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Shale Oil Value Enhancement Research

First Quarterly Technical Progress Report

prepared for

**U. S. Department of Energy
James Westhoff, COR
Contract #DE-AC21-93MC29240**

prepared by

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Summary Management Report

Concurrent progress is being made in all key areas, namely, separation, characterization and market assessment. The market area, not one of our traditionally strong areas, has been going better than expected. We believe this is due mainly to the emerging interest in new and unconventional materials.

The characterization work has been progressing solidly with the fundamental Z-BASIC correlations providing information not heretofore available in the chemical literature. Our agreement with Hewlett-Packard regarding the purchase of equipment at a reduced price is complete and the gc-ms will be ordered shortly.

The separation work has progressed satisfactorily although an unexpected amount of time has been required for "facilities" and "equipment" related issues. Some of these issues have dealt with safety and regulatory compliance when storing larger quantities of samples. These now seem to be solved. We have a lot of direct experience in shale oil separations dating back to the OXY project and before. Also, we will streamline our work by going to prepacked micro-separation tools for some of our separation characterization work. This will allow us to stay on schedule.

Overall, we are on schedule with the project. All administration requirements are in place and the accounting and financial records are current.

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Technical Progress Report

Objectives for the reporting period were:

- To initiate project tasks and formalize management assignments,
- To provide information required for the National Environmental Policy Act (NEPA).
- To distill a barrel of shale oil into broad cuts for separations.
- To develop Z-BASIC correlations for prediction of boiling points for various heteroatom containing compounds
- To initiate marketing and subcontract tasks.

These objectives were aimed at balancing the progress in each task according to the project schedule of phase-I. Long term project planning, assignment of task leaders, reporting requirements and project management controls have been streamlined to assure successful completion of the project.

Accomplishments

Submitted the draft copy of Information Required for NEPA and developed policies and procedures for Environmental Safety and Health

Fractionated one barrel of shale oil into three fractions for downstream separations processing

Developed methodology to predict boiling points of heteroatom containing compounds not available in the literature to assist in characterization of shale oil fractions

Made initial contacts with major chemical companies to evaluate narrow concentrates of shale oil for valuable chemicals

Negotiated with HP to procure GC-MS system at subsidized cost in return for option on rights to HyMAT.

Task 1.

Task Manager: P A. V. Devineni

The objective of Task 1 is to provide DOE with environmental impact information from the project. This information will be used by DOE to determine the appropriate level of NEPA documentation.

The status of Task 1 is 95% complete. A preliminary draft report was submitted to the COR for review in April. Comments and suggestions were received from the COR. Additional data and documentation as requested by the COR have been provided in the draft final report early in May. After receiving final comments and/or acceptance, a final report will be submitted to DOE to conclude task 1.

To evaluate the overall environmental impact of the three phase project, the scope of work included:

- (a) Estimation of facilities requirement for process development units, laboratory and instrumentation;
- (b) Estimation of shale oil and chemicals consumption and calculation of solid and liquid waste production;
- (c) Estimation of volatile organic carbon (VOCs), SO_x, NO_x and particulate emissions from the operation of units;
- (d) Development of a hazardous waste management plan;
- (e) Extention of permits;
- (f) Development of policies and procedures for environmental safety and health (ESH).

Figure 1 shows the hazardous waste management plan for the project. The operational scale of the project and types of waste generated from the project qualify JWBA as a 'conditionally exempt small quantity waste generator'. The overall impact of the shale oil value enhancement research in various classes of environmental concerns is shown in Table 1.

Table 1
The Impact of 'Shale Oil Value Enhancement Research' on the Environment

Class	Impact
Air Emissions (VOCs)	20 Kgs/year
Water Use	12,000 bbls/year
Land/Facilities	Modifications within project boundaries
Waste, Liquid	2 bbls/year
Waste, Solid	100 lbs/year
Socioeconomic	Providing Employment
OSHA	Compliance

In summary, we have concluded that the proposed work for three phases is similar in scope to work previously performed by JWBA under sponsorship of DOE and Occidental Oil Shale Company. The previous facility operational permit is being renewed for

the proposed work. Similar waste disposal practices will be followed as the nature of waste will be similar. At this scale of process development operation, the impact on the environment will be insignificant.

After detailed analysis of environmental impacts in conjunction with scale of operation, this project shall be categorically excluded under class B. The final report on 'Information required for National Environmental Policy Act' is in DOE review.

Task 2.

Task Manager: D. E. Cogswell

Assistant: J. W. Wiser

The objective of task 2 is to process raw UNOCAL shale oil according to a thermodynamically logical separation sequence. The process sequence includes distillation, liquid-liquid extraction, and liquid-solid adsorption.

The first step in the separation sequence is the distillation of shale oil. In order to complete the separation sequence and generate samples of various chemicals or concentrates, it was decided to distill one barrel of shale oil. We used an existing distillation column for the atmospheric pressure distillation steps.

Table 2 shows the properties of raw shale oil as supplied by UNOCAL.

Table 2
Typical Raw Shale Oil Properties (from UNOCAL)

Gravity, Deg API	22.8	
ASTM D2887		
Distillation	deg F	deg C
IBP/10	200/400	93/204
50/90	710/950	375/510
EP	1080	582
Nitrogen, wt.%	1.8	
Sulfur, wt.%	0.95	
Pour Point, DEG F	+20	
Rams Carbon Residue, wt.%	0.3	
Arsenic, WPPM	45	

To improve the efficiency of the existing column and quality of distillation fractions, column modifications were required. The following is a list of activities regarding the distillation:

1. Conversion of steam stripping plate distillation column to packed tower to increase number of theoretical stages;

2. Provision of stripping section by adding reboiler and changing feed tray location;
3. Addition of reflux facility and control;
4. Addition of total and partial condensers to improve column temperature profile;
5. Modification of process control software to accommodate all hardware changes in the distillation column and addition of flowrate control mechanism.

Operational factors include:

1. Determination of the packed column efficiency using a Cyclohexane and Toluene system;
2. Characterization of shale oil for boiling point distribution using a homogenous sample;
3. Blending of overhead product with the feed to increase vapor loading thus increasing the rectification efficiency;
4. Optimization of reflux ratio and feed rate.

When a 50-50 mixture of cyclohexane (B.P. = 80.7) and toluene (B.P. = 110.6) was distilled, the overhead was essentially free of toluene (>99% cyclohexane) while the bottoms were 82% toluene. This showed that the rectification section was working well, but that the stripping section was experiencing some inefficiencies. Modification to improve the stripping efficiencies would have required an unacceptable amount of time and effort, so it was decided that we would live with the lower efficiency.

The shale oil distillation effort encountered certain problems associated with shale oil composition and fixed column geometry. The low overhead make caused problems of low vapor traffic and inadequate heat at the top of the column. However, with operational experience, the problems were effectively solved.

Figure 2 illustrates the difference between the boiling point distribution of a grab sample compared to a sample which had been heated and stirred until homogenous. Examination of the bottom-of-the-barrel sample indicated the presence of waxes and other polymerized products that skewed the results. It is worthwhile to note that UNOCAL cut temperatures match with the boiling point distribution of homogenous sample.

The overall distillation scheme was modified to four fractions as opposed to five fractions as originally anticipated. The amount of +535°C is relatively small and, for

purposes of characterization, it was decided to leave this material in the +400°C fraction. Figure 3 illustrates the modified distillation scheme with process yields and status of completion.

The overall material accountability for these runs is better than 98%. Current plans call for making the final fractionation on the thin-film molecular still at the University of Utah. Results of the characterization of distillation fractions will be provided in the second quarterly report.

Task 3.

Task Manager: D. E. Cogswell

Assistants: C. P. Russell, P. A. V. Devineni

One objective of Task 3 is to develop algorithms for routine Z-BASIC characterization of shale oil fractions. The purpose is to use the GC-MS data to identify structures of commercial importance from complex shale oil fractions.

The first step in this development is to predict boiling points of heteroatom containing compounds for which little or no data are available. The methodology, so developed in this reporting period, is outlined and results of the correlations are presented.

According to the Z-BASIC method, any molecule can be represented by the formula $C_nH_{2n+z}N_uO_vS_w$, where 'z' is a classification parameter. For a given homologous series, 'z' is constant and the addition of -CH₂- groups increases the value of 'n'. The prediction methodology is based on previously developed correlations between boiling point and molecular weight for paraffins(z=+2), alkylmonocycloparaffins(z = 0), alkylbenzenes(z =-6) and alkylnaphthalenes(z =-12).

For a new parent compound, we obtain from the literature its boiling point and as many of its paraffinic substituted compounds as are available. According to the location of the compound, the two neighboring curves are chosen. That point lies at some fraction 'f', of the distance between the two selected curves, as do any additional points that data provide. If we have more than one data point, we correlate this 'f' with molecular weight, otherwise we force 'f' to have the value of the parent compound at higher molecular weights. Thus, with 'f' as a function of molecular weight and the two selected curves, boiling point of any member of the series can be calculated.

To estimate the boiling point for a parent compound (limited to polycondensed ring systems), the following procedure is used:

1. We identify the basic ring skeleton of the compound. Treating it as a pure hydrocarbon, we obtain its boiling point from the literature or calculate it from an empirical correlation we developed, based on 'z' and on the number of saturated rings in the skeleton.

2. To this boiling point value, we add empirical corrections which we generate using existing literature data. These corrections are functions of the final molecular weight of the parent compound. The two types of corrections are:
 - (a) for changing a carbon in the basic skeleton to a specific heteroatom;
 - (b) for adding onto the basic skeleton some heteroatom functionality, such as -OH- or -SH-.

This procedure was used to generate curves of estimated boiling point vs molecular weight for parent compounds with from one to four condensed rings of varying degrees of saturation and functionalities. Table 3 shows various heteroatom containing compounds that have been correlated for boiling points from molecular weight using Z-BASIC methodology and prediction routines. The corresponding number of homologous curves generated is also given.

Figures 4 to 7 illustrate the nature of the homologous series curves for these heteroatom containing compounds. The legend for plots is shown in molecular structure for illustration purposes.

Table 3
B. P. Correlations Completed

Compound	# of Curves
Nitrogen containing compounds	
1. Pyrroles	14
2. Pyridines	14
3. Anilines, primary amines	9
4. Anilines, secondary amines	9
5. Anilines, tertiary amines	3
Oxygen containing compounds	
1. Furans	12
2. Ethers	6
3. Phenols	14
4. Acids	10
5. Aldehydes	10
Sulfur Containing Compounds	
1. Thiophenes	11
2. Thiols	10
3. Sulfides	6
Nitrogen & Oxygen	
1. -OH on Pyridines	10
2. -OH on Pyrroles	10

Table 3 (Continued)

3. -C=O on Pyridines	10
4. -C=O on Pyrroles	10
5. Furans & Pyridines	10
Nitrogen & Sulfur	
1. -SH on Pyridines	10
2. -SH on Pyrroles	10
3. Thiophenes & Pyridines	10
Polycyclic Hydrocarbons	8

This procedure will assist us in identifying functional types seen in GC analysis of fractions obtained in tasks 2, 3, 5 and 6. For a given peak from the GC, retention time approximates boiling point. From elemental analysis and mass spectroscopic data, the most probable 'z' and 'n' are calculated. These boiling point curves then tell us which among the possibilities is the one with the appropriate boiling point.

Task 4.

Task Manager: P. A. V. Devineni

Assistant: J. W. Bunger

The objective of task 4 is to conduct market research to determine current market needs and anticipate directions of future market needs of the target products from shale oil. Even though Task 4 was scheduled to start after this quarter, there were some leads that developed out of the ACS meeting, in March, which we have pursued.

The activities of the marketing task include:

1. Contacting majors to accept and evaluate shale oil concentrates for valuable chemicals. We have received verbal expressions of interest from Dow, duPont and Monsanto.
2. Initiating subcontract tasks with Sinor and Zahradnik;
3. Reorganizing the database structure to assemble the marketing information, specifications and feedback data;
4. Approached the Oil Shale Consortium of LLNL about a possible agreement.

Contacts with the chemical industry have been highly encouraging. Apparently, the search for new compounds with unique activities has been formalized in many of the major companies. What these companies are concerned about is if they find something interesting and valuable, will we be able to reproduce the data, back them up in focusing the search and ultimately to produce larger quantities of sample. For these reasons, it is already becoming important that there are assurances of funding to complete the project. JWBA is initiating formal, written dialogue with these majors.

Work statements have been agreed upon between JWBA and Sinor and Zahradnik, respectively. Subcontracts will be in place in the next quarter pending the approval from DOE. Mr. Sinor, who in the past has examined the potential of chemicals from shale oil, will concentrate on technical and production aspects of marketing task while Dr. Zahradnik will investigate the business approach of the marketing task. Details of the subcontract Statement of Work will be reported, when approved by DOE.

Modifications to the database model are underway which include database structure, data retrieval and data manipulation. Figure 8 shows the Structure of the Market Database and Database Files. Work is progressing well on completion of the modules. The product and manufacturers models are essentially complete. The program for the market file is about 15% complete. This file will receive data from subcontractors and that developed in-house.

The target chemicals from the shale oil required SIC code to facilitate other online database searches. Table 4 shows the result of the database search conducted by Dun & Bradstreet. The 8-digit SIC codes of the target chemicals and respective business entities whose line of business include these chemicals are shown. The JWBA database is organized by the SIC codes of the target chemicals. The data in Table 4 is exemplary of the formalized approach we will take to find a market for shale oil-derived chemicals.

Table 4
Listing of 8-digit SIC Codes for Target Chemicals
and Corresponding Number of Businesses
(from Dun & Bradstreet Database)

8-digit SIC	Description	Businesses
2843 01 01	Soluble Oils or greases	5
2843 01 02	Sulfonated Oils, fats or greases	2
2851 01 05	Paints, asphalts or bituminous materials	19
2865 02 07	Phenols, alkylated cumene	4
2865 04 02	Distillates, coal tar	14
2865 04 03	Tar	9
2869 99 01	Accelerators, rubber processing	1
2869 99 28	Organic solvents	27
2879 99 03	Fungicides, herbicides	42
2895 00 00	Carbon black	32
2899 99 18	Fire Retardant chemicals	58
2911 02 06	Petroleum Solvents	11
2911 03 03	Fuel oils	49

Table 4 (Continued)

2911 04 02	Mineral oils	1
2911 04 03	Mineral waxes	2
2911 04 04	Lubricating oils	26
2911 04 05	Paraffin wax	1
2911 05 01	Asphalt, Refining	39
2911 05 02	Petroleum coke	4
2911 05 03	Lubricating Greases	10
2911 05 04	Petrolatum	4
2992 01 01	Brake Fluid	10
2992 01 02	Cutting oils	45
2992 01 04	Transmission Fluid	6
2992 99 02	Rerefining oils	88
2999 01 01	Coke, petroleum	7
2999 02 02	Petroleum waxes	18

Objectives for the Next Quarter

- Complete and submit the final NEPA document;
- Complete the distillation to obtain the bottom cut;
- Generate fractions based on molecular types and functionalities using separation techniques;
- Set up GC/MS system and develop operating experience on initial sample;
- Extend Z-BASIC methodology for other thermodynamic properties such as enthalpies and entropies of adsorption and vaporization;
- Complete subcontracts and initiate marketing tasks by Sinor and Zharadnik;
- Continue marketing efforts and complete testing agreements, where possible, for evaluation of shale oil derived specialty chemicals.
- Continue work on market database and make entries as available,
- Complete subcontract with the University of Utah and initiate work under that subcontract.
- Continue dialogue with LLNL consortium.

Figure 1: Hazardous Waste Management Plan

Figure 2: Boiling Point Distribution of Shale Oil

Figure 3: Shale Oil Distillation Scheme

Figure 4: Boiling Point Vs Molecular Weight
5-Membered N-Heterocyclic Ring Systems

Figure 5: Boiling Point Vs Molecular Weight
Polycyclic N-Heterocyclic Ring Systems

Figure 6: Boiling Point Vs Molecular Weight
One & Two Ring N-Heterocyclic Ring Systems

Figure 7: Boiling Point Vs Molecular Weight

Phenolic Ring Systems

Structure of Market Data Base Files

Product File	Sales File	Manufacturer File	Market File
Product Name JWBA ID SIC Number Price Unit Trade Assocn. Specifications	JWBA ID Manufacturer ID Sales Volume Unit Source	Manufacturer ID Name Division Contact Phone & Fax Address Update	JWBA ID Demand Region State Imports Exports Growth

Structure of Markets Data Base

Figure 8

**DATE
FILMED**

10/04/93

END