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CHEMICALS FROM COAL

Quarterly Technical Progress Report
for January - March 1976

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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 ethylene 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 DECEMBER 31, 1975

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

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

ACTIVITIES OF THE FIRST QUARTER OF 1976

SUMMARY

Progress on the Coal Oil Crudes

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 hydrocracking of COED mid-distillates was combined and hydrotreated. The hydrotreated product was then successfully reformed.

Hydrotreating of the combined H-Coal two stage hydrocrackate naphthas was begun.

First pass hydrocracking of the Synthoil mid-distillate was completed, and second pass hydrocracking of the resulting hydrocrackate mid-distillate fraction was commenced.

Liquid samples from the SRC II run at Tacoma were received.

DISCUSSION OF EXPERIMENTAL PROCESSING

Petrochemical Processing Experiments

FMC COED Syncrude -

Reforming Hydrotreated Naphtha--The hydrotreated straight run naphtha (B-4) was dried to less than 10 ppm water and reformed over American Cyanamid Aeroform PHF-4 platinum reforming catalyst. Linde 4-A molecular sieves were used in the drying step. The product analyzed 6 ppm nitrogen, 2 ppm sulfur. The oxygen analysis is not available.

During the reforming runs, the proportion of aromatics in the C_6-C_9 fraction decreased significantly. The catalyst was unloaded and it analyzed 13.6% coke with a 0.6 hydrogen to carbon ratio.

The conditions and results are presented in the first half of Table 76-3-1.

TABLE 76-3-1

REFORMING OF COED NAPHTHAS

Catalyst: Cyanamid Aeroform PHF-4
Diluted with 1 volume 6-8 Mesh, Tabular Alumina

	--------Hydrotreated Straight Run Naphtha (B-4)--------							------Hydrotreated B-1+C-1 Naphtha------				
Run Number	Feed	010876	010976	011276	011376	011476	011576	Feed	8-2-2	8-2-3	8-2-4	8-2-5
Temperature, °F		955	955	954	954	955	950		968	968	968	968
Pressure, Psig		250	250	250	250	250	250		500	500	500	500
LHSV, vol/(vol)(hr)		2.0	2.0	2.0	2.1	2.0	1.9		1.9	2.0	2.0	2.1
Hydrogen Ratio, SCF/bbl		4000	4000	3940	3750	3910	4260		4250	3920	3920	3900
Hydrogen Prod., SCF/bbl		1157	839	1097	779	681	585		976	980	943	991
$C_1 - C_3$	--	7.5	7.4	6.8	6.9	7.3	7.1	--	6.2	5.1	5.2	5.0
$C_4 - C_5$	--	5.2	5.3	4.2	5.0	5.0	4.9	0.4	5.8	5.3	5.4	5.2
$C_6 - C_9$												
Paraffin	10.9	4.0	7.6	6.0	7.7	8.0	8.5	13.3	6.4	7.2	8.4	8.3
Naphthene	50.1	0.9	5.5	2.2	8.2	10.9	13.9	35.7	2.2	3.1	3.0	3.9
Aromatic	28.7	73.4	62.7	67.1	58.1	54.6	52.7	33.4	70.2	69.7	68.1	70.5
C_{10} +	10.3	6.0	8.6	10.1	11.1	11.1	10.1	17.2	6.6	7.4	7.2	4.3
% Aromatic $C_6 - C_9$	32.0	93.8	82.7	89.1	78.5	74.3	70.2	40.5	89.1	87.2	85.7	85.3

Hydrotreating Hydrocrackate Naphthas--The naphtha (B-1) produced during the hydrocracking of the COED mid-distillate and the second stage hydrocrackate naphtha (C-1) were combined and hydrotreated. Table 76-2-1 summarizes the data. Pressures on the order of 1500 psig will apparently be necessary to reduce the sulfur levels to the less than 1 ppm necessary to prevent poisoning of a bimetallic reforming catalyst. The oxygen data will be added as they become available.

Reforming Hydrotreated Hydrocrackate Naphthas--The hydrotreated composite of naphthas (B-1 & C-1) from hydrocracking was reformed over Cyanamid Aeroform PHF-4 catalyst at 500 psig. At this pressure, double that at which the straight run naphtha was reformed, the catalyst deactivation rate was substantially decreased. Conditions and data for the reforming of the two types of hydrotreated naphthas are compared in Table 76-3-1. The limited amount of feed available allowed only a 100 hour run. Thus it is difficult to determine if the catalyst is simply "breaking in" or if the slowed deactivation rate at the higher pressure will continue.

Further Processing--No further processing of the COED material is planned.

HRI H-Coal -

Hydrotreating Hydrocrackate Naphthas--The naphtha fractions (B-1 & C-1) of the hydrocrackate were combined and subjected to hydrotreating over Harshaw HT-100 nickel molybdenum catalyst (Table 76-3-2). Only two runs were performed, after which a serious difficulty was identified. Increasing the space velocity resulted in less nitrogen removal as expected, but the sulfur level was decreased. The sulfur level should not go down upon increasing the space velocity. This set of data, the first time we have gone to less severe conditions chronologically, indicates the following possible problems.

1. Substantial backmixing in the reactor -- not likely, however, or the nitrogen data would show the same anomaly.
2. A catalyst induction period wherein the fresh catalyst is less active than the broken-in catalyst -- not uncommon.

Table 76-2-1

HYDROTREATING COED B-1 & C-1 NAPHTHA

Catalyst: Harshaw HT-100 E 1/8" diluted
with 1.5 volumes of 6-10 mesh
tabular alumina

Run No.	Feed	103-6-2	103-6-4	103-6-5
Temperature, °F		756	756	752
Pressure, psig		800	800	1500
LHSV, vol/(vol)(hr)		1.9	1.0	1.0
H_2 Ratio, SCF/bbl		2100	2200	3500
C_1-C_3 Gas	--	0.1	0.2	0.2
C_4-C_9 Material				
Paraffin	12.4	12.7	13.9	13.1
Naphthene	23.8	35.3	32.6	36.2
Aromatic	37.4	34.8	38.3	32.7
Unidentified	7.5	0	0	0
C_{10} +	19.0	16.9	14.9	16.1
Nitrogen ppm	1	0.6	0.5	0.4
Sulfur ppm	41	3.8	1.7	0.4
Oxygen ppm	--	--	--	--

TABLE 76-3-2

HYDROTREATING H-COAL B-1 & C-1 NAPHTHA

Catalyst: Harshaw HT-100 E 1/8"
Diluted with 2 volumes of 6-10 mesh,
tabular alumina

Run Number	Feed	103-6-7	103-6-9
Temperature, °F		756	752
Pressure, Psig		1500	1500
LHSV, vol/(vol)(hr)		1.9	4.0
H_2 Ratio SCF/bbl		2150	2000
$C_1 - C_3$ Gas, %		0.09	0.06
$C_4 - C_9$ Material, %			
Paraffin	10.4	12.2	10.1
Naphthene	29.1	42.9	36.8
Aromatic	49.7	29.8	36.4
C_{10} + Oil & Residue, %	10.80	14.8	16.7
Heteroatoms, ppm			
Nitrogen	8	1.7	4.6
Sulfur	100	2.3	1.6

3. Poor purging after the presulfiding of the catalyst.

4. Inaccuracies in the sulfur analysis.

Items 3 and 4 are being investigated before continuing the run. Hydrotreating of the composite naphtha (B-1 & C-1) will continue when warranted.

Further Processing--Reforming of the hydrotreated hydrocrackate naphthas (B-1 & C-1) will follow and this will complete the planned processing.

USBM Synthoil -

Hydrocracking of Straight Run Mid-distillate--Hydrocracking of the straight run mid-distillate was begun. A comparison of the boiling range data for this stock compared to the COED and H-Coal mid-distillates is shown in Table 76-2-2. The Synthoil material is heavy (10.5°API) and contains about 0.74% sulfur and 0.28% nitrogen.

The initial conditions for the hydrocracking were:

Temperature:	932°F
Pressure:	2,500 psig
LHSV:	0.62 (vol)/(vol)(hr)
Hydrogen Feed Rate:	20,000 SCF H_2/bbl

Various mechanical problems have made it difficult to maintain mass balances during these experiments. One of the difficulties arose from the need to handle approximately 4% water produced (due to O_2 in the feed) along with the liquid product. This was not a problem with the COED and H-Coal samples since the water was present in sufficiently small quantities to be carried out with the vent gas.

The computer programs for data reduction were modified to handle the water produced.

It is interesting to note that conversion of the feed to material boiling at less than 350°F has been about 50% or, nominally, about what would be expected based on previous experience with the COED mid-distillate.

Table 76-2-2

SIMULATED DISTILLATIONS OF MID-DISTILLATES

% Distilled	Boiling Point, °F		
	H-Coal	COED	Synthoil
IBP	217	364	360
5	351	411	402
10	366	434	426
20	378	468	462
30	395	499	490
40	408	525	516
50	417	555	543
60	432	581	570
70	449	611	596
80	471	637	622
90	500	671	654
95	522	689	680
FBP	564	733	820

A major difficulty was encountered with this particular feed. After approximately 100 hours of operation, a plug was built up in the reactor, downstream from the catalyst at a point where the temperature is 400-600°F. X-ray diffraction indicates the plug, or "salt", to be primarily ammonium chloride. X-ray fluorescence picks up percentage levels of iron, chromium and lower levels of Mn, Ti, S, K, and Ca in the "salt". The formation of this salt plug necessitates a reactor cleaning, reloading and presulfiding, a procedure which can take 3 to 5 days.

All of the mid-distillate on hand was given a first pass hydrocracking. Approximately 60 pounds of liquid product was accumulated.

The difficulties encountered in these runs make the data reduction and interpretation considerably more difficult.

Further Processing--Second stage hydrocracking, using the mid-distillate fraction (B-2) of the above product, has commenced. Additional processing along the lines of the COED and H-Coal materials is being considered.

PAMCO SRC Product -

Characterization--The new samples of liquid produced during the SRC II (recycle ash mode) run at Tacoma were received in February. Received were about 20 gallons each of light oil and wash solvent and about 35 gallons of process solvent. These will be combined in the ratio of 25:29:46 (light oil: wash solvent: process solvent) in order to simulate the net yield, and then the mixture will be distilled into the IBP-350°F naphtha and the 350-650°F mid-distillate.

Chart 1

OUTLINE SUMMARY OF PROJECT PROGRESS

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

Chart 1 Cont'd.

Petrochemicals Processing Experiments	
Straight run distillations (Fig. 2)	
Atm. still product as feed	Jan., 1975
Vac. still bottoms as feed	July-Aug., 1975
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	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	To be Planned
Petrochemicals Processing Experiments	
Straight run distillations	Planned
Hydroprocessing	To be Planned

Figure 1

Petrochemicals Liquid Processing Flowchart

for

FMC COED Syncrude

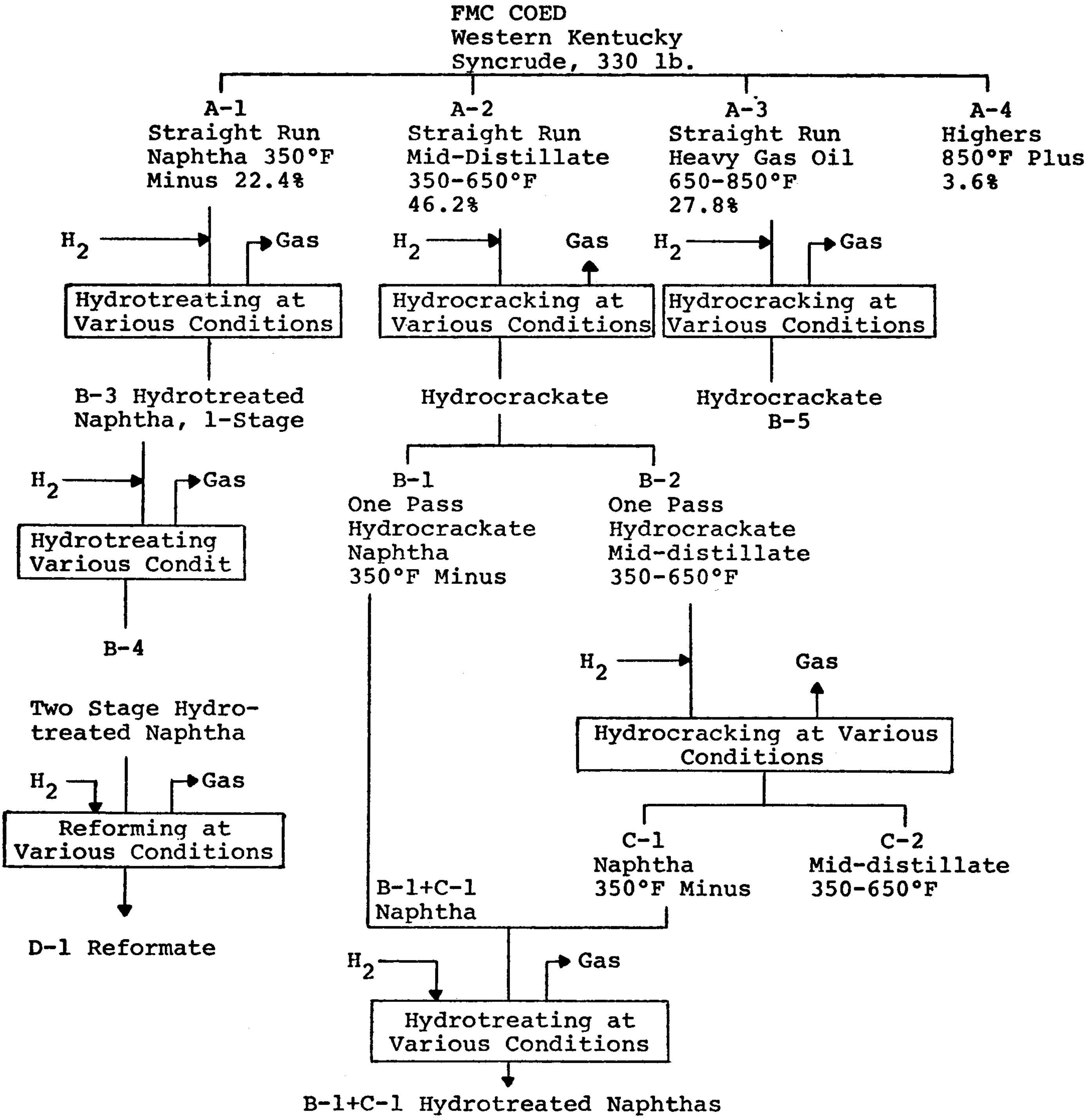

Figure 2

Petrochemicals Liquid Processing Flowchart

for

HRI H-Coal Oil

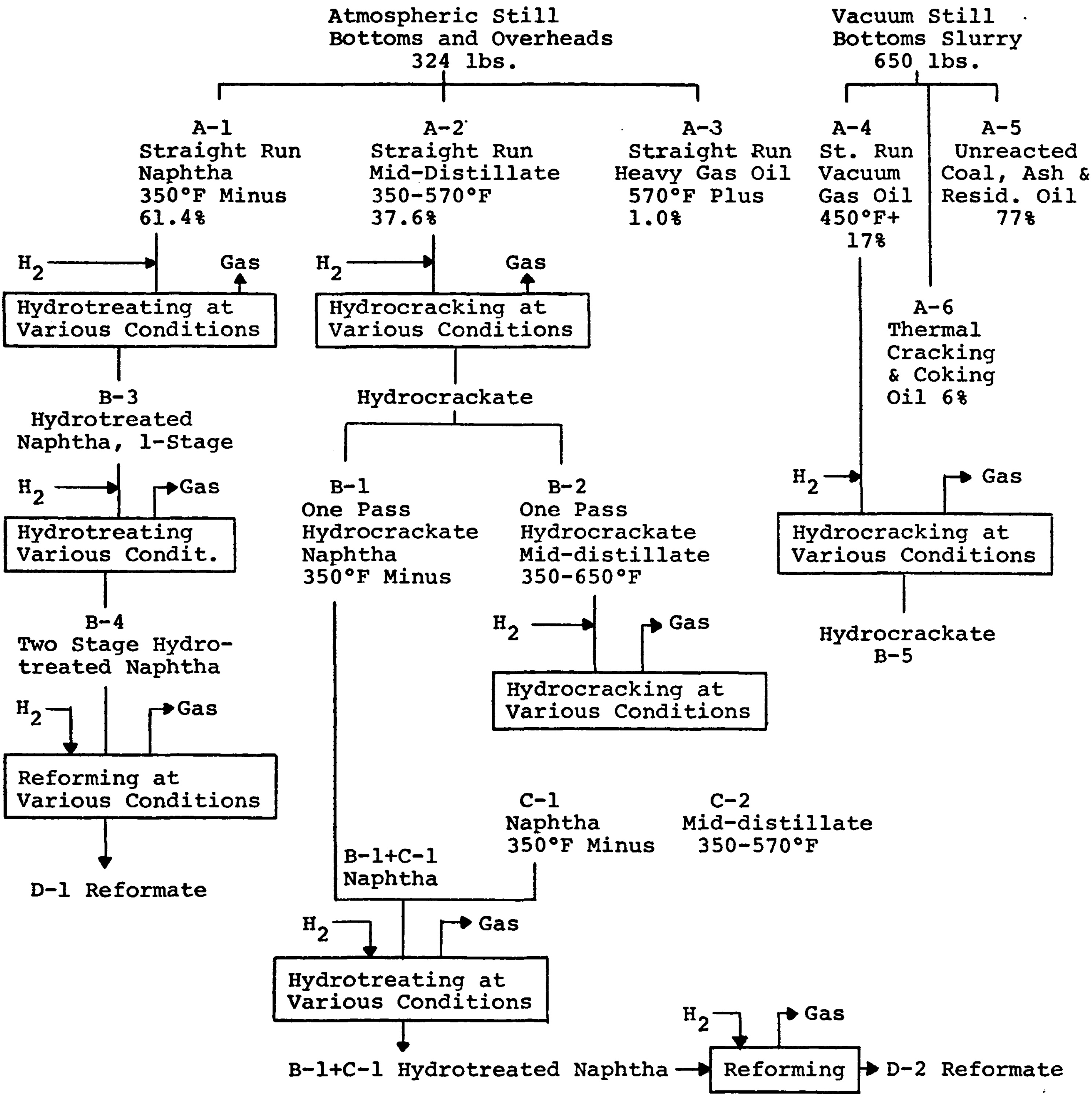

Figure 3

Petrochemicals Liquid Processing Flowchart
for
USBM Synthoil