Shale Oil Value Enhancement Research

**Quarterly Report
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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.

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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.
2207 W. Alexander Street
Salt Lake City, Utah 84119

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Summary Management Report

The focus of the phase-I research effort is now on exploratory level verification of the candidate process schemes. We are quite confident of the basic strategy, namely, division of the barrel by polarity and separate processing of the polar and non-polar streams. Processing of the non-polar stream must necessarily focus on the high value products found in the +400 °C fraction. We expect that waxes will meet high quality paraffin-wax specifications (partly because of the high initial boiling point) but the lube oil quality is not yet known.

Verification of the polars processing scheme is aimed at determining the balance between broad-range concentrates and pure compounds. We have identified buyers for both types of streams but it is not yet clear how much value-addition is economically desirable. In the early stages of this work, we showed that there is an optimum level of processing and that over-processing might actually reduce the IRR (Reference: Bunger, et al 25th Annual Shale Oil Symposium at CSM, 1992).

We are proceeding with the pilot plant developments in areas where we are confident of the process steps, eg. distillation and liquid-liquid extraction while completing the verification work before deciding what to do about piloting HDA, catalytic hydrotreating and liquid-solid adsorption. The loss of equipment capabilities at the University of Utah may make it more expedient for us to pilot these processes in-house. The availability of the new WISER coal liquefaction equipment at the University of Utah for use in HDA experiments is being given careful consideration.

The principal investigator traveled to company A to help coordinate with their screening efforts. This international company is conducting a complete screening of shale oil fractions for activity as insecticides, herbicides and fungicides. Initial results will be available within the next 2-3 months. We are expecting to extend our agreement with Company A to include pharmaceutical testing as well. This type of testing should yield information on both biological activity and toxicology. During the next quarter, additional samples will be sent for testing.

Technical Progress Report

Objectives for the Quarter were:

- 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.

Discussion

Task 1.

The NEPA task has been completed. Approval for CX-B has been granted for Phase-I on June 20, 1994 and for phase-II on December 19, 1994.

Task 2.

The separations characterization task is completed. Any developments related to this task are reported in other sections of the report.

Task 3.

Major focus during this quarter has been on completing the development of the Z-BASIC peak identification. The progress to this date shows that our objectives have been met within the available resources of phase-I. The detailed approach of this methodology based on the past developments in the project is presented in this section.

We tested a way to get the boiling point of a parent mass in a GC-peak using two retention times from two different temperature program runs. From column parameters and operating conditions, it has been shown (refer; 3rd quarterly report) that enthalpy (ΔH_a) and entropy (ΔS_a) of adsorption could be calculated for a given peak using two retention times. The enthalpy and entropy values are average values calculated from the program conditions using temperature and pressure programming.

The calculation procedure includes:

- a) modeling of carrier gas flow to obtain gas velocity at any position in the capillary column and at any time;
- b) obtaining the local ratio of migration velocity of an adsorbing material to the carrier gas velocity in terms of column parameters and an equilibrium adsorption constant;
- c) modeling of the equilibrium adsorption constant in terms of ΔH_a , ΔS_a , temperature and pressure;

These theoretical models along with the temperature programming information for a given run yield retention time. Since only ΔH_a and ΔS_a are unknown, two retention times from two different runs allow the theoretical determination of ΔH_a and ΔS_a .

In each chromatogram, normal paraffins are identified using a standard library and BP, ΔH , ΔS for these paraffins are correlated with molecular weights. These are labelled BP_p , ΔH_p , ΔS_p . Then the actual boiling point of the peak material is BP_p plus a correction based on how its ΔH_a and ΔS_a differ from values for a comparable (pseudo) paraffin. The pseudo paraffin is the compound having the same molecular weight as the compound present in the peak.

$$BP = BP_p + a (\Delta H_a - \Delta H_p) + b (\Delta S_a - \Delta S_p) \quad \text{-----(1)}$$

This concept is tested on <200 °C shale oil distillate fraction. The operating conditions for GC runs are same except for heating rate. These conditions are as follows:

<i>Initial Temperature</i>	50 °C	
<i>Initial Hold Time</i>	0	
<i>Final Temperature</i>	275 °C	
<i>Initial Pressure</i>	15 psig	
<i>Initial pressure hold time</i>	1 min.	
<i>Pressure drop rate</i>	99 psi/min	
<i>Final Pressure</i>	3 psig	
<i>Heating Rate</i>	1 °C/min.	or 4 °C/min.

Also, after inlet pressure reaches 3 psig, it is adjusted with column temperature to maintain constant flow of carrier gas through the column.

Table 1 shows specific identified components in this shale oil fraction as well as their mw, BP, the two retention times and the calculated ΔH_a and ΔS_a . For normal paraffins these values are correlated with molecular weights as:

$$BP_p = \frac{a_1 m + b_1}{m + c_1} \quad \text{-----}(2)$$

$$\Delta H_p = a_2 m^3 + b_2 m^2 + c_2 m + d_2 \quad \text{-----}(3)$$

$$\Delta S_p = a_3 m^3 + b_3 m^2 + c_3 m + d_3 \quad \text{-----}(4)$$

Table 1

Compound	mw	BP	Retention Time		ΔH_a cal/mol	ΔS_a cal/mol K
		deg C	1 °/min	4°/min		
n-Octane	114	125.7	271.9	236.5	6823	32.9
n-Nonane	128	150.8	502.9	379.9	6106	32.0
n-Decane	142	174.2	903.1	567.1	5286	30.4
n-Undecane	156	195.9	1481.5	777.1	4509	28.7
n-Dodecane	170	216.3	2176.9	991.3	3885	27.3
Ethylbenzene	106	136.2	393.1	319.3	6119	31.6
m-Xylene	106	139.1	417.1	334.3	6037	31.5
p-Xylene	106	138.4	417.1	334.3	6037	31.5
o-Xylene	106	144.4	475.9	370.3	5803	31.0
2,6-Dimethyloctane	142	160.4	610.9	436.9	5813	31.4
1,3,5-trimethylbenzene	120	164.7	720.7	493.9	5434	30.5
1,2,4-trimethylbenzene	120	169.4	788.5	526.3	5271	30.2
1-Decene	140	170.6	855.7	547.9	5356	30.5
Naphthalene	128	217.9	1773.1	959.5	3525	30.1
1-Dodecene	168	213.4	2108.5	972.1	3931	27.4

From this data, it is possible to obtain a corresponding paraffin for each molecular ion of the peak. The difference in enthalpies and entropies between (pseudo) paraffin and the compound is calculated. These differences in basic thermodynamic properties are the basis for correlation with molecular properties. The approach has been tested for boiling points for various classes of compounds that are found in the shale oil distillate fractions. These results are very encouraging.

The resulting correlation for the non-normal paraffins (mostly pure hydrocarbons) based on equation (1), gives degree of prediction as shown in figure 1.

This methodology has also been applied to extracts from 200 - 275 °C and 275 - 400 °C distillate cuts of shale oil. The GC run conditions are similar to the previous case. The normal paraffins identified are given in table 2 and other compounds are shown in table 3. The same correlating methodology has been applied and the accuracy of fit is shown in figure 2. The deviations are greater for the di, tri and tetra methyl phenols, as well as for the dimethylnaphthalene. This error might be due to improper isomer assignments.

Table 2

Compound	mw	BP <i>deg C</i>	RT		ΔH_a <i>cal/mol</i>	ΔS_a <i>cal/mol K</i>
			<i>1 °/min</i>	<i>4 °/min</i>		
n-Decane	142	174.2	882.8	542.0	-11827	-20.52
n-Undecane	156	195.9	1439.0	739.1	-12605	-21.22
n-Dodecane	170	216.3	2110.4	942.8	-13364	-21.89
n-Tridecane	184	235.5	2828.6	1142.0	-14149	-22.68
n-Tetradecane	198	253.6	3548.3	1334.0	-14894	-23.37
n-Pentadecane	212	270.7	4248.8	1517.0	-15629	-24.07
n-Hexadecane	226	286.9	4917.8	1690.4	-16337	-24.72
n-Heptadecane	240	302.0	5561.6	1857.2	-17098	-25.53

So far this approach has been shown to calculate boiling points with low error. In general any property based on thermodynamics, as is the case, is expected to correlate as well with ΔH and ΔS as boiling point does where:

$$\Delta H = \Delta H_a - \Delta H_p \text{ ----- (5)}$$

$$\Delta S = \Delta S_a - \Delta S_p \text{ ----- (6)}$$

Furthermore, a linear form of correlation can be expected because ΔH and ΔS are relatively small compared to ΔH_a and ΔS_a as indicated by the data. In a Taylor series expansion of the functional form that relates ΔH_a and ΔS_a to the property, second order and higher terms of the series are not needed if the first order terms are small enough, as they are in the illustrated case.

Table 3

Compound	mw	BP	Retention	Time	ΔH_a	ΔS_a
		deg C	1 °/min	4°/min	cal/mol	cal/mol K
2,6-Dimethyloctane	142	160.4	598.4	423.2	-10839	-18.68
1,3,5-Trimethylbenzene	120	164.7	716.0	478.4	-11017	-18.70
1,2,4-Trimethylbenzene	120	169.4	789.2	511.4	-11061	-18.54
Naphthalene	128	217.9	1917.8	912.8	-12051	-18.48
1-Dodecene	168	213.4	2049.8	924.8	-13320	-21.90
2,4,6-Trimethylpyridine	121	171.0	836.0	527.0	-11453	-19.55
Indene	116	182.6	1086.2	632.6	-11302	-18.28
1-Undecane	154	192.7	1383.2	721.4	-12510	-21.08
2,5-Dimethylphenol	122	211.5	1791.8	828.8	-14011	-24.50
2,3-Dimethylphenol	122	216.5	1948.4	891.8	-13363	-22.25
2,4,6-Trimethylphenol	136	221.0	2648.0	1097.6	-13768	-21.95
2,3,5,6-Tetramethylphenol	150	247.0	3194.0	1263.8	-13650	-20.50
1,5-Dimethylnaphthalene	156	264.0	3568.0	1374.8	-13642	-19.90

In principle, other thermodynamic properties can be calculated for a peak using this approach include vapor pressure, viscosity, refractive index, etc. These calculated properties can be used to delineate a peak for better identification. The overall impetus in developing and consolidating this approach is to identify valuable components in the shale oil to help devise a better economic separation approach.

The significance of this effort is that **we are able to calculate the properties (and partition behavior) of any species in shale oil without having to know its structure.** This information can be highly useful for deducing the structure if necessary, but the capability eliminates the age-old problem of analytical breakdown at higher molecular weights. This allows us to track a species (by its Z-BASIC parameters) one of the original requirements for success on this project. This has now been achieved.

Task 4.

Market research work for the compound types work is almost completed. Market research information on plausible shale oil value-added chemicals has been reported in our previous quarterly and monthly reports. This information is organized in the market database for data retrieval and management. A business plan has been prepared as a document to

market the shale oil project to majors. Also, market research has identified potential players for each chemical and type of industry.

Market research has been assisted by a sub-contract to Sinor consultants and by using published reports and on-line databases. For phase-I work, this approach seemed to be cost-effective and sufficient to compile information. As the project is entering into phase-II, there is need to obtain more detailed information on manufacturers and access to professional research reports to compile information on specifics of market growth. To meet these growing needs, a DIALOG subscription has been obtained. In the phase-II of marketing efforts, a DIALOG search will be used to obtain profiles of manufacturers and growth in the product markets.

The overall scope and status of the shale oil research has been presented to one of the major chemical companies, who is involved in the activity testing of shale oil fractions. A lot of interest has been generated due to this presentation which has laid the groundwork for future involvement in the project. Marketing efforts are continuing to generate interest with other majors. A firm time-table has been set to complete these marketing efforts through a systematic approach.

Task 5.

Liquid-Liquid extraction of the +400°C fraction has proven problematic for the following reasons. The high wax content has dictated that either an elevated temperature be used or the waxes be solvated by an appropriate non-polar solvent. When the temperature is raised, a less volatile extraction solvent is needed. Lower volatility extraction solvents tend to yield reduced selectivity (although improved recovery). Many of these solvents do not form two phases.

Mixed solvents eg. alcohol/water/carboxylic acids have shown promise in shake tests but control of solvent quality in a commercial process may be difficult. Use of hydrocarbon co-solvents have also shown useful in shake tests. For broad range solvents any aromatics present tend to partition in the extract. Work is continuing to find the best combination of solvents and temperature which will give high coefficients-of-separation (CS) for the +400°C fraction.

Confirmation studies of scheme 1 i.e. extraction of the total shale oil has been conducted in the laboratory with various solvent systems. Results of single stage shake tests are very encouraging. In a single stage, the extract-to- raffinate split is 15/85 with 40% recovery of nitrogen. Future experiments in six-stage counter-current extraction are expected to improve the split ratio and nitrogen recovery. The results will be used for cost analysis and the fractions generated will be used for downstream processing.

Modifications to the extraction unit are underway to handle +400 °C fraction. Pumps to handle hot fluids are on order. These experiments will be completed in this quarter.

Task 6.

Development of the best process strategy for the +400°C material is important to the overall viability of a shale oil value enhancement venture. Approximately 50% of the mass and over 60% of the nitrogen is found in this fraction. The +400°C material is potentially the highest value fraction, not only for its nitrogen components, but also for the more conventional products (waxes and lube oils) that may be manufactured from the non-polar fraction.

Focus on the +400°C material has been reserved for the later stages of phase-I so as to adequately understand the partition behavior of lower molecular weight species and to develop the analytical procedures on lighter distillates needed to deal with this heavier, complex mixture. The emphasis now is on this interesting fraction.

The main choices for primary processing are a) liquid-liquid extraction followed by Hydrodealkylation (HDA) of the polar fraction and refining of the non-polar fraction; b) hydrovisbreaking followed by liquid-liquid extraction; and c) processing as part of the total shale oil. Work is progressing on each of these options.

Hydrovisbreaking (HVB) lowers the overall molecular weight and generates a more easily extractable feedstock. Because hydrovisbreaking has been carried out at the University of Utah in microreactors there has been insufficient quantities to study the extraction behavior of the HVB product in detail. Analytical results show that nitrogen compounds are being broken down and based on partition behavior of the distillates studied, should be highly extractable. Work with in-house equipment begin built for phase-II is expected to resolve this problem.

In any of these schemes Hydrodealkylation (HDA) of the larger nitrogen compounds is needed. In hydrodealkylation alkyl groups are clipped at the ipso position (leaving the parent ring compound in an ideal reaction) in practice there is also dealkylation at the alpha position (leaving a methyl substituent), dehydrogenation of naphthenic rings, yielding larger condensed ring systems, and coke formation. Because nitrogen heterocyclics promote coke formation, any resulting coke results in a loss of valuable nitrogen. A single batch type coke/visbreaker is being constructed to study conversion of +400°C material and to measure yields of lower molecular weight nitrogen compounds.

Hydrodealkylation work will be conducted on the extract of +400°C fraction. The two options are: a) build an experimental unit at JWBA facilities and b) use existing facilities at University of Utah. A final decision will be made after evaluating the options regarding costs and time commitments. But this work is planned to be completed during this quarter to complete the proof of concept work.

Task 7.

The process modeling task is progressing as expected except for the data i.e. required to translate material balance information to cost analysis. A cost estimation model has been developed which includes flowsheeting, mass balance, cost analysis and economic

analysis. All these four aspects of process development and process evaluation are integrated in this consolidated model. Any changes in flowsheet will automatically take effect in the downstream calculations. Provisions are made to include process models that yield kinetic data for equipment sizing. The ability to rapidly estimate the economic impact of various schemes and operating conditions is important to finding an optimum preferred scheme.

At present, the flow sheet in the model is based on scheme-I (refer: sixth quarterly report). However, other schemes can also be easily implemented with minor changes to the flowsheet. In the costing, the capital cost and utility costs are obtained from the refining economics data for a given capacity. Scale-up factors are also needed in the data input to scale the data to the required stream capacity in the flowsheet.

Process modeling of various units is underway. Liquid-liquid extraction will be modeled for kinetics to size the equipment from the existing data of various shale oil extractions.

Task 8.

During this quarter, the separations development task has been initiated. The objective of this task is to obtain engineering data for process units to enable us to perform scale-up and sizing of the equipment. The data will be used to increase the accuracy of cost estimates. The plan for pilot operations include distillation and liquid-liquid extraction units which are needed for front-end processing while process development is continuing on the downstream processing.

The distillation is a once-through operation and fractions will be cut based on the phase-I data. The liquid-liquid extraction pilot unit will be operated in block mode as solvent systems and operating conditions differ for each fraction. Other process units such as adsorption, HDA and hydrotreating will be added to complete the pilot operation as more experimental data become available.

Objectives for the Next Quarter

- Perform six-stage extraction of total shale oil using the dual solvent system
- Complete modifications to the extraction unit to extract +400 °C fraction
- Conduct hydrodealkylation experiments on the shale oil fractions
- Complete cost and economic analysis for both schemes
- Continue marketing efforts aimed at identifying additional majors as candidate partners for commercialization

Calculated Vs Actual Boiling Point Differential between a compound and its corresponding paraffin

Figure 1

Calculated Vs Actual Boiling Point Differential between a compound and its corresponding paraffin

Figure 2