Shale Oil Value Enhancement Research

Final Report

March 1, 1993 – November 30, 2006

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July 12, 2007

DOE Award Number – DE-AC21-93MC29240

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DISCLAIMER

ABSTRACT

Raw kerogen oil is rich in heteroatom-containing compounds. Heteroatoms, N, S & O, are undesirable as components of a refinery feedstock, but are the basis for product value in agrochemicals, pharmaceuticals, surfactants, solvents, polymers, and a host of industrial materials. An economically viable, technologically feasible process scheme was developed in this research that promises to enhance the economics of oil shale development, both in the US and elsewhere in the world, in particular Estonia. Products will compete in existing markets for products now manufactured by costly synthesis routes. A premium petroleum refinery feedstock is also produced. The technology is now ready for pilot plant engineering studies and is likely to play an important role in developing a US oil shale industry.

EXECUTIVE SUMMARY

Production of oil from oil shale has, historically, proven non-profitable, due primarily to the low price of petroleum with which it needed to compete in the marketplace. Prior research by J. W. Bunger and Associates, Inc. (JWBA) suggested that raw kerogen oil from oil shale contained valuable nitrogen compounds and if these compounds could be extracted and manufactured to saleable products, revenues would be enhanced and the development of oil shale may be made profitable, even if oil prices remained modest. In 1993 the US Dept. of Energy awarded the present contract to JWBA to research this concept.

Detailed molecular analysis of whole kerogen oil shows 62.1% hydrocarbons (paraffins, naphthenes and aromatics) and 37.9% heteroatom-containing compounds (pyridines, pyrroles, phenols, sulfides and thiophenes). Among this latter class of compounds pyridines, pyrroles and phenols, representing 23.4% of the whole oil, are targets for manufacturing high value compounds. Pyridines are used in the manufacture of vitamins for animal feeds and environmentally-benign herbicides for the agrochemical industry; pyrroles are used for specialty products in the fragrance industries as well as industrial solvents; and phenols are used for resin manufacture for the wood industry.

Pyridines, which are Lewis bases, are selectively extracted by low molecular weight carboxylic acids to yield an extract concentrate that can be refined into high value chemicals and commodities, and a raffinate that is readily upgraded to a premium refinery feedstock. Research of various process schemes revealed a choice between complex schemes that would maximize the value and the number and value of products, or simpler schemes that would focus on just a few, high value products.

The market and economic analyses point to a process scheme that produces a few, high value products. The simplicity reduces the number of process steps that need to be proven and the number of products that need to be qualified in the marketplace. The optimum product slate consists of about 7% pure, specialty chemicals, 8% commodities such as asphalt additives, and 85% premium refinery feedstock. The potential additional market opportunities establish future growth opportunities, but for a first-generation plant the additional market and process uncertainty outweighed the revenue advantages.

When the development opportunity was presented to industry in the late 90s, there was universal interest in the technology and products, but the absence of a source of kerogen oil served as an impediment to investment. About 1999 DOE became interested in applying the Value Enhancement Process concept to Estonia Kukersite kerogen oil. Estonia has been producing kerogen oil for more than 80 years and has a reliable supply of oil. If the VEP concept could be proven with Kukersite oil and a venture developed around this feedstock, a business model would be proven for replication in the US. A key benefit of this synergistic relationship is that high-value products from Kukersite oil are primarily phenolic compounds whereas high-value products from Green River Formation (US) oil are pyridinic and pyrrolic compounds; hence, both ventures could proceed without competing in the same marketplace.

The simplified VEP process was shown to be applicable to Estonia Kukersite kerogen oil. In this case yields were 7% pure, specialty chemicals, 13% commodity products, and 80% refinery feedstock. More research is still required to achieve process assurances on the production of Estonia products, especially in the area of dealkylation of resorcinols, but the goal of the development is clear.

The added revenue afforded by the kerogen oil products allows the VEP venture to pay more for raw kerogen oil than a refiner could afford to pay, offering a market pull to those interested in producing kerogen oil. For both the US and Estonia cases, there will be market volume limitations for the pure, specialty chemicals that will prevent the VEP process from being applied at a massive scale, e.g. 100,000 bbl-feed/day, or greater. However, the cost advantage of the extracted chemicals, compared to synthesized chemicals, assures the VEP venture a competitive advantage on price, and in time could come to dominate world markets for these select chemicals. The first player in this market space will create a barrier to entry to successive developments because the pricing advantage will already have been realized.

Meanwhile, prices of oil have now risen to levels not seen in several decades. Based on today's prices, and using $50/bbl crude oil as the reference price, the US product slate would be valued at about $105/bbl and the Estonia product slate would be value at about $90/bbl. The specialty products from Estonia oil are at least as valuable as those from the US and will be more readily marketed, but the oils are more aromatic and refining is more difficult, accounting for the differences.

The research concludes there is a clear profit potential for VEP and that the economics have improved with higher oil prices. This favorable trend is due to the fact that synthesis chemicals, with which kerogen oil products would compete, are becoming even more costly to produce because of the escalating prices for energy and feedstocks. This trendline bodes well for future economics and reinforces the notion that for those oils rich in heteroatoms, extraction methods will be able to compete on a cost basis with synthesis methods, thereby facilitating market penetration on a world-wide scale.

The final report includes details of laboratory experience and the rationale leading to the principal conclusions.

- Raw kerogen oil is rich in heteroatoms that are costly to remove if simply processing as a petroleum substitute, but afford an opportunity to extract and process for high value products.
- Commercially-reasonable liquid-liquid extraction conditions have been found that selectively separate polar compounds, desired for their heteroatom functionality, from non-polar compounds, desired for their fuel value, thereby upgrading both sides of the separation.
- Conversion processes have been shown by laboratory methods to yield products of interest to the marketplace.
- A simplified process scheme emphasizing a few high-yield, high-value products gives the best process and market assurances and shows attractive investment economics.

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INTRODUCTION

By the early 90s it was apparent that oil from oil shale could not compete with petroleum, so long as the price of crude oil was below about $30/bbl. Petroleum prices had remained modest for a decade and the US Synfuels Corporation had been defunded in 1985. More recently, the last two industrial ventures, Unocal's surface demonstration project and Occidental Oil Shale's modified in-situ (MIS) project had been abandoned. During these years the question was raised; "if oil shale could not compete with petroleum at then-current prices could it be rendered profitable if it were processed into higher value products?" Higher value products would increase the revenue stream and partially uncouple the economics from petroleum prices.

In 1993 JWBA was awarded a competitively-procured contract to explore and develop a value-enhancement process concept, known as VEP. The essential approach of the concept is to first extract heteroatom-containing compounds (principally the nitrogen-containing compounds) from kerogen oil fractions,[1] and to subsequently process the heteroatom-rich stream(s) for chemicals. The heteroatom-lean stream(s), or raffinate, is processed for fuels. JWBA held extensive experience in analysis of the molecular composition of highly complex multi-component mixtures, as well as process experience with shale oil and petroleum, and offered to use this experience to develop chemically effective processes that maximize the value of the products streams, while minimizing costs.

Changing dynamics in the field, coupled with evolving needs of DOE resulted in a number of contract modifications and extensions of time. A significant modification was the application of composition and processes knowledge to studies of Estonia shale oil. Oil shale has been commercially produced in Estonia for nearly 90 years. Today, three enterprises produce about 10,000 bbl/day of oil. The reliable supply of raw shale oil is a major step toward commercialization, a situation that did not exist in the US. If the VEP concept could be proven with Estonia shale oil, then a business model would be demonstrated for possible replication in the US.

Ultimately, 19 tasks were completed. For reporting purposes results have been aggregated into task topics even though work may have been done toward the task objectives in different phases. The tasks with their principal objectives are briefly outlined as follows:

1. NEPA – To assure compliance with all applicable regulations.

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[1] In this report the terms 'kerogen oil' and 'shale oil' are used somewhat interchangeably. However, 'kerogen oil' reflects the actual chemical origin of the oil, namely 'kerogen' not 'shale', and is used in the context of value-enhancement processing (VEP). The distinction; 'kerogen oil' is manufactured for its inherent chemical values, while 'shale oil' is manufactured for its traditional fuel values. This distinction could become important when selecting recovery approaches and during recovery process optimization.

2. Separation Characterization – To understand the separation behavior of raw kerogen oil as a basis for separation process design.

3. Analytical Procedures and Oil Characterization – To develop more routine analytical procedures needed to study the molecular composition and properties of kerogen oil and to apply those procedures for optimizing separation, conversion and product manufacturing design.

4. Marketing Research – To identify the commodity volumes, product characteristics and companies engaged in potential markets for kerogen oil products.

5. Separation Exploration – To identify plausible separation schemes including applicable feedstocks, process conditions, and product characteristics.

6. Conversion Exploration – To identify plausible conversion processes for increasing yields and improving qualities of target products.

7. Process Modeling and Preliminary Economics – To explore the process economics as a guide for further process development.

8. Separation Development – Using plausible separation process schemes identified in Task 5 and guided by Task 7, to measure the effects of separation process variables on yield and product qualities.

9. Conversion Development – Using plausible conversion process schemes identified in Task 6 and guided by Task 7, to measure the effects of conversion process variables on yield and product qualities.

10. Product and Process Integration – To design and test a plausible process scheme at the bench level.

11. Simulation and Economics – To update the cost and profitability estimates and determine the sensitivities to product yields and qualities.

12. Product manufacture – To generate samples of key products in the laboratory.

12a. Product manufacture - Estonia – To apply separation and conversion techniques to Estonia shale oil, and characterize products.

12b. Process Integration – Estonia – To design and test plausible process schemes at the bench level for Estonia oil.

13. Test Marketing – To identify potential buyers for products and to compare product specifications with market-accepted specifications.

13a. Test Marketing – Estonia - To identify potential buyers for Estonia products and to compare product specifications with market-accepted specifications.

14. Venture Development – To identify the impediments to development and prepare an investment-attractive path forward.

14a. Venture Development – Estonia - To identify the impediments to Estonia development and prepare an investment-attractive path forward.

14b. US Venture Development – Update – To update the US venture development path in view of renewed (2006) interest in US oil shale resulting from escalating oil prices.

EXPERIMENTAL

1. NEPA – Environmental information was provided to DOE for their determination of the appropriate level of NEPA Documentation. Permits were applied for and granted based on information provided by DOE, as well as all local regulatory requirements.

2. Separation Characterization –

   2.1. Study sample - The study oil was raw Unocal production oil drawn during their semi-commercial operation. It was decided early in the project that selection of a single commercially-representative shale oil for thorough examination would provide future investors some assurance that the feedstock for a Value Enhancement Process could be reproduced at the commercial level. A general description of the Unocal process and oils produced from it is given in Reeg.[1] It was requested, and it is believed, the samples received from Unocal were produced under typical operating conditions.

   2.2. Separation methods - The behavior of raw kerogen oil in distillation, liquid-liquid extraction and liquid-solid adsorption or precipitation, was characterized. A thermodynamically logical process scheme was sought. Process conditions were selected to yield the maximum amount of commercially important information. A rigorous material balance was performed around the separation. Separation products were characterized according to the analytical procedures developed in other tasks.

   2.3. General method for material balances – Through prior experience Contractor has developed a laboratory procedure for minimizing the effect of weighing errors on research results. Balances owned by Contractor were specified and procured to possess minimum capacity-to-precision ratios of 10^5 whenever available. Using the appropriate balance allows results to be calculated to 3 significant figures without introducing weighing errors. The balances available for this research are summarized in Table 1. Wherever possible all experiments were done by mass, rather than by volume.

Table 1: Description of Analytical Balances

Balance	Capacity	Precision	Capacity/Precision
Precision	250 g	± 0.0001 g	2.5 E6
Top Load #1	1200 g	± 0.01 g	1.2 E5
Top Load #2	10,000 g	± 0.1 g	1.0 E5
Bulk scale	400 kg	± 0.1 kg	4.0 E3

Distillation – Five distillation units were used in the course of the research.

2.3.1. 4"- semicontinuous tower – A 10 tray 4" x 6' stainless steel distillation unit was used for bulk distillation of kerogen oil. The tower was outfitted with an immersion heater in the reboiler, guard heaters at each tray level, a preheater (with immersion heater) and a water-cooled condenser with reflux. Bottoms product was withdrawn by a calibrated variable-speed gear pump. Mass flow rates were measured by on-line electronic balances used to weigh feed and recovery vessels.

Throughput rates were approximately 4 liter/hr. The column was operated as a splitter, not a fractionator. That is, only overhead and bottoms were collected; no side draws were taken. For general operation the column was brought to steady state before study samples were collected. The bottoms from the first cut would be used as feedstock for the next cut taken at higher temperature. Although the column is capable of operating at reduced pressure, all distillations were made at ambient atmospheric pressure (~640 mm Hg at Contractor's location)

Several distillations were made, but the essential study samples were a > 150 °C topped whole shale oil and a fractionated shale oil. The > 150 °C oil was used for extraction of whole oil. (For liquid-liquid extraction it is necessary for solvent recovery that lower boiling components of the oil be removed; these lower boiling components are readily processed by conventional technologies.) A second batch of whole shale oil was cut at 200 °C and 275 °C to produce a <200 °cut, a 200-275 °C cut and a > 275°C bottoms. The > 275 °C bottoms were sent to a thin-film still for further splitting.

2.3.2. Thin film still – A glass Distact 6" thin film still (housed at the Univ. of Utah) was used to distill the > 275 °C bottoms into a 275 – 400 °C distillate and a > 400 °C residue.

2.3.3. ASTM D-2892 still – A 15/5 packed column with a 5 liter pot, meeting ASTM D-2892 specifications, was used for higher efficiency fractionation of kerogen oil fractions or raffinate products. The apparatus was computer controlled with respect to boil-up rate and reflux ratio.

2.3.4. Bench scale pot still – A bench scale pot still with a simple distillation head and vigraux tube was used for small-scale fractionations. Like the D-2892 apparatus, multiple cuts could be taken as the pot temperature was increased. In all distillations care was taken not to exceed pot wall temperatures of 320 °C, the maximum safe temperature to avoid thermal cracking. A vacuum distillation head was also used for vacuum distillations.

2.3.5. Rotovap – A commercial rotary evaporator was used to evaporate solvents from samples. For recovery of organic acid solvents from base extracts a small bleed of CO_2 was bubbled into the liquid by a tube inserted through the flask stem. The CO_2 acted to 'spring' the solvent by displacing the association of the acid with the base.

2.4. Extraction- Liquid-liquid extractions were carried out at 3 different scales.

2.4.1. Test tube tests - Tests were conducted to screen solvents, to ascertain conditions for phase separation, and to note preliminary (wet) volumes of extracts and raffinates.

2.4.2. Shake tests – Tests were conducted using separatory funnels, typically using 1 or 3 stages. When 3 stages were used solvent-to-oil ratios were calculated from the sum of the solvent volumes used for the 3 stages. Most shake tests were conducted at ambient temperatures, although some were conducted at controlled, elevated temperatures.

In a typical shake test a measured amount of oil would be added to a measured amount of solvent. The separatory funnel would be well-shaken and phases allowed to separate. The bottom layer, typically the extract, would be drawn off into a pre-weighed round-bottom flask and weighed. The top layer, typically the raffinate, would be successively drawn off and weighed. Solvents would be stripped by rotary evaporation and the resulting dry extract and raffinate would be weighed. Solvent and product mass balances would be calculated.

2.4.3. Semi-continuous multi-stage extraction tests – Tests were conducted in a seven-stage 2” x 4’ glass, pulsed perforated tray extraction (PPTE) column. These runs were made for preparatory purposes and designed to simulate commercial extraction conditions. It may be noted that for separation processes that scale-ups of 1000 to 1 are possible, provided that the thermodynamics are well-understood.

In PPTE the extraction solvent is metered to the top of the column (below the top tray), oil is metered to the bottom (above the bottom tray), extract is withdrawn at a metered rate from the bottom, and raffinate is withdrawn from the top (the default leg). The feedstock oil is generally pre-saturated with solvent so that the next contact with extraction solvent induces phase separation.

In typical operation the system is brought to steady state conditions. Feedstock vessels are weighed, and product is switched to clean, weighed vessels. Runs are continued until the target volumes of product are accumulated. Solvents are stripped by rotary evaporator to generate the dry extract and raffinate samples. Weight measurements are used to close the mass balances. Process conditions for the various runs are reported in the results section.

2.5. Dewaxing – Dewaxing of raffinate was accomplished by batch solvent dewaxing typically using methylethylketone (MEK) and toluene in a 50-50 volume mixture. Solvent to oil ratios were typically 4:1. Waxes were filtered by vacuum filtration, sparingly rinsed with chilled, dewaxing solvent, air dried and weighed.

3. Analytical Procedures and Oil Characterization

3.1. Summary - Algorithms, methods and procedures for routine Z-BaSIC (Z-Based Structural Index Correlation) characterization of kerogen oil fractions and products were formally developed. The procedures so developed were applied to the whole study oil as well as kerogen oil fractions derived in the separations characterizations task. The Z-BaSIC characterization was subsequently used to evaluate products. The technique established the computerized relationship between composition and properties needed for specification matching and process optimization.

3.2. GC-MSD method - The essential tool for Z-BaSIC analysis is the GC-MSD equipment manufactured by Hewlett-Packard. This equipment was procured early in the contract with cost-sharing from JWBA. After some experimentation a standard method was selected.

Conditions and Method

GC: HP 5890
Carrier: Helium 0.826 ml/min constant flow
Column: HP-5MS 30m x 0.25mm x 0.25 µm
Inlet: 275°C Split mode (50:1), 0.1µ neat injection
Oven: Initial - 0°C, 5°C/min to 310°C (5 min hold)
Detector: HP 5972A MSD, TIC mode (50-500 amu)

Procedure

One tenth of a micro liter of the sample to be analyzed is injected neat into a Hewlett Packard model 5890 series II Gas Chromatograph (GC) using a Hewlett Packard model 7673 automatic liquid sampler (ALS). The injection port is pressure programmable and is set for constant flow with an initial pressure of 4 psig and a temperature of 275°C. The injection port is operated in the split mode with the split ratio set at approximately 50:1. This ratio may need to be optimized to give a total ion chromatogram (TIC) with a maximum abundance of 0.5-1.5 million counts. The GC is equipped with an HP-5MS capillary column 30 meters long and 0.25 mm internal diameter. The stationary phase consists of a 5%-Diphenyl-95%-Dimethylpolysiloxane Copolymer with a film thickness of 0.25 micrometer. The Helium carrier gas is flowing at approximately 0.826 ml/min. in constant flow mode. The GC oven temperature is initially set to 0°C and programmed to heat up to 310°C at 5°/min. with a 5 min. final hold. The analytes are detected with a Hewlett Packard 5972 series mass selective detector (MSD). The data.ms file is analyzed using Hewlett Packard MSD ChemStations software, and proprietary methods developed by JWBA.

3.3. MW measurements – Determining average MW of multi-component mixtures is difficult. For all known techniques there are errors due to intermolecular association that are difficult to quantify. Two methods were used in this work. The first uses Vapor Pressure Osmometry (VPO) with various compatible solvents. A novel method for calculating the true molecular weight from VPO results, and referred to as the BRD method, was employed. In the BRD method molecular weights would be calculated from VPO measurements of differing concentrations and a specialized thermodynamic procedure was used to arrive at a true dissociated state. The method is fully described in US patent 5,574,215.

In a second method, a total ion current trace (TIC) from the GC MSD would be integrated to find the average retention time. From a retention-time vs. boiling point correlation established for n-paraffins, and correcting for average cyclic character of the sample an average molecular weight was calculated. Because this latter technique was simpler, it was the most commonly used technique in this work.

3.4. Z-correlations – Details of the Z-BaSIC method are provided in reference[2,3,4]. A necessary step in the interpretation of GC-MSD information to understand the retention time for each molecular type. For this, the parent ion for each molecular type was manually sought by inspection of the extracted ion chromatograms (EICs), over the expected retention time window based on boiling point. From this inspection a correlation of parent ions with retention time windows was developed.

Properties of pure compounds, density, critical temperature and vapor pressures (coefficients of the Antoine equation) were correlated against the number of carbons for each molecular type (see also results section). Full utilization was made of API RP-44 database on properties of petroleum-based compounds, as highlighted by Steele[5] Correlating properties with the numerical values of Z-BaSIC allows us to know the parent structure and some key properties of components eluting from the GC by merely knowing their retention time and parent mass. The molecular structure is not needed in order to know the properties.

3.5. Partition Function Analysis – For each companion extract and raffinate a GC-MSD would be run and for each desired component a comparison would be made between the integrated area under the parent peak in the extract and raffinate, normalized to the total areas under the curves. The beauty of this technique is that it was not necessary to know the response factor of the peak, as it could be assumed that the response factor for a given compound was the same in the extract as in the raffinate. By normalizing the total areas to the gravimetric yields determined in the laboratory, the need to know the relative response factors of the entire fractions were likewise eliminated.

3.6. Potentiometric titrations for basic nitrogen were conducted according to ASTM D-4739.

3.7. Ion-exchange chromatographic separations were conducted according to the method described in reference[6]

3.8. Elemental analyses were conducted by a commercial analytical laboratory.

4. Marketing Research

   4.1. Summary – Markets for anticipated products were analyzed for volumes and trends. Markets were classified according to types of materials needed including composition, if known, and volume and price relationships. Results of market analysis and product compositions were compared with the compositional data obtained in Tasks 2 and 3 above. A candidate list of target products was developed by using experience and knowledge of composition of matter.

   4.2. Process and Product Analysis - The assessment was used to draw a plausible separation and conversion scheme for each of the target products. Products which appeared to have complementary relationships from a processing point of view were grouped. Products which appear to be exclusive of one another were identified. This latter category may include multiple products for a specific compound type. Specific difficulties in preparing the product were identified and such difficulties were considered during the later phases of the project. Based on this analysis, a target set of products was prioritized. This information was used to design laboratory-scale separation and conversion processes for manufacture of products.

5. Separation Exploration

   5.1. Summary - Separations approaches for isolation of each of the priority target products were devised. Preparative scale separations were conducted according to the devised schemes. Separations included distillation and liquid-liquid extraction.

   5.2. Product streams were subjected to elemental and physical property analysis, specifications testing or further processed by conversions processing.

6. Conversion Exploration

   6.1. Summary - Processes for conversion of separated concentrates into marketable products were explored. Candidate conversion processes included catalytic hydrogenation and oxidation, thermal hydrodealkylation (THDA), chemical dealkylation, polymerization, hydrolysis, derivatization and other possible chemical processes. At this stage of the project only batch THDA, a critical step in the identified process schemes, was examined. In the development phase of the project, additional methods were employed.

   6.2. Batch THDA – Experiments were conducted in a stirred stainless steel batch autoclave at the University of Utah. In a typical experiment >400 °C oil was weighed into the autoclave, the system was pressurized with hydrogen to 800 – 1600 psig and stirring was initiated. The temperature of the autoclave was raised to a desired holding temperature, typically 400 °C, where the system was held for a period of time (10min to 1 hr). These temperature and pressure conditions are analogous to hydrovisbreaking conducted in the petroleum industry. During this process gases were released (holding the pressure constant) through a metering device and their volume measured. At the end of the holding time the system was cooled and liquid sample was withdrawn and weighed.

7. Process Modeling and Preliminary Economics

7.1. Summary - Results were used to prepare flow diagrams of at least two alternative process approaches. Process units were specified and material balances were calculated. Process conditions identified in the separations and conversion tasks were used to determine heat duties and solvent recycle requirements. A cost analysis of the processes was performed using factored estimates and analogy to currently-practiced technologies. Prices were assigned to the products and profitability (cash flow) analysis was conducted. The economic sensitivity to various economic assumptions was performed. Based on these results, a recommendation was made as to the most promising direction to pursue in a process development phase.

8. Separation Development

8.1. Summary - Process apparatus for separations were designed, constructed and operated. The operations were conducted to obtain information on engineering parameters including, but not limited to, temperature, contact ratios, solvent quality, partition function values, stage efficiency, and other important parameters. Data were obtained in a form which allows for rigorous and fundamental process modeling.

8.2. Distillation – Preparatory distillation apparatus and procedures are described in Task 2 above.

8.3. Extraction – Preparatory extraction apparatus and procedures are described in Task 2 above.

9. Conversion Development

9.1. Summary - Conversion apparatus for selected conversion process trains were designed constructed, and operated. Engineering data, including kinetic data, and the effect of process variables on product yield and composition were obtained. The process reaction models for use in process simulators were developed.

9.2. THDA – In addition to the thermal hydrovisbreaking, thermal hydropyrolysis conversion was conducted. A downflow, open tube SS reactor 1” ID by 12” in length was used. Oil was preheated to about 400 °C and introduced through a dispersion nozzle at the top of the reactor. Hydrogen was superheated to about 650 °C and fed to the reactor at pressures ranging from 800 to 1800 psig. The preheat temperatures and the hydrogen to oil ratios were controlled to result in a desired reaction temperature, typically 500 – 575 °C. An electric guard heater was installed around the tube to avoid heat losses through the reactor walls. The resulting residence time in the reactor was on the order of 1 to 3 seconds. Product leaving the reactor was quenched, and gases were separated from liquids in a high pressure flash vessel. Further details regarding hydropyrolysis processing of hydrocarbons can be found in references[7,8].

9.3. Catalytic Hydrotreating – the same reactor used for hydropyrolysis was used as a trickle-bed reactor. In this mode the oil was introduced to a dispersion plate positioned at the top of the catalyst bed. Commercially available Ni-Mo catalysts were used. The catalyst was pre-sulfided before use. Temperatures were held in the range of 320-390 °C, pressures at 800 – 1800 psig, and LHSVs of 0.5 to 1.0.

10. Product and Process Integration

10.1. Summary – The various process options were analyzed for simplicity, estimated product yields and integration to develop a preferred process scheme. Heteroatom-containing products from kerogen oil may be classified as either pure compounds or concentrates. The preferred process scheme was tested using equipment from Tasks 8 and 9 to verify anticipated product yields and quality.

10.2. Details - Preparation of refinery feedstock and heteroatom concentrates where conducted according to sequences reported in the results section of this report. In general, purification schemes for pure compounds were developed theoretically. To accomplish this objective, the feedstocks for the purification process (generally the light ends extracts) were quantitatively analyzed for their composition by GC-MSD and from known pure compound thermodynamic properties a distillation sequence would be designed.

11. Simulation and Economics

11.1. Summary - A base case was defined which considered the state of conventional processing, scale, market limitations and other factors. The preferred scheme was cost-estimated and profitability analyses were performed. Values for the base case parameters were varied to determine the economic sensitivity of each economic variable on profitability. This sensitivity analysis was conducted on a process and product specific basis to determine areas of highest risk and greatest economic impact. The prime economic variables considered were revenue, capital cost, operating cost, debt interest, transportation and marketing costs, raw materials (kerogen oil) cost, royalties and taxes.

12. Product Manufacture

12.1. Summary - Using the equipment on hand, target products were manufactured in liter quantities for market inspection. A suite of products were produced representing the range of target products. The products were analyzed by Z-BaSIC and specification methods.

12.2. Products

12.2.1. THDA Feedstocks - A concentrate of higher alkyl pyridines amenable to dealkylation to produce marketable lower alkyl pyridines were produced as a distillation overhead from a solvent extract.

12.2.2. Asphalt additives – A polar extract distillation residue containing basic nitrogen useful for their antistrip properties (resisting moisture-induced de-adhesion of asphalt binder from aggregate) were produced as a distillation bottoms from a solvent extract.

12.2.3. Refinery feedstocks – A low N and S, full range process stream (acceptable to Western US refineries) were produced by catalytic hydrotreating of the raffinate from solvent extraction. Upgraded raffinate is superior in quality to Alberta syncrude currently being processed in Western US refineries and is expected to successfully compete, especially in the small amounts, e.g. 5,000-10,000 bbl/day that would initially be produced.

12.2.4. Pure compounds – Primarily pyridine, pyrroles, phenol, thiophene and their lower alkyl homologs would be produced by high efficiency distillation of low boiling extracts. Thermodynamic modeling was used to assess the necessary distillation conditions and stage efficiency.

12a. Product Manufacture – Estonia

12a.1 Experimental – Oil soluble phenols were extracted from Kukersite kerogen oils in JWBA laboratories using non-ionic solvents similar to those used for US (Green River Formation) kerogen oils. Oil soluble phenols were extracted in Estonia using ionic caustic wash, followed by acidification of resulting salts.

12a.1.1 Source of Oil. Samples of Kukersite kerogen oils (KKO) were obtained from commercial operations in Estonia in 1993, 2000 and 2002. Oils were topped by distillation at either 150 or 200 °C to remove light ends to simplify the solvent recovery step from the extraction process. The total residue from this topping step was used directly for extraction. Toppings from the distillation were scheduled directly for the purification step.

12a.1.2 Extraction. A semi-continuous, counter-current, pulsed perforated tray column was used for the extraction. Extraction solvents were selected from the following list: formaldehyde, formic acid, methanol, acetaldehyde, acetic acid, ethanol, propylalcohol, isopropylalcohol, furfural, phenol, sulfolane, N-methyl-2-pyrrolidone. Solvents were removed by distillation, prior to analysis and subsequent processing.

12a.1.2.1 Galoter Oil. Two experiments were run, one in which the Galoter oil was washed with neutral water, the other by washing with 0.1N NaOH solution. The experiments were carried out in a test tube using 1cc of aqueous solution and 1 cc of cyclohexane. Approximately 200mg of raw oil was added heated to 50 °C, shaken, ultrasonicated, and allowed to separate at 50 °C. The raffinate phase was decanted from the top with a pipette and used directly for GC–MS analysis. The aqueous phase was decanted from the bottom with a pipette, neutralized with HCl and back extracted with 1 cc ethyl acetate. The ethyl acetate solution was used directly for GC-MS analysis.

12a.1.3 Conversion Processing. The principal objective of conversion processing was to dealkylate the hydroxyaromatics, without dehydroxylation. Test methods used included pyrolysis, hydropyrolysis, reverse Friedel-Crafts and aquathermolysis.

12a.1.4 Analyses. Density, viscosity and elemental compositions were measured by conventional methods. Average molecular weights were estimated from GC-MSD. Molecular compositions were analyzed by the Z-BaSIC method

12b. Process Integration – Estonia

12b.1 Much of the work done on process integration was done in Estonia, at no expense to the current project. Full reports of the Estonia work are available from the Office of Petroleum Reserves, NPOSR[9, 10,11].

13. Test Marketing

13.1. Summary - A survey was conducted for market interest in products manufacturable from kerogen oil. The target products and analytical data for the optimum product slate were provided for inspection. Interested parties were asked to comment on the acceptability and value of the product for its applications and, most importantly, cite any deficiencies that they perceived in the product character. This information was incorporated into considerations of optimum process design.

13.2. Agrochemical testing – samples were submitted to an agrochemical company for testing as herbicides and insecticides. Procedures were not disclosed per confidentiality agreements.

13.3. Antistrip asphalt additive testing - samples were submitted to one testing laboratory and one industry company for testing as antistrip additives. Results are reported in the results sections. Procedures used by the industrial lab were not disclosed per confidentiality agreements.

13.4. Sweet refinery feed – A specification sheet was prepared for inspection by a local refinery. A written response was received indicating the sample submitted possess premium refining qualities.

13.5. Pure compounds – Visits were made to various buyers or users of pure compound products. A list of key contaminants to avoid (for their particular uses) was identified. Purification schemes were devised to take this information into account.

13a. Test Marketing – Estonia

13a.1 Pure compounds. The pure compounds manufacturable from Estonia kerogen oil are all water soluble. Compounds such as resorcinol, 5-methyl resorcinol and various phenols and cresols are targets for pure compound manufacture. Estonia has an on-going program to develop pure compounds from water soluble extracts, and this program did not duplicate this effort.

13a.2 Broad Range concentrates. The bulk extract produced in this program is referred to as ‘oil-soluble phenols’. Uses are for wood preservatives, UV blockers, industrial solvents, fuel additives, etc. The market qualifying research was done in Estonia, at no cost to this contract. Efforts in the US were aimed at converting these ‘oil soluble phenols’ to lighter alkyl products that would feed into the refining scheme under development in Estonia. More experimental details are found in reference 9.

14. Venture Development

14.1. A Venture Development Plan was prepared. The plan specifies the technical, market and economic potential discovered in this research and the requirements for the next phase of development. This plan forms the basis for kerogen oil venture development involving private sector funding. The Plan was presented at a Venture Capital Conference sponsored by the US Dept. of Energy.

14a. Venture Development – Estonia

14a.1 A Venture Development plan was prepared. The plan emphasized the need to engage an industrial consortium in the next phase of development. A consensus among Estonia stakeholders is needed to execute the plan.

14b. US Venture Development – Update

14b.1 New mass balances were performed in view of improved analytical results and new interest in larger scale production in the US. Economic analysis was updated to current costs and prices. The role of VEP in industry development was detailed.

RESULTS AND DISCUSSION

PHASE I – EXPLORATORY RESEARCH

Task 1 - Information Required for the National Environmental Policy Act (NEPA)

Statement of Work

Information will be developed to satisfy NEPA requirements for permitting and regulatory compliance. A description of the process in terms of unit operations and a flow diagram will be projected. Special attention will be paid to any possible discharges, effluents or disposal requirements. NEPA requirements addressed include but are not limited to air quality, water resources, land use, waste management, ecological impacts, sociological impacts, archaeological, cultural and historic resources, noise, occupational safety and health and related issues. A Table specifying required local permits, the responsible agencies and contacts will be prepared. An overall assessment of the prospective compliance of the proposed technology with NEPA's requirements will be performed.

Results

1.1 NEPA

The information required for National Environmental Policy Act (NEPA) to determine the overall project classification include:

(a) Materials consumption
(b) Waste generation
(c) Facilities modification
(d) Waste disposal
(e) Overall impact on the environment

The total anticipated consumption of the raw kerogen oil is expected to be between 4-8 barrels (bbls) for all three phases of the kerogen oil value enhancement research. (Actual consumption was less than 3 barrels, including Estonia shale oil.) The use of various solvents for liquid-liquid extraction is expected to be not more than 1 bbl. The consumption of solid adsorbent will not be more than 100 pounds. The amount of anticipated waste generation is shown in Table 1.1.

The waste disposal has been addressed by developing a hazardous waste management plan. The waste will be picked-up by a suitable contractor or incinerator operator depending on its type. Appropriate procedures have been implemented to handle waste and gas streams without affecting the operating personnel. An environmental safety and health safety code has been written. The overall impact as shown in Table 1.1 illustrates that there are no significant environmental impacts from the project during the period of performance.

Approval for categorical exclusion-B (CX-B) was granted for The Base Program (Phase I) on June 20, 1994 and for the optional phases on December 19, 1994. JWBA's laboratory facilities are located in an industrial zone in West Valley City (WVC), Utah. The Company annually renews its business license and Hazardous Materials permit with WVC.

Table 1.1: Environmental Impacts of Kerogen Oil Value Enhancement Research

Class	**Anticipated Impact**	**Estimated Actual Impact**
Air Emissions (VOCs)	44 lbs/year	< 44 lbs/year
Water Use	12000 bbls/year	<1000 bbls/year (cooling water)
Land/Facilities	Modifications within project boundaries	Modifications within project boundaries
Waste, Liquid	2 bbls/year	< 1 bbl/year (to licensed hazardous waste incineration)
Waste, Solid	100 lbs/year	~ 100 lbs/year (mostly disposable labware)
Socioeconomic	Providing Employment	Providing Employment
OSHA	Compliance	Compliance

Task 1 Conclusions

The environmental impact of the project was substantially less than originally anticipated. Release of VOC, production liquid waste and use of water were all below anticipated quantities. Liquid waste was disposed of by incineration through a licensed hazardous waste disposal company. All solid waste generated was non-hazardous and did not require special handling for disposal. The reduced environmental impact was due in large part to careful design of and precise measurement during small-scale laboratory experiments, thereby generating high quality data without the requirement for massive scale.

Task 2 - Separation Characterization

Statement of Work

Raw kerogen oil will be separated according to a thermodynamically logical separation sequence. A process sequence of distillation, liquid-liquid extraction and liquid-solid adsorption or precipitation, will be employed. Process conditions will be selected to yield the maximum amount of commercially important information. A rigorous material balance will be performed around the separation. Separation products will be characterized according to the analytical procedures developed in Task 3. A generalized process/product map will be prepared.

Results

2.1 Study Sample

Eight 55 gallon barrels of Unocal kerogen oil were obtained for the value-enhancement research program. Table 2.1 shows properties of raw kerogen oil. When drawing samples for study a barrel was first heated to 80 °C and thoroughly mixed. This procedure ensured that waxes would be melted and a representative sample was drawn. The observed solid nature of the shale oil at cool, room temperature is consistent with the estimated pour point, although the pour point of the original sample was inadvertently not measured. Because the contents of the samples were kept under N2, it was assumed they remained unchanged over time. Various analytical tests conducted during the course of the research (density, GC analysis, etc.) did not reveal any obvious changes with time.

Kerogen oil is comprised of molecules exhibiting a wide range of boiling points and polarities. Prior work of others, most notably researchers at the Laramie Center of the USBM and successor organization, was used as a starting point. Nitrogen bound in shale oil is known to occur in 5-membered pyrrolic rings and 6-membered pyridinics rings, and is known to be concentrated in the higher boiling range. However, at the beginning of this work, it was not known how the nitrogen was bound in the higher boiling ranges, whether predominately in single ring compounds, multi-ring compounds, or some other functionality. It was important that this question be answered

2.2 Distillation

To characterize the separation behavior the kerogen oil was first distilled into narrower boiling range fractions. These distillate fractions were subsequently separated by liquid-liquid extraction into a polar extract and a non-polar raffinate. The separation of kerogen oil into distinct fractions by their molecular weight and polarity is the first step in the approach to producing value-added chemicals.

Table 2.1: Raw Kerogen Oil Properties

Property	Typical Results supplied to JWBA in personal communications - 1992	Study Sample Results
API Gravity	22.8	22.8
ASTM D 2887 Distillation °F		
IBP	200	193*
10	407	384*
50	710	715*
90	950	935*
FBP	1080	1062*
Nitrogen Wt %	1.8	1.53
Sulfur Wt %	0.95	0.92
Pour Point °F	>20	58*
Carbon Residue, Wt %	0.3	0.13*
		* Z-BaSIC results

The 10 tray column described in the experimental section was run in a packed column mode. The efficiency of the column was tested with the cyclohexane-toluene system, which showed that rectification was very good but the stripping efficiency was lower.

Figure 2.1 shows the overall distillation scheme and their yields. The >275 °C was fractionated using a thin film distillation apparatus under vacuum to generate a 275 – 400 °C overhead and a > 400 °C underflow. Table 2.2 shows results of elemental analysis and estimated average molecular weight (from GC-MS) for these fractions. Figures 2.2-2.5 show total ion chromatograms (TICs) of these fractions as analyzed by GC-MS. For this research program, this distillation efficiency is acceptable. It is important to note almost 50% of the barrel is in the > 400°C residue fraction that contains 2% by weight of nitrogen.

Table 2.2: Elemental Analysis of Distillate Fractions of Kerogen Oil

Fraction	Wt.%	C	H	N	S	O	H/C	Avg. MW
<200 °C	11.9	85.8	12.6	0.28	1.02	0.3	1.76	124
200-275 °C	13.1	85.4	12.8	0.59	0.94	0.29	1.79	173
275-400 °C	24.6	85.4	12.1	1.13	0.99	0.43	1.7	232
> 400 °C	50.4	85.5	11	1.96	0.82	0.75	1.54	391
Wtd. Avg. Total	100	85.5	11.7	1.38	0.9	0.55	1.64	246

Figure 2.1: Kerogen Oil Distillation

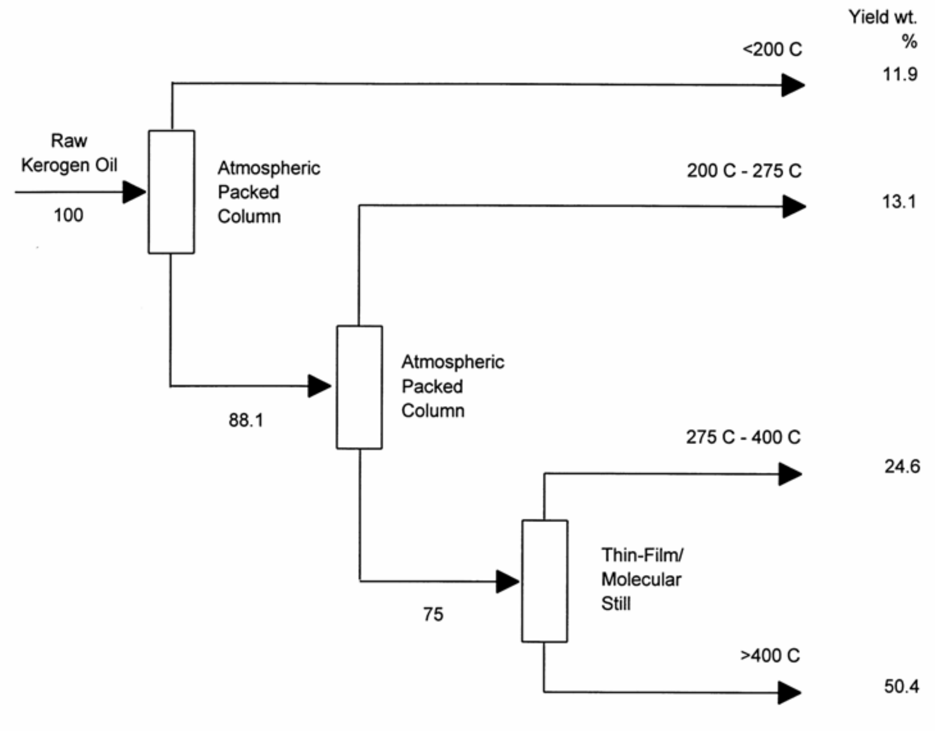
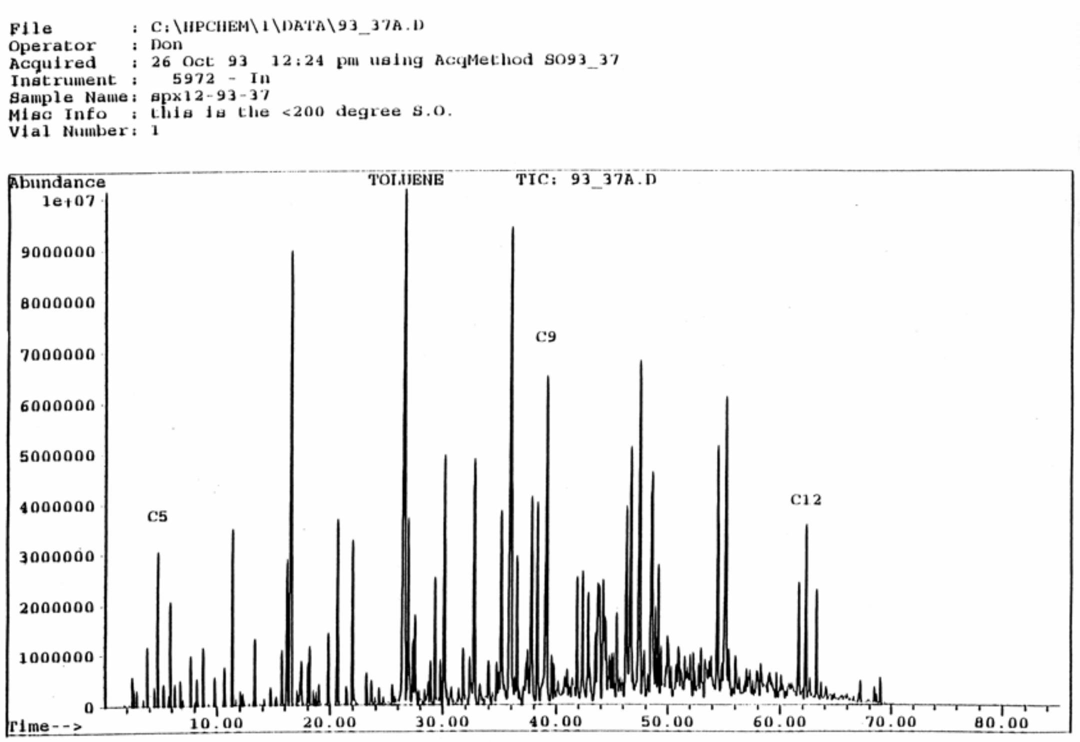


Figure 2.2: GC-TIC of < 200 °C Distillate



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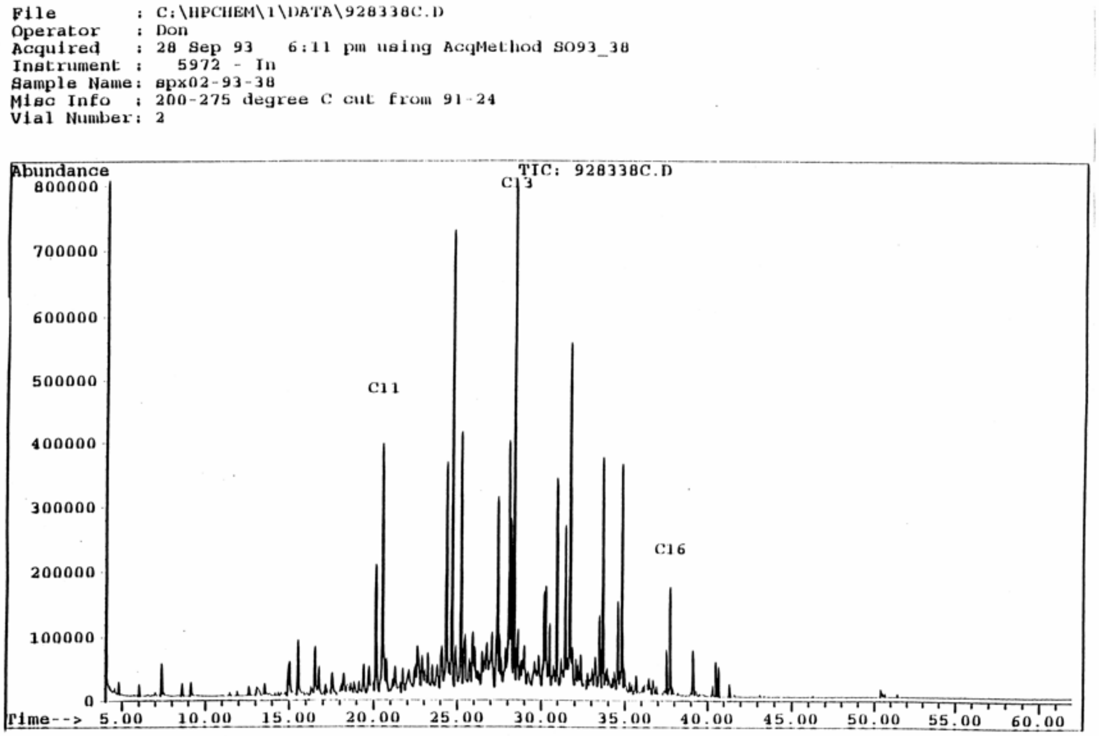
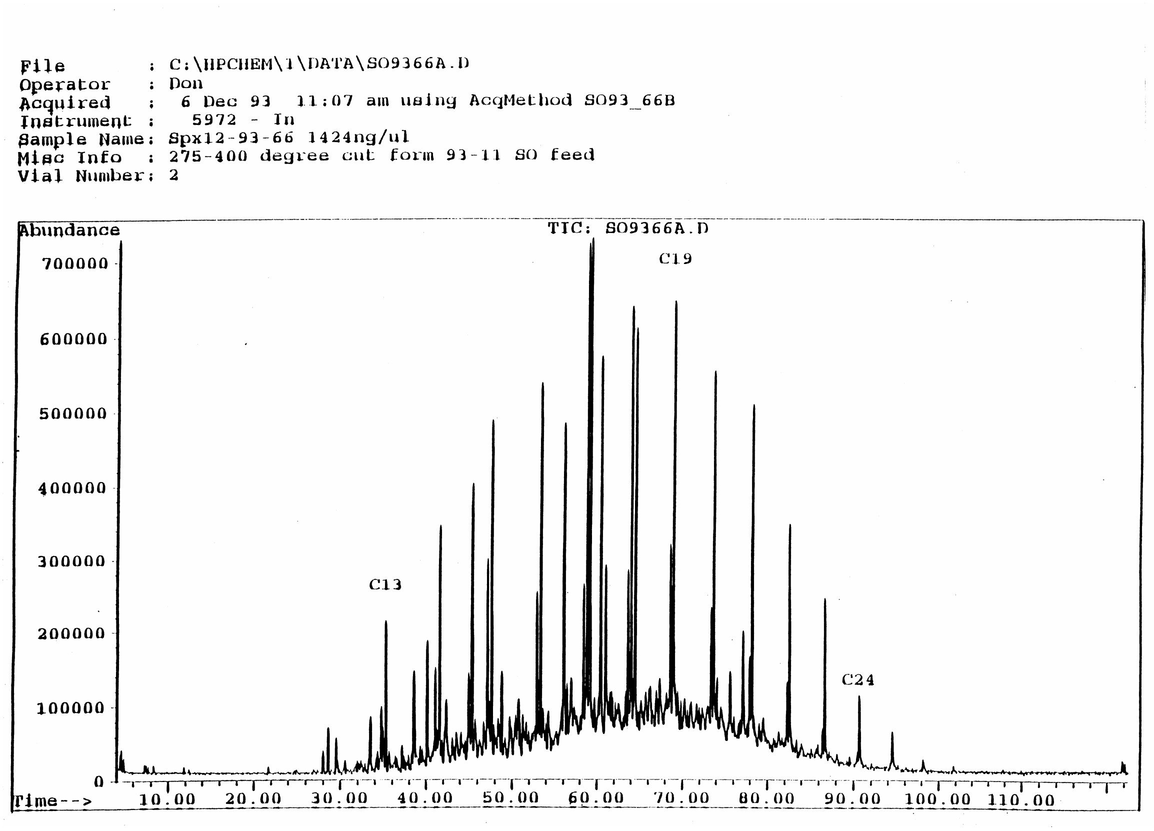
Operator   : Don
Acquired   : 26 Oct 93 12:24 pm using AcqMethod SO93_37
Instrument :   5972 - In
Sample Name: spx12-93-37
Misc Info   : this is the <200 degree S.O.
Vial Number: 1

Figure 2.3: GC-TIC 200 – 275 °C Distillate



File   : C:\HPCHEM\1\DATA\928338C.D
Operator   : Don
Acquired   : 28 Sep 93   6:11 pm using AcqMethod SO93_38
Instrument :   5972 - In
Sample Name: spx02-93-38
Misc Info   : 200-275 degree C cut from 91-24
Vial Number: 2

Figure 2.4: GC-TIC 275-400 °C Distillate



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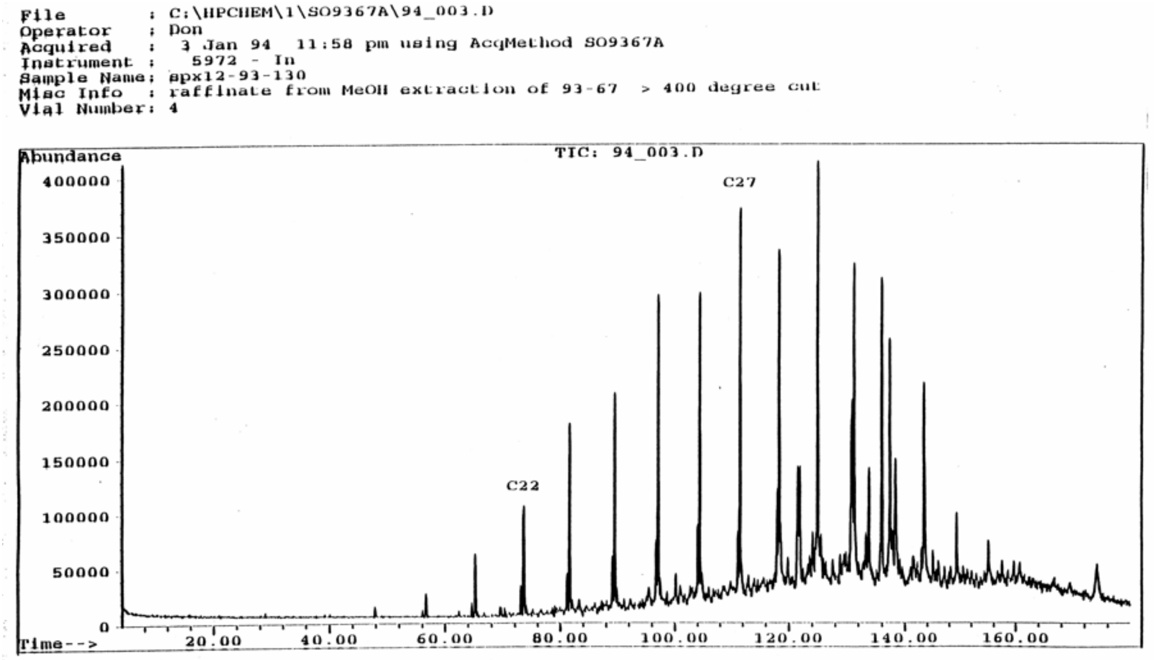
Operator    : Don
Acquired    :  6 Dec 93  11:07 am using AcqMethod SO93_66B
Instrument  :   5972 - In
Sample Name: Spx12-93-66 1424ng/ul
Misc Info   : 275-400 degree cut form 93-11 SO feed
Vial Number: 2
```

Figure 2.5: GC-TIC >400 °C Residue



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File        : C:\HPCHEM\1\SO9367A\94_003.D
Operator    : Don
Acquired    :  3 Jan 94  11:58 pm using AcqMethod SO9367A
Instrument  :   5972 - In
Sample Name: spx12-93-130
Misc Info   : raffinate from MeOH extraction of 93-67  > 400 degree cut
Vial Number: 4
```

2.3 Liquid-Liquid Extraction

Liquid-liquid extraction processing is used to separate polar compounds from non-polar compounds. Liquid-liquid extraction is a commonly practiced, reasonably-priced operation. It is used for lube oil finishing and other petroleum and chemical process applications. A suitable solvent is needed to selectively extract various functionalities in the distillate fraction. Table 2.3 shows the matrix of solvent types that were thought to be commercially viable candidates for conducting screening tests. These solvent types include mineral and organic acids, mineral and organic bases, neutral polar compounds and hydrocarbons. The polar compounds selected for study are reasonably priced and possess the requisite polarity. Ethers, aldehydes and anhydrides were avoided because their instability would result in a poor commercial choice. Each of these may be used in the presence of controlled amounts of water. The criteria for final solvent selection are based on process selectivity, cost, ease of recovery and safety in handling.

Table 2.3: Solvent Matrix for Extractions

Solvent Type	**Solvent Systems**
1. Mineral Acids	H_2SO_4
2. Mineral Bases	NaOH
3. Organic Acids	Acetic Acid, Formic Acid
4. Organic Bases	Isopropylamine
5. Polar Hydrocarbons	N-Methyl-2-pyrolidinone, Furfural, Phenol, Methanol, Ethanol
6. Non-Polar Hydrocarbons (co-solvents)	n-hexane, cyclohexane

The primary variables used in the test tube screening tests were solvent to oil ratio and effects of water. Most screening results were based on visual observations, and only those systems that produced two, proportional phases were examined in further detail. (The term proportional in this context is derived from the observation that for each fraction the quantity of nitrogen containing compounds is known and extracts that produce much greater or much less yield than those known quantities are unlikely to lead to high coefficients of separation. This separation characteristic is implied throughout this work.) The effectiveness of solvent screening was measured by tracking desired compound types and their partition selectivity. Qualitative observations showed that acid extractions were more selective than bases.

- 200 °C cut extraction – The low molecular weight distillate responded well to extraction by methanol. Of the various solvents, methanol has the lowest boiling point and was readily separable from the oil fractions. Small amounts of water, about 2-5%, caused two phases to form (methanol phase on top). Excessive water, however, resulted in phase inversion. Other solvents were screened but their results were unremarkable. Mineral acids resulted in discoloration over time; a sign of chemical reaction. In general, some water is needed to induce two phases when using organic solvents.

- 200 – 275 °C cut extraction - Based on the positive results for methanol with the > 200 °C cut, a systematic test was conducted using anhydrous methanol. Shake tests were conducted at 50°C. Yield results are shown in Figure 2.6. Nitrogen analysis of the fractions are given in Table 2.4 and reveal that while the percent of nitrogen extracted increases with increasing solvent ratio, the concentration of nitrogen in the extract decreases. These opposing trends are exemplary of the tradeoffs inherent in liquid-liquid extraction and show that, economically, it is not sufficient to simply maximize the recovery of nitrogen containing compounds, it is also important that the quality of the extract be considered. This recognition led to the development of a Coefficient of Separation (COS) as an optimizing function for extraction development.

Figure 2.6: Methanol Extraction of 200-275 °C Kerogen Oil

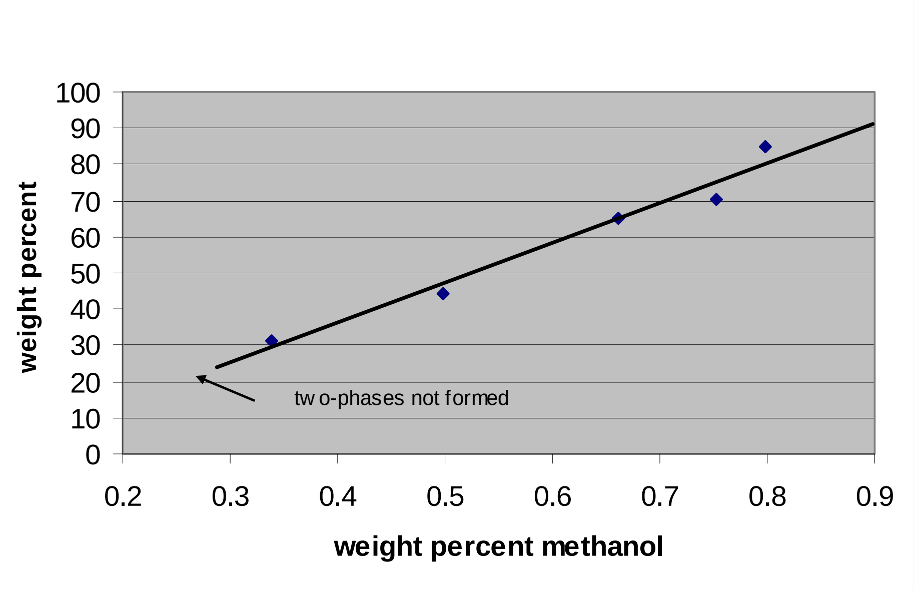


Table 2.4: Results of Shake Tests on 200-275 °C Distillate

Solvent/oil ratio	Weight % extract	% nitrogen in extract	% of feed nitrogen in recovered in extract
1:2	31.4	1.16	61.7
1:1	44.5	1.15	86.7
2:1	65	0.84	92.5
3:1	70.5	0.84	100.0
4:1	84.8	0.685	98.5

- 275 – 400 °C cut - This cut is quite viscous and readily dissolves anhydrous methanol. Methanol with 2% water forms two phases, however. A matrix of tests was conducted similar to those done for the 200- 275 °C cut. Results showed the extract quantity ranged from 12.9% to 34.7% for solvent to oil ratios that ranged from 2:1 to 1:2. The results are described by the equation:

  $$\% \text{ Ext} = 58.8 \times \%\text{solvent} - 6.4$$

  Considering that the nitrogen content of the distillate fraction is going up, and the yield of extract is going down, it was apparent that the methanol system was losing its extraction power as molecular weight increased. This led to the conclusion that stronger, perhaps higher molecular weight solvents would be needed for these higher molecular weight fractions.

- > 400 °C cut – This cut was too viscous to extract even at elevated temperatures (50 °C) and needed to be diluted with paraffinic solvent (n-hexane). Methanol extraction yielded only 7.5% extract. Acetone and water in a ratio of 75/25 was employed with a 50/50 oil/hexane ratio. This system yielded only 1% extract. Because this cut is in the lube oil range, an extraction was performed with N-methyl-2-pyrrolidone (NMP). This extraction yielded 33% extract. From this work it was concluded that separation efficiency was going to prove a strong function of molecular weight, and that the selection of solvent would be driven by molecular weight range.

2.4 Characterization of Distillate Cuts

Potentiometric titration results of distillate cuts are shown in Table 2.5. Both basic and non-basic nitrogen types increase with increasing boiling range. The basic nitrogen types include six-membered rings such as pyridines, quinolines and higher analogs whereas non-basic nitrogen types the five-membered rings such as pyrroles, indoles and higher analogs. The proportion of basic to non-basic nitrogen shows a maximum in the 200 – 275 °C range, or about $C_8 - C_{14}$. A dramatic falloff in basic nitrogen is not expected, however, and it is possible that not all of the basic nitrogen titrates quantitatively.

Table 2.5: Potentiometric Titration Results for Nitrogen Types

	% Total Nitrogen	**% Basic Nitrogen**	**% Non-Basic Nitrogen (by difference)**	**Basic Nitrogen as a percent of Total Nitrogen**
< 200 °C	0.28	0.14	0.14	50
200-275 °C	0.59	0.42	0.17	71
275-400 °C	1.13	0.54	0.59	48
> 400 °C	1.96	0.74	1.22	38

2.5 Type and Heteroatom Distributions

The heteroatom distribution is shown in Figure 2.7. The significant results show that nitrogen compounds are the most abundant on a mole % basis and that at an average molecular weight of 292 (see Table 2.2) nearly 40 percent of molecules contain a nitrogen compound.

Figure 2.7: Heteroatom Type Distribution in Raw Kerogen Oil

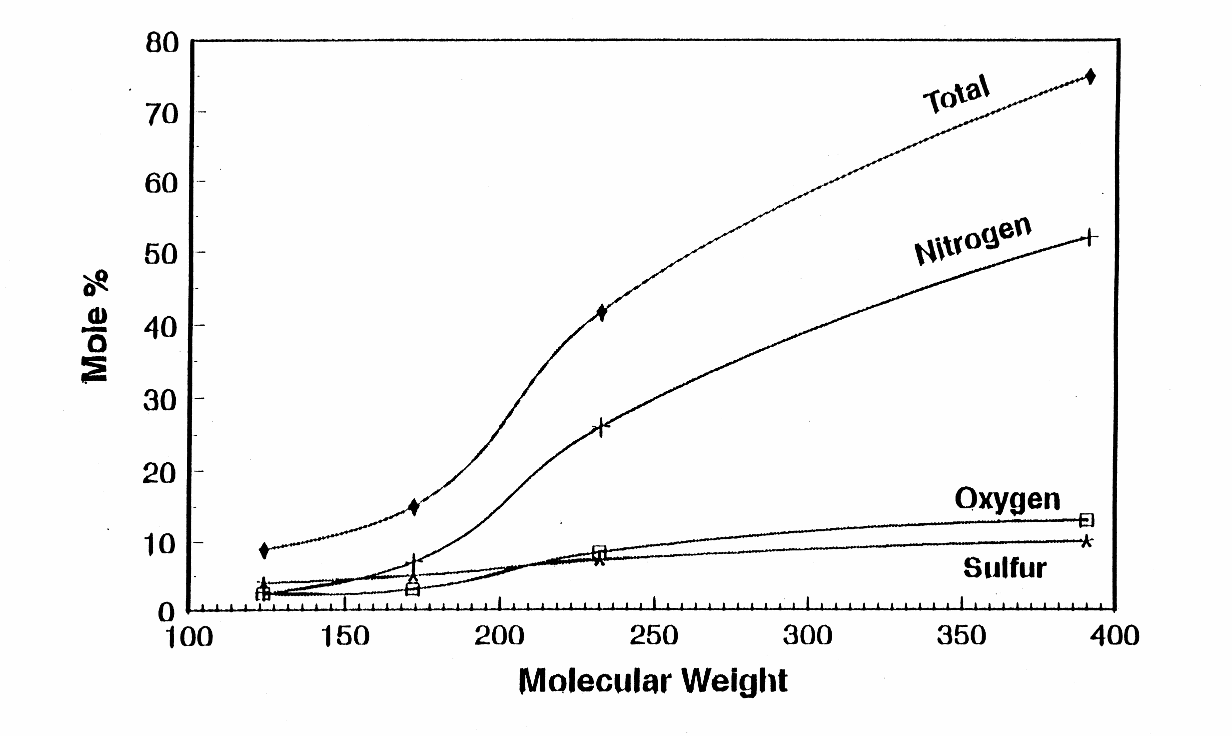
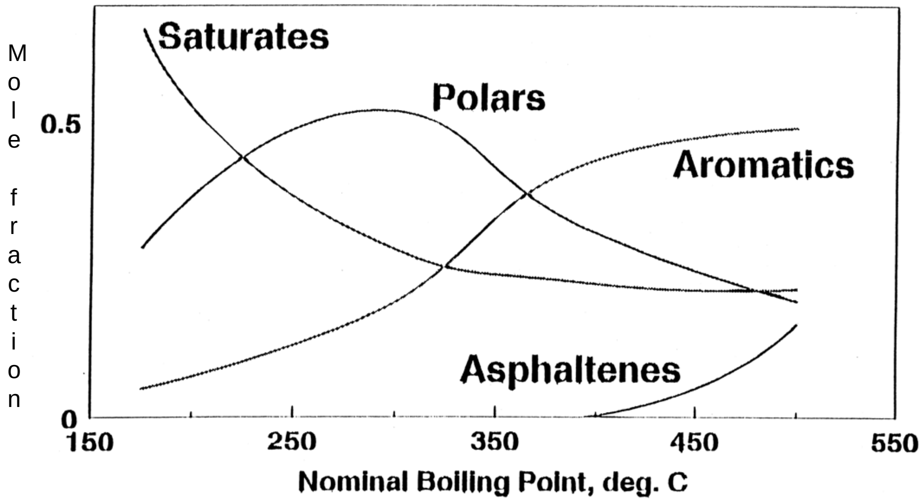


Figure 2.8 shows how the classes of compounds behave in an extraction environment using alcohols as an extraction solvent. Note that the decline of the polar compounds at higher molecular weights reflects the reduced solubility of large molecules in low molecular weight alcohols. This phenomenon was later shown in the program to reduce the effectiveness of alcohols for high recovery of nitrogen types and indicate that stronger solvents were needed if higher recovery of high molecular weight nitrogen compounds was to be achieved. (In subsequent work with Estonia shale oils, the use of mineral acids or bases was found to be effective for higher molecular weight polar compounds because with these strong acids and bases ions are formed and the partitioning to an aqueous solution is favored; however, recovery of the solvents in mineral acids and bases is problematic and for that reason was deemphasized in the current program.)

Figure 2.8: Mole Fraction Type Composition



2.6 Separation of Extract and Raffinate

Non-aqueous ion-exchange adsorption is known to be highly selective to organic acids, bases, and neutrals separation. Two samples (as a paired extract-raffinate) obtained from extraction of the >150 °C kerogen oil sample were separated into acids, bases and neutrals fractions. The quantitative results are given in the Table 2.5.

The data in Table 2.6 show that more than 80% of the bases are recovered and more than 70% of the neutrals are rejected. Acids are about evenly divided as a class. This is a significant finding because it is well-known that basic nitrogen is more difficult to remove during catalytic hydroprocessing than is non-basic nitrogen, meaning that extraction will render the raffinate much more amenable to hydrotreating. Later results bear this out.

Table 2.6: Summary of Acid-Base-Neutral Separation of Kerogen Oil Samples

Sample Name	SPX29-95-453 (extract)			SPX29-95-455 (raffinate)		
Distribution	% of >150 °C	% of type	% of Ext.	% of >150 °C	% of type	% of Raf.
Acids	5.2	14.1	43	6.9	10.9	57
Bases	15.5	41.9	83	3.2	5.1	17
Neutral	16.3	44.0	24	52.9	84.0	76
Subtotal	37.0	100		63.0	100	

Elemental composition of the above mentioned samples were also investigated. The results of nitrogen distribution are given in the Table 2.7.

Table 2.7: Nitrogen Distribution of Acid-Base-Neutral Samples of Kerogen Oil >150 °C Fraction

Fraction	Wt% of oil	Wt% of type in Fraction	Wt% N in fraction	%wt x % N in oil	% N in type
Extract					
Acid	5.2	43	4.54	.236	14.6
Base	15.5	83	5.77	.894	55.4
Neutral	16.3	24	1.88	.306	19.0
Subtotal	37.0				89.0
Raffinate					
Acid	6.9	57	0.54	0.037	2.3
Base	3.2	17	2.72	0.087	5.4
Neutral	52.9	76	~0.1	0.053	3.3
Subtotal	63.0				11.0
Total	100.0				100.0

Prior experience of the P.I. (Jewell, et. al.[6]) has shown that six-membered nitrogen heterocyclic rings (e.g. pyridine-types) are basic, whereas five-membered rings (e.g. pyrrolic-types) are either acid-base neutral, or titrate as weak acids. Pyridinic nitrogen is much harder to remove by catalytic hydrotreating than pyrrolic nitrogen. Both types are valuable in the specialty chemical world.

The data in Table 2.7 show about 89% of the nitrogen is concentrated in the extract fraction. This is highly desirable, both from the standpoint of high yields of pyridines and improved values of the raffinates for petroleum refinery products. The concentration of nitrogen in the total raffinate is less than 0.3%, somewhat high by Rocky Mountain crude oil standards but much less than the original 1.6~1.8%. This nitrogen content may be low enough to avoid the need for hydrotreating the kerogen oil to make it refinery-acceptable.

Acids are about evenly divided as a class. The analysis also showed high nitrogen content in the acid fraction in the extract. The GC/MSD showed that these nitrogen compounds are mainly substituted indoles and substituted carbazoles (pyrrolic-type nitrogen). The indoles and carbazoles have apparently hydrogen-bonded with the extraction solvent and are carried into the extract but show up as acids in the ion-exchange separation. We have postulated that non-aqueous ion exchange separations may play a role in separating acidic nitrogen compounds from basic nitrogen and the above results are confirmation that such an approach is thermodynamic feasible. Until a target product is identified that requires ion-exchange separation the technical and economic feasibility of this approach cannot be examined.

2.7 Separation of Non-Polar Fractions

The non-polar fraction of the kerogen oil was further processed. First, the light ends (<350 °C) were distilled and characterized as a refinery feed. This material exhibits an API gravity of about 40° and a low 0.13% nitrogen.

The heavy fraction was extracted by NMP (N-methyl-2-pyrrolidinone) solvent and aromatic oils were recovered as an extract. The wax in the raffinate fraction was removed by a 50/50 methyl-ethyl ketone/toluene solvent. So far, about three kilograms of the non-polars have been processed. The distribution of the products among refinery feed, aromatic oil, waxes, and lube oils are roughly 40%, 14%, 18% and 28%, respectively, of the total non-polar fractions.

Task 2 Conclusions

The amenability of the various distillate cuts to solvent extraction was elucidated. Lower molecular weight fractions were highly responsive to extraction by highly polar solvents. The higher molecular weight fractions did not respond as well to solvent extraction as the hydrocarbon portion of the heteroatom-containing molecules resisted solvation in the low molecular weight polar solvents. As would later be discovered, this problem would be overcome by extracting the whole oil such that the polar light ends of the kerogen oil assisted in the solvation of these higher molecular weight components. The analysis conducted on the distillation fractions and their solvent-partitioned fractions showed that basic nitrogen was more readily extracted than non-basic nitrogen. This helped focus research attention on basic nitrogen products as first-generation products. Non-basic nitrogen products are equally valuable, but because of their lower responsiveness to extraction (and their relative ease of removal by catalytic hydrotreating) these types were considered second-generation products.

Task 3 - Analytical Procedures and Characterization

Statement of Work

Algorithms, software and procedures for routine Z-BaSIC (Z-Based Structural Index Correlation) characterization of kerogen oil fractions and products will be formally developed. The procedures so developed will be applied to kerogen oil fractions derived in the separations characterizations task. The Z-BaSIC characterization will be subsequently used to evaluate concentrates produced in the separation and conversion exploration tasks (Tasks 5 and 6). The technique will establish the computerized relationship between structure and properties needed for specification matching and process optimization. The analytical methodology software will be written so as to interface with the market and product specification databases developed in Task 4.

Results

3.1 Boiling Point - Molecular Weight Database

For heteroatom-containing compounds, the availability of boiling point data is limited. Using the Z-BaSIC method, it is possible to predict the boiling point data for the entire homologous series from the parent compound data and its neighboring series. In the Z-BaSIC notation, any molecule can be represented by the empirical formula $C_nH_{2n+z}N_uO_vS_w$. In the Z-BaSIC method ‘z’, ‘u’, ‘v’, and ‘w’ are classifying parameters and ‘n’ is the primary correlating variable. For each class increases in the value of 'n' results in regular additions of -CH_2- groups making properties highly correlatable with 'n'.

The methodology is useful for estimating properties of compounds for which literature data is not available. Some data is required for each series. If literature data is available, even for just one compound of a series, the properties of the remainder of the series can be estimated by recognizing that in the infinite 'n', all properties approach the properties of an infinitely long paraffin. Correlating equation forms are chosen to correspond with this behavior (see 3.2 below). If no literature data is available a reasonable estimate of the series curves can be made by interpolating or extrapolating from neighboring series. A point along the curve may be estimated from the basic ring skeleton of the heteroatom-containing compound. Empirical correction factors are added to this boiling point value based on (a) changing a carbon in the basic skeleton to a specific heteroatom and (b) adding onto the basic skeleton some heteroatom functionality such as -OH- or -SH-.

Figures 3.1-3.4 show results of the boiling prediction methodology for nitrogen-containing compounds and oxygen-containing compounds. The legend for plots is shown in molecular structure for illustration purposes. Other compound types include thiophenes, thiols, sulfides and carboxylic acids. These constants for correlations form the basis for the database.

In general, once the chain lengthens, the properties become quite predictable. In fact, at the infinitely long chain the properties approach (but never quite equal) the properties of an infinitely long paraffin. Knowledge of the properties of an infinitely long paraffin establishes the limit for all other series. Using this knowledge, equations can be selected that behave properly in extreme. This approach is powerful, because properties of high molecular weight compounds can be accurately estimated even though pure compound data base values are absent.

Figure 3.1: Boiling Point vs. Molecular Weight
5-Membered N-Heterocyclic Ring Systems

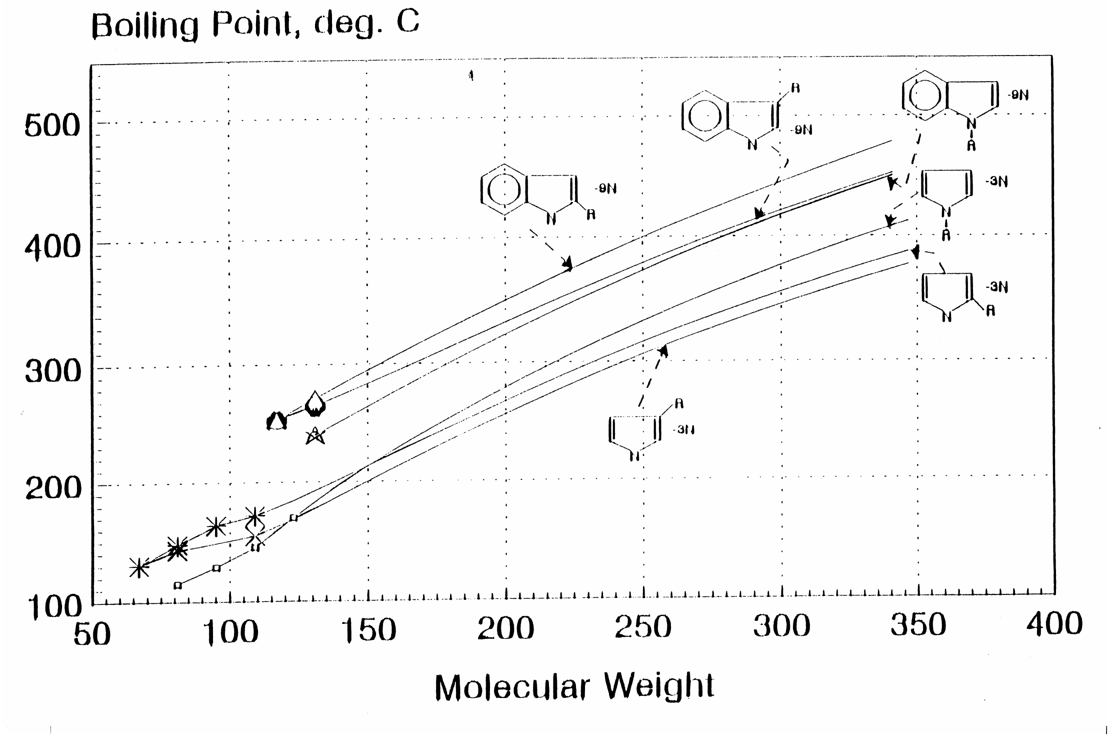


Figure 3.2: Boiling Point vs. Molecular Weight
Polycylic N-Heterocyclic Ring Systems

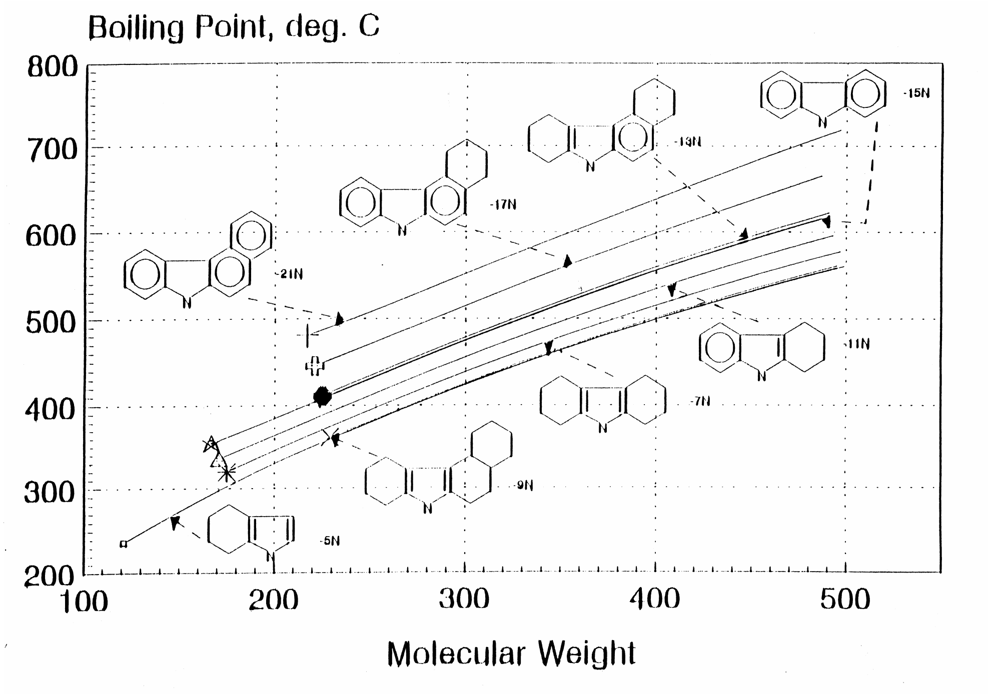


Figure 3.3: Boiling Point vs. Molecular Weight
One and Two Ring N-Heterocyclic Ring Systems

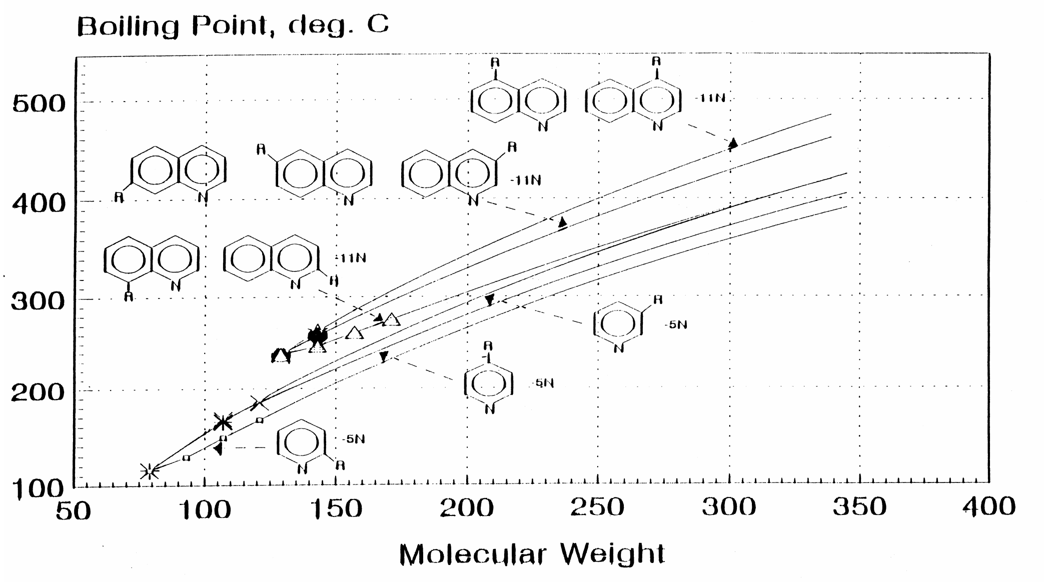
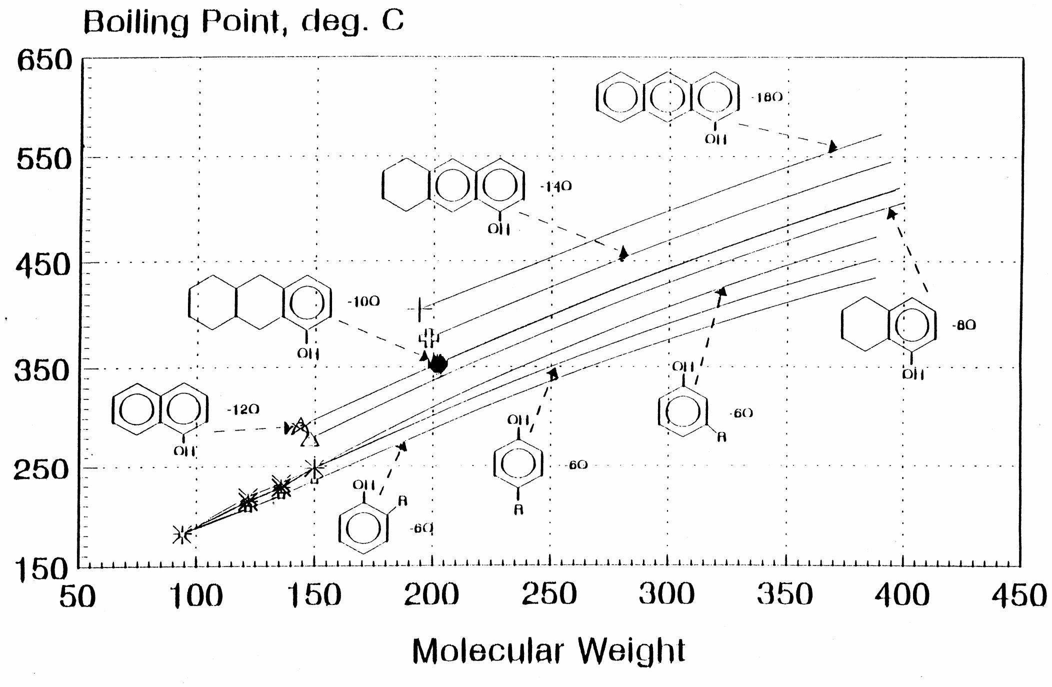


Figure 3.4: Boiling Point vs. Molecular Weight
Phenolic Ring Systems



3.2 Boiling Point - Retention Time Database

The development of boiling point-retention time correlations has been undertaken to expand the capabilities of GC-MS system to identify heteroatom containing compounds in the heavy fractions of kerogen oil. The conventional spectral libraries have limitations to their applicability in the range of kerogen oil fractions, in large part because of coeluting peaks, but also because most components in kerogen oil have never been isolated, synthesized or studied.

The Z-BaSIC correlating methodology has been applied to vapor pressure, density and critical temperature. To develop correlations, the 200-275 °C distillate fraction of kerogen oil was used to identify compounds and their retention times for each series.

The mathematical data treatment is as follows:

$$y = \frac{a\,x^2 + b\,x + c}{x + d}$$ eq. 3.1

$$y = \frac{a\,x^3 + b\,x^2 + c\,x + d}{x^2 + e}$$ eq. 3.2

$$y = \frac{a\,x^3 + b\,x^2 + c\,x + d}{x^2 + e\,x + f} \qquad \text{eq. 3.3}$$

where x is retention time (min.)
and y is boiling point (deg. °C)

Note that all expressions in the denominators are polynomials one order lower than the polynomials in the numerators. This assures that the behavior of the boiling point in the extreme x behaves as a sloping asymptote and not in any oscillatory fashion. (In practice this can occasionally lead to denominator values equal to zero and each correlation needs to be examined for this possibility.)

The following table shows values for constants for the compound types of interest that are present in the kerogen oil fraction. These constants for equations are obtained by multiple regression analysis. Also, boiling point-retention time correlation curve for paraffins is used as reference series for all other compound types (that is why the 'a' value, 2.8583 for paraffins remains the same for other series).

Table 3.1: Constants for BP-RT Correlations

Compound		**a** = 2.8583				
Type	**b**	**c**	**d**	**e**	**f**	**Equation**
Alkanes	120.46	-878.64	-6.15			3.1
Alkenes	119.43	-881.54	-6.21			3.1
Benzenes	140.46	-236.69	-0.58			3.1
Indanes	144.77	-326.66	-0.22			3.1
Naphthalenes	144.77	14.39	0.00			3.1
Pyridines	136.58	-493.54	-2.91			3.1
Quinolines	132.35	-951.79	-6.15			3.1
Ketones	141.34	-176.04	-0.48			3.1
Thiophenes	141.69	-161.93	0.06			3.1
Nitriles	136.43	846.61	9987.23	105.43		3.2
Pyrroles	134.64	1074.85	616.53	101.71		3.2
Phenols	128.49	101.43	-55154.	-297.26		3.2
Indoles	180.87	3097.14	-2348.4	15.09	4.95	3.3
Carboxylics	180.87	3097.14	-2348.41	15.09	4.95	3.3

Figures 3.5 and 3.6 show correlation curve fits for nitrogen types and hydrocarbons that are present in the kerogen oil fraction. Points represent actual literature data and lines represent calculated values for a given series predicted up to the final carbon number of paraffin series. These correlations constituted the basis for the database development for compound type identification.

Figure 3.5: BP vs RT Correlation Plot – Nitrogen Compounds

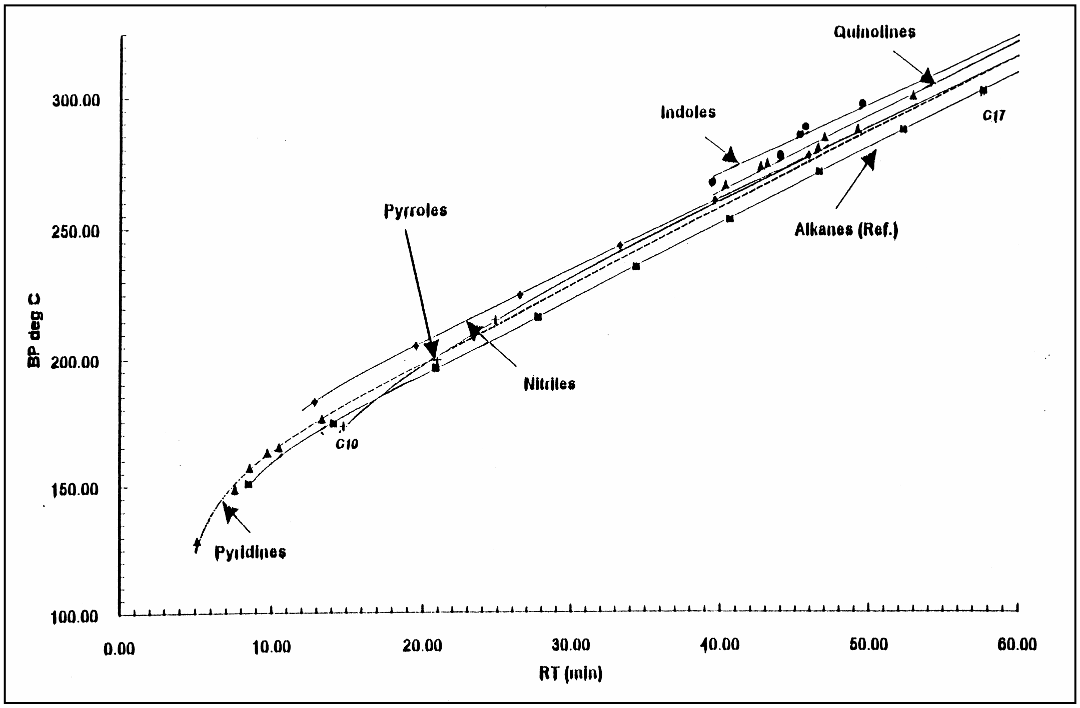
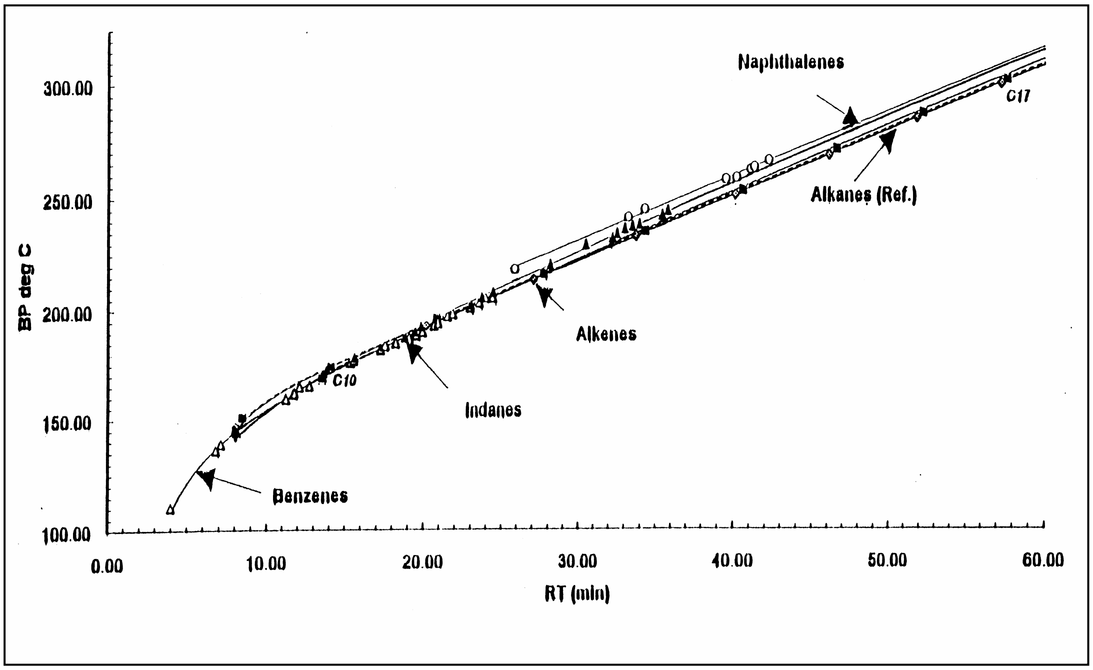


Figure 3.6: BP vs RT Correlation Plot – Hydrocarbon Compounds



3.3 Z-NUM.P Computational Method

Figure 3.7 shows the Z-NUM.P program flow sheet, which is the product of Z-BaSIC methodology to track heteroatom (N, S, O) types. The input to the program is acquired from the integration of GC-MS data. Other inputs include elemental analysis of the sample and boiling point - retention time data to account for changes in the temperature programming. The calculation sequence consists of:

- Interpretation of isotopes
- Calculation of elemental probabilities
- Calculation of possibilities of elemental combinations
- Assignment of molecular formula based on the BP-MW and BP-RT databases
- Check the probability of the match
- Sort output results by compound type distribution and retention time distribution

The testing of the program has been done by comparing its output with Wiley Library (an electronic library of mass fragmentation patterns of pure compounds) results using gasoline and the light fractions of kerogen oil. We use motor gasoline as a test sample because it contains a mixture of paraffins, isoparaffins, olefins and aromatics and possesses a known molecular composition. The output of the program has matched well (better than 90%) and in some cases better.

Z-NUM.P method is the analytical procedure by which the computer assigns a probable type to a parent mass of a known retention time. In Z-NUM.P, 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 illustrates the Z-NUM.P output for an extract sample peak at 23.33 minutes. 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 are the alkylpyridine series and an agreement index of six is observed for this type.

Figure 3.7: ZNUM.P Program Flowsheet

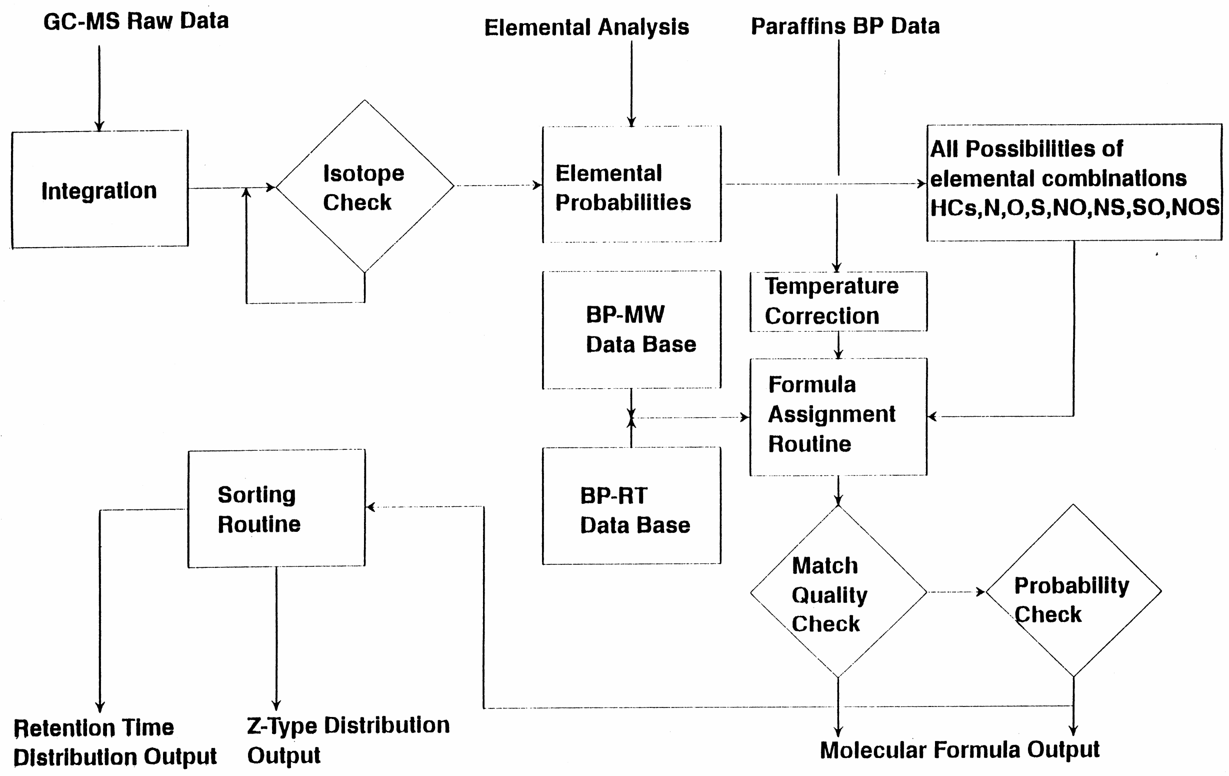


Table 3.2: Z-NUM.P Output for Extract at Retention Time of 23.33 Minutes

(200-275 °C Kerogen Oil Fraction)
An Illustration

RT (Min.)	**Mass #**	**%Rel. Abun.**				
C	H	#Z#N#O#S	Prob.	Quality	BPM	BPR
23.33	**146**	**2.23**				
11	14	-8N0O0S0	9.20e-01	1	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	-12N0OS1	2.80e-03	U	na	na
7	14	0N0O1S1	1.30e-03	U	na	na
23.33	**136**	**7.23**				
10	16	-4N0C0S0	9.90e-01	U	na	na
8	12	-4N2O0S0	4.70e-03	U	na	na
9	12	-6N0OaS0	8.00e-02	2	229	216.3
8	8	-8N0O2S0	1.40e-03	U	na	na
8	8	-8N0O0S1	6.90e-03	U	na	na
23.33	**135**	**67.53**				
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

3.4 Partition Function Analysis

Partition function analyses were run on specific chromatographic peaks (Table 3.3). Higher numbers indicate a preference for the extract. Lower numbers show preference for the raffinate. If a peak is missing in one or the other mass spectrum, the program assigns an E or R to designate in which fraction the fragment was found. These partition functions are valuable for scale-up design. The analytical technique also provides a means for tracking individual compounds, which can be used to economically optimize separation systems.

Table 3.3: An Illustration of Partition Function Analysis[+]

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

[+] GC elution time 48.9 min; m/z is the mass fragment

* E means detected only in Extract; R means detected only in Raffinate. Partition ratio is the concentrate in the extract divided by the concentration in the raffinate. A value of 1.0 implies no preference for the extract or the raffinate.

3.5 Z-BaSIC Analysis of Total Kerogen Oil

The Z-BaSIC analytical technique was improved substantially in the past several years, primarily through non-contract applications to petroleum. This improved analytical technique has now been applied to the whole kerogen oil to produce a quantitative data file (referred to as a composition-property file, or ‘cp’ file) of all the chemical types by their carbon number. The ‘cp’ file agrees with the measured hydrogen, carbon, nitrogen, and sulfur content, and the density and high-temperature simulated distillation data on the oil. Results are summarized in Table 3.4.

Table 3.4: Compositional Analysis of Surface Retort Oil
(higher carbon numbers continued on next page)

Table 3.4		Unocal kerogen oil - composition															
		Units in weight percent															
Compound Type	Total	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n-paraffins	6.427	0	0.00997	0.176	0.04314	0.1981	0.2011	0.2173	0.2533	0.2969	0.2856	0.2887	0.2285	0.2277	0.2032	0.2445	0.1802
i-paraffins	6.673	-	0	0.1243	0.04998	0.1899	0.3685	0.17694	0.63578	0.52649	0.41102	0.47865	0.32735	0.24606	0.35917	0.42156	0.31791
monolefins	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
mononaphthenes	8.369	-	-	0.03916	0.00843	0.32977	0.38291	1.17468	1.25741	0.92275	0.24312	0.48878	0.28142	0.51257	0.61043	0.37532	0.25697
dinaphthenes	2.48	-	-	-	-	-	0.24657	0.30611	0.13588	0.52124	0.31783	0.26574	0.172	0.24237	0.08655	0	0.07214
trinaphthenes	1.361	-	-	-	-	-	-	-	-	0.11785	0.18573	0.22192	0.14931	0.11825	0.02557	0	0.01627
tetranaphthenes	6.888	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02809	0.21019	0.17765
pentanaphthenes	7.545	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0	0.20877
hexanaphthenes	0.449	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
heptanaphthenes	0.178	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
octanaphthenes*	2.379	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
monoaromatics	4.471	-	-	-	0.2722	0.3507	0.3061	0.35749	0.35148	0.52499	0.29273	0.32762	0.18102	0.21325	0.07532	0.02521	0.03488
naphthenomonoaromatics	3.38	-	-	-	-	-	-	0.00222	0.1932	0.12104	0.39606	0.17332	0.25428	0.2496	0.18991	0.26075	0.05445
dinapthenomonoaromatics,indenes	2.442	-	-	-	-	-	-	0	0	0.34473	0.24358	0.22967	0.33729	0.18494	0.32066	0.17093	0.19932
trinaphthenomonoaromatics	1.337	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0	0.1233
tetranapthenomonoaromatics	0.421	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.06246
diaromatics	2.38	-	-	-	-	-	-	-	0.01469	0.12979	0.12547	0.16511	0.32261	0.37274	0.36486	0.36264	0.15127
acenaphthene/naphthenodiaromatics	1.787	-	-	-	-	-	-	-	-	-	0.00152	0.02247	0.06635	0.23347	0.03148	0.07312	0.17223
dinaphthenodiaromatics	0.319	-	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0
acenaphthalenes/fluorenes	0.513	-	-	-	-	-	-	-	-	-	0.00168	0.00906	0.03566	0.06637	0.03863	0.03424	0.00041
triaromatics	0.335	-	-	-	-	-	-	-	-	-	-	-	0.00807	0.01696	0.06097	0.02109	0.02358
phenylnaphthalenes	0.185	-	-	-	-	-	-	-	-	-	-	-	-	-	0.00178	0.04038	0.01797
tetraaromatics (peri-condensed)	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02128	0.01041	0.00736
tetraaromatics (cata-condensed)	0.019	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
naphthenoflourenes	0.055	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0	0
pentaaromatics (peri-condensed)	0.004	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
naphthenosulfides/thiols	1.224	-	0	0	0	0	0.01743	0	0.00594	0	0	0.00003	0.00484	0.08719	0.04919	0.2196	0.1052
dinaphthenosulfides/thiols	1.688	-	-	-	-	-	0	0	0	0.00397	0	0.00544	0	0.00757	0	0.11778	0.14336
thiophenes	0.792	-	0	0.07029	0.10169	0.11019	0.02544	0.1204	0.05092	0.05051	0.02744	0.01456	0.01284	0.02613	0.03747	0	0.00006
trinaphthenosulfides/thiols	0.807	-	-	-	-	-	-	-	-	0	0	0	0	0	0	0	0
thiophenol	0.045	-	-	-	0	0	0	0	0	0	0.04461	0	0	0	0	0	0
tetrahydrobenzothiophene	0.141	-	-	-	-	-	0.01147	0.01289	0.00374	0.00225	0.00378	0.00216	0.01071	0.01126	0	0	0
benzothiophenes	1.456	-	-	-	-	-	0.043	0.0955	0.14126	0.13037	0.13545	0.19342	0.10128	0.05535	0.08974	0.04406	0.02687
benzodithiophenes	0.305	-	-	-	-	-	-	-	0	0.00748	0.02129	0.02007	0.00259	0.00444	0.00514	0.00485	0.00811
dibenzothiophenes	0.266	-	-	-	-	-	-	-	-	-	0.0059	0.04798	0.03948	0.00349	0	0.01674	0.0149
epithiophenanthrenes	0.066	-	-	-	-	-	-	-	-	-	-	-	0	0	0	0	0
benzodibenzothiophenes	0.185	-	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0.01571
5-ring thiophenes*	0.008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pyrroles	1.216	-	0.00741	0.01546	0.03819	0.04036	0.01838	0.04972	0.0292	0.01626	0.02929	0.03262	0.0249	0.01168	0	0	0
indoles	5.494	-	-	-	-	-	0.04862	0.0418	0.06086	0.09231	0.18302	0.28808	0.48493	0.67085	0.08949	0.14646	0.1843
carbazoles	1.836	-	-	-	-	-	-	-	-	-	0.03275	0.05206	0.10311	0.08146	0.04521	0.06858	0.07698
4-ring pyrrolics*	1.952	-	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0.21474
5-ring pyrrolics*	0.045	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pyridines	1.369	-	-	0.00768	0.00449	0.07075	0.03612	0.0479	0.05303	0.03409	0.07629	0.09336	0.06354	0.06706	0.01852	0.08168	0.06231
quinolines	7.293	-	-	-	-	-	-	0	0.02585	0.01821	0.05478	0.06578	0.11467	0.02943	0.17982	0.16119	0.78741
phenanthridines	0.576	-	-	-	-	-	-	-	-	-	-	0	0	0.02152	0.0155	0.01391	0.01821
4-ring pyridinics*	2.703	-	-	-	-	-	-	-	-	-	-	-	-	-	0	0.06367	0.11644
5-ring pyridinics*	0.009	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
phenols	0.424	-	-	-	0.00567	0.02425	0.16804	0.05228	0.06858	0.04207	0.05636	0.00176	0.00464	0	0	0	0
hydroxy tetralins	0.278	-	-	-	-	-	0	0.00723	0.01953	0.01218	0.0346	0.05775	0.03773	0.0298	0.05097	0.02828	0
naphthols	0.314	-	-	-	-	-	-	-	0.03551	0.08117	0.09415	0.03553	0.04591	0.02186	0	0	0
dibenzofuran	0.027	-	-	-	-	-	-	-	-	-	-	0.00943	0.01758	0.00022	0	0	0
resorcinols	0.231	-	-	-	0	0.00289	0.05238	0.08962	0.00734	0.03576	0.0178	0.0176	0.00753	0	0	0	0
dihydroxy tetralins	0.127	-	-	-	-	-	-	-	0.01842	0.02435	0.0243	0.03697	0.02285	0	0	0	0
unidentified	0.267	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C36+ unidentified	8.35																

Table 3.4 (continued)																	
Compound Type	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
n-paraffins	0.2067	0.1944	0.483	0.2974	0.2698	0.2316	0.23	0.2477	0.2144	0.2038	0.1891	0.1408	0.1361	0.1195	0.0519	0.08155	0.07542
i-paraffins	0.71174	0.74717	0.32219	0.25786	0	0	0	0	0	0	0	0	0	0	0	0	0
monolefins	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
mononaphthenes	0.8591	0.52124	0	0.03589	0.021	0.01981	0.00952	0.00576	0.00798	0.00538	0	0	0	0	0	0	0
dinaphthenes	0	0.08096	0	0	0	0	0.00657	0.00253	0.00329	0.00374	0.00214	0.00103	0	0	0.00057	0.0074	0.0057
trinaphthenes	0.16907	0.04568	0.0017	0.00481	0.00629	0.00506	0.00505	0.00474	0.00493	0.00607	0.01644	0.10575	0.12924	0.00426	0.00298	0.01372	0
tetranaphthenes	0.48647	0.45086	0.4654	0.56947	0.75167	0.67645	0.62196	0.63888	0.46746	0.37529	0.32436	0.30601	0.1359	0.07955	0.06288	0.05659	0.00335
pentanaphthenes	0.32739	0.28033	0.3051	0.48741	0.46094	0.46635	0.47035	0.62705	0.53733	0.40259	0.69212	0	0.68488	0.72712	0.78044	0.08325	0.00359
hexanaphthenes	-	0.00612	0.01088	0.01593	0.01585	0.01889	0.01798	0.05969	0.03239	0.01647	0.01404	0.02511	0.02174	0.00582	0.01496	0.06876	0.1044
heptanaphthenes	-	-	-	0	0.00628	0.00585	0.00723	0.00761	0.01663	0.00906	0.0032	0.00116	0.00043	0.00153	0	0	0.119
octanaphthenes*	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5985	0.7052	0.6091	0.4666
monoaromatics	0.07958	0.02065	0	0.24388	0.18752	0.19535	0.13199	0.09586	0.05751	0.04014	0.04943	0.02417	0.01544	0.00988	0.00054	0.00338	0.00234
naphthenomonoaromatics	0.05332	0.16759	0.2332	0.23832	0.18481	0.15414	0.12131	0.10191	0.05096	0.03769	0.03866	0.02949	0.01648	0.00291	0.01491	0.03278	0.00712
dinapthenomonoaromatics,indenes	0.05819	0.05169	0.05076	0.03635	0.03442	0.0353	0.02284	0.01724	0.01378	0.00866	0.00796	0.00585	0.00175	0.01322	0.02177	0.0245	0.00649
trinaphthenomonoaromatics	0.01149	0.16246	0.23709	0.13789	0.15016	0.09883	0.08345	0.1044	0.0471	0.04858	0.02238	0.04534	0.0332	0.01422	0.00086	0.00629	0.0097
tetranapthenomonoaromatics	0.05061	0.04219	0.04714	0.04296	0.02516	0.02594	0.01909	0.01639	0.00995	0.01734	0.01527	0.02378	0.00343	0.0064	0.00402	0.00277	0.00627
diaromatics	0.06883	0.07455	0.05874	0.03422	0.02738	0.01548	0.01007	0.00828	0.00742	0.00611	0.00398	0.00227	0.00064	0.00039	0.0142	0.01538	0.0228
acenaphthene/naphthenodiaromatics	0.20691	0.19128	0.21582	0.15292	0.09446	0.07326	0.0653	0.04096	0.02853	0.02373	0.02025	0.02093	0.00493	0.00123	0.00129	0.01787	0.02639
dinaphthenodiaromatics	0.04665	0.04988	0.05619	0.04793	0.02605	0.02675	0.01361	0.00985	0.00723	0.00734	0.00457	0.01058	0.00422	0.0013	0.00504	0.00087	0.00088
acenaphthalenes/fluorenes	0.05463	0.05692	0.06237	0.04997	0.02511	0.01696	0.00864	0.00672	0.00732	0.00544	0.00445	0.00482	0.0019	0.00132	0.00856	0.00373	0.00788
triaromatics	0.0221	0	0.02175	0.0146	0.01088	0.00761	0.00862	0.00704	0.00528	0.00271	0.0017	0.00668	0.01809	0.02029	0.03302	0.02268	0.00111
phenylnaphthalenes	0.01062	0.02482	0.01818	0.01343	0.0077	0.00795	0.00614	0.00554	0.00359	0.00156	0.00012	0.00814	0.00551	0.00491	0.00264	0.00383	0
tetraaromatics (peri-condensed)	0.03064	0.00647	0.00624	0.002	0.00225	0.00441	0.00104	0.00093	0.00066	0.00039	0.004	0.0072	0.00381	0.00051	0.00016	0	0
tetraaromatics (cata-condensed)	0.00177	0.00217	0.00257	0.00369	0.00102	0.00137	0.00102	0.00028	0.00012	0.00062	0.00136	0.00011	0.00061	0.00191	0	0	0
naphthenoflourenes	0	0	0.00166	0.00228	0.00065	0.0008	0.00068	0.00043	0.01372	0.02245	0.0035	0.00061	0.00802	0	0	0	0
pentaaromatics (peri-condensed)	-	0	0	0.0001	0.00009	0.00001	0.00002	0.00259	0.00003	0.00156	0	0	0	0	0	0	0
naphthenosulfides/thiols	0.07655	0.1083	0.08023	0.07301	0.07098	0.04665	0.06402	0.03378	0.03155	0.0124	0.00767	0.00327	0.01181	0.01532	0.02004	0.03711	0.04185
dinaphthenosulfides/thiols	0.15017	0.12507	0.09387	0.08811	0.13503	0.13131	0.13508	0.10621	0.10192	0.10956	0.10806	0.01405	0.01626	0.01843	0.03826	0.01987	0.01824
thiophenes	0	0.00692	0.00953	0.01048	0.06572	0.01927	0.00871	0.00988	0.00645	0.00249	0.0007	0.00137	0.00115	0.00129	0	0	0
trinaphthenosulfides/thiols	0.00752	0.00639	0.01467	0.01891	0.05596	0.03114	0.0219	0.02452	0.06535	0.1008	0.1035	0.16068	0.03443	0.06353	0.04425	0.0413	0.01235
thiophenol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
tetrahydrobenzothiophene	0	0	0.00242	0.0007	0.01426	0.00452	0.00338	0.00481	0.00281	0.00773	0.00491	0.03238	0.00446	0	0	0	0
benzothiophenes	0.03369	0.05743	0	0.03846	0.02979	0.02994	0.03346	0.03107	0.02149	0.01796	0.00958	0.00375	0.01567	0.01699	0.02406	0.01409	0.02222
benzodithiophenes	0.00432	0.00473	0.00701	0.00895	0.01215	0.0158	0.02034	0.02031	0.02024	0.01747	0.00566	0.03392	0.04245	0.01398	0.00345	0.00001	0.00003
dibenzothiophenes	0.01845	0.01002	0.00727	0.00565	0.00702	0.006	0.00522	0.00579	0.00269	0.00296	0.01854	0.00778	0.00866	0.01494	0.01681	0	0
epithiophenanthrenes	0.00478	0.00452	0.00392	0.00604	0.00271	0.00332	0.00326	0.00105	0.00408	0.01851	0.00043	0.00927	0.00394	0.00001	0	0	0
benzodibenzothiophenes	0.02525	0.03033	0.0292	0.00776	0.00828	0.0089	0.00083	0.00093	0.00599	0.01797	0.02822	0.0045	0.00119	0	0	0	0
5-ring thiophenes*	-	-	-	-	-	-	-	-	-	-	-	0	0.00754	0	0.00001	0	0
pyrroles	0	0	0	0	0	0	0	0	0.0068	0.01317	0.02522	0.167	0.06779	0.12245	0.2189	0.1924	0.08894
indoles	0.16639	0.18563	0.22559	0.21563	0.24004	0.24161	0.26879	0.18436	0.17827	0.24826	0.17449	0.2317	0.23035	0.18814	0.17552	0.0385	0.01012
carbazoles	0.0763	0.06733	0.05661	0.0547	0.05424	0.05561	0.14761	0.15845	0.17378	0.23322	0.18323	0.08896	0.01164	0.00162	0.01212	0.00069	0.00001
4-ring pyrrolics*	0.1933	0.226	0.40913	0.34824	0.30206	0.03714	0.09325	0.08107	0.02734	0.00433	0.0001	0	0	0	0.00143	0.00888	0.00499
5-ring pyrrolics*	-	-	-	-	-	0	0	0	0	0.0126	0.03259	0	0	0	0	0	0
pyridines	0.05522	0.02177	0.026	0.0205	0.01894	0.0253	0.01547	0.03104	0.01129	0.05181	0.09145	0.14063	0.00459	0.02824	0.03724	0.02782	0.04448
quinolines	0.7658	0.84152	0.5358	0.47429	0.47467	0.3848	0.4306	0.56081	0.4423	0.42634	0.30587	0.0459	0.02945	0.04005	0.056	0.03898	0.00258
phenanthridines	0.01855	0.02401	0.01581	0.01241	0.00977	0.00933	0.01063	0.05729	0.05898	0.05726	0.06304	0.05883	0.06908	0.02678	0.00715	0.00091	0.00748
4-ring pyridinics*	0.42199	0.70376	0.61623	0.42355	0.00604	0.04327	0.03968	0.00415	0.00001	0.00004	0	0	0.00188	0.02067	0.04574	0.09443	0.1015
5-ring pyridinics*	-	-	-	-	0.00039	0.00888	0	0	0	0	0	0	0	0	0	0	0
phenols	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
hydroxy tetralins	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
naphthols	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
dibenzofuran	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
resorcinols	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
dihydroxy tetralins	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
unidentified	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.04877	0.21773

Task 3 Conclusions

The analytical methods development promoted the success of the project for two reasons. First, prior to this project the chemical structure of the higher boiling portion of the kerogen was largely unknown. It was not known quantitatively how most of the nitrogen was bound nor was it known if the functionalities were of any value. The analysis showed that all nitrogen types were present in a few homologous series of alkyl substituted rings, and that single ring nitrogen compounds were much more prevalent than previously thought. Second, the methodology could be, and was, used to track the behavior of the target compounds in conversion and separations processes.

When developing the Z-BaSIC methodology it became clear, however, that the quantitative part would not lend itself readily to automation. This had been an early goal, but when it became obvious that the automation would consume resources and become a distraction to the central objectives of the project, and in consultation with the DOE COTR, a decision was made not to pursue automation of Z-BaSIC. The project got full benefit from the development of the Z-BaSIC methodology; it just didn't result in a spin-off product.

Task 4 - Market Research and Product Identification

Statement of Work

Market application research will be conducted to determine current market needs and to anticipate directions of future markets. Markets will be classified according to types of materials needed including composition, if known, and volume and price relationships. Worldwide markets will be examined with an emphasis on North American markets. Results of market analysis will be compared with the compositional data obtained in Tasks 2 and 3 above. A candidate list of target products will be developed.

A plausible separation and conversion scheme for each of the target products will be prepared. Products will be grouped if they have complementary relationships from a processing point of view. Products which appear to be exclusive of one another will also be identified. This latter category may include multiple products for a specific compound type. Products derivable from kerogen oil will be ranked according to their price-yield multiplier. The leading candidates on this list will be viewed for their process synergism. Any special difficulties in preparing the product will be identified. Based on this analysis, a target set of products will be prioritized. This information will be used to design laboratory-scale separation and conversion processes for manufacture of products.

Results

The market research was systemized by structuring database files on products, sales, manufacturing and markets. This work, conducted in 1993, is shown in Figure 4.1.

4.1 Search by Standard Industrial Code (SIC)

The target chemicals from the kerogen oil required a SIC code to facilitate other on-line database searches. Table 4.1 shows the result of the database search conducted by Dunn & Bradstreet. The 8-digit SIC codes of the target chemicals and respective business entities whose line of business include these chemicals are shown. The data in Table 4.1 is exemplary of the formalized approach we have taken to find a market for kerogen oil-derived chemicals.

4.2 Classification by Company Profile

A further search along company profile lines revealed the data summarized in Table 4.2. Some of these companies specialize in commodity chemicals comprised of multiple components, while others specialize in specialty, pure chemicals.

The market research showed that product specifications for specialty and commodity products are highly exacting and that if kerogen oil products were to substitute for conventional products in the marketplace they must:

a. meet all specifications if they are to be accepted as a direct substitute for current supplies, or
b. be qualified through R&D testing as an alternative material in existing markets, or

c. form the basis of new markets developed around unique or useful properties or performance.

It became clear in the Phase I that the closer we could come to satisfying currently accepted specifications the easier time we would have gaining market acceptance. For pure compounds these specifications almost always relate to purity, but in some applications specific impurities are important. Pure compounds are generally manufactured synthetically today, so extracts from shale oil may include impurities not present in currently-accepted products.

Figure 4.1: Structure of Market Data Base and Data Base Files

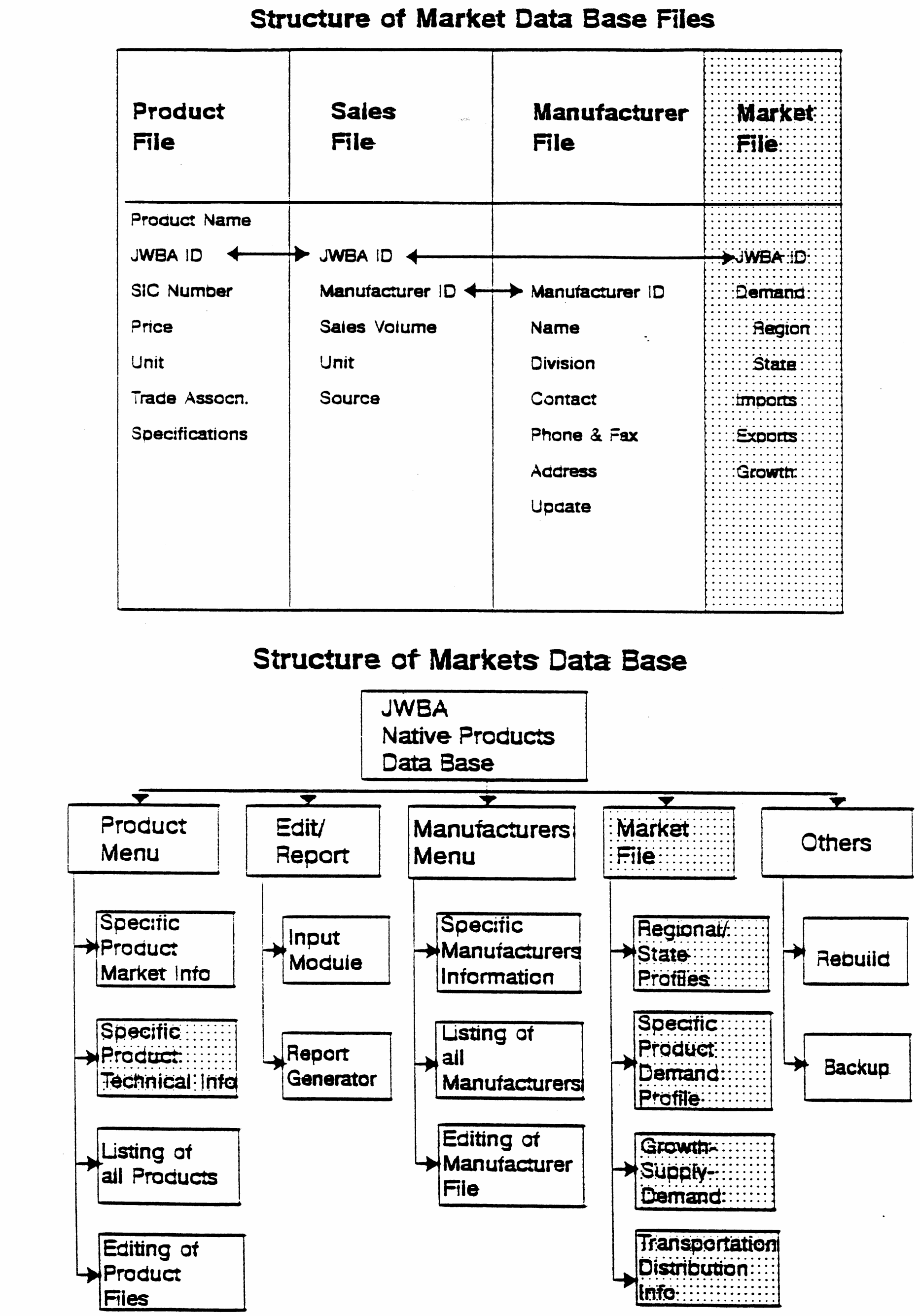


Table 4.1: Listing of 8-digit SIC Codes for Target Chemicals and Corresponding Number of Businesses

(from Dunn & Bradstreet Database -1993)

8-digit SIC	Description	Businesses
2843 01 01	Soluble oils or greases	5
2843 01 02	Sulfonated oils, fats or greases	2
2851 01 05	Paints, asphalts or bituminous	19
2865 02 07	Phenols, alkylated cumene	4
2865 04 02	Distillates, coal tar	14
2865 04 03	Tar	9
2869 99 01	Accelerators, rubber processing	1
2869 99 28	Organic solvents	27
2879 99 03	Fungicides, herbicides	42
2895 00 00	Carbon black	32
2899 99 18	Fire retardant chemicals	58
2911 02 06	Petroleum solvents	11
2911 03 03	Fuel oils	49
2911 04 02	Mineral oils	1
2911 04 03	Mineral waxes	2
2911 04 04	Lubricating oils	26
2911 04 05	Paraffin wax	1
2911 05 01	Asphalt, refining	39
2911 05 02	Petroleum coke	4
2911 05 03	Lubricating greases	10
2911 05 04	Petrolatum	4
2992 01 01	Brake fluid	10
2992 01 02	Cutting oils	45
2992 01 04	Transmission fluid	6
2992 99 02	Rerefining oils	88
2999 01 01	Coke, petroleum	7
2999 02 02	Petroleum waxes	18

Table 4.2

SIC	**Product Type Search**	**# of Potential Companies**
2833	Chemical Manufacturing/Medicinal and Botanical	96
2821	Plastic Resins	84
5169	Chemical Products n.e.c.* (Misc.)	97
5169	Resins, Chemical Products	5
2992	Lubricating Oil	200
2911	Petroleum and Coal Products	23
3624	Carbon Products	35
5172	Petroleum Products n.e.c.* Oils	21
2899	Chemical Preparations n.e.c.* Oils	25
2911	Petroleum Refining	235
2834	Pharmaceutical Preparations n.e.c.*	66
2843	Surface Active Agents	32
2865	Cyclic Crudes and Intermediates	82
2869	Amines, Acids & Esters	6
2879	Agricultural Chemicals	71
2869	Fragrance Chemicals	4
2865	Tar Products	4

* Not elsewhere classified.

For concentrates, the specifications pertain more to physical properties and performance. Most industries have a set of specification tests for their products. It is a matter of determining which market will be approached and then designing the processes and conditions to produce products that meet those specifications.

The prospect of developing new markets is significant to the long-term growth of a value-enhancement process. As with phenolic compounds with Estonia kerogen oil, the nitrogen compounds in US kerogen oil are inexpensive to produce in their raw state. It is highly likely that markets exist for these compounds that have not heretofore been developed because the historic expense of synthesizing the heteroatom containing compounds exceeded their commercial benefits. Examples of high-volume new markets are industrial and oil-field surfactants, polymers with special antimicrobial properties, water-proof wood laminating adhesives, etc.

While the current market volumes will pose some limitations to the capacity of the initial venture, it is conceivable that with continuing research and development, along with increasing market penetration of existing synthesis-supplied markets that a VEP venture could grow by several factors over the initial plant scale.

Task 4 Conclusions

In practical terms, the markets for the products were not as diverse as originally expected and there was no need for a massive, linked database. Commodity products are marketed on the basis of product quality and price, and generally have a broader market base of customers. Petroleum products are all commodity products. Specialty products will necessarily be marketed to customers who have made a business based on a narrow product line. Here product quality can be influenced by trace impurities, some of which may be acceptable to the buyer, but others may not (thiophene in pyridine being an example). Customers for specialty products are particularly concerned about supply and quality assurance. In fact, because there was no reliable source of kerogen oil, this concern, as much as any other single factor deterred investment in VEP in the early days of project marketing.

The foregoing investigation was conducted in the general time frame of 1993-95 and prices and companies reflect that era. An update of relevant companies and economics was conducted in the time frame of 2005-06 and those results are contained in the report on Task 14b.

Task 5 - Separations Exploration

Statement of Work

Separations approaches for isolation of each of the priority target products will be devised. Preparative scale separations will be conducted according to the proposed schemes. Products will be subjected to Z-BASIC analysis, specifications testing or further processed by conversions processing.

Results

Results of the distillation and liquid-liquid extraction of the light fractions have been combined with Task 2 results reported above. Extraction of the >400°C fraction (Heavy Vacuum Gas Oil, HVGO) proved highly problematic because of the high wax content. Task 5 focused on solving this issue. Elevating the temperature restricted the solvent choices that could be run at atmospheric pressure, and it was deemed beyond the scope of the exploratory phase to build a pressure extractor.

Hence, exploratory extraction studies were done with N-methyl-2-pyrrolidone. These extractions resulted in yields of 33% extract and 67% raffinate. Because the extract was comprised of both alkyl-polar and alkyl-aromatic compounds, the extract would be scheduled for dealkylation in the THDA process. Subjecting the entire HVGO to THDA was considered, but the value of avoiding the extraction step did not offset the higher cost of cracking valuable waxes and, therefore, this route did not appear promising. Alternatively, as was learned in later phases, this extract may be useful as an antistrip asphalt additive.

The >400°C raffinate was further subjected to dewaxing with MEK/Toluene. About 18% waxes and 82% dewaxed oil was produced. Waxes are valuable commodities in their own right with values in the mid-90s of at least double the price of crude oil. Because of the bottomless nature of kerogen oil, however, it is not expected that kerogen oil waxes will have the value of a fully-refined microcrystalline wax that have carbon numbers ranging above about 40. The high yields of paraffin waxes offer a product option to VEP concept.

Task 5 Conclusions

If prior distillation is performed and extraction of the heavy vacuum gas oil fraction is desired, then N-methylpyrrolidone is an acceptable solvent for polar extraction of the >400° C. Based on work conducted in tasks 6 and 9 described below, THDA processing of the extract would add appreciably to the yield of lower alkyl pyridines (LAPs). The difficulty of extracting the >400° C cut, which represents approximately 50% of the mass and contains approximately 70% of the nitrogen was a finding that called for a refocus of approach. Combined with the negative economic impact of the complexity resulting from pre-distillation, the results of this task contributed to the decision to focus on extraction of whole kerogen oil (see also conclusions of Task 7).

Task 6 - Conversions Exploration

Statement of Work

Processes for conversion of separated concentrates into marketable products will be explored. Candidate conversion processes include catalytic hydrogenation and oxidation, hydrodealkylation, chemical dealkylation, polymerization, hydrolysis, derivatization and other possible chemical processes. These processes will be applied where required to explore means of conversion of separation concentrates to marketable products.

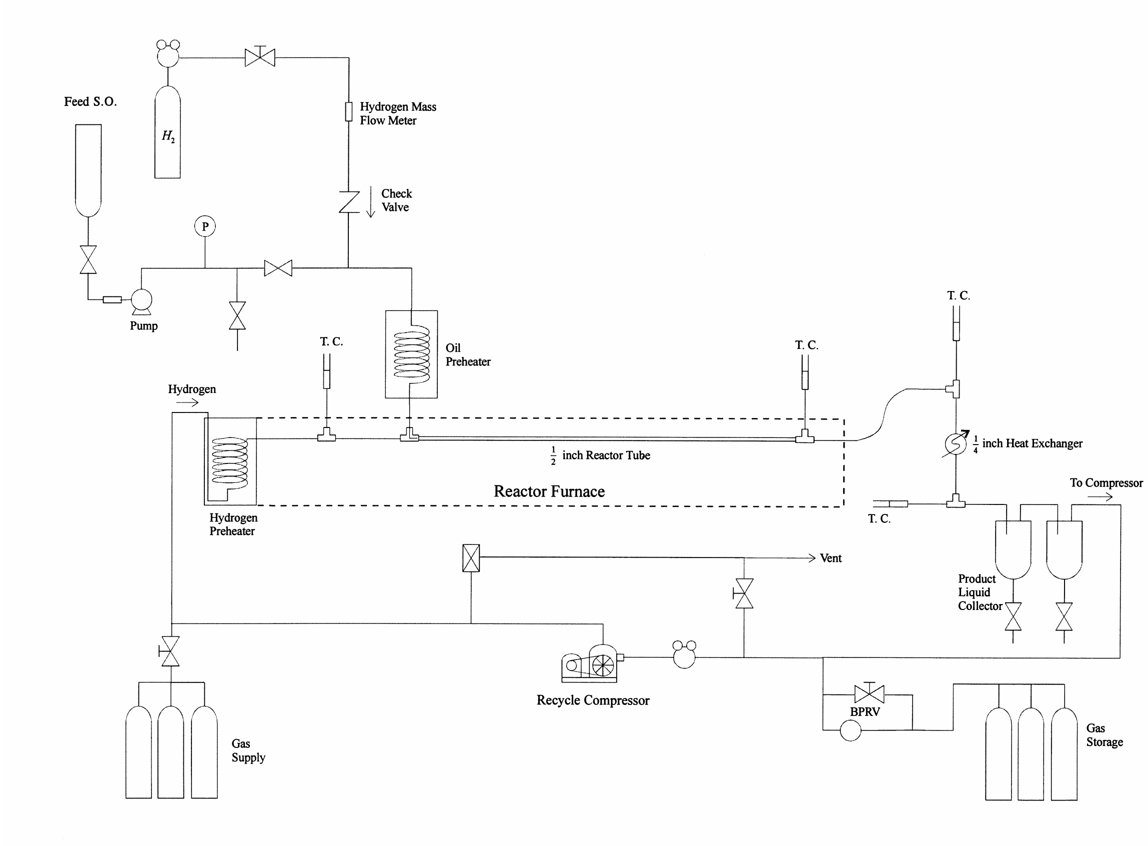
Results

The conversions exploration task was conducted under subcontract with the University of Utah. The University has a once-through thermal hydrodealkylation (THDA) unit originally constructed by the PI during his tenure there. A diagram of this equipment is provided in Figure 6.1.

Difficulties caused by unfamiliarity of the students with the flow-through equipment resulted in a change in approach. THDA experiments on a flow through system would be conducted in later phases. Batch THDA (hydrovisbreaking) work was completed. The work at the University of Utah showed that >400 °C kerogen oil, when further visbroken in the presence of hydrogen, produced lower molecular weight pyridines. This demonstrated the tractability needed to warrant further study of this process. Results of the THDA experiments are included in the task 9 conversion process development described below.

The polar fraction from the > 400°C fraction is of high molecular weight and a candidate for higher temperature thermal hydrodealkylation (THDA). It was learned through investigations of industrial interest (task 13) that THDA is, in fact, used commercially to dealkylate higher alkyl pyridines to pyridine and picolines. This gives increased confidence to include this unit in a commercial sequence As a result of this success, chemical dealkylation such as reverse Friedel-Crafts dealkylation is not needed.

Figure 6.1: Flow Diagram of Shale Oil THDA Process Apparatus



Other types of conversion processes such as polymerization, hydrolysis, or derivatization were not indicated based on the characterization results. This was a convenient discovery and allowed the efforts to more quickly focus on product development.

Task 6 Conclusions

Based on conversion processing and in view of the compositional analysis, market analysis, and separation work, it was concluded that a two conversion processes, THDA and catalytic hydrotreating, would be sufficient to produce a suitable product slate from kerogen oil. THDA could be used in a hydropyrolysis mode for cracking of higher alkyl pyridines to lower alkyl pyridines, and the traditional THDA mode could be used to dealkylate lower alkyl pyridines to pyridine and picolines. Catalytic hydrotreating is a commercially practiced technology and is known to be an acceptable means of removing residual nitrogen from feedstocks such as the raffinate. (This process was demonstrated in the laboratory in subsequent phases, justifying this conclusion). Further finishing of raffinates to produce waxes, aromatic oils, or lube oils, while adding value also added complexity.

Task 7 - Process Modeling and Preliminary Economics

Statement of Work

Results of Tasks 2-6 will be assembled and flow diagrams of at least two alternative process approaches will be devised. Process units will be specified and material balances will be calculated. Process conditions identified in the separations and conversion tasks will be used to determine heat duties and solvent recycle requirements. Process simulation software will be utilized to supplements experimentally determined data. A cost analysis of the processes will be performed using factored estimates and analogy to currently-practiced technologies. Prices will be assigned to the products and profitability analysis will be conducted. An economic sensitivity analysis of the various economic assumptions will be performed. Based on these results, a recommendation will be made as to the most promising direction to pursue in a process development phase (Option-I).

Results

7.1 High Selectivity Separation Case

During Phase I a comprehensive approach was taken to determine the processability of kerogen oil by distillation, extraction, and conversion processing. The general approach is shown in Figure 7.1. At the outset of this research it was not known where the greatest profitability existed and it was important that every possibility be given a fair examination so as not to miss a prime opportunity.

The Phase I results led to a ‘high-selectivity’ process scheme as shown in Figure 7.2. This scheme was thermodynamically sound and promised to produce products in a highly selective way. Further, it was aimed at maximizing the value of the products, aiming not only at recovering pyridines and quinolines, but recovering indoles, pyrroles, phenols and thiophenes.

The High Selectivity case produces four (4) distillate cuts which in turn are extracted to form four (4) pairs of extracts and raffinates. Heavy polars are combined and sent to THDA (by extracting the two heavy fractions separately, each extraction can be better optimized for extraction selectivity). Heavy THDA products are recycled to extinction. Light ends from the THDA are extracted and the polars are combined with the original polar extracts from the lighter distillates for purification into pure compound products. Heavy raffinate is processed for its oil and wax values.

Overall, more than a dozen process units are needed as there will undoubtedly be multiple units required for pure compound finishing. Based on experimental results the estimated product slate is given in Table 7.1. The high yield of pure compounds would greatly enhance the value of the final product slate, if costs were acceptable. It is believed that a mature industry could achieve these results by incremental additions to the process facilities and market conditions warrant. Note that the high selectivity mode also favors production of lube oils and waxes over refinery feedstock. However, markets might not support these products at a local or regional level.

Figure 7.1: Shale Oil Value Enhancement Research Project Connectivity

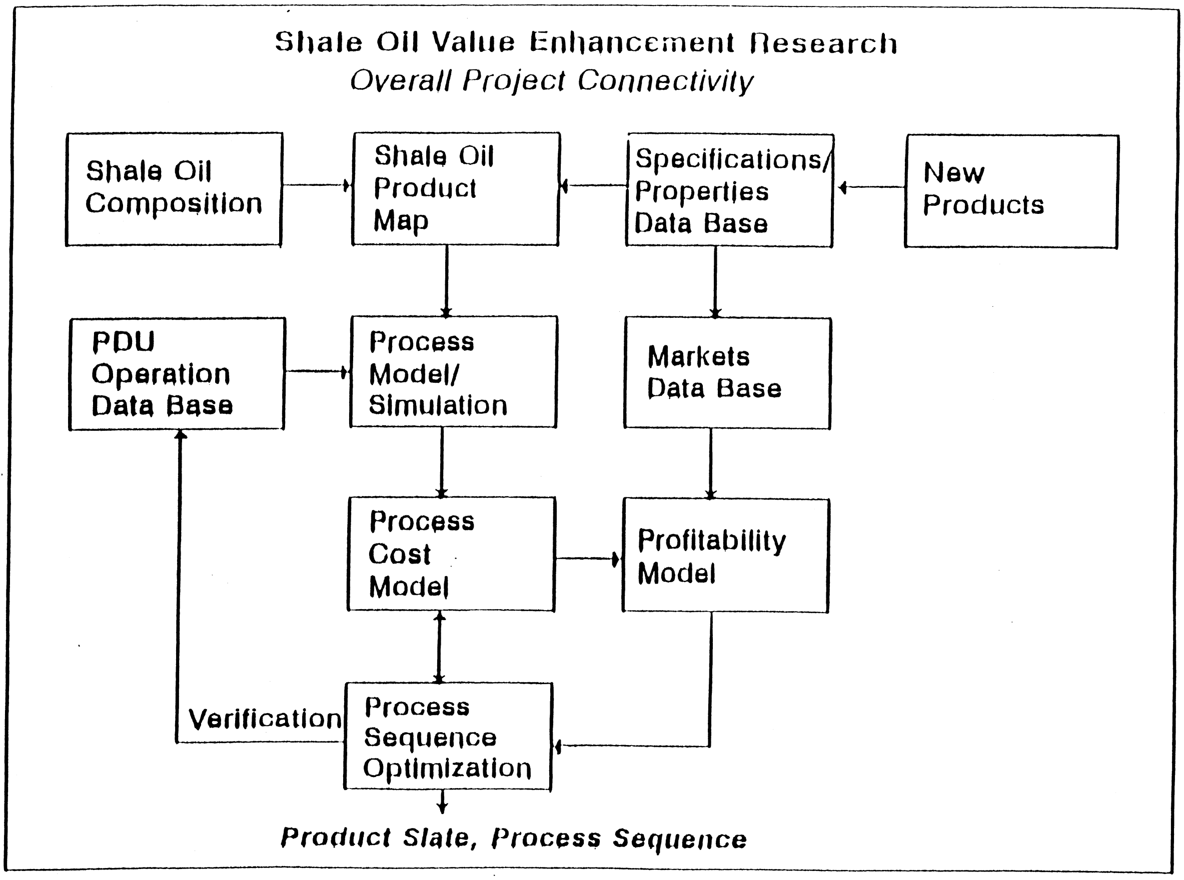


Table 7.1: High Selectivity Process Yields - Weight Percent

Product Stream	Estimated Yield
Pure Compounds (all)	12.9
Light solvents/naphtha	10.7
Refinery feed (middle distillate)	18.6
Paraffin waxes	5.8
Aromatic oils	16.0
Lube oils	26.6

7.2 Economic Analysis

An economic analysis was performed according to the logic shown in Figure 7.3. The logic shown in the figure is used throughout the program. The approach of fractionating the oil by both boiling range and polarity was to assess the overall product map, and to assure that any particularly valuable components would be discovered. However, when economic analysis of the high selectivity process sequence was performed it became apparent that the economics could not support 12 (or more) major process units. The vast majority (~88%) of products are conventional petroleum products selling at, or slightly above crude oil prices. In this phase of work the base-case petroleum price of \$20/bbl was assumed, and feedstock costs (raw kerogen oil) costs of \$18/bbl were assumed (the latter from estimates of minimum production costs).

7.3 Simplified Process

7.3.1 Process Sequence

Consequently, the process sequence shown in Figure 7.4 became the basis for work initiated in Option-I(a). In the simplified process polars are sent to THDA, where a secondary extraction splits the THDA product into lower molecular weight polars and a naphtha-range raffinate. The polar extract is sent to a purification process (unspecified in this phase of work). The raffinate is successively processed to recover middle distillate for conventional refining and the heavy ends for commodity petroleum products. (In practice, these heavy ends may be simply catalytically cracked, but this would be a lower value use). Estimated process yields are given in Table 7.2

Figure 7.2 Flow Diagram – High Selectivity Process

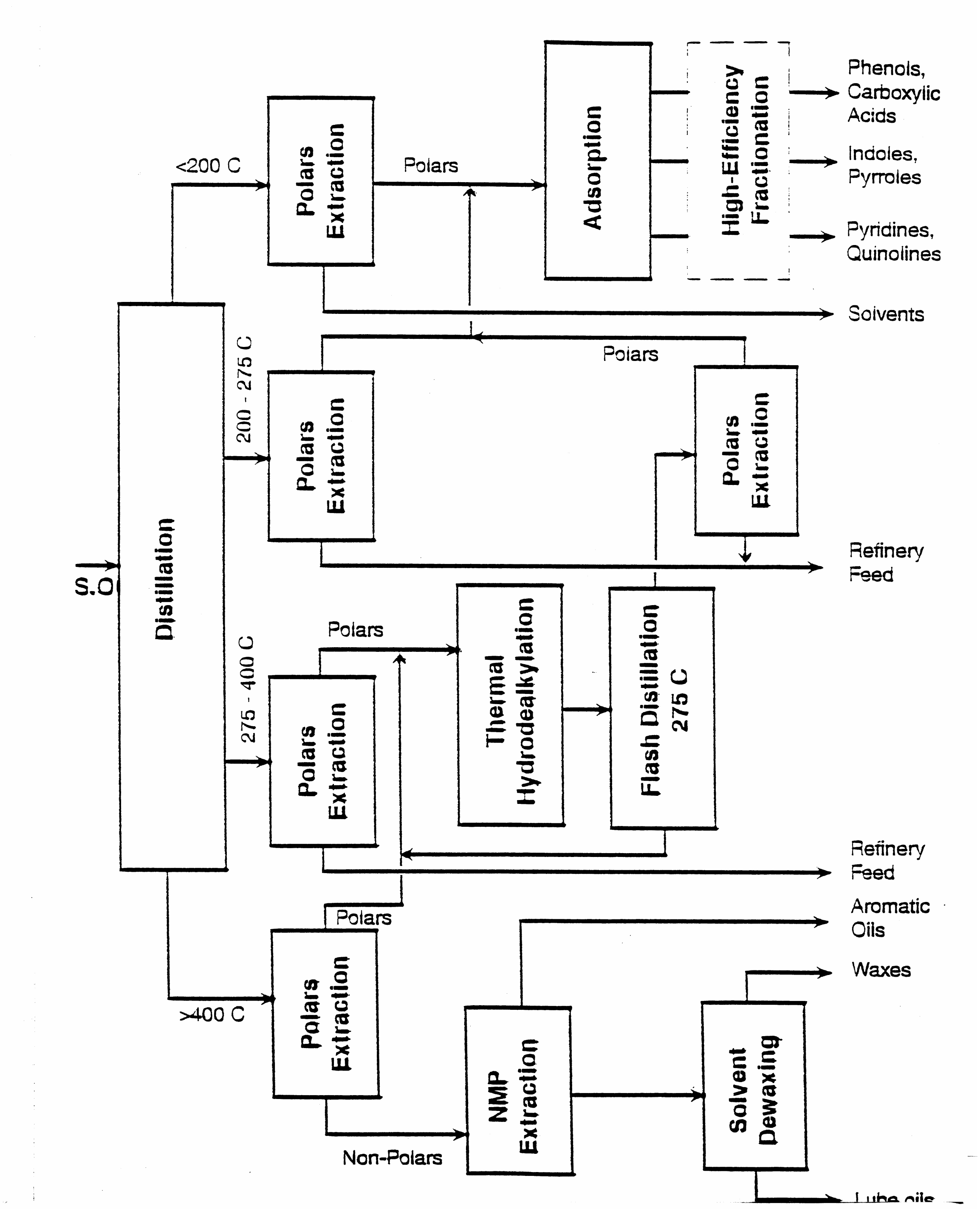


Figure 7.3: Economic Analysis Model for Process Evaluation

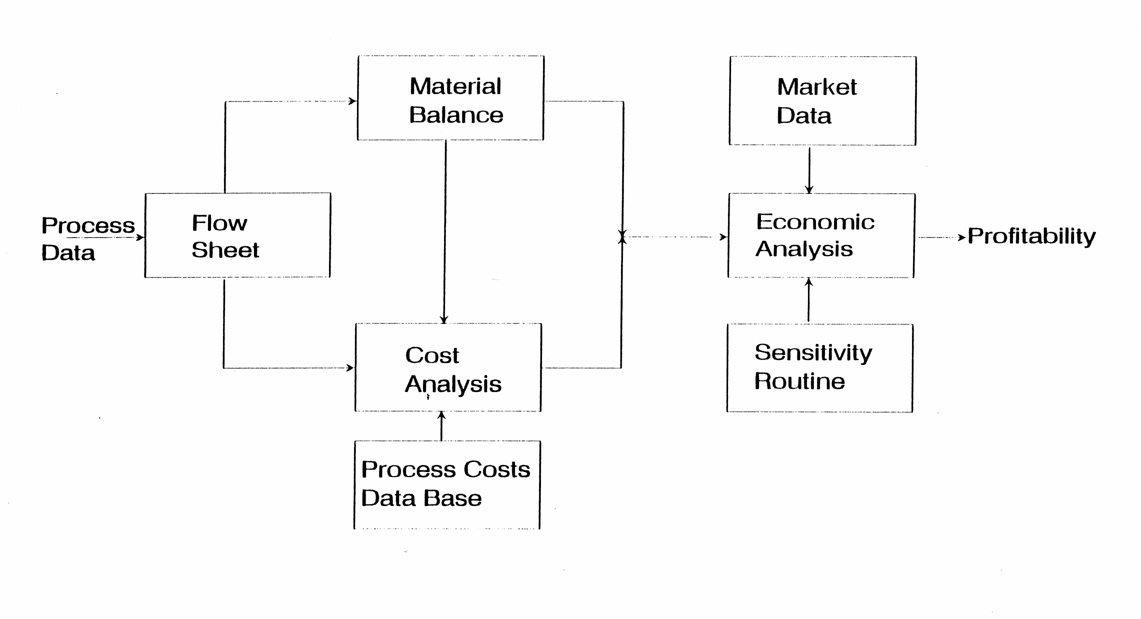
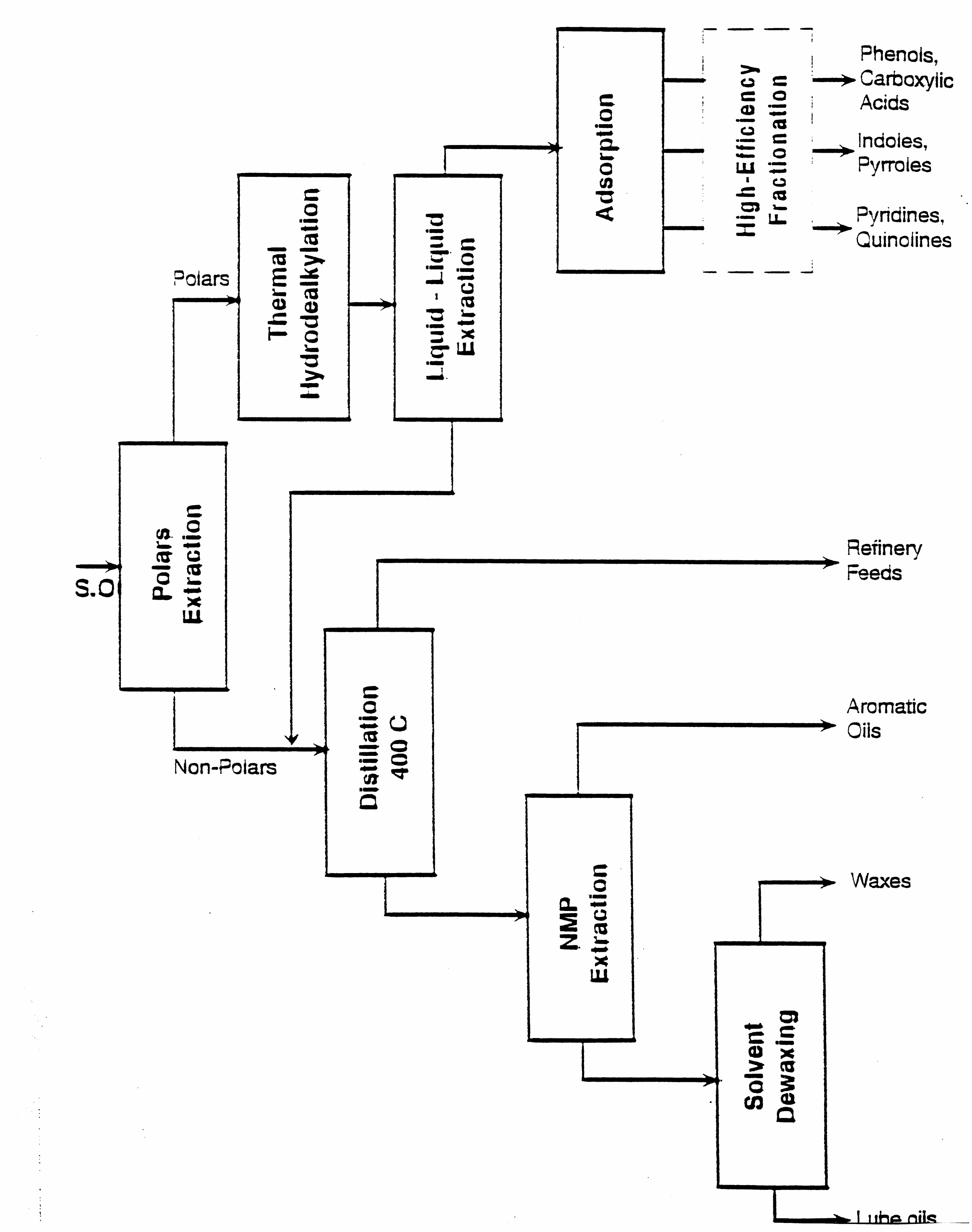


Table 7.2: Simplified Process Yields

Product Stream	Estimated Yields – Wt %	Unit Cost $/bbl*	Product Revenue** $/bbl	Net $/bbl on Unit	Net $/bbl on Process
Pure Compounds (all)	19.1	25	90	65	12.42
Refinery feed (middle distillate)	44.7	6	20	14	6.26
Paraffin waxes	4.3	10	25	18	0.77
Aromatic oils	11.9	8	25	17	2.02
Lube oils	19.8	10	28	18	3.56
	100.0		Net process revenue		25.03
			Less feedstock cost		-18.00
* includes CAPEX at 15% IRR and total OPEX ** revenue data circa 1995 prices WTI crude = $20/bbl			Net gross profit		$7.03

Figure 7.4: Flow Diagram – Simplified Process



7.3.2 Economics

The overall economics are shown in the aforementioned table. Typical capex and opex costs were simply taken from petroleum literature for the distillation and extraction processes. The purification process assumed that multiple units of high efficiency distillation would be needed. The state of development at this phase of the project did not justify more detailed economics.

Extraction of basic nitrogen types is expected to make the remaining raffinate more valuable for conventional refining because brute force catalytic hydrotreating is not needed. Hence, even though catalytic hydrotreating is not included in the current schemes, the products are expected to be marketable. It may be noted that the petroleum products are essentially breakeven; that the profit margin comes from the pure compounds. A transfer price of \$18/bbl for raw shale oil is assumed. This price is higher than what a petroleum market would bear for an a non-upgraded material, but was chosen higher than the market to illustrate the market-pull that VEP could bring to oil shale commercialization. It should also be noted however, that the scheme as currently outlined could not support a project if the raw oil shale costs were \$30/bbl and crude oil prices remained at \$20/bbl. This would be too large a differential to ask the pure compounds to make up.

Task 7 Conclusions

The complex, multi-step process as originally conceived was not economical. The highest value products did not promise enough revenue to overcome the number of process steps required. Some process simplification was needed. The obvious simplification was to eliminate the initial distillation unit and combine the extraction units into one unit. This approach might lead to reduced recovery and selectivity toward target compounds. However, economic necessity showed that this simplification was needed.

While it is generally understood that simplicity leads to better economics, it might be remembered that the original objective of this work was to identify the maximum amount of high value products. The original proposal anticipated a matrix of more than a dozen commodity and specialty products. The possibilities of developing a large suite of products was explored in this first phase, and these possibilities are available for future development in a growth phase. But to succeed in achieving commercial viability for a first generation project, the product slate needed to be simplified, and producing pyridinics compound products from the extract and producing petroleum product products from the raffinate showed promise. Consequently, the Department of Energy elected to exercise its option and pursue process development, Phase II.

PHASE I - CONCLUSIONS

1. About 40 % of raw kerogen oil is comprised of molecules that contain a heteroatom, with nitrogen types representing more than half of this. These are the target molecules for specialty products.

2. About half of the study oil boils above 400 °C, with nitrogen compounds representing more than half of this fraction on both a molar and mass basis. A successful VEP must make valuable use of the heteroatoms in this fraction.

3. Methanol is an excellent extraction solvent for lower molecular weight fractions, but higher molecular weight fractions will require higher molecular weight solvents.

4. Pure compound targets contain pyridinic, pyrrolic and phenolic groups, and broad range concentrates include aromatic oils, lube oils and waxes. The balance of the products will be hydroprocessed and sold as a sweet refinery feedstock.

5. Pyridinic rings are known to respond to thermal hydrodealkylation and kerogen oil was shown to respond to hydrovisbreaking. Concentrates of higher alkyl pyridines will produce large quantities of lower alkyl pyridines.

6. Economic considerations show that the overall scheme must be as simple, with fewest units possible that result in markets for all the production.

7. Economic results show that if petroleum products can break even with the cost of feedstock including upgrading that the valuable heteroatom-containing compounds can make the venture profitable.

8. Results are sufficiently positive that a development phase is warranted. DOE elected to proceed with Phase II - Process Development.

PHASE II - PROCESS DEVELOPMENT

Task 8 - Separations Development

Statement of Work

Process apparatus for separations will be designed, constructed and operated. The operations will be conducted to obtain information on engineering parameters including, but not limited to, temperature, contact ratios, solvent quality, partition function values, stage efficiency, and other important parameters. Data will be obtained in a form which allows for rigorous and fundamental process modeling.

Results

8.1 Apparatus

Apparatus for this task are as describe in the experimental sections for tasks 2 and 8. Whether the extraction is by test tube, shake test or semicontinuous counter-current extraction, for each experiment, one raffinate and one extract is produced. Unless otherwise specified, results for the following sections are done as shake tests in separatory funnels. See also Figure 10.1, below, for the context of Task 8 work.

8.2 Coefficient of Separation

In the Phase I Program it was learned that there will be a tradeoff between recovery and selectivity. An engineering objective will be to minimize this tradeoff. This kind of problem is common also in the extractive metallurgy industry, which considers both recovery and quality of concentrate. Adopting techniques practiced in extractive metallurgy, a Coefficient of Separation (COS) was defined as:

COS = mole % of desired compounds recovered in the fraction

mole % of undesired compounds recovered in the same fraction eq. 8.1

To illustrate, if a kerogen oil consisting of 40 mole % nitrogen-containing compounds and 60 mole % non-nitrogen-containing compounds is extracted for the purpose of concentrating nitrogen-containing compounds, a perfect separation would be one in which all of the nitrogen-containing compounds would be recovered in the extract and none of the non-nitrogen-containing compounds would be recovered in the extract. Under these circumstances the calculated COS would be:

100 = 100% of nitrogen-containing compounds recovered

0% of non-nitrogen-containing compounds recovered eq. 8.2

As another example, if 75% of the nitrogen compounds are recovered in the extract and 25% of the non-polar hydrocarbons are recovered in the extract then the calculated COS would be 50 = 75 -25. As a rule, economic viability requires a COS of greater than 50%, and ideally the COS should be maximized, as long as it does not require additional process steps. Maximum COS is achieved by varying the selection of solvent, the concentration of water, the temperature, the solvent-to-oil ratio, the number of extraction stages, the throughput rate and other process variables.

8.3 Selection of Solvent Systems

8.3.1 Selection of Polar Solvent

It had been learned in Phase I research that alcohols were inadequate for extracting the >400 °C material. It had also been concluded that liquid-liquid extraction of individual distillate cuts resulted in too many units for economic viability. Therefore, to simplify the process scheme the whole, topped shale oil was used as the study oil. It was hypothesized that the low molecular weight polar compounds may assist in solvating the higher molecular weigh polar compounds in the >400 °C portion. This hypothesis proved to be true.

The selection of polar solvent is made based on COS, ease of recovery, low reactivity and low cost. The newly defined COS is used as the measure of selectivity. Ease of recovery considers both recovery efficiency, defined as the percentage of solvent recovered per pass, and other handling characteristics such as low toxicity or corrosivity. Low reactivity is defined as exhibiting negligible chemical effects on the composition of the extract. Low cost implies that the solvent should readily available in commodity markets.

In general, small molecules possessing dipole moments of greater than 1.0 Debyes are candidates for the selected polar solvent. Chlorinated or halogenated solvents are to be avoided, both because of the additional environmental hazards and the adverse effects the presence of halogens have on downstream processing. Other undesirable solvents are oxidizing solvents, reducing solvents, mineral acids and solvents that promote free radical or ionic polymerization reactions.

Examples of compounds that may be considered for polar extraction solvents and their gas phase dipole moments (in Debyes) are shown in Table 8.1. Results of shake tests of selected solvents are given in Table 8.2.

Table 8.1: Selected Solvents and Polarity Properties

Solvent	*Dipole Moments (Debyes)*
Formaldehyde	2.33
Formic Acid	1.41
Methanol	1.70
Acetaldehyde	2.69
Acetic Acid	1.74
Ethanol	1.69
Propyl Alcohol	1.68
Isopropyl Alcohol	1.66
Furfural	>1.00 est.
Phenol	1.45
Sulfolane	>1.00 est.
N-methyl-2-pyrrolidone	>1.00 est.

Table 8.2: Results of Shake Tests with Selected Solvents

Feedstock - > 150°C Kerogen Oil
N Content - 1.6%
Avg. M.W. - 246 Dalton
Method - Single Stage Extraction (shake tests)

Solvent System	**% Extract**	**% Raffinate**	**%N in Extract**	**%N in Raffinate**	**COS**
98% methanol/2% water	10.0	90.0	3.2	1.4	16
100% acetic acid	16.6	83.4	2.9	1.3	22
80% formic acid/20% water	17.4	82.6	3.5	1.2	32
23% formic acid/77% acetic acid	36.3	63.7	3.3	0.6	61
100% formic acid‡	31.8	68.2	3.9	0.5	73
85% formic acid/15% water	28.7	71.3	4.1	0.5	75
90% formic acid/10% water	40.8	59.2	3.6	0.2	82
95% formic acid/5% water	32.3	67.7	4.0	0.4	79
90% formic acid/10% water*	30.0	70.0	4.3	0.4	80
*Multiple stage PPTE countercurrent extraction.					

It is clear from the results in Table 8.2 that the solvent system selection has a strong effect on the COS. It is also apparent that the concentration of water will be an important variable. In commercial operation it will not be practical to maintain anhydrous conditions, so the beneficial effects of small amounts of water is convenient.

To illustrate the effects of water in a system familiar from Phase I research, equal portions of a methanol and the 200-275°C distillate were extracted in a shake test. In the first case the selected solvent was pure methanol, in the second case the selected solvent was pure methanol to which 2.0 weight percent water was added. Other proportions of water were tested, but for the 200-275° C fraction used, 2% water gave the best combination of clean phase separation and selectivity. The results are shown in Table 8.3.

The results show that adding a very small amount of water dramatically improves the COS for this solvent system and distillate feed. The improved results are achieved because of the antisolvent effects of water that acts to reject non-polar oils from the extract. The improvement in recovered nitrogen is due also to the antisolvent effect of water in reducing the solubility of the polar solvent, methanol, in the raffinate phase.

Table 8.3: Effect of Added Water on Extraction Results

Feedstock 200 - 275° distillate, Green River Formation Kerogen Oil
N content – 0.6 %
Average MW - 173 Dalton

	Methanol Only	Methanol + 2% Water
Extract (wt %)	44.7	33.3
Raffinate (wt %)	55.3	66.7
% N Compounds recovered in extract	82.3	88.0
% Non-N compounds recovered in extract	41.6	29.6
COS	40.7	58.4

The solubility of the nitrogen compounds in the raffinate is directly related to the amount of water and polar compounds remaining in the raffinate. Addition of water to the solvent system makes the solvent system less compatible with the raffinate and reduces the amount of solvent constituents in the raffinate phase. Reducing the amount of the solvent system constituents, the water and polar solvent, results in a less favorable partitioning of the nitrogen types into the raffinate phase.

In general, the addition of small amounts of water to any of the selected organic solvent systems is favorable. The percentage of water added should be determined so as to maximize the COS[12]. The limit to how much water should be added is determined by the solubility of the extract oil in the selected solvent system.

The results of the shake tests with carboxylic acids provided COS values of 80%, or greater, very positive results. To test whether carboxylic acids may catalyze polymerization reactions, or otherwise cause chemical reactions, a sample of 200-275°C distillate was heated and stirred with an equal portion of 90F/10W.

Solvent was removed and a GC-MSD trace was compared with the original trace. Except for some losses of light ends, no differences were detectable. These were positive results and encouraged further development of carboxylic acid solvent systems.

8.3.2 Selection of Non-Polar Solvent

Selection of a non-polar co-solvent is made based on COS, ease of recovery, low reactivity and low cost, as defined above. In general, the non-polar co-solvent serves to enhance the antisolvent effect of water.

Small molecules possessing a dipole moment of less than 0.1 Debyes are candidates for selection as non-polar solvents. Aromatic hydrocarbons are to be avoided because of their adverse effects on selectivity and olefins are to be avoided because of their instability and reactivity. Chlorinated or halogenated solvents are to be avoided because of their adverse effects on selectivity and undesirable environmental effects.

Suitable non-polar solvents include, but are not limited to normal paraffins, isoparaffins, and cycloparaffins with less than 7 carbon atoms. Examples, all of which exhibit dipole moments (in Debyes) less than 0.1, are:

n-propane
n-butane
n-pentane
n-hexane
n-heptane
cyclopentane
methylcyclopentane
cyclohexane
methylcyclohexane

As an example, Kukersite kerogen oil from Estonia is, itself, a highly polar mixture, being comprised almost entirely of phenolic and aromatic compounds. Dihydric phenols such as resorcinols are extremely valuable and if they could be separated from the aromatics, could become a concentrate for further refining. To demonstrate the value of using a non-polar solvent to enhance the selectivity of separating polar compounds from aromatics, a 200-550 °C distillate of Estonia Kukersite kerogen oil was vigorously shaken with 1.5 parts of polar solvent, comprised of 90% formic acid and 10% water, and 1.0 parts non-polar solvent, comprised of n-hexane (all parts by weight) and allowed to settle until 2 phases were formed. The bottom extract phase was separated from the top raffinate phase and the solvent was separately removed from each phase by distillation according to the practice of the invention. The extract amounted to 19% of the total distillate and raffinate amounted to 81% of the total distillate. The extract and raffinate were separately analyzed by a gas chromatograph equipped with a mass selective detector (GC-MSD) in a total ion current (TIC) mode.

Three compound-types of approximately the same molecular weight were selected to evaluate the separation; methylnaphthalenes, MN (142 amu), naphthols, NOH (144 amu), and dimethylresorcinols, DMR (138 amu). Each of these specific ions were integrated in the chromatograms for both the extract and the raffinate. Using customary methods for comparing relative concentrations and accounting for the yields of extract and raffinate in the extraction step it was determined that the recovery in the extract of MN was 4%, NOH was 51% and DMR was 88%. From this information three coefficients of separation can be determined as follows:

For the separation between DMR and MN; 84 = 88 - 4

For the separation between NOH and MN; 47 = 51 – 4

For the separation between DMR and NOH; 37 = 88 – 51

For this example the separation between DMR and MN is high. However, the separation of NOH from MN or DMR from NOH is less than optimum and may be improved by varying the selection of polar solvent, water-to-polar solvent ratio, selection of non-polar solvent, solvent-to-oil ratio, temperature, number of contact stages and the like and measuring the effect of variations on the COS.

It will be noted by the example that it is not possible to maximize both the separation of the NOH from the MN *and* the DMR from the NOH while at the same time maintaining a nearly ideal separation between the DMR and the MN. This example reveals that the choice of which species to consider the desirable species and which species to consider the less-desirable species must be made by the practitioner and that optimization of all of the practitioner's objectives may require successive and multiple extractions, if it profitable to do so.

It was not known at the time of this experiment, but these results were highly useful when phase IV of the project, the USA/Estonia cooperative agreement on oil shale was implemented.

8.4 Effect of Process Variables

8.4.1 Solvent-to-Oil-Ratio

It is desirable to minimize the solvent-to-oil ratio in order to reduce requirements for solvent recovery. For all selected solvent systems there will be a minimum amount of solvent that must be added to the oil in order to create two phases. This amount of solvent is the least amount that can be used in practice and will depend on the nature and composition of the oil, the structure of the solvent, the presence of other solvents, the temperature and the configuration of the extraction system. In practice, it may be desirable to use more than the minimum amount of solvent required to induce two phases, if by increasing the solvent-to-oil ratio the COS is increased correspondingly. In all practical systems it is expected that there will be a limit to the maximum amount of solvent that can be introduced to a fixed amount of oil before the COS will no longer rise and will begin to fall. The desired amount of solvent will be between the limits of the minimum amount required to create two phases and the amount required to maximize the COS. In the practice of the invention the selection of solvent and the temperature of extraction are chosen to maximize the COS while minimizing the solvent-to-oil ratio. For example Table 8.4 shows the effect of solvent-to-oil ratio on extraction of a kerogen oil distillate.

The data shows that the minimum solvent to oil ratio is between 0.5 and 0.6, below which two phases are not formed. As the solvent-to-oil ratio is increased above this minimum the percent of the total oil extracted increases and the percent of total nitrogen recovered increases. The optimum COS is exhibited at a ratio of about 1, below this ratio the recovery of nitrogen is not as effective and above this ratio the undesirable recovery of non-nitrogen compounds into the extract increases.

In prior-art processes that aim to maximize the recovery of nitrogen compounds[13], the highest recovery of nitrogen into the extract would be considered the most desirable, which in the above example would be at a solvent/oil ratio of 4. However, to achieve such a high recovery of nitrogen compounds in the extract there is also a much higher recovery of non-nitrogen compounds into the extract, which devalues the extract. Thus, by minimizing the nitrogen content of the raffinate to achieve the highest value raffinate, the value of the extract would be seriously compromised. In addition, the solvent requirements are much higher, increasing solvent recovery costs.

Table 8.4: Effect of Solvent-to-Oil Ratio on COS

Feedstock - 200-275°C distillate from Green River Formation kerogen oil
N Content 0.6 wt.%
Average M.W. Nitrogen Compounds - 173 Dalton
Solvent System - 98% methanol, 2% water

Solvent/Oil Ratio	% Raffinate	% Extract	% N Recovered in Extract	COS
0.5	TWO PHASES NOT FORMED			
0.6	67	33	68	38
1.0	67	33	87	59
2.0	47	53	94	45
3.0	41	59	98	42
4.0	19	81	99	20

By increasing the COS, the combined value of the raffinate and extract fractions is optimized, rather than optimizing one fraction while seriously devaluing the other. In addition, this increase in value is achieved by a significant saving in solvent, as compared to typical prior-art practice, which utilized solvent/oil ratios far in excess of 1 to 1. It should be pointed out here that the methanol/water system is effective for light distillate cuts; it is easily recovered and inexpensive. However, as is pointed out below, for the whole oil greater hydrocarbon solvation power is needed, and the preferred systems for the whole oil are lower carboxylic acids.

8.4.2 Effect of Temperature

Raw Green River Formation kerogen oil possessing 1.6% nitrogen and an average molecular weight of 246 Daltons was subjected to a single-stage extraction in a separatory funnel. Solvent was added in a ratio of 1 part solvent to 1 part oil, shaken, brought to 42°C by a heating bath, reshaken and phases allowed to separate. The extract and raffinate were recovered as described above and samples were subjected to elemental analysis. The coefficient-of-separation was calculated as described. The process was repeated under identical procedures except that the temperature was brought to 79.2°C. The results of the two tests along with a prior test done at ambient (20 °C) conditions are shown in Table 8.5.

The results show that the COS decreases with increasing temperature. Increasing temperature appears to increase the solubility of the polar compounds in the raffinate. The underlying thermodynamics reflect complex changes in intermolecular associations, some of which are exothermic and others endothermic. Hence, this result may not be general for all hydrocarbonaceous oils and all solvent systems. However, first-principle thermodynamic argues that polar solvents may become more soluble in non-polar oils with increasing temperatures, which explains what is observed. The results show that higher temperature decreases selectivity as measured by COS and therefore must be considered when optimizing solvent systems and process variables. In other words, while it is tempting to operate at higher temperatures, in order to reduce viscosity, improve mass transfer rates, and increase phase disengagement rates, as well as improve operability (lower propensity to form rags), there is a penalty that may be paid in selectivity, resulting in the requirement for more stages to achieve the same COS.

Table 8.5: Effect of Temperature on Extraction Results
Feed-Total >150°C Unocal Kerogen Oil
N-content 1.6 wt.%
Average M.W. = 246 Dalton

Solvent	T°C	% Extract	%N in Ext	% Raffinate	%N in Raffinate	COS
90% Formic Acid 10% Water	79.2	30.8	4.22	69.2	0.7	71.8
same	42.0	30.8	4.36	69.2	0.69	74.8
same	20.0	40.8	3.60	59.2	0.2	82

8.5 Recovery of Solvent

In general, the lower the boiling point the easier the solvent recovery process will be, albeit the lowest boiling of acceptable solvents may not necessarily provide the desired COS. Recovery of higher boiling solvents may be enhanced if they form convenient azeotropes with components of the oil. Such systems, if they simultaneously provide a high COS, are preferred. For example, Figure 10.2 (page 81) shows a diagram of a preferred solvent recovery scheme for the selected solvent of formic acid and water. In the recovery scheme extract and raffinate are sent to separate distillation apparatus where they are heated to distill the solvent. Formic acid forms an azeotrope with cyclic hydrocarbons and the boiling point of this azeotrope is lower than the boiling point of either formic acid or water. Likewise, water forms an azeotrope with certain light aromatics typically found in hydrocarbonaceous oils. The consequence is that solvent recovery is aided by the azeotropic distillation of components naturally occurring in the oil. Upon condensation these azeotropic distillates disengage into separate liquid phases, a low density, upper hydrocarbon phase and a high-density solvent phase. The light hydrocarbon phase can be recycled to the distillation apparatus to further assist the stripping of the solvent, reintroduced to the feed system to assist extraction selectivity, or withdrawn as product.

8.6 Process Performance

8.6.1 Distribution of Nitrogen Types with Extraction

The extract and raffinate from the 90F/10W extraction were analyzed by GC with a nitrogen-selective detector. A nitrogen-selective detector was used to track the general fate of nitrogen as a function of boiling range. The data are shown in Table 8.5. As had been learned in Phase I, the vast majority of nitrogen (71.8%) is contained in the >400 °C material, which amounts to 50% of the kerogen oil. The data show that the selectivity is high for the material boiling below 400 °C, but extraction selectivity for the >400 °C may need to be improved. Even so, the selectivity for the >400 °C portion is substantially better than when the actual fraction was extracted. This data tends to confirm the hypothesis that lower molecular weight, naturally occurring polars are assisting in the recovery of higher molecular weight polars.

Table 8.5: Nitrogen Distribution after Extraction of Total Kerogen Oil
90% Formic 10% Water Case
Nitrogen content of Feed = 1.65
Nitrogen content of Extract = 3.36
Nitrogen content of Raffinate = 0.20

B.P. Fraction	wt% of Oil	% of Feed N in fraction before extraction	Distribution of Extract Nitrogen % of total		Distribution of Raffinate Nitrogen % of total	
< 200 °C	11.9	2.4	5.7	(4.7)*	0.3	(0.05)*
200-275 °C	13.1	5.6	20.2	(16.6)	5.5	(1.0)
275-400 °C	24.6	20.2	49.1	(40.3)	38.1	(6.9)
> 400 °C	50.4	71.8	25.0	(20.4)	56.1	(10.05)
Total	100.0	100.0	100.0	(82.0)	100.0	(18.0)
* values in parenthesis ( ) are % of feed nitrogen.						

8.6.2 Effectiveness of Formic Acid System

While 82% of the nitrogen is recovered in the extract, more than 90% of the basic nitrogen is recovered. The Total Ion Chromatograms for the dry extract and raffinate are given in Figures 8.1, and 8.2, respectively. The featureless characteristics of the extract result because of the extraordinary complexity of the fraction; no one component stands out. The raffinate shows the strong paraffin peaks, not detectable in the extract because of the high COS. Typical of kerogen oils, and consistent with the analysis that shows the nitrogen content concentrated in the heavy ends, the extract is strongly skewed to the heavy distillate range compared to the raffinate.

The 121 m/z extracted ion chromatogram (EIC) is shown in Figure 8.3. By looking only at the 121 ion the C_3-alkyl pyridines are highlighted and show that an entire homologous series of alkyl pyridines is present in the extract, which would be subject to dealkylation. After a THDA process, the long alkyl chains on the pyridine rings are shortened considerably and the selectivity to extraction is improved. This kind of 'filtering' can be done with any ion and is a powerful tool for assessing process performance.

The overall separation efficiency is expected to be improved greatly in a commercial process because of multistage efficiency. What is the most important is that the majority of the nitrogen compounds are recovered in the first stage of the process. Several liters of >150 °C kerogen oil were extracted to produce feedstock for conversion processing and secondary extraction.

Figure 8.1: GC-TIC of Formic Acid Extract from Topped Shale Oil

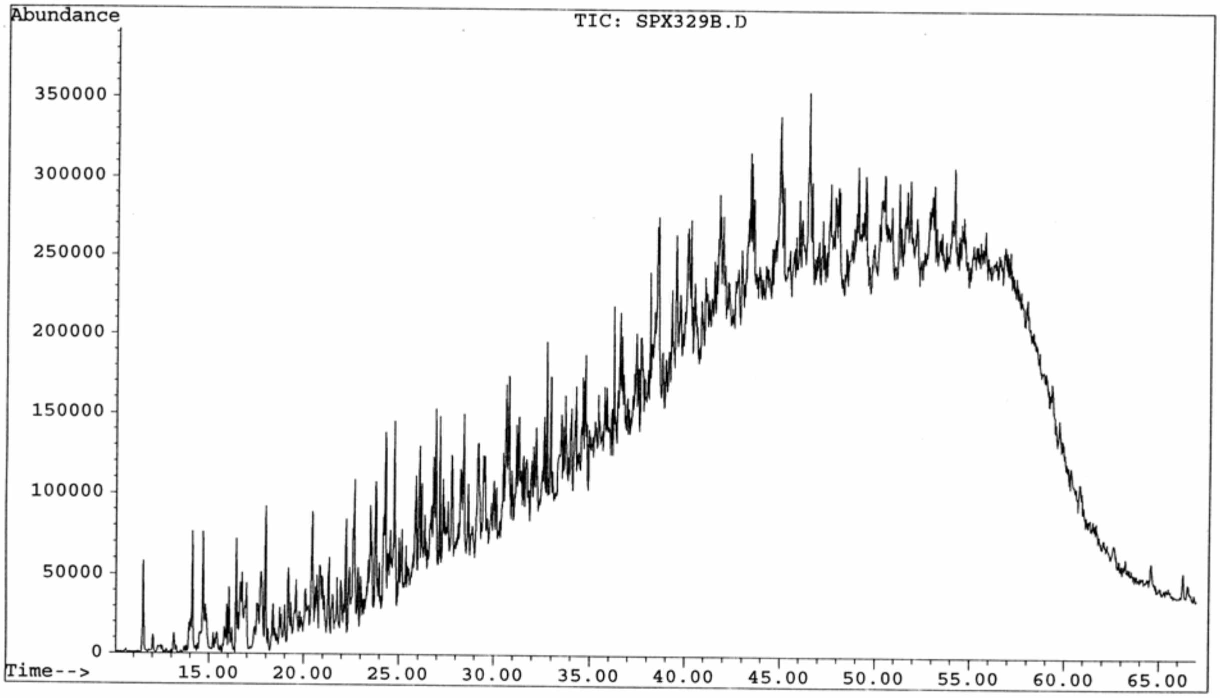


Figure 8.2: GC-TIC of Formic Acid Raffinate from Topped Shale Oil

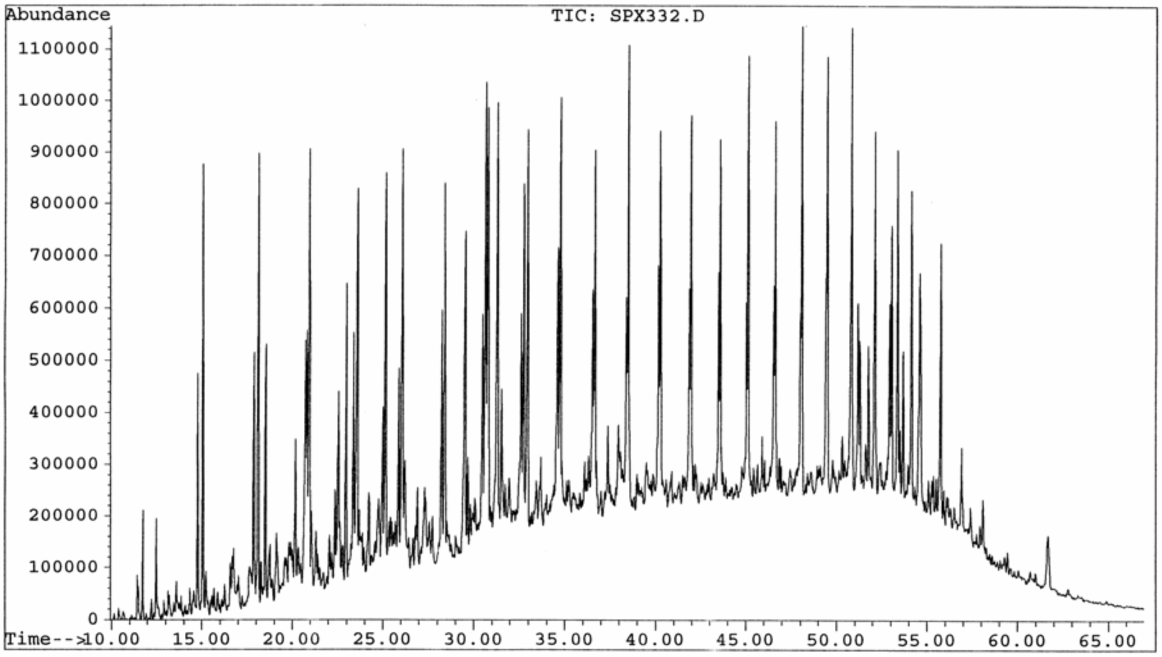
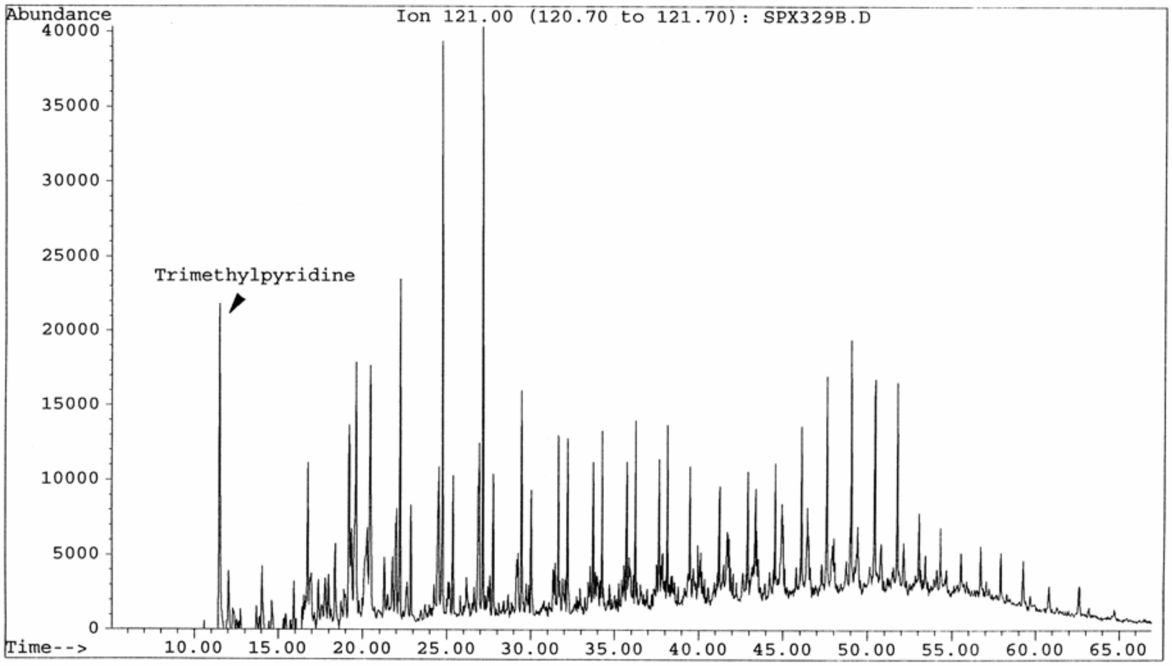


Figure 8.3: Extracted Ion 121 Chromatogram of Formic Acid Extract



Task 8 Conclusions

For the whole kerogen oil (topped at 150° C for operability purposes), a formic acid -10% water solvent system operating at a 1:1 solvent-to-oil ratio and 20° C gave a high COS (82%) for target nitrogen compounds. The solvent-system is readily recovered under conditions amenable to commercial practice. Maintaining solvent quality in process recycle appears achievable, especially since a small amount of water is desired.

The conditions found in this development step may not be commercially optimum, but have framed the problem narrowly enough that future development work can proceed at an expedited pace. At an appropriate point in the development path, a continuous pilot plant test should be performed at the conditions identified, and the process conditions varied over a reasonable range to develop a model of the COS vs. process variables.

Task 9 - Conversions Development

Statement of Work

Conversion apparatus for selected conversion process trains will be designed constructed, and operated. Engineering data, including kinetic data, and the effect of process variables on product yield and composition will be obtained. The process reaction models for use in process simulators will be developed.

Results

9.1 Trial THDA Runs

The molecular structure of nitrogen containing components dictates that the primary conversion process for the extract will be some form of dealkylation. Dealkylation of the higher alkyl pyridines to lower alkyl pyridines will greatly enhance the overall yields of the most valuable products. Hydropyrolysis (HP), a thermal hydrocracking process previously studied by the PI[6,7] is a robust method for dealkylation. It is a non-catalytic, fast reaction and the process is not affected by residue, minerals, metals or heteroatoms, as long as the mineral content is under about 2%. Thermal hydrodealkylation (THDA), a higher temperature version of HP, is operated entirely in the vapor phase, whereas HP can be operated in mixed phases utilizing spray nozzle injectors. (For additional information on HP conducted later in this research refer to Section 12.1 of this report.)

Results from this study provide initial confirmation of a) the analytical results showing the predominance of small rings and long chains and b) the predicted responsiveness of kerogen oil to THDA. Although it was not clear at the time task 9 research was conducted, the ultimate outcome of this work was to formulate the process scheme shown in Figure 10.1 below.

The University of Utah 1 liter/hour flow apparatus was initially used to study the conversion in HP. This system was equipped with a gas recycle compressor. In theory, this system could operate on a semi-continuous basis with run lengths of many hours. In practice, the system suffered from feed problems and plugging of tubes with minerals and coke. (These types of problems had been previously solved by the P.I. in work on an apparatus no longer available at the University.) The cost to fix the problems on the available reactor and the labor effort needed to obtain significant data were, in the end, deemed too high to continue in this direction. Instead, HP experiments were conducted at JWBA facilities at a smaller scale.

9.2 THDA Conversions

Figure 9.1 illustrates the conversion of pyridines by HP. The m/e 121 ion is thought to be representative of tri-substituted pyridines. Even at a modest temperature of 440 °C substantial conversion (>50%) is seen.

Higher severity THDA causes almost complete conversion of alkyl pyridines to their methylated homolog. Figure 9.2 is the TIC of the feedstock and Figure 9.3 is the TIC of the products. All of the material boiling below a time equivalent of 30 minutes was generated in the HP process (note that the x-axis is expanded on in Figure 9.2).

The specific ion chromatograms for the m/e 121, 135 and 149 for the feedstock are shown in Figure 9.4. These chromatograms show the multiple series of alkyl pyridines that are concentrated in the extract. The corresponding specific ion chromatograms for the total HP product are shown in Figure 9.5. There are two features of these latter chromatograms that are significant. First is the simplicity of the chromatograms; only a few isomers are present. The second, and perhaps most significant, is the virtually total conversion of the +30 min. (~ C_{10}) alkyl pyridines.

Figure 9.1: m/z = 121 Extracted Ion Chromatograms of a) HP Feed and b) HP Liquid Product

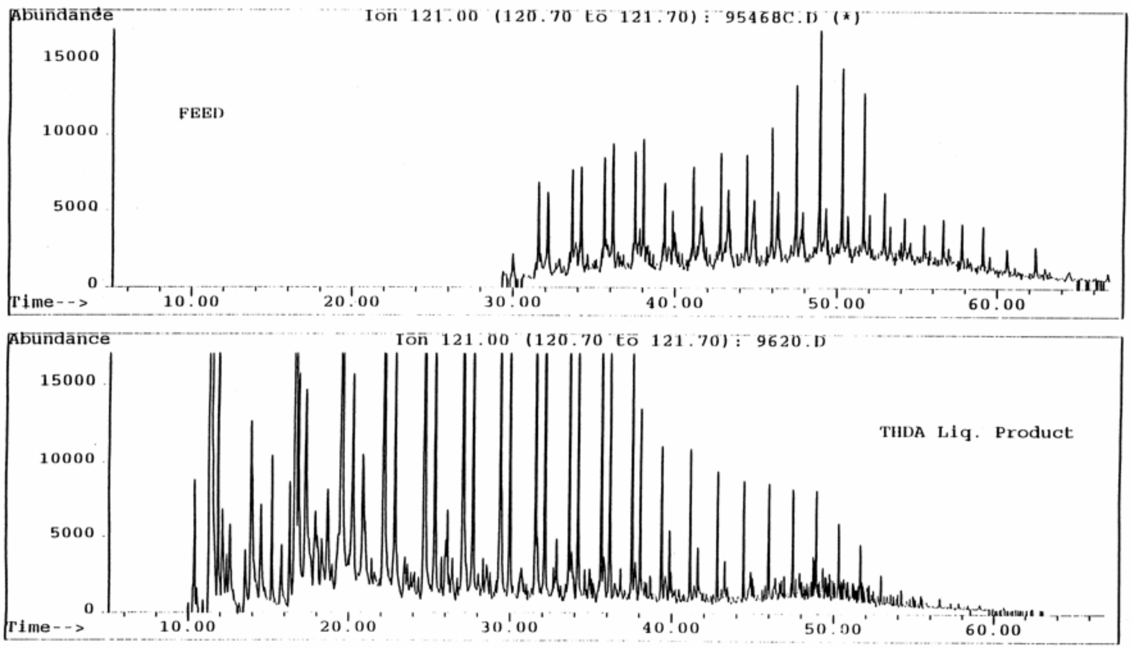
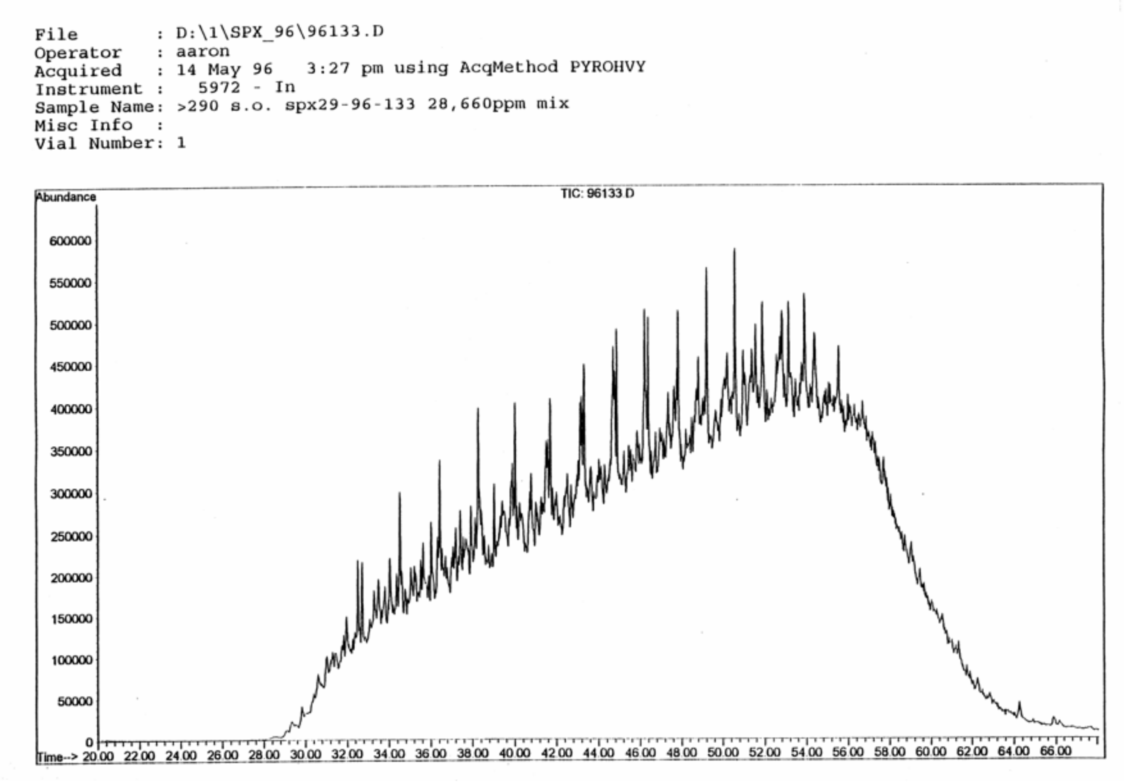
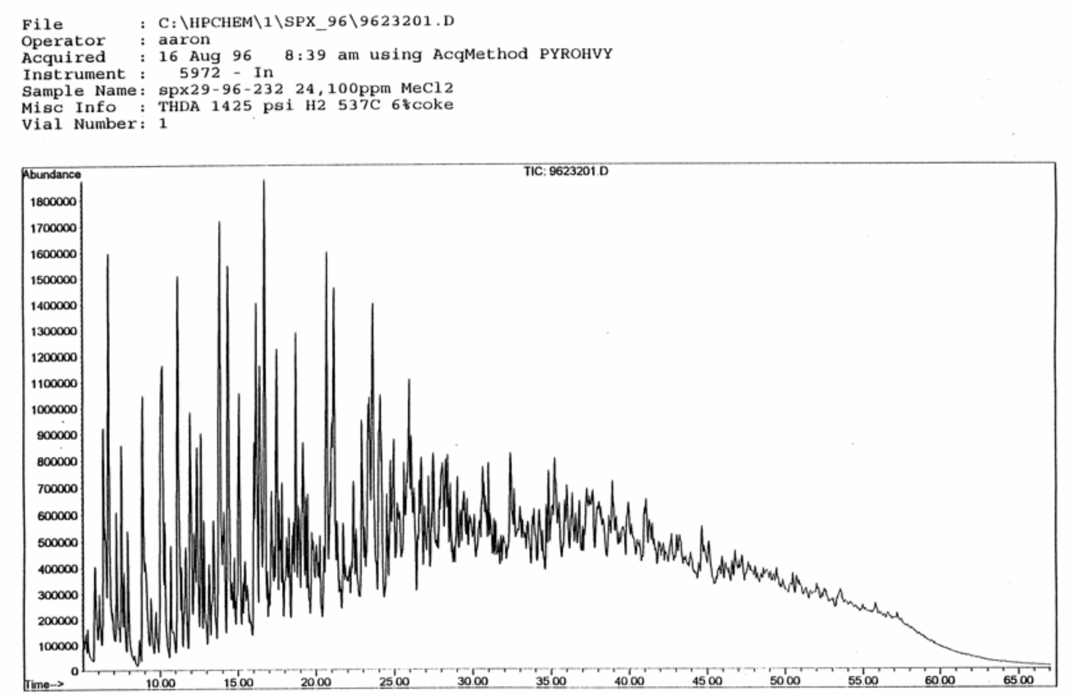


Figure 9.2: GC-TIC > 290°C Polar Extract Feedstock to HP



```
File        : D:\1\SPX_96\96133.D
Operator    : aaron
Acquired    : 14 May 96   3:27 pm using AcqMethod PYROHVY
Instrument  :   5972 - In
Sample Name: >290 s.o. spx29-96-133 28,660ppm mix
Misc Info   :
Vial Number: 1
```

Figure 9.3: GC-TIC of Total HP Products >290 °C Polar Extract Feed



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File        : C:\HPCHEM\1\SPX_96\9623201.D
Operator    : aaron
Acquired    : 16 Aug 96   8:39 am using AcqMethod PYROHVY
Instrument  :   5972 - In
Sample Name: spx29-96-232 24,100ppm MeCl2
Misc Info   : THDA 1425 psi H2 537C 6%coke
Vial Number: 1
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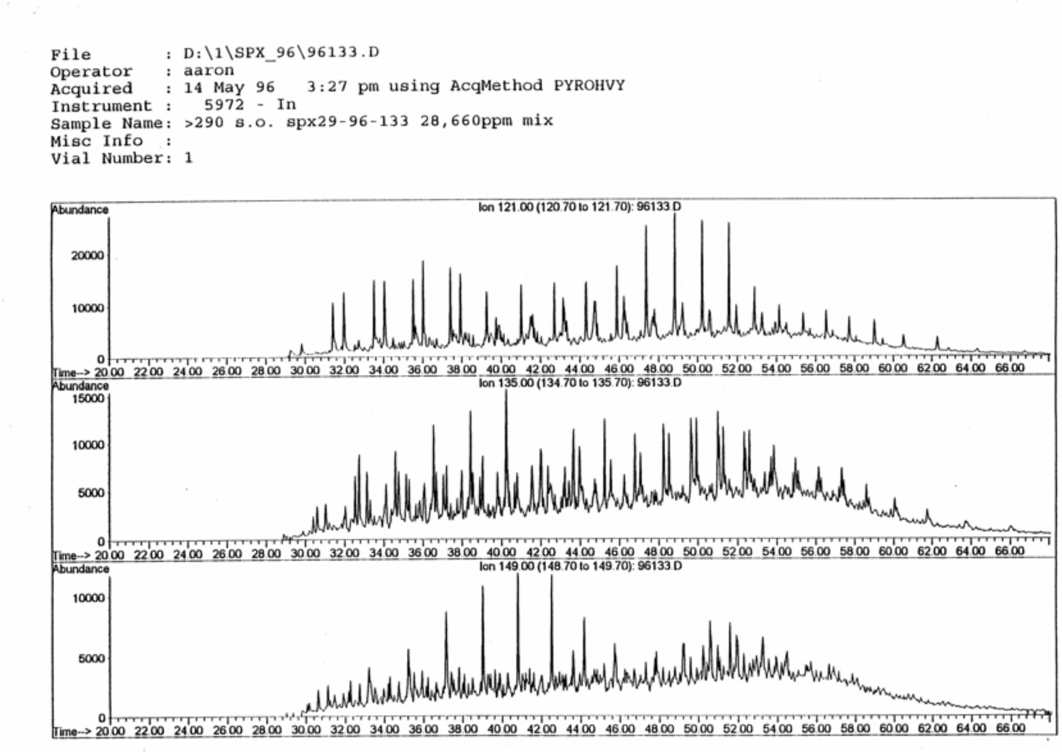
Figure 9.4: m/z = 121, 135, 149 for >290 °C HP Polar Extract Feedstock



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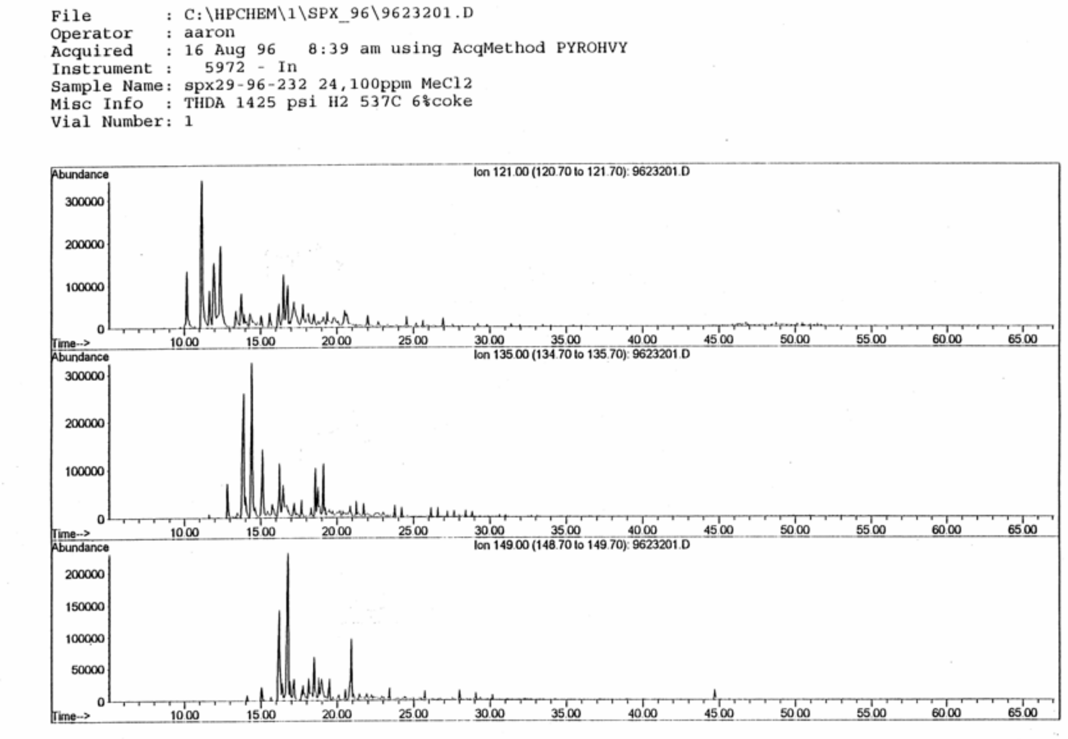
File        : D:\1\SPX_96\96133.D
Operator    : aaron
Acquired    : 14 May 96   3:27 pm using AcqMethod PYROHVY
Instrument  :   5972 - In
Sample Name: >290 s.o. spx29-96-133 28,660ppm mix
Misc Info   :
Vial Number: 1
```

Figure 9.5: m/z =121, 135, 149 for HP Product from >290 °C Polar Extract Feedstock



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Operator    : aaron
Acquired    : 16 Aug 96   8:39 am using AcqMethod PYROHVY
Instrument  :   5972 - In
Sample Name: spx29-96-232 24,100ppm MeCl2
Misc Info   : THDA 1425 psi H2 537C 6%coke
Vial Number: 1
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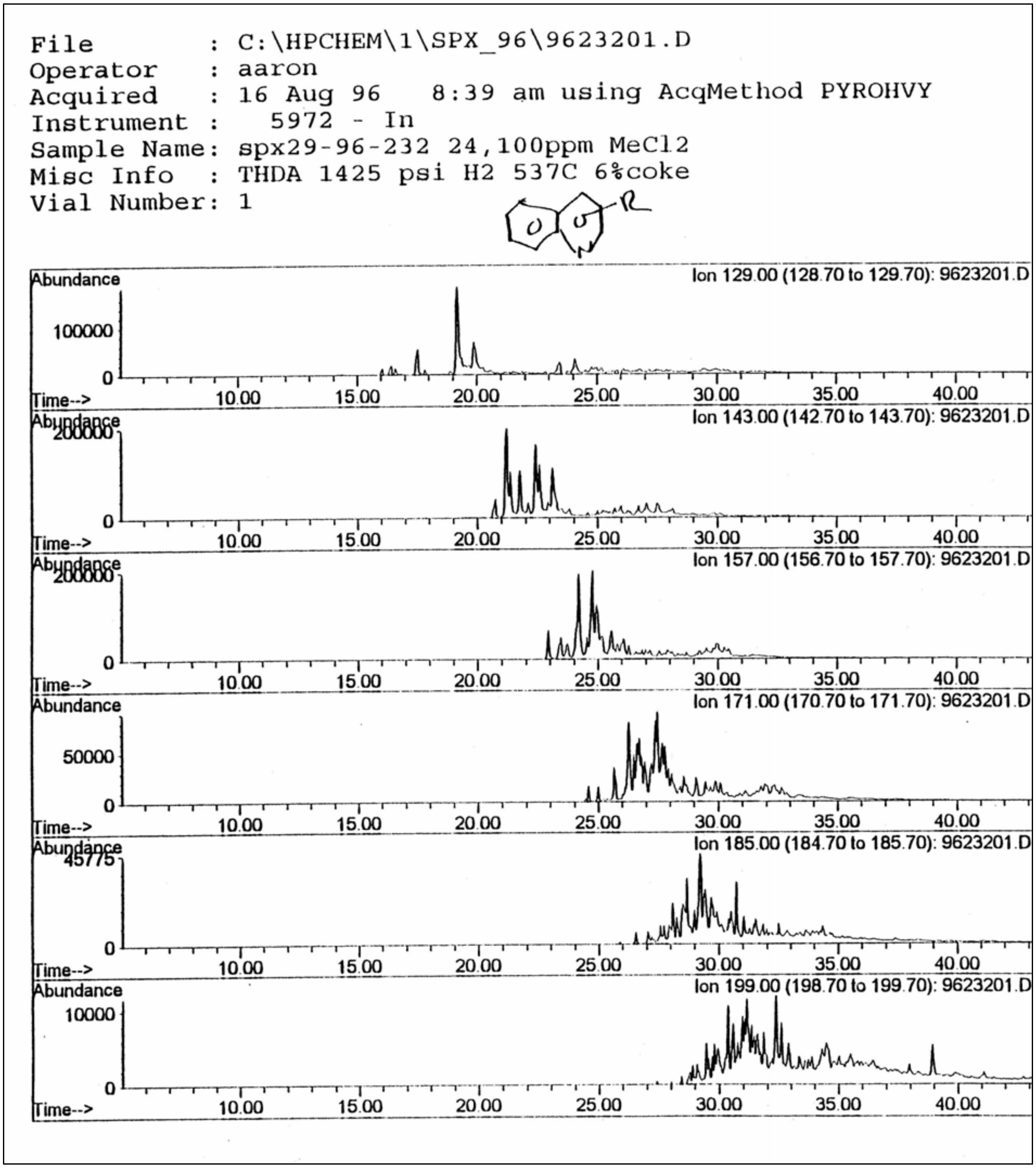
Figure 9.6 Extracted Ion Series for Quinolines and iso-Quinolines



File : C:\HPCHEM\1\SPX_96\9623201.D
Operator : aaron
Acquired : 16 Aug 96 8:39 am using AcqMethod PYROHVY
Instrument : 5972 - In
Sample Name: spx29-96-232 24,100ppm MeCl2
Misc Info : THDA 1425 psi H2 537C 6%coke
Vial Number: 1

9.3 Quinolines

To further illustrate the "clean" THDA reaction Figure 9.6 provides extracted ion chromatograms of the quinoline/isoquinoline series. The lack of ion response in the products at residence times greater than 30 minutes testifies to the total hydrodealkylation to the methylated analog. It should be noted that THDA is a commercially-accepted technology for dealkylating pyridines produced by synthesis routes, thus lending a high degree of certainty to the applicability of this technology in the Value Enhancement Process technology.

9.4 Other Conversion Processes

Other conversion processes such as quaternization of pyridinic nitrogen, chlorination, sulfonation, hydroxylation and direct hydrogenation (not HDN) were contemplated in this work but were not needed to achieve the objectives of this phase. Ultimately such derivatization will become part of a mature process industry, as full use is made of the heterocyclics contained in kerogen oil. However, for purposes of identifying a plausible sequence that could meet market assurances and satisfy investment criteria for a first generation plant, the focus remained on a few simple products for reasons discussed in task 7 above.

Task 9 Conclusions

Reliance on THDA, as the primary conversion step, has been validated by work in this task. Specifically, THDA does not appear to destroy the ring system inherent to the value of the product. Combining the results of this research with theoretical considerations and prior research by the PI suggests that THDA will play two roles. One will be to manufacture lower alkyl pyridines from higher alkyl pyridines, and the other is to finish lower alkyl pyridines to pyridine and alpha-picoline. Being able to rely on one technology for two purposes (commercially using two units) will result in process and cost advantages in any commercial operation.

Task 10 - Product and Process Integration

Statement of Work

Various process options will be analyzed to develop a preferred process scheme. The analysis will be based on a computerized database of all acquired product and process data. The preferred process scheme will be tested using equipment from Tasks 8 and 9 to verify anticipated product yields and quality.

Results

10.1 Product Focus

As a consequence of the separation and conversion process development work it was concluded that pyridines (and quinolines) were selectively concentrated by extraction; whereas, pyrroles and indoles were less selectively concentrated (see also Table 2.6). The projected products from selective separation consist of a concentrate of pyridines and a petroleum refining feed. The pyridine concentrate is expected to be marketable as follows:

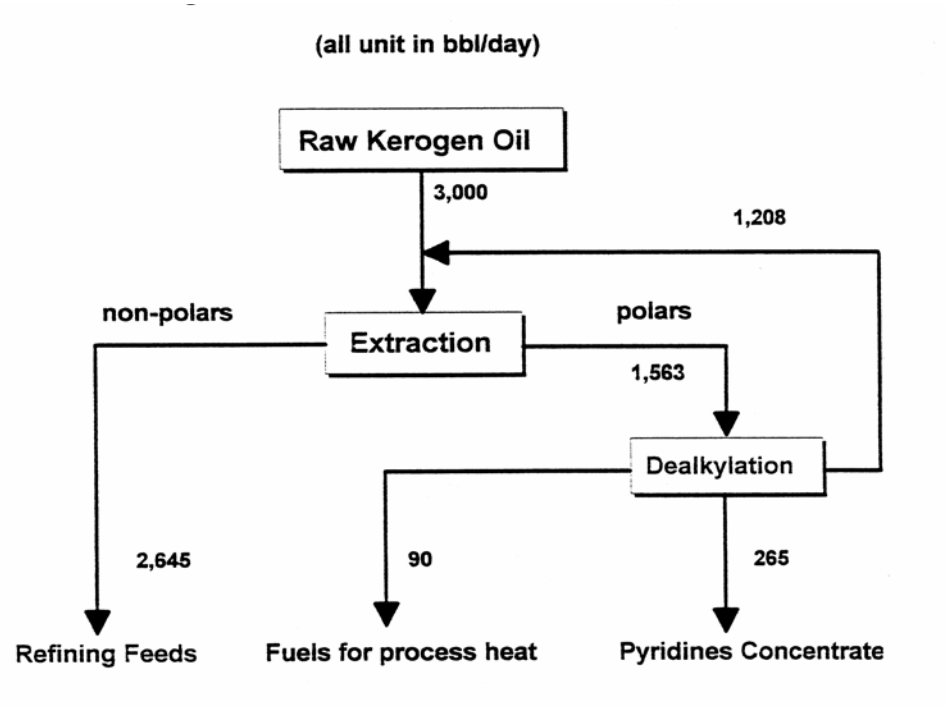
a) As a concentrate for further refining to specification pyridine products.
b) As an antistripping asphalt additive.
c) As an industrial solvent for sludge dispersion, pipeline cleaning and similar applications.
d) As a concentrate for conversion to cationic surfactants for use in drilling muds or other industrial applications.

The other major product is a reduced nitrogen feed for conventional petroleum refining. The non-polar raffinate is low in nitrogen (0.4%) compared to the starting material (1.6%) and consequently its value for refining is upgraded. As will be shown in the discussion to follow the remaining nitrogen is easily removed by catalytic hydrotreating.

10.2 Process Focus

The essential VEP process is described by a process flow diagram as shown in Figure 10.1. The scheme is referred to as ‘essential’ because it is the minimum number of process units that can effect the goals of value-enhancement; namely, highly selective separation of heteroatom-containing compounds from hydrocarbons and conversion of high molecular weight heteroatom-containing compounds (the majority of compounds) to more marketable, lower molecular weight compounds. The essential process shows a final product slate consisting of 88% raffinate for petroleum refinery feed (N<0.4%), 9% pyridines concentrate and 3% non-condensable gases used for process fuel.

Figure 10.1: KPX Essential Process



The extraction step employs a countercurrent extraction of a suitable configuration. For work done on this project a six-stage pulsed, perforated tray system was employed. A mass and nitrogen balance for the first pass in a six-stage extraction unit are shown in Table 10.1.

Table 10.1: Mass and Nitrogen Balance for 6 Stage Extraction

	wt%	C	H	N	O+S (by diff.)
Total kerogen oil	100	85.1	11.9	1.6	1.4
Raffinate	72.2	86.2	12.3	0.4	1.1
Extract	27.8	83.6	10.3	4.1	2.0

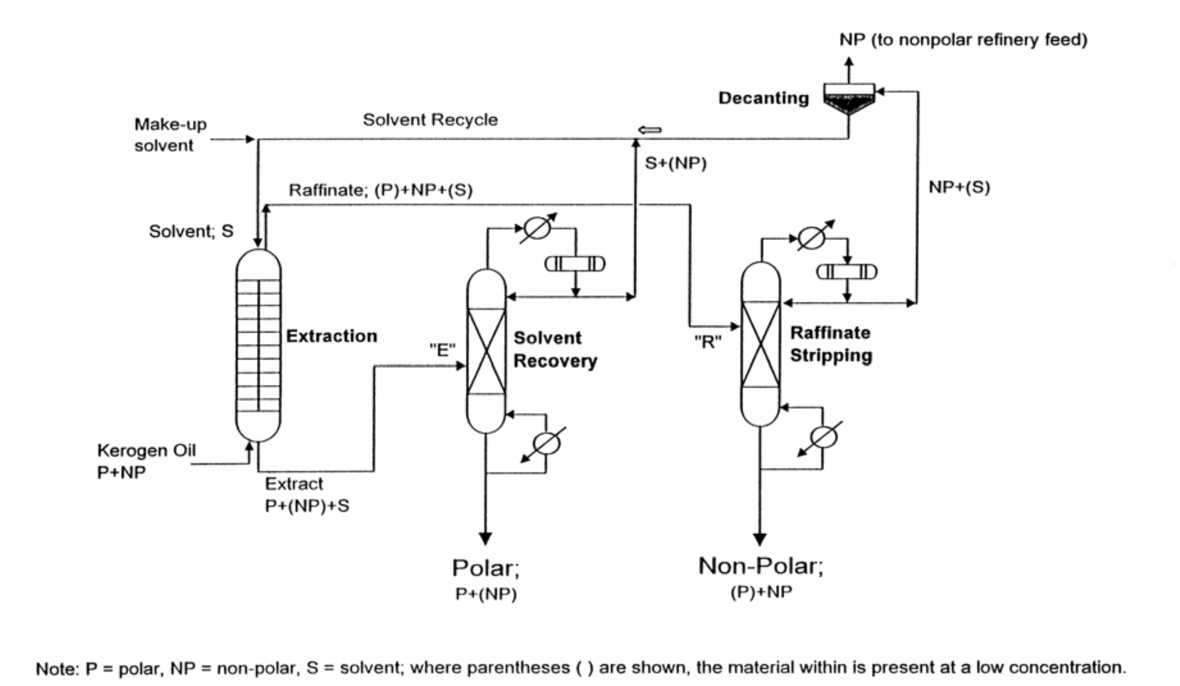
The results show the total yield of extract is 27.8% with a nitrogen content of 4.1%. The coefficient of separation (COS) is calculated to be 74.4% based on an assumed molecular weight for nitrogen compounds of 325 Dalton. This COS is quite acceptable and shows that the lower yield of extract (compared to earlier results) is due to rejection of non-nitrogen compounds. 80% of the nitrogen is recovered in the extract and the extract is comprised of 95% nitrogen compounds. It is fully expected that the 0.4% nitrogen remaining in the raffinate will be easily removed by catalytic hydrotreating, as experienced in earlier tests. The results of the six-stage extraction are realistic and the COS of 74% is very likely to be the minimum achievable at a commercial scale.

In any liquid-liquid extraction process solvent recovery is essential. A solvent recovery scheme is shown in Figure 10.2. Both the extract and the raffinate must undergo solvent recovery, although the vast majority of the solvent appears in the extract. Solvent may be recovered by fractional distillation. The boiling point of formic acid is 100.7°C, conveniently very close to that of water. Hence both components are recovered simultaneously in the distillation.

Process monitors and controls will be needed to maintain solvent quality in the recycle loop, but with respect to the water ratio, this does not appear to be a difficult problem. One of the areas of needed study will be the amount of light hydrocarbons that find their way into the recycle loop, and attention will need to be paid to the beneficial or deleterious effects of these. This kind of experiment cannot be conducted, however, at the batch or semicontinuous scale. A full pilot plant with on-line solvent recycle will be needed to answer these questions, which will be addressed in future developments of a commercial nature.

The raffinate possesses low amounts of solvent. It is anticipated that solvent recovered from the extract and raffinate will simply be combined and controlled for recycle purposes.

Figure 10.2: Extraction and Solvent Recovery Scheme



Note: P = polar, NP = non-polar, S = solvent; where parentheses ( ) are shown, the material within is present at a low concentration.

Table 10.2 shows the mass balance for the solvent recovery system. The vast majority of the solvent is found in the extract; only 5% of the raffinate stream is solvent. The table shows a high level of solvent recovery which is a requirement for an economic process. The high level of solvent recovery is aided by the azeotropic distillation effects between cycloparaffins and carboxylic acids. This is a key discovery of the research[11] and not only will afford high solvent recoveries for these systems, but also assists in the solvent quality control for the recycle loop.

Table 10.2: Composition of Solvent Recovery Unit Process Streams

Product Stream	Composition, wt%		
	Polar	Nonpolar	Solvent
Extract; feed to the Solvent Recovery (SR) unit	33.28	0.16	66.56
Raffinate, feed to the Raffinate Stripping (RS) unit	0.48	94.52	5.00
Distillate of SR unit to solvent recycle	0.005	0.024	99.97
Bottom of SR unit, polar products	99.58	0.42	0
Distillate of RS unit to decanting unit	0	63.66	36.34
Bottom of RS unit, nonpolar products*	0.43	99.51	0.05
Solvent Recycle	0.004	0.07	99.92

*including nonpolar product obtained from the decanting unit.

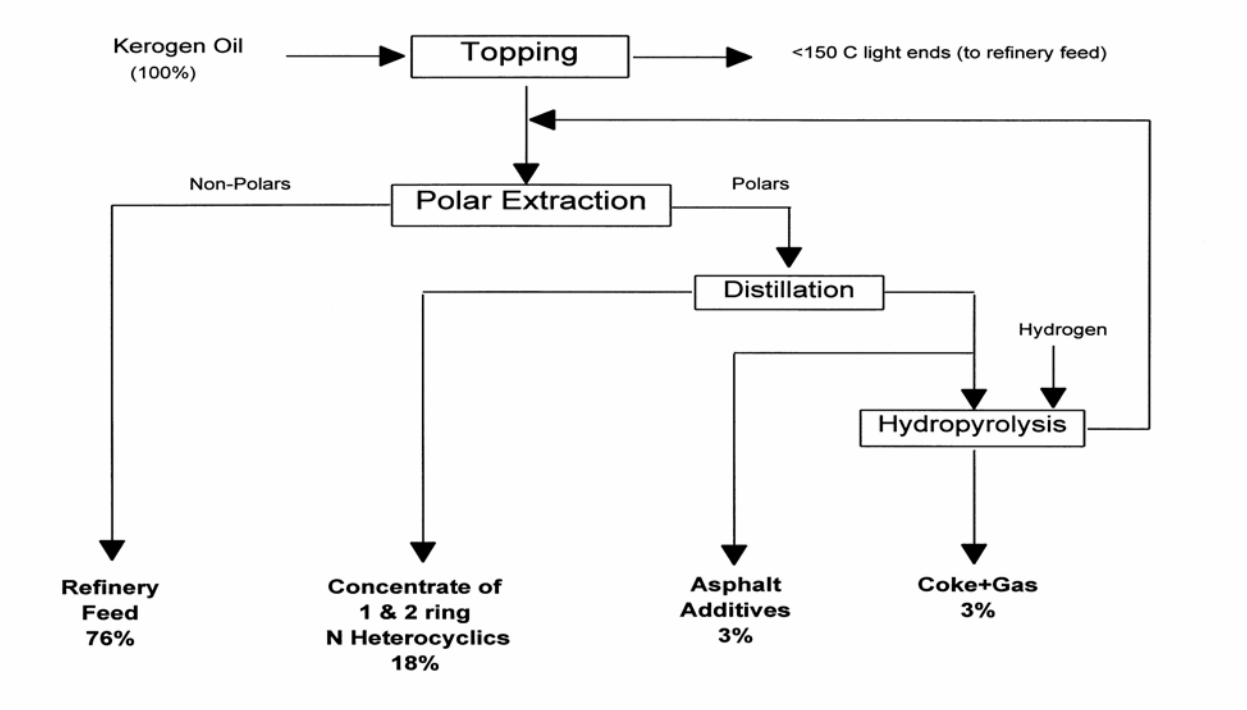
10.3 Process Integration

Additional process steps were integrated with the essential process to enhance the overall technology value. This enhanced process scheme took into account the fact that neither the pyridine concentrate nor the petroleum refinery feed obtained directly from extraction were highly marketable products. Neither of these met existing specifications for currently practiced technology. The petroleum feed could be used in existing refineries, but at a discount in price. New capital investment would be required to refine the pyridine concentrate.

Consequently, an advanced process system was devised. This system is shown in Figure 10.3. In the enhanced scheme the pyridine concentrate is topped to remove lower alkyl pyridines (LAPs). Higher alkyl pyridines (HAPS) are sent to a hydropyrolysis unit where the long alkyl chains are cracked from the parent ring system. The total (condensable) hydropyrolyzate is then recycled to the extraction unit where the lower molecular weight polars assist with the extraction of higher molecular weight polars from the fresh feedstock. By combining the liquid-liquid extraction into a single unit, not only is performance enhanced, but costs are reduced.

The hydropyrolysis process is a mixed phase process and the heaviest, non-volatile products are recycled to the system, removing a drag stream as an asphalt additive. A description of the hydropyrolysis unit is given in Figure 10.4. The hydropyrolysis unit operates at T, P and t conditions not unlike catalytic hydrocracking, but without catalyst. The results of the enhanced process scheme provide more marketable products, thereby enhancing the economic viability.

Figure 10.3: KPX High Value Process Flow Diagram

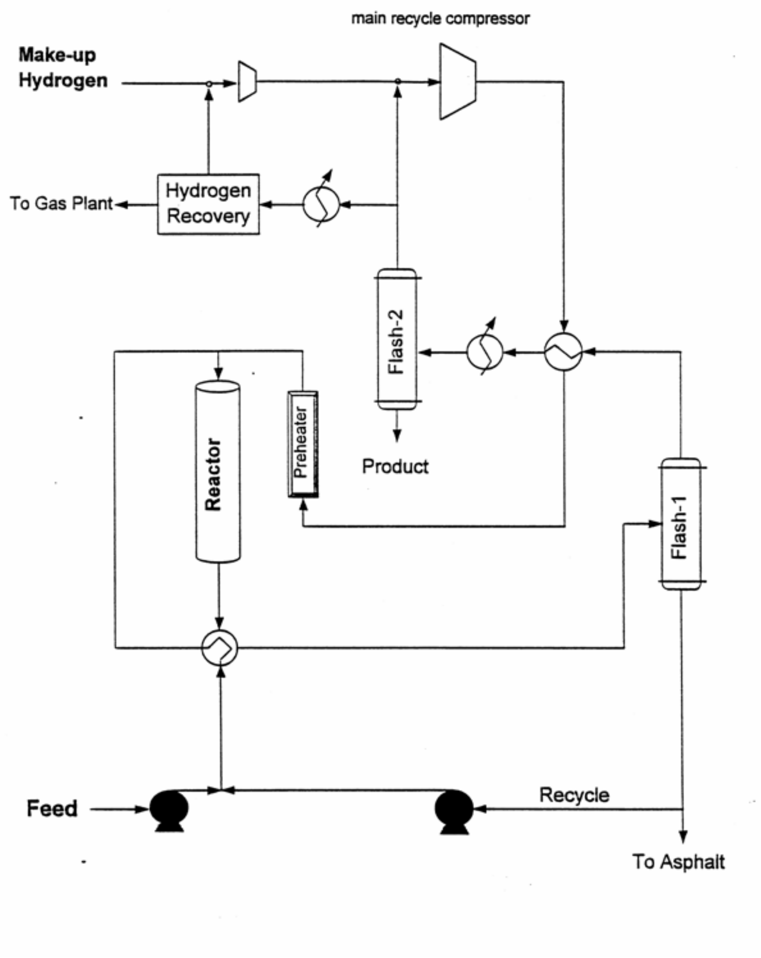


Task 10 Conclusions

Process and product integration results show how important it is to select process steps and process conditions that yield marketable products. The optimization of a new industry, such as being studied in this research is quite iterative. Process sequences must be run, products evaluated, and adjustments made to accommodate markets. Preferred products are those for which markets already exist, but whenever a new feedstock such as kerogen oil is being introduced to the manufacturing industry, it can be expected that new markets may need to be developed. A large part of the research optimization is to find that balance point that minimizes the need for developing new markets while at the same time maximizing the volume of products acceptable to existing markets while minimizing costs.

In research conducted to this point it has been shown that raw kerogen oil can be separated and converted with reasonable-cost processes to several concentrates that with further refining could produce marketable products. The next logical question is what secondary refining must be made of these concentrates to achieve that objective.

Figure 10.4: High Energy Efficiency Hydropyrolysis Process



Task 11 - Simulation and Economics

Statement of Work

The preferred scheme will be cost-estimated, and profitability analyses of the base case will be performed by the Contractor. Values for the base case parameters will be varied to determine the economic sensitivity of each process variable on profitability. This sensitivity analysis will be conducted on a process and product specific basis to determine areas of highest risk and greatest economic impact. The prime economic variables considered will be revenue, capital cost, operating cost, debt interest, transportation and marketing costs, raw materials (kerogen oil) cost, royalties and taxes.

Results

11.1 Economics of Essential Scheme

Economics of the simplified process illustrated in Figure 10.1 (p. 76) is a marginal 10.4% IRR. Further, as discussed above the pyridine concentrate may prove difficult to market. Recent discussions with potential industrial partners reveal that there is not much interest in these alkylated pyridines. The greater excitement is shown when we discuss production of pure pyridine and picolines.

11.2 Projected Economics of Enhanced Scheme

Enhancements to the essential scheme are shown in Figures 11.1 and 11.2. These are secondary refining processes used to make the products more valuable and more readily marketed. The scheme shows processing to refined pyridines and higher value petroleum products. Results of these economics are given in Table 11.2 and show a healthy 34% IRR. Further, the target products are more like those being currently manufactured synthetically or from petroleum, and hence, the market assurance will be made easier.

11.3 Sensitivity to Capacity

The overall effect of capacity and cost on profitability is shown in Figure 11.3. This figure shows that as capacity goes up the cost per unit output goes down and the profitability increases. A major component of the optimization problem is maximizing the capacity while maintaining market prices, and consequently maintaining anticipated revenues. It will be desirable to maintain some capacity flexibility in the high value market space for the purpose of responding to opportunities to capture market share. Because of the high concentrations of pyridines in shale oil (approximately 50 times the concentrations historically found in coal tars), extraction pyridines will be able to compete with synthesis pyridines on a cost basis. The question will be whether or not extraction pyridines can meet the quality specification of the market-place. Because of the approximate nature of the economics at this stage, additional sensitivity analysis was not conducted.

Task 11 Conclusions

Process, product and economic integration reveal that a slate of products consisting of pure compound pyridines, LAP mixtures, HAP mixtures, oils, waxes and refinery feedstocks will promise high returns on invested capital under conditions existing at the time (ca. 1996).

Figure 11.1: KPX Secondary Process Pyridines Concentrate

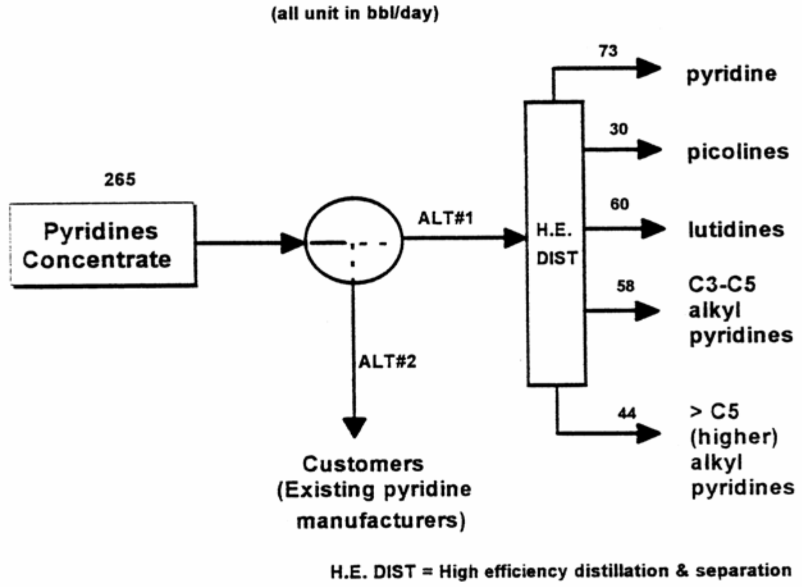


Figure 11.2: KPX Secondary Process - Refinery Products

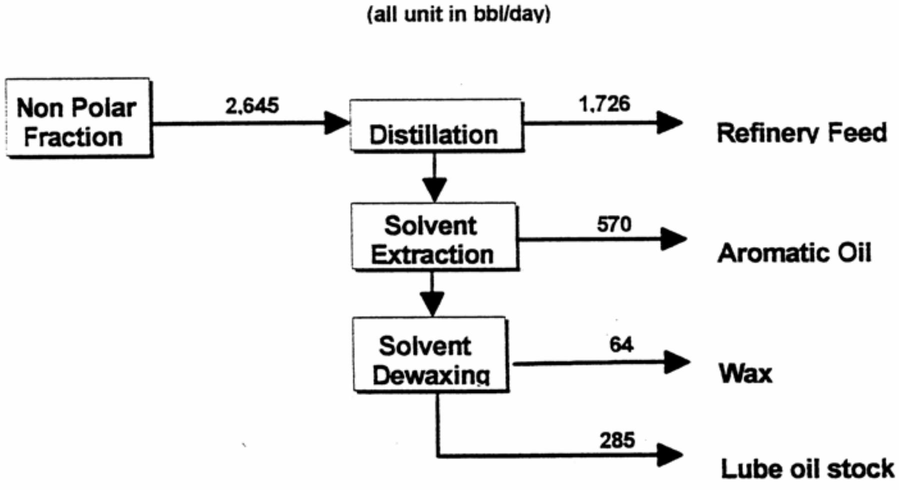
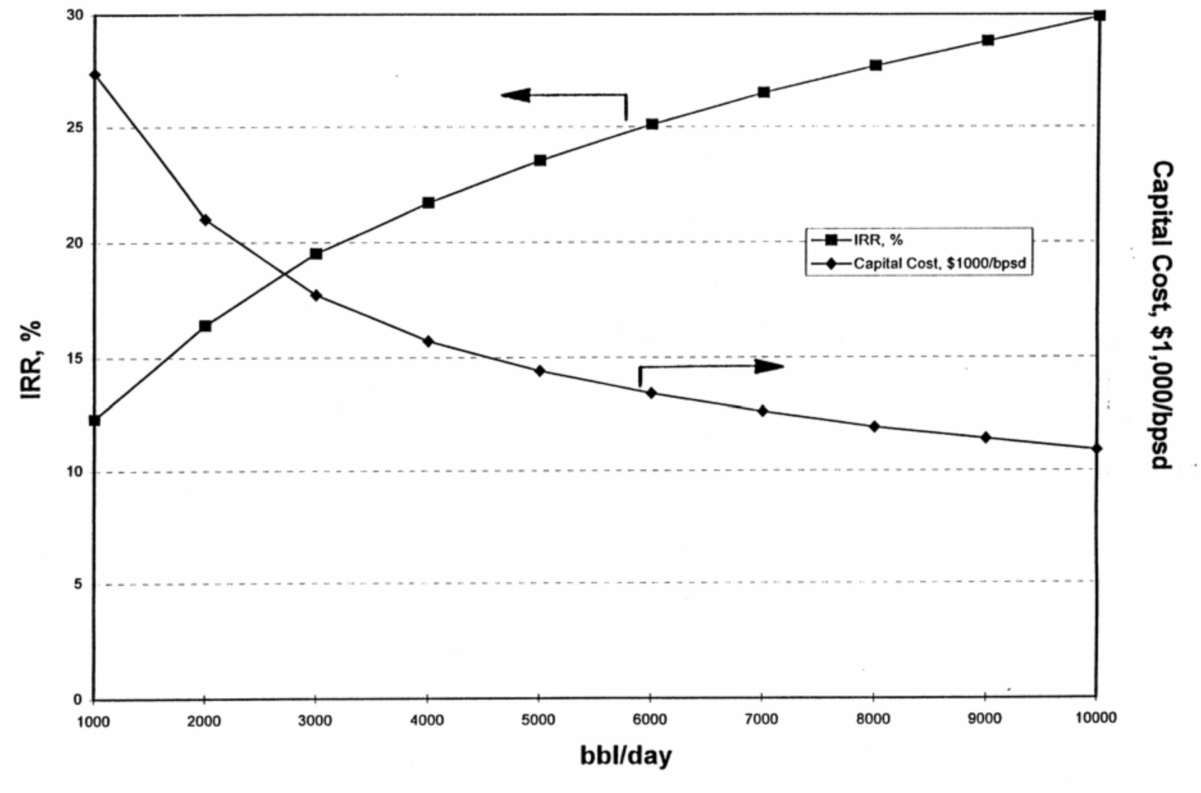


Figure 11.3: Effect of Capacity on Capital Cost and Profitability



PHASE II - CONCLUSIONS

Research conducted in Phase II showed that plausible processes were identified for all key steps. In particular, HP and THDA can be used to dealkylate pyridines without a loss of ring structures. An effective solvent system, namely formic acid/water, amenable to recovery and recycle was identified. Hydrotreating of raffinate was shown to produce high quality refinery feedstock. Thus, the processes of liquid-liquid extraction, distillation, THDA/HP, and catalytic hydrotreating, all accepted commercial units, give confidence to the technical viability of the processes under development. The continuing simplification of the process also enhances the economic viability. The technology results were sufficiently positive that DOE elected to exercise its option to research product qualities and markets (Phase III).

PHASE III - PRODUCT AND VENTURE DEVELOPMENT

Task 12 - Product Manufacture

Statement of Work

Using the equipment on hand, target products were manufactured in liter quantities for market inspection. A suite of products were produced representing the range of target products. The products were analyzed by Z-BaSIC and specification methods.

Results

The overall product slate determined in prior phases is shown in Figure 12.1. The product slate is divided at the initial extraction phase between a pyridines concentrate and a petroleum fraction. The priority selection of products was based on considerations of value, market volume and market readiness. It was determined that targeting well-established markets was the best way to attract private interest. To establish a new market adds a layer of risk that is presently unattractive to investment. The potential for long-term growth through development of new products and new markets deserves emphasis, however. There are numerous structural isomers of the various heterocyclic types that may prove to have unique market values and the economics assessment allows for an ongoing research and development budget.

Figure 12.2 shows the priority products. Priority One products are those that are necessary for the viability of the venture. Pyridine, the lower alkyl pyridine concentrate, and the premium refinery feed belong to the Priority One products. Priority Two products are those products which are important to the venture, but for which failure to gain market acceptance would not jeopardize the overall venture. The higher alkyl pyridines and higher value petroleum products (aromatic oils, waxes, etc.) are examples of the Priority Two products. At least one broad range concentrate product is necessary to provide capacity flexibility and economy of scale.

Pyridines are currently manufactured by a synthesis process using ammonia, alcohols and aldehydes over a zeolitic catalyst. The reaction selectivity is not ideal. While the primary targets are pyridine, α-picoline and β-picoline, lutidenes, collidines, other lower alkyl pyridines (LAPs) and higher alkyl pyridines (HAPs) are produced. The mixed LAPs and HAPs do not have a high market value but certain markets do exist as described below. Priority products will need to compete on price, provided there are no quality deficiencies.

12.1 Hydropyrolysis (HP)

Hydropyrolysis is a short contact time, thermal hydrocracking process. The objective of hydropyrolysis is to crack alkyl chains without producing coke from the pyridines and aromatics. Further, it is desirable to inhibit dehydrogenation of naphthenes. The elevated hydrogen pressure and short contact times accomplish this. Because the feedstock contains material that cannot be vaporized at the reaction T&P the reactor system must accommodate a mixed phase. It is undesirable to ‘over-crack’ because to do so generates non-condensable gases which are of less value than liquids and which results in high hydrogen consumption.

Figure 12.1: KPX General Product Slate

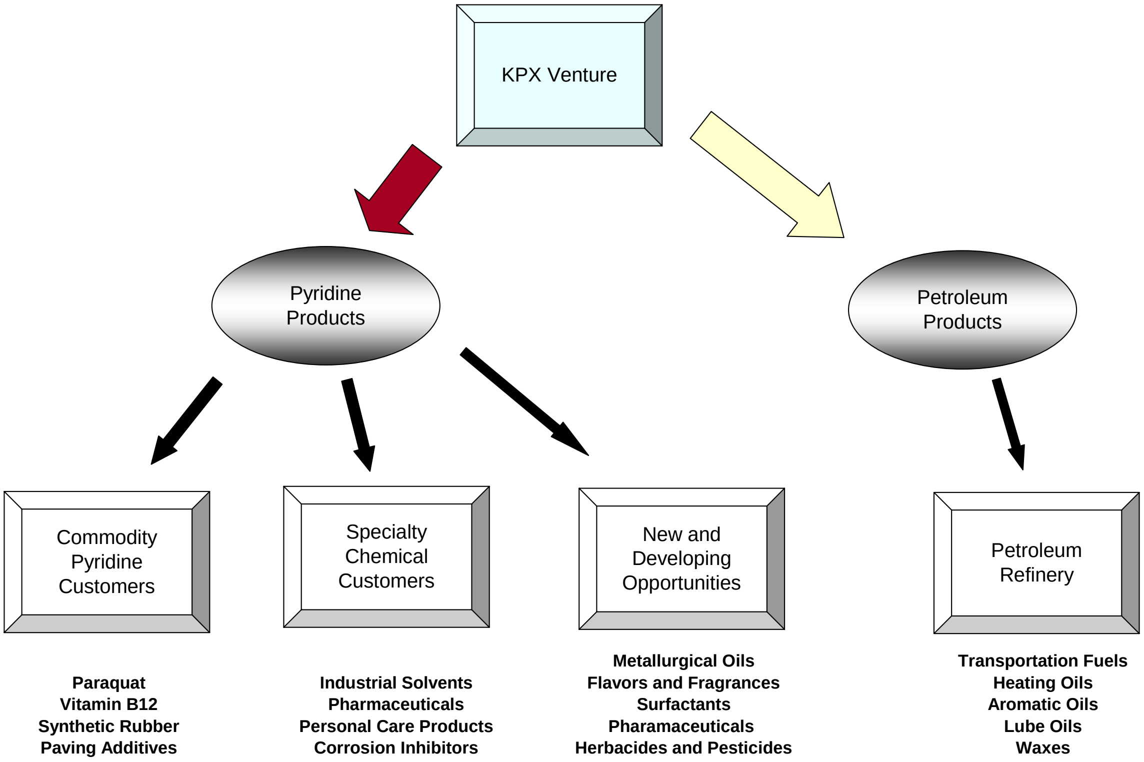
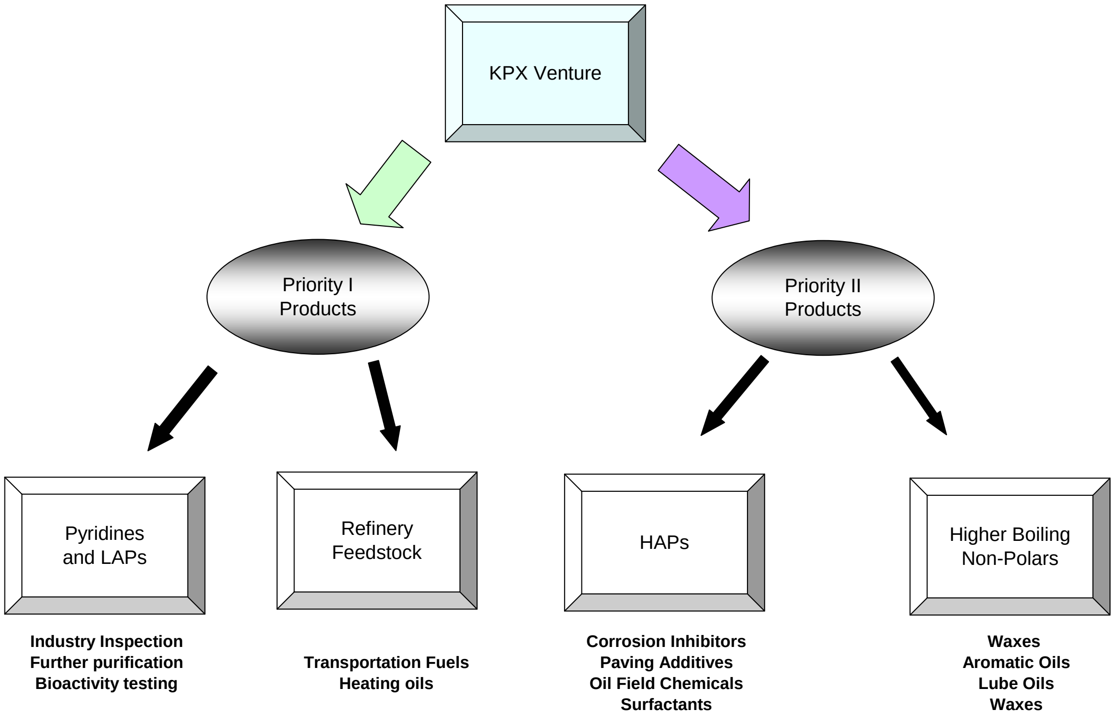


Figure 12.2: KPX Test Marketing Plan



It is not desirable to hydropyrolyze whole kerogen oil because cracking of non-pyridine compounds requires a larger reactor and unnecessarily consumes hydrogen. The most economic approach is to subject only the pyridine concentrate to HP. This was done with the following results.

Hydropyrolysis of the >290 °C kerogen oil polar fraction yielded 82 to 85% liquids, 7 to 12% gases and 5 to 9% coke. In a larger reactor the amount of coke can be reduced to nearly zero because coke is formed only when droplets impinge on the reactor walls. A small amount of water was also observed (which probably results from hydropyrolysis of oxygen-containing compounds). Methane is the predominant gaseous component. The analysis of the coke showed its hydrogen-to-carbon molar ratio is 0.46. The nitrogen content in coke is 5.2%, which is about 20% greater concentration than that in the feed and is consistent with known chemistry of coke forming reactions.

Simulated distillation of the liquid products showed that the amount of distillable material increased from 32% to 71%. The hydrogen-to-carbon molar ratio of the liquid products remained about the same as that of the feed (1.37), nevertheless, the amount of nitrogen increased from 3.79% to 4.49%. This enrichment comes from the fact that the gases derive from non-nitrogen segments of the polar species. The HP liquid products were recycled to polar extraction to separate the nitrogen compounds from liquid hydrocarbons. The hydrocarbon portion of the hydropyrolyzate is predominantly diesel range material. The addition of this material to the refinery feed significantly enhances its value for petroleum refining. Thus, there are economic benefits that accrue from HP in addition to the upgrading from pyridine dealkylation.

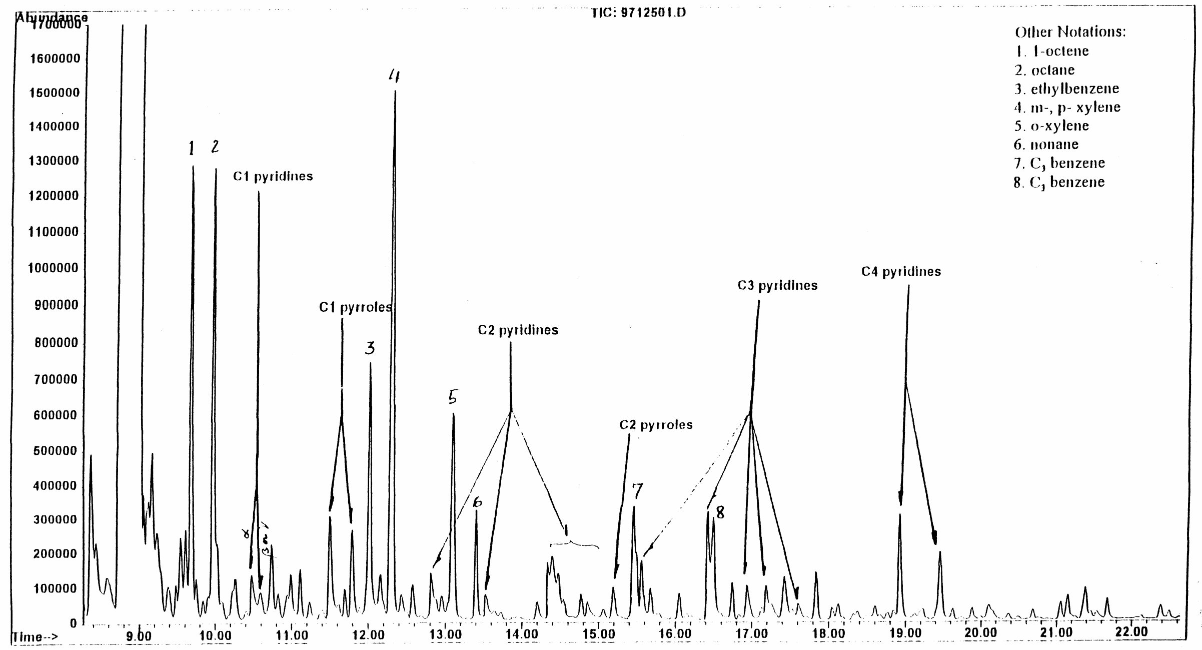
The analysis of the HP liquid products showed small amounts of pyridine and picolines but larger amounts of tri- and tetra-methylated pyridines. Most of the pyridines in the kerogen oil are tri- and tetra- substituted and HP is not designed to demethylate the ring (cracking at the ipso position). Therefore, the low concentration of picoline and pyridine is expected. The observed results are consistent with the compositional analysis and expected chemistry.

Lower boiling compounds, pyridine and the picolines, were identified in the lightest condensate. As indicated in Figure 12.3, the analysis of the cold condensate containing 2.5% of the feed showed that it contains a variety of light alkylpyrroles and alkylpyridines. One important observation is that the amount of higher-valued α-picoline produced is about twice that of β- and γ-picoline. With current pyridine synthesis technology a certain proportion of the yield is β-picoline. While β-picoline has a high market value it has a limited volume (used primarily for manufacture of niacin). The ability to produce pyridine and α-picoline without placing additional pressure on the β-picoline market is seen as a unique opportunity that complements the existing pyridine business.

12.2 Polar Separation of the HP Products

The liquid product obtained from HP of the >290 °C polar fraction was extracted to separate the polar fraction. After the extraction, the solvent was carefully removed by distillation with a stream of carbon dioxide bubbling through the distillation pot to more effectively remove the polar solvent. The distribution of the resulting extract and raffinate are 76% and 24%, respectively. Compositional analysis of the two fractions show that an exceedingly sharp (selective) separation results. The test scheme is shown in Figure 12.4.

Figure 12.3: GC-TIC of Cold Trap Products from HP of >290 °C Polar Extract



The nitrogen content of the polar fraction was measured at 6.0%. GC/MSD analysis of the polar fraction of the HP products is given in Figure 12.5. It was found that the majority of the identifiable compounds are pyridine derivatives (as peaks pointed out with an arrowhead in Figure 12.5). A m/e=121 and m/e=135 ion-extracted chromatogram is given in Figure 12.6 to demonstrate the possible distribution of the multi-substituted alkyl pyridines in this polar fraction. Alkyl pyrroles, pyrazines, quinolines, isoquinolines, quinoxalines, indoles, naphthyridines, and carbazoles are also identified. As indicated in Figure 12.4, the composition of the HP polar fraction is still quite complicated.

12.3 Simplification of the Polar Concentrate

Since the composition of the polar concentrates obtained from the HP process is still quite complicated, it is logical to further simplify it before it is sent to the final THDA process. The simplification can be achieved by increasing the initial HP process severity with the trade-off of higher coke and gas yield. Another approach is to operate the HP under mild conditions and recycle the products to the extraction step. This was deemed the preferred route.

Figure 12.4: Test Scheme – Hydropyrolysis with Extraction

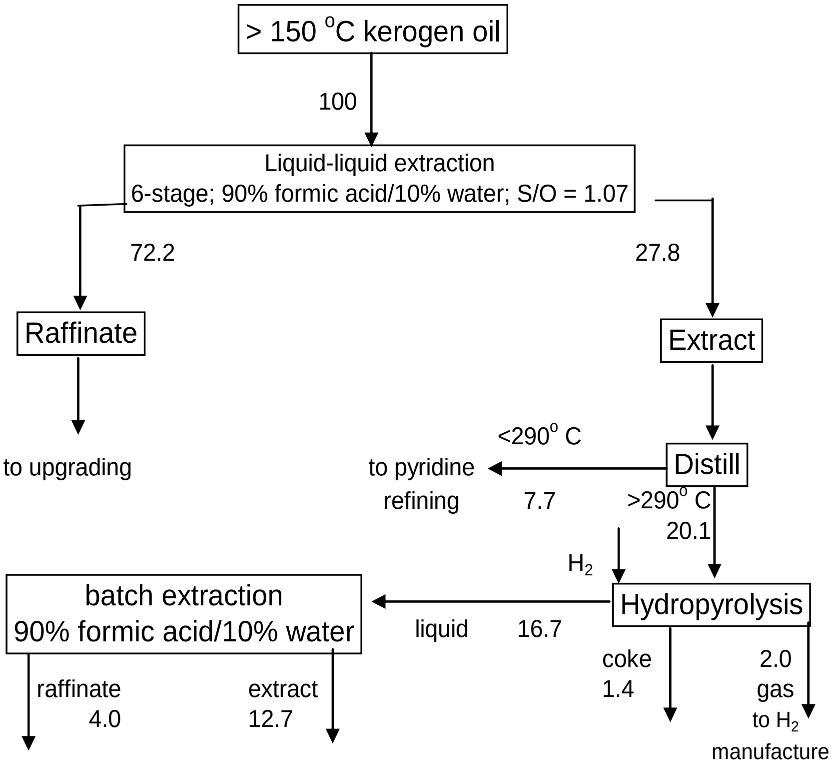


Figure 12.5: N-compounds found in Extract of Hydropyrolyzate of >290 °C Extract

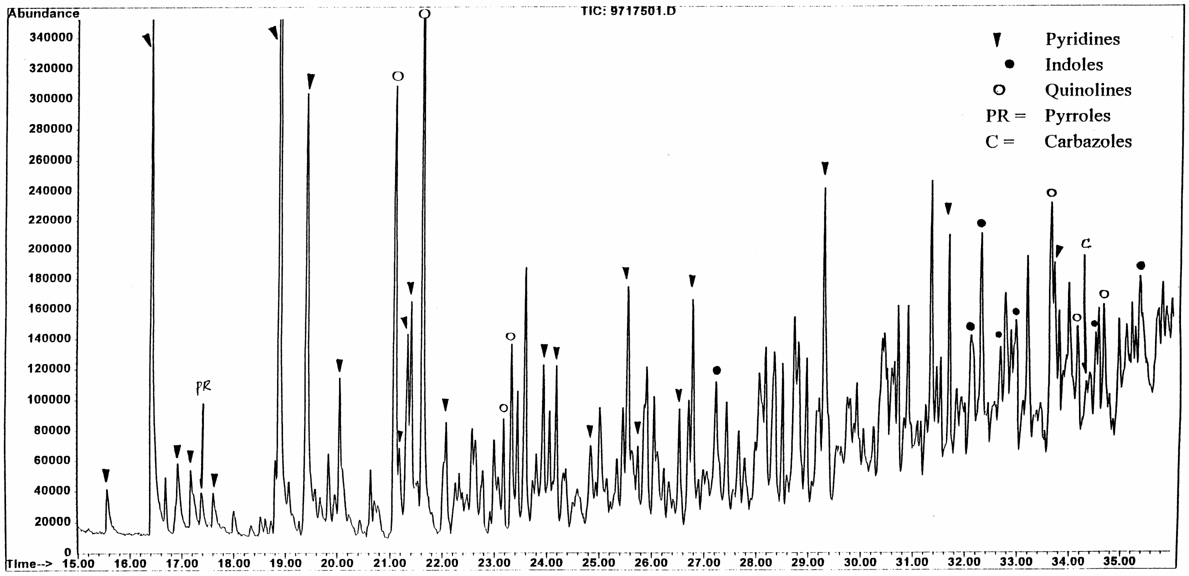
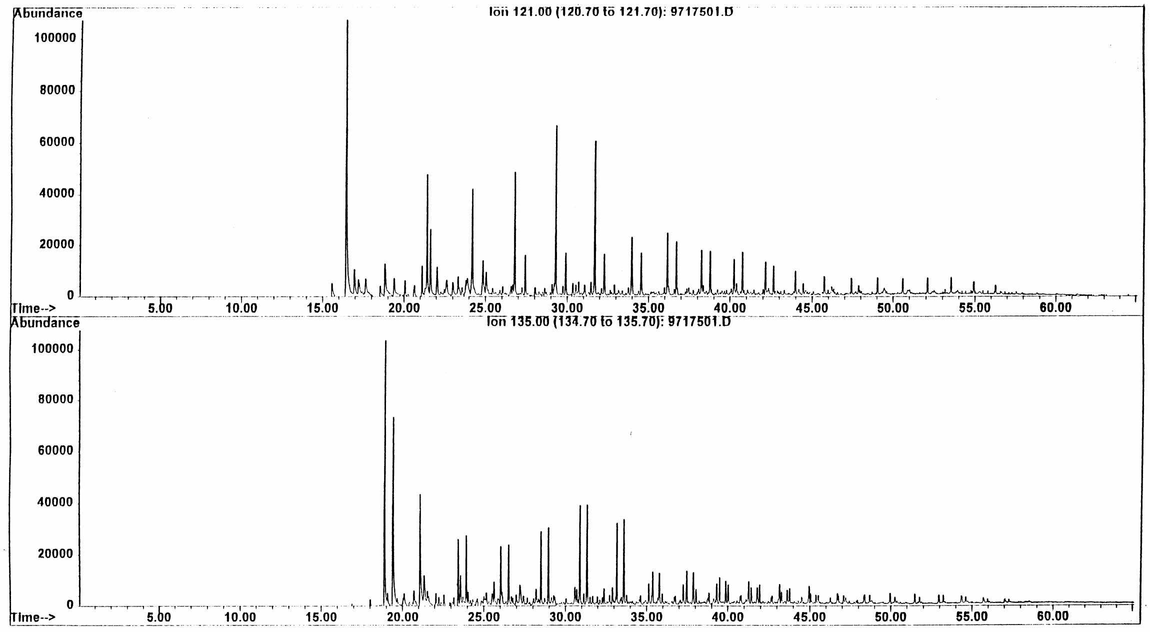


Figure 12.6: GC-EIC of Polar Extract of Hydropyrolyzate of >290 °C Extract



With the recycle of the HP products, the efficiency of the primary polar separation also improved. The lower viscosity and the ‘solvating’ effect of lower alkyl pyridines helps extract the higher alkyl pyridines. The HP products are recycled to the primary extraction unit where they are mixed with the topped kerogen oil. This mixture is further processed by polar separation and distillation; with light polar compounds fed to the THDA unit and heavy polar compounds re-introduced to the HP unit.

Upon extraction of polar components the polar concentrate may be topped. The choice of topping temperature is made to control the composition of the pyridine concentrate. For example, if naphthalene, quinoline and other resulting aromatics are not a desired product then the topping might be conducted at 220 °C. If these dicyclic types are desired, the topping temperature may be raised to include these types. In practice, fractionation of the polar concentrate may be made flexible enough to change product objectives as market conditions dictate.

A key feature of the preferred scheme is the use of HP to crack alkylated types to their methylated homologs thereby concentrating these types in a narrow and predictable boiling range. Figure 12.7 shows the relative simplicity of the <220 °C fraction (a commercial distillation will have a sharper end point). The <220 °C polar fraction may now be subjected to vapor-phase thermal hydrodealkylation THDA, to demethylate the rings. THDA is used in the chemical industry to dealkylate toluene to benzene.

THDA is also practiced commercially for the purpose of demethylating higher alkyl pyridines (HAPs) to pyridine and picolines. In the course of pyridine synthesis the higher alkyl pyridines are produced by uncontrollable runaway reactions. The fact that THDA is economically profitable under these conditions, where the HAPs were produced at large expense, argues strongly that THDA will be highly economical when feeding low-cost kerogen oil extracted HAPs. The commercial maturity of THDA also adds certainty to the technology sequence, thus reducing risk to investment.

The flow diagram for THDA is shown in Figure 12.8. In THDA the primary products are pyridine and α-picoline. Higher boiling HAPs that fail to convert on the first pass are recycled to the THDA unit.

A separation scheme for product refinement is given in Figure 12.9. The scheme is designed to maximize the purity of pyridine and α-picoline. The major separation problem for purifying pyridine (boiling point 115 °C) is the presence of toluene (bp 110.6 °C), 2-methyl thiophene (bp 112.6 °C) and 3-methyl thiophene (bp 115.4 °C) that possess similar boiling points. The major separation problem for α-picoline (bp 128 °C) is pyrrole (bp 130 °C) and, to a lesser extent, C_8 aromatics (bps 136 – 144 °C). The 'other' category shown in Figure 12.8 represents these aromatic byproducts that also have an appreciable market value. The purification scheme is based on known thermodynamics and the yields and purity are based on model results. Ultimately, as the market demands particular purity specifications this scheme may require modification.

12.4 Refinery Feedstock

The other half of the product slate, the raffinate, was characterized for its refinery acceptability. Discussions with local refineries indicated that while the product had acceptable boiling range and sulfur content, it would not be acceptable without further nitrogen removal, even though the nitrogen content had been reduced to less than 0.4% through extraction. Area refiners do not have very much hydrotreating capacity and adding new capacity to accommodate kerogen oil raffinates is not in their business plans. Catalytic hydrotreating was then conducted under task 13, product refinement.

Figure 12.7: Specialty Compounds found in <220 °C Distillate from Hydropyrolyzate

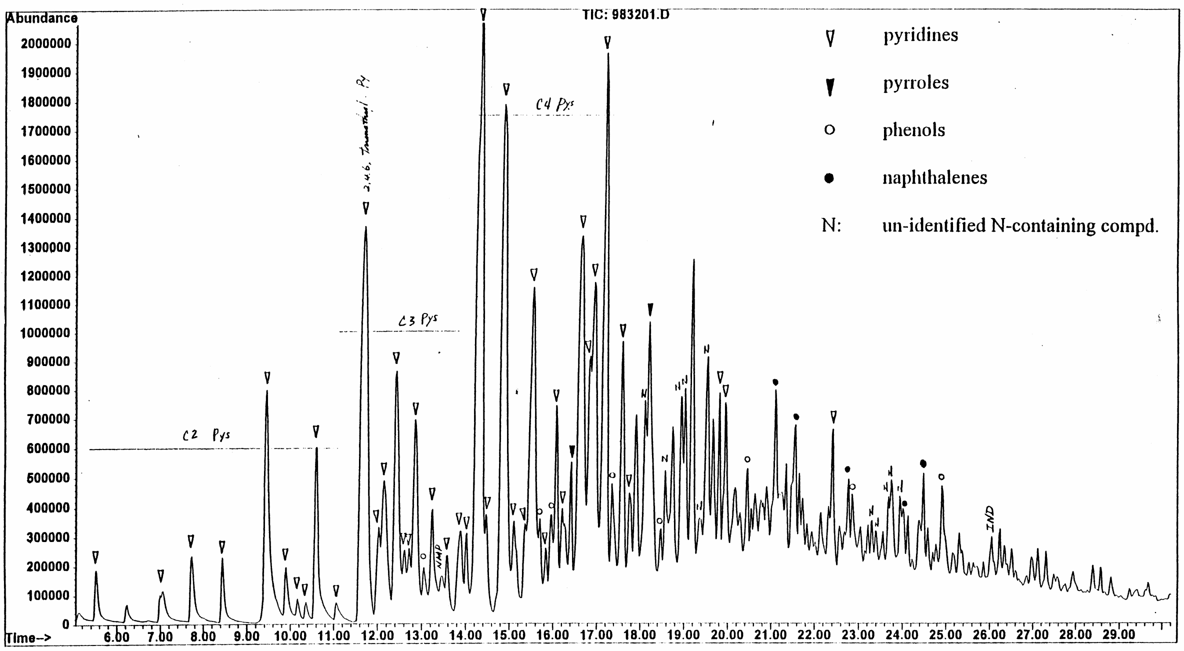


Figure 12.8: THDA Process Flow Diagram

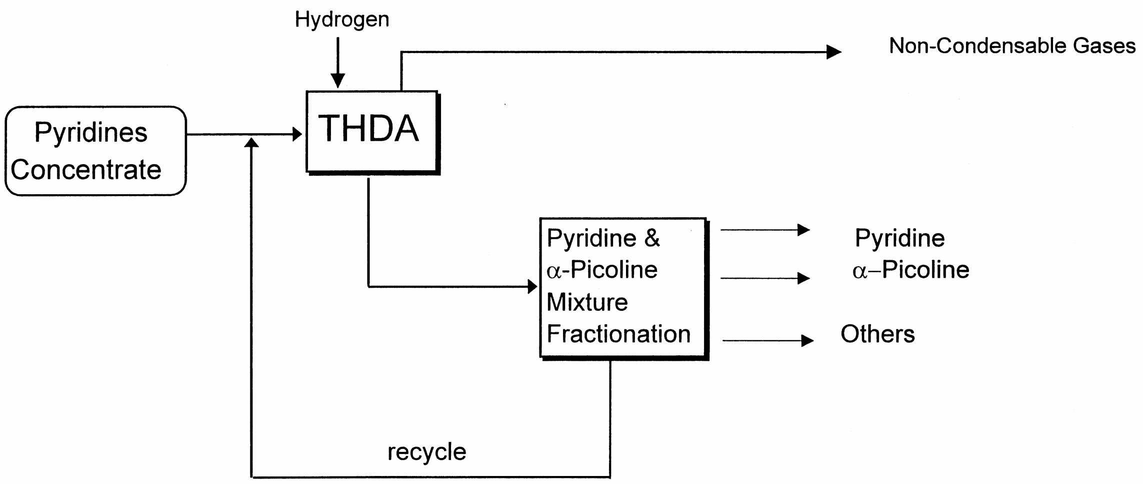
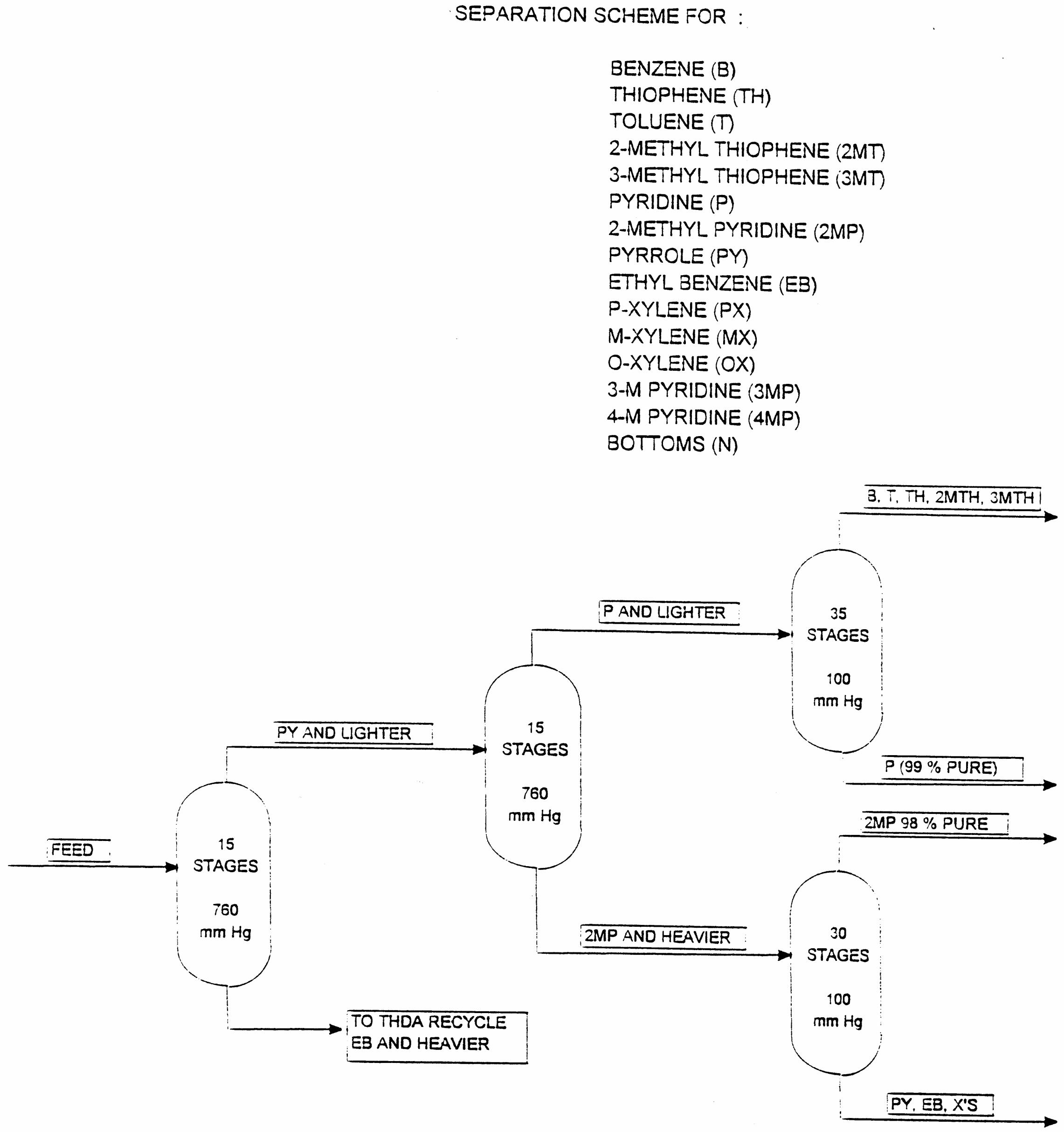


Figure 12.9: KPX Pure Compound Purification Scheme



Task 12 Conclusions

Task 12 focused on proving the process integration in the laboratory by putting the system through a simulated flow. While each process was conducted on a batch scale, an authentic mass balance was obtained. Results showed that the high boiling extract would yield the expected lower alkyl pyridines and that when combined with the initially extracted pyridines would form a common stream for purification. GC-MSD analysis provided the composition of this extract distillate cut, and a thermodynamically plausible separation scheme was devised. Anticipated purities of these separation fractions were used in discussions with potential buyers during task 13. The issues of producing marketable products were more clearly defined as the composition of possible impurities in pure compound products was determined and the need for hydrotreating the raffinate was reinforced.

Task 13 - Test Marketing

Statement of Work

A survey was conducted for market interest in products manufacturable from kerogen oil. The target products and analytical data for the optimum product slate were provided for inspection. Interested parties were asked to comment on the acceptability and value of the product for its applications and, most importantly, cite any deficiencies that they perceived in the product character. This information was incorporated into considerations of optimum process design.

Results

Early in this task we coined the term KPX, short for Kerogen Products Extraction, as a way to brand the products from VEP. This greatly assisted the communications with potential customers of kerogen-derived products.

A 1996 survey was completed of companies known to be either manufacturers or consumers of pyridines.

The primary users for pyridines by application are:

Paraquat and Diquat (herbicides)
    Zeneca AG Products

Other Insecticides and Herbicides
    Dow Chemical
    Monsanto
    DSM

Personal Care Products (antidandruff shampoos, topical disinfectants, antifungals, mouthwash germicidals)

- Olin Corp.
- Ruetgerswerke AG
- Hexcel Corp.

Pharmaceuticals and Pharmaceutical Processing

- Eli Lilly
- Upjohn
- American Cyanamid
- Merck
- Rhone-Poulenc (France)
- Laboratori Mag Smc (Italy)
- Bayer AG

Rubber Products (tires, belts, polymers)

- Goodyear
- Firestone
- Bayer Elastomers (France)
- Huels Aktiengesellschaft (Germany)

Industrial Solvents

- Oil field and oil refinery companies
- Metallurgical processors

Pyridine Manufacture/Consumption

- Robinson Brothers LED
- Abbott Laboratories
- Reilly Industries
- R. T. Vanderbilt Company
- Upjohn
- BASF
- Nepera

B-Vitamin Manufacture

- Degussa Antwerpen N.V.
- Lonza AG
- Reilly Industries
- Nepera

13.1 Pyridine Products

13.1.1 Pyridine and α-Picoline

Pyridine and α-picoline produced from kerogen oil will be used interchangeably with synthesized pyridines. Concern was expressed by some potential customers about purity.

The industry has established standards for impurities when synthesizing paraquat and diquat or in chlorination to form chlorpyriphos. However, the current standards are aimed primarily at coproducts and partially reacted feedstocks accruing from the synthesis route. As a result it is not clear whether small amounts of coproducts from the KPX route will cause any difficulties. Discussions with end users and considerations of chemistry suggest that the identified impurities in KPX products would be inert to downstream processing, and therefore may not pose a problem. Confirmation of this preliminary conclusion must be made in future development work.

13.1.2 Lower Alkyl Pyridines (LAPs)

Other LAPs will meet existing market applications with similar considerations. In the preferred scheme all LAPs boiling higher than ∝-picoline are recycled in the THDA unit to manufacture more pyridine and ∝-picoline. If such products are desired for market a slipstream of the THDA feedstream or recycle stream could be drawn and subsequently refined to specifications. These polar types may have interesting additive and detergent properties that, through product development research, could prove marketable.

13.1.3 Higher Alkyl Pyridines (HAPs)

Higher alkyl pyridines (HAPs) are the predominant type found in the extract. As such, HAPs from kerogen oil are low cost; whereas, HAPs from synthesis routes are high cost and are actually undesirable byproducts. Use of low-cost HAPs in traditional applications offers significant market growth potential because of the large cost difference.

Kerogen oil HAPs may be effectively substituted in many traditional applications even though they may not be the exact structures currently being marketed. The field of herbicides and fungicides may accept a substituted pyridine, perhaps at some advantage in properties because of the single alky chain not commonly present in synthesized HAPs. Product R&D will need to be completed, but it is expected that the cost saving of kerogen oil derived HAPs ($1/Kg) will appear very attractive to customers who are accustomed to paying $2-3/Kg. HAPs may find their first markets as solvents and process oils, displacing HAPs inadvertently generated during pyridine synthesis. Kerogen oil HAPs will have a lower degree of substitution on the ring, and will have longer alkyl chains. The performance of these HAPs as solvents is superior in solvent strength to petroleum-derived aromatic solvents and similar to pyridine-based solvents. Properties, as well as price, will be the competing factors in the solvent markets.

HAPs have a strong potential for market growth. The characteristics that make higher alkyl pyridines attractive for new markets are:

1) Longer alkyl groups reduce the water solubility. This lower solubility will have beneficial effects in agrochemicals because the compounds will be more strongly absorbed on the plant and less susceptible to washing by rain and pollution of

ground water. The lower solubility also reduces the absorbability through the skin making compounds made of higher alkyl pyridines safer to handle.

The longer chains will increase the oil/water partition function used to measure bioavailability. A problem in the pharmaceutical and agrochemical business is the high water solubility of currently used pyridine products. HAPs may help solve this problem because the long alkyl chain reduces water solubility.

2) HAPs have a higher boiling point and are less volatile than lower alkyl pyridines. This means agrochemicals or other products manufactured from HAPs evaporate at a much slower rate, and pose less of a respiration hazard in the manufacture and handling. Flammability and combustibility are also reduced.

The foregoing issues were discussed with industry experts, and all agreed that there is room to develop new markets for kerogen oil HAPs; current production of HAPs is an inadvertent byproduct of pyridine and picoline manufacture, and therefore costly by synthesis routes. For example, to the extent they have been produced and marketed, HAPs have been used as metal corrosion inhibitors. Historically, there has been little product R&D for HAPs. Yet, theoretical chemistry will suggest that the biological and chemical activity of the nitrogen center should be substantially the same in HAPs as it is in LAPs. If low-cost HAPs are available to the marketplace (for the first time), the chemistry of LAP-based products could be deployed to guide product development research for HAPs.

Examples of new product/market development area are:

- Advanced agrochemicals with lower environmental impact,
- Metal winning additives for the metallurgical industry,
- New detergents and surfactants for industrial and home product application,
- New solvents for industrial processing, and
- New intermediates for chemical and pharmaceutical synthesis.

Product and market development opportunities identified would provide significant growth opportunities to a VEP venture.

13.2 Asphalt Additives

A high nitrogen antistrip additive produced from raw kerogen oil (the >290° C extract described above) was tested for its antistripping characteristics by the Western Research Institute (WRI) developed, Water Susceptibility Test (WST). The antistrip additive was mixed with SHRP (Strategic Highway Research Program) core asphalt AAF-1. Rheological measurements were made on the stripping-prone, neat asphalt and the asphalt-additive mixture to ensure that the additive did not adversely affect the asphalt viscosity. Viscosity measurements at 25°C and 60°C showed the viscosity reduction to be within acceptable limits.

Briquets consisting of five mass percent asphalt AAF-1 and AAF-1-KPX with 20-35 mesh aggregate particles were made following the Plancher, et al. procedure,[14] except that the briquets were compacted at 4000 psi instead of 6200 psi. The briquets were tested by subsequent freeze thaw cycles until failure. The results are given in Table 13.1.

The cycles to failure increased with the addition of the KPX additive. The results indicate that KPX additive imparts measurable improvement to the moisture damage resistance of the above described asphalt-aggregate mixtures. Examination of the data in Table 13.1 also shows that moisture damage resistance is also sharply dependent upon aggregate composition but in each case for a given aggregate the KPX antistripping additive showed beneficial effects. The prospect of marketing an asphalt antistrip additive dramatically reduces the production capacity limitations imposed by pyridine markets.

It may be noted that the KPX antistripping additive, at more than 6% nitrogen, possesses more than 4 meq/g active nitrogen. This is higher than the 2.5 meq/g for the successfully tested SOMAT asphalt additive product and roughly equivalent to the 4 meq/g activity of synthesized amine additives. This is additional evidence for potential marketability of KPX antistrip additives.

A 1-liter sample of the asphalt additive was provided to a major asphalt company operating throughout the United States. Terms of agreement did not allow JWBA to receive results of testing. Results were positive with respect to binding and antistrip activity. However, some lowering of asphalt viscosity occurred. This latter deficiency could be remedied in a variety of ways, including topping distillation of additive, deeper distillation of petroleum residue (using the additive to blend back to asphalt viscosity specs), air blowing, or mild polymerization of additive. It was decided that results were sufficiently positive, that if and when production of shale oil appeared probable, that additional effort to fit market specifications would be warranted.

Table 13.1: Moisture Sensitivity Test Results, Cycles to Failure*

	Aggregates (20-35 mesh size)					
Sample	RJ		RA		RG	
	R1	R2	R1	R2	R1	R2
AAF-1	1	1	2	2	8	8
AAF-1 4% KPX-98-107	1	2	3	3	>16	>16

*Cycles to failure greater than 12 are considered to be essentially equivalent and very moisture insensitive.

The positive results of laboratory testing, the industrial inspection of the total extract as an asphalt additive and the success that SOMAT had with pavement test qualification gives confidence that such material can be made acceptable to the marketplace. Costs of asphalt additives have been difficult to ascertain, but in general alkyl amines exhibit 1996 prices in the vicinity of \$1/kg or greater. Anecdotal information placed SOMAT asking prices at about \$1.20/kg. Therefore, at a cost substantially lower than these prices, KPX asphalt additive should be competitive on a price basis.

13.3 Ionic Surfactants

Alkyl-substituted pyridines extracted from kerogen oil can be converted to cationic surfactants by reaction with alkyl chlorides. The resulting quaternary pyridinium surfactants ("quats") will be quite different from commercial quats, which have the alkyl group on the nitrogen, because kerogen oil quats have the long-chain alkyl group attached to the aromatic ring. This will result in unique behavior and properties, which may prove desirable in certain applications, especially where chemistry applied to the quaternary salt is important.

Most commercially available cationic surfactants are quaternary aliphatic ammonium compounds, but the marketplace includes quite a variety of variations on these themes. An example of the pyridine derivatives is cetylpyridinium chloride, used in a number of personal care products. During the course of research, it was learned that the C_{16} moiety has special antibacterial properties that alkyl groups of differing lengths may not have.

Quaternary ammonium surfactants are used in a broad variety of consumer and industrial formulations (Table 13.2). A major traditional application is in disinfectants, taking advantage of the bactericidal properties of many of these compounds. Consultation with industry suggests that the length of the alkyl chain influences the antimicrobial effectiveness, with C_{16} alkyl groups being the most effective.

The largest businesses are in consumer products, because of the importance of fabric softeners, virtually all of which are quats made from aliphatic amines. The other rapidly growing application is in hair conditioners, the largest application in personal care products.

Table 13.2: Cationic Surfactants
(share of 1.16 million metric tonnes/year world market)

End-Product	Market Share
Fabric softeners	23%
Personal care (especially shampoo conditioners)	19%
Textile auxiliaries	12.6%
Dishwasher detergents	10.5%
Household cleaners	7.8%
Biocides	4%
Industrial and institutional laundry and cleaning	3.6%
Laundry detergents	2%

Other (asphalt emulsifiers, corrosion inhibitors, fuel additives, plastics additives)	remainder

Data from Chemical Market Reporter, 26 Jan 1998.

Commercial pyridine-derived quats have the nitrogen buried in the middle, with a long alkyl chain on the nitrogen. Surfactant properties are controlled by altering the lengths of the chain to give varied solubility, etc.

The quats made from kerogen oil would be similar, except that the long chain would be on the ring. The opportunity comes from using a methyl or ethyl group on the nitrogen and relying on the long alkyl chain attached to the ring as the fatty end. The cationic site thus has the acid/base properties one would expect from the nitrogen atom in a pyridine ring yet the oleophilic/hydrophilic properties are those of a long-chain alkyl making a “fatty pyridine”. Some industry experts have found this combination intriguing and warrants investigation. This potential market opportunity was discovered during dialog with industry, and was not demonstrated in the laboratory during this research.

In some applications, kerogen-derived pyridines could be used as surfactants without N-alkylation. In these, small amounts of mineral acid could be added to form the pyridinium cation. In some systems, naturally occurring acidic species would convert the pyridine to a pyridinium. The cost for production of such quats is also low because methyl or ethyl substitution is inexpensive on a molar basis. This again takes advantage of the natural long-chains accruing to the KPX alkyl pyridines.

Making a “fatty pyridine” from conventional synthetic pyridine requires something akin to Friedel-Crafts alkylation of benzene, except that the reaction will probably require an extra step to protect the N from substitution by the alkyl chloride. There is currently no identified market for these materials, however, and for these reasons it was not possible to test for market acceptability of these potential products.

13.4 Agrochemicals

Agrochemical testing programs were established with several agrochemical R&D facilities. Tests for herbicidal, fungicidal and insecticidal activity were performed on a number of concentrates produced from kerogen oil. Companies expressed a concern about spending large sums of money to identify and develop products before a reliable source of material was available. Consequently, only preliminary screening was justified. At the initial trials none of the screening tests showed results sufficiently positive that a ‘lead’ was discovered. No derivatization such as quaternization or chlorination was conducted however, and such derivatives would almost certainly yield activity of interest. The screening tests were not exhaustive and additional work is warranted under a future program. Any such activity, should it be discovered would be high value. Such biologically active products should be considered ancillary to the prime products and while enhancing the economics, are not of sufficient volume to support a venture alone.

13.5 Petroleum Products

13.5.1 Raffinate

The raffinate from the KPX process represents about 80 wt.% of the total kerogen oil. It consists of 7.5% of <150 °C fraction (recovered in the initial topping process), 67.5% of the non-polar fraction of the first extraction product and 25% of the non-polar fraction of the HP products (or recyclate). This sequence is shown in Figure 12.4 above. It is possible that the raffinate may be directly marketable as a refinery feedstock.

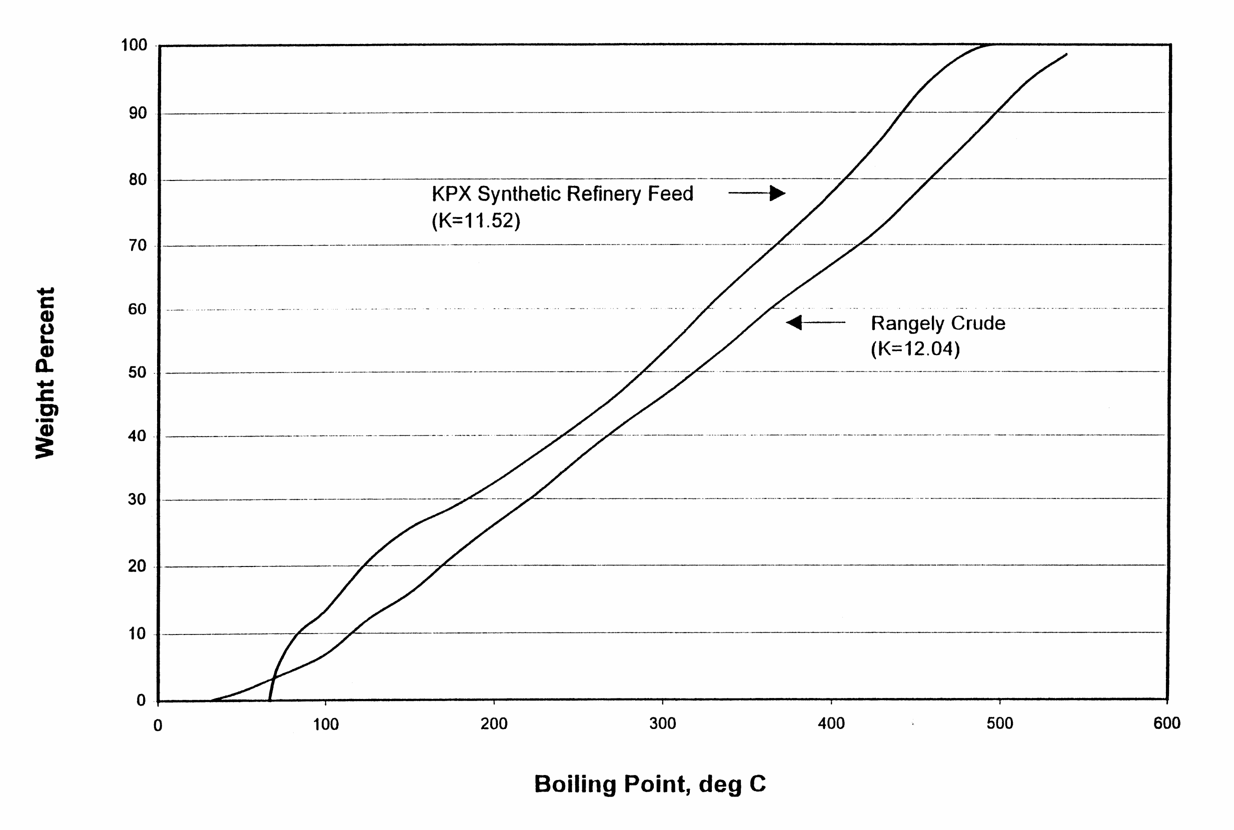
The raffinate exhibits no Conradson Carbon and low (0.25%) asphaltene content. The density of this raffinate is 0.870 g/cc (60 F/60 F), or 31 API gravity. Its initial boiling point is about 66 °C. The result of simulation distillation of this refinery feed is tabulated as shown in Table 13.3.

The boiling-point curve of KPX total raffinate is shown in Figure 13.1 and is compared to the boiling-point curve for a Rangely Colorado crude, a well-established locally available crude oil. The Rangely crude is slightly lighter (°API=34.8) than the KPX raffinate. The K-factor of the Rangely crude (K=12.04) is also higher than that of KPX raffinate (K=11.52).

Table 13.3: Boiling-Point Distribution of the KPX Raffinate

Fraction	**Total, wt.%**
Naphtha, <200 °C	32.6
Kerosene, 200 - 275 °C	14.4
Gas Oil, 275 - 325 °C	12.5
Heavy Gas Oil, 325 - 400 °C	18.5
Vacuum Gas Oil, 400 -538 °C	22.0

Figure 13.1: Boiling Point Distribution of KPX Total Raffinate

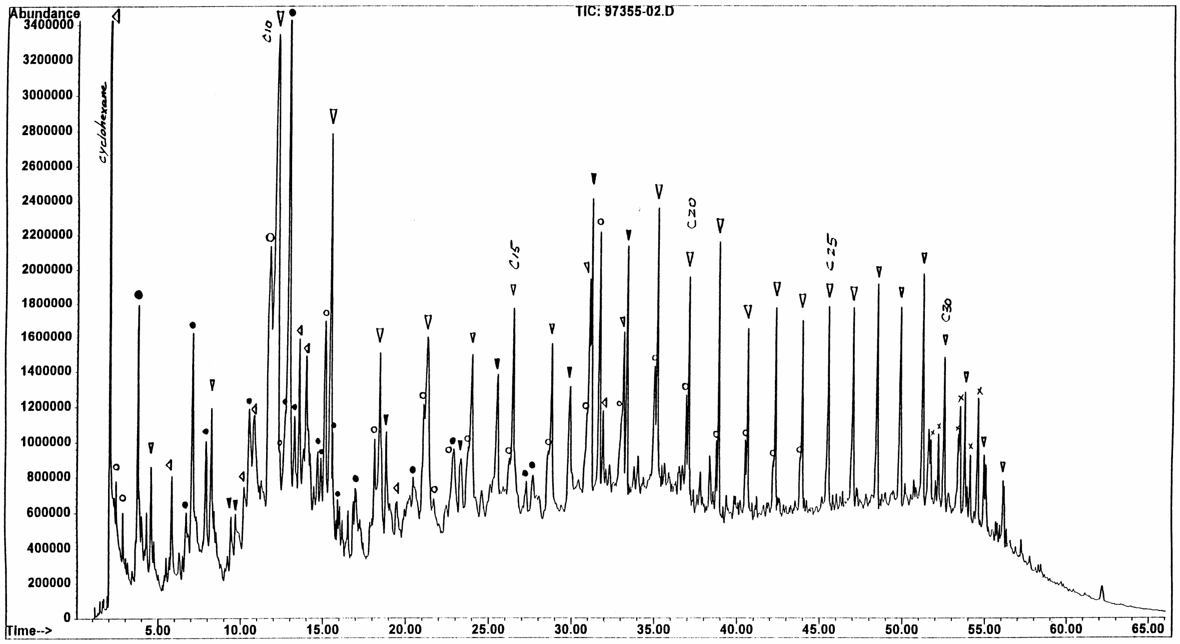


13.5.2 Compound Type Analysis of a KPX Raffinate

The total ion chromatogram of the KPX raffinate is shown as Figure 13.2. With the aid of the Z-BaSIC techniques, the compound types of this KPX raffinate were analyzed. The types and amounts of the hydrocarbons within this fraction are tabulated in Table 13.4.

The high olefins (mostly terminal alkenes) contents are consistent with the nature of the pyrolytically derived kerogen oil. The elemental analysis showed that the nitrogen and sulfur contents are 0.35% and 0.97%, respectively. The type of sulfur compounds are primarily C_1 to C_5 alkyl-substituted thiophenes. S-compounds are distributed evenly throughout this sample, nevertheless, more N-compounds are found in the higher boiling fractions than in the lower boiling fractions.

Figure 13.2: Compound Type Analysis of KPX Total Raffinate



Compound Types in the KPX Synthetic Refinery Feed; in Which ∇=Paraffins, ▼ = Isoparaffins, ● = Aromatics, ◁=Naphthenes, ○ =Olefins, and ×=Biomarkers Such as Hopane.

Table 13.4: Compound Types Analysis of KPX Raffinate

Compd. Types	Z-series	norm. wt. %*	Descriptions
Paraffins	+2	31.3	From C_8 to C_{34}
Isoparaffins	+2	10.7	From C_9 to C_{22}
Aromatics	-6, -12, -18	19.8	Alkylbenzenes and Alkylnaphthalenes
Naphthenes	0	15.4	Cycloalkanes and Alkylcycloalkanes
Olefins	0, -2	22.8	Alkenes and Alkylcycloalkenes
*Normalized from 81% of the total material (19% of the components were not identified).			

The types of the nitrogen compounds found are pyrroles and indoles. It is believed that basic nitrogen compounds not processed for pyridine, such as quinolines and higher benzologs, have been almost quantitatively recovered as part of the extract and end up in the asphalt additive.

The predominate non-basic nitrogen compounds present in the KPX raffinate are more amenable to catalytic hydroprocessing than those of basic nitrogen type. These nitrogen compounds can be easily removed by the hydrotreating units even under moderate conditions. The addition of the KPX raffinate at 5,000-10,000 bbl/day will not overload the capacity of the existing hydrotreating units of the refineries in the production area. Salt Lake area refineries have a combined capacity of about 135,000 bbl/day and are becoming increasingly crude-short. (In the intervening years, the capacity has risen to about 160,000 bbl/day of which approximately 30% is being fed by syncrude from Alberta oil sands; the original statement is, nevertheless, still valid.)

A specification sheet of the KPX raffinate is listed as Table 13.5. The KPX raffinate contains less than 5 ppm of vanadium and nickel. Its pour point is -20 °C (-4 °F) and the viscosity at 100 F is 4.9 cSt. Due to the relative high API gravity and low viscosity, the KPX raffinate can be blended directly with the heavier petroleum-based crudes. After secondary processing, this stream itself is expected to yield 45% light (b.p. <350 °C) refinery feedstock, 19% aromatic oils, 25% lube oils, and 11% waxes; according to laboratory tests.

The specification sheet was sent to prospective refinery buyers for inspection. Feedback indicated that this material still contained levels of sulfur and nitrogen that would make it difficult to market in the Salt Lake area in large part because the area is accustomed to very sweet crudes. Also, the high olefins content makes its stability suspect for pipelining and storage. Based on this feedback it was decided that field hydrotreating might be necessary**.** Because the HP unit already requires a hydrogen plant, adding a catalytic hydrotreater would not introduce a new ancillary unit.

13.5.3 Preparation of Sweet Refinery Feed

About one liter KPX raffinate (see Figure 12.4 for sequence) was subjected to a mild hydrotreating step to obtain a stabilized sweet refinery feed. A sulfided commercial hydrotreating catalyst (Englehard HPC 50) was employed. Reactor conditions were 290 °C and 800 psig hydrogen partial pressure. The oil was fed at 1.55 LHSV. Hydrogen flow rate was held at a hydrogen-to-oil ratio of 680 SCF/bbl. These conditions are relatively mild compared to those commercially operated when feeding gas oils which may operate at 375 °C, 2000 psig hydrogen, and 2200 SCF/bbl hydrogen-to-oil ratio.

After hydrotreating, the API gravity of the stabilized refinery feed improved from 31.0 to 36.8 °API. Sulfur and nitrogen contents were reduced to 200 ppm and 1200 ppm, respectively. These are below the locally-allowable concentrations of 3000 ppm sulfur and 1500 ppm nitrogen.

The boiling-point curve of the KPX stabilized refinery feed is shown in Figure 13.3 and compared to the boiling-point curve for Rangely, Colorado crude, a well-established locally available crude oil. The KPX refinery feedstock is now slightly lighter than the Rangely crude (°API=36.8 vs 34.8) and the K-factor is about equivalent (K= 12.00 vs. 12.04.)

Table 13.5: Specification of the KPX Raffinate

DESCRIPTION: Kerogen Oil Non-polar Fraction

ORIGIN: Green River Formation Pyrolysis Oil Raffinate

CRUDE PROPERTIES

Gravity, degrees API	31.0
Specific Gravity (60 °F/ 60 °F)	0.870
Total Sulfur, wt. Pct.	0.97
Total Nitrogen, wt. Pct.	0.35
Pour Point, °F	- 4
Viscosity at 100 °F, cSt	4.9
Vanadium, ppm wt	<5
Nickel, ppm wt	<5
Conradson Carbon, wt. Pct.	0
Asphaltenes, wt. Pct.	0.25
Hydrogen Sulfide, ppm wt.	0
Ash Content, wt. Pct.	0

PRODUCT PROPERTIES (obtained from Simulated Distillation)

Distillation Fraction	*Yield, wt%*	*Cumm. wt%*
Gasoline, <200 °C	32.6	32.6
Kerosene, 200 - 275 °C	14.4	47.0
Gas Oil, 275 - 325 °C	12.5	59.5
Heavy Gas Oil, 325 - 400 °C	18.5	78.0
Vacuum Gas Oil, 400 - 538 °C	22.0	100.0

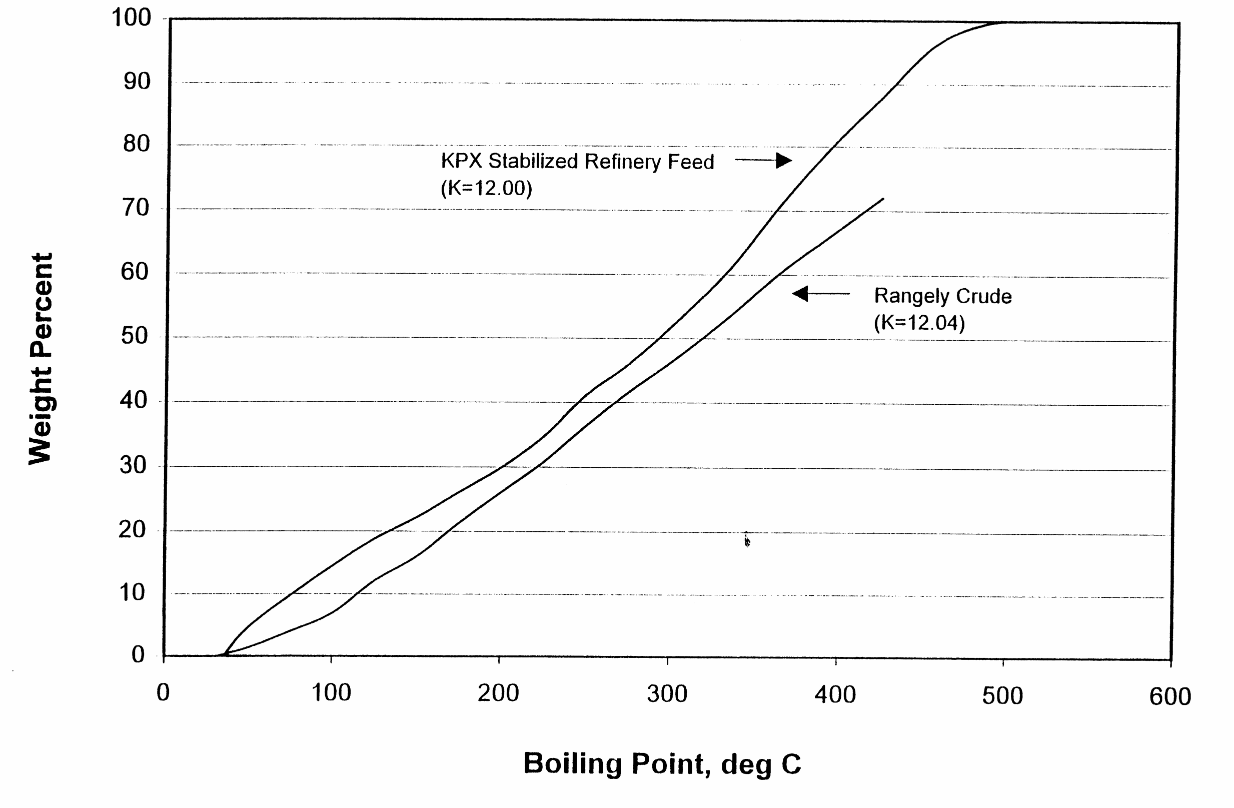
Boiling Point Cuts

Fraction wt%	*Boiling Point, °C*
10%	82
50%	291
90%	441

Atmospheric Reside, >350 °C	33.7
Vacuum Reside, >538 °C	0

A new specification sheet of this stabilized refinery feed, as seen in Table 13.6, was sent to local refineries for their inspection. Reaction was highly positive. This KPX synthetic refinery feed is expected to command a premium market price once it becomes available. The KPX feed was evaluated by one refinery at $5.17/bbl premium over NYMEX prices at a time when NYMEX was $20/bbl. The premium character of KPX refinery feed will be maintained in the future, even as the refinery diets are increasingly feed by Alberta syncrude. The hydrogen content of the KPX product is higher (13.0 vs 12.4), the API gravity is higher (37 vs 35), the sulfur content is lower (0.02 vs 0.4) but the nitrogen content is higher (1200 ppm vs 623 ppm), making the KPX product equivalent or better in quality. It is observed, at the time of this final report writing (October, 2006), that samples stored in clear glass vials under nitrogen have shown no discoloration in the nine (9) years since production in late 1997. With shale oil, discoloration due to polymerization of unsaturated species is the first sign of instability. Lack of discoloration shows the hydrotreating of olefins and pyrroles was complete.

Figure 13.3: Boiling Point Distribution of KPX Stabilized Refinery Feed



13.5.4 Compound Types Analysis of a KPX Stabilized Refinery Feed

With the aid of the Z-BaSIC techniques, the compound types of the KPX stabilized refinery feed (after hydrotreating) was analyzed. The types and amounts of the hydrocarbons within each sample are tabulated in Table 13.7.

The main difference between the two samples is the reduction of olefin content and increase of the isoparaffins which results from hydrogenation of the olefins and ring opening of the heteroatom-containing compounds. The large increase in isoparaffins is somewhat inexplicable, however, given the modest process temperature. The amount of paraffins increased slightly from hydrogenation of the olefins. The aromatic content decreased as a result of hydrogenation. The amount of naphthenes decreased slightly, apparently the consequence of ring opening of the naphthenes to isoparaffins. These results show that once the polar compounds are removed from kerogen oil by extraction, the remaining non-polar compounds are easy to upgrade.

Table 13.6: Specification of KPX Refinery Feed

DESCRIPTION: Stabilized (Hydrotreated) Kerogen Oil Non-polar Fraction

CRUDE PROPERTIES

Gravity, degrees API	36.8
Specific Gravity (60 °F/ 60 °F)	0.841
Total Sulfur, wt. Pct.	0.02
Total Nitrogen (mostly non-basic), wt. Pct.	0.12
UOP K Factor	12.00
Pour Point, °F	39
Viscosity at 100 °F, cSt	3.3
Vanadium, ppm wt	<1
Nickel, ppm wt	<1
Conradson Carbon, wt. Pct.	nil
Asphaltenes, wt. Pct.	<0.25
Hydrogen Sulfide, ppm wt.	nil
Ash Content, wt. Pct.	nil

DISTILLATION PROFILE (obtained from Simulated Distillation)

Distillation Fraction	*Yield, wt%*	*Cumm. wt%*
Naphtha, <200 °C	29.8	29.8
Kerosene, 200 - 275 °C	16.2	46.0
Gas Oil, 275 – 325 °C	12.3	58.3
Heavy Gas Oil, 325 - 400 °C	23.2	81.5
Vacuum Gas Oil, 400 - 538 °C	19.5	100.0

Boiling Point Cuts

Fraction	*Boiling Point, °C*
10%	76
50%	299
90%	433

		wt. Pct
Atmospheric Reside,	>350 °C	34.1
Vacuum Reside,	>538 °C	nil

The remaining small amounts of heteroatom-containing compounds are difficult to trace because their existence is masked by co-eluting large hydrocarbon peaks. It is believed that sulfur compounds are primarily alkyl-substituted benzothiophenes. The nitrogen compounds found are pyrroles and indoles. These heterocyclic compounds can be removed at more severe hydrotreating conditions in subsequent refining processes. Since the amount of nitrogen and sulfur in the hydrotreated stabilized crude is well below the ordinary refinery feed, this material is now highly marketable. Regional crude oil supplies are declining and local refiners are bringing in syncrude derived from Canadian tar sand bitumen.

Table 13.7: Comparison of Compound Types of KPX Non-Polar Fraction and Stabilized Refinery Feedstock

Compound Types	**Z-series**	**norm. wt. %***		**Descriptions**
		crude raffinate	stabilized	
Paraffins	+2	31.3	34.8	From C_8 to C_{34}
Isoparaffins	+2	10.7	35.7	From C_9 to C_{22}
Aromatics	-6, -12, -18	19.8	14.7	Alkylbenzenes and Alkylnaphthalenes
Naphthenes	0	15.4	12.1	Cycloalkanes and Alkylcycloalkanes
Olefins	0, -2	22.8	2.7	Alkenes and Alkylcycloalkenes
*Normalized from 81% (crude raffinate) and 85% (stabilized products) of the total samples.				

Task 13 Conclusions

Raffinate from extraction of total kerogen oil (>150° C) is readily hydrotreated under moderate conditions to produce a premium refinery feedstock. Prior extraction of basic nitrogen compounds accounts for the ease in hydrotreating. There is substantial technical and market certainty regarding the price and acceptability of the hydrotreated raffinate to regional refineries.

Products from the extract will consist of pure compounds and heavier mixtures. Markets for both product types are already established; however, because these are specialty products the prices and specification requirements are much harder to determine. Pyridine suppliers claim there is no unmet market need. On the other hand pyridine consumers are highly dependent upon a few suppliers and have been highly receptive to the prospect of a lower-cost, long-term alternative supply. Compositional analysis suggests that the pure compound pyridine products can be manufactured in the purities required.

Higher molecular weight extract can be marketed as an anti-strip asphalt additive. Additional market development is possible for these materials, as long-chain alkyl pyridines have not been available at a sufficiently low price to promote market development. This prospect affords market diversification to the KPX venture and provides growth opportunities for the future.

Task 14 - Venture Development

Statement of Work

A Venture Development Plan was prepared. The plan specifies the technical, market and economic potential discovered in this research and the requirements for the next phase of development. This plan forms the basis for kerogen oil venture development involving private sector funding.

Results

14.1 Venture Description

The KPX Venture will involve sourcing raw kerogen oil, upgrading this oil to a refinery stream and a pyridinic concentrate, using a portion of the concentrate for an asphalt additive, a high volume use, and processing the remainder for its chemical values. This sequence requires the following critical components.

1) a resource base,
2) a retorting technology,
3) an oil processing technology (this study),
4) a market outlet for petroleum products, and
5) a market outlet for pyridine products.

The possible participants in such a venture are displayed in Figure 14.1. The business relationship between these participants will be determined through discussions with specific companies.

14.2 Resource Base

The scale anticipated for the first generation facility is on the order of 12,000 bbl/day, or less. This modest scale allows the process to be sited on locations that are accessible and rich, but not necessarily large. These criteria point to a preferred location in Utah where rich oil shale zones can be found near the surface or which are accessible through outcrops in beds of modest dip. Figure 14.2 is a richness profile for a mineable section of the mahogany zone in Utah showing that an average grade of 35 gal/ton may be realized from a pay zone of 28 feet. It is possible that Colorado possesses zones of this richness but it is believed that such zones are not as accessible, being covered with large depths of overburden. Even so, favorable sites exist in Utah or Colorado for small scale operations.

14.3 Retorting Technology

A number of retorts including the Unocal, Paraho, Tosco, Chevron and Oxy modified in-situ designs have been tested in prior attempts at synfuels development. The Petrosix process, a variation of the Paraho process has operated at about 3000 bbl/day in Brazil since the early 90s. The Alberta Taciuk Process is under consideration for Australian resources. A combined 10000 bbl/day are being produced in Estonia using two different technologies, the Kiviter and the Galoter designs. The Lofreco modified in-situ process was demonstrated at a sizable scale in Utah and is also a strong candidate for kerogen oil production technology. These technologies are briefly reviewed in Volume II of reference[15].

At a sufficient transfer price raw kerogen oil can be economically produced. The upper limit that can be paid for this raw oil will be dictated by the prices of the refinery feed and the pyridine products, less the process and capital costs.

For purposes of economic analysis a base-case transfer price was chosen at $18/bbl. This is in the range of expected prices for NYMEX crude in a stable petroleum pricing environment. Discussions with potential producers of kerogen oil (at the time of analysis, in the late 90s) indicate that raw kerogen oil could be profitably manufactured at that transfer price. It should be noted that without VEP, there would be no market for raw kerogen oil, at any price, and upgrading costs and transportation costs may add as much as $9 to the required sales price. Hence, $18/bbl is a better transfer price for the raw kerogen oil than a producer could expect as a feedstock to a hydrotreating operation. This price was used as the base price to the VEP venture. The ability of a VEP venture to pay a competitive price for the raw kerogen oil is seen as key to stimulating the start of a shale oil industry. (See also results of Task 14b for a 2006 update)

14.4 Markets

14.4.1 Pyridine Products

The high end pyridine products will have the same uses as current products made synthetically. Ideally, current manufacturers will participate in the venture, expanding their growth opportunities and reducing average manufacturing costs. Alternatively, the venture could qualify KPX pyridines for the generic market and compete with synthesis pyridines based on price. Because of the limited manufacturing base for pyridines, supply reliability will be an important factor to achieving market penetration.

14.4.2 Antistrip Asphalt Additives

The acceptance of nitrogen-based antistrip additives is growing. Certain antistrip additives containing amines are in the marketplace and have an established pricing structure. Success has been achieved in introducing shale-derived asphalt additives to the marketplace.

14.4.3 Refinery Feed

The hydrotreated, sweet refinery feed product is conventional and of low technical and market risk. If the overall economics are proved, this product will be readily marketed in the region as a premium, high-distillate-yield feedstock.

By all accounts, the three primary products, pyridine pure compounds, antistrip asphalt additives, and sweet, light refinery feed, will supply growth markets. The primary applications of pyridines, namely agrochemical herbicides and vitamins, relate to growing food production needs and much of the growth in demand is being seen in areas of population growth.

Figure 14.1: KPX Cooperative Agreement and Joint Venture Plan

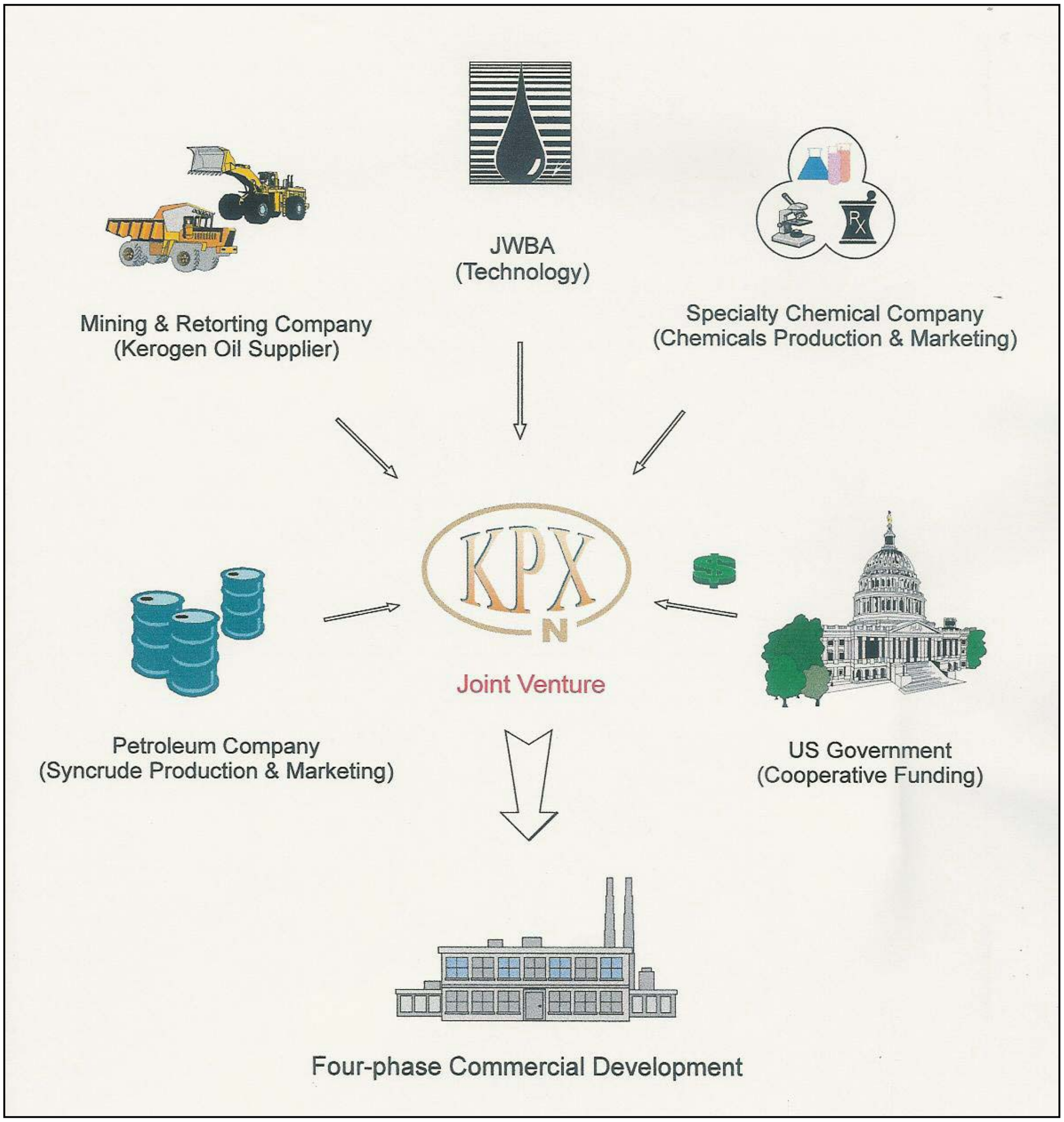
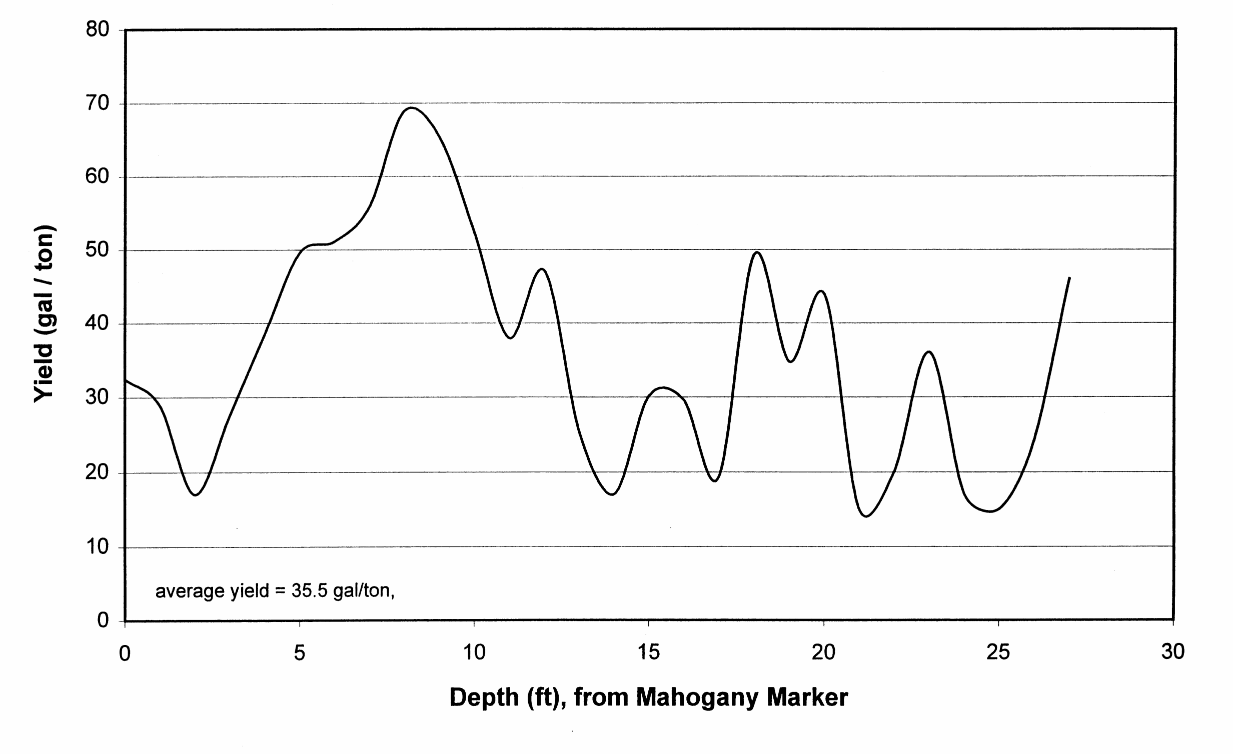


Figure 14.2: Illustration of Kerogen Oil Yield from Mahogany Zone, Uinta Basin, Utah



14.5 Process Technology

Three process configurations were constructed around the preferred product slate. They are labeled and described as follows.

14.5.1 High Value Case

The high value case maximizes the product value by extracting the maximum amount of pyridines. The total plant capacity will be limited by the pyridine markets. The process flow diagrams for the full sequence are given in Figures 14.3, 14.4. The purification step is given in Figure 12.8 on page 91.

14.5.2 High Capacity Case

The high capacity case removes some of the limitations imposed by pyridine market volumes by taking the heaviest extract for asphalt additive and processing only the middle distillate extract for pyridines. This allows for a higher oil production capacity, reducing per unit costs. In this configuration, the HP unit will be simpler because it can be run at a much higher vapor to liquid (V/L) ratio with substantially less heavy recycle. The process flow diagrams are given in Figures 14.5 and 14.6. The purification step (Figure 12.8) is the same as with the high value case.

Figure 14.3: KPX Process Flow Diagram - High Value Case

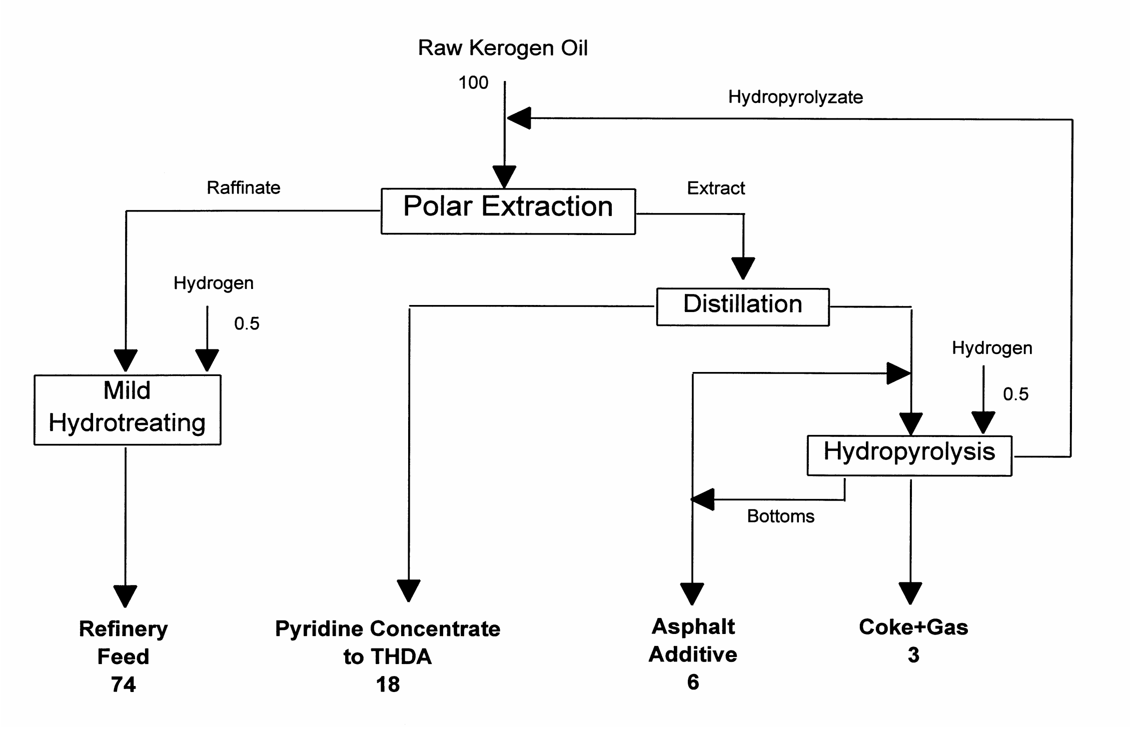


Figure 14.4: THDA Flow Diagram for High Value Case

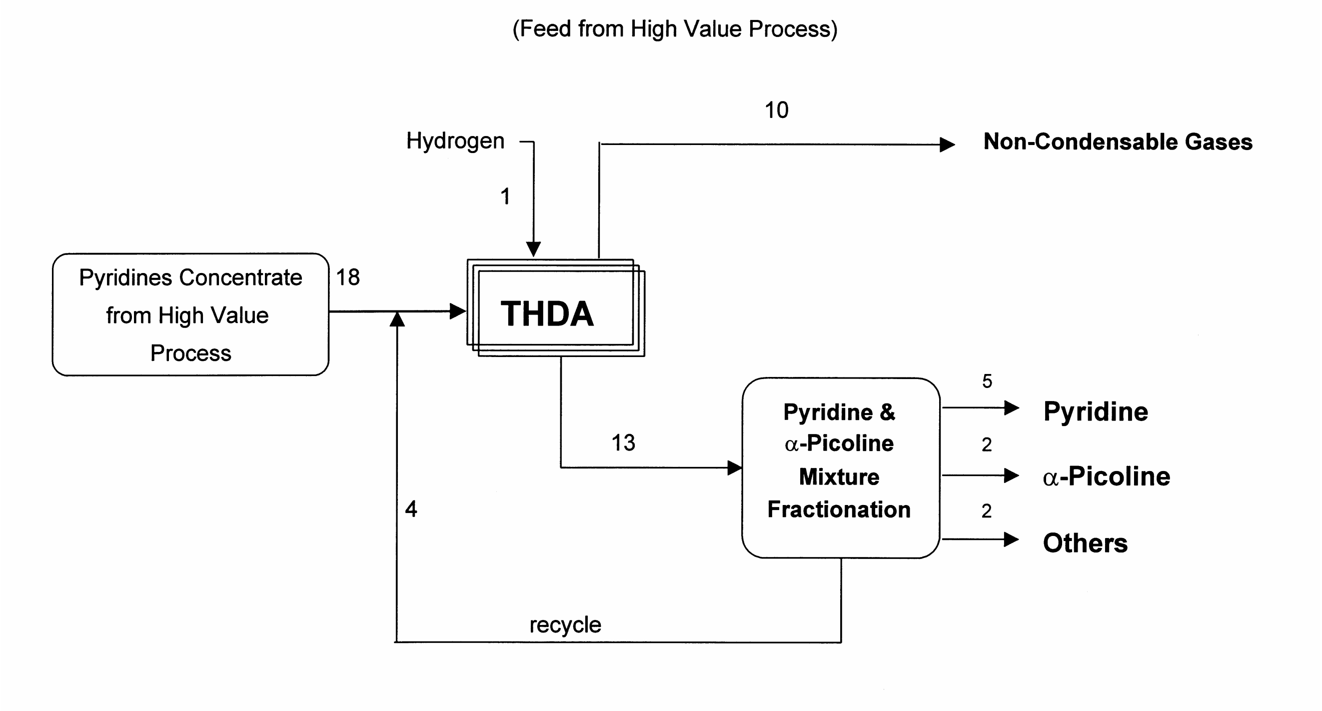


Figure 14.5: KPX Process Flow Diagram – High Capacity Case

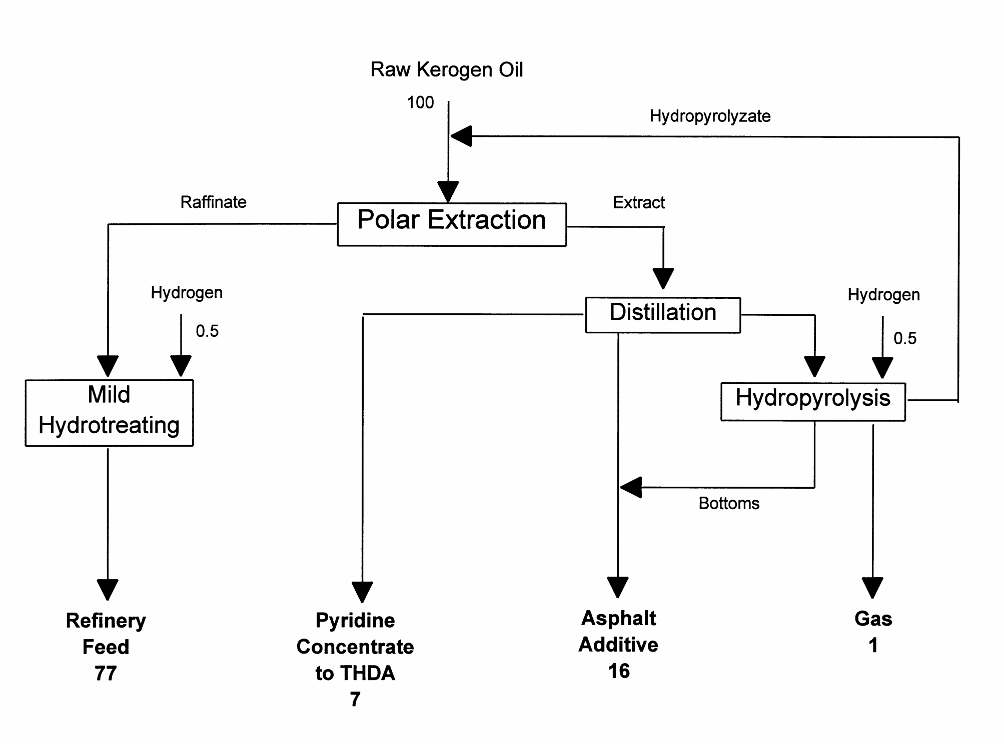
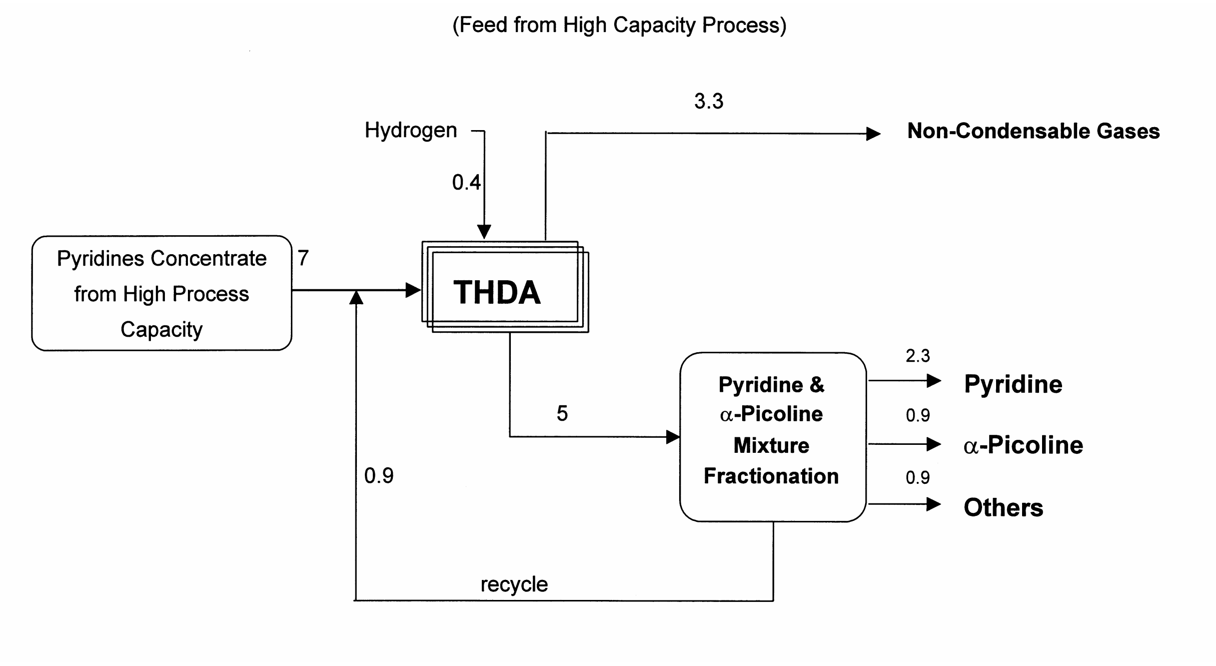


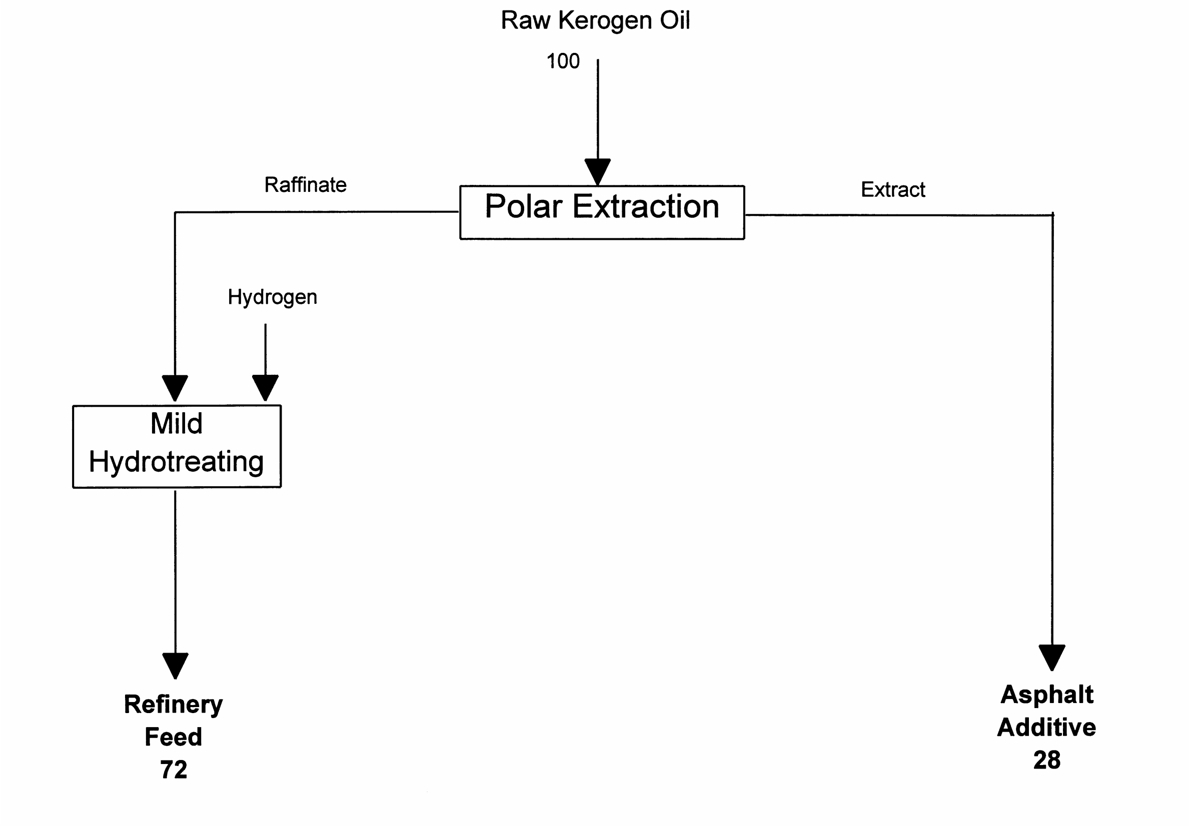
Figure 14.6: THDA Process Flow Diagram for High Capacity Case



14.5.3 Low Capital Case

The low capital case produces the minimum product slate with no secondary processing to pyridines. This case upgrades the raffinate by extraction and utilizes the extract for its use as an asphalt additive. Product market limitations will not be as significant at the scale contemplated as with the other two cases. This configuration is shown in Figure 14.7.

Figure 14.7: KPX Process Flow Diagram – Low Capital Case



14.6 Economics

14.6.1 Capacities and Capital Costs

Unit capacities are shown in the data in Figures 14.3-14.7 and are summarized in table form in Table 14.1. Inspection of the data in Table 14.1 shows significant differences in the cases. Pyridine and α-picoline production have been arbitrarily limited to 5% of the total world markets, a small enough amount that the product can be absorbed without seriously influencing the pricing structure. Asphalt additive is expected to readily penetrate North American markets (as they compete with expensive alkyl amines) and represents less than 1% of these markets. In addition to the economic promise of each case, the choice of process configuration and capacity will be influenced by the potential business partners that may have more or less interest in the various products.

Table 14.1: Summary of Unit Capacities

Unit	Capacity units	Low Capital 12,000 bbl/day	High Capacity 10,000 bbl/day	High Value 5,000 bbl/day
Extraction	bbl/day	12,000	11,300	6,650
Hydropyrolysis	bbl/day		1,500	2,350
THDA	bbl/day		800	1,100
Distillation	bbl/day		3,600	2,950
Hydrotreating	bbl/day	9,000	7,700	3,700
Purification	bbl/day		500	650
Hydrogen Plant	Mscf/day	4,000	7,000	5,000

14.6.2 Installed Costs

Installed costs for various units specified in Table 14.2, which are estimated based on commercial experience for similar units. The data used for reference capacities and their source is given in the table. The scaling factor is used in the traditional manner to adjust costs for actual capacities to the costs for the reference capacities.

Table 14.2: Installed Costs – 1999 (reference capacities)

Unit	Scaling Factor	Daily Capacity Bbl or MMscf	Installed Cost USD per daily bbl capacity	Source
Extraction	0.75	10,000	2,500	Hydrocarbon Processing (NMP)
Hydropyrolysis	0.75	20,000	4,000	HP (hydrocracking)
		2,000	7,000	Add extra for coke make
THDA	0.75	2,000	3,500	HP (toluene to benzene)
Distillation	0.70	10,000	2,500	HP
Hydrotreating	0.75	9,000	4,000	HP (UOP process)
Purification	n/a	650	5,000	Sommerville, 1972 (Nelson index adjusted)
Hydrogen Plant	0.75	3	\$5 million	Vendor estimate
		10	\$12 million	Vendor estimate

Combining the data in Tables 14.1 and 14.2 leads to the installed costs for units for each configuration. This data is given in Table 14.3. Common costs such as tankage and pipelines are added to each case. The high value case has more, smaller tanks and the low capital case has fewer, larger units, hence, no scaling factor was used. A remoteness and grass roots factor of 20% was added to adjust the costs, which are based on Gulf Coast installation. Capital costs will be adjusted in future evaluations as more details come to light. The costs shown in Table 14.3 are thought to be reasonable and provide a basis upon which to evaluate the profitability potential of a KPX value-enhanced processing venture.

Table 14.3: Installed Costs - 1999 Case Studies

	Millions - USD		
Unit	**Low Capital 12,000 bbl/day**	**High Capacity 10,000 bbl/day**	**High Value 5,000 bbl/day**
Extraction	29	27	19
Hydropyrolysis		12	18
THDA		4	5
Distillation		12	11
Hydrotreating	36	32	19
Purification		3	3
Hydrogen Plant	6	8	8
Tankage and Pipeline	4	4	4
Subtotal	75	102	87
Remoteness and Grass Roots Factor (20%)	15	20	17
Totals	90	122	104

14.6.3 Operating Costs

Operating costs were estimated for each of the units based on utility requirements and published information from sources similar to those shown for capital costs shown in Table 14.2. The data for each of the configurations are shown in Tables 14.4-14.6. Because published costs are based on \$/bbl a normalization is needed to account for the size of the units relative to the nameplate capacity. This is seen in the stream multiplier column. The weighted contribution of each unit to total operating costs is given in the final column and the sum is the average operating costs per barrel of feed.

Operating costs for the hydrogen plant were are more than offset by the value of the co-produced steam. This co-product was not factored as a credit, but will be highly important to supplying the heat energy for preheating, extraction and distillation. The hydrogen plant will be of a steam reformer type and will run on natural gas. Natural gas is produced in the same general locale of the probable site of a KPX operation and is expected to be available at reasonable cost. For the 1999 case fuel credits and costs, including natural gas, were taken at \$18/bbl-equivalent, or \$3/MM Btu.

14.6.4 Product Prices

Note to reader: This portion of the work was completed in the late 90s and reflects market prices at the time. A subsequent update is included in Task 14(b) below. The following economic assessments should be viewed as relative values, but not necessarily indicative of recent economic conditions, which now may be better because of firmness in commodity prices.

Five products, sweet refinery feed, pyridine and α-picoline, asphalt additive, aromatic chemicals (other chemicals) and fuel, are anticipated. Prices on a per barrel basis are shown in Table 14.7

Table 14.4: KPX High Value Case Operating Cost (5,000 bbl/day)

Unit	$/bbl	Stream Multiplier (1.0 = 5,000 bbl/day)	Weighted $/bbl
Extraction	1.76	1.33	2.34
Hydropyrolysis	3.52	0.47	1.65
THDA	2.51	0.2	0.55
Distillation	0.68	0.59	0.40
Hydrotreating	3.08	0.74	2.28
Purification	2.64	0.13	0.34
Total			7.56

Table 14.5: KPX High Capacity Case Operating Cost (10,000 bbl/day)

Unit	$/bbl	Stream Multiplier (1.0 = 10,000 bbl/day)	Weighted $/bbl
Extraction	1.55	1.13	1.75
Hydropyrolysis	4.00	0.15	0.60
THDA	2.72	0.08	0.22
Distillation	0.65	0.36	0.23
Hydrotreating	2.56	0.77	1.97
Purification	2.80	0.05	0.14
Total			4.91

Table 14.6: KPX Low Capital Case Operating Cost (12,000 bbl/day)

Unit	$/bbl	Stream Multiplier (1.0 = 12,000 bbl/day)	Weighted $/bbl
Extraction	1.52	1.00	1.52
Hydrotreating	2.50	0.72	1.80
Total			3.32

Table 14.7: Estimated Product Prices $/bbl

Pyridine and α-Picoline	500
Asphalt Additive	65
Other Chemicals (Pyrroles, etc.)	40
Sweet Refinery Feed	23
Fuel	18

The prices for the refinery feed are based on its projected value of \$5 over NYMEX prices, taken as \$18/bbl. The pyridine and α-picoline are priced at what is believed to be a competitive price for these chemicals. The asphalt additive price is derived by assuming that asphalt will increase in value by \$20/ton with 5% KPX additive blended. Such enhanced values are typical of current practice. The value of other chemicals, primarily aromatics, methylthiophenes and pyrroles, are taken at an average of about \$1.00/gallon. This value may prove either high or low depending on a number of factors including markets, purities, secondary processing requirements, etc. In any case the volume of such products is small and deviations in the average value do not have a major impact on economics. The fuel value is assumed to be equivalent to the feedstock price, which is a reasonable number for purposes of internal accounting.

14.6.5 Investment Analysis for Fixed Kerogen Oil Transfer Prices

Details of the economic analysis are given in Tables 14.8-14.10 for the high value, high capacity and low capital cases, respectively. These analyses are self-explanatory and provide the economic assumptions in the upper left hand boxes. Results show that at a transfer price of \$18/bbl for raw shale oil, all three cases present an attractive investment opportunity of greater than 25% IRR.

A summary of the investment analysis is given in Table 14.11. Table 14.11 shows that all three options provide an attractive return on investment. The high capacity case appears to have a slightly better investment opportunity in terms of IRR and NPV. This result suggests that the optimum plant will be a mix of high value pyridine products and asphalt additives.

The low capital option has the attractiveness of avoiding the pyridine markets for the first generation facility. Such markets may involve some early stage risk. The high value option has the attractiveness of maximizing the high value byproducts which could position the venture for diversification and growth. The high capacity option, in addition to showing good economics, has the attractiveness of lower severity and more conventional processing in the HP and THDA steps reducing some technical risk and costs in these areas. In the final analysis, market volume limitations on the key products will probably dictate the capacity and configuration of the process.

Table 14.8: KPX Venture Economic Analysis

High Value Case 4/28/99

Data

		User	Input	S.Factor
Products	bbl/day	5000	5000	1.00
Capital	$	**1.04E+08**	1.04E+08	1.00
Operating	$/bbl	**7.56**	7.56	1.00
Raw Material	$/bbl	**18.00**	18.00	1.00
Revenue (1)	$/yr	101878500	101878500	1.00
Revenue (2)	(wt.avg.) $/bbl	59	59	1.00
Royalties	% of Sales	4	4	1.00
Operation	days/yr	345	345	1.00
Life	Years	15	15	1.00
Admin.(incl. marktg) % of Op.		17%	17%	1.00
R&D	% of Sales	4%	4%	1.00
Equity		100.0%	100%	1.00
Debt Interest Rate		10.0%	10%	1.00
Discount Rate		10.0%	10%	1.00
Tax Rate		40.0%	40%	1.00
Loan	Years	15	15.0	1.00
Day	Hours	24	24	1.00

Revenue (1): based on pyridine products = 3.37 $/kg

Revenue (2): from petroleum products = 23 $/bbl

Products **1,725,000** **bbl/yr**

value $/bbl	revenue $/yr	101878500	Yield bbl/day
23	ref. feed	74	3700
500	pyridines	7	350
65	asphalt add.	6	300
40	other chem	2	100
18	fuel	13	650

IRR **25.5%**

NPV **9.89E+07**

Investment Schedule

year	amount
1	$3,924,528
2	$7,849,057
3	$86,339,623
4	$5,886,792
total	$104,000,000

Cash Flow Analysis

Production		0%	0.0%	75%	100%			
Year	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**18**
Revenue		0	0	76,408,875	101,878,500	101,878,500	101,878,500	101,878,500
-op.cost		0	0	(44,091,000)	(44,091,000)	(44,091,000)	(44,091,000)	(44,091,000)
-admin		0	0	(2,216,970)	(2,216,970)	(2,216,970)	(2,216,970)	(2,216,970)
-Dep.		0	0	(6,933,333)	(6,933,333)	(6,933,333)	(6,933,333)	(6,933,333)
-Royalties		0	0	(3,056,355)	(4,075,140)	(4,075,140)	(4,075,140)	(4,075,140)
-R&D		0	0	(3,056,355)	(4,075,140)	(4,075,140)	(4,075,140)	(4,075,140)
-Interest		0	0	0	0	0	0	0
Gross Income		0	0	17,054,862	40,486,917	40,486,917	40,486,917	40,486,917
-Tax		0	0	(6,821,945)	(16,194,767)	(16,194,767)	(16,194,767)	(16,194,767)
Net Income		0	0	10,232,917	24,292,150	24,292,150	24,292,150	24,292,150
+Dep				6,933,333	6,933,333	6,933,333	6,933,333	6,933,333
-Principal				0	0	0	0	0
+Borrowed Capital	0	0	0	0				
-Equity Capital	-3.92E+06	(7,849,057)	-8.634E+07	(5,886,792)				
Cash Flow	-3.92E+06	(7,849,057)	-8.634E+07	11,279,458	31,225,483	31,225,483	31,225,483	31,225,483
Cum. Cash Flow	-3.92E+06	(11,773,585)	-9.811E+07	-8.683E+07	-5.561E+07	(24,382,783)	6,842,700	350,323,017
DCF	-3.92E+06	(7,135,506)	-7.136E+07	8,474,424	21,327,425	19,388,568	17,625,971	6,177,795
NPV	-3.92E+06	(11,060,034)	-8.242E+07	-7.394E+07	-5.261E+07	(33,224,677)	(15,598,706)	98,883,053
IRR	**25.5%**							

Table 14.9: KPX Venture Economic Analysis

High Capacity Case 4/28/99

Data

		User	Input	S.Factor
Products	bbl/day	10000	10000	1.00
Capital	$	**1.22E+08**	1.22E+08	1.00
Operating	$/bbl	**4.91**	4.91	1.00
Raw Material	$/bbl	**18.00**	18.00	1.00
Revenue (1)	$/yr	156091800	156091800	1.00
Revenue (2)	(wt.avg.) $/bbl	45	45	1.00
Royalties	% of Sales	4	4	1.00
Operation	days/yr	345	345	1.00
Life	Years	15	15	1.00
Admin.(incl. marktg) % of Op.		17%	17%	1.00
R&D	% of Sales	4%	4%	1.00
Equity		100.0%	100%	1.00
Debt Interest Rate		10.0%	10%	1.00
Discount Rate		10.0%	10%	1.00
Tax Rate		40.0%	40%	1.00
Loan	Years	15	15.0	1.00
Day	Hours	24	24	1.00

Revenue (1): based on pyridine products = 3.37 $/kg

Revenue (2): from petroleum products = 23 $/bbl

Products **3,450,000** **bbl/yr**

value $/bbl		revenue $/yr	Yield bbl/day
		156091800	
23	ref. feed	77	7700
500	pyridines	3.2	320
65	asphalt add.	16	1600
40	other chem	0.9	90
18	fuel	4.3	430

IRR **27.5%**

NPV **1.35E+08**

Investment Schedule

year	amount
1	$4,603,774
2	$9,207,547
3	$101,283,019
4	$6,905,660
total	$122,000,000

Cash Flow Analysis

Production		0%	0.0%	75%	100%			
Year	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**18**
Revenue		0	0	117,068,850	156,091,800	156,091,800	156,091,800	156,091,800
-op.cost		0	0	(79,039,500)	(79,039,500)	(79,039,500)	(79,039,500)	(79,039,500)
-admin		0	0	(2,879,715)	(2,879,715)	(2,879,715)	(2,879,715)	(2,879,715)
-Dep.		0	0	(8,133,333)	(8,133,333)	(8,133,333)	(8,133,333)	(8,133,333)
-Royalties		0	0	(4,682,754)	(6,243,672)	(6,243,672)	(6,243,672)	(6,243,672)
-R&D		0	0	(4,682,754)	(6,243,672)	(6,243,672)	(6,243,672)	(6,243,672)
-Interest		0	0	0	0	0	0	0
Gross Income		0	0	17,650,794	53,551,908	53,551,908	53,551,908	53,551,908
-Tax		0	0	(7,060,317)	(21,420,763)	(21,420,763)	(21,420,763)	(21,420,763)
Net Income		0	0	10,590,476	32,131,145	32,131,145	32,131,145	32,131,145
+Dep				8,133,333	8,133,333	8,133,333	8,133,333	8,133,333
-Principal				0	0	0	0	0
+Borrowed Capital	0	0	0	0				
-Equity Capital	-4.60E+06	(9,207,547)	-1.013E+08	(6,905,660)				
Cash Flow	-4.60E+06	(9,207,547)	-1.013E+08	11,818,149	40,264,478	40,264,478	40,264,478	40,264,478
Cum. Cash Flow	-4.60E+06	(13,811,321)	-1.151E+08	-1.033E+08	-6.301E+07	(22,747,235)	17,517,243	460,426,501
DCF	-4.60E+06	(8,370,497)	-8.370E+07	8,879,150	27,501,180	25,001,073	22,728,248	7,966,112
NPV	-4.60E+06	(12,974,271)	-9.668E+07	-8.780E+07	-6.030E+07	(35,297,842)	(12,569,594)	135,051,764
IRR	**27.5%**							

Table 14.10: KPX Venture Economic Analysis

Low Capital Case 4/28/99

Data

		User	Input	S.Factor
Products	bbl/day	12000	12000	1.00
Capital	$	**9.00E+07**	9.00E+07	1.00
Operating	$/bbl	**3.32**	3.32	1.00
Raw Material	$/bbl	**18.00**	18.00	1.00
Revenue (1)	$/yr	143906400	143906400	1.00
Revenue (2)	(wt.avg.) $/bbl	35	35	1.00
Royalties	% of Sales	4	4	1.00
Operation	days/yr	345	345	1.00
Life	Years	15	15	1.00
Admin.(incl. marktg)	% of Op.	17%	17%	1.00
R&D	% of Sales	4%	4%	1.00
Equity		100.0%	100%	1.00
Debt Interest Rate		10.0%	10%	1.00
Discount Rate		10.0%	10%	1.00
Tax Rate		40.0%	40%	1.00
Loan	Years	15	15.0	1.00
Day	Hours	24	24	1.00

Products **4,140,000** **bbl/yr**

value $/bbl	revenue $/yr	143906400	Yield bbl/day
23	ref. feed	72	8640
500	pyridines		0
65	asphalt add.	28	3360
40	other chem		0
18	fuel		0

IRR **24.4%**

NPV **8.26E+07**

Investment Schedule

year	amount
1	$3,396,226
2	$6,792,453
3	$74,716,981
4	$5,094,340
total	$90,000,000

Cash Flow Analysis

Production		0%	0.0%	75%	100%			
Year	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**18**
Revenue		0	0	107,929,800	143,906,400	143,906,400	143,906,400	143,906,400
-op.cost		0	0	(88,264,800)	(88,264,800)	(88,264,800)	(88,264,800)	(88,264,800)
-admin		0	0	(2,336,616)	(2,336,616)	(2,336,616)	(2,336,616)	(2,336,616)
-Dep.		0	0	(6,000,000)	(6,000,000)	(6,000,000)	(6,000,000)	(6,000,000)
-Royalties		0	0	(4,317,192)	(5,756,256)	(5,756,256)	(5,756,256)	(5,756,256)
-R&D		0	0	(4,317,192)	(5,756,256)	(5,756,256)	(5,756,256)	(5,756,256)
-Interest		0	0	0	0	0	0	0
Gross Income		0	0	2,694,000	35,792,472	35,792,472	35,792,472	35,792,472
-Tax		0	0	(1,077,600)	(14,316,989)	(14,316,989)	(14,316,989)	(14,316,989)
Net Income		0	0	1,616,400	21,475,483	21,475,483	21,475,483	21,475,483
+Dep				6,000,000	6,000,000	6,000,000	6,000,000	6,000,000
-Principal				0	0	0	0	0
+Borrowed Capital	0	0	0	0				
-Equity Capital	-3.40E+06	(6,792,453)	-7.472E+07	(5,094,340)				
Cash Flow	-3.40E+06	(6,792,453)	-7.472E+07	2,522,060	27,475,483	27,475,483	27,475,483	27,475,483
Cum. Cash Flow	-3.40E+06	(10,188,679)	-8.491E+07	-8.238E+07	-5.491E+07	(27,432,634)	42,850	302,273,165
DCF	-3.40E+06	(6,174,957)	-6.175E+07	1,894,861	18,766,125	17,060,113	15,509,194	5,435,878
NPV	-3.40E+06	(9,571,184)	-7.132E+07	-6.943E+07	-5.066E+07	(33,599,655)	(18,090,461)	82,642,700
IRR	**24.4%**							

Table 14.11: Summary Investment Analysis

	Low Capital	High Capacity	High Value
Nameplate Capacity bbl/day	12,000	10,000	5,000
Investment (millions USD)	90	122	104
Average Product Value $/bbl	35	45	59
Revenues (millions USD/year)	144	156	102
IRR (15 yr)	24.4	27.5	25.5
DCF-NPV (10% discount rate, millions USD)	83	135	99

14.6.6 Investment Analysis at Fixed Return and Variable Transfer Price

To illustrate how significant the added value is to the kerogen oil price, consider the transfer price that could be paid and still maintain a 15% IRR for the three cases. Table 14.12 summarizes the results for the 3 cases.

Table 14.12: Raw Kerogen Oil Transfer Price for a Fixed 15% IRR

	Low Capital	High Capacity	High Value
Demand bbl/day	12,000	10,000	5,000
Transfer Price for Raw Kerogen Oil $/bbl	22.95	27.45	30.80
Revenues $/bbl (avg)	35	45	59
‘Spread’ (revenue-cost)	12.05	17.55	28.20

The table clearly illustrates that the high value process can afford to pay more for the kerogen oil. Should market volumes prove less limiting than projected, the capacity of the high value case may be increased with an even greater promise of profitability. The economic analysis shows that there is some price (the transfer price), higher than $18/bbl, that could be paid for raw kerogen oil and still establish a profitable venture.

14.7. Venture Plan

The next step will be to assemble a consortium of interested parties to carry the venture forward. This consortium will consist of selected parties from the candidates described in Figure 14.1 above. The projected development plan is based on the high capacity process. It is expected that consortium partners and their business interests along with market conditions will play an important role in the final configuration. Four future phases of development are contemplated:

Phase I - Confirmation and Feasibility - This planning phase will confirm the optimum plant configuration, market feasibility, and update the economics. Confirmation of process and product data will be performed, and this work will be used to specify the pilot plant work for Phase II. During this phase decisions will be made regarding plant location, utility and product transportation requirements, kerogen oil production technologies, product marketing options, permitting and licensing, venture agreements, financing options and other factors needed to complete the feasibility study. The cost for this phase is estimated at $ 2M (1999 estimate). Figure 14.8 "Milestone Schedule" illustrates the time line currently envisaged for the development program.

Phase II - Pilot plant studies will be performed on those units necessary to develop engineering data for detailed commercial design. Retorting, extraction, dealkylation and possibly the catalytic hydroprocessing technologies will all need to be run at a reasonable scale over a period of time. Because most of these technologies are already commercially established for other applications, it is expected that the piloting will be accomplished on a toll basis, reducing the cost of design and construction of equipment. During this phase environmental baseline studies needed for the permitting process will begin. Costs for this phase are estimated at $ 8M.

Phase III - The engineering phase consists of the final design, engineering and detailed cost estimates. Final permitting will be completed in this phase. The costs for this phase are $12M and are included in the capital cost estimate. A one year time frame is allocated for this phase.

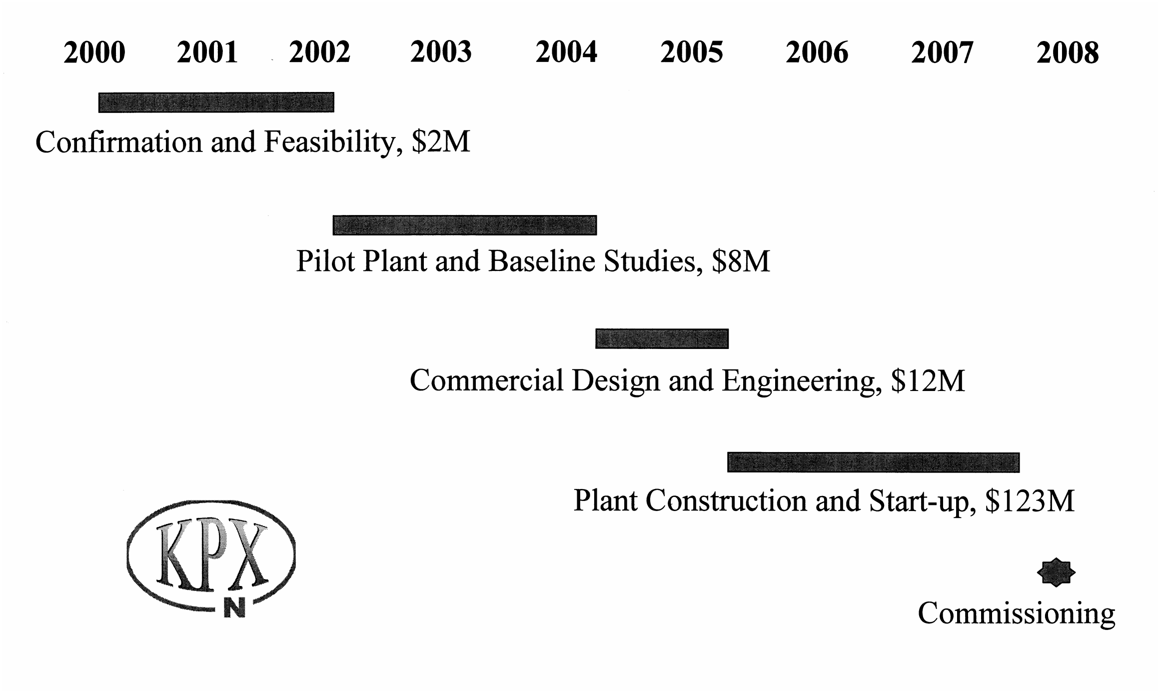
Phase IV - A two year plant construction period is expected. The construction will be conducted by a qualified engineering firm. Several firms have shown an interest in this project in part because it represents a first-generation facility that will tap the largest undeveloped hydrocarbon resource in the U.S.

Task 14 Conclusions

A central conclusion of this work is that value-enhanced technology provides a market for raw shale oil at prices substantially higher than this material could command as a refinery feed. At what transfer price it becomes economical to produce raw kerogen oil is a matter for the upstream sector to determine. Even so, KPX can provide a market incentive at a higher sales price for raw kerogen oil than for conventional processing to fuels. This result is very probably the most significant result of the current study.

Assurances that the economics are reasonable come from market (product) assurances and price trends. Production of competing products by synthesis routes are experiencing escalating feedstock costs even greater than petroleum costs are escalating. Entering an era where supply of commodities of all types are increasingly strained, it bodes well for VEP that kerogen oil is naturally rich in types that are experiencing escalating prices.

Figure 14.8: Milestone Schedule (ca 1999)



PHASE III CONCLUSIONS

Research showed strong and growing markets for products manufacturable from kerogen oil. On the extract side, markets exist for pure compounds, such as pyridine, picolines, pyrroles, indoles and phenols. Products for alkyl pyridine concentrates exist but some product and market development may be required. Asphalt additive products promise an outlet for the majority of nitrogen compounds. On the raffinate side, a premium refinery feedstock is manufactured by hydrotreating the low nitrogen raffinate. Product is acceptable to local refineries and with declining conventional oil production in the region, will not have difficulty with finding pipeline capacity or refinery acceptance.

Economics show:

a) The VEP process is most viable when the process is simple and the number of products requiring marketing is small.
b) At least one polar compound commodity product is needed to provide economy-of-scale to the venture.
c) Pure compounds command a high value, but will be required to meet exacting quality specifications.
d) There will be no price or market capacity limitations on the refinery feedstock product, as long as sulfur and nitrogen specifications are met.

Investment in the VEP process is deterred by lack of raw kerogen oil. All prospective buyers of products, or potential investors in VEP development cited lack of assured access to kerogen oil as a critical uncertainty. It was not sufficient that demand for the high value products might draw kerogen oil producers into the market. Under economic conditions that existed in the late 90s, the difficulty in bringing the disparate partners together proved problematic. However, the country of Estonia was already producing shale oil and the issues of assured supply would not exist in Estonia. Consequently, an additional phase of research was requested by DOE. Could the technology be applied to Estonia shale oil, creating a venture in Estonia, and thereby set a business model example that could be applied in the US?

PHASE IV - ESTONIA VEP

Introduction

In 2000 a cooperation agreement was signed between the US Dept. of Energy and the Ministry of Economy of Estonia[16]. Three phases of research were conducted under this program, somewhat analogous to the 3 phases previously completed on US kerogen oil.

- Phase-1 was an Exploratory Research phase in which processes concepts were explored for their effectiveness in producing high value products.

- Phase-2 was a Development phase in which process concepts were tested to obtain quantitative yield and product quality data under commercially-reasonable conditions.

- Phase-3 was a Feasibility Analysis phase in which the technical, market and economic feasibility of the process concepts developed in phases 1 and 2 were evaluated and a development plan was prepared.

Like US shale oil, Estonia shale oil is rich in heteroatoms that are the building blocks for potentially valuable products. Raw kerogen oil from Estonian shale contains high concentrations of oxygen compounds, primarily phenolics, while US kerogen oil contains high concentrations of nitrogen compounds, primarily pyridinics and pyrrolics. These heteroatoms (O and N) are undesirable for refinery feedstocks and are costly to remove when manufacturing a petroleum substitute. If the kerogen oil is to be used solely to produce a substitute for petroleum, the final product value will be dictated by world crude oil prices. But these same heteroatom-containing compounds may prove of higher value if extracted from the oil to produce commodity and specialty chemicals. The prospect of producing high yields of high-value chemicals, which partially uncouples the revenue ceiling from world crude oil prices, helps mitigate risks of low oil prices, and enhances investment attractiveness.

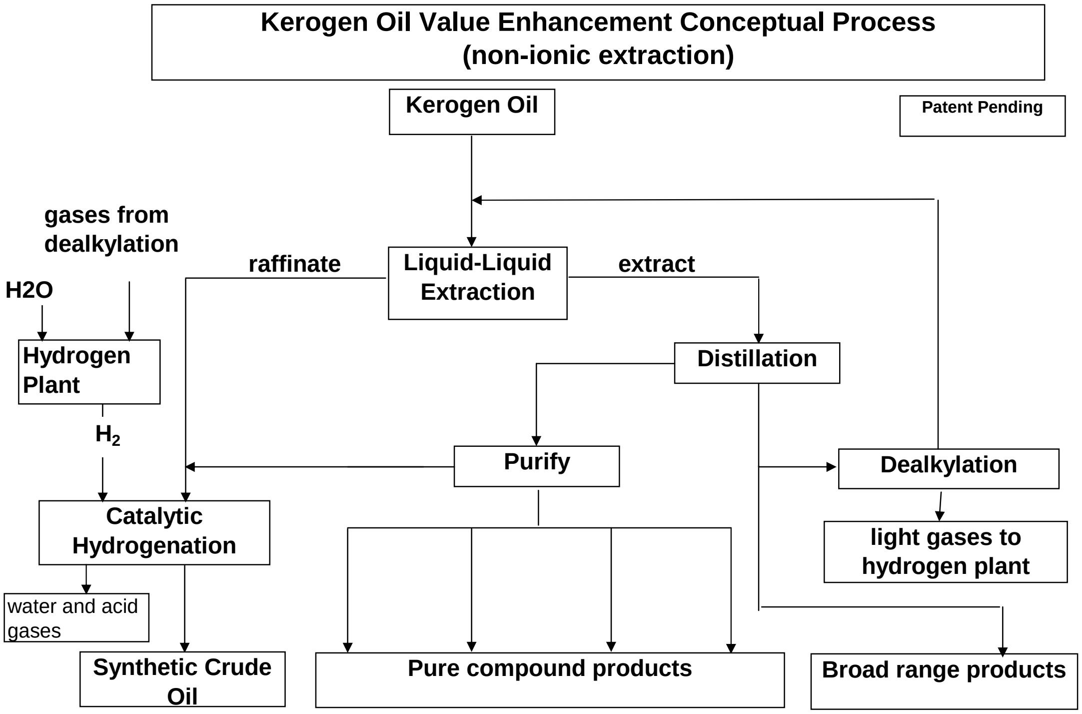
Task 12a - Product Manufacturing – Estonia

The generalized process scheme applied to Estonia shale oil (sometimes referred to as Kukersite kerogen oil, or KKO) is the same as that employed for the US case (see Figure12a.1). The techniques developed in the Phase – I - III of the US program were employed for the Estonia case, namely sophisticated analytical techniques, laboratory research on extraction systems, conversion process research, purification and product formulation studies and market research.

The research was performed on the Estonian kerogen oil manufactured in Kiviter and Galoter retorts. Economically, the most attractive scale for VEP processing in Estonia is for one plant that accepts all of the oil production. Hence, the two sources of oil were combined in their production proportions, 65% Kiviter and 35% Galoter, to simulate a possible commercial feedstock.

While some pure compound chemicals are produced in Estonia their production is derived from the 2% of the oil that is soluble in water. The present research does not duplicate this historic and current effort and instead focuses on the oil-soluble phenols. If the oil soluble phenols could be extracted, refined and marketed, this sequence would be highly analogous to that contemplated for US Green River Formation kerogen oil. Also, a greater percentage of the higher alkyl phenolics would be recovered enhancing overall yield. What is ideal is that if expanded markets could be found for Estonia products, which are predominately centered around hydroxyaromatics (mono- and di-hydric phenols) they would not compete with markets for US products, which are predominately centered around pyridines and pyrroles.

Figure 12a.1: VEP Process Scheme Applicable to Kerogen Oil



Statement of Work

Using existing equipment and techniques developed for the Green River Kerogen Oil produce products from Kukersite (Estonia) kerogen oil and estimate a plausible product slate.

Results

12a.1 Compositional Analysis

Analytical methods developed in prior tasks were applied to Kukersite kerogen oil (KKO) to identify compound types and develop the means of tracking partitioning in separation and conversion processing. A sample obtained by the PI during a visit in 1993, representing a middle distillate (~175 – 400 °C), was examined for its compound type composition. Table 12a.1 provides the range of homologous series for the 175- 350 °C portion. (At the time of original analysis Z-BaSIC was limited to types boiling above 350 °C. Subsequent analysis shows that all homologous series extend to the endpoint of the fraction.) Neutral oxygen types such as ketones and furans were searched for, but their presence could not be confirmed.

Table 12a.1: Compound Types and Carbon Range Found in Estonia Middle Distillate

Compound type (Series name)	‘z’ number $C_nH2_{n+z}N_uS_vO_w$	Carbon range Initial – 356 °C	Estimated Concentration wt% (similar, but not identical sample)
n-paraffins	+2	10-21	1-5
i-paraffins	+2	10-21	
monocycloparaffins	0	9-19	5-10
dicycloparaffins	-2	9-20	
tricycloparaffins	-4	12-15	
alkylbenzenes	-6	9-20	10-20
alkyltetralins	-8	10-20	
alkylindenes/dihydronaphthalenes	-10	11-19	
naphthalenes	-12	10-18	5-10
acenaphthenes	-14	12-18	
acenapthalenes/fluorenes	-16	12-16	
phenanthrenes/anthracenes	-18	14-15	0-5
thiophenes	-4S	7-17	1-5
benzothiophenes	-10S	8-18	
dibenzothiophenes	-16S	12-15	
phenols	-6O	10-18	10-20
vinylphenols	-8O	8-17	
naphthols	-12O	10-16	5-10
fluorenols	-16O	13-15	
resorcinols	$-6O_2$	8-14	10-20
dihydroxytetralins	$-8O_2$	10-15	

The major heteroatom distributions for the two oils are given in Figure 12a.2. The data show that the mole concentration of the nitrogen types in the GRKO are skewed to the heavy ends, as is typical of nitrogen distributions in fossil hydrocarbons. The oxygen distribution in the KKO is generally flat on a weight basis and actually declines on a mole basis with increasing molecular weight. Because kerogen oils are pyrolysis products with an upper boiling point limit, the average molecular weight of the heteroatom-containing compounds is lower than that for the hydrocarbons. This effect is more pronounced in the KKO than in the GRKO.

The study kerogen oils exhibit the characteristics shown in Table 12a.2. In general, only one nitrogen atom is found in each nitrogen-containing compound and the concentration of nitrogen is weighted toward the higher molecular weight (MW) range. The molar concentration of nitrogen-containing compounds is calculated to be about 37%. The KKO has high concentrations of resorcinols that contain more than one oxygen atom per oxygen-containing compound. The molar concentration of oxygen-containing compounds, assuming an average MW of 250 amu for oxygen-containing compounds and an average of 1.5 oxygen atoms per oxygen-containing molecule, is calculated to be about 60%. The mole percent concentration of heteroatom-containing compounds establishes the theoretical limits for an ideal separation between heteroatom-containing compounds and those hydrocarbons containing only H and C.

Figure 12a.2: Heteroatom Type Distribution in Kerogen Oils

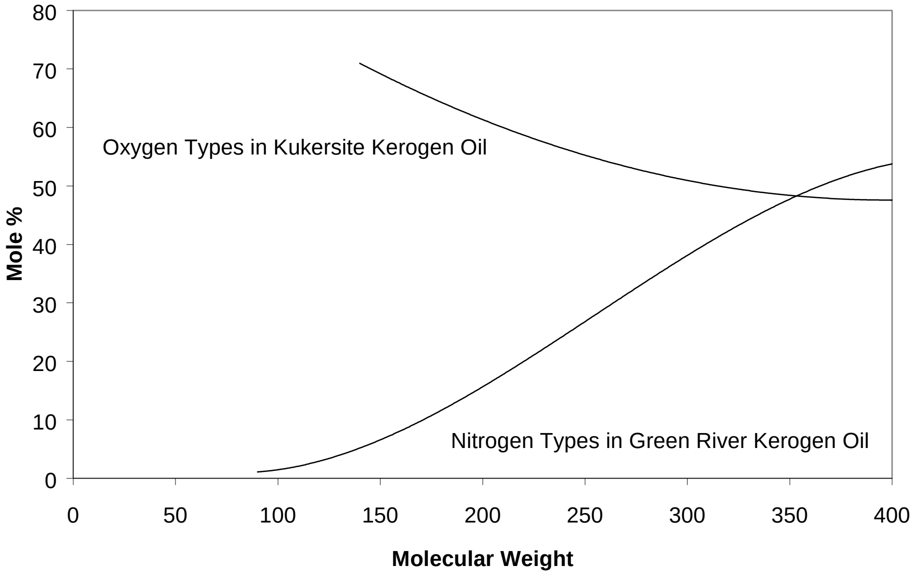


Table 12a.2: Elemental Composition and Bulk Properties of GRKO and KKO

Property	GRKO	KKO (water-free basis)
Carbon wt%	85.5	83.4
Hydrogen	11.7	9.9
Nitrogen	1.6	0.1
Sulfur	0.9	0.8
Oxygen	0.3 (by diff)	5.8 (direct)
Density g/cc	0.922	1.018
Avg. MW amu	325	290

12a.2 Extraction of KKO

Results of liquid-liquid extraction for the KKO are given in Table 12a.3. Results show an extract yield of 16% for the KKO. The extract is comprised almost entirely of oxygen-containing compounds. The overall extraction efficiency shows that while the extract is enriched, there remains a substantial amount of oxygen in the raffinate. It is not clear how the oxygen is bound in the raffinate molecules but GC-MSD analysis fails to reveal substantial quantities of phenolics, implying that the oxygen is bound in less polar environments such as furans.

Assuming an average of 1.7 oxygen atoms per oxygen-containing molecule (the extract is enriched in resorcinols compared to the unextracted oil) reveals a COS of 24% (27-3). A reasonable target for an economic separation is about 50%. Above this level, both recovery and selectivity are high.

Table-12a.3: Multi-stage Countercurrent Extraction of KKO

Property	Extract	Raffinate
Yield wt %	16	84
Avg. MW, amu	220	300
Oxygen wt%	11.3	4.8
Percent of O(5.8%) in feed	31	69
Avg # of O in molecule	1.55	0.9

The extraction of the KKO shows a low COS, however, which is due to the low recovery of heteroatom-containing compounds. The selectivity is very high as the extract is virtually 100% phenols and resorcinols. Additional research is required to improve the recovery without sacrificing selectivity.

To better understand the KKO extraction at the molecular level, key compounds were analyzed. Results are given in Table-12a.4. The partition ratio is the concentration of a given component found in the extract divided by the concentration in the raffinate. A partition ratio of 1 means the concentrations are equal. Comparison is made between compounds of like molecular weight. Because higher molecular weight favors partitioning toward the raffinate, holding this variable constant is necessary to interpret polar and aromaticity effects. (Selected aromatic hydrocarbons are included in the comparison as a benchmark for compounds not desired in the extract.)

Table 12a.4: Partition Ratio and Recovery Results (KKO)

Light components	Partition ratio	% recovery in extract
C_1 alkyl naphthalenes 142amu	0.77	12.8
C_3 phenols 136amu	14.2	73.1
Naphthols 144amu	6.62	55.8
C_2 resorcinols 138amu	164	96.9
Mid-range components		
C_1 triaromatics 192amu	0.84	13.9
C_7 phenols 192amu	2.03	27.9
Phenanthrenols 194amu	5.61	51.7
C_6 resorcinols 196amu	66.0	60.5
Coefficient of separation	COS	
C_2 resorcinols - C_1 alkyl naphthalenes	84.1	
C_3 phenols - C_1 alkyl naphthalenes	60.3	
naphthols - C_1 alkyl naphthalenes	43.0	
C_6 resorcinols - C_1 triaromatics	46.6	
phenanthrenols- C_1 triaromatics	37.8	
C_7 phenols - C_1 triaromatics	14.0	

Results show that phenols and resorcinols are preferentially extracted compared to aromatic hydrocarbons, as expected. However, the recoveries fall off with increasing molecular weight as the longer alkyl chains drive the oxygenated compounds toward the raffinate. Recoveries of heavy, e.g. >250 Dalton, components are even less.

The COS results show similar trends. When deciding how to optimize the COS a choice must be made. Improving the recovery of monohydric phenols runs the danger of simultaneously recovering undesirable polycondensed aromatic hydrocarbons. Clearly, optimum recovery and selectivity has not yet been achieved and additional work will be required to optimize the extraction of KKO before commercial design can commence. Nevertheless, well over half of the most desirable components, resorcinols, are recovered in only 16% of the oil as extract. The analytical tools exist to perform this optimization at the fundamental, molecular level, a significant advancement over prior empirical methods.

12a.3 Conversion

The objective of conversion processing of the extract is to make the oxygenated compounds more marketable or to increase the yield of marketable products. For this latter case dealkylation of phenolic compounds to lower alkyl phenols is desirable.

12a.3.1 Catalytic Cracking

Kukersite extract was subjected to catalytic cracking in a semi-batch micro-reactor (fixed bed – flowing feed). The catalyst was an equilibrium catalyst supplied by a local Salt Lake City refinery. Temperature of the bed was 497 °C. Conditions were deliberately chosen so as not to overcrack. Results are shown in Table 12a.5.

Table 12a.5: Results of Catalytic Cracking of KKO Extract

Compound/fraction	Feedstock Concentration %	Product concentration % (Feed Basis)	% change in yield
phenol	.0044	.0366	732
cresols	.0396	.205	418
dimethylphenols	.0867	.349	303
resorcinol	.049	.072	47
5-methylresorcinol	0.61	0.43	-30
5-heptylresorcinol	0.84	0.48	-43
5-dodecylresorcinol	0.11	0.08	-27
Total <230°C material	1.74	18.80	980
Total <300°C material	20.58	38.78	88

Results of catalytic cracking show substantial conversion of higher molecular weight material to lower molecular weight. Results show that monohydric phenols were increased by several hundred percent, and the concentration of resorcinol was also increased. However, the net loss of 5-methyl resorcinol suggests that some of the mono-hydric phenol production is occurring through dehydroxylation of dihydric phenols. Because dihydric phenols are more valuable than monohydric phenols, this competing reaction is undesirable and further efforts are needed to determine how dihydric phenols can be dealkylated without the loss of hydroxyl groups.

12a.3.2 Aquathermolysis

The prospect of using aquathermolysis was explored. KKO extract was first converted to its sodium salt with NaOH and then exposed to pressurized water at 314°C for 9 minutes and

320°C for 13 minutes. The samples were acidified, extracted with ethyl acetate and the recovered organics analyzed by GC-MSD. Results are given in Table 12a.6. The data show the change in parent phenol (94), resorcinol (110), mono-substituted phenols (108, carbon numbers 1 to 9) and mono-substituted resorcinols (124, carbon numbers 1 to 12).

Table 12a.6: Aquathermolysis Results

FEED					Product #1					Product #3			
					314°C (9 min into run)					320°C (13 min into run)			
Total area	7,159,571,722				Total area	5,382,611,483				Total area	7,609,799,682		
Conc.	19,338	mg/l			Conc.	12,747	mg/l			Conc.	15,299	mg/l	
counts/mg	370,233				counts/mg	422,265				counts/mg	497,405		
					Corr fact	0.876780				Corr fact	0.744330		
ion	No.	Time	Area		Time	Area	Corr area	% of feed		Time	Area	Corr area	% of feed
94	1	10.897	660123		10.937	255585	224091.716	33.95		10.887	1153568	858635	130.1
108	1	14.006	2280610		14.021	657318	576323.018	25.27		14.029	2910158	2166117	95.0
	2	22.2	1028791		22.229	506499	444087.995	43.17		22.211	1165758	867708	84.3
	3	24.722	1651580		24.714	1044480	915778.765	55.45		24.72	2345071	1745506	105.7
	4	27.128	1283097		27.112	831270	728840.585	56.80		27.125	1803360	1342294	104.6
	5	29.437	1358216		29.416	1095316	960350.733	70.71		29.436	1846106	1374111	101.2
	6	31.632	1746168		31.613	1611541	1412966.29	80.92		31.63	2122098	1579540	90.5
	7	33.733	1025031		33.719	767163	672632.874	65.62		33.731	1230096	915597	89.3
	8	35.737	887008		35.722	711080	623460.444	70.29		35.736	996260	741546	83.6
	9	37.671	537977		37.651	545881	478617.329	88.97		37.672	559083	416142	77.4
110	1	20.596	3968098		20.563	2554824	2240017.58	56.45		20.599	3439106	2559828	64.5
124	1	23.135	61627113		22.983	36426626	31938122.9	51.82		23.048	11661916	8680310	14.1
	2	27.384	9241689		27.345	6392292	5604631.27	60.65		27.365	1769377	1317000	14.3
	3	29.631	24164311		29.6	15392878	13496161.5	55.85		29.62	4009512	2984399	12.4
	4	31.761	45517430		31.72	38813119	34030551.3	74.76		31.704	8430323	6274939	13.8
	5	33.788	37912365		33.761	35633654	31242861.2	82.41		33.752	6406700	4768697	12.6
	6	35.783	60736625		35.757	54942885	48172801.2	79.31		35.736	12685398	9442118	15.5
	7	37.668	59995377		37.643	58090723	50932761.3	84.89		37.638	12833939	9552681	15.9
	8	39.456	29105480		39.451	25945937	22748868.5	78.16		39.45	5647723	4203768	14.4
	9	41.196	17032994		41.198	14961337	13117795.2	77.01		41.204	3212755	2391349	14.0
	10	42.885	11944109		42.89	11648846	10213470.6	85.51		42.887	2514339	1871497	15.7
	11	44.513	4738652		44.522	5679156	4979368.17	105.08		44.517	906422	674677	14.2
	12	46.084	2010937		46.096	3033345	2659575.04	132.26		46.084	736235	548002	27.3

Compared to the feedstock material, phenol appears to initially decline, but gains in yield as the reaction progresses. The yield of alkyl phenols also increases with time. Conversely, the higher alkyl resorcinols are cracked in the pyrolysis, but do not result in higher concentrations of parent resorcinol. These results are interpreted as evidence that dehydroxylation of the first hydroxy group on resorcinol is faster than dealkylation. Because the parent molecules (of both phenol and resorcinol) show a greater loss than the higher alkyl homologs at 314 °C of each type, we further conclude that the monohydric hydroxy group is also preferentially lost, compared to the alkyl groups.

The observation that the parent molecules have a higher yield at the higher temperature than at the lower temperature suggests that the activation energy for the dehydroxylation reaction is lower than that for the dealkylation. Theoretically, this suggests that a flash pyrolysis at higher temperature and shorter residence time would enhance the relative rate of dealkylation compared to dehydroxylation. However, since both are occurring and dehydroxylation is faster at lower temperature, it is unlikely that satisfactory results would be achieved even under flash pyrolysis conditions. For these reasons it was decided to postpone further work using this approach.

12a.3.3 Reverse Friedel Crafts

The need for a viable dealkylation step still looms as an important hurdle to cross. Reverse Friedel-Crafts has been proposed as a possible approach. The theoretical basis for this is that in thermodynamically controlled catalytic reactions the reverse reaction should be favored at higher temperatures if the reaction is endothermic and lower temperatures if the reaction is exothermic. The dealkylation reaction is slightly endothermic. However, the dehydroxylation reaction is also slightly endothermic, but less so than the dealkylation reaction. This suggests that higher temperatures will favor dealkylation relative to dehydroxylation, and it may prove that a Friedel-Crafts catalyst would provide a degree of selectivity.

Anhydrous $AlCl_3$ was added at 5.5% weight percent of a total Kiviter extract and gradually heated in a pot still at ambient pressures. Vapor production and overhead liquid production were monitored as a function of temperature. At about 80 °C when the sample softened and the first integral mixing of the $AlCl_3$ occurred, a strong exothermic reaction was observed, raising the temperature quickly to over 90 °C.

As the temperature was raised periodic liquid samples were taken for GC-MSD analysis. At about 280 °C a small surge of gas production was observed. Above 300 °C reaction water was seen condensing in the condenser. This gave cause to be concerned that dehydroxylation was occurring. The reaction was terminated at 320 °C. Above this termination temperature thermal reactions will occur and would not necessarily be catalytic. In addition to the periodic samples taken, final liquid from the pot was analyzed by GC-MSD. All samples were found to exhibit little change from the starting material.

The interpretation of this experiment is that the catalyst in Friedel-Crafts alkylation does not act as a catalyst for the reverse reaction. This finding is consistent with the mechanism that when alkylating the catalyst first forms carbonium ion from the olefin bond in the alkylating group, and it is this ion that attacks the aromatic ring. The reverse reaction does not occur, apparently because the catalyst is not directly involved with the actual alkylation step. Resolving the alkyl phenol dealkylation problem is one of the remaining technical challenges for maximizing the value of KKO.

12a.4 Analysis and Extraction of Galoter Oil

Because much of the historic value enhancement work had been conducted on Kiviter oil, a special study of the Galoter oil was warranted.

12a.4.1 Elemental Composition

Approximately 65 kg of Galoter oil was received from the Oil Shale Institute of Tallinn Technical University. The oil was dried by Dean Stark distillation and found to contain 0.4% water. The elemental composition of the water-free Galoter oil is given in Table 12a.7.

Table 12a.7: Elemental Composition and Density of Galoter Oil (wt %)

Carbon	81.81
Hydrogen	9.68
Nitrogen	0.20
Sulfur	0.74
Oxygen (direct)	7.57
H/C (atomic)	1.41
Density g/cc	0.987

12a.4.2 Chromatographic Traces

A chromatographic trace of the total oil is shown in Figure-12a.3 and reveals substantial light ends that are not present in the Kiviter study oil (see Figure -12a.4 to follow). Analysis of the chromatograms indicates that the Galoter oil contains lower concentrations of resorcinols than the Kiviter oil. However, the elemental composition shows a higher oxygen content for the Galoter oil (7.57% vs 5.8%).

Figure 12a.3: GC-TIC Total Galoter Oil

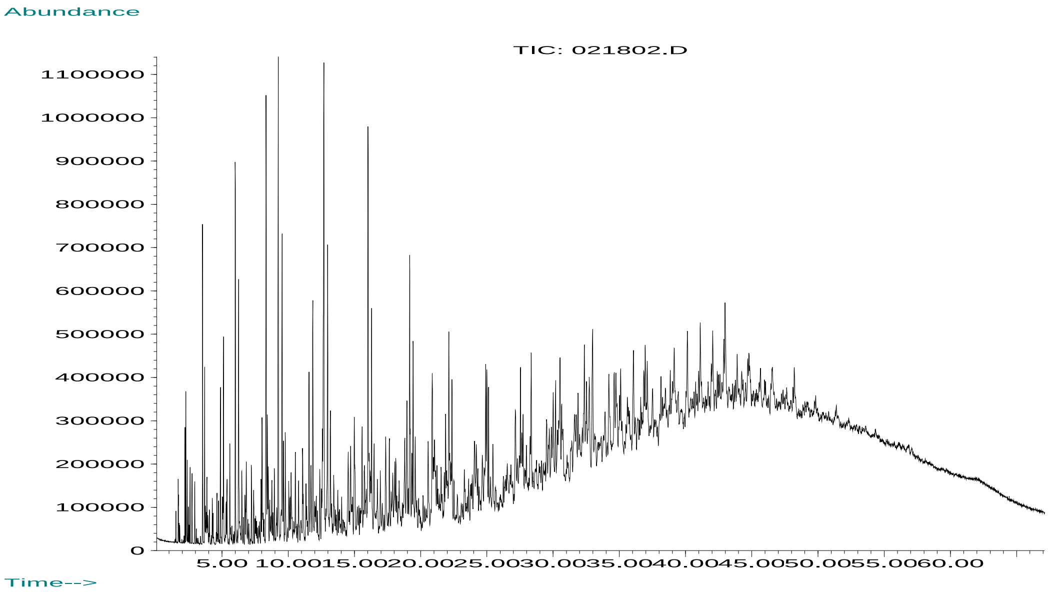
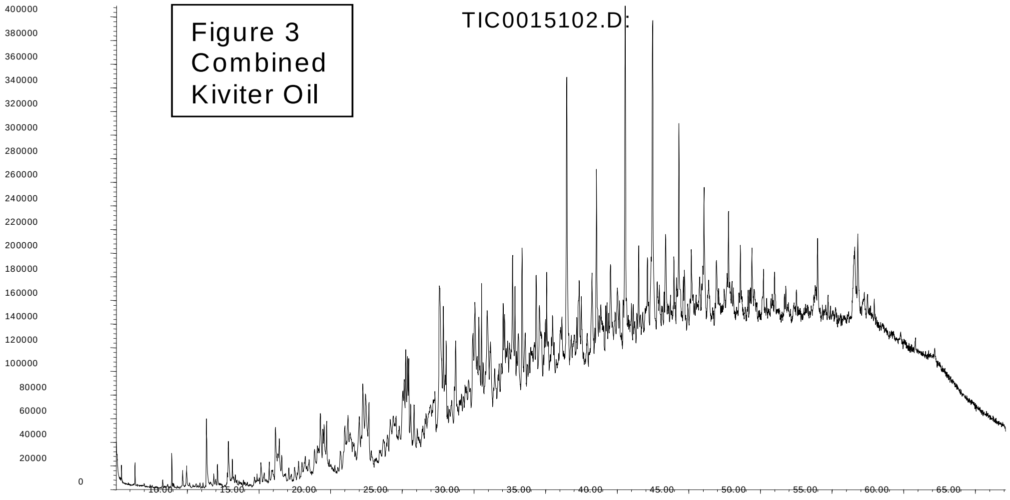


Figure 12a.4: GC-TIC Total Kiviter Oil



12a.4.3 Compound Types found in Galoter Oil

A Z-BaSIC™ analysis of the Galoter oil was performed. The Z-BaSIC™ method provides a quantitative analysis by compound type and carbon number. A survey was first made of the compound types present. Table 12a.8 lists the oxygen types found. High-value pure compounds will very likely derive from the types listed.

Because some of these types were not identified in the earlier Kiviter oil there is some development work required to complete the quantitative portion.

Table 12a.8: Oxygen Compound Types found in Galoter Oil

aliphatic ketones
hydroxy-biphenyl or vinyl naphthalenol
keto-olefins
dibenzofuran
fluorenols
resorcinols
furans
phenols
dihydroxy styrenes or dihydroxy tetralins
dihydroxy benzofurans (possible)
pyrene diol
phenyl naphthalenol
vinyl phenol or hydroxy tetralin
alkyl phenones (possible)
dihydroxy indenes (possible)
pyrene-ol
benzofuran
indenols
naphthalene diols (possible)
naphthalenols or vinyl indenols

12a.4.4 Extraction of Galoter Oil

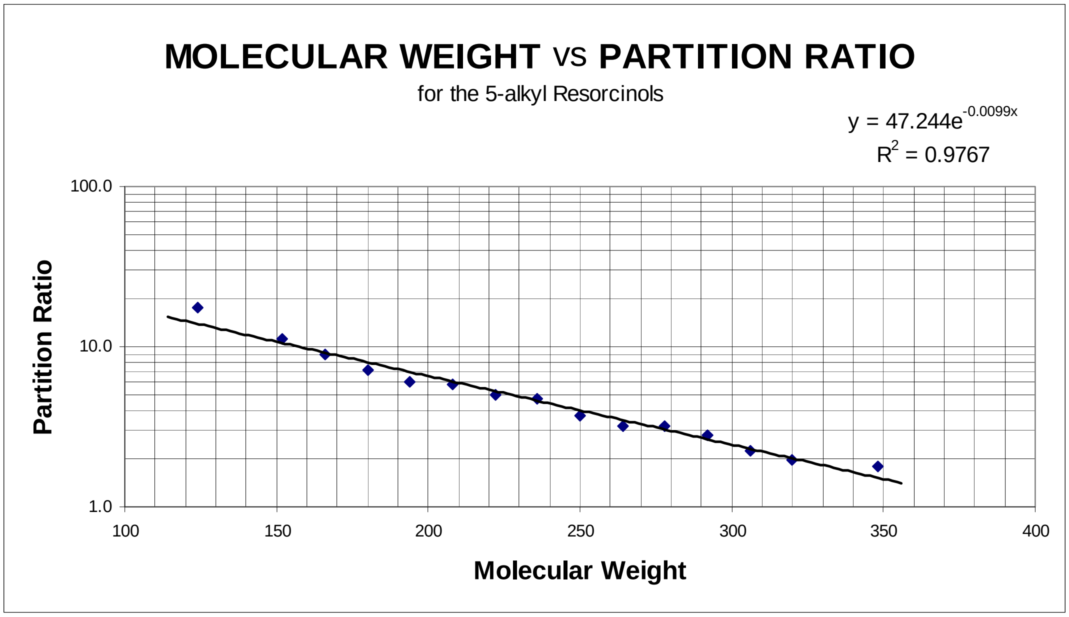
A sample of total Galoter Oil was extracted by the non-ionic batch system. The overall mass balance was 22.3% extract and 77.7% raffinate. Elemental analyses of the water-free feed, extract, and raffinate are shown in Table 12a.9.

Table 12a.9: Elemental Balance on Galoter Oil Extraction

	Feed	**Calc. Feed**	**Extract**	**Raffinate**
			Yield Fr. 0.223	**Yield Fr. 0.777**
C	81.81	81.81	78.79	82.72
H	9.68	9.56	8.63	9.83
N	0.20	0.22	0.42	0.17
S	0.74	0.65	0.77	0.62
O	7.57	7.72	11.40	6.66
H/C	1.41	1.39	1.30	1.42

A chart of partition ratio vs. MW was prepared for the 5-alkyl resorcinols (see Figure 12a.5). The partition ratio is the relative concentration of a component in the extract compared to the raffinate. A ratio of 1 indicates there is no preference for the compound between the extract and the raffinate. Results show a strong partition ratio (>10) for the lower molecular components, but less than 2 for the 5-heptadecyl resorcinol. The reduction in partition ratio with increasing molecular weight is generally observed for all oils and reflects the fact that as alkyl chain length increases, the molecule becomes more oleophilic. For a yield of extract of 22.3%, this means that 34% of the 5-heptadecyl resorcinol is recovered. Further research will be needed to find the extraction conditions that recover a higher percentage of the higher alkyl resorcinols.

Figure 12a.5: Molecular Weight vs Partition Ratio for 5-alkyl Resorcinols



Analysis of the separation was conducted on individual species. These results are shown in Table 12a.10. The low coefficient-of-separation (COS) for the higher molecular weight compounds illustrates the nature of the problem. For the conditions studied the raffinate is not rejecting enough of the polar compounds, while the extract is solvating too many of the non-polar aromatic hydrocarbons. Note, that all COS comparisons made in Table 12a.10 are between components of like molecular weight in an attempt to interpret the performance based on ring systems and polar functionality. A COS of 50% for the key separation is thought to be in the economic regime. The current results suggest that a target for improving the coefficient-of-separation between the C_7 phenols and the methyl phenanthrenes may result in the desired separation for the broader goal of selective isolation of phenols from aromatics.

Results show high enrichment of oxygen in the extract, but less-than-desired recovery. Using a MW of 220 Dalton for the oxygen types and an average of 1.5 oxygen atoms per molecule a coefficient of separation for all oxygen compounds of 33% is calculated. These results are similar to those determined for the Kiviter oil.

12a.4.5 Lower Alkyl Resorcinol Products from Galoter Oil

Because the Kiviter retort produces a water soluble phenol stream as part of its process could a similar stream be produced from the Galoter oil by simply washing the oil with water? In other words, if a first generation product comprised of lower alkyl resorcinols is developed, could the Galoter oil also be a source of these products?

Table 12a.10: Water Extraction Results

Parameter	single-stage	
Process yields (weight percent)		
Extract	22.3	
Raffinate	77.7	
Partition ratio and recovery results		
Light components	Ratio	Recovery
C_1 alkyl naphthalenes	1.01	22.40
C_3 phenols	2.78	44.38
Naphthols	3.46	49.82
C_2 resorcinols	21.96	86.31
Mid-range components		
C_1 triaromatics	1.06	23.26
C_7 phenols	1.95	35.93
Phenanthrenols	2.86	45.04
C_6 resorcinols	5.89	62.82
COS results	COS	
C_2 resorcinols - C_1 alkyl naphthalenes	63.91	
Naphthols - C_1 alkyl naphthalenes	27.42	
C_3 phenols - C_1 alkyl naphthalenes	21.98	
C_6 resorcinols - C_1 triaromatics	39.56	
Phenanthrenols- C_1 triaromatics	21.79	
C_7 phenols - C_1 triaromatics	12.67	

Results show that the lower alkyl phenols are nearly completely extracted by both systems (see Figures 12a.6 and 12a.7). The NaOH system extracts a much higher percentage of the higher alkyl phenols. Neither give a clean separation of phenols from non-phenols and the orcinol is a small percentage of the total extract in both cases. In fact, orcinol (marked with arrows) is a higher concentration in the water-only extract. The results suggest that such phenols could readily be recovered, the question being whether this sequence would be economically feasible. It was determined that a suite of products could be manufactured from the Galoter oil similar to those identified from the Kiviter oil, albeit the yields were somewhat different.

12a.5 Summary Results of Research conducted in Estonia

During the course of research, the Estonia side concentrated on ionic extraction of oil-soluble phenols. To add this perspective to the value-enhancement process, this research is summarized below.

Figure 12a.6: GC-TIC Water Extract

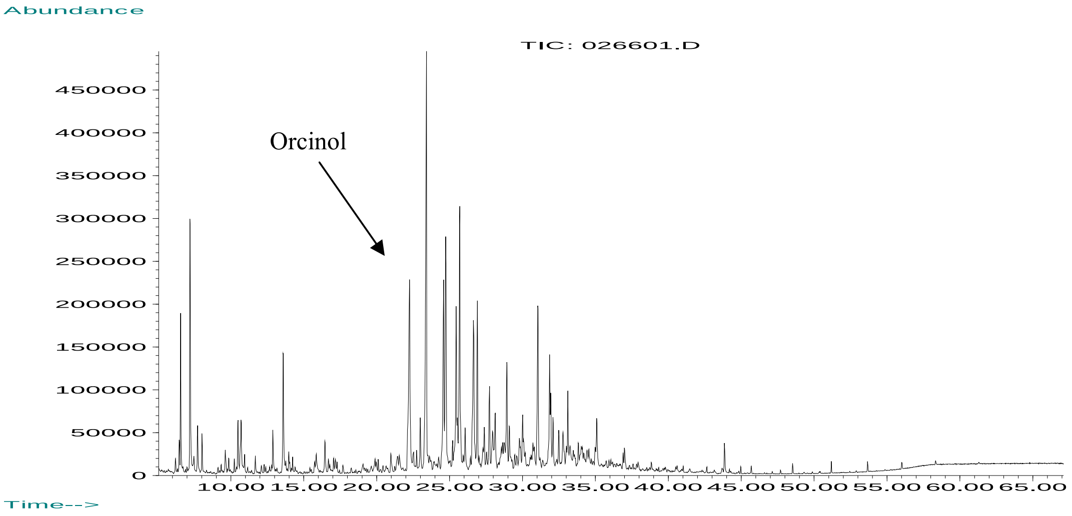
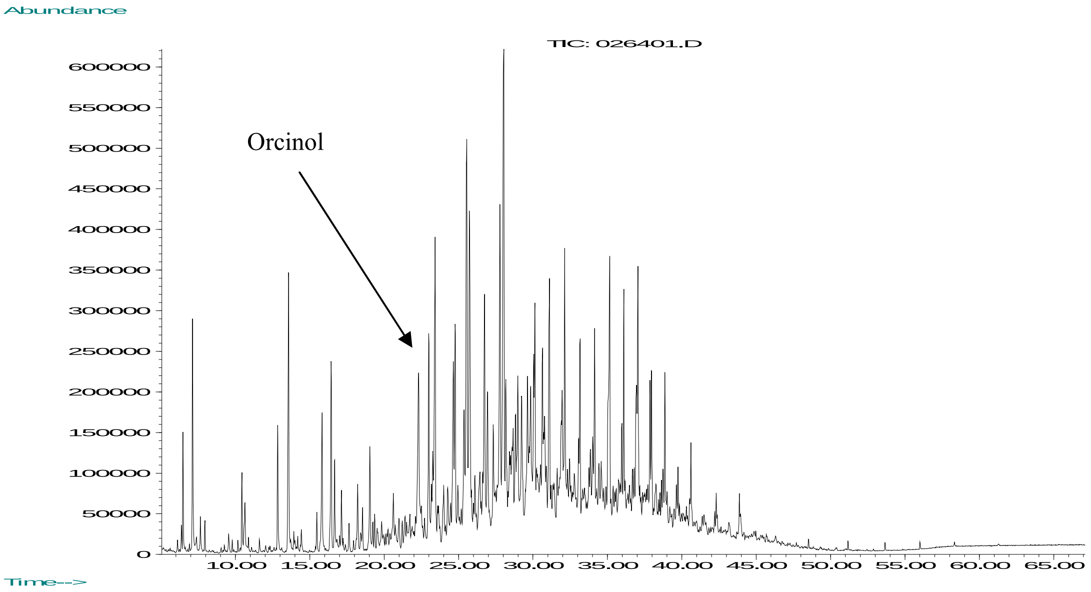


Figure 12a.7: GC-TIC NaOH Extract from Galoter Oil



12a.5.1 Extraction of Phenols from Mixture of Kiviter and Galoter Shale Oils

The extraction of oil-soluble phenols from shale oil with alkali is an alternative method to the non-ionic extraction method. Ionic extraction has the advantage of greater selectivity and recovery, but has the disadvantage of high solvent consumption and greater waste product management. The process involves a sequence of chemical reactions as follows:

1. Phenols are extracted from distillate or residue shale oil fractions with water solution of 10% caustic soda. In this step phenols are converted to sodium phenolates, which

dissolve in water: (PhOH)oil + NaOH = PhONa + H_2O. Significant amounts of neutral oil compounds are co-dissolved or entrained in the phenolates solutions, although high efficiency countercurrent extraction may be employed to minimize this effect.

2. Neutral oils are extracted from phenolate solution with hydrocarbons (petrol, benzene, toluene).

3. Phenolates are neutralized with carbon dioxide or other mineral acid:
PhONa + CO_2 + H_2O = PhOH (free phase) + $NaHCO_3$.

4. Neutralized phenol oil (dephenolized oil) is washed with water to remove salts.

5. Caustic soda is recovered from sodium bicarbonate solution with lime.
$NaHCO_3 + CaO \rightarrow NaOH + CaCO_3$.

The sum equations of chemical separation of phenols from oil is:
PhOH (in oil) + CaO + CO_2 = PhOH (free phase) + $CaCO_3$.

The material balance of extraction of phenols from total shale oil of the Kiviter and Galoter processes and washing of dephenolized oil with water is shown in Table 12a.11. The experimental data were obtained from enlarged laboratory scale separation tests of the oil. The data are based on 1 tonne of cleaned shale oil.

Table 12a.11: Material Balance of Extraction of Phenols and Neutral Oils from Total Shale Oil of Kiviter and Galoter Processes and Washing of Dephenolized Oil

Input Item	Kg	Output Item	Kg
Clean shale oil	1,000	Raffinate	590
10% NaOH solution	1,600	Neutral oils	132
Wash water	1,700	Phenolate solution	1,828
		Alkaline phenol water	1,750
Totals	4,300		4,300

The phenolate solution is fed into neutralization column by high-pressure pumps from the phenol extraction unit through heat exchanger, where it is heated to 70–75 °C. Gas containing 14–15 % vol. of CO_2 enters under 25-30 bar pressure is contacted countercurrently with the phenolates to form sodium carbonate and bicarbonate and free phenols:

$$2\ ArONa + CO_2 + H_2O \rightarrow 2\ ArOH + Na_2CO_3$$
$$Na_2CO_3 + CO_2 + H2O \rightarrow 2\ NaHCO_3$$
(Ar = aryl radical)

For better separation of phenols from the soda solution, toluene is added and mixed with the solution. The mixture is separated in a decanter and phenols solution is processed for its chemical values and the solution of sodium carbonates is moved to caustic soda recovery unit.

The steps are summarized as follows:

1. Neutralization of phenols with sulfuric acid, separation of sulfate solution and draining off the solution.

2. Washing of phenol-toluene mixture with phenol or industrial water.
3. Separation of phenol-toluene mixture from phenol water.
4. Distillation of phenol-toluene mixture.

The material balance of neutralization of phenolates is shown in Table 12a.12. The phenolates originate from processing of Kiviter and Galoter total shale oil at the phenol extraction unit. The input quantity of phenolate solution corresponds to 1 tonne of cleaned oil. Consumptions of retort gas and sulfuric acid for neutralization are based on design figures for commercial unit that had been operating.

Table 12a.12: Material Balance for Neutralization and Recovery of Phenolates

Input Item	Kg	Output Item	Kg
Phenolate solution*	1,828	Phenols	270
Retort gas including 130 kg CO_2	520	Carbonate solution	1,558
Concentrated H_2SO_4	3	Fuel Gas	432
Wash water	270	Phenol water	361
Totals	2,621		2,621

12a.5.2 Oil Hydrogenation

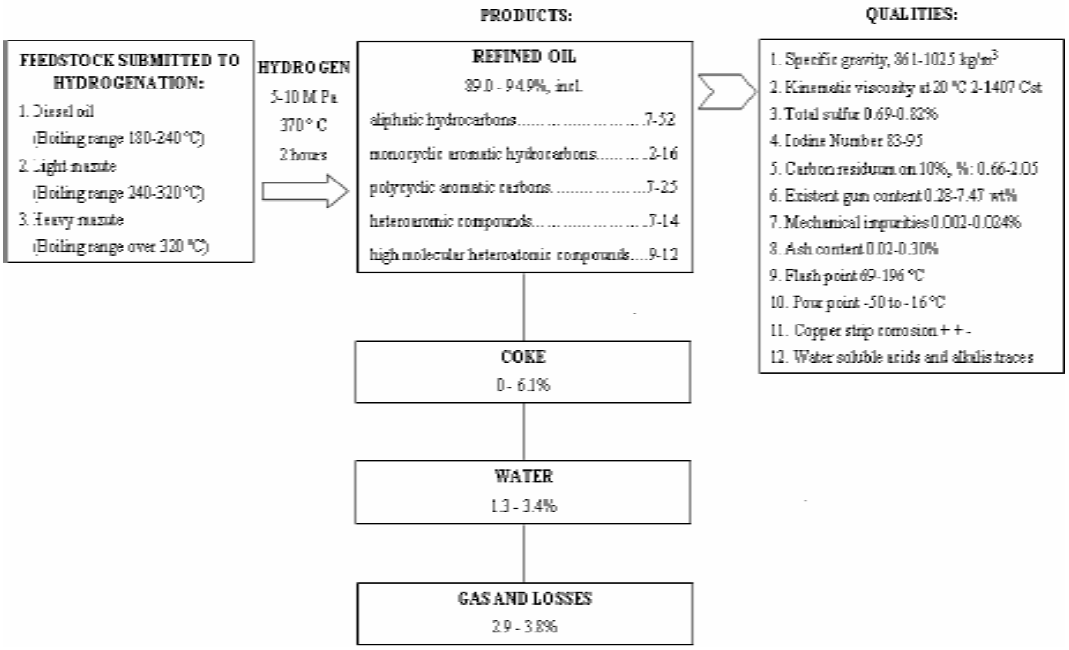
Catalytic hydrogenation of ~ 100 g charges of total raffinate (and other oil components and fractions as well) was performed in a flow reactor at various conditions (e.g. temperature 340-360 ºC, pressure 8-11 MPa, space velocity 4, 1/h). Material balances were compiled (typical yield of refined oil was about 90%) and preliminary economic calculations were performed. The results show the feasibility of hydrogenation process in improving quality of the refined oil. Additionally, gas and gasbenzine are transformed via Zeoforming process and used as components of petrol and diesel fuels (plus some amount of propane-butane fraction). The schematic shown in Figure 12.8 summarizes the results.

12a.5.3 General Process Scheme

Based on results given above and previous experience of cooperation partners a common scheme of treatment of shale oil was developed (see Figure 12a.9). The central process of the treatment is extraction. The raffinate from the extraction step is hydrotreated to a refinery feedstock. The extract is processed to produce commodity products. Residue and rejects from the extract processing are coked to produce fuel, coke and gas.

This process scheme differs from non-ionic extraction scheme researched by the Contractor in two important respects. The Estonia scheme does not rely on a dealkylation step and instead uses a coker to crack higher alkyl phenols to fuel and gas. The dealkylation step pursued by the US side has yet to be technically proven and so the Estonia scheme has greater commercial assurances by relying on more conventional technology. The Estonia scheme does not recycle the coker distillate to the extraction unit, which would maximize the recovery of lower alkyl phenols (the most valuable components), but which reduces the size of the [relatively costly] extraction unit.

Figure 12a.8: Summary Results of Hydrotreating KKO Raffinate



The key features of this scheme are the separation of the total oil into three components, the catalytic hydrogenation of the hydrocarbon component and the fractionation of the heteroatomic component. The outputs of the scheme are fuels, commodity products and coke. In principle, the yield of the latter depends on the "horizontal and vertical" extent of the hydrogenation process, i.e. which oil components are hydrogenated to varying extents. In development of oil shale processing the attention must be given that gases cleaned from sulfur can be used in economic way to produce energy[17].

12a.5.3 Process Waters Treatment

Process water treatment was improved for both phenolic compounds and nitrogen containing compounds; experiments were carried out in a continuous flow mode laboratory unit. Biological aerobic treatment reduces the di-basic phenol content (mainly LARs) below the concentrations required to comply with current regulations (15 mg/L). The nitrogen content (ca 500-550 mg/L, so far not regulated for chemical plants in Estonia, but regulated for urban-waters at 10mg/L) was cut in half in a combined anaerobic/aerobic treatment. For additional nitrogen removal it is recommended that ozonation be included in the aerobic oxidation stage. The results are useful in the designing of semicoking process waters purification for US retort waters which are richer in organic nitrogen compounds.

Process conditions for decontaminating process water to class 3 standards (industrial recycle) have been identified. The current phenolic water processing systems might be upgraded at acceptable costs with the goal of approaching zero discharge for new facilities, while reducing the discharge for current facilities.

12a.6 Plausible Pure Compound and Mixture Products

Phenolic pure compounds include phenol, cresols, resorcinol, orcinol and higher alkyl mono- and di-hydric phenols. Mixture products include:

- light-thermal stabilizer for the technical rubber industry, produced from water-soluble phenols;
- fungicide for building materials, lubricants and paints, produced from oil-soluble phenols;
- fuel additives produced from specified oil fractions;
- other modified products developed in prior research on the basis of water-soluble phenols include individual crystalline alkylresorcinols, epoxy-resins, clues, leather tannides, backfill and curing resins;
- petrol, diesel and heavy fuels can be produced using processes of petrochemistry, i.e. catalytic hydrogenation/zeoforming, and use of additives;
- bitumen and coke.

Task 12a Conclusions

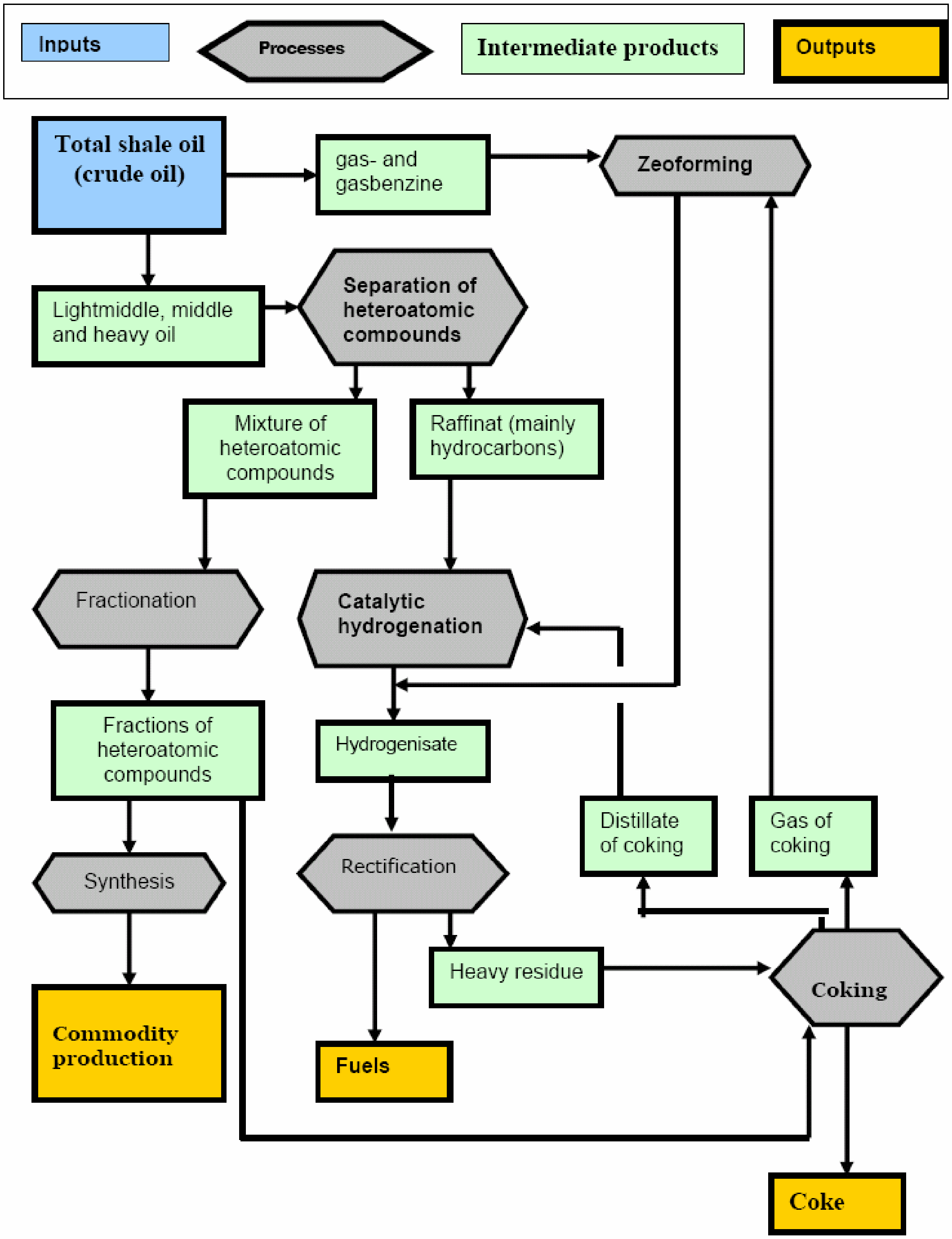
Extractions with both the ionic and non-ionic method were made on study oils. End uses of the extract may be bulk commodity products, such as asphalt additives, industrial surfactants, dispersants or solvents. Or the extract may be processed and refined for its pure compound chemical value. Results supported conclusions of Phase I, namely, as much as 5 to 7 % of Estonia kerogen oil can be manufactured into products valued at $400 - 600/bbl. Another 15 - 20 % can be manufactured into products valued at $100/bbl, or more. For a complete report of the Phase I Estonia project see reference[18].

Application of the technology developed for US Green River Formation kerogen oil to Estonia Kukersite kerogen oil demonstrated the efficacy of the overall process scheme. In addition to extraction of higher molecular weight phenolic compounds by non-aqueous extraction, a selective aqueous extraction method was shown, albeit solvent recovery is more problematic from this latter approach.

Compositional analysis revealed that the most valuable, highest concentration constituents were the alkyl resorcinols (so-called dihydric phenols), with important contributions from alkyl phenols (so-called monohydric phenols). The existence of these alkyl resorcinols and phenols was previously known to Estonia researchers; however, targeting the extraction of these higher molecular weight polar compounds (referred to as the oil soluble phenols) was a new research direction and made promise of greatly enhancing the yield of these valuable constituents.

Dealkylation of alkyl phenols proved more difficult than dealkylation of alkyl pyridines in the US work. Whereas in the US research the valuable moiety is preserved, in the case of phenolics a substantial amount of dehydroxylation occurred. Loss of the hydroxyl group results in loss of value. Further research is needed to find a selective dealkylation step.

Figure 12a.9: Overall Process Scheme for Estonia Research Approach



Task 13a - Product Specifications

Statement of Work

The Contractor shall survey the marketplace for interest in products manufactured from Estonia Kukersite shale oil. Inspections will be prepared on available products. Improvements will be made to products possessing deficiencies that make them not yet acceptable in the marketplace. Results will be incorporated into the product and market specifications database. Updates of the product and process integration results performed under prior tasks will be completed as required.

Results

13a.1 Classification of Products

Five groups of products, representing two levels of market maturity, were studied:

Within the high level of market maturity two product lines have been identified.

- Alkylphenols and alkylresorcinols in both mixtures and pure form (5-methyl-, 2,5-dimethyl-, 5-ethylresorcinol). These products are used as raw materials for foundry resins, tanning chemicals, plugging resins, and feedstocks for synthesis of fine chemical products.

- Epoxy resins synthesized from alkylresorcinols for use in preparation of wood adhesives, laminating glues, rigid plastics, building composites.

Three potential new commercial products marketable for their performance their specifications have been identified, each of which will require additional development work:

- Diesel fuel additives (modifiers) – based on the hydrocarbon portion of the shale oil. The additives are added in small quantities to fuel to improve their combustion and lubricating properties.

- Biocides based on alkylresorcinols separated from shale oil for use as ingredients in building materials such as drywall, paints and lacquers for protection from biodegradation and molds.

- Light- and thermostabilizers based on alkylresorcinol based benzo- or acetophenones for use as additives in plastics and rubber compositions for UV blockers, antioxidants, to protect from degradation under heat and light.

These latter two are particularly interesting uses for higher alkyl phenols, because these compounds have low volatility and solubility and will therefore be stable in their functional environment. Growing markets for specialty chemicals provide good opportunities for shale oil products. The main chemical and market potential have lower alkyl phenols and products as their base. The most promising market for alkylphenols and alkylresorcinols is chemical feedstock market. The straightforward conclusion is to develop synthesis chemistry around these building blocks and sell more expensive end-products. The separation of individual compounds (5-methylresorcinol) is also a very good prospect.

Analogues to oil-soluble phenols on world market were not found. But the potential resources of oil-soluble phenols (higher alkyl phenols) are much greater then water-soluble phenols (lower alkyl phenols). There is a great opportunity for a venture to find useful applications and market opportunities for higher alkyl phenols, and this could provide long-term growth opportunities.

New commercially valuable products based on the shale oil hydrocarbon portion, such as diesel fuel additives, could be developed. The conventional petroleum refining industry is large enough that hydrotreated raffinate could be sold directly to these markets, provided that specifications are within reasonable limits for refinery feedstocks.

13a.2 Industry Prospects by Product Type

The following list of companies has been gleaned from various directories as having a business interest in the products, as listed. In general, these companies are manufacturers or suppliers of these products as contrasted with being customers for the products. The prospect of manufacturing products cheaper from kerogen oil should be of interest to these companies. It will be noted that some companies appear under more than one product title. These companies may have multiple interests in the value-enhancement process venture and may be candidates for consortium partnership. This preliminary listing of companies will need to be refined to ascertain specific interests.

13a.2.1 Pure Compounds

Resorcinol, phenols and phenolic resins

- Aceto Corp.
- Allchem Industries
- American International Chemical Inc.
- Ashland Specialty Chemical Co.
- Bayer Corp. Fibers, Additives and Rubber Div.
- BF Goodrich Kalama, Inc.
- Biddle Sawyer Corp.
- Bimex Corp
- Cardolite Corp.
- ChemMatch
- The Chemical Co.
- Chemicals Incorporated
- Columbus Chemical Industries, Inc.
- Concord Chemical Co., Inc.
- Davos Chemical Corp.
- Dynea Canada Limited, Dynea USA, Inc.
- Encal Specialties
- Fabrichem, Inc.
- Focus Chemical Corp.
- Fuji Hunt Specialty Products Company
- Georgia-Pacific Resins, Inc.
- GFS Chemicals, Inc.
- H. Interdonati, Inc.
- He-Ro Chemicals, Inc.
- ICC Chemical Corporation
- Indspec Chemical Corp.
- Itochu Specialty Chemicals, Inc.
- J. H. Calo Co., Inc.
- JSL Chemical Corporation
- Kessler Chemical, Inc.
- Loos and Dilworth, Inc.
- Maypro Industries, Inc.
- Mays Chemical Co., Inc.
- Mitsui and Co (USA) Inc.
- Napp Technologies, Inc.
- P.A.T. Products, Inc.
- Penta Manufacturing Co.
- Reagents, Inc.
- Rhodia Inc.
- Ruger Chemical Co., Inc.
- Rütgers Organics Corp., Specialty Chemicals Division
- Sattva Chemical Div., Pechiney World Trade (U.S.A), Inc.
- Seegott Inc.
- Solutia, Inc.

- Spectrum Chemical Manufacturing Corp.
- Sunoco Chemicals
- Supreme Resources, Inc.
- Synasia Fine Chemical, Inc.
- Tembec Inc., Chemical Products Group
- Tomen America Inc. Specialty Chemicals
- Total Specialty Chemicals, Inc.
- Universal Preserv-A-Chem, Inc.
- U. S. Chemicals, Inc.
- Westco Chemicals, Inc.
- Vopak USA Inc.

Naphthalenols and higher aromatic phenols

- Aceto Corp.
- Alchemie USA, Inc.
- Austin Chemical Co., Inc.
- Biddle Sawyer Corp.
- Davos Chemical Corp.
- Fanwood Chemical, Inc.
- GL Synthesis Inc.
- KIC Chemicals, Inc.
- Maypro Industries, Inc.
- Multi Organics Ltd.
- Ronas Chemicals Ind., Ltd.
- Spectrum Chemical Mfg. Corp.,
- Total Specialty Chemicals, Inc.
- Wego Chemical and Mineral Corp.

Monoaromatics (primarily BTX)

- Ashland Distribution Chemical Co., Industrial Chemicals and Solvents, Inc.
- CheMatch
- Corco Chemical Corp.
- Coyne Chemical Co.
- G. J. Chemical Co., Inc.
- ICC Chemical Corporation
- Mitsui & Co. (U.S.A.) Inc.
- Multichem Inc.
- Phancorp.
- Soltex
- Spectrum Chemical Manufacturing Corp.
- Sunoco Chemicals
- U. S. Petrochemical Industries, Inc.

Polyaromatics (naphthalene, phenanthrene and related)

- Advanced Aromatics, L.P.
- Advanced Synthesis Technologies, S.A.
- Alfa Aesar-Johnson Matthey
- Allchem Industries
- Bayer Corp. Industrial Chemicals Division
- Biddle Sawyer Corp.
- CBC (America) Group
- Cindu Chemicals, B.V.
- Crowley Tar Products Co., Inc.
- Dudley Chemical
- Geo Specialties Chemical Process Industries Group
- GFS Chemicals Inc.
- R. W. Greeff and Co., L.L.C
- RECA Reuter Chemische Apparatebau KG
- Recochem Inc.
- Spectrum Chemical Manufacturing Corp.
- Solutia Inc.
- Tulstar Products Inc.

13a.2.2 Mixture Products

Surface Active Agents

- ACME-Hardesty Co.
- Air Products and Chemicals, Inc.
- Alco Chemical
- Allchem, Inc.
- Amerchol Corp.
- Amtrade
- Angus Chemical Co., a subsidiary of Dow Chemical Company
- Ashland Distribution Chemical Co., Ind. Chemical and Solvents Div.
- Atlas Refinery, Inc.
- Avatar Corp
- BASF Corporation
- Bayer Corp, Industrial Chemicals Division
- Brown Chemical Co. Inc.
- Cary Co., The
- Chemron Corp.
- Condea Vista Company
- Corsicana Technologies, Inc.
- Coyne Chemical Co.
- Croda, Inc.
- Crompton Corporation
- Cytec Industries, Inc.
- Davidson Labs LLC
- Deeks & Co.
- Degussa Corporation
- Diamond Chemical Co., Inc.
- Dow Chemical Company
- Dusa Chemical Co., Inc.
- E. I. du Pont de Nemours and Company
- EMCO Chemical Distributers, Inc.
- Ethox Chemicals, Inc.
- Expo Chemical Co., Inc.
- GFI Chemicals, L.P.
- Hampshire Chemical Corp., A subsidiary of The Dow Chemical Company
- King Industries, Inc.
- Kraft Chemical Co.
- Lignotech USA, Inc.
- Lonza Group
- MFG Chemical, Inc.
- Mason Chemical Co.
- Mcintyre Group Ltd.
- Milliken Chemical Div. Milliken & Co.
- Niacet Corp.
- Norman, Fox and Co.
- Noveion Inc., Performance Coatings
- OSI Specialties, A Crompton Business
- Pilot Chemical Co.
- Rütgers Organics Corp., Specialty Chemicals Division
- Sanyo Corp. of America
- Scher Chemicals, Inc.
- Seegott Inc.
- Solar Process Corp.
- Surfactants, Inc., Distributer
- TR – Metro Chemicals, Inc.
- Tilley Chemical Co., Inc.
- Tomah Products
- Troy Corp.
- Universal Preserv-A-Chem, Inc.
- Vopak USA Inc.
- Vulcan Performance Chemicals

UV absorbers

- Ashland Distribution Chemical Co. Ind. Chem. & Solvents Div.
- BASF Corporation
- Crompton Corporation
- Cytec Industries Inc.
- Fairmont Chemical Co., Inc.
- Fanning Corp., The
- Ferro Corp., Polymer Additives Div.
- R. W. Greeff and Co., L.L.C.
- International Specialty Products
- Lycus Ltd.
- Mayzo, Inc.
- Rich Yu Chemical Co., Ltd.
- Seegott Inc.
- Universal Preserv-A-Chem, Inc.

Biocides and Fungicides

- Alco Chemical
- ARCH Chemicals Inc.
- The Cary Co.D. B. Becker Co., Inc.
- DAR-TECH, Inc.
- Degussa Corporation
- Dow Chemical Company
- Ferro Corp. Polymer Additives Div.
- Ideas, Inc.
- Kraft Chemical Co.
- LONZAGROUP
- Quimica Sagal, S. A.
- Spartan Chemical Services, Inc.
- Surfactants Inc. Distributer
- TCR Industries, Inc.
- TETRA Chemicals
- Troy Corp.
- R.T. Vanderbilt Co., Inc.
- Verichem
- Vulcan Performance Chemicals

Oilfield Chemicals

- Air Products and Chemicals, Inc.
- Altivia
- Anedco Division of CPI Engineering Services, Inc.
- Angus Chemical Co. A subsidiary of The Dow Chemical Company
- Ashland Distribution Chemical Co. Industrial Chemical and Solvents Div.
- The Chemical Co.
- Chemron Corp.
- Codea Vista Company
- Crompton Corp.
- Ethox Chemicals, Inc.
- Expo Chemical Co. Inc.
- Georgia Pacific Resins, Inc.
- KMCO Inc.
- Geo. Pfau's Sons Co., Inc.

Coaltar and Creosote Oil

- Cindu Chemical B. V.
- Crowley Tar Products Co., Inc.
- Penta Manufacturing Co.
- Ruger Chemical Co. Inc.
- Spectrum Chemical Mfg. Corp.
- R. W. Greeff & Co., L.L.C.

13a.3 Patent Search

Patents in the field of biocides were searched in order to evaluate the patentability of the biocide composition developed by TTU. Subject matter of the described invention was the use of oil-soluble phenolic compounds as biocide, i.e. as antibacterial and antifungal agent. Use of phenolic compounds (including alkyl-phenols and -resorcinols) for antibacterial and antifungal purposes in wood, paints, fuels, construction materials and as fungicides and stabilizers of plastic materials is well known. Several patent opportunities were revealed and patents are being pursued by Estonia researchers.

A patent search was conducted on light- and thermo-stabilizers in order to evaluate patentability of the light- and thermo-stabilizers developed by TTU. Use of benzophenones as light- and thermo-stabilizers is well known. In principle, the use of shale oil resorcinols for synthesis of light-thermostabilizers is possible. There was no information on patents that would be infringed by using Estonian oil shale products as light- and thermo-stabilizers. A number of patent opportunities were revealed and patents are being pursued.

A process patent application based on the scheme shown in Figure 12.1 was filed for in May, 2000 and has been granted in the US (6,875,341 B1) and has recently been allowed in Estonia. This patent, as well as others to be filed by Estonia researchers could form the basis of additional ventures.

13a.4 Product Slate and Values

Tying all the research results together, a plausible product slate was identified and potential yields calculated. This slate avails itself of the maximum amount of pure compounds that could be manufactured by combining the water soluble products with the oil extraction products. The building materials, UV blockers and related additives from the broad range concentrates are lumped together as the distinction between these has yet to be fully specified.

Summary results show that combined estimated product values are about $55/bbl. This analysis was done at a time when crude oil prices were $20/bbl. The refinery feed was given a premium of $5/bbl over benchmark because of its resid-free, low-sulfur character.

Table 13a.1: Products, Yields and Revenues for a Conceptual 10,000 bbl/day Estonia Value Enhancement Processing Venture (feeding 60% Kiviter 40% Galoter oil)

Product	Yield %	Unit Value (2001 $/kg)	Revenues $/feed-bbl
Phenols	2.86	1.90	8.64
Naphthols	1.63	1.80	4.68
Resorcinols	2.45	4.00	15.59
Aromatics	1.63	0.50	1.30
Broad Range Concentrates	8.17	0.20	2.60
Refinery Feed	79.52	0.164	20.74
CO_2	7.19	0.08	0.91
Totals*	103.45		54.45
* Total differs 100% of feed due to production of H_2 and CO_2 less fuel gases			

Task 13a Conclusions

The markets for these products are generally established. Pure compounds are used as feedstocks for manufacture of foundry resins, wood adhesives, laminating glues, rigid plastics, UV blockers, antioxidants, and feedstocks for manufacturing of fine chemical products. Broad range concentrates are expected to find markets as industrial surfactants, industrial antimicrobials, moldicides, solvents, oil-field chemicals, fuel additives, asphalt stability enhancers and other possible products that can utilize the properties of phenolic functionality. The main high-volume product is a low-sulfur fuel, expected to compete favorably with petroleum-derived fuels.

Task 14a - Venture Development – Estonia

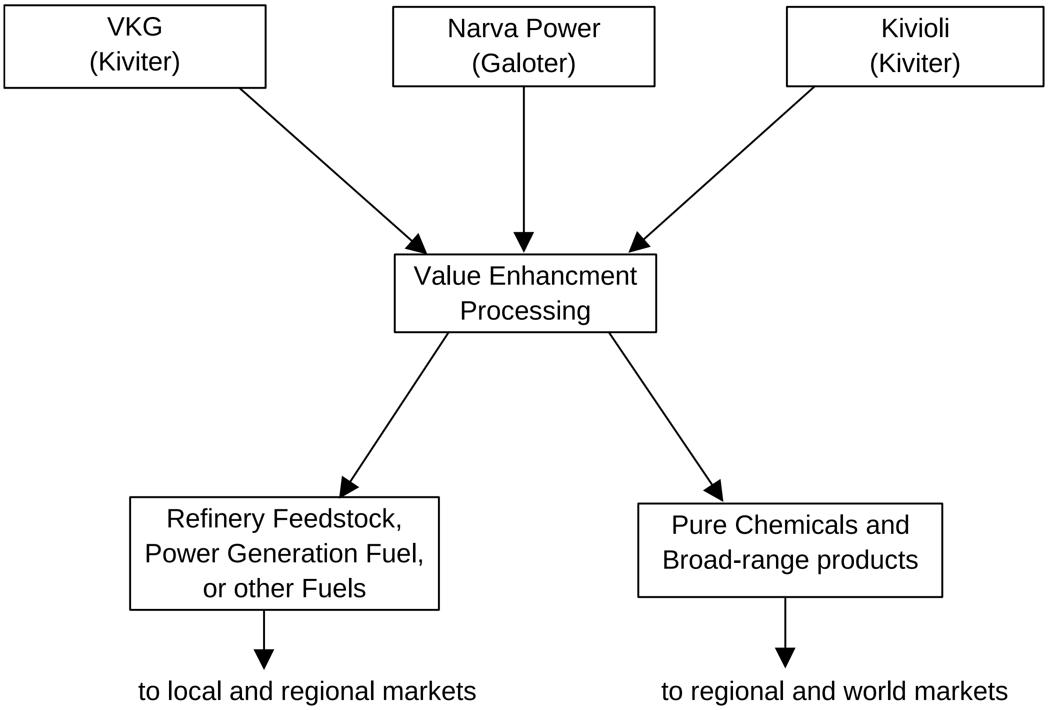
Statement of Work

The Contractor shall prepare a Venture Development Plan which specifies the technical, market and economic potential for the Estonia case and describe how these findings enhance the United States plan. This plan is to form the basis of future oil product development involving private sector funding. Implications to the US product development and enhanced recovery of domestic oil will be included.

14a.1 Introduction

It has previously been estimated that a Value Enhancement Venture in Estonia would be more economical at throughputs greater than are currently being produced by a single production facility. The Galoter retorts produce several thousand barrels/day of raw Kukersite kerogen oil. To improve the economics it may be desirable to combine the outputs of both the Kiviter and Galoter retort facilities. A possible process configuration is shown in Figure 14a.1.

Figure 14a.1: Generalized Venture Approach

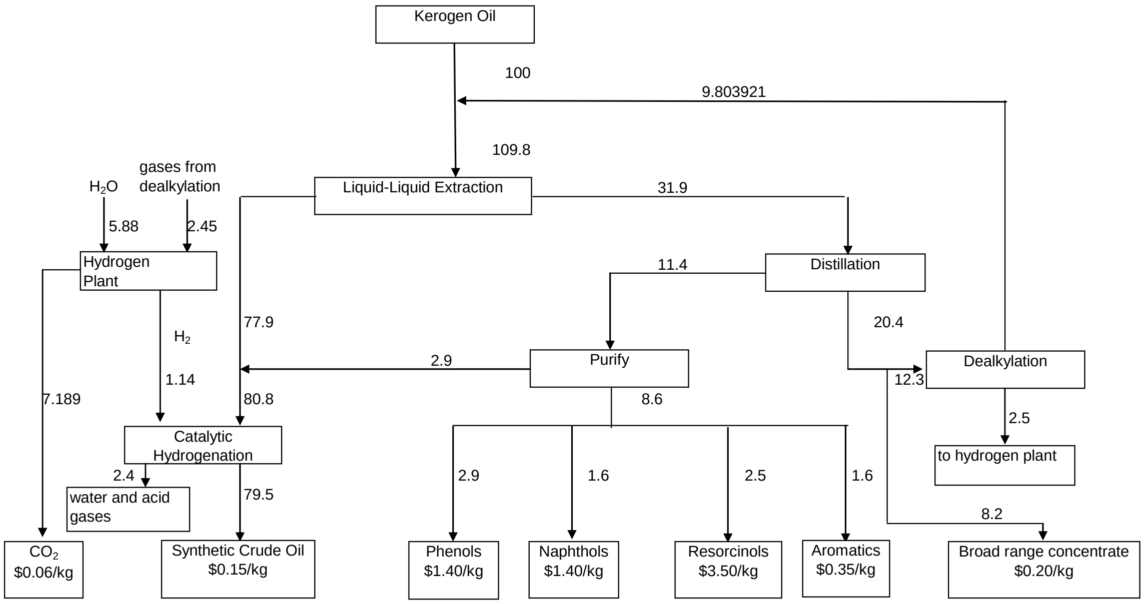


14a.2 Process Description

A plant with the flexibility of shifting product between high-value pure compounds and intermediate-value broad range products is desirable because it can respond to changing conditions in the product markets. It is also advisable to integrate the oil production from oil shale and value-enhancement processing into the same plant.

The overall mass balance for the process scheme, as well as the estimated product values are shown in Figure 14a.2. This is diagram and product slate is based on the US non-ionic extraction scheme.

Figure 14a.2: Kukersite High Value Process Flow Diagram and Mass Balances



14a.3 Process Economics and Investment Analysis

Capital Cost estimates are provided in Table 14a.1. These costs are estimated based on analogy to similar processes in the industry as well as work done for the US case. Operating cost estimates are provided in Table 14a.2. The profitability estimate, assuming a stream factor of 92% (335 days), is provided in Table 14a.3.

The potential profitability for investment appears highly attractive. What is needed is a plan that will reduce the technical and market uncertainty and warrant investment.

Table 14a.1: Kukersite High Value Case - Capital Costs

Basis - 10,000 bbl/day feed (500,000 tonne/annum)

Process	Capacity bbl/day	Unit cost $/daily-bbl-capacity	Installed Cost Million USD
Extract	12,000	3,000	36.00
Distill	3,900	2,500	9.75
Dealkylate	2,500	4,200	10.50
Hydrotreat	8,850	4,100	36.29
Purify	1,400	6,000	8.40
Hydrogen Plant	7MMscf/day		9.20
Installed Capital Cost			110.14
Working Capital			22.03
Total Investment			132.16

Table 14a.2: Kukersite High Value Case – Operating Costs

Basis 10,000 bbl/day

Process	Unit Costs $/bbl	Stream factor	Weighted $/bbl
Extract	1.76	1.10	1.93
Distill	0.69	0.32	0.22
Dealkylate	3.00	0.12	0.37
Hydrotreat	2.25	0.81	1.82
Purify	4.00	0.11	0.46
Hydrogen Plant	3.00	1.00	3.00
Total Operating Cost			7.80

Operating Costs include Direct Labor, Benefits, Utilities, Maintenance

Table 14a.3: Investment Analysis (USD millions)

Investment Cost*	132.16
Annual Revenues	177.46
Annual Costs	
Raw kerogen oil	-63.00
Labor, benefits, utilities	-21.60
Administration and Mkting	-14.85
Research and royalties	-17.75
Gross revenue	60.26
Taxes (social + dividend)	-30.13
Net Revenue	30.13
IRR	16.02%
NPV at 15%	5.12

*10 yr depreciation and capital amortization

14a.4 Development Plan Outline

The goal of the development plan is to establish a VEP venture in Estonia, and replicate that business model in the US. To reach the goal four major milestones must be achieved.

1. Assemble a consortium of interest parties to complete the R and D requirement and to form a pool of potential investors.
2. Complete the R and D.
3. Demonstrate the process at the field demonstration level
4. Perform the commercial design and engineering, finance the venture and construct the project.

The primary audiences for the development plan are:

- Potential investors.
- Product markets and users.
- Governmental and other public institutions, including education.
- Scientists in the field of shale oil processing.

14a.4.1 Investor Needs

Whether the investment is from a venture capital fund, a business, corporation, bank, government, or a combination of sources, financing requires rewards that are commensurate with risks. High risk requires a high rate-of-return on capital.

Development plan activities will focus on value enhancement and risk reduction at each development (financing decision) point. To establish the consortium we will need to succinctly answer the questions:

- What is the unmet market need and what opportunity does that need present?
- Why is Estonia the one to meet that need?
- Who will buy the product and what assurances can be made of prices?
- What human, technology, manufacturing, and natural resources does Estonia have that can facilitate achieving the goal.
- What benefits will the investor realize by joining the consortium now?

14a.4.2 Product Users

Product users require a reliable, quality-controlled, competitively-priced commodity. In both the US and Estonia case there has been strong interest in products manufacturable from shale oil. For shale oil products that serve as feedstocks for manufacturing downstream end user products, the manufacturer is especially interested in lower costs, compared to their current supply, which often is derived by synthesis routes.

14a.4.3 Government and Education

Governments, on behalf of their citizens are interested in development of domestic economies, promoting manufacture of goods for domestic use and export, enhancing high-paying employment opportunities, and educating a labor force. If government needs can be met, the prospect of achieving 'permission to practice' is greatly enhanced.

14a.4.4 Scientists and Engineers

The front-line technical personnel have incentives to enhance their opportunities for innovation and for sharing in profits from innovating work they create. In Estonia, where there is a long history of oil shale science, there is an interest in utilizing this expertise for the benefit of employing businesses and institutions and for personal reward.

14a.5 Business Planning

14a.5.1. Market Need and Estonia's Role in Filling that Need

14a.5.1.1 Unmet market needs -There is a World-wide need for low-cost monohydric and dihydric phenols for use as chemical intermediates. Market prices for these chemicals are high, owing to the high cost of synthesis routes currently used to manufacture these phenols. There is a need for low-cost, effective performance additives for polymers and building materials. A market may be developed for specialty performance products derivable from higher alkyl phenols, heretofore not available on world markets.

14a.5.1.2 Estonia is the Country to meet that need - Estonia's unique oil shale resource is rich in phenolic compounds. No other country has this unique advantage for meeting the market needs for phenolic products. The resource is sufficiently large to continue shale oil production for a century, at expected outputs. Estonia has a long tradition (more than 80 years) in oil shale mining, processing, and utilization. There is an economically successful shale oil industry today, currently producing 3 million tonnes/year. Certain markets for Estonian shale oil products are already established. Estonia has the human resources to assure competitive labor costs. Oil shale is Estonia's principle natural resource; Government policy favorable to development reflects the importance of this resource to the National Economy.

14.5.1.3 Emerging investment opportunity - Positive differential between oil prices and cost of shale oil production is widening. There is a strong prospect for becoming the dominant World supplier of phenolic compounds from Estonia oil shale or pyridinic and pyrrolic compounds from United States oil shale. Existing industry in Estonia reduces front-end costs and risks. High value chemicals afford attractive profitability at more modest scales than unconventional resource developments that produce only petroleum substitutes. Investors in Estonia will be plausible candidates for investment in the US.

14a.5.2. Technology and Products

14a.5.2.1 Slate of products to be produced - Pure compound chemicals will compete on a price basis with identical chemicals in established markets. Primary chemical products (phenols, epoxy resins, different modifiers) are derived from water-soluble and oil-soluble phenols. Biocides and fuel additives need yet to be market-qualified. Different grades of shale oil fuels will be manufactured based on fractionation (distillation) of crude oil.

14a.5.2.2 Technologies - Production of crude oil is done in existing factories using two different methods – Kiviter and Galoter retorts. Future production may be derived from advanced retorts such as the Alberta Taciuk Process (ATP), or other economic means. Dephenolated fractions of crude oil are treated according to ordinary petrochemical processes to produce high grade fuels. Liquid-liquid extraction of crude oil produces raw material for pure compound manufacture and broad range products. Custom chemical transformation will be needed and key processes require some development. Purification and refinement technologies are used to manufacture products of specification values. A key remaining step is to identify the optimum dealkylation process.

14a.5.2.3 Facilities - Conceptual process schemes have been prepared that maximize the market value of the products. The separation units will be priority items: renovation of water soluble phenols separation units and building industrial units for separation of oil-soluble phenols. The building of completely new shale oil treatment plants will be possible in the future by significantly expanding production of crude shale oil. The scale and complexity of the Value-Enhancement Process facility must yet be determined.

14a.5.2.4 Environmental technologies and standards - Estonia has harmonized its national environmental standards with current EU standards. For shale oil processing plants the most important standards pertain to discharge of process water. Breakthrough progress was made under the current study. Emissions technologies will utilize best-available-practices. New generation facilities will not produce semi-coke, a traditional product that does not meet modern waste disposal standards.

14a.5.3 Government/Industry Consortium

A Government/Industry Consortium will be established to pursue commercial development of the Value-Enhancement Process (VEP) concept. Government participation of Estonia, the United States, and potentially other countries containing oil shale resources is expected. Industry participation may include Estonia industry, parties interested in product use, technology/engineering companies, petroleum producers and refiners, and natural resource development companies. The Agreement must be viewed as attractive to current Estonia industry.

The Consortium funding will be provided by the participants. A Cooperative Research and Development Agreement (CRADA) is one potential mechanism, but there are other formats to consider. Funding for the commercial plant will be provided by the private sector through customary investment decisions.

14a.5.3.2 Initial Tasks - Select early product opportunities that require minimal investment for manufacture and sale. Establish specialized research tasks with industrial participants. Perform pilot and demonstration scale studies for near term product manufacture and qualify products, as necessary. Establish supply, production and purchase agreements. Perform cooperative research with member Countries relative to World oil shale resources.

14a.5.3.3 Intermediate-range tasks - Complete proof-of-concept tasks for key process steps needed for full integration of VEP. Perform pilot and demonstration scale studies for intermediate-term product manufacture, and qualify products, as necessary. Design and conduct studies for advanced products and market development needed for improved process integration and greater value-enhancement.

14a.5.3.4 Long-Range Goals

- Create attractive natural resource, private sector investment opportunities.
- Enhance economic base of participating countries.
- Enhance the economic and education cooperation between countries.

14a.5.4. Benefits of Consortium Membership

14a.5.4.1 Governments

- Low-cost means of stimulating economic growth.
- Development of intellectual property assets of investment and export value.
- Improved availability of competitively priced fuels and consumer products.
- Enhanced workforce skill level.
- Enhanced employment and wages.
- Creation of economic wealth.

14a.5.4.2 Industry

- Cost-shared development of technology and products.
- Favorable access to product purchase.
- Low-risk, high-potential investment in a unique industry with high growth potential and high barriers to competitive entry.
- Early access to emerging commercial investment opportunities.
- Favorable investment climate; low taxes, skilled and educated workforce, accredited research and technology university (TTU), entrepreneurial support, welcoming and proactive Government policy.

14a.5.4.3 Academia

- Funding for research of practical value in the market place.
- Opportunity to develop valuable intellectual property for the benefit of the institution and its faculty and students.
- Student and scholar exchange with participating countries.
- Faculty consulting opportunities for broadening experience.

14a.6 Field Demonstration

During the Demonstration phase a field unit will be constructed. The capacity of the unit will be on the order of 100 bbl/day. It will consist of the primary recycle loop, namely extraction, distillation and dealkylation. Product for hydrotreating will be shipped to existing facilities to obtain engineering data. Lower alkyl phenols will be purified in semicontinuous units. Particular care will be given to thermodynamic properties, which will allow scale-up factors of up to 1000 to 1. Likewise, refining of broad range concentrates will be conducted in semi-continuous units. Process waters will be subjected to treatment to assure water process design.

14a.7 Commercial Development

Consortium participants will have the first opportunity to invest in the venture. Non-participants may buy-in to the opportunity at some multiple (typically 3 to 5) of the participant's costs. Feedstock supply and product off-take agreements will be secured. A site will be selected and permits acquired. Construction is expected to require 2 years.

Task 14a Conclusions

Development of a Value Enhancement Venture in Estonia will require a coordinated effort between Estonia industry and government, as well as the investment community. An industrial consortium has been proposed as one path forward, but there may be other approaches. At present there is understandably some competition between the interested parties that has slowed the pace of assembling the proposed consortium.

The moderate scale of production in Estonia, combined with the much larger markets for phenolic products (compared to pyridinics products), strongly suggests that one VEP industry of the largest possible scale be developed in Estonia. There are ample markets to absorb products from a VEP venture feeding more than 10,000 bbl/day of Kukersite kerogen oil. One industry group is actively pursuing specialty chemical production from the water-soluble phenols (about 1%), but to our knowledge is not pursuing the oil soluble phenols.

An Estonian patent has been issued to JWBA #04818, dated April 20, 2007. This is the same patent that was issued in the US. JWBA will make this patent available to Estonia industry for licensing. Direct involvement of JWBA in Estonia VEP development will depend on investment interest, as well as continuing interest and activities of the US Departments of State and Energy.

PHASE IV - CONCLUSIONS

The overall approach to improving the value of kerogen oil is to selectively separate polar heteroatom-containing compounds from non-polar hydrocarbon compounds. The process selected to accomplish this objective is liquid-liquid extraction. Many variations of solvents and process conditions exist for this step and further research is needed to discover the optimum conditions. Once the polars are separated from the non-polars, the streams can be independently processed to make the final products acceptable to the market place.

Overall economics show strong investment potential. Potential business arrangements in Estonia were not agreed, however, as there was a change in enterprise management that did not fully embrace the policies of the former officials. Nevertheless, the investment worthiness of the opportunities are well known in Estonia, and it is a matter of putting additional effort into bringing these opportunities to fruition. The results were used to catalyze discussion in the US, ultimately resulting in the publication Strategic Significance of America's Oil Shale Resources. This seminal publication has been oft-cited since its publication in March, 2004.

The next step for Estonia is to reinstate the Government to Government Agreement. The first task of this Agreement will be to form a consortium of interested parties to develop the opportunity further.

PHASE V - PROJECT UPDATE

Task 14b - Project Update

Statement of Work

The Contractor shall perform the following tasks:

1. Review current status of products, markets, prices and economics.
2. Update conceptual value-enhancement process as applied to US kerogen oil, including mass balances and energy requirements.
3. Update Venture Development Plan for US resources including estimates of capital requirements and economic viability as a function of crude oil prices.

Results

14b.1 Emerging Investment Climate

When this program was originally conceived in the late 80s, oil prices were hovering around $20/bbl, which is where they held for another decade. A temporary drop to about $10/bbl in the late 90s preceded the current rise to $60/bbl and more. A key to understanding the recent rise in oil prices, which may be more permanent than many think, is recognition of the fundamental shift from a demand-constrained market to a supply-constrained market underway.

In a demand-constrained market the minimum price of crude oil is dictated by the marginal cost of the *cheapest* barrel, generally considered to be Middle East oil at less than $10/bbl. In a supply-constrained market the minimum price of crude is dictated by the marginal cost of the *highest-cost* barrel, generally considered to be unconventional fuels or ultra deep-water oil at about $30/bbl. Indeed, most E and P companies are now basing their investment decisions on $30 or $35/bbl oil.

The fact that current oil prices are substantially higher than the marginal highest-cost barrel, however, is evidence that prices are beginning to uncouple from costs. The uncoupling of prices from production costs is strong evidence for this emerging supply-constrained market. To keep demand at the same volume as supply, demand must be destroyed through pricing.

The case for large scale commercialization of oil shale is becoming more compelling. The realization that conventional oil may be reaching limits of production rate, sometimes referred to as ‘peak oil’ is now being discussed in broader circles, including Congress. This peak in production has already occurred in 54 of the 65 countries that produce oil[19], and will occur in most, if not all of the remaining 11 countries within the next 10 to 15 years. The implications of potential supply shortfalls are already being felt in the petroleum, natural gas, and chemical markets, where commodity futures are already factoring in higher long-term prices.

There are three circumstances that have emerged that change the view of the oil shale world. First, the floor price of oil now appears to be set by the marginal high-cost base, which is about $30/bbl. This factor alone changes the attractiveness of investment. The effect of this anticipated price floor is being witnessed in the phenomenal growth of Alberta oil sands developments.

Second, Congress is becoming increasingly concerned over future supplies of oil[20], particularly because the US derives a majority of its oil from imports. Congress is now viewing unconventional oils (which includes shale oil) as strategically import to future supply. It has placed the primary responsibility for this initiative in the Office of Petroleum Reserves, as a long-term complement to the Strategic Petroleum Reserve. If the US could develop its unconventional resources at the commercial level, the US could add billions of barrels to its proven reserve base.

Third, Sec. 369 (d) and (e) of the Energy Policy Act of 2005 (EPACT 05) calls for the Bureau of Land Management to make commercial leases available for oil shale for the first time in nearly a century. (The Prototype leases of the 1970s were highly restricted compared to the anticipated lease program). Under Sec 369 (c) of EPACT 05 they have now awarded a number of R D and D leases designed to help the investment community gain confidence in the technology and to obtain data useful for permitting. The prospect of obtaining commercial leases for oil shale on federal land has now energized industry to begin paying attention to oil shale.

This set of conditions, in which supply shortfalls are anticipated and price substantially exceeds costs, virtually dictates that there will be a transition to unconventional fuels to fill the supply gap[21]. The growth in investment in Alberta oil sands is on this track. *A substantial supply of raw shale oil can be expected in the future, based on these market fundamentals.*

14b.2 Review of Prior Status

In the original concept, oil shale was to be brought on-line through ‘market pull’ using the VEP technology. While this may have attracted interest from prospective shale oil producers (such as Oil Tech) lack of kerogen oil supply was seen by both the investment community and the product users as the major impediment to a VEP venture.

Now that there is a market-driven need for shale oil the focus should now be placed on product development and markets as the next biggest remaining uncertainty. Also, because there may be substantially more raw shale oil available in the future than was anticipated for a ‘first generation’ plant built on the market-pull incentive, the optimum process configuration and conditions have changed.

Whereas before there was a premium on maximum recovery of nitrogen heterocyclics, thereby maximizing the yield of high value products while minimizing the cost of upgrading the raffinate, now the optimization problem is maximizing the nitrogen heterocyclic concentration in the extract, while minimizing the yield of the extract.

Because large-scale development would overwhelm the specialty chemical markets, if all of the nitrogen heterocyclics were extracted and processed for chemicals, it is anticipated that VEP will operate on a slip stream of a larger project. This objective would be more like skimming the best cream and leaving the remaining problem of heteroatoms to the large-scale upgrader.

An even greater emphasis may now be put on the individual types present in the raw shale oil, so as to target specific types for production. This update takes a new look at the types present, and places the VEP process in the context of a larger production profile.

It is assumed that extracted pyridines/pyrroles/phenols can always compete with synthesized chemicals, so long as the concentrations of these types are above some threshold limit. The reason for this is that as energy prices increase, the incremental cost of synthesis increases faster than the incremental cost of extraction (a favorable cost trendline). This suggests that extracted heterocyclics could conceivably dominate world markets, in time.

We may recall that in the early days of coal tar production, a vast industry was built around the heteroatom containing compounds in coal tar. This resource fell out of favor only because abundant natural gas, petroleum and new small molecule building block chemicals became readily available. In the future, the abundant feedstocks will be shale oils, which are many times as rich in nitrogen heterocyclics as was coal tar. (Raw oil shale has about 50 times the concentration of pyridines compared to coal tar, a primary source of pyridines a century ago.) The value-added processing of coal gasification tar from SASOL today[22] is further evidence of the current and future viability of the approach.

Consequently, from the standpoint of energy supply trends and relative increases in costs for chemicals, there can be some assurances that VEP has a future role to play in oil shale development.

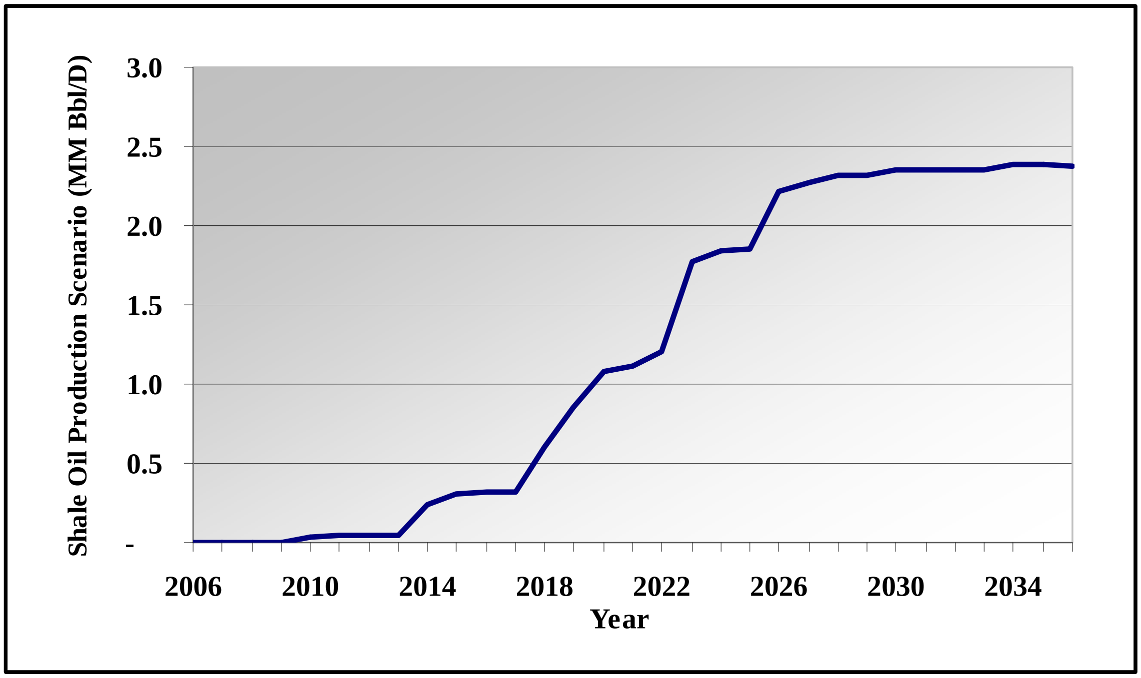
14b.3 Government Activities Leading to an Oil Shale Industry

The Energy Policy Act of 2005 (EPACT 2005) established a multiagency Strategic Unconventional Fuels Task Force to “develop a program to coordinate and accelerate the commercial development of strategic unconventional fuels, including but not limited to oil shale and tar sands resources within the United States, in an integrated manner.” (Sec. 369 (h) (1)). This Task Force has identified the major impediments to development and has made preliminary recommendations to mitigate those impediments.

Briefly, the major impediments relate to a) lack of resource access, b) immature technology, with uncertain costs and reliability, c) uncertain product prices, d) unsupportive tax and royalty structures, e) uncertain regulatory requirements and permitting timelines, e) timelines and responsibilities for community and project infrastructure development, and f) uncertain community acceptance. Remedies for each of these impediments are included in the Task Force recommendations, contained in the DOE report "Development of America's Strategic Unconventional Resources" Office of Petroleum Reserves, June, 2006[23].

The shale oil development scenario anticipates initial production by 2010 with major growth (from both in-situ and mining based technologies) in the 2017-2022 timeframe and target production of about 2.4 million bbl/day by 2035. This is depicted in the following chart (Figure 14b.1).

Figure 14b.1: Shale Oil Production Scenario – Accelerated Case (ref [20])



14b.3.1 Analogy to Alberta Oil Sands – Production History

The experience of the Province of Alberta, Canada in transforming its oil sands resources from a promising unconventional resource to a thriving million barrel per day oil producing industry, can serve as an analog for the development of America's unconventional fuels resources. An Alberta analog is found for all of the major development challenges described above.

The Alberta experience has demonstrated that:

- Oil sands technology, initially supported primarily by government Research, Development, and Demonstration (RD&D), has matured significantly. Today most of the improvements in performance, reliability, and efficiency, are funded by industry with shared public investments in RD&D.

- Per barrel capital costs have dropped by 1/3 and operating costs by 2/3 through experience and technology improvements. Private investment was effectively stimulated by public fiscal measures that reduced investment risk by deferring royalty and other tax revenues until project investment payback is achieved.

- Net water use requirements have dropped from about five barrels (Bbl) per Bbl of syncrude produced to three Bbl per Bbl as new approaches for use minimization, water conservation, and water re-use have been implemented.

- Energy efficiency has improved from the original 71 percent to 83 percent today, and sulfur and CO_2 emissions have been cut, correspondingly.

- Net revenues to Provincial and local communities have provided for schools, utilities, roads, public safety, recreation and other public services and infrastructure. The Provincial Government is debt-free, a desirable objective for U.S. local and state governments. Various working groups have been established to facilitate frequent public input on all aspects affecting communities and quality of life. With assurances of long-term investment and employment, public and industry support for community development, communities have granted this unconventional fuels industry their "permission to practice."

Perhaps the most important feature of the Alberta analog is the bond of public-private partnership that has been forged by engaging and valuing the input of all stakeholders having interest in the development of the oil sands resource.

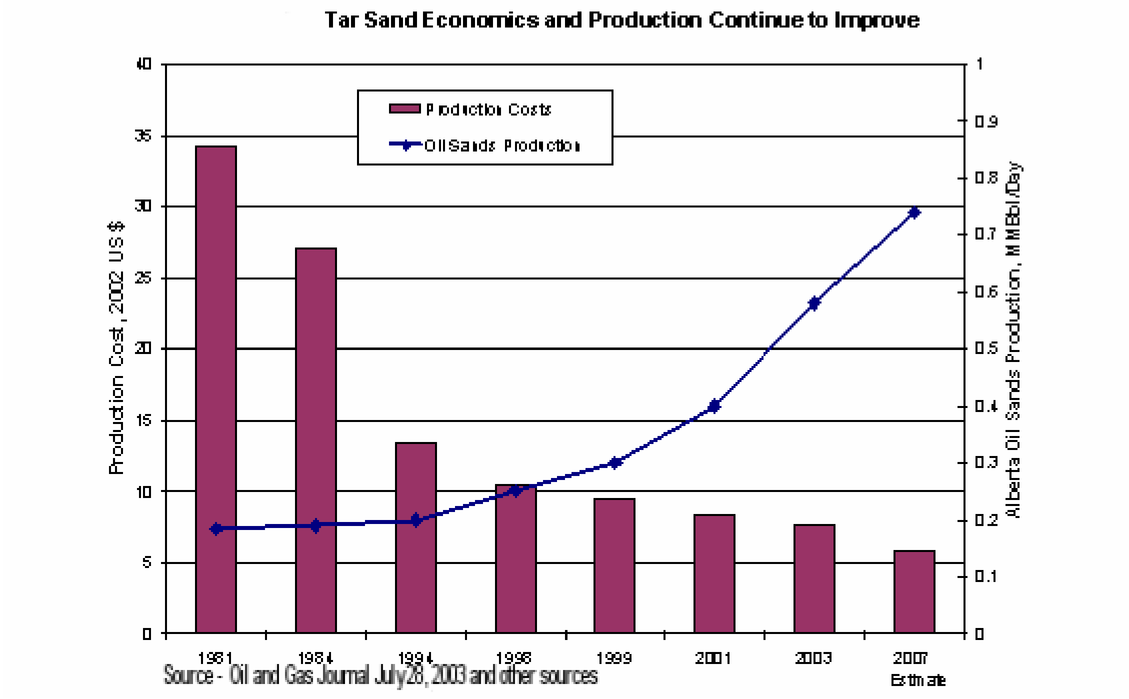
The Alberta production and cost history, shown in Figure 14b.2 provides compelling evidence that America's unconventional resources, too, can be developed efficiently, economically, and with respect for the environment and for the communities and regions where these vital resources exist.

14b3.2 Analogy to Alberta Oil Sands – Cost Trends

Oil sand development costs in Canada are rising due to shortfalls in skilled labor and materials, both of which contribute to project delays. Whereas in a well-supplied labor market, capital costs run about $30,000 per daily-barrel-capacity, recent costs have been as high as $50,000. For an expected 15% IRR, including amortization of capital, the $30K figure translates to about $18/bbl for capital costs and the $50K figure translates to about $30/bbl. Operating costs, on the order of $10-12/bbl must be added to this to obtain the minimum price to achieve 15% IRR.

Using the history of the Alberta industry as a guide, a first-generation oil shale facility will experience capital costs about 33% higher than a mature industry plant and operating costs will be about 60% higher. From the standpoint of capital investment decisions, it may prove that first-generation oil shale development in the US, which is not as labor- or materials-constrained may be on a par with mature, but currently constrained, Alberta oil sands development. Of course there are other uncertainties of US development that demand a higher hurdle rate, but as mentioned above, the US government is expected to take some action to mitigate these uncertainties.

Figure 14b.2: Tar Sand Economics and Production Efficiency Improve with Time



Source - Oil and Gas Journal July 28, 2003 and other sources

Because the VEP process will take a slipstream from a large facility the transfer cost will enjoy the economy of scale of the larger unit. Surface processing for sweet synthetic crude oil is estimated to be profitable at $45/bbl. Less $8.60/bbl allocated for upgrading the raw kerogen oil, the transfer price to the VEP process (the feedstock cost) is estimated to be $36.40. For an in-situ process which is believed to be profitable at $35/bbl the similarly-calculated raw kerogen oil transfer price for in-situ oil is $29.00. For in-situ production the nitrogen content is about 40% lower, which translates into lower costs of about 30%, or $6/bbl. The yield of nitrogen-containing compounds for in-situ oil is substantially lower than for surface retorted oil. The economic analysis to follow shows that both are profitable. The foregoing transfer prices were used as the feedstock cost values for the VEP 2006 case.

14b.4 Scope of Update Tasks

Updates of prior work were indicated in the following areas:

1. Kerogen oil composition - Significant progress has been made on the Z-BaSIC™ technology since 1999, which now allows for a closed mass balance by carbon number of specific compound types. A Z-BaSIC analysis is a quantitative description at the molecular level that when composition is summed the results agree with measured properties of density, C, H, N, S, and boiling point distribution according to high temperature simulated distillation (HTSD).A closed mass balance at the molecular level is important to understanding the mass balances and process efficiencies for the conceptual process.

2. Update target product slate - Kerogen oil products are essentially of three categories of products;

    a. those products for which markets are already established and for which kerogen oil products will compete on the basis of specifications and price,
    b. those products for which markets are already established, but for which kerogen oil products will compete as an alternative to existing products that meet that need, and
    c. products for which markets need yet to be developed, based on unique or unusual characteristics of kerogen oil-derived products, or the first-time availability of low-cost nitrogen compounds.

3. Improved Technology - The purification scheme for the light extract is currently based on thermodynamic properties and theoretical considerations. Some experimental verification strengthens the overall business plan by presenting validated arguments for product specifications. Also, new tools have been developed for measuring extraction efficiency and these tools were applied to experimental results. In past work hydropyrolysis efficiency had not been optimized. Sufficient funds are not available to attack this problem experimentally, but an improved understanding was achieved through stoichiometric calculations and modeling based on the new Z-BaSIC results.

4. Update conceptual processes and economics - In the prior work there were three (3) processes conceptualized. They were labeled the ‘high-value’ case, ‘high capacity’ case and the ‘low capital’ case. The differences between these processes related to the extent of upgrading targeted and with it the product slate produced. The greater volume of kerogen oil anticipated now skews the consideration to the high capacity case.

5. Update business development strategy – In prior work we characterized the markets (uses, volumes, specifications), and identified the companies involved, along with their possible interests for becoming engaged with VEP. The results of feedback from engagements with producers, consumers and venture capital

communities were used to develop a strategy for integrating these interests with newly identified fuel production interests. Generic economics were developed as a new foundation for kerogen oil production economics (prior economics assumed a transfer price of $18/bbl, which was a reasonable number 5 years ago, but is not current today). Of significant importance is an assessment of the role VEP might play in initiating an industry today and how that makes business sense in today's energy economic climate. The results of this assessment form the basis for the business approach to Venture Development.

14b.5 Z-BaSIC™ Compositional Analysis Update

The 'cp' file gives a molecular representation of a hydrocarbon oil. The 'cp' file is an input file for process simulation and property estimation. The file can be 'distilled' and fraction composition and properties assessed. Further details of the Z-BaSIC methodology can be found in reference[24].

The 'cp' file is comprised of molecular components found by GC-MSD whose concentrations agree with the boiling point distribution, density, hydrogen, nitrogen, and sulfur contents. Information obtained in the earlier phases of the project was used to make certain assumptions about distributions of properties with boiling point. It needs to be emphasized that the actual compound types used to construct the 'cp' file are representative of those found in the surface retorted raw shale oil.

Z-BaSIC™ was used to construct a composition-property file 'cp' for the Unocal study oil. This file was then adjusted to agree with the reported Shell ICP product properties. This latter file provides a reasonable estimate of the composition of an in-situ oil produced by the Shell ICP method, at least for purposes of estimating the application of VEP to this oil.

Table 14b.1 shows that there is about 23% of the raw surface retort shale oil and about 16% of the raw in-situ shale oil that could be a target for pure compound production. To manufacture pure compounds these targets would first be extracted, then dealkylated and then purified for market. According to the VEP scheme each of these steps has an efficiency, or process loss, factor associated with it. Semi-quantitative estimations of these efficiency factors, based on prior experience, were used to estimate a final yield profile. This yield profile in tons/yr is given in the Table 14b.2. The high yield of oxygenated compound types shown for the In-situ case requires further confirmation.

Table 14b.2: Potential Annual Production of Pure Compounds

Compound class	Production –ton/yr per 100,000 bbl-oil/yr	
	Surface process	In-situ
Pyrroles and indoles	190,576	135,456
Pyridines and quinolines	209,215	143,332
Phenols and resorcinols	23,756	84,078
Net pure compound production	423,548	362,867

World production of chemicals has become difficult to obtain in the post 9/11 world. Based on information from the 1990s, it would appear that the volumes shown in the Table 14b.2 would be a substantial portion of the world markets. Value-enhancement processing for pure compounds will be market-limited, even for the lower nitrogen in-situ product. However, enhanced revenues will still add incremental value even if only a portion of a large scale facility is split for VEP.

To remind, the business strategy for any of these extracted pure compounds is to compete with synthesis chemicals on the basis of price. Once established in the marketplace, taking over market share is a matter of time as the oil shale industry grows and costs continue to decline.

14b.6 Process and Product Update

The generalized Value-Enhancement Process (VEP) concept is given in Figure 14b.3. Numbers on the streams are mass percent. New emphasis is placed on process flexibility that can quickly respond to changes in market opportunity. This process flexibility is achieved primarily through the severity of the extraction step; greater severity increases the yield of extract, but results in greater extract processing costs, lower severity results in a purer extract and lower extract processing costs.

In the updated scheme the liquid-liquid extractor will be run to maximize the recovery of lower molecular weight compounds, minimizing the recovery of higher molecular weight compounds. This will have the effect of reducing the size of the hydrodealkylation unit, as well as the yield of the total extract. However, the extract will contain a higher concentration of the most desirable low molecular weight components. Process flexibility can be gained by changing the solvent properties and the solvent to oil ratio thereby changing the ratio of broad range concentrates to pure compound products.

The fractionation (distillation) unit is designed to send those target compounds present directly to the purifier; higher alkyl rings are sent to a THDA unit. The cutpoint temperature of 230°C is set to minimize the amount of dicyclic compounds being sent to the THDA unit. In practice, either of these cutpoints can be changed to afford flexible optimization as the markets demand. The purification process is outlined in Figure 12.8 above.

Heavy ends are split for manufacture of broad range products, such as asphalt additive, or sent to dealkylation (hydropyrolysis) to remove alkyl chains from nitrogen heterocyclic compounds. This asphalt additive serves as a drag stream to prevent inordinate buildup of intractable compounds. The total condensable product from dealkylation is recycled to extraction where the alkyl groups report to the raffinate and the nitrogen heterocyclic compounds report to extract.

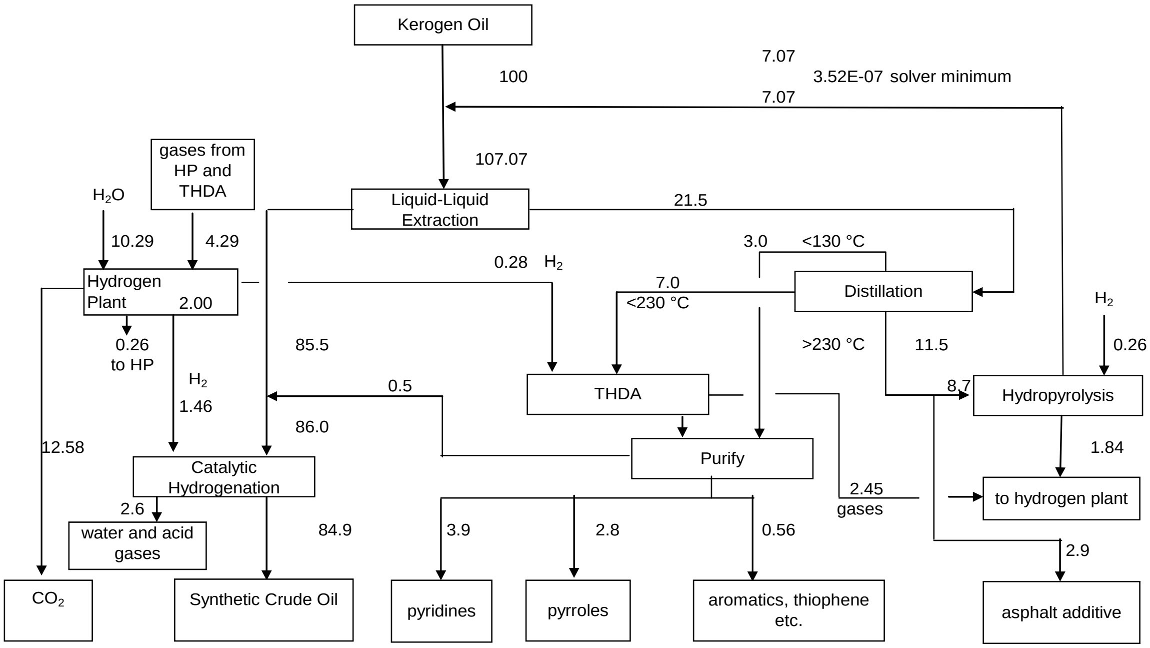
Table 14b.1: Compound Type Analysis of Surface and in-Situ Produced Shale Oil

Compound Type	Unocal surface % of Total	Shell ICP* % of Total
n-paraffins	9.332	26.629
i-paraffins	8.467	10.615
mononaphthenes	6.582	7.772
dinaphthenes	1.565	15.65
trinaphthenes	1.222	4.417
tetranaphthenes	6.327	2.809
pentanaphthenes	6.835	1.68
hexanaphthenes	0.421	0.002
heptanaphthenes	0.188	0
octanaphthenes*	3.448	0
monoaromatics	5.532	4.919
vinyl benzenes	0	0.001
naphthenomonoaromatics	2.851	1.77
dinapthenomonoaromatics,indenes	1.424	0.608
trinaphthenomonoaromatics	1.449	0.042
tetranapthenomonoaromatics	0.461	0.981
diaromatics	1.467	0.437
acenaphthene/naphthenodiaromatics	2.044	1.563
dinaphthenodiaromatics	0.44	0
acenaphthalenes/fluorenes	0.648	0.405
triaromatics	0.474	0.034
naphthenotriaromatics/dihydropyrenes	0	0.027
phenylnaphthalenes	0.429	0.732
tetraaromatics (peri-condensed)	0.4	0.015
tetraaromatics (cata-condensed)	0.053	0
naphthenoflourenes	0.061	0
pentaaromatics (peri-condensed)	0.003	0
naphthenosulfides/thiols	1.114	0.868
dinaphthenosulfides/thiols	1.471	0.434
thiophenes	1.045	0.419
trinaphthenosulfides/thiols	0.76	0.339
thiophenol	0.037	0.001
tetrahydrobenzothiophene	0.202	0.093
tetranaphthenosulfides/thiols	0	0.002
benzothiophenes	1.015	0.272
benzodithiophenes	0.422	0.331
dibenzothiophenes	0.299	0.198
epithiophenanthrenes	0.092	0
benzodibenzothiophenes	0.405	0.023
4-ring thiophenes*	0.013	0
pyrroles	0.986	3.522
indoles	5.296	3.383
carbazoles	2.383	0.499
4-ring pyrrolics*	3.406	0
5-ring pyrrolics*	0.034	0
pyridines	1.425	2.588
quinolines	4.722	2.717
phenanthridines	0.53	0.348
4-ring pyridinics*	3.275	0
5-ring pyridinics*	0.003	0
phenols	0.818	0.784
hydroxy tetralins	0.218	1.097
naphthols	0.053	0.24
dibenzofuran	0.024	0.036
resorcinols	0.064	0.674
dihydroxy tetralins	0.115	0.025
unidentified	0.249	0
C36+	7.398	-0.001
Totals	99.997	100
Total Target compounds	23.352	15.913

Target compound types highlighted in yellow.

* The Shell ICP molecular composition is estimated by Z-BaSIC comprised of compounds likely to be contained in shale oil and in proportions to agree with the reported elemental composition, density and boiling point distribution. This estimation is not an actual analysis of a sample of ICP oil and actual compositions may differ signficantly from estimated.

Figure 14b.3: Updated KPX Process Flow Diagram and Mass Balances



The raffinate is sent to a catalytic hydrotreater where remaining sulfur and nitrogen are removed, to manufacture a sweet, high quality synthetic crude oil. Because a lower percentage of the nitrogen will be removed in the extractor, the catalytic hydrotreater unit will need to be larger. Hydrogen is manufactured from the non-condensable gases obtained from the dealkylation unit. Hydrogen is used in both the hydrotreating and dealkylation steps. Products of the process scheme include the syncrude, a variety of pure compounds and broad range (mixture) products. A patent has recently issued on this process[25] (cf. US 6,875,341 April 5, 2005).

The following controls are possible with the process scheme.

1. The severity of the extraction step determines the percent recovery of nitrogen compounds and the sharpness of the split, quantified by a coefficient-of-separation. Lower severity is indicated when processing for pure compounds is the objective. Higher severity is indicated when asphalt additive is the primary market objective and a higher quality raffinate is desired.

2. The bottom distillation cutpoint determines which ring systems report to the purification process. A deep cutpoint includes bicyclic compounds such as quinoline, whereas a light cutpoint sends bicyclic compounds to the downstream processing. The cutpoint also affects the quality of the asphalt additive.

3. The severity of the dealkylation step (at steady state) determines the size of the recycle stream, but can result in excessive costs in the process step; over-cracking lowers liquid yield. If pure compounds are not a target, then a dealkylation step is not needed.

4. The conceptual process is in hydrogen balance. In general, the system will operate close to hydrogen balance over a wide range of severities, because higher severity, while consuming more hydrogen also produces more hydrogen. The high hydrogen content of the shale oil at 11.7%, and a full percentage point higher than coker distillate from Athabasca tar sands, is what allows this flexibility.

Raffinate is hydroprocessed in a conventional refining unit. The kerogen in Green River oil shale contains substantial quantities of nitrogen compounds, not all of which are removed in the extraction process. The concentration of nitrogen compounds in the raw shale oil from surface retorts are of the following characteristics (Table 14b.3).

Table 14b.3: Characteristics of Raw Kerogen Oil

Characteristic	Units	Range of Values
Gravity	API degrees	20-25
Pour Point	°C	25-30
Distillation midpoint	°C	375-400
Nitrogen content	Weight percent	1.6 – 2.0
Basic nitrogen content	Weight percent	1.2 – 1.5
Non-basic nitrogen content	Weight percent	0.4 – 0.5
Sulfur content	Weight percent	0.3 – 0.5
Percent nitrogen compounds	Mole percent	30 - 40

The advantage of extraction processing by VEP is that virtually all (>85%) of the basic nitrogen compounds are recovered in the extract. These are the most difficult to hydroprocess. The resulting raffinate is now much more readily hydrotreated, because the nitrogen compounds have been substantially removed, and particulates and metals report to the extract, where they are relatively easily filtered from the dilute extract stream. Hydrotreating of the raffinate may be accomplished at pressures of less than 1000 psig H2, and consumption of hydrogen of less than 600 scf/bbl. Process costs are likely less than $5/bbl, even when capital amortization is taken into account.

The hydrotreated raffinate from the VEP is a high quality product, low in sulfur and nitrogen and stable to transportation and storage. It is readily marketable to ordinary refineries and has been valued at a premium to NYMEX traded West Texas Intermediate, WTI. The nitrogen and sulfur levels can be controlled by the level of severity of the hydrotreater. In the example shown, extremely mild conditions were used for manufacturing the VEP refinery feed (Table 14b.4).

Hydrotreated raffinate will be acceptable to all refineries. This material will be an excellent diluent for waxy crudes produced in the region, or even for blending with tar sand bitumen, such as what Canadian producers market with their dil-bit product.

Table 14b.4: Characteristics of Hydrotreated Refinery Feedstock

Properties	Unocal oil shale refinery feed	VEP raffinate refinery feed	Alberta Oil Sands synthetic crude
API Gravity	40	36.8	35.5
Sulfur ppm	5	200	400
Nitrogen, pm	20	1200	129
UOP K factor	12. 3	12.0	11.7
Pour Point °C	< -4	4	NA
Viscosity @ 37 °C cSt	NA	3.3	NA
Distillation Yields			
<200 °C	24	30	28
200-275	23	16	27
275-325	17	12	21
325-400	22	23	15
400-538	14	19	7
>538 °C	0	0	2

The market acceptance of products from the extract has yet to be confirmed, and this confirmation will come through future R and D. The total extract contains properties that are valuable as an anti-strip asphalt additive, for the same reasons that SOMAT, the Paraho product, achieved market acceptance from the State of Wyoming and other entities. That is, the basic nitrogen compounds form a bond with aggregate that resists moisture damage and increase the life of the road.

The classic evidence of this beneficial behavior is the road leading from I-70 to the Anvil points mine in Colorado. This road was paved more than 50 years ago with shale oil-derived asphalt and even with daily truck traffic is still in use today with virtually no maintenance.

The highest value, highest volume pure compound targets are the pyridines and picolines used in the agrochemical industry for products ranging from herbicides to vitamins for animal feed. Pure compound values are estimated at more than $5/kg and yields up to 5% (~7 kg/bbl) of the total raw shale oil can be produced. Oil shale extracted products will compete with products made today by synthesis routes; which are experiencing unprecedented increases in feedstock costs as natural gas, ammonia and formaldehyde prices rise along with crude oil prices.

The high-value markets are large enough to support an initial venture of about 20,000 bbl/day, using the VEP extraction approach. This would produce pure compounds that would supply about 5% of the world markets for pyridines and picolines. This volume would be enough to provide buyers an incentive to help qualify the products with the promise of lower cost, but not so much that it greatly alters the world pricing structure.

In time, it conceivable that US shale-derived nitrogen heterocyclic compounds could command the majority of world markets, because the extraction route offers a substantially lower cost base compared to the alternative synthesis rout. The first production facility in this market space will command a competitive advantage over those who follow because the second-generation plant would now need to compete for market share with the first-generation extraction plant which gained the price advantage of extraction over synthesis routes.

14b.7. Economic Update

14b.7.1 Costs

The high capacity case is used as the base case. In reality, it is unlikely that the low capital case will be deployed because it misses the opportunities presented by the pure compounds. Similarly, the high value case is unlikely to attract capital, because there is a desire to maximize capacity through a fully integrated product slate.

To run the high capacity case with today's economics the CAPEX and OPEX were updated using the Nelson-Farrar cost indices as published annually in the Oil and Gas Journal. Costs for kerogen oil feedstocks are per discussion in the Alberta Analogy section above, namely, $35.40/bbl for surface retorted oil and $29.00/bbl for in-situ oil.

Table 14b.5: High Capacity Case CAPEX

Installed Costs – 2006 (escalated and resized from Tables 14.2 and 14.3)				
Unit	**Daily Capacity Bbl or Mscf**	**Installed Cost USD per daily bbl capacity**	**Installed Cost USD**	**OPEX $/feed-bbl**
Extraction	21,415	6,023	128,979,401	2.10
Distillation	4,307	1,887	8,127,018	0.18
THDA	1,400	3,474	4,863,026	0.24
Hydropyrolysis	1,731	8,144	14,093,436	0.44
Hydrotreating	8,850	5,122	45,333,144	1.43
Purification	1,566	11,624	18,203,261	0.28
Hydrogen Plant	21,555	5,876	126,661,702	1.27
Tankage and Pipeline			8,745,323	5.93
Grass Roots Factor – 20%			69,252,200	1.19
Total Installed Cost (CAPEX)			415,513,197	7.12

Table 14b.6: High Capacity Case OPEX

Installed Costs – 2006 (escalated and resized from Table 14.5)				
Unit	**Daily Capacity Bbl or Mscf**	**$ per stream barrel**	**Stream Factor**	**OPEX $/feed-bbl**
Extraction	21,415	1.962	1.07	2.10
Distillation	4,307	0.823	0.22	0.18
THDA	1,400	3.442	0.07	0.24
Hydropyrolysis	1,731	5.062	0.09	0.44
Hydrotreating	8,850	3.240	0.44	1.43
Purification	1,566	3.543	0.08	0.28
Hydrogen Plant	21,555 mscf			1.27
Tankage and Pipeline				1.00
Subtotal				6.93
Admin factor – 20%				1.39
Total OPEX				8.32

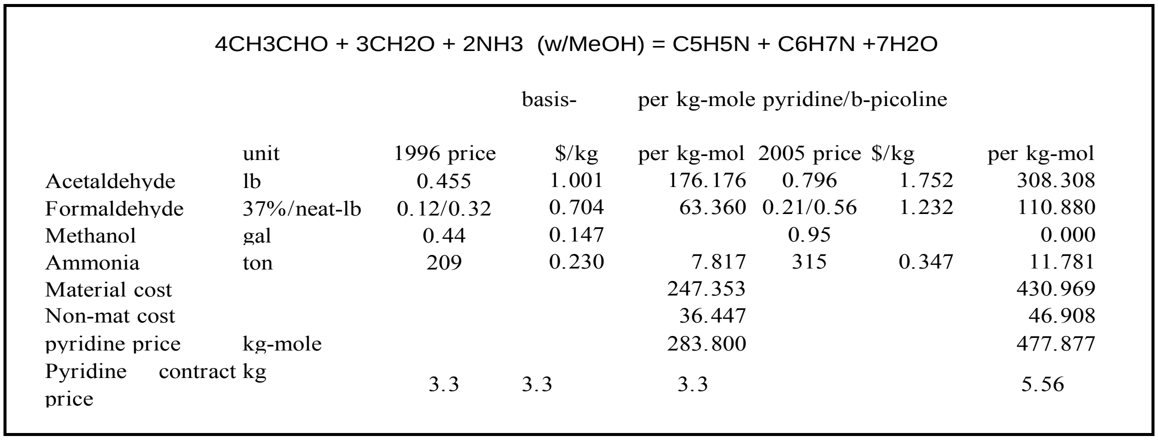
14b.7.2 Revenues

Pyridine and Pyrrole Prices

Bulk, contract prices for pure nitrogen heterocyclics are hard to come by, simply because long-term contract prices are locked in at lower rates than prevailing rates, as-well-as the fact that published prices are often substantially higher than bulk commodity prices. In 1996 JWBA was able to confirm the long-term contract price of pyridine at $3.3/kg.

To update this product price, an estimate was made by comparing raw material prices from 1996 with raw material prices today, and escalating the non-raw material prices by the employment index inflation rate, assuming the majority of non-material costs were related to labor costs. The methodology and results are shown in Table 14b.7

Table14b.7: Costs of Synthesis Chemicals used in Manufacture of Pyridine



4CH3CHO + 3CH2O + 2NH3 (w/MeOH) = C5H5N + C6H7N +7H2O

			basis-	per kg-mole pyridine/b-picoline			
	unit	1996 price	$/kg	per kg-mol	2005 price	$/kg	per kg-mol
Acetaldehyde	lb	0.455	1.001	176.176	0.796	1.752	308.308
Formaldehyde	37%/neat-lb	0.12/0.32	0.704	63.360	0.21/0.56	1.232	110.880
Methanol	gal	0.44	0.147		0.95		0.000
Ammonia	ton	209	0.230	7.817	315	0.347	11.781
Material cost				247.353			430.969
Non-mat cost				36.447			46.908
pyridine price	kg-mole			283.800			477.877
Pyridine contract price	kg	3.3	3.3	3.3			5.56

The result is a current estimated product price of $5.56/kg FOB-midwest for either pyridine or b-picoline. Pyrrole products are generally more valuable than pyridine products, but their markets are more limited. Hence, the same revenue value was used for pyrroles.

Asphalt Additive Prices

Asphalt additive will vary according to prices of crude oil. Amine based antistrip asphalt additives sell for about $0.70/lb (2004 prices calculated from reference[26]). This is consistent with prior information that amine-based antistrip additives are expensive, synthesized chemicals. Often the cost-basis for synthesis chemicals is about 30-40% of list prices but 70-80% of wholesale, long-term contract prices. This would imply that costs are about $0.21-0.28/lb and prices that would compete for contract volumes are about $0.28-0.36/lb. For purposes of economic estimates we have used $0.30/lb, or $100/bbl.

Carbon Dioxide Prices

CO_2 prices vary considerably by application and purity. Industrial grade CO_2 fit for enhanced oil recovery may sell for as little as $4/ton, while higher purity CO_2 may sell for $100/ton or more. The European trading markets, artificially created for carbon sequestration, have ranged widely, but $20/ton is in the middle of the range. For purposes of this economic analysis, $20/ton is used.

Crude Oil Prices

For 2006 crude oil prices averaged about $61/bbl. Several cases were run on prices ranging from $30 to $70/bbl. For the $50 case (shown in Table 14b.8 below), the IRR is 40.3%. For the $30 case (not shown), the IRR is 27.8%. It would appear that the economics have improved since 1999 providing a strong incentive to include VEP in a shale oil venture.

14b.8 Role of VEP in Large Scale Development of Oil Shale

What is the role that Value Enhancement Processing (VEP) will take with 1) the production of byproducts of shale oil, 2) a comprehensive list of multiple projects in which to apply the VEP, and 3) a thorough discussion of how to make shale oil recovery self-sufficient? This latter requirement is interpreted to mean what role VEP can take to make shale oil recovery investment-worthy.

Much of the answer to these questions has been given in the discussion above for a small scale plant; but what about for a whole industry. By 2035 up to 2.4 million bbl/day of shale oil might be produced[20]. At 5% yield this would imply the production of 120,000 bbl/day nitrogen compounds. This would be a substantial portion of the total world market, including asphalt additives and would require a number of years to displace synthesis chemicals, assuming that specifications can be met for all markets.

Table 14b.8: KPX Investment Analysis – High Capacity Case (Updated)

High Capacity Case 2006

Data

		User	Input	S.Factor
Products	bbl/day	20000	20000	1.00
Capital	$	415513197	4.16E+08	1.00
Operating	$/bbl	8.32	8.32	1.00
Raw Material	$/bbl	**35.40**	35.40	1.00
Revenue (1)	$/yr	689070207	689070207	1.00
Revenue (2)	(wt.avg.) $/bbl	100	100	1.00
Royalties	% of Sales	4	4	1.00
Operation	days/yr	345	345	1.00
Life	Years	15	15	1.00
Admin.(incl. marktg) % of Op.		17%	17%	1.00
R&D	% of Sales	4%	4%	1.00
Equity		100.0%	100%	1.00
Debt Interest Rate		10.0%	10%	1.00
Discount Rate		10.0%	10%	1.00
Tax Rate		40.0%	40%	1.00
Loan	Years	15	15.0	1.00
Day	Hours	24	24	1.00

Products **6,900,000 bbl/yr**

alue $/bbl or Tor	revenue $/yr	689070206.6	Yield bbl/day
50	ref. feed	85	16985.18035
792.3	pyridines & pyrr	6.8	1351.876285
100	asphalt add.	2.9	576.8364001
100	other chem	0.6	112.5733898
20	CO2	12.6	400.6684862
		108	

IRR **40.3%**

NPV **8.68E+08**

Investment Schedule

year	amount
1	$15,679,743
2	$31,359,487
3	$344,954,352
4	$23,519,615
total	$415,513,197

Cash Flow Analysis

Production		0%	0.0%	75%	100%			
Year	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**18**
Revenue		0	0	516,802,655	689,070,207	689,070,207	689,070,207	689,070,207
-op.cost		0	0	(301,664,137)	(301,664,137)	(301,664,137)	(301,664,137)	(301,664,137)
-admin		0	0	(9,758,703)	(9,758,703)	(9,758,703)	(9,758,703)	(9,758,703)
-Dep.		0	0	(27,700,880)	(27,700,880)	(27,700,880)	(27,700,880)	(27,700,880)
-Royalties		0	0	(20,672,106)	(27,562,808)	(27,562,808)	(27,562,808)	(27,562,808)
-R&D		0	0	(20,672,106)	(27,562,808)	(27,562,808)	(27,562,808)	(27,562,808)
-Interest		0	0	0	0	0	0	0
Gross Income		0	0	136,334,722	294,820,869	294,820,869	294,820,869	294,820,869
-Tax		0	0	(54,533,889)	(117,928,348)	(117,928,348)	(117,928,348)	(117,928,348)
Net Income		0	0	81,800,833	176,892,522	176,892,522	176,892,522	176,892,522
+Dep				27,700,880	27,700,880	27,700,880	27,700,880	27,700,880
-Principal				0	0	0	0	0
+Borrowed Capital	0	0	0	0				
-Equity Capital	-1.57E+07	(31,359,487)	-3.450E+08	(23,519,615)				
Cash Flow	-1.57E+07	(31,359,487)	-3.450E+08	85,982,098	204,593,401	204,593,401	204,593,401	204,593,401
Cum. Cash Flow	-1.57E+07	(47,039,230)	-3.920E+08	-3.060E+08	-1.014E+08	103,175,319	307,768,720	2,558,296,136
DCF	-1.57E+07	(28,508,624)	-2.851E+08	64,599,623	139,740,046	127,036,406	115,487,641	40,477,714
NPV	-1.57E+07	(44,188,367)	-3.293E+08	-2.647E+08	-1.249E+08	2,101,466	117,589,107	867,688,383
IRR	**40.3%**							

Total world markets for asphalt additive at 2% concentration would be about 80,000 – 100,000 bbl/day (2% of 5-6% of 80-85 million barrels). Estimates of world markets for nitrogen-based oil-field chemicals and industrial surfactants have not been made, but are undoubtedly smaller (but still significant) than the asphalt additive market. Pure compound markets are a small fraction of these totals. This simple exercise shows that it is highly unlikely that markets exist, or can be developed before 2035 to consume all of the possible available nitrogen-containing compounds. Hence, we can expect that a large portion will need to undergo direct hydrodenitrogenation. Note, that while expensive, HDN produces ammonia, a valuable by-product in its own right.

The role of VEP will be to enhance the economics of a mega-project, as contrasted to being the 'market-pull' for a small-scale project. This change of role has impacts on several optimization criteria, including scale, extraction process severity and product slate.

To elaborate, with increases in oil prices and likelihood of shortfalls in conventional petroleum supply there will be a strong push to grow and oil shale industry focused on producing a substitute refinery feed (sweet syncrude). Large-scale shale oil production will lower VEP feedstock costs. The optimum extraction may be aimed at recovering the lower alkyl pyridines, pyrroles and phenols, leaving the higher alkyl homologs for the HDN unit.

Of the total oil shale production about 75% of it, or about 1.8 million, is expected to come from in-situ production, probably by slow heating similar to what Shell is developing with their ICP process. Liquid products from the ICP exhibit a nitrogen content of about 1 % by weight (cf. Table 2, Strategic Significance of America's Oil Shale Resource, DOE Office of Petroleum Reserves, March, 2004). The distribution of this nitrogen content with respect to boiling point is has not been disclosed, but it is likely that the concentration increases with increasing boiling point, not dissimilar to the trends observed with conventional surface retorting.

For the other production, or about 600 thousand barrels/day from surface retorts, raw kerogen oil product will exhibit nitrogen contents ranging from about 1.4 to 2.2 % by weight. For this material the high nitrogen content may be more problematic for conventional hydrotreating and there will be a greater incentive to use VEP as part of the upgrading step.

Using VEP for large quantities of raw kerogen oil will face market constraints and beyond a certain volume, market penetration will require that discounts on price be offered. Once this point is reached, then the oil shale industry will need to be prepared to supply a growing share of the world markets, as it may not be possible for synthesis chemicals to continue to compete on a cost basis.

It is also clear that if VEP is to have more than an incidental role in the economics of an oil shale industry, markets for large volume commodities will need to be developed. In prior work, these large volume markets were identified as anti-strip asphalt additive, industrial surfactants, and oil-field chemicals, to name the principal products.

Based on prior market research, and in view of the magnitude of the potential production, it is likely that the first plant to produce commodity and specialty chemicals from oil shale will enjoy the best pricing power, with the greatest likelihood of drawing market share from the synthesis producers. Thus, the first plant may establish a barrier to entry for successive producers, or alternatively, become the outlet for extraction products manufactured by others in the upgrading process.

The significance of this changing dynamic is that:

a) VEP will take on the role of production of byproducts, rather than the main economic driver earlier contemplated.
b) There may be multiple projects in which to apply VEP, some more profitable than others,

c) There will be increasing pressure to make shale oil recovery energy self-sufficient, placing demands on residuals for heat and power generation, influencing the final product slate.
d) VEP may serve the role of easing the severity of the hydrotreating process, and hence, the optimum extraction conditions may be quite different from those previously identified.
e) The large-scale nature of the developments point to a more world-wide marketing effort, as compared to the narrow markets previously contemplated.

14b.9 Venture Development Update

New interest in the development of oil shale has been shown by major corporations and smaller companies alike. For the first time in more than 20 years we see that industry is becoming interested in developing oil shale at a large scale. The approaches include both in-situ and ex-situ recovery. The thinking in the industry is to build megaprojects, not unlike the scale practiced in Alberta, Canada. This is quite different than the small-scale projects for which economics were originally run on the VEP concept.

Emerging trends point to indirect heating of retorts. The significance of this trend is that oil is more stable, and very likely to be lower in nitrogen content than direct-fired retorts. (It is not yet clear if this will result in lower retort yield.) The more stable oil product is likely to result in better operability, less fouling in the extraction system, but also lower yield of the extract.

The Shell process claims to produces very light oil, with very low nitrogen content. While theoretical calculations can be made on the basis of prior models, understanding the product slate when applying VEP to an ICP product will require laboratory testing. It is not known at this time whether or not agreements can be made to perform such testing. Suffice it to say, additional work will need to be done to assess the relationship of VEP to in-situ produced oil using indirect heat.

The OilTech (OT) process is a surface retort that also uses indirect heat. JWBA is in contact with OT and is negotiating terms by which VEP evaluation can be completed on OT oil. Cost for such evaluation may be borne by non-DOE funds. Since the prior study oil was a Unocal oil manufactured from a direct-fired retort, the results of an evaluation of the OT oil could serve as an important benchmark in the project assessment.

With the trends toward large-scale projects, the question now is ‘how large an extraction unit represents the economic optimum?’ A large scale extraction unit might completely avoid the hydrodealkylation step, by recovering the lower alkyl pyridines for pure compounds and recovering the higher alkyl pyridines for a combination of asphalt additives, detergents and as a supplemental fuel for power generation.

An assessment of VEP in the context of a megaproject was not contemplated in the original Statement of Work, but now seems to be a fruitful pursuit, in view of this newly emerging industrial interest in large-scale projects.

On June 9, 2005 the BLM placed a Federal Register Notice for R, D & D leases for oil shale. The significance of this event is that this is the first time in 85 years that industry has been able to nominate oil shale tracts and bid for rights on these tracts (the 1970s Prototype leasing program was highly controlled and limited to specific blocks selected by the Government). Along with the R, D and D lease tract (160 acres) companies could select an additional 4960 acres for preference rights, the combined 5120 acres being the maximum allowable by law at the time.

The effect of this lease offering was to awaken industry to the prospect that oil shale leases may soon be made available (subsequent energy legislation passed in August, 2005 expanded on the prospective availability of resource). There were 8 applications in each of Utah and Colorado and 1 in Wyoming. Applicants ranged from the largest petroleum companies to small entrepreneurs. It now appears as if industry is taking an interest in developing oil shale. With the prospect that lease holdings will no longer be restricted to 5120 acre blocks, oil companies are looking at much larger plant capacities, on the order of 100,000 bbl/day. (A 5120 acre block in Utah would only support a plant capacity of about 50,000 bbl/day at the very best locations, more in Colorado and less in Wyoming).

The significance of these events to VEP is four-fold.

1. The need to 'pilot' an industry at 10,000 bbl/day, using the economics of VEP to make a small unit profitable may be obviated by the renewed interest at a larger scale.

2. The price of oil, exceeding $30/bbl for more than two years now, is expected to be substantially higher than the $20/bbl the original VEP economics were based on. Congress is considering price floors for oil shale production, probably in the range of $35 – 40/bbl. Legislatively controlled price floors, probably through production tax credits on a sliding scale will be used as one of the cases for performing economic analysis.

3. It will no longer be necessary to justify oil shale economics on the basis of making up the difference between prices and costs by the Value-Enhancement products alone. VEP capacity and product slate can now be optimized based on markets and internal stream values, with less regard for carrying a minimum production capacity.

4. The Value-Enhancement product margins are growing, because the raw materials for synthesis feedstocks are growing even faster than the price of crude oil.

All of these factors change the optimizing functions. In prior analysis, it was essential that a broad range concentrate be manufactured to provide the economy-of-scale needed for the extraction. Now the extraction capacity may be more strongly driven by savings on the hydrotreating end. Further, it may be desirable to extract only the heavy ends, while directly hydrotreating the light ends. In prior studies the penalty for taking this tack was reduced yield of nitrogen compounds, but with a larger raw kerogen oil production, this penalty may prove not to be as important.

JWBA is making its VEP technology available for license and has been in discussions with several companies who are making progress with retort technologies.

14b.9.1 Patent Awarded

US patent # 6,875,341 B1 "Process for Enhancing Value of Hydrocarbonaceous Resources" was issued by the US Patent and Trademark Office. The patent contains the Statement of Government Interest "This invention was made in part with United States Government support under contract No. DE-AC21-93MC29240 awarded by the Department of Energy (DOE) The government may have certain rights in this invention."

The patent covers the extraction and processing of high-value products from hydrocarbonaceous resources. "Oils for treatment by the invention are those derived by extraction or heat treatment of carbonaceous materials, e.g., oil shale, oil sands tar sands, coal, gilsonite and biomass." Further, "Any hydrocarbonaceous product having sufficient amounts of heteroatom-containing molecules to justify their recovery as a valuable product are contemplated as an oil source for the process of the invention."

The invention claims extraction processes applied to hydrocarbonaceous oils, which use a solvent system of a polarity greater than 1 Debye, with a minor portion of water acting as an antisolvent, under process conditions that yield a Coefficient of Separation (COS) of greater than 50%.

The patent describes in detail the solvent systems and process conditions used to achieve the desired results. A coefficient of separation (COS) is defined as the "mole % of desired compounds recovered in the fraction minus the mole % of undesired compounds recovered in the same fraction." The effectiveness of the separation is optimized when the coefficient of separation is the highest. It is believed that this definition will closely track the economic optimum.

It is worthy for emphasis and clarity to summarize the value of using the defined COS as a process objective function. In the prior art, emphasis has been placed on the percentage of nitrogen compounds recovered in the extract. This objective ignores the amount of hydrocarbons that are co-extracted and results in unacceptable loss of oil and dilution of the nitrogen compounds.

When optimizing the COS function we find that the solvent-to-oil ratio cannot be too high or too low. At high ratios too many non-nitrogen compounds are extracted and economics suffer. At low ratios, insufficient nitrogen compounds are extracted, and at very low ratios it becomes difficult to maintain two liquid phases.

Likewise, the effectiveness of the solvent system is directly measured by the COS. When a number of solvent systems are tested at a constant solvent-to-oil ratio, the COS is a direct measure of the selectivity toward the target compounds, and hence, a sound tool for screening solvent candidates.

It should be noted that the optimum solvent composition will vary based on 1) the composition of the feedstock, including boiling range 2) the target compounds for extraction, 3) ease of solvent recovery and control of recycle quality, 4) effects of water content, 5) operational considerations, including propensity to form emulsions or rags, 6) cost of makeup solvent, 7) acceptability to downstream processing and 8) health and safety considerations, among possibly others. For work with kerogen oils, it has been found that lower carboxylic acids (formic and acetic) have consistently shown favorable characteristics for extraction of pyridinic nitrogen compounds from US kerogen oil and phenolic oxygen compounds from Estonia kerogen oil.

Now that this patent has issued, JWBA will be seeking licensees for the technology. Successful licensing will improve the investment attractiveness in oil shale and help advance the prospect for commercialization. Additional patents are possible in the area of processing of nitrogen- or oxygen-rich extracts.

Deciding factors today may include competition for energy-related capital. Oil shale ventures will be measured against oil sands and other unconventional fuels such as Fischer Tropsch liquids.

Comparisons with Alberta Oil Sands suggest that large-scale syncrude production (without VEP) from oil shale will need to compete with energy-capital at oil prices of about $30/bbl. That is, if oil shale is more costly than about $30/bbl and this additional cost is not offset by favorable government treatment, then capital will preferentially flow to Alberta Oil Sands (or conventional oil and gas resources that are undervalued).

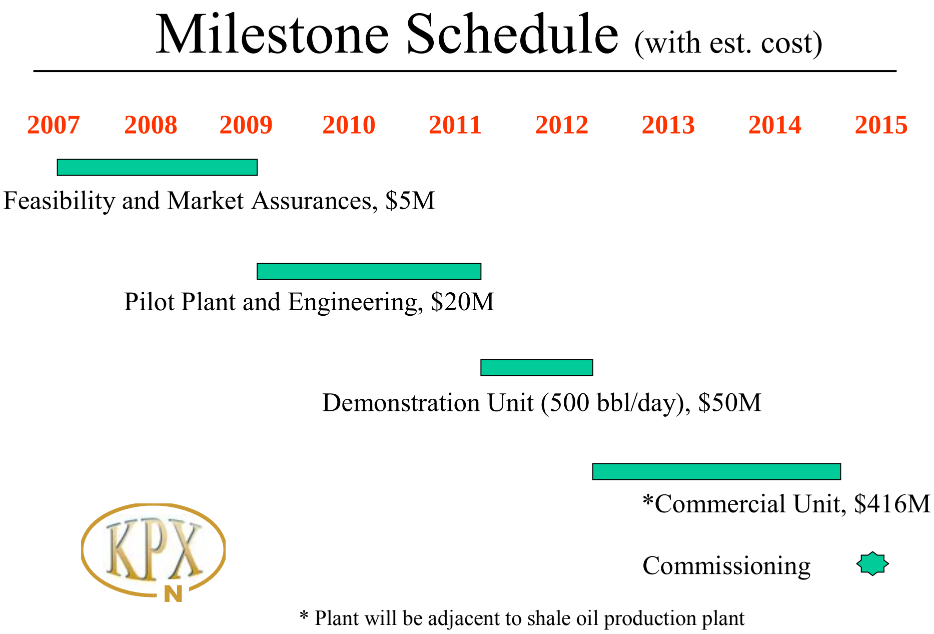
14b.9.2 Next Development Steps

The reported activities have been based on laboratory analysis and processing of a commercially available shale oil sample. While processes were run in semi-continuous mode and careful measurements have been made of the mass balances, the process has not been integrated. Piloting of certain processes such as extraction, THDA and HP are necessary in the next phase of development. The current study, and this report, serve to some extent to validate the feasibility and from discussions with industry are likely to warrant further private sector development.

The four major milestones are given in Figure 14b.4. A full feasibility analysis must be completed, along with market assurances (who will accept the products and what price will they pay). At this stage equity participants are likely to be identified. Candidates will include those companies previously consulted. Piloting is expected to be conducted on a toll basis. That is, feedstock will be moved to existing facilities for testing. Generally, these pilot plants will operate on a scale of a few barrels/day. Samples will be prepared upon which to base market letters of intent.

Once market agreements are in place, investment in an integrated field project will be warranted. Final market agreements, conditioned on agreed specifications will be put in place. Agreement with a kerogen oil supplier will also be made. The field pilot will be as such a scale that scale-up to 20,000 bbl/day is justified. Generally, for fluids-only systems, scale-ups of 100-200 to 1 are prudent. The field demonstration will probably fall between about 100 – 500 bbls/day, depending on the confidence obtained at the pilot plant study level.

Figure 14b.4: Milestone Schedule (Updated)



PHASE V (Task 14b) - CONCLUSIONS

Kerogen oil is rich in valuable heteroatom containing compounds. Liquid-liquid extraction is an efficient, cost-effective step to recover the heteroatom-containing compounds for manufacture of chemicals and simultaneously producing a raffinate, readily upgraded to premium petroleum refinery feedstock.

Markets exist for the highest value products; those that contain lower alkyl groups. Yields of these products are maximized using commercially practiced process for dealkylating rings. Markets for broad range concentrates include anti-strip asphalt additives, oil field chemicals, surfactants and fuel additives. Production of such concentrates enhances the overall plant capacity and adds flexibility to the operation.

The first-generation plant will require simplicity and products should address existing markets. Once established, greater world wide market penetration and development of new markets is likely. Cost trends show that VEP extraction products will be able to compete with synthesis products over the long-term. There is some possibility that production of refinery feedstock becomes sufficiently attractive in its own right that VEP may not be necessary to start an industry; however, if an economic fence is drawn around VEP, the IRR will still exceed that of simple fuels production, and that opportunity is expected to attract the necessary capital.

VEP adds economic value to an oil shale venture and reduces the risk of price declines. Anticipating that with firm world oil prices, a large oil shale industry will ultimately be developed, VEP will play a valuable role in improving the economics of first-generation technologies. Efforts are underway to attract private investment for piloting and eventual commercialization of the technology.

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List of Acronyms, Abbreviations and Glossary of Terms

Alkylate – A term used in the petroleum industry to designate a branched chain paraffin derived from an isoparaffin and an olefin. The product is used as a high-octane blending component of aviation and civilian gasolines. Also, the addition of an alkyl group to a ring system.

Antistrip asphalt additive - Additives, generally of comprised of amines, which are added to paving asphalts to resist moisture stripping of the asphalt binder from the aggregate. Addition of high quality antistrip additives extend the life of paved highways and runways, especially in climates where there is frequent freezing and thawing cycles.

Aquathermolysis - A term used to describe pyrolysis in the presence of liquid water, as compared with steam pyrolysis, which is a vapor phase reaction.

Azeotrope – A liquid mixture of two or more substances which behaves like a single substance in that the vapor produced by partial evaporation of liquid has the same composition as the liquid. The constant boiling mixture exhibits either a maximum or minimum boiling point as compared with that of other mixtures of the same substances.

Carbon number - In this context, the number of carbons found in alkyl groups bonded to a ring system. Thus a C_7 resorcinol would possess seven carbons bonded in various methyl groups or longer alkyl chains to the resorcinol ring.

Compound type - The term compound type is used in the context given in Reference 6 and means any distinguishing functionality of rings or heteroatom (N, S, O) which forms the basis for a homologous series. In the development of Z-BaSIC there have been found more than 60 compound types as illustrated in the left hand column of Table 3.4.

COS - Coefficient Of Separation. Defined as the mole percent of desired components extracted less the mole percent of non-desired components extracted.

Data.ms file - the computer file generated by the MSD consisting of the ions produced and their intensity (currents) as a function of time since injection.

Distillation – A separation process in which a liquid is converted to vapor and the vapor then condensed to a liquid.

EIC - Extracted Ion Current, a chromatogram showing the detector response to a particular mass as a function of time since injection, extracted from the data.ms file.

Galoter - The name given to a type of retort in operation near Narva, Estonia and consisting of a rotary kiln heated by recycled, combusted, spent ore.

GC - Gas Chromatography, a method for separating volatile components according to their thermodynamically controlled partitioning between a flowing gas phase and a stationary bonded phase.

HVGO - Heavy Vacuum Gas Oil for this report is considered that portion of the kerogen oil boiling above 400° C atmospheric equivalent boiling point.

HAPs - Higher Alkyl Pyridines are pyridines that contain more than 2 alkyl carbons, either as methyl groups or in longer chains. In the case of Green River kerogen oil the number of total carbons in the highest MW examples is about 26.

HARs - Higher Alkyl Resorcinols are resorcinols that contain more than 2 alkyl carbons, either as methyl groups or in longer chains. In the case of Estonia kerogen oil the number of total carbons in the highest MW examples is about 16.

IRR - Internal Rate of Return is the interest rate received for a cash flow consisting of an investment (negative value) and net revenues (positive values) that occur over a specified period of time.

Kiviter - The name given to a type of retort in operation near Kohtle Jarve and Kivioli, Estonia and configured as a down-flow vertical chamber heated by cross-flow direct combustion. The Kiviter retort is characterized by a water seal in the bottom zone to cool the produced semicoke and isolate the retort chamber from the atmosphere.

KPX - Kerogen Products Extraction is a brand applied to kerogen-oil-derived products from the VEP scheme.

LHSV - Liquid Hourly Space Velocity is calculated by dividing the volume of the feedstock flow per hour by the volume of the reactor, resulting in a numerical value of reactor volumes per hour. Use of LHSV is a convenient method of specifying average residence time without the need to specify flow rate and reactor dimension details.

LAPs - Lower Alkyl Pyridines are pyridines that contain 1-2 methyl groups. These types may be separated into pure compounds and markets for these compounds either already exist or can be relatively easily developed.

LARs - Lower Alkyl Resorcinols are resorcinols that contain 1-2 methyl groups. These types may be separated into pure compounds and markets for these compounds either already exist or can be relatively easily developed.

MSD - Mass Selective Detector, in this case electron impact ionization (70 electron volts) of a quadrapole configuration and having a nominal mass resolution of 1 atomic mass unit.

MW - Molecular Weight, expressed in atomic mass units, amu, or Dalton.

Rp - Partition ratio is defined as the ratio of the concentration of a component in the extract divided by the concentration of that same component in the raffinate. A partition ratio of 1 implies that there is no preference of that component for the raffinate or the extract. In thermodynamic terms, the free energy in both phases is the same.

SOMAT - Shale Oil Modified Asphalt is a shale oil-derived antistrip product developed and marketed by the New Paraho Corporation. It has been placed in test strips in eight states and one (Wyoming) has accepted it for state highway paving purposes.

THDA- Thermal hydrodealkylation is a thermal, non-catalytic process performed under hydrogen pressure. At proper temperature, residence time and pressure conditions alkyl groups are removed from aromatic ring systems, leaving the bare ring or a mildly methylated ring as product.

TIC - Total Ion Current is a chromatogram showing the total detector response as a function of time since injection.

VEP - Value Enhancement Processing, the subject of this research, is the processing of kerogen oil to extract and convert naturally occurring nitrogen- and oxygen-containing constituents to valuable chemicals. The term ‘enhancement’ follows from the observation that these same constituents are of very low value as fuel and without the value enhancement processing would result in low production revenues.

VOC – Volitile organic compounds pertains to those organic vapors that may escape to the atmosphere if left uncontained. VOC releases is the quantity of VOCs that are allowed to be released to the atmosphere.

ACKNOWLEDGEMENTS

The majority of this work was supported by the US Department of Energy, **National Energy Technology Laboratory**, under contract DE93-AC21-93MC29240. The technical assistance of DOE Contracting Officer's Technical Representatives, in order of their assignment, James Westhoff, Keith Westhusing, the late Hugh Guthrie, Sue Mehlhoff, and Betty Felber is gratefully acknowledged. The assistance of David Olsen for his review and comments on the final report added substance and clarity to the report.

A portion of this work was conducted under an agreement between the US DOE and the **Estonia Academy of Sciences** with assistance from the **Oil Shale Institute of Tallinn Technical University**. US sponsorship was obtained from the **Office of Naval Petroleum and Oil Shale Reserves**. Portions of Phase IV of this report have been taken directly from References 7-10. JWBA acknowledges these sources of text.

The following **JWBA Scientists and Engineers** contributed to the technical research: C.P. Russell, D.E. Cogswell, P. A. V. Devineni, J. Tsai, J. Wiser, A Wright, H. Mihamou, J. Daghlian, and H. Huai.

University of Utah the contributors were J. B. DuBow, L. L. Anderson, and J. Pu. Subcontractors to JWBA were R. Zahradnik, the late J. Sinor, G. Dolbear and D. Purpi.

Estonia Researchers and Program Managers were: Mr. Anthony P. Dammer, Ms. Kitty Kubo, Prof. Mihkel Veiderma, Dr. Mihkel Koel, Dr. Jüri Tanner, Dr. Jüri Soone; Mr. Hugh Guthrie, Dr. Don Repici, Dr. Peep Sürje, Mr Jaanus Purga, Mr. Nikolai Golubev, Dr. E. Raidma; Prof. M. Kaljurand; Prof. M. Lopp, Dr. J. Zirjakov; Dr. E. Roo; Prof. R. Munter; Dr. R. Kuusik, S. Doilov, Dr. V. Sitnik; Dr. L. Kekisheva, Dr. H. Luik, Dr. H. Riisalu, Prof. Y. Lille, Dr. I. Rooks, Prof. J. Järv, Prof. R. Küttner

Organizational Acknowledgements are due for:

US Dept. of Energy - National Energy Technology Laboratory, Office of Naval
Petroleum and Oil Shale Reserve, Rocky Mountain Oilfield Testing Center
Ministry of Economic Affairs and Communication of Estonian Republic
US State Department/ US Embassy in Tallinn
Estonian Academy of Sciences
Tallinn University of Technology (TTU), Institute of Oil Shale
Tartu University
Viru Keemia Grupp
Narva Power Station Oil Factory AS
Kiviõli Oil Factory
Carboshale
NRG Energy, John Francis Co.
Shell Oil Company
Ashland Chemical Co