Pressurized Carbonization of Coal Liquefaction By-Product Materials: Fluor Advanced Liquefaction and Parsons' POGO Processes

R. E. Barker
J. R. Hightower, Jr.
J. B. Gibson III
S. M. Gibson

OAK RIDGE NATIONAL LABORATORY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ORNL/TM-6452
Dist. Category UC-90d

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

PRESSURIZED CARBONIZATION OF COAL LIQUEFACTION
BY-PRODUCT MATERIALS: FLUOR ADVANCED
LIQUEFACTION AND PARSONS' POGO PROCESSES

R. E. Barker
J. R. Hightower, Jr.
J. B. Gibson III*
S. M. Gibson

November, 1978

*Present address: Dow Chemical Company, Baton Rouge, Louisiana.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

PRESSURIZED CARBONIZATION OF COAL LIQUEFACTION BY-PRODUCT MATERIALS: FLUOR ADVANCED LIQUEFACTION AND PARSONS' POGO PROCESSES

R. E. Barker
J. R. Hightower, Jr.
J. B. Gibson III
S. M. Gibson

ABSTRACT

Experiments were performed to determine the results of carbonization under pressure of three coal liquefaction product (or by-product) materials and thus supply data needed as a design base for two concepts for advanced coal liquefaction plants. Solid-liquid separation underflow (SLSU) and solvent from a hydroextraction process were carbonized at 900°F in an inert atmosphere at pressures up to 400 psig. Vacuum still bottoms from the H-Coal process were pyrolyzed at 1100°F in a methane atmosphere at 400 psig.

Results from carbonization of hydroextraction solvent and SLSU show that (1) only 1 to 7% of the solvent is degraded during carbonization at 900°F and 400 psig, (2) the heavier fraction of the residue contributed the most toward coke formation, and (3) increased pressure increases the degree of coking of the heavier fractions.

Results from pyrolysis of the vacuum still bottoms material at 1100°F and 400 psig indicated that (1) small amounts of liquid are produced, (2) a significant quality of gas is produced, and (3) higher temperatures will probably be required to produce free-flowing char.

1. INTRODUCTION

Experiments were performed at the request of the former Division of Major Facilities Projects Management in the U.S. Energy Research and Development Administration* to evaluate the process feasibility of unit operations proposed by two of their contractors: Fluor Engineers and Constructors, Inc., and the Ralph M. Parsons Company. The purpose of this report is to summarize these experiments and the results obtained.

---

*Now the Department of Energy.

Fluor Engineers and Constructors, Inc., has prepared a conceptual design for a hydroextraction demonstration[1] in which it has proposed that the solid-liquid separation underflow (SLSU) be gasified under pressure for hydrogen production after low-temperature carbonization solvent recovery. To avoid lock-hoppers, it was suggested that the carbonizer be pressurized, allowing the char simply to overflow from the carbonizer to the gasifier. Information was needed concerning the quantity of solvent which would be thermally degraded at 900°F with pressures of 50 and 400 psig. An experimental, pressurized carbonizer using small quantities of SLSU and solvent was used to estimate fraction of feed thermally degraded in a fluidized-bed carbonizer.

The Ralph M. Parsons Company has prepared a conceptual design for an advanced coal liquefaction plant[2] in which it has proposed that vacuum still bottoms be treated by rapid pyrolysis in an entrained flow reactor to recover hydrocarbon liquids and gases. Since there are no existing data on yields of liquids and gases for pyrolysis at the desired operating conditions (1100°F, 500 psi, and gas space time between 0.1 and 1 sec), and since extrapolation of data taken near atmospheric pressure was felt to be too unreliable for process evaluation, the equipment built previously was used to provide timely estimates of product yields as a basis for evaluation of Parsons' proposed process step. Since the existing equipment used in this experiment was not designed for the extreme conditions proposed by Parsons, these experiments were done at 1100°F and 400 psig in a fluidized bed (fluidized with methane). The Parsons' flowsheet also calls for the vacuum still bottoms to be fed to the pyrolysis reactor with an equal amount of coal. Therefore, these experiments were conducted with three feeds: coal, vacuum still bottoms, and a mixture of coal and vacuum still bottoms.

The remaining sections of this report discuss the experimental equipment, the various feedstocks examined in the experiments, the experimental procedures, the measured results, and some conclusions that can be drawn from the observations.

2. EXPERIMENTAL

The materials that were investigated in these experiments, the equipment, and the procedures are described in this section.

2.1 Characterization of Feed Materials

SLSU and solvent for the studies in support of the hydroextraction process designed by Fluor had much different properties from the vacuum still bottoms material used for the studies in support of the residue treatment step proposed by Parsons. These materials are described below.

2.1.1 Hydroextraction SLSU and solvent

Three materials were used as feedstocks for the study of hydroextraction SLSU carbonization: (1) SLSU consisting of solids suspended in solvent similar to the expected carbonizer feed obtained from Conoco Coal Development Corporation (CCDC) in December 1976; (2) another quantity of a similar SLSU obtained from CCDC in June 1977; and (3) solids-free solvent (defined as the -700°F boiling fraction of the SLSU) also obtained from CCDC in June 1977. Ultimate and proximate analyses of these materials are shown in Table 1. Both SLSU samples are quite viscous, though definitely fluid at room temperature, and contained visible solid particles. However, as seen in Table 1, the SLSU obtained from CCDC in June 1977 contains considerably fewer solid materials, as reflected in the ash content. This difference in the two SLSU samples is also reflected in the results, which are discussed in Sect. 3. The solvent, which is the -700°F boiling fraction of the residue, (also obtained from CCDC in June 1977) is a much less viscous liquid with no solids and a very small sulfur and ash content. Similated boiling curves for the two SLSU and solvent are shown in Figs. 1, 2, and 3. These boiling curves are obtained by the ASTM chromatographic technique and do not account for any of the material which is nonvolatile.

2.1.2 Vacuum still bottoms materials

The residue used for the studies in support of the Parsons' design was a vacuum still bottoms (VSB) material produced by the H-Coal process.

Table 1. Analyses of pressurized carbonization feed materials

| Materials | Proximate analysis (wt % as received) | | | | Ultimate analysis (wt % maf) | | | | Heating value (Btu/lb) |
	Moisture	Ash	Volatile matter	Fixed carbon[a]	Carbon	Hydrogen	Nitrogen	Sulfur	
SLSU (12/76)	1.76	17.5	43.8	36.9	88.7	6.45	1.07	4.52	13,356
SLSU (6/77)	--	0.08	94.02	5.90	91.12	8.00	0.16	0.44	17,504
Solvent[b]	0.14	<0.2	<100	--	91.83	8.06	0.02	0.07	17,762
Vacuum still bottoms	0.21	18.05	35.9	45.8	85.43	6.07	1.84	2.63	15,374
Illinois No. 6 coal	1.19	11.14	14.2	73.5	89.31	4.32	1.27	1.57	9,454

[a]By difference.

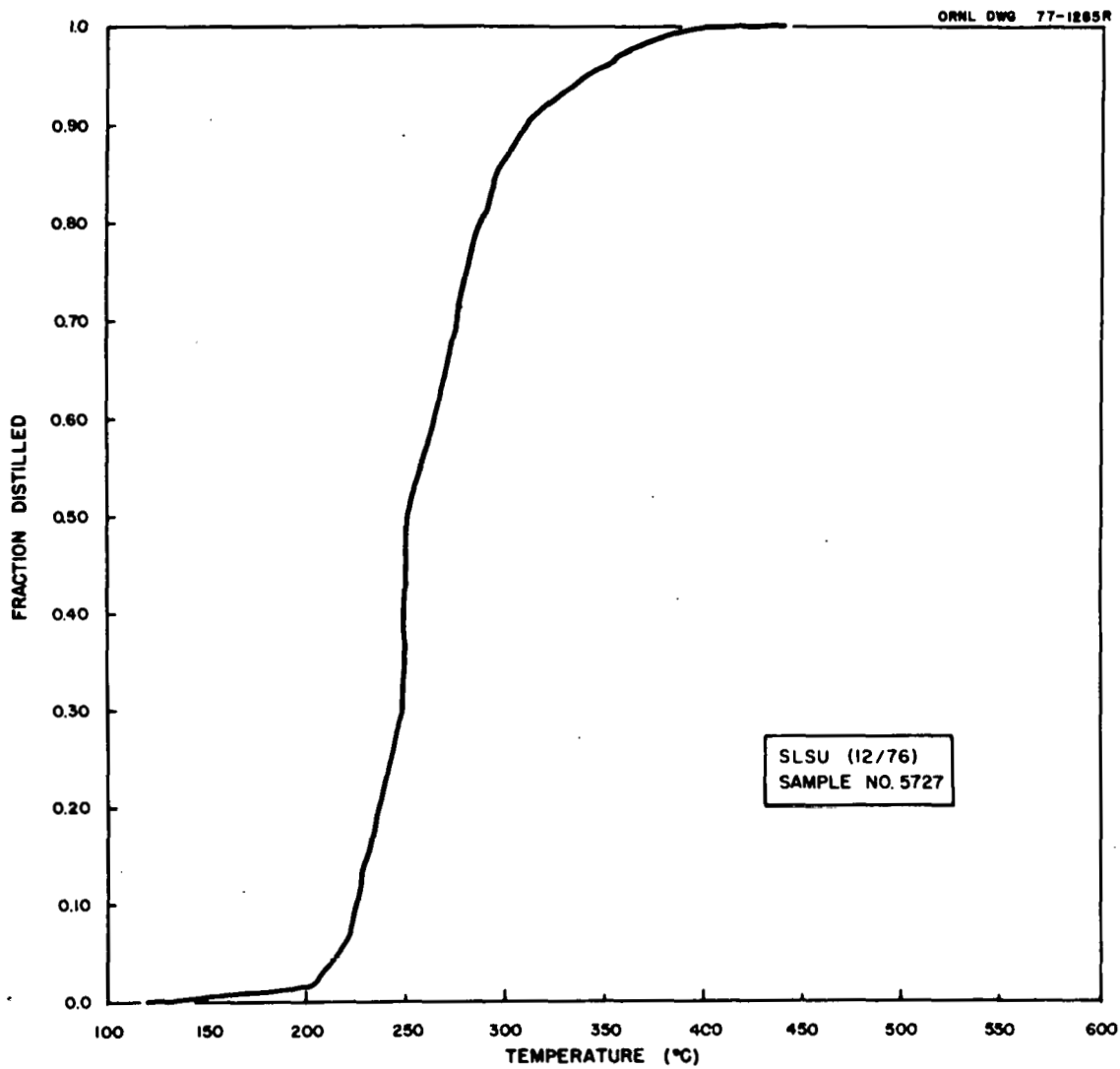[b]Solvent denotes the -700°F boiling fraction of residue (6/77).

Fig. 1. Simulated boiling curve for SLSU received December 1976.
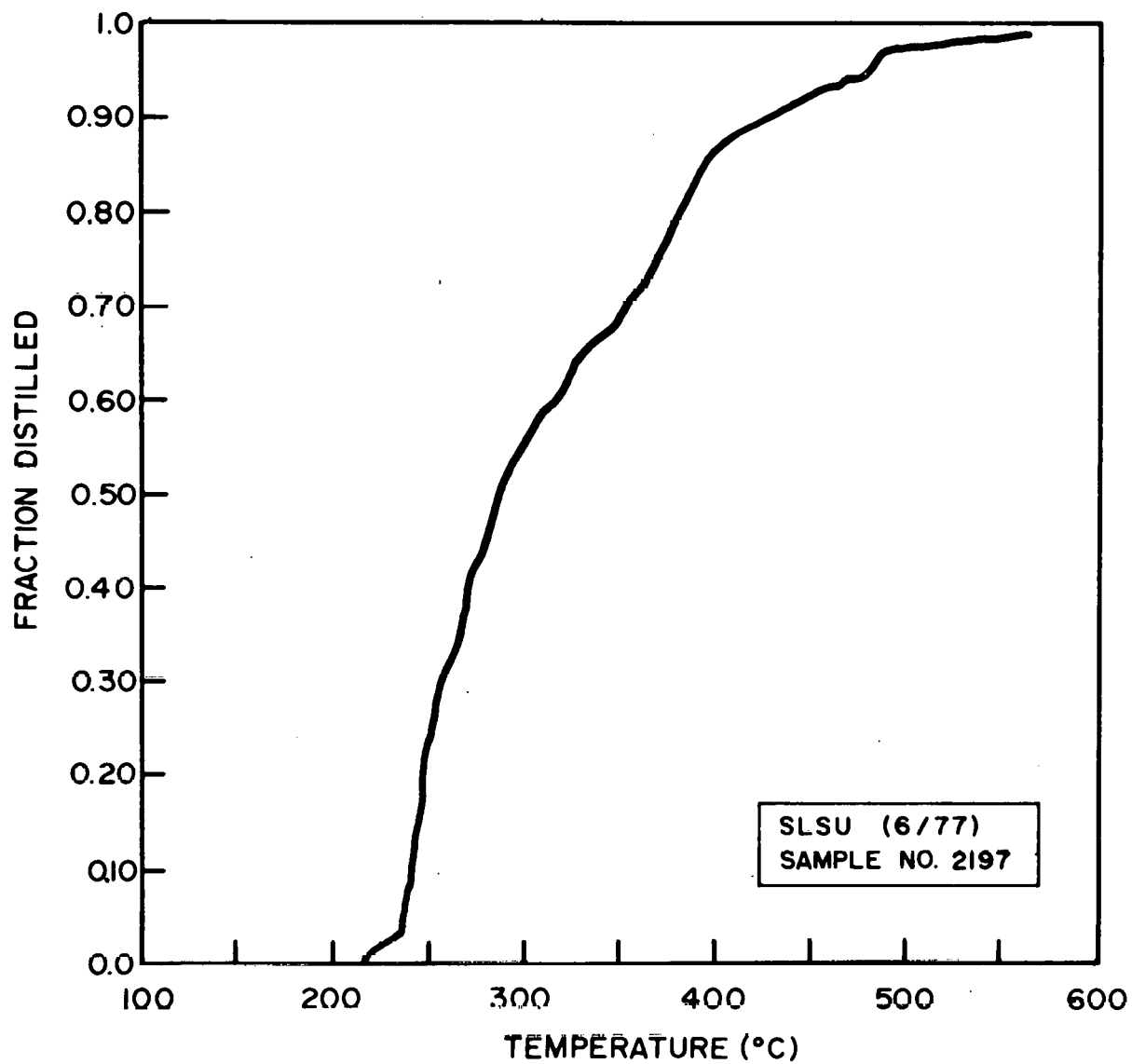
ORNL DWG. 77-966R2

Fig. 2. Simulated boiling curve for SLSU obtained from CCDC in June 1977.
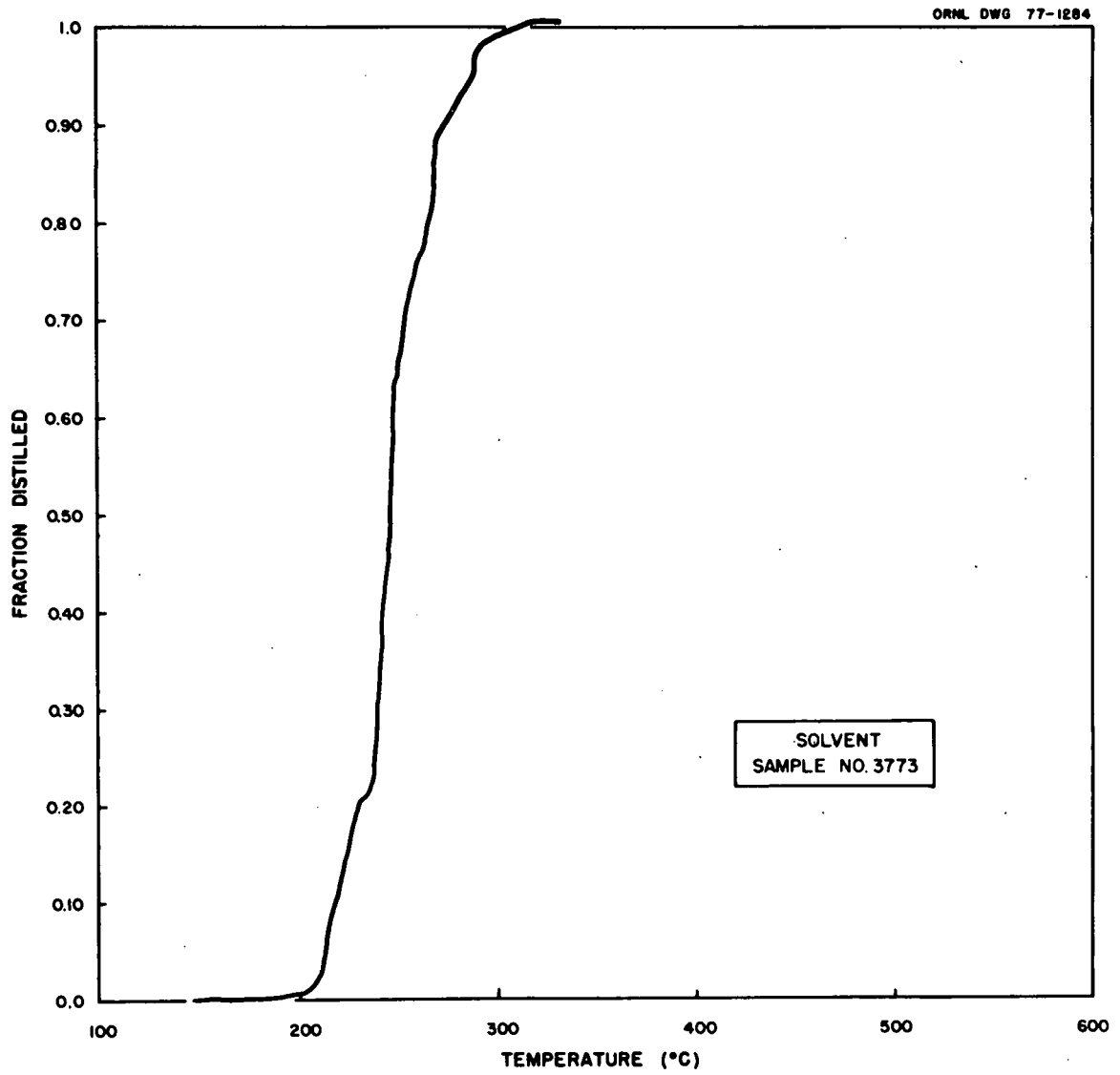
ORNL DWG 77-1264

Fig. 3. Simulated boiling curve for solvent.

The material had been obtained from Hydrocarbon Research, Inc. (sample LO-282) in late 1975 for an earlier project. Ultimate and proximate analyses and heating values for this VSB material are also tabulated in Table 1. The VSB material is quite intractable and solid at room temperature. As seen in Table 1, the H-Coal VSB is not a premium material since it contains high concentrations of sulfur and ash. In addition to H-Coal VSB, Illinois No. 6 coal was also used as a feed material for the second phase of this project. The ultimate and proximate analyses for the Illinois No. 6 coal used are also shown in Table 1.

2.2 Experimental Equipment Procedures

Because of the significant differences in the feed materials for these studies (hydroextraction SLSU and VSB), different experimental techniques were required, necessitating slightly different flowsheets for the experimental apparatus. The flowsheet variations and the experimental procedure for each variation are described.

2.2.1 Equipment and procedures for experiments using hydroextraction residue and solvent feedstock

The flowsheet used for pressurized carbonization of hydroextraction SLSU and solvent is shown in Fig. 4. The equipment consists of a 500-ml feed tank, a Milton Roy Model A packed plunger positive-displacement pump for SLSU slurries or solids-free solvent, a fluidized-bed carbonization vessel, a water-cooled condenser, a primary-condensate receiver, a cyclone for aerosol removal, a secondary-condensate receiver, an activated charcoal bed for additional vapor removal, and a train of 10 gas-sample bombs for sampling the gas stream from the carbonizer. The carbonization vessel contained a bed of alumina fluidized by preheated argon. The carbonizer vessel, the condenser, the primary-condensate receiver, the gas preheater, and the slurry atomizing nozzle are described in detail in the Appendix.

Since the Fluor design called for continuous fluidized-bed carbonization of the SLSU, an attempt was made to simulate continuous operation as closely as possible without continuous solids removal from the bed.
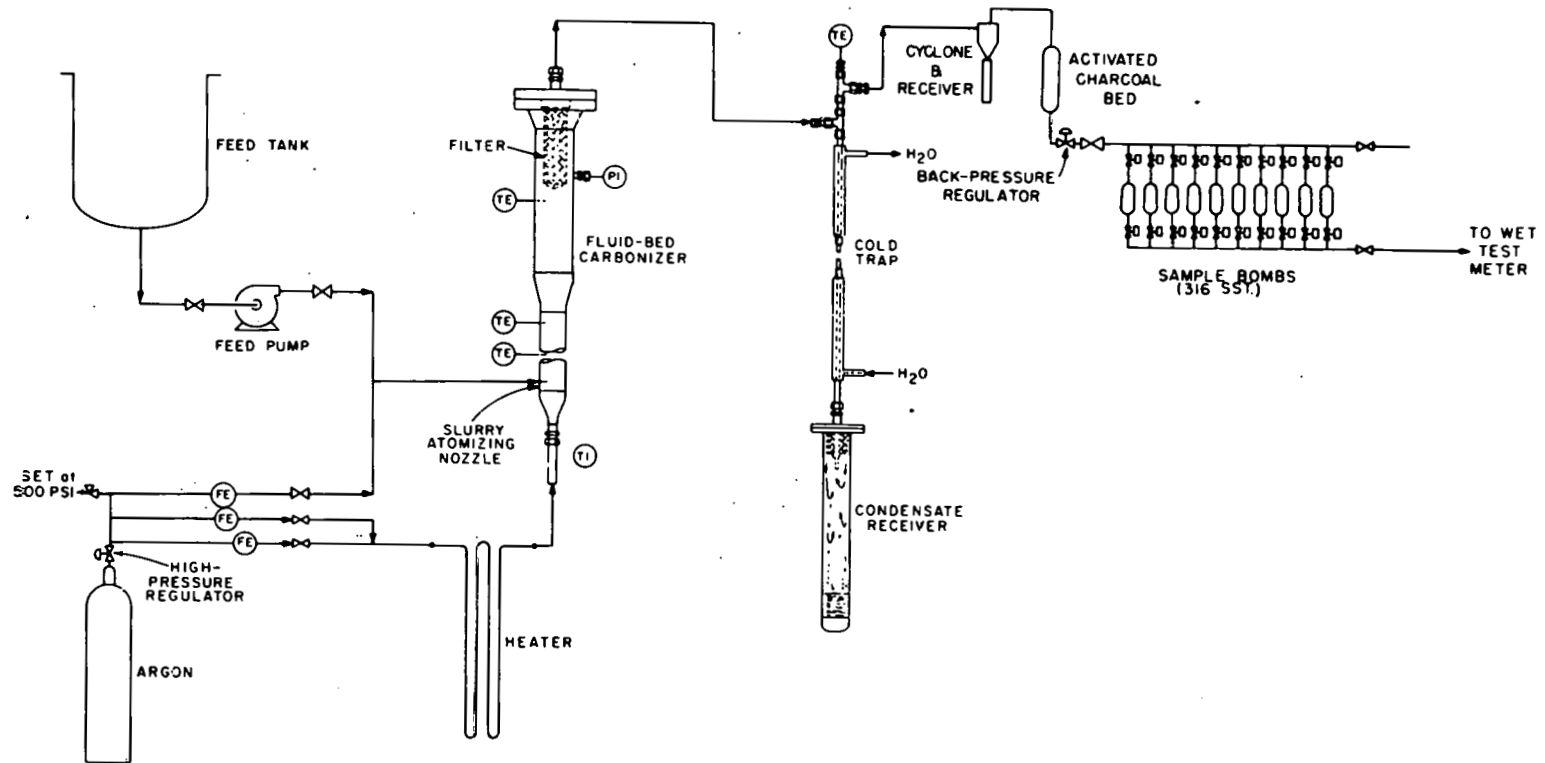
Fig. 4. Schematic of experimental system for pressurized carbonization of SLSU.

The experimental procedure was as follows:

1. The bed material (alumina or char) was charged to the carbonization vessel, and the system was sealed and leak-tested.

2. Fluidizing argon flow was begun at flow rates of 0.15 to 2.0 SCFM (controlled using calibrated orifice flow meters), and power to the electrical heaters on the gas preheater and carbonizer was turned on. Cooling water flow to the condenser was started.

3. As the system was being heated, the feed tank was filled with the feed liquid. With the feed line disconnected from the system, the feed pump was started so that the tubing between the feed tank and the carbonizer was filled with feed.

4. The feed tank was removed, its weight recorded, and then it was reinstalled. A sample of the feed was set aside for future analysis.

5. When the temperatures (recorded on multipoint recorders) became stable, the pump was turned on to introduce feed into the carbonizer at a rate of 10 to 20 ml/min.

6. During the run, grab samples of the gas leaving the cyclone were taken at 10-min intervals. Readings on the wet-test meter were recorded at 5-min intervals. Power to the heaters was adjusted to maintain a constant temperature in the carbonizer, which was usually constant to $\pm 10°F$.

7. The run continued until ~ 200 g of feed was pumped into the reactor; at that time, the pump was stopped, the feed tank removed, and its weight recorded. The amount of feed was assumed to be the difference between this weight and the weight recorded in step 4. Run temperature was maintained in the system for at least 20 min after the feed was stopped; gas samples and readings on the wet-test meter were also taken during this time.

8. The system was purged overnight with a small flow rate of argon. Char was removed from the carbonizer, weighed, and sampled. Liquid products were removed from the condensate receiver, cyclone receiver, and activated carbon trap, as well as from tubing connecting those vessels. These products were weighed and sampled.

2.2.2 Flowsheet for experiments with vacuum still bottoms material and experimental procedure

The equipment was modified to allow feeding the coal and VSB to the pressurized carbonizer vessel. Also, to simulate the Parsons' process as closely as possible, methane was used as the fluidizing gas to the carbonizer. The flowsheet of the modified experimental equipment is shown in Fig. 5.

The initial scheme to feed the VSB material was to slurry the solids in a relatively inert organic liquid (e.g., benzene) and pump the slurry into the reactor using existing equipment. However, the volume of liquid required to make a pumpable slurry was too large for this scheme to be practical. Therefore, a plan using several small feed injection tubes operating similarly to lock-hoppers was used, although this did not rigorously simulate the Parsons' process. The feed tubes are described in detail in the Appendix.

The activated charcoal trap was also removed from the experiment since it was predetermined that it was not needed for these experiments with VSB material.

The experimental procedure was as follows:

1. The bed material (alumina) was charged to the carbonization vessel, and the system was sealed, leak-tested, and flushed with argon to remove air from the system.

2. The alumina bed was fluidized with argon, and the power to the electrical heaters was turned on. When the temperatures were near run conditions, argon flow was stopped and methane flow started; the temperatures were then allowed to stabilize.

3. When run conditions were stabilized, the VSB/coal was fed to the reactor in the following sequence:

   a. With valve 1 (see Fig. 5) closed, a feed tube previously filled with VSB/coal was installed.

   b. With valves 3, 4, and 5 closed, valves 1 and 2 were opened to pressurize (to ∿1800 psig) the tubing upstream of the feed tube.

   c. With valve 1 closed and valve 2 still open, valves 3, 4, and 5 were opened in succession to impel the VSB into the reactor.
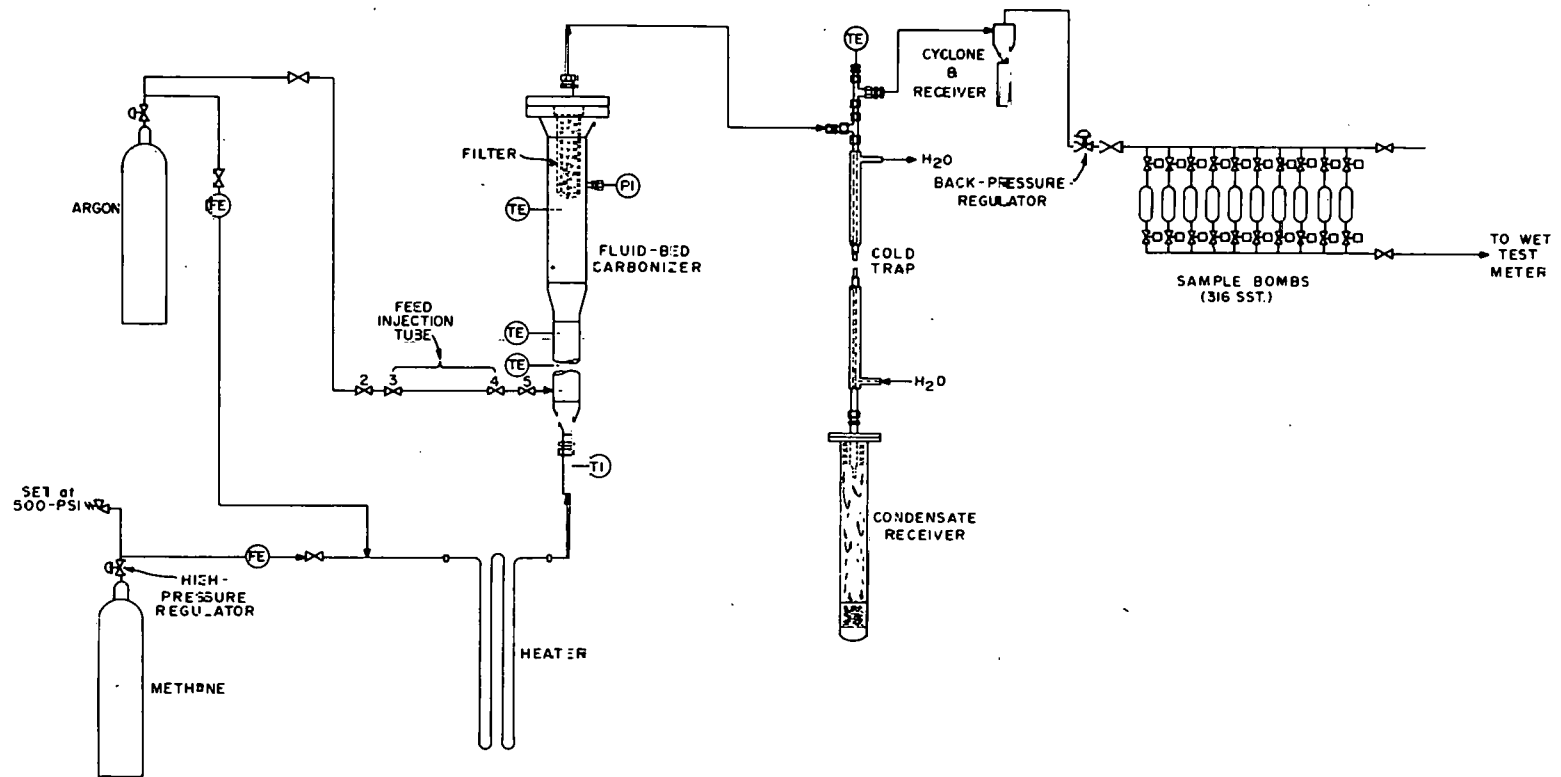
Fig. 5. Schematic of experimental system for rapid-pressurized pyrolysis of VSB/coal.

    d. All valves were closed, and the procedure repeated until the contents of all feed tubes were fed. In order to simulate continuous operation as closely as possible, the feed tubes were fed at intervals of approximately 3 to 5 min. The feed tubes were weighed before and after injection to determine the amount of VSB/coal fed.

4. During the run, grab samples of the gas leaving the cyclone were taken at 10-min intervals. Readings on the wet-test meter were recorded at 5-min intervals. Power to the heaters was adjusted to maintain a constant temperature in the carbonizer, which was usually constant to $\pm 10°F$.

5. The system was purged overnight with a small flow rate of argon. Char was removed from the carbonizer, weighed, and sampled. Liquid products were removed from the condensate receiver, cyclone receiver, and activated carbon trap, as well as from tubing connecting those vessels. These products were weighed and sampled.

3. RESULTS

Thirty experimental runs were performed in support of the two conceptual designs. The first seven runs were shakedown operations for the experiments supporting hydroextraction residue carbonization and used methylnaphthalene as feed; sixteen runs were made using either hydroextraction SLSU or solvent; four runs were made testing methods for feeding VSB material and coal; and four runs were made using VSB material, coal, or VSB/coal mixtures. The results from the experiments in support of the two conceptual designs are discussed separately in the following sections.

3.1 Pressurized Carbonization of Hydroextraction SLSU

Hydroextraction SLSU was carbonized in a fluidized bed at 65 and 415 psia and 900°F (one run was at 1050°F). Two bed materials, alumina and hydrocarbonization char (obtained from the ORNL Bench-Scale Hydrocarbonization Facility) were used as the fluidized solid. In each case, argon was the fluidizing gas. Experiments were operated such that gas and liquid (slurry) feeds were continuous but were batch experiments with respect to the fluidized solids (i.e., there was an unsteady-state buildup of coke in the bed during a run).

The results of hydroextraction SLSU carbonization are summarized in Table 2. As mentioned earlier, the objective of this work is to estimate solvent losses in pressurized carbonization. The measure of solvent loss was the coke formation in the reactor, with the gas and liquid yields (i.e., material balance closure) of secondary importance. The coke production was measured by the weight gain of the bed, and this analysis was the most reliable measurement of solvent degradation. As can be seen from the runs using solvent as the feed material, the solvent losses are quite low (1 to 7% of feed). For most of these runs, no significant gas production was detected. As discussed earlier, the SLSU received in June 1977 is a much lighter material with a lower solids content; this difference is reflected in the considerably lower coke formation in runs using this SLSU. It should also be noted that coke formation is not the sole measure of liquid losses since the reaction that produces coke also produces some gas. The gas formed from the CSF residue carbonization consisted mainly of H_2 and CH_4.

The liquids recovered were a light, high-Btu liquid having low concentrations of ash and sulfur. Table 3 shows the ultimate and proximate analyses of the liquid products recovered. The quality of these materials can be compared with that of the feed materials by reference to Table 1. In addition, representative simulated boiling curves for liquid products of the three feedstocks are shown in Figs. 6 (product of pressurized carbonization of SLSU received in December 1976, 7 (product of pressurized carbonization of SLSU received in June 1977), and 8 (product of pressurized carbonization of solvent).

Reference to Table 2 reveals that the material balance closures are consistently deficient 20 to 30%; this deficiency was probably caused by incomplete recovery of liquid products. When one considers the small amount of liquid present in a fairly large piece of equipment, it can be easily seen that the amount of liquid needed to make up the material balance deficiency could easily be lost in fittings, tube bends, etc. In addition, the material balance measurements associated with the solid and gas products were reliable and reproducible.

Table 2. Summary of results for pressurized carbonization of hydroextraction SLSU

Run[a]	Bed material	Pressure (psig)	Temperature (°F)	Fluidizing gas	Feed	Feed wt (g)	Coke wt (g)	Fraction coked	Liquid wt (g)	Gas wt (g)	Material balance closure (%)
PRC-7	Alumina	400	900	Argon	SLSU (12/76)	181	77	0.425	61	0.97	77
PRC-8	Alumina	50	900	Argon	SLSU (12/76)	151	45	0.298	58	1.43	69
PRC-9	Alumina	400	900	Argon	Solvent	161	12	0.074	89	∿0	63
PRC-10	Alumina	50	900	Argon	Solvent	179	13	0.073	111	∿0	69
PRC-11	Char	400	900	Argon	SLSU (6/77)	167	Results invalid due to improperly devolatized char				
PRC-12[b]	Alumina	400	900	Argon	Solvent	177	---	---	140	∿0	---
PRC-13	Alumina	400	900	Argon	SLSU (6/77)	211	39.7	0.188	99	∿0	66
PRC-14	Alumina	50	900	Argon	SLSU (6/77)	262	40.8	0.156	152.6	∿0	74
PRC-15	Alumina	50	1050	Argon	Solvent	271	2.7	0.010	208.2	∿0	78
PRC-17	Char	50	900	Argon	Solvent	161	4.4	0.027	110	1.3	72
PRC-18[b]	Char	50	900	Argon	SLSU (6/77)	346	---	---	199.3	---	---
PRC-19[b]	Char	50	900	Argon	SLSU (6/77)	238	---	---	---	---	---
PRC-20	Char	50	900	Argon	SLSU (6/77)	Run aborted due to filter failure					
PRC-21	Char	50	900	Argon	SLSU (6/77)	183	9	0.049	110	1.6	61
PRC-22	Char	400	900	Argon	SLSU	209	11	0.053	147.5	5.3	79

[a] Runs 1 to 7 were shakedown runs using methylnapthalene as feed; run 16 was to test char devolatilization.

[b] Results invalid due to operating difficulties.

15

Table 3. Analysis of hydroextraction residue carbonization product materials

Run	Proximate analysis (wt % as received)			Ultimate analysis (maf)[c]				Heating value (Btu/lb)(maf)[a]
	Moisture	Ash	Volatile matter	Carbon	Hydrogen	Nitrogen	Sulfur	
PRC-7[b]	----	----	----	89.95	7.75	0.10	0.18	----
PRC-8[b]	----	----	----	88.36	7.82	0.08	0.23	----
PRC-9	0.004	0.04	>99	91.49	8.08	0.08	0.23	17,603
PRC-10	0.023	0.06	>99	91.99	8.14	0.05	0.05	17,738
PRC-11	0.52	0.04	>99	92.03	8.02	∿0	0.11	17,743
PRC-12	0.046	0.05	>99	92.24	7.92	0.03	0.09	----
PRC-13	0.053	0.06	>99	91.03	7.84	0.05	0.22	17,626
PRC-14	0.052	0.05	>99	91.00	8.13	0.09	0.19	17,523
PRC-15	0.040	0.04	>99	89.97	7.91	0.02	0.07	17,349
PRC-17	0.811	0.04	>99	92.05	7.88	0.03	0.05	17,634
PRC-21	1.16	0.05	>99	91.43	8.23	0.03	0.05	17,613
PRC-22	1.16	0.05	>99	92.18	8.32	∿0	0.07	17,710

[a]Moisture and ash free.

[b]Ultimate analysis for runs 7 and 8 are on as-received basis.

16

ORNL DWG.77-967RI

Fig. 6. Simulated boiling curve for product of pressurized carbonization of SLSU obtained in December 1976.
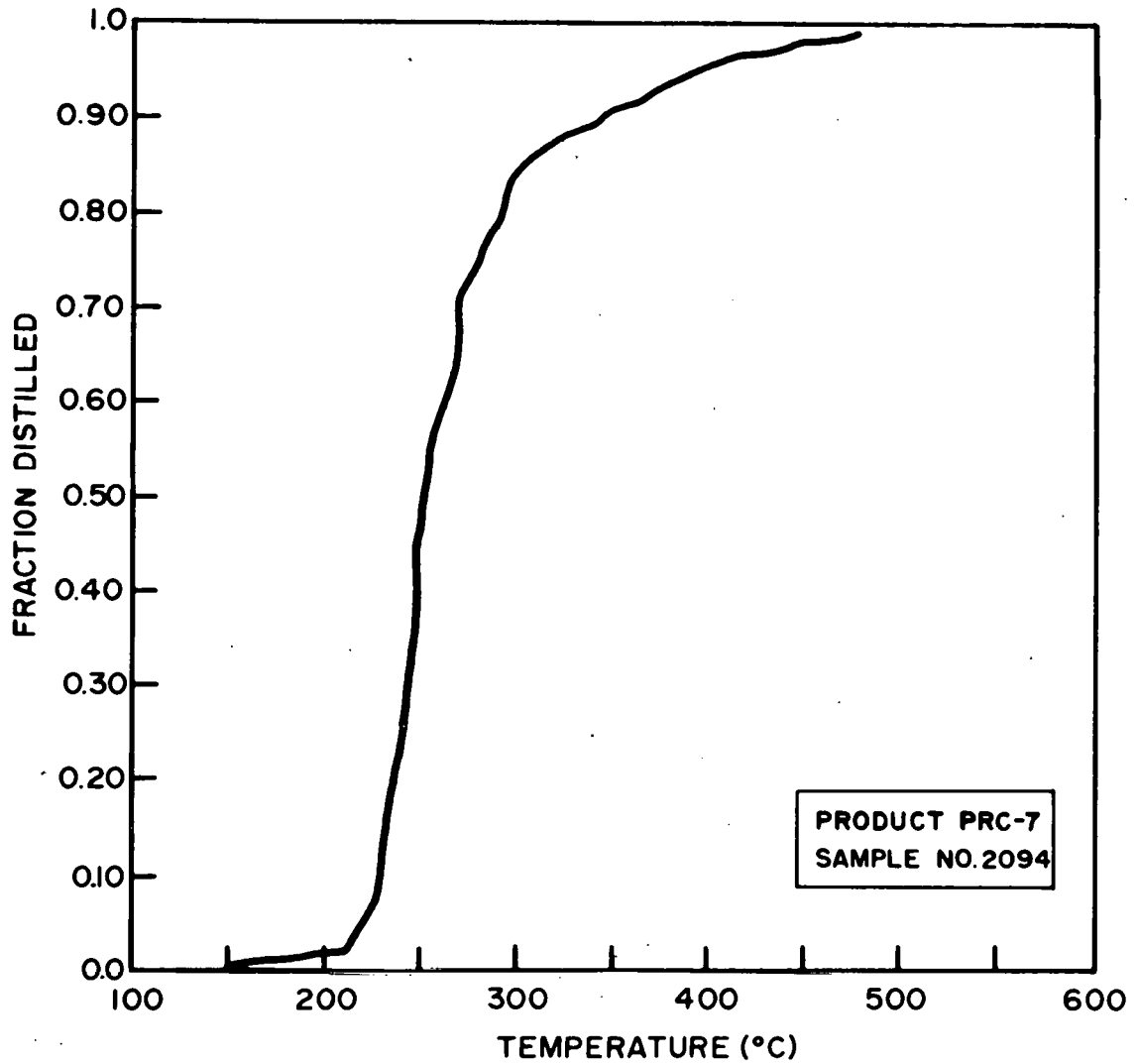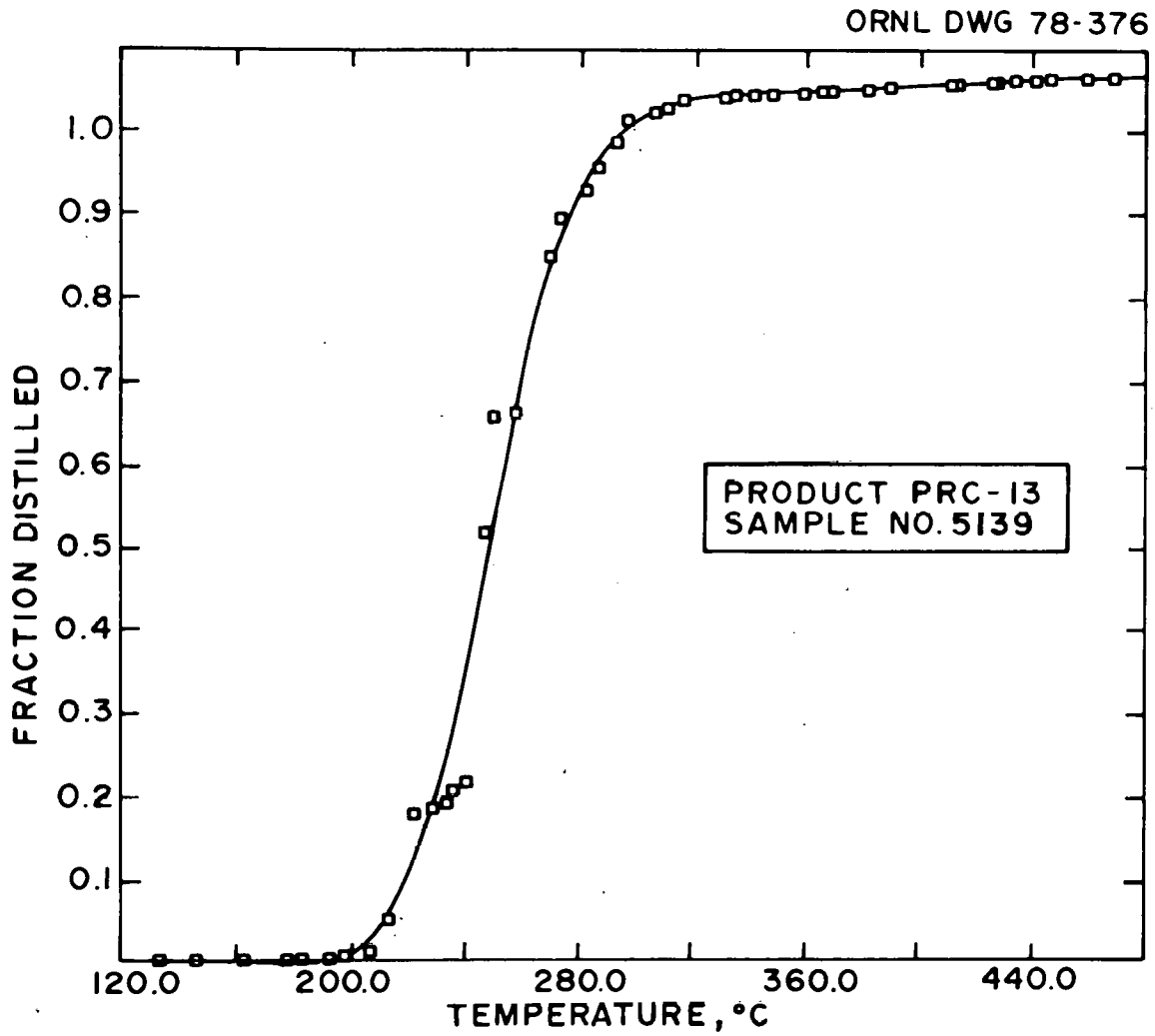
ORNL DWG 78-376

Fig. 7. Simulated boiling curve for product of pressurized carbonization of SLSU obtained June 1977.
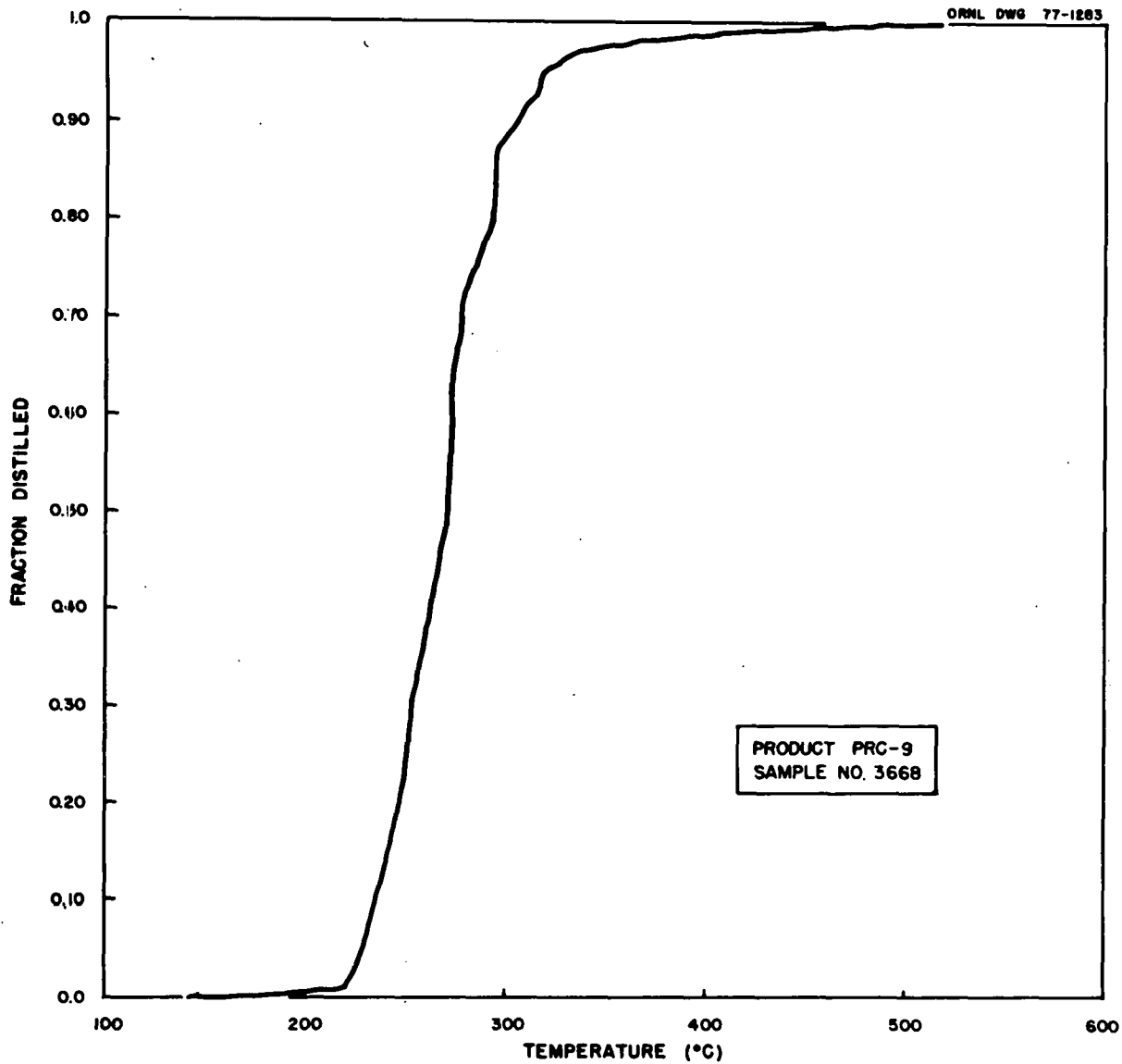
Fig. 8. Simulated boiling point curve for product of pressurized carbonization of solvent received December 1976.

The solids left in the carbonizer were always free flowing; however, for some of the runs using SLSU as the feed materials, some small agglomerates were present. It should also be noted that the liquids produced in these experiments were of high quality, showing low ash and sulfur contents and a high heating value.

As noted in Sect. 2, two batches of SLSU were used in these experiments. Although these materials were obtained from the same source, there were differences in the two materials (as noted in Table 1) and reflected in the results shown in Table 2. The second batch of SLSU contained less solids (ash and fixed carbon) and produced a smaller fraction of coke.

3.2 Rapid Pressurized Pyrolysis of
Vacuum Still Bottoms and Coal

Vacuum still bottoms (VSB), coal (Illinois No. 6), and a 1:1 mixture of VSB/coal were carbonized at 1100°F, 415 psia in a methane atmosphere. Using the method of feeding described in Sect. 2, the gas residence time at the time of feeding was estimated to be 3 sec. The experiments were continuous with respect to methane, semicontinuous with respect to VSB/coal, and batch with respect to fluidized solids, again causing unsteady-state accumulation of coke in the fluidized bed.

Table 4 summarizes the results of the pressurized carbonization of the VSB/coal. As seen from this table, the material balance closures are somewhat deficient; however, since methane was used as the fluidizing gas for these runs, it was not possible to estimate methane production. Therefore, the methane produced may account for a large portion of the material balance deficit.

The liquid product recovered from pressurized carbonization of H-Coal VSB was not of the high quality of the liquid recovered in earlier experiments. The product was not fluid at room temperature and had unacceptably high sulfur concentrations. The ultimate and proximate analyses of the products of H-Coal VSB are shown in Table 5.

Significant gaseous products were recovered from the pressurized carbonization of H-Coal VSB; the gas-analysis data are summarized in Table 6. Because of the ambiguity introduced by using a discontinuous

Table 4. Summary of results of pressurized
carbonization of VSB/coal

Run number	PRC-72	PRC-28	PRC-29	PRC-30
Temperature, °F	1100	1100	1100	1100
Pressure, psig	400	400	400	400
Average methane flow rate, scfm[a]	0.46	1.65	1.56	1.22
Feed material[b]	VSB	coal	{50% VSB {50% coal	VSB
Feed weight, g	67	125	118	118
Feed weight (maf),[c] g	55	111	101	97
Char weight (maf),[c] g	58.7	58.3	50.0	51.6
Char yield, $[d]	--	57.8	56.8	61.3
Char yield (maf),[c] %	--	52.5	49.5	53.2
Mass gas recovered (CH_4, CO_2, Ar, air-free), g	1.8	13.9	21.7	18.4
Mass liquid recovered, g	--	--	5.3	10.7
Material balance closure, %	--	--	80	86

[a]Standard conditions = 20°C, 1 atm.

[b]VSB = H-Coal vacuum still bottoms; coal = Illinois No. 6.

[c]Moisture- and ash-free basis.

[d]Moisture-free, ash included.

Table 5. Summary of VSB/coal product analyses

	Proximate analysis (wt %)				Ultimate analysis (maf)[a] (wt %)				Heating value (Btu/lb)
	Moisture	Ash	Volatile matter	Fixed carbon[b]	Carbon	Hydrogen	Nitrogen	Sulfur	
H-Coal VSB	0.21	18.03	35.9	45.9	85.43	6.07	1.84	2.62	15,375
Illinois No. 6 coal	1.19	11.14	14.2	73.5	89.31	4.32	1.27	1.57	9,454
Liquid product PRC-27	--	0.79	--	--	85.12	6.90	1.59	0.09	--
Liquid product PRC-29	5.46	1.15	68.1	25.29	88.77	7.08	1.32	1.69	15,899
Liquid product PRC-30	8.02	0.06	70.1	21.82	93.34	7.91	1.68	1.14	17,284

[a]Moisture- and ash-free basis.

[b]By difference.

22

Table 6. Summary of gas analyses from pressurized carbonization of VSB/coal

Gas	PRC-27 Concentration (mole %)[a] Average	Peak	Total weight (g)	PRC-28 Concentration (mole %)[a] Average	Peak	Total weight (g)	PRC-29 Concentration (mole %)[a] Average	Peak	Total weight (g)	PRC-30 Concentration (mole %)[a] Average	Peak	Total weight (g)
H_2	0.28	0.51	0.15	0.36	0.59	1.39	0.30	0.39	0.75	0.44	0.61	0.67
H_2O	0.15	0.34	0.74	0.13	0.25	4.69	0.02	0.02	0.34	0.01	0.01	0.14
CO		0.01			0.03		0.03	0.11	1.12			
N_2	0.23	0.47					0.02	0.07	0.76	0.01	0.03	0.24
CO_2	0.05	0.10	0.65	0.05	0.18	4.60	0.01	0.02	0.58	0.01	0.02	0.40
CH_4				BALANCE								
C_2H_4	0.02	0.04	0.12	0.01	0.02	0.31	0.01	0.02	0.18	0.01	0.02	0.26
C_2H_6	0.09	0.13	0.73	0.07	0.13	4.07	0.23	0.27	8.80	0.04	0.05	1.17
C_3H_6	0.01	0.03	0.11	0.01	0.07	1.20	0.03	0.06	1.79	0.04	0.05	1.17
C_3H_8				0.03	0.11	2.34	0.15	0.20	8.51	0.22	0.32	6.38

[a] Argon- and air-free.

feeding method and taking grab samples, both volume-averaged and peak gas concentrations are shown. The total weight of each species was calculated from the volume-averaged concentration. As can be seen, the gas contains significant quantities of H_2, C_2H_6, and C_3H_8, as well as H_2O and CO_2. In addition, C_4, C_5 aliphatics and mono-olefins, as well as benzene, toluene, and xylene, were analyzed for but were not detected.

The VSB/coal proved to be a very difficult material to carbonize in a fluidized bed. The VSB appeared to form a stable liquid at operating conditions. When cooled for cleanout of the reactor, this liquid hardened to form an agglomerate over the entire cross section of the reactor. The overhead product, when condensed, also formed very stubborn plugs in the condenser tubing.

4. CONCLUSIONS

Since the studies discussed in this report were not an exhaustive investigation of pressurized carbonization of coal liquefaction by-products but were intended to be scouting or preliminary tests, caution must be used in drawing conclusions. From the results presented in Sect. 3, the following conclusions are offered.

4.1 Carbonization of Hydroextraction SLSU

Several conclusions can be drawn from an analysis of the results of the SLSU experiments. The following conclusions are presented:

1. Pressurized carbonization of SLSU causes only small amounts (1 to 7%) of solvent degradation.
2. Pressurized carbonization of SLSU produces a high-quality liquid, low in ash and sulfur.
3. Pressurized carbonization of SLSU formed a free-flowing char with only small agglomerates.
4. Char is formed primarily from the higher boiling fraction of the SLSU.
5. Increased pressure has a small effect on the production of char from the solvent fraction of the SLSU.
6. Increased pressure has a significant effect on the production of char from the higher boiling fraction of the SLSU.

4.2 Pressurized Rapid Pyrolysis of Vacuum
Still Bottoms and Coal

Several conclusions can be made from an examination of the results of the rapid pyrolysis of vacuum still bottoms and coal:

1. Significant quantities of gaseous products (primarily H_2, CH_4, C_2H_6, and C_3H_8) are produced from pressurized carbonization of H-Coal VSB.

2. Pressurized carbonization of H-Coal VSB produces small amounts of liquid product under the conditions investigated (1100°F, 400 psig).

3. Pressurized carbonization of H-Coal VSB does not produce a free-flowing char(solid) product (i.e., the nonvolatile materials are liquid at carbonization conditions) under the conditions investigated (1100°F, 400 psig).

5. ACKNOWLEDGMENTS

6. REFERENCES

1. Fluor Engineers and Constructors, Inc., Conceptual Design for Advanced Coal Liquefaction Commercial Plant, - Annual Technical Progress Report, April 21, 1976 - April 30, 1977, FE-2251-28 (June 1977).

2. J. B. O'Hara, N. E. Jentz, H. T. Syverson, G. H. Hervey, and R. V. Teeple, Project POGO, Total Coal Utilization, COG Refinery Design Criteria, R&D Report No. 114 - Interim Report No. 5, FE-1775-11. Prepared for the Energy Research and Development Administration (August 1977).

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

7. APPENDIX: DETAILS OF EXPERIMENTAL EQUIPMENT

28

7.1 Carbonization Vessel

The carbonizer consisted of a 2-ft section of 2-in. NPS sched-40 pipe and a 1-ft section of 3-in. NPS sched-40 pipe—both of SST 304. Pressure and thermocouple taps were located as shown in Fig. 9. The top flange was a 1500-lb metal ring joint flange of 316 SST. An internal porous stainless steel filter (average pore diameter of 7 μm) removed particles from the exit-gas stream. This design proved entirely adequate except that for the VSB/coal work, better access to the lower portion would have been desirable.

7.2 Condenser

The condenser, shown in Fig. 10, consisted of three concentric tubes: a 1-in.-diam, 0.049-in.-wall tube containing the cooling water, a 1/2-in.-diam, 0.035-in.-wall tube containing hot gas from the carbonizer and a 3/8-in.-diam, 0.035-in.-wall tube containing the cooled gas from the condensate receiver. All tubing and sheet metal used in the condenser was 300-series SST; compression fittings were of 347 SST. A thermocouple, located at the top of the condenser, monitored exit-gas temperature. Two problems were encountered with the condenser: (1) during the VSB/coal studies, the heavy product condensed in the 0.055-in.-wide annulus between the 3/8-in. and 1/2-in. tubes, causing stubborn plugging; and (2) during the hydroextraction residue carbonization studies, the condensate formed an aerosol that was difficult to recover.

7.3 Condensate Receiver

The condensate receiver was a 2-in. NPS sched-40, 304-SST pipe, capped at the bottom and flanged at the top, as shown in Fig. 11. The flanges were 316 SST (300-lb, raised-face flanges) sealed with spiral-wound asbestos/stainless steel gasket.

7.4 Gas Preheater

The gas preheater, see Fig. 12, consisted of a 1/4-in.-OD SST-347 tube fitted with four 2.5-kW electrical heaters. Thermocouples were tack-welded to the tube to monitor wall temperatures.
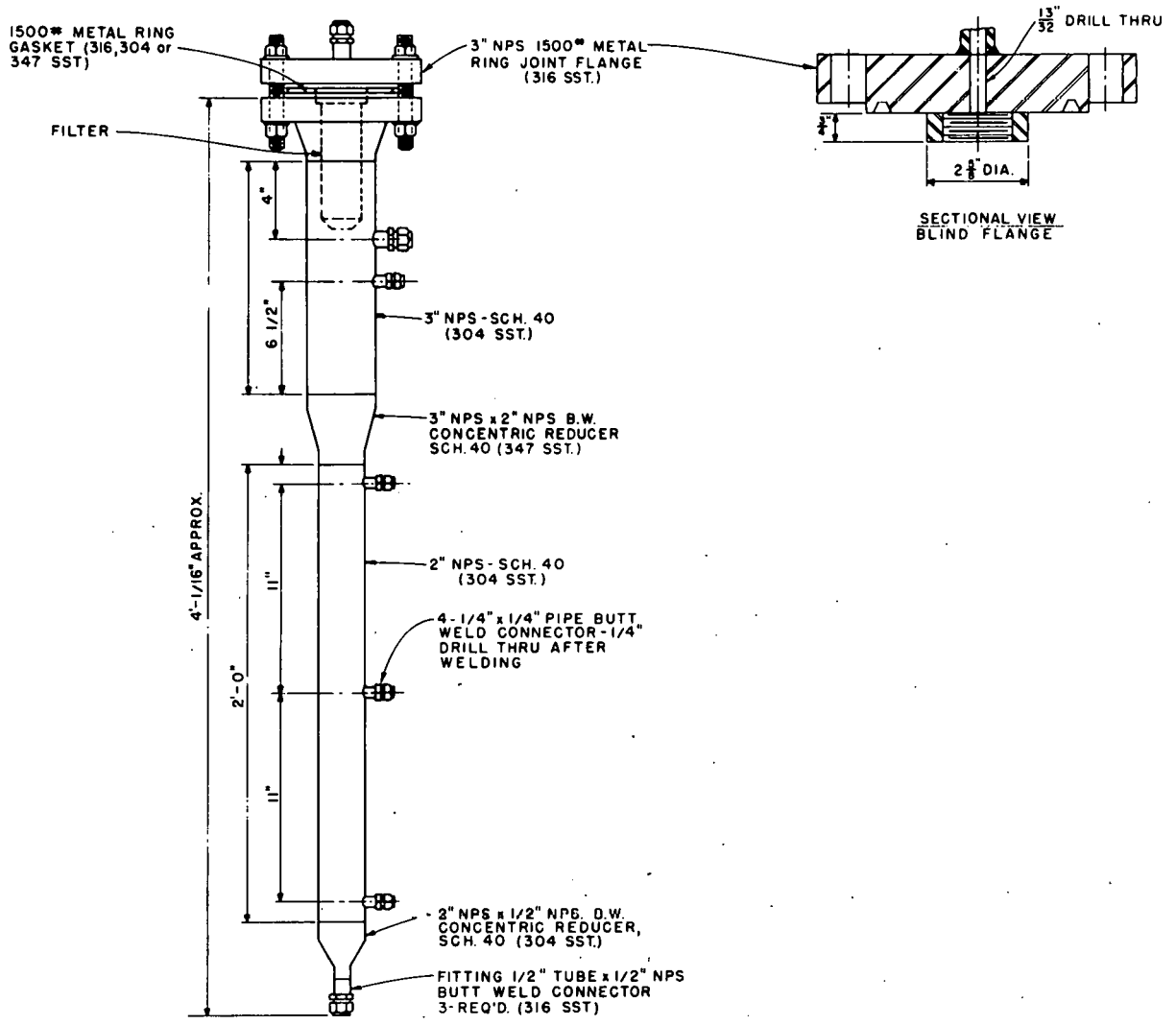
ORNL DWG 77-223R

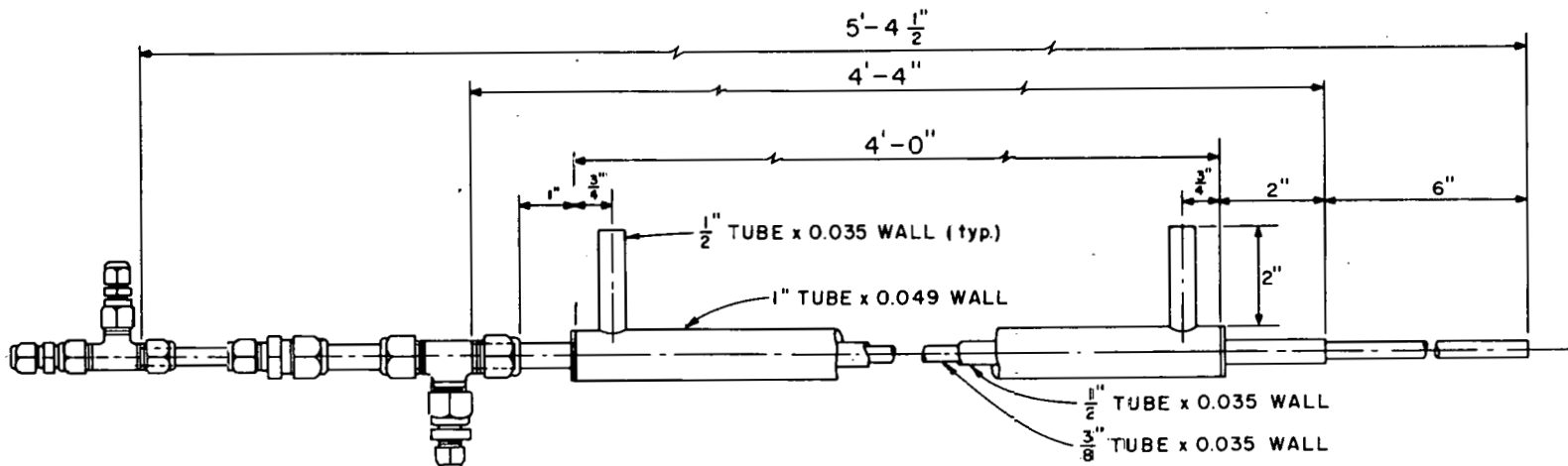1500# METAL RING GASKET (316,304 or 347 SST)

FILTER

3" NPS 1500# METAL RING JOINT FLANGE (316 SST.)

$\frac{13}{32}$" DRILL THRU

4"

6 1/2"

3" NPS-SCH. 40 (304 SST.)

3" NPS x 2" NPS B.W. CONCENTRIC REDUCER SCH.40 (347 SST.)

4'-1/16" APPROX.

11"

2'-0"

2" NPS-SCH. 40 (304 SST.)

4-1/4" x 1/4" PIPE BUTT WELD CONNECTOR-1/4" DRILL THRU AFTER WELDING

11"

2" NPS x 1/2" NPS D.W. CONCENTRIC REDUCER, SCH. 40 (304 SST.)

FITTING 1/2" TUBE x 1/2" NPS BUTT WELD CONNECTOR 3-REQ'D. (316 SST)

2 $\frac{3}{8}$" DIA.

SECTIONAL VIEW BLIND FLANGE

Fig. 9. Carbonization vessel.

Fig. 10. Condenser.

ORNL DWG 77-227R2

FITTING-1/2" TUBE x 1/2" NPS
BUTT WELD CONNECTOR(316SST)

2-300# R.F. BLIND FLANGE
(316 SST)

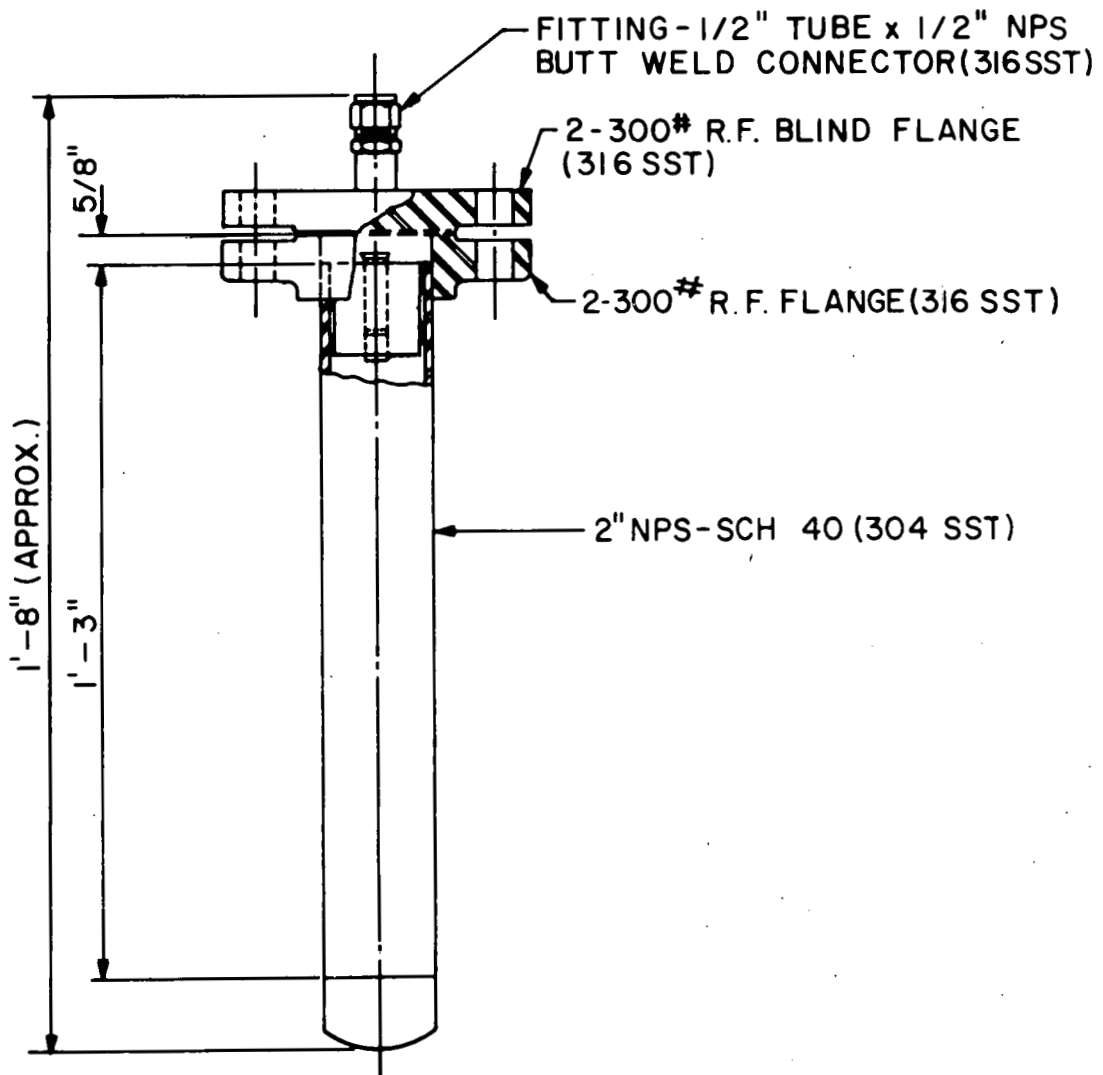2-300# R.F. FLANGE(316 SST)

2" NPS-SCH 40 (304 SST)

5/8"
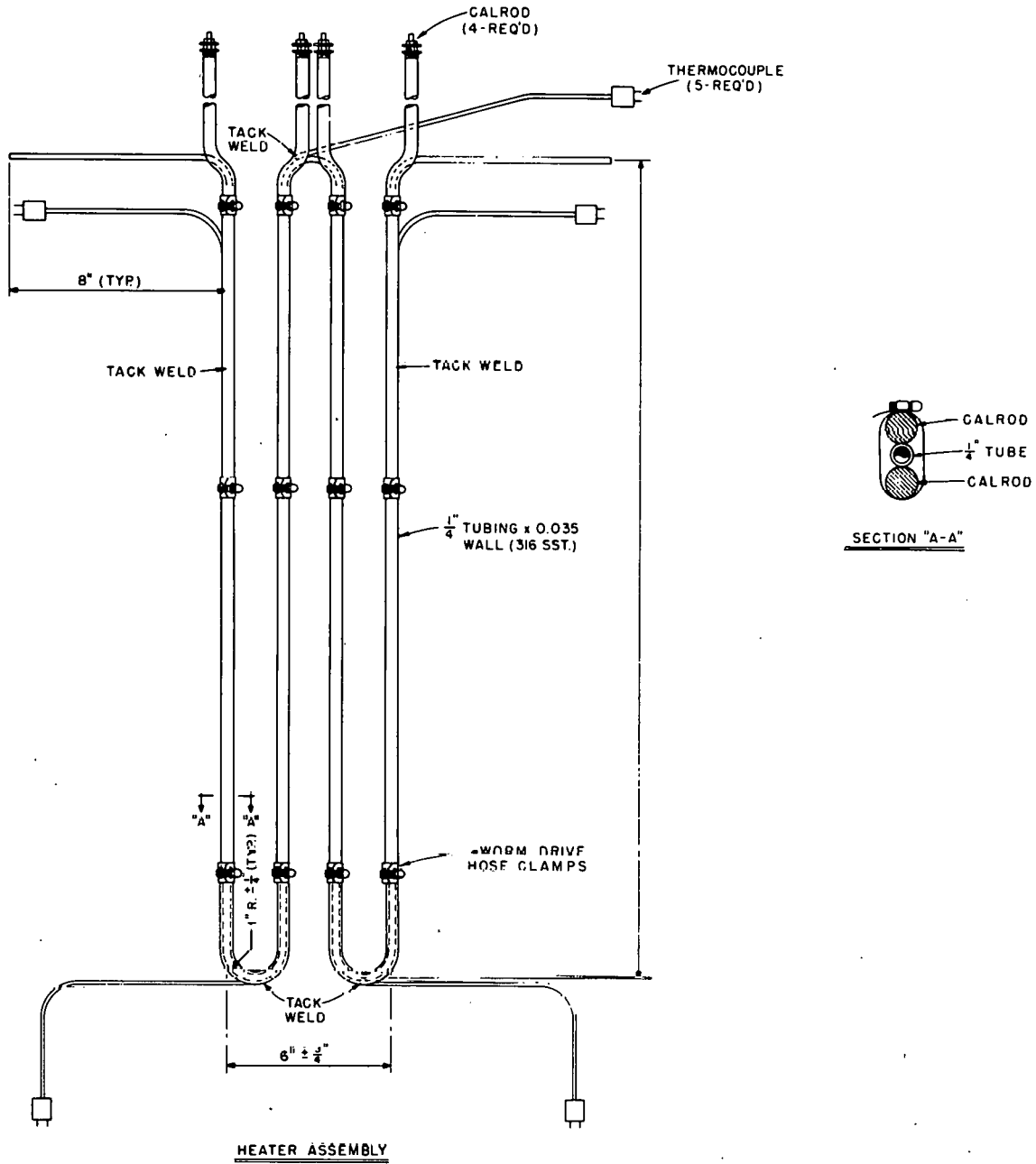
1'-8" (APPROX.)

1'-3"

Fig. 11. Condensate receiver.

Fig. 12. Gas preheater.

7.5 Atomizing Nozzles

The atomizing nozzles, as seen in Fig. 13, consisted of two concentric tubes and a compression fitting. The slurry liquid to be atomized flowed through the inner tube, and the atomizing gas flowed through the annulus. The gas mixed with the liquid at a high velocity upon existing the 1/32-in.-diam holes at the mouth of the nozzle.

7.6 Feed Injection Tubes

The feed injection tubes, shown in Fig. 14, were composed of 3/8-in.-OD tubing that was 20 in. long with a ball valve at each end. Each tube held ~10 g of VSB/coal.
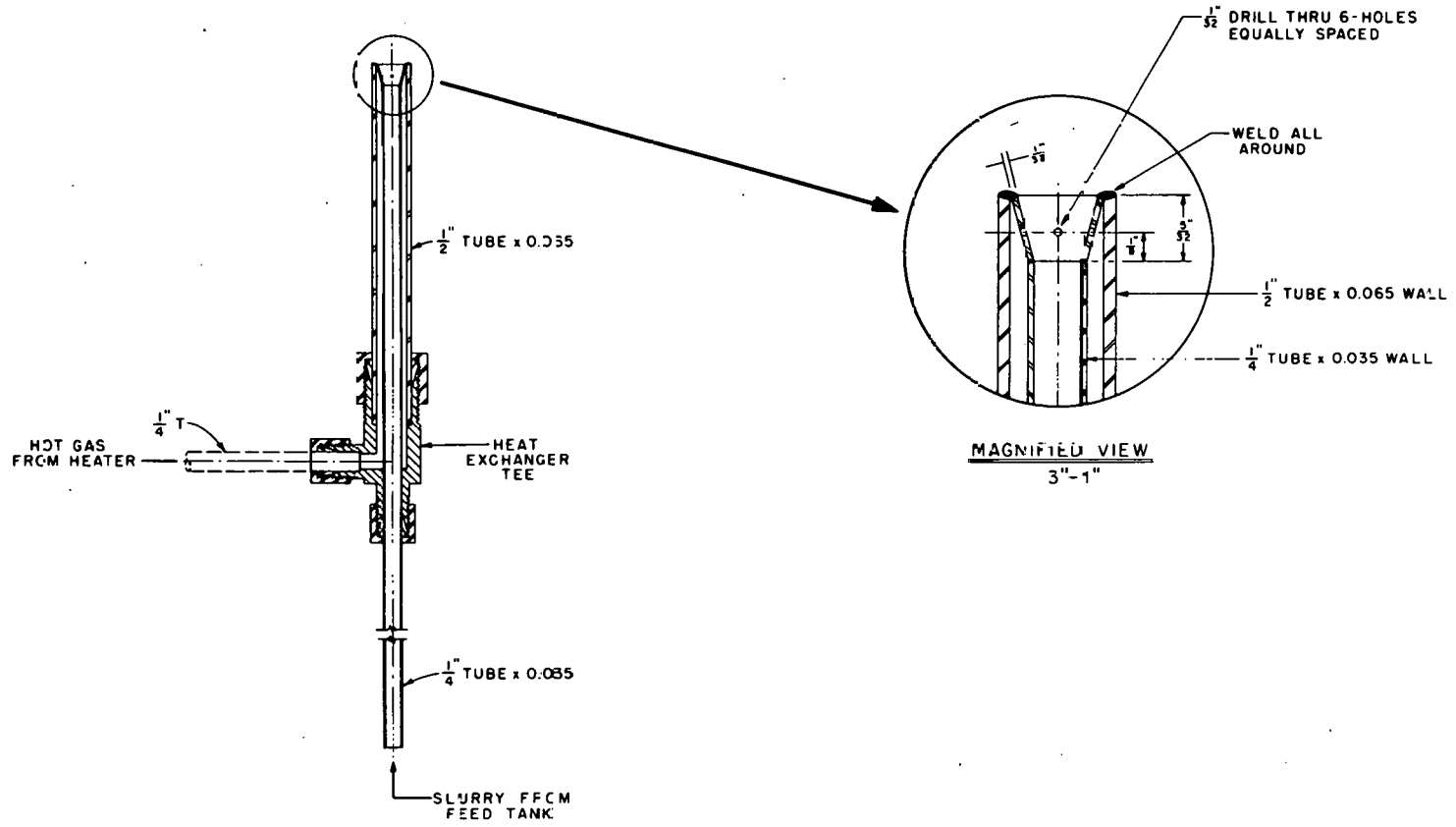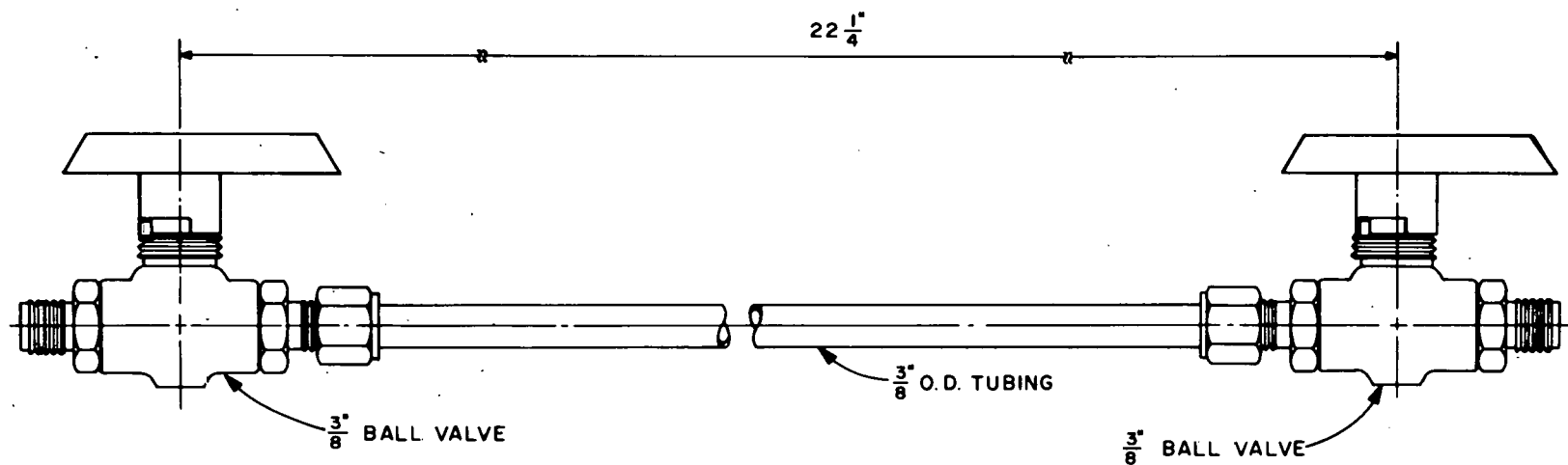
$\frac{1}{32}$ DRILL THRU 6-HOLES
EQUALLY SPACED

WELD ALL
AROUND

$\frac{1}{58}$

$\frac{5}{32}$

$\frac{1}{8}$

$\frac{1}{2}$ TUBE x 0.065 WALL

$\frac{1}{4}$ TUBE x 0.035 WALL

MAGNIFIED VIEW
3"-1"

$\frac{1}{2}$ TUBE x 0.035

HOT GAS
FROM HEATER

$\frac{1}{4}$ T

HEAT
EXCHANGER
TEE

$\frac{1}{4}$ TUBE x 0.035

SLURRY FROM
FEED TANK

Fig. 13.   Atomizing nozzle.

$22\frac{1}{4}$"

$\frac{3}{8}$" O.D. TUBING

$\frac{3}{8}$" BALL VALVE

$\frac{3}{8}$" BALL VALVE

Fig. 14. Feed injection tube.

35

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

INTERNAL DISTRIBUTION

1-10.	R. E. Barker	31.	M. Siman-Tov
11.	C. R. Boston	32.	S. P. N. Singh
12.	J. E. Campbell	33.	R. A. Strehlow
13.	H. D. Cochran	34.	D. B. Trauger
14.	S. G. DeCicco	35.	J. S. Watson
15.	D. E. Ferguson	36.	P. R. Westmoreland
16.	J. F. Fisher	37.	R. G. Wymer
17.	R. C. Forrester	38.	E. L. Youngblood
18.	E. L. Fuller	39.	S. Alpert (consultant)
19.	S. M. Gibson	40.	H. Beuther (consultant)
20.	R. W. Glass	41.	C. Streed (consultant)
21.	J. R. Hightower	42.	G. R. Choppin (consultant)
22.	J. M. Holmes	43.	L. James Colby, Jr. (consultant)
23.	J. K. Huffstetler	44.	L. E. Swabb, Jr. (consultant)
24.	L. E. McNeese	45-46.	Central Research Library
25.	J. P. Meyer	47.	Document Reference Section
26.	G. R. Peterson	48-49.	Laboratory Records
27.	B. R. Rodgers	50.	Laboratory Records - RC
28.	R. Salmon	51.	ORNL Patent Office
29.	G. Samuels	52-53.	ORNL - Y-12 Technical Library
30.	C. D. Scott		

EXTERNAL DISTRIBUTION

54. R. H. Fischer, Department of Energy, 400 1st Street, Washington, D. C. 20545
55. J. B. Gibson, 1213 Quail Hollow, Baton Rouge, Louisiana 70810
56. N. E. Jentz, Ralph M. Parsons Company, 100 W. Walnut Street, Pasadena, California 91124
57. E. B. Neben, Fluor Engineers and Constructors, Inc., P. O. Box 4051, Anaheim, California 92803
58. T. B. Simpson, Department of Energy, 400 1st Street, Washington, D. C. 20545
59. Office of Assistant Manager, Energy Research and Development, DOE, ORO, Oak Ridge, Tennessee 37830
60-370. Given distribution as shown in TID-4500 under Coal Conversion and Utilization - Liquefaction category (25 copies - NTIS).