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MASS SPECTROMETRIC ANALYSIS OF PRODUCT WATER FROM COAL GASIFICATION

by

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C. E. Schmidt,[1] A. G. Sharkey, Jr.,[2] and R. A. Friedel[3]

ABSTRACT

Condensate waters from the Bureau of Mines Synthane process for coal gasification have been investigated by mass spectrometric methods to determine the organic contaminants. Waters from the gasification of six coals were extracted with methylene chloride, yielding 0.6 to 2.4 weight-percent extractable material. Using high-resolution mass spectrometry (HRMS), combined gas chromatography-mass spectrometry (GC-MS), and low-voltage mass spectrometry, 60 to 80 percent of the extract was found to be phenolic. About 20 organic contaminants have been identified and are present in the condensate waters from each coal gasified. The relative distribution of contaminants in the condensate water was nearly the same for the six coals gasified under various conditions; phenolic compounds were the most abundant in all cases.

INTRODUCTION

As part of a program at the Federal Bureau of Mines to produce an environmentally acceptable synthetic natural gas, the Synthane process (2-3)[4] has been developed for the gasification of coal. This process has several advantages over other gasification processes for the manufacture of high-Btu gas from coal, including the fact that any type of coal, even the caking varieties, can be used. The four steps in the process are (1) pretreatment of the coal, (2) gasification, (3) purification of the gas, and (4) methanation.

The condensate water, resulting mainly from unused steam fed to the gasifier, is a possible major source of pollution because 0.4 to 0.6 ton of water is recovered for every ton of coal gasified (4). Detailed information concerning the trace constituents is required so that proper purification systems can be devised and implemented. This report describes the analytical techniques used for determination of the major contaminants inherent in condensate water from the laboratory-scale Synthane gasification unit.

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL PROCEDURE AND RESULTS

Organic material in the condensate water was concentrated by a methylene chloride extraction technique. Typically, 2 liters of condensate water was extracted with methylene chloride under both acidic and basic conditions. The condensate water as received generally had a pH of 7 to 9. Hydrochloric acid and sodium hydroxide were used to adjust the pH for the two extractions. About 1 percent sodium chloride was added to the condensate water for "salting-out" organic compounds with relatively high water solubility. Excess methylene chloride was distilled off at 41° C.

The organic extracts were analyzed by high-resolution mass spectrometry (HRMS), combined gas chromatography-mass spectrometry (GC-MS), and low-voltage mass spectrometry (6). HRMS was used to determine the formulas of the organic compounds shown in table 1. Individual compounds were then identified by GC-MS as illustrated in figure 1. Semiquantitative data were obtained using low-voltage mass spectrometry.

Byproduct waters used in this study were from the gasification of six coals--Illinois (hvBb), Wyoming (sub), Western Kentucky (hvBb), Pittsburgh

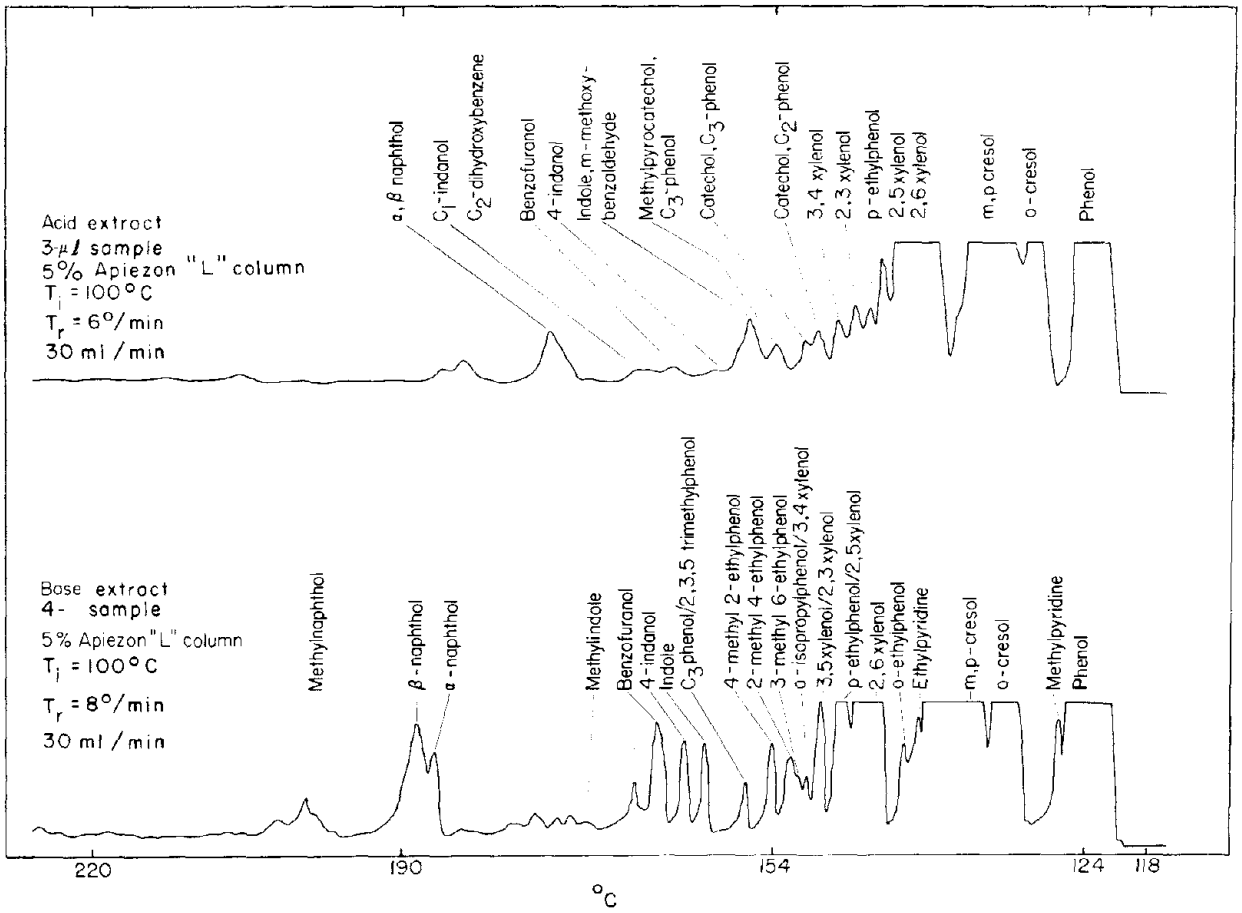

FIGURE 1. - Contaminants in product water from coal gasification: Gas chromatography-mass spectrometry data.

(hvAb), Montana (sub), and North Dakota (lig)--under various experimental conditions including use of "promoters" (5) such as limestone to alter the gasification characteristics.

TABLE 1. - Contaminants in product water from coal gasification: High-resolution mass spectrometer data

Mass (nominal)	Precise mass, amu		[1] $\Delta \times 10^3$	Formula	Possible compound type
	Meas.	Calc.			
79	79.004	79.002	2	C_5H_5N	Pyridine.
93	93.058	93.057	1	C_6H_7N	Methylpyridine.
94	94.041	94.042	1	C_6H_6O	Phenol.
107	107.071	107.074	3	C_7H_9N	C_2-pyridine.
108	108.055	108.057	2	C_7H_8O	Cresol.
110	110.036	110.037	1	$C_6H_6O_2$	Dihydroxybenzene.
117	117.057	117.058	1	C_8H_7N	Indole.
120	120.056	120.057	1	C_8H_8O	Acetophenone.
121	121.088	121.089	1	$C_8H_{11}N$	C_3-pyridine.
122	122.036	122.037	1	$C_7H_6O_2$	Benzoic acid, hydroxybenzaldehyde.
	122.073	122.073	0	$C_8H_{10}O$	C_2-phenol.
124	124.052	124.052	0	$C_7H_8O_2$	C_1-dihydroxybenzene.
129	129.055	129.058	3	C_9H_7N	Quinoline.
132	132.055	132.058	3	C_9H_8O	Indenol.
134	134.035	134.037	2	$C_8H_6O_2$	Hydroxybenzofuran.
	134.070	134.073	3	$C_9H_{10}O$	Indanol.
135	135.144	135.145	1	$C_9H_{13}N$	C_4-pyridine.
136	136.051	136.052	1	C_8H_8O	C_1-benzoic acid, methoxybenzaldehyde.
	136.087	136.088	1	$C_9H_{12}O$	C_3-phenol.
138	138.066	138.068	2	$C_8H_{10}O$	C_2-dihydroxybenzene.
143	143.057	143.058	1	$C_{10}H_9N$	Methylquinoline.
144	144.056	144.058	2	$C_{10}H_8O$	Naphthol.
146	146.069	146.073	4	$C_{10}H_{10}O$	C_1-indenol.
148	148.052	148.052	0	$C_9H_8O_2$	C_1-benzofuranol.
150	150.013	150.014	1	C_8H_6OS	Hydroxybenzothiophenol.
	150.069	150.068	1	$C_9H_{10}O_2$	C_2-benzoic acid, C_2-hydroxybenzaldehyde.
157	157.172	157.170	2	$C_{11}H_{11}N$	C_2-quinoline.
158	158.073	158.073	0	$C_{11}H_{10}O$	C_1-naphthol.
186	186.066	186.068	2	$C_{12}H_{10}O$	Biphenol.

[1] Difference between measured and calculated precise mass.

DISCUSSION

Organic compounds containing oxygen, sulfur, and nitrogen were found in the condensate water. As shown by the data in table 2, oxygen compounds are by far the most abundant contaminants. Phenolic-type compounds were present in concentrations ranging from 2,000 to 7,000 ppm. Data in figure 1 confirm that nearly all of the substituted cresols, xylenols, and C_3 phenols were present. Meta- and para-cresol were not separable under the chromatographic conditions employed. Identification of all the isomeric C_2 phenols was not possible because of the closeness of retention times and the similarity of mass spectral patterns. Reference spectra were not available for all the compounds listed in table 2. Identification of some of the compounds listed was based on comparison of HRMS data with compounds previously identified in various coal derivatives (1). Tentative identifications were also made by comparing the sample with a synthetic blend of substituted phenols and by "spiking" the samples with small amounts of pure compounds.

The dihydroxybenzenes along with their alkyl derivatives were also in high concentration, with up to 500 ppm being detected in several samples. Compounds containing nitrogen were also detected in condensate waters from gasification runs; substituted pyridines and quinolines were the most prevalent, generally in concentrations of 200 to 500 ppm. Indole was detected in concentrations of less than 100 ppm.

The only sulfur compound detected was hydroxybenzothiophenol. The concentration of hydroxybenzothiophenol paralleled the amount of sulfur in the feed coal. The Illinois and Western Kentucky coals contained about the same percent sulfur, 2-4; however, the Wyoming coal contained less than 1 percent sulfur, and the water showed a lower concentration of hydroxybenzothiophenol.

The relative distribution of contaminants in the condensate water was approximately the same for the six coals gasified. More data are needed before conclusions can be made on the effects of promoters on the contaminants in the condensate water.

TABLE 2. - Contaminants in product water from coal gasification: Low-voltage mass spectrometer data, ppm by weight

Promoter.....	Illinois No. 6 (hvBb)										Montana (sub)			N. Dak. (lig)		Wyo. (sub)	W. Ky. (hvBb)	Pgh. (hvAb)
	None	None	2 pct limestone		2 pct quick-lime	5 pct quick-lime	Air instead of O_2	Coal fed directly into gasifier bed			None	Air instead of O_2		None	Air instead of O_2	None	None	None
			1	2				1	2	3		1	2					
Phenol.....	3,400	2,660	2,640	2,890	2,490	1,130	2,770	1,300	1,270	1,000	3,160	4,480	4,230	2,790	3,590	4,050	2,040	1,880
Cresols.....	2,840	2,610	1,760	2,720	2,470	3,580	2,860	530	890	930	870	2,100	2,400	1,730	1,450	2,090	1,910	2,000
C_2-phenols...	1,090	780	560	800	660	1,170	860	140	270	330	240	440	560	450	260	440	620	760
C_3-phenols...	110	100	70	130	90	150	110	20	50	50	30	60	80	60	40	50	60	130
Dihydrics....	250	540	140	60	170	300	30	60	20	20	130	70	-	70	170	530	280	130
Benzofuranols	70	100	70	120	100	80	110	30	40	50	80	100	120	60	50	100	50	70
Indanols..... Acetophenones	150	100	100	140	140	130	150	40	50	60	140	70	80	110	50	110	90	120
Hydroxy-benzaldehyde Benzoic acids	60	110	100	40	60	210	40	20	10	10	-	-	-	40	-	60	50	80
Naphthols....	160	110	180	290	170	270	210	110	140	180	160	180	160	140	30	80	160	170
Indenols.....	90	90	70	110	90	60	90	30	40	30	70	80	70	50	30	60	80	20
Benzofurans..	-	-	10	10	30	10	20	10	10	80	10	10	10	10	-	-	-	110
Dibenzofurans	-	-	-	-	-	-	-	-	-	10	-	-	-	-	-	-	-	-
Biphenols....	40	20	-	-	-	110	-	-	-	10	-	-	-	-	-	40	20	60
Benzothio-phenols.....	110	60	100	150	130	20	120	70	90	120	-	-	-	10	-	20	70	20
Pyridines....	-	60	210	240	180	250	580	130	270	320	270	160	270	220	300	120	30	540
Quinolines...	-	-	20	-	20	10	20	40	30	100	20	10	20	10	-	-	-	10
Indoles.....	-	20	40	60	40	70	40	70	100	110	70	70	70	30	-	20	40	40

CONCLUSIONS

The environmental impact of any coal process must be thoroughly evaluated, and purification schemes must be devised to rid the effluent streams of potential health hazards. As evidenced by the data for the condensate water, phenolic compounds are the largest contaminants in this stream. Since phenol can be detected by taste in concentrations in the parts-per-billion range, essentially complete removal is necessary before the byproduct waters can be released. Additional investigations should be conducted to determine precisely the amounts of the isomeric phenolic compounds present. Other techniques such as the concentration of trace impurities by an ion-exchange resin are being used to determine other contaminants present in levels too low for conventional extraction procedures.

While the Synthane process for conversion of coal to natural gas shows great promise, thorough investigation of all streams is necessary to determine potential environmental hazards.

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