Shale Oil Value Enhancement Research

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

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Summary Management Report

The first year of this effort was focussed on the following broad objectives:

- ▶ Analyze the molecular types present in shale oil (as a function of molecular weight distribution);
- ▶ Determine the behavior of these molecular types in liquid-liquid extraction;
- ▶ Develop the analytical tools needed to systematize the process development;
- ▶ Survey the markets to assure that these have high value uses for the types found in shale oil;
- ▶ Explore selective process means for extracting / converting shale oil components into concentrates of potentially marketable components;
- ▶ Compile overview of the venture development strategy and begin implementation of that strategy;

Each of these tasks has been completed in sufficient detail that we can now focus on filling in the knowledge gaps evident from the overview.

Status

Task-1: NEPA

NEPA requirements for the laboratory-scale processes have been examined in detail and qualify for a categorical exclusion-B as a small generator. This information has been submitted and the task is completed.

Task-2: Separations Characterization

Analysis of the heteroatom distribution of fractions obtained by distillation, extraction and adsorption confirm our projections of high concentrations of valuable products and have identified those regimes providing the greatest economic promise. Partition behavior of heteroatom types demonstrate that it will be possible to separate shale oil along the compound-type class lines needed to manufacture an identified slate of products. The task is 90% completed.

Task-3: Analytical Procedures and Characterization

To rapidly monitor separation processes, methodologies have been successfully developed which include Z-BASIC characterization, boiling point calculations and thermodynamic properties estimation. These methodologies have been extended to the higher boiling regimes and for the first time provides a molecular profile of these residual

materials . The task is 85% completed and remainder of the work will focus on integrating Z-BASIC methodologies with GC-MS software.

Task-4 Market Research and Product Identification

Specialty and commodity chemical markets exist for all of the target compounds and compound types identified. All these compounds sell for \$100 - 1000 /bbl. Demand for these chemicals is high enough to support a shale oil facility of 5000 BPSD without disrupting the market structure. The specialty chemical market is expected to grow at 5% per year. The U.S. is currently importing raw materials and finished products in several target market areas. The task is 70% completed.

Task-5 Separations Exploration

Low-cost processes have been identified for key product separation steps. Maximum use of distillation and liquid-liquid extraction have been employed. Thermodynamic modeling promises to lead to new process options for a shale oil value-enhancement venture. This task is 50% completed. In the remainder of the task, we will focus on formulating the most direct and least costly means for separating shale oil into the desired polar and non-polar concentrates.

Task-6 Conversions Exploration

Hydrodealkylation holds great promise for conversion of higher molecular weight nitrogen-containing structures to lower molecular weight products with greater market demand. Initial results of hydrovisbreaking have shown that these types are dealkylated to form lower molecular weight analogs without the formation of coke. The task is 40% completed. In the remainder of this task, attention will be paid to the process conditions regime most likely to improve yields of desirable nitrogen heterocyclics.

Task-7 Process Modeling and Preliminary Economics

A thermodynamically logical process approach shows that shale oil can be used for both specialty chemicals manufacture and conventional refining. A conceptual process flow diagram is developed from which economic projections will be made. The task is 30% completed. The remainder of this task will be focused on consolidating the information obtained in tasks 1-6 into a concise technical and economic description of shale oil value-enhancement research.

Overall progress of the project is on schedule. The results and findings support the need for obtaining engineering data in phase-II.

Technical Progress Report

Objectives

Objectives for the quarter were:

- 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.

Discussion

Task 1.

NEPA task has been completed.

Task 2.

Primary solvent screening studies for all shale oil fractions have been completed. In this quarter, solvent screening studies on 400 °C+ fraction have been conducted. For heavy fractions which are complex, multiple extraction steps are required to achieve the polar compounds separation.

GC-MS analysis of shale oil distillate fractions have been carried out for compound type identification. Table 2.1 shows the extent of completion. The methodology developed in task-3 would enable us to complete the identification of compound types in the remaining spectrum of each fraction.

Table 2.1 Compound Type Identification

Fraction	% Completion
<200 °C	95
200 - 275 °C	90
275 - 400 °C	85
>400 °C	20-40

Completion of task-2 has been deferred until we have settled on a solvent for each fraction as carried out in task-5.

Task 3.

Major emphasis was placed on the completion of the development of peak identification software and integration with the Mass Spectroscopy data handling. We have achieved this goal and made some preliminary analysis of complex chromatogram. Also, the thermodynamic properties estimation program has been modified to include gas chromatographic column effects. Hardware changes include the installation of the low voltage EI system to enhance the parent peak recognition capability. A discussion of each subtask follows:

A. Peak Identification by Z-BASIC Methodology

To analyze and characterize heavy fractions of shale oil, we have developed data treatment software routines based on Z-BASIC methodology. The overall scheme of development is shown in figure 3.1. A patent application is in preparation based on the logic and results. The major blocks in the flow diagram are:

(i) Probable Structures: The probable structures routine is designed to find all probable structures for a given mass number and the elemental analysis of the fraction. The number of probable structures are controlled by the cut-off probability. The logical sequence of calculations include: (a) determination of atomic probabilities based on elemental analysis, (b) determination of molecular probabilities (product of atomic probabilities) of all possible structures and (c) normalization of all molecular probabilities. The output includes exact molecular weights, z-number and probable empirical formula for the molecule.

(ii) B.P.- MW Database: The boiling point / molecular weight database consists of constants for correlations between boiling point and molecular weight for all compound types (classified by z-number e.g. z=+2 for paraffins, -6 for alkylbenzenes, etc.). Database also provides information from extrapolative and interpolative techniques. The output from probable structures routine i.e. structure ($C_nH_{2n+z}NuSvOw$) and Z number are input parameters for the database. Currently, boiling point is the only output. However, constants are available for other physical properties based on molecular weight.

(iii) B.P.- RT Database: The boiling point / retention time database consists of constants for correlations between boiling point and retention time for compound types that are identified from shale oil fractions. The retention time data from GC/MS analysis of shale oil fractions were obtained from selected ion chromatograms and fragmentation patterns of compound types of interest. Correlations have been developed between boiling point data from literature and observed retention times. These correlations (reference: third quarterly report) have the ability to extrapolate for data on compounds of the same series. These correlations, however, are column dependent and future work will aim at obtaining correction factors for column variables. The output from bp-rt database is boiling point based on retention time.

Based on the comparison of two boiling points and accounting for the isomeric variations, match index is calculated. Index of 1-10 indicate the relative closeness of two boiling points and '10' being the best. The probability of the given compound and the match index will determine the exact compound. The index of '0' implies that the specific compound type is not in the database or outside of the limits. The alternative for this case is to identify the compound structure, if possible from reference library using fragmentation pattern or use the thermodynamic properties estimation routine. This routine, based on three temperature programmed GC/MS runs, will calculate enthalpy and entropy of adsorption and will calculate boiling point dependent on adsorption thermodynamics. Details of this program were given in the third quarterly report.

Table 3.1 summarizes the program output for various compound types that are identified in the 200-275 °C fraction of shale oil. The program was run using the indicated retention time and molecular weight data for identified compounds. It is important to note the program response for isomers (e.g. m.w. 120 of alkylbenzene has retention times from 11 to 15 mins and quality varied from 10 to 6). This illustrates the complexity of isomers.

Table 3.1

Compound Type	Molecular Weight	Retention Time	Match Index
Alkanes	128	8.486	10
	170	27.743	10
	240	57.641	10
Alkenes	126	8.063	10
	182	33.737	10
	238	57.25	10
Alkylbenzenes	120	11.206	10
	120	12.083	9
	120	15.36	6
	134	17.271	10
	134	20.91	8
	134	23.904	5

Alkyl naphthalenes	156	39.554	10
	156	41.116	6
	156	43.152	1
	170	46.192	9
	170	48.59	5
	170	50.794	1
Ketones	100	4.442	5
	170	33.935	2
	226	57.543	2
Carboxylic Acids	74	2.74	9
	130	21.621	10
	186	45.829	10
Phenols	122	21.133	8
	122	26.404	1
	136	29.556	9
	136	32.707	5
	150	33.767	9
	150	38.494	8
Pyridines	107	7.593	9
	107	10.48	1
	121	13.324	8
	121	17.996	3
	135	18.512	10
	135	23.378	6
Pyrroles	123	19.613	5
	123	22.695	2
	137	23.839	8
	151	27.325	10
Indoles	145	43.989	10
	145	45.718	2
	159	49.539	10
	159	51.268	5
	173	53.178	2
	173	55.214	9
	173	58.38	2
Quinolines	157	40.335	1
	157	43.082	7
	171	46.555	1
	171	49.232	7

Thiophenes	112	6.952	7
	112	7.942	1
	126	11.316	7
	126	14.733	2

Currently, the program is completely integrated with the GC/MS data handling macros system and runs on any selected chromatogram. Future developments include the expansion of databases and integration of thermodynamic properties routine.

B. Installation of Low-Voltage E.I

The installation of low voltage EI has been completed. The various settings for low voltage range from 70 - 8.7 eV. Low voltage eV mass spectroscopy offers several advantages which include:

- (i) less fragmentation of the molecule due to low ionizing energy
- (ii) increase in relative abundance of parent peak
- (iii) selection of eV to match compound types

Low voltage system is an important factor in the overall z-basic methodology. It helps to simplify the decision making criterion with fewer peaks for any given scan. Increased relative abundance of parent peak enables the program to choose the molecular weight of the compound. Figure 3.2 shows an example of the 1,2,4-trimethylbenzene spectrum from two different runs at different voltages. The difference is very significant in terms of parent peak ($m/z=120$) and relatively fewer peaks. It is also important to note the reproducibility of the instrument i.e retention time comparison.

Other considerations of low eV mass spectroscopy include that the parent peak should be present at higher voltage i.e. compound should be stable to give parent peak. It is also implied that the absolute abundance of peaks decreases with low voltage. Standard reference libraries based on fragmentation patterns will not function with low eV. However, in complex mixtures simplifying the higher end of the mass range to essentially parent peaks improves the quality of the Z-BASIC treatment and works to our advantage when analyzing shale oil fractions.

Task 4.

Major activities in market research include compilation of market profiles for target chemicals and preparation of venture development prospectus for shale oil value enhancement products. Market profile report presents market information from production statistics to outlook. A sample of market profile for pyridine bases is shown in Table 4.1. Other market profile reports include products such as phenols, naphthalenes, n-alkanes, waxes, lube oil, cresilic acids and resorcinols. The information is obtained from published sources and online market databases. Efforts are continuing to prepare profiles for other target chemicals.

Table 4.1 Market Profile for Pyridine Bases

Producers		Capacity (millions Lbs)
Nepera Inc.		25
Reilly Industries		35
	TOTAL	<hr/> 60
Demand		

The U.S. demand for pyridine bases has been around 30 million pounds a year. About 50% of the demand is for pyridine. The demand in 1988 is 32 millions pounds.

Growth

The growth in consumption over the past 15 years has been around 2% per year. The future growth is expected to remain at the same level.

Price

	<i>Pyridine</i>	<i>Picoline</i>
Historical(1978-92)	2.2	1.2 \$ per pound
Current	3.2	1.3 \$ per pound

Uses

	%
Agricultural Chemicals	33
Pesticides	25
Niacin	20
Vinyl Pyridine	9
Pyrrithone Salt	5
Solvents	5
Misc.	3

Strength

Agricultural chemical market is strong and the use of pyridine bases will continue to meet the market demand.

Weakness

Pesticide market is expected to slow down due to toxicity and competition from biopesticides.

Outlook

The declining supply coal tar, which is the conventional source for extraction of pyridine bases, presents a need for alternate sources.

The development prospectus for shale oil value enhancement products is a concise version to the detailed business plan for the commercialization. Various sections include markets, products, technology, economic strategy and profitability. This prospectus will be used to market the shale oil venture to the industrial sponsors.

The economic strategy as shown in figure 7.1 classifies value enhanced products into four general categories. Examples of these broad categories are given in Table 4.2.

Table 4.2

<u>Category</u>	<u>Examples</u>
Polar Compounds	Pyridines, Phenols, Carboxylic Acids
Chemical Intermediates	Alkylheterocyclics, Monomers
Petroleum Products	Aromatic Oils, Lube Oils, Mineral Oil
Refinery Feedstocks	Distillates and Residues

Table 4.3 shows selected market data for target chemicals/molecular types that are present in shale oil.

Table 4.3

Product	Market Size (10 ⁶ lbs/yr)	Value \$/lb	Manufacturers
Pyridines	30	3.0	Reilly, Nepera
Quinolines	n/a	1.5	Koppers, Crowley
Pyrroles	n/a	9.0	Detrex
Indoles	n/a	27.5	Penta
Carboxylic Acids & salts	725	0.6	Texas Chemicals, Westvaco, Mona
Phenols	3900	0.3	Allied, Merichem, Aristech
Nitriles	1060	0.7	DuPont, Akzo
Ketones	653	0.6	Union Carbide, Eastman

Task 5.

During this quarter, shale oil distillate fractions and polar fractions have been analyzed for determining thermodynamic properties of association and partition. The thermodynamics of association is an important consideration to obtain average molecular weights of these fractions. Apparent molecular weight is a measure of the association of solute molecules in the liquid phase and effects the partitioning when performing liquid-liquid extractions. These molecular weights were compared with data from GC-MS and found to be in good agreement.

Studies of the partition behavior show relatively efficient concentration of heteroatom types boiling below about 275 °C. Between 275 and 400 °C, the coefficient of separation falls off but high heteroatom recoveries are still achieved in a single stage. Preliminary results of >400 °C fraction indicate that multiple liquid-liquid extraction steps will be required .

Molecular Weight Measurements of Shale Oil Fractions

Molecular weight measurements of shale oil fractions have been made by vapor pressure osmometry (VPO) using toluene as the solvent. As expected, thermodynamic associations have been proved to be a factor in conventional extrapolation of calculation of molecular weights from vapor pressure osmometry data. To solve the problem of association and to get more reliable molecular weights from experimental data, a model has been developed and tested using the molecular weight measurements data from three shale oil fractions.

The description of the thermodynamic model (referred to as BRD model) and equations governing the model are shown in figure 5.1 (slides from ACS presentation). This model has been tested using the molecular weight measurements from shale oil fractions of <200 °C, 275-400 °C and asphaltene fraction of 400 °C+. The results of the model are shown in figure 5.2. The following table 5.1 shows results of molecular weights by various methodologies.

The conventional method is a linear extrapolation or statistical curve fitting of the data without accounting for the interactions of the molecule. The weighted average molecular weight is calculated from the major of peaks of the spectrum and adjusting for the heteroatom content i.e. obtained from the elemental analysis. The molecular weight from the BRD model is calculated using the concentration and apparent molecular weights data from VPO measurements. The calculated molecular weights (for 200-275 and 275-400 °C) from the BRD model agree with the molecular weight data from GC-MS which demonstrates the applicability of the model. When this model is applied to asphaltene fraction of shale oil 400 °C+ fraction, the molecular weight is 582 as opposed to 641 from the experimental data.

Table 5.1 Comparison of Molecular Weights

Fraction	Traditional	GC-MS	BRD
200 - 275 °C	735	173	172
275 - 400 °C	245	232	235
400 °C+ Asphaltenes	641	n/a	582

Table 5.2 shows thermodynamic values for association and constants for BRD model. The thermodynamics of association for 200-275 °C is stronger than other fraction where 8 monomer molecules are involved in association and is the evidence for difference in molecular weights between BRD and experimental methods. The reason for this stronger association is due to higher polarity of the fraction. Other fractions exhibit associations which included only 2 molecules. This methodology sheds light on thermodynamics of association when heteroatoms are involved such as shale oil and concludes that the conventional method of extrapolation needs some modification.

Table 5.2: Thermodynamics of Association for Shale Oil Fractions

Fraction	# of Molecules n	Equilibrium Constant, k	kT	Free Energy Association G,cal/mole
200 - 275 °C	7.8	1.9×10^{19}	9×10^{25}	-5096
275 - 400 °C	1.96	3.5	30.4	-1163
400 °C+ Asphaltenes	2.4	153	3159	-2285

Task 6.

The conversions exploration experiments are conducted at the University of Utah under subcontract. The objective of this quarter is to determine aromatic nitrogen containing functionalities in 400 °C+ shale oil residue and to investigate possible methods for their dealkylation. Four analytical instrumental techniques were used to investigate dealkylation and these are:

- Pyrolysis Gas Chromatography/Mass Spectroscopy (Py-GC/MS)
- Thermogravimetry with on-line Mass Spectroscopy (TG/MS)
- High Pressure Thermogravimetry in a Hydrogen atmosphere with on-line GC/MS (HPTG/MS)
- Tubing Solution Reactor with on-line GC/MS (TSR-GC/MS)

The sample preparation consists of separation of paraffins on an open liquid chromatography column of silica gel using elution with various solvents of increasing polarity ranging from pentane to methanol. For analytical purposes, both whole fraction and polar fraction are used.

Py-GC/MS :

Experiments were conducted in various desorption or pyrolysis modes. The desorption was performed at 358 °C while pyrolysis was most effective at 650 °C. The pyrolysis was done by coating the sample on to a silica/alumina column, which was then wrapped in a Curie point foil.

Results of TIC of total fraction show normal paraffins distribution with an unresolved hump of higher boiling compounds. SICs were obtained for alkyl substituted quinolines, indoles and carbazoles for both total and polar fractions. Figure 6.1 shows the selected ion chromatograms of alkylindole from polar fraction.

TG/MS :

A thermogravimetry/mass spectroscopy run was performed on the total sample to gain preliminary information on its temperature range for evaporation/decomposition. Low voltage (12) eV EI mode was used for MS to simplify the resultant spectrum. The main sample weight loss has occurred between 140 - 360 °C (10 min.) leaving 3% residue at a final temperature of 660 °C in helium. Figure 6.2 shows weight loss and rate of weight loss curves. Even with low EI, extensive fragmentation could not be avoided for interpretation of data.

HPTG/GC/MS :

The main objective of this unique system is to monitor the products of thermal decomposition of the shale oil in hydrogen atmosphere at 900 psi pressure. Experiments were conducted in the presence of silica-alumina. The temperature programming conditions are 15 °C/min from 25 to 350 °C and 3 °C/min from 350 to 500 °C. Alkanes and alkenes of up to 22 carbons are the predominant products through the main weight loss range followed by various aromatics from recondensed tar/char gasification at higher temperatures. Approximately, 20-30 % weight loss has occurred depending on the catalyst loading.

Runs were also conducted using silica gel as sorbent. Figure 6.3 shows benzene and pyridine profiles whereas the later is the most predominant product. Figure 6.4 shows similar behavior with naphthalene and quinoline.

TSR-GC/MS :

Thermal decomposition behavior of shale oil fraction (400 °C+) was studied in a flow reactor using solvents such as pentane and methanol (20-30%) under hydrogen flow at 200 psig (1-2%). The initial decomposition products were observed at 380 °C. These products were alkylbenzenes in the beginning and later replaced by highly methylated pyrroles and pyridines. Smaller products than the C₃ pyridines could not be observed due to the overloaded solvent peak. Figure 6.5 shows selected ion chromatogram of alkylpyrrole.

All these techniques are very powerful in the study of dealkylation. However, the best technique with flexibility to change operating conditions will be chosen for optimizing conditions for dealkylation in the future work.

Hydrodealkylation :

A probable means for reducing molecular structure while preserving the ring structure of the molecule is some form of dealkylation. The candidate methods are: hydrodealkylation (575-650 °C), hydropyrolysis (500-575 °C), hydrovisbreaking (420-460 °C) and catalytic hydrocracking (420-525 °C).

A sample of >400 °C residue was subjected to hydrovisbreaking at 420 °C. The sample readily cracked into lower molecular weight species. Figure 6.6 shows the TIC chromatogram. The vast majority of recovered liquids boil below 300 °C (C₁₇). Pyridines, pyrroles, nitriles and phenols were readily found in this distillate.

Task 7.

The development of economic strategy for optimizing shale oil product slate has been given priority in this quarter. A refinery process cost database has been completed which contains information on capital investment and operating costs. This database is integrated with economic evaluation model. A preliminary profitability analysis has been conducted.

Figure 7.1 shows an overall economic strategy based on the currently understood separation behavior and product match. The strategy involves the selective division of shale oil into heteroatom containing compounds. The strategy shows that each stream is subsequently processed for its highest value components. Both sides of the separation are upgraded. No residuals or waste streams are produced. All material is either manufactured into high value products or sent to refining for transportation fuels. Mass balances will vary as we now begin to test a specific sequence.

A preliminary economic analysis has been conducted based on the economic strategy. Figure 7.2 shows the results of economic sensitivity analysis. The base case values are based on the economic strategy diagram. The internal rate of return of 30% is projected for the base case with raw shale oil cost of \$30/bbl and average product value of \$78/bbl. Economic analysis shows product value is the most sensitive factor when compared to capital and operating costs. These projections will be revised for optimum process sequence.

Objectives for the Next Quarter

- 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

Figure 3.1 **Peak Identification by Z-BASIC Methodology**

Figure 3.2 Comparison of Mass Spectra

Compound: 1,2,4-Trimethyl Benzene

Figure 5.1

Description of BRD Model

- Molecules In Solution Associate Into Clusters of Many Sizes
- Solvent Molecules do not Associate
- All Clusters are in Equilibrium with Unassociated Molecules
- The Solution is Dilute

BRD Model

$$k_n = \frac{[B_n]}{[B]^n}$$

k_n - Equilibrium Constant
[B] - Monomer, moles/lit.
[B_n] - Cluster, moles/lit.

BRD Model

$$X_1 = \frac{C_1 MW_s}{1000 \rho_s}$$

C₁ - Concentration, mol/l
X₁ - Mole Fraction
ρ_s - Solvent Density, g/cc
MW_s - Solvent MW

$$(k_n)_T = k_n \left[\frac{1000 \rho_s}{MW_s} \right]^{n-1}$$

BRD Model

$$[B_n] = \frac{B_o R_n}{n}$$

R_n - Association Ratio
B_o - [B], No Association

$$[B] = B_o Y$$

$$Y = 1 - \sum_{j=2}^{\infty} R_j$$

$$C = B_o MW_o$$

MW_o - Monomer MW
C - Solute Concentration, g/l

BRD Model

$$R_n = \frac{nk_n}{(MW_o)^{n-1}} Y^n C^{n-1}$$

$$1 - Y = \sum_{j=2}^{\infty} \frac{[k_j C^{j-1}]}{(MW_o)^{j-1}} Y^j$$

$$MW = \frac{MW_o}{Y + \sum_{j=2}^{\infty} \frac{R_j}{j}}$$

BRD Model

Example of relationship between 'k_n' and 'n':

$$\ln(k_n) = a(n-1)^b$$

Figure 5.2

BRD Model (Simplified)

$$C = \left[\frac{R(MW_o)^{n-1}}{nk(1-R)^n} \right]^{\frac{1}{n-1}}$$

$$MW = \frac{MW_o}{1-R+R/n}$$

Application to MW vs C Data

1. Improved Determination of Molecular Weight
2. Thermodynamic Characterization of Association
 - a. ΔG as a function of 'n'
 - b. ΔH , ΔS as a function of 'n'
 - c. average ΔG
 - d. average ΔH , ΔS

Results of BRD Model to Characterize Molecular Association Thermodynamics Shale Oil Fraction (275-400 C)

Prediction of
the Model

Results of BRD Model to Characterize Molecular Association Thermodynamics Shale Oil Fraction (200-275 C)

Application of BRD Model to Asphaltenes Asphaltene Fraction of Shale Oil Residue (400 C+)

Figure 6.1

Chromatogram C:\ITMS\BLSHOIL4 Acquired: Mar-04-1994 16:02:57
Comment: SHOIL X3/SIAL, 4ul; 4m SPB-5; 6psi270; 45-300@20(0,5), SP10mL/mn, 650f10s
Scan Range: 1 - 1560 Scan: 1 Int = 13024 @ 0:00 100% = 115657
100%

Figure 6.2

a.

b.

c.

TG/MS data showing a) weight loss (TG) and rate of weight loss (DTG) curves, b) total ion curve and c) average mass spectrum (m/z 278 from oil background).

Figure 6.3

Comparison of benzene and pyridine signals

Figure 6.4

Comparison of m/z 128 from naphthalene and m/z 129 from quinoline

Figure 6.5

Selected ion chromatograms for alkylpyrrole molecular ions from TSR/GC/MS data

Figure 6.6

File : C:\HPCHEM\1\DATA\S094_37\943701.D
Operator : Don
Acquired : 4 Mar 94 2:22 pm using AcqMethod S093_66F
Instrument : 5972 - In
Sample Name: spx16-94-37 13337 ng/ul
Misc Info : Thermal hydro visbroken product from 93-67
Vial Number: 1

Figure 7.1 Economic Strategy
Shale Oil Value Enhanced Products

Figure 7.2

Economic Sensitivity Analysis

Value-Added Chemicals from Shale Oil

(Projections as of Feb. 28, 1994)