

Shale Oil Value Enhancement Research

**Quarterly Report
September 1 - November 30, 1995**

By
James W. Bunger, Ph.D.
Christopher P. Russell, Ph.D.
Jesse C.H. Tsai, Ph.D.
Donald E. Cogswell, M.S.
Jerry W. Wiser, B.S.
Houssine Mihamou
Aaron D. Wright

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MAR 17 1997
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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

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

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Summary Management Report

Activities during this quarter focused on compound type analysis of shale oil extraction products and improvement of the continuous extraction process. We have installed a walk-in fume hood to improve the ventilation of our working environment while handling of larger amounts of shale oil and volatile solvents in our Phase-II(a) work. The fume hood accommodates the distillation column, rotary evaporator, and the CLLX column. During the construction period, experimental work was carried on at a smaller scale.

Modifications to the thermal hydrodealkylation process unit at the University of Utah have been completed. The higher boiling polar fraction of shale oil was fed and the preliminary run showed promising results.

The search for potential industrial partners is continuing. During this period, the P.I. has visited six industrial companies that are candidates for partner/buyer relationship. Currently, we are pursuing confidentiality agreements with four of them. It is the intent to focus our research toward addressing the objectives of those companies who show sufficient interest in the shale oil value enhancement project to enter the next level of discussions.

The assignment of Dr. Jesse Tsai and the availability of the student technicians to the SPX project has accelerated the pace of results.

Technical Progress Report

Objectives for the Quarter were:

- Complete economic analysis and capital cost estimation;
- Complete the software to track the efficiency of separation of the LLX process;
- Further improve the continuous LLX process;
- Conduct initial thermal HDA experiments for the conversions task;
- Perform preliminary adsorption processing for acid/base/neutral separation of concentrates;
- Continue industrial contacts.

Discussion

Task 7. Integration and Economics

Depending on the product specifications and economics, two alternative process scheme were proposed (see the Ninth Quarterly Report) for the shale oil value enhancement. In this report, we summarize the material balance of the preferred scheme, as shown on Figure I. The estimation was based on feeding 5,000 bbl/day of raw shale oil. The operation parameters used are

- a). 94% yield on the initial topping process (or 6% of the $< 150\text{ }^{\circ}\text{C}$)
- b). 40% extract yield on the first polar extraction, and 50% yield after the second pass;
- c). 25% yield of the below $290\text{ }^{\circ}\text{C}$ fraction on the $290\text{ }^{\circ}\text{C}$ distillation;
- d). 93% liquid yield of the THDA process;
- e). 60% yield of the below $400\text{ }^{\circ}\text{C}$ fraction on the $400\text{ }^{\circ}\text{C}$ distillation;
- f). 18% aromatic oils yield on the NMP extraction; and
- g). 7% wax yield on the solvent dewaxing process.

A cost summary around the preferred scheme is as following:

The cost of raw shale oil is \$30/bbl;

The product values (per barrel) used are:

- N-concentrates, \$220;
- higher quality refinery feed, \$25;
- aromatic oils, \$50;
- waxes, \$70; and

lube oil stock, \$60.

The total weighted value of the enhanced products is calculated to be \$62.8/bbl.

The operating cost is calculated to be \$12.3/bbl, including utilities, labor, make-up solvents, and maintenance.

The total capital investment is estimated to be about \$ 60 MM for the 5,000 bbl/day unit.

Task 8. Separation Development

Analysis of total shale oil extraction products: At the present time, we have analyzed the shale oil extraction products obtained from the formic acid - water solvent system by a nitrogen sensitive detector. The results were presented in the September Monthly Report (SPX2-31-95). With the information obtained from the nitrogen scans, we have assessed the change of nitrogen distribution along with the boiling point fractions. The result is shown as Table 1. It can be seen that the nitrogen was concentrated in the >400 °C fraction before the extraction, yet the nitrogen is more concentrated in the extract of the lower 200-400 °C boiling range after the polar extraction process. This is consistent with earlier partition coefficient results which shows that increased mass of hydrocarbon favors appearance in the raffinate.

Two extract fractions obtained from the distillation of S.O. extraction products were analyzed by H-1 and C-13 n.m.r. spectroscopy. The two samples were (a) a narrow distillation fraction with a boiling range from about 210 to 225 °C and (b) the >290 °C fraction. The n.m.r. spectra of these samples were presented in the November Monthly Report (SPX2-33-95).

For the 210-225 °C boiling fraction sample, the ratio of the aliphatic carbon to aromatic carbon (C_{Al}/C_{Ar}) is 1.42 and aliphatic hydrogen to aromatic hydrogen (H_{Al}/H_{Ar}) is 4.81. These results suggest that this sample contains a mixture of molecules with the average molecular structure of mainly di-substituted pyridines with seven carbons in the alkyl-substituents, i.e., $C_{12}H_{19}N$, and lesser amount of di-substituted aromatics with eight carbons in the alkyl-substituents, i.e., $C_{14}H_{22}$. These results further confirmed the extracted ion scan (obtained from GC/MS) of methyl-substituted pyridines as we presented in the October Monthly Report (SPX2-32-95). We have proved that the <290 °C shale oil extract fractions are rich in polysubstituted pyridine compounds. These compounds are building blocks and intermediates of numerous agrochemicals and pharmaceuticals.

For the heavier extract (>290 °C fraction), the ratio of the aliphatic carbon to aromatic carbon (C_{Al}/C_{Ar}) is 2.16 and aliphatic hydrogen to aromatic hydrogen (H_{Al}/H_{Ar}) is 12.78. This heavier fraction contains multiple (at least tri-) substituted pyridines and aromatics with considerably longer alkyl-substituents. These results promise for high responsiveness of the >290 °C fraction for the consecutive THDA process.

Besides the aboved mentioned analytical techniques, we are preparing the adsorption column for the separation of acid/base/neutral fractions. An automatic potentiometric titrator is also set up in our laboratory for the non-aqueous basic nitrogen determination. The purpose of these work is to better understand the quantitative relationship of pyridine-type nitrogen to non-pyridine nitrogen and how the relationship affects the extraction selectivity. The results will be provided in the next report.

Solvent selection for the continuous LLX process: For optimizing the polar extraction process, we have conducted a systematic study to investigate the effect of acid-water solvent system on total shale oil extraction. Formic acid, acetic acid and their mixtures are mixed with proper amount of water as solvent system. The results are tabulated in the Table II. So far, the use of 90% formic acid-10% water and 80% formic acid-20% acetic acid solvent system yield the best results. Since it is more economic to have some water in the extraction process, we intend to use the 90% formic acid-10% water solvent system in the CLLX process.

Improvement of the CLLX process: As reported previously, using a formic acid/water solvent to extract a topped whole shale oil, the nitrogen recovery for the continuous six stage column operation was only 55% (and a coefficient-of-separation, C.S.=0.38). This was less than the recovery of small scale batch single stage shake test of 82% (and C.S.=0.64). The poor results in the CLLX show a lack of contact efficiency and probably some turn-around. To improve the separation efficiency of the CLLX, a pretreatment stage was added to the process. The purpose of the pretreatment is to saturate the feed oil with solvent before it is fed into the column. Under these conditions the next incremental addition of solvent drives a phase separation.

To further improve the separation efficiency, we have increased the volume of both settling zones (or disengaging zones) of the CLLX column and increase the distance between the perforated-plates. The overall length of the column increased from 60 cm to 100 cm, the internal six-stage configuration remained the same.

The major difficulty we experience with the CLLX process is the lack of visibility of the column operation, i.e., the interface is too dark to be seen. We are currently evaluating the use of capacitive sensors to detect the interface. The dielectric constant (K) of the oil is 2.0-2.2 and K values for aqueous solutions vary from 50 to 80. This very high dielectric constant difference suggest that capacitive sensors would be an excellent choice for liquid level sensing.

Task 9. Conversion Development

Thermal Hydrodealkylation of the N-concentrates: In order to obtain the lower molecular weight shale oil derived nitrogen-concentrates, we have converted the coal hydrolysis reactor at the University of Utah to accept shale oil feedstock. The flow diagram of the THDA process is shown as Figure X. We are utilizing the existing recycle hydrogen compressor, gas handling system, liquid collector, reactor furnace and hydrogen preheater. For thermal hydrodealkylation of shale oil, we have installed a new 10 feet long, 0.334 inch ID reactor tube. With the recycle compressor running at full capacity, the residence time is calculated to be 0.6 second at reaction conditions. Other new components we installed include: a water-cooling condenser, an oil injector, and a high pressure liquid pump.

In a preliminary run, a mixture of two parts of >290 °C extract fraction and one part of methylcyclohexane solvent was fed into the system at 525 °C and 1300 psig hydrogen partial pressure; the calculated residence time was 0.75 second. After feeding about 500 cc of oil, the run was terminated unexpectedly because of plugging in the oil feed line. It was discovered later that the inadequately makeup hydrogen flow may contribute to the plugging. To resolve the

problem, a hydrogen pulse injection valve and a hydrogen mass flow meter will be installed on the pre-saturation stream.

The analysis of the liquid product, as showed in Figure XI, indicated that less than 10 % conversion was achieved on this preliminary run. However, the majority of the light fractions were paraffins. Because the feedstock consists entirely of polar species, these paraffins represent the alkyl side chains removed in the THDA process, as expected. It is believed that the hydrodealkylation, by using this flow apparatus, can be improved by increasing the process severity, i.e., higher temperature or longer residence time. In addition, we plan to carry out THDA at lower temperature (~ 465 °C) and much longer residence time ($\sim 1/2$ hour) in a batch system. The purpose of the preliminary THDA is to reduce the molecular weight of the pyridine ring-containing molecules, rendering them more volatile, hence, more susceptible to secondary THDA, chemical reactions, or other process step.

Reactions of N-concentrates: We have proved that the < 290 °C shale oil extract fractions are rich in alkyl pyridine compounds. These compounds are building blocks and intermediates of numerous agrochemicals and pharmaceuticals. We are planning to investigate reactions of shale oil derived nitrogen concentrates. Reaction types of interest are oxidation, chlorination and polymerization.

Task 10. Product and Process Integration

The industrial marketing efforts is continuing as part of the product and process integration work. During this period, the PI visited Nepera, Reiley Tar Products, Koppers, Amoco, Lubrizol, and Ricerca. Interest was found with each company with particular steps indicated with Nepera, Reiley, and Lubrizol. Most of these companies are interested in producing lower molecular weight alkyl pyridines at lower cost than from synthesis routes. Currently, we are pursuing confidentiality agreements with potential industrial partners. It is the intent to focus our research toward the objectives of those companies who show sufficient interest in the shale oil value enhancement project to enter the next level of discussions.

Objectives for the Next Period

- Continue compound type analysis on shale oil extract fractions;
- Continue investigation of the LLX process to improve overall extraction efficiency;
- Conduct hydrodealkylation of the >290 °C shale oil extract fraction;
- Investigate reaction types (e.g., oxidation, chlorination, and polymerization) of the <290 °C shale oil extract fraction in order to obtain higher value products;
- Continue industrial contacts and marketing efforts.

Table I

Change of Nitrogen Distribution After Extraction of Total Shale Oil

| B.P. Fraction | wt.% of Oil | % of Feed N in fraction (wt.% N = 1.65) | % of Extract N in fraction (wt.% N = 3.36) wt. $f_{\text{ext}} = .403$ | % of Raffinate N in fraction (wt.% N = 0.50) wt. $f_{\text{raf}} = .597$ |
|--------------------------|--------------------|--|--|--|
| < 200 | 12 | 2.4 | 5.7 (4.7)* | 0.3 (.05) |
| 200-275 | 13.1 | 5.6 | 20.2 (16.6) | 5.5 (1.0) |
| 275-400 | 24.6 | 20.2 | 49.1 (40.3) | 38.1 (6.9) |
| >400 °C | 50.4 | 71.8 | 25.0 (20.5) | 56.1 (10.1) |

* values in () are % of total nitrogen

Table II. Effect of Solvent System on Total Shale Oil Extraction

| Solvent System* | 100F | 95F/5W | 90F/10W | 85F/15W | 80F/20W | 80F/20A | 23F/77A | 100A |
|------------------|-------|--------|---------|---------|---------|---------|---------|-------|
| Ext. sample ID | 473 | 475 | 377 | 477 | 401 | 453 | 462 | 461 |
| %N as reported | 3.85 | 4.02 | 3.61+ | 4.13 | 3.46+ | 3.99 | 3.33 | 2.89 |
| %O by difference | 6.0 | 4.02 | 7.88 | 4.08 | 20.1 | 2.72 | 1.95 | 2.16 |
| % ext. yield | 31.8 | 32.3 | 40.8 | 28.7 | 17.4 | 37.0 | 36.3 | 16.6 |
| H/C molar | 1.405 | 1.409 | 1.432 | 1.405 | 1.507 | 1.405 | 1.464 | 1.486 |
| C.S. | 0.43 | 0.47 | .49 | .44 | .19 | .53 | .38 | .13 |

* : F=formic acid, W=water, A=acetic acid

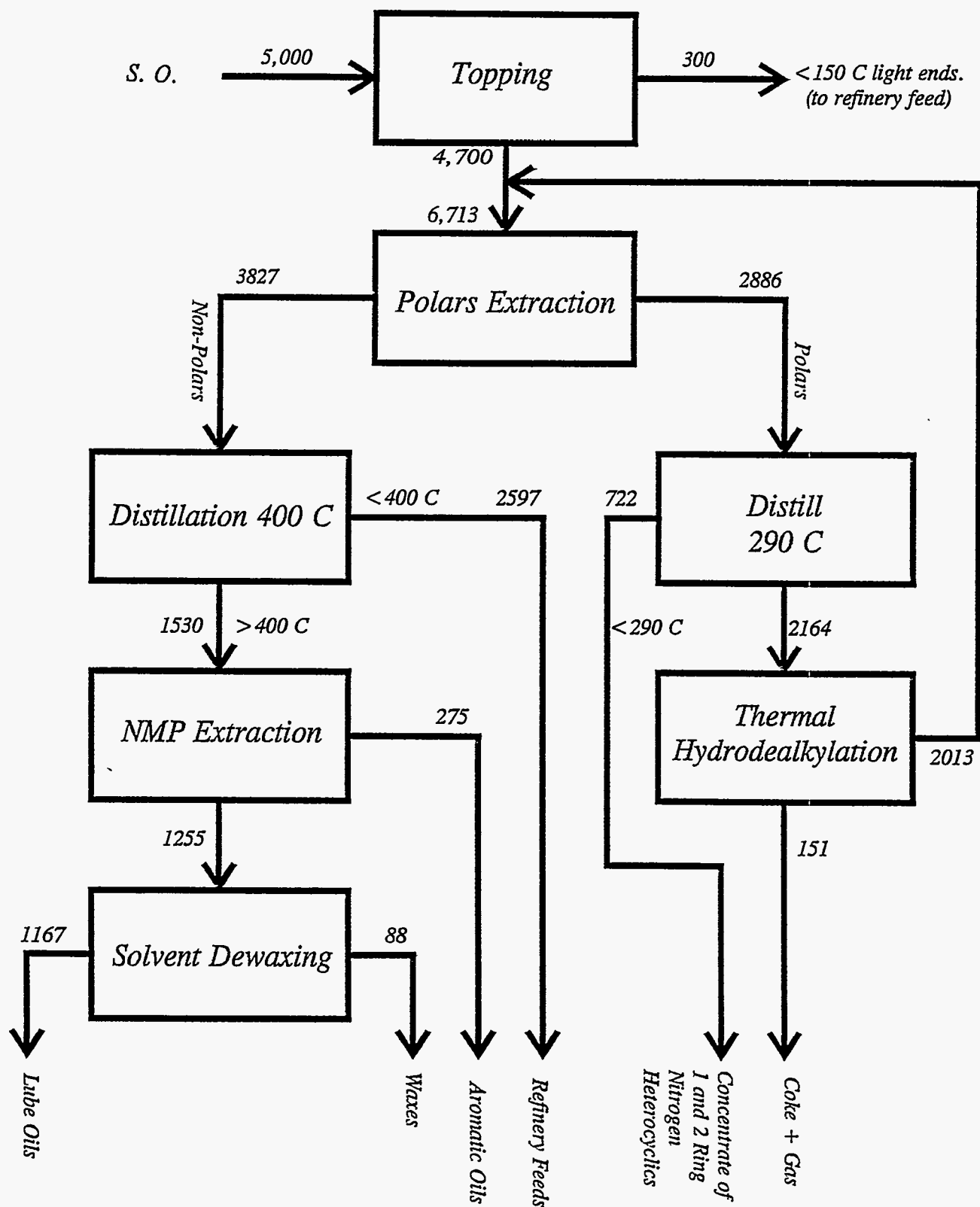
"+" : excess acid solvent remained, actual value could be higher

sample # 377 and 401 were dried w/o gas stripping

sample # 453 was dried with nitrogen stripping

sample # 461, 462, 473, 475 and 477 were dried with CO₂ stripping

Figure 1 Flow Diagram - Preferred Process



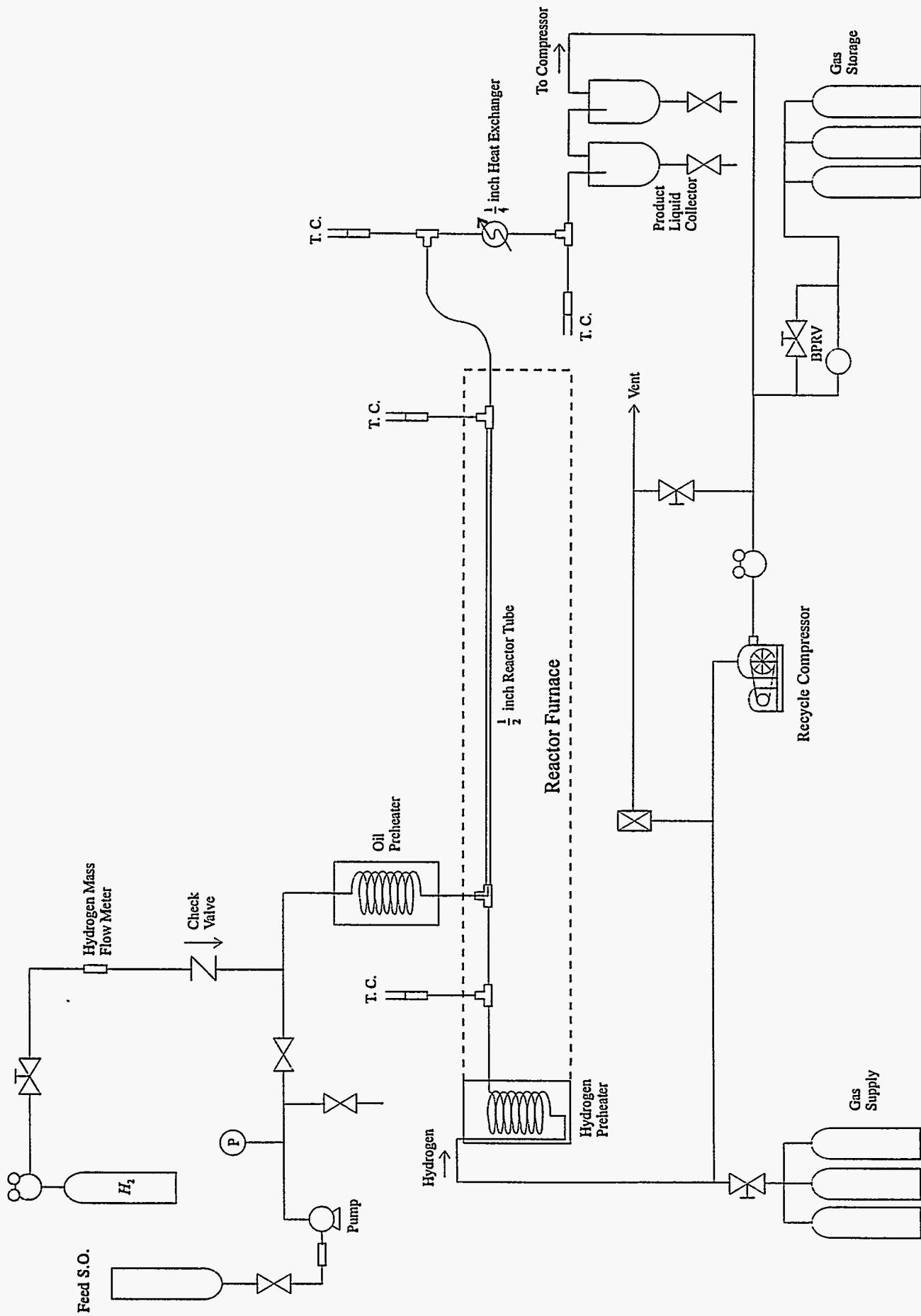


Figure 2. Flow diagram of shale oil THDA process apparatus.

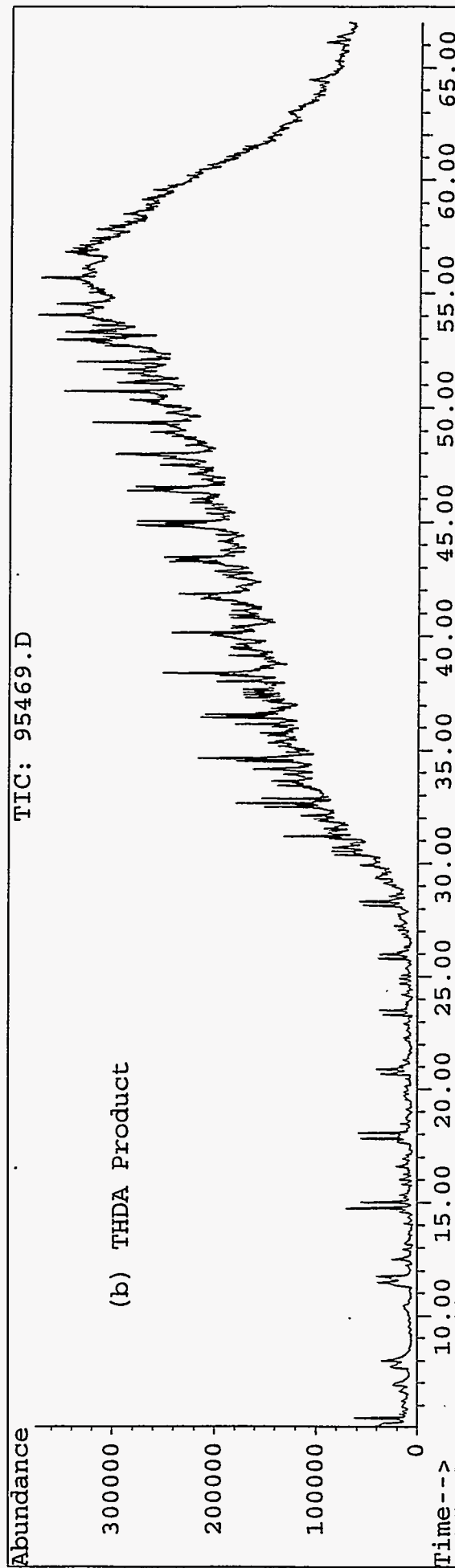
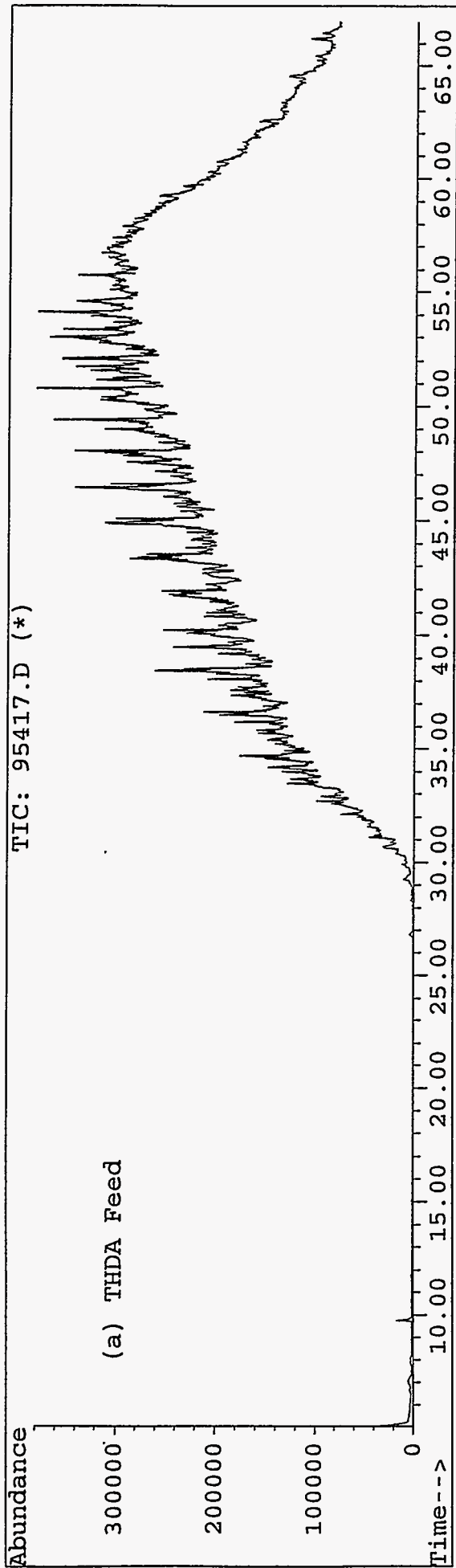


Figure 3. Total ion chromatograms of (a) THDA feed, and (b) THDA liquid product obtained from a preliminary run at 525°C and 1300 psig H₂.