

# Shale Oil Value Enhancement Research

**Quarterly Report  
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## Summary Management Report

The main activities during this quarter were: (a) separation and characterization of kerogen oil non-polar fractions, (b) participating in the Dawnbreaker Commercial Assistance Program, (c) continuing the liaison with potential industrial partners, and (d) submitting a Phase II final report.

In October, we submitted a draft of the final report for the base program and option 1a activities. In this final report, it was concluded that the industry is showing interest in the concept of producing pyridines from kerogen oil. Our economic analysis showed that with current technologies, pyridines can be effectively and economically manufactured from kerogen oil and is competitive with the synthesis manufacturers. It was also recommended that the Government elect to exercise its option to complete the originally proposed program. Performance of research under Option-1(b) will focus on the alternative scheme for refining the pyridine concentrates into pyridine and lower alkyl pyridines which are more valuable and easier to market to the current consumers. Performance of research under Option-II will focus on assuring the market acceptability of kerogen oil products.

At the end of November, the U.S. Department of Energy exercised their option to require JWBA to complete the contract as originally awarded. The work on tasks contained in these options will be initiated in the following quarter.

# Technical Progress Report

## Objectives for the Quarter were:

- 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 proceed to next phase of dialog with interested parties.
- Prepare final report for the Base Program and Option-1(a) activities.

## Discussion

### Task 10. Product and Process Integration

#### Review of THDA Equipment

One of the main objective of Option 1b research is to focus on an improved scheme for refining the pyridine concentrates into pyridine and lower alkyl pyridines. We have demonstrated that the majority of the high boiling polar fraction can be converted into <C5 substituted pyridines in a primary THDA step. It is also believed that, with process conditions similar to those in the hydrodealkylation of toluene to benzene, the methyl substituted pyridines can be striped to the bare-ring system.

We have carried out the THDA reactions (of the polar concentrates) in a 150 cc bomb reactor at 535 °C and 1500 psig hydrogen pressure and found that coke formation can be limited to 6 % or less. This result is quite encouraging. In historic work conducted by the P.I. it has been postulated that in a larger scale reactor, where wall effects are less, THDA could be operated without making appreciable amount of coke, even for feeds with 10%

or more CCR. In the earlier work on this project, we have analyzed the composition of the coke and found that the coke was not enriched in nitrogen. It is believed that the loss of nitrogen compounds *via* coke formation can be minimized in the flow process due to shorter contact time and the hydrogen rich environment. For purposes of completing the bench scale process development and enhancing the overall product values, we would like to reduce the coke formation and maximize the pyridine yield.

In the previous work, the flow THDA experiments were subcontracted to the University of Utah. Although the results are promising, the modification of the equipment reached the limitation that the reactor temperature can not go above 510 °C. During this period, we are designing a simple, once through flow THDA system which is able to handle process up to 650 °C and 500 psig (or 525 °C and 1500 psig) hydrogen pressure. The calculated gas residence time is 3 to 30 seconds. The oil feed rate is 40 to 240 cc/hour. The reactor system is expected to be completed by the end of February, 1997.

### **Separation of Non-Polar fractions**

The non-polar raffinate from the acid extraction of kerogen oils was further processed. First, the raffinate was topped at 350 °C. This below 350 °C fraction has a nitrogen content of only 0.13% and about 40° API gravity. This premium refinery feed represents about 30% (by weight) of the total KPX products. This relatively light feedstock with low nitrogen and low metals is expected to command a premium market price. The KPX refinery feed will be readily salable because of increasing demand for transportation fuels in the Rocky Mountain region where the population growth has reached historic highs and is expected to continue growing while regional crude oil supplies are declining.

The above 350 °C fraction was extracted with NMP (N-methyl-2-pyrrolidinone) to recover the aromatic oils. The yield of the aromatic oil is 23% of the +350°C raffinate and about 10 wt. % of the total KPX products. The aromatic oil has a specific gravity (@ 60°F) of 0.989, its viscosity at 100°F is 328 cSt and its pour point is determined to be 64°F (ASTM D97). The other properties of the aromatic oils are still under investigation.

The raffinate fraction resulting from the NMP extraction was further treated with a 50/50 methyl-ethyl ketone/toluene solvent and then cooled to separate the lube oils and waxes. The distribution of the products between waxes and lube oils is roughly 40% and 60%, respectively. The initial analysis showed the so-obtained dark waxes has a specific gravity of 0.917 and its melting point is 43-45 °C. The specific gravity of the lube oil is 0.889, viscosity @ 60 °F is 98 cSt, VI is 90.8 (ASTM D567) and the melting point (ASTM D127) is 2°C. Both lube oil and waxes contains 0.2-0.3 wt. % nitrogen, which may be responsible

to the dark color of the products. A finishing process such as catalytic hydrotreating may be employed to meet the product specification.

The nitrogen content of the aromatic oil is 0.8 % by weight. It is found that the higher nitrogen content may be in part associated with the residual NMP (N-methyl-pyrrolidinone) solvent used in the extraction process, as indicated in the Figure 1. It is also postulated that the remaining nitrogen types are not basic nitrogen (e.g., pyroles, indoles, and carbazoles) and therefore they were not separated completely by the primary acid extraction process.

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

### **Industrial Liaison**

Over the last three years, we have made contact with 57 potential KPX venture industries. 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)

Most of contacts were made to the new business development, R&D, or technology transfer. Some of the contacts were made to the top management level. To date, about a dozen of contacts are active; among them, four confidentiality agreements are in place and negotiations with others are in progress.

In November, the PI visited a major pyridine manufacturer. A confidentiality agreement was in place and in-depth technology information was exchanged. The company has expressed their interest for the KPX development. Their primary interest was found to be in pyridine itself. They also agreed the economic forecast we proposed. In addition, we also initiated contact with other pyridine manufacturers and major consumers. The contacts have been made to the top management level and the initial feedback has been positive. Contact to the companies through the DOE Commercialization Assistance

Program are also in progress. From these contact, we expect a venture partnership to emerge.

### **Economics Analysis**

Economic analysis of the preferred scheme has been performed. The analysis shows that the market value of the pyridine concentrate could be enhanced by further refinement of the preferred scheme. Additional process steps (an alternative process sequence) will produce more pyridine and less alkyl pyridines. Refining the concentrate to make more concentrate to make more pyridine will enhance the marketability of the products by expanding the customer base several times. Further, the products are about five times the value of the pyridine concentrate which will yield a higher return on investment.

The economic calculations were revised to determined the lowest price of pyridine that would be offered and still sustain a profit. It was found that the main economic variable relates to the price/cost differential between the petroleum feedstock and the cost of the Kerogen oil. Figure 2 shows this relationship. The sensitivity analysis shows that KPX could drop the price of pyridine to \$2.50/kg, if the price cost differential was only \$4/bbl. It is believed that below \$2.50/kg, synthesis manufacturers could not sustain a business. If KPX can achieve this objective, the products successfully entry in the pyridine market are initially assured.

### **Dawnbreaker Commercial Assistance Program**

In October, we participated in the DOE sponsored Commercialization Assistance Program Conference at Washington DC. During the conference, we:

- (1) presented a business plan, and
- (2) initiated discussions with 10 interested companies.

The conference was more focused on utilities and environmental technologies. Among the 112 potential investors, there were six chemical companies. We have made direct contact with all of the participated chemical companies. Other interested parties include two engineering companies, an investment & financial firm and an instrumentation company.

In addition to the above-mentioned companies, we have continued to receive inquires from the companies who have received a business plan abstract but were not able to participate in the DOE Conference. As a result of this conference, we have sent confidentiality agreements to the potential partners (including a major pyridine manufacturer and a major pyridine consumer) for their review in order to enter the next phase of dialog. It is our

intent to establish a consortium of interested parties that will become more directly involved in high level discussions during the Option 1b and Option 2 programs.

### **KPX Consortium Development**

We have spent several months to prepare the DOE Commercialization Assistance Program. The purpose of this presentation was to attract commercial interest in the KPX venture opportunity. We have successfully accomplished the presentation and made direct contact with several interested industrial participants. During the post-program period, we are focusing our effort to formulate a KPX Consortium. Partners are sought with the following interest areas:

1. Pyridine manufacturers
2. Pyridine consumers
3. Synthesis companies
  - a) agrochemicals
  - b) pharmaceuticals
  - c) vitamins
4. Industrial consumers (solvents, detergents and surfactants)
5. Petroleum companies
6. Engineering companies
7. Resource owners
8. Kerogen oil producers
9. Equity investors

Contacts have been made with qualified firms in most of these categories and confidentiality agreements have been, and are being, completed. The plan calls for obtaining the interest of qualified representatives in each of these categories and from that group begin focusing the research to enhance their individual interests. From this select group we expect a venture partnership to emerge.

### **Final Report**

During this period, major effort was devoted to prepare the final report of the current project. On October 23rd, we submitted a draft of the final report for the base program and option 1a activities. In this final report, it was concluded that the industry is showing interest in the concept of producing pyridines from kerogen oil. Our economic analysis showed that with current technologies, pyridines can be effectively and economically manufactured from

kerogen oil and remains competitive with the synthesis manufacturers. It is also recommended that the Government elect to exercise its option to complete the originally proposed program. Performance of research under Option-1(b) will focus on the alternative scheme for refining the pyridine concentrates into pyridine and lower alkyl pyridines which are more valuable and easier to market to the current consumers. Performance of research under Option-II will focus on assuring the market acceptability of kerogen oil products.

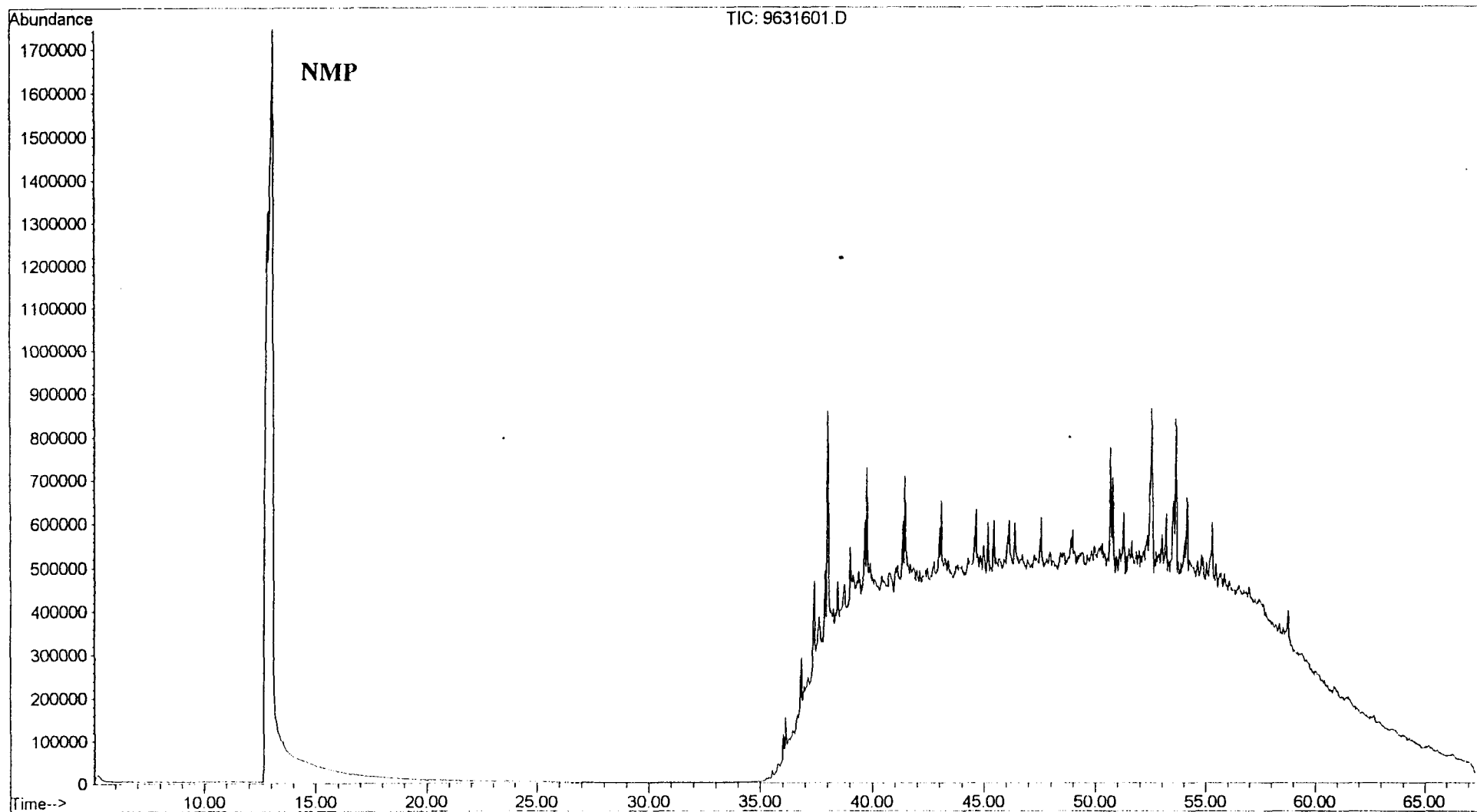
### **Exercise of Option 1b and Option II**

During this period, the U.S. Department of Energy exercised their option to require JWBA to complete the contract as originally awarded. The work on tasks contained in these options will be initiated in the following quarter.

## **Objectives for the Next Period**

- Design and Construct a Multi-purpose THDA unit,
- Continue Industrial liaison of KPX consortium,
- Collect information on KPX commercial products specification,
- Initiate preparation of non-polar KPX commercial products in liter-quantity.

**Figure 1. Gas Chromatogram showed residual amount of NMP solvent in aromatic oil fraction.**



## KPX Economic Sensitivity

