Shale Oil Value Enhancement Research

**Quarterly Report
July 1 - September 30, 1994**

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Work Performed Under Contract No.: DE-AC21-93MC29240

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
James W. Bunger and Associates
P. O. Box 520037
Salt Lake City, Utah 84152-0037

MASTER

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Summary Management Report

Activities during this quarter focused on using the phase-I results to define process sequence alternatives for phase-II. Two process alternatives have been devised while obtaining the desired marketable product slate. The status of required process units has been evaluated. While there are some units that need to be designed and fabricated, the upstream process units are in place to proceed with the process plan.

Separations have been completed and analyzed on three of the four shale oil fractions. The extraction work on the heaviest fraction has run into difficulties due to equipment design limitations. Modifications are in progress to rectify this problem and to complete the planned work. The separations and analytical work on the middle distillate fraction (275-400 C) have been completed. The solvent system has performed as expected and will be used in the pilot system in phase-II.

The work on conversions task has steered in the direction of using thermal hydrodealkylation (THD) process to dealkylate polar fractions. The THD process is expected to yield low molecular weight polar compounds/concentrates that are suitable for market needs. The design and fabrication will be initiated in the next quarter.

The analytical procedures and characterization task is in the final stages of refinement to complete the software as expected. The Z-BASIC software, eventually, will be used to monitor separations by tracking compound types or z-types. Present modifications are expected to provide z-type distributions. The decision-making routines need further refinement.

The progress of the development work slowed a little during this quarter due to work load demand from other projects. However, serious efforts will be made to meet the original project schedule.

Technical Progress Report

Objectives for the Quarter were:

- Complete liquid-liquid extraction runs on shale oil fractions
- Analyze chromatograms using Z-NUM software
- Develop process flow diagram for Phase-II research
- Complete activity testing of shale oil fractions
- Continue marketing efforts to major chemical companies
- Complete profitability analysis

Discussion

Task 1.

NEPA task has been completed.

Task 2.

Separations characterization task is almost completed. Work is continued and related results are reported in separations explorations task.

Task 3.

Analytical procedures development and characterization is nearing completion. Z-BASIC software development is in the final stages of conclusion. During this quarter, the improvements to the Z-BASIC program include:

- (i) Boiling point-molecular weight data base was expanded to about 80 z- types and several sub-classes for each z-type. Data base verification and testing have been completed. In phase-II, data gathered during routine GC-MS analysis will be used to compile data for boiling point-retention time data base.
- (ii) Equations have been developed to obtain a window of molecular weight range for a given retention time. This molecular weight window is an integral part of decision making routine for selection of representative fragments in a given scan. This will help us decide the parent ion when multiple compounds co-elute at the same time. However, further modifications are needed for the case of low eV MS.

- (iii) A generalized methodology has been developed and incorporated into the program to adjust the data from BP-RT data base for variations in the temperature programming of the data acquisition. It is common practice to run different fractions at different temperature programming conditions to get better resolution. As retention times are related to run conditions, these modifications based on paraffin series will normalize retention times of those used to build the data base. The effect of pressure conditions is being investigated.
- (iv) Major modifications have been made in the integration of GC-MS routines with Z-BASIC routines. These modifications have reduced run time from hours to minutes. The GC-MS macro creates one data input file for the whole spectrum and then passes to the Z-BASIC program for execution thus making only one call instead of a call for each scan.
- (v) From probable structures, peak integration data and relative abundance, z-type distribution can be calculated. Routines to obtain z-type distribution are in place and debugged. The z-type report also includes distribution with retention times. The main objective is to track z-types in separation fractions. Refinements will be made and results will be reported in the next quarter.

The analytical procedures development has progressed and being completed as planned. The phase -II work will take advantage of the phase-I analytical tools for better design, operation and monitoring of process units.

Task 4.

The market research and product identification task is nearing completion as required by phase-I. Samples have been submitted to an industrial agrochemical company (company A) for activity testing according to our negotiated agreements. Results from activity testing will be reported later.

Based on the phase-I results, two process sequences have been developed for phase-II and reported in task-7. The target product slate consists of value-added chemicals from polar fractions and valuable products from non-polar fractions.

For specialty polar products, the process sequence to be piloted in phase-II involves how much processing should be done prior to marketing. Is there a market for broad-range concentrates or must these concentrates be processed to pure compounds. As reported in the previous quarterly reports, markets already exist for pure compounds derivable from shale oil. But, the project could be simplified if we could show technically how pure compounds can be derived and then to market concentrates and technology to an established chemical producer. Present marketing efforts with chemical companies will provide a clearer direction within the next few months.

Based on material balances and cost analysis, profitability evaluation will be made for these two process sequences (figures 7.1 and 7.2) to establish a reasonable selling price

for the product slate or cost of production plus margins. While the definitive answer will not come until phase-III, this preliminary analysis will help to address markets.

We have conducted on-line data base search for target chemicals/compounds and accumulated data need to be evaluated and compiled to devise market strategy. These summaries will be reported in the next quarter.

Task 5.

During this quarter, separations exploration work has been completed on 275 - 400 C fraction. Design limitations of liquid-liquid extraction system have hindered the progress of separations of 400 +C fraction. Details of this work are presented below.

275-400 C Distillate Fraction: A six-stage extraction of 275 - 400 C distillate fraction has been completed. Process variables for this extraction include solvent to oil and water to solvent ratios. Table 5.1 shows operating conditions and normalized yields. The yield of extract, in genera, is proportional to the solvent to oil ratio.

Table 5.1: Liquid-Liquid Extraction of 275 - 400 C Shale Oil Fraction

	Run #			
	1	2	3	4
Solvent	MeOH + 2%H ₂ O	MeOH + 2%H ₂ O	MeOH + 2%H ₂ O	MeOH
Solvent/Oil	1.94	1.66	1.14	0.94
Extract%	34	35	28	40
Raffinate%	66	65	72	60

Results show approximately 2/3 to 1/3 split toward the raffinate. Noticeable difference is observed when solvent is used without water. Overall material balances are good. Raffinate fractions retained an extremely small percentage of methanol suggesting that the partition was quite sharp. Elemental analysis and GC-MS analysis have been conducted on both extracts and raffinates.

Table 5.2 shows results of elemental analysis along with coefficients of separation. Results of elemental analysis show good partition of nitrogen types between extracts and raffinates. Sulfur compound types, as expected, are less influenced by the solvent system. Raffinate is low in nitrogen content (av. <.45%) while extract is high in nitrogen (av. >2.3%) and agrees with feed nitrogen of 1.1 from material balance calculations.

Coefficients of separation (CS) have been calculated using the same methodology as presented in the 2nd quarterly report. Values for CS range from 0.47 to 0.57 which are, as

expected, better than bench scale separations (with an average value of .35). Six stage extractions have increased the partition of nitrogen types. However, the effectiveness of the solvent system is dropping as fractions become heavier (i.e. effect of molecular weight) which is indicated by CS (68 for 200 -275 C vs 57 for 275 - 400 C). This trend will be confirmed with extraction results from 400 +C fraction.

Table 5.2: Results of Extraction of 275-400° C Distillate Fraction

<i>Solvent/Oil</i>	<i>Fraction(%)</i>	<i>Carbon</i>	<i>Hydrogen</i>	<i>Nitrogen</i>	<i>Sulfur</i>	<i>CS</i>
1.94	E(34)	82.72	10.42	2.47	1.07	56.80
	R(66)	85.23	12.70	0.37	0.88	
1.66	E(35)	82.27	10.51	2.55	1.09	51.70
	R(65)	85.36	12.66	0.44	0.93	
1.14	E(28)	81.75	10.54	2.60	1.08	56.79
	R(72)	85.25	12.54	0.45	0.95	
0.94	E(40)	82.87	10.81	2.34	1.12	47.73
	R(60)	85.33	12.68	0.44	0.88	

The total ion chromatograms of extract and raffinate from run #1 are shown in figures 5.1 and 5.2. The chromatograms show differing selectivities to specific peaks. A superimposed section of the chromatograms is given figure 5.3 showing variations in concentrations of compounds in the region portrayed. Figures 5.4 and 5.5 provide the fragmentation pattern (70 eV) for the peaks at 42.3 minutes of the extract and raffinates respectively. The patterns show significantly different fragmentations between the extract and the raffinate.

As a next step, partition function analyses were run on specific chromatographic peaks. Table 5.3 shows an example of this partitioning. Higher numbers indicate a preference for the extract. Lower numbers show preference for the raffinate. If a peak is missing in one or the other mass spectrum, the program assigns an E or R to designate in which fraction the fragment was found.

Table 5.3 : An Example of Partition Function Analysis

Extract = 48.89, Raffinate = 48.955

m/z	Partition	m/z	Partition	m/z	Partition	m/z	Partition
27	E	28	1.0035	29	1.4430	32	1.2374
39	E	41	0.8714	43	0.6155	51	E
55	0.8407	57	0.5590	63	E	65	E
67	0.985	69	1.0536	70	R	71	0.8447
76	E	77	1.7185	79	0.9882	81	0.6456
82	1.4892	83	1.0277	84	1.4704	85	1.2971
91	1.5924	95	0.6627	96	R	97	0.8237
105	2.1451	106	E	107	E	109	0.6512
110	R	111	1.2913	115	1.9518	116	E
117	E	119	E	120	E	121	E
123	1.0614	127	2.1099	128	2.1149	129	2.0969
130	E	131	E	132	E	134	E
135	E	136	E	137	E	139	1.4739
141	1.9804	142	E	143	E	144	E
145	E	146	E	147	E	149	E
150	E	151	1.5757	152	1.7959	153	1.9273
154	2.0879	155	2.1546	156	2.3941	157	1.4074
159	1.6626	160	E	161	E	162	E
163	E	164	E	165	1.3545	167	E
169	2.0689	170	2.0021	171	2.3701	172	E
173	1.0365	174	E	175	E	176	E
179	R	188	E	189	E	216	E

Attempts have been made to analyze the chromatograms using Z-BASIC analysis. As described earlier in task 3, the decision making criteria needs refining to obtain meaningful assignments for peaks and calculate z-type distribution. Results of the Z-BASIC analysis will be reported in the next quarter.

400+ C Distillate Fraction: Attempts have been made to complete six-stage counter-current liquid extraction on 400 +C fraction with proven solvent systems in the laboratory. While the system operated as anticipated, it was not designed to handle waxy raffinate streams. Equipment modifications are being done to handle waxy raffinates and feedstocks from heavy fractions of shale oil. These modifications include choosing different pumps to operate at elevated temperatures to maintain good flow rates without choking the lines.

Work on extraction of resinous materials from 400+ C fraction showed encouraging results which warrant continuation in the similar direction. The details of extraction procedure are:

(a) The 400 +C fraction was solvent extracted with NMP to form an aromatic oil and a non-aromatic oil.

(b) The non-aromatic oil was then solvent dewaxed using 75:25 MEK:Toluene at -30 C. The solvent to oil ratio was 4:1.

The dewaxed oil was then analyzed for resin materials using GC-MS. Figure 5.6 shows TIC of resin concentrate from 400 +C fraction. The GC-MS analysis shows the presence of hopanes and hopenes. These compounds are useful in the printing and adhesive industries for their softening behavior, solubility, chemical compatibility and acid number. Numerous triterpenoids and their alcohol derivatives (principally hopanes and friedelanes) have been identified in coal derived chemicals and crude oils. One of these is 1,2,3,4-tetrahydro-2,2,9-trimethylpicene. Identification of such compounds in shale oil confirms our belief that this fraction of shale oil could be a valuable source for resinous materials.

Task 6.

The objective of conversions exploration is to select a process to convert higher molecular weight polar compounds to lower molecular weight species to enhance both marketability and value. Conversion response of shale oil fractions has been studied and reported (refer 4th quarterly) with several explorative analytical techniques such as TSR-GC/MS, TG/MS and Py-GC/MS. These studies have concluded that shale oil fractions can be easily dealkylated to lower molecular weight compounds.

Hydrovisbreaking experiments have been conducted on shale oil distillate fraction (400 +C). Alkylated nitrogen types have been effectively dealkylated by visbreaking process. These results were presented in the last quarterly report.

Main focus during this quarter was to evaluate thermal hydrodealkylation (THD) as a possible candidate process for conversion processing. The 400 +C shale oil distillate fraction has been used for the experiments. Figure 6.1 compares the total ion chromatogram (TIC) of the 400 +C fraction from total shale oil to the TIC of the THD product. Preliminary GC-MS analysis indicates that significant amount of material has been cracked to lower boiling constituents. Olefin peaks seen just before the paraffin peaks in the feed are missing in the THD product which indicates saturation of the molecules. In

the next quarter, compound type analysis will be conducted to estimate relative selectivity.

Other candidate processes include hydropyrolysis, hydrocracking and catalytic processes. The difference between hydropyrolysis and THD is the severity of operating conditions. It is possible, however, to convert the basic THD process development unit to hydropyrolysis unit if required. This is essentially the case with hydrovisbreaking. Catalytic processes are basically very sensitive to heteroatom types and their applicability to extract fractions, thus, are limited.

The foregoing analysis concludes that a generic THD unit will satisfy our requirements for dealkylation to produce valuable products from shale oil extracts. So, efforts in the next quarter will focus on the design and fabrication of THD unit at our facilities. This is an important step in the proposed process alternatives (see task 7). THD will help us reach the specification testing of products faster with minimum risk.

Task 7.

The prime objective of Phase-I research is to determine a plausible suite of products and a reasonable process sequence to achieve that product slate. Target high value products must necessarily include nitrogen heterocyclics because these are the types most prevalent in shale oil compared to other 'natural' sources of nitrogen types. Non-nitrogen high value products (waxes, solvents, resins etc.) are sought as secondary high value products.

To develop a reasonable process sequence to maximize the value of nitrogen compounds, several critical steps had to be taken. These are:

Analysis: How is the nitrogen distributed according to type and do the types present in the lower boiling fractions present in the higher boiling fractions as alkyl substituted parents. The answer to this latter question appears to be affirmative although new types (higher ring structures) are present in higher boiling fractions than in lower boiling fractions.

Separation: How selectively can the nitrogen types be separated from non-nitrogen types. The emphasis in this research has been on low cost, non-corrosive polar solvents eg. alcohols. Results of these studies are encouraging. Coefficients of separation of greater than 0.50 are achieved along with recoveries of >85% of nitrogen. Further, low cost separation of nitrogen types from non-nitrogen types provides upgrading for refinery feedstock at a cost which promises profitability for high value petroleum products as well.

Secondary separation processes, eg. adsorption(acid & base separation) and high-efficiency distillation appear practical when the feedstock concentration is high in target compounds and the number of isomers is small. This is achieved if the number of rings is limited to 1 or 2. Since these are also the products the market currently accepts focusing on fractionation of the <275 C components is a reasonable objective.

Conversions: While it may be possible to find markets for concentrates (feedstocks to the coal tar industries, solvents for agrochemicals, etc.), conversion of concentrates is important to assessing that there is a conventional market 'home' for the entire barrel. The analysis and chemistry point to thermal hydro-dealkylation (THD) as such a process.

In phase-I, thermalhydrovisbreaking has been completed to illustrate the fact that lower molecular weight pyridines can be produced from higher molecular weight fractions through THD (refer task 6). Correspondingly, THD is thought to be a key technology for shale oil value enhancement research. The contractor has nearly twenty years of experience in THD technology and will utilize this experience in optimizing the process in phase-II.

The foregoing considerations have been incorporated into the general process scheme approaches. One, labeled the simplified process minimizes the number of steps at the possible expense of selectivity (and yield). The other scheme, high selectivity takes advantage of pre-fractionation to improve yield and product quality.

Simplified Process: Figure 7.1 depicts the flow diagram for simplified process for extracting value-added chemicals from shale oil. This process sequence starts by subjecting the total shale oil to liquid-liquid extraction with a strong polar solvent. The polar fraction is then subjected to thermal hydrodealkylation (THD) to reduce molecular weight. The THD product is then extracted with a polar solvent to separate lower molecular weight polars from non-polars.

The polar stream is further separated according to compound types in a solid-liquid adsorption process such as ion-exchange chromatography, followed by high-efficiency fractionation into compounds and functional type concentrates. These product streams include bases such as pyridines and quinolines, acids such as phenols and carboxylic acids and neutrals such as indoles, pyrroles. Market needs will dictate if further processing such as crystallization or finishing processes are needed.

The non-polar stream is mixed with non-polars from the first extraction. This stream is distilled at 400 C to obtain a light fraction, premium refinery feedstock with low heteroatom content. The heavy fraction is subjected to NMP extraction followed by dewaxing to produce valuable petroleum products such as lube oils, aromatic oils and waxes.

The simplified process sequence is based on the concept of economic viability while maintaining required selectivities to produce valuable products. Preliminary shake test results show good partition with total shale oil. The viability of simplified process sequence will be tested in the next quarter.

High Selectivity Process: Figure 7.2 shows the flow diagram for high selectivity process for shale oil processing. The high-selectivity process sequence starts by fractionating the shale oil into four fractions i.e. <200, 200-275, 275-400 and 400 +C. Each fraction is then subjected to liquid-liquid extraction to separate the polars and non-polars individually.

The two heaviest polar fractions are then subjected to THD followed by flash distillation where it is flashed at 275 C and 275 + C fraction is recycled to extinction. The light product from flash distillation is then subjected to solvent extraction. The polar fraction is then mixed with -275 C polars. The description of down stream processing is similar to the illustrated in simplified process sequence.

The non-polar stream from -200 C is suitable as solvents. The non-polar stream with a boiling range between 275 - 400 C is sent to refineries for conventional refining. The 400 +C non-polar fraction is subjected to similar processing as described in simplified process scheme.

The high-selectivity process option, as indicated by its name, offers high selectivity with better control over separation processes in terms of process conditions and selection of solvent systems. However, the process complexity increases simultaneously. It is expected that selectivity and better yields will offset economic penalties.

Economic analysis and profitability estimates will be conducted on these two alternatives, when material balance data become available. In phase-II, we will examine these two alternatives to devise a preferred scheme. The units for phase-II are listed in table 7.1. These units will be modeled as process data are obtained.

Table 7.1 Unit Operations for Phase-II

Unit	Status
Distillation	Existing and requires no modifications
Liquid-liquid Extraction	
Polar Solvent	Existing unit needs modifications to handle heavy feeds
NMP	Same unit - no modifications
THD	To be designed and fabricated in coming months
Adsorption	To be designed and fabricated in phase-II
High-Efficiency Fractionation	Equipment selected and needs to be ordered
Flash Distillation	Prototype exists and easy to fabricate

Objectives for the Next Quarter

- Complete liquid-liquid extraction runs on 400+ C fraction.
- Obtain preliminary mass balance data for alternate process sequences for Phase-II work.
- Develop, design and fabricate thermalhydrodealkylation facility to aid in conversion processing of heteroatom concentrates.
- Contact and present the project business plan to potential phase-III partners.
- Conduct economic analysis of two process sequences.
- Initiate phase-II design and development work for batch PDU operation.

File : C:\HPCHEM\1\DATA\SPXEXT01.D
Operator : Jerry
Acquired : 5 Aug 94 6:13 pm using AcqMethod SO93_66B
Instrument : 5972 - In
Sample Name: SPX-94-99, 4589 mg/L Methanol
Misc Info : Extract - 1.9/1 MeOH+2%H2O; 275-400 C
Vial Number: 1

Figure 5.1

File : C:\HPCHEM\1\DATA\SPXRAF01.D
Operator :
Acquired : 4 Aug 94 4:07 pm using AcqMethod S093_66B
Instrument : 5972 - In
Sample Name: SPX-94-100, 4553 mg/L hexane
Misc Info : Raffinate - 1.9/1 MeOH+2%H2O; 275-400 C
Vial Number: 1

Figure 5.2

File : C:\HPCHEM\1\DATA\SPXEXT01.D
Operator : Jerry
Acquired : 5 Aug 94 6:13 pm using AcqMethod S093_66B
Instrument : 5972 - In
Sample Name: SPX-94-99, 4589 mg/L Methanol
Misc Info : Extract - 1.9/1 MeOH+2%H2O; 275-400 C
Vial Number: 1

Figure 5.3

File : C:\HPCHEM\1\DATA\SPXRAF01.D
Operator :
Acquired : 4 Aug 94 4:07 pm using AcqMethod S093_66B
Instrument : 5972 - In
Sample Name: SPX-94-100, 4553 mg/L hexane
Misc Info : Raffinate - 1.9/1 MeOH+2%H2O; 275-400 C
Vial Number: 1

Figure 5.4

File : C:\HPCHEM\1\DATA\SPXEXT01.D
Operator : Jerry
Acquired : 5 Aug 94 6:13 pm using AcqMethod S093_66B
Instrument : 5972 - In
Sample Name: SPX-94-99, 4589 mg/L Methanol
Misc Info : Extract - 1.9/1 MeOH+2%H2O; 275-400 C
Vial Number: 1

Figure 5.5

File : D:\DATA\SO9367A\94_5001.D
Operator : Don
Acquired : 12 May 94 10:03 am using AcqMethod SO9367A
Instrument : 5972 - In
Sample Name: spx16-94-50 7940 ng/ul in tol
Misc Info : H.P. prod from 93-67
Vial Number: 1

Figure 6.1

Figure 7.1 Flow Diagram - Simplified Process

Figure 7.2 Flow Diagram - High Selectivity Process