

# Shale Oil Value Enhancement Research

## Quarterly Report

June 1 - August 31, 1996

By  
James W. Bunger  
Christopher P. Russell  
Jesse C.H. Tsai  
Donald E. Cogswell  
Houssine Mihamou  
Aaron D. Wright

RECEIVED  
MAR 04 1997  
OSTI

Work Performed Under Contract No.: DE-AC21-93MC29240

For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
P.O. Box 880  
Morgantown, West Virginia 26507-0880

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

By  
James W. Bunger and Associates, Inc.  
P. O. Box 520037  
Salt Lake City, Utah 84152-0037

**DISCLAIMER**

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

## Disclaimer

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

## Summary Management Report

The quarter's efforts were concentrated on (a) THDA and reaction of alkylpyridines at elevated conditions, (b) compound type analysis of kerogen oil and its derived products, (b) thermal hydrodealkylation of the  $>290$  °C polar fraction, (c) secondary reactions of pyridinic type compounds to form marketable products, and (d) preparation of presentation to the Dawnbreaker Commercial Assistance Program. Excellent progress is being made in all cases.

The liaison with potential industrial partners is continuing. During October, we will participate in Commercial Opportunity Forum of the Dawnbreaker Commercialization Assistance Program. We qualified for their program because the initial thrust for value-added products research originated in the SBIR program. The reviewers believe that both our technologies and products are marketable and deserved further attention.

Our market analysis and industrial feedback indicate that the low molecular weight pyridines are the main market driving force. We are concentrating our effort toward increasing the yield of "light" pyridines before the end of Phase II(a). Our current laboratory set-up can only produce analytical quantity of samples, which is not sufficient for marketing purpose. However, the completion of a secondary flow THDA unit for a pilot-scale production depends on the availability of the Phase-II(b) and Phase-III funding.

# Technical Progress Report

## Objectives for the Quarter were:

- Conduct THDA and reaction of alkylpyridines at elevated conditions,
- Perform acid-base separation on the raffinate fractions and assess the separation efficiencies of the extraction process,
- Perform reaction types (e.g., oxidation, chlorination, and polymerization) of the <290 °C kerogen oil extract fraction in order to obtain higher value products;
- Refine commercialization business plan, proceed with industrial liaison and update market evaluation.

## Discussion

### Task 8. Separation Development

**Acid-base Separation** The purpose of this work is to both help quantify the type of polar compounds present in the kerogen oil and to obtain a better understanding on their thermodynamic behavior and to measure separation selectivity. We have prepared anion and cation exchange resins for separating acid and base fractions of the kerogen oil samples. The detailed resin preparation procedures and separation conditions have been described in a previous Monthly Report (SPX2-39-96, April 20, 1996).

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 the formic acid extraction of the > 150 °C shale oil sample were separated into acids, bases and neutrals fractions. The quantitative results are given in the following table.

**Table 1. Summary of Acid-Base-Neutral Separation of Kerogen Oil Samples.**

Sample #	SPX29-96-453 (extract)			SPX29-96-455 (raffinate)		
	Distribution, wt%	% of > 150°C	% of Ext.	% of type	% of > 150°C	% of Ext.
Acid	5.2	14.1	43	6.9	10.9	57
Base	15.5	41.9	83	3.2	5.1	17
Neutral	16.3	44.0	24	52.9	84.0	76
Subtotal	<u>37.0</u>	<u>100</u>		<u>63.0</u>	<u>100</u>	

The data in Table 1 show that the formic acid recovers more than 80% of the bases and rejects more than 70% of the neutrals. Acids are about evenly divided as a class. Work is continuing to ascertain the difference between the acids in the extract and those in the raffinate, if any.

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

**Table 2. Nitrogen distribution of Acid-Base-Neutral samples of kerogen oil > 150 °C fraction after being extracted by formic acid**

Fraction	%wt.	% of type	%N in each frac.	%wt. x %N	%N distrib.
<b>Extract</b>					
Acid	5.2	43	4.54	0.236	14.6
Base	15.5	83	5.77	0.894	55.4
Neutral	16.3	24	1.88	0.306	<u>19.0</u>
					89.0
<b>Raffinate</b>					
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	<u>3.3</u>
					11.0
Subtotal	<u>100</u>			<u>1.61</u>	<u>100</u>

The data in Table 2 show that the formic acid recovers more than 80% of the bases and rejects more than 70% of the neutrals. About 90% of 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 is 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. The indoles and carbazoles have apparently hydrogen-bonded with the formic acid (used as extracting solvent) and are carried into the extract but show up as acids in the ion-exchange separation. We have previously 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. The technical and economic feasibility of this approach have yet to be examined.

The overall separation efficiency is expected to be improved greatly in a commercial process. After the THDA process, the long alkyl chains on the pyridine rings are shortened considerably and the basicity of the pyridines will be more available for interaction with the solvent. Most importantly is, the majority of the nitrogen compounds are recovered in the first stage of the process.

Separation of non-polar fractions The non-polar fraction of the kerogen oil was further processed. First, the light ends (below 350 °C) were distilled and characterized as a refinery feed. Properties of this fraction are being assessed. The heavy fraction was extracted by NMP (N-methyl-2-pyrrolidinone) solvent and aromatic oils were then recovered as an extract. The wax of the raffinate fraction was then removed by a 50/50 methyl-ethyl ketone/toluene solvent. So far, about three kilograms of the non-polars has been processed. The distribution of the products among the refinery feed, aromatic oil, waxes, and lube oils are roughly 40%, 14%, 18% and 28%, respectively, of the total non-polar fractions. We are analyzing the properties of these products and the results will be reported in the next Report.

## **Task 9. Conversion Development**

High pressure THDA experiments: A high pressure 150 cc bomb reactor was assembled to test the THDA activity. This batch setup has proven much less costly to operate and is providing us adequate information at the current stage of development.

In less than 30 minutes, the pressurized bomb can be heated up from ambient to 540 °C. During the THDA of the >290 °C kerogen oil polar fraction, it was observed that the coke yield was suppressed from 21% to 6% as the initial hydrogen pressure increased from 50 to 550 psig. Additional high severity THDA of the kerogen oil heavy polar fraction runs were performed. The objective of X the experiment was to improve the yield of pyridine and lower alkylpyridines without making substantial amount of coke. Reactions were carried out at 535 °C and 1500 psig hydrogen pressure. Initial results showed that under controlled conditions (by cutting the heat-up time from 30 min to 15 min), the coke yield was further reduced to 2%. These results will be confirmed.

The benefit of excess hydrogen in the THDA of kerogen oil residue is consistent with that of THDA of heavy crudes and bitumens as we observed in the previous studies (Bunger et al., 1985a, 1985b, 1988, Tsai, 1987). In the batch system tested, the hydrogen-to-oil molar ratio is calculated to be about 12 to 1, which is far less than the 70~100 to 1 ratio practiced in a flow system. In light of this, low coke yield is possible in a commercial THDA operation.

The condensable products obtained from the high pressure THDA run consists of mainly low boiling alkylpyridines and a small amount of pyridine. We will further process the low-boiling alkylpyridines *via* THDA at higher temperature but shorter residence time in order to recover pyridine as the final product.

Previous work of Yokoyama et al. (1978) showed that oxides of V, Ag, and Mo, or W can be used as dealkylation catalyst for converting picolines into pyridine. However, unless the catalytic reaction can be carried out at reasonably low temperature and pressure, we feel that the secondary THDA will still be commercially viable.

In parallel with the THDA work, we have investigated an alternative process means as suggested by the COR. The works of Louis Strumskis (1982, 1983, 1994) incorporated acetic acid and steam in the oil shale retorting process. He claims that a denitrified hydrocarbons (as referred to as high-quality, low-nitrogen oil) and distillable nitrogen compounds (mostly amines and anilines) are recovered. The overall economics appear to be poor due to:

- (1) the exposure of acid and steam at high temperature create an extremely corrosive environment; the retort itself and some of the downstream equipments would need to be made of special alloy or equipped with a special liner.
- (2) the value of anilines (\$1/kg) are significantly less than that of pyridines (\$8.50/kg) we are proposing.

For the time being, most of the THDA experiments were carried out in the batch mode. The plan to set up a laboratory scale flow unit was deferred during this quarter due to funding uncertainties. In view of the benefit of the flow system and the likelihood of receiving funds to complete the project, this option will be reviewed in the following quarter.

## TASK 10. Product and Process Integration

**Chlorination of the Pyridinic Compounds:** The chlorinated pyridines are intermediates of many agrochemicals. For example, 2,3,4,5-tetrachloropyridine can be converted to the insecticide chlorpyrifos, and trichloropyridinol was converted to the herbicide trichlopyr. Direct chlorination can be achieved by the contact of chlorine and pyridine in the vapor phase. The alkyl-substituents of the alkylpyridines block the (chlorinating) sites and make chlorination more difficult than that of the unsubstituted pyridine. We have successfully synthesized chlorinated pyridines from a mixture of lower alkyl pyridines (obtained from a commercial source) in the JWBA laboratory. An alkylpyridines sample was chlorinated with chlorine gas at 50 °C in carbon tetrachloride for chlorination reaction. The purpose of this work is to generate chlorinated derivatives to be tested for agrochemical activity. Chlorinated pyridines are known to be good insecticides and it is important to discover if such activity is present in Kerogen derived pyridines.

The alkylpyridine concentrates consists of about 60% of dimethylpyridines and 20% of neutral oil; the balance of the mixture consists of ethyl-, trimethyl-, and ethylmethyl-pyridines and substituted indoles.

Various polychlorinated pyridines were identified with pentachloropyridine as a main product. The overall conversion is estimated to be 20%. This discovery is important because chloropyridines are starting material for various agrochemicals, e.g., the tetrachloropyridine can be converted to the insecticide chlorpyrifos. We have submitted these samples to our industrial partners who are testing these materials for bioactivity.

A preliminary chlorination reaction of the base fraction of the 150 - 290 °C polar extract of kerogen oil sample was also explored. The result showed that substantial polymerization was carried out. The identifiable chlorination products were polychloro-paraffins, e.g., hexachloroethane. This may result from the residual olefins remaining in the polar extract. The work on the secondary reactions of kerogen oil derived sample is still continuing.

**Non-polar fractions** The products obtained from the non-polar fraction of the kerogen oil will be analyzed and their market values determined accordingly. The types of the non-polar products are premium refinery feed, aromatic oil, waxes, and lube oils. More than 90% of the kerogen oil fractions are converted into the non-polar categories, these products will be readily marketed as a petroleum substitute at prevailing prices.

**Industrial Liaison** The liaison with potential industrial partners is continuing. Based on our contact with the industries over the last three years, the total of the KPX venture contact companies has reached 57.

These companies are classified as:

pyridines manufacturing (3)

pyridine related agrochemicals (3)  
coal and coal-tar processing (5)  
natural resource development (2)  
chemical synthesis (13)  
pharmaceutical preparations (4)  
petroleum refining and related chemicals (26)  
production engineering and construction (1)

## **Task 11. Simulation and Economics**

During this period, we have refined the business plan entitled "Pyridines from Kerogen Oil" and prepared material for the presentation to the Dawnbreaker Commercialization Assistance Program. In the meantime, we have assisted in making contact and invitations to the strategic partners.

An abstract and non-confidential executive summary of the business plan, as attached, has been sent to each of the contacts. Invitations from the CAP are also on the way to these companies. The marketing effort will proceed within the available resources until a major investor commits to the development plan.

### **Objectives for the Next Period**

- Characterize kerogen oil non-polar fractions.
- Continue and confirm THDA work for improving yield of low-boiling pyridines.
- Complete presentation materials to the Dawnbreaker Commercialization Assistance Program (CAP), follow up on mailings to industrial contacts. Make presentation and get into next phase of dialog with interested parties.
- Prepare final report for the Phase-II(a) activities.

## Reference:

1. Bunger, et al., "Upgrading of Bitumen by Hydrolysis", Proc. Third Intl. Conf. on Heavy Crude and Tar Sands (1985a); "Inhibition of Coke Formation in Hydrolysis of Residual Oils" Preprints, Div. Petro., ACS, (1985b); "Development in Upgrading of Bitumen by Hydrolysis" Proc. Fourth Intl. Conf. on Heavy Crude and Tar Sands (1988).
2. Strumskis, L., U.S. Patents 4,325,787 (1982); 4,396,487 (1983); 5,360,537 (1994).
3. Tsai, C. H., "Reaction Kinetics and Mechanisms of Hydrolysis Processing of Tar Sand Bitumen and Related Material", M.S. Thesis, University of Utah, (1987)
4. Yokoyama, et al., CA 88: 152439e (1978)

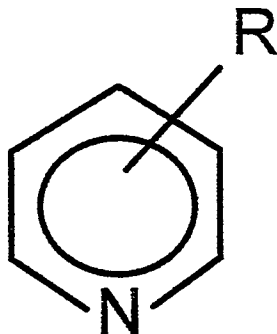
# Pyridines from Kerogen Oil

## ABSTRACT

Kerogen Products Extraction (KPX) will be a joint venture of James W. Bunger and Associates, Inc. (JWBA) and a Strategic Industrial Partner (PARTNER). The KPX venture will extract valuable pyridines from raw kerogen oil produced from rich oil shale deposits. Raw kerogen oil contains about 20% pyridines, a chemical commodity in growing demand and of high market value. These pyridines can be economically concentrated from kerogen oil and converted to saleable products.

JWBA is the first to identify the presence of these valuable pyridines in kerogen oil and has developed low-cost processes for their extraction and conversion. A first-generation plant of 500 ton/day is planned. The product slate will consist of about 45 ton/day of pyridine products and 455 ton/day of petroleum products. A 35% IRR is projected on a \$53 million investment with annual revenues of \$102 million and operating costs of \$49 million. The venture promises strong growth potential.

In 1993, the U. S. Department of Energy awarded JWBA a \$1.93 million contract to perform the R&D necessary to develop a venture based on high value components found in kerogen oil. The contract is in the 3rd year of a 4.5-year effort. The U.S. Government owns the majority of Kerogen oil resources and success in this research will improve the value of these vast resources to our domestic economy. JWBA is seeking a PARTNER to leverage the funds remaining on the contract and to capitalize on the Pyridines from Kerogen Oil venture opportunity.



**ALKYL PYRIDINES**

## EXECUTIVE SUMMARY

### *Mission Statement*

KPX will be the sole source of low-cost alkyl pyridines extracted from kerogen oil and will sell pyridine products into growing and developing markets in the agrochemical, pharmaceutical, metallurgical, food supplement, and rubber processing industries.

### *The Market Opportunity*

Pyridines are unique chemical compounds with important applications in agrochemicals (herbicides, fungicides and insecticides), human and animal nutrition (B-vitamins), personal care products (antidandruff shampoos and disinfectants), pharmaceuticals (antihistamines), and industrial solvents (extraction and synthesis).

The total domestic market for pyridine chemicals is estimated at 65,000 ton/year and world demand is thought to be 2 to 3 times this much. Because most of the uses for pyridines relate to fundamental human needs; food, nutrition and health, the long-term growth trend is expected to equal or exceed population growth. The current market is being supplied by synthesized pyridines, which are costly to produce.

### *Core Technology*

The KPX technology consists of three key components: a) selective separations for the isolation, concentration and purification of pyridines, b) processing to convert kerogen oil pyridines to market-qualified pyridines, and c) a proprietary and powerful analytical methodology that can be used to accelerate process and product development.

### *Sustainable Competitive Advantages*

Pyridines from kerogen oil can be manufactured at costs substantially lower than the costs for synthesizing pyridines. KPX will be located in the Utah/Colorado area where the richest kerogen oil deposits are located. The source material is consistent in composition and is not subject to cost

variations that are often experienced with raw materials used in synthesis routes. Barriers to entry by competing interests include: sole-source supply of raw material, competition for market share by the KPX venture, sound technology protection, and proprietary methods for advanced process and product development.

### ***The Investment Opportunity***

Annual revenues of \$102 million are expected against operating costs (including feedstock costs) of \$49 million, yielding an after-tax internal rate-of-return (IRR) of 35%. Economic growth is expected through increasing market share and new product/market developments. Growth potential for the facility is projected at 10% per year, which could result in a \$700 million/year (constant dollars) industry by the year 2020.

### ***Commercialization Strategy***

The path to commercialization and investment profits consists of:

1. Completing an agreement with a strategic industrial partner.
2. Completing the market qualification of products.
3. Completing commercial design and engineering.
4. Completing kerogen oil supply agreements.
5. Constructing a process facility.
6. Operating the facility for a profit.
7. Growing revenues through capacity expansion and new product developments.

### ***Partner Qualifications***

The ideal PARTNER will be a major company with a competency in pyridines or pyridine products. Other suitable PARTNERS are companies interested in natural resource developments.

## *Use of Investment Funds*

The investment of \$53 million will be used as follows.

1. \$1 million to leverage remaining federal contract funds and to prepare a comprehensive venture development plan.
2. \$5 million for commercial design and engineering, securing intent-to-purchase contracts, completing a kerogen oil supply agreement, and plant permitting. It is likely that this phase would be cost-shared with the federal government.
3. \$47 million for construction and start-up of a 3,000 bbl/day commercial facility.

## *Management Team and JWBA*

Staffing of the KPX venture will be completed with the direct involvement of the joint venture PARTNER. Key personnel from both JWBA and the PARTNER's organization will be required. Additional personnel, including a CEO, will be engaged through the joint efforts of JWBA and PARTNER.

## *The Current JWBA Team*

Dr. James W. Bunger is the President and CEO of JWBA. He has nearly 30 years experience in structure of multicomponent mixtures and processing of these mixtures for manufacture of consumer and industrial products. Other principals are Jesse Tsai, Ph.D., Research Engineer, Christopher P. Russell, Ph.D., Research Mathematician and Donald E. Cogswell, M.S., Research Scientist. Associates include Ray Zahradnik, Ph.D., former President of Occidental Oil Shale Company, J. D. Seader, Ph.D. (author of Chapter 13, Distillations, in Perry's Handbook), James U. Jensen, J. D., M.B.A. (Director of JWBA and founding member of the Licensing Executive Society, LES), and Geoff Dolbear, Ph.D. (formerly with UNOCAL, W.R. Grace and Occidental Petroleum). Employees and Associates of JWBA are primarily doctoral-level people who possess recognized experience in thermodynamics, analytical and organic chemistry, process development, economics, business management, and technology licensing and marketing.