.64	0.57	0.43	0.59	ND
	O	1.80	1.59	2.71	1.59	ND
9492/1786 (middle distillate)	C	85.35	85.54	79.91	85.30	76.76
	H	9.11	9.21	6.50	9.16	6.58
	N	0.94	1.03	3.73	1.06	4.14
	S	0.28	0.26	1.07	0.26	1.92
	O	4.82	4.13	8.81	4.15	*
9493/9125 (naphtha)	C	84.19	84.43	68.11	ND	67.33**
	H	12.95	12.51	6.65	ND	7.37
	N	0.51	0.22	3.60	ND	4.69
	S	0.64	0.78	2.97	ND	6.22
	O	3.18	1.89	14.39	ND	*
9792/LO-1928 (atmospheric overhead)	C	85.56	85.82	70.79	85.78	70.59
	H	11.53	11.25	7.23	10.87	6.87
	N	0.64	0.46	4.09	0.45	2.16
	S	0.31	0.29	7.5	0.30	4.7
	O	3.65	2.14	*	2.42	*
9793/LO-1930 (vacuum overhead)	C	89.81	88.95	89.10	88.74	ND
	H	8.34	8.33	7.36	8.35	ND
	N	0.72	0.64	1.45	0.59	ND
	S	0.20	0.15	0.3	0.14	ND
	O	1.62	1.59	1.74	1.07	ND

ND - Not determined.

* Insufficient gum for analysis.

** Four-week samples.

TABLE 7. KINEMATIC VISCOSITY AT 40°C, cSt

<u>AL-Code No.</u>	<u>Description</u>	<u>Unaged</u>	<u>Aged 24 weeks</u>	<u>Difference</u>
AL-9491	Heavy distillate - unfiltered	160.7	166.7	6.0
AL9491	Heavy distillate - filtered	152.7	168.9	16.2
AL9492	Middle distillate - unfiltered	3.19	3.27	0.08
AL9492	Middle distillate - filtered	3.44	3.46	0.02
AL9793	Vacuum overhead - unfiltered	26.19	26.03	0.16
AL9793	Vacuum overhead filtered	25.53	*	*

* Insufficient sample.

data were obtained for all of these samples; however, the soluble gum data were obtained only through the 4-week samples because the values were so large that they were no longer meaningful. After 24 weeks of storage, insoluble precipitate values were generally higher for the unfiltered samples than for the filtered ones where data are available. Adherent gum values seem to be higher in the filtered samples. Insufficient samples were available initially to store 16- and 24-week aliquots of unfiltered sample AL-9699 (hydrotreated Occidental Shale Oil at 775°F), and 24-week aliquot of sample AL-9702 (hydrotreated Occidental Shale Oil at 650°F). The data are summarized further in Table 9. Based on total gum data shown in Table 9, it appears that filtration improved the stability of the Occidental shale oils hydrotreated at 750°F and 775°F more than the shale oil hydrotreated at 650°F. The unfiltered hydrotreated Occidental shale oils had the highest increase in total gums. Some values such as 13.0 mg/100 mL for the Occ. HT at 650°F, unfiltered, and 73.0 mg/100 mL for Occidental HT at 775°F, unfiltered, 8 weeks appear to be out of line with other values and cannot be explained. Filtration did not affect the stability characteristics of the two hydrotreated Paraho shale oils. In 24 weeks of storage at 43°C, none of these shale oils showed a dramatic increase in total gum content. The data in Table 9 seem to show a slight trend of improved storage stability with severity of hydrotreatment.

The untreated crude shale oils were too viscous for measurements of precipitate, adherent and existent gum, therefore, the heptane insoluble procedure was used to monitor the progress of the storage tests. The results obtained are shown in Table 10 and indicate little deterioration of these

TABLE 8. STORAGE TESTS OF HYDROTREATED SHALE SYNCRUDEs AT 43°C - mg/100 mL

Code AL-	Description	Initial (1), Soluble Gum	2 Weeks			4 Week		
			Insoluble Precipitate	Adherent Gum	Soluble Gum (2)	Insoluble Precipitate	Adherent Gum	Soluble Gum (3)
9702	Occ. HT at 650°F-Unfiltered	13,227	22.8	0.3	3,084	25.0	0.9	8,678
9702	Occ. HT at 650°F-Filtered	13,668	12.4	0.2	9,051	8.5	3.1	7,569
9700	Occ. HT at 750°F-Unfiltered	6,832	21.8	0.7	5,727	34.6	8.4	5,143
9700	Occ. HT at 750°F-Filtered	10,074	1.7	0.6	5,650	4.0	6.4	4,384
9699	Occ. HT at 775°F-Unfiltered	4,953	29.2	1.2	1,286	36.2	4.4	1,613
9699	Occ. HT at 775°F-Filtered	4,548	3.2	0.5	1,637	4.2	1.7	1,865
9703	Par. HT at 650°F-Unfiltered	29,361	26.8	1.2	23,805	24.5	1.7	20,435
9703	Par. HT at 650°F-Filtered	27,806	22.4	1.4	24,403	18.6	3.0	19,896
9701	Par. HT at 700°F-Unfiltered	29,579	23.1	1.5	22,146	27.6	1.4	19,664
9701	Par. HT at 700°F-Filtered	28,891	13.4	2.0	23,933	22.5	3.7	20,937

Code AL-	Description	8 Weeks		12 Weeks		15 Weeks		24 Weeks	
		Insoluble Precipitate	Adherent Gum	Insoluble Precipitate	Adherent Gum	Insoluble Precipitate	Adherent Gum	Insoluble Precipitate	Adherent Gum
9702	Occ. HT at 650°F-Unfiltered	67.3	0.9	12.6	0.4	63.3	0.7	(4)	(4)
9702	Occ. HT at 650°F-Filtered	43.7	0.6	21.1	0.2	25.6	2.1	26.3	1.6
9700	Occ. HT at 750°F-Unfiltered	29.9	3.3	27.5	2.4	42.6	2.4	44.2	1.6
9700	Occ. HT at 750°F-Filtered	8.9	12.3	7.7	4.9	12.4	6.7	12.4	1.9
9699	Occ. HT at 775°F-Unfiltered	52.6	20.4	37.1	5.3	(4)	(4)	(4)	(4)
9699	Occ. HT at 775°F-Filtered	6.6	1.6	3.4	1.2	7.8	1.8	11.6	2.9
9703	Par. HT at 650°F-Unfiltered	35.6	2.2	32.0	2.0	24.4	2.6	38.9	1.5
9703	Par. HT at 650°F-Filtered	45.8	5.8	27.0	3.4	17.5	4.3	23.1	4.8
9701	Par. HT at 700°F-Unfiltered	41.7	1.9	21.2	1.3	25.8	2.0	26.6	1.2
9701	Par. HT at 700°F-Filtered	32.1	3.9	21.6	3.4	22.4	3.8	24.6	5.4

(1) Determined on single 50 mL samples, evaporated for 2 hours.

(2) Determined on duplicate 25 mL samples evaporated for 2 hours.

(3) Determined on unfiltered, 25 mL samples evaporated for 2 hours.

(4) Insufficient sample for tests at this storage period.

TABLE 9. SUMMARY STORAGE TEST OF HYDROTREATED SHALE OILS
Total "Gum" = Insoluble Precipitate plus Adherent Gum (mg/100 mL)

Code AL-	Description	2 Weeks	4 Weeks	8 Weeks	12 Weeks	16 Weeks	24 Weeks
9702	Occ. HT @ 650°F-Unfiltered	23.1	25.9	68.2	13.0	69.0	(1)
	Occ. HT @ 650°F-Filtered	12.6	11.6	44.3	21.3	27.7	27.9
9700	Occ. HT @ 750°F-Unfiltered	22.5	43.0	33.2	29.9	45.0	45.8
	Occ. HT @ 750°F-Filtered	2.3	10.4	21.2	12.6	19.1	14.3
9699	Occ. HT @ 775°F-Unfiltered	30.4	40.6	73.0	42.4	(1)	(1)
	Occ. HT @ 775°F-Filtered	3.7	5.9	8.2	4.6	9.6	14.5
9703	Par. HT @ 650°F-Unfiltered	28.0	26.2	37.8	34.0	27.0	40.4
	Par. HT @ 650°F-Filtered	23.8	21.6	51.6	30.4	21.8	27.9
9701	Par. HT @ 700°F-Unfiltered	24.6	29.0	43.6	22.5	27.8	27.8
	Par. HT @ 700°F-Filtered	15.4	26.2	36.0	25.0	26.2	30.0

(1) Insufficient Sample for tests at this storage period.

samples over 24 weeks at 43°C. Both unfiltered and filtered samples of Paraho shale crude yielded adherent material on the flasks during storage. The weight of this material was determined for each aliquot and is shown in Table 10 as "Flask adherent insolubles." These values were added to the heptane insoluble values to give total insolubles. Differences between unfiltered and filtered samples were insignificant. Elemental analyses for unaged and aged, unfiltered and filtered hydrotreated and crude shale oils are shown in Table 11. The oxygen analysis values show no particular trend, although, an increase in oxygen content may have been expected after 24 weeks of 43°C storage. No appreciable difference between the filtered and unfiltered samples was observed.

Table 12 contains kinematic viscosity data measured at 40°C for unaged and aged shale oils. No startling differences were observed between the unaged and aged samples and no trends were noted between filtered and unfiltered samples.

GC ANALYSIS AT RETC

After the coal and shale liquids were stored at 43°C for 24 weeks, aliquots of the unfiltered and filtered unaged samples, and of the unfiltered and filtered aged samples, were sent to the Bartlesville Energy Technology Center for gas chromatographic analysis to provide hydrocarbon, sulfur and nitrogen distribution data.

EXPERIMENTAL

A Perkin-Elmer Sigma 2 temperature-programmable gas chromatograph equipped with a heated, flash vaporizing injector was used. A three-way divider was installed at the outlet of the packed column to split the effluent into each of three detectors: a flame ionization detector (FID), a flame photometric detector (FPD) selective for sulfur compounds, and a nitrogen/phosphorus detector (NPD) selective for nitrogen compounds. The column was a nonpolar glass tubing coil 1.8 m long, 2 mm I.D., packed with 3% OV-1 on 80-100 mesh Chromosorb G-HP. The injector was held at 300°C, while the detector block was set at 350°C. The oven was programmed to ramp from 70° to 350°C at 12°/min. Each detector was calibrated with compounds of the type to which it was most sensitive (e.g., sulfur compounds were used for the FPD).

RESULTS

Samples of plots of data generated by the gas chromatograph runs are presented in Appendix A. As expected the FID, being sensitive to all hydrocarbons, rarely showed definitive differences between original and aged samples. The quantity of material involved in degradation for even a very unstable syncrude is too small to observe. However, it can be observed that the vacuum filtration technique used to prefilter part of the samples has a tendency to remove some of the lighter material. For example, in Figure A-1 in which the filtered and unfiltered samples from a hydrotreated shale oil (AL-9701) are compared there is a noticeable difference at the front end. This produces the unexpected result of making it seem like there is more

TABLE 10. STABILITY OF SHALE CRUDES, 43°C -
HEPTANE INSOLUBLE MATTER - UOP METHOD 614-68, WT%

Code AL No.	Description	Unaged	2 Weeks	4 Weeks	8 Weeks	12 Weeks	16 Weeks	24 Weeks
9704	Paraho crude unfiltered	---	0.23	0.17	0.13	0.13	0.14	0.19
	Flask adherent insolubles	---	0.60	0.61	0.77	0.63	0.69	0.60
	Total	0.48	0.83	0.78	0.90	0.76	0.83	0.79
9704	Paraho crude filtered	---	0.39	0.19	0.24	0.19	0.14	0.21
	Flask adherent insolubles	---	0.18	0.40	0.37	0.43	0.48	0.49
	Total	0.51	0.57	0.59	0.61	0.62	0.62	0.70
9705	Geokinetics crude unfiltered	0.41	0.42	0.40	0.40	0.38	0.38	0.48
9705	Geokinetics crude filtered	0.41	0.42	0.47	0.40	0.43	0.43	0.50
9706	Occidental crude unfiltered	0.37	0.52	0.40	0.47	0.47	0.45	0.56
9706	Occidental crude filtered	0.41	0.50	0.42	0.47	0.47	0.47	0.52

TABLE 11. ELEMENTAL ANALYSES OF SHALE OIL SYNCRUDES

Code No. AL	Description	wt%	Unaged	Aged-24 Weeks at 43°C	
				Unfiltered	Filtered
9706	Occidental	C	84.29	85.12	84.92
		H	11.28	12.02	11.94
		N	1.53	1.43	1.43
		S	0.63	0.63	0.63
		O	1.46	1.19	1.75
9702	HT Occidental at 650°F	C	85.60	85.75(1)	85.52
		H	12.90	12.99	12.97
		N	0.82	0.80	0.85
		S	0.08	0.06	0.07
		O	0.65	0.27	0.32
9700	HT Occidental at 750°F	C	86.10	86.01	86.12
		H	13.09	13.10	13.24
		N	0.55	0.54	0.57
		S	0.06	0.06	0.04
		O	0.40	0.29	0.20
9699	HT Occidental at 750°F	C	86.11	85.88(2)	86.21(1)
		H	13.34	13.22	13.35
		N	0.26	0.25	0.25
		S	0.012	0.002	0.002
		O	0.76(3)	0.057	0.067
9704	Paraho	C	84.88	84.66	84.58
		H	11.87	11.60	11.48
		N	2.11	2.33	2.01
		S	0.63	0.67	0.64
		O	1.42	1.47	1.68
9703	HT Paraho at 650°F	C	84.83	84.57	85.12
		H	12.32	12.24	12.28
		N	1.64	1.99	1.93
		S	0.21	0.27	0.22
		O	0.88	0.83	0.62
9701	HT Paraho at 700°F	C	85.40	85.47	85.38
		H	12.58	12.53	12.50
		N	1.42	1.62	1.57
		S	0.14	0.16	0.14
		O	0.60	0.48	0.38
9705	Geokinetics	C	84.51	84.46	84.55
		H	12.08	12.05	12.05
		N	1.74	1.78	1.84
		S	0.55	0.55	0.58
		O	1.35	1.44	1.27

(1) Aged 16 weeks; (2) Aged 12 weeks; and (3) Suspect value.

TABLE 12. KINEMATIC VISCOSITIES AT 40°C, cSt

AL-Code No.	Description	Unaged	Aged 24 weeks*	Difference Unaged-Aged
AL-9706	Occidental Crude unfiltered	35.63	35.11	+0.52
AL-9706	Occidental Crude filtered	35.20	34.51	+0.69
AL-9702	Occidental HT at 650°F unfiltered	11.59	10.99 (16 wks)	+0.6
AL-9702	Occidental HT at 650°F filtered	11.25	11.33	-0.08
AL-9700	Occidental HT at 750°F unfiltered	7.99	7.71	+0.28
AL-9700	Occidental HT at 750°F filtered	7.95	7.89	+0.06
AL-9699	Occidental HT at 775°F unfiltered	4.80	4.92 (12 wks)	-0.12
AL-9699	Occidental HT at 775°F filtered	5.01	4.92 (16 wks)	+0.09
AL-9704	Paraho Crude unfiltered	40.84	41.25	-0.61
AL-9704	Paraho Crude filtered	42.06	42.15	-0.09
AL-9703	Paraho HT at 650°F unfiltered	22.87	23.78	-0.91
AL-9703	Paraho HT at 650°F filtered	22.13	22.60	-0.47
AL-9701	Paraho HT at 700°F unfiltered	17.05	16.67	+0.38
AL-9701	Paraho HT at 700°F filtered	16.79	16.56	+0.23
AL-9705	Geokinetics Crude unfiltered	13.91	14.17	-0.26
AL-9705	Geokinetics Crude filtered	14.01	13.28	+0.73

* Except where noted

heavy material (B.P. above 900°C) in the filtered sample than in the unfiltered. As shown in Table 9, it is found that total gum value for the filtered sample shows considerable difference initially, but, as corroborated by the gas chromatograph, after 24 weeks of accelerated aging, the two samples are essentially identical. This theory is further confirmed by the absence of this difference in viscous samples filtered using positive pressure (e.g., AL-9706, Figure A-2).

A second observation made from the gas chromatography results was that the nitrogen and sulfur often seem to be present in fewer, more distinct compound types, as implied by the sharp peaks in the chromatographs. This was not confirmed by mass spectral analysis, so there must be a large number of compounds present in each of these fairly narrow regions.

The differences in boiling point distribution of the various compound types are of interest, however. For example, in shale crude AL-9704, the hydrocarbons peak around 850°F, then fall off at higher temperatures (Figure A-3). Yet the nitrogen compounds are concentrated in the 800+°F fraction (Figure A-4), while the sulfur compounds are almost uniformly distributed between 275° and 1000°F (Figure A-5). These sulfur plots imply a rather significant difference between filtered and unfiltered samples, which seems to be reflected in the adherent insolubles data (Table 10). Even after 24 weeks of aging at 43°F, the filtered sample shows less adherent gum.

The unusual temperature shift of middle- to higher-boiling components of sample AL-9704 displayed by the sulfur compounds without affecting the lowest or highest boiling compounds is difficult to explain. In fact, the sulfur distribution from a Geokinetics shale crude (AL-9705) shows the more predictable loss of lower and middle distillates during the aging process as dimers, trimers, and other reaction products are formed (Figure A-6).

If one compares boiling point distributions for samples differing only by degree of hydrotreating (AL-9704, AL-9701, and AL-9703; or AL-9706, AL-9702, AL-9700, and AL-9699) one finds that the initial treatment produces a significant shift towards lighter components, while more severe conditions do not affect the overall distribution pattern for either nitrogen or hydrocarbons proportionately more (Figures A-3, A-1, A-7, A-2, A-8, A-9 and A-10, respectively). Thus, once the more reactive species have been hydrogenated, further upgrading seems to occur fairly uniformly across the boiling range.

One of the hydrotreated shale liquids (AL-9702) yielded almost perfectly identical nitrogen distributions before and after aging for both filtered and unfiltered samples (Figure A-11), yet the storage test results show the insolubles precipitate and adherent gum levels rather high with a factor of 2.5 difference between filtered and unfiltered results (27.6 vs. 60.3 at 16 weeks) (Table 8). This would indicate that gum formation involves all nitrogen species present or that the G.C. technique was not sensitive enough. While seeming to contradict the established theory that some species are more reactive than others, considerable evidence for interactions in which reactive species stimulate the reactivity of normally stable species is beginning to be published (6). This uniform decrease in nitrogen compounds would support that theory, especially since 69 mg/100 mL of insolubles were formed in the unfiltered sample (Table 9), yet no change is seen in the nitrogen distribution curve.

It is obvious from this mass of data that simulated distillation is not a sensitive test for the broad range of samples investigated here. Samples that produced large quantities of deposits gave identical chromatograms before and after aging. Where significant changes were found, causes were sometimes difficult to establish. Thus, while simulated distillation is important for processing and utilization considerations, it was not found here to be a reliable tool for stability predictions.

ANALYSIS OF AGED COAL AND SHALE LIQUIDS VIA ^1H NMR AND LOW-RESOLUTION MASS SPECTROMETRY AT PETC

The coal and shale liquids studied in this work were analyzed by both ^1H NMR and Low Resolution Mass Spectrometry (LRMS) before and after aging. The goal of this investigation was to determine the utility of these techniques for monitoring the disappearance of reactive components during the aging process. The samples used were readily amenable to study by these techniques since they were sufficiently volatile to allow direct syringe injection into the mass spectrometer's inlet system and were readily soluble in the solvent (CDCl_3) used for ^1H NMR. The NMR spectra were obtained on a Varian HA-100 spectrometer. The mass spectra were obtained in the m/e range 15-150 using an ionizing voltage of 70 ev on a CEC 103 mass spectrometer.

Both of these techniques have been shown to be very useful for screening purposes and give good overall views of the nature of the sample. The LRMS data yield an accurate picture of the molecular weight distribution in the sample and will detect significant changes in this distribution. The major difficulty with this technique is that in order to observe the saturate components of the sample, the ionizing voltage used was 70 ev. This ionizing voltage results in extensive fragmentation, so that any m/e ion signal consists of contributions from a wide variety of source molecules. Quantitative measurement of small changes in concentration of specific components is virtually impossible. If the ionizing voltage is reduced to 10 ev, where little fragmentation occurs, the saturate fraction of the sample is not ionized and thus is not observed. Under these low voltage conditions, only the parent ions of the heteroatomic and aromatic species are observed. Spectra obtained under low-voltage conditions have been used to monitor changes in the relative concentrations of polar and aromatic species which occur on aging; however the magnitude of the changes occurring under the conditions of this work is too small to interpret unambiguously.

The ^1H NMR spectra of samples used in this work give a simple and accurate picture of the distribution of proton types present in the sample. The complexity of the sample together with the similarity in position of resonances due to protons of the same type on different molecules (for example: $-\text{CH}_2$, $-\text{CH}_3$ or OH) makes it very difficult to assign unambiguously a resonance to a particular compound or class of compounds. The technique has proven useful in following relatively large changes in sample composition, but in most cases it has insufficient resolution to follow changes as small as those observed in this work. In several of the aged samples, significant changes in proton distribution were observed. These changes were in the aliphatic region of the ^1H distribution and can be adequately explained by small losses of light hydrocarbons on handling. Experiments in other laboratories, involving much more highly accelerated aging, have found the ^1H NMR

technique to be useful in characterizing the reactive components (8), but in this work, where only small amounts of material are reactively removed from solution, the technique is not sufficiently sensitive. ¹H NMR spectra for sample AL-9792 (atmospheric overhead coal syncrude) unfiltered, before and after 24 weeks of aging are shown in Appendix B.

Analysis of data obtained via these two analytical methods indicates that both techniques are useful for broad characterization of coal distillates, but they have insufficient resolution to measure reliably the small changes in composition occurring under the conditions used in this aging study. If, on aging, a sample reacts to form 0.1 percent gum (100 mg/100 mL) the sample which remains after gum removal is 99.9 percent identical to the original. It is difficult to detect quantitatively such small changes, except by using very high resolution techniques, either chromatographic or spectroscopic.

The alternative approach is to characterize the gum, which is almost totally composed of material which reacted. Although this material is much more difficult to characterize, the information concerning the chemistry of precipitate formation is more highly "concentrated" in this fraction.

STORAGE CHARACTERISTICS OF EXPERIMENTAL REFEREE BROADENED-SPECIFICATION FUELS

Three samples of experimental referee broadened-specification (ERBS) fuels were placed in dark storage at 43°C. The basic difference among these three petroleum-derived fuels was the hydrogen content. Thus the fuels were identified as ERBS 3B 12.8, containing a nominal 12.8 wt% H; ERBS 3B 12.3, containing a nominal 12.3 wt% H, and ERBS 3B 11.8, with a nominal 11.8 wt% H. Additional analyses for these fuels are shown in Table 13. The variation in hydrogen content was achieved by blending a base kerosene fuel with xylene bottoms, a highly aromatic refinery fraction. As can be seen in Table 13, many other properties are affected by varying the hydrogen content in this manner.

Table 14 contains the storage stability for the three fuels and indicates that changes observed in precipitate, insoluble, and soluble gum over the 24-week period were insignificant. These experimental fuels appear to be quite stable under these conditions.

To determine if changes had occurred in the fuels during storage, gas chromatography boiling point distributions were determined on the original and aged samples. Chromatograms for ERBS 3B 12.8 fuel, before and after 43°C storage are shown in Figure 7. A loss in light-end components is quite apparent. Chromatograms for ERBS 3B 12.3 in Figure 8 show the difference in front-end composition from the 12.8 ERBS fuel and also show the loss of lighter components. The chromatograms in Figure 9 show the difference in composition between ERBS 3B 11.8, and the other two fuels and also shows the loss in lighter components.

The change in front-end composition for all three samples has been attributed to the fact that, as the samples were removed from storage, they were filtered with vacuum to measure the precipitate remaining on the filter membrane. The application of vacuum apparently removed some light-ends from the samples. The change in composition was observed when these same samples

TABLE 13. ANALYSES OF ERBS FUELS

Code No.	AL-10669	AL-10667	AL-10668
Description	<u>ERBS 3B 12.8</u>	<u>ERBS 3B 12.3</u>	<u>ERBS 3B 11.8</u>
<u>Property</u>			
Aromatics, vol% (FIA)	31	41	50
Olefins, vol% (FIA)	1	1	1
Aromatics, wt% (HPLC)	32.4	45.0	55.4
Saturates, wt% (HPLC)	67.6	55.0	46.6
Aromatic Types (UV)			
Mono, wt% ring C	9.9	15.6	20.5
Di, wt% ring C	10.8	11.8	13.2
Tri, wt% ring C	0.5	0.5	0.6
Carbon, wt%	86.93	87.43	87.78
Hydrogen, wt%	12.93	12.39	11.88
Sulfur, wt%	0.04	0.05	0.05
Nitrogen, ppm	66	78	86
Distillation, °C			
D 86 (D 2887)			
Initial Boiling Point	181(131)	161(114)	150(113)
10 vol% recovered	201(188)	184(168)	172(143)
20 vol% recovered	208(202)	198(194)	186(171)
50 vol% recovered	228(235)	229(234)	229(234)
90 vol% recovered	288(305)	289(307)	294(309)
Final Boiling Point	330(370)	332(371)	335(372)
% Residue	1	1	1
% Loss	0	0	0
Gravity, °API	36.8	34.6	32.6
Specific Gravity,			
15.6/15.6°C	0.8408	0.8519	0.8623
Freezing Point, °C	-21	-21	-22
Kinematic Viscosity at			
-20°C, cSt	7.88	6.67	5.85
Cetane Number	40.8	39.5	31.0
Cetane Index	39.6	36.4	33.2
Particulate, mg/L	2.8	1.5	1.0

TABLE 14. STORAGE OF ERBS FUELS AT 43°C

Fuel	mg/100 mL				
	Initial Soluble Gum	Precipitate	Soluble Gum*	Insoluble Gum	Total Gum
4 Weeks					
AL-10669					
ERBS 3B 12.8	1.0	0.2	1.8	0.0	2.0
AL-10667					
ERBS 3B 12.3	0.9	0.1	3.2	0.6	3.9
AL-10668					
ERBS 3B 11.8	1.5	0.1	2.4	0.2	3.1
8 Weeks					
AL-10669					
ERBS 3B 12.8		0.1	1.0	0.0	1.1
AL-10667					
ERBS 3B 12.3		0.1	1.8	0.4	2.3
AL-10668					
ERBS 3B 11.8		0.1	1.1	0.3	1.5
12 Weeks					
AL-10669					
ERBS 3B 12.8		0.1	2.8	0.5	3.4
AL-10667					
ERBS 3B 12.3		0.2	3.9	0.2	4.3
AL-10668					
ERBS 3B 11.8		0.1	3.8	0.3	4.3
16 Weeks					
AL-10669					
ERBS 3B 12.8		0.2	2.2	0.0	2.4
AL-10667					
ERBS 3B 12.3		0.3	2.2	0.3	2.8
AL-10668					
ERBS 3B 11.8		0.2	2.4	0.3	2.9
24 Weeks					
AL-10669					
ERBS 3B 12.8		0.1	1.7	0.3	2.1
AL-10667					
ERBS 3B 12.3		0.1	1.9	0.3	2.3
AL-10668					
ERBS 3B 11.8		0.1	2.8	0.3	3.2

*Existent gum by steam jet evaporation

FIGURE 7. ERBS 3B 12.8, AGED AND UNAGED

FIGURE 8. ERBS 3B 12.3, AGED AND UNAGED

ERBS 3B 11.8 UNAGED

ERBS 3B 11.8 AGED

FIGURE 9. ERBS 3B 11.8, AGED AND UNAGED

were analyzed by differential scanning calorimetry, as shown later in this report. To confirm that light-ends were being removed by vacuum filtration, an unaged sample of ERBS 3B 12.8 was vacuum filtered and analyzed by DSC, giving data very similar to the unfiltered sample. This experiment is reported in more detail later in this report.

SOLVENT SEPARATIONS

A procedure for measuring n-heptane insolubles in a heavy petroleum fraction described earlier(9) was used to compare the insolubles in unaged shale crude oils with aged samples. The same procedure was followed using a variety of solvents, i.e., toluene, cyclohexane, methyl-iso-butyl ketone (MIBK) and decane. The data obtained for the Paraho shale crude (AL-9704), Geokinetics shale crude (AL-9705), and Occidental shale crude (AL-9706), unaged and stored 24 weeks, unfiltered and filtered, are presented in Table 15. Generalizations about these data can be made. The aging procedure caused no significant change in insoluble levels regardless of solvent used. N-heptane and n-decane produced about the same level of insolubles in each crude sample analyzed. The Paraho crude generated insolubles that adhered to the flask using both n-heptane and n-decane. These insolubles were measured by weighing the flask with the adherent insolubles after drying and after they were removed with an aromatic solvent. The difference in weights represented the adherent insolubles which were added to the filterable insolubles to obtain a total as shown in Table 15. Toluene and MIBK produced very low levels of insolubles, and cyclohexane gave insolubles levels considerably lower than the paraffinic solvents. In most cases, the filtered samples had slightly lower insolubles than the unfiltered samples, and aged samples had more insolubles than unaged samples. The data are presented graphically for the individual solvents in Figure 10 for n-heptane, Figure 11 for toluene, Figure 12 for cyclohexane, Figure 13 for MIBK and Figure 14 for n-decane.

The experiments conducted with the various solvents show that the paraffinic solvents n-heptane and n-decane produced the highest level of separation, and it appears that the materials separated were principally asphaltenes. In materials less stable than the shale syncrudes this solvent treatment may produce higher levels of insolubles after the aging process.

AGING OF OCCIDENTAL CRUDE AND REFINERY INTERMEDIATES AT 80°C

A sample of Occidental shale crude oil and samples of refinery intermediate materials generated by the Extractacacking® process to produce JP-4 and JP-8 at Ashland Oil Company under contract with Wright-Patterson AFB,(10) were obtained for stability evaluations. These samples were aged at 80°C for 3, 7, and 14 days to generate aged samples and gum residues from these samples in a shorter period than 24 weeks. A schematic diagram of the Extractacacking® process is shown in Figure 15, and the locations where the intermediate samples were taken are indicated. The properties of the original Occidental crude, a crude hydrotreated prior to processing (supplied by Laramie Energy Technology Center), and the four intermediate samples are shown in Table 16.

TABLE 15. SOLVENT SEPARATIONS

	Paraho Crude 9704 - Unaged				Paraho Crude 9704 - Aged 24 Wks*				Geokinetics Crude 9705 - Unaged				Geokinetics Crude 9705 - Aged 24 Wks*				Occidental Crude 9706 - Unaged				Occidental Crude 9706 - Aged 24 Wks*			
	Unfiltered		Filtered		Unfiltered		Filtered		Unfiltered		Filtered		Unfiltered		Filtered		Unfiltered		Filtered		Filtered		Unfiltered	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
n-Heptane																								
Filterable insols	0.17	0.14	0.35	0.31	0.18	0.17	0.34	0.22	0.55	0.56	0.51	0.51	0.49	0.51	0.61	0.60	0.52	0.54	0.57	0.55	0.71	0.67	0.58	0.55
Adherent insols	0.65	0.71	0.43	0.44	0.74	0.73	0.47	0.61	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	0.82	0.85	0.78	0.76	0.92	0.90	0.81	0.83	0.55	0.56	0.51	0.51	0.49	0.51	0.61	0.60	0.52	0.54	0.57	0.55	0.71	0.67	0.58	0.55
Average	0.84		0.79		0.91		0.82		0.56		0.51		0.50		0.61		0.53		0.56		0.69		0.57	
Toluene																								
Filterable Insols	0.05	0.04	0.02	0.01	0.03	0.03	0.01	0.01	0.07	0.07	0.07	0.08	0.07	0.07	0.08	0.09	0.01	0	0.01	0	0.01	0	0.02	0.02
Adherent Insols	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	0.05	0.04	0.02	0.01	0.03	0.03	0.01	0.01	0.07	0.07	0.07	0.08	0.07	0.07	0.08	0.09	0.01	0	0.01	0	0.01	0	0.02	0.02
Average	0.05		0.02		0.03		0.01		0.07		0.08		0.07		0.09		0.01		0.01		0.01		0.02	
Cyclohexane																								
Filterable Insols	0.30	0.24	0.19	0.18	0.21	0.17	0.25	0.25	0.19	0.24	0.16	0.16	0.20	0.18	0.23	0.21	0.08	0.10	0.05	0.05	0.07	0.04	0.08	0.06
Adherent Insols	0.04	0.07	0	0	0.09	0.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	0.34	0.31	0.19	0.18	0.30	0.29	0.25	0.25	0.19	0.24	0.16	0.16	0.20	0.18	0.23	0.21	0.08	0.10	0.05	0.05	0.07	0.04	0.08	0.06
Average	0.33		0.19		0.30		0.25		0.22		0.16		0.19		0.22		0.09		0.05		0.06		0.07	
MIBK**																								
Filterable Insols	0.07	0.06	0.01	0.01	0.07	0.06	0.01	0.01	0.11	0.11	0.08	0.09	0.13	0.11	0.08	0.09	0.09	0.09	0.02	0.03	0.15	0.15	0.03	0.04
Adherent Insols	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	0.07	0.06	0.01	0.01	0.07	0.06	0.01	0.01	0.11	0.11	0.08	0.09	0.13	0.11	0.08	0.09	0.09	0.09	0.02	0.03	0.15	0.15	0.03	0.04
Average	0.07		0.01		0.07		0.01		0.11		0.09		0.12		0.09		0.09		0.03		0.15		0.04	
n-Decane																								
Filterable Insols	0.45	0.24	0.78	0.71	1.02	1.02	0.74	0.55	0.80	0.73	0.67	0.68	0.33	0.27	0.80	0.80	0.52	0.54	0.62	0.66	0.70	0.70	0.70	0.69
Adherent Insols	0.35	0.53	0	0.02	0	0	0.01	0.08	0	0	0	0	0.46	0.53	0	0	0	0	0	0	0	0	0	0
Total	0.80	0.37	0.78	0.73	1.02	1.02	0.75	0.73	0.80	0.73	0.67	0.68	0.79	0.80	0.80	0.80	0.52	0.54	0.62	0.66	0.70	0.70	0.70	0.69
Average	0.84		0.75		1.02		0.74		0.77		0.68		0.80		0.80		0.53		0.64		0.70		0.70	

*Aged at 43°C.

**Methyl isobutyl ketone - Teflon® filter.

FIGURE 10. N-HEPTANE-INSOLUBLES

FIGURE 11. TOLUENE-INSOLUBLES

FIGURE 12. CYCLOHEXANE-INSOLUBLES

FIGURE 13. MIBK-INSOLUBLES

FIGURE 14. DECANE-INSOLUBLES

FIGURE 15. THE EXTRACTACRACKING[®] PROCESS

TABLE 16. PROPERTIES OF CRUDE AND INTERMEDIATE FRACTIONS TAKEN DURING REFINING OF OCCIDENTAL SHALE OIL

Sample Code	AL-11561	AL-11692	AL-11502	AL-11503	AL-11504	AL-11505
Description	Oxy Shale Crude	HT Oxy Shale Crude	Raffinate	III Tower Overhead	CSHT,* Recycle	JP-8 GCHT,** Off-Spec
Property						
Gravity, °API	22.8	26.2	36.9	37.4	26.4	40.0
Specific Gravity, 16/16°C	0.9170	0.8973	0.8403	0.8378	0.8961	0.8251
Distillation D 86, °C (D 2887, °C)						
IBP	(117)***	(160)	121(89)	83(60)	188(52)	142(101)
10% Recovered	(256)	(270)	182(172)	123(117)	252(257)	187(175)
20% Recovered	(294)	(302)	209(211)	141(145)	280(297)	207(208)
50% Recovered	(388)	(384)	251(267)	201(218)	353(390)	244(260)
90% Recovered	(520)	(303)	283(315)	292(323)	404(527)	283(311)
FBP	(626)	(603)	307(429.6)	307(407)	(621)****	308(407)
Residue, vol%	*****	-	0.5	1.0	*****	1.0
Loss, vol%	0	0	0	0	-	0
FIA, vol%						
Aromatics	-	-	-	-	-	28.4
Saturates	-	-	-	-	-	71.6
Olefins	-	-	-	-	-	0
HPLC, vol%						
Aromatics	-	-	49.6	83.2	-	33.1
Saturates	-	-	50.4	16.8	-	66.9
UV aromatic carbon						
wt% mono	9.06	9.14	12.7	18.1	9.7	12.5
wt% di	5.80	5.12	6.0	9.5	4.9	1.7
wt% tri	1.03	0.65	0.21	0.41	0.64	0.01
Viscosity @ 40°C, cSt	33.28	29.09	1.98	1.17	20.10	1.89
Flash Point D 93, °C	60	135	35	6	60	42
Pour Point, °C	-2	14	-30	-30	-7	-29
Steam jet gum, mg/100 mL	-	-	107.2	53.0	14,231	27.7
Particulates D 2276, mg/L	-	-	1.2	2.2	-	71.0
XRF analysis,						
Fe, ppm	95	12	16	17	16	10
Cu, ppm	<10	<10	16	<10	14	15
Cr, ppm	<15	24	-	-	-	-
Pb, ppm	50	<60	-	-	-	-
As, ppm	13.4	<1	-	-	-	-
Elemental Analysis,						
Carbon, wt%	84.17	86.05	86.56	87.19	85.57	86.60
Hydrogen, wt%	11.89	12.49	12.90	11.92	12.43	13.64
Nitrogen, wt%	1.16	0.96	0.318	0.528	0.921	0.028
Oxygen, wt%	1.47	0.35	0.24	0.10	0.45	0.06
Sulfur, wt%	0.49	0.08	0.04	0.03	0.20	<0.01

* CSHT-Crude shale hydrotreater

** GCHT-Guard case hydrotreater

*** Numbers in parentheses are boiling point distribution temperatures measured gas chromatography ASTM D2887.

**** FBP past thermometer range

***** Not determined

***** Residue became semi-solid.

Three bottles of each sample, containing 100 mL each, were stored for the different periods at 80°C. The aliquots in the three bottles stored for three days were filtered to measure filterable residue; the bottles were washed with triple solvent TAM (equal portions of toluene, acetone, and methanol), to remove adherent insolubles which were then weighed after evaporation of the triple solvent. This is standard procedure for working up the aged samples in this test.

The aliquots from the 7- and 14-day aged samples were worked up differently. Bottle No. 1 was treated by the standard procedure as described above. Bottle No. 2 was diluted 1 to 1 with heptane, heated in a hot water bath held at 80°C, and filtered with slight pressure if needed. The heptane-insoluble filterable residue and adherent insolubles were measured by weight. Bottle No. 3 was blanketed with nitrogen and temporarily put aside.

The standard filterable residue and adherent insolubles for the six shale oil samples aged at 80°C for 3, 7, and 14 days are shown in Table 17. Table 18 has the data for heptane-diluted samples unaged and aged for 7 and 14 days. The total insolubles determined by the standard procedure after 3, 7, and 14 days are presented graphically in Figure 16, and those obtained by diluting the samples with heptane are shown in Figure 17.

The data obtained by the standard technique and by heptane dilution indicate that the tower overhead and raffinate are much less stable than the other materials. The whole hydrotreated shale crude, and CSHT recycle and the JP-8 off-spec GCHT, all of which were hydrotreated during the process, were relatively stable. Hydrotreatment evidently imparts storage stability to these process streams. The Occidental crude shale oil appears to have an induction period somewhere between 7 and 14 days, based on the heptane dilution data.

The heptane-dilution procedure increases the level of deposits observed, but shows no significant change in the ranking of the samples. The dilution procedure does facilitate the filtration of highly viscous samples such as the Occidental crude and permits determination of insoluble residue.

Samples of unaged and aged Occidental crude and process intermediates were submitted to thermal gravimetric analyses. The procedure and results are discussed in the next section of this report.

THERMAL ANALYSES

The purpose of the thermoanalytical experiments reported here was to determine if differential scanning calorimetry (DSC) and/or thermogravimetric analysis (TGA) could be applied to a quantitative evaluation of gums formed during degradation of various coal and shale derived liquids. Shale crudes, coal liquids, experimental fuels, various liquids from selected points in a process stream, and "blind" samples from National Bureau of Standards (NBS) were included in the protocol. The latter samples were also analyzed using a procedure developed at NBS. Comparison of data to standard laboratory results was made.

TABLE 17. AGING TEST 80°C STANDARD WORK-UP

Code AL-	Description	3 Days			7 Days			14 Days		
		Filterable Residue mg/100 mL	Adherent Insolubles mg/100 mL	Total Insolubles mg/100 mL	Filterable Residue mg/100 mL	Adherent Insolubles mg/100 mL	Total Insolubles mg/100 mL	Filterable Residue mg/100 mL	Adherent Insolubles mg/100 mL	Total Insolubles mg/100 mL
11561	Oxy crude shale oil	11.3	0.2	11.5	10.7	0.9	11.6	16.5	1.7	18.2
11692	Whole hydrotreated Oxy crude	0.5	0.4	0.9	0.2	0.4	0.6	0.1	0.2	0.3
11504	CSHT recycle	0.03	0.2	0.2	0	0.5	0.5	0.3	0.1	0.4
11503	Tower overhead	35.8	10.3	46.2	58	140	198	36.2	358	394
11502	Raffinate	16.1	7.8	23.6	65	148	213	14.5	563	578
11505	JP-8 off-spec GCHT	1.1	1.8	2.9	2.0	7.1	9.1	0.5	17.5	18.0

TABLE 18. AGING TEST 80°C HOT HEPTANE DILUTION

Code AL-	Description	Unaged Filterable Residue mg/100 mL	7 Days			14 Days		
			Filterable Residue mg/100 mL	Adherent Insolubles mg/100 mL	Total Insolubles mg/100 mL	Filterable Residue mg/100 mL	Adherent Insolubles mg/100 mL	Total Insolubles mg/100 mL
11561	Oxy crude shale oil	29.6	7.6	1.3	8.9	114	1.5	115
11692	Whole hydrotreated Oxy crude	1.6	0.5	0.2	0.7	0	0	0
11504	CSHT recycle	0.4	0	0.5	0.5	0	0.2	0.2
11503	Tower overhead	12.6	142	107	249	126	320	446
11502	Raffinate	14.5	150	83	233	91	583	674
11505	JP-8 off-spec GCHT	8.6	2.9	8.0	10.9	4.9	13.0	17.9

FIGURE 16. 80°C STABILITY TEST FOR CRUDE SHALE OIL AND REFINING INTERMEDIATES

FIGURE 17. HEPTANE-INSOLUBLES IN ORIGINAL SAMPLES AND AFTER 80°C AGING

Experimental Procedure

General conditions for all experiments are set forth here. Variations or specific details will be noted as necessary in the sections describing each data set.

A duPont model 990 DSC and model 951 TGA were employed for generation of data. The atmosphere around the sample could be varied using air, oxygen, nitrogen or argon. In later experiments a high pressure (up to 500 psig) cell was used on the DSC. Normally the gas flow rate was 40-60 cc/min and the rate of temperature increase was 20°C/min. The maximum temperature to which the sample was scanned was 600°C (DSC) and 800°C (TGA). Sample size ranged from 3 mg to 20 mg while the sample containers were either aluminum (DSC) or platinum (TGA).

Results

A. Crude Shale Oil

The materials tested in this phase of the program are shown in Table 19.

TABLE 19. EXPERIMENTAL LIQUIDS		
Origin	Code No.	Condition
Paraho crude shale oil	AL-9704	unaged, unfiltered , filtered aged 24 wks (43°C), unfiltered , filtered
Geokinetics crude shale oil	AL-9705	unaged, unfiltered aged 24 wks (43°C), filtered
Occidental crude shale oil	AL-9706	unaged, unfiltered

A summary of the data obtained by TGA (averaged where applicable) for the three crude shale oils in air and in nitrogen is given in Table 20. The column which indicates % residue is applicable to N₂ atmospheres only since all the organic materials oxidized under air. The weight loss is designated in three regions (1,2,3) because the actual sample temperature varies from the thermocouple reading to a certain extent. A typical thermogram (TGA) is shown in Figure 18. The transition temperatures recorded for peak positions 1, 2 and 3 were generally in the range of 300°C, 450°C and 550°C respectively, indicating volatile fuel components and two peaks, where gums are indicated. Variations in these temperatures have been noted between different samples which are inherent in the procedure due to the variability in positioning of the sample thermocouple.

It is obvious that the residue is relatively non-volatile in nature due to the much lower (or non-existent) weight loss under an inert atmosphere versus air. In air, oxidation takes place causing the sample to react completely with total weight loss.

TABLE 20. WEIGHT LOSS (%) UPON HEATING (TGA)

Sample	Condition	Weight Loss (%) (air)			Weight Loss (%) (N ₂)			Residue (N ₂)
		1	2	3	1	2	3	
Paraho crude shale oil	aged*, filtered	72.7	10.7	16.6	96.6	-	-	3.4
	, unfiltered	73.6	9.2	14.9	91.3	2.8	2.9	2.8
	unaged, filtered	74.0	9.6	16.4	91.6	-	-	0.2
	unaged, unfiltered	76.0	7.9	15.9	96.9	-	-	3.1
Geokinetics crude shale oil	unaged, unfiltered	84.6	5.0	10.5	98.0	-	-	2.0
	aged*, filtered	86.6	5.8	7.6	93.7	3.0	2.9	0.43
Occidental crude shale oil	unaged, unfiltered	81.5	6.3	12.2	99.6	7.6	-	2.8

*Samples aged 24 weeks at 43°C.

FIGURE 18. THERMOGRAM SHOWING MAJOR AREAS
OF WEIGHT LOSS (IN AIR)

Heptane-insoluble components of the unaged and aged materials were isolated by filtration. Portions of the filter entrained insolubles were analyzed by both DSC and TGA. The major weight loss corresponded to regions 2 and/or 3 in Table 20. Although a peak still occurred at position 1 it was greatly reduced in comparison to that in the whole liquid. Therefore, indications show that peaks 2 and 3 in Figure 18 are due to degradation products while peak 1 is most probably due to the base fuel.

DSC scans of the liquid samples repeatedly indicated sample evaporation in the range of 250°C to 350°C corresponding to the first weight loss noted by TGA. Other notable exotherms are shown in Table 21.

TABLE 21. SUMMARY OF DSC DATA FOR SHALE CRUDE OILS
Major Exotherms, °C

Sample	Condition	Peak	Maximum
		Air	N ₂
Paraho crude shale oil	aged, filtered	550	endotherm
	, unfiltered	550	—*
	unaged, filtered	550	—
	, unfiltered	550	500+
Geokinetics crude shale oil	unaged, unfiltered	510	550
	, filtered	—	600
Occidental crude shale oil	unaged, unfiltered	—	—

*—No peaks observed.

B. Coal Liquids

The two samples used in this phase are listed in Table 22.

TABLE 22. COAL LIQUID SAMPLES

Origin	I.D. No.	Condition
Coal liquid, middle distillate	AL-9492	aged 24 wks (43°C), unfiltered
Coal liquid, atm., overhead	AL-9792	aged 24 wks (43°C), unfiltered

These materials are quite volatile with respect to the previous samples analyzed. Therefore, the temperature program rate was reduced to 2°C/min. Residue after evaporation appeared to be minimal for both materials. The DSC and TGA data summary appears in Table 23. TGA and DSC data are in gen-

TABLE 23. SUMMARY OF DSC AND TGA DATA

Sample	Evaporation Complete (DSC), °C		Temperature of Maximum Rate of Weight Loss, °C	
	Air	N ₂	Air	N ₂
Coal liquid, middle distillate	150	175	—	160
Coal liquid, atm., overhead	115	80	105	75

eral agreement; with the maximum rate of weight loss (TGA) occurring at a slightly lower temperature than that obtained for complete evaporation (DSC).

C. ERBS Fuels

The three ERBS fuels: ERBS 3B 12.8, 12.3 and 11.8, unaged and aged at 43°C for 24 weeks, were examined by DSC and TGA under air and nitrogen. The DSC data were obtained initially in hermetically sealed pans which indicated significant differences between aged and unaged samples. It was observed that a vacuum filtration was performed on the aged samples prior to submission for analysis. Therefore, unaged ERBS fuels were filtered in a manner similar to that used for aged samples. Thermograms, obtained by DSC, for the three filtered and unfiltered pairs were then compared. In each instance the unfiltered materials exhibited a lower temperature for both the peak minimum and return to baseline after evaporation. This would indicate that at least some of the more volatile materials are lost during application of a vacuum to the filters (and filtrate). Reruns of DSC data were in non-sealed cups, which eliminated a "sawtooth" response on the initial curves due to pressure buildup and release in the "sealed" pans. A data summary is given in Table 24. Sample weights were between 1.9 and 2.5 mg.

TABLE 24. DSC DATA FOR ERBS FUELS

Time Base (Rerun Thermograms) in Air						Endotherm	Temperature	
Sample						Minimum	Return to	
No.	Description					(°C)	Baseline	Cup
						(°C)		
AL-10669	ERBS	3B	12.8	Unaged	Unfiltered	125	185	Non-sealed
AL-10669	ERBS	3B	12.8	Unaged	Filtered	140	200	Non-sealed
AL-10668	ERBS	3B	11.8	Unaged	Filtered	146	210	Non-sealed
AL-10667	ERBS	3B	12.3	Unaged	Filtered	144	206	Non-sealed
AL-10667	ERBS	3B	12.3	Aged	Filtered	144	206	Non-sealed
Run in Nitrogen								
AL-10668	ERBS	3B	11.8	Aged	Unfiltered	150	198	Hermetic
AL-10667	ERBS	3B	12.3	Aged	Unfiltered	210	286	Hermetic
AL-10668	ERBS	3B	11.8	Aged	Filtered	115	178	Non-sealed
AL-10668	ERBS	3B	11.8	Aged	Filtered	150	226	Hermetic
AL-10667	ERBS	3B	12.3	Aged	Filtered	200	254	Hermetic
AL-10667	ERBS	3B	12.3	Aged	Filtered	116	180	Hermetic
Temperature Base (Original Thermograms) in Air								
AL-10669	ERBS	3B	12.8	Unaged	Unfiltered	235	350	Hermetic
AL-10668	ERBS	3B	11.8	Unaged	Unfiltered	215	305	Hermetic
AL-10667	ERBS	3B	12.3	Unaged	Unfiltered	142	290	Hermetic
AL-10669	ERBS	3B	12.8	Aged	Filtered	200	255	Hermetic
AL-10668	ERBS	3B	11.8	Aged	Filtered	200	255	Hermetic
AL-10667	ERBS	3B	12.3	Aged	Filtered	185	365	Hermetic
Run in Nitrogen								
AL-10669	ERBS	3B	12.8	Unaged	Unfiltered	115	175	Hermetic

The data obtained from DSC analysis of the ERBS fuels were not particularly consistent with respect to the temperature at which the minimum of the endotherm occurred, although 7 of the 18 data points occurred between 140 and 150°C. A relationship between filtered and unfiltered fuels was not determined nor was there a notable difference between aged and unaged fuels. Integration of the time base peaks may yield some information not provided by direct observation of the temperatures during a scan. A greater number of replicates should also be run to determine the actual precision of this technique.

D. Intermediate Materials from Refining of Occidental Shale Oil

Unaged and aged samples of Occidental shale crude, whole hydro-treated Occidental crude and intermediate materials from the refining of the Occidental crude, described earlier in Table 16, were analyzed by TGA in air, in a manner similar to previous experiments. The values determined for TGA gums in these samples (normalized to a 10 mg sample wt) are compared in Table 25 to total insolubles and soluble gum (steam jet gum) measured before and after aging at 80°C for 7 and 14 days.

The data show that the TGA-determined gum values decrease as the degree of refining of the intermediate samples are increased and that the 80°C stability test did not increase the TGA-measured gum significantly; no correlation was observed between the total insolubles and TGA-measured gum levels.

E. Cooperative Evaluation of Techniques for Studying Gum Formation between the National Bureau of Standards (NBS) and Southwest Research Institute (SwRI)

To conduct a cooperative evaluation of the TGA and DSC techniques for measuring the gum content of liquid syncrudes, eight unidentified (except for code numbers) samples were received from NBS, and six of these were selected for evaluation. Two procedures were to be followed: a routine TGA analysis as described earlier and a DSC/TGA procedure provided by NBS. The latter consisted of oxidizing the test sample in the presence of steel under 600 psig oxygen for one hour at 160° to 170°C, followed by determination of the amount of gum in the oxidized residue using the TGA procedure. The weight loss in the TGA procedure was assumed to be the gum formed during the DSC-aging process.

Table 26 shows the data from duplicate runs by TGA and the values obtained at NBS by their DSC/TGA technique.

Two runs on these samples using the NBS procedure resulted in values shown in Table 27, which failed to agree with values reported by NBS. There appears to be differences in techniques and in use of correction factors for calculation of results, which have not been resolved.

Samples of unaged coal- and shale-derived syncrudes and the same materials unfiltered and prefiltered, aged at 43°C for 24 weeks, were evaluated by TGA in an argon atmosphere and in air. The results appearing in Table 28 indicate little change in the gums during aging as determined by this technique except in a few cases which may be experimental error. The level of gum determined in air is considerably more than that determined in argon which

TABLE 25. INSOLUELES AND TGA ANALYSIS OF OXY SHALE PROCESS SAMPLES

Code AL-	Description	Unaged			7 Days		14 Days	
		Steam Jet gum mg/100 mL	Particulates mg/L	TGA mg/10mg	Total Insolubles mg/100 mL	TGA mg/10mg	Total Insolubles mg/100 mL	TGA mg/10mg
11561	Oxy crude shale oil	--	--	1.98	11.6	1.98	18.2	2.04
11692	Whole hydrotreated Oxy crude	--	--	0.94	0.6	1.15	0.3	*
11504	CSHT recycle	14,231	--	1.10	0.5	0.96	0.4	1.14
11503	FCC tower overhead	530	2.2	0.26	198	0.47	394	0.75
11502	Raffinate	107	1.2	0.33	213	0.56	578	0.43
11505	JP-8 off-spec GCHT	27.7	71.0	0.05	9.1	0.05	18.0	0.00

*Data not available.

TABLE 26. PERCENT GUM

<u>Specimen</u>	<u>Original TGA</u>	<u>Rerun TGA</u>	<u>NBS/DSC-TGA</u>
F07636	6.0	4.9	6.9
F07637	1.3	1.2	--
F07638	10.0	11.3	5.3
F07639	1.0	1.2	12.8
F07640	1.0	1.2	1.3
F07641	7.5	1.3	16.7

TABLE 27. COMPARISON OF DSC/TGA GUM DATA
FROM TWO LAD3

<u>Sample</u>	<u>NBS</u>	<u>SwRI</u>	
		<u>1st run</u>	<u>2nd run</u>
F07636	6.9	43.5	38.5
F07637	--	2.5	1.6
F07638	5.3	30	27.0
F07639	12.8	7.8	32.0
F07640	1.3	(charred)	33
F07641	16.7	nil	nil

indicates that oxidation and/or polymerization is occurring along with volatilization of the sample. The level of gum determined by this technique does not compare with that determined by measuring filterable insolubles, adherent gum, or soluble gum reported earlier in Tables 4, 5, and 10.

Unaged samples of coal- and shale-derived syncrudes were submitted to NBS for evaluation by the DSC/TGA technique. The same samples were analyzed at SwRI by the NBS procedure with the results shown in Table 29. The NBS results for these samples have not been received.

TABLE 28. THERMAL GRAVIMETRIC ANALYSES OF COAL AND SHALE LIQUIDS GUM, WT%

AL- No.	Description	TGA in Argon			TGA in Air		
		Unaged	Aged 24 weeks at 43°C Unfiltered	Filtered	Unaged	Aged 24 weeks in 43°C Unfiltered	Filtered
9491	Coal liquid - heavy dist.	6	15.8	3	16	16	16
9492	Coal liquid - mid. dist.	0.5	trace	0.5	0	trace	0
9490	Coal liquid - naphtha	*	*	*	*	*	*
9704	Shale oil - Paraho	6.5	6	5.2	28	27	26
9705	Shale oil - Geokinetics	5	3	2	11	9	8.5
9706	Shale oil - Occidental	2	4.5	3.5	17.5	14	18

* Sample too volatile for this analysis.

TABLE 29. DSC/TGA ANALYSIS USING NBS PROCEDURE

<u>AL- No.</u>	<u>Description</u>	<u>% Gum</u>
9704	Shale oil - Paraho	18.6
9705	Shale oil - Geokinetics	14.3
9706	Shale oil - Occidental	9.5

CONCLUSIONS

As was pointed out at the beginning of this report, the work was conducted in two phases. Therefore, the conclusions will also be divided into two phases and several sub-phases:

STABILITY EVALUATIONS

Coal-Derived Syncrudes

- The results of storage stability tests conducted on the coal-derived liquids indicate that the lighter naphthas and middle distillates seem to form proportionately less deterioration products during storage under these conditions than the heavy distillate and vacuum still overhead.
- Elemental analyses of gum samples show more heteroatom concentration in coal-derived naphtha and middle distillate gums than in the gum from heavier fractions.
- Pre-filtrations did not produce large differences for the coal-derived naphtha samples, but did reduce the deposits formed in the middle distillate and in the atmospheric still overhead. Results for the vacuum still overhead were not conclusive with respect to the effect of pre-filtering.

Shale Syncrudes

- The hydrotreated shale oils did not produce large quantities of deterioration products in 24 weeks of storage although some increases in precipitate and adherent gum values were observed between 2 and 24 weeks of storage.
- In general the filtered hydrotreated shale oil samples produced lower levels of precipitate and adherent gum than the unfiltered materials.
- The shale crudes showed increases in heptane insoluble matter over the 24-week period; however, only slight differences between filtered and unfiltered samples were observed.
- Elemental analyses of unaged and aged hydrotreated and crude shale oils show no significant changes in composition after 24 weeks at 43°C and no differences between filtered and unfiltered samples.
- Aging for 24 weeks at 43°C did not change materially the kinematic viscosities of the shale oils.

SPECIAL ANALYSES

- GC simulated distillation techniques providing hydrocarbon, nitrogen and sulfur distribution failed to show significant and/or consistent differences between unaged and aged syncrudes, even though large quantities of deposits were formed during aging.
- Analyses of unaged and aged samples by ^1H NMR and low-resolution mass spectrometry showed that these techniques have insufficient resolution to measure the small changes in composition occurring during storage.
- The ERBS fuels which are petroleum derived, appear to be considerably more stable than the syncrudes investigated in this program, which would have been anticipated.
- The use of several solvents to attempt to promote the precipitation of deterioration products in shale crudes resulted in little difference between unaged and aged samples indicating that these crudes are reasonably stable under the conditions of storage.
- The aging test at 80°C for 3, 7, and 14 days conducted on Occidental shale crude and several refinery intermediates showed a wide range of stability under these conditions. The hydro-treatment steps in the refining of this material apparently stabilized the intermediate fractions. The extremely unstable streams were those that were distilled at temperatures above 600°F.
- Thermal gravimetric analyses and differential scanning calorimetry have shown promise as useful techniques for monitoring gum formations, heavy syncrudes and petroleum products stability. Naphthas and middle distillates which are more volatile, may require pressure for analyses by these procedures.
- TGA and DSC procedures as employed in this work will require modification and refinement if they are to be used as standard tests. Therefore, although the procedures used here were satisfactory at this time further technique development is necessary if expanded application of this procedure is anticipated.

RECOMMENDATIONS

- Stability characterization studies of syncrudes, intermediate/upgraded materials and finished synfuels/streams should be conducted as extraction/upgrading and refining processes evolve.
- Cooperative work between SwRI and NBS on the TGA and DSC methods should be continued to establish standard procedures for use of these methods.

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FIGURE A-1. HYDROCARBON DISTRIBUTION OF 700°F HYDROTREATED
PARAHO SHALE CRUDE (9701)

FIGURE A-2. HYDROCARBON DISTRIBUTION OF OCCIDENTAL SHALE CRUDE (9706)

FIGURE A-3. HYDROCARBON DISTRIBUTION OF PARAHO SHALE CRUDE (9704)

FIGURE A-4. NITROGEN DISTRIBUTION OF PARAHO SHALE CRUDE (9704)

FIGURE A-5. SULFUR DISTRIBUTION OF PARAHO SHALE CRUDE (9704)

FIGURE A-6. SULFUR DISTRIBUTION OF GEOKINETICS SHALE CRUDE (9705)

FIGURE A-7. HYDROCARBON DISTRIBUTION OF 650°F HYDROTREATED
PARAHO SHALE CRUDE (9703)

FIGURE A-8. HYDROCARBON DISTRIBUTION OF 650°F HYDROTREATED
OCCIDENTAL SHALE CRUDE (9702)

FIGURE A-9. HYDROCARBON DISTRIBUTION OF 750°F HYDROTREATED OCCIDENTAL SHALE CRUDE (9700)

FIGURE A-10. HYDROCARBON DISTRIBUTION OF 775°F HYDROTREATED OCCIDENTAL SHALE CRUDE (9699)

FIGURE A-11. NITROGEN DISTRIBUTION OF 650°F HYDROTREATED OCCIDENTAL SHALE CRUDE (9702)

APPENDIX B

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA

FIGURE B-1. AL-9792/L01918, ATMOSPHERIC OVERHEAD
UNAGED, UNFILTERED

FIGURE B-2. AL-9792/L01928 ATMOSPHERIC OVERHEAD
AGED 24 WEEKS, UNFILTERED

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