ANALYSES OF TARS, CHARS, GASES, AND WATER FOUND IN EFFLUENTS FROM THE SYNTHANE PROCESS

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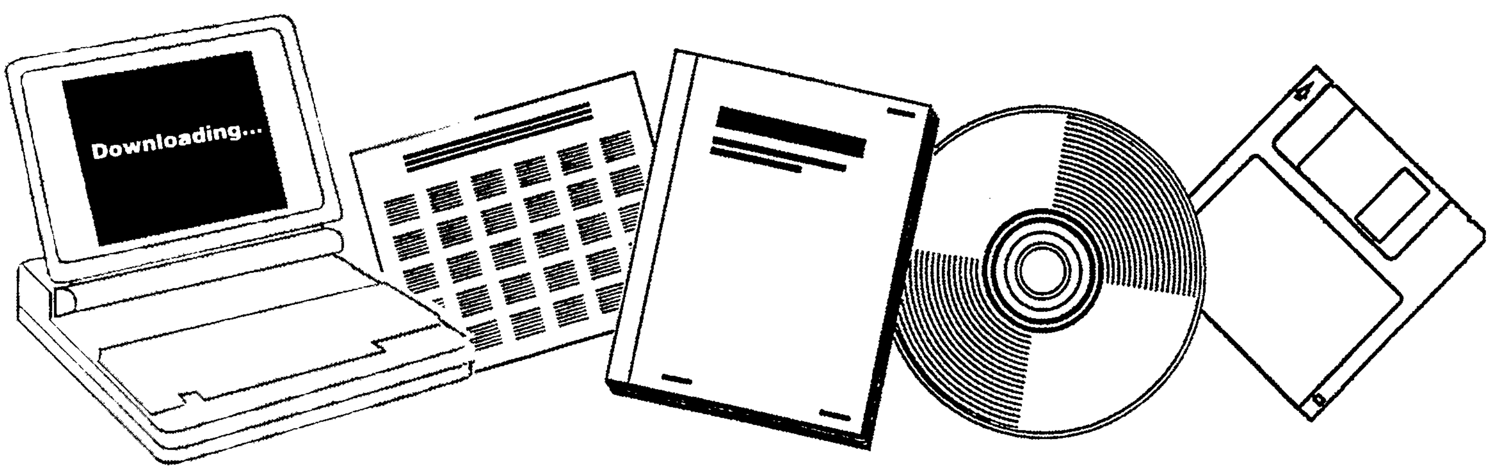

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Pittsburgh, Pennsylvania

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ANALYSES OF TARS, CHARS, GASES, AND WATER FOUND IN EFFLUENTS FROM THE SYNTHANE PROCESS

by

Albert J. Forney,[1] William P. Haynes,[2] Stanley J. Gasior,[3]
Glenn E. Johnson,[3] and Joseph P. Strakey, Jr.[2]

ABSTRACT

Extensive studies have been made of the various effluents found in the Synthane coal-to-gas process. Analyses have been made of the waters, gases, and trace elements present in some of the streams. Results of analyses show the water effluents are the area where extensive research is needed.

INTRODUCTION

One of the answers to the shortage of natural gas is to convert coal to a high-Btu gas. Four coal-conversion projects are proceeding to the prototype plant scale (75 to 120 tpd coal utilization) (2).[4] An aspect of coal gasification that is of major importance is the possible pollution resulting from the process. While the four prototype plants have different types of processing units, they will have similar effluents. This paper discusses this aspect of the Synthane process, based on the Bureau of Mines laboratory-scale gasifier at Bruceton, Pa.

The advantage of the Bruceton laboratory-scale Synthane gasifier in studying effluent problems is that the waters, tars, gases, and solids streams are representative of those that will be obtained from a commercial operation. There will be some difference due to temperatures and variations in steam-oxygen feed quantities, but the samples of streams discussed in the following tables will be quite representative of larger scale operation. This will also be true of the byproducts of the methanation step. Most of our knowledge of these effluents is based on the work at the Bruceton laboratories of the Pittsburgh Energy Research Center (PERC).

[1]Research supervisor.
[2]Supervisory chemical engineer.
[3]Chemical engineer.
[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ACKNOWLEDGMENT

At PERC the solids, water, and tar analyses were mostly performed by the General Analysis group headed by H. Schultz, with special thanks due to F. E. Walker, J. F. Smith, and M. F. Ferrer. Other water, tar, and gas analyses were made by the Spectro-Physics group headed by R. A. Friedel with A. G. Sharkey and C. E. Schmidt. Trace element analysis (table 2) of the waters was done by Charles E. Taylor of EPA, and the tar and gas were analyzed by Bernard Keisch of Carnegie-Mellon University. The HCN analyses were performed by Dr. Schultz's group.

THE OVERALL PROCESS

The overall process is schematically shown in figure 1. This is the 75-tpd pilot plant designed by the Lummus Co. and being built at Bruceton, Pa., by the Rust Engineering Co. Figure 1 shows the major units--the gasifier, shift converter, purification systems, and methanators. Each of these units has its byproduct streams.

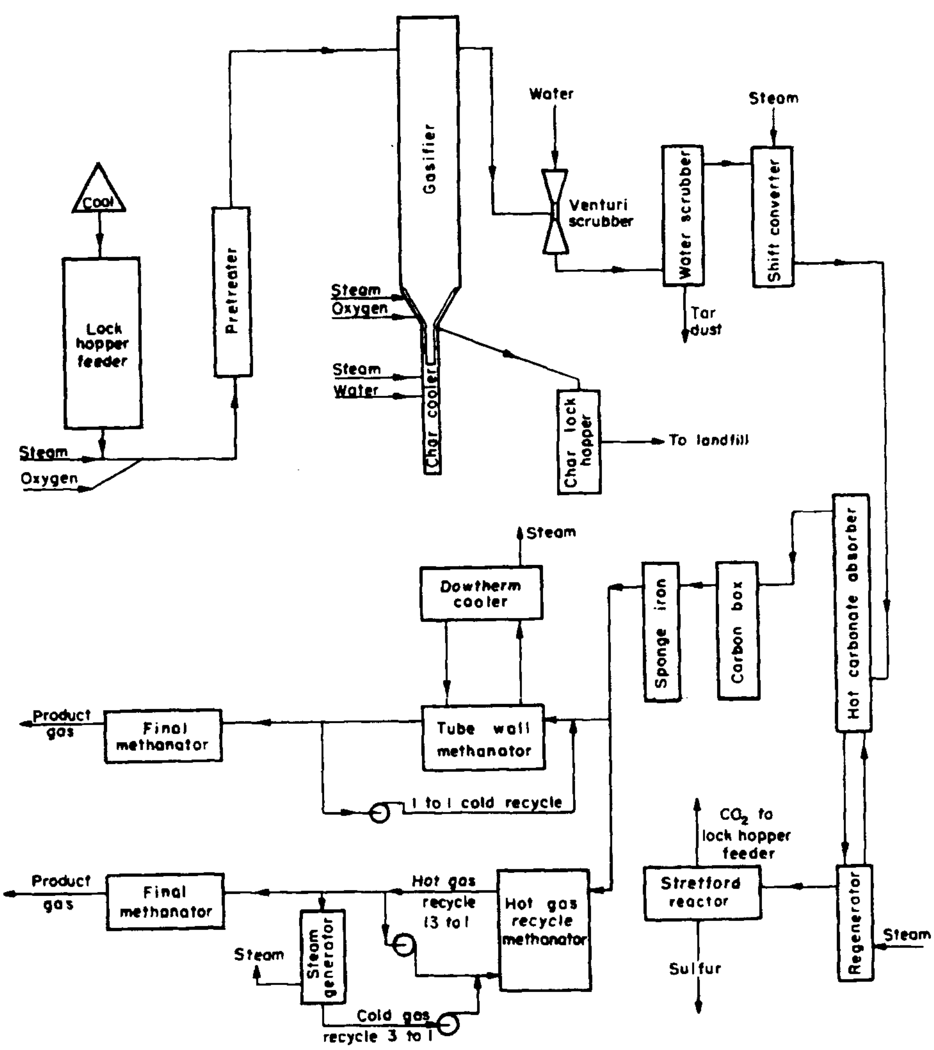

FIGURE 1. - Flowsheet of prototype Synthane process.

WATER ANALYSIS

The major effluent problem is the contaminated condensate from the gasifier. The Bruceton laboratory gasifier shown in figure 2 condenses the water, tars, and dusts in two water-cooled condensers operated at 100° and 50° C. Table 1 shows the analysis of the condensate from gasification tests with a number of different coals compared with a coke-plant weak ammonia liquor. Bethlehem Steel Co. at its

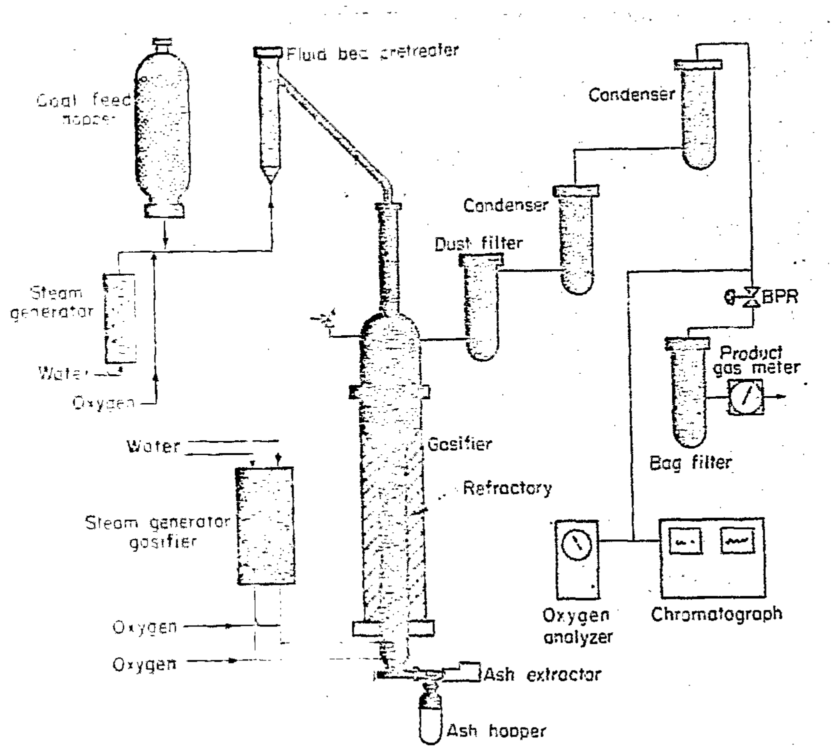

FIGURE 2. - Forty-atmosphere fluid-bed gasifier.

Bethlehem, Pa., plant (4) has reduced the phenol level of its weak ammonia liquor to 100 ppb by biological oxidation and has reduced the thiocyanates by an average of 70 percent. This plant has been operating at Bethlehem for over 10 years, and the effluent of the plant satisfactorily meets Pennsylvania pollution requirements. Therefore, we consider this system a satisfactory means of solving the effluent problems of the Synthane plant. However, work is continuing on new and better methods of alleviating these problems.

TABLE 1. - Byproduct water analysis from Synthane gasification of various coals, mg/l (except pH)

	Coke plant	Illinois No. 6 coal	Wyoming subbituminous coal	Illinois char	North Dakota lignite	Western Kentucky coal	Pittsburgh seam coal
pH	9	8.6	8.7	7.9	9.2	8.9	9.3
Suspended solids	50	600	140	24	64	55	23
Phenol	2,000	2,600	6,000	200	6,600	3,700	1,700
COD	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Thiocyanate	1,000	152	23	21	22	200	188
Cyanide	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3	5,000	[1]8,100	9,520	2,500	7,200	10,000	11,000
Chloride	-	500	-	31	-	-	-
Carbonate	-	[2]6,000	-	-	-	-	-
Bicarbonate	-	[2]11,000	-	-	-	-	-
Total sulfur	-	[3]1,400	-	-	-	-	-

[1]85 percent free NH_3.
[2]Not from same analysis.
[3]$S^{=}$ = 400
$SO_3^{=}$ = 300
$SO_4^{=}$ = 1,400
$S_2O_3^{=}$ = 1,000

Additional analyses of the condensate were performed by the Environmental Protection Agency at its Southeast Environmental Research Laboratory; the trace elements in the water are shown in table 2.

TABLE 2. - Trace elements in condensate from an Illinois No. 6 coal gasification test

	No. 1	No. 2	Average (by weight)
Ppm:			
Calcium	4.4	3.6	4
Iron	2.6	2.9	3
Magnesium	1.5	1.8	2
Aluminum	0.8	0.7	0.8
Ppb:			
Selenium	401	323	360
Potassium	117	204	160
Barium	109	155	130
Phosphorus	82	92	90
Zinc	44	83	60
Manganese	36	38	40
Germanium	32	61	40
Arsenic	44	28	30
Nickel	23	34	30
Strontium	33	24	30
Tin	25	26	20
Copper	16	20	20
Columbium	7	5	6
Chromium	4	8	6
Vanadium	4	2	3
Cobalt	1	2	2

For a commercial coal-to-gas plant this water would be purified as completely as possible and then used as a recycled cooling water; therefore, it could not possibly contaminate any streams.

GAS ANALYSIS

Besides the large quantities of H_2, CO, CO_2, CH_4, and C_2H_6 made in the gasifier, there are a number of trace components which are of interest. These are shown in table 3 which shows the sulfur compounds plus the BTX (benzene-toluene-xylene) components. The sulfur compounds must be removed before methanation because of their poisoning effect on the nickel catalyst. The use of Benfield[5] hot carbonate gas purification followed by sponge iron and activated carbon traps should accomplish this goal.

TABLE 3. - Components in gasifier gas, ppm

	Illinois No. 6 coal	Illinois char	Wyoming subbituminous coal	Western Kentucky coal	North Dakota lignite	Pittsburgh seam coal
H_2S	9,800	186	2,480	2,530	1,750	860
COS	150	2	32	119	65	11
Thiophene	31	.4	10	5	13	42
Methyl thiophene	10	.4	-	-	-	7
Dimethyl thiophene	10	.5	-	-	11	6
Benzene	340	10	434	100	1,727	1,050
Toluene	94	3	59	22	167	185
C_8 aromatics	24	2	27	4	73	27
SO_2	10	1	6	2	10	10
CS_2	10	-	-	-	-	-
Methyl mercaptan	60	.1	.4	33	10	8

In industrial practice, the BTX would be removed in the oil scrubber (fig. 1). A commercial plant (250,000,000 scfd) will produce about 25,000 gpd of BTX.

TAR ANALYSIS

Tar analyses were made by our own and other laboratories as shown in tables 4 and 5. Table 4 shows analyses of tars from various coals and the variety of products found in the tar.

Elemental analyses of tars are shown below, in percent:

	Illinois No. 6	Illinois No. 6	Lignite
Carbon	82.6	83.4	83.8
Hydrogen	6.6	6.6	7.7
Nitrogen	1.1	1.1	1.0
Sulfur	2.8	2.6	1.1

These analyses are reported on a moisture- and ash-free basis. Oxygen can be obtained by difference from 100 percent. It is planned to burn the tars

[5]Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

in the boiler because it would be too expensive to try to separate the chemical compounds for sale.

TABLE 4. - Mass spectrometric analyses of the benzene-soluble tar, volume-percent

Structural type (includes alkyl derivatives)	Run HP-1 No. 92, Illinois[1] No. 6 coal	Run HPL No. 94, lignite	Run HPM No. 111, Montana subbituminous coal	Run HP-118 No. 118,[1] Pittsburgh seam coal
Benzenes	2.1	4.1	3.9	1.9
Indenes	[2]8.6	1.5	2.6	[2]6.1
Indans	1.9	3.5	4.9	2.1
Naphthalenes	11.6	19.0	15.3	16.5
Fluorenes	9.6	7.2	9.7	10.7
Acenaphthenes	13.5	12.0	11.1	15.8
3-ring aromatics	13.8	10.5	9.0	14.8
Phenylnaphthalenes	9.8	3.5	6.4	7.6
4-ring pericondensed	7.2	3.5	4.9	7.6
4-ring catacondensed	4.0	1.4	3.0	4.1
Phenols	2.8	13.7	5.5	3.0
Naphthols	([2])	9.7	9.6	([2])
Indanols	.9	1.7	1.5	.7
Acenaphthenols	-	2.5	4.6	2.0
Phenanthrols	2.7	-	.9	-
Dibenzofurans	6.3	5.2	5.6	4.7
Dibenzothiophenes	3.5	1.0	1.5	2.4
Benzonaphthothiophenes	1.7	-	-	-
N-heterocyclics[3]	(10.8)	(3.8)	(5.3)	(8.8)
Average molecular weight	212	173	230	202

[1]Spectra indicate traces of 5-ring aromatics.
[2]Includes any naphthol present (not resolved in these spectra).
[3]Data on N-free basis since isotope corrections were estimated.

SULFUR ANALYSIS

Sulfur analyses of the various coals tested and products are shown in table 5.

TABLE 5. - Sulfur content of coals and products, weight-percent (except gas)

	Coal type			
	Pittsburgh seam coal	Illinois No. 6 coal	Montana subbituminous coal	North Dakota lignite
Coal	1.5	3.5	0.6	1.1
Char	.5	1.1	.4	.6
Tar	.8	2.7	.5	1.0
Condensate	<.1	<.1	<.1	<.1
Gas........vol-pct.	.3	1.1	.4	.3

SOLIDS ANALYSIS

The residue (char) from the gasifier in a commercial plant is to be burned along with the tars to raise steam for the process. The ultimate and proximate analyses of the chars are shown in table 6. The chars would contain a percentage of trace elements shown in ash analyses done by the Bureau (1, 3). A problem may exist with SO_x in stack gases when burning the char and tars from the gasification of high-sulfur coal.

TABLE 6. - Representative analyses of coals and chars, weight-percent

	Illinois No. 6 coal	Western Kentucky coal	Wyoming subbituminous coal	North Dakota lignite	Pittsburgh seam coal
Coals:					
Moisture..........	8.3	4.3	18.1	20.6	2.5
Volatile matter...	37.5	34.6	31.9	32.9	30.9
Fixed carbon......	43.0	44.5	32.0	38.2	51.5
Ash...............	11.2	16.6	18.0	8.3	15.1
Hydrogen..........	5.3	4.7	5.4	5.7	4.7
Oxygen............	15.9	10.9	30.3	32.6	9.3
Carbon............	63.0	62.7	45.2	51.5	68.4
Nitrogen..........	1.1	1.2	.6	.7	1.2
Sulfur............	3.5	3.9	.5	1.2	1.3
Chars (from above coals):					
Moisture..........	.8	1.2	.5	1.2	1.4
Volatile matter...	4.0	4.8	5.1	10.0	1.6
Fixed carbon......	69.9	63.3	38.1	50.2	69.3
Ash...............	25.3	30.7	56.3	38.6	27.7
Hydrogen..........	1.0	1.0	1.0	.9	1.0
Oxygen............	1.3	1.1	1.2	.0	1.7
Carbon............	70.4	64.5	40.6	58.9	68.9
Nitrogen..........	.6	.7	.4	.2	.5
Sulfur............	1.4	2.0	.5	2.0	.2

OTHER STREAMS

Since we operate both gasification and methanation laboratory-size equipment at PERC, we have analyzed these streams extensively. No serious contaminants have been detected in the water from the methanation reactors. The other process steps are not being investigated by PERC, but some assumptions can be made. It would be reasonable to assume the contaminated condensate from the shift converter would be similar to but more dilute than the gasifier condensate shown in table 1. There should be no effluent from the hot carbonate unit if the feed gas contains the proper partial pressure of water. The Stretford unit should have a gas effluent low enough in sulfur for air pollution requirements for the 75-tpd plant at Bruceton.

TRACE ANALYSIS

Other analyses that took special methods are shown in table 7. The HCN analysis is of special significance since it could effect the operation of the Stretford unit in the 75-tpd pilot plant. However the low level (ppb) indicates no serious problem. Mercury is present in the gas from the gasifier, but none was detected in the final product; that is, in the high-Btu gas. The mercury and arsenic in the tars, if burned, would probably end up in the stack gas.

TABLE 7. - Trace components in gas and tar

	Gas (by volume)		Tar (by weight)	
	HCN, ppb	Mercury, ppm	Mercury, ppm	Arsenic, ppm
Illinois char...............	5	-	-	-
Illinois No. 6 coal.........	20	0.00001	0.003	0.7
Western Kentucky coal.......	11	-	-	-
North Dakota lignite........	3	-	-	-
Wyoming subbituminous coal..	2	-	-	-

CONCLUSION

While we have obtained much data, we are continuing to analyze these effluent streams exhaustively and hope to completely characterize these effluents and have solutions available for handling them before the 75-tpd plant is operating. No serious problems are foreseen at this time.

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