

PRODUCTS OF LIQUEFACTION OF LIGNITE WITH SYNTHESIS GAS BY PRODUCT SLURRY RECYCLE

Bruce W. Farnum, Curtis L. Knudson and Del A. Koch

Grand Forks Energy Technology Center, U. S. Department of Energy
Box 8213 University Station, Grand Forks, ND 58202

Liquefaction of lignite is under study at the Grand Forks Energy Technology Center using a 5 lb coal per hour continuous processing unit (CPU) with various reactor configurations (1). The objectives of the experiment reported in this paper were (a) to test CPU operability under conditions of extensive product slurry recycle with fresh coal addition, (b) to produce a quantity of "lined out" lignite derived liquids for analytical characterization, and (c) to ascertain the function of reaction yields with the degree of line out or number of slurry passes. Objectives (a) and (c) have been discussed at a recent symposium by Willson et al. (2). A one gallon stirred autoclave reactor was operated at 460°C and 4000 psig with an average residence time of about one hour. Redistilled anthracene oil (IBP 296°C at 10 Torr.) was used as a pasting solvent for the initial pass. A 30% slurry of high ash Beulah seam lignite (10.7% ash, 29.6% fixed carbon, 29.5% moisture, 30.2% volatile matter) in pasting solvent was prepared for each pass. The lignite had been pulverized to 100% minus 60 mesh and 90% minus 200 mesh. Batch recycling was carried out through 34 cycles using the unfiltered product as pasting solvent for each subsequent pass. Gases, water and high pressure volatile oils were removed during each cycle. A mixture of equal parts of carbon monoxide and hydrogen was fed through the system at a rate of 1/2 scfm.

Separation of gas and liquid phases at 4000 psig and 300°C was carried out in the unit after the products exited the reactor (Figure 1). The gas phase was then cooled and depressurized producing a water layer, a high pressure volatile oil layer, and tail gases. Yields calculated on a moisture and mineral free coal basis were: C₁-C₄ hydrocarbons 19%, high pressure volatile oils 19%, vacuum distillate 36%, THF soluble vacuum bottoms 9%, and THF insoluble organic polymers 11%.

During Run 27 (64 hours) a slight leak in the autoclave head closure caused loss of the gas head in the reactor with the result that the liquid level rose above the level of the liquid removal tube, and the relatively poorly stirred liquid contacted the overheated wall surfaces. The reactor filled with coked slurry around the space occupied by the stirrer blade and shaft. The suspended solids (minerals and organic polymers) normally present in the product were deposited in the reactor by a process of polymerization of the organic high molecular weight material with inclusion of the mineral particles. Run 27 was terminated after the sixteenth pass. Operation of the CPU was resumed (Run 28) using product from Run 27 as pasting solvent for the first cycle. After the 34th recycle pass, conditions were changed, doubling the slurry feed rate. Coke was found in the reactor at the end of Run 28 and probably occurred for the same reason as in Run 27. However, as indicated in Figure 2 the disproportionate increase in the amount of THF soluble vacuum bottoms was not observed in Run 28, indicating this coking occurred later in the run.

Figure 2 depicts on an MAF coal basis a summation of the yields of the various product fractions obtained. Ash concentration in the product stream paralleled the THF insoluble values showing the same inclusion of inorganic fraction as coke formed in the reactor.

Gas samples were analyzed by on-line gas chromatography. Effluent water samples were characterized by standard analytical methods for waste water and

standard EPA methods (3,4). The average analysis of four samples of condensate water produced under lined out conditions is reported in Table 1.

The aromatic to aliphatic proton ratio of the high pressure volatile oils was monitored as a function of recycle pass number by infrared spectrophotometry and by proton nuclear magnetic resonance spectrometry. 90MHz proton NMR spectra were integrated over the range 9.7 to 6.4 ppm in the aromatic region (Har), 4.2 to 1.7 ppm in the benzylic region (Halp), and 1.7 to 0.25 ppm in the aliphatic methyl and methylene region (Ho). Water and phenolic OH proton signals were omitted, and solvent (deuteropyridine) contributions were subtracted from the total integrated area. Calculation of molecular parameters, f_a , sigma and Haru/Car were carried out as defined by Brown and Ladner (5).

Figure 3 illustrates the approach to constant composition of the high pressure volatile oils collected during each pass. The discontinuity of the curves following the sixteenth pass was caused by the operational problem previously discussed. Agreement of the two methods of analysis was good. A plot of IR ratio versus NMR ratio was linear with a correlation coefficient of 0.96. NMR data is listed in Tables 2 and 3. Gas chromatographic separation indicated about 269 resolved components using a 50 meter OV-101 glass capillary column. There were 30 components present in 1 to 4% concentration, 23 in 0.5 to 1%, 110 in 0.1 to 0.5%, and 106 in 0.01 to 0.1% concentration. Identification of the components of the light oil is in progress and will be reported at a future date.

Low voltage low resolution mass spectrometry provided an indication of the organic oxygen compound type distribution of the high pressure volatile oils (Figure 4). The build up of phenolic oxygen observed by mass spectrometry was also observed by measuring the phenolic OH proton concentration by NMR. The total oxygen content by neutron activation analysis equaled the organic oxygen content from LVMS plus the water oxygen content measured by Karl Fischer titration in the lined out volatile oil. The computer program for analysis of mass data was originally developed for analysis of gasifier tar (6) and accounted for 76% of the total ion current.

Determination of the molecular weight distribution (MWD) of the THF soluble fraction of the product stream was carried out using gel permeation HPLC with uv detection at 365 nm (7). The startup solvent was mostly replaced by lignite derived oil by pass number 5 (Figure 5). The THF soluble fraction of the product stream yields an average MW of 300 relative to Water's polystyrene standards.

Gel permeation chromatography of the non-distillable but THF soluble fraction of the product stream indicated an increase in molecular weight during passes 6-14 which paralleled the trend in percent vacuum bottoms. This is another indication that organic polymerization was the probable cause of coke formation in the reactor. Temperature was held constant during processing. Reactor temperature has been previously observed to be the predominant factor in lowering molecular weight in both batch autoclave studies (8) and stirred autoclave continuous process unit studies (1,2). Figure 6 illustrates the ratio of uv absorbance at 254 nm of high molecular weight to low molecular weight materials versus reactor temperature in studies carried out with the batch autoclave and the continuous stirred autoclave unit. The strong temperature dependence of the MWD between 400 and 500°C is readily observed. That a CPU yielded similar dependence can also be noted.

The ashes obtained from the feed slurry, product slurry and reactor coke material have been examined to determine if the coke contains any enrichment of Ca, Mg, Fe, or Na content. None was observed, supporting the hypothesis that coking was due to polymerization of the organic phase rather than agglomeration and deposition of minerals. Figure 7 depicts the locations where samples were obtained from coke removed from the reactor after Run 28. Three distinct differ-

ently colored regions were observed. The center (B3-1) was softer and slightly sticky, while the other areas were hard and brittle. Ash and sulfur content indicated little variability in composition of the coke from the reactor (Table 4). Analysis of the ashes of feed slurry, product slurry and coke samples with an inductively coupled argon plasma (ICAP) spectrometer after digestion indicates that the Ca, Fe, Mg and Na contents are essentially identical. The data does indicate that no build up of calcium carbonate occurred in the stirred autoclave reactor to cause reactor plugging as has been observed in tubular reactors (9). The presence of 5.7 wt. percent carbonate was observed by TGA analysis indicating carbonates were present. Since much of the sodium and calcium content of low rank coals is dispersed throughout the organic matrix as humate salts, the formation of bicarbonate-carbonate salts is expected from decarboxylation of the humates early in the process. High CO₂ and water concentrations in the reactor may account for not observing carbonate agglomeration.

Acknowledgement: We are indebted to Dr. Warrack Willson (Liquefaction Project Manager), Gene Baker, Raymond Majkrzak and James Tibbetts for operation of the CPU and calculation of yield data. We also thank Dr. Sylvia Farnum, Dr. Warren Reynolds, William Barton, David Miller, Ed Bitzan, Diane Rindt, George Montgomery and Steven Benson for contributions of data and helpful discussions.

References

1. Sondreal, E. A., Knudson, C. L., Majkrzak, R. S., and Baker, G. G., "Liquefaction of Lignite by the CO-Steam Process", A.I.Ch.E. National Meeting, Miami, Florida, November 12-16, 1978.
2. Willson, Warrack, Baker, G. G., Knudson, C. L., Owens, T. C., and Severson, D. E., "Applications of Liquefaction Processes to Low-Rank Coals." Proceedings of the 1979 Symposium on Technology and Use of Lignite, Grand Forks Energy Technology Center, Grand Forks, ND 58202, May 1979.
3. American Public Health Assn. Standard Methods for Examination for Examination of Water and Wastewater, 14th Ed, APHA, AWWA, and WPCF, Washington (1975).
4. EPA Methods for Chemical Analysis of Water and Wastes EPA #5501-0067 (1976).
5. Brown, J. K. and Ladner, W. R., Fuel (London) **39**, 87-96 (1960).
6. Miller, D. J., Olson, J. K., and Schobert, H. H., Preprints, ACS Div. of Fuel Chemistry, in press.
7. Barton, W. F., Knudson, C. L., Ruud, A. L. and Farnum, B. W. Symposium on Characterization of Coal Derived Materials, Pittsburgh Energy Tech. Ctr, May 10-11, 1979.
8. Knudson, C. L., Schiller, J. E. and Ruud, A. L. "Temperature Effects on Coal Liquefaction", in Organic Chemistry of Coal, American Chemical Society, Washington, DC, J. Larsen, Editor, 1978.
9. Dr. Ray Anderson, Pittsburg and Midway Co., Merriam, KS, Private Communication.

Table 1
Effluent Water Composition^a
(Averages of Recycle Passes 21, 24, 29 and 32)
(Concentrations in ppm)

pH at analysis	8.6
Alkalinity as CaCO ₃	80,400
Ammonia	27,300
Total sulfur	2,380
Total carbon	31,200
Inorganic carbon	12,400
Organic Carbon	18,800
Phenol	6,430
<u>o</u> -cresol	579
<u>m,p</u> -cresols	1,640

a. Analysis carried out under contract by Stearns-Roger, Inc.

Table 2
NMR Analysis of Light Oils^a

Sample	Pass No.	%Har	%H α	%H ω	fa	σ	Haru/Car	%Hphenolic
27L01	0.5	8.0	13.0	79.0	0.167	0.455	1.602	0
L02	4.2	12.7	15.7	71.6	0.264	0.416	1.395	0.79
L03	8.7	19.3	20.1	60.7	0.387	0.364	1.191	1.84
L04	13.6	22.6	20.9	56.4	0.432	0.348	1.182	2.53
28L02	18	21.7	23.2	55.1	0.415	0.393	1.224	2.08
L04	20	17.1	18.3	64.6	0.346	0.404	1.230	1.72
L06	22	19.6	22.0	58.4	0.386	0.413	1.246	2.02
L08	24	19.5	18.8	61.7	0.378	0.380	1.216	2.43
L010	26	21.9	22.8	55.2	0.406	0.392	1.282	2.51
L012	28	20.9	19.5	59.6	0.393	0.370	1.228	2.49
L013	29	21.3	19.7	59.0	0.393	0.373	1.257	2.74
L014	30	22.6	20.7	56.7	0.406	0.383	1.286	2.86
L015	31	21.9	20.7	57.4	0.398	0.376	1.286	2.63
L016	32	22.0	20.4	57.5	0.405	0.384	1.256	2.59
L017A	33	22.5	20.3	57.2	0.410	0.368	1.244	2.74
L018	34	18.6	18.9	62.5	0.351	0.378	1.363	2.07

a. Analyses performed on a Varian EM-390 Spectrometer located at the University of North Dakota Department of Chemistry.

Table 3
NMR Analysis of Unfiltered Product^a

Sample	Pass No.	%Har	%H α	%H β	f α	σ	Haru/Car
27-Y1	1	33.4	28.6	38.0	0.650	0.296	0.762
27-B2B	3	35.8	28.5	35.7	0.670	0.294	0.774
27-B2D	5	38.0	28.6	33.5	0.693	0.304	0.756
28-2B	18	42.6	28.7	28.7	0.730	0.303	0.750
28-4B	20	43.4	29.3	27.3	0.737	0.284	0.741
28-6B	22	42.7	28.8	28.4	0.734	0.287	0.734
8B	24	43.1	28.3	28.6	0.735	0.286	0.741
10B	26	43.5	27.1	29.5	0.739	0.274	0.723
12B	28	43.0	28.6	28.4	0.741	0.289	0.718
13B	29	43.9	27.7	28.5	0.746	0.278	0.713
14B	30	43.1	28.3	28.6	0.745	0.286	0.701
15B	31	42.5	28.0	29.5	0.737	0.291	0.713
16B	32	44.1	28.2	27.7	0.753	0.289	0.697
17B	33	41.5	30.2	28.3	0.718	0.295	0.770
18B	34	41.1	29.3	29.5	0.735	0.317	0.701
22B	38	41.6	30.8	27.6	0.745	0.326	0.687

a. Analyses performed on a Varian EM-390 Spectrometer located at the University of North Dakota Department of Chemistry.

Table 4
Analyses of the Feed Slurry (FS), Product Stream (PB)
and Reactor Coke (CK) by ICAP after High Temperature Ashing^a

Run 28										
Element/ Sample ^b	FS4	FS13	FS15	FS16	FS Ave	PB8	PB13	PB15	PB16	PB Ave
Ca, x10 ⁻³ ppm	83.1	80.3	81.6	83.4	82.1	85.0	78.8	83.2	80.7	81.9
Fe	86.2	84.7	84.5	85.5	85.2	89.0	85.4	89.5	86.2	87.5
Mg	23.4	22.8	23.0	23.6	22.9	24.1	23.0	23.2	23.2	23.4
Mg ₂	22.5	22.6	23.2	22.3		23.6	23.2	23.9	22.9	
Na	28.7	29.4	30.9	27.1		26.9	31.3	29.7	29.7	
Na ₂	27.9	29.4	30.7	27.3	28.9	27.9	31.2	29.7	29.8	29.5
Run 28 Coke										
Element/ Sample ^c	CKB1				CKB3-4					
Ca, x10 ⁻³ ppm	83.9				86.3					
Fe	83.4				87.2					
Mg	23.8				24.2					
Mg ₂	22.9				23.7					
Na	29.4				31.3					
Na ₂	24.9				30.6					

a. Determinations.

b. As an example FS4 = feed slurry on the fourth recycle pass.

c. See Figure 7 for locations where coke samples were obtained.

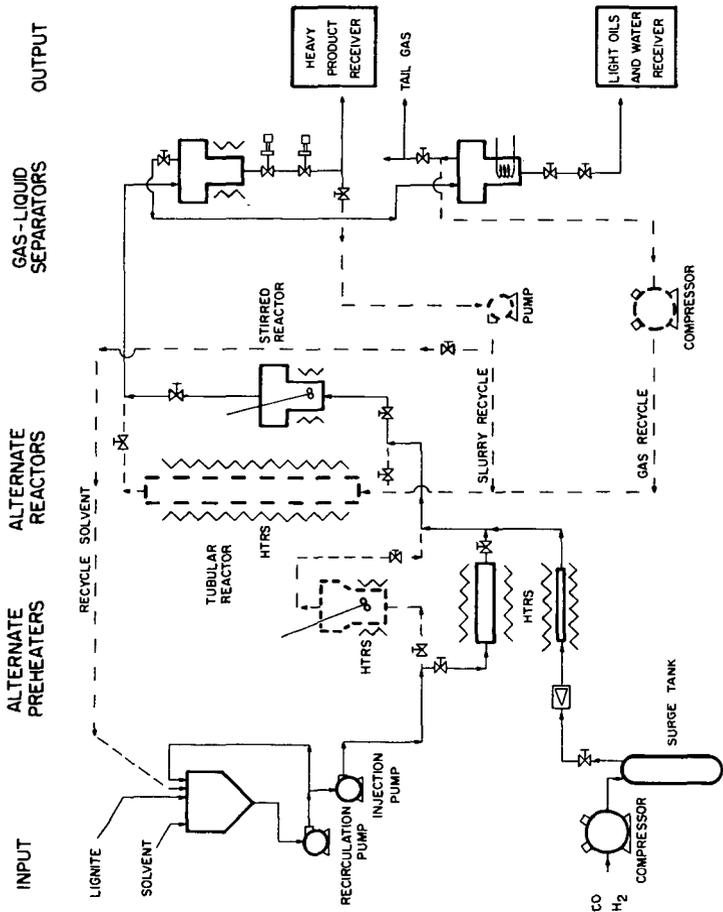


Figure 1. - Schematic diagram of the 6FETC 5-lb coal/hr continuous process unit.

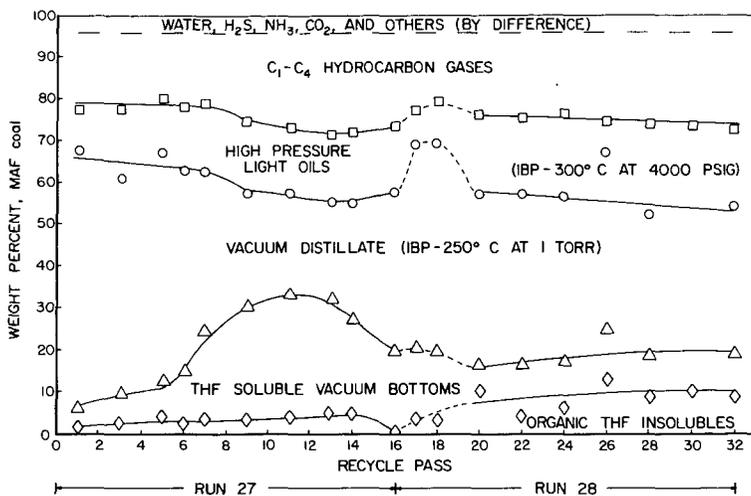


Figure 2. - Runs 27 & 28: Distribution of MAF coal conversion products versus recycle pass.

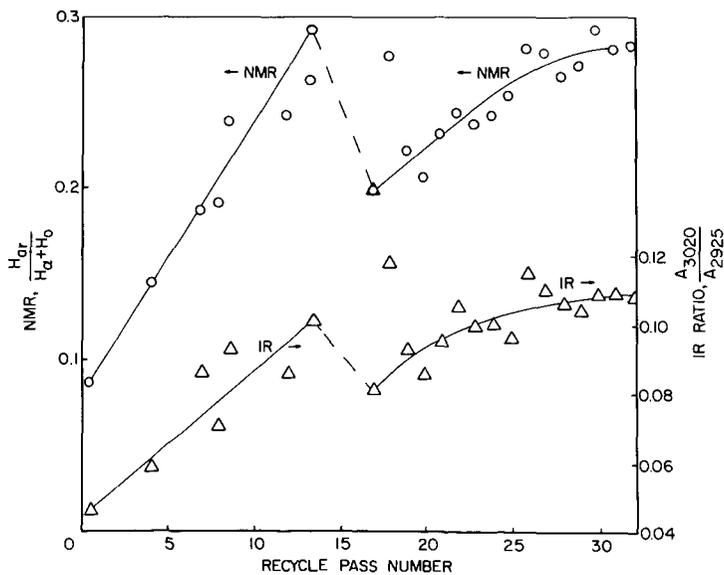


Figure 3. - Aromatic to aliphatic proton ratio by NMR and IR versus recycle pass number.

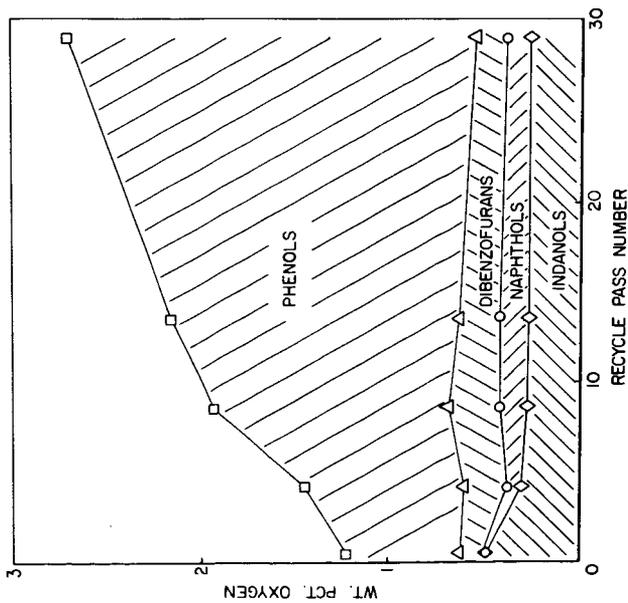


Figure 4. - Oxygen distribution in the high pressure light oils as determined by LVMS.

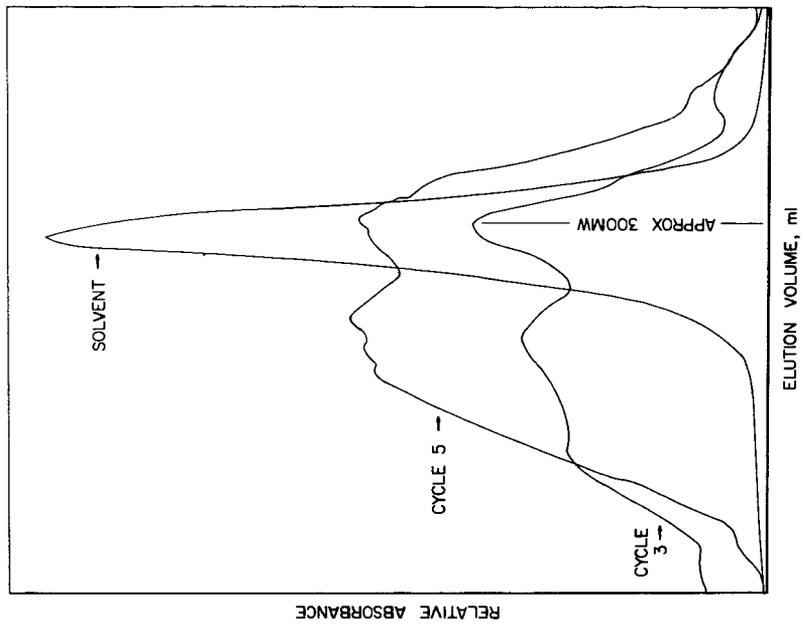


Figure 5. - Changes in the molecular weight distribution with recycle (Run 27). Detection was at 365 nm.

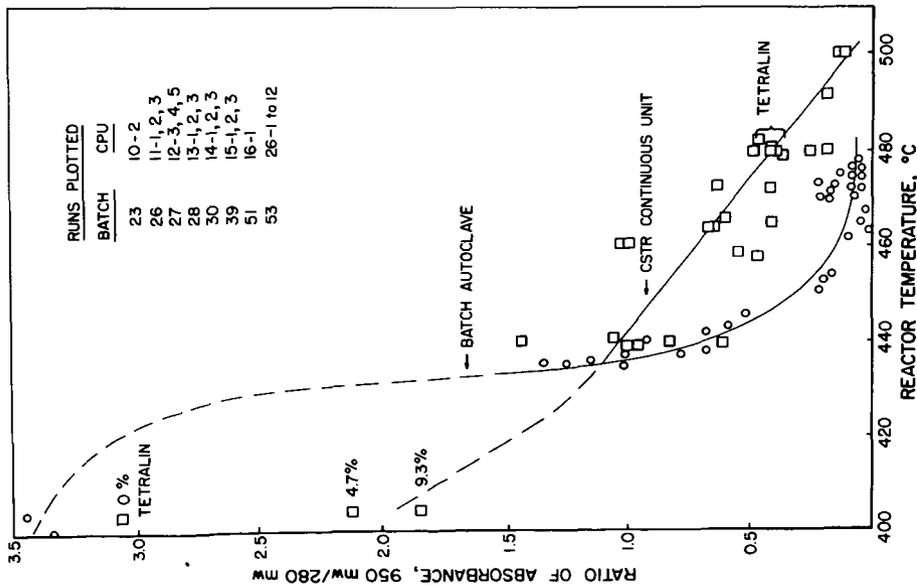


Figure 6. - Ratio of U.V. absorbance at 254 nm of 950 MW to 250 MW material versus reactor temperature for reaction times under 30 minutes.

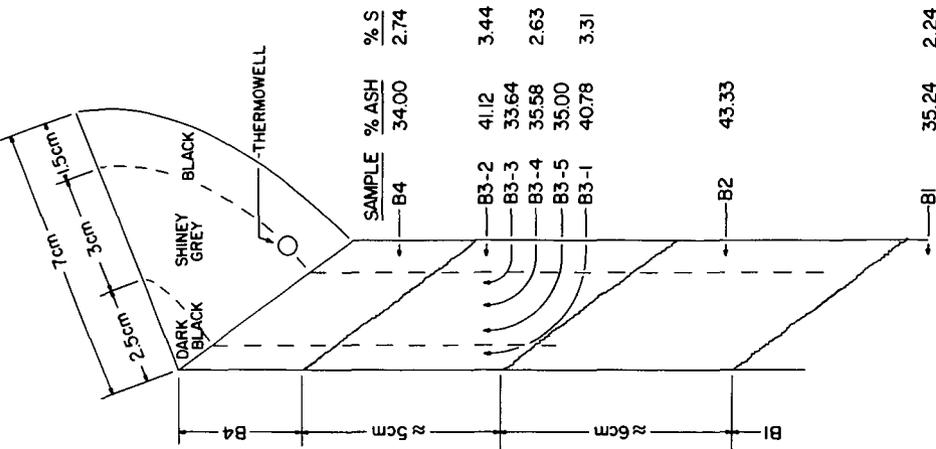


Figure 7. - Location of reactor coke samples from Run 28 and their ash and sulfur contents.