Shale Oil Value Enhancement Research

**Quarterly Report
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Summary Management Report

Concurrent activities are ongoing in all key area, namely, (a) construction and startup of a flow THDA reactor system, (b) development of KPX product slate, and (c) conducting industrial liaison for assembly of the KPX consortium. Excellent progress is being made in all cases.

Our market analysis and industrial feedback have caused us to focus on pyridine itself. We are concentrating our effort toward increasing the yield of pyridine at present. To produce sufficient quantity of sample for marketing purpose, we needed an in-house flow THDA unit. This unit is in its startup phase. The completion of the flow THDA unit will allow us to produce pyridine effectively.

The liaison with potential industrial partners is continuing. At the present time, we have a confidentiality agreement with many of the major target companies. Follow-up work has been initiated and excellent progress has been made. To expedite the process, we reached an agreement with Mr. David Purpi as a consultant to assist on the industrial liaison. Mr Purpi has served many years as a marketing executive for a major pyridine manufacturer and has extensive experience in pyridine production and marketing. His appointment to work on this project has been approved by the DOE.

Technical Progress Report

Objectives for the Quarter were:

- Design and construct a multi-purpose THDA unit,
- Continue industrial liaison of KPX consortium,
- Develop KPX process and products strategy,
- Initiate preparation of non-polar KPX commercial products.

Discussion

Task 8 & 9. Process Development

A main objective of the current research is to focus on refining the pyridine concentrates into pyridine and lower alkyl pyridines. We have demonstrated that the majority of the high boiling polar fraction can be hydrolyzed into <C5 substituted pyridines in a hydrolysis step. It is also believed that, with process conditions similar to those in the commercial hydrodealkylation of toluene to benzene, the methyl substituted pyridines can be de-methylated to the bare ring system. For production of larger quantity of sample for marketing purpose, we are constructing a multiple purpose THDA unit. The THDA unit can be employed in both hydrolysis (490–535 °C, 1500 psig H₂, 10–60 seconds residence time) and THDA (575–650 °C, 500 psig H₂, 3–15 seconds residence time) conditions for hydroprocessing the pyridine concentrate fraction of the kerogen oil.

Testing of the THDA Flow Reactor The construction of the flow THDA reactor system was completed near the end of this period. The reactor assembly is an up-flow co-current configuration, i.e., both hydrogen and oil are fed from the bottom. The up-flow configuration is especially beneficial to the heavier fractions, because they are allowed to stay in the reaction zone longer than the lighter fraction and the longer residence time results in greater conversion. Theoretically, the heavy molecules would have to be cracked into smaller units until the unit mass is small enough to be carried out by the up-flow gas stream, or form coke. The disadvantage of

the latter is the coke built-up which has to be periodically burned out.

To conserve the valuable polar extract, topped (b.p. > 150 °C) kerogen oil was employed to perform the shake down tests. The process conditions employed for the shakedown tests are: reactor temperature, 540 °C and hydrogen pressure, 1500 psig. The hydrogen is preheated to 625 °C at a flow rate of 8.6 SLM and the residence time is calculated to be 60 seconds. The oil is preheated to 390 °C and the feed rate is 88 cc/hr.

The analysis of the products showed that the specific gravity (60°F/60°F) of the topped kerogen oil decreased from 0.92 to 0.87. The TIC of both feed and product, as shown in Figure 1 (a) and (b), indicated that the boiling point distribution of the > 350 °C fraction shifted from 47% to less than 7% (see Table 1). The material balance showed that the weight loss due to coking and gasification is close to 20%. This is rather high compare to a "stabilized" reactor. It is believed that the excessive amount of retrogressive products is a result from the catalytic effect of fresh metal surface. The surface catalytic effect can be overcome by sulfiding (e.g., H₂S) or deliberately leave a thin layer of the coke on the surface to inhibit the contact with the active sites.

Table 1.
Boiling Point Distribution of the > 150 °C kerogen oil and its THDA product at 540 °C, 60 seconds gas residence time.

	> 150 °C kerogen oil		THDA product	
Fraction, °C	Total, wt.%	Cum., wt%	Total, wt.%	Cum., wt%
Gasoline (<200)	5.6	5.6	49.8	49.8
Kerosene, (200 - 275)	21.5	27.1	28.8	78.6
Gas Oil, (275 - 325)	17.6	44.6	12.1	90.9
Heavy Gas Oil, (325 - 400)	23.1	67.7	7.2	97.8
Vacuum Gas Oil, (400-538)	32.3	100.0	2.2	100.0
Vacuum Residue, > 538	0	100.0	0	100.0

The THDA reactor system seemed to be functioning properly during the initial shake down. In addition to the topped kerogen oil, we also processed about one liter of the > 290 °C polar concentrates at hydropyrolysis conditions. Material balance of the run and the properties of the products obtained from the polar concentrates are currently being assessed. The results will be given in the next Monthly Report.

At present, we expect that the performance of the current THDA set-up can still be improved. We are currently working on

- improvement of the heat transfer between the oil preheater and reactor, and
- optimization of the nozzle performance.

After refining the operating procedure and the yield of coke and gas is reduced to a satisfactory level, we intend to

- perform the reaction on the polar fractions, and
- perform the reaction on a commercial alkyl pyridine mixtures to verify system performance.
- produce a product high in pyridine from THDA of a methylated pyridines fraction obtained from kerogen oil.

TASK 10. Product and Process Integration

KPX Process and Products Strategy

According to the product characteristics, the KPX products can be divided into two major categories, pyridine products and petroleum products. This is illustrated in Figure 2, as KPX Master Product Slate. In this plan, we are also providing examples for the finished products and grouping the major customers in each category. The pyridine product represents only about one-tenth of the total products by volume but close to two-thirds of product revenue. The remaining one-third revenue comes from petroleum product (~90 volume percent of the total products). It is unlikely that a single customer would take both products. It is obvious that we would have to find homes for both products simultaneously. The viability of the KPX development is greatly dependent on the successful penetration of the pyridine market.

According to the economic optimization analysis, we divide the KPX products into two categories for test marketing. As shown in Figure 3, KPX Test Marketing Plan, Priority One products are those which are critical to the viability of the venture. Pyridine, lower alkyl pyridine concentrates, 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.) derived from kerogen oil are examples of the Priority Two products.

In our product manufacturing work, we will first manufacture Priority One precursory products, e.g., a $<C_3$ pyridines concentrate and a $<350^\circ\text{C}$ refinery feedstock, and submit them to our potential industrial partners for inspection. It is expected that after reasonably minimum amount of purification work (as suggested by the industrial partner), the quality of the purified precursory

products should match the specifications of compatible commercial products. Refining the precursory products may be required depending on the industrial feedback. The subsequent Priority Two products will also be produced and submitted for inspection.

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 are expected to be readily marketed as a petroleum substitute at prevailing prices.

Task 11. Simulation and Economics

Economics Analysis The KPX economics was further assessed to incorporate the factor of capacity into overall evaluation. Based on a fixed operating cost of \$10/bbl, the effect of capacity on the capital investment and profitability is plotted as Figure 4. The calculation was also based on a base case of 3,000 bbl/day and \$53M capital investment. A scaling factor of 0.6 was used to calculate the capital cost for the operating capacity from 1,000 to 10,000 bbl/day. It can be seen that a minimum capacity of 1700 bbl/day is required in order to achieve a 15% Internal Rate of Return (IRR). As the capacity increases, the unit capital cost decreases gradually, while the resulting IRR increases more drastically. To illustrate, based on a yield of 6% pyridine, a 7,800 bbl/day KPX operation would supply 23,000 tonnes of pyridine a year, the estimated demand of the target pyridine consumer. The resulting IRR is 27%. This estimate is somewhat conservative, since the discounted factor for the operating cost of larger capacity operation was not included.

Task 12. Product Manufacturing

In parallel to the preparation of the pyridine products, we also initiated the preparation of the refinery feed for the industrial inspection. The refinery feed includes the <150 °C boiling fraction (~ 6% of the total kerogen oil) and the <350 °C fraction of the non-polar fraction. The preparation work includes blending and characterization of the blend. This blend will be sent to a local refinery for their inspection. The criteria would be that the content of the nitrogen and the amount of residual extraction solvent remaining in the blend meet the refinery specification.

We have examined that the below 350°C non-polar fraction has a nitrogen content of only 0.13% and its API gravity is about 39. We have specified this fraction as a premium refinery feedstock. This refinery feed represents more than half 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.

Task 14. Venture Development

Industrial liaison and KPX consortium

The liaison with potential industrial partners is continuing. At the present time, we have a confidentiality agreement with several of the major target companies. With the in-depth information (both technology and business) exchanged, we have learned a lot of limitations and difficulties which the current manufacturers are experiencing. We have presented the ideal of KPX consortium on the last Quarterly Report (15th SPX Quarterly Report, December 31, 1996). The Consortium part of the venture development (see Figure 5 attached) is trying to pull the expertise and resources together to overcome the limitations and difficulties the current producers are experiencing. We have made a concerted effort to put the KPX Consortium together, the goal is to have at least one partner in each critical category.

Follow-up work with the potential industrial partners has been initiated and excellent progress has been made. To expedite the process, we hired Mr. David Purpi as a consultant to assist on the industrial liaison. Mr Purpi has served many years as a marketing executive for a major pyridine manufacturer and has extensive experience in pyridine production and marketing. His appointment to work on this project has been approved by the DOE.

Objectives for the Next Period

- Optimize the performance of the THDA unit,
- Prepare a refinery feed for industrial inspection,
- Continue industrial liaison and institute KPX consortium.

Figure 1.

Total Ion Chromatograms of (a) the $>150^{\circ}\text{C}$ kerogen oil and
(b) its THDA product at 540°C , 60 seconds gas residence time.

Figure 2. KPX Master Product Slate

Figure 3. KPX Test Marketing Plan

Figure 4.
Effect of Capacity on Capital Cost and Profitability

Figure 5. KPX Consortium Venture Development

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