ARD 2880 FE-2306-15

RESEARCH AND DEVELOPMENT OF AN ADVANCED PROCESS FOR THE CONVERSION OF COAL TO SYNTHETIC GASOLINE AND OTHER DISTILLATE FUELS

Quarterly Technical Progress Report No. 5
for the Period May 1977
through July 1977

MASTER

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I. OBJECTIVE AND SCOPE OF WORK

The objective of this program is (1) to produce coal liquids that can be converted to high-octane gasoline and distillate motor fuels in conventional petroleum refining processes and equipment, the entire operation being economically and technically viable, and (2) to perform an engineering assessment of (1) and its economic potential in a continuous bench-scale unit employing a practical reactor design and catalyst system at a scale not exceeding 1-3 pounds of coal per hour under steady state conditions.

Specifically, the course of action is to apply very deep hydrogenation during the dissolution of coal, while minimizing cracking, to achieve hydrogen to carbon atomic ratios suitable for catalytic cracking, hydrocracking, etc. of the total products of deep hydrogenation or of distillate fractions thereof. It is recognized that substantial removals of nitrogen and oxygen compounds probably will not occur during the catalytic hydrogenations, and chemical removal of these non-hydrocarbons, for example by precipitation with hydrogen choloride after the hydrogenation step, but prior to the catalytic cracking or hydrocracking operations, is necessary and will be carried out.

II. SUMMARY OF PROGRESS TO DATE - (See Time-Line Chart-Figure 1)

This report describes the progress in the development of a process to convert coal to gasoline for the period May 1, 1977 through July 31, 1977. During the fifth quarterly period of effort on this contract we accomplished the following:

1. We installed two new peripheral assemblies on our one-liter reactor. The first is a hydrogen reservoir feed system which permits determination of the amount of hydrogen which is absorbed during a reaction. The second is a quick-feed system which should permit injection of reactants after the reactor has been heated.

2. We carried out fourteen reactions in our one liter reactor. Nine of these were carried out to generate solvents from anthracene oil and dimethylnaphthalenes. Five of these reactions were hydrogenations of mixtures of hydrogenated anthracene oil and Illinois No. 6 coal which were carried out at 425°C and featured continual gas bleeding. The results from these reactions indicated that:

a. Reaction in hydrogenated anthracene oil at 425°C and 2500 PSIG for one to two hours is sufficient to produce a conversion of about 90 wt. % of MAF coal to liquids and gases.

b. Hydrogen absorption under these conditions is about 12 to 20 MSCF H_2 per ton of coal (MAF basis); 11 to 17 MSCFH_2 per ton of coal (dry basis) - an estimated 3 to 5 MSCF H_2 per barrel of product.

c. About 80 to 85 wt. % of the coal-derived liquids which are produced are distillable below 1000° F.

3. We treated the <1000°F distillate fractions of the filtered liquid products of three coal-solvent hydrogenation reactions with gaseous hydrogen chloride. The data indicate that:

a. The amine-hydrochloride complex is apparently formed but is soluble in the bulk of remaining liquids and does not precipitate.

b. Removal of basic nitrogen via this treatment will require more severe hydrogenation or substantial dilution with an appropriate solvent.

c. Precipitation of the amine-hydrochloride complex was achieved via dilution with toluene. Nitrogen levels of about 0.25 wt. % were attained and appear to be independent of the tested hydrogenation severity.

d. Problems encountered previously with the wash steps were essentially solved by the use of more concentrated wash solutions.

4. We examined the 754 to 927°F distillate fraction from one of the filtered liquid products of our 425°C reactions in detail. The data suggest that the material is of poor catalytic cracking quality. Further treatment of this material will be necessary to convert it to an acceptable petroleum refinery feed.

5. We carried out one reaction at 425°C in our 300 ml stirred reactor using tetralin as the solvent. Hydrogen transfer took place but hydrogenation of created naphthalene was largely suppressed by the high vapor pressure of the solvent and the low partial pressure of hydrogen under the conditions of the reaction.

6. Previous reactions in the one liter stirred reactor compared the Filtrol HPC-5 Co-Mo catalyst with our Sun 740711-1% CoO-2% MoO_3 on 8 to 20 mesh bauxite at 400°C. The data, now complete, indicate that under these conditions, the Filtrol HPC-5 catalyst is superior to the Sun catalyst in terms of oxygen and nitrogen reduction and hydrogenation ability.

7. Design of the bench-scale continuous unit (BSCU) continued. Detailed evaluation of our concept of the BSCU has resulted in our recommendation of a conventional single ebullating bed reactor as used by Hydrocarbon Research, Inc. in lieu of our previous design which was a stirred tank coupled to a bank of three ebullating bed reactors. The preliminary design should be completed by September 30, 1977.

We propose that a final design phase be added as a task. We will seek approval of our current BSCU concept from the Program Manager, Dr. John Shen.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. REACTIONS AND DISCUSSION

1. INSTALLATION OF PERIPHERAL EQUIPMENT

We have installed two new peripheral assemblies on our one-liter reactor. Figure 2 is a detailed drawing of our reactor as it now stands. The first assembly which we installed is a hydrogen reservoir feed system. This system consists of an empty 800 ml hydrogenation bomb which is fitted with an accurate pressure gage and the proper fittings, valves, etc. to enable us to fill the autoclave with hydrogen and to use it as a hydrogen reservoir. By calibrating the volume of hydrogen delivered as a function of pressure we can accurately measure the quantity of hydrogen delivered to our reactor. A wet test meter and gas analyses measure the volume of hydrogen removed as gas. We will now know accurately the amount of hydrogen which is absorbed by reactants.

The second assembly which we installed is a quick-load system. It consists of a Hoke cylinder and two severe-service valves fitted with appropriate fittings to enable us to charge the contents to our reactor quickly when it is at reaction temperature. We have not yet tested this system. The biggest anticipated problem with this system is the possibility of plugging the delivery valves and tubes. Our current experience with reactions at 425°C, indicates that we should prove this equipment as soon as possible to minimize the amount of hydrogen which is absorbed before the reactor gets to the desired temperature. At 425°C about one-half of the hydrogen is absorbed before we reach operating temperature.

2. HYDROGENATIONS OF MIXTURES OF COAL AND ANTHRACENE OIL

a. GENERAL

During this quarter, we carried out fourteen reactions in our one liter reactor. Nine of these reactions were carried out to generate solvents for subsequent reactions. Five of these reactions were hydrogenations of mixtures of hydrogenated anthracene oil and Illinois No. 6 coal. Appendix A is a summary of all the material balances and reaction conditions of reactions carried out in our one liter reactor. The order of presentation in this appendix is chronological. It is intended to serve as a compendium of all reactions carried out in the one liter reactor. Analyses of gaseous and liquid reaction products are presented in various tables of this report. These data are so voluminous and varied that we will not follow our previous pattern of including the gas and liquid product analyses in separate appendices.

Nine of the fourteen reactions completed this quarter were carried out to generate solvent for subsequent reactions. Since these were all run under the same reaction conditions only one (755500) was subjected to detailed workup. Most of these solvents, however, were filtered and analyzed so that we could calculate the charge analyses. In general, several runs were made to generate enough solvent for several coal hydrogenations. The filtered products from these runs then were combined and analyzed in one batch.

b. REACTIONS AND RESULTS

Five hydrogenations of Illinois No. 6 coal were carried out in the one liter reactor this quarter. Table I summarizes the data obtained from these reactions. The reactions examine the effects of reaction time and catalyst concentration at 425°C and 2500 PSIG. Only the first three reactions, 755546, 755552, and 755566 have been worked-up sufficiently to judge product quality.

Figure 3 illustrates the actual weight of hydrogen absorbed by these three reactions as determined by our new hydrogen reservoir systems. The data indicate that about 4 to 6 grams of hydrogen were absorbed in these reactions. Calculations indicate that this is about 11 to 17 MSCF hydrogen per ton of dry coal, or assuming four barrels of product per ton of coal, about 3 to 5 MSCF of hydrogen per barrel of product. The data also indicate that about one-half of the hydrogen which is absorbed is absorbed before the reactants get to 425°C (about 2 1/2 hours). We try to suppress this by keeping the hydrogen pressure below 2000 PSIG until the reactants get to 425°C. In our present set-up, the time required to reach 425°C from 350°C is about one hour. We plan to try our quick-load system as soon as possible to eliminate this problem.

Work-up is continuing on 755572 and 755580. All of these reactions were run under conditions such that gas was bled continually from the reactor during the run and hydrogen was added continually so that the content of hydrogen in the gas phase was always above 75%.

The liquid products from these reactions were filtered and then distilled to about 1000°F. Three distillation cuts were taken: gasoline, gas oil, and bottoms. The gasoline and gas oil fractions were recombined to give a composite which represented the proper proportions of all material which boiled below 1000°F. Table II is a summary of distillation data of two batches of hydrogenated anthracene oil solvent and the filtered liquid products of reactions 755546, 755552, and 755566. Included in the table are the nitrogen contents of the filtrates and all distillation cuts. It should be noted that the gasoline cuts of the hydrogenated anthracene oils contain as much nitrogen as those of the reaction product filtrates. Thus, the hydrogenated anthracene oil solvent and not the coal may be a major source of nitrogen in this cut. We plan to try to differentiate positively between solvent-derived and coal-derived material by the next quarter by using dimethyltetralins as the solvent. The distillation curves for the solvents and the filtered liquid products are shown on Figure 4.

The results indicate that:

1) Reaction for one to two hours at 425°C, 2500 PSIG in the presence of hydrogenated anthracene oil and 10 wt. % catalyst is sufficient to convert about 90 wt. % MAF coal to gases and liquids.

2) Under these reaction conditions, about 80 to 85 wt. % of the coal-derived liquids are distillable below 1000°F.

These are important results and we wish to emphasize that these are major findings of our current work. We derive these results as follows:

1. Conversion of Coal (MAF Basis):

$$1 - \left(\frac{\text{Solids} - (\text{catalyst} + \text{ash})}{\text{MAF coal}} \right) \times 100\%$$

where, ash = 10.44% and MAF coal = 87.13% of charged coal.
Thus for reaction 755552, conversion is:

$$1 - \left(\frac{65.0_g - (40.2_g + 13.9_g)}{115.9_g} \right) \times 100\% = 90.6\%$$

2. Conversion to liquids distillable below 1000°F:

It is difficult to differentiate between coal-derived products and solvent-derived products, since we use a hydrogenated anthracene oil solvent. However, by assuming that the solvent undergoes no change in the reaction, one can force a calculation of solvent-free, coal-derived products.

In addition to a VBR distillation (Modified ASTM D-1160 - Table II), we also carefully distilled the filtered liquid product of reaction 755552 through a 1/2" I.D. x 3" long Vigreux column. In both the VBR and the Vigreux distillation, the charge to the pot was 100 ml. The VBR distillation is essentially a fast, simple distillation which involves no reflux. The Vigreux distillation is carried out at a relatively slower rate through a Vigreux column with considerable reflux. The results are summarized on Table III. Use of these results and those on Tables I and II enable us to calculate the data summarized in Table IV. Here we assumed that the solvent emerged unchanged from the reaction and that 95 volume percent of the solvent boiled below 750°F. The data indicate that over 90 wt % of the MAF coal is converted to gases and liquids and, further, that about 82 wt % of the coal-derived liquids boil below about 1016°F.

We consider these results quite satisfactory since they were obtained from a two-hour reaction even though some of the data were calculated by making several assumptions. In the next quarter, we hope to use dimethyltetralins as the solvent and to separate positively coal-derived from solvent-derived products.

c. QUALITY OF THE PRODUCTS

We now have some idea of the quality of the distillable liquids obtained from coal. We again assumed that the distillate fraction of Reaction 755552 (Table III) which had a boiling range of 754°F to 927°F contained only coal-derived product since 95 volume percent of the hydrogenated anthracene oil solvent boiled below 750°F. We subjected this fraction to analysis via clay-gel separation (D-2007) and mass spectrographic analyses of the fractions via ASTM Methods D-2786 and D=3239). Results of these analyses are summarized on Table V. The data indicate that this fraction contains about 0.9 wt % nitrogen, is predominately aromatics and, further, contains large quantities of tri- and tetra- aromatics,in particular, pyrenes.

Consequently this fraction is a poor catalytic-cracking stock and will require further hydrogenation to convert it to an acceptable petroleum refinery feed. Also, since the nitrogen content of this fraction is about 0.9, it is far too high to be handled even by a hydrocracker. Pretreatment to reduce the nitrogen level to <0.3 will undoubtedly be necessary and experiments along this line are discussed in the next section.

3. HYDROGEN CHLORIDE TREATMENT OF COAL-DERIVED LIQUID PRODUCTS

a. GENERAL

We treated the 1000°F⁻ fractions of the filtered liquid products of Reactions 755546, 755552, and 755566 with gaseous hydrogen chloride. Treatment was at room temperature and pressure was carried out simply by bubbling HCL through the liquids, separating the solids when formed by filtration or centrifugation, and washing the raffinate with 10 wt. % aq. KOH and 10 wt. % aq. KCL solutions.

b. RESULTS

In no case was a precipitate formed after HCL treatment of these distillates. The amine-hydrochloride complex was apparently formed but it is soluble in the bulk of the remaining liquids. We achieved precipitation by diluting the liquids with 40 wt. % toluene and then treating them with HCL. All fractions were analyzed for total nitrogen via the Kjeldahl method. Table VI summarizes the results.

The data indicate that the nitrogen content of the HCL-treated product is independent of the severity of hydrogenation within the tested range. From this series of reactions the lowest level of nitrogen reached was 0.25 wt. %. It must be remembered that about 70 wt. % of this material is solvent. Our goal is 0.10 wt. % nitrogen in coal-derived liquid products.

The apparent solubility of the amine-HCL complex in the bulk fluids suggests that further removal of nitrogen via this technique will require much more severe hydrogenation or substantial dilution with a more effective solvent. We plan to try hexane as the diluent next in the hopes that it will precipitate more nitrogenous material.

We wish to point out that our new processing scheme of treating only the 1000°F product and washing with 10 wt. % aq.KOH and KCL solutions solved all of the separation problems previously encountered. In all of the present cases, separations were clean and sharp. No emulsions were formed.

4. HYDROGENATION WITH TETRALIN

We carried out one coal-solvent reaction at 425°C in our 300 ml stirred reactor using tetralin as the solvent. Hydrogen transfer took place but hydrogenation of the created naphthalene was largely suppressed by the high vapor pressure of the tetralin. We aborted the reaction and did not work up the products. We opted, instead, to use dimethyltetralin as the solvent in the next quarter. We believe the higher boiling range of the dimethyltetralins will solve our vapor pressure problem.

5. COMPARISON OF FILTROL HPC-5 CATALYST WITH THE SUN CATALYST

Previous reactions in the one-liter stirred reactor compared the Filtrol HPC-5 catalyst with our Sun 740711-1% CoO-2% MoO_3 on 8-20 mesh bauxite catalyst at 400°C and 2500 psig at 456 minutes of reaction time. The analyses are finally complete and the results are summarized on Tables VII, VIII, IX, X, and XI and Figure 5. Both reactions were carried out while bleeding gases during the reaction to maintain a high hydrogen partial pressure. The gas analyses indicate that the Sun catalyst ran at a lower average hydrogen partial pressure than the HPC-5 catalyst. Perhaps these reactions should be repeated under more comparable circumstances.

The data clearly show that the Filtrol HPC-5 catalyst is superior to Sun catalyst in terms of nitrogen and oxygen removal and in hydrogen insertion. It must be remembered, however, that the Filtrol catalyst contains about 3% CoO and 12% MoO_3 and is more expensive.

We plan to compare these two catalysts at 425°C and short reaction times in the next quarter.

B. DESIGN OF THE BENCH-SCALE CONTINUOUS UNIT

1. DELAY IN THE DESIGN OF THE BSCU.

Our project schedule, Figure 1, indicates a delay in the completion of the preliminary design of the BSCU. We currently plan completion of the preliminary design by September 30, 1977. This has been necessitated by current laboratory findings and further changes in the design concept. Pending approval of the design by the Project Manager, we have labelled Task 3 of the Time-Line Chart (Figure 1) as "Undergoing Revision".

2. CHANGE IN THE BSCU REACTOR CONCEPT

Detailed evaluation of our concept of the BSCU has resulted in our recommendation of a conventional single ebullating bed reactor, as used by Hydrocarbon Research, Inc. (HRI), in lieu of our previous design which was a stirred tank coupled to a bank of three ebullating bed reactors. The new concept does not incorporate a provision for continuous replenishment of catalyst. Figure 6 is a general flow sheet for this revised concept. We will seek approval for this revision from Dr. John Shen, the Program Manager.

The reasons for our change in concept are detailed in Appendices B and C.

Our preliminary design of this concept is well underway and should be complete by September 30, 1977. From this we will devise a construction timetable and cost estimate before moving on to a final design.

We have contacted some vendors for individual equipment costs. Further, we have contacted HRI to explore the possibility of renting time for catalyst-life studies on their bench unit and for acquiring ebullating bed technology. Appendix D summarizes this visit with HRI.

C. WORK FORECAST

1. Continue workup and analyses of hydrogenation products.

2. Carry out dilutions of HCL-treated products with hexane and analyze all fractions.

3. Generate dimethyltetralin for use as solvent in coal hydrogenation.

4. Carry out coal-dimethyltetralin solvent hydrogenation.

5. Carry out a 425°C reaction with Filtrol HPC-5 catalyst.

6. Seek approval for the BSCU revision from the Program Manager.

7. Continue preparation of the preliminary BSCU design.

IV. CONCLUSIONS

We conclude from our present work that:

1. Reaction times of one to two hours at 425°C, 2500 PSIG in the presence of hydrogenated anthracene oil and 10 wt. % catalyst are sufficient to convert about 90 wt. % MAF coal to gases and liquids.

2. Hydrogen consumption under these conditions is about 12 to 18 MSCF H_2 per ton of MAF coal; 11 to 17 MSCF H_2 per ton of dry coal - an estimated 3 to 5 MSCF H_2 per barrel of product.

3. Under these reaction conditions, about 80 to 85 wt. % of the coal-derived liquids which are produced are distillable below 1000°F.

4. The heavy gas oil fraction of these coal-derived liquids contains relatively large amounts of nitrogen and three and four-ring aromatics. It is, therefore, a poor catalytic cracking stock and will require additional processing to convert it to an acceptable petroleum refinery feed.

5. Treatment with hydrogen chloride of the 1000°F$^-$ distillate fraction of the filtered liquid products of coal-solvent hydrogenations produced under these reaction conditions does not result in a precipitation of nitrogenous material. Removal of basic nitrogen by this treatment will require more severe hydrogenation or substantial dilution with an appropriate solvent. Nitrogen levels of 0.25 wt. % have been achieved with toluene dilution.

6. In the hydrogenation of coal in a solvent at 400°C, the Filtrol HPC-5 catalyst appears to be superior to the Sun CoMo on bauxite catalyst in terms of oxygen and nitrogen removal and hydrogenation ability.

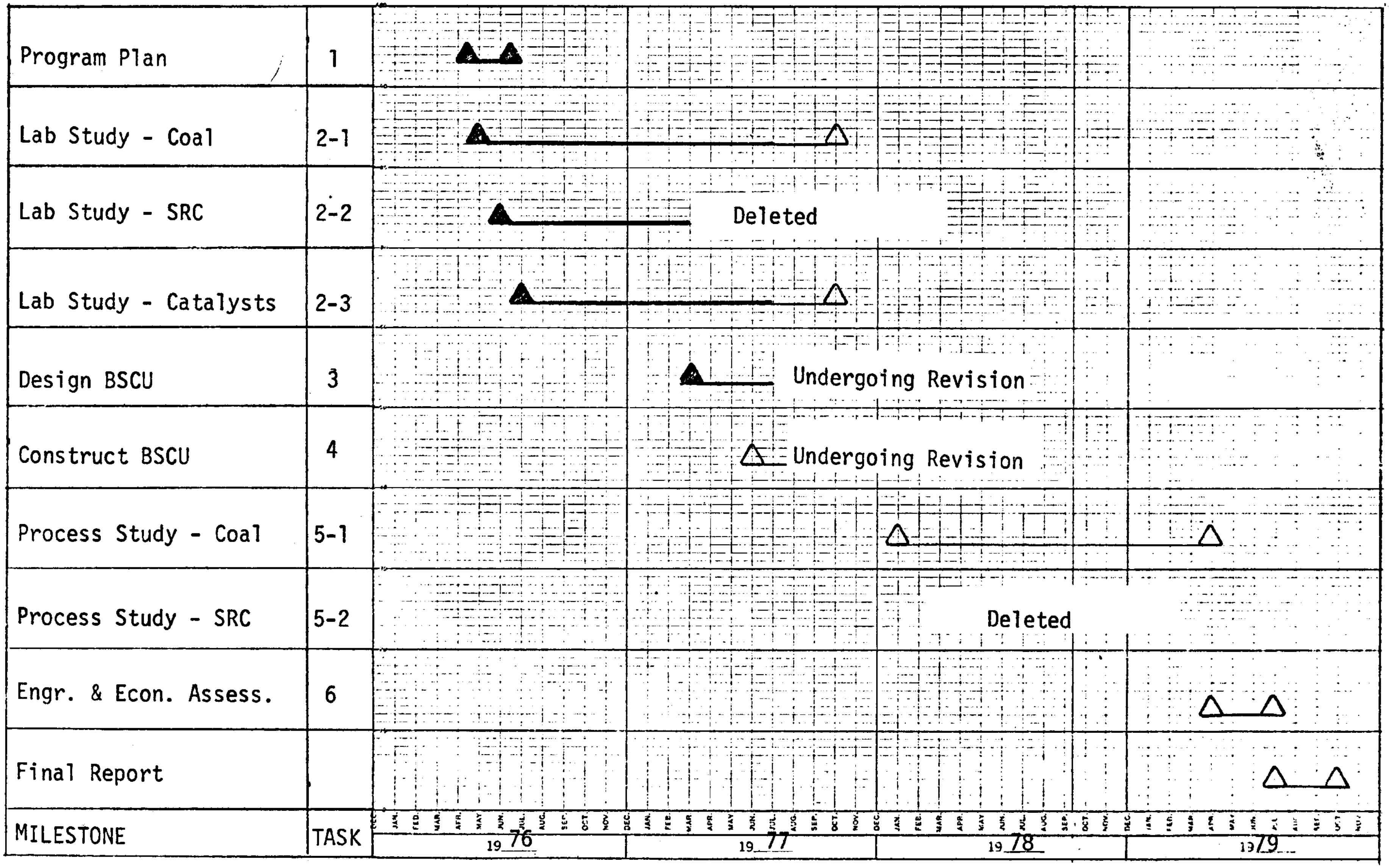
7. The single ebullating bed reactor, a la HRI, is preferable to our previous design (a stirred tank coupled to a bank of three ebullating bed reactors) for the BSCU we plan to construct and operate.

FIGURE 1

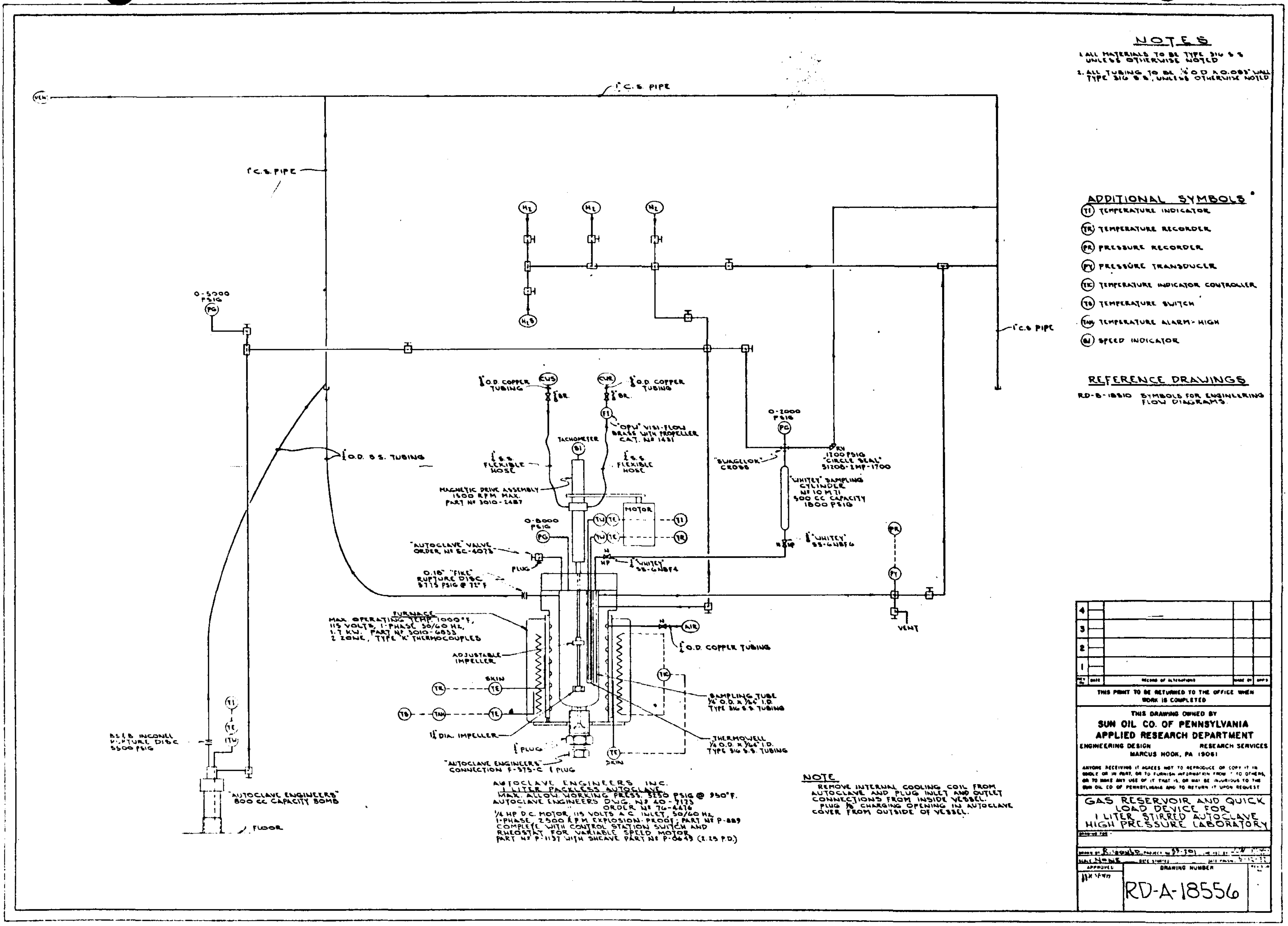
TIME-LINE CHART (1)

Quarterly Technical Progress Report No. 5

Contract E(49-18)-2306



(1) Indicates timing of tasks only. This does not indicate manpower loading.



AUTOCLAVE ENGINEERS INC.
1 LITER PACKLESS AUTOCLAVE
MAX. ALLOW. WORKING PRESS. 5250 PSIG @ 950°F.
AUTOCLAVE ENGINEERS DWG. Nº 40-7173
" " ORDER Nº 76-4476
¼ HP D.C. MOTOR, 115 VOLTS A.C. INLET, 50/60 HZ,
1-PHASE, 2500 R.P.M. EXPLOSION-PROOF; PART Nº P-889
COMPLETE WITH CONTROL STATION SWITCH AND
RHEOSTAT FOR VARIABLE SPEED MOTOR
PART Nº P-1137 WITH SHEAVE PART Nº P-0643 (2.25 P.D.)

NOTE

REMOVE INTERNAL COOLING COIL FROM AUTOCLAVE AND PLUG INLET AND OUTLET CONNECTIONS FROM INSIDE VESSEL.
PLUG ⅛" CHARGING OPENING IN AUTOCLAVE COVER FROM OUTSIDE OF VESSEL.

NOTES

1. ALL MATERIALS TO BE TYPE 316 S.S. UNLESS OTHERWISE NOTED
2. ALL TUBING TO BE ¼" O.D. x 0.083" WALL TYPE 316 S.S., UNLESS OTHERWISE NOTED

ADDITIONAL SYMBOLS

TI TEMPERATURE INDICATOR
TR TEMPERATURE RECORDER
PR PRESSURE RECORDER
PY PRESSURE TRANSDUCER
TIC TEMPERATURE INDICATOR CONTROLLER
TS TEMPERATURE SWITCH
TAH TEMPERATURE ALARM - HIGH
SI SPEED INDICATOR

REFERENCE DRAWINGS

RD-B-18810 SYMBOLS FOR ENGINEERING FLOW DIAGRAMS

REV. No.	DATE	RECORD OF ALTERATIONS	MADE BY	APP'D
4				
3				
2				
1				

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GAS RESERVOIR AND QUICK LOAD DEVICE FOR 1 LITER STIRRED AUTOCLAVE HIGH PRESSURE LABORATORY

DRAWN BY R. GOULD PROJECT No 33-301
SCALE NONE DATE STARTED DATE FINISH. 5-12-77
APPROVED
DRAWING NUMBER
RD-A-18556

FIGURE 2

HYDROGEN ABSORPTION CURVES- DIRECT MEASUREMENT

REACTION CONDITIONS: Reactor = 1 liter 316 SS stirred autoclave; Time = as indicated; temperature = 425 ± 5°C; Pressure = 2500 PSIG; Reactants = Illinois No 6 coal and hydrogenated anthracene oil (H/C = 1.2) 1:2 by weight

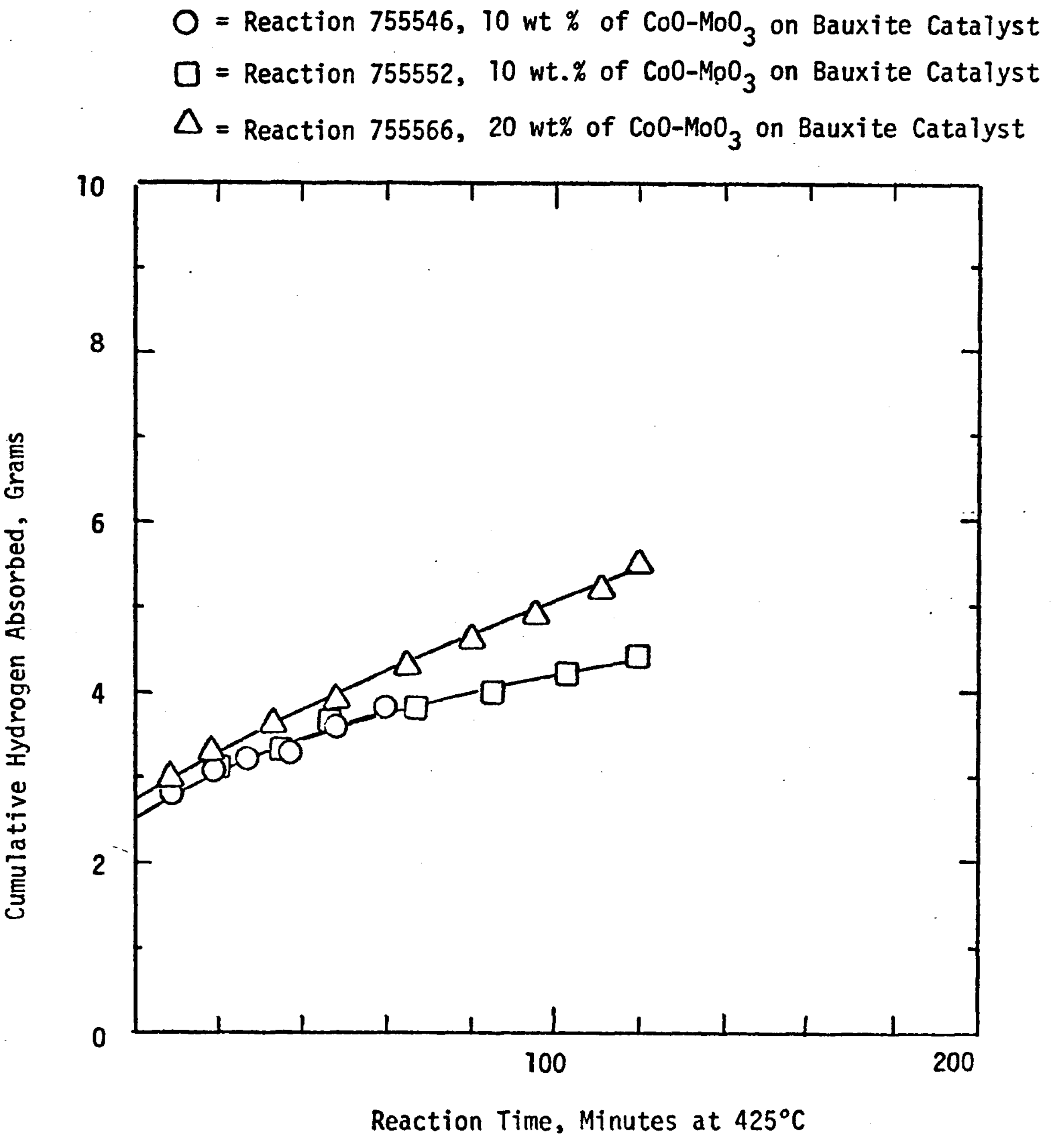


Figure 4

BOILING RANGES OF SOLVENTS AND FILTERED LIQUID PRODUCTS

(Via Modified ASTM D-1160)

Note: Additional data on Table II, this report

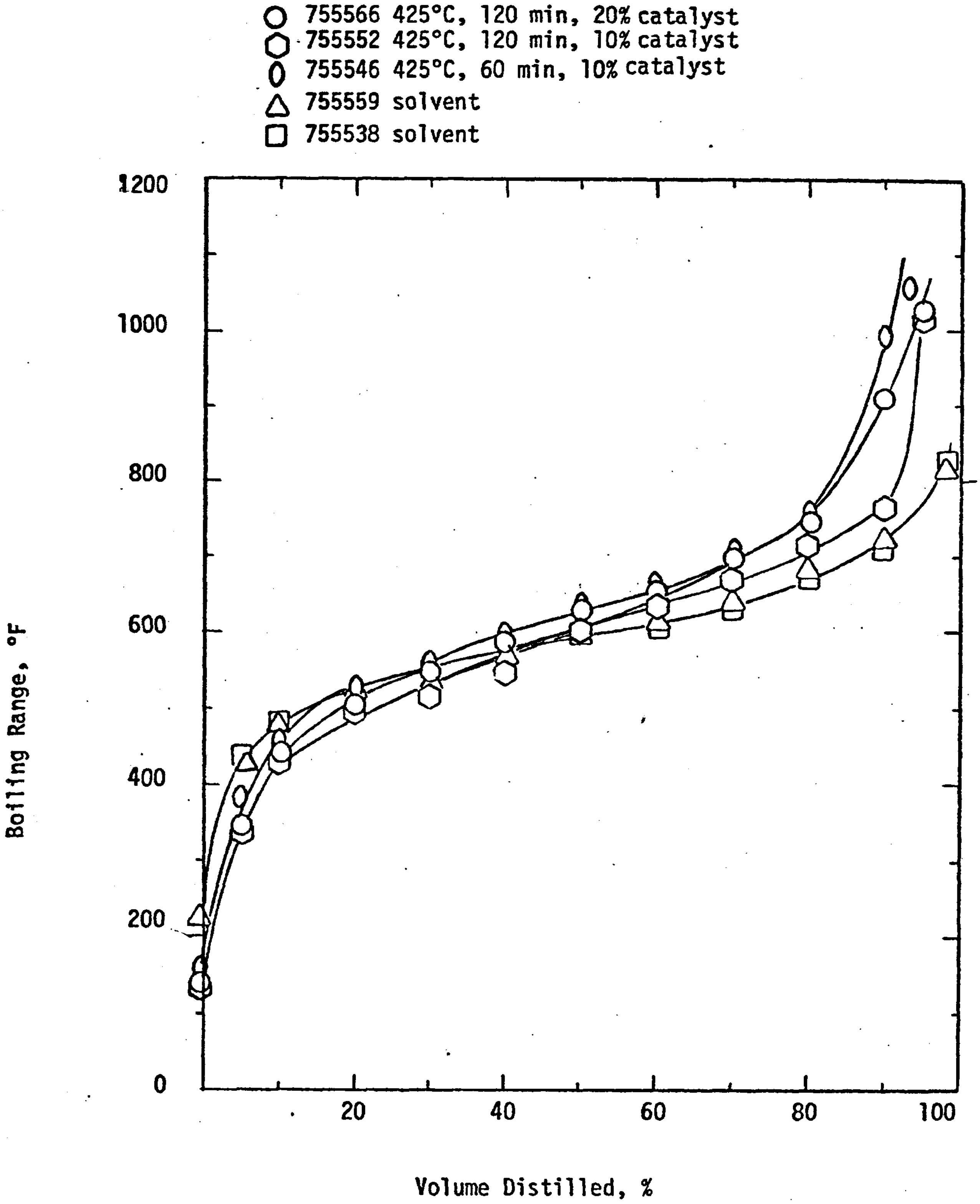


FIGURE 5

HYDROGEN ABSORPTION RATE: HYDROGENATION OF A MIXTURE OF ILLINOIS NO. 6 COAL AND HYDROGENATED ANTHRACENE OIL IN THE ONE LITER REACTOR

Reaction Conditions: Temperature = 400°C; Pressure = 2500 ± 100 PSIG Reactor = One liter stirred autoclave; Catalyst = as indicated; Charge = 1:2 (by weight) Illinois No. 6 coal; hydrogenated anthracene oil (H/C = 1.19). Gases were periodically bled from reactor to maintain high hydrogen partial pressure.

* Indicates where reaction was stopped and the reactor cooled, vented, and repressured with fresh hydrogen.

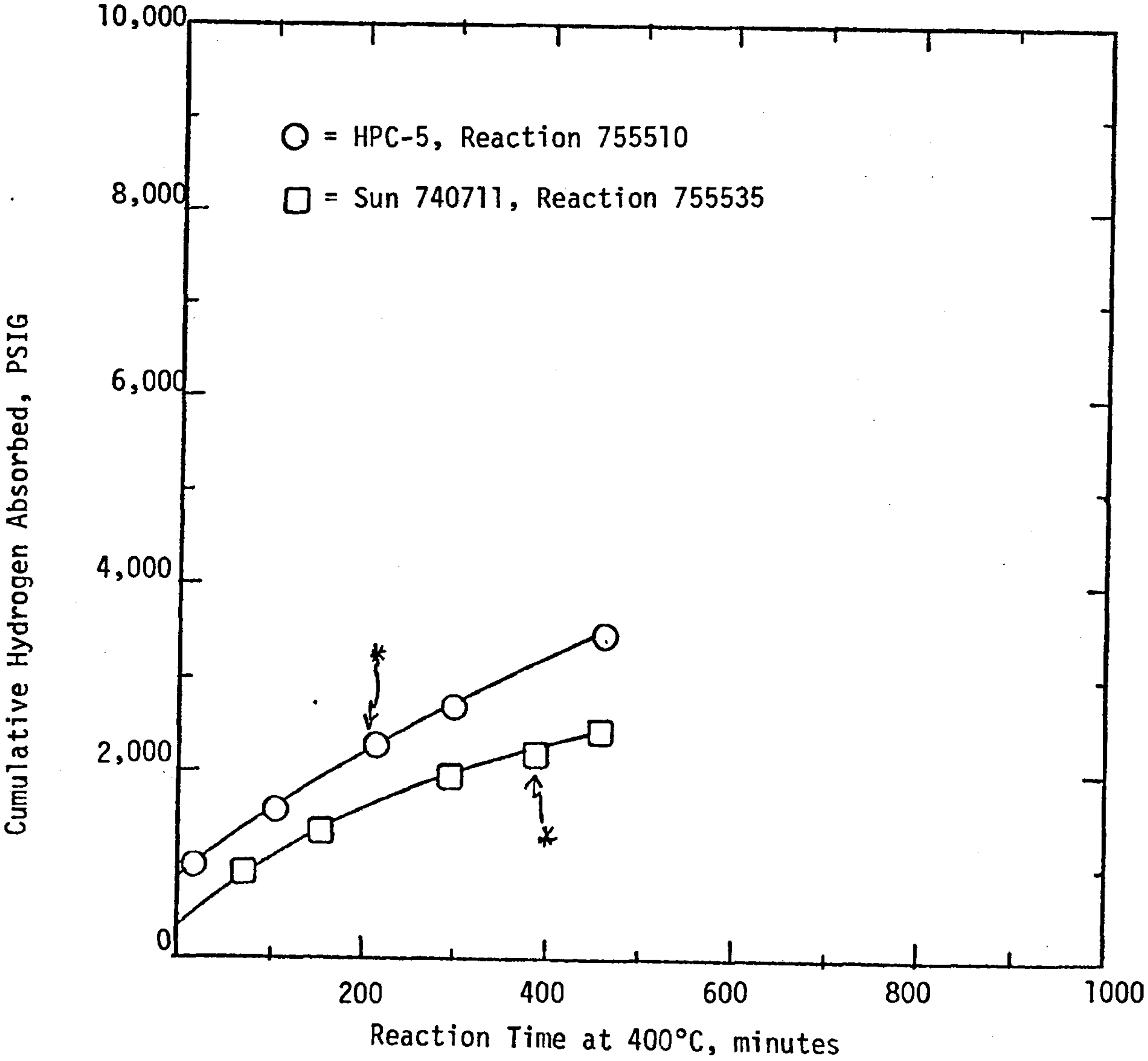


FIGURE 6

GENERAL FLOW SHEET

EBULLATING BED COAL HYDROGENATION UNIT

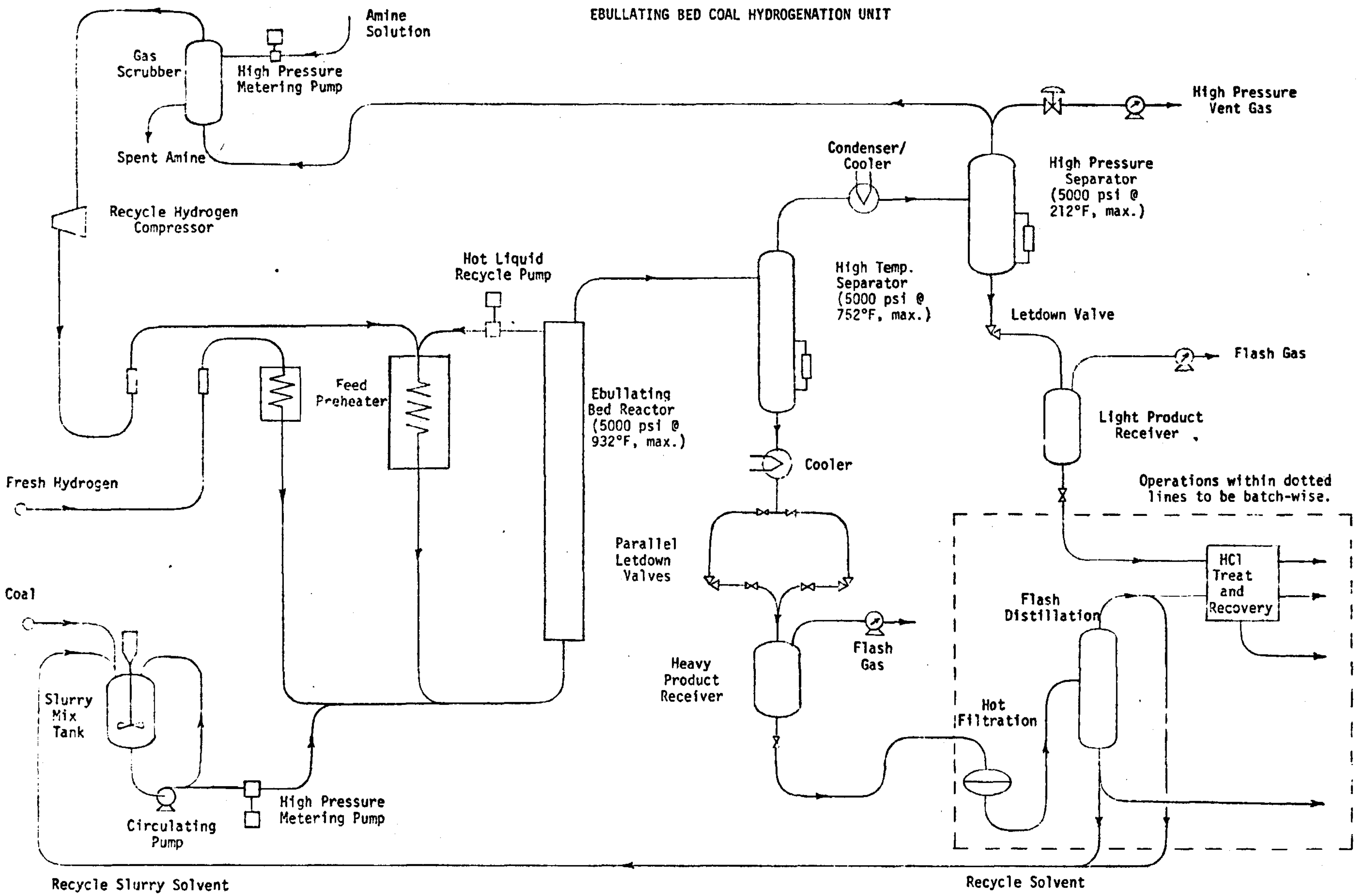


TABLE I

Summary of Reaction Data: One Liter Reactor Reactions

Reaction Number	Coal (1)	Solvent	Catalyst	H_2 (4)	Total	Time (min) (12)	Temp. (°C)	Pressure (PSIG)	H_2 Absorbed, gms (7)	gms H_2 Absorbed per 100 gms coal	H_2 Absorbed per ton MAF coal (MSCF)	H_2 Absorbed per ton dry coal (MSCF)	H_2 Absorbed per bbl Product (MSCF)(11)	Conversion (wt %) ~~(9)~~
755546	133.0	267.2(2)	40.0(3)	6.8	447.0	60	425	2500	3.8	3.3	12.3	11.0	3.1	89.2
755552	133.0	268.6(2)	40.2(3)	7.3	449.1	120	425	2500	4.4	3.8	14.3	12.7	3.6	90.6
755566	133.0	267.0(5)	80.0(3)	9.2	489.2	120	425	2500	5.5	4.7	17.8	15.9	4.4	87.3
755572	133.0	268.0(5)	20.1(3)	9.0	430.1	120	425	2500	5.0	4.3	16.2	14.5	4.1	93.3
755580	135.0	272.5(13)	40.8(3)	8.2	456.5	120	425	2500	6.1	5.2	19.5	17.4	4.9	91.2

	Products, gms								Elemental Analysis, wt.%										
Reaction Number	Gas (6)	Wet Ice Trap	Wash Liquids	Soxhlet Liquids	Filtered Liquids	Solids	Total	Recovery wt.%	C	H	O	N_T (8)	N_B (10)	S	H/C	Mol wt.	Kin.Vis.(cs) 100°F	Kin.Vis.(cs) 210°F	Gravity
755546	12.6	1.4	51.0	0.3	302.1	66.4	433.8	97.0	89.13	8.25	1.62	0.62	(14)	(14)	1.11	(14)	(14)	(14)	1.0604
755552	15.8	6.8	35.8	10.5	303.8	65.0	437.7	97.5	89.96	8.10	1.12	0.51	(14)	(14)	1.08	233	12.54	2.50	1.0724
755566	16.5	0.0	63.3	0.3	268.0	108.6	456.7	93.4	90.01	8.36	0.94	0.43	(14)	(14)	1.11	312	(14)	(14)	1.0545
755572	18.6	4.2	41.6	1.1	299.0	42.1	406.6	94.5	←			→	(14)	←					→
755580	17.6	3.8	53.5	1.2	297.4	65.6	439.1	96.2	←			→	(14)	←					→
Calculated Analysis of Charge to: 755546									86.38	7.56	4.12	0.60	...	1.14	1.05				
755552									86.39	7.56	4.11	0.60	...	1.13	1.05				
755556									86.42	7.48	4.12	0.60	...	1.15	1.04				

(1) Sun 740700 - Illinois No. 6 Coal
(2) Hydrogenated Anthracene Oil 755538-D
(3) Sun 740820 1% CoO 2% MoO_3 on 8 to 20 mesh Bauxite
(4) Indicates total hydrogen gas admitted to reactor measured directly.
(5) Hydrogenated Anthracene Oil 755559-D
(6) Includes all vented gas samples and residual gases
(7) Measured directly
(8) Total nitrogen content, via Kjeldahl analysis
(9) Calculated from ((1-(Solids-(catalyst + ash)•MAF Coal))x 100%
(10) Basic nitrogen
(11) Assumes 4 bbl product per ton coal
(12) Time at 425°C. Heat up time from 350°C to 425°C is about one hour
(13) Hydrogenated Anthracene Oil 755558 (H/C=0.9)
(14) Data not available yet

TABLE II

Distillation Data of Some Filtered Liquid Products and Solvents and Nitrogen Contents of Some Fractions(3)
(Via Modified ASTM D-1160)

	Filtered Liquid Products			H.A.O. Solvents (1)	
Reaction Number	755546	755552	755566	755538	755559
Reaction Conditions					
Time, Minutes	60	120	120	--	--
Catalyst, Wt. %	10	10	20		
Nitrogen Content, wt. %					
Filtrate	0.62	0.51	0.43	--	0.28
Gasoline (2)	0.27	0.29	0.22	--	0.27
Gas Oil (2)	0.46	0.46	0.36	--	--
Bottoms (2)	1.53	1.49	1.34	--	--
Composite	0.42	0.44	0.35	--	--
Vol.% Distilled, °F					
IBP	154	134	139	144	222
5	386	336	346	436	431
10	457	430	444	480	483
20	506	496	499	503	511
30	549	514	553	551	531
40	587	548	592	578	571
50	617	592	626	595	600
60	645	631	654	610	623
70	700	667	688	637	640
80	757	711	747	674	671
90	993	861	910	717	716
Final	1057	1016	1018	824	819
Vol % Yield at Crack	93	95	94	98	98

(1) These data refer to the hydrogenated anthracene oil solvents used in reactions 755546, 755552, and 755566.

(2) Volume percent of these cuts via VBR:

Cut	755546		755552		755566	
	Vol %	B.R., F	Vol %	B.R.,°F	Vol %	B.R.,°F
Gasoline	11	154-457	22	134-496	12	139-444
Gas Oil	82	458-1057	73	497-1016	82	445-1018
Bottoms	7	>1057	5	>1016	6	>1018

(3) These data refer to VBR distillations via Modified ASTM Method D-1160. The terms "filtered liquid products" refers to the product obtained by washing or soxhleting the solids of the reaction.

TABLE III

Distillation of the Filtered Liquid Product
of Reaction 755552 (3,4)

	Boiling Range (°F)	Wt. % Distilled	Total Nitrogen, Wt. %(1)
Filtered Liquid Product			0.51
(755552)	---	---	0.51
Distillate Fractions			
Trap Material	----------	4.2	0.08 (5)
Gasoline	173 to 457	0.8	0.01
Gas Oil	457 to 754	72.8	0.38
Heavy Gas Oil	754 to 927(2)	10.2	0.88
Bottoms	927	12.1	1.64

(1) Via Kjeldahl; nitrogen balance = 111%

(2) This fraction analyzed via ASTM Methods D-2007, D-2786, and D-3239, see Table V.

(3) Reaction Conditions: 2 hrs., 425°C, 2500 PSIG, 10 wt. % catalyst Further details on Table I, this report.

(4) Distilled in mini-lab glassware through a 1/2" I.D. x 3" long Vigreux column - not a VBR distillation.

(5) Note the difference in the nitrogen content here and in a similar fraction obtained via VBR distillation on Table II. We attribute this difference to the two widely different distillation methods.

TABLE IV

Calculated Coal-Derived Products of Reaction 755552

Note: Data given in weight percent

$$96.3\ \text{MAF Coal} + 3.7\ H_2 \xrightarrow[\text{10\% Catalyst}]{\text{2 hrs. @ 425°C 2500 PSIG}}$$

wt.%	
11.8	gases
78.9	raw liquids (1)
9.3	unconverted organics

Wt.%	Boiling Range,°F	
16.3	173-754°	
38.3	754°-927°	(2)
27.7	927°-1016°	
17.6	> 1016°	

(1) Called "raw liquids" because we are unable to resolve water content

(2) This fraction was further analyzed via ASTM Methods D-2007, D-2786, and D-3239 - see Table V, this report.

TABLE V

Analysis of the 754°F to 927°F Distillate Fraction of the Filtered Liquid Products of Reaction 755552(1)

I. ASTM D-2007 Clay-Gel Separation Data

Nomenclature	Amount in fraction, wt.%
Asphaltenes	4.1
Saturates*	2.0
Aromatics**	83.9
Polars	10.0

*Analyzed below, Section II

**Analyzed below, Section III

II. Analysis of Saturate Fraction via Mass Spectroscopy - ASTM Method D-2786

Component	Amount, Vol %
paraffins	33.9
1-ring naphthenes	27.1
2-ring naphthenes	11.4
3-ring naphthenes	9.8
4-ring naphthenes	7.6
5-ring naphthenes	4.1
6-ring naphthenes	2.2
aromatics	3.9
Total	100.0

III. Analysis of the Aromatic Fraction via Mass Spectroscopy - ASTM Method D-3239

Component	Amount, Wt.%
monoaromatics	
alkylbenzenes	0.0
naphthenebenzenes	1.3
dinaphthenebenzenes	4.1
diaromatics	
naphthalenes	0.0
acenaphthenes, dibenzofurans	6.8
fluorenes	7.2
triaromatics	
phenanthrenes	6.4

TABLE V CONTINUED

Component	Amount, Wt.%
naphthene phenanthrenes	10.3
tetraaromatics	
pyrenes	24.3
chrysenes	9.1
pentaaromatics	
perylenes	2.6
dibenzanthracenes	0.0
thiophenoaromatics	
benzothiophenes	2.6
dibenzothiophenes	2.1
naphthobenzothiophenes	1.6
unidentified aromatics, class IV	4.8
Total Identified	83.2

(1) See Table I for reaction conditions and other details

TABLE VI

Nitrogen Content of Hydrogen Chloride Treated Samples of Reactions 755546, 755552, and 755566 (4)

	Nitrogen Contents, wt.%(1) Reaction Number		
	7555546(4)	755552(4)	755566(4)
	0.60	0.60	0.61
Filtered Liquid Product	0.62	0.51	0.43
Distillate, 1000°F	0.42	0.44	0.35
First HCL Treat (2)	0.44	0.40	0.35
Second HCL Treat-Toluene Dilution(3)			
Raffinate	0.28	0.25	0.25
Extract	2.59	2.20	2.47
Water washes	0.0065	0.0042	0.0037
Amount of extract, wt.%	6	3	1

(1) Via Kjeldahl analysis
(2) HCL added but no precipitate formed. Neutralized, washed, and dried
(3) 40 wt.% Toluene added then HCL treated.
(4) See Table I for reaction condition details.

TABLE VII

Comparison of the Filtrol HPC-5 and Sun Catalyst 740711

	← Reactants, gms				→	← Reaction Conditions		→
Reaction Number	Solvent	Coal	Catalyst	H_2	Total	Time (min)	Temp. (°C)	Pressure (PSIG)
755510	330.0(1)	167.0	50.0(3)	3.0	553.0	456	400	2500
755535	333.0(2)	167.0	50.0(4)	2.1	552.1	456	400	2500

Reaction Number	Gas	Wet Ice Trap	Wash Liquids	Soxhlet Liquids	Filtered Liquids	Solids	Total	Recovery (wt.%)	Conversion (wt.%)(6)
755510	13.8	0	60.8	3.3	370.2	79.1	527.2	95.3	92.0
755535	7.8	0	33.8	7.0	363.0	94.6	506.2	91.7	81.3

Analysis of Filtered Liquid Product

	C	H	O	N_t(7)	N_b (7)	S	H/C
Calculated Charge to Rxn 755510	86.83	7.94	3.69	0.48	-----	1.07	1.10
Calculated Charge to Rxn 755535	86.88	7.78	3.71	0.54	-----	1.01	1.17
Product of 755510	90.22	9.45	0.42	0.16	0.07	0.01	1.26
Product of 755535	90.45	8.46	0.82	0.38	0.02	0.03	1.12

(1) Hydrogenated anthracene oil 755500
(2) Hydrogenated anthracene oil 755530
(3) Filtrol HPC-5 Catalyst
(4) Sun Catalyst 740711 $CoO-MoO_3$ on 8-20 mesh Bauxite
(5) Time at 400°C
(6) Calculated from {{1- {[solids-(catalyst+ash)] MAF coal x100%
(7) N_t = Total Nitrogen via Kjeldahl; N_b = Basic Nitrogen

TABLE VIII

SUMMARY OF GAS ANALYSES FROM REACTION 755535

Reaction Time, min.	11	24	32	74	110	158	188	219	298	(2) 339	456
Total Volume Removed, liters	1.0	1.9	2.9	5.4	8	10.5	12.5	15.3	17.9	20.5	21.8
Total H_2 Absorbed, PSIG	400	480	580	920	1120	1340	1490	1840	1940	2140	2440
Total Moles H_2 Absorbed (1)	0.2	0.2	0.2	0.4	0.5	0.6	0.8	0.8	0.8	0.9	1.1
Analysis, Mole %, Air-free											
Hydrogen	92.4	86.8	85.0	79.0	77.9	76.3	75.3	74.9	72.9	73.3	82.8
Methane	1.2	2.5	3.2	5.8	6.7	7.9	8.4	8.6	9.7	10.0	10.4
Ethane	0.5	1.0	1.3	2.3	2.7	3.0	3.2	3.4	3.9	4.1	3.1
Propane	0.2	0.5	0.7	1.5	1.6	2.0	2.2	2.3	2.7	3.0	1.2
Butenes	0.0	0.1	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.3	0.0
Butanes	0.1	0.2	0.3	0.5	0.7	0.8	0.9	1.0	1.2	1.4	0.2
Pentenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pentanes	0.0	0.2	0.1	0.2	0.3	0.3	0.4	0.4	0.4	0.4	0.0
Hexenes	0.1	0.0	0.5	0.7	0.8	0.9	1.0	1.2	1.4	1.2	0.1
Hexanes	0.0	0.0	0.0	0.2	0.1	0.2	0.2	0.2	0.2	0.3	0.1
Carbon dioxide	0.7	1.2	1.4	1.6	1.4	1.3	1.2	1.1	0.8	0.7	0.2
Hydrogen Sulfide	4.8	6.9	7.4	8.1	7.5	7.1	6.9	6.6	6.4	5.2	1.9

(1) Calculated from ideal gas laws

(2) Reaction was stopped after 385 minutes, cooled, vented, repressured, started.

TABLE IX

SUMMARY OF GAS ANALYSES FROM REACTION 755510

Reaction Conditions are Shown in Table VII

								(2)					
Reaction Time, min.	10	30	50	102	143	178	212	224	254	298	353	407	456
Total Volume Removed, liters	2.9	4.6	7.3	10.0	12.5	15.1	18.0	19.8	20.9	23.5	25.7	28.1	29.9
Total H_2 Absorbed, PSIG	900	1100	1320	1760	1760	1960	2210	2340	2480	2690	2930	3210	3470
Total Moles H_2 Absorbed (1)	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.0	1.1	1.2	1.2	1.4	1.5
Analysis, Mole %, Airfree													
Hydrogen	82.0	80.1	79.0	74.6	73.7	73.6	74.7	84.3	83.4	85.0	82.2	81.4	80.9
Methane	2.5	3.3	4.2	7.0	7.9	8.1	8.0	2.7	3.4	4.1	4.8	5.2	5.6
Ethane	0.9	1.2	1.6	2.6	2.9	3.1	3.1	2.2	2.5	2.8	3.1	3.4	3.6
Propane	0.7	1.1	1.1	1.8	2.1	2.1	2.2	2.3	2.4	2.2	2.8	3.1	3.0
Butenes	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.2	0.3	0.2	0.4	0.4	0.5
Butanes	0.3	0.6	0.6	0.9	1.3	0.9	1.1	1.0	0.9	0.9	1.1	1.2	1.4
Pentnes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pentanes	0.0	0.0	0.0	0.0	0.2	0.6	0.8	0.4	0.3	0.3	0.3	0.3	0.4
Hexenes	1.3	1.6	1.5	1.8	1.8	2.1	1.8	1.4	1.5	1.0	1.6	1.7	2.1
Hexanes	0.0	0.0	0.0	0.2	0.2	0.0	0.0	0.3	0.2	0.0	0.2	0.2	0.2
Carbon dioxide	1.4	1.2	1.2	0.8	0.6	0.6	0.4	0.3	0.2	0.0	0.0	0.0	0.0
Hydrogen sulfide	10.6	10.5	10.4	9.9	9.0	8.4	7.4	4.9	4.7	3.5	3.5	3.0	2.3

(1) Calculated from ideal gas laws

(2) Reaction was stopped after 212 min., cooled, vented, repressured, started

TABLE X

Distillation of the Filtered Liquid Product of 755535

	C	H	O	N_t(1)	N_b(1)	S	H/C	wt%	B.R.°C
755535-D	90.45	8.46	0.82	0.38	0.02	0.03	1.12	100	-----
Cut 1	86.12	12.95	0.63	0.10	0.02	0.08	1.80	7.0	65-300
2	89.90	9.38	0.62	0.20	0.01	0.06	1.25	61.9	200-356
3	91.78	7.66	0.50	0.39	0.02	0.06	1.00	8.0	356-381
4	89.33	7.49	0.08	0.65	0.04	0.06	1.01	11.6	381-493
5	89.01	7.19	0.11	1.38	0.07	0.12	0.97	11.5	7493

(1) N_t = Total nitrogen via Kjeldahl; N_b = Basic nitrogen.

TABLE XI

DISTILLATION OF THE FILTERED LIQUID PRODUCT OF 755510

Reaction Conditions: 400°C, HPC-5 Catalyst, 2500 PSIG, Hydrogenated Anthracene Oil Solvent. See Table III

	ELEMENTAL ANALYSIS, WT.%												
	C	H	O	N_t (1)	N_b (2)	S	H/C	Wt.%	Vol.%	Boiling Range, °C, (S.D)(4)			
Charge to Reaction (3)	86.83	7.94	3.69	0.48		1.07	1.07	------	-------	------------------------------			
755510-D	90.22	9.45	0.42	0.16	0.07	0.01	1.26	100.0	100.0	------------------------------			
Cut 1	85.87	13.97	0.16	0.00	0.02	0.03	1.95	6.6	8.0	78	-	192	Gas. Range
2	88.38	11.46	0.16	0.00	0.03	0.004	1.56	12.8	14.2	179	-	259	Kerosine
3	89.12	10.48	0.34	0.10	0.02	0.002	1.41	16.1	17.2	224	-	301	Lt. Gas Oil
4	90.18	8.62	0.43	0.17	0.07	---	1.15	57.7	50.9	272	-	499	Hv. Gas Oil
5	85.26	7.42	0.36	0.74	0.25	0.006	1.04	6.8	9.7	449+		Lube Oil	

(1) Total nitrogen analyzed via the Kjeldahl Method
(2) Basic Nitrogen
(3) Calculated
(4) Simulated distillations of fractions previously distilled

APPENDIX A

Summary of Reaction Conditions and Material Balances
For One Liter Reactor

		Reactants, gms.					Reaction Conditions			Products, gms.							
Reaction Number (755:xxx)	Reaction Date (mo/day)	Solvent	Coal(5)	Catalyst	Hydrogen(15)	Total	Time (min.)	Temp. (°C)	Pressure (PSIG)	Gas	Wet Ice Trap	Wash Liq.	Soxhlet Liq.	Filtered Liq.	Solids	Total	Recovery Wt.%
500	1/12	507.4(1)	0.0	50.7(2)	7.8	565.9	305	375	3000	4.0	0	48.2	----	459.2	55.6	567.0	100.2
510	1/19	333.0(3)	167.0	50.0(2)	3.0	553.0	456	400	2500	13.8	0	60.8	3.3	370.2	79.1	527.2	95.3
517	2/10	508.5(1)	0.0	51.0(2)	8.0	567.5	403	375	3000				(10)				
522	3/2	524.0(1)	0.0	52.4(2)	8.1	584.5	370	375	3000				(10)				
530	3/16	537.0(1)	0.0	53.7(2)	8.2	598.9	383	375	3000				(10)				
532	3/18	505.5(1)	0.0	53.7(2)	7.7	566.9	440	375	3000				(10)				
535	4/6	360.8(4)	167.0	50.0(6)	2.1	552.1	456	400	2500	7.8	0	33.8	7.0	363.0	94.6	506.2	91.7
538	5/3	522.0(1)	0.0	52.2(2)	8.0	574.2	442	375	2500				(10)				
540	5/6	428.0	0.0	52.2(2)	6.5	486.7	385	375	2500				(10)				
546	5/17	267.2(7)	133.0	40.0(8)	3.8(9)	444.0	60	425	2500	12.6	1.4	51.0	0.3	302.1	66.4	433.8	97.0
552	5/21	268.6(7)	133.0	40.2(8)	7.3(9)	449.1	120	425	2500	15.8	6.8	35.8	10.5	303.8	65.0	437.7	97.5
559	6/3	507.0(1)	0.0	50.7(2)	15.6(9)	573.3	304	375	3000				(10)				
563	6/6	505.0(1)	0.0	50.5(2)	(10)	(10)	379	375	3000				(10)				
566	6/9	267.0(1)	133.0	80.0(8)	9.2(9)	489.2	120	425	2500	16.5	0.0	63.3	0.3	268.0	108.6	456.7	93.4
572	7/20	268.0(11)	133.0	20.1(8)	9.0(9)	430.1	120	425	2500	18.6	4.2	41.6	1.1	299.0	42.1	406.6	94.5
580	7/26	272.5(12)	135.0	40.8(8)	8.2(9)	456.5	120	425	2500	17.6	3.8	53.5	1.2	297.4	65.6	439.1	96.2
588	7/29	441.5(13)	0.0	44.2(2)	(14)	(14)	253	300	2000				14				

(1) Non-hydrogenated Anthracene Oil-Sun 740701
(2) Filtrol HPC-5 Co-Mo Catalyst
(3) Hydrogenated Anthracene Oil-Sun 755500
(4) Hydrogenated Anthracene Oil-Sun 755530
(5) Illinois No.6-Sun 740700
(6) Sun 1% CoO-2% MoO_3 on 8 to 20 mesh Bauxite-740711
(7) Hydrogenated Anthracene Oil-Sun 755538
(8) Sun 1% CoO-2% MoO_3 on 8 to 20 mesh Bauxite-740820
(9) Measured via hydrogen reservoir method
(10) Not measured
(11) Hydrogenated Anthracene Oil-Sun 755559
(12) Hydrogenated Anthracene Oil-Sun 755558 (H/C=0.9)
(13) Charge here was a mixture of dimethylnaphathalenes - Sun Code 616616
(14) Data not available yet.
(15) Calculated from pressure drop data

INTEROFFICE CORRESPONDENCE DATE June 21, 1977

SUBJECT COAL HYDROGENATION PILOT UNIT;
REVISED REACTOR SECTION

LOCATION Marcus Hook - Processes

FROM A. F. Talbot

TO Dr. A. Schneider

SUMMARY

Our contract with ERDA to study the conversion of coal to gasoline calls for construction of a continuous pilot unit (capacity $\leq$ 3 lb coal/hr.) for the coal hydroliquefaction step. In the past few months several quite different high pressure/high temperature lab reactor concepts have been proposed and evaluated. Chronologically, these were:

1. A plug flow type reactor, with once-through use of powdered catalyst slurried with the coal/solvent feed.
2. A CSTR, with granular catalyst continuously supplied from and removed via lock hoppers.
3. A CST, coupled to a bank of 3 small ebullating bed catalytic reactors. A fourth "swing" reactor allows for periodic replacement of 1/3 the catalyst inventory.

Thus, each proposal included a mechanism for introducing fresh catalyst to the reaction zone.

After considering the most recent design concept (proposal #3 above) I recommend we modify the reactor section of the proposed pilot unit once more, adopting a single ebullating bed reactor ala the H Coal process of Hydrocarbon Research, Inc. with no provision for continuous replenishment with fresh catalyst. This recommendation is based on considerations of current lab data, and possible design problems and operating restrictions, which are discussed in more detail below.

DISCUSSION

Design Basis

The design criteria for the proposed pilot unit were derived in part from operating conditions as now practiced in 300 ml and 1000 ml batch stirred autoclave runs. These include use of a proprietary catalyst (1% C_oO-2% M_oO_3 on bauxite) at low concentration, e.g. 3-10% of reactants (coal plus solvent) charged to the autoclave. Some means of replenishing the "disposable" catalyst was considered necessary to maintain satisfactory system activity. A residence time target of 1 hour at hydrogenation conditions was chosen, although autoclave runs to date have not established that acceptable quality liquid product can be obtained within this time for the reactor conditions employed (375-400°C at 2000-2500 psig). Maximum design temperature of 500°C and pressure of 5000 psig were selected to encompass those conditions which might reasonably be expected to be necessary. Coal throughputs of up to 3 lb/hr. were agreed upon in discussions with ERDA personnel.

The current proposal for a coal hydrogenation pilot unit (item #3 in the Summary section) meets these general requirements, coupling a bank of three small ebullating beds (catalytic) to a large stirred autoclave (non-catalytic). A general flow sheet is shown in Figure 1; more details of the design have been reported (AFT:AS, 5/23/77). Some aspects of this arrangement are discussed below.

The Recycle Reactor

The reaction section of the current proposal bears a close resemblance to a recycle reactor system as described by Carberry (IEC 56 p. 39, Nov. 1964) and shown in Figure 2a. This type of lab reactor is useful for kinetic studies of heterogeneous (usually gas/solid) catalytic reactions, provided that the only reactions occurring are within the catalyst bed, that perfect mixing prevails, and that the recycle rate (q) is very much larger than the fresh feed rate (F). Mahoney (AIChE 74th Nat'l. Mtg., 3/13/73) indicates recycle rates of 20-100 are adequate for valid kinetic studies of vapor phase reactions when the flow across the catalyst bed is closely controlled to give gradient-free conditions. Total time lag for mixing on the order of 1-2 seconds has been measured (C.E.P. 70 p. 78, May 1974) in internal gas recycle reactors.

Figure 2b shows schematically the reaction section for our pilot unit proposal #3. Feed and product rates of about 1 gal/hr. are estimated. Given a total reaction volume of ~ 1 gallon, the nominal design base residence time of 1 hour is realized. The central question is to what degree this arrangement approaches a recycle reactor, and thus performs as a perfectly mixed tank reactor. In this design, the recycle rate through the ebullating bed reactors cannot be varied independently; otherwise it might be sufficient to set and maintain the recycle rate at, say 100X the fresh feed rate. The rate through the beds is defined within relatively narrow limits -- enough to expand the catalyst bed to the desired void fraction, but not enough to blow it up to the top of the reactor.

To estimate the liquid rates for bed ebullation, I've had to rely heavily on information presented in Hydrocarbon Research Inc's. basic patent (U.S. #2,987,465) on ebullated bed reactors. These and other data are summarized in Figure 3, which shows superficial liquid velocities for ebullation of various particulates. A roughly exponential relationship with particle size is shown, in spite of the variety of liquid/gas/particle systems represented. From this, a liquid recycle rate of ~ 30 GPH was estimated for the pilot unit (about 10 GPH for each of the three beds) when operating with ~ 10/20 mesh granules. In the operating pilot unit, this rate would be additionally affected by uncontrollable catalyst factors (size distribution and shape, deposits, attrition) and operating conditions (hydrogen rates, coal/solvent ratio, conversion level, ash and coke levels, recycle solvent properties, etc) so that a several-fold variation from the 30 GPH estimated by particle size alone seems likely.

The estimated liquid recycle rate of 30 GPH, based only on particle size, is at the bottom of the range recommended for gas reactions by Mahoney. Should unit operating conditions dictate a decreasing recycle rate, kinetic results become increasingly misleading and the pilot unit results compromised due to bypassing of feed to product. Use of fixed bed satellite reactors would remove the restrictions on recycle rate posed by the ebullating beds. This alternative is not recommended, however, for reasons brought out in subsequent discussions.

Catalyst Loading

Pilot unit proposal #3 contains about 400 ^{cc} catalyst (200^{cc} before bed is expanded 100%) in ~ 4 liter reaction volume. Thus, ~ 90% of the reaction volume is "non-catalytic". Autoclave studies have shown that some homogeneous chemical reactions occur e.g. about 95% conversion of coal to coal liquids can be realized in the absence of any catalyst (note comment above about absence of homogeneous reactions in an ideal recycle reactor). Hydrogen transfer from solvent to coal undoubtedly occurs as well under non-catalytic conditions. In recent catalyzed autoclave runs, the rate of removal of hetero-atoms proceeds in the order $S>O>>N$. However, conversion of N compounds within the one hour target has not been adequate, so higher reaction temps. are now being investigated. The attendant higher rates of cracking reactions may produce undesirably high hydrogen consumption. Therefore, operation at significantly higher catalyst concentration than the 5% of the design case seems a worthwhile alternative to higher reaction temperatures. This could be accomplished in a single ebullating bed type reactor, as is now being proposed.

Some comment by Mr. Mike Chervenak of HRI (AFT:AS, 6/15/77), along similar lines, is informative. When I asked about the effect of reducing L/D of an ebullating bed reactor, he advised against drastic changes from their geometry simply because the proposed reduction leads to lower catalyst concentrations within the system.

Pilot Unit Design and Operation

The unique feature of proposal #3 is that of swinging a fourth ebullating bed reactor in and out of a bank of three other ebullating bed reactors operating in parallel. This allows for periodic replenishment of the hydrogenation catalyst to maintain high activity level. However, to isolate any one of the four reactors from the others would require double block and bleed valving on the hot feed and product lines of each reactor. Each reactor also requires an auxiliary system (heat-up, cool-down, purging, safing, etc.) for starting it up before swinging and shutting it down after swinging. It's uncertain whether this can be a gas-only system or must use both gas and liquid, but these too require isolation valves. Not only must all these valves confine material at reaction conditions (e.g. 850°F and 2500 psig) they must be so located that there are no stagnant zones where coal liquid can coke up or ash settle out. In all likelihood, motor operated valves operated in a programmed sequence would be necessary to reduce the possibility that an improper valving sequence would be attempted manually. The complexity of this system poses an extraordinary challenge for the design and layout engineer as well as the operating crew. It should not be underestimated.

Bed Ebullation

The small satellite reactors were selected to contain 65^{cc} catalyst before bed expansion. For a 1" I.D. vessel, this represents a bed depth of 5 inches; 10 inches if 100% expansion can be achieved. Some means for measuring/estimating bed height is necessary, so that it can be controlled. We learned from HRI that the type of positive detection system (1) used in their 8 1/2" I.D. reactor won't fit into a 1" I.D. unit. It's likely that we too would have to resort to some indirect sensing system, possibly multiple differential pressure measurements, to estimate where the top of the bed is. Obtaining reliable data over a range of 5-10" in bed height at 2,000-3,000 psig may be beyond the precision of available instrumentation and our ability to calibrate ΔP's with bed behavior. Alternatively, ΔP measurements on bed heights which range from 3 to 6 feet or from 4 to 8 feet, as might be typical of a "conventional" ebullating bed reactor, would give us a much more reliable estimate of the condition and location of the catalyst bed.

Catalyst Life

As noted earlier, each of the preceeding pilot unit proposals included some technique for introducing fresh catalyst during unit operation. The alternate proposed here does not, and this significant departure in concept should be fully appraised for it's effect on pilot unit operations.

The proprietary catalyst now being used in our autoclave studies consists of a relatively low concentration of metals on an inexpensive support (i.e. 1% CoO-2% MoO_3 on granular bauxite). This mode of preparation allows us to think of the catalyst as a "throwaway" or disposable item, but at the same time suggests periodic replenishment may be necessary to maintain acceptable system activity during continuous operation of the pilot unit. We have no data on the stability of this catalyst in a coal hydrogenation application, since all autoclave runs are made on a batch of fresh catalyst. Neither do our batch autoclave runs, as presently conducted, lend themselves to generating this kind of data. Of related

(1) A moveable radiation source with multiple detectors spaced along the reactor length.

interest, similar catalyst preparations were used in fixed bed hydrodesulfurizing of vacuum residua (Memo's RD71-92 and RD 72-43) and catalyst life of 3 to 6 months was extrapolated. Thus, if even a reasonable fraction of this catalyst life can be achieved in coal operations, we would be able to sustain operations long enough to obtain representative data for lined out recycle operations, and provide sufficient product for subsequent testing. In our contacts with HRI personnel, they noted that catalyst make-up in lab units of this capacity are not necessary or recommended.

Dr. Chong has projected that, to be approximately competitive, our catalyst should have a life of several hundred lbs. coal/lb catalyst (VMC:AS, 4/28/77). For a 1 hour residence time in a single ebullating bed reactor, this would require about 2 weeks of continuous operation. This does not seem unreasonable, given the results observed in resid processing noted above. Should catalyst life be substantially shorter than this, the problem confronting us would not be that there is no facility on the pilot unit for catalyst make-up. Rather, we'd be facing the technical challenge of providing a more stable catalyst preparation for competitive reasons.

CONCLUSION

An ebullating catalyst bed for coal hydroliquefaction studies has a number of attractive features (temperature control, reduced coking tendency, process already scaled up to 600 TPD level) compared to alternative(s) such as a fixed bed reactor (Synthoil). Thus, inclusion of this type reactor in a Sun pilot unit designed to study our proprietary catalyst and downstream treatment is a reasonable strategy. However, the current proposal (#3) of a large, non-catalytic reactor coupled to 3 small ebullating catalyst beds has potential disadvantages in the following areas:

low catalyst loading
operation as a CSTR is doubtful
design and operating complexity

which could make acquisition of sound pilot unit data difficult, if not impossible. It's advantage is that it provides a mechanism for fresh catalyst make-up during pilot unit operation.

As an alternative, I propose we design and construct a single ebullating bed type reactor similar to H Coal bench units, making no provision for fresh catalyst make-up. While substantial operating problems can still be expected, this alternative is judged to be significantly more feasible than proposal #3. If catalyst stability is inadequate to get reliable process data at lined out conditions, it appears it would also be inadequate for a competitive process, in which case a catalyst development program would be necessary.

A. F. Talbot

A. F. TALBOT

AFT:jmr

APPENDIX B

FIGURE 1

OVERALL FLOW SHEET FOR CONTINUOUS UNIT

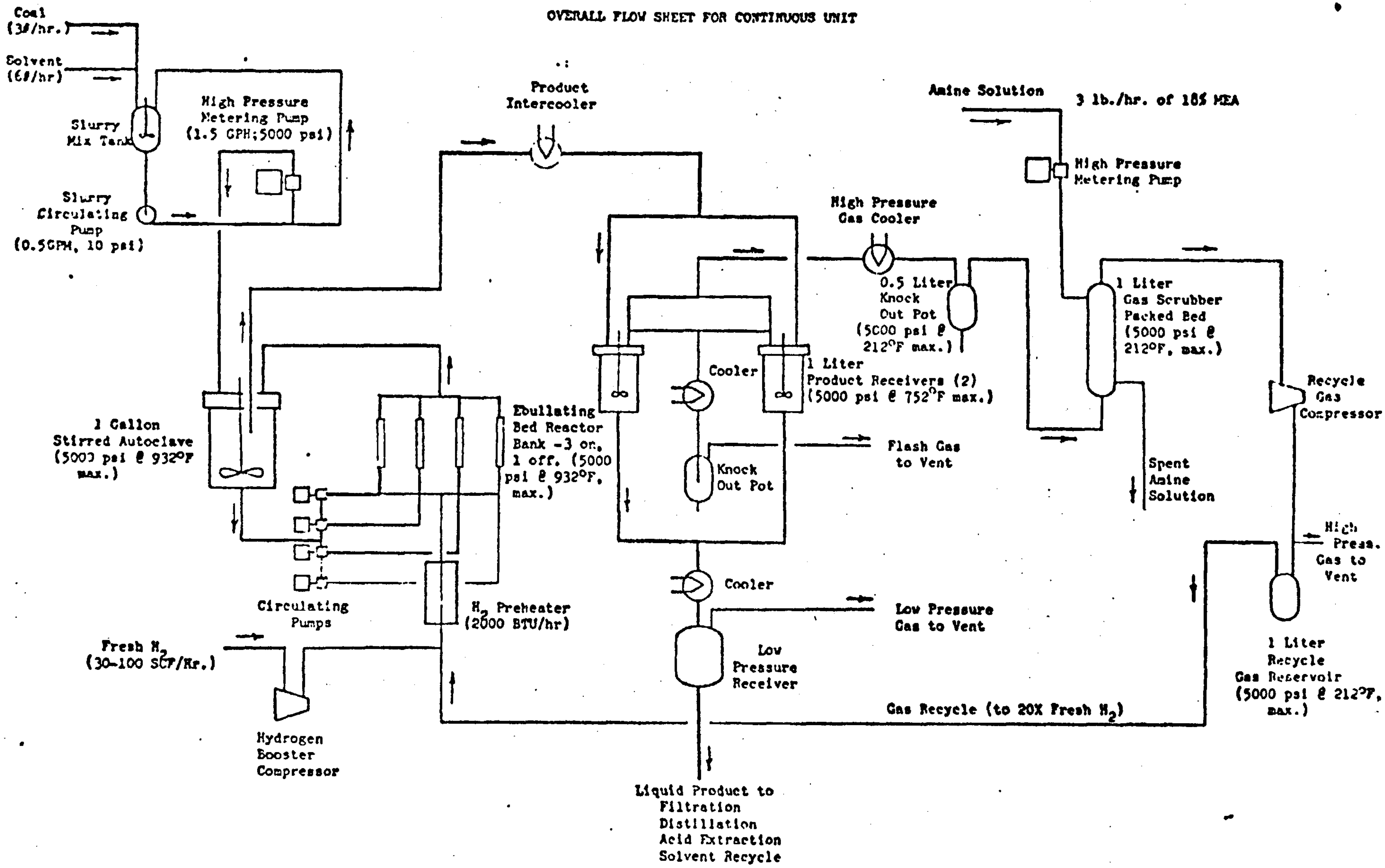


FIGURE 2a
Recycle Reactor
(q >> F)

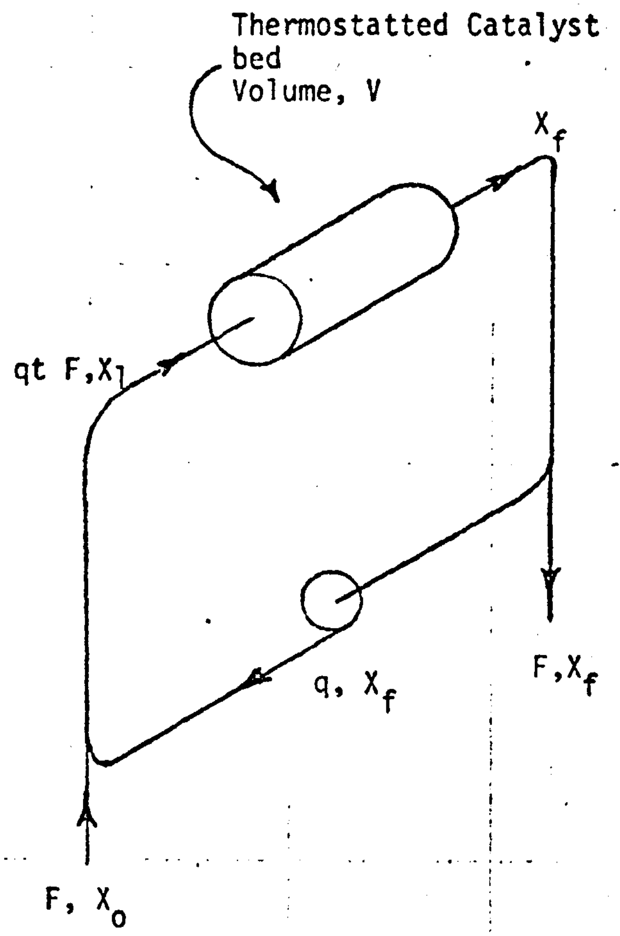
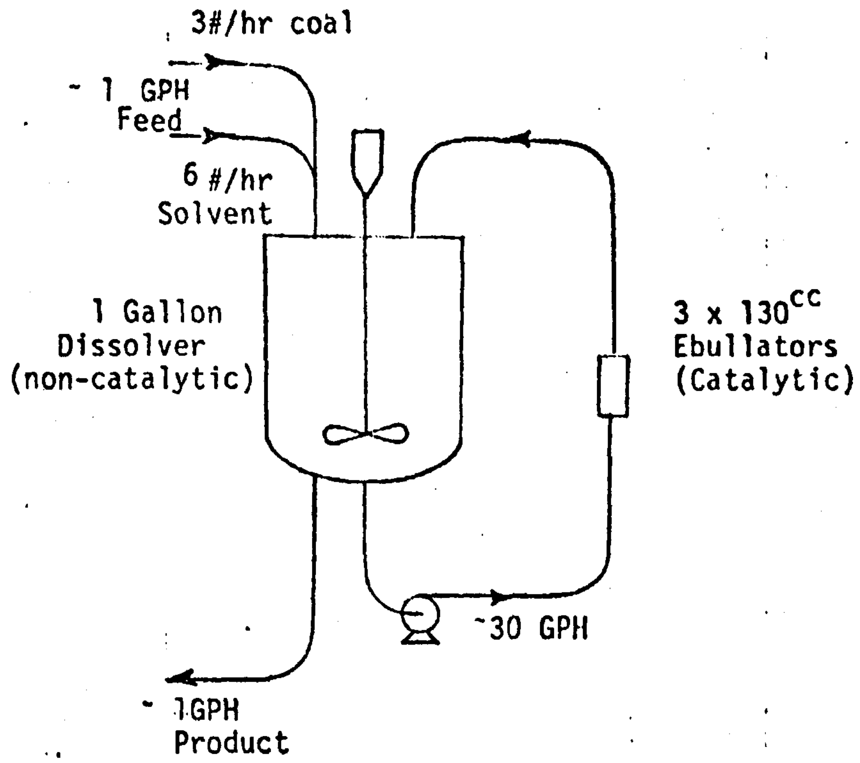
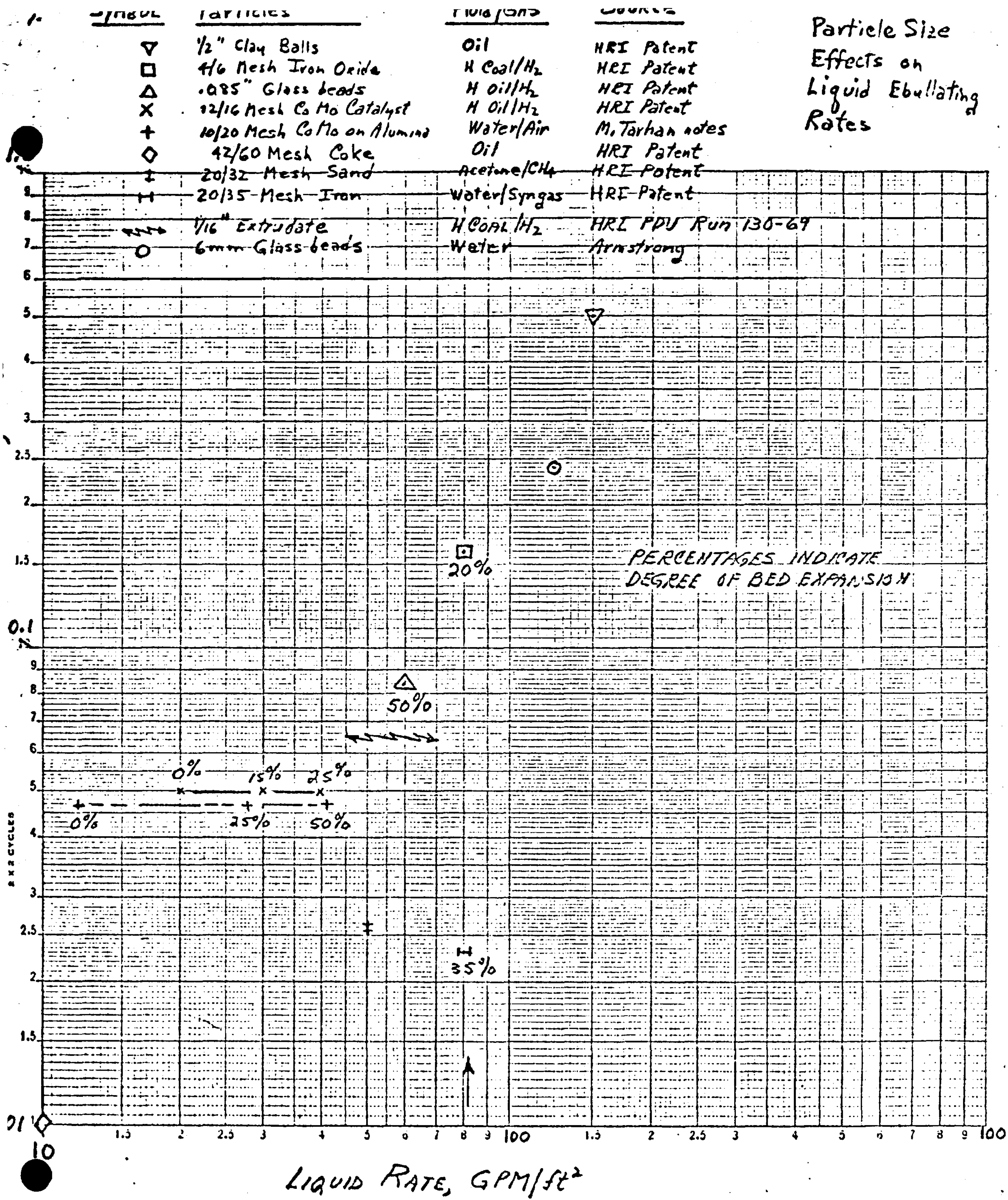


FIGURE 2b
Reaction Section,
Pilot Unit Proposal #3



Particle Size Effects on Liquid Ebullating Rates



INTER-OFFICE CORRESPONDENCE

DATE June 23, 1977

SUBJECT MONTHLY PROGRESS REPORT
JUNE, 1977

LOCATION ARD - Processes - Marcus Hook

FROM A. F. Talbot

TO Mr. I. Steinmetz

Advanced Process for Coal Liquids - ERDA Contract E(49-18)-2306
Project Number 59-201

Work on a general process flow sheet for a coal hydrogenation pilot unit continues, with special emphasis on the reaction zone of the most recent proposal (AFTalbot/ASchneider, 5/23/77).. This version (our third concept) couples a 1 gallon (non-catalytic) stirred autoclave to a bank of three 200 cc ebullating bed (catalytic) reactors. A fourth swing reactor allows for periodic replacement of 1/3 the catalyst inventory without shutting the others down.

A more detailed evaluation of this concept is being issued separately (AFTalbot/ASchneider, 6/21/77). In summary, features of this proposal include:

PRO - allows catalyst replenishment
utilizes ebullating bed technology

CON - may not be operable as a CSTR
low catalyst concentration (e.g., 5 wt.%)
piping/valving layout intricate, with many dead spots
operating complexity

As an alternative, I am recommending a "conventional" single ebullating bed reactor, as used by Hydrocarbon Research, Inc. in development of their H-Coal process. It offers:

PRO - higher catalyst concentration
technology already scaled up to 200-600 TPD
relative simplicity in design and operation

CON - no mechanism for catalyst replenishment during run.

The disadvantage of no catalyst replacement in the single ebullating bed unit is difficult to evaluate. The Sun proprietary catalyst is relatively inexpensive because it utilizes low levels of hydrogenation metals on a cheap support. Thus, we tend to think of it as an "expendable" material, although we have no information on its stability under coal hydrogenation conditions. Dr. Chong had estimated that to be competitive, a life of at least several hundred pounds of coal per pound of catalyst would be required. This is equivalent to several weeks of pilot plant operation, which should be ample time to obtain data and samples at lined out conditions. Thus, the inability to replenish catalyst becomes significant about when catalyst life is too brief to be competitive with other processes. Of related interest, similar catalyst preparations have been used in resid hydrodesulfurization (Memo's RD71-92 and RD72-48), and catalyst life of 3-6 months extrapolated. Thus, I conclude that providing catalyst replenishment in this pilot unit does not justify the increased design and operating complexity.

A general flow sheet for this revised concept is attached. Detailed design will proceed.

A. F. Talbot

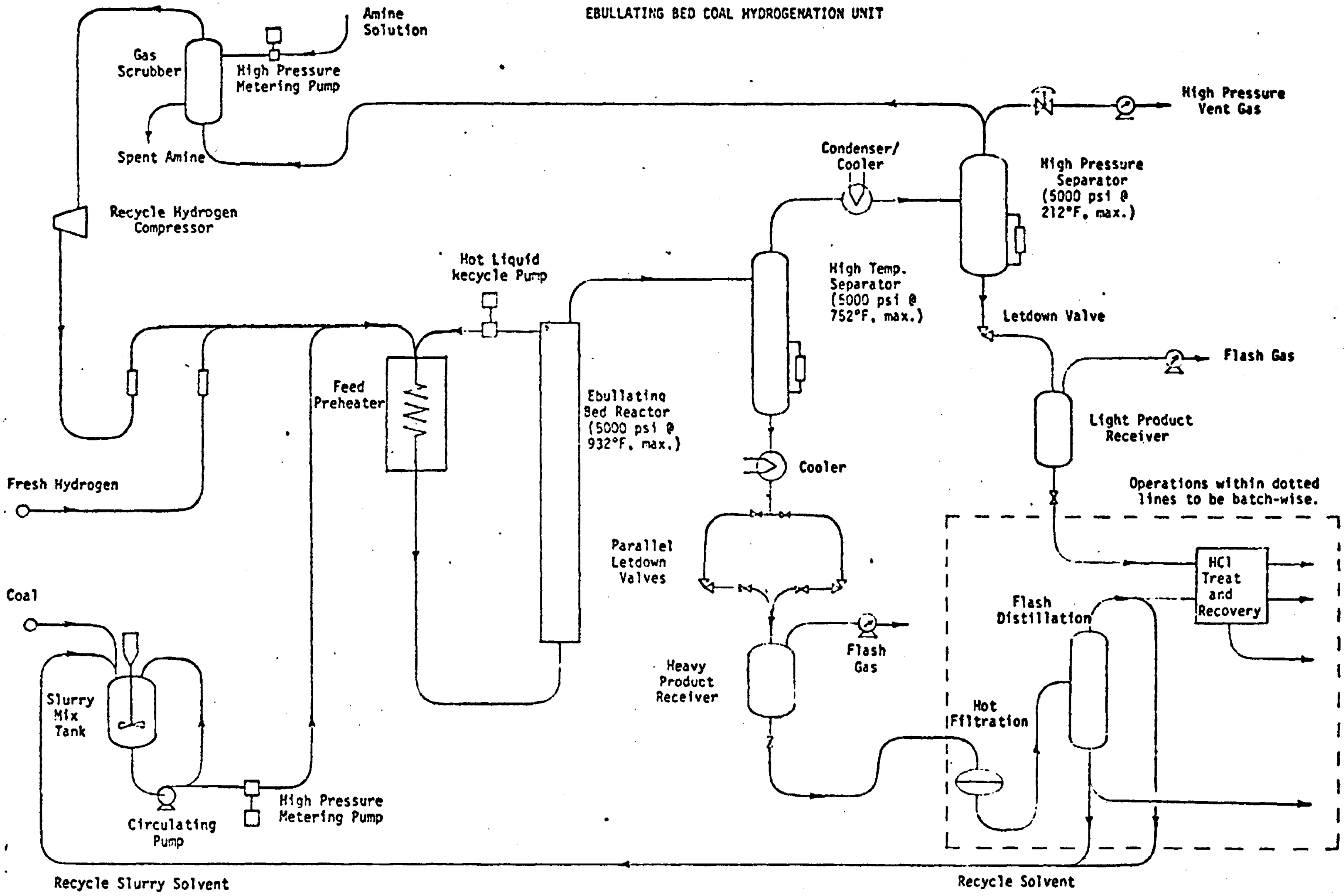
A. F. TALBOT

AFT/mjdf

APPENDIX C

GENERAL FLOW SHEET

EBULLATING BED COAL HYDROGENATION UNIT



INTEROFFICE CORRESPONDENCE

DATE: June 15, 1977

SUBJECT CONTACTS WITH HRI RE
H COAL TECHNOLOGY

LOCATION ARD, Processes

FROM. A. F. Talbot

TO Dr. A. Schneider

On May 10, 1977 we (Fred Eisen, you, and I) visited the Hydrocarbon Research, Inc. laboratories in Trenton, New Jersey, meeting with Dr. Paul Kydd, Vice President - Technology. Purpose of the visit was to explore with HRI the possibility of our a) renting time on HRI's H Coal bench unit for a test of catalyst activity/stability, and b) acquiring and using HRI's ebullating bed technology in a pilot plant Suntech is to build under our ERDA contract covering coal liquefaction studies. This letter is written to make details of this visit, and my subsequent phone call to Mr. Mike Chervenak of HRI, part of the record.

Our talk with Dr. Kydd was very general in nature. He indicated HRI would consider specific proposals from Sun. We suggested these might take the form of either a consulting role during the design stages of a pilot plant, or as a contractor to fabricate an ebullating bed - based coal hydrogenation pilot unit. Despite numerous inquiries, HRI apparently has not performed either function for third parties, to date. In the absence of a specific proposal from Sun, Dr. Kydd did not discuss fees for their help in design and/or construction of a pilot unit. Dr. Kydd indicated a one month catalyst life test in their H Coal bench unit might cost in the neighborhood of $100,000.

We were given a brief tour of the HRI H Coal facilities. Due to extensive maintenance operations, neither the bench unit (0.8" ID by 10' reactor) nor the pilot unit (8.5" ID by 22' long reactor) were operating. In general, we obtained little detailed information on their pilot unit design and operations. Some general comments follow.

A "bench scale" H Coal unit needs a pretty big bench! Structure dimensions were about 10' x 15' x 25' high (they need at least 2x reactor height to remove the thermocouple bundle). The bench unit is usually operated by a two-man crew, with batch product filtrations and distillations done on the spot. Unit turn-around time (i.e. a new run with fresh catalyst) is about 3-4 days. Once coal is unloaded from rail hopper cars, all subsequent handling and storage is under inert atmosphere. So far this has been effective in avoiding any coal dust incidents. Spare coal slurry feed pumps (Milton Roy) are essential for continuous operation. Erosion of lines, valves, etc., in the high pressure let-down of coal liquids (which may contain ash, unreacted coal) is reduced by minimizing the amount of gas contained in the high pressure liquid. Let-down valves are of tungsten carbide trim.

HRI runs catalyst life tests out to 1000-2000 lb coal/lb catalyst (equivalent to 1-2 months operation), to estimate stabilized yield and operating conditions. In the bench unit, no fresh catalyst make-up is used during a run; instead the effect of fresh catalyst addition is back-calculated from stabilized conditions. HRI feels this is quite adequate for a bench unit. The larger (8.5" ID) unit was being equipped with lock hoppers for fresh catalyst addition, during our visit.

Much of HRI's experience has been with ebullating beds containing 1/16" or 1/32" catalyst extrudates. Dr. Kydd would not speculate on the effect of other particle size or shape. He views the ebullation phenomenon as essentially one-dimensional;thus, reactor L/D ratio was not viewed as critical to the ebullation process. Catalyst strength and abrasion resistance were viewed as critical properties, although no values were mentioned.

Our current pilot unit design consists of a bank of three small (1" ID x 16" inside length) ebullating beds operating in parallel (AFT:AS, 5/23/77). I've been concerned about their operability, considering the drastic departure in geometry from HRI's lab units. So, after several unsuccessful attempts to contact Dr. Kydd, I talked to Mr. Mike Chervenak of HRI by phone on 5/23/77 to get a feel for the effect of reducing L/D. In reply, Mr. Chervenak stated he would be very leery of substantially reducing reactor height, for a given lab reactor diameter. While feeling comfortable with a nine or possibly eight foot length for their 0.8" x 10 ft bench reactor, Mr. Chervenak recommended against a scale-down of, say, 50%. He explained that a certain amount of the reactor length is for feed distribution and catalyst-liquid-vapor disengaging space, and this is relatively fixed. Thus, reductions in reactor length come directly from catalyst bed depth. Therefore, significant changes in total length lower substantially the proportion of catalytic to non-catalytic volume within the system.

Since the ebullating beds in our "mini-reactors" could range from 5 to 10 inches deep, we'd need an extremely sensitive measurement system to identify the degree of bed expansion. I asked how catalyst bed height was measured in HRI's bench unit, but received no information. A moveable radiation source, as used in the 8.5" unit, won't fit into a 1" reactor, according to Mr. Chervenak, so other techniques are used.

At this point, Mr. Chervenak became reluctant to answer more questions, suggesting further requests for information be directed to Dr. Kydd. It was his opinion that HRI would be unwilling to disclose its 20-some years of design and operating experience (read art) in exchange for several days of consulting services.

If, after our ideas on the pilot unit flow sheet harden, we still feel that an ebullating catalyst bed is desirable, we should re-open discussions with HRI to see if we can reach a reasonable basis for a transfer of useful information.

A. F. Talbot

A. F. TALBOT

AFT:emj