Shale Oil Value Enhancement Research

Quarterly Report March 1 - May 31, 1994

By
James W. Bunger, Ph.D.
C.P. Russell, Ph.D.
P.A.V. Devineni, Ph.D.
D.E. Cogswell, M.S.
J. W. Wiser, B.S.

RECEIVED
MAR 17 1997
OSTI

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, Inc.
P. O. Box 520037
Salt Lake City, Utah 84152-0037

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

dy

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Summary Management Report

RECEIVED
ACQUISITION SERVICES

Activities during this quarter focused on integrating the various tasks and elements. During Phase-I, substantial effort was placed on designing and automating the identification of molecular types present in shale oil. The ability to know the molecular composition and to track a given "target" species through the initial concentration steps was deemed critically important to the ultimate success of the three-phase project. It has been this molecular tracking ability that clearly distinguishes the JWBA work from prior shale oil research. The major software and hardware tasks are not in place to rapidly perform these analytical efforts. Software improvements are expected as new questions arise.

The existence of the major nitrogen and oxygen types in shale oil has been confirmed. Most importantly, the ability to convert higher molecular weight types to lower molecular weight types was preliminarily confirmed in the present quarter. This is significant because it confirms earlier hypothesis that values are found though out the boiling range. Potential yields of extremely high value chemicals, e.g., \$1000 /bbl of upto 10% by weight of the barrel remain a feasible objective.

Market and economic assessment continue to show encouraging results. Markets for specialty and fine chemicals containing a nitrogen atom are expanding both in type and application. Initial discussions with pharmaceutical and agrochemical industries show a strong interest in nitrogen-based compounds.

Major progress was made during this quarter in completing agreements with industry for testing of shale oil components for biological activity. Positive results of such testing will add to the previously known applications of shale oil components as pure compounds and concentrates.

During this quarter, we will formulate the pilot plant strategy for Phase-II(a). Process steps will be comprised of distillation (both fractional and thin-film), liquid-liquid extraction, thermal hydroprocessing, catalytic hydroprocessing, solvent dewaxing/deasphalting, adsorption processing and derivitization/functionalization. Several of these pilot plants are already in place, others will be designed and constructed in phase-II(a).

Technical Progress Report

RECEIVED
ACQUISITION SERVICES

Objectives

94 JUL -5 AM 11:07

Objectives for the quarter were:

- ▶ Complete solvent selection for liquid-liquid extraction of shale oil fractions
- ▶ Use peak identification routines on shale oil extracts of heavy fractions for completion of compound type analysis
- ▶ Summarize market research data for target chemicals
- ▶ Develop specific process sequence based on target products
- ▶ Analyze candidate processes for dealkylation
- ▶ Continue marketing efforts to major companies
- ▶ Complete economic analysis model

Discussion

Task 1.

NEPA task has been completed.

Task 2.

Separations characterization task is almost completed. This effort is continued under separations exploration task.

Task 3.

During this quarter, major emphasis was given to completion of the analytical methodology development task which include (a) model for calculation of partition coefficient distribution for continuous liquid-liquid extraction system, (b) Z-NUM software development and testing for low-voltage mass spectroscopy, (c) extension of BP-MW data base. With these analytical tools, for the first time it is now possible to characterize shale oil fractions according to compound types and identification of heteroatom molecules from separations followed by GC-MS analysis. These methods and tools, though exclusively developed for shale oil, are applicable to other hydrocarbon resources.

A. Partition Coefficient Model for Liquid-Liquid Extraction System

A model has been developed to simulate liquid-liquid extraction system based on the

distribution of partition coefficient 'k'. Details of the distribution of partition coefficient were reported in the third quarterly report. The k-distribution which is used to characterize feed as well as raffinate and extract phases at each tray of extraction is similar in concept to the simulated distillation used in the modeling of distillation column. The total area for the k-distribution is equivalent to the total number of moles of oil in the stream.

The k-distribution data from methanol extractions of 200-275 °C fraction (refer to third quarterly report) is used as input to the model. The effect of solvent to oil ratio on extractions is also taken into account by the model for tray calculations. Figure 3.1 helps to explain the results of computer simulation model of liquid-liquid extraction.

Table 3.1 shows results of k-distribution output for various solvent to oil ratios at 80% tray efficiency.

Table 3.1: Results of Computer Simulation of Counter Current Liquid-Liquid Extraction
(200 - 275 °C Shale oil Extraction with Methanol, Tray Efficiency = 0.8)

Solvent/Oil	#of Stages	$K'_{\max}$ Raffinate	$K'_{\max}$ Extract	$R_{\max}$	$K'_{1/2}$
1.0	3	.46	.67	.59	.57
	5	.45	.67	.63	.60
	10	.45	.67	.64	.61
1.5	3	.41	.65	1.43	.61
	5	.41	.66	1.67	.68
	10	.41	.67	1.85	.70
2.0	3	.38	.64	2.41	.62
	5	.38	.66	3.12	.70
	10	.38	.67	3.93	.76
2.5	3	.37	.63	3.10	.61
	5	.36	.65	4.39	.71
	10	.37	.67	6.15	.79
3.0	3	.36	.63	3.44	.62
	5	.36	.65	5.21	.71
	10	.36	.67	7.81	.80

$K_{\max}^*$ = K^* value where the distribution is at a maximum (refer figure 3.1a)

$K_{1/2}^*$ = K^* value where the extract/raffinate ratio is half its maximum value (figure 3.1b)

$R_{\max}$ = Ratio of extract to raffinate for components with the highest partition coefficient

The results shown in table 3. 1 indicate that solvent/oil ratio, as expected, has influence on the relative shift of k-distribution between the raffinate and the extract. but this ratio is less influenced by the number of stages. A measure of separation of the most polar components is represented by $R_{\max}$ value. As indicated, it increases with both solvent/oil ratio increase and increase in number of stages. These trends are consistent with the expected performance of liquid-liquid extraction units.

Using the model: (a) stage efficiencies and k-distribution for feed can be calculated using the data from actual runs, (b) operating conditions can be obtained for a desired separation and products of interest and (c) design of liquid-liquid extraction columns for a given system.

B. Z-NUM Software for Peak Comparison

Z-NUM software is the analytical procedure by which the computer assigns a probable type to a parent mass of a known retention time. In Z-NUM, the integrated chromatogram is used to select the scan number corresponding to the maximum intensity of the integrated interval. The mass spectrum is examined beginning with the heaviest mass. The possible empirical formulas of that mass are calculated. Using an overall elemental composition of the mixture, a statistical probability is assigned to each formula. This process is repeated until a mass is encountered which is outside of the feasible region for a parent mass, i.e., the mass number is due to the fragment.

For each mass number, boiling points are calculated based on molecular weight and retention time databases. The methodology is explained in detail in the fourth quarterly report. Table 3.2 shows the Z-NUM output for the extract peak at 23.33 minutes whereas table 3.3 shows that of raffinate at 25.64 minutes retention time. Figure 3.2 shows corresponding segment of the chromatograms for an extract and a raffinate.

In figure 3.2, the partitioning of components between extract and raffinate is evident. Z-NUM will provide a rapid output of probable types. Table 3.2 shows that there are five ions in the 'feasible region'. These are: 146, 136, 135 134 and 131. The most intense ion is 135 (67.63% of full scale). The most probable types based on elemental analysis is the alkyipyridine series and an agreement index of six is observed for this type. Table 3.3 shows that three ions: 165, 151 and 148, that are in the feasible region. For the 166 ion, the most probable type is an alkyldecalin, $z=-2$. The boiling point database, at this time, does not include this type. The 151 peak is attributed to an alkylpyrrole and the 148 peak is attributed to an alkylbenzene. The agreement index for this latter type is 10.

Table 3.2: Z-NUM Output for Extract at Retention time of 23.33 minutes
(200 - 275 °C Shale Oil fraction)

RT (Min.) C	Mass# H	%Rel. Abun. #Z#N#O#S	Prob.	Quality	BPM	BPR
23.33	146	2.23				
11	14	-8N0O0S0	9.20e-01	1.0	222.1	204.7
9	10	-8N2O0S0	3.50e-03	U	na	na
10	10	-10N0O1S0	5.30e-02	U	na	na
8	18	2N0O2S0	4.60e-03	U	na	na
8	18	2N0O0S1	1.40e-02	U	na	na
9	6	-12N0O0S1	2.80e-03	U	na	na
7	14	0N0O1S1	1.30e-03	U	na	na
23.33	136	7.23				
10	16	-4N0O0S0	9.90e-01	U	na	na
8	12	-4N2O0S0	4.70e-03	U	na	na
9	12	-6N0O1S0	8.00e-02	2	229.0	216.3
8	8	-8N0O2S0	1.40e-03	U	na	na
8	8	-8N0O0S1	6.90e-03	U	na	na
23.33	135	67.63				
9	13	-5N1O0S0	9.20e-01	6	189.0	208.0
8	9	-7N1O1S0	4.40e-02	U	na	na
9	5	-9N1O0S1	2.00e-03	U	na	na
23.33	135	11.64				
10	14	-6N0O0S0	9.90e-01	5	183.9	202.0
8	10	-6N2O0S0	3.60e-03	U	na	na
9	10	-8N0O1S0	6.20e-02	U	na	na
8	6	-10N0O0S1	3.80e-03	U	na	na
23.33	131	3.16				
9	9	-9N1O0S0	7.80e-01	0	265.7	227.3
6	13	1N1O2S0	4.00e-03	U	na	na
6	13	1N1O0S1	1.60e-02	U	na	na

Table 3.3: Z-NUM Output for Raffinate at Retention time of 25.64 minutes
(200 - 275 °C Shale Oil fraction)

RT (Min.) C	Mass# H	%Rel. Abun. #Z#N#O#S	Prob.	Quality	BPM	BPR
25.64	166	6.21				
12	22	-2N0O0S0	7.40e-01	U	na	na
13	10	-16N0O0S0	1.60e-01	U	na	na
10	18	-2N2O1S0	6.60e-03	U	na	na
11	18	-4N0O1S0	9.20e-02	U	na	na
10	14	-6N0O2S0	3.30e-03	U	na	na
10	14	-6N0O0S1	2.80e-03	U	na	na
25.64	151	4.45				
10	17	-3N1O0S0	9.20e-01	1	225.2	222.3
8	13	-3N3O0S0	1.40e-03	U	na	na
9	13	-5N1O1S0	7.10e-02	U	na	na
8	9	-7N1O2S0	1.30e-03	U	na	na
8	9	-7N1O0S1	5.40e-03	U	na	na
25.64	148	6.61				
11	16	-6N0O0S0	9.90e-01	10	206.3	209.3
9	12	-6N2O0S0	4.90e-03	U	na	na
10	12	-8N0O1S0	7.50e-02	U	na	na
9	8	-10N0O2S0	1.20e-03	U	na	na
9	8	-10N0O0S1	5.60e-03	U	na	na
7	16	2N0O1S1	1.20e-03	U	na	na

Partition Ratio : The partition ratio calculator compares the intensity of data taken from an extract analysis and a raffinate analysis. The calculator can be applied to either the integration data (area ratios) or the mass data on an ion-specific basis (intensity ratios).

Table 3.4 provides area ratio data for the same peaks as shown in tables 3.2 and 3.3. As observed, that the peak at about 23.4 minutes partitions more strongly into the extract (R=6.6, 1.0 = equal partitioning). At 25.6 minutes, the peak partitions more strongly in the raffinate (R = 0.54). This agrees with basic chemistry principles which would predict that

alkylpyridines, which are polar molecules, would partition toward the polar extract and decalins and alkylbenzenes, non-polar hydrocarbons, would partition toward the raffinate.

Table 3.4

Raffinate Peak#	Retention Time	Area	Extract Peak#	Retention Time	Area	Area Ratio
105	23.42	5.6E5	99	23.37	3.5E6	6.60
116	25.54	2.9E6	109	25.54	1.5E6	0.54

However, we saw from Z-NUM that these peaks may constitute a mixture of unresolved compounds. These mixtures may be resolved by examining the mass spectra on an ion-by-ion basis (for a given scan). A partition ratio can be calculated on an ion basis. Mass spectra for the two cases discussed above are given in figures 3.3 and 3.4 respectively. Ion-by-ion results provide behavioral proof of compound type identification. The synergism between separations and analysis is evident.

C. Extended Boiling Point- Molecular Weight Database

Preliminary results of Z-BASIC analysis of shale oil fractions with low-voltage GC-MS has shown the need for extending BP-MW database. Previously, the database consisted of 14 z-series for molecular weight and retention time based boiling points. In the phase-II of the shale oil research, retention time database will be extended. The extended database has been incorporated in the Z-NUM software for peak identification and matching.

BP-MW and BP-RT time databases are arranged according to 'z' vector ($C_nH_{2n+z}N_uS_vO_w$). However, each z-vector may correspond to several parent compounds (i.e. sub-classes). Boiling point data for various parent compounds are obtained from the literature and then prediction methodologies are used to generate data for the homologous series. Correlation constants are calculated by regression analysis and then used in the database.

At present, the database consists of 89 z-vectors encompassing a total of 273 parent compounds. Table 3.5 lists database compound types that are unassociated ring systems. Table 3.6 shows database compound structures that are of ring types. Table 3.7 is the output of the program with the extended database for a molecular weight of 269. These results show subclasses of z-vector along with calculated boiling points using BP-MW database. When BP-RT database is completed, this method of comparison offers valuable information for peak identification and can be an effective tool.

Table 3.5: Compound Types without Ring Systems

Paraffins	Ethers
Alkenes	Ketones & Aldehydes
Amines	Carboxylic Acids
Nitriles	Thiols
Alcohols	Sulfides

Table 3.6: Compound Types with Ring Systems

Cyclopentadiene	Benzene	Diphenylmethane
Pyrrole	2,3-Dihydroindole	Pyridine
Aniline	Diphenylamine	Furan
2,3-Dihydrobenzofuran	Phenol	Diphenylether
Benzoic Acid	Benzaldehyde	Thiophene
Thiophenol	Diphenylsulfide	2-Pyridol
2-Hydroxypyrrole	Pyridines,2-mercapto	2-Pyridinecarboxaldehyde
2-Pyrrolecarboxaldehyde		Pyrrole, 2-mercapto

Table 3.7: ZNUM Output for Molecular Weight 269

Formula	Z-Number	Prob.	Match Index	BP-MW	BP-RT	Structure
C19H27N	-11	4.00e-01	9	400.3	388.9
C19H27N	-11	4.00e-01	U	441.1	na
C19H27N	-11	4.00e-01	U	422.5	na
C19H27N	-11	4.00e-01	U	432.1	na
C19H27N	-11	4.00e-01	U	370.4	na
C19H27N	-11	4.00e-01	U	421.6	na
C19H27N	-11	4.00e-01	U	423.7	na
C19H27N	-11	4.00e-01	U	392.0	na
C19H27N	-11	4.00e-01	U	427.5	na
C19H27N	-11	4.00e-01	U	390.7	na

C20H15N	-25	2.50e-02	U	470.9	na
C16H35N3	3	2.30e-03	U	na	na	
C17H23N3	-11	1.50e-03	U	na	na	
C17H35NO	1	7.50e-02	U	na	na	
C18H23NO	-13	4.70e-02	U	513.9	na
C18H23NO	-13	4.70e-02	U	459.7	na
C18H23NO	-13	4.70e-02	U	400.5	na
C18H23NO	-13	4.70e-02	U	395	na
C18H23NO	-13	4.70e-02	U	413.1	na
C18H23NO	-13	4.70e-02	U	462.1	na
C16H31NO2	-1	6.00e-03	U	na	na	
C17H19NO2	-15	1.70e-03	U	na	na	
C16H31NS	-1	3.80e-02	U	na	na	
C17H19NS	-15	1.40e-02	U	456.9	na
C17H19NS	-15	1.40e-02	U	423.7	na
C17H19NS	-15	1.40e-02	U	498.6	na
C15H27NOS	-3	5.80e-03	U	na	na	

Task 4.

Major accomplishments during this quarter include:

- negotiated agreements with 3 major pharmaceutical/agrochemical companies to test shale oil for biological activity;
- completed business plan for shale oil value-added chemical venture;
- completed compilation of market data on target compound types;

JWBA has negotiated agreements with major pharmaceutical/agricultural companies to conduct activity testing of shale oil fractions. These tests are designed to evaluate the biological activity of shale oil fractions for use as biocides and herbicides. As shale oil contains nitrogen functionalities that may be similar to conventional biocides, the opportunity exists for exploration. The biological activity potential of shale oil has never been studied. If these tests are positive, shale oil may become a potential raw material for agricultural chemical intermediates. These results are expected before the initiation of phase-II.

Marketing efforts will be continued to generate interest with major chemical companies. A business plan has been completed based on the available information from phase-I data. The main purpose of this business plan is to explain the economic opportunity of 'shale oil based value-added chemicals'. At present, we have submitted the business plan to a major specialty chemical company for their review. Other chemical companies will be actively pursued in the near future.

Sinor consultants has submitted a report of findings regarding the market opportunities for the target chemicals. Production cost data for target chemicals is difficult to obtain, but efforts are continuing to search other financial databases. A brief description of the market information for target chemicals is summarized:

Carboxylic Acids: Uses for alkylcarboxylic acids also known as fatty acids include lubricants, polymers and plasticizers. Hydrocarbon based fatty acids are used in alkyd resins and as plasticizers in the rubber industry. Applications for higher fatty acids and their derivatives include surface-active agents and synthetic detergents. These markets are growing at an annual rate of 3%. Low-end market prices are at least \$100/bbl.

Indoles: Indoles are primarily used in pharmaceuticals and perfume industries. Indole derivatives of commercial value include: indole and skatole(perfume base), indigoid (dyes and pigments), indole-3-acetic acid (plant hormones), and reserpine (tranquillising agent). Current price is at \$60 /kg. The many and varied pharmacological effects of indole derivatives known already makes continued growth of applications in this area likely. Medicinal chemicals are a strong growth area.

Carbazoles: Carbazole and its derivatives are primarily used as photographic chemicals. Among carbazole compounds, the practical application for the polymer n-vinylcarbazole, which is a photoconductive substance, has been of particular significance. It is one of the photosensitive substances which can be used as the photoactivator in xerography. Market information for carbazoles is rather limited due to very few producers.

Pyridines: Numerous pyridine and its derivatives are the building blocks for commercially important compounds which include niacin, vinylpyridine and pyriothione salts. Pyridines are mainly used as agricultural chemicals and pesticides. Market for pyridine has grown approximately 2% per year. Current prices for pyridines range from \$1.2-2.2 per lb. Annual capacity of 60 million pounds is shared between Reilly and Nepera industries.

Phenols and Naphthols: Phenols are categorized as a high volume chemical in this class. The four principal markets for phenols are nonionic surfactants, phenolic resins, polymer additives and agrochemicals. United States phenol production capacity is approximately 4 billion pounds per year. The market growth has been 3-4% per year and is expected to continue at the same rate. Market for phenolic resins and bis-phenol is especially strong. Currently, phenol prices range from \$ 0.30 to 0.40 per pound.

Quinolines: Quinoline and its derivatives have a wide variety of applications. They are used in antioxidants, corrosion inhibitors, pesticides, catalysts and electroplating processes. Annual demand for quinoline is in the order of 200 tons. Its current price is about \$1.5 per pound. Market demand for quinoline will remain at the same level.

Pyrroles: Commercially important derivatives of pyrrole include 2-pyrrolidone and 1-methyl-2-pyrrolidone(NMP). The largest use of NMP is in the extraction of aromatics from lube oil but it is also used in the recovery of aromatics from mixed feedstock. The practical application of pyrroles is heavily centered on the pharmaceutical area. The production capacity of pyrrole is estimated at 24,000 tons. The current price of pyrrole is about \$1.25 per pound.

Related end-use markets are also examined which include adhesives, antioxidants, dyes, pesticides, and hydrocarbon resins. Shale oil derived chemical intermediates and concentrates are ideal candidates to these markets. In the Phase-II of the program, these markets will be explored through product introduction.

Task 5.

During this quarter, separations exploration was continued with various solvents at laboratory scale. Extract and raffinate fractions are characterized for compound types of interest. Dielectrophoresis, a novel separation process, has been developed and tested for the separation of polar compounds.

A formic acid extraction was conducted to evaluate its effectiveness in separating polar compounds from total shale oil. Preliminary results are encouraging. The yield of extract is about 30% of the total shale oil when extracted with 90% formic acid. Elemental analysis

results show efficient partition of nitrogen compounds. The extract phase is very complex in nature and analysis requires the characterizational tools under development.

Continuous counter-current liquid-liquid extraction will be performed on 275-400 and 400+ °C fractions followed by acid-base separations in the next quarter. These fractions will be characterized for compound types of interest and their partition behavior. Ion exchange resins will be used for acids, bases and neutral separations. The raffinate will be extracted to separate aromatic oils and then dewaxed to recover valuable waxes.

Dielectrophoresis: Dielectrophoresis is the migrational motion of polar neutral matter caused by polarizational effects in a nonuniform electric field. The neutral object under the influence of Dielectrophoresis tends to move steadily into a region of higher field intensity no matter which electrode is charged positive and which is negative. On the other hand, the charged body, if under only the influence of Dielectrophoresis will be attracted toward the electrode of opposite polarity.

The molecular movements may result either from permanent dipoles in a spatially varying field or from the van der Waals forces. Equations governing these movements are well postulated from basic principles. According to the Debye equation:

$$P = P_e + P_a + P_p$$

where:

P = total polarization

P_e = electronic polarization

P_a = atomic polarization

P_p = polarization due to permanent dipole

$P_e + P_a$ corresponds to the polarization of those constituents whose field is determined by the van der Waals forces. The non-polar molecules are composed of $P_e + P_a$. On the contrary, if the molecules are polar, association of permanent molecule dipoles makes a great difference to the value of total polarization.

Based on the fundamental principles, a preparative scale Dielectrophoresis apparatus was constructed as shown in figure 5.1. The main system is composed of two tube electrodes which have different diameters and a nylon membrane between two electrodes. The power source is capable of supplying a high voltage of 10kv to the system. Online gas chromatograph is used for analysis of the products.

Figure 5.1

Preliminary results with a Hexane-Methyl Ethyl Ketone show 2:1 enrichment in polar compound concentration in a single pass. Its low power dissipation compared to electrophoresis values suited for large scale, inexpensive separations. In the next quarter, the efficiency of dielectrophoresis system will be measured with shale oil fractions.

Task 6.

A key part of the phase-I research was to show that nitrogen compounds present in the higher molecular weight range were convertible to lower molecular weight species. An unknown of this fraction was the level of polycondensation of aromatic ring systems. If the ring systems were highly condensed, then conversion would be difficult.

In prior work JWBA had projected that the nitrogen was not present in highly condensed systems. The projections were based on the properties of homology seen in the z-basic analysis and the fact that the hydrogen/carbon/nitrogen relationships could not allow very much aromaticity.

Figure 6.1 & 6.2 show the 135 specific ion chromatograms from the +400 °C residue and a hydrovisbreaker liquid produced from that residue. The 135 ion is characteristic of alkylpyridines and is prevalent in all fragmentation patterns containing pyridines. The EIC shows numerous pyridine molecules have been created at less than 100 minute residence time that are not present in the original feed. 100 minute residence time is equivalent to about n-C₂₅ in boiling point.

During the next quarter we will quantify the specific nitrogen types, using our automated z-basic analysis. During phase-II(a) we will propose hydrovisbreaker products in large enough quantities that extraction and purification of these nitrogen types can (and will) be performed.

Task 7.

During this quarter, process and economic strategies have been finalized for the target products of shale oil. This strategy is explained in the following paper to be presented at the Washington, D.C. ACS conference in August, 1994.

An economic analysis model has been automated to conduct routine tasks such as sensitivity analysis and plotting. As more data become available for specific process sequences, profitability analysis will be conducted and estimates will be revised. Process modeling tasks are continued from the laboratory data. It is anticipated that process simulation will be conducted in phase-II based on the PDU operation data.

At the conclusion of Phase-I effort, a conceptual PDU flow diagram for shale oil value enhancement research will be developed and operating parameters will be decided. A preliminary profitability analysis will be presented in the final report.

Objectives for the Next Quarter

- 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

↓
cycled
as
separate
conf
paper

DE97006002

Figure 3.1

(a)

F

$$R = \frac{F(\text{extract})}{F(\text{raffinate})}$$

(b)

Shale Oil

Figure 3.2

Figure 3.3

Figure 3.4

File : D:\DATA\S09367B\94_019.D
Operator : Don
Acquired : 13 Jan 94 12:18 am using AcqMethod S09367A
Instrument : 5972 - In
Sample Name: spx12-93-67 in Toluene
Misc Info : 400 degree + cut from 93-11
Vial Number: 6

Figure 6.1

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 6.2