FE-1534-33
Distribution Category UC-90d

# CHEMICALS FROM COAL

## Quarterly Technical Progress Report

## for April - June 1976

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Submitted - July 15, 1976

Prepared for:

THE UNITED STATES ENERGY

RESEARCH & DEVELOPMENT ADMINISTRATION

Washington, D. C. 20545

Under Contract No. E(49-18)-1534

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## OBJECTIVE

The objective of this contract is to conduct laboratory studies in metal reactors and perform computer simulations to provide comparative data from which will be estimated preliminary capital requirements and operating costs for a commercial plant which would use coal liquefaction products for the production of useful aliphatic and aromatic compounds.

## INTRODUCTION AND PROGRAM DESCRIPTION

Because of the recent rising costs and lessened availability of petroleum and natural gas, The Dow Chemical Company, under the sponsorship of ERDA, is studying the possibility of using coal-derived liquids as chemical feedstocks. Specifically, Dow is testing the liquids produced from four coal liquefaction processes (COED, SRC, Synthoil, and H-Coal) in standard petrochemical processing experiments and is evaluating these results to select one process for further study, based on process design, quality of chemicals produced, and overall plant economics. For the process selected, further development will include material balances and utility requirements for each major process step, a preliminary process flowsheet, and estimates of capital and operating costs for a commercial plant.

The liquids produced by the four processes are subjected to standard petrochemical processing operations. The experimental work is being carried out in miniplants capable of operating unattended at pressures up to 3000 psi, temperatures to 1300°F, and feed rates from 25 ml/hr to 400 ml/hr. Two of these miniplants were described in the April-June, 1975 progress report.

The processing sequence used for all of the samples is as follows: 1) distillation into nominally three cuts--straight run naphtha <350°F, mid-distillate 350-650°F, and heavy gas oil 650-950°F; 2) hydrocracking of the mid-distillate and heavy gas oil to reduce molecular weight; 3) hydrotreating of the straight run naphtha and hydrocrackate naphtha to remove heteroatoms; and 4) reforming of the hydrotreated naphthas to maximize aromatics. Steam coil cracking of some of the fractions is also performed to evaluate potential ehtylene yields.

Characterization studies on the crude samples and on the intermediates in the hydroprocessing experiments are done using the following procedures:

- componential analysis of the hydrocarbons
- atmospheric, vacuum, and simulated ASTM distillations
- elemental analysis (C, H, O, N, S)
- trace metal analysis
- liquid chromatography for class separations (aliphatics, monoaromatics, diaromatics).

Four procedures have been developed to coordinate the reporting.

1. Outline Summary of Project Progress - Chart 1 is being maintained for each coal-derived material to show the chronology of completed processing and the sequence of projected steps.

2. Petrochemical Liquid Processing Flowcharts - A flowchart method of showing the main processing steps for evaluating the synthetic crudes is used (Figures 1-3). For general presentation and discussion of the data, the composite feed and product liquids are identified by the numbers designated on the flowcharts, e.g., COED straight run naphtha (A-1), H-Coal mid-distillate hydrocrackate (B-2).

3. Numbering of Tables and of Samples - The data tables presented in each report are numbered by year, month and sequence, e.g., 75-3-2. Non-repetitive numbering of samples and run numbers is practiced.

4. Discussion of Current Activities - The narrative discussion of the program follows a pattern complimentary to the Outline Summary of Project Progress

## SUMMARY OF PROGRESS TO JUNE 30, 1976

### 1974-1975

The laboratory investigation began on April 18, 1974. The FMC COED Syncrude and the HRI H-Coal Oil were obtained in early 1974. The processing progress for these can be readily followed on the attached Chart 1 and Figures 1 & 2.

Characterization studies and straight run distillations were completed on the COED material during 1974. Two stage hydrocracking of the mid-distillate and steam coil cracking of naphtha, mid-distillate, and first stage hydrocrackate products followed in early 1975. Hydrocracking of the straight run heavy gas oil was done in September 1975 and two stage hydrotreating of the straight run naphtha followed.

The H-Coal processing followed the pattern of the COED, but a separate step was necessary. The material was received as atmospheric still bottoms and overheads--they were processed in a manner similar to the COED Syncrude--and vacuum still bottoms slurry. It was necessary to build a disposable still to separate the heavy gas oil from this solidified slurry for further processing. This was done, and the resulting vacuum gas oil was hydrocracked in October 1975. Processing of the atmospheric still material had proceeded and by the end of the year had caught up to that performed on the COED Syncrude. In addition, the two stage hydrotreated H-Coal naphtha was reformed in December 1975.

Samples of USBM Synthoil and PAMCO SRC materials were obtained during 1975. Based on characterizations of the samples, it was decided to limit the study of the Synthoil to the mid-distillate and to obtain a new set of samples of the SRC Product. The Synthoil straight run distillation was completed in December 1975. See Figure 3.

Interim conclusions from the individual petrochemical processing runs were given in a review in the October - December 1975 technical progress report.

1976

The COED hydrotreated naphtha was catalytically reformed as had been done with the H-Coal hydrotreated naphtha. The naphtha fractions from each stage of the COED mid-distillate hydrocracking were combined and hydrotreated, and the product was then successfully reformed.

The H-Coal hydrocrackate naphthas were hydrotreated over a different catalyst system than was used for the COED naphtha fractions.

First and second pass hydrocracking of the Synthoil mid-distillate were completed and the product naphtha was hydrotreated in the manner of the H-Coal hydrocrackate naphthas.

Liquid samples of the SRC II run (ash recycle mode) at Tacoma were received, combined and distilled into naphtha and mid-distillate fractions. Hydrocracking of the mid-distillate continues. (See Figure 4).

## ACTIVITIES OF THE SECOND QUARTER OF 1976

### SUMMARY

Progress on the Coal Oil Crudes

Second pass hydrocracking of the USBM Synthoil mid-distillate was completed in April. Hydrocracking data for both the first and second pass hydrocracking are presented.

Presulfiding procedures for the hydrotreating catalyst were changed, and the H-Coal B-1 + C-1 naphtha and the Synthoil B-1 + C-1 naphtha were each hydrotreated over American Cyanamid Aero HDS-9A catalyst.

The Solvent Refined Coal product oils were recombined and distilled into the IBP-350°F naphtha and the 350-650°F mid-distillate. This was followed by hydrocracking, which is continuing.

DISCUSSION OF EXPERIMENTAL PROCESSING

## Petrochemical Processing Experiments

### FMC COED Syncrude -

The petrochemical processing was essentially completed during the first quarter.

### HRI H-Coal -

Hydrotreating Hydrocrackate Naphthas - During attempts to hydrotreat the B-1 + C-1 naphtha for sulfur and nitrogen removal, a serious difficulty was identified (See March 1976 Monthly Progress Status Report). As there have been continuing difficulties with the sulfur analysis in the parts-per-million range, considerable effort was expended in satisfactorily establishing that the sulfur analysis was correct. A new catalyst loading was made. The catalyst was presulfided with 1% $CS_2$ in light naphtha as is the standard presulfiding procedure, and then toluene was run over the catalyst for 100 hours. The sulfur level of the product liquid was monitored. It was over sixty hours before the liquid product sulfur level could be considered the same as the toluene feed (less than 1 ppm).

The presulfiding procedure was changed to use hydrogen sulfide gas and the appropriate mechanical modifications to the hydrotreating reactor system were made. A new catalyst loading of Cyanamid Aero HDS-9A was made and presulfided with 7-8% by vol. $H_2S$ in hydrogen at atmospheric pressure. The hydrotreating of the B-1 + C-1 naphtha was completed in June. Analytical results on sulfur and nitrogen removal are incomplete.

### USBM Synthoil -

Second Pass Hydrocracking of Mid-distillate - The weight of recovered liquid hydrocrackate from the first pass experiments was 59.5 pounds. This material was distilled to recover 23.1 pounds of naphtha (B-1) and 33.4 pounds of mid-distillate (B-2). The mid-distillate (B-2) was subsequently hydrocracked over Harshaw HT-400 E-1/8 cobalt-molybdenum catalyst under conditions comparable to those used during the first pass experiments (Tables 76-4-1 and 76-4-2). It should be noted that the feed to the

TABLE 76-4-1 - SYNTHOIL A-2 HYDROCRACKING DATA

| Run No. | Temp. °F | LHSV (v)/(v)(hr) | Press PSIG | $C_1$-$C_9$ Yield[a] | HYDROCRACKING PATTERN, PERCENT[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Methane | Ethane | Propane | Butane | $C_5$ - $C_9$ Paraffins | $C_5$ - $C_9$ Naphthenes | $C_5$ - $C_9$ Aromatics | % Water Make |
| 7- 5-2 | 917 | 0.91 | 2500 | 41.8 | 5.2 | 8.1 | 8.7 | 9.1 | 11.1 | 31.7 | 26.1 | 3.7 |
| 7- 6-4 | 926 | 1.04 | 2500 | 47.4 | 5.5 | 6.9 | 8.9 | 12.8 | 13.1 | 26.3 | 26.4 | 3.6 |
| 7- 2-3 | 932 | 0.62 | 2500 | 52.1 | 4.3 | 6.4 | 6.5 | 6.7 | 13.7 | 36.1 | 26.3 | 3.4 |
| 7- 8-2 | 932 | 1.30 | 2500 | 42.8 | 6.2 | 8.5 | 7.2 | 5.2 | 8.7 | 31.2 | 32.9 | 3.7 |
| 7-10-2 | 916 | 1.47 | 2500 | 45.7 | 5.7 | 10.1 | 9.5 | 8.7 | 11.3 | 27.7 | 26.9 | 2.6 |
| 7-14-2 | 947 | 0.88 | 2500 | 59.5 | 6.8 | 9.8 | 11.2 | 10.0 | 11.8 | 24.2 | 26.2 | 2.7 |
| 7-14-3 | 950 | 0.97 | 2500 | 60.9 | 6.9 | 10.8 | 11.6 | 10.7 | 11.9 | 22.7 | 25.4 | 3.4 |
| 7-14-4 | 950 | 1.04 | 2500 | 61.8 | 6.7 | 10.4 | 10.7 | 9.6 | 11.0 | 24.8 | 26.8 | 3.1 |
| 7-11-2 | 910 | 1.11 | 1500 | 37.5 | 5.9 | 10.1 | 8.5 | 6.9 | 10.5 | 24.8 | 33.3 | 1.7 |
| 7-12-2 | 946 | 0.95 | 1500 | 47.0 | 7.8 | 9.9 | 11.0 | 8.5 | 11.3 | 19.6 | 31.8 | 3.2 |

TABLE 76-4-2 - SYNTHOIL B-2 HYDROCRACKING DATA

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7-17-2 | 950 | 0.98 | 2500 | 66.1 | 5.8 | 7.2 | 9.5 | 11.2 | 15.5 | 22.3 | 28.6 | 0 |
| 7-17-3 | 944 | 0.97 | 2500 | 56.8 | 5.9 | 7.8 | 10.3 | 11.7 | 14.2 | 21.0 | 29.0 | 0 |
| 7-17-4 | 946 | 1.00 | 2500 | 51.8 | 5.8 | 7.6 | 10.9 | 11.6 | 13.2 | 20.5 | 30.4 | 0 |
| 7-17-5 | 949 | 1.00 | 2500 | 53.1 | 5.9 | 7.5 | 10.1 | 11.4 | 14.3 | 20.2 | 30.6 | 0 |
| 7-21-2 | 984 | 0.99 | 2500 | 74.2 | 7.0 | 9.0 | 12.5 | 12.2 | 13.7 | 17.7 | 27.8 | 0 |
| 7-21-3 | 983 | 1.00 | 2500 | 72.3 | 7.1 | 9.1 | 12.4 | 11.7 | 14.8 | 16.1 | 28.9 | 0 |

[a] - basis: 100 gm of liquid feed.

[b] - etc., see 75-3-1.

TABLE 76-4-3

Simulated Distillations of Synthoil Mid-Distillates
Boiling Point, °F

| % Distilled | First-Pass Feed (A-2) | Second Pass Feed (B-2) |
|---|---|---|
| IBP | 360 | 330 |
| 5 | 402 | 354 |
| 10 | 426 | 365 |
| 20 | 462 | 389 |
| 30 | 496 | 399 |
| 40 | 516 | 412 |
| 50 | 543 | 436 |
| 60 | 570 | 456 |
| 70 | 596 | 484 |
| 80 | 622 | 513 |
| 90 | 654 | 541 |
| 95 | 680 | 565 |
| API Gravity | 10.5° | 32.8° |

second pass (B-2) was significantly different from the feed to the first pass (A-2). Table 76-4-3 shows the difference in boiling range and the change in gravity.

When considering the hydrocracking data, the following points should be considered:

> The temperature stated in the table is the average bed temperature. Since this reaction is moderately exothermic, the catalyst bed had temperature profiles of from 15°F to 35°F higher than the inlet temperature.
>
> In none of the experiments on the first pass feed (A-2) was the catalyst much older than 100 hours. Thus any catalyst property changes during the induction period would also tend to obscure the data.

As elemental analyses become available, these hydrocracking data will be rechecked and hydrogen consumption calculated. Further discussion may be introduced at that time.

Hydrotreating Hydrocrackate Naphthas - The hydrocracked naphtha (B-1 + C-1) was hydrotreated over the same catalyst loading as was the HRI H-Coal naphtha, i.e., $H_2S$ presulfided Cyanamid Aero HDS-9A. Analytical results on sulfur and nitrogen removal from this stock are also incomplete.

PAMCO SRC II Product -

Distillation of Straight Run Material - The products of the SRC II (ash recycle) mode of operation were combined to make up a "net liquid" of 25% light oil, 29% wash liquid and 46% process solvent. The "net liquid" was distilled in a batch column to make 110 pounds of IBP-350°F naphtha, 307 pounds of 350-650°F mid-distillate and 74 pounds of heavy oil.

Hydrocracking of Straight Run Mid-distillate - Hydrocracking experiments on the mid-distillate over Harshaw HT-400 cobalt-molybdenum catalyst commenced in early June and continue. While the elemental analysis are not yet complete, the hydroprocessing data work-up indicates about 65% yields of $C_1$-$C_9$ at 2500 psig and 967°F and 48% yields of $C_1$-$C_9$ at 2500 psig and 925°F. The yields of water indicate a minimum oxygen level of about 2 to 2.5 weight %.

Chart 1

OUTLINE SUMMARY OF PROJECT PROGRESS, June 30, 1976

The date when a substantial portion of an item had been completed and was reported is given. The sample designations, such as A-2, refer to the Petrochemicals Liquid Processing Flowchart for the respective crude starting material.

## LABORATORY STUDIES

### FMC COED Syncrude

| | |
|---|---|
| Coal Oil Sample Procurement | July, 1974 |
| Characterization Studies | Aug., 1974 |
| Petrochemicals Processing Experiments | |
| Straight run distillations (Fig. 1) | Sept., 1974 |
| Hydrocracking and separation of products (Fig. 1) | |
| A-2 mid-distillate as feed | Dec., 1974 |
| B-2 hydrocrackate mid-distillate | Jan., 1975 |
| A-3 straight run heavy gas oil | Sept., 1975 |
| Steam coil cracking | |
| Feedstocks A-1, A-2, B-1, B-2 | March, 1975 |
| Hydrotreating (Fig. 1) | |
| A-1 straight run naphtha | Oct., 1975 |
| B-1 + C-1 hydrocrackate naphthas | Feb., 1976 |
| Reforming (Fig. 1) | |
| B-4 naphtha | Jan., 1976 |
| B-1 + C-1 hydrotreated naphtha | March, 1976 |

### HRI H-Coal Oil

| | |
|---|---|
| Coal OIl Sample Procurement | Early 1974 |
| Characterization Studies | Oct.-Dec., 1974 |
| Petrochemicals Processing Experiments | |
| Straight run distillations (Fig. 2) | |
| Atm. still product as feed | Jan., 1975 |
| Vac. still bottoms as feed | July-Aug., 1975 |

Chart 1 Cont'd.

| | |
|---|---|
| Steam coil cracking | |
| Feedstock A-1 naphtha | March, 1975 |
| Feedstock A-2 mid-distillate | August, 1975 |
| Hydrocracking (Fig. 2) | |
| A-2 mid-distillate as feed | March, 1975 |
| B-2 hydrocrackate mid-distillate | March, 1975 |
| A-4 vacuum gas oil as feed | Oct., 1975 |
| Hydrotreating (Fig. 2) | |
| A-1 straight run naphtha | July-Aug., 1975 |
| B-1 + C-1 hydrocrackate naphthas | In Progress |
| Reforming (Fig. 2) | |
| B-4 naphtha | Dec., 1975 |
| B-1 + C-1 hydrotreated naphtha | Planned |

USBM Synthoil

| | |
|---|---|
| Coal Oil Sample Procurement | March, 1975 |
| Characterization Studies | In Progress |
| Petrochemical Processing Experiments | |
| Hydrogenation of Synthoil crude | Evaluating data |
| Straight run distillations (Fig. 3) | Dec., 1975 |
| Hydrocracking and separation (Fig. 3) | |
| A-2 mid-distillate as feed | March, 1976 |
| B-2 hydrocrackate mid-distillate | April, 1976 |
| Hydrotreating (Fig. 3) | |
| B-1 + C-1 hydrocrackate naphthas | In Progress |

PAMCO Solvent Refined Coal (SRC Product)

| | |
|---|---|
| Coal Conversion Product Procurement | Oct., 1975 |
| Characterization Studies, Spl. No. 1 | Dec., 1975 |
| Characterization Studies, Spl. No. 2 | In Progress |
| Petrochemicals Processing Experiments | |
| Straight run distillations (Fig. 4) | May, 1976 |
| Hydrocracking and Separation (Fig. 4) | |
| A-2 mid-distillate as feed | In Progress |

Figure 1

Petrochemicals Liquid Processing Flowchart

for

FMC COED Syncrude

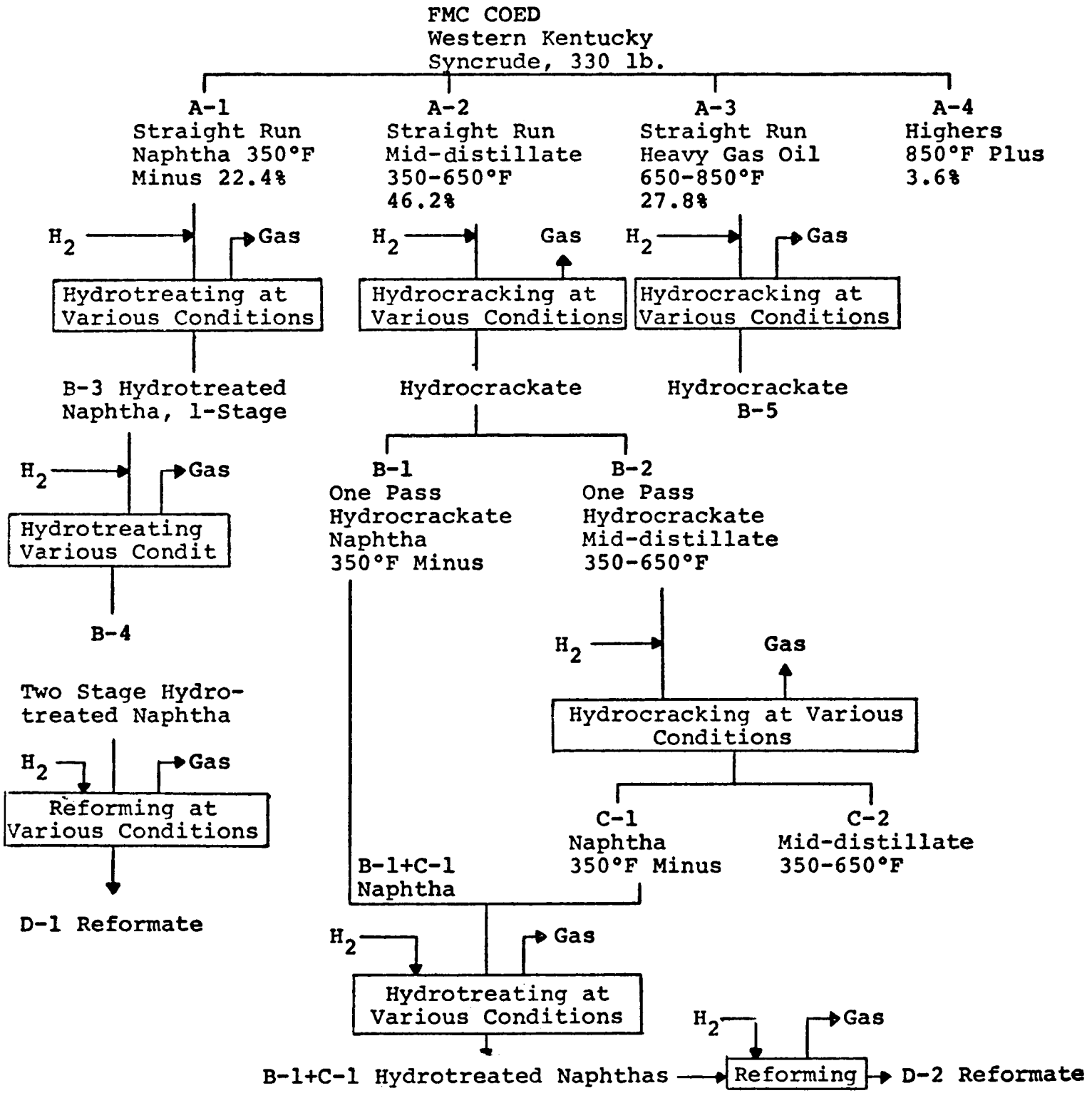

Figure 2

Petrochemicals Liquid Processing Flowchart

for

HRI H-Coal Oil

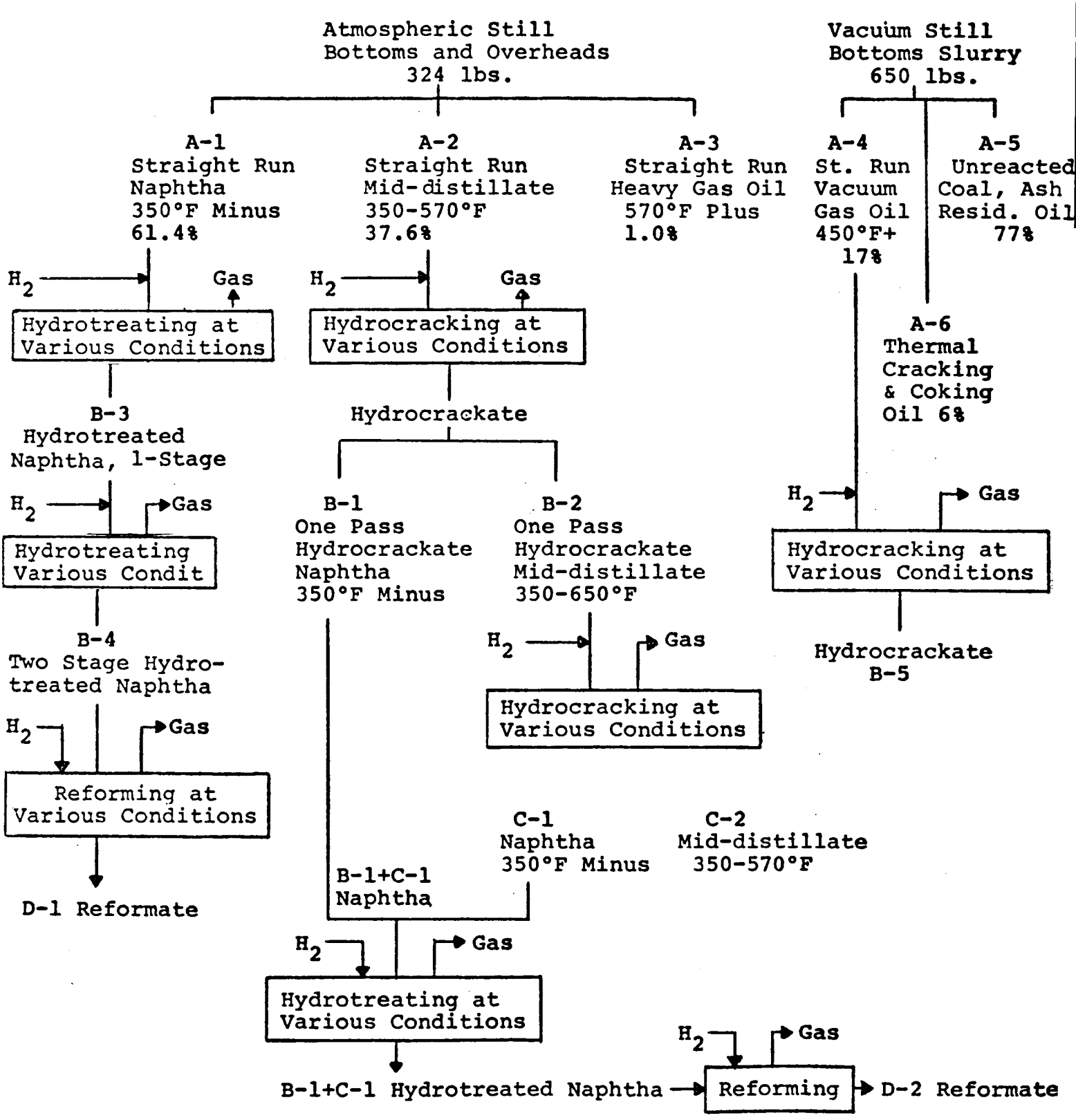

Figure 3

Petrochemicals Liquid Processing Flowchart

for

USBM Synthoil

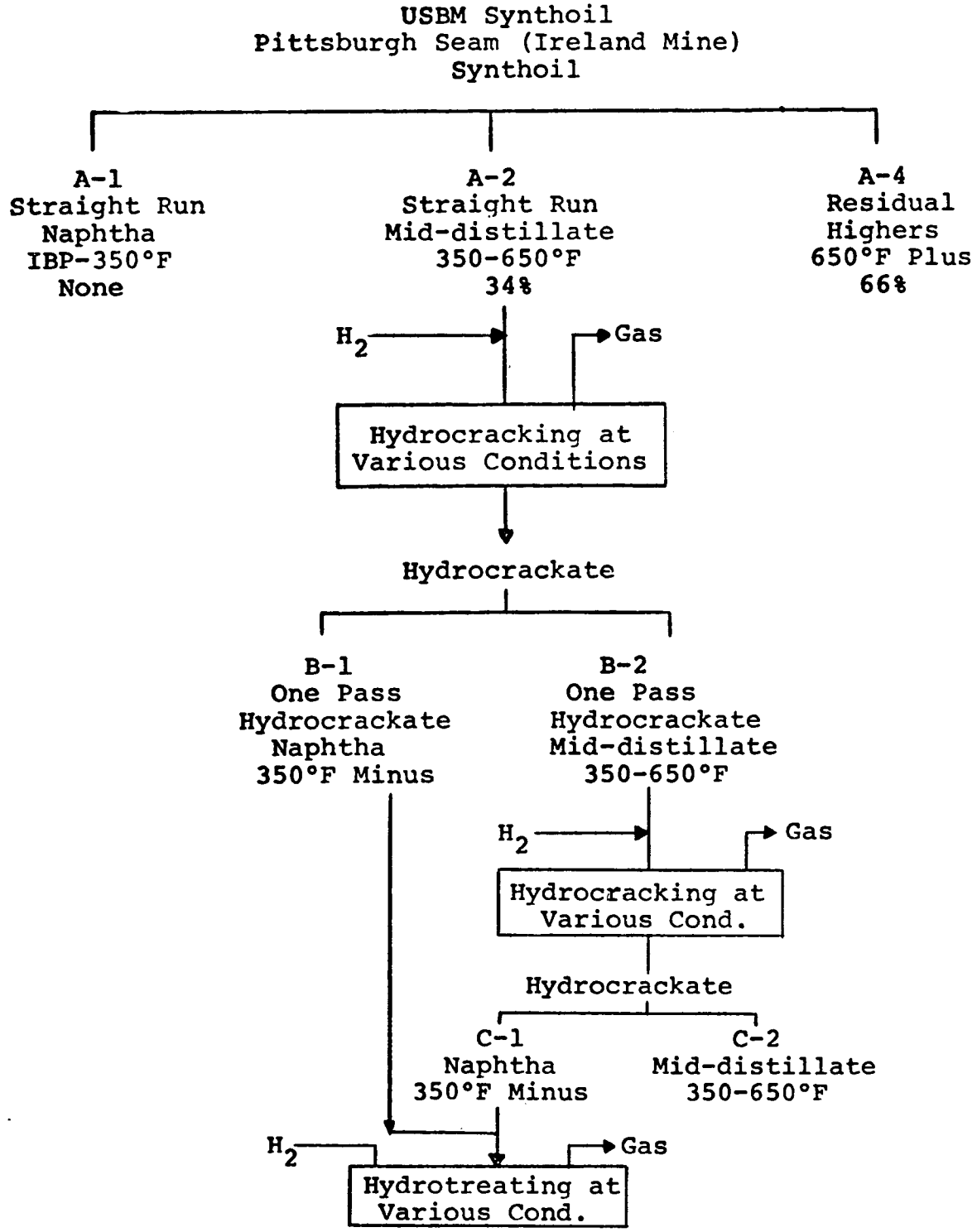

Figure 4

Petrochemicals Liquid Processing Flowchart

for

PAMCO SRC II Product Oil