Shale Oil Value Enhancement Research

**Quarterly Report
October 1 - December 31, 1993**

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Summary Management Report

A major push was made to identify the hydrocarbon and heteroatom types present in raw shale oil. A comprehensive, qualitative picture of the $<400^{\circ}\text{C}$ material has been obtained. In addition to the expected types, e.g., pyridines, pyrroles, indoles and phenols, the presence of aliphatic carboxylic acids, ketones and nitriles was confirmed. Most importantly, heteroatom types are able to be concentrated nearly quantitatively by liquid-liquid extraction with polar solvents.

Compound types characterization of the $>400^{\circ}\text{C}$ material, as well as rapid, routine analysis of separations fractions, requires new methodologies founded in the Z-BASIC concept. Advances were made in establishing the interface protocol needed to utilize Z-BASIC methodologies for interpretation of gc-ms output data. It is anticipated that all interface protocols will be completed and a computerized reporting system will be in place by the end of the next quarter.

Progress reports were made at the Contractor's Review Meeting (METC), November 16th and at the Eastern Oil Shale Symposium (Lexington), November 17th. Research results continue to be well-received. The concept of a thermodynamically logical map of potential products from shale oil is a sound approach to value-enhancement research. From a commercial perspective, the concept of establishing a demand for raw shale oil at a reasonable purchase price of, say \$30/bbl, is increasingly being recognized as the best means of pulling shale oil into the marketplace.

In the next quarter, a framework will be established for a conceptual commercial process. The main consideration in establishing a framework is the interrelationship between specialty/commodity chemicals and conventional petroleum refining products. Another consideration is the anticipated depth of processing and the level of refinement of the product slate. As part of the conceptual commercial process development, a preliminary process scheme for the pilot plant development (Phase-II) will be developed.

Overall, the project is on schedule and on budget.

Technical Progress Report

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Objectives

Objectives for the Quarter were:

- Generate gc/ms data on extraction samples and find prominent target chemicals in the chromatograms;
- Generate an initial batch of 25 samples for activity testing by major chemical companies;
- Finalize the methodology and program development for marketing data base and conduct test runs;
- Continue efforts to market shale oil project to potential companies;
- Present results at METC Contractors Meeting and Eastern Oil Shale Symposium;
- Conduct exploratory continuous liquid-liquid extractions and analyze results;
- Conduct exploratory studies of hydrodealkylation to produce low molecular weight nitrogen compounds.

Discussion

Task 1.

NEPA check list has been signed by the contractor and COR and submitted to DOE for its final approval. According to the NEPA checklist, this project is recommended for categorical exclusion B. A final NEPA requirement report will be submitted to DOE upon final approval.

Task 2.

During this quarter, the following sub-tasks have been completed:

- (a) Fractionation of 275°C+ cut at 400°C.
- (b) Solvent screening for higher fractions.

Distillation of shale oil has been completed. The four distillate fractions have been analyzed for elemental analysis and GC-MS characterization. The following table shows results of elemental analysis:

Table 2.1
Analysis of Distillates

Fraction	Wt.%	C	H	N	S	O	H/C	Avg. MW
<200 C	11.9	85.84	12.56	0.28	1.02	0.30	1.76	124
200-275	13.1	85.42	12.76	0.59	0.94	0.29	1.79	173
275-400	24.6	85.36	12.09	1.13	0.99	0.43	1.70	232
>400	50.4	85.48	10.99	1.96	0.82	0.75	1.54	391
Wtd. Avg. Tot.	100.0	85.49	11.68	1.38	0.90	0.55	1.64	292

Figure 2.1 to 2.4 show the total ion chromatogram of the four fractions. Column program conditions, i. e., starting temperature, temperature ramp and end temperature were customized for each fraction to provide the best resolution of the chromatogram. GC-MS data were used to estimate the average molecular weight shown in Table 2.1.

The molar heteroatom type distribution is given in Figure 2.5. UNOCAL raw shale oil is slightly lower in nitrogen than many reported raw shale oils. This factor was known entering this project, but it was decided that the UNOCAL shale oil would make a good study oil because:

- a) it was relatively fresh and the retorting process conditions were well-documented;
- b) a slightly lower concentration of heteroatoms would make the separations and analysis tasks easier; and
- c) the partition modeling would be made on a molecular thermodynamic basis, lending the results of our study directly applicable to other Green River shale oil samples irrespective of prior process history.

Potentiometric titration data were obtained on all four fractions according to ASTM D-2896 using perchloric acid as a titrant. This work was conducted by the University of Utah. Average results of duplicate analysis are given in Table 2.2.

Table 2.2 Potentiometric Titration Results

Fraction	%N	%N	%N	Basics as a
Basic	Non-Basic	(diff)	Total	% of Total
<200°C	0.14	0.14	0.28	50
200-275	0.42	0.17	0.59	71
275-400	0.54	0.59	1.13	48
>400	0.74	1.22	1.96	38

The basic nitrogen types are thought to be nitrogen contained in six-membered types such as pyridines, quinolines and higher analogs. A half-neutralization potential (HNP) of about 425 mv was observed for the basic nitrogen types (see Figures 2.6 and 2.7). The non-basic nitrogen is thought to be nitrogen contained in five-membered ring systems such as pyrroles, indoles and higher analogs.

The data show that both types increase with increasing boiling range but that the non-basic types are relatively more concentrated in the higher boiling fractions. We will attempt to confirm these results with gc-ms data, as a check against any unusual titration behavior (non-titratability), due to high molecular weights.

Solvent screening studies for three distillate fractions have been completed. These screening studies are done by shake tests to find the best solvent loading and to measure the effectiveness (selectivity) of the solvent. Both extract and raffinate phases are analyzed by elemental analysis for polars distribution and by GC-MS for compound type identification. Solvents used for screening studies were listed in the previous quarterly report.

Task 3.

During this quarter, the following sub-tasks were emphasized. GC-MS system has been installed, tested and put into operation for the project. Analytical methodologies development is nearing completion. Compound-type analysis of the resolved peaks is essentially complete. Software development is in progress.

Distribution of Partition Coefficients

The development of the computer program for partition coefficient distribution has been completed. In this quarter, the program was tested with actual data from shale oil separations and results are presented. The shale oil distillate fraction (200-275 C) was extracted with methanol and also methanol with 2% water. The shake tests data were used to run the partition distribution program.

The distribution of partition coefficient 'k' can be explained by analogy to simulated distillation. In simulated distillation, the y-axis represents the weight fraction of the sample that has a specific boiling point i.e. x-axis. While, in the k-distribution, the y-axis corresponds to the molar fraction of the sample that has partition coefficient 'k' i.e. x-axis.

Figure 3.1 shows the effect of solvent loading on the distribution of partition coefficient, and Figure 3.2 corresponds to the effect of wet solvent loading. The range of values for 'k' increases with an increased oil/solvent ratio in both cases. The factor 'F' is defined as:

$$F = BK(A-K)$$

where $B = 6/A^3$ i.e area under the distribution = 1 mole.

'A' is the maximum 'k' value allowed in the distribution. Figure 3.3 shows the effect of solvent loading on the 'A'. The width of the distribution narrows with the addition of an antisolvent (water). Because the plateau between 1 and 2 (s/o) is seen with both solvents, we believe the phenomenon is real but its significance is yet to be determined.

Results of distribution of partition coefficient obtained from the shake tests will be used to evaluate the actual run data from counter current liquid-liquid extraction with the same solvent system. The effectiveness of the solvent matrix is thus estimated quantitatively to rank various solvent systems.

Determination of Enthalpies and Entropies

An original hypothesis of the program stated that the physical and chemical behavior of a molecule were governed, in large part, by the thermodynamic properties of the molecule. Enthalpy, being a measure of the electronic properties of a molecule, could be related to chemical reactivity in addition to the obvious relationships with heat of vaporization, solubility, partitioning, etc. Entropy, being a measure of the geometric properties of a molecule, could be related to crystallization structure, adsorption and biologic receptor chemistry (odor, taste, toxicity, etc.) for example, in addition to the more obvious relationship with size and equilibrium thermodynamics.

Therefore, a key task of our program is to measure the thermodynamic behavior of shale oil components. From such measurements, we obtain fundamental information which can be used both for process design and for prediction/correlation of applications.

The technical details of the computer program for calculating enthalpies and entropies were reported in the Second Quarterly report. During this quarter, the development of the computer has been completed and debugged. The program was tested using data from different temperature programmed GC runs. Initially, a simple model compound system was used to test the program output.

GC run conditions for various temperature programs are given in the following table along with the results of program output. To calculate thermodynamic properties, at least three runs are necessary. Retention time for air is used as a standard reference. Data were obtained using naphthalene spiked standard diesel and peaks were identified by the Wiley Mass Spectra Library.

Compound	Temp. Program	Enthalpy (cal/mole)	Entropy (cal/mole °K)
Naphthalene	1,2	-12,373	-19.56
	1,3	-12,125	-18.92
	2,3	-11,749	-17.79
n-Dodecane	1,2	-13,903	-23.55
	1,3	-13,574	-22.70
	2,3	-13,088	-21.27
n-Eicosane	1,2	-21,208	-32.21
	1,3	-20,367	-30.46
	2,3	-18,751	-26.76

Where GC Run Conditions are:

Temp. Program	Initial Temp.C	Hold min.	Rate C/min	End Temp.C	Pres. (psi)	Air RT (min)
1	50	2	25	275	10	1.38
2	50	10	4	250	5	1.78
3	50	30	2	250	5	1.78

As expected, these results show that enthalpies and entropies depend on the temperature program conditions. Future modifications will include the addition of heat capacity term to the model to add flexibility to the program and give one more degree of freedom for the calculation of thermodynamic properties. These results will be used to calculate enthalpies and entropies at standard conditions.

Development of Boiling Point - Retention Time Correlations

One of the limitations of using standard spectral libraries for analysis of shale oil fractions, is the lack of spectral information for heavy molecules in the higher boiling fractions. Analysis of data from residual fractions using conventional techniques would be an onerous task. Z-BASIC solves this problem by anticipating the compound types present based on the presence of lower members of a homologous series. Data from 200-275°C fraction can be used to identify most of the precursor molecules that could be found in heavier fractions. Molecules, in the 200-275 region, are simpler than >250°C boiling molecules and can be identified from fragmentation patterns.

The data treatment includes:

- GC-MS analysis of the light fraction (200 - 275 C)
- Peak identification using fragmentation pattern (Wiley Library)
- Search by compound types (Z-BASIC) classification.
- Assign retention time data and obtain boiling point information from literature
- Determine the equation forms that best match the data
- Obtain constants for these equations for use as a database
- Predict boiling points at higher retention times

The following non-linear equation types are used:

$$y = \frac{a(x)^2 + b(x) + c}{x + d}$$

$$y = \frac{a(x)^3 + b(x)^2 + c(x) + d}{(x)^2 + e}$$

$$y = \frac{a(x)^3 + b(x)^2 + c(x) + d}{(x)^2 + e(x) + f}$$

where

x is retention time (min.)

y is Boiling Point (deg. C)

The following table shows values for constants for the compound types of interest that are present in the shale oil fraction. These constants for equations are obtained by multiple regression analysis. Also, the boiling point-retention time correlation curve for paraffins is used as the reference series for all other compound types. By holding the 'a' value constant at 2.8583 (the value determined for n-paraffins), the correlation curves are forced to converge asymmetrically to the paraffin curve at infinite m.w., which is the expected behavior.

Constants for BP-RT Correlations (ACQ Method SO-93)

Compound Type	b	<u>a = 2.8583</u> c	d	e	f
Alkanes	120.46	-878.64	-6.15		
Alkenes	119.43	-881.54	-6.21		
Benzenes	140.46	-236.69	-0.58		
Indanes	144.77	-326.66	-0.22		
Naphthalenes	144.77	14.39	0.00		
Pyridines	136.58	-493.54	-2.91		
Quinolines	132.35	-951.79	-6.15		
Ketones	141.34	-176.04	-0.48		
Thiophenes	141.69	-161.93	0.06		
Nitriles	136.43	846.61	9987.23	105.43	
Pyrroles	134.64	1074.85	616.53	101.71	
Phenols	128.49	101.43	-55154.	-297.26	
Indoles	180.87	3097.14	-2348.4	15.09	4.95
Carboxylic acids	180.87	3097.14	-2348.41	15.09	4.95

Figures 3.4 and 3.5 show the correlation curve fit for nitrogen types and hydrocarbons that are present in the shale oil fraction. Points represent actual literature data and the line represents calculated values for a given series predicted up to the final carbon number of paraffin series. These correlations will be used for peak identification as boiling points for a given series can be calculated from retention time. Results, when

compared with the B.P. vs. M.W. correlations (see Second Quarterly report) will establish the "allowability" of the peak identification.

Software development for mapping, peak identification and comparison

As the need for advanced data treatment became apparent, we have embarked the phase of software development for GC-MS data. The main goal is to use advanced programming tools of HP Chemstation for better management of mass spectra. Program routines will be used for:

- (a) Spectra comparison
- (b) 3-D mapping of spectra
- (c) Peak identification
- (d) Quantification

Previously developed Z-BASIC programs, i. e., executable files, are used for obtaining possible empirical formulas. Also, correlations between molecular weight, retention time and boiling point will be part of this program to narrow the possible structures and help identify the structure for a given peak.

The programming concept has been formalized and the development is in progress. The successful completion of this program will be very advantageous for the overall progress of the research. Because this capability allows for rapid tracking of individual species through a separation sequence, an original goal of the program.

Figure 3.6 shows the 3-D spectra of a shale oil extract. It illustrates various compound types that are present in the extract. Data treatment includes stacking of characteristic ions for each compound type. Future work will involve the development of techniques for integration of Z-BASIC programs and decision making logic for peak identification and confirmation.

Task 4.

During this quarter, the specific goals in the marketing task include:

- Mail letters of introduction to selected companies;
- Follow-up on industrial contacts;
- Complete the development of marketing database;

Following is the list of selected companies for first go-round in the effort of marketing and commercialization of the project:

AMOCO Chemical Company
Ashland Chemical Company
Calgon Carbon Corp.
Chevron Chemical Company
CSX Corporation
GE Petrochemicals
Marathon Petroleum
Nepera, Inc.
Neville Chemical Company
PPG Industries
Occidental Chemical Company
Reilly Industries, Inc.
SUN Company
UNOCAL
W.R. Grace & Co.
Westates Carbon

The criteria for the selection of initial companies include: a) broad spectrum of companies, b) personal contacts at higher level, c) producers of chemical intermediates, specialty chemicals and heterocyclics, and d) high probability for support. Dr. Zahradnik's experience, contacts and suggestions have been utilized in this effort. The purpose is to generate interest in the project by explaining the product slate and potential profitability. The difficulty of this task involves educating some of these companies about the nature of shale oil and its potential as a feedstock for specialty chemicals.

Some of these companies expressed interest in receiving more information about the project and its progress. Currently, we are in the process of preparing information package which includes prospectus, program description, summary of progress reports and published papers.

The development of market database has reached the stage of completion. All required routines to handle data input, management and report generator are in-place and debugged. It has been tested with sample data sets. As more marketing data become available on value-added chemicals/products, the performance and utility of database can be evaluated.

The P.I. traveled to the country of Estonia in October (no cost to current contract). Estonia has been producing Kukersite shale oil for more than 70 years and extracts high value chemicals (mostly hydroxy aromatics) to enhance their revenues. Philosophically, the Estonian shale oil industry is 30 years ahead of the U. S., although their technology (design) is presently behind modern engineering capabilities. The case history of the Estonian experience is highly encouraging because even with a managed economy, the profitability brought to the venture by value-added chemicals was clearly the difference between economic viability and non-viability. Green River shale oil contains components of potentially higher value than Estonian shale oil

lending additional impetus to the prospect of a viable U.S. shale oil industry based on value-added components.

In the next quarter, efforts will be made to gather marketing data for the target compound types that are found in the shale oil fractions. Market profiles will be developed for target compounds.

Task 5.

The following subtasks have been accomplished:

- (a) Operation of Liquid-liquid counter current extractor
- (b) Compound type identification
- (c) Evaluation of partition coefficient

Liquid-liquid extractor has been modified to 1" column to match the throughput rates. Fraction (200-275 C) was used in the first batch of counter current runs. The conditions for this operation have been obtained from shake tests (from task 2). Operating conditions include solvent system (2% H₂O, MeOH), solvent loading (1:0), flow rates .5l/hour, and temperature (17.2°C). Mass balance, physical properties and elemental analysis data were gathered to determine the efficiency. Characterization of extract and raffinate phases is in progress.

One of the objectives of this task is to identify compound types that have commercial potential i.e adding value to the overall scheme. Figure 5.1 shows the overall distribution of compound types present in the total shale oil. The middle distillate fractions seem to contain the bulk of the compounds which exhibit polar behavior. These compounds are primarily alkylated one and two ring systems. Depending on the length of side chain, it may or may not be necessary to dealkylate to obtain a specification product.

Figure 5.2 shows specific heteroatom containing molecules in the acid extract of <200 C fraction. It also illustrates the effectiveness of extraction i.e. absence of polar compounds in raffinate phase. The average substitution of polar ring systems in the <200° fraction is up to three carbons.

For these compound types, a system dependent (six-step counter-current extraction) partition coefficient distribution has been calculated. Results are shown in the following table:

Compound Type	'K' Values
Alkanes	.0317
Alkenes	.0370
Dicycloparaffins	.0436
Monoaromatics	.155
Indanes	.165
Indenes	.174
Diaromatics	.215
Thiophenes	.332
Pyridines	4.73

The following types are completely (99%+) extracted in the extract phase; phenols, pyrroles, indoles, nitriles, ketones and carboxylic acids.

The distribution of 'K' values suggest that liquid-liquid extraction can partition between hydrocarbons and polars for this solvent system. Compound types having 'K' values below .113 will preferentially be found in the raffinate.

The analytical methodologies and characterization results can be effectively used to design a continuous separation process. The major break seen between the thiophenes and pyridines (including the types listed at the bottom of the table) bodes well for a highly selective process for enriching desirable types.

Task 6.

The conversions exploration task has been initiated. The University of Utah, under subcontract, has been evaluating the feasibility of hydrodealkylation for shale oil fractions. The University has also been assisting in potentiometric titration characterization of basic and non-basic compound types. Results are reported under Task 2 above.

Task 7

During this quarter, the process modeling task has been initiated as it is the logical extension of the marketing task. The specific goals include:

- Initiation of process cost and economics
- Integration of market database with economic models

The current phase of development involves the integration of marketing information with cost and economic models. The preliminary economic model for shale oil has been developed in our previous project funded by JWBA and the State of Utah. The original model, shown in figure 7.1, was developed using Lotus 2.1 which involved the development of command language routines. However, this model is upgraded using Excel for windows software to take advantage of built-in routines such as what-if analysis,

goal seeker and scenario manager. This approach will reduce the development time. Costing routines will be based on the process flow diagram and product slate. A preliminary diagram will be prepared in the following quarter.

Figure 7.2 shows the overall connectivity of data flow from various tasks of the current research program. Data are connected between process sequence, analytical results, process models, cost analysis and economic evaluation. The purpose of this connectivity is to reflect changes in process sequence or product slate on overall project economics and constrained by market forces.

Objectives for the Next Quarter

- Complete solvent screening studies for 275-400 and +400°C fractions
- Perform continuous liquid-liquid extraction runs for the 275-400°C fraction
- Develop routines for rapid peak identification
- Continue the characterization of shale oil extract and raffinate phases from different solvent systems
- Research market profiles for target chemicals that are present in the shale oil
- Select candidates for conversion process for dealkylation
- Initiate costing and economic analysis blocks for process modeling
- Continue marketing efforts to major companies
- Draft a process concept framework based on first 12-month results.

File : C:\HPCHEM\1\DATA\93_37A.D
Operator : Don
Acquired : 26 Oct 93 12:24 pm using AcqMethod S093_37
Instrument : 5972 - In
Sample Name: spx12-93-37
Misc Info : this is the <200 degree S.O.
Vial Number: 1

Figure 2.1

File : C:\HPCHEM\1\DATA\928338C.D
Operator : Don
Acquired : 28 Sep 93 6:11 pm using AcqMethod SO93_38
Instrument : 5972 - In
Sample Name: spx02-93-38
Misc Info : 200-275 degree C cut from 91-24
Vial Number: 2

Figure 2.2

File : C:\HPCHEM\1\DATA\S09366A.D
Operator : Don
Acquired : 6 Dec 93 11:07 am using AcqMethod S093_66B
Instrument : 5972 - In
Sample Name: Spx12-93-66 1424ng/ul
Misc Info : 275-400 degree cut form 93-11 SO feed
Vial Number: 2

Figure 2.3

File : C:\HPCHEM\1\S09367A\94_003.D
Operator : Don
Acquired : 3 Jan 94 11:58 pm using AcqMethod S09367A
Instrument : 5972 - In
Sample Name: spx12-93-130
Misc Info : raffinate from MeOH extraction of 93-67 > 400 degree cut
Vial Number: 4

Figure 2.4

Heteroatom Type Distribution in Raw Shale Oil

Figure 2.5

Potentiometric Titration for
Basic Nitrogen (BN) determination.
(Sample #38)

Figure 2.6

Potentiometric Titration for
Basic Nitrogen (BN) Determination.
(Sample #67)

Figure 2.7

K Distributions for Partitioning Between Shale Oil(200-275 C) and Solvent A

Figure 3.1

K Distributions for Partioning Between Shale Oil(200-275 C) and Solvent B

Figure 3.2

Dependence of K Range on Solvent/Oil

Figure 3.3

BP and RT Correlation Plot

Nitrogen Type Compounds in Shale Oil Fraction

Figure 3.4

Figure 3.5

Shale Oil Extract (200-275)

Figure 3.6

Compound Type Distribution of Western Shale Oil

Figure 5.1

Acid Extraction of -200 C Fraction Total Ion Chromatogram(Excerpt)

Figure 5.2

General Effect of Molecular Weight on Partition Coefficient 'K'

Figure 5.3

Economic Analysis Model

Figure 7.1

Shale Oil Value Enhancement Research *Overall Project Connectivity*

Figure 7.2