Market Enhancement of Shale Oil by Selective Separations

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Introduction

The recent history of petroleum availability and price has shown that petroleum substitutes are not economically viable as long as there is a stable supply of conventional petroleum. The additional costs for recovery and upgrading are not sufficiently offset by product values to attract private risk capital without supports or subsidies. In order to create an economically viable synthetic fuels industry, it is becoming clear that some research must be directed at market enhancement technologies, in addition to the more traditional view of cost reduction (recovery and processing) technologies.

Recognizing this requirement, James W. Bunger and Associates, Inc. (JWBA), in concert with the Center for Microanalysis and Reaction Chemistry (MARC), at the University of Utah, has initiated a program aimed at technology for isolation and manufacture of high-value products from unconventional hydrocarbon resources. We refer to this technology as the Natural Products Extraction (NPX) technology. One such initiative is aimed specifically at high-value products from shale oil -- a U. S. natural resource of more than 1-trillion bbls-oil, in place. When compared with conventional crude oil, shale oil is characterized by its high percentage of heteroatom (N, S and O) containing molecules, its high level of mono- and di-cyclic compounds and relatively high percentage of vacuum gas oil.

For successful development of a high-value product slate from shale oil, we must focus on those structural characteristics which are present in higher concentrations in shale oil than in crude oil and which possess proven, or unique, chemical applications. Also, it is clear that isolation of distinctive structural types must, of necessity, adhere to fundamental thermodynamic principles. Therefore, separations process technology must be based on a fundamental understanding of shale oil composition and the relationship of that composition to partitioning during separation.

This paper reports results of our initial attempts to identify and isolate fractions from shale oil of potential market value, to confirm a suitable analytical methodology as a basis for process and product development, and to delineate the economic parameters of market enhancing technology.

Analytical Methodology

In prior work (1-3), it had been determined that thermodynamic properties of molecules correlate well with structural parameters 'n' and 'z' (defined by the formula $C_nH_{2n+z}N_uS_vO_w$) and 'i', a non-integer number which relates to isomeric variations. The indices 'n' and 'z' (with 'u', 'v' and 'w'), establish the molecular weight and define the essential skeletal structure. These parameters, which can be obtained from high resolution, parent peak mass spectroscopy, correlate well with enthalpic properties of the molecule. The parameter 'i', is a strong function of entropic properties. Preliminary evidence suggests that 'i' may be measured indirectly through chromatographic retention time (2).

The development of the classifying system and correlating functions has been collectively labeled the Z-Based Structural Index Correlation Method (Z-BASIC) (2). The Z-BASIC method allows, for the first time, the ability to track the separation behavior of individual species from shale oil. This provides the theoretical basis for process modeling on a molecular level. Coupled GC-MS-FTIR technologies available at the MARC, were used to demonstrate the viability of Z-BASIC for calculation of partition functions of molecular species.

Given the ability to develop separations technologies using fundamental molecular science, we organized a logical development strategy. Figure 1 shows the information flow for this strategy. The flow diagram shows that detailed analytical data is translated into mathematical terms which provide a rigorous basis for process simulation. The simulation becomes the controlling function for modifying the processes to manufacture a specification product. Where specifications cannot be met by

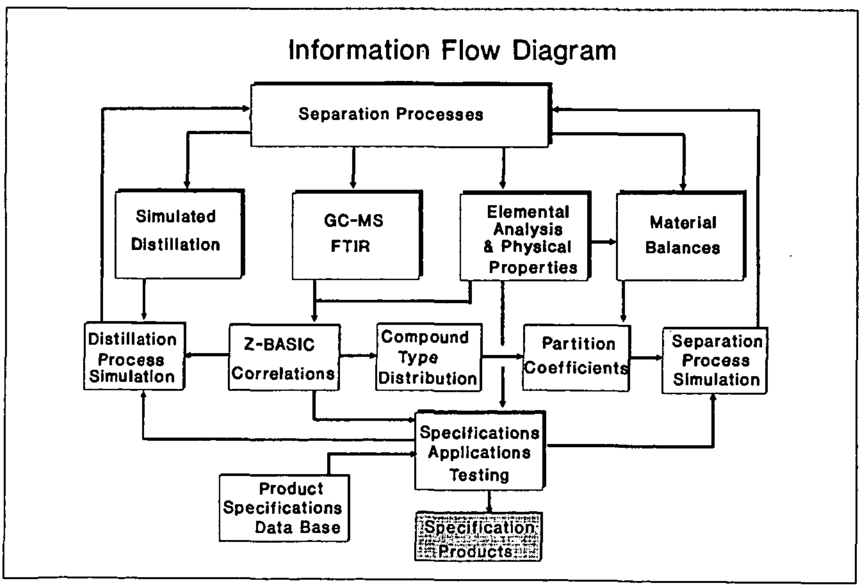

Figure 1

separations processing alone, a comparison between actual concentrate structure and desired concentrate structure will help delineate any additional processes required.

Separation of Shale Oil

Theoretical arguments suggest that attempts to separate a broad molecular weight mixture on the basis of polarity, will suffer from lack of definitiveness between molecular weight and polarity effects. Therefore, the logical initial step in a separation sequence is distillation, a process which provides fractions of narrower molecular-weight ranges.

Figure 2 shows the distillation scheme used in this study and the resulting weight percent yield of each fraction. Figure 3 shows the total ion chromatograms of the individual fractions showing the complexity of the fractions. In general, shale oil lacks homology on the basis of distillation alone, with the notable exception of the concentration of paraffins in the 350 - 440°C fraction.

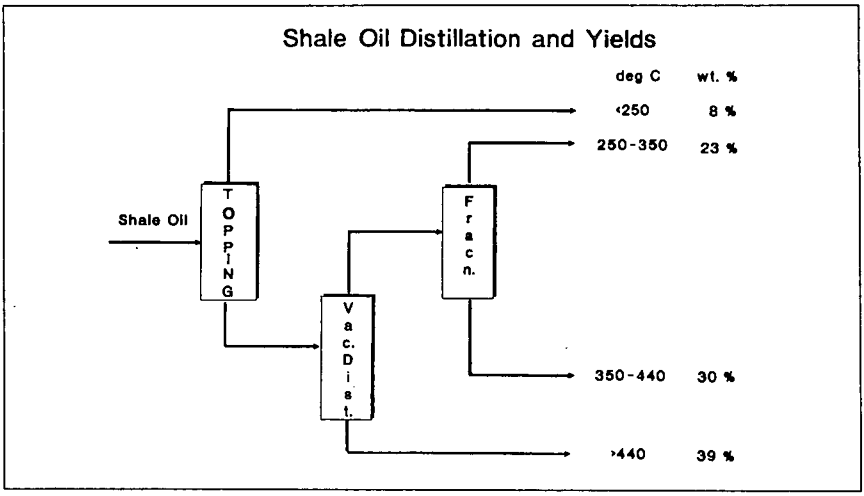

Figure 2

Figure 4 represents the heteroatom distribution as a function of boiling point and shows that while sulfur and oxygen are less dependent on boiling point, nitrogen increases significantly with boiling point. The unusual shape of the oxygen distribution is thought to be indicative of differing types dominating the lower-molecular-weight range as compared to the higher-molecular-weight range. These types have not been fully characterized.

Distillate fractions may be subjected to liquid-liquid extraction with polar solvents to separate concentrates according to polarity. Candidates for polar solvent separation include phenol, furfural, N-methyl-2-pyrrolidone and other polar solvents such as alcohols, ketones, organic and mineral acids, and organic bases. Two-phase partitioning was successfully achieved with several of the aforementioned solvent systems.

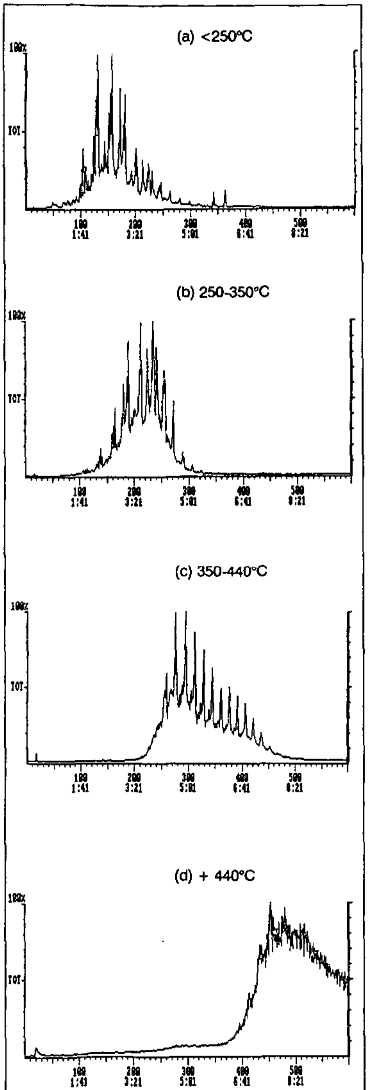

Figure 3.
Total Ion Chromatogram of Shale Oil Distillate Fractions

Laboratory separations were conducted in a small-scale, batch-type processes and quantitative results must be further confirmed before publication. Laboratory conditions were designed to simulate commercially-realistic conditions, e.g., solvent-to-oil ratios of 1:1. In commercial practice, up to five sequential separation/distillation steps are envisioned.

The laboratory separations produced 16 specific concentrates covering four boiling ranges and four polarities. The overall yield and elemental composition of the fractions separated are given in Table 1. For purposes of illustration, the fractions were lumped according to similar polarities. The four major concentrates are labeled "White Oils and Waxes", "Aromatic Oils", "Low Polarity Nitrogen Compounds" and "High Polarity Compounds".

The elemental compositions of these concentrates illustrate the differences achievable with relatively straight-forward and inexpensive separations. The white oils and waxes are extremely low in heteroatoms, including sulfur. Oxygen is calculated by difference and is, therefore, subject to a wider margin of error. The aromatic oil fraction is particularly interesting because it possesses a low nitrogen content while constituting a significant portion of the shale oil barrel.

The major fraction is the low-polarity nitrogen compounds. These materials are of a higher molecular weight and thought to possess carbazolic and aromatic nitrogen. The high-polarity compounds are of a lower molecular weight and contain acidic, phenolic, nitrilic, pyrrolic and pyridinic functionalities.

Product Slate

Based on our laboratory separations and knowledge of the structural types present, a projected product slate for shale oil was constructed. The product slate is compared to current U. S. market volumes and prices. Results are shown in Table 2.

The product slate includes oils, waxes, aromatic oils, aromatics for manufacture of sulfonates, acids, bases and resins. Functionalized intermediates are compounds containing nitrogen or oxygen and which are thought to be of particular value as starting materials for derivatization to pharmaceuticals, industrial chemicals and other pure compound systems. Pure compounds are those with particularly high market

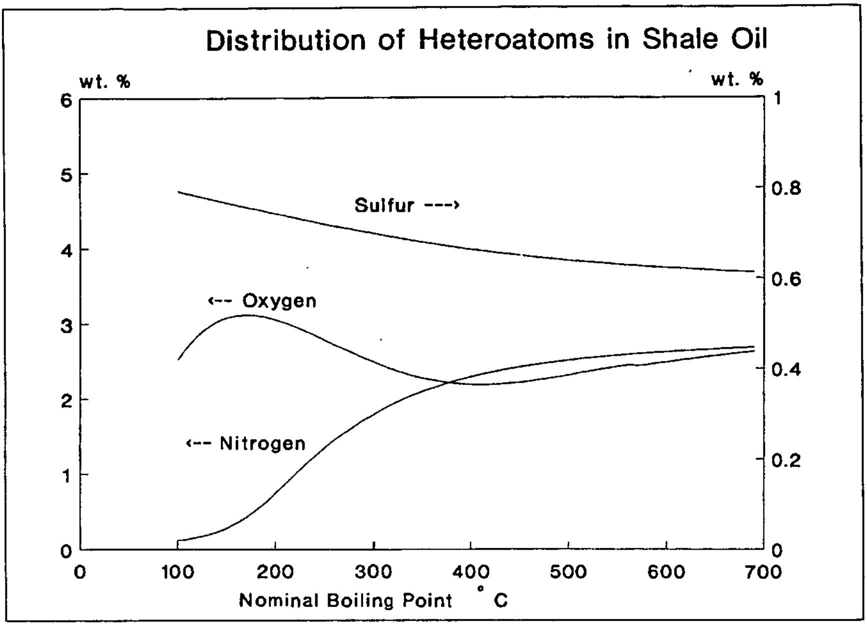

Figure 4

Table 1
Summary of Elemental Composition by Functional Concentrate

Concentrate	Wt % of Shale Oil	C	H	N	S	O (Diff)	H/C
White Oils and Waxes	13	85.7	13.8	0.05	0.02	0.26	1.92
Aromatic Oils	22	87.0	12.1	0.2	0.6	0.5	1.66
Low-Polarity Nitrogen Compounds	35	83.6	10.4	3.2	0.7	3.4	1.47
High-Polarity Compounds	30	82.7	10.6	2.8	0.8	3.2	1.52

value that may be isolable in a pure form from shale oil. Target compounds include nitriles, pyridines, quinolines, amines, amides, phenols, naphthols and carboxylic acids.

The special applications concentrates represent mixtures of particular properties which makes the concentrate marketable in its mixed form. Examples include industrial antimicrobials, coatings, wood preservatives, industrial surfactants and asphalt additives. We currently project that less than 10% of the shale oil barrel may require marketing as a fuel or refinery feed.

Table 2
Demand and Value of Products
Output of SO/NPX = 170,000 Tons/year (3,000 bbl/day)

Product	Market Volume Tons/year	Recent Price $/bbl-equivalent		SO/NPX Projected Yield Wt. % of Feed	% of Market	Revenue $/feed-bbl
White Oils	4,575,000	84	Ref (4)	13.3	0.5	11.2
Waxes	882,000	133	Ref (4)	5.0	1.0	6.6
Aromatic/ Lubricating Oils	9,526,365	60	Ref (4)	30.5	0.5	18.3
Sulfonate Feeds	333,900	142	Ref (5)	11.7	5.9	16.6
Tar Acids and Bases	830,000	210	Ref (6)	4.0	0.8	8.4
Resins	542,000	120	Ref (7)	14.7	4.6	17.6
Functionalized Intermediates	130,000	178	Ref (7)	4.3	5.6	7.6
Special Application Concentrates	500,000	28	Ref (6)	10.3	3.5	2.9
Pure Compounds	200,000	135	Ref (7)	0.7	0.6	0.9
Fuels and Refinery Feeds	large	15	Ref (8)	5.5		0.8
Totals				100		$90.90/bbl

The majority of the anticipated products are targeted for conventional commodity markets for which the market is well established. Maximum economic enhancement of a commercial shale oil facility will occur most readily when a large percentage of the shale oil product slate addresses large, well-established markets. The primary questions which remain and must be addressed in future research relate to the quality of the product and the finishing steps that are required to make the shale oil products market-acceptable.

It is recognized that certain products such as functionalized intermediates and special application concentrates may require significant market development. While this requirement may be an inhibiting factor in the short term, in the long term it raises exciting prospects for development of new materials, new chemical routes and new precursor chemicals, unique to shale oil.

Cost and Profitability Estimates

In order to establish the economic framework for our research, an attempt was made to estimate the process costs, and from projections of the product value, to estimate the profitability of a Shale Oil Native Products Extraction venture. The feed stream to the process facility is a raw, retorted shale oil which we charge to the facility, in the base case, at $30/bbl.

The capacities of the unit operations required to produce the product slate shown in Table 2, were estimated based on conceptual flow diagrams (not shown). Costs for the unit operations were determined from analogy to commercially-practiced technologies. The results are given in Table 3.

Results show that process costs of approximately $15/bbl are anticipated. Results also show that the shale oil barrel is subjected to an average of five process steps to make the product slate priceable at the values given in Table 2. Item -7 represents unspecified finishing steps through which the entire

Table 3 Estimated Process Costs for SO/NPX (Basis: 1,065,000 bbl/year)				
Unit		Process Cost $/bbl	Throughput bbl/yr	Operating Costs $M/yr
1.	Distillation	1.5	1,065,000	1.60
2.	Liquid-Liquid Extraction	2.7	1,065,000	2.88
3.	Adsorption	4.2	958,500	4.03
4.	Dewaxing	3.2	95,850	0.31
5.	High-Efficiency Separation	4.5	60,705	0.27
6.	Hydrofinishing	2.1	777,400	1.63
7.	Miscellaneous (Filtration, Precipitation, Crystallization, etc.)	4.0	1,065,000	4.26
Annual Manufacturing Costs				$14.98M

output of the process facility is charged. This represents a contingency to account for currently unknown process requirements.

In order to account for marketing and distribution costs, a $5/bbl charge is added to the operating costs. This allows for an average shipping radius of about 500-750 miles. Higher value products, e.g., $100/bbl +, may be shipped further. Lower value products, e.g., asphalt additives, may be used locally or regionally.

Capital costs were estimated by summing the unit costs weighted for throughput capacities. A capital cost of $120-million is projected for the 5,000 bbl/day case.

The profitability estimates are shown in Figure 5. Part a) shows the capital cost and return on investment as a function of capacity; parts b) and c) provide the sensitivity to the weighted average product value and raw shale oil costs, respectively; part d) shows the profitability analysis as a function of cost of raw shale oil and plant capacity. The profitability estimates have been made for the 100% equity case, using a 10% discount rate. The profit on investment for various debt-to-equity ratios can easily be estimated by multiplying the DCF/ROI for the 100% equity case by the ratio.

The economic assessments show that an increase in average product value rapidly offsets the process and raw material costs. The incremental price/cost differential promises significant profits on investment capital and a significant return on investment could be made, even if shale oil costs were $40/bbl. Maximum profitability comes from the largest SO/NPX facility that the market will bear.

Conclusions

Commercial viability of synthetic fuels may be enhanced through technology for producing products of high market value. To pursue this objective, we have developed and demonstrated an analytical methodology which forms the basis for a process development strategy. This strategy promises an effective approach to maximizing the value of products isolable, or derivable, from shale oil.

Shale oil has been fractionated according to a simplified laboratory scheme using distillation, liquid-liquid extraction and liquid-solid adsorption, and the products have been characterized. Based on these results, a projected product slate has been constructed. The promised value of the product

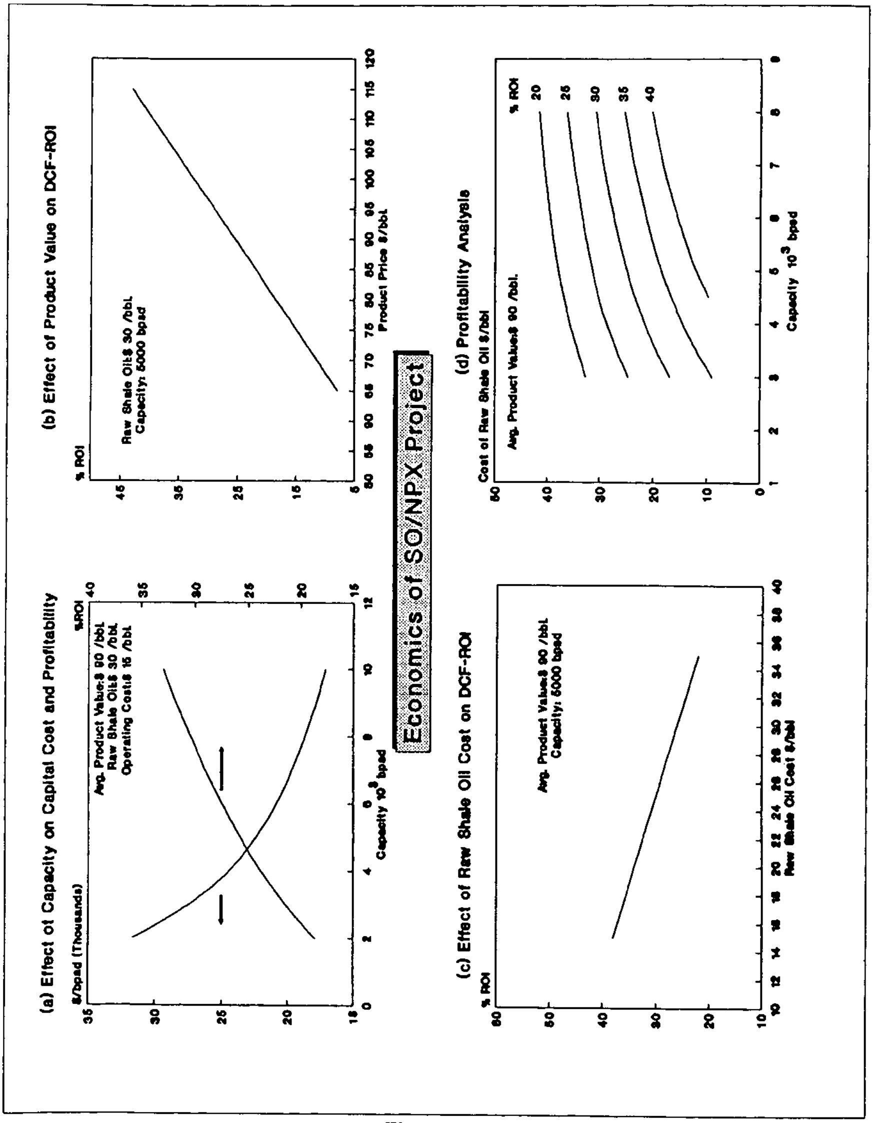
Economics of SO/NPX Project
(a) Effect of Capacity on Capital Cost and Profitability
$/bpsd (Thousands)
%ROI
Avg. Product Value:$ 90 /bbl.
Raw Shale Oil:$ 30 /bbl.
Operating Cost:$ 15 /bbl.
Capacity 10³ bpsd
(b) Effect of Product Value on DCF-ROI
% ROI
Raw Shale Oil:$ 30 /bbl.
Capacity: 5000 bpsd
Product Price $/bbl.
(c) Effect of Raw Shale Oil Cost on DCF-ROI
% ROI
Avg. Product Value:$ 90 /bbl.
Capacity: 5000 bpsd
Raw Shale Oil Cost $/bbl
(d) Profitability Analysis
Cost of Raw Shale Oil $/bbl
Avg. Product Value:$ 90 /bbl.
% ROI
Capacity 10³ bpsd

Figure 5

slate readily offsets the incremental process costs and shows promise for economic profitability. This work provides a sound basis for detailed process and product research and development.

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