



SYNTHANE GASIFIER EFFLUENT STREAMS

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SYNTHANE GASIFIER EFFLUENT STREAMS

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ABSTRACT

A substantial number of experiments have been carried out with the 4-inch SYNTHANE PDU gasifier, primarily using three coals: North Dakota lignite, Illinois No. 6 bituminous and Montana subbituminous coal. These experiments were performed over a wide range of operating conditions using several coal feeding configurations. Operating pressures ranged from 10 to 40 atmospheres and the steam-to-coal and oxygen-to-coal ratios varied from 0.45 to 2.46 and 0.12 to 0.51, respectively. The effluent streams of the gasifier have been analyzed with regard to composition.

In this report the yields of potential environmental pollutants resulting from the gasification of various coals in the SYNTHANE PDU gasifier are reported and an attempt is made to identify relationships between these yields and gasifier operating conditions and coal type. Whenever possible direct comparison of the effluent streams for various conditions and modes of operation and coal rank are given in this report.

INTRODUCTION

The industrial and residential use of natural gas has steadily increased because of its low cost per Btu and clean burning characteristics. In recent years the finiteness of natural gas supplies has become apparent. As supplies of natural gas dwindle the highly industrialized northeastern United States will be the first to feel the economic effects. However, large coal fields lie east of the Mississippi. Processes are being developed in which this coal can be converted to substitute natural gas (SNG) in a manner consistent with environmental regulations, thus alleviating short gas supplies. The SYNTHANE process, which was initially developed under the Bureau of Mines and is being further developed by ERDA, is one such process for converting coal to SNG.

In the SYNTHANE process, both caking and noncaking coals can be converted to a satisfactory substitute for natural gas. At the heart of this

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process are two fluidized bed reactors which perform the following basic process steps: (1) coal pretreatment to destroy caking properties of various coals and (2) carbonization plus steam-oxygen gasification of the pretreated coals. The effluent gas from the gasifier is cleaned up, passed through a shift converter, purified and methanated to produce a high-Btu gas having a heating value greater than 900 Btu/scf and a carbon monoxide concentration less than 0.1 percent. An overall schematic of the 75 ton per day SYNTHANE unit which was designed by C. E. Lummus Co. and built at the Bruceton, Pennslyvania site of the Pittsburgh Energy Research Center (PERC) by Rust Engineering Company is shown in figure 1.

The shift conversion and purification processes necessary in the SYNTHANE process are technologically well developed and have been used in commercial applications for a number of years. (The gas purification step used in the SYNTHANE process is the hot carbonate process which was developed at PERC in the 1950's.) For these reasons the current research and development effort at PERC has been focused upon developing viable methanation and fluidized bed coal gasification units.

The development work done so far on the SYNTHANE gasifier has been in a small unit which typically treats about 25 pounds of coal per hour. A simplified flow diagram of this unit, which is located at PERC, is shown in figure 2.

One of the most important considerations which must be dealt with in developing a coal utilization process such as SYNTHANE is that of eliminating potential environmental pollutants found in the effluent streams of these processes. The SYNTHANE gasifier has several streams which could be sources of environmental problems.

As shown in figure 2 there are three effluents associated with the SYNTHANE gasifier: (1) condensate which includes water, tar and oil condensed out of the gas stream; (2) gas product stream; and (3) solids which are the extractor char and filter dust.

The purpose of this report is to summarize information on the potential environmental pollutants in the effluent streams of the SYNTHANE gasifier and to describe the effects of operating conditions and coal type on yields of these materials.

The data presented in this report covers experimental runs on the SYNTHANE PDU carried out before January 1975.

PERC SYNTHANE PDU

The major elements of the SYNTHANE PDU gasifier are shown in figure 2. These are: (1) the fluidized bed pretreater; (2) the free-fall carbonizer; and (3) the fluidized bed gasifier.



FIGURE 1. - Flowsheet of Prototype SYNTHANE Process

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FIGURE 2. - Schematic of the Fluid Bed Gasifier

Briefly, pulverized coal is partially oxidized in the pretreater to destroy the caking properties of the coal. The pretreated coal and pretreater fluidizing gas pass to the carbonizing section of the gasifier where the coal particles fall by gravity countercurrent to the gas passing upward from the fluidized bed gasification section. Upon passing through the carbonization zone the solid particles enter the fluidized bed gasification section where they are partially gasified by reactions with steam and oxygen.

A more detailed description of the SYNTHANE PDU gasifier is given below.

<u>Pretreater</u>: Coals with a free-swelling index of two or greater must be pretreated if they are to be used in the fluidized bed gasifier. The SYNTHANE PDU pretreater consists of an 8-foot long, 3/4-inch pipe topped with a 2.5-foot long, 1-inch pipe. Both sections are schedule 80 pipe and made of 304 stainless steel. Four individually controlled heaters enclosed the pretreater and provide heat for start-up and to counter radiation losses.

It is well known that the caking properties of coal can be destroyed by fluidizing the pulverized coal with an inert gas containing oxygen. In the SYNTHANE PDU the initial oxygen content of the fluidizing pretreater gas is maintained at 10 to 15 volume percent. In addition to this concentration range, other operating parameters associated with the pretreater operation are: (1) oxygen to coal ratio of 0.5 to 0.8 scf/lb of coal; (2) superficial gas velocity of 0.5 to 1.0 ft/sec; (3) a temperature of 770° F to 805° F; and 4) a minimum residence time of two minutes.

The gases formed during the pretreatment contain in part methane, carbon monoxide and hydrogen. These gases enter the gasifier and become part of the final product, adding to the overall methane recovery of the system.

<u>Carbonizer</u>: The carbonizer is a 6-foot long, 10-inch diameter, schedule 40 pipe of 304 stainless steel located directly above the gasification section. Electric heaters surround the carbonizer and maintain it at a nominal temperature of 550° C during the gasification.

Pretreated caking coal enters the top of the carbonizer from the fluidized bed pretreater and falls by gravity through the carbonizer countercurrent to the gas leaving the gasification section. The carbonizer can be by-passed by conveying the coal directly into the fluidized gasification section through a dip-tube.

Experiments at the Bruceton center have been carried-out with both caking and non-caking coals in which the coals have been injected directly into the fluidized bed of the gasifier at several depths. As will be discussed later, direct injection has a significant effect on the formation of condensate compounds in the process. <u>Gasifier</u>: The PDU gasifier is a 6-foot long, 4-inch diameter schedule 40 pipe of 310 stainless steel. Surrounding this pipe are three individually controlled electric heaters which provide start-up heat and counter radiation losses during operation. The heaters are surrounded by a 3inch thick layer of insulation. The entire assembly is enclosed in a 10inch diameter pipe. The transition zone between the gasification section and carbonizer is a 60° cone of 310 stainless steel.

During operation the fluidized bed height in the gasifier is maintained around 66 to 68 inches. The height can be adjusted by a variable speed screw extractor located at the base of the gasification section.

A mixture of steam and oxygen or air enters the gasifier at the center of the base through a 1/8-inch pipe as shown in figure 3. Also shown in this figure is the thermowell which is made of 3/8-inch pipe. It extends from 1 inch above the gas inlet to the top of the carbonizer traversing the entire length of the gasifier and carbonizer. The thermowell contains twelve thermocouples which measure the temperature distribution along the bed. It can be situated along the axis of the gasifier or in an asymmetric position.

Effluents of the SYNTHANE PDU Gasifier

The effluent gas of the SYNTHANE PDU is first filtered to remove small particulate matter. The filter consists of a perforated tube around which fiber-glass is wrapped. The flow of gas is radially inward through the fiber-glass and perforated tube. This filter is apparently very efficient since very few particles are observed in the condensate from the condenser.

The condensers are concentric tube heat exchangers in which the effluent gas flowing on the tube side is cooled to 100° C in the first condenser and to 50° C in the second condenser.

The condensers operate by passing the raw gas from the bottom of the condenser through the inner pipe where the gas is cooled. During the course of operation the condensate level builds and the raw gas begins to bubble through the trapped condensate. The condensate builds to a specified level, then the excess passes to the condensate receiver.

The aqueous condensate typically contains about 95 percent water with the balance being significant quantities of ammonia and phenols plus traces of sulfur-bearing compounds. The condensate water is primarily unused steam fed to the gasifier. The tar which is condensed simultaneously with the aqueous phase is considered to be that portion of the condensed material which sinks below the aqueous phase in the condensers and condensate receiver. The tar is primarily a mixture of heavy aromatics having boiling points above 190° C.



Symmetric position

Asymmetric position

FIGURE 3. - Gasifier and Thermowell Details of the SYNTHANE PDU

The gas leaving the second condenser (tail gas) is sampled for chemical analysis by a chromatographic column and infra-red analyzers.

The third major effluent leaving the SYNTHANE PDU gasifier is the char. The char is withdrawn from the gasification section by a variable speed screw extractor.

FEED MATERIALS

The principal materials fed to the SYNTHANE gasifier are coal, oxygen (sometimes supplied by air), steam and nitrogen (nitrogen is the purge gas.)

In this report attention is restricted to three ranks of coal: Illinois No. 6, Montana subbituminous and North Dakota lignite. Of the three only the Illinois No. 6 is a caking coal. Although many other coals have been gasified in the SYNTHANE PDU, the number of experiments for each of these coals was small, and it was questionable whether conclusions should be drawn about these coals until further testing has taken place. The average proximate and ultimate analyses of the three major coals to be discussed in this report are listed in table 1. The analyses are given for coals which have been spread on a floor and air dried for 12 to 14 hours.

The coal is crushed before it is fed to the SYNTHANE PDU. Table 2 gives the representative size distribution of the gasifier feed coals.

A major portion of the steam and oxygen is fed to the bottom of the gasification section as described previously. The steam is fed at about 600 psia and 400° C. Oxygen can be supplied as pure oxygen or as oxygen contained in air. Both pure oxygen and air (when used) are preheated and fed to the gasifier at approximately operating pressure.

SYNTHANE CONDENSATE

The SYNTHANE condensate consists of two portions, aqueous phase and tar phase.

The aqueous phase of the condensate stream is potentially the major source of environmental pollution associated with the SYNTHANE process. Extensive treatment will be required before reuse or discharge. An estimate of the size of the stream can be obtained from figure 4. In this figure the pounds of condensate water per pound of coal on a moistureand ash-free basis (maf) is shown as a function of pounds of steam fed to the gasifier per pound of coal, maf. It can be seen that, regardless of the coal rank and the conditions under which the coal was gasified, most of the data lies tightly about a single line. The equation of the best line through the data points is:

$$\frac{\# \text{ Condensate}}{\# \text{ Steam}} = 0.85 \tag{1}$$

This empirical equation should not be used outside the range of data from which it was obtained. It serves only to estimate the amount of the aqueous condensate from the SYNTHANE PDU.



FIGURE 4. - Aqueous Condensate Production Rate as a Function of the Steam Feed Rate to the SYNTHANE PDU Gasifier

	(Weight Percent)				
Coal	North Dakota	Montana	Illinois #6		
Rank	Lignite	Subbituminous	Bituminous HVC		
Proximate:					
Moisture	$17.9 \pm 4.2(36)^{\frac{1}{2}}$	15.5 <u>+</u> 3.8(16)	5.1 <u>+</u> 2.4(30)		
Volatile Matter	34.5 + 2.0(36)	$31.6 \pm 1.4(16)$	38.1 <u>+</u> 1.3(30)		
Fixed Carbon	39.5 <u>+</u> 2.5(36)	41.5 + 2.4(16)	43.3 + 2.2(30)		
Ash	8.1 ± 1.0(34)	11.4 ± 2.2 (15)	13.5 ± 2.2(30)		
Ultimate:					
Hydrogen	$5.5 \pm 0.3(34)$	$5.3 \pm 0.3(15)$	$5.0 \pm 0.2(30)$		
Oxygen	31.4 + 3.3(33)	25.8 <u>+</u> 2.4(15)	13.3 + 2.5(30)		
Carbon	$53.4 \pm 2.8(34)$	55.8 <u>+</u> 2.2(15)	$63.6 \pm 2.1(30)$		
Nitrogen	$0.8 \pm 0.2(34)$	$0.8 \pm 0.1(15)$	$1.1 \pm 0.1(30)$		
Sulfur	0.8 ± 0.2(34)	$0.9 \pm 0.1(15)$	$3.5 \pm 0.2(30)$		

TABLE 1.Proximate and ultimate analysis of coals air dried
and gasified in the SYNTHANE PDU

1/Number in parenthesis indicates number of tests.

******		(Percent Ret	ained On Sieve)	
Coal	North Dakota	North Dakota	Montana	Illinois No. 6
Rank	Lignite .	Lignite	Sub-bituminous	Bituminous
Generic Size	8x0	10x0	10x0	20x0
8	0			
10		0	0	
20	14.9	10.5	9.4	trace
50	40.2	39.8	36.6	18.7
100	17.0	15.7	17.4	25.1
140	12.2	17.5	15.3	21.6
200	5,6	6.4	6.6	11.7
325	4.2	5.1	9.6	14.8
fines	5.8	4.9	5.2	7.8

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TABLE 2. - Size distribution of feed coals

It is interesting to note that the data varies about a single line (Equation 1) even though the different ranks of coal have different moisture contents as shown in table 1, indicating that coals with a higher moisture content appear to have an enhanced water decomposition. This can be more easily seen in figure 5 which shows the relationship between total water fed to the SYNTHANE PDU and the condensate water. It can be seen by comparing figures 4 and 5 that the steam decomposition is directly related to moisture content of the coal.

Based on Equation 1 and assuming the moisture contents of the char, tar and nominally dry tail gas are small compared to that of the feed coal, the fractional decomposition of the steam plus moisture of the coal, X_{H_00} , can be estimated by

$$X_{H_20} = 1 - 0.85$$

$$1 + \frac{(H_20) f}{f_{H_20}}$$
(2)

where (H₂0) is the fractional moisture content of the coal and f coal and f $_{\rm H_20}$ are the feed rates of the coal and steam, respectively.

Equation 2 indicates that high water conversions can be obtained for coal with high moisture content being gasified at low steam feed rates to the gasifier. Water decompositions of over 40 percent have been observed in the SYNTHANE PDU under these conditions. The implication of high moisture content is not well understood except that higher moisture contents usually indicate lower rank coals which are known to be more reactive in the gasification reactions. Low steam feed rates should favor higher temperatures in the gasifier bed which would kinetically favor water decomposition.

The yields of various chemical species in the aqueous condensate are presented in tables 3, 4 and 5. In these tables averaged data and sample deviations are presented in terms of pounds of compounds produced per ton of coal (maf) fed. The reason for this is that, while the total water feed to the gasifier can vary several fold, the yields of many of the constituents of the condensate remain relatively constant with other operating conditions remaining fixed. For example, the yield of phenol in the aqueous condensate is relatively constant under a varying total water feed as can be seen in figure 6. Since approximately 85 percent of the feed water ends up as condensate, the concentration data for many of the condensate constituents is as random as the steam feed rate.

Tables 3, 4 and 5 show averaged operating conditions for groups of data. Examination of the averaged conditions and associated standard deviations shows that, for a given coal type, pressure and mode of operation, the average temperature and coal, oxygen and steam feed rates are fairly



FIGURE 5. - Aqueous Condensate Production Rate as a Function of the Total Water Feed Rate to the SYNTHANE PDU Gasifier



FIGURE 6. - Effect of Total Water Feed Rate on the Production of Phenol in the Aqueous Condensate for the Gasification of North Dakota Lignite at 40 atm Without a Dip Tube

	SYNTHANE condensate for the gasification of North Dakota lignite coal							
conditions:								
Dip Tube	No ¹ /	No	No	Yes <u>-</u> /				
Pressure(atm)	10	20	40	40				
Avg. Temp. (°C) $\frac{3}{}$	833 <u>+</u> 2(2)	852 ± 8(3)	834 <u>+</u> 15(8)	814 + 22(8)				
Coal Feed Rate (lb/hr)	15.0 <u>+</u> 0.0(2)	29.7 <u>+</u> 0.3(3)	29.4 <u>+</u> 4.2(8)	28.2 + 5.2(8)				
0 ₂ /Coal Ratio (Ib/lb)	0.36 ± 0.03(2)	0.23 ± 0.02(3)	0.20 <u>+</u> 0.03(8)	0.19 ± 0.06(8)				
Steam/Coal Ratio (lb/lb)	1.21 ± 0.47(2)	0.62 + 0.05(3)	1.10 ± 0.23(8)	1.15 ± 0.31(8)				
Additives	No	No	No	No				
<u>Yields</u> : (1b/ton maf co	al)							
Phenol	7.93 + 2.70(2)	5.99 <u>+</u> 1.76(3)	8.91 <u>+</u> 2.31(9)	4.42 <u>+</u> 1.70(8)				
Ammonia	12.79(1)	11.6 + 5.3(3)	14.3 + 1.5(5)	15.5 <u>+</u> 2.8(7)				
COD	40.6 <u>+</u> 7.5(2)	8.8 ± 10.7(3)	49.2 + 16.1(9)	15.6 <u>+</u> 6.5(7)				
Chloride x 10^2	4.20 <u>+</u> 0.09(2)	5.95 + 3.52(3)	4.43 + 2.53(9)	1.81 ± 1.05(8)				
Thiocyanate x 10^2	1.75 <u>+</u> 0.78(2)	2.78 ± 1.22(3)	3.24 + 2.50(9)	1.73 <u>+</u> 0.59(8)				
Cyanide x 10^4	1.36 + 1.78(2)	10.3 ± 10.0(3)	2.40 <u>+</u> 3.31(6)	0.34 <u>+</u> 0.32(8)				
Phosphate x 10^4	$ND^{4/}$	1.26(1)	54.5 + 9.2(2)	22.1 <u>+</u> 6.7(7)				
Tar	$51.0 \pm 9.0(2)$	72.7 + 43.4(3)	51.9 <u>+</u> 29.7(9)	11.4 <u>+</u> 7.3(16)				

TABLE 3. - Average yields of various components in the

1/"No" indicates coal fed through carbonizer by free fall. 2/Immersion of dip tube ranged from 0 to 54 inches. 3/Average temperature in the fluid bed gasifier. 4/ND means "not determined."

	Of Montana subbituminous coal							
Cond	itions:							
	Dip Tube	No	No	Yes	Yes	Yes		
	Pressure (atm)	20	40	10	20	40		
	Avg. Temp.(°C)	899 <u>+</u> 24(5)	845 <u>+</u> 10(4)	980 <u>+</u> 8(2)	904 <u>+</u> 14(3) ·	842 <u>+</u> 2(2)		
	Coal Feed Rate (1b/hr)	22.0 <u>+</u> 2.0(5)	29.9 <u>+</u> 4.5(4)	16.8 <u>+</u> 0.6(2)	28.2 <u>+</u> 2.3(3)	22.9 <u>+</u> 0.4(2)		
	0 ₂ /Coal Ratio (Ib/lb)	0.29 <u>+</u> 0.04(5)	0.20 ± 0.02(4)	0.38 ± 0.01(2)	0.28 ± 0.04(3)	0.22 ± 0.02(2)		
	Steam/Coal Rat: (1b/1b)	io 0.89 <u>+</u> 0.09(5)	1.10 ± 0.14(4)	0.28 ± 0.01(2)	0.62 ± 0.14(3)	1.46 ± 0.24(2)		
	Additives	No	No	No	No	No		
Yiel	<u>ds</u> : (1b/ton maf	coal)						
	Phenol	5.48 <u>+</u> 1.48(5)	6.92 <u>+</u> 3.19(4)	3.32 <u>+</u> 0.82(2)	4.00 <u>+</u> 1.63(3)	2.13 <u>+</u> 2.02(2)		
	Ammonia	12.7 <u>+</u> 0.8(3)	ND	ND	12/5 + 2.5(3)	ND		
	COD	29.1 <u>+</u> 4.2(5)	43.3 <u>+</u> 33.0(4)	16.8 <u>+</u> 1.2(2)	16.9 <u>+</u> 3.4(3)	11.4 <u>+</u> 10.0(2)		
	Chloride x 10^2	7.37 <u>+</u> 5.20(5)	4.22 <u>+</u> 1.13(4)	3.03 <u>+</u> 0.31(2)	1.01 <u>+</u> 0.83(3)	3.17 <u>+</u> 0.50(2)		
	Thiocyanate x 10 ²	8.92 <u>+</u> 3.81(5)	2.16 <u>+</u> 2.50(4)	5.93 <u>+</u> 2.90(2)	2.67 <u>+</u> 0.78(3)	1.60(1)		
	Cyanide x 10^4	28.1 <u>+</u> 14.2(5)	$0.65 \pm 0.65(4)$	5.85 <u>+</u> 7.41(2)	8.40 <u>+</u> 5.45(3)	0.19 <u>+</u> 0.00(2)		
	Phosphate x 10 ⁴	2.06 <u>+</u> 0.35(3)	ND	ND	1.27 <u>+</u> 0.36(3)	32.0(1)		
	Tar	64.1 <u>+</u> 14.0(5)	44.0 <u>+</u> 36.2(4)	36.6 <u>+</u> 14.5(2)	30.1 <u>+</u> 7.4(3)	20.3 <u>+</u> 13.4(2)		

TABLE 4. - Average yields of various components in the

15

1/"No" indicates coal fed through carbonizer by free fall. 2/Immersion of dip tube ranged from 0 to 54 inches. 3/Average temperature in the fluid bed gasifier. 4/ND means 'not determined."

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TABLE 5. <u>Average yields of various components in the</u> SYNTHANE condensate for the sasification						
	-	of Illinois M	No. 6 bituminou	s coal		
onditions:	<u></u>					
ip-Tube	No	No	No	No	Yes	
ressure(atm)	20	30	40	40	40	
vg. Temp. (°C)	923 + 16(5)	916 + 1(2)	909 <u>+</u> 13(4)	913 + 9(8)	895 + 10(6)	
oal Feed Rate lb/hr)	20.3 ± 3.2(5)	18.6 + 3.3(2)	18.7 <u>+</u> 1.5(4)	23.7 + 2.1(8)	23.8 <u>+</u> 3.7(6)	
/Coal Ratio Ib/lb)	0.33 <u>+</u> 0.07(5)	0.45 ± 0.08(2)	0.35 <u>+</u> 0.05(4)	0.24 ± 0.04(8)	0.26 + 0.05(6)	
team /Coal Ratio (1b/1b)	1.06 <u>+</u> 0.31(5)	2.13 ± 0.47(2)	1.51 ± 0.13(4)	1.08 ± 0.28(8)	1.12 <u>+</u> 0.33(6)	
dditives	No	No	No	Yes	No	
lelds: (lb/ton mag	f c oal)					
Phenol	5.81 ± 1.90(5)	10.4 + 2.9(2)	8.84 <u>+</u> 1.23(3)	8.85 + 1.97(8)	$6.22 \pm 0.76(4)$	
mmonia	11.8 ± 2.8(2)	ND	18.62(1)	21.6 ± 5.3(8)	20.0 ± 2.1(2)	
COD	54.0 ± 15.7(5)	66.5 <u>+</u> 10.9(2)	57.5 <u>+</u> 12.0(3)	50.9 <u>+</u> 9.3(8)	27.6 ± 4.4(4)	
Chloride x 10^2	58.5 ± 5.1(5)	40.1 + 8.7(2)	70.9 ± 10.8(3)	77.9 <u>+</u> 13.3(8)	66.8 <u>+</u> 9.7(4)	
Thiocyanate x 10^2	59.1 ± 20.5(5)	28.1 ± 9.8(2)	25.0 + 9.4(3)	28.6 + 9.9(8)	24.3 + 9.3(4)	
Cyanide x 10^4	24.0 ± 20.4(5)	3.55 ± 2.97(2)	4.69 ± 4.94(3)	12.5 <u>+</u> 5.1(8)	10.6 + 5.8(4)	
Phosphate x 10^4	12.3 ± 14.3(4)	< 36.0(1)	ND	12.3 + 24.3(8)	10.2 <u>+</u> 14.3(3)	
Car	198 ± 59.0(6)	138.0 ± 1.0(2)	114.9 + 38.9(3) 131.4 ± 19.4(8)	45.8 + 36.4(6)	

//"No" indicates coal fed through carbonizer by free fall.
//Immersion of depth of dip tube ranged form 0 to 54 inches.
/Average temperature in the fluid bed gasifier.
/ND means "not determined."

uniform. Because of this nature of the data, it is difficult to separate the effect of coal type on pollutant yields from, say, temperature effects. However, some interesting general observations can be drawn from these tables.

The production rate of condensate compounds can be significantly dependent on the rank of the coal being gasified. It is not clear how to separate coal rank from temperature since in general the lower rank coals were gasified at lower temperatures. However, previous workers have found coal rank more important to tar formation than carbonization temperature. (This will be discussed below.)

As can be seen from tables 3 through 5 the production rates of the major contaminants in the aqueous condensate (e.g. phenol, COD and NH₃) are not significantly different for the various coals gasified. However, trace contaminants such as chlorides, thiocyanates, cyanides and phosphates, vary greatly with coal type. The variation of the chloride and phosphates in the condensate is probably directly related to the amounts of these compounds in the feed coal; but this has not been established as of now.

The production of tar is greatly affected by coal rank; roughly, the higher the rank the greater the tar production. This functionality parallels the observations of Rhodes ($\underline{1}$) on coal tar production in coke ovens.

Rhodes also lists carbonization temperature as one of the major parameters affecting the distribution of product in coal carbonization processes. In the case of the SYNTHANE gasifier the temperature effect cannot be readily distinguished from the effect of coal rank on the condensate compounds production. In general for the SYNTHANE PDU tests, higher average bed temperatures were associated with the higher ranked coal. Table 6 shows the average bed temperature for the various coals studied.

Rhodes has presented a correlation for predicting tar and light oil production in coal carbonization experiments carried out in a retort of 13-inch diameter and 26-inch height. The correlation is given by:

$$(T + L0) = a + b(VM) + C(H_20)$$
(3)

$$a = -17.13 + 0.03166T_c - 0.1656 \times 10^{-4} T_c^2$$

$$log_{10} b = \frac{498.7}{T_c + 273} - 0.9411$$

$$c = 4 \times 10^{-5} T_c - 0.242$$

		North Dakota	Montana	Illinois No. 6
Average of Average Bed	8.0	<u></u>		
lemperature,	-0	840	876	912
Range of Average Bed				
Temperatufe,	°C	812 to 871	834 to 930	893 to 937

TABLE 6. - Average gasification temperature in the SYNTHANE PDU

TABLE 7. - Ultimate analysis of dewatered SYNTHANE Tar

		percent, weight	
	North Dakota Lignite	Montana Subbituminous	Illinois No.6 Bituminous
Carbon	83.00 + 1.67(7)	84.93 ± 0.75(3)	83.17 ± 1.65(10)
Hydrogen	$7.40 \pm 0.24(7)$	$7.45 \pm 0.21(2)$	$6.43 \pm 0.22(10)$
Nitrogen	$0.89 \pm 0.11(7)$	$0.93 \pm 0.06(3)$	1.25 + 0.11(10)
Sulfur	$0.96 \pm 0.36(6)$	$0.65 \pm 0.17(3)$	$2.58 \pm 0.18(10)$
0xygen ¹ /	7.75	6.04	6.57

1/By difference.

where (T + LO) is the percent coal converted to tar (T) and light oil (LO),

(VM) is the percent volatile matter in the coal,

and T is the carbonization temperature, °C.

Rhodes (1) emphasized that the water as such does not have a direct effect on the production of tar and light oils but is a measure of the coal rank.

Figure 7 shows the results of applying Equation 3 to the three coals under consideration. As can be seen from this figure, the rank of the coal has far greater influence on the production of tars and light oil than the temperature.

The effect of temperature variation on the tar production is probably less than the inherent experimental error associated with PDU operations and data analysis. In the SYNTHANE gasifier, because of complicated gas-solid contacting and the unknown kinetics and mechanism of carbonization and gasification, it is difficult to determine the temperature history of the coal particles. Therefore, the temperature effect on the production of condensate conpounds cannot be accurately determined. However, coal particles fed from the same position in the gasifier probably experience similar temperature histories. The lack of agreement between Equation 3 and the SYNTHANE PDU experimental data in figure 7 is not suprising due to the unknown particle temperature history and different pressures and gasification reactors involved. The averaged ultimate analysis of the tar is given in table 7. It can be seen that with respect to carbon, hydrogen, and nitrogen the tars are the same. However, the sulfur concentration in the tars parallel the sulfur content of the coal.

Tables 3 through 5 also show the effect on effluent compound production of feeding the coal to the gasification section through the carbonizer or feeding the coal directly to the gasification section through a dip tube. The dip tube feeder is a pipe which extends from the top of the gasification vessel through the carbonization zone and penetrates into the gasifier bed from 0 to 54 inches. Coal is fed to the top of the dip tube and is heated (but more slowly than in free-fall feeding) as it passes down toward the gasifier bed; also the countercurrent contact of coal particles and gas rising through the carbonization zone is eliminated. Table 8 summarizes the data from tables 3, 4 and 5 on the effects of dip tube coal injection. A detailed account of dip tube injection of coal into the SYNTHANE PDU has been reported by Nakles et al.(2) It can be seen that a significant reduction in the phenol, COD, thiocyanate, cyanide and tar production can be realized by dip tube coal injection.



FIGURE 7. - Demonstration of the Effect of Coal Rank and Temperature on the Production of Tar and Light Oil

Coal Rank	North Dakota		Montana Subbituminous		Illinois No. 6 Bituminous	
Dip Tube	Yes	No	Yes	No	Yes	No
Phenol	4.42 <u>+</u> 1.70(8)	8.91 <u>+</u> 2.31(9)	2.14 ± 2.02(2)	6.92 <u>+</u> 3.19(4)	6.22 <u>+</u> 0.76(4)	8.84 ± 1.23(3)
Ammonia	$15.5 \pm 2.8(7)$	14.3 <u>+</u> 1.5(5)	ND	ND	$20.0 \pm 2.1(2)$	18.62 (1)
COD	15.6 ± 6.5(7)	49.2 <u>+</u> 16.1(9)	11.3 ± 10.0(2)	43.3 ± 33.0(4)	27.6 ± 4.4(4)	57.5 ± 12.0(3)
Chloride x 10 ²	1.81 ± 1.05(8)	4.43 <u>+</u> 2.53(9)	3.17 ± 0.50(2)	4.22 <u>+</u> 1.13(4)	66.8 <u>+</u> 9.7(4)	70.9 <u>+</u> 10.8(3)
Thiocyanate x 10 ²	1.73 ± 0.59(8)	3.24 <u>+</u> 2.50(9)	1.60(1)	2.16 + 2.50(4)	24.3 + 9.3(4)	25.0 <u>+</u> 9.4(3)
Cyanide x 10 ⁴	0.34 <u>+</u> 0.32(8)	2.40 ± 3.31(6)	0.19 ± 0.00(2)	0.65 + 0.65(4)	10.6 ± 5.8(4)	4.69 <u>+</u> 4.94(3)
Phosphate x 10 ⁴	22.1 + 6.7(7)	54.5 <u>+</u> 9.2(2)	32.0(1)	ND	10.2 ± 14.3(3)	ND
Tar	11.4 ± 7.3(16)	51.9 <u>+</u> 29.7(9)	20.3 <u>+</u> 13.4(2)	44.0 <u>+</u> 36.2(4)	45.8 <u>+</u> 36.2(6)	114.9 <u>+</u> 38.9(3)

TABLE 8	8.	 Effect	of	coal	feed	posit	ion	on	the	yield	l of	condens	ate	compounds
		fro	n ti	he SYI	THANE	PDU	oper	ati	on a	at 40	atm	with no	ad	ditives
					(a	11 ur	uits	16/	ton	maf o	coal)		

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The apparent difference in the yields of these compounds when the dip tube is or is not used could be attributed to the radically different temperature histories which the coal undergoes when fed to the gasifier by the two methods.

When particles are fed directly into the bed, they will undergo a much more rapid heating than particles dropped through the carbonization section because of the higher temperatures in the fluidized bed. Therefore, the average temperature of the particles fed directly to the bed will be much higher than the average temperature of those which fall through the carbonizer. Thus, in accordance with Equation 3, the tar production for the particles fed directly to the bed should be less than for those fed through the free-fall carbonizer. Also, in the fluidized bed of char, the char could act as sites for the cracking and decomposition of the tars, phenols and other organic compounds evolved from the coal particles.

The depth of the dip tube injection does not appear to significantly affect the production of condensate compounds. This can be seen by examining table 9 which summarizes the dip tube data for lignite coal gasified at 40 atmospheres. The data in this table are averaged data. This observation is not suprising since particle mixing is very good in fluidized beds. However, if the dip tube is placed in the vicinity of the oxygen inlet where the local bed temperature can be extremely high, the make of tar and condensable organic compounds could be considerably different than when coal is fed to other parts of the bed.

The effect of pressure on the formation of condensable compounds has been studied in the SYNTHANE PDU. Unfortunately this cannot be strictly isolated from the effects of gas residence time in the gasifier and carbonizer since these residence times are proportional to the pressure. Also, for the data presented in this paper, in all the runs carried out at 40 atmospheres oxygen was fed to the gasifier, and in essentially all the runs at lower pressures the gasifier was fired with air. Gasification of coals with oxygen at 20, 30 and 40 atmospheres has been carried out in the PERC SYNTHANE PDU; however, only fragmentary analyses of the condensate and gas for trace contaminents are available and these runs were not included in this report.

Examination of tables 3 through 5 reveals that the only condensable whose production rate is significantly affected by pressure-associated effects is the tar. This occurs when the coal is being fed through the carbonizer zone of the SYNTHANE PDU. In this case the tar production falls with in-7 creasing pressure as shown in table 10 and figure 8.



FIGURE 8. - The Effect of Factors Associated with Gasification Pressure on the Yield of Tar

Dip Tube Position (inches below bed level)	feed to top	12 to 18	54
Yields: (lb/ton maf coal)			
Phenol	4.42 ± 1.59(2)	4.13 ± 1.89(6)	ND
Ammonia	12.5 ± 3.1(2)	16.0 <u>+</u> 3.2(5)	ND
COD	18.1 + 1.1(2)	14.7 ± 6.8(5)	ND
Chloride x 10 ²	0.29 ± 0.12(2)	2.47 ± 0.59(6)	ND
Thiocyanate x 10 ²	2.17 ± 0.44(2)	1.57 ± 0.65(6)	ND
Cyanide x 10^4	3.43 <u>+</u> 4.73(2)	0.20 ± 0.16(6)	ND
Phosphate x 10^4	8.55 ± 6.77(2)	25.9 ± 1.6(5)	ND
Tar	9.91 <u>+</u> 4.58(2)	13.7 + 9.8(9)	13.2 ± 8.0(5)

TABLE 9. - Effect of dip tube depth on condensate yield duringthe gasification of North Dakota lignite in theSYNTHANE PDU at 40 atmospheres

	(Tar Make in 1	b/ton coal, ma	f)	• ··· • • • • • •
Coal	Gasi	fication Press	ure (atm.)	
	20	30	40	
Lignite	73 <u>+</u> 43(3)		52 ± 30(9)	
Subbituminous	64 <u>+</u> 14(5)		44 <u>+</u> 36(4)	
Bituminous	198 <u>+</u> 59(6)	138 <u>+</u> 1(2)	115 <u>+</u> 39(3)	

TABLE 10. - Effect of pressure on tar formation in the SYNTHANE PDU

The only exception to this is the tar yield in the gasification of lignite at 10 atm.

The effects of feeding additives with the coal on methane and total gas production, carbon conversion, slag formation and condensate and gas composition in the SYNTHANE gasifier have been reported by Forney et al. $(\underline{3})$ and Haynes et al. $(\underline{4})$

The effects of additives at various concentrations on the condensate components are compared in table 11 with the average of the data for experiments with similar operating conditions but no additives. It can be seen from this table that no significant differences between the entries or trends in the data are established. In the case of cyanide and tar production the use of additives has apparently increased both of these yields. However, because of the large scatter in the data (as signified by the sample deviation), the averages presented here could be misleading.

The analysis of condensate water from the SYNTHANE gasifier for trace elements and compounds has been discussed by Forney, et al. (5) and Schmidt et al. (6). A more detailed analysis of these trace components has been published by Forney et al. (7). The condensate water has been shown to be similar in composition to the waste water from coking operations. Strakey et al. (8) have proposed a process for clean-up of the SYNTHANE condensate water as well as estimated the cost of this clean-up.

The effects of operating conditions on the production rate of condensate compounds has been discussed above. Included in these compounds is tar, whose production rate has been shown to be one of the most sensitive to coal rank and mode and conditions of operation.

SYNTHANE TAIL-GAS AND CHAR

Yield data for the gas leaving the condenser of the SYNTHANE PDU is summarized below in tables 12 and 13. In table 12 the direct injection of the coal into the gasification bed is compared to experiments where

Additive	None	2 pct Quick 5 Lime	pctQuick 2 Lime	pct Hydrated 5 Lime	pct Hydrated 5 Lime	pct Limestone
Operating Conditions						
Coal Feed Rate (1b/hr)	23.7 + 2.0(11)	24.2 + 2.1(2)	24.2 + 0.0(2)	$22.9 \pm 5.2(3)$	$21.1 \pm 0.6(2)$	25.7 ± 0.4(2)
0 /Coal Ratio (1b/1b)	0.25 + 0.04(11)	- 0.24 + 0.02(2)	- 0.21 + 0.00(2)	$0.27 \pm 0.04(3)$	$0.29 \pm 0.06(2)$	$0.24 \pm 0.00(2)$
2 Steam/Coal Ratio (1b/1b)	1.08 + 0.30(11)	- 0.87 + 0.13(2)	- 0.79 + 0.01(2)	$1.30 \pm 0.37(3)$	$1.37 \pm 0.11(2)$	$0.98 \pm 0.00(2)$
Ave. Temp. (°C)	$911 \pm 10(11)$	$904 \pm 1(2)$	914 <u>+</u> 2(2)	913 <u>+</u> 7(3)	923 ± 20(2)	901 ± 1(2)
Yields (lb/ton coal maf)						
Phenol	8.84 + 1.23(4)	10.10 + 0.57(2)	ND	8.60 ± 3.32(3)	$8.41 \pm 0.50(2)$	7.98(1)
Ammonia	18.6(1)	18.7 + 1.0(2)	ND	$21.1 \pm 1.8(3)$	$18.9 \pm 0.4(2)$	34.2(1)
COD	57.5 + 12.0(4)	41.8 + 1.2(2)	ND	57.0 <u>+</u> 12.6(3)	$51.0 \pm 2.4(2)$	50.2(1)
Chloride x 10^2	-70.9 + 10.8(4)	-65.1 + 2.3(2)	ND	78.5 <u>+</u> 1.2(3)	79.2 <u>+</u> 20.9(2)	99.2(1)
Thiocyanate x 10^2	-25.1 + 9.4(4)	- 16.7 + 4.4(2)	ND	31.9 <u>+</u> 5.4(3)	$26.8 \pm 1.5(2)$	45.6(1)
$\frac{1}{2}$	-6.19 + 4.79(3)	- 9.77 + 0.10(2)	ND	$12.3 \pm 5.0(3)$	$12.7 \pm 9.2(2)$	18.2(1)
Phosphate x 10 ⁴	ND	- ND	ND	$2.87 \pm 0.73(3)$	2.92 ± 0.25(2)	2.28(1)
Tar	115 <u>+</u> 39(4) 1	28 ± 13(2) 13	1 <u>+</u> 2(2)	151 <u>+</u> 28(3)	124 ± 3(2)	113 <u>+</u> 1(2)

TABLE 11.- Comparison of the gasification of Illinois No. 6 coal in the SYNTHANE PDU at 40 atmospheres with and without additives

Coal Rank	North Dako Lignite	ta	Montana Subbitumin	ous	111inois No. 6 Bituminous		
Dip-Tube?	Yes	No	Yes	No	Yes	No	
Coal Feed Rate (1b/hr)	27.8 <u>+</u> 4.7(19)	29.4 <u>+</u> 4.7(19)	22.9 ± 0.4(2)	29.9 <u>+</u> 4.5(4)	23.8 ± 3.7(6)	18.7 ± 1.5(4)	
0 ₂ /Coal Ratio (Ib/1b)	0.21 ± 0.06(19)	0.20 ± 0.03(8)	0.22 ± 0.02(2)	0.20 ± 0.02(4)	0.26 ± 0.05(6)	0.35 ± 0.05(4)	
Steam/Coal Ratio (1b/1b)	1.24 ± 0.27(19)	1.10 ± 0.23(8)	1.46 ± 0.24(2)	1.10 ± 0.14(4)	1.12 ± 0.33(6)	1.51 ± 0.13(4)	
Ave. Temperature (°C)	814 ± 20(8)	834 <u>+</u> 15(8)	842.2 <u>+</u> 2(2)	845 <u>+</u> 10(4)	895 <u>+</u> 10(6)	909 <u>+</u> 13(4)	
Product Yields: (sc	f/1b coal maf)						
CH ₄	3.21 <u>+</u> 0.32(19)	3.34 ± 0.47(8)	3.70 <u>+</u> 0.42(2)	4.18 ± 0.21(4)	3.28 ± 0.26(6)	$3.33 \pm 0.45(4)$	
$(CH_4 + CO + H_2)$	17.1 <u>+</u> 1.7(19)	$16.6 \pm 2.0(8)$	16.1 + 2.0(2)	$16.4 \pm 2.0(4)$	12.8 ± 2.9(6)	$13.6 \pm 1.6(4)$	
Equivalent CH_4 (CH_4 + (CO + H_2)/4)	6.68	6.66	6.80	7.24	5.66	5.90	
By-Product Yields:	(scf/ton coal mag	af)					
H ₂ S	235 ± 118(11)	260 ± 114(5)	144(1)	205(1)	198 <u>+</u> 204(2)	168 <u>+</u> 11(4)	
Methyl Mercaptan	0.86 ± 0.59(11)	$1.39 \pm 0.97(5)$	0.59(1)	0.60(1)	0.67 <u>+</u> 0.59(2)	$1.05 \pm 0.45(4)$	
COS	4.58 ± 1.85(11)	3.70 ± 1.7(5)	. 4.70(1)	6.30(1)	11.8 ± 15.4(2)	8.46 ± 4.37(4)	
so ₂	$0.42 \pm 0.2(11)$	$0.70 \pm 0.23(5)$	0.59(1)	0.90(1)	0.40 ± 0.35(2)	$0.63 \pm 0.38(4)$	
Thiophene	0.50 ± 0.34(11)	0.78 <u>+</u> 0.72(5)	0.29	0.24(1)	4.47 <u>+</u> 0.18(2)	4.96 ± 1.35(2)	
Methyl Thiophene	$0.29 \pm 0.09(11)$	0.36 ± 0.20(5)	0.15(1)	0.12(1)	0.75 ± 0.86(2)	$2.89 \pm 1.19(4)$	
Dimethyl Thiophene	0.34 ± 0.02(11)	$0.30 \pm 0.14(5)$	≃ O(1)	<pre>~ 0(1)</pre>	$0.23 \pm 0.06(2)$	$0.46 \pm 0.21(4)$	
Benzene	93.9 ± 68.6(11)	53.9 <u>+</u> 22.9(5)	71.2(1)	39.3(1)	76.0 + 8.2(2)	46.9 + 22.0(4)	
Toluene	6.06 <u>+</u> 5.50(4)	5.65 <u>+</u> 2.36(5)	4.70(1)	3.00(1)	7.26 + 1.57(2)	14.2 + 8.3(4)	
Xylene	1.20 ± 1.00(11)	2.14 ± 1.15(5)	1,18(1)	0.30(1)	$1.21 \pm 0.58(2)$	3.32 ± 2.01(4)	

TABLE	12	Comparison	of	SYN	THANE	ta11	l-gas	s vields	tor	several	coalg
		gasified with	Lth	and	with	out t	he d	lip-tube	at	40-atmost	heres

Additive	None	2 pct Quick Lime	5 pct Quick Lime	2 pct Hydrated Lime	5 pct Hydrated Lime	5 pct Limestone
Operating Condition	s:					
Coal Feed Ratio (lb/hr)	23.7 ± 2.0(11)	24.2 ± 2.1(2)	24.2 + 2.1(2)	22.9 ± 0.0(2)	21.1 + 0.6(2)	25.7 ± 0.4(2)
0 ₂ /Coal Ratio (Ib/lb)	0.25 ± 0.04(11)	0.25 ± 0.02(2)	$0.21 \pm 0.00(2)$	0.27 ± 0.04(3)	$0.29 \pm 0.06(2)$	0.24 ± 0.00(2
Steam/Coal Ratio (1b/1b)	1.08 ± 0.30(11)	0.87 ± 0.13(2)	0.79 <u>+</u> 0.01(2)	1.30 ± 0.37(3)	1.37 ± 0.11(2)	.98 ± 0.00(2)
Average Bed Temperature °C	911 <u>+</u> 10(11)	904 <u>+</u> 1(2)	914 <u>+</u> 2(2)	913 <u>+</u> 7(3)	923 ± 20(2)	901 <u>+</u> 1(2)
Product Yields: (sc	f/lb coal maf)					
CH,	3.33 + 0.45(4)	4.04 + 0.23(2)	$4.21 \pm 0.32(2)$	3.90 ± 0.30(3)	4.10 ± 0.14(2)	$3.40 \pm 0.00(2)$
$(CH_{1} + CO + H_{2})$	$13.55 \pm 1.62(4)$	$11.93 \pm 1.51(2)$	12.89 ± 0.79(2)	$13.83 \pm 1.97(3)$	$16.40 \pm 3.54(2)$	12.00 ± 0.140
Equivalent CH_{4} (CH_{4} + (CO + H_{2})/4)	5.89	6.01	6.38	6.38	7.18	5.55
By-Product Yields (scf/ton coal maf)					
H_S	143.6 + 48.8(4)	ND	201.8(1)	$221.3 \pm 189.0(2)$	384.50 <u>+</u> 194(2)	ND
2 ⁻ Methvl Mercaptan	_ 1.05 + 0.49(4)	ND	1.35(1)	$0.67 \pm 0.36(2)$	$1.00 \pm 0.62(2)$	ND
cos	- 8.46 + 4.37(4)	ND	0.27(1)	$9.40 \pm 12.70(2)$	18.9 <u>+</u> 16.6(2)	ND
S0	- <0.63 + 0.38(4)	ND	0.24(1)	$0.22 \pm 0.13(2)$	$0.81 \pm 0.03(2)$	ND
2 Thiophene		ND	1.08(1)	$3.37 \pm 0.22(2)$	4.88 ± 0.17(2)	ND
Methyl Thiophene	$-2.85 \pm 1.19(3)$	ND	0.16(1)	$1.18 \pm 0.81(2)$	$3.33 \pm 0.37(2)$	ND
Dimethyl thiophene	- 0.46 + 0.21(3)	ND	0.13(1)	$0.19 \pm 0.18(2)$	$0.94 \pm 0.33(2)$	ND
Benzene	46.9 + 22.0(3)	ND	13.7(1)	53.5 + 9.62(2)	76.2 ± 1.5(2)	ND
Toluene	- 14.2 + 8.3(3)	ND	2.29(1)	8.53 <u>+</u> 0.49(2)	$15.4 \pm 2.1(2)$	ND
Xvlene	3.32 + 2.01(3)	ND	0.54(1)	$2.09 \pm 0.07(2)$	4.26 <u>+</u> 1.30(2)	ND

TARLE 13 Comparison of the SYNTHANE Tail-Gas Yields for the gasification of Illinois No. 6 at
40 atmospheres with and without additives

coal was fed to the gasification section through the free-fall carbonization zone. Because of the scatter of the data no definite conclusions can be drawn from this table. However, it appears that (1) the mode of coal feed apparently has no significant effect on the yield of the gaseous components reported in table 9; and (2) the type of coal significantly affects the total gas (i.e., $CH_4 + CO + H_2$) make, which averages about 16.5 scf per pound of coal maf for the lignite and subbituminous coal and about 13.2 for Illinois No. 6 bituminous coal at a gasifier pressure of 40 atmospheres. It is interesting to note that the methane yield is about the same for the North Dakota lignite and Illinois No. 6 coal whereas the Montana subbituminous coal gives slightly higher methane yields.

The effect of pressure-associated factors (e.g., gas residence time) on the gas yield is most pronounced for the case of methane. Figure 9 shows the relationship between the methane yield and the gasification pressure. It can be seen that the Montana subbituminous coal is the superior methane producer. The data for the Illinois No. 6 and North Dakota lignite tend to group together.

The effect of feeding various additives mixed with the Illinois No. 6 coal in the SYNTHANE PDU is shown in table 13. Because of the high degree of scatter, it is not possible at this time to draw definite conclusions with regard to the effects of additives on the byproduct yields. However, the product yield data is less scattered and several trends can be seen in this data. The methane yield increases substantially and in similar amounts with the addition of quick and hydrated lime to the feed coal. However, there is not a clear distinction between adding 2 percent or 5 percent of these components. Limestone apparently does not effect the methane yield. Examination of the equivalent methane yield shows that hydrated lime is the most effective additive since it enhances both methane and the quantity of synthesis gas produced. Pukanic et al (9) have reported in more detail the effect of additives.

Char extracted from the bottom of the SYNTHANE gasifier is another major effluent stream of the SYNTHANE process. The average percentage of coal converted to char is given in table 14 along with the char composition.

In a commercial scale SYNTHANE plant, the production of char will be adjusted so that burning it will produce all process power and steam required in the SYNTHANE plant. For the gasification of high sulfur coal, stack gas clean-up will be required in the burning of the char. Before burning, a portion can possibly be used to absorb organics out of the SYNTHANE waste water. This possiblity is being explored at PERC.

In the 75 TPD SYNTHANE pilot plant the char will not be utilized to produce process power. One alternative scheme to dispose of the char will be to send it to a landfill. In order to assess the environmental aspect of this mode of disposal, experiments on the leaching of compounds from the SYNTHANE char by water have been carried out. In table 15, results



FIGURE 9. - Effect of Pressure on the Methane Make in the SYNTHANE PDU

			•
Coal Rank	North Dakota Lignite	Montana Subbituminous	Illinois No. 6 Bituminous
#Char/#Coal	0.196 + .048(35)	0.216 ± 0.039(17)	0.345 ± 0.044(31)
Proximate:			
Moisture, %	1.1 ± 0.7	0.8 ± 0.6	1.0 ± 0.8
Volatile Matter	8.9 <u>+</u> 1.9	4.9 ± 1.5	2.8 ± 1.0
Fixed Carbon	55.6 ± 9.5	49.7 <u>+</u> 15.0	61.6 <u>+</u> 6.7
Ash	34.4 <u>+</u> 9.8	44.6 <u>+</u> 15.2	34.6 ± 6.2
Oltimate:			
Hydrogen	1.2 ± 0.3	1.0 ± 0.3	0.9 ± 0.1
Oxygen	2.5 <u>+</u> 1.8	1.2 ± 1.1	1.1 ± 1.3
Carbon	60.8 <u>+</u> 8.6	52.0 <u>+</u> 14.6	61.8 <u>+</u> 6.0
Nitrogen	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
Sulfur	0.7 ± 0.4	0.8 ± 0.5	1.2 ± 0.4

TABLE 14. - Average rate of production and composition of SYNTHANE chars

are given for the leaching of one part by weight of Illinois No. 6 char to two parts distilled water for various periods of time at room temperature. The water and char were mixed manually daily to insure intimate contacting between the two phases; however, not all of the char would wet and some floated on the water.

As can be seen from table 15, the COD increases with longer contact time. The other results are questionable because of the detection limits of the analyses. Also reported are the results of a Soxhlet extraction of SYNTHANE chars. The char was leached with water for 10 days at 190° F. Since the conditions of the Soxhlet and other tests listed in Table 15 are quite severe, the results shown in this table can perhaps serve as an estimate for the leaching of contaminants from char by rainfall. These results are pertinent only to the 75 TPD plant where the char may be sent to a landfill. In a commercial SYNTHANE plant the char will be burned and the only solid byproduct will be ash.

The sulfur content of the char represents all the sulfur in the coal which was not gasified. Therefore, the percent of sulfur gasified can be calculated by

> Percent S Gasified = $[S]_{coal} f_{coal} - [S]_{char} E_{char}$ $\frac{[S]_{coal} f_{coal}}{[S]_{coal} f_{coal}}$

where [S] and [S] are the weight fractions of sulfur in the coal and char, respectively, and E is the rate of extraction of char from the gasifier, 1b/hr. Using this definition of percent sulfur gasified, figure 10 and table 16 were prepared. It can be seen in figure 10 that the percent sulfur gasified is not a function of the carbon conversion. Table 16 shows the average percent sulfur gasified. It can be seen from this table that the sulfur conversion increases with increasing gasification pressure. Also, the small standard deviations indicate that the percent sulfur gasified was essentially constant at a fixed pressure regardless of percent carbon gasified, solid residence time, etc. One interpretation of this observation could be that reactant partial pressure (possibly hydrogen partial pressure) or gas residence time are important factors influencing sulfur gasification.

CONCLUSIONS

The yields of potential pollutants in the effluent streams of the SYNTHANE gasifier and the effects of operating conditions and type of coal gasified on these yields have been presented and discussed in this report. In some cases it was found that definite conclusions could not be drawn because operating parameters were not varied independently. For example, variation in pressure was accompanied by variation in the gas residence time in both the gasifier and carbonizer. Also, the scatter of the experimental data in most cases was quite large, making the observation of trends in yields with operating conditions difficult. PERCENT SULFUR GASIFIED



Figure 10. - Effects of Carbon Conversion and Gasification Pressure on the Conversion of Sulfur in Coal to Gaseous Sulfur Products

Test	рН	Phenol	COD	Thiocyanate	Cyanide	Chloride	Phosphate	Ammonia
3-day	8.8	1.8	10	<u><</u> 2	<0.012	2	<u><2</u>	ND
7-day	9.6	<u><0.8</u>	14	<u><2</u>	<u><</u> 0.03	4	<u><2</u>	ND
30-day	9.1	<u><</u> 2.0	52	<u><</u> 10	<u><</u> 0.03	ND	ND	ND
Soxhlet Extraction		0.21	680	4.6	ND	ND	ND	46

TABLE 15. - Results of SYNTHANE char leaching studies(except for pH, all units mg/1000g char)

(Coal Type	North Dakota Lignite	Montana Subbituminous	Illinois No. 6 Bituminous
ssure	10	70.7 <u>+</u> 8.0(3)	57.8 <u>+</u> 5.4(2)	
l Pre	20	70.2 + 4.8(4)	80.4 + 3.7(7)	84.9 <u>+</u> 3.5(7)
ttion	30			92.0 ± 3.5(2)
Gastfica (at	40	88.6 ± 7.8(21)	89.0 ± 2.4(7)	90.4 <u>+</u> 3.5(18)

TABLE 16.Effects of gasification pressure on the extent
of sulfur gasification in various coals

The most influential factors affecting pollutant yields appear to be coal type and the method of feeding coal to the fluidized bed of the gasifier (i.e. free fall through the carbonizer or by-passing carbonizer using a dip tube.) The dip tube feeding of the coal was found to substantially reduce phenol, COD, thiocyanate, cyanide and tar yields associated with the condensate stream. However, dip tube feeding did not make significant changes in the contaminants found in the gas stream. The rank of the coal being gasified was by far the most influential factor affecting the production of possible environmental pollutants.

The effect of additives on the yield of contaminants in both the gas and condensate effluent streams was considered. Due to scatter of the data no significant effect on the production of condensate or gaseous contaminants due to feeding additives with the coal could be observed.

Although the data presented in this report is from a small scale SYNTHANE unit and has a significant amount of scatter, it can serve to estimate the production of potential environmental pollutants which must be treated in commercial SYNTHANE gasifiers and those with similar operational principles.

REFERENCES

- Rhodes, E.O. The Chemical Nature of Coal Tar. <u>Chemistry of Coal</u> <u>Utilization</u>, ed. by H. H. Lowry, Chapter 31, John Wiley and Sons, Inc., New York, N.Y., v. II, 1945, pp. 1287-1291.
- Nakles, D. V., M. J. Massey, A. J. Forney and W. P. Haynes. Influence of SYNTHANE Gasifier Conditions on Effluent and Product Gas Production. U.S. ERDA PERC/RI-75/6, 1975, 50 pp.
- Forney, A. J., W. P. Haynes, S. J. Gasior and R. F. Kenny. Effect of Additives Upon the Gasification of Coal in the SYNTHANE Gasifier. Proc. 167th National Meeting, Div. Fuel Chemistry, ACS, Los Angeles, Calif., v. 19, no. 1, pp. 111-122, April 1-5, 1974.
- Haynes, W. P., S. J. Gasior and A. J. Forney. Catalysis of Coal Gasification at Elevated Pressure. <u>Advances in Chemistry Series</u>, Number 131, <u>Coal Gasification</u>, p. 179, published by the ACS, 1974.
- Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson and J. P. Strakey. Analyses of Tars, Chars, Gases and Water Found in the Effluents from the SYNTHANE Process. U.S. BuMines TPR-76, 1974, 9 pp.
- Schmidt, C. E., A. G. Sharkey and R. A. Friedel. Mass Spectrometric Analysis of Product Water from Coal Gasification, U.S. BuMines TPR-86, 1974, 7 pp.
- Forney, A. J., W. P. Haynes, S. J. Gasior, R. M. Kornosky, C. E. Schmidt, and A. G. Sharkey. Trace Element and Major Component Balances Around the SYNTHANE PDU Gasifier. U.S. ERDA PERC/TPR-75/1, 1975, 23 pp.
- Strakey, J. P., A. J. Forney, W. P. Haynes and K. D. Plants. Effluent Treatment and Its Cost for the SYNTHANE Coal-to-SNG Process. Annual ACS Meeting, Atlantic City, N. J., Div. of Fuel Chemistry, ACS, v. 19, no. 5, 1974, pp. 94-103.
- Pukanic, G. W., W. P. Haynes, and R. R. Schehl. Statistical Analysis and Linear Programming Model for Illinois #6 Coal Gasification Data from the SYNTHANE Process. U.S. ERDA PERC/RI-77/1, 1977, 26 pp.

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