



## *Project Summary*

# **Coal Gasification/Gas Cleanup Test Facility: Volume III. Environmental Assessment of Operation with New Mexico Subbituminous Coal and Chilled Methanol**

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This report concerns the second major study carried out on a pilot-scale coal-gasification/gas-cleaning test facility: the steam-oxygen gasification of a New Mexico subbituminous coal using refrigerated methanol as the acid gas removal solvent. The report briefly describes the facility; summarizes gasifier operation using the New Mexico coal; gives results of mathematical modeling of the gasifier, detailed chemical analyses of gasifier effluent streams, and operation of the acid gas removal system using the gasifier make gas as feed; and summarizes results of mathematical model development for the acid gas absorber column. Several trace sulfur compounds and aliphatic hydrocarbons were found to distribute among all exit streams from the acid gas removal system. In addition, a wide range of simple aromatic hydrocarbons were found to accumulate in the recirculated methanol.

*This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## **Introduction**

As a part of a continuing research program on the environmental aspects of fuel conversion, the EPA has sponsored a research project on coal gasification at North Carolina State University. The facility used for this research is a small coal-gasification/gas-cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification/gas-cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters.

The plant, described in detail in Volume I (EPA-600/7-80-046a; NTIS PB80-188378) consists of a fluidized-bed reactor, a cyclone and venturi scrubber for particulates, condensables, and solubles removal, and absorption and stripping columns for acid gas removal and solvent regeneration. The plant has a nominal capacity of 23 kg/hr (50 lb/hr) of coal feed for steady state operation. Figure 1 is a schematic of the gasifier, the acid gas removal system (AGRS), and other major components.

In an initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and

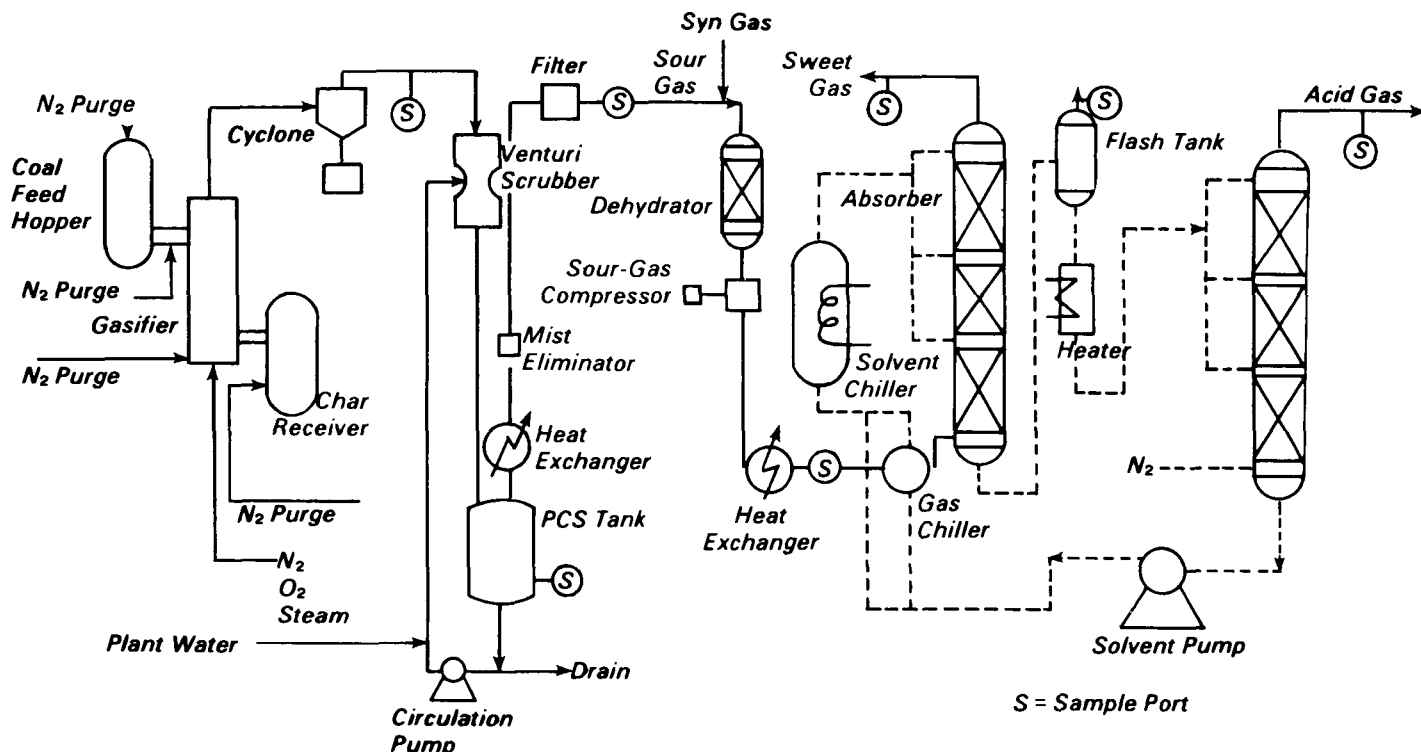


Figure 1. Pilot plant facility.

oxygen. The results of this work and a detailed list of project objectives are in Volume II (EPA-600/7-82-023).

This report concerns the second major study carried out on the facility, the steam-oxygen gasification of a New Mexico subbituminous coal using refrigerated methanol as the AGRS solvent. This coal, from the Navaho mine of the Utah International Co., was ground and screened by the Morgantown Energy Technology Center of the Department of Energy. Table 1 shows an average analysis of the char and coal used in studies to date.

This report briefly describes the facility; summarizes gasifier operation using New Mexico coal; gives results of mathematical modeling of the gasifier, detailed chemical analyses of gasifier effluent streams, and operation of the AGRS using the gasifier make gas as feed; and summarizes results of mathematical model development for the AGRS absorber.

## Results and Discussion

Fifteen gasification runs were made using the pilot plant facility with New Mexico coal. Six runs made use of the

gasifier-PCS system only, and nine runs were integrated and included the acid gas removal system.

To evaluate the ability of the system to handle the tars associated with the coal feedstock, gasifier runs were commenced by feeding mixtures of the subbituminous coal and devolatilized Western Kentucky coal char used in previous studies. The first four runs used 10, 30, 30, and 50 wt % subbituminous coal; the rest used char. After some system

modification to accommodate tars, these runs indicated that 100% New Mexico subbituminous coal could be used as a feedstock, so 100% coal was used for the rest of the runs.

Sampling and chemical analysis methods were developed for all feed and effluent streams. Methods used to sample and analyze gaseous streams were satisfactory for the major gases and for all minor components of the gaseous streams in concentrations

Table 1. Coal and Char Analysis

	Coal Char wt %	New Mexico Coal wt %
Proximate Analysis %		
Fixed Carbon	86.0	36.2
Volatile Matter	2.4	31.1
Moisture	0.9	9.7
Ash	10.7	23.0
Ultimate Analysis %		
Carbon	83.8	50.2
Hydrogen	0.6	4.2
Oxygen	2.2	20.7
Nitrogen	0.1	1.1
Sulfur	2.6	0.8
Ash	10.7	23.0

greater than a few parts per million. Detailed chemical compound analyses for solid and liquid streams are generally satisfactory, but are still under development.

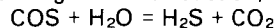
A major effort was made to develop methods to detect trace metal elements in the feed and effluent streams. Methods now used for As analysis are satisfactory, both for ease of application and reliability. The main problem with As is the ineffectiveness of the impinger solutions in trapping it from the gas stream. Reproducibility of Pb concentration measurements has been less than satisfactory, although considerable improvement has been made recently by diluting all samples to fall within the linear range of the atomic absorption spectrometer calibration, and by adding dibasic ammonium phosphate to the injected sample, thereby binding the Pb and enabling higher charring temperatures. The cold-vapor technique used for Hg is satisfactory; the main difficulty with Hg is its volatility: samples must be analyzed soon after they are taken.

The most important quality assurance test for the evaluation of the experimental data was good closures on the mass balances for total mass and for all major elements. In general, the mass balance results for both the gasifier-PCS and the acid gas removal systems are excellent: they indicate no gross errors in either chemical analyses or mass flow measurements. Frequent calibration checks were necessary to achieve the mass balance results shown.

Reactor temperature and steam-to-carbon feed ratio were the main operating parameters varied for the gasifier: results show that the make gas flow rate and the carbon conversion both increase with increasing temperature. This increase is expected: the degree of devolatilization and the gasification reaction rates all increase with increasing temperature. Although the effects of operating parameters on reactor performance are not easily determined directly from the experimental data, a mathematical model developed in this study correlates run results reasonably well, and is useful in evaluating the effects of operating parameters.

Previous studies with a char feed indicated that the sulfur conversion could be roughly estimated by assuming it to equal the carbon conversion. For New Mexico coal, this crude approximation also seems applicable. In addition,

results of a detailed analysis of the reactor make gas for the various sulfur gases indicate that the distribution between H<sub>2</sub>S and COS may be predicted by assuming that the reaction,



is at equilibrium at the temperature above the fluidized bed. Figure 2 shows the equilibrium constant ( $K_1$ ) for this reaction plotted versus the temperature at the top of the fluidized bed for both the char and the coal runs.

The gasification of New Mexico coal produces many hydrocarbon gases. Aliphatics up to butene and butane and simple aromatic compounds have been detected in the gasifier make gas stream. Analyzing these hydrocarbon emission rates indicates that they generally increase with increasing reactor bed temperature. Table 2 shows the gas compositions measured at six gas sample locations shown on Figure 1.

After leaving the PCS system, the reactor make gas is compressed to about 3610 kPa (525 psig) and then cooled to approximately 10°C. During this process higher molecular weight compounds in the gas stream in very low concentrations are condensed and separated from the gas in a knockout drum. This drum eliminates pressure

fluctuations at the sour gas flow meter and also collects liquids which may condense after compression and cooling.

A sample of this liquid was collected after Run GO-79 and was analyzed by GC-MS. The mass spectrogram is shown in Figure 3; results of compound identification are listed in Table 3. While a variety of hydrocarbon compounds were found in this liquid, no aromatic compounds heavier than substituted benzenes were found. This fact, together with results of analyses of the methanol AGRS solvent, indicates that no detectable polynuclear aromatic compounds are in the gases leaving the PCS system.

No unusual results were noted from the proximate and ultimate analyses of the solid streams; however, the ultimate analysis of the spent char generally correlates with gasifier run conditions. For example, higher temperatures result in higher carbon conversions and a lower carbon content in the spent char.

The tars collected from the cold trap downstream from the cyclone were subjected to a solvent partitioning scheme to separate them into groups of compounds of varying polarities. The groups were then quantified as to their wt % contribution to total tar composition. In addition to the partitioning

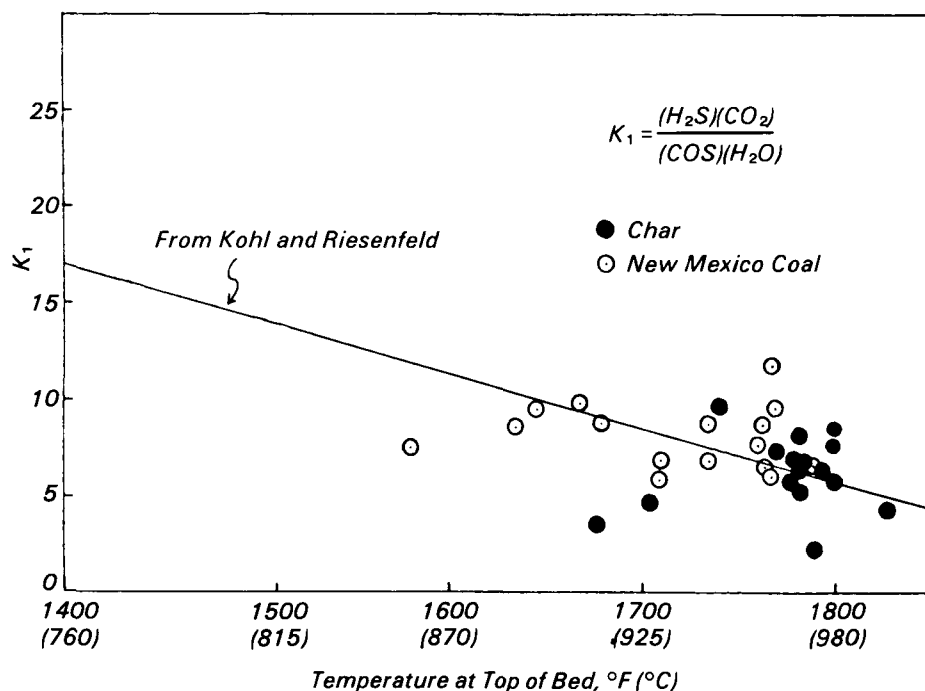


Figure 2. Comparison of experimental values of  $K_1$  with data of Kohl and Riesenfeld.

**Table 2.** Gas Analysis Summary for AMI-60/GO-79

Species	Sample Train	PCS Tank	Sour Gas	Sweet Gas	Flash Gas	Acid Gas
H <sub>2</sub>	32.13	32.57	32.60	43.01	21.55	—
CO <sub>2</sub>	21.68	21.82	21.68	—	27.16	63.82
Ethylene	0.30	0.30	0.32	0.065	0.69	0.95
Ethane	0.33	0.33	0.36	0.081	0.82	1.03
H <sub>2</sub> S	0.206	0.174	0.214	0.026	0.108	0.597
COS	0.0084	0.0078	0.0084	0.0019	0.0044	0.0233
N <sub>2</sub>	21.33	20.62	20.71	27.62	24.40	24.71
CH <sub>4</sub>	6.78	6.65	6.61	7.44	—	2.60
CO	17.06	17.17	17.25	21.90	25.18	2.06
Benzene	N/A	0.0272	0.0391	—	—	0.0592
Toluene	N/A	0.0278	0.0393	—	—	—
Ethyl Benz.	N/A	N/A	N/A	N/A	N/A	N/A
Xylenes	N/A	N/A	N/A	N/A	N/A	N/A
Thiophene*	99	97	83	—	—	13
CH <sub>3</sub> SH*	37	29	35	—	—	26
C <sub>2</sub> H <sub>5</sub> SH*	1	1	2	—	—	65
Carbon disulfide*	2	2	2	—	1	5
Propylene*	925	940	1012	212	381	1053
Propane*	273	277	314	66	364	5004
Butane*	451	1730	224	—	145	434
Methanol**	—	—	—	—	—	3.49

\*Parts per million (volume)

\*\*Estimated

**Table 3.** Compressor Knockout Sample from AMI-60/GO-79 Peak Numbers from Figure 3

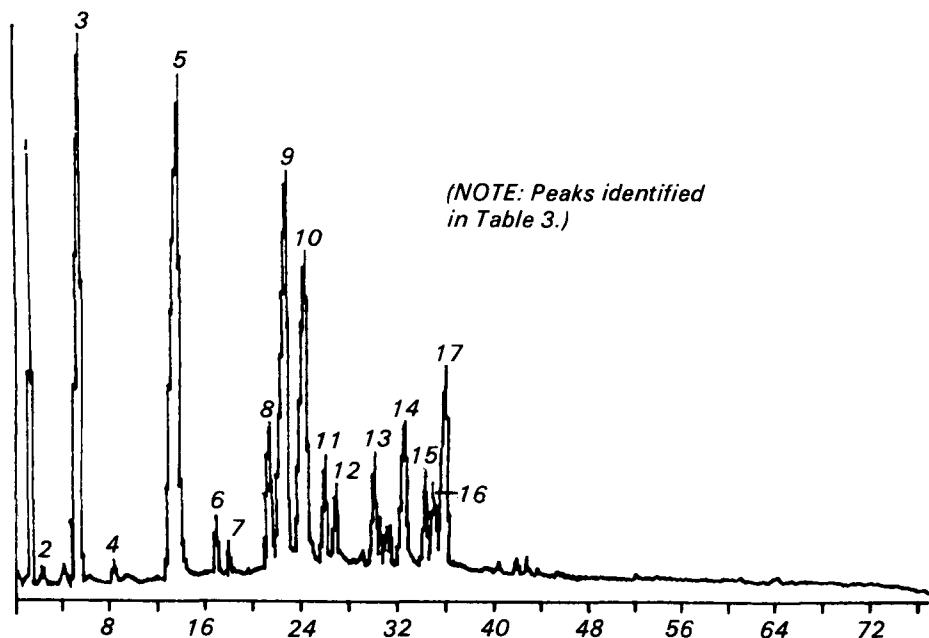
1.	1-pentene
2.	Hydrocarbon
3.	Benzene
4.	Hydrocarbon
5.	Toluene
6.	Cyclo C4-C5
7.	Hydrocarbon
8.	Ethyl benzene
9.	Dimethyl benzene
10.	Substituted benzene
11.	C <sub>8</sub> hydrocarbon
12.	C <sub>9</sub> hydrocarbon
13.	Propyl or ethyl methyl substituted benzene
14.	Propyl or ethyl methyl substituted benzene
15.	1-decene
16.	2-propyl benzene
17.	1-ethyl-4-methyl benzene

The analyses of the tars indicate that a significant amount of PAHs is in the gas stream as it leaves the reactor, and emerge primarily in the stream condensed by the venturi scrubber. Compounds with boiling points higher than that of naphthalene do not seem to be in the gas stream past the PCS system.

The concentrations of various species in the water condensate from the sample train were normalized to determine rates of evolution in milligrams per kilogram of coal fed to the gasifier. No clear trends with reactor temperature are evident, indicating that (for the temperature range covered) the reactor temperature has little effect on the emission rates of wastewater species.

Water samples were analyzed by high-performance liquid chromatography (HPLC) for phenolics. The sample preparation consisted of filtering to remove particulates prior to direct injection into the HPLC. The results, shown in Table 7, are not reported as specific phenolic compounds, but are categorized as phenols, cresols, and xylenols. Also, the samples (except GO-70) were analyzed for total organic extractables. A methylene chloride extraction was performed and the extract evaporated to dryness to determine the weight percent of organic extractables in the sample.

In addition, both the trap water and water from the PCS tank were analyzed by standard methods. Table 8, summarizing these results, shows average values for all runs, general levels of



**Figure 3.** GC/MS scan of compressor knockout condensate for AMI-60/GO-79.

analysis, the tars were analyzed for polynuclear aromatic hydrocarbons (PAHs) and organic sulfur compounds. The PAHs were analyzed by glass capillary gas chromatography with a

flame ionization detector; the sulfur-containing species were analyzed by gas chromatography with a flame photometric detector. Tables 4, 5, and 6 show results of these analyses.

**Table 4. Tar Partition Results\***

	GO-69B PCS	GO-70 PCS	GO-76 Trap	GO-76 PCS	GO-78 Trap
Acids	10.9	34.7	16.5	11.2	17.29
Bases	20.9	27.5	4.7	6.7	6.05
TOTAL NEUTRALS	68.3	37.7	78.8	80.1	76.66
Non polar	25.1	5.5	24.7	30.0	11.53
PAHs	36.0	26.7	10.7	11.5	26.85
Polar	7.2	5.5	15.3	15.2	16.45
Cyclohexane Insolubles	—	—	28.1	23.4	21.83

\*wt %

**Table 5. Capillary GC Tar Analyses\***

No.	Compound	GO-69B PCS	GO-76 Trap	GO-76 PCS	GO-78 Trap
1	Phenol	0.15	—	—	—
2	Indene	0.87	—	—	—
3	Naphthalene	3.50	2.11	1.30	2.10
4	Benzothiophene	0.13	0.09	0.06	0.08
5	Quinoline	0.08	0.16	0.09	0.13
6	2-Methylnaphthalene	1.60	0.79	0.60	0.97
7	1-Methylnaphthalene	1.10	0.52	0.37	0.81
8	Biphenyl	0.36	0.16	0.14	0.28
9	Acenaphthylene	1.50	0.71	0.53	0.60
10	Acenaphthene	0.57	0.34	0.30	0.26
11	Dibenzofuran	0.74	0.53	0.46	0.53
12	Fluorene	1.00	0.53	0.51	0.43
	Dibenzothiophene	0.09	0.07	0.08	0.09
13	Phenanthrene	1.30	0.62	0.67	0.47
14	Anthracene	0.73	0.38	0.32	0.49
15	Fluoranthene	0.45	0.36	0.32	0.23
16	Pyrene	0.32	0.26	0.25	0.17
17	Benzo(a)anthracene	0.09	0.16	0.07	0.05
18	Chrysene	0.14	0.13	0.09	0.04
19	Triphenylene	0.14	0.06	0.03	0.02
20	Benzo(b)Fluoranthene	0.04	0.11	0.05	0.013
21	Benzo(k)Fluoranthene	0.02	0.06	0.01	0.007
22	Benzo(e)Pyrene	0.05	0.05	0.01	0.007
23	Benzo(a)Pyrene	0.04	0.11	0.03	0.015
24	Perylene	0.02	0.05	0.01	0.01
	Total Wt%	15.03	8.36	6.30	7.802

\*wt %

concentrations found, and differences between the two kinds of samples collected.

Efforts continued to determine the fate of several of the more volatile trace metal elements in the feed coal. Closures on As mass balances consistently vary between 35% and 70%, suggesting that a significant fraction of this substance is passing undetected from the system, either in the gas phase or adsorbed on fine particles that are not trapped by the cold trap or impingers. Similar results are obtained for Pb, for which closures never exceeded 34%,

indicating a higher volatility for this element.

The problem with Hg is reproducibility, rather than failure to detect a portion of the total emitted element. The quantity of Hg appearing in the trapped tar and solids varies dramatically from one run to another. In some instances the apparent amount of Hg in one stream or other exceeds the quantity fed in with the coal.

To aid in formulating gasifier performance correlations, a simple mathematical model of the fluidized bed gasifier has been developed which considers

the gasification process in three stages: instantaneous devolatilization of coal at the top of the fluidized bed, instantaneous combustion of carbon at the bottom of the bed, and steam/carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage. The model is significant in and of itself, but its particular importance to the project is that it enables the specification of gasifier conditions required to produce a feed to the acid gas removal system with a predetermined flow rate and composition.

Using optimal parameter values, the model was run for all gasifier runs and gave excellent predictions of carbon conversion, dry make gas flow rate, and the production rate of all major gases. Figure 4 shows an example. The model does a good job of correlating data on the evolution of individual species and may be used to predict the composition of the gasifier make gas for a specified set of reactor conditions, and also to study the effects of individual reactor variables on yield.

Results from the acid gas removal system show that refrigerated methanol is an effective solvent for cleaning gases produced by coal gasification. CO<sub>2</sub>, COS, and H<sub>2</sub>S can be removed to sufficiently low levels with proper choice of operating conditions and effective solvent regeneration.

The presence of several trace sulfur compounds, mercaptans, thiophenes, organic sulfides, and CS<sub>2</sub>, complicates the gas cleaning process. These compounds were found to distribute among all exit streams from the AGRS. Since no provision was made to treat these sulfur gases, they may be emitted to the atmosphere and must be dealt with to avoid significant environmental problems (see Table 2).

A wide variety of aliphatic and aromatic hydrocarbons are present in the gas stream fed to the AGRS. The aliphatic hydrocarbons, from methane to butane, cover a wide range of solubilities. Their presence in all AGRS streams must be anticipated to prevent their emission to the atmosphere.

While a wide range of simple aromatics were identified in the gas stream fed to the AGRS, essentially no polynuclear aromatic compounds were found. Apparently, the gas quenching process effectively removes these compounds from the gasifier product gas. However, significant quantities of simple aromatics were found to accumulate in the recirculating methanol increasing the

**Table 6. Quantitative Analysis of Sulfur Species\***  
(Tar Sample, Run GO-69B)

No.	Compound	Concentration
1	Thiophene	0.01
2	Methylthiophenes	0.02
3	C <sub>2</sub> -thiophenes	0.03
4	C <sub>3</sub> -thiophenes	0.03
5	Benzothiophene	0.13
6	C <sub>1</sub> -benzothiophenes	0.05
7	C <sub>2</sub> -benzothiophenes	0.06
8	C <sub>3</sub> -benzothiophenes	0.05
9	Dibenzothiophenes	0.09
10	Naphthothiophenes	0.08
11	Phenanthrothiophenes	0.06
12	Naphthobenzothiophenes	0.09
	Total	0.70

\*wt %

**Table 7. Water Analyses\***

	GO-69B PCS	GO-70 PCS	GO-76 Trap	GO-76 PCS	GO-78 Trap
Phenols	870	637	1250	220	1584
Cresols	690	398	693	166	783
Xylenols	230	881	161	97	510
Organic extractables	1620		2040	460	1900

\*mg/l

**Table 8. Water Analysis for All Runs\***

	PCS water	Trap water
Ammonia	700	6,000
Carbon	725	3,200
Chloride	20	40
COD	1,500 - 3,000	6,000 - 10,000
Cyanate	500	2,000 - 5,000
Cyanide	45	25 - 200
Fluoride	5	10
Nitrogen	600	6,000
pH	7.7	8.5
Phenolics	200 - 400	600 - 1,100
Sulfate	35	40 - 300
Sulfite	15	40
Thiocyanate	50	250
TOC	400 - 600	2,600
TVC	325	1,500

\*mg/l (except pH); values shown are averages or minimum-maximum values.

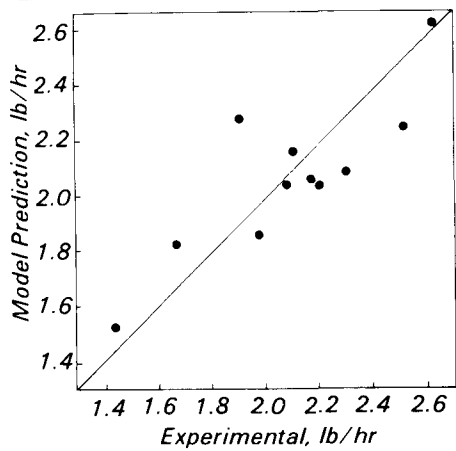
potential for their discharge to the atmosphere. Provision must be made to purge the solvent of these compounds or to remove them prior to the AGRS through cold traps. Table 9 shows results of a GC/MS scan of a sample of the methanol solvent taken at the stripper exit after Run GO-76.

In an environmental context, use of refrigerated methanol as an acid gas removal solvent for coal gas cleaning must be accompanied by safeguards to avoid several potential problems. The need for polishing steps on any discharge stream appears necessary because of the wide distribution of several potential

pollutants throughout the AGRS. The nature and design of these polishing steps will depend on the required discharge levels of specific pollutants manufactured in the gasification process.

As a part of the AGRS research program, a mathematical model of the absorber was developed. The model assumes adiabatic operation of the column and uses appropriate mass and energy balances, physical and transport property information, and phase equilibrium relationships to simulate steady-state behavior of the absorber. The model was tested by comparing its predictions with experimental data for runs made with a mixture of nitrogen and CO<sub>2</sub> only (syngas runs) and with reactor make gas from the PCS system.

For the syngas runs the measured and predicted liquid temperature profiles showed excellent agreement. For runs using reactor make gas there was very good agreement between the predicted and experimental concentrations for most compounds. However, experimental data and model predictions for H<sub>2</sub>S, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> show some small differences. These differences were shown to be related to the fact that the entering methanol was not adequately stripped and contained some H<sub>2</sub>S (input data to the model assumed that clean methanol was fed to the column). The difference between the values for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> may be related to the fact that Henry's law does not provide an accurate correlation of vapor/liquid equilibrium data for these species. Figure 5 gives examples.



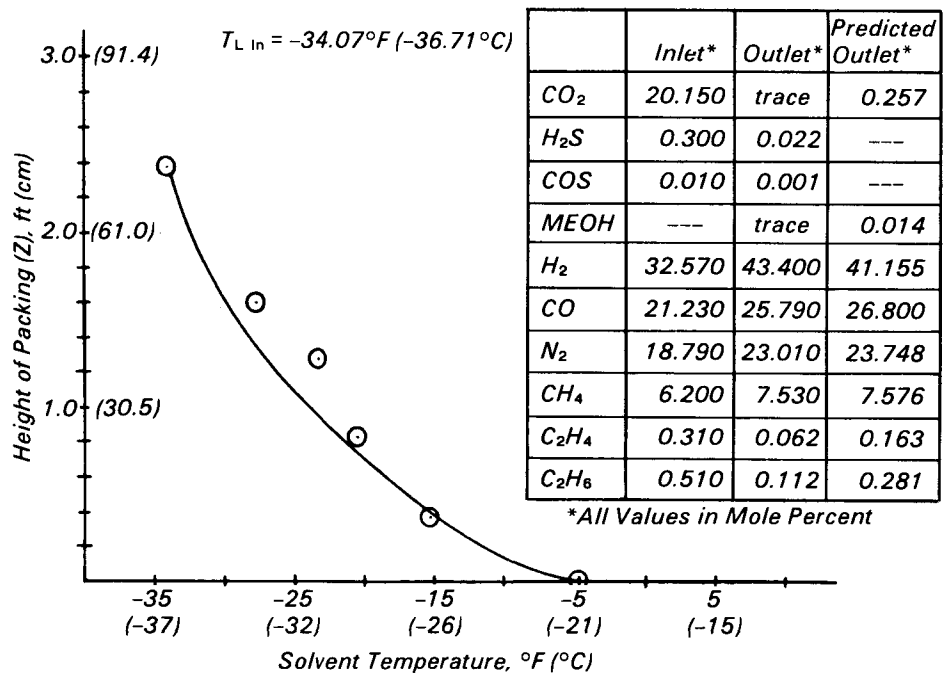
**Figure 4.** Predicted vs. experimental production rate of  $H_2$  from gasification of New Mexico coal.

**Table 9.** AMI-57/GO-76 Stripper Exit Methanol

1. S at'd hydrocarbon
2.  $CO_2$
3.  $C_4H_8$  isomer
4. Tetramethylsilane
5. Trichlorofluoromethane
6.  $C_5H_{10}$  isomer
7. Unknown
8. Freon 113
9. Cyclopentadiene
10.  $C_6H_{12}$  isomer
11.  $C_6H_{14}$  isomer
12.  $C_6H_{10}$  isomer
13. Benzene
14.  $C_7H_{14}$  isomer
15.  $C_7H_{16}$  isomer
16.  $C_7H_{16}$  isomer
17.  $C_7H_{12}$  isomer
18.  $C_7H_{12}$  isomer
19.  $C_7H_{12}$  isomer
20. Unknown hydrocarbon
21. Toluene
22. Methyl thiophene isomer
23.  $C_8H_{16}$  isomer
24.  $C_8H_{16}$  isomer
25.  $C_8H_{16}$  isomer
26.  $C_8H_{16}$  isomer (trace)
27.  $C_8H_{14}$  isomer (trace)
28. Hexamethyl cyclotrisiloxane
29.  $C_9H_{20}$  isomer
30.  $C_9H_{18}$  isomer
31. Ethyl benzene
32. Xylene (M,P)
33. Styrene
34. Xylene (O)
35.  $C_9H_{18}$  isomer
36.  $C_9H_{20}$  isomer

**Table 9.** (Continued)

37.  $C_3$  alkyl benzene
38.  $C_{10}H_{22}$  isomer
39. Unknown hydrocarbon
40. Unknown hydrocarbon
41.  $C_{11}H_{24}$  isomer
42.  $C_3$  alkyl benzene
43.  $C_3$  alkyl benzene
44.  $C_{10}H_{22}$  isomer
45.  $C_{10}H_{22}$  isomer
46.  $C_4$  alkyl benzene
47.  $C_{10}H_{22}$  isomer
48.  $C_{10}H_{20}$  isomer
49. Unknown hydrocarbon
50.  $C_9H_{10}$
51.  $C_9H_8$  isomer
52. Alkyl benzene isomer
53.  $C_{11}H_{24}$  isomer
54.  $C_8H_{10}O$  isomer
55.  $C_{11}H_{24}$  isomer
56.  $C_8H_{10}O$  isomer
57. Unknown siloxane
58. Unknown siloxane
59. Unknown siloxane
60.  $C_{14}H_{30}$  isomer
61.  $C_{14}H_{30}$  isomer
62. Unknown
63.  $C_{15}H_{32}$  isomer



**Figure 5.** AMI-43/GO-68B ONDA correlation.

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*The complete report, entitled "Coal Gasification/Gas Cleanup Test Facility: Volume III. Environmental Assessment of Operation with New Mexico Sub-bituminous Coal and Chilled Methanol," (Order No. PB 83-107 417; Cost: \$19.00, subject to change) will be available only from:*

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