

GAS CHROMATOGRAPHIC METHODS DEVELOPED ON THE
BCR TWO-STAGE SUPER-PRESSURE
GASIFICATION PROGRAM

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INTRODUCTION

Under a project sponsored by the Office of Coal Research, Bituminous Coal Research, Inc., (BCR) has been developing a two-stage super-pressure process for coal gasification. (1) The development work began with a small high-pressure rocking autoclave, then was transferred to a 5 lb/hr externally-heated continuous flow reactor (1), and now is being scaled up to a 100 lb/hr internally-fired process and equipment development unit.

Fixed gases plus some light hydrocarbons comprise the principal products of interest from this coal gasification process. Their composition varies with the experimental conditions and upon the kind and amount of inert gas used. For rigorous interpretation of results of the gasification experiments, accurate determination of the product gas composition is a prerequisite. The analytical methods employed have to be not only accurate but also rapid and simple to meet the desired time schedule.

At the outset, a search of the technical literature for suitable methods revealed several procedures using gas-solid or/and gas-liquid chromatography which might be suitable. (2,3,4) Unfortunately, they were found to be either too complicated and time consuming, or did not determine all the desired components. This paper describes the three gas chromatographic methods and two sampling devices which have been developed for the analysis of the various product gases obtained on the coal gasification program.

EXPERIMENTAL

A. Methods for Batch Autoclave Tests

In the batch autoclave experiments, small quantities of a coal slurry were injected into a preheated autoclave that was partially pressurized with nitrogen. At the end of the reaction period, the product gas was exhausted at atmospheric pressure and room temperature to an all-glass gas holder using additional nitrogen as a purge gas. (1)

The nature of this product gas was thoroughly studied by both gas-solid and gas-liquid chromatography. It was found to be composed of H₂ (major), CO₂ (major), CH₄ (major), CO (minor), C₂H₆ (minor to trace), C₂H₄ (trace to 0), C₃H₈ (trace to 0), and H₂S (trace). Because nitrogen was used to purge the autoclave before and after gasification, it was also present in the product in varying quantities.

Based on the composition of the product gas, a G.C. method, using an 11.5-ft silica gel column, was developed to determine all components except H_2S . The trace quantity of H_2S was determined separately by conventional iodometric titration.

1. Sample Collection: For the batch autoclave tests, gas samples were taken from the gas holder at normal pressure and collected in 500 ml glass tubes using 15 percent H_2SO_4 in saturated Na_2SO_4 solution as the confining liquid.

2. Analytical Method: After being conditioned by removal of H_2S by absorption in $CdCl_2$ and of H_2O by adsorption on Drierite, the gas sample (0.5 ml) is injected into an 11.5-ft silica gel column operated at 50 C, with 50 ml/min of helium carrier gas. Changes in composition of the column effluent as detected by a thermoconductivity cell are automatically recorded. From the resultant chromatogram, the amounts of the individual components are calculated. (5) A chromatogram of a synthetic mixture produced on such a column is shown in Figure 1.

The analysis of a single sample required about 35 minutes, including the conditioning of the sample. Six samples or more can be analyzed in duplicate during a normal working day.

3. Discussion of Results: The composition of a number of gaseous products collected at room temperature from the autoclave experiments, as determined by this G.C. method is listed in Table 1 together with similar data by Orsat method for comparison. The results obtained with the two methods for CH_4 , C_2H_6 , and H_2 are not in agreement. By the Orsat method, CO_2 , O_2 , total olefins, and CO were determined by absorption; H_2 and CH_4 by slow combustion and absorption; and, lastly, N_2 was determined by difference. The H_2 and CH_4 values by this Orsat method were accurate only when the sample contained no other saturated hydrocarbons. If C_2H_6 or any other saturates were present, they were combusted and estimated together with CH_4 , making the observed values for CH_4 high and those for H_2 low. Thus, when a significant amount of C_2H_6 was present as in these samples, the CH_4 and H_2 values were not as accurate as those determined by the G.C. method.

Precision of the G.C. method using the 11.5-ft silica gel column in an F & M Model 720 gas chromatograph was determined by replicate analyses of a mixture containing 15 percent H_2 , 1.0 percent CO , 20 percent CO_2 , 35 percent CH_4 , 2 percent C_2H_6 , and 0.5 percent C_2H_4 (balance helium). From six analyses, the absolute standard deviations were estimated as 0.420 (H_2), 0.042 (CO), 0.212 (CO_2), 0.230 (CH_4), 0.234 (C_2H_6), and 0.030 (C_2H_4). These deviations are small; therefore, the precision of the G.C. method is high.

B. Methods for 5 lb/hr Continuous Flow Reactor (CFR) Tests

In the 5 lb/hr continuous reactor, coal is gasified under conditions simulating those that prevail in Stage 2 of the two-stage super-pressure gasifier. In these experiments, coal entrained in a simulated Stage 1 gas (CO , H_2 , CO_2 , H_2O) is partially gasified by passage through an externally-heated metal reactor at elevated pressures. (1)

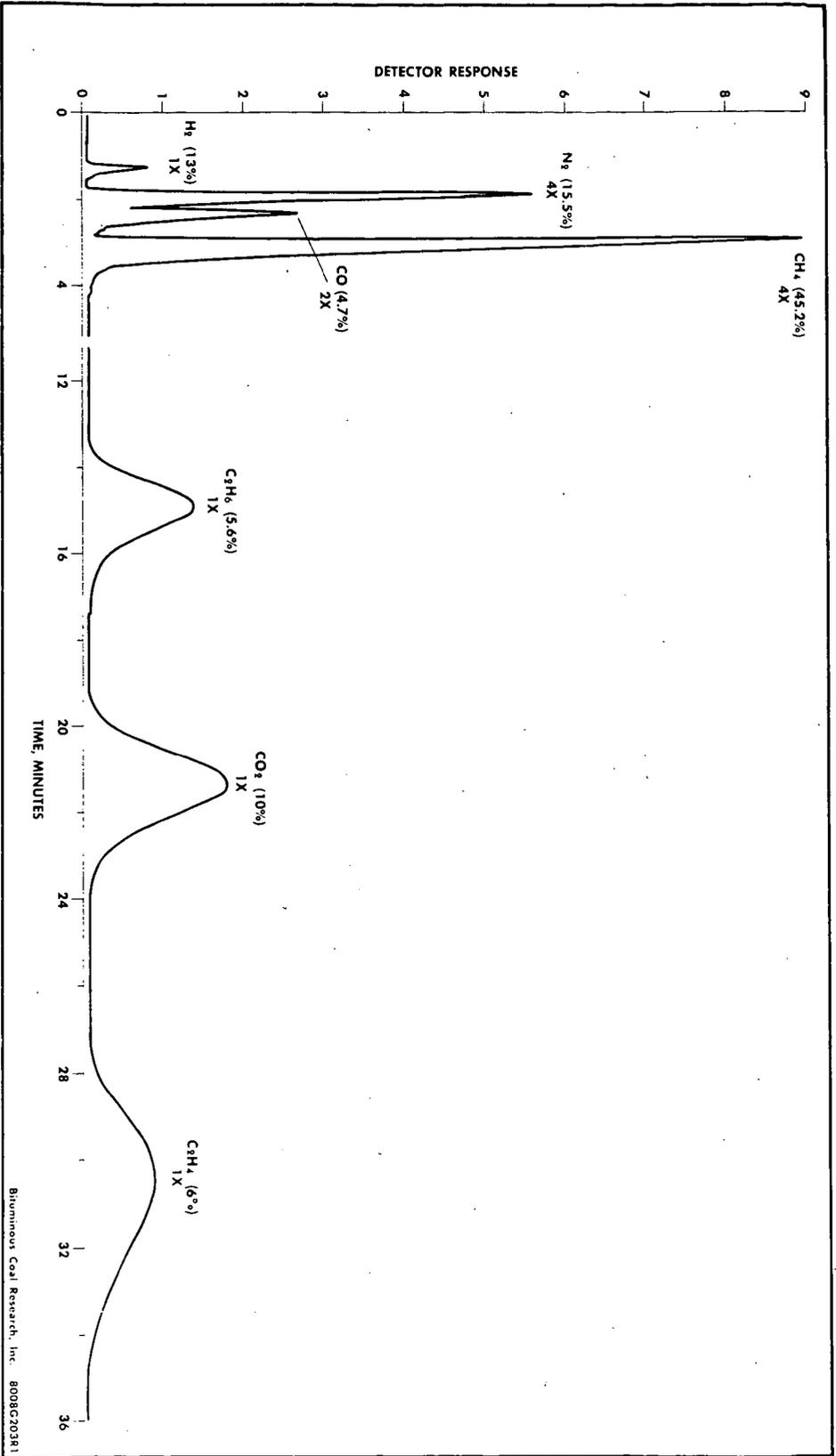


Figure 1. Chromatogram of a Mixture on the 11.5 ft Silica Gel Column

TABLE 1. COMPARISON OF G.C. ANALYSIS AND ORSAT ANALYSIS OF COAL GAS SAMPLES FROM AUTOCLAVE EXPERIMENTS

COMPONENT, VOLUME PERCENT

Sample No.	H ₂		O ₂		CO		CO ₂		CH ₄		C ₂ H ₆		C ₃ H ₈		N ₂			
	GC	Orsat	GC	Orsat	GC	Orsat	GC	Orsat	GC	Orsat	GC	Orsat	GC	Orsat	GC	Orsat		
202	22.2	23.3	0.3	0.4	1.7	1.9	22.4	22.0	48.4	47.6	0.5	-	0.5	0.6	tr	-	4.0	4.2
212	31.2	33.0	0.4	0.5	1.5	1.8	24.2	25.2	38.1	33.4	tr	-	tr	0.3	0	-	4.6	5.8
222	32.0	36.0	0.2	0.2	2.8	3.5	17.1	18.0	40.5	35.7	0.1	-	0.5	0.6	0	-	6.8	6.0
342A	7.1	5.3	-	0	4.1	4.0	3.4	3.7	21.2	26.4	3.1	-	1.1	1.3	<0.05	-	60.0	59.3
342B	21.2	23.8	0	0.2	1.2	1.3	17.3	19.7	42.5	41.5	0.3	-	tr	0.3	0	-	17.5	13.2
382A	14.9	13.3	0	0.1	3.0	2.9	10.4	11.7	41.5	47.3	2.9	-	0.5	0.5	<0.05	-	26.8	24.2
382B	22.9	25.5	0	0	1.6	1.6	21.6	21.2	40.7	38.2	0.2	-	tr	0.4	0	-	13.0	13.1
382C	23.9	26.9	0	0.2	1.3	1.4	21.9	21.0	39.8	37.7	tr	-	0	0.2	0	-	13.1	12.6
392A	12.8	8.4	0	0.2	0.3	0.3	12.4	15.0	30.1	37.8	4.6	-	1.0	0.8	tr	-	38.8	37.5
392B	29.0	30.0	0	0.2	2.1	2.0	21.4	25.0	33.0	29.6	0.2	-	tr	0.4	0	-	14.3	12.8
412A	16.9	15.7	0	0.1	0.5	0.6	17.6	19.2	36.6	38.5	2.5	-	0.1	0.3	0	-	25.8	25.6
412B	19.3	11.2	0	0.1	0.6	0.7	15.9	18.8	32.2	39.0	3.5	-	tr	0.6	0	-	28.5	29.6
412C	23.9	25.5	0	0.2	1.2	1.2	22.8	24.5	36.9	33.3	0.4	-	0	0.3	0	-	14.8	15.0

tr = trace

* as olefin

To enable calculation of material balances, argon gas was added to the simulated Stage 1 gas as an internal reference and thus constituted a major component of the product gas. Other major components of the dry product gas were H_2 , CO , CO_2 , CH_4 , and sometimes N_2 from the purge gas. Minor to trace components were C_2H_6 , C_2H_4 , and H_2S . The trace amounts of H_2S were determined by the conventional iodometric titration, as in the analysis of the autoclave products. As the 11.5-ft silica gel column does not resolve mixtures of A, N_2 , and O_2 , the presence of argon precluded the procedure for batch autoclave samples from being applied to samples from the 5 lb/hr flow reactor tests. New procedures, therefore, were developed.

1. Sampling System: At the sampling point of the flow reactor, the product gas was already quenched with water and reduced in pressure from about 1000 psi down to 10 to 40 inches of water.

The sampling method for the 5 lb/hr reactor was essentially the same as for the autoclave, except that several glass sampling bulbs were connected in parallel to a common manifold in such a way that several samples could be collected at two minute intervals during each test. This system was found very satisfactory at this pressure range.

2. Analytical Methods: Under normal operating conditions, there was no O_2 in the product gas from the 5 lb/hr CFR tests. However, at times air becomes admixed with the sample and an accurate method for determining O_2 as well as A was required. A molecular sieve column separates A and N_2 at room temperature, but not A and O_2 . To solve this problem, a method using a differential technique was developed for the determination of these two components using only the 6-ft molecular sieve 5A column.(6) The overall G.C. method as finally developed for analysis of the product gas involved two columns: a 3-ft silica gel column and a 6-ft molecular sieve 5A column. On the silica gel column, CO_2 , C_2H_6 , and C_2H_4 were measured, and on the molecular sieve, using the differential technique, H_2 , A, O_2 , N_2 , CH_4 , and CO .

However later, significant loss of CO_2 to the confining liquid in the sampling system was observed whenever the CO_2 concentration in the sample was higher than 20 percent; this was found to occur even when the confining liquid was 15 percent H_2SO_4 saturated with Na_2SO_4 . It was found that for samples containing 25 percent CO_2 , the observed value was only 22-23 percent, and for those having 35 percent CO_2 , the observed value was 31-32 percent. To avoid this error, CO_2 was determined separately by the Orsat apparatus before gas chromatography on dual columns in an F & M Model 700-231 gas chromatograph.(5)

a. Determination of CO_2 : Prior to gas chromatography, a separate analysis of CO_2 is made by conventional Orsat procedures.

Immediately after sampling, the sampling tube contains gas at a pressure slightly higher than 1 atmosphere with less than 5 ml confining liquid saturated with CO_2 from the sample left inside. The first portions of the sample are released for CO_2 determination without admitting additional confining liquid into the tube. The observed CO_2 result so obtained represents the true concentration in the sample.

b. Preconditioning of sample for gas chromatography: Prior to gas chromatography, the sample is preconditioned by passage through a CdCl_2 absorbent to remove H_2S and then through a Drierite tube to remove H_2O . (5)

The sample is not processed to remove CO_2 prior to being measured for chromatography as a CO_2 absorption unit (Indicarb cartridge) may be connected to the system between the inlet valve and the column as desired.

c. Determination of C_2H_6 and C_2H_4 : A portion (0.5 ml) of the preconditioned dry, H_2S -free gas sample is analyzed for C_2H_6 and C_2H_4 using the 3-ft silica gel column operated at 50 C with 50 ml/min helium carrier gas and with automatic recording of changes in composition of the column effluent. A typical chromatogram is shown in Figure 2A.

d. Determination of H_2 , A, O_2 , N_2 , CH_4 , and CO: Another portion (0.5 ml) of the preconditioned gas sample is analyzed for H_2 , A (or O_2), N_2 , CH_4 , and CO using the 6-ft molecular sieve 5A column located in the same oven and operated under the same conditions as for the silica gel column in (c) above. A typical chromatogram is shown in Figure 2B.

e. Calculation of sample composition: The overall composition of the sample on a dry, H_2S -free basis is calculated as follows:

- (1) Percent CO_2 as determined by Orsat
- (2) Percent of other components by normalization of the values from gas chromatography to the CO_2 -containing basis, using the formula:

$$f_n = \frac{100 - \text{CO}_2\% \text{ (from Orsat)}}{(\text{H}_2 R\% + \text{N}_2 R\% + \text{CH}_4 R\% + \text{-----})}$$

where

f_n = normalization factor

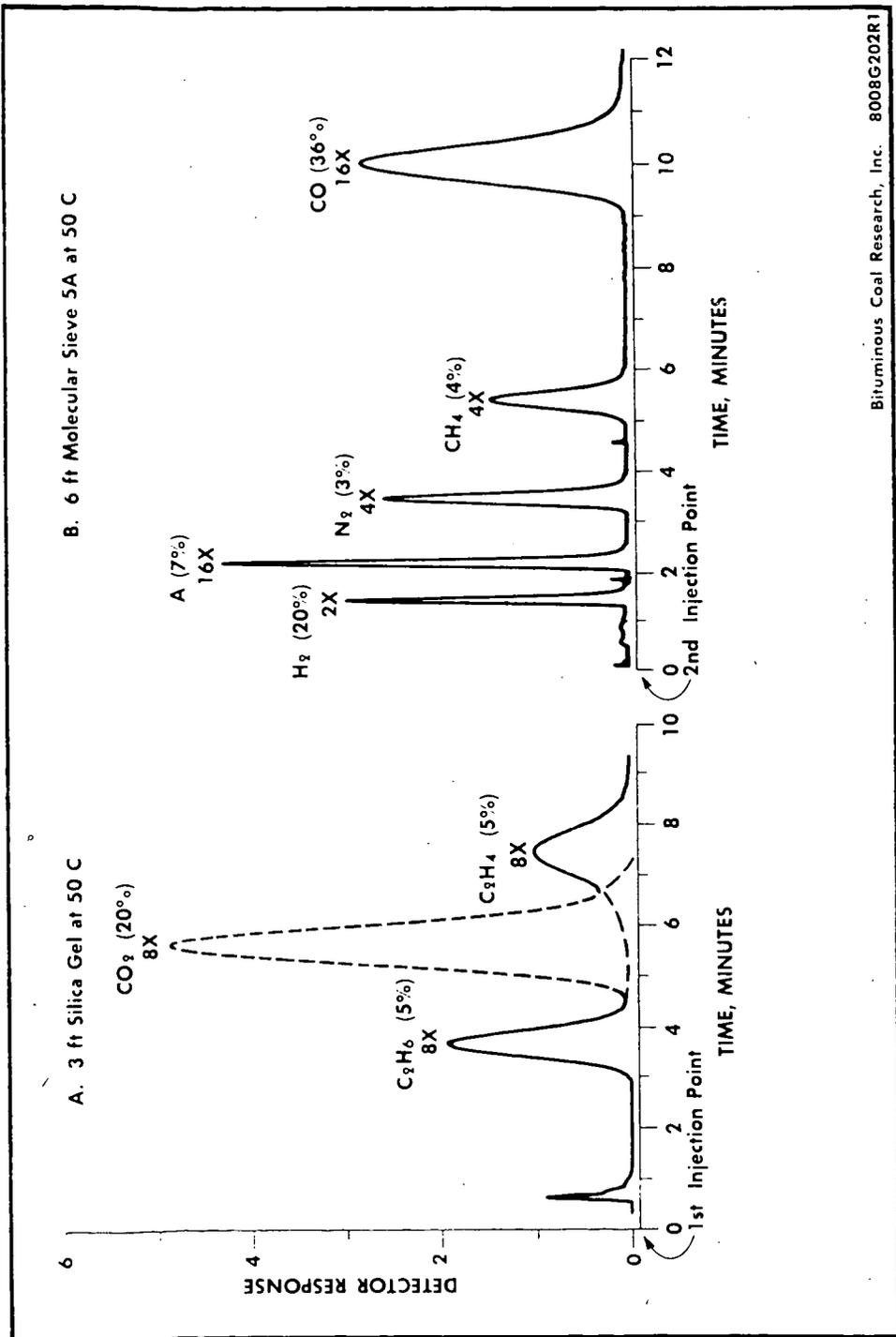
$$\text{H}_2\% = f_n (\text{H}_2 R\%)$$

$$\text{N}_2\% = f_n (\text{N}_2 R\%)$$

$$\text{CH}_4\% = f_n (\text{CH}_4 R\%), \text{ and}$$

$\text{H}_2 R\%$, $\text{N}_2 R\%$, $\text{CH}_4 R\%$ ---are observed values from the G.C. chromatogram

Time required for a complete analysis in duplicate is about one hour including calculation. During a normal working day seven samples can be analyzed by one operator.



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Figure 2. Chromatograms Produced on the 3 Ft Silica Gel and the 6 Ft Molecular Sieve Columns

3. **Results and Discussion:** Precision of this method, using the Orsat CO_2 analyzer and the F & M gas chromatograph Model 700-231, may be expressed as standard deviations of the components in a gas sample. The observed precision, as shown in Table 2, is considered high and quite satisfactory.

The product gases from more than 100 CFR experiments have been collected by the glass sampling system and analyzed by this combined method. Tables 3, 4, and 5 show the composition of several samples collected during experiments using three different coals.

In all three tables, sample "S" represents the simulated Stage 1 gas as purchased for use in the experiments. The three samples of Stage 1 gas were fairly consistent in composition showing only slight deviations. Sample "1" represents the composition of the product gas before introduction of coal feed. It is apparent that CO in the feed gas reacted with H_2O by the water gas shift reaction to form H_2 and CO_2 , thus making the product gas higher in CO_2 and H_2 and lower in CO than the original feed gas. A small amount of CH_4 was also detected in the product gas, possibly due to the reaction of CO and H_2 .

After coal feeding began, two or more samples were collected, each over a period of 2 minutes. These, designated as Sample 2, Sample 3, etc., contained CH_4 in amounts consistent with the operating conditions. Only trace amounts (less than 0.02%) of C_2H_6 , and even less C_2H_4 were found in these samples.

The last sample shown in the tables is the total composite product gas as accumulated in a gas holder during the total period of each CFR test. This sample, naturally, contained less CH_4 , as the gas holder also accumulated the N_2 used to purge the reactor system before and after the test and an extra amount of the Stage 1 feed gas used to establish equilibrium with steam at the start of the test.

C. Methods for 100 lb/hr Process and Equipment Development Unit

Construction of a 100 lb/hr internally-fired process and equipment development unit (PEDU) is nearing completion. Except for use of an ash-free fuel in Stage 1, this PEDU will simulate closely the conditions expected in both Stage 1 and Stage 2 of a full-scale two-stage super-pressure pilot plant. In the main zone (Stage 2) of the 100 lb/hr reactor, steam and fresh coal will react with Stage 1 gas to form a second stage product gas relatively rich in CH_4 and will leave a residue of partially reacted coal.

It is expected that the final product gas of the PEDU may deviate in composition from that produced in the 5 lb/hr CFR unit by possible presence of C_2 and C_3 hydrocarbons. In view of this possibility, a rapid G.C. column capable of separating CO_2 and minute quantities of C_2 to C_3 hydrocarbons has been developed.

A stainless steel sampling system, eliminating the use of a confining liquid, has also been developed for the taking of samples directly from the PEDU system.

TABLE 2. REPLICATE ANALYSES OF A GAS SAMPLE BY
COMBINED ORSAT AND DIFFERENTIAL G.C. METHOD

Run No.	Component, Percent by Volume						
	CO ₂ *	C ₂ H ₆	H ₂	A	N ₂	CH ₄	CO
1	18.6	1.8	24.8	11.9	1.9	10.5	30.5
2	18.5	1.9	24.6	11.9	2.0	10.7	30.4
3	18.5	1.8	24.8	11.9	1.9	10.7	30.4
4	18.3	1.3	25.9	11.8	1.8	10.7	30.2
5	18.6	1.5	25.9	11.8	1.9	10.2	30.1
6	18.5	1.5	25.1	11.7	1.9	10.8	30.5
Mean	18.50	1.63	25.18	11.84	1.90	10.60	30.35
Std. Dev. (σ)	0.110	0.233	0.577	0.082	0.100	0.219	0.164

* CO₂ by Orsat Method

TABLE 3. COMPOSITION OF GAS PRODUCTS IN GASIFICATION
OF PITTSBURGH SEAM COAL IN 5 LB/HR CFR, TEST NO. 79

Sample No.		Component, Percent Volume						
		<u>CO₂</u>	<u>H₂</u>	<u>A</u>	<u>N₂</u>	<u>CH₄</u>	<u>CO</u>	<u>C₂H₆</u>
3	Simulated Stage 1 gas	15.7	18.5	9.9	0	0	55.9	0
1	Product gas with- out coal	29.8	31.8	8.3	0	T	30.1	0
2	First sample with coal feeding	26.4	28.1	7.7	0	7.2	30.6	T
3	Second sample with coal feeding	25.5	26.7	7.6	0	8.0	32.2	0
4	Third sample with coal feeding	24.2	25.4	7.6	0	8.9	33.9	0
5	Total accumulated product	17.7	20.8	5.8	29.6	2.6	23.5	0

TABLE 4. COMPOSITION OF GAS PRODUCTS IN GASIFICATION
OF LIGNITE IN 5 LB/HR CFR, TEST NO. 82

Sample No.	Sampling	Component, Percent Volume						
		CO ₂	H ₂	A	N ₂	CH ₄	CO	C ₂ H ₆
S	Simulated first stage gas	15.5	18.5	9.9	0	0	56.1	0
1	Product gas without coal	29.7	31.6	8.4	0	0.1	30.2	0
2	First sample with coal feeding	29.0	28.0	6.2	0	9.6	27.2	T
3	Second sample with coal feeding	29.0	28.6	6.3	0	9.6	26.5	T
4	Third sample with coal feeding	28.7	28.8	5.6	0	11.3	25.6	T
5	Total accumulated product	23.8	25.6	6.5	14.3	3.5	26.3	-

TABLE 5. COMPOSITION OF GAS PRODUCTS IN GASIFICATION
OF ELKOL COAL IN 5 LB/HR CFR, TEST NO. 93

Sample No.	Sampling	Component, Percent Volume						
		CO ₂	H ₂	A	N ₂	CH ₄	CO	C ₂ H ₄
8	Simulated first stage gas	15.6	20.1	10.1	0	0	54.2	0
1	Product gas without coal	26.6	30.2	8.7	0	0.1	34.4	0
2	First sample with coal feeding	30.5	28.2	6.9	0	11.6	22.8	0.02
3	Second sample with coal feeding	30.1	28.3	6.9	0	11.5	23.2	T
4	Third sample with coal feeding	30.0	28.1	6.8	0	11.8	23.3	T
5	Fourth sample with coal feeding	30.5	27.9	6.9	0	11.7	23.0	T
6	Total accumulated product	22.6	24.6	6.5	16.5	4.2	25.6	T

1. Sampling System: To eliminate the use of a confining liquid in the sampling system, an evacuated stainless steel (s.s.) device, as shown in Figure 3, was developed. It consists of eight 1500 ml s.s. sampling bulbs (A.C. Tank Co.) each equipped with a Hoke packless valve and connected in parallel to a common 1/4-inch OD manifold. For sampling prefiltered gas, the inlet of the system is provided with a single-stage, corrosion-resistant regulator and a 0-30 psi gauge. For sampling unfiltered gas, an MSA filter cartridge is inserted between the regulator and the sampling point. At the outlet of the manifold, a control valve is installed, together with a trap and a flow indicator flask containing silicon fluid.

After the fully evacuated system is connected to the sampling point, the manifold is purged at a regulated pressure of 4 psi. The outlet of the manifold is closed and bulb No. 1 is immediately opened. The pressure of gas in the bulb is then gradually increased at a constant rate to about 20 psi during the period of operation to be sampled, usually one to two minutes. At the end of the sampling period, bulb No. 1 is closed and the outlet of the manifold is again opened; the manifold gas pressure is immediately reduced to 4 psi and purging is continued.

The procedure is repeated for collection of the next sample using bulb No. 2.

2. An Improved G.C. Method for the 100 lb/hr PEDU Tests: Recently, a new column packing known as Porapak Q was reported to be better than silica gel for resolving many types of organic compounds and gases (7, 8). So an investigation of Porapak Q for resolution of CO_2 , H_2S , and light hydrocarbons was made. In experiments with an 8-ft Porapak Q column, it was found that mixtures of C_1 - C_3 , CO_2 , and H_2S could be completely separated in a shorter time and eluted in much sharper peaks than on a 3-ft silica gel column.

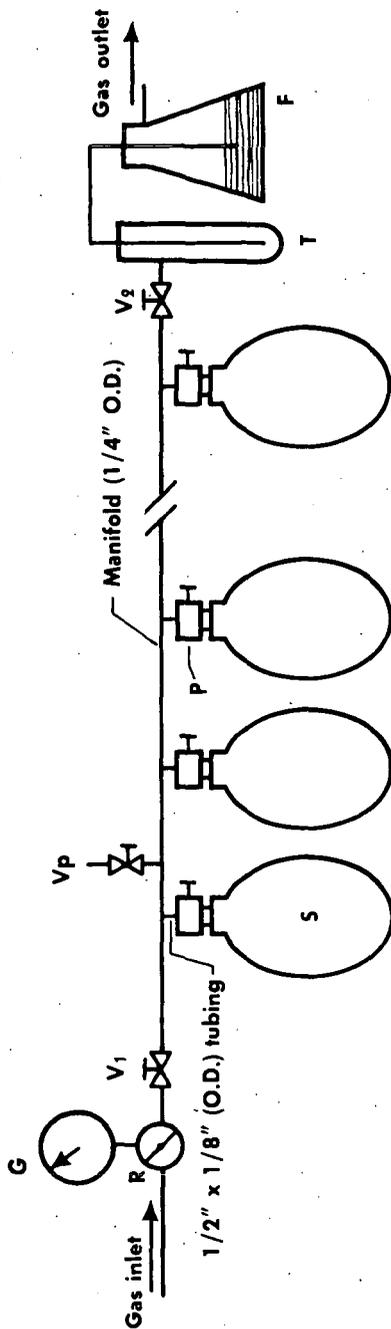
Figure 4 shows a chromatogram produced by a synthetic mixture on the 8-ft Porapak Q column operated at 50 C with 50 ml/min of helium carrier gas. The elution sequence of the components is as follows: Composite (N_2 , H_2 , O_2 , CO), CH_4 , CO_2 , C_2H_4 , C_2H_6 , H_2S , and C_3H_8 . Good precision on the analysis of C_1 - C_3 hydrocarbons and H_2S has been achieved on this column. Standard deviations of these components in a synthetic mixture are shown in Table 6. Since H_2S can be rapidly and accurately determined on this Porapak Q column, the iodometric titration of H_2S as used for the 5 lb/hr CFR tests can be eliminated.

Therefore, in the future an 8-ft Porapak Q will be used in combination with a 6-ft molecular sieve 5A for product gas analysis. Time required for a complete analysis of inorganic gases and C_1 - C_3 hydrocarbons, in duplicate, is about 2 hours.

CONCLUSION

Each of the three phases encountered so far in the development of the BCR two-stage super-pressure gasification process has presented some specific analytical problems. By development of three G.C. methods and two sampling devices, these analytical problems have been satisfactorily solved.

- | | | | |
|---|---|---------------------------------|---|
| S | Sampling bulbs under vacuum before sampling | V ₁ , V ₂ | Control valve |
| P | Packless valve | T | Trap |
| R | Pressure Regulator | F | Heavy wall flask containing silicon fluid |
| G | Gauge with large dial face | VP | To vacuum pump |



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Figure 3. Stainless Steel Sampling System

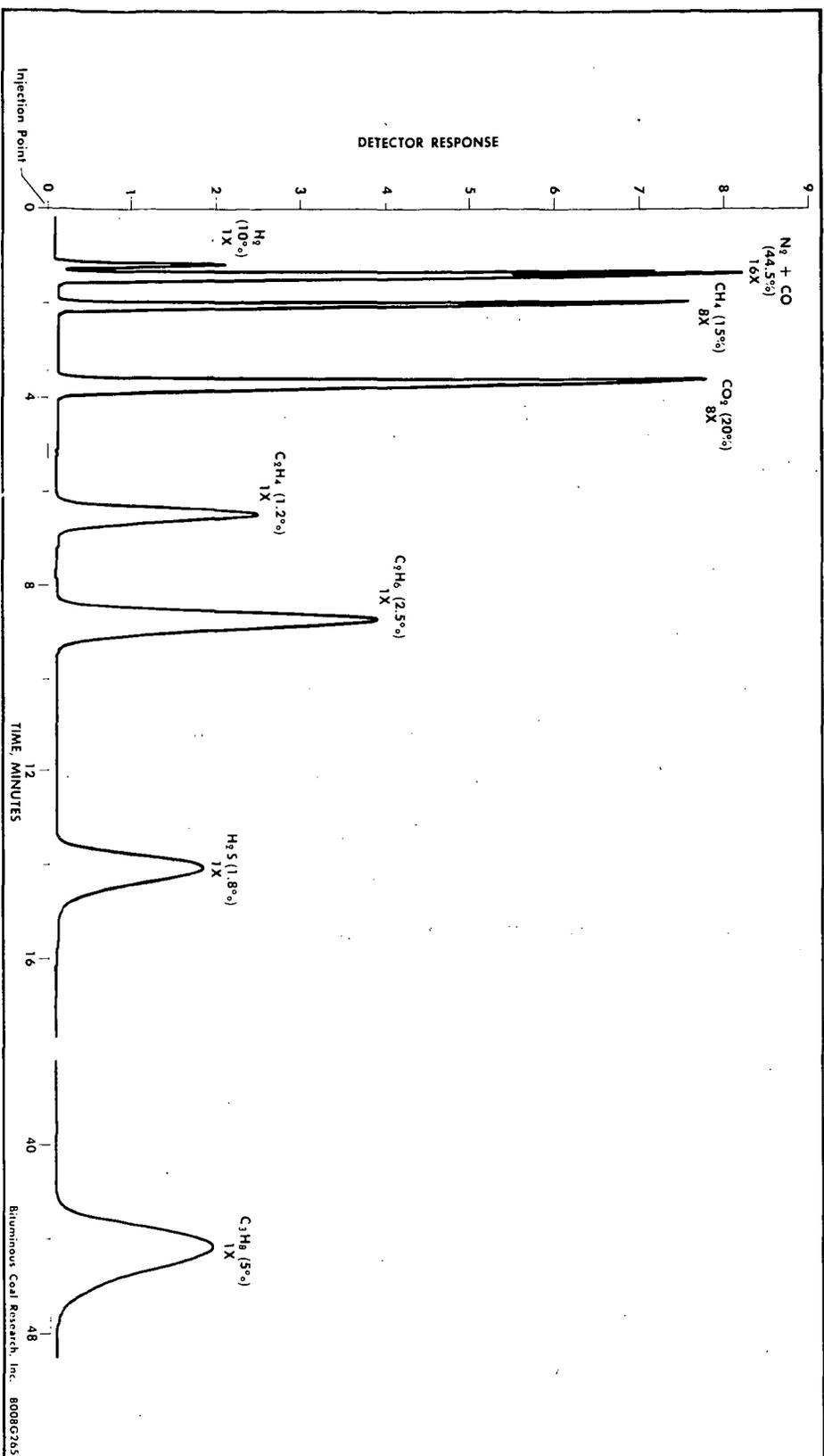


Figure 4. Chromatogram Produced on the 8 ft Poropak Q Column

TABLE 6. REPLICATE ANALYSES OF A SYNTHETIC MIXTURE*
ON THE 8-FT PORAPAK Q COLUMN

Run No.	Component, Percent by Volume					
	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈	H ₂ S	C ₃ H ₆
1	10.1	30.5	0.48	0.49	0.21	0.47
2	10.0	30.8	0.50	0.50	0.18	0.48
3	10.1	30.6	0.50	0.50	0.18	0.50
4	9.8	30.4	0.52	0.48	0.20	0.46
5	10.0	30.5	0.50	0.49	0.21	0.47
6	9.9	30.8	0.49	0.49	0.21	0.50
Mean	9.983	30.600	0.498	0.492	0.198	0.480
Absolute σ	0.117	0.168	0.013	0.022	0.015	0.167

* Balance of the mixture was nitrogen.

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