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CHARACTERIZATION OF GFETC COAL-GASIFICATION CONDENSATE WATERS

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INTRODUCTION

The overall objective of our project at the Lawrence Berkeley Laboratory is to develop and assess physicochemical processing technology suitable for coal-gasification condensate waters. In association with this goal, analytical techniques are being developed to characterize individual organic compounds which contribute substantially to the chemical oxygen demand (COD). Liquid-liquid phase equilibria of various conventional and novel solvents are being investigated so as to identify solvents that can remove large fractions of the COD at low solvent/water ratios. A third area of investigation is a novel approach that combines stripping and solvent extraction to remove and isolate ammonia and acid gases (CO_2, H_2S)from sour waters such as condensate waters from coal conversion. This paper is limited to the characterization of the organic compounds in condensate-water samples from the Grand Forks Energy Technology Center (GFETC) slagging fixed-bed gasifier.

High-performance liquid chromatography (HPLC) and gas chromatography (GC) have been employed to resolve and detect quantitatively organic compounds in condensate waters. A novel GC-MS technique has been developed to provide qualitative identification of polar organic compounds in HPLC fractions. Laboratory procedures have been used for quantitative measurement of chemical oxygen demand (COD), organic nitrogen and organic sulfur. In addition, solvent extraction, distillation, and ultrafiltration techniques have been employed to yield information about physical properties of various constituents of the condensate water.

EXPERIMENTAL PROCEDURE

Condensate-Water Samples. Four samples of condensate water were obtained from the GFETC gasifier. The samples were collected and all experiments were performed under an inert atmosphere to prevent oxidation by air. The samples were shipped by air freight and analyzed as rapidly as possible. After receipt, the samples were stored in dark glass bottles in a cold room at 4°C.

Analyses of Condensate Waters by HPLC and GC. In reversed-phase HPLC the stationary phase is a non-polar hydrocarbon and the mobile phase is a polar solvent. A major advantage of this technique is that the aqueous condensate water can be injected directly into the mobile phase without a preliminary solvent extraction.

In this work a Spectra-Physics SP 8000-B HPLC pump was utilized. The HPLC column was a Waters Associates Radial Compression Module with an octadecyl silane stationary phase. A Perkin-Elmer LC-75 variable-wavelength UV absorbance detector was employed.

Two solvents were used to form the mobile phases. The first was water buffered to pH 3 with 0.004 M $K_2H_2PO_4$ and 0.0017 M H_3PO_4. The second solvent was HPLC-grade methanol (Burdick & Jackson Co.).

The samples were eluted following two different sets of HPLC operating conditions. The first involved a linear gradient from 100% pH 3 water to 30% v/v water and 70% v/v methanol at an elution volume of 42 mL with a flow rate of 1 mL/min and UV absorbance detection at 280 nm. These conditions provided an effective analysis for phenols, including compounds 1-7 in Table 1. Inspection of

this chromatogram showed that no major components were detected in the first portion of the chromatogram where the more polar compounds would be expected to elute. Therefore, the sample was eluted a second time with an isocratic mobile phase of pure water. This "weak" solvent maximizes the resolution of polar compounds and is sufficiently transparent in the far UV so that the detector can be operated at 192 nm where many more compounds absorb strongly. Compounds 8-12 in Table 1 were detected with these conditions.

Quantitative measurements were obtained by calibrating the UV absorbance detector with mixtures of known composition. The precision of the HPLC measurements was approximately ±5%. These techniques are described in greater detail elsewhere (1).

A GC technique was employed to analyze for methanol, acetone, and acetonitrile. The aqueous sample was injected directly into a Varian Model 3700 gas chromatograph, containing an 18-inch Porapak R column. The temperature was programmed from 80 to 100°C, and the compounds were detected with a flame-ionization detector. The precision of the GC measurements was about ±2%.

Qualitative Identification Procedures. Once the solutes were resolved and detected with the HPLC, it was necessary to obtain a qualitative identification. In the first qualitative identification procedure, HPLC co-chromatography, a known compound was added to the condensate-water mixture and the liquid chromatography was repeated. If there was no resolution between the added compound and the peak of interest, then the unknown solute was assigned the structure of the added compound.

Mass spectrometry is an effective tool for identifying compounds. LC-MS interfaces are at an early stage of development and are not readily available. Therefore, a novel sample-preparation technique was developed which allowed GC-MS identification of indiviual compounds after they were isolated by means of the HPLC.

In this procedure, fractions containing individual HPLC peaks were collected in dilute aqueous solution. This solution (5 mL) was mixed with 50 mL of isopropanol (Burdick & Jackson Co.) to form a solution near the azeotropic composition. The mixture was evaporated to 1 mL. More isopropanol (10 mL) was added and the mixture was evaporated to 0.1 mL. This azeotropic distillation produced a water-free isopropanol concentrate suitable for GC-MS analysis. The operating conditions of the GC-MS are described by Mohr and King (1). The recovery of a solute with this technique depends strongly on its volatility in the isopropanol-water solution. However, moderately volatile compounds can be concentrated to the GC-MS detection limit even though the total solute recovery may be quite low. This technique was intended for qualititative identification only.

The principal advantage of this azeotropic-distillation procedure is that the solute, which may be very polar, does not have to distribute between an aqueous and an organic phase. In the standard methylene chloride/GC-MS technique many hydrophilic compounds may not be detected due to inadequate extraction.

Generic Analyses. Organic nitrogen is defined as the difference between Kjeldahl nitrogen and ammonia nitrogen. The condensate waters had a low concentration of organic nitrogen (200 mg/L), compared to a high concentration of ammonia (5,000 mg/L). To improve the precision of the organic-nitrogen measurement, most of the ammonia was removed by stripping with 4 moles N_2/mole H_2O at 25°C and high pH. This procedure may have removed some volatile organic-nitrogen compounds. Organic nitrogen and organic sulfur were measured according to standard procedures (2) by the Microanalytical Laboratory of the College of Chemistry at the University of California, Berkeley. The COD was measured according to standard procedures (2) with a precision of ±2%.

Liquid-Liquid Extraction. Liquid-liquid equilibria were measured by contacting the condensate waters with several solvents in simple batch equilibrations. The solvent-to-water ratio in all of the extractions was 1:1 by volume. If several extractions were performed in series, then the raffinate from the previous

extraction was contacted with fresh solvent in a 1:1 volume ratio.

In order to measure the fraction of the feed COD remaining in a raffinate, it was necessary to remove the residual dissolved solvent from the solution. Methyl isobutyl ketone (MIBK) was obtained from Burdick and Jackson Co. and was purified by repeated washing with 0.1 N NaOH, 0.1 N H_2SO_4, and then water. In tests with distilled-water raffinates the purified MIBK was removed by stripping with 1.5 moles N_2/mole H_2O at 25°C to an MIBK concentration equal to or less than 5 mg/L, as determined by GC, and a COD less than 25 mg/L. With this procedure, the COD of condensate water raffinates could be measured with an estimated uncertainty of ±100 mg/L. Extractions were also performed with tributyl phosphate (TBP) and 25% w/w trioctyl phosphine oxide (TOPO) in MIBK. The removal of these solvents from the raffinates is discussed elsewhere (1).

RESULTS AND DISCUSSION

Analyses of Water Samples. Table 1 presents the quantitative analysis of four GFETC condensate-water samples. The compounds are divided into four groups. The first group is the hydroxybenzenes, or simple phenols. These compounds have been detected in many condensate waters. The estimated precision of ±5% in this work is a considerable improvement over the standard GC-MS analysis for these compounds.

The second group of compounds is the dihydroxybenzenes. These compounds are more polar and more difficult to extract than simple phenols. It is therefore important to have accurate quantitaive analyses of these compounds in condensate waters. However, the recovery of these compounds in the standard GC-MS technique is probably much lower than that for the simple phenols due to incomplete extraction.

The Lurgi Phenosolvan process and the Chem-Pro process are two solvent extraction processes which have been proposed for commercial-scale treatment of condensate waters. The solvents in these processes are diisopropyl ether (DIPE) and MIBK, respectively. DIPE exhibits K_D = 36 for phenol and K_D = 1 to 4 for the dihydroxybenzenes (3). Here K_D is the equilibrium distribution coefficient, defined as the ratio of the weight fraction of phenol in the organic phase to that in the aqueous phase at equilibrium. If the Phenosolvan process is designed to remove 99% of the phenol from a condensate water, then a much lower fraction of the dihydroxybenzenes will be removed. MIBK gives K_D's equal to 100 for phenol and equal to 10 to 19 for the dihydroxybenzenes (3). Since MIBK gives higher values of K_D for the dihydroxybenzenes than does DIPE, the presence of these compounds is an economic incentive to employ MIBK instead of DIPE in a solvent extraction process.

The third group of compounds is the hydantoins. The major component is 5,5-dimethyl hydantoin ($C_5H_8O_2N_2$). An earlier communication from this work (4) was the first report of hydantoins in condensate waters. Dimethyl hydantoin was identified by HPLC co-chromatography and by the isopropanol/GC-MS technique. The electron ionization (EI) GC-MS data were compared to the mass spectra obtained from the pure compound and from a literature report as described elsewhere (1). The identification of hydantoins, including dimethyl hydantoin, in a GFETC condensate was has been confirmed by Olson et al. (5).

Dimethyl hydantoin is a very polar compound with a low activity coefficient in water. Values of K_D for extraction of this compound into several solvents have been reported by Mohr and King (1) [methylene chloride, <0.05; MIBK, 0.25; TBP, 2.6]. Several other solvents were studied, but TBP gave the highest value of K_D. Since K_D for methylene chloride is so low, dimethyl hydantoin could have been present in many other condensate waters and not have been detected by the standard GC-MS technique. The low value of K_D into MIBK also indicates that dimethyl hydantoin may by difficult to remove in a solvent extraction process with conventional solvents.

Dimethyl hydantoin was detected in all four GFETC samples. The concentration of this compound changed with time in some of the samples (1). When the condensate-

water samples were removed from the gasifier, part of the sample was adjusted to pH 2 with conc. H_2SO_4, and the remainder was stored without pH adjustment. No time dependence was observed for the pH 2 samples, and these concentrations are shown in parentheses in Table 1. The concentration in the pH 8.5 samples started out higher than in the pH 2 samples, increased gradually over a period of one month, and then remained nearly constant. From these data it appears that dimethyl hydantoin is the product of a chemical reaction that proceeds slowly at pH 8.5 and does not occur at pH 2. Therefore, the composition in the pH 2 samples is probably equal to the concentration at the time the sample was taken.

The fourth group of compounds includes methanol, acetone, and acetonitrile. These compounds have been identified in other GFETC samples (6). Acetone is of interest because it may react with cyanide, ammonia, and carbon dioxide to form dimethyl hydantoin by the Bucherer-Bergs reaction (7). Acetonitrile is an EPA Priority Pollutant.

Comparison of the four samples shows significant differences in composition. The fraction of the COD due to phenols is nearly constant, but there are large percentage changes in the concentrations of the dihydroxybenzenes and the hydantoins. The changes in composition were most likely due to changes in the operation of the coal gasification process. Variations in feed composition can cause difficulties with biological oxidation treatment processes.

The total fraction of the COD identified in Table 1 varied from 70 to 84%. This is an improvement over the standard GC-MS technique, as summarized elsewhere (1). However, a significant fraction of the COD remains unidentified in these condensate waters.

Characterization of Unidentified Constituents. The second phase of this work employed solvent extraction and other processes to determine the physical properties of the unidentified solutes. Table 2 shows the fraction of the COD that was removed by several solvent-extraction procedures for one sample. The small increase in COD removal for successive extractions with MIBK indicates that most of the remaining solutes have low values of K_D. MIBK extraction removed nearly all of the phenols and dihydroxybenzenes. Only a small fraction of the hydantoins were removed, but they account for only 1.3% of the COD in this sample. K_D for methanol has not been reported, but it is probably low. Therefore, methanol could be an important component of the poorly extracted COD. The methanol concentration has not yet been measured in this sample. Acetone and acetonitrile are sufficiently volatile that they would be removed by the stripping procedure used to remove MIBK; therefore, these compounds should not contribute to the measured raffinate COD.

Extraction at low pH suppresses the ionization of acidic functional groups and should thereby increase K_D for acidic compounds. Since no increase in removal was obtained at pH 3, ionization of acidic functional groups is not the explanation for the low values of K_D for the remaining solutes.

MIBK extraction at increasing sample ages removed progressively less of the COD. This indicates that chemical reactions occurred during storage, leading to solutes with lower K_D values. At a sample age of 190 days, five successive extractions showed that the remaining 10% of the COD had nearly a zero K_D into MIBK, and that the organic-nitrogen compounds also had a low values of K_D. Additional extractions at pH 12 with MIBK and methylene chloride did not improve the removal of the nitrogen compounds. Therefore, ionization of basic functional groups is not the explanation for the low values of K_D. The molecular weight of the unextracted solutes was found by ultrafiltration to be less than 1,000.

For a sample age of 15 days in Table 2, three different solvents can be compared. TBP is a stronger Lewis base than MIBK, and it removes a greater fraction of the COD. This indicates that some of the solutes may be Lewis acids. TOPO is a still stronger Lewis base, but it removed only the same fraction of the COD as MIBK.

In extractions not shown in Table 2, the removal of organic-sulfur compounds

was studied for the GFETC RA-106 sample. This sample contained 383 mg/L of organic sulfur. Extraction with MIBK and methylene chloride at pH 2 removed none of the sulfur compounds. At pH 9 MIBK and methylene chloride removed 57 and 24% of the sulfur compounds respectively. One possible interpretation of these results is that the organic-sulfur compounds protonate at low pH, but have some Lewis-acid properties at higher pH.

Some additional information about the physical properties of the solutes was obtained from the single-stage batch-distillation experiments described in Table 3. It is important to know the volatility of these compounds because there would be many advantages to using treated condensate water as make-up for a cooling tower. Volatile compounds would be stripped out of the cooling tower and become an air pollution problem.

The first data in Table 3 show that more than one third of the COD remaining after MIBK extraction was volatile for one sample. Distillation of the same sample without MIBK extraction showed that nearly all of the organic-sulfur compounds were non-volatile with respect to water. The third set of data show that more than one third of the COD remaining after MIBK extraction of a different sample was volatile. All of the organic nitrogen in this sample had a low volatility. When the pH of this sample was raised to 12, the volatility of the nitrogen did not increase. Therefore, ionization of basic functional groups is not the explanation for the low volatility of these compounds. Methanol may account for a substantial portion of the volatile COD in the MIBK raffinates.

CONCLUSIONS

A novel sample preparation technique has been developed which allows GC-MS identification of polar compounds. Dimethyl hydantoin has been identified with this technique. Analytical techniques have been described which are an improvement over the standard GC-MS technique, particularly for polar compounds. These techniques identified 70 to 84% of the COD in four condensate-water samples. Solvent extraction, distillation, and ultrafiltration techniques were employed to obtain physical properties of the unidentified COD, organic nitrogen, and organic sulfur compounds.

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Table 1: Quantitative Analyses of GFETC Condensate Waters[a,c,f]

GFETC Run No.:	RA-78	RA-97	RA-106	RA-120
Sample age interval (days)[b]:	150-500	40-150	1.7-38	0.7-110
Compound[c]				
1. phenol	4,750	7,250	3,450	4,300
2. C_1-phenols	2,850	3,750	2,140	2,350
3. C_2-phenols[d]	450	470	430	410
4. o-methoxy phenol[d]	260	450	165	260
5. p-hydroxy acetophenone[d]	50	35	5	ND
6. catechol	990	860	40	2
7. 4-methyl catechol[d]	610	500	20	ND
8. resorcinol	60	28	2	ND
9. hydroquinone	35	24	1	ND
10. 5,5-dimethyl hydantoin[d,e]	1,720 (660)	300 (150)	460 (230)	165 (40)
11. 5-methyl hydantoic acid	95	130	ND	10
12. 5-methyl hydantoin	135	40	ND	35
13. methanol	NA	NA	1,000	NA
14. acetone	NA	NA	500	NA
15. acetonitrile	NA	NA	280	NA
COD (mg/L)	34,900	46,700	22,900	23,400
Fraction of COD due to:				
hydroxybenzenes	0.586	0.624	0.663	0.764
dihydroxybenzenes	0.095	0.059	0.006	0.0002
hydantoins	0.082	0.014	0.030	0.013
methanol, acetone,& acetonitrile	-	-	0.140	-
Total COD Identified:	0.763	0.697	0.839	0.777

a. Concentrations in mg/L. Estimated precision: ±5%.
b. No change in concentration was observed over these time intervals, with the exception of the dimethyl hydantoin concentration.
c. All of these compounds were identified by co-chromatography.
d. The qualitative identification of these compounds was confirmed by the isopropanol/GC-MS technique.
e. This is the concentration at long sample ages. The value in parentheses is the concentration in the sample stored at pH 2, which is thought to represent the concentration at the time the sample was collected.
f. ND--none detected, NA--not analyzed.

Table 2: Fraction of COD Removed by Solvent Extraction from GFETC Run No. RA-120 Condensate Water

Solvent[a,b]	No. of Batch Extractions[c]	Fraction of COD Removed vs. Sample Age[d,f,g,h]			Fraction of Organic N Removed at 190 Days[i,j]
		0.7 Days	15 Days	190 Days	
1. MIBK	1	0.890(6)	0.883(2)	0.856(3)	0.28
2. MIBK	2	0.927(2)	0.911(2)	0.878(2)	0.28
3. MIBK	3	-	-	0.890(1)	0.35
4. MIBK	4	-	-	0.900(1)	0.35
5. MIBK	5	-	-	0.902(1)	0.41
6. MIBK	1 and 1 @ pH 3	0.923(1)	0.913(1)	-	
4. TBP	1	-	0.915(1)	-	
5. TBP	2	-	0.938(1)	-	
6. TBP	1 and 1 @ pH 3	-	0.945(1)	-	
7. 25% w/w TOPO/MIBK	1	-	0.88e(2)	-	
8. 25% w/w TOPO/MIBK	1 and 1 @ pH 3	-	0.92e(2)	-	

a. Solvents: MIBK--methyl isobutyl ketone, TBP--tributyl phosphate, TOPO/MIBK--25% w/w trioctyl phosphine oxide in MIBK.
b. 1:1 volume phase ratio in all extractions.
c. Extractions performed at the condensate water pH of about 8.5 unless indicated differently.
d. Experimental uncertainty: ±0.005
e. Experimental uncertainty: ±0.02
f. The number of replicates is shown in parentheses. The ratio standard deviation/mean for each extraction was about 0.004.
g. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before COD measurement.
h. Condensate water COD: 23,400 mg/L.
i. Condensate water organic nitrogen: 220 mg/L.
j. Experimental uncertainty: ±0.10

Table 3: Fractionation of COD, Organic Nitrogen, and Organic Sulfur Compounds by Batch Distillation

I MIBK Raffinate from GFETC Run No. RA-106 (distillation pH: 8.5)

	Distillate 1	Distillate 2	Bottoms	Total	Feed Conc. (mg/L)
% Water from Feed:	45	45	-	-	-
% COD from Feed:[a,c]	25	13	-	-	3,770

II GFETC Run No. RA-106 without extraction (distillation pH: 2)

	Distillate 1	Distillate 2	Bottoms	Total	Feed Conc. (mg/L)
% Water from Feed	27	46	27	100	-
% Organic Sulfur from Feed	1	2	97	100	383

III MIBK Raffinate from GFETC Run No. RA-120 (distillation pH: 2)

	Distillate 1	Distillate 2	Bottoms	Total	Feed Conc. (mg/L)
% Water from Feed:	43	46	11	100	-
% COD from Feed:[a,c]	38	4	44	86[b]	3,220
% Org. N from Feed:[a]	0	3	90	93[b]	175

IV MIBK Raffinate from GFETC Run No. RA-120 (distillation pH: 12)

	Distillate 1	Bottoms	Total	Feed Conc. (mg/L)
% Water from Feed:	71	29	100	-
% Org. N from Feed:[a]	2	98	100	175

a. Experimental uncertainty: ±5% of COD or organic nitrogen in feed.
b. Mass balance did not close because a solid precipitate formed in the bottoms product during the distillation.
c. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before distillation.

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