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D.H. Mohr, Jr.* and C.J. King
(*Ph.D. Thesis)

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IDENTIFICATION AND SEPARATION OF THE ORGANIC COMPOUNDS IN COAL-GASIFICATION CONDENSATE WATERS

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ABSTRACT

A substantial fraction of the organic solutes in condensate waters from low-temperature coal-gasification processes are not identified by commonly employed analytical techniques, have low distribution coefficients (K_D) into diisopropyl ether (DIPE) or methyl isobutyl ketone (MIBK), and are resistant to biological oxidation. These compounds represent an important wastewater treatment problem.

Analytical techniques were developed to detect these polar compounds, and the liquid-liquid phase equilibria were measured with several solvents.

A high-performance liquid chromatography (HPLC) technique was employed to analyze four condensate-water samples from a slagging fixed-bed gasifier. A novel sample-preparation technique, consisting of an azeotropic distillation with isopropanol, allowed identification of compounds in the HPLC eluant by combined gas chromatography and mass spectrometry.

5,5-dimethyl hydantoin and related compounds were identified in condensate waters for the first time, and they account for 1 to 6% of the chemical oxygen demand (COD). Dimethyl hydantoin has a K_D of 2.6 into tributyl phosphate (TBP) and much lower K_D values into six other solvents. It is also resistant to biological oxidation. Phenols (59-76% of the COD), dihydroxy benzenes (0.02-9.5% of the COD), and methanol, acetonitrile, and acetone (15% of the COD in one sample) were also detected.

Extraction with MIBK removed about 90% of the COD. MIBK has much higher K_D values than DIPE for dihydroxy benzenes. Chemical reactions occurred during storage of condensate-water samples. The reaction

products had low K_D values into MIBK. About 10% of the COD had a K_D of nearly zero into MIBK. These compounds were not extracted by MIBK over a wide range of pH; therefore, some of them may be amphoteric. These compounds have molecular weights less than 1,000, some of them contain organic nitrogen, and some of them are more volatile than water. Solvents containing trioctyl phosphine oxide (TOPO) have high K_D values for phenol and dihydroxy benzenes. A fraction of the compounds which are not removed by MIBK may be Lewis acids, because some of them were extracted by the strong Lewis bases, TBP and TOPO.

... to my daughter, Teresa,

and the love of learning that we share.

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Chapter 1: INTRODUCTION

Gasified coal is a promising alternative to crude oil and natural gas. Coal gasification can produce a clean, high-BTU, synthetic natural gas compatible with existing distribution systems, as well as a low- or medium-BTU gas which can be used as boiler fuel or for synthesis of liquid fuels. Recent declines in the price of petroleum on the world market have delayed the expected dates of commercialization of all synthetic fuel processes. However, research is still needed so that these processes will be well understood before it becomes desirable or necessary to build commercial-scale units. This is particularly true for the environmental aspects of these processes. Environmental control technology will be an important factor in the economics and social acceptability of all synthetic fuels processes, including coal gasification.

In the gasification process, coal reacts with water and oxygen to form a hydrocarbon product with a greater ratio of hydrogen to carbon than that in the original coal. A large quantity of waste heat must be dissipated. This heat can be transferred as sensible heat to the atmosphere, or it can be dissipated by evaporative cooling. The most economical balance between wet and dry cooling depends on the cost of the evaporated water. In most designs a large fraction of the heat removal will be by evaporative cooling, and this represents a large water requirement for the process. This water requirement is a concern because many coal deposits are located in arid regions.

In the gasification reactor, coal reacts with steam and air or oxygen. The hot product gases are then quenched, usually by injection of recycled water, and the excess steam condenses to form a condensate water. The condensate waters from high-temperature processes, such as the Texaco and Koppers-Totzek processes, are comparatively clean. However, the condensate water from a low-temperature gasification process is highly contaminated. The condensate-water flow rate is large and approximately equal to the cooling water requirement. It has been estimated that a 250×10^6 SCF/day Lurgi-type gasification plant will generate about 1×10^6 lb/hr of contaminated condensate water (1). The condensate water is buffered at a pH between 8 and 9 because of large concentrations of ammonia and acid gases (CO_2 and H_2S). It also contains high concentrations of phenols and other organic and inorganic compounds. The treatment of this condensate water is important because the release of potential pollutants must be controlled. Also, the overall water requirements of the process can be reduced substantially if the condensate water can be recycled within the process. The general aspects of condensate-water management and treatment have been discussed previously (1, 2, 3).

The goal of this work is the separation of the organic compounds from coal-gasification condensate water. A review of the literature, discussed below, shows that there is a significant lack of understanding of the chemical composition of condensate waters. It is difficult to design wastewater-treatment systems or interpret experimental studies of treatment processes without detailed knowledge of the feed composition. Therefore, a major part of this study was devoted to the identification of organic compounds in condensate waters.

Chemical Analyses of Condensate Waters

Condensate waters are complex mixtures containing many organic compounds. In order to simplify the analyses of complex wastewaters, a number of generic tests have been developed, and the procedures have been standardized (4). Four tests that are relevant to this discussion are those for phenols, chemical oxygen demand (COD), total organic carbon (TOC), and biochemical oxygen demand (BOD). The phenols test is a colorimetric method which does not respond to p-cresol and other para substituted isomers of phenol and may be subject to interferences from other components of the sample (4). The COD and TOC analyses are measures of the total concentration of organic compounds in solution. The COD is the amount of oxygen required to oxidize the compounds and the TOC is the amount of organic carbon in solution. As an example, a solution containing 1 mg/l of phenol has a COD of 2.38 mg/l and a TOC of 0.77 mg/l. The BOD is the amount of oxygen consumed when microorganisms use the organic solutes as a substrate.

The TOC or COD can be compared, in consistent units, to the sum of the individual compounds identified in a mixture. This is a useful way of demonstrating how complete an analysis is. Fourney, et al. (5) report the concentration of phenols and COD, as measured by the generic techniques, for several condensate waters from the Synthane gasification process. The phenols ranged from 200 to 6,600 mg/l and the COD ranged from 1,700 to 43,000 mg/l. These ranges are typical for a condensate water from a low-temperature gasification process. However, Singer, et al. (6) compared these phenol and COD measurements and found that the phenols accounted for only 21 to 46% of the COD. Also, phenols accounted for only 38 to 84% of the COD in the condensate waters from the gasification of five coals at the Lurgi facility in Westfield, Scotland (7). In the discussion that follows it will become apparent that most analyses of condensate waters fail to account for a large fraction of the COD or TOC. This lack of information is an important limitation in the design and operation of wastewater-treatment facilities.

Reported analyses of condensate waters from coal-gasification, coal-liquefaction, and oil shale retorting processes are presented in Table 1-1. These investigators employed direct injection of aqueous samples into a gas chromatograph (GC) with flame ionization detection. The COD or TOC were not available for comparison. The gasification and liquefaction condensate waters are similar. They have high concentrations of phenols and lower levels of aliphatic acids and other compounds. The oil-shale-retort water has much lower levels of phenols and higher concentrations of aliphatic acids. It appears to be generally true that wastewaters from oil shale retorting have less phenols and more acids compared to gasification and liquefaction condensate waters. The remainder of this discussion will focus on coal-gasification condensate waters.

Table 1-2 shows the analyses of many condensate waters from three coal-gasification processes. In these analyses the aqueous samples were extracted with methylene chloride and the extracts were analyzed with combined gas chromatography-mass spectrometry (GC-MS). All of the condensate waters contained high levels of hydroxy benzenes including phenol and alkylated phenols. Some samples contained dihydroxy benzenes. Other classes of compounds included nitrogen aromatics and aliphatic acids.

In three cases where the COD and TOC were available for comparison, the identified components accounted for only 34 to 54% of the COD or TOC. Therefore, a large fraction of the organic solutes remains unidentified after this GC-MS analytical procedure.

Table 1-1: Chemical Analyses of Coal-Gasification, Coal-Liquefaction, and Oil Shale Retort Waters.[a]

Compound	Coal Gasification[b]	Coal Liquefaction[c]	Oil Shale Retorting[d]
phenol	2,100	2,100	10
C_1-phenols	2,470	2,450	50
C_2-phenols	680	1,450	ND
acetic acid	620	600	600
propanoic acid	60	90	210
n-[C_4 through C_{10}]-acids	50	100	1,240
acetamide	ND	ND	230
propionamide	ND	ND	50
butyramide	ND	ND	10
1- and 2-naphthol	40	ND	ND

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[a] Data from Ho, et al. (8). Concentration units: mg/l. ND--not detected.

[b] Synthane fluidized-bed gasifier, Pittsburgh, PA.

[c] COED coal liquefaction process, FMC Corp., Princeton, NJ.

[d] 150 ton/day retort, Laramie Energy Research Center, Laramie, WY.

Table 1-2: Chemical Analyses of Condensate Waters from Coal-Gasification Processes.[a]

Compound	Lurgi[b]	Lurgi[c]	Lurgi[d]	Synthane[e]	Chapman[f]
hydroxy benzenes:	1833-4560	2360	3940	4300-7400	4083
dihydroxy benzenes:	546-1750	NR	NR	70-540	NR
polycyclic hydroxyl compounds:	NR	NR	NR	250-360	NR
monocyclic N-aromatics:	NR	231	137	30-540	63
aliphatic acids:	NR	226	NR	NR	NR
other compounds:	NR	NR	NR	170-340	NR
COD:	NR	12,500	20,200	NR	28,500
TOC:	NR	4,190	6,490	NR	9,430
Fraction of COD Identified:		0.539	0.487	-	0.360
Fraction of TOC Identified:		0.511	0.470	-	0.336

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a. Concentration units: mg/l. NR--not reported.

b. Lurgi fixed-bed gasifier, Westfield, Scotland. Range of values reported from one study, summarized by Singer, et al. (6).

c. Lurgi fixed-bed gasifier, Sasolburg, South Africa. Data summarized by Singer, et al. (6).

d. Lurgi fixed-bed gasifier, Kosovo, Yugoslavia. Data reported by Collins, et al. (9).

e. Synthane fluidized-bed gasifier, Pittsburgh, PA. Range of values from the gasification of six coals reported by Schmidt, et al. (10) as summarized by Singer, et al. (6).

f. Chapman fixed-bed gasifier, Kingsport, TN. Data reported by Collins, et al. (9).

The information shown in Table 1-3 was obtained by GC analysis with direct injection of aqueous samples. Several components not reported in Table 1-2 were found in substantial concentrations. The most significant of these are methanol, acetonitrile, and acetone. It is possible that these compounds were not in the analyses of Table 1-2 due to incomplete recovery in the methylene chloride extraction procedure before GC-MS analysis. These compounds are polar and may have low distribution coefficients (K_D) into methylene chloride.

Table 1-4 is a summary of GC-MS analyses of two condensate waters. The methylene chloride extraction was performed at different pH values to isolate acid, base, and neutral fractions. A large number of compounds were identified, and the most important classes of compounds are listed in the table. However, comparison to the COD shows that only about one-third of the organics was identified.

Table 1-5 shows analyses of two condensate waters with two different analytical techniques. The Synthane condensate water was analyzed with a methylene chloride/GC-MS technique. The other condensate water was analyzed with a high-performance liquid chromatography (HPLC) technique similar to the techniques employed in this study. The HPLC technique detected dihydroxy benzenes in the condensate water and identified a greater fraction of the COD and TOC (92 and 77%, respectively). This may be due to differences in the composition of the two samples, or the methylene chloride/GC-MS technique may have low recoveries for the polar dihydroxy benzenes. Hubik and Ferrell (15) found that some of the components degraded during storage of the condensate water. In the present study all of the phenols and dihydroxy benzenes remained stable during storage of GFETC condensate waters.

Table 1-3: Chemical Analyses of Condensate Water from Coal-Gasification Processes.[a]

Compound	GFETC[b]	Synthane[c]
hydroxy benzenes	4,840	5,280
methanol	900	140
other alcohols	<10	<10
acetonitrile	500	210
other nitriles	80	60
acetone	540	950
other ketones	150	340
acetic acid and/or CS_2[d]	400	1400
other acids	140	160
furans	170	110
aniline	40	30

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a. Data reported by White and Schmidt (<u>11</u>). Concentration units: mg/l.
b. GFETC slagging fixed-bed gasifier, Grand Forks, ND.
c. Synthane fluidized-bed gasifier, Pittsburgh, PA.
d. The analytical technique employed could not distinguish between acetic acid and CS_2.

Table 1-4: GC-MS Analyses of GFETC and HYGAS Condensate Waters.[a]

GFETC[b] Condensate Water [Luthy, et al. (13)]

	Acid Fraction	Base Fraction	Neutral Fraction
Fraction of COD Identified:	0.33	<0.003	<0.01
Compound Classes Identified:[c]	hydroxy benzenes hydroxy indans naphthols	pyridines anilines azonaphthalenes	cycloalkenes benzonitrile acetophenone naphthalenes indole

HYGAS[d] Condensate Water [Stamoudis and Luthy (12)]

	Acid Fraction	Base Fraction	Neutral Fraction
Fraction of COD Identified:	<0.34	<0.002	<0.002
Compound Classes Identified:[c]	hydroxy benzenes dihydroxy benzenes naphthol	pyridines anilines picolines	benzonitrile benzenes cycloalkenes acetophenone benzothiophene naphthalenes indole

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[a] Gas chromatography-mass spectrometry (GC-MS) analysis of methylene chloride extracts. Samples were partitioned into acid, base, and neutral fractions as described in (12).

[b] GFETC slagging fixed-bed gasifier, Grand Forks, ND.

[c] The classes of compounds present in the highest concentration are listed in the table. A large number of individual compounds were identified in the original studies.

[d] HYGAS fluidized-bed gasifier, Chicago, IL.

Table 1-5: Chemical Analyses of Condensate Waters from Two Coal-Gasification Processes.[a]

Compound	Synthane[b]	N. C. State[c]
Hydroxy benzenes:		
phenol	2,209	950
C_1-phenols	1,626	450
C_2-phenols	559	470
C_3-phenols	106	NR
Dihydroxy benzenes:		
catechol	NR	250
C_1-catechol	NR	320
resorcinol	NR	150
C_1-resorcinol	NR	90
C_2-resorcinol	NR	50
hydroquinone	NR	70
Other compounds:	417	100
COD	17,160	7,300
TOC	5,800	2,800
Fraction of COD Identified:	0.712	0.924
Fraction of TOC Identified:	0.655	0.765

---

a. Concentration units: mg/l. NR: not reported.

b. Synthane fluidized-bed gasifier, Pittsburgh, PA. Data from Neufeld and Spinola (14).

c. Fluidized-bed gasifier, North Carolina State University. Data from Hubik and Ferrell (15).

Table 1-6 shows the compounds identified in the condensate water from a hydrocarbonization unit. These compounds were analyzed by preparative-scale anion exchange chromatography, gas chromatography, and mass spectrometry. This condensate water contained phenol, dihydroxy benzenes, and other polar compounds, including hydroxy pyridines. Hydroxy pyridine is one example of an amphoteric compound which is ionized over wide ranges of pH. Any compound that is ionized in water has a low activity coefficient and is difficult to remove with most processes. The analysis in Table 1-6 accounted for only 20% of the TOC. This was due in part to the approximate methods employed to obtain quantitative analyses.

Table 1-7 shows analyses of two effluent waters from an oil shale retorting process. These waters were separated into fractions with solid adsorbents, and individual components were identified with HPLC and GC techniques. Many classes of polar compounds were identified, including the hydroxy pyridines which were reported in Table 1-6 for a coal-gasification condensate water. Although only 50% of the TOC was identified in both cases, fractionation techniques based on solid adsorbents appear to be useful for separating the polar organic solutes in condensate waters. Such separations could be used to simplify complex mixtures before chemical analysis, or they could be used to determine physical properties of unidentified solutes.

In summary, Tables 1-1 to 1-7 show some generalities in the published analyses of condensate waters. Phenol and alkylated phenols usually comprise a large fraction of the COD. The most common analytical technique employs a methylene chloride extraction followed by GC-MS analysis. This technique detects phenols and a large number of less

Table 1-6: Analysis of Organic Compounds in the Condensate Water from a Hydrocarbonization Unit.[a]

Compound	Conc. (mg/l)[b]	Identification Method[c]
catechol and phenol[d]	1,700±	AC,GC,MS
methyl resorcinol	2,000±	AC,GC,MS
5-methyl resorcinol	2,000±	AC,GC,MS
other dihydroxy benzenes	70	AC,GC,MS
hydroxy pyridines	40	GC,MS
palmitic, oleic, linoleic, and steric acids	1.5	GC,MS
methyl carbazole	4	MS
TOC	22,000	
Fraction of TOC Identified:	0.20±	

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a. Data reported by Pitt, et al. (16). Bench-scale hydrocarbonization unit, Oak Ridge TN.

b. The concentration of some of the components was determined with a semi-quantitative procedure.

c. AC--anion exchange chromatography retention time.
GC--gas chromatography retention time.
MS--mass spectrometry.

d. These compounds were not resolved with the analytical technique employed.

Table 1-7: Analyses of the Organic Compounds in Condensate Water and Process Water from an Oil Shale Retorting Process.[a,b]

Compound Class	Condensate Retort Water Conc. as mg/l of TOC	Process Retort Water Conc. as mg/l of TOC	Analysis Technique
aliphatic monocarboxylic acids	2.9	1,264	HPLC,GC
aliphatic dicarboxylic acids	NA	41.6	GC
aromatic carboxylic acids	ND	16.6	HPLC
phenols	140.2	64.5	HPLC
aromatic amines	152.1	9.7	HPLC
hydroxy pyridines	ND	31.5	HPLC
pyridine carboxylic acids	NA	0.7	HPLC
aliphatic amides	2.5	38.5	HPLC,GC
nitriles	34.3	3.4	GC
aliphatic alcohols	27.3	1.5	GC
aliphatic ketones	20.7	2.4	GC
aliphatic aldehydes	ND	1.3	HPLC
lactones	12.1	16.7	GC
pyrole	3.6	ND	HPLC
TOC	790	3,000	
Fraction of TOC Identified:	0.50	0.50	

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a. Data reported by Leenheer, et al. (17). Occidental Oil Shale, Inc., Logan Wash, CO. ND--not detected; NA--not analyzed.

b. The samples were separated into fractions using a "dissolved organic carbon fractionation procedure" that employs polymeric resins.

polar compounds which are usually present at low concentrations. This technique occasionally detects dihydroxy benzenes, but usually at low concentrations. Other analytical techniques which do not employ a preliminary extraction with methylene chloride tend to detect more polar components in the condensate waters. These polar compounds include methanol, acetonitrile, acetone, acetic acid, hydroxy pyridines, higher concentrations of dihydroxy benzenes, and other components. Most importantly, all of the analyses fail to account for a large fraction of the COD or TOC. This represents an important lack of understanding about the composition of coal-gasification condensate waters.

Condensate-Water Treatment Goals

The treatment goals for condensate water depend strongly on the final use of the treated water. Treated condensate water could be used as a boiler feed water, discharged to a natural body of water, fed to a cooling tower, or recycled directly into the coal gasifier. Boiler feed water must be very clean to avoid fouling heat exchange surfaces in the boiler and throughout the plant. The treatment necessary to prepare boiler feed water from condensate water would be very expensive. It is more likely that condensate water would be used in other ways that require less extensive treatment.

The treatment requirements for release to the environment would also be very strict. The effluent requirements for individual components in condensate waters have been estimated (2, 3) for the time when coal-gasification facilities may be commercialized. Most coal-gasification processes have a net consumption of water, and released water would have to be nearly as clean as surface water in the area. Therefore, it is unlikely that condensate water will be treated for release to the environment.

The amount of water required for cooling-tower feed is approximately equal to the flow of condensate water (1). Although the quality requirements are not well established, cooling-tower feed can have higher levels of contaminants than boiler feed water or water released to the environment. Therefore, recycle of condensate water to the cooling tower is a promising design alternative.

Quality requirements for cooling-tower feed are determined by two criteria. Scaling, fouling, and corrosion of heat exchange surfaces in the cooling tower and throughout the plant must be kept to acceptable levels. Also, components in the cooling water may evaporate or be lost in the drift from the tower and present an air pollution problem.

Scaling results from the precipitation of inorganic species such as calcium carbonate. The solubility products and scaling properties of these inorganic species are well known. The presence of organic compounds in the water may change some of these properties. Heat exchange surfaces can also be fouled by biological growth. If a substrate such as phenol is present in the cooling water, then microorganisms will grow, and the resulting sludge can adversely affect heat transfer properties. Goldstein and Aiyegbusi (18) operated a small biologically active cooling tower with dilute solutions of phenol and concluded that the rate of biological fouling would be acceptable if a commercial cooling tower was operated with a feed containing 600 mg/l of phenol. Willson, et al. (19) have operated a pilot-scale cooling tower with condensate water that was first extracted with diisopropyl ether (DIPE) and then steam stripped to remove ammonia. Their preliminary results showed fouling of heat exchange surfaces, increases in pressure drop through heat exchangers, and high corrosion rates of carbon steel parts.

The second constraint on the composition of the cooling water is the loss of potential pollutants through evaporation or in the liquid-phase drift. In the study by Willson, et al. (19) the air leaving the tower was sampled, but the analyses are not yet available. They did find that most of the ammonia and phenols were either lost to the atmosphere or biologically degraded.

More work is needed to determine the treatment goals for cooling-tower feed. It is apparent that high concentrations of volatile compounds cannot be tolerated, particularly if their toxicity is poorly understood. Although some biological activity may be acceptable, high levels of organic compounds may cause operating problems and may increase the blowdown requirement.

One final option for condensate-water reuse is to recycle the liquid water directly into the gasifier. This would require little if any water treatment, and the organic compounds would be gasified with the coal. However, this would require major modifications to most gasifiers. There would be a decrease in thermal efficiency with this approach because the heat of vaporization of the water would be supplied at a high temperature in the gasifier. Netzer and Ellington (20) report that quench-water organics were recycled to extinction in a Texaco entrained-bed gasifier. However, this is a high-temperature gasification process which produces a less contaminated condensate-water.

The most probable use of treated condensate-water is as make-up to a cooling tower. The treatment goals for this use are not well defined, but they must be stringent enough to minimize atmospheric emissions and to allow reliable operation of the cooling tower. More effective treatment would be required to use the condensate water as boiler feed water or to release it to the environment. Very little treatment would be required if liquid condensate-water was recycled directly into the gasifier; however, major process modifications would be necessary.

Unit Operations for Condensate-Water Treatment

Gravity Separation Techniques: These techniques include settling ponds with skimmers, API separators, centrifuges, etc., and are frequently used for pretreatment. They can remove oil, grease, tar, and suspended solids, but they are not effective for very small particles, stable emulsions, and suspended particles with the same density as the aqueous phase. The separation can often be improved with dissolved-air flotation. In this process small bubbles are formed in the water, and as the bubbles rise particulates and other surface-active species collect at the gas-liquid interface and rise to the top. Many non-polar organics are either suspended in condensate waters as a second phase or adsorbed on particulates.

Steam Stripping: Steam stripping can remove NH_3, CO_2, H_2S, and other volatile species. One factor that influences the performance of a stripping process is the ratio of the non-volatile anions to the non-volatile cations (21). An excess of non-volatile anions decreases the volatility of ammonia. As an example, ammonia is much less volatile in an ammonium chloride solution than in an ammonium carbonate solution. Ammonia combined with non-volatile anions is called "fixed ammonia". The volatility of fixed ammonia can be increased by addition of a base such as calcium oxide; however, the cost could be prohibitive and the concentration of salts would be increased. Conversely, the volatility of acid gases is suppressed by an excess of non-volatile cations.

The operating cost for a stripping process is determined by the boil-up ratio, which is the fraction of the water which must be converted into steam in the reboiler. In processes where the ammonia and acid gases are both collected in the overhead product, the boil-up ratio can range from 5 to 20% (23, 24, 25). As the concentration of ammonia in the feed increases, it becomes economically feasible to separate ammonia from the acid gases and sell the ammonia. The PHOSAM W process of the U. S. Steel Co. and the Chevron process are established processes capable of separating ammonia, although greater boil-up ratios are required. Another approach, based on simultaneous extraction of ammonia and stripping of acid gases, is being explored in a companion project to the present work (22). This approach may reduce the energy requirements for ammonia separation.

Stripping processes will also remove volatile organic compounds. Although this may be an advantage in some cases, it will complicate the design of the process. After ammonia and acid gases have been removed, the buffering capacity of the water is greatly reduced. This reduces the expense of any pH adjustments which may be necessary for other processing steps.

Solvent Extraction: Solvent extraction is capable of removing phenols and many other organic compounds from condensate waters. The phase equilibrium in a solvent extraction process is characterized by the equilibrium distribution coefficient (K_D), defined as the weight fraction in the organic phase divided by the weight fraction in the aqueous phase. The solvent-to-water ratio (S/W) is an important factor in the economics of this process. In a countercurrent extraction process K_DS/W must be greater than one to remove the solute effectively.

Solvent extraction has a number of advantages over biological oxidation. Solvent extraction processes can recover the organics either for sale or for the fuel value. The cost of a solvent extraction process is determined primarily by the solvent-to-water ratio and the number of stages. Once these variables are fixed, the process will remove approximately a constant fraction of a given solute, regardless of the feed concentration. In biological-oxidation processes the cost is nearly proportional to the mass of solute oxidized. Therefore, extraction processes become more economical at high feed concentrations. Also, extraction processes are not sensitive to fluctuations in feed composition which can cause operating problems in a biological-oxidation reactor.

Two solvent extraction processes have been proposed for commercial-scale treatment of condensate waters. The Lurgi Phenosolvan process employs diisopropyl ether (DIPE) as solvent and the Chem-Pro process employs methyl isobutyl ketone (MIBK). In both of these processes the solvent is removed from the condensate water by steam stripping. Greminger, et al. (26) report that MIBK has a higher K_D for phenol and much higher K_D values for dihydroxy benzenes as compared to DIPE. They also show that vacuum steam stripping is an economical way to remove residual MIBK. The phase equilibria of these two solvents are discussed in greater detail subsequently.

Although MIBK has several advantages over DIPE, both of these solvents fail to remove an important fraction of the COD in condensate waters (see Chapters 1 and 3). The effectiveness of extraction processes can be improved by selecting a solvent with higher K_D's for the solutes of interest. MacGlashan (27) has shown that a solvent of 25%

w/w trioctyl phosphine oxide (TOPO) in MIBK gives very high K_D's for phenol, dihydroxy benzenes, and trihydroxy benzenes. TOPO is a strong Lewis base and is one example of an extractant that has favorable equilibrium properties for very polar solutes.

Biological Oxidation: In a biological oxidation process microorganisms use the contaminants as a substrate and oxidize them to CO_2 and H_2O. The economics are controlled by the large reactor volume required and the amount of oxygen that must be transferred to the microorganisms. The hydraulic residence time is usually more than one day, and this results in large reactor volumes. The oxygen can be supplied by sparging air or oxygen through the water. Since the cost of the process is approximately proportional to the concentration of BOD in the feed, biological oxidation becomes more attractive for dilute feeds.

Biological oxidation can remove a wide variety of compounds from wastewaters. However, many organic compounds in coal-gasification condensate waters are resistant to biological oxidation. A second limitation to these processes is that changes in the feed composition can cause severe upsets. Many of the contaminants are toxic to the microorganisms at high concentrations.

Addition of powdered activated carbon to the activated-sludge reactor (PAC/AS) improves the performance of the biological treatment in a number of ways, as discussed by Castaldi, et al. (28). Addition of PAC improves the removal of BOD and components which would otherwise be resistant to biological treatment. In many cases the removal of organic compounds is better than if the biological-oxidation and the carbon adsorption processes were used in series. One possible explanation for this is that compounds which degrade slowly have additional time to react because they adsorb on the carbon and remain in the reactor for the residence time of the solids, which is much longer than the hydraulic residence time. Also, the presence of PAC provides a buffer against fluctuations in the feed composition and improves the operating characteristics of the reactor. This process has been employed commercially at the DuPont Chambers Works treatment plant in Deepwater, NJ. In this process the excess biomass is incinerated and the activated carbon is regenerated in a multiple-hearth furnace. Regeneration of the carbon is an important factor in the ecomonics because replacement carbon is expensive. Castaldi, et al. (28) estimate that 50% of the carbon may be lost per cycle in a PAC/AS system with regeneration in a multiple-hearth furnace.

Another promising alternative is to use biological oxidation to treat the effluent from a solvent extraction process. The solvent extraction process would treat a concentrated feed and would dampen fluctuations in the feed composition. Solvent extraction has economic advantages over biological oxidation at high feed concentrations and the organic compounds could be recovered for fuel or for sale. The biological oxidation would receive a relatively dilute feed at a nearly constant composition. The presence of the biological treatment can reduce the number of stages required in a countercurrent solvent extraction process because a higher effluent concentration is acceptable.

Adsorption: Solid adsorbents can be used to remove organic compounds from water. Activated carbon is the most common sorbent, but coal char, spent oil shale, open pore polyurethane, and others have been considered (3). The cost is proportional to the amount of the solute adsorbed, so this process is best suited for dilute streams. The controlling factors in the economics are the cost of the sorbent, the equilibrium isotherms of the solutes, and the cost and effectiveness of the regeneration. Activated carbon is usually regenerated thermally. Some adsorbents can be regenerated by washing with solvents.

Other Processes: Additional unit operations for the removal of organics from water include incineration, ozonation, and wet-air oxidation. Incineration can be economical for small streams containing high concentrations of organic compounds. High residence time at high temperature is necessary to oxidize the organics completely and reduce air emissions.

Ozonation can be used to oxidize organics completely to CO_2 and H_2O. Partial ozonation may make some organics more susceptible to treatment by biological oxidation or other processes. The cost is proportional to the amount of ozone consumed.

In a wet-air oxidation process the water reacts with air at high temperature and pressure above the critical point. This process is very expensive due to the reactor volume and the heat exchange area required at high pressure. This process may be able to oxidize compounds that are difficult to treat by other processes.

Removal and Disposal of Inorganic Salts: The separation and ultimate disposal of the inorganic compounds in condensate waters has been identified as an important environmental problem (2). Evaporation and reverse osmosis are two methods of separating inorganic species from water. Multi-effect or vapor-compression evaporation can be employed to reduce the energy requirements. In the design of evaporation systems there is a trade-off between the capital cost of heat exchange area and the energy requirement. Evaporators can be operated to produce a concentrated slurry in the bottom product with nearly all of the water recovered in the overhead product. Organic compounds in the feed will also partition between the two products depending on their volatility.

The economics of reverse osmosis (RO) are controlled by the cost of the membrane area and the pressure drop across the membrane. A major uncertainty is the effect of organic compounds on the RO membrane. Organic compounds may decrease the membrane life or increase the pressure drop.

The ultimate disposal of these salts is difficult because they are very soluble in water and may contain hazardous metals. Two possible disposal methods are encapsulation with sand or slag and deep-well injection.

Experimental Studies of Condensate-Water Treatment Processes

Solvent Extraction: The fraction of the COD or TOC removed by a solvent extraction procedure provides information about both the effectiveness of a process employing that solvent and the physical properties of the solutes. The data in Table 1-8 summarize several extraction experiments. All of the extractions in Table 1-8 removed nearly all of the phenol and alkylated phenols; however, the TOC or COD removed ranged from 65 to 88%. Additional extraction data are presented in Chapter 3.

Bombaugh, et al. (31) report that a commercial Lurgi Phenosolvan solvent extraction process removed 70% of the TOC, 58% of the COD, and 89% of the phenols from the condensate water produced by a Lurgi coal-gasification process. Singer, et al. (6) report that a Phenosolvan process removed 89% of the COD and 99.7% of the phenol from another Lurgi condensate water. Luthy and Campbell (32) found that extraction with n-butyl acetate removed 99% of the phenol and 75% of the COD from the condensate water from HYGAS run No. 72.

Table 1-8: Removal of COD and TOC from Condensate Waters by Various Solvent Extraction Procedures.

Coal Gasification Process	Ref.	Solvent[a]	Phase Ratio S/W (v/v)	No. of Batch Extractions	Fractional Removal of TOC	Fractional Removal of COD
Lurgi[b]	(9)	DIPE	0.33	3	0.69	0.76
Lurgi[b]	(9)	DIPE MC DEE	0.33 0.33 0.33	3 3 @ pH 12 3 @ pH 2	0.71	0.79
Chapman[c]	(9)	DIPE	0.33	3	0.65	0.46
Chapman[c]	(9)	DIPE MC DEE	0.33 0.33 0.33	3 3 @ pH 12 3 @ pH 2	0.81	0.75
Chapman[c]	(30)	BA	0.10	3	0.68	0.67
GFETC[d]	(13)	MIBK	0.067	5	0.82	0.88

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a. Solvents: DIPE--diisopropyl ether, MC--methylene chloride, DEE--diethyl ether, BA--butyl acetate, MIBK--methyl isobutyl ketone.
b. Lurgi fixed-bed gasifier, Kosovo, Yugoslavia.
c. Chapman fixed-bed gasifier, Kingsport, TN.
d. GFETC slagging fixed-bed gasifier, Run RA-52, Grand Forks, ND.

These data show that, although extraction with these solvents effectively removes phenol, an important fraction of the COD or TOC is not removed. These compounds which remain in the raffinate are more polar and hydrophilic than phenol.

Luthy, et al. (13) detected eleven polynuclear aromatic hydrocarbons (PAH) in a condensate water from the GFETC slagging fixed-bed gasifier with a reversed-phase HPLC technique. The total concentration of these compounds was about 10 mg/l. Nearly all of the PAH were adsorbed on particulate matter suspended in the water. MIBK extraction removed all of these compounds to levels below the detection limit. MIBK extraction removed 99.98% of the acid-fraction, 97.0% of the neutral-fraction, and 99.0% of the base-fraction compounds listed in Table 1-4 for the GFETC gasifier. Most non-polar compounds should have high distribution coefficients, and therefore high removals, for MIBK and other solvents. However, Table 1-8 shows that MIBK extraction removed only 88% of the COD and 82% of the TOC from this condensate water.

Biological Oxidation and Other Processes: The results of activated sludge treatment of two condensate waters are presented in Table 1-9. The effluents from activated sludge treatment of the GFETC condensate water had a COD value of 1,260 mg/l despite the fact that the water had been diluted to 33% before treatment. Activated sludge treatment removed only 85% and 83% of the COD from the GFETC and HYGAS condensate waters, respectively. This treatment did remove the compounds identified by the methylene chloride/GC-MS procedure to a total concentration of less than 1 mg/l. Therefore, this analytical technique cannot be used to identify the compounds that remain after biological treatment.

Table 1-9: Activated Sludge Treatment of Two Coal-Gasification Condensate Waters.[a]

				GC-MS Fractions[b]		
GFETC Run No. 52	COD	Phenols	Org. N	Acid	Neutral	Base
Raw water (mg/l)	25,400	5,100	90	-	-	-
After NH_3 stripping and 33% dilution (mg/l)	6,780	1,510	43	>700	3.2	1.6
After activated sludge treatment (mg/l)	1,260	1	21	<0.2	0.18	0.05
Fraction removed compared to raw water	0.851	0.999	0.3	0.999	0.944	0.970
HYGAS Run No. 64[d]						
Raw water (mg/l)	4,050	710	10	-	-	-
After NH_3 stripping (mg/l)	3,710	625	10	>500	4.6	4.6
After activated sludge treatment (mg/l)	710	0.3	7	<0.005	0.64	0.37
Fraction removed compared to raw water	0.825	0.999	0.3	0.999	0.86	0.92

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a. Data reported by Stamoudis and Luthy (12).
b. Compounds in GC-MS fractions are identified in Table 1-4.
c. GFETC slagging fixed-bed gasifier, Grand Forks, ND.
d. HYGAS fluidized-bed gasifier, Chicago, IL.

The data in Table 1-10 show that MIBK extraction combined with activated sludge (AS) or powdered activated carbon/activated sludge (PAC/AS) treatment increased the COD removal to 96 and 98%, respectively. This increase in removal indicates that MIBK extraction removes some of the compounds which are not biodegradable, and Table 1-10 shows that activated-sludge treatment removes some of the compounds that are difficult to extract. The additional advantages of combining extraction and/or PAC addition with biological treatment have already been discussed. The effluent from the MIBK-PAC/AS treatment still had a COD of 640 mg/l.

Additional reports show that activated sludge treatment without solvent extraction removed about 70% of the TOC from a Synthane condensate water (33), 85% of the TOC from a different sample of Synthane condensate water (34), and 96.3% of the TOC from a bench-scale hydrocarbonization unit (16).

The data in Table 1-11 show the toxicity of a condensate water from a Chapman gasifier before and after biological treatment. The effluent from the treatment process contained 5,080 to 7,200 mg/l of COD. Although the treatment process reduced the observed toxicity by an order of magnitude, the effluent was still toxic to the organisms used in the bioassays. In this investigation the ammonia was not removed from the condensate water before the toxicity measurements were made. Therefore the toxicity of the ammonia cannot be separated from the toxicity of other components.

Table 1-12 shows the results of several condensate-water treatment processes. Extraction with n-butyl acetate and activated sludge treatment removed 94.5% of the COD from a HYGAS condensate water. Activated

Table 1-10: Cumulative Removal of GFETC Condensate-Water Solutes[a]

	Raw Water (mg/l)	After MIBK Extraction	After NH_3 Stripping	AS[b]	PAC/AS[c]
TOC	11,100	0.82	0.88	0.948	0.965
COD	32,000	0.88	0.91	0.958	0.980
BOD	26,000	0.89	0.93	0.999	0.999
phenols	5,500	0.99	0.99	0.999	0.999
Organic N	115	0.56	0.71	0.913	0.965
Acid fraction[d]	4,320	0.99	-	0.999	0.999
Neutral fraction[d]	146	0.97	-	0.999	0.999
Base fraction[d]	38	0.99	-	0.999	0.999

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a. Data reported by Luthy, et al. (13). GFETC slagging fixed-bed gasifier, Run No. RA-52, Grand Forks ND.
b. Activated sludge treatment after MIBK extraction and ammonia stripping
c. Powdered activated carbon/activated sludge treatment after MIBK extraction and ammonia stripping.
d. Compounds from GC-MS analysis are identified in Table 1-4.

Table 1-11: Toxicity Data for a Chapman[a] Condensate Water Before and After Activated-Sludge Treatment.[b]

Water Quality Parameter	Influent	Effluent	% Reduction
TOC	6,540	1600-2400	63.4-75.6
COD	17,960	5080-7200	59.9-71.7
Phenol	6,800	104	98.5

	48-hr LC-50[d]	
Aquatic Bioassays[c]	Influent	Effluent
Daphnia	0.1%	1.0%
Fathead Minnow	0.1%	1.5%

Mammalian Cytotoxicity Bioassay[c]	LC-50 Influent	LC-50 Effluent
Chinese Hamster Ovary System	0.1%	1.0%

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[a] Chapman fixed-bed gasifier, Kingsport, TN.

[b] Data reported by Singer, et al. (35).

[c] The data reported in this table have been adjusted to a basis of undiluted condensate water. In the study by Singer, et al. the water was diluted to 25% before biological treatment.

[d] A value of 0.1%, for example, means that a 0.1% solution of condensate water in distilled water produced a 48-hr LC-50 toxicity in the indicated system.

Table 1-12: Experimental Results of Condensate-Water Treatment Processes.[a]

HYGAS Run No. 72[b]	TOC	COD	Phenols	Org. N
Raw water	-	10,000	-	-
n-butyl acetate extraction	-	2,500	-	-
Activated sludge treatment	-	550	-	-
Cumulative fraction removed	-	0.945	-	-
HYGAS Run No. 79[b]				
Raw water	-	10,400	1,950	70
Lime pretreatment	-	10,200	1,970	60
NH_3 stripping	-	6,930	1,140	26
Activated sludge treatment	-	715	0.75	11
Cumulative fraction removed	-	0.931	0.999	0.843
Lime-soda softening	-	600	0.50	10
Carbon adsorption	-	110	0.23	5
Reverse osmosis	-	20	0.04	2
GFETC[d]				
Raw water	13,500	-	9,800	-
Lime precipitation and ammonia stripping	6,700	-	6,800	-
MIBK extraction[e]	1,450	-	200	-
Activated sludge treatment	720	-	20	-
Cumulative fraction removed	0.947	-	0.998	-
Raw water	13,500	-	9,800	-
Lime precipitation and ammonia stripping	6,700	-	6,800	-
DIPE extraction[e]	1,550	-	520	-
Activated sludge treatment	550	-	20	-
Cumulative fraction removed	0.959	-	0.998	-

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a. Units in mg/l except for "Cumulative fraction removed".

b. Data reported by Luthy and Campbell (32). HYGAS fluidized-bed gasifier, Chicago, IL.

c. Countercurrent extracion designed to remove 99% of the phenol.

d. Data reported by Hung, et al. (36). GFETC slagging fixed-bed gasifier, Grand Forks, ND.

e. Four-stage countercurrent extraction with methyl isobutyl ketone (MIBK) or diisopropyl ether (DIPE). Solvent-to-water ratio = 0.1 by volume.

Table 1-12: (continued)

Experimental Results of Condensate-Water Treatment Processes

METC Run No. 95[f]	TOC	COD	Phenols
Raw water	5,390	12,750	3,750
Pretreatment[g]	3,910	10,800	2,900
Activated sludge treatment[h]	430	1,600	2.3
Cumulative fraction removed	0.920	0.874	0.999
SRC-I[i]			
Raw water	10,700	-	1,900
Ammonia stripping	9,800	35,000	840
Pretreatment[j]	7,220	22,700	680
Activated sludge treatment	1,070	3,100	2
Carbon adsorption	490	1,600	1
Cumulative fraction removed	0.954	0.954	0.999

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f. Data reported by Neufeld, et al. (37). Morgantown Energy Technology Center, fixed-bed gasifier, Morgantown, WV.

g. Pretreatment included lime precipitation, ammonia stripping, and alum clarification.

h. The results are reported here on the basis of full-strength wastewater. The condensate water was actually diluted to 40% for activated sludge treatment.

i. Data reported by Drummond, et al. (38). Solvent Refined Coal liquefaction process, Fort Lewis, WA.

j. Pretreatment included adjusting the pH to 5, dissolved air flotation, and adjusting the pH to 7.

sludge treatment of HYGAS run No. 79 condensate water removed 93% of the COD. Lime-soda softening and activated carbon adsorption produced an effluent containing only 110 mg/l of COD. The economics of a carbon adsorption process depend strongly on the phase equilibria of the adsorbed solutes. Luthy and Tallon (39) measured the adsorption of the effluents from biological treatment of the HYGAS run No. 64 condensate water on activated carbon and coal-gasification chars. Since these effluents are complex mixtures, the adsorption data cannot be interpreted as a pure-component isotherm. However, the solutes remaining after biological treatment were about an order of magnitude more difficult to adsorb than phenol.

A reverse osmosis unit was operated successfully on the effluent from the carbon adsorption of the HYGAS run No. 79 water. The permeate contained 20 mg/l of COD. The presence of organic compounds in the feed to the RO unit may foul the membrane. This would have a significant effect on the economics of the process.

One alternative to reverse osmosis for the separation of inorganic species is evaporation. Wakamiya (40) successfully operated a small vapor-compression evaporator with an oil shale retort water. The evaporator was operated at a concentration factor of 25. The distillate contained 500 mg/l of TOC, which was 30% of the TOC in the feed.

Hung, et al. (36) investigated combined solvent extraction and biological oxidation of a GFETC condensate water as described in Table 1-12. Extraction with MIBK and DIPE combined with activated sludge treatment removed 94.7 and 95.9% of the TOC, respectively. MIBK extraction alone removed a greater fraction of the TOC than did DIPE extraction, but the cumulative removal for extraction and biological treatment was somewhat greater with DIPE as solvent.

Table 1-12 shows that 92% of the TOC and 87% of the COD were removed by activated-sludge treatment of a METC condensate water. Activated sludge treatment and carbon adsorption removed 95% of the TOC and COD from an SRC-I coal liquefaction wastewater.

In many of the studies of biological treatment cited above, pretreatment of the condensate water was necessary before the reactor could be operated satisfactorily. This pretreatment often included pH adjustment, nutrient addition, and/or dilution. The chemicals cost for pH adjustment can be very high, even if most of the ammonia has been removed by steam stripping. If dilution is required, the volume and cost of the reactor increase.

Modification of the Coal-Gasification Reactor: The design of the gasifier can have an important effect on the production of organic contaminants in the condensate water. Phenol and many of the other organic compounds in condensate waters are formed during pyrolysis of the coal and by gas-phase reactions within the gasifier. Pyrolysis, or devolatilization, is defined as the decomposition of organic matter by heat in the absence of oxygen. Coal pyrolysis during gasification is discussed by Probstein and Hicks (41). The effect of pyrolysis conditions on the production of phenols during coal gasification has been experimentally studied by Nakles (42) and Fillo and Massey (43).

Phenols, oils, and tars are formed by pyrolysis reactions and then decompose further in the gas phase. The important variables for the pyrolysis reactions are temperature, composition of the organic material in the coal, composition of inorganic material in the coal which may act as a catalyst, composition and pressure of the gas phase, and the heat- and mass-transfer rates between the reacting coal particles and the surrounding gas. The important variables for the gas-phase decomposition are temperature, pressure and composition of the gas phase, the residence time of the gas, the catalytic effects of the char or coal particles, and the mass-transfer rates between the gas and the solid particles with catalytic activity.

Nakles (42) measured the effect of coal feed location on the production of phenol and other pollutants by the Synthane gasifier. (Table 1-13). This study showed that the production of phenol, COD, TOC, and tars and oils could be reduced by an order of magnitude by changing the coal feed from the normal position above the fluidized bed to a position near the bottom of the bed.

Fillo and Massey (43) measured reaction rates of phenol decomposition in the gas phase and found that char formed by the Synthane gasification of lignite catalyzed the reaction significantly. In a separate experiment, they studied the formation of phenol in the CO_2-Acceptor gasification process. In this process coal is injected into a fluidized bed of coal and calcined dolomite ($CaO \cdot MgO$) which reacts exothermicly with CO_2 and supplies the heat necessary for gasification. The condensate water from this process contains less than 0.01 lb phenol/ton MAF coal. However, a specially designed collector was used to detect about 1 to 2 lb phenol/ton MAF coal within the fluidized bed near the coal injection point.

A conclusion from these studies (42, 43) was that a relatively constant amount of phenol is formed per ton of coal over the pyrolysis conditions studied, and it then decomposes in the gas phase. They also concluded that the formation of tars and oils is strongly influenced by the pyrolysis conditions. These compounds also decompose in the gas phase.

Table 1-13: Effect of Coal Feed Geometry on Condensate-Water Pollutant Production in a Synthane Gasifier.[a]

Coal Injection Location[b,c]	Effluent Production lb/ton MAF coal			
	Phenol	COD	TOC	Tars & Oils
Free fall injection above fluidized bed[d]	12±1	78±14	22±3	74±27
Within fluidized bed near the top	3.5±2	12±5	4.8±1	10±5
Within fluidized bed near the bottom	0.5±0.6	3.6±2	2.7±0.7	6±2

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a. Data reported by Nakles (42).

b. The Synthane gasifier has a fluidized bed with a temperature of about 900°C at the bottom and 700°C at the top. There is a gas disengaging zone above the fluidized bed where the temperature is about 400°C.

c. Coal: North Dakota Lignite.

d. This is the normal operating mode of the Synthane gasifier.

The formation and destruction of phenols and other compounds in coal gasification is complex. It is difficult to isolate experimentally the effects of the many variables identified above and arrive at a fundamental understanding of pollutant production. However, changes in the design of the gasifier can have a dramatic effect on the type and quantity of organic compounds produced in the condensate water. Table 1-14 lists some common gasifier designs. The contacting geometry is described as fixed bed, fluidized bed, or entrained flow. Cocurrent and countercurrent refer to the directions of flow of the coal and the product gas. The pyrolysis temperature is the approximate temperature in the region of the gasifier where the fresh coal is fed. The amount of condensate-water phenols produced by the different gasifier configurations varies widely. Low pyrolysis temperature and low residence time of the gas-phase pyrolysis products in the coal bed (countercurrent flow) promote phenol production. High pyrolysis temperature and longer residence time of the pyrolysis products in the coal bed (cocurrent flow) decrease phenol production by several orders of magnitude. These same trends apply to the total organic carbon production.

It is apparent that there are significant differences in condensate water composition between the different gasifier designs. The gasifiers that produce clean condensate waters have an important advantage, and this may improve public acceptance of the commercialization of these technologies.

Generalizations About Condensate-Water Characterization and Treatability

It is generally true that an important fraction of the organic compounds in condensate waters has not been identified. Condensate waters are complex mixtures of many organic solutes. The polarity of

Table 1-14: Comparison of Phenol Production for Different Coal-Gasification Designs.[a]

Fixed-Bed Gasifiers	Contacting Geometry	Pyrolysis Temperature[b]	Phenol Production[c]
Lurgi Dry-Ash	countercurrent	low (44)	high (42)
Slagging Fixed-Bed	countercurrent	low (43)	high (43)
Fluidized-Bed Gasifiers			
Synthane	countercurrent	low (43)	high (43)
HYGAS	countercurrent	low (43)	high (43)
CO_2-Acceptor	cocurrent	medium (44)	very low (43)
Entrained-Flow Gasifiers			
Koppers-Totzek	cocurrent	high (44)	very low (42)
Texaco	cocurrent	high (44)	very low (42)

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a. Literature references are given in parentheses.
b. Pyrolysis temperature ranges: high >1,000°C; medium 750-1,000°C; low <750°C.
c. Phenol production rates: high 1-30 lb phenol/ton MAF coal; very low <0.01 lb phenol /ton MAF coal.

these solutes varies widely, from polynuclear aromatic hydrocarbons on one extreme to methanol, dihydroxy benzenes, and other very polar compounds on the other extreme. It is difficult to design one analytical technique to detect all of these compounds. Many analytical techniques employ a sample-preparation procedure to fractionate the sample and decrease its complexity and/or to concentrate the solutes in an appropriate solvent. Many compounds may escape detection because they are not recovered in the sample preparation technique.

The literature data discussed above show that solvent extraction processes with common solvents fail to remove a large fraction of the COD, although these processes do remove nearly all of the phenols and other identified compounds. This indicates that many of the unidentified compounds are polar and hydrophilic.

Finally, activated sludge processes also fail to remove an important fraction of the COD. Figure 1-1 is a schematic Venn diagram which illustrates the relationships among the condensate-water solutes that are poorly characterized, poorly extracted, and poorly removed by biological oxidation. A substantial fraction of the organic solutes in condensate waters is unidentified and is not removed by either biological oxidation or extraction with common solvents. This represents an important problem for the design of condensate-water treatment systems.

It is difficult to design new wastewater treatment processes or to correlate the results of experimental tests without detailed knowledge of the physical properties of the solutes. Generic analyses alone are not sufficient to characterize the composition of a condensate water because the composition may vary with time or between processes. A treatment process may perform differently on two condensate waters with equivalent COD and TOC values. Also, the generic analyses do not provide enough information to evaluate the acceptability of the effluent from a given process. A detailed chemical analysis that accounts for all of the major components is necessary to evaluate the toxicity and other properties of an effluent.

The purpose of this work was to develop analytical techniques which can account for a larger fraction of the COD in condensate waters than previous analyses. A second purpose was to study the phase equilibria of condensate water solutes with several solvents. Phase equilibrium studies provide information about the physical properties of the solutes and the capabilities of solvent extraction processes. The investigations in both of these areas focused on polar and hydrophilic compounds which had not been characterized in previous studies.

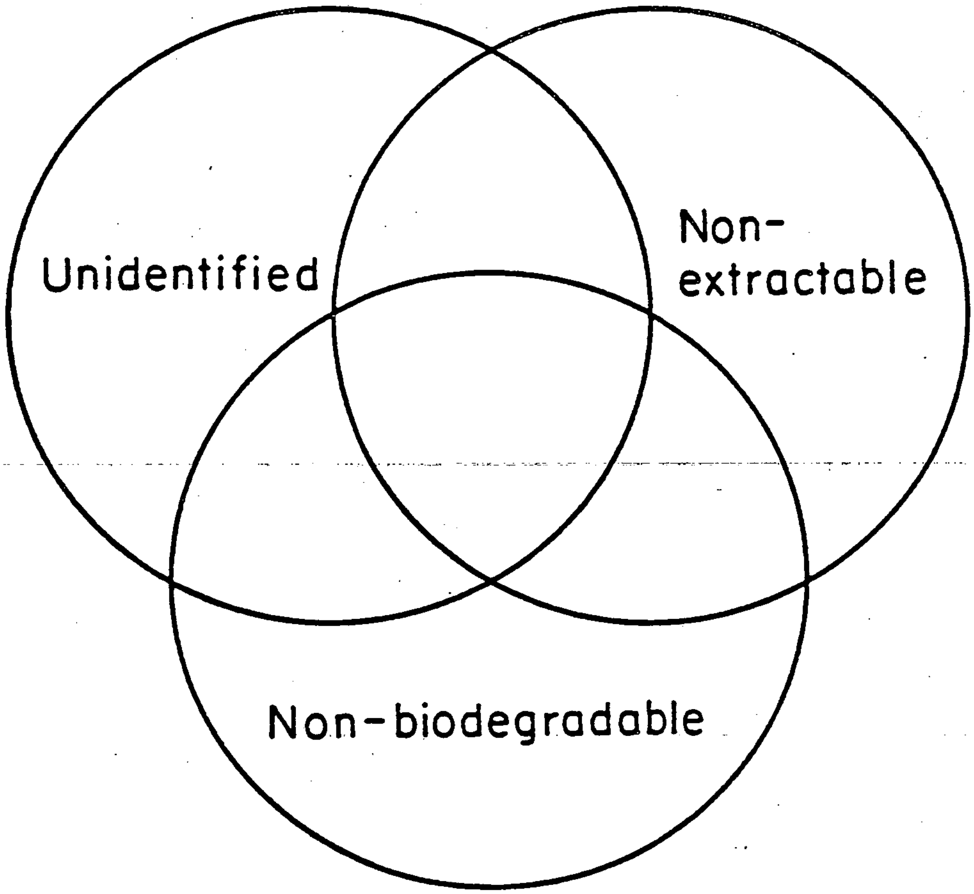

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Figure 1-1: Schematic Venn Diagram of Condensate-Water Solutes Which are Not Identified by Commonly Employed Analytical Techniques, Have Low Distribution Coefficients into Diisopropyl Ether or Methyl Isobutyl Ketone, and are Resistant to Biological Oxidation.

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Chapter 2: Experimental Procedure

Condensate-Water Samples

Samples of condensate water were obtained from a slagging fixed-bed gasifier which was operated by the Grand Forks Energy Technology Center (GFETC) of the U. S. Department of Energy. Indian Head lignite was fed to the top of the gasifier at a rate of 25 tons/day, steam and oxygen flowed up through the bed, and molten slag was continuously withdrawn from the bottom. When the product gases were cooled, an aqueous condensate was produced. Samples of this condensate were collected during steady-state operation from gasifier runs Nos. RA-78, RA-97, RA-106 and RA-120.

Condensate-water samples must be protected from air to prevent oxidation of phenols and dihydroxy benzenes. After even a brief exposure to oxygen the solution darkens and precipitates form. Therefore, the samples were collected under an inert atmosphere. All subsequent handling and analyses of the samples were also performed under nitrogen. The oxidation of phenols can be slowed by lowering the pH of the solution below the pK_A's of these compounds, and this is frequently employed as a sample preservation procedure. Therefore, half of each sample was adjusted to pH 2 with concentrated sulfuric acid at the time of sample collection. Then 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.

Analysis of Condensate Waters by High-Performance Liquid Chromatography

Compounds in the condensate-water mixture were resolved and detected with a reversed-phase high-performance liquid chromatography

(HPLC) technique. This method has advantages over previous analyses, particularly for the quantitative analysis of very polar and hydrophilic solutes.

Many previous analyses of condensate waters (see Chapter 1) have been performed with a standard analytical technique consisting of methylene chloride extraction followed by gas chromatography-mass spectrometry (GC-MS) analysis of this extract. An important disadvantage of this technique is that some solutes may be incompletely recovered by the solvent extraction sample-preparation technique. Stamoudis and Luthy (1) report recoveries of 82% for phenol and 65% for C_2-phenols using the methylene chloride/GC-MS technique. Solvent extraction results from the literature and this work show that many compounds in coal-conversion condensate waters are more polar and difficult to extract than phenol. These compounds would be poorly recovered by this technique. It is also possible that some very polar solutes would have such low distribution coefficients into methylene chloride that they would not be detected. The analysis of these very polar compounds is important for the design of solvent extraction treatment processes because these compounds are the most difficult to remove by solvent extraction. In summary, the methylene chloride/GC-MS technique has poor precision for the quantitative analyses of compounds such as phenol due to incomplete extraction. This problem is more pronounced for solutes which are more polar than phenol. Some compounds in condensate waters may be so polar and difficult to extract that they would not be detected with this technique.

These problems do not occur in reversed-phase HPLC analyses of condensate waters. In reversed-phase HPLC the stationary phase is a non-polar hydrocarbon and the mobile phase is a polar solvent. Therefore, the aqueous sample mixture can be injected directly into the mobile phase, and a preliminary solvent extraction is not required.

In reversed-phase HPLC a separation occurs because the solutes distribute, or partition, to different extents between the two phases. The more polar solutes have a greater affinity for the mobile phase and elute quickly from the HPLC column. Less polar compounds have a greater affinity for the stationary phase and elute more slowly.

The retention of solutes on the non-polar stationary phase can be controlled by adjusting the composition of the solvent. Water is called a "weak" solvent because it elutes only the more polar solutes while the less polar compounds are retained by the stationary phase. Methanol is a "strong" solvent since it elutes the less polar compounds. Solvent strength in liquid chromatography is analogous to temperature in gas chromatography. With isocratic elution the solvent composition remains constant during the chromatographic analysis. Isocratic elution with a weak solvent is analogous to isothermal elution at a low temperature in gas chromatography.

In isocratic elution the solvent strength is adjusted to optimize the retention times of the solutes. If the solvent is too weak, then the solutes elute too slowly. The result is a long analysis time and short, wide peaks which are difficult to detect. If the solvent is too strong, then all of the solutes elute in the beginning of the chromatogram and are poorly resolved.

Even though the solvent strength is adjusted to give the appropriate retention times, two closely eluting compounds may still be poorly resolved. The resolution of these compounds can be improved by increasing the efficiency of the column or by improving the separation factor by modifying the solvent. The most effective way to improve the resolution is to change the compostion of the solvent while maintaining the solvent strength constant. This can be accomplished by changing the strong solvent. For example, a mixture of water and methanol could have approximately the same strength as a mixture of water and acetonitrile, but the separation factors could change significantly. If the separation factor cannot be improved by changing the solvent composition, then the stationary phase can be changed.

If the sample contains solutes with a wide range of polarity, then it may not be possible to optimize the solvent strength for all of the solutes in one isocratic elution. In this case gradient elution is required to resolve all of the solutes in one analysis. In gradient elution the solvent composition is changed in a controlled manner from a weak solvent to a strong solvent. Polar compounds are eluted by the weak solvent at the beginning of the gradient. Then the solvent strength increases and the less polar compounds elute. In this way all of the solutes have an acceptable retention time. The initial and final solvent strength as well as the rate of change of solvent strength can be varied to optimize the separation of the solutes. Gradient elution in liquid chromatography is analogous to temperature programming in gas chromatography. The resolution of mixtures by isocractic and gradient elution HPLC has been reviewed by Snyder, et al. (2) and Dolan, et al. (3).

In this work the stationary phase was octadecyl silane, which is a C_{18} hydrocarbon chemically bonded to a silica support. Specifically, a Waters Associates Radial-Pak A with 5-micron particle size was employed in a Waters Associates Radial Compression Module. This type of column provides lower pressure drop and higher efficiency than steel columns.

Precise control of the mobile-phase flow rate and composition was achieved with a Spectra-Physics SP 8000-B liquid chromatography pump. This microprocessor-controlled pump can be programmed to mix as many as three solvents to provide a mobile phase of known composition at a constant flow rate at pressures up to 6000 psi. The composition of the mobile phase can be changed over time in a precisely controlled manner.

Two solvents were used to form the HPLC mobile phases. The first was water buffered to pH 3 with a mixture of 0.004 $\underline{M}$ $K_2H_2PO_4$ and 0.0017 $\underline{M}$ H_3PO_4. This low pH prevented the ionization of acidic compounds such as phenol, which would result in poor resolution on the HPLC. Before the buffer was prepared, inorganic ions and organic contaminants were removed from the water with a Millipore Milli-Q system. The second solvent was HPLC-grade methanol (Burdick and Jackson Co.). All solvents were filtered to remove particles larger than 0.45 microns.

A Perkin-Elmer LC-75 variable wavelength UV absorbance detector was employed to detect the compounds which eluted from the HPLC. This detector has a wavelength range of 190-600 nm, and a bandwidth of 4 nm. The wavelength can be reset to a precision of ±0.3 nm.

Condensate-water samples were prepared for HPLC analysis by slow addition of concentrated H_2SO_4 to pH 3. This solution (5 ml) was filtered through a Waters Associates Sep-Pak which contained an octadecyl silane liquid chromatography packing. The Sep-Pak was then washed with 5 ml of water (pH-3 phosphate buffer) and 5 ml of methanol. All of the eluant from the Sep-Pak was combined for subsequent analysis. The purpose of this procedure was to remove compounds which might contaminate the HPLC stationary phase. Tests with synthetic solutions verified that this procedure quantitatively recovered all of the compounds reported subsequently.

Information from the literature reports discussed in Chapter 1 about the polarity of condensate-water solutes was used to develop the HPLC separation of the solutes in the GFETC samples. It was expected that dihydroxy benzenes, phenols and alkylated phenols would be present in these samples. Solvent extraction results from the literature and this work indicated that solutes were present which are even more polar than dihydroxy benzenes. Since the mixture contained solutes with such a wide range of polarity, it was analyzed by gradient elution. The initial solvent composition was 100% water since very polar compounds were thought to be present. The final solvent composition was chosen to be 70% methanol because no significant peaks were detected as the solvent strength increased further. The slope of the gradient was adjusted by trial and error to optimize solute resolution and analysis time. The result of this method development was that the samples were eluted in a linear gradient from 100% pH-3 water at injection to 30% water and 70% methanol at an elution volume of 42 ml, with a flow rate of 1 ml per minute. A trial-and-error procedure established that the detector response was optimized for many of the compounds in the sample at 280 nm. Phenols absorb strongly at this wavelength. A chromatogram with these conditions is shown in Figure 3-1.

Inspection of this chromatogram shows that no major components were detected in the beginning of the chromatogram where the most polar compounds would be expected to elute. Therefore, a second set of HPLC conditions was developed to improve the detection of the most polar solutes. The samples were eluted a second time with 100% pH-3 water. This weak solvent maximized the resolution of very polar compounds. Also, water is sufficiently transparent in the far UV that the detector could be operated at 192 nm where many more compounds absorb UV radiation. Figure 3-2 shows that several additional compounds were detected with these conditions.

Quantitative measurements of the solutes were obtained by integrating the peaks from the UV absorbance detector. The detector was calibrated by eluting mixtures of known composition with identical chromatographic conditions. Table 2-1 shows the sources of the compounds employed in this study. Compounds not listed in Table 2-1 were readily available from commercial sources. Several of the hydantoins were synthesized from the corresponding ketones by the Bucherer-Bergs synthesis (4). Methyl hydantoin was purchased from both Chemical Procurement Laboratories and Lachat Chemicals. When this compound was chromatographed in isocratic pH-3 water with detection at 192 nm, two peaks were found. In the sample from Chemical Procurement Laboratories the smaller peak was 30% of the total. In the sample from Lachat Chemicals the smaller peak was 15% of the total. It is known (4) that hydantoins can hydrolyze in water to form the hydantoic acid. Therefore, it was assumed that the large peak in each sample was 5-methyl hydantoin and that the smaller peak was 5-methyl hydantoic acid. However, there is appreciable uncertainty about the identities of these compounds.

In two instances the isomers of a compound could not be resolved. The C_1-phenols could not be separated, so the detector was calibrated with an equimolar mixture of the three isomers. The relative absor-

Table 2-1: Sources of Compounds Used to Calibrate the UV Absorbance Detector.

Compound	Source
hydantoin	Aldrich Chemical Company
hydantoic acid	Chemical Procurement Laboratories
5-methyl hydantoin Lachat Chemicals (see text)	Chemical Procurement Laboratories
5-methyl hydantoic acid	(see text)
5,5-dimethyl hydantoin	Aldrich Chemical Company
5-ethyl-5-methyl hydantoin	Frinton Laboratories
5,5-diethyl hydantoin	Synthesized[a]
5-isobutyl-5-methyl hydantoin	"
5,5-di-n-propyl hydantoin	"
5-methyl-5-phenyl hydantoin	"

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a. Synthesized from the corresponding ketones by the Bucherer-Bergs synthesis (see ref. 4).

bances of the three isomers at 280 nm are: o-methyl phenol (1.00), m-methyl phenol (0.95), and p-methyl phenol (1.25). Therefore, this approximation should not have caused a large error. Similarly, the C_2-phenols could not be resolved. In this case the detector was calibrated with 2,4-dimethyl phenol. From the data for methyl phenols cited above it is reasonable to expect that the absorbance of the C_2-phenol isomers would be nearly constant.

Several additional factors affect the precision of the quantitative information obtained from the HPLC system. The peak area from the UV absorbance detector is inversely proportional to the mobile-phase flow rate. Therefore, the precision of the detector response is determined by the precision of the flow-rate measurement. The reproducibility of the detector response is affected by any uncontrolled changes in the wavelength of the monochromatic UV radiation. The magnitude of this effect is determined by the precision of the wavelength setting (±0.3 nm) and by the change in absorbance with wavelength for the solute of interest. The precision is also affected by the chromatographic resolution of the solute from closely eluting compounds. Finally, the sample volume must be reproducible. The sample is injected into the HPLC with a six-port rotary valve. If the seals on this valve become scratched or worn, the valve can leak and the sample volume can change. HPLC samples were filtered before injection to prolong the life of the valve seals.

The precision of the HPLC quantitative analyses was approximately ±5%.

Qualitative Identification Procedures

Once the solutes from the condensate water samples were resolved and detected with the HPLC, it was necessary to obtain a qualitative identification of these compounds. The first qualitative identification procedure employed HPLC co-chromatography. In this procedure 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. This technique is experimentally simple. However, if the possible identity of a solute cannot be limited to a small number of alternatives, this procedure becomes too lengthy.

Mass spectrometry is an effective tool for identifying compounds. A direct interface between a liquid chromatograph and a mass spectrometer would be very desirable for the identification of polar organic compounds in condensate waters. However, 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 gas chromatography-mass spectrometry (GC-MS) identification of individual compounds after they eluted from the liquid chromatograph.

Individual peaks were collected in dilute aqueous solution as they eluted from the HPLC. In many cases the concentration of the solute in this solution was below the detection limit of the GC-MS. Also, water is not compatible with many GC stationary phases, and removing this water in a rotary evaporator is difficult. Therefore, the samples were concentrated by an azeotropic distillation with isopropanol. The aqueous solution (typically 5 ml) containing the unidentified solute was mixed with about 50 ml of high-purity isopropanol (Burdick and Jackson Co.) to form a solution at about the azeotropic composition. The mixture was evaporated to a final volume of about 1 ml in a rotary evaporator. More isopropanol (10 ml) was added and the mixture was evaporated to a final volume of about 0.1 ml. The resulting solution contained almost no water.

In order to obtain qualitative identification with this sample-preparation technique, the solute concentration in the final isopropanol solution must be greater than the detection limit of the GC-MS. Under the conditions stated above and assuming 100% recovery, the concentration of the solute is increased by a factor of 50 in the final isopropanol solution. The actual recovery of a solute depends strongly on its volatility in the isopropanol-water solution. The measured recoveries for several solutes were: dimethyl hydantoin--63%, phenol--86%, and catechol--89%. The solute must have a relative volatility substantially less than one. However, moderately volatile compounds can be concentrated to the GC-MS detection limit even though the total solute recovery may be quite low. The solute must be soluble and unreactive in isopropanol, and the isopropanol must be free of non-volatile impurities which would concentrate during evaporation.

This technique was intended for qualitative identification only. Quantitative information was obtained from the HPLC with the UV absorbance detector.

The principal advantage of this azeotropic distillation procedure is that the solute, which may be very hydrophilic, 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 incomplete extraction of the solutes.

GC-MS analyses were performed with a Finnigan 4000 GC-MS system with an Incos data system. The mass spectrometer was operated in the electron ionization mode with electron energies of 70 eV. The spectrometer scanned the mass range 33-450 at a rate of one scan per second. The gas chromatograph stationary phase was a 60-m glass capillary (0.32 mm i.d.) SP 2250 column manufactured by J & W Scientific, Inc. The mobile phase was helium with a linear flow velocity of 20 cm/sec. The temperature was programmed from 10 to 250°C at 4°C per minute. The Grob injection technique was used. The data system could compare the mass spectrum of an unknown solute to a library of known spectra and give a statistical indication of how closely the two spectra matched. The mass spectrum of 5,5-dimethyl hydantoin was measured from the pure compound because this spectrum was not available in the computer library.

In the case of dimethyl hydantoin, chemical ionization mass spectrometry data were also obtained. The chemical ionization reagent was methane. The spectrometer scanned the mass range of 50-700. The gas chromatograph stationary phase was a 60-m glass capillary DB-5 column manufactured by J & W Scientific, Inc. The temperature was programmed from 60-300°C at 10°C per minute. All of the other conditions were the same as for the electron ionization data. The GC conditions were different for the chemical ionization data only because the measurements were made at different times.

In summary, two methods were employed for qualitative identification. All of the compounds reported in this work were identified with the HPLC co-chromatography procedure. This technique alone yields an identification with a good level of confidence. Some of the compounds reported here were also identified with the isopropanol/GC-MS technique. The combination of these two techniques yields an identification with a high confidence level.

Generic Analyses

The procedures described above provided information about specific compounds in the condensate-water samples. Liquid-liquid extraction experiments and general water-quality parameters, such as the Chemical Oxygen Demand (COD) and organic nitrogen, were used to obtain additional information about the physical properties of the organic solutes and to estimate the performance of continuous solvent extraction processes.

The COD was measured according to standard procedures (5). In the COD test the sample is oxidized by potassium dichromate in boiling 50% H_2SO_4 in the presence of a Ag_2SO_4 catalyst. Nearly all organic compounds oxidize to CO_2 and H_2O under these conditions. The result is reported as the amount of oxygen that would be required to complete the same oxidation. As an example, Equation (1) shows the oxidation of phenol. Phenol has a theoretical COD of 2.38 mg oxygen/mg phenol.

$$C_6H_6O + 7\ O_2 = 6\ CO_2 + 3\ H_2O \qquad (1)$$

Experimental tests showed that phenol has an actual COD equal to 100% of the theoretical value, within the experimental uncertainty. Some of the compounds detected in GFETC condensate waters contained nitrogen. Equation (2) shows that dimethyl hydantoin has a theoretical COD of 1.125 mg oxygen/mg dimethyl hydantoin.

$$C_5H_8N_2O_2 + 4.5\ O_2 = 5\ CO_2 + 2\ NH_3 + H_2O \qquad (2)$$

Experimental tests showed that the actual COD of dimethyl hydantoin was 83% ± 1% of the theoretical value. The theoretical value of the COD was used in all comparisons of analytical results to measured values of the condensate-water COD.

In previous reports from this work (6, 7) the theoretical COD was calculated with the assumption that nitrogen in organic compounds reacted to form N_2. If this assumption is applied to dimethyl hydantoin (Equation 3), then the theoretical value of the COD is 1.5 mg oxygen/mg dimethyl hydantoin.

$$C_5H_8N_2O_2 + 6\ O_2 = 5\ CO_2 + N_2 + 4\ H_2O \qquad (3)$$

Although some compounds oxidize to form a mixture of ammonia and molecular nitrogen (8), most compounds react to form ammonia (8, 9). Therefore, in this paper it was assumed that all nitrogen-containing organic compounds reacted to form ammonia in the COD analysis, and the theoretical COD was calculated as exemplified by Equation 2.

Some inorganic compounds respond to the COD measurement. $HgSO_4$ is added to the reaction mixture in the COD analysis to prevent interferences due to chloride ion. Sulfide and cyanide do not interfere because the samples were acidified and degassed before analysis. Thiocyanate (SCN^-) has a COD of 1.35 g COD/g SCN^-, but the concentration of this ion is usually small compared to the total COD.

Organic nitrogen is defined as the difference between Kjeldahl nitrogen and ammonia nitrogen. These measurements were performed by the Microanalytical Laboratory of the College of Chemistry at the University of California, Berkeley, according to standard procedures (5). In the ammonia measurement the aqueous sample is adjusted to a high pH, and the ammonia is removed by distillation and then titrated. In the Kjeldahl nitrogen measurement the sample is heated with K_2SO_4, $HgSO_4$, and H_2SO_4 until SO_3 fumes are liberated. This procedure converts the nitrogen in many organic compounds into ammonia. In the final step of the Kjeldahl analysis the original ammonia combined with the ammonia from the organic compounds is measured by the distillation procedure. The organic nitrogen test does not respond to any compound in which the formal oxidation state of the nitrogen is greater than zero. Also, some pyridines and tertiary amines are resistant to the test (10).

Tests with synthetic solutions showed that thiocyanate (SCN^-) responded to the organic nitrogen test (0.24 g N/g SCN^-). Therefore the concentration of SCN^- was measured by the Microanalytical Laboratory described above according to a procedure described by Luthy (11). The concentration of SCN^- in the pH-2 portion of the condensate water from GFETC run No. RA-120 was 45 mg/l. The corresponding value of organic nitrogen (11 mg/l) was subtracted from the measured organic nitrogen to obtain the results reported subsequently.

The condensate waters had a low concentration of organic nitrogen, typically 200 mg/l, compared to a high concentration of ammonia, typically 5,000 mg/l. In this situation the organic nitrogen was the small difference between the high concentrations of Kjeldahl and ammonia nitrogen. To improve the precision of the measurement, most of the ammonia was removed from the sample by adjusting to a high pH and stripping with four moles of water-saturated nitrogen per mole of solution at 25°C. This procedure may have removed some of the volatile nitrogen-containing compounds.

The COD and organic nitrogen measurements are useful because they provide a bulk characterization of the organic solutes although the individual components need not be identified.

Liquid-Liquid Extraction

Liquid-liquid phase 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. The two phases were shaken by hand in a separatory funnel for five minutes. The mixture was then centrifuged at 1,000 g, if necessary, to obtain clear phases. The phases were separated and the raffinate was analyzed. If several extractions were performed in series, then the raffinate from the previous extraction was contacted with a fresh volume of solvent. These procedures were performed in an inert atmosphere to prevent oxidation of the condensate-water samples as discussed earlier.

In order to measure the COD of a raffinate, it was first necessary to remove the residual dissolved solvent from the solution. The first solvent studied was methyl isobutyl ketone (MIBK). MIBK has a high volatility relative to water and can be removed from aqueous solution by nitrogen stripping.

Two grades of MIBK and two solvent-removal procedures were employed in this study. For the extraction of condensate-water samples from GFETC run Nos. RA-78 and RA-97 the MIBK was reagent grade (Matheson, Coleman, and Bell). Reagent-grade MIBK was removed from aqueous solution by stripping with water-saturated nitrogen (5 moles N_2/mole H_2O @ 25°C) to an MIBK concentration of less than 5 mg/l as determined by gas chromatography. However, it was subsequently determined that an impurity in the reagent-grade MIBK was distributing into the aqueous phase and contributing to the measured COD. The magnitude of this effect is shown in Table 2-2. The values in Table 2-2 were subtracted from the COD measurements of condensate-water raffinates to account for this effect. However, an experimental uncertainty of ±1,000 mg/l was assigned to the COD of the raffinates due to the uncertainties involved in quantifying the effect of the impurity.

Table 2-2: Residual Concentration of COD in Distilled Water Raffinates Due to Impurities in MIBK

Organic Phase [a,b]	No. of Successive Batch Extractions	Residual COD After Nitrogen Stripping (mg/l)
MIBK	1 @ pH 12	1,000
MIBK	2 @ pH 12	2,000
MIBK	1 @ pH 12 & 1 @ pH 2	1,000

a. Unpurified, reagent grade MIBK (Matheson, Coleman, & Bell)

b. The phase ratio in all of the extractions was 1:1 v/v.

The procedure was improved for the extraction of condensate waters from GFETC run Nos. RA-106 and RA-120. MIBK was obtained from Burdick and Jackson Company. The MIBK was purified by repeated washes with 0.1 N NaOH, 0.1 N H_2SO_4, and then water. The purified MIBK was then used in the condensate-water extractions. 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 less than 5 mg/l, as determined by gas chromatography, and a COD concentration less than 25 mg/l. The temperature and nitrogen flow were kept as low as possible to minimize the loss of volatile solutes. With this procedure, the COD of condensate-water raffinates could be measured with an estimated uncertainty of ±100 mg/l.

The second solvent that was studied was a mixture of 25% w/w trioctyl phosphine oxide (TOPO) in MIBK. TOPO was obtained from American Cyanamid Co. and has a solubility less than 4 mg/l in water (American Cyanamid Co.). Therefore, only the residual MIBK and any water-soluble impurities in the TOPO/MIBK mixture contribute to the measured COD of the raffinate. For the extraction of condensate water from GFETC run No. RA-78 reagent-grade MIBK (Matheson, Coleman, and Bell) was employed, the raffinates were stripped with 5 moles N_2/mole H_2O, the corrections in Table 2-2 were applied, and the estimated uncertainty was ±1,000 mg/l in the condensate-water raffinates. In the extraction of condensate water from GFETC run No. RA-120 the MIBK (Burdick and Jackson Co.) was purified by washing with acid and base as described above, and the raffinates were stripped with 1.5 moles N_2/mole H_2O. When distilled water was contacted with the TOPO/purified-MIBK mixture and stripped with nitrogen, the residual COD was about 500 mg/l. This COD was probably due to impurities in the TOPO since the purified MIBK alone produced a raffinate with a lower residual COD. This residual COD of 500 mg/l was subtracted from the measured COD's of condensate-water raffinates from GFETC run No. RA-120, and the uncertainty of the raffinate COD's was estimated to be ±500 mg/l.

When condensate-water samples were contacted with the TOPO/MIBK mixture, the two phases did not separate as rapidly or as completely as compared to extraction with MIBK. After ten minutes of centrifugation at 1,000 g the condensate-water raffinates were still cloudy. This problem was not observed if the condensate water had been acidified to pH 3 before extraction. This problem was solved in the experimental procedure by centrifuging the two phases, withdrawing the cloudy aqueous phase, adding conc. H_2SO_4 to pH 3, and centrifuging a second time to obtain a clear aqueous phase.

The third solvent employed in condensate-water extractions was tributyl phosphate (TBP). TBP was obtained from Mobil Chemical Co. and was purified by washing with 0.1 $\underline{N}$ NaOH, 0.1 $\underline{N}$ H_2SO_4, and water. Residual COD was removed from the condensate-water raffinates by adding conc. H_2SO_4 to pH 2, extracting the raffinate a second time with n-heptane (Burdick and Jackson Co.) at a solvent-to-water ratio of 1:4 by volume, and removing the heptane by stripping with 1.5 moles N_2/mole H_2O. Heptane removed very little, if any, of the solutes remaining after TBP extraction because heptane is a very non-polar solvent. A test of this procedure with distilled water gave a residual COD of 150 mg/l. For each condensate-water raffinate, this residual COD of 150 mg/l was subtracted from the measured COD, and the uncertainty of the raffinate COD was estimated to be ±150 mg/l.

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Chapter 3: Results and Discussion

Condensate-Water Samples

Four condensate-water samples were obtained from the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) according to the procedure described in Chapter 2. The gasifier operating conditions are listed in Table 3-1. The chemical oxygen demands (COD) of these samples are shown in Table 3-2. The COD was measured for the samples stored at pH 2 and for the samples stored without pH adjustment. When the samples stored without pH adjustment were acidified with conc. H_2SO_4 to pH 3, a small amount of precipitate formed. This solution was centrifuged for 5 minutes at 1000 g, and the COD was measured. This value of the COD was used in all subsequent calculations.

Qualitative Identification of Organic Solutes in Condensate Waters

Condensate-water samples were eluted from the HPLC stationary phase with two sets of mobile-phase conditions. The samples were first eluted with a linear gradient from water (pH 3) to 70% methanol with UV absorbance detection at 280 nm. The details of the HPLC conditions and the chromatogram for one condensate water are shown in Figure 3-1. The peaks in the chromatogram are identified in Table 3-3.

The samples were eluted a second time with a mobile phase of 100% pH 3 H_2O and UV absorbance detection at 192 nm. These conditions were chosen to maximize the resolution of very polar compounds, as discussed in Chapter 2. With these conditions several more compounds were detected in the HPLC chromatogram of Figure 3-2. Table 3-4 is a list of the compounds detected in Figure 3-2.

Table 3-1: Operating Conditions
for the GFETC Slagging Fixed-Bed Gasifier[a].

GTETC Run No.:	RA-78	RA-97	RA-106	RA-120
Operating pressure (psi):	300	300	350	300
Moles steam/mole oxygen:	1.0	0.9	0.9	0.9
Oxygen rate (SCF/hr):	6,000	4,500	5,000	6,500
Coal feed rate (ton/day):	25	25	25	25

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[a] Data from Paulson (1). Feed coal: Indian Head Lignite.

Table 3-2: Chemical Oxygen Demand (COD) of GFETC Condensate Water Samples

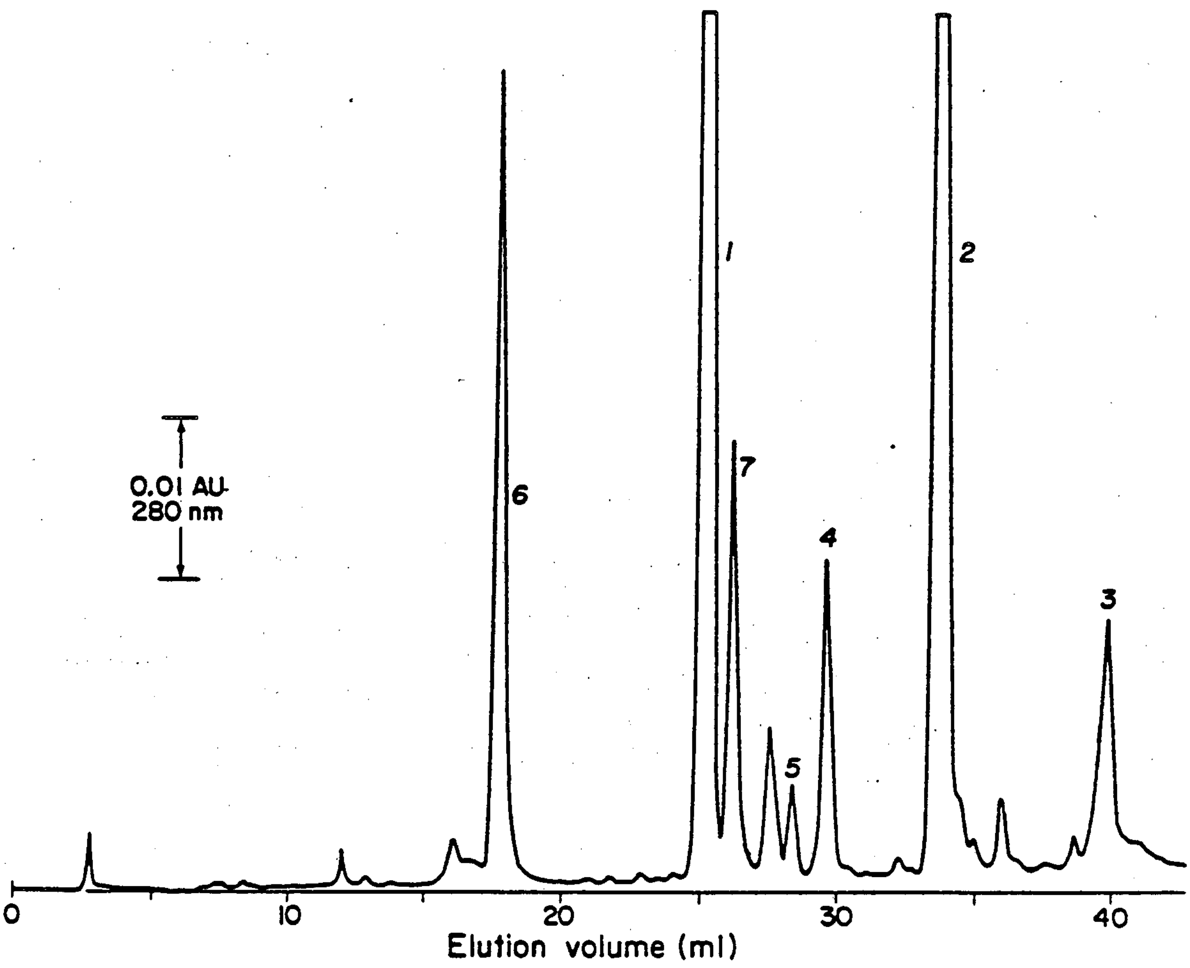
GFETC Run No.:	RA-78	RA-97	RA-106	RA-120
COD (mg/l) of sample stored @ pH 2:	31,700	47,100	23,400	22,800
No. of replicates:	2	1	3	3
Standard deviation/mean:	0.026	-	0.010	0.028
COD (mg/l) of sample stored without pH adjustment:	35,800	-	23,500	24,700
No. of replicates:	4	-	3	3
Standard deviation/mean:	0.011	-	0.025	0.014
COD[a,b,c,d] (mg/l) of sample stored without pH adjustment after precipitation at pH 3:	34,900	46,700	22,900	23,400
No. of replicates:	5	1	3	4
Standard deviation/mean:	0.021	-	0.015	0.012
Sample age interval (days)[e]:	70-400	50-60	1.7-22	0.7-40

---

a. The sample was adjusted to pH 3 with conc. H_2SO_4 and centrifuged immediately before analysis. Some precipitate was observed.
b. This COD value was used in subsequent calculations.
c. No significant change was observed if the pH was lowered to 2.
d. The estimated precision of the COD measurements is ±2%.
e. No significant change was observed in the COD concentrations over this time interval.

Figure 3-1: HPLC Chromatogram of

GFETC Run No. RA-97 Condensate Water



XBL 8112-1665

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a. Mobile phase: linear gradient from 100% pH-3 H_2O at injection to 30% pH-3 H_2O and 70% methanol at 42 ml elution volume. Flow rate: 1 ml/min

b. Stationary phase: Waters Associates Radial Pak A C_{18}.

c. UV absorbance detection at 280 nm.

d. Peak Nos. identified in Table 3-3.

Table 3-3: Qualitative Identification of Condensate-Water Components Eluted in Figure 3-1.

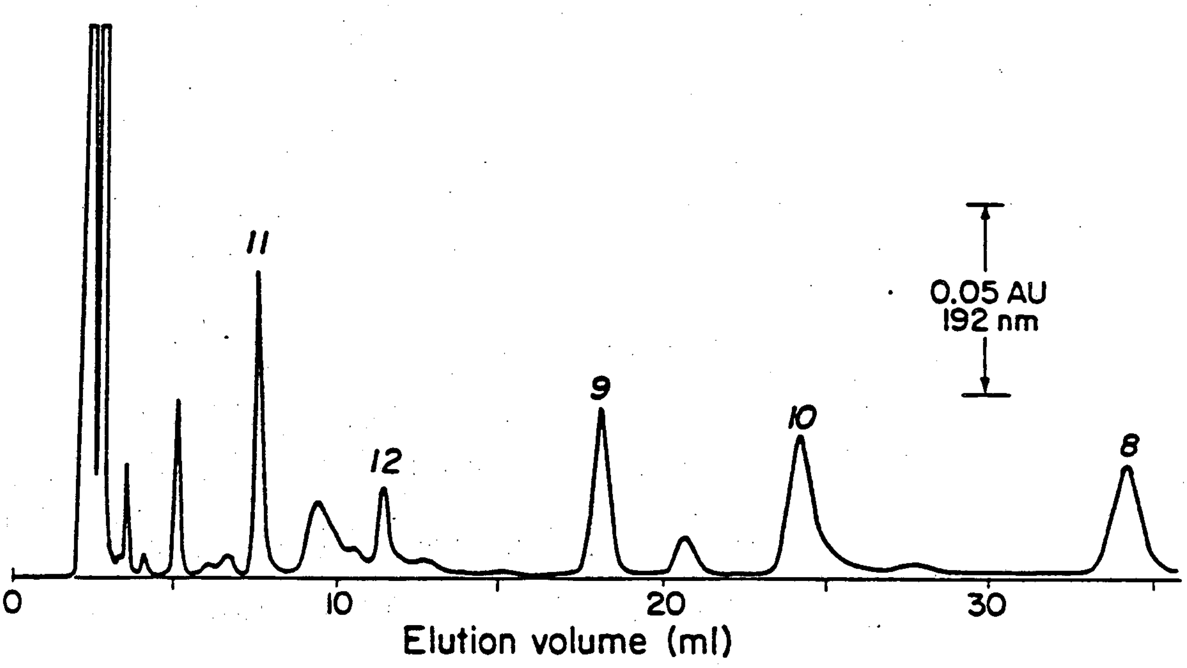
Compound	Qualitative Identification by HPLC Co-chromatography	Qualitative Identification by the Isopropanol/GC-MS Technique[a]
1. phenol	*	
2. C_1-phenols	*	
3. C_2-phenols	*	*
4. o-methoxy phenols	*	*
5. p-hydroxy acetophenone	*	*
6. 1,2-dihydroxy benzene (catechol)	*	
7. 1,2-dihydroxy 4-methyl benzene (4-methyl catechol)	*	*

---

[a] HPLC fractions were collected in aqueous solution, the solutes were concentrated by an azeotropic distillation with isopropanol, and the components were identified by GC-MS. This procedure is described in Chapter 2.

Figure 3-2: HPLC Chromatogram of

GFETC Run No. RA-97 Condensate Water.



XBL 8112-1666A

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a. Mobile phase: 100% pH-3 H_2O. Flow rate: 1 ml/min.
b. Stationary phase: Waters Associates Radial Pak A C_{18}.
c. UV absorbance detection at 192 nm.
d. Peak Nos. identified in Table 3-4.

Table 3-4: Qualititative Identification of Condensate Water Components Eluted in Figure 3-2.

Compound	Qualitative Identification by HPLC Co-chromatography	Qualitative Identification by the Isopropanol/ GC-MS Technique[a]
8. 1,3-dihydroxy benzene (resorcinol)	*	
9. 1,4-dihydroxy benzene (hydroquinone)	*	
10. 5,5-dimethyl hydantoin	*	*
11. 5-methyl hydantoic acid	*	
12. 5-methyl hydantoin	*	

---

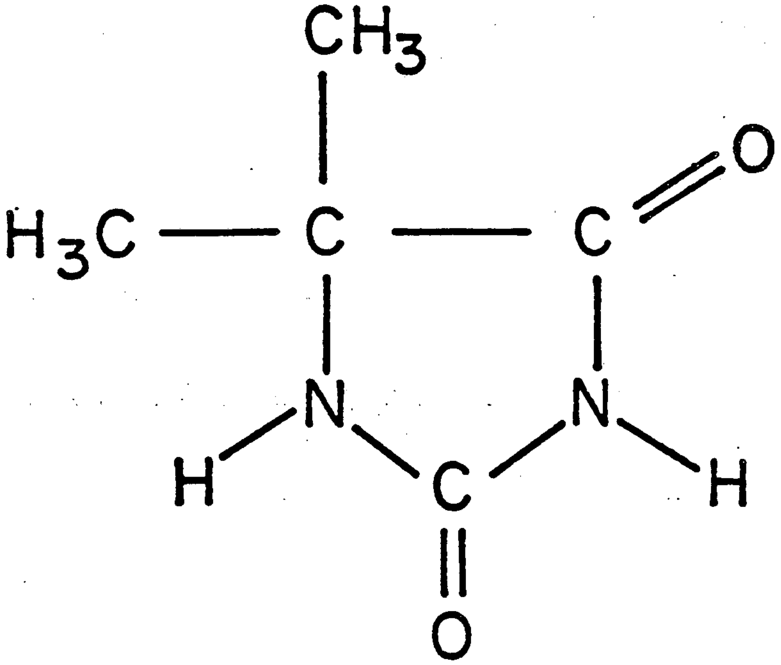
[a] HPLC fractions were collected in aqueous solution, the solute was concentrated by an azeotropic distillation with isopropanol, and the component was identified by GC-MS. This procedure is described in Chapter 2.

Earlier reports from this work (2,3) were the first reports of hydantoins in condensate waters. Therefore, the qualitative identification of these compounds will be discussed in more detail. Figure 3-3 shows the structure of 5,5-dimethyl hydantoin. This compound is very polar and is a weak acid with pK_A of about 10 (4). Figure 3-4 is a comparison of the electron ionization (EI) mass spectrum of a compound isolated from GFETC run No. RA-78 condensate water and the mass spectra of dimethyl hydantoin as measured in this work and by Rucker et al. (5). The condensate-water solute spectrum closely matches the dimethyl hydantoin data. Figure 3-5 is a comparison of the chemical ionization (CI) mass spectra of the condensate-water solute and dimethyl hydantoin. These spectra also match closely. On the basis of the EI and CI mass spectrometry data and HPLC co-chromatography, 5,5-dimethyl hydantoin was identified with a high level of confidence.

Dimethyl hydantoin has a low activity coefficient in water because it is very polar and hydrophilic. The distribution coefficient (K_D) of this compound between methylene chloride and water is less than 0.05 (Table 3-9). Therefore, hydantoins may have been present in many other condensate-water samples, but would not have been readily detected by the standard methylene chloride/GC-MS analytical technique due to negligible recovery in the extraction step. Both the direct injection of aqueous samples on the HPLC and the isopropanol/GC-MS technique are advantageous for these hydrophilic compounds because the solutes do not have to be extracted out of water.

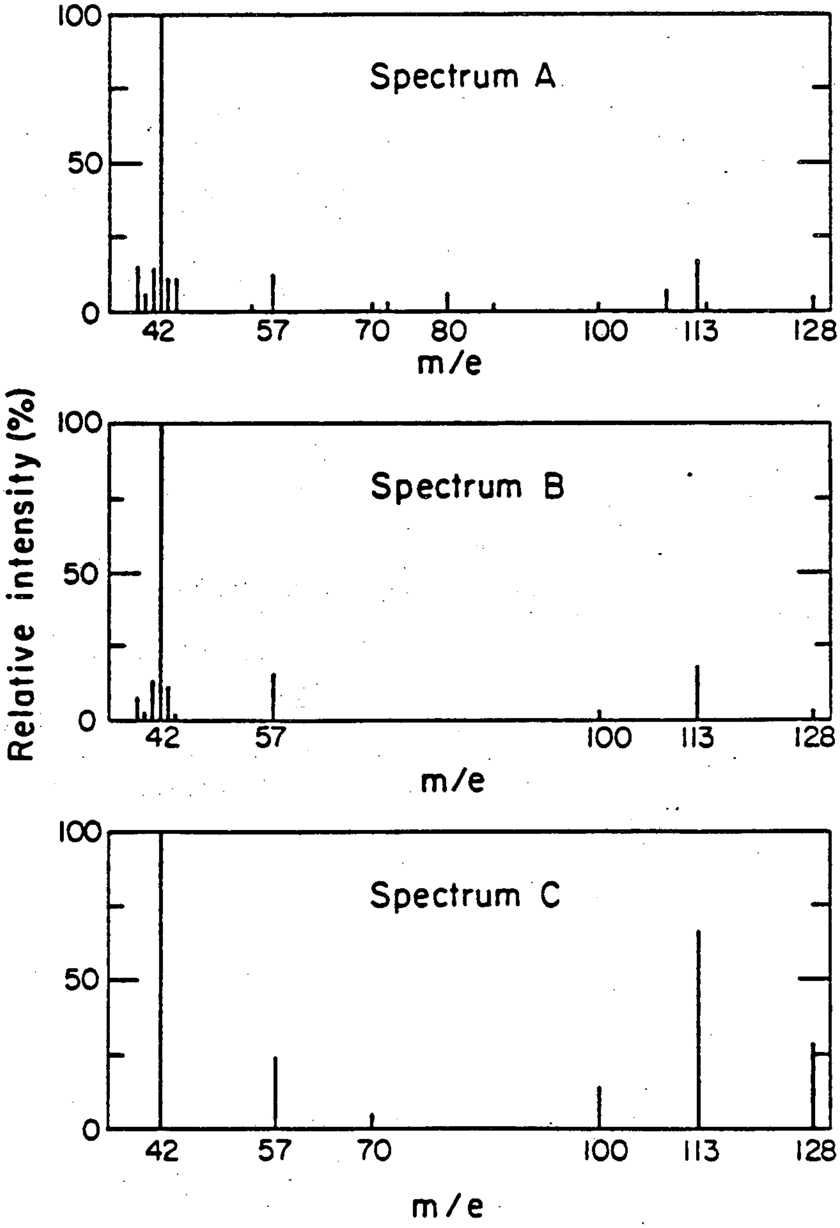
After the initial communications from this work (2,3) the identification of hydantoins in GFETC condensate waters was confirmed by Olson, et al. (6) at the Grand Forks Energy Technology Center. Olson, et al.

Figure 3-3:



5, 5 – Dimethyl Hydantoin

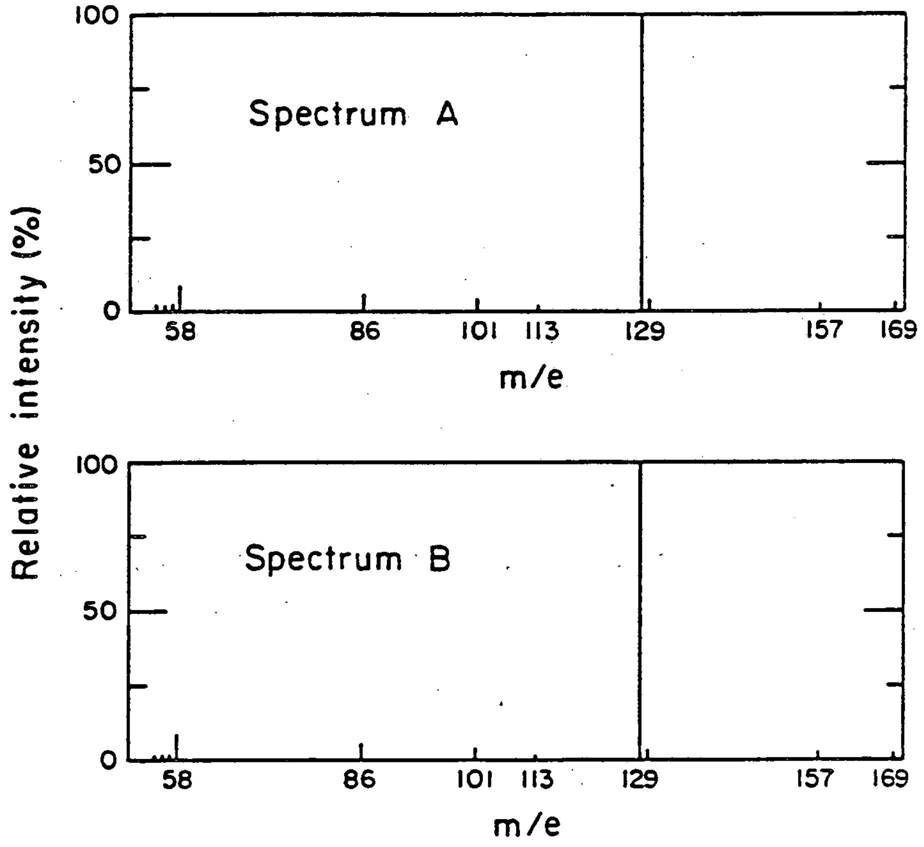
Figure 3-4: Comparison of the 70 eV Electron-Ionization Mass Spectra of a Condensate-Water Solute and Dimethyl Hydantoin.



XBL837-973

Spectrum A: Solute isolated from GFETC run No. RA-78 condensate water with the isopropanol/GC-MS technique described in Chapter 2.
Spectrum B: 5,5-dimethyl hydantoin standard. Mass spectrometer conditions described in Chapter 2.
Spectrum C: 5,5-dimethyl hydantoin from Rucker, et al. (5).

Figure 3-5: Comparison of the Chemical Ionization Mass Spectra of a Condensate-Water Solute and Dimethyl Hydantoin



XBL837-810

Spectrum A: Solute isolated from GFETC run No. RA-78 condensate water with the isopropanol/GC-MS technique described in Chapter 2.
Spectrum B: 5,5-dimethyl hydantoin standard analyzed with the isopropanol/GC-MS technique described in Chapter 2.

adsorbed the hydantoins from condensate-water samples with activated carbon at pH 8.5 and pH 2. The compounds were removed from the carbon with boiling ethanol and evaporated to dryness. The compounds were identified with electron ionization (EI) mass spectrometry, chemical ionization (CI) mass spectrometry with methane, GC retention index matching, and EI mass spectrometry of the 1,3-dimethyl derivatives. This information, summarized in Table 3-5, provides a definitive identification of hydantoins in a GFETC condensate water.

Quantitative Analyses of Condensate-Water Solutes

Table 3-6 gives the results of quantitative analyses of four GFETC condensate waters for the compounds identified in Tables 3-3 and 3-4. The compounds have been arranged into three groups. The first group is the hydroxy benzenes or simple phenols. These compounds are moderately polar; Stamoudis and Luthy (7) report recoveries of 82% for phenol and 65% for C_2-phenols with the standard methylene chloride/GC-MS technique. The estimated precision of ±5% in this work is a considerable improvement in the quantitative analysis of these compounds.

The second group of compounds is the dihydroxy benzenes. The data in Table 3-7 show that these compounds have much lower distribution coefficients (K_D) into diisopropyl ether (DIPE) and methyl isobutyl ketone (MIBK) than simple phenols.

If, for example, a solvent extraction process which employed DIPE was designed to remove 99% of the phenol from a condensate water, then a much lower fraction of the dihydroxy benzenes would be removed. Similarly, a solvent extraction process which employed MIBK would remove a much smaller fraction of the dihydroxy benzenes as compared to phenol

Table 3-5: Confirmation of the Qualitative Identification of Hydantoins in GFETC Condensate Waters[a] [Olson, et al. (6)]

	Identification Method			
Compound	GC-MS EI Mode	GC-MS CI Mode	GC Retention Index	GC-MS EI Mode of 1,3 Dimethyl Derivatives
5-methyl hydantoin	*	*	*	*
5,5-dimethyl hydantoin	*	*	*	*
5-ethyl hydantoin	*		*	*
5-ethyl 5-methyl hydantoin	*	*	*	*
5,5-diethyl hydantoin		*	*	*
5-methyl 5-propyl hydantoin		*	*	*
5-isopropyl 5-methyl hydantoin		*	*	*
5-ethyl 5-propyl hydantoin			*	
5-butyl 5-methyl hydantoin			*	
spiropentyl hydantoin	*	*	*	
spirohexyl hydantoin	*	*	*	

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a. GFETC run No. RA-85.

Table 3-6: Quantitative Analyses of GFETC Condensate Waters[a]

GFETC run No.:	RA-78	RA-97	RA-106	RA-120
Date of sample:	6/80	6/81	9/81	4/82
Sample age interval (days)[b]:	150-500	40-150	1.7-38	0.7-110
Compound				
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	450	470	430	410
4. o-methoxy phenol	260	450	165	260
5. p-hydroxy acetophenone	50	35	5	ND
6. catechol	990	860	40	2
7. 4-methyl catechol	610	500	20	ND
8. resorcinol	60	28	2	ND
9. hydroquinone	35	24	1	ND
10. 5,5-dimethyl hydantoin[c]	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[d]	-	-	1,050	-
14. acetonitrile[d]	-	-	365	-
15. acetone[d]	-	-	505 (620)[e]	-
COD (mg/l)	34,900	46,700	22,900	23,400
Fraction of COD due to:				
hydroxy benzenes:	0.586	0.624	0.663	0.764
dihydroxy benzenes:	0.095	0.059	0.006	0.0002
hydantoins:	0.061	0.010	0.023	0.010
methanol, acetonitrile, acetone:	-	-	0.151	-
Total Fraction Identified:	0.742	0.693	0.843	0.774

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a. Concentrations in mg/l. Estimated precision: ±5%. ND--none detected.

b. No change in concentration was observed over this time interval with the exception of the dimethyl hydantoin concentration.

c. This is the concentration at long sample ages. The value in parentheses is the estimated concentration when the sample was removed from the gasifier. The time dependence of the dimethyl hydantoin concentration is discussed in Table 3-8. The concentrations of all of the other solutes did not change with time and were the same in the sample portions which were stored at pH 8.5 and pH 2.

d. Data from Senetar (8). Sample age: 600 days.

e. The concentration in parentheses is for the sample stored at pH 2.

Table 3-7: Equilibrium Distribution Coefficients (K_D) of Phenol and Dihydroxy Benzenes into DIPE and MIBK[a,b,c]

Compound	DIPE	MIBK
phenol	36.5	100.
catechol	4.86	18.7
resorcinol	2.06	17.9
hydroquinone	1.03	9.92

---

a. K_D is defined as the weight fraction in the organic phase divided by the weight fraction in the aqueous phase at equilibrium.
b. Solvents: DIPE--diisopropyl ether, MIBK--methyl isobutyl ketone.
c. Data from Greminger and King (9).

at a constant solvent-to-water ratio. However, the K_D's of the dihydroxy benzenes are considerably larger for MIBK than for DIPE. Therefore, the presence of dihydroxy benzenes in a condensate water creates an economic incentive to employ MIBK instead of DIPE as solvent. The presence of dihydroxy benzenes requires a significant increase in the solvent-to-water ratio for either process.

Since these compounds are more difficult to remove than phenols with a solvent extraction treatment process, it is important to have accurate quantitative analyses of these compounds in condensate waters. However, the recovery of these compounds in the standard methylene chloride/GC-MS technique is probably much lower than the simple phenols due to less complete extraction.

The third group of compounds is the hydantoins. Dimethyl hydantoin was detected in all four GFETC samples. The concentration of this compound changed with time in some of the samples as illustrated in Table 3-8. When the condensate-water samples were removed from the gasifier, part of the sample was acidified to pH 2 and the remainder was stored without pH adjustment. No time dependence was observed for the dimethyl hydantoin concentration in the samples stored at pH 2. The concentration in the samples stored at pH 8.5 started out higher than that in the pH 2 samples, increased gradually over a period of one month, and then remained constant.

Two additional experiments were performed to determine the effect of pH on dimethyl hydantoin concentration. When the sample from run RA-78 was about 500 days old the concentration of dimethyl hydantoin was 1720 mg/l in the pH-8.5 portion of the sample and 660 mg/l in the pH-2 portion. The pH-8.5 portion was adjusted to pH 2 with conc. H_2SO_4 and

Table 3-8: Time Dependence of Dimethyl Hydantoin Concentration

	Sample Stored at pH 8.5		Sample Stored at pH 2	
GFETC Run No.	Age (Days)	Conc. (mg/l)	Age (Days)	Conc. (mg/l)
78	200	1720		
	500	1720	500	660
97	40	300	40	150
	130	300		
106	1.7	290	1.7	230
	24	410		
	38	460	38	230
120	0.7	70	0.7	40
	10	110		
	30	150		
	110	165	110	40

stored for one month. The concentration of dimethyl hydantoin remained constant. The pH-2 portion was adjusted to pH 8.5 with NaOH and sufficient Na_2CO_3 to replace the carbonate originally present in solution. After one month the concentration of dimethyl hydantoin had increased to about 1700 mg/l.

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 concentration in the samples stored at pH 2 is probably equal to the concentration in the condensate water at the time the sample was taken.

The fourth group of compounds includes methanol, acetonitrile, and acetone. These compounds were measured by Senetar (8) with a GC technique, and account for 15% of the COD in one condensate-water sample. These compounds have been identified in other condensate waters (see chapter 1). Distribution coefficients for these compounds into MIBK, DIPE, and methylene chloride are not available, but they are probably low. Acetone may react with ammonium carbonate and hydrogen cyanide to form dimethyl hydantoin in condensate waters by the Bucherer-Bergs reaction (eq. 1) as described by Ware (4):

$$\underset{\text{acetone}}{C_3H_6O} + NH_3 + CO_2 + HCN = \underset{\text{dimethyl hydantoin}}{C_5H_8O_2N_2} + H_2O \qquad (1)$$

In the sample from GFETC run No. 106 the concentrations of acetone and dimethyl hydantoin were different in the portions of the sample which had been stored for many months at pH 2 and pH 8.5. The acetone concentration was 10.7 mmoles/l in the pH-2 sample and 8.7 mmoles/l in the pH-8.5 sample—a difference of -2.0 mmoles/l. The concentration of dimethyl hydantoin was 1.8 mmoles/l in the pH 2 sample and 3.6 mmoles/l in the pH-8.5 sample—a difference of +1.8 mmoles/l. This suggests that acetone reacted during storage of the pH-8.5 sample to produce dimethyl hydantoin. Ammonium carbonate is present at high concentration in the condensate water. Hydrogen cyanide has been reported in GFETC condensate waters at concentrations as large as 200 mg/l (10). As discussed above, the chemical reaction that produces dimethyl hydantoin stops when the pH is lowered. The Bucherer-Bergs reaction could not occur appreciably at low pH because CO_2 and HCN are not soluble in acidic solutions.

It is important to conduct laboratory tests of condensate-water treatment processes with fresh condensate-water samples because chemical reactions can change the composition of the samples.

The measured distribution coefficients of dimethyl hydantoin into several solvents are listed in Table 3-9. Methylene chloride is a Lewis acid and is the solvent in the standard GC-MS analytical technique. This solvent has a low K_D (<0.05) for dimethyl hydantoin. Di-(2-ethyl hexyl) phosphoric acid (D2EHPA) is a high-molecular-weight phosphoric acid that also gives a low K_D. The K_D was also measured for Lewis-base solvents because dimethyl hydantoin is a Lewis acid. MIBK is a weak Lewis base and gives a low K_D. Tricresyl phosphate (TCP) is a stronger Lewis base than MIBK and gives a low K_D (0.11). Tributyl phosphate (TBP) is a somewhat stronger base than TCP because of the electron-withdrawing characteristics of the aryl substituents of TCP. Trioctyl phosphine oxide (TOPO) is a stronger Lewis base than TBP. Solvents containing TOPO have been found to give high K_D values for phenols (11). A mixture of 25% w/w TOPO in MIBK gave a lower K_D (1.2) than TBP (2.6), possibly because the concentration of basic phosphoryl groups is

Table 3-9: Equilibrium Distribution Coefficients for Dimethyl Hydantoin[a]

Solvent	K_D[b]
Methylene chloride	<0.05
25% w/w di(2-ethyl hexyl) phosphoric acid in kerosene	<0.05
Methyl isobutyl ketone (MIBK)	0.25
Tricresyl phosphate (TCP)	0.11
Tributyl phosphate (TBP)	2.6
25% w/w trioctyl phosphine oxide in MIBK	1.2
25% w/w Adogen 363 (R_3N, Sherex Chemical Co.) in kerosene	<0.05

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a. Data from Schonberg (12).
b. Experimental uncertainty: ±20%.

greater in TBP than that in the TOPO-MIBK solvent. Adogen 363 is a tertiary amine and is a stronger Lewis base than TOPO. However, this solvent gave a very low K_D, possibly because the basic nitrogen is sterically hindered.

TBP had the highest K_D (2.6) for dimethyl hydantoin of the solvents studied; however, TBP may be difficult to regenerate in a continuous countercurrent extraction process. TBP has a sufficiently low volatility that it could not be regenerated as the overhead product in a distillation process. It may be possible to separate some solutes from TBP by distillation. However, if non-volatile solutes were present, they would accumulate in the bottoms product with the TBP, and the performance of the solvent might deteriorate. It may be possible to remove acidic solutes such as phenol from TBP by extraction with aqueous base. However, the chemicals cost would be high and some of the solutes in condensate waters may not be acidic. Also, a solvent-to-water ratio (S/W) of about 0.6 would be required to give $K_DS/W = 1.5$. This approximate value of K_DS/W would be required to remove dimethyl hydantoin with a reasonable number of stages.

After the initial reports from this work (2, 3) Willson, et al. (13) at the Grand Forks Energy Technology Center measured the concentration of hydantoins and other compounds in the effluent from a condensate-water treatment process. The results are shown in Table 3-10. The treatment process consisted of diisopropyl ether (DIPE) extraction and ammonia stripping of a condensate water from the GFETC slagging fixed-bed gasifier. The treated water was then fed to a pilot-scale cooling tower. The analysis of the raw water included phenols, hydantoins, and other compounds (#7-12 in Table 3-10), and accounted for

Table 3-10: DIPE Extraction and Ammonia-Stripping Treatment of a GFETC Condensate Water for Use in a Cooling Tower.[a]

Compound	Raw Water	After DIPE Extraction[b]	After NH_3 Stripping	Cooling Tower Blowdown[c]
1. phenol	4,560	210	160	160
2. o-cresol	650	0	0	2
3. p-cresol	880	3	0	25[d]
4. m-cresol	950	3	0	-
5. dimethyl hydantoin	2,280	2,340	2,140	17,080
6. ethyl methyl hydantoin	510	520	490	4,160
7. methanol	1,450	1,440	230	NR
8. ethanol	5	5	0	NR
9. acetonitrile	420	370	2	NR
10. propionitrile	85	38	0	NR
11. acetone	40	50	10	NR
12. acetic acid	16	11	0	NR
COD (mg/l)	27,900	-	5,700	45,200
Fraction of COD Due to:				
hydroxy benzenes (#1-4)	0.617	-	0.670	0.010
dihydroxy benzenes	NR	-	NR	NR
hydantoins (#5-6)	0.117	-	0.539	0.550
other compounds (#7-12)	0.122	-	0.064	NR
Total Fraction Identified:	0.856	-	0.067	0.560

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a. Data from Willson, et al. (13). GFETC slagging fixed-bed gasifier, Grand Forks, ND. NR--not reported.

b. Countercurrent extraction, S/W=0.091 v/v. Extraction column had the equivalent of six equilibrium stages.

c. The pilot-scale cooling tower was operated at about 10 cycles of concentration.

d. Combined concentrations of m- and p-cresol.

85.6% of the COD. No dihydroxy benzenes were reported. DIPE extraction removed 95% of the phenol, 99.8% of the cresols, 55% of the propionitrile, and 12% of the acetonitrile. However, DIPE extraction removed almost none of the hydantoins and methanol. It was not possible to compare the measured compounds to the COD in the raffinate because a large concentration of DIPE remained dissolved in the water.

Stripping to remove ammonia also removed 85% of the methanol and nearly all of the acetone and nitriles. In a commercial process these compounds might have to be separated from the ammonia product. Ammonia removal by stripping removed very little of the hydantoins. Dimethyl hydantoin and ethyl methyl hydantoin accounted for 53.9% of the COD in the effluent from the steam stripper.

The effluent was then fed to a cooling tower operated at about ten cycles of concentration. The cooling tower was seeded with some activated sludge that had been acclimated to the condensate water. Therefore, the cooling tower acted as a biological reactor because the water was warm and well aerated. Nearly all of the phenols fed to the cooling tower were either biologically degraded or stripped into the air. The concentration of hydantoins in the cooling-tower blowdown was about a factor of 8 greater than in the feed. This indicates that the hydantoins are resistant to biological oxidation. Although most of the hydantoins remained in the water, emissions due to volatilization and cooling tower drift may be an important environmental concern. The hydantoins had a total concentration of 21,000 mg/l in the cooling-tower blowdown and accounted for 55% of the COD.

The data in Table 3-9 show that dimethyl hydantoin is difficult to remove by solvent extraction. The cooling-tower study discussed above indicates that dimethyl hydantoin is resistant to biological oxidation. Little is known about the toxicity of dimethyl hydantoin (<u>14</u>), but diphenyl hydantoin is a suspected carcinogen (<u>15</u>). Because this compound may pose a difficult treatment problem and its toxicity is poorly characterized, the quantitative analysis of dimethyl hydantoin is important

Another important aspect of the quantitative analyses of the condensate waters was the difference in the concentrations of some solutes among the different gasifier runs. The concentration of COD, shown in Table 3-6, varied considerably among the four samples. The phenols, compounds 1-5 in Table 3-6, represented 58 to 76% of the COD in the four samples. The dihydroxy benzenes represented 0.02 to 9.5% of the COD. This is a large percentage difference in dihydroxy benzene concentration. Similarly, the hydantoins accounted for 1.0 to 6.1% of the COD. The change in hydantoin concentration between runs was statistically significant compared to the time-dependent changes shown in Table 3-8. The changes in condensate-water composition were most likely due to changes in the operation of the coal-gasification process and/or the gas quenching system, despite the fact that the operating conditions, listed in Table 3-1, were nearly constant.

Variation in the feed concentration is an important consideration in the design of wastewater treatment processes. Sudden changes in solute concentration can cause operating problems in a biological-oxidation process. In contrast, changes in the feed composition do not cause operating problems in a solvent extraction process.

The total fraction of the COD identified in Table 3-6 varied from 69 to 84%. This is an improvement over the literature results discussed in Chapter 1. However, a significant fraction of the COD remains unidentified in these condensate waters. In an attempt to increase the identified fraction of the COD, HPLC co-chromatography was performed with a number of compounds which were expected to be present in the condensate water. None of the compounds listed in Table 3-11 were detected in the GFETC run No. RA-78 condensate water at the estimated limit of detection. Trihydroxy benzenes have been reported in coal-conversion condensate waters (9), and these compounds are very polar and difficult to extract. However, trihydroxy benzenes were not detected in the GFETC condensate waters.

There are several possible reasons why the compounds representing the unidentified fraction of the COD were not detected with the techniques employed in this study. Some of the lesser peaks that were eluted and detected in the HPLC chromatograms of Figures 3-1 and 3-2 were not identified and therefore could not be quantitatively analyzed. About 95% of the UV-absorbance peak area in Figure 3-1 can be accounted for by the compounds in Table 3-6. Therefore, it is unlikely that compounds representing a significant fraction of the unidentified COD are detected in Figure 3-1. More than 50% of the UV-absorbance peak area in Figure 3-2 can be accounted for by the compounds in Table 3-6. Most of the unidentified peak area in Figure 3-2 is contained in two peaks at the beginning of the chromatogram. These two peaks represent very polar compounds which are not retained by the non-polar stationary phase. These two peaks are probably inorganic species. However, if they are organic compounds, then they could represent a large fraction of the unidentified COD.

Table 3-11: Compounds not Detected in GFETC Condensate Water No. RA-78 by HPLC Co-chromatography

Compound	Estimated Detection Limit (mg/l)	HPLC Conditions	UV Absorbance Wavelength (nm)
1. acetic acid	20	b	210
2. acetone	300	a	270
3. acetophenone	10	a	230,240,254,280
4. aniline	10	a	230,240
5. benzoic acid	20	a	230,240,270
6. 5,5-diethyl hydantoin		a	230
7. dimethyl phthalate	10	a	280
8. di-n-butyl phthalate	10	a	280
9. 5-ethyl 5-methyl hydantoin	-	a	230
10. glycine	100	b	192
11. hydantoic acid	10	b	192
12. hydantoin	10	b	192
13. methyl benzoate	10	a	280
14. 5-methyl 5-isobutyl hydantoin	-	a	230
15. 5-methyl 5-phenyl hydantoin	-	a	230
16. 1-naphthol	5	a	230,240,270
17. 2-naphthol	20	a	230,280
18. pyridine	35	a	230,240,254,270
19. thiophenol	5	a	230,240
20. 1,2,4-trihydroxy benzene (hydroxyquinol)	5	a	230,270,290
21. 1,3,5-trihydroxy benzene (phloroglucinol)	25	a	210,230,270,290
22. 1,2,3-trihydroxy benzene (pyrogallol)	5	a	230,240,270,280

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a. HPLC conditions were the same as in Figure 1.
b. HPLC conditions were the same as in Figure 2.

A second possibility is that the unidentified solutes have very low extinction coefficients for the UV wavelengths used in this study. Alcohols and nitriles are two examples of compound classes which would not be detected by UV absorbance at 192 or 280 nm.

A third possibility is that some of the solutes were not eluting from the HPLC column. This question was addressed by measuring the elution of the unidentified COD from a Waters Associates Sep-Pak. The Sep-Pak was described in Chapter 2 and is a small packed bed of C_{18} HPLC stationary phase. The fourth condensate-water sample, from GFETC run No. RA-120, was extracted with MIBK and the residual MIBK was removed by nitrogen stripping. This extraction removed nearly all of the identified compounds and, as shown in Table 3-16, left many of the unidentified solutes in the raffinate. The raffinate (5 ml) was pumped through the Sep-Pak, the Sep-Pak was eluted with 15 ml of water, and the COD of the combined effluents was measured. This procedure eluted about 90% of the COD in the raffinate. The remaining 10% of these solutes would probably be eluted from the Sep-Pak if the solvent strength was increased, but methanol or any other strong solvent would interfere with the COD measurement. In summary, this experiment showed that most of the unidentified solutes which are not removed by MIBK extraction are very polar compounds which elute easily from a Sep-Pak C_{18} stationary phase. Since the analytical HPLC stationary phase is similar to the Sep-Pak material, these compounds are probably eluted from the HPLC column.

Separation and Characterization of COD by Solvent Extraction Processes

The second phase of this work employed solvent extraction and other processes to predict the performance of commercial-scale treatment processes and to determine the physical properties of the unidentified solutes.

The fraction of the chemical oxygen demand (COD) removed from a condensate-water sample by various solvent-extraction procedures is shown in Table 3-12. The solvent-to-water ratio was 1:1 by volume in all of the extractions. As discussed in chapter 2, residual dissolved solvent was removed by nitrogen stripping prior to measurement of the raffinate COD, and the experimental uncertainty is about 3% of the original condensate-water COD. Condensate water which had been stored without pH adjustment was contacted with methyl isobutyl ketone (MIBK); and, as shown in the first line of the table, 81% of the COD was removed. A second extraction with MIBK increased the overall removal to 86%. This indicates that most of the components that remain after the first MIBK extraction have fairly low distribution coefficients (K_D) into MIBK. As part of this study, the total organic carbon (TOC) of the raffinate after one MIBK extraction was measured by Langlois (16). In the TOC measurement inorganic carbonates are removed from solution and the organic compounds are oxidized to CO_2 (17). The ratio TOC/COD gives some information about the average oxidation state of the carbon in the solutes. The measured ratio TOC/COD was 0.37 ±0.01. This shows that the average oxidation state of the carbon in the solutes was equivalent to the oxidation state of the carbon in a compound with the formula of $C_xH_{2x}O_x$. The carbon has a significantly higher oxidation state than phenol (C_6H_6O), for example, which has a TOC/COD ratio of 0.32.

The extraction in line three of Table 3-12 was designed to test for acidic functional groups on the poorly extracted solutes. The raffinate from the first extraction was adjusted to pH 3 with conc. H_2SO_4 and

Table 3-12: Fraction of COD Removed by Solvent Extraction from GFETC Run No. RA-78 Condensate Water

Solvent[a,b]	No. of Batch Extractions[c]	Fraction of COD Removed[d,e,f,g]	Sample Age Interval (Days)
1. MIBK	1	0.81(4)	90-200
2. MIBK	2	0.86(3)	135-200
3. MIBK	1 and 1 @ pH 3	0.88(2)	135
4. MIBK MC	2 1	0.88(1)	150
5. MIBK MC	2 1 @ pH 12	0.88(1)	150
6. 25% w/w TOPO/MIBK	1	0.86(3)	100-140
7. 25% w/w. TOPO/MIBK	2	0.89(2)	140
8. 25% w/w TOPO/MIBK	1 and 1 @ pH 3	0.94(3)	100-140
9. 25% w/w TOPO/MIBK	1 @ pH 3	0.91(1)	200
10. 25% w/w TOPO/MIBK	2 @ pH 3	0.94(1)	200
11. 25% w/w TOPO/MIBK	3 @ pH 3	0.96(1)	200
12. 25% w/w TOPO/MIBK	4 @ pH 3	0.97(1)	200

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a. Solvents: MIBK--methyl isobutyl ketone, MC--methylene chloride, TOPO/MIBK--25% w/w trioctyl phosphine oxide in MIBK.

b. 1:1 volume phase ratios in all extractions.

c. Extractions performed at the condensate water pH of about 8.5 unless indicated differently.

d. Experimental uncertainty: ±0.03.

e. The number of replicates is shown in parentheses. The ratio of standard deviation/mean was about 0.01.

f. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before measurement of the COD.

g. Condensate water COD: 34,900 mg/l.

extracted a second time. Many organic compounds with weakly acidic functional groups would be ionized, and therefore difficult to extract, at the condensate-water pH of 8.5. The purpose of the low-pH extraction was to suppress the ionization of these compounds and improve their distribution coefficients. However, comparison of lines 2 and 3 in Table 3-12 shows that only a small increase in COD removal was obtained by the low-pH extraction. Therefore, acidic functional groups are not the only reason for the low distribution coefficients of these compounds into MIBK.

The extractions of lines 4 and 5 in Table 3-12 were designed to test for the presence of organic bases. Many organic compounds with basic functional groups would be ionized, and therefore difficult to extract at the condensate-water pH of 8.5. Increasing the pH to 12 by dissolving solid NaOH would suppress the ionization of these compounds and increase their distribution coefficients. Also, a Lewis-acid solvent, methylene chloride, was employed to increase the K_D of basic compounds. Comparison of lines 4 and 5 of Table 3-12 shows that basic functional groups are not the only reason for the low distribution coefficients of these compounds into MIBK.

The second solvent in Table 3-12 is a mixture of 25% w/w trioctyl phosphine oxide (TOPO) in MIBK. TOPO is a strong Lewis-base extractant which is a solid at room temperature, is non-volatile, and is available in commercial quantities at about $8/lb. A mixture of TOPO in a diluent such as MIBK or diisobutyl ketone (DIBK) gives a solvent with very high K_D's for phenol and the dihydroxy benzenes, as shown in Table 3-13. This suggests the possibility that solvents containing TOPO would also have high K_D's for the other solutes in the condensate water.

Table 3-13: Equilibrium Distribution Coefficients of Phenol and Dihydroxy Benzenes into 25% w/w TOPO in DIBK[a]

	Stoichiometric Ratio[b]					
Solute	10.0	5.0	2.5	1.2	0.6	0.4
phenol	810	650	460	255	110	76
catechol	-	270	200	92	-	-
resorcinol	-	-	98	-	-	-
hydroquinone	-	-	35	-	-	-

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a. Data from MacGlashan (11). Solvents: TOPO--trioctyl phosphine oxide, DIBK--diisobutyl ketone.

b. The stoichiometric ratio is the moles of TOPO/moles of phenol in the organic phase at equilibrium.

Comparison of lines 6 through 8 with lines 1 through 3 in Table 3-12 shows that, although an important fraction of the COD has a low K_D into TOPO/MIBK, this solvent mixture does remove a greater fraction of the COD than MIBK alone. As discussed in Chapter 2, the experimental uncertainty was the result of impurities in the MIBK which distributed into the raffinate and increased the measured COD. Since the same lot of MIBK was used to prepare the MIBK and TOPO/MIBK solvents, the magnitude and direction of this effect was probably the same for both solvents. This means that the difference between two measurements is known with a greater degree of accuracy. As an example, in Table 3-12 the COD removal was 0.81 ±0.03 for one MIBK extraction and 0.86 ±0.03 for one TOPO/MIBK extraction. If the experimental uncertainty was completely random, the difference would be 0.05 ±0.06. However, since the experimental uncertainty has the same magnitude and direction for both solvents, the difference between the MIBK and TOPO/MIBK extractions is statistically significant.

Four repeated extractions with TOPO/MIBK at pH 3 removed 97% of the COD from this condensate-water sample. However, lines 9 through 12 of Table 3-12 show that a very large solvent-to-water ratio would be required to increase the COD removal from 91 to 97% in a continuous extraction process. Also, pH adjustment of the highly buffered condensate water would require an expensive consumption of chemicals and increase the total dissolved solids in the water.

The K_D data in Tables 3-7 and 3-13 show that a solvent containing TOPO has higher K_D values for phenols than MIBK or DIPE. This suggests that a solvent containing TOPO may be able to remove phenols and other components of the COD at a lower solvent-to-water ratio than MIBK.

However, TOPO-containing solvents may be difficult to regenerate in a continuous solvent extraction process. If a diluent of sufficiently low volatility was employed, then phenol could be separated from the solvent as a distillate. However, non-volatile solutes could accumulate in the solvent and degrade its performance. The dihydroxy benzenes have such high boiling points [catechol 245°C, resorcinol 277°C, hydroquinone 285°C, (18)] that they could not be recovered as distillates.

It may be possible to recover acidic solutes such as phenols from a TOPO solvent by back extraction of the loaded solvent with aqueous base. Acidic solutes form a salt at high pH, and these salts may have extremely low distribution coefficients into the organic phase. A stable emulsion formed when 25% w/w TOPO in MIBK was contacted with 0.1 N NaOH. However, the phase separation can be improved by increasing the ionic strength of the aqueous phase. An aqueous phase containing 13% w/w NaOH and 20% phenol (0.67 mole phenol/mole NaOH, pH of about 14) was contacted with a solvent mixture of 25% w/w TOPO in MIBK. The two phases were agitated on an orbital shaker at 250 rpm for three minutes, and two clear phases resulted after a settling time of three minutes. This aqueous phase composition may not represent the most economical conditions for recovering phenol from the loaded solvent. However, it does suggest that a promising regeneration method for acidic solutes may be to back extract the loaded solvent with an aqueous solution which has a high pH and a high ionic strength. In the case of the coal-gasification condensate waters, however, some solutes are probably not acidic. Since these solutes would not be back extracted by the basic solution, they could accumulate in the solvent and cause operating problems in the solvent extraction process.

As illustrated in Table 3-13, the K_D values for phenols depend on the stoichiometric ratio of phenols to TOPO in the organic phase, As the concentration of phenols in the solvent increases, K_D decreases, and this phenomenon may increase the required solvent flow for a given separation. As an example, consider an aqueous phase containing 2,000 mg/l of phenol in equilibrium with an organic phase of 25% w/w TOPO in DIBK. The organic-phase concentration of phenol would be 15.2% w/w and the K_D would be 76. In a countercurrent solvent extraction process the ratio of K_DS/W, where S and W are the mass flow rates of solvent and water, must be greater than one throughout the extraction column in order for there to be a high degree of solute removal. In this case the required solvent flow would be determined by the value of K_D near the feed end of the column where the concentrations are high and K_D is low. In a multicomponent mixture the stoichiometric ratio, TOPO/total phenols, must be considered. A typical condensate water has a concentration of phenol and dihydroxy benzenes greater than 5,000 mg/l. Therefore, the TOPO/phenols ratio would be low at the feed end of the column, the K_D values would be comparatively low, and the required solvent flow would be correspondingly large.

In summary, the results from one condensate-water sample indicate that 25% w/w TOPO in MIBK may be able to remove more of the COD than MIBK alone. This solvent may also be capable of removing phenols and dihydroxy benzenes at a lower solvent-to-water ratio. However, solvents containing TOPO may have economically important disadvantages.

The second condensate-water sample, GFETC run No. RA-97 also contained an important fraction of COD with low K_D values into MIBK. Table 3-14 shows that MIBK extraction at pH 8.5 and pH 3 removed 90% of the COD from this sample.

Table 3-14: Fraction of COD Removed by Solvent Extraction of GFETC Run No. RA-97 Condensate Water

Solvent[a,b]	No. of Batch Extractions	Fraction of COD Removed[c,d,e,f]	Sample Age (Days)
MIBK	1 @ pH 8.5 and 1 @ pH 3	0.90(2)	140

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a. Solvents: MIBK--methyl isobutyl ketone.
b. 1:1 volume phase ratio in all extractions.
c. Experimental uncertainty: ±0.02.
d. The number of replicates is shown in parentheses. The ratio of standard deviation/mean was about 0.005.
e. Residual dissolved solvent was removed from the raffinate before COD measurement.
f. Condensate water COD: 46,700 mg/l

The third condensate-water sample, GFETC run No. RA-106, was extracted with MIBK at sample ages ranging from 1.7 to 190 days and was also extracted with tributyl phosphate (TBP) at a sample age of 240 days. The results are listed in Table 3-15.

A dependence upon sample age was observed for the extraction of COD by MIBK. Condensate water which had been stored without pH adjustment was extracted with MIBK at pH 8.5 and then at pH 3. This procedure removed 96% ±4% of the COD at a sample age of 1.7 days and 88% ±2% of the COD after 75 days. The observed variations were larger than the experimental uncertainty. Also, the experimental uncertainty was due to impurities in the solvent, as discussed in Table 2-2. Any error due to solvent impurities would have the same magnitude and direction for all three extractions. Therefore, the changes in the fraction of COD removed with respect to time are statistically significant. This time-dependent behavior indicates that chemical reactions occurred while the samples were stored which led to solutes with lower K_D values into MIBK.

The K_D data in Table 3-7 show that MIBK extraction should remove nearly all of the phenols and dihydroxy benzenes. MIBK has a low K_D for dimethyl hydantoin, but hydantoins represent only 3% of the identified COD. Acetone and acetonitrile are very volatile and would be removed from solution by the nitrogen stripping procedure used to remove residual MIBK. However, only about 25% of the methanol would be removed by the nitrogen stripping. Distribution coefficient data are not available for methanol and MIBK, but the K_D is probably low. Therefore, methanol could account for a substantial portion of the unextracted COD. The remainder of the unextracted solutes have not been identified.

Table 3-15: Fraction of COD Removed by Solvent Extraction from GFETC Run No. RA-106 Condensate Water

Solvent[a,b]	No. of Batch Extractions[c]	Fraction of COD Removed[h,i,j]	Sample Age Interval (Days)
1. MIBK	1 and 1 @ pH 3	$0.96^{d(2)}$	1.7
2. MIBK	1 and 1 @ pH 3	$0.92^{d(2)}$	24
3. MIBK	1 and 1 @ pH 3	$0.88^{e(2)}$	75-190
4. MIBK	2 @ pH 2[f]	$0.90^{e\ (2)}$	50
5. MIBK	1	0.85^{e} 190	
6. TBP	1	$0.900^{g(2)}$	240
7. TBP	2	$0.922^{g(2)}$	240
8. TBP	1 and 1 @ pH 3	$0.931^{g(1)}$	240

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a. Solvents: MIBK--methyl isobutyl ketone, TBP--tributyl phosphate.
b. 1:1 volume phase ratios in all extractions.
c. Extractions performed at the condensate water pH of about 8.5 unless indicated differently.
d. Experimental uncertainty: ±0.04
e. Experimental uncertainty: ±0.02
f. Sample stored and extracted at pH 2. All other extractions performed with samples stored without pH adjustment.
g. Experimental uncertainty: ±0.005
h. The number of replicates is shown in parentheses. The ratio of standard deviation/mean for each extraction was about 0.002.
i. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before COD measurement.
j. Condensate water COD: 22,900 mg/l.

On the fourth line of Table 3-15 the portion of the sample that had been acidified to pH 2 at the time the sample was collected from the gasifier was extracted twice with MIBK at pH 2 and a sample age of fifty days. Recall that the chemical reaction that produced dimethyl hydantoin at pH 8.5 does not occur at pH 2. The purpose of the extraction on line 4 of Table 3-15 was to determine if pH-2 storage affected the chemical reaction or reactions responsible for the changes in lines 1 through 3 of Table 3-15. However, comparison of lines 1 through 3 with line 4 of Table 3-15 shows that pH 2 sample storage did not prevent the reaction that resulted in solutes of lower K_D as the sample aged.

In lines 5 through 8 of Table 3-15 the effectiveness of MIBK is compared with that of TBP at long sample age. TBP removed an additional 5% of the COD when compared to MIBK for a single batch extraction. Of the solvents listed in Table 3-9, TBP exhibits the highest K_D (2.6) for dimethyl hydantoin. Hydantoins represent only 3% of the identified COD in this sample. Two batch extractions with TBP removed a total of 92.2% of the COD. TBP has a low volatility and may be difficult to regenerate in a continuous countercurrent condensate-water extraction process. Phenol and other volatile solutes could be separated as distillates, but dihydroxy benzenes and other solutes of low volatility would require a different regeneration process. TBP is considerably less expensive ($1.2/lb) than TOPO.

The fourth condensate-water sample, GFETC run No. RA-120, was extracted with MIBK at sample ages ranging from 0.7 to 190 days and was also extracted with TBP and 25% w/w TOPO in MIBK at a sample age of 15 days. The results are shown in Table 3-16. The portion of the COD removed by two batch extractions with MIBK decreased from 92.7% at a

Table 3-16: Fraction of COD Removed by Solvent Extraction from GFETC Run No. RA-120 Condensate Water

		Fraction of COD Removed vs. Sample Age[d,f,g,h]		
Solvent[a,b]	No. of Batch Extractions[c]	0.7 Days	15 Days	190 Days
1. MIBK	1	0.890(6)	0.883(2)	0.856(3)
2. MIBK	2	0.927(2)	0.911(2)	0.878(2)
3. 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	-	0.88[e](2)	-
8. 25% w/w TOPO/MIBK	1 and 1 @ pH 3	-	0.92[e](2)	-

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[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 replicate is shown in parentheses. The ratio of 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.

sample age of 0.7 days to 87.8% at 190 days. This decrease is large compared to the experimental uncertainty. This is again strong evidence that chemical reactions occurred in the condensate water during storage, forming solutes with lower distribution coefficients into MIBK.

The occurrence of chemical reactions during storage of condensate-water samples is important because many analyses and experimental tests of treatment processes are performed with condensate-water samples that have been stored for long periods of time. The chemical reactions in this study occurred even though the samples were stored under an inert atmosphere, in the dark, and at 4°C. As discussed in Chapter 2, condensate waters darken and form precipitates after even a small exposure to oxygen. Samples stored in contact with air would be even less representative of actual condensate waters. Analyses or process tests performed with samples stored in this way would therefore have a large experimental uncertainty.

In Table 3-16 extraction with TBP and 25% w/w TOPO in MIBK can be compared to extraction with MIBK at a sample age of 15 days. TBP removed about 3% more of the COD as compared to MIBK under similar conditions. This is consistent with the results for the third GFETC sample in Table 3-15. However, TOPO/MIBK removed only the same fraction of the COD as did MIBK alone. This result is different from the observations in Table 3-12 where TOPO/MIBK removed a greater fraction of the COD than did MIBK alone from the first GFETC sample. This is probably due to differences in the composition of these two samples.

Additional Characterization of the COD and Organic Nitrogen Compounds

The results in Table 3-17 display the fractions of COD and of nitrogen-containing organic compounds removed by a series of MIBK

Table 3-17: Fractions of COD and Organic Nitrogen Removed by Solvent Extraction from GFETC Run No. RA-120 Condensate Water

Solvent[a,b]	No. of Batch Extractions[c]	Fraction of COD Removed[d,e,f,g,h]	Fraction of Organic N Removed[i,j]
1. MIBK	1	0.856(3)	0.30
2. MIBK	2	0.878(2)	0.30
3. MIBK	3	0.890(1)	0.37
4. MIBK	4	0.900(1)	0.37
5. MIBK	5	0.902(1)	0.43
6. MIBK	1 and 1 @ pH 12	0.878(1)	0.25
7. MIBK MC	1 1 @ pH 12	0.880(1)	0.11

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a. Solvents: MIBK--methyl isobutyl ketone, MC--methylene chloride.
b. 1:1 volume phase ratios in all extractions.
c. Extractions performed at condensate water pH of about 8.5 unless indicated differently.
d. Experimental uncertainty: ±0.005
e. Sample age: 190 days
f. The number of replicates is shown in parentheses. The ratio of standard deviation/mean for each extraction was about 0.004.
g. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before COD analysis.
h. Condensate-water COD: 23,400 mg/l.
i. Condensate-water organic nitrogen: 210 mg/l.
j. Experimental uncertainty: ±0.10.

extractions from the fourth condensate-water sample. A single batch extraction removed 85% of the COD. Four additional extractions increased the cumulative removal to 90% of the initial COD. Comparison of lines 4 and 5 in Table 3-17 shows that the final 10% of the COD has a vanishingly small K_D into MIBK. These solutes could not be removed by MIBK at these conditions with any realistic solvent-to-water ratio or number of stages.

Organic nitrogen is defined as the difference between Kjeldahl nitrogen and ammonia nitrogen. This condensate-water sample contained 220 mg/l of organic nitrogen before extraction. The quantitative analysis reported in Table 3-6 accounts for only 48 mg/l of organic nitrogen. The extractions in Table 3-17 show that most of the nitrogen-containing organic compounds also have low K_D's into MIBK. The ratio of COD to organic nitrogen can be as high as 20 for many compounds. Therefore, the nitrogen-containing compounds may represent a large fraction of the COD which is not extracted by MIBK.

The condensate water was extracted with MIBK and methylene chloride at a high pH to test for the presence of organic bases. Comparison of lines 2, 6, and 7 of Table 3-17 show that no statistically significant increase in removal was obtained at high pH. Therefore, basic functional groups are not the only reason for the low distribution coefficients of the nitrogen-containing compounds into MIBK.

Some additional information about the solutes which remain after MIBK extraction was obtained from batch distillation of MIBK raffinates. The condensate water was contacted with an equal volume of MIBK, the phases were separated, and dissolved MIBK was removed by nitrogen stripping (1.5 moles N_2/mole H_2O). Then the raffinate was distilled in a one-stage, batch apparatus. The analyses of the products are reported in Table 3-18. The condensate-water raffinate from GFETC run No. RA-106 contained 3,770 mg/l of COD. The first distillate fraction contained 25% of the measured COD, and 13% was in the second distillate fraction. The remainder had a low volatility with respect to water. The condensate-water raffinate from GFETC run No. RA-120 contained 3,220 mg/l of COD. The first distillate fraction contained 38% of the COD, and 4% was present in the second fraction. The remainder of the solutes, including nearly all of the nitrogen-containing organic compounds, had a low volatility with respect to water. Raising the pH of the raffinate to 12 before distillation did not increase the volatility of the nitrogen compounds. This indicates that, although the compounds could have basic functional groups, ionization of basic functional groups is not the only reason for the low activity coefficients of these compounds in water. This observation is consistent with the results of the extractions at high pH discussed previously.

It is important to know the volatilty of the solutes which remain after MIBK extraction. There would be many advantages to using treated condensate water as make-up for a cooling tower. If volatile compounds were present in a cooling tower, then they would be stripped into the atmosphere and become an air-pollution problem. The results in Table 3-18 indicate that MIBK extraction of these condensate waters would fail to remove a large concentration of volatile organic compounds.

The molecular-weight distribution of the solutes in condensate-water raffinates after MIBK extraction was assessed by ultrafiltration. Condensate waters from GFETC runs Nos. RA-106 and RA-120 were

Table 3-18: Batch Distillation of the COD and Organic Nitrogen Compounds which Remain after MIBK Extraction[a,b]

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

	Dist. 1	Dist. 2	Bottoms	Total	Feed Conc. (mg/1)
% Water From Feed:	45	45	-	-	-
% COD From Feed:	25	13	-	-	3,770

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

	Dist. 1	Dist. 2	Bottoms	Total	Feed Conc. (mg/1)
% Water From Feed:	43	46	11	100	-
% COD From Feed:	38	4	44	86[c]	3,220
% Org. N From Feed:	0	3	90	93[c]	165

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

	Dist. 1	Bottoms	Total	Feed Conc. (mg/1)
% Water From Feed:	71	29	100	-
% Org. N From Feed:	2	98	100	165

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a. Experimental uncertainty: ±5% of COD or organic nitrogen in feed.

b. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before distillation.

c. Mass balance did not close because a solid precipitate formed in the bottoms product during the distillation.

extracted with an equal volume of MIBK, the MIBK was removed by nitrogen stripping, and conc. H_2SO_4 was added to pH 3. The raffinate was then pumped through an ultrafiltration membrane (Amicon No. UM-02) with a nominal molecular-weight cutoff of 1,000. In both cases less than 5% of the solutes were retained by the membrane; therefore, most of the solutes remaining after MIBK extraction have a low molecular weight.

Summary of the Separation and Characterization of the COD

Table 3-19 is a summary of much of the information from the preceding tables. The purpose of this summary is to combine all of the available information about the physical properties and chemical nature of the condensate-water solutes which are unidentified and difficult to extract. The preceding discussion contains the experimental detail in support of the following statements.

The first five lines of Table 3-19 are the COD of each sample and the fraction of the COD due to phenols, dihydroxy benzenes, hydantoins, and methanol, acetonitrile and acetone. The sixth line is the fraction of the COD removed by extracting the sample with MIBK twice at pH 8.5. This extraction procedure removed nearly all of the phenols and dihydroxy benzenes and less than half of the hydantoins. The values in parentheses were obtained at short sample ages. The change in the fraction of the COD removed by MIBK extraction shows that chemical reactions occurred during storage of the samples. During this time interval the concentrations of all of the identified compounds remained constant, except for dimethyl hydantoin. The increase in dimethyl hydantoin concentration was not sufficient to explain the decrease in COD removal by MIBK. Extraction at low pH did not improve the distribution coefficients of the solutes. This means that the ionization of

Table 3-19: Characterization of COD and Organic Nitrogen--A Summary[a]

GFETC Run No.:	RA-78	RA-97	RA-106	RA-120
COD (mg/l)	34,900	46,700	22,900	23,400
Fraction of COD Due to:				
Hydroxy benzenes	0.586	0.624	0.663	0.764
Dihydroxy benzenes	0.095	0.059	0.006	0.0002
Hydantoins[b]	0.061 (0.027)	0.010 (0.006)	0.023 (0.011)	0.010 (0.003)
Methanol,acetonitrile,acetone	-	-	0.151	-
Fraction of COD Removed by Two Extrs. with MIBK @ pH 8.5[c]	0.86	-	-	0.88 (0.93)
Fraction of COD Removed by Extraction with MIBK @ pH 8.5 and pH 3[c]	0.88	0.90	0.88 (0.96)	0.88 (0.92)
Extraction Improved @ pH 3[d]	No	-	No	No
Extraction Improved @ pH 12[d]	No	-	-	No
Extraction Improved with TBP[d]	-	-	Yes	Yes
Extr. Improved with 25% w/w TOPO/MIBK[d]	Yes	-	-	No
Molecular Weight of Solutes in MIBK raffinate	-	-	<1,000	<1,000
Volatile Compounds Present in MIBK Raffinate	-	-	YES	YES
TOC/COD in MIBK Raffinate	0.37	-	-	-
Organic Nitrogen in MIBK Raffinate (mg/l)	-	-	-	150

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a. Refer to preceding discussion for greater detail.
b. Values in parentheses are an estimate of the concentration of hydantoins at a sample age of zero. See Table 3-8.
c. Values in parentheses were obtained at small sample ages. See Tables: 3-11, 3-13, 3-14 and 3-15.
d. Extraction improvement was measured by comparison to MIBK extraction at the same solvent-to-water ratio without pH adjustment.

acidic functional groups was not the only reason for the hydrophilic nature of the unextracted solutes. Similarly, extraction at high pH indicated that ionization of basic functional groups was not the only reason for the hydrophilic nature of these solutes. Extraction with tributyl phosphate increased the COD removal for two samples. This may indicate that the solutes which are not removed by MIBK have some Lewis-acid functional groups, since TBP is a stronger Lewis base than MIBK. Extraction with 25% w/w trioctyl phosphine oxide in MIBK increased the COD removal in one sample and gave no improvement in another sample as compared to MIBK. This is another indication of Lewis-acid functional groups, because TOPO is a stronger Lewis base than MIBK. The solutes remaining after MIBK extraction were shown to have molecular weights less than 1,000 for two samples. Important fractions of these compounds were volatile with respect to water in the same two samples. The TOC/COD ratio after MIBK extraction showed that the average oxidation state of the carbon in the solutes was high compared to phenol. Finally, 150 mg/l of organic nitrogen remained after extraction of one sample. These nitrogen compounds had a low K_D values into MIBK and low volatility compared to water.

The information in Table 3-19 can be used to estimate the performance of commercial-scale treatment processes and to infer some of the physical properties of the solutes. Two-stage extraction with MIBK removed 86 to 93% of the COD without pH adjustment. This degree of COD removal could probably be accomplished in a continuous countercurrent extraction process with an economically reasonable solvent-to-water ratio. However, MIBK extraction would fail to remove a substantial concentration of COD. Many of these unextracted compounds are sufficiently volatile so that they could not be fed to a cooling tower without causing an air-pollution problem. Tributyl phosphate and 25% w/w trioctyl phosphine oxide in MIBK can remove a greater fraction of the COD in at least some cases, but these non-volatile solvents may be difficult to regenerate.

The unidentified and difficult-to-extract compounds are very polar and hydrophilic. They have low activity coefficients in water at all pH values. This suggests that they may be amphoteric or zwitterionic compounds. The high oxidation state of the carbon and the presence of the organic nitrogen are important characteristics of these compounds.

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SUMMARY

Coal-gasification processes produce large quantities of highly contaminated condensate water. The management of this wastewater is important to the economics and environmental impact of the gasification process. The most likely use of treated condensate water is as feed to the cooling tower which dissipates waste heat from the process. Condensate-water treatment processes must remove volatile compounds which would present an air pollution problem and compounds which would foul the heat exchangers. Treated condensate water could be used in other ways, but more expensive treatment would be required.

The design of the coal gasifier can affect the quality of the condensate water. Gasifiers with a high pyrolysis temperature and long residence time of the gas in the coal bed produce condensate waters which are relatively clean. This important advantage is offset by the lower thermal efficiency for these gasifiers. Also, very little treatment would be required if liquid condensate water could be recycled directly to the gasifier. However, this would require major modifications to the gasifier. The remainder of this discussion is limited to contaminated condensate waters from low-temperature gasifiers.

Published analyses of condensate waters fail to account for a substantial fraction of the chemical oxygen demand (COD). This represents an important lack of information about the chemical composition of condensate waters. It is difficult to design wastewater-treatment systems or interpret experimental studies of treatment processes without detailed knowledge of the composition and physical properties of the solutes.

The most common analytical technique employs a methylene chloride extraction with analysis of the extract by combined gas chromatography and mass spectrometry (GC-MS). This technique has poor precision in the quantitative analysis of phenol and alkylated phenols due to incomplete recovery in the extraction step. The recovery is even lower for compounds which are more polar than phenol. Some condensate-water solutes may be so polar that they would escape detection with this technique.

The three most common unit operations for removal of organic compounds from condensate waters include solvent extraction, biological oxidation, and carbon adsorption. Solutes can be recovered by solvent extraction for sale or for use as fuel. Also, the fraction removed is independent of the feed concentration at a given set of conditions. Therefore solvent extraction has economic advantages for concentrated feeds with fluctuating composition. In biological oxidation systems the cost is proportional to the quantity of the solutes oxidized. Therefore, biological oxidation is most suitable for dilute streams. Also, fluctuations in the feed composition can be toxic to the microorganisms. Adsorption processes can be used for dilute streams. The economics depend on the equilibria of the solutes and the regeneration of the sorbent. Addition of powdered activated carbon to the activated sludge system (PAC/AS) can increase the removal of organic compounds and improve the stability of the reactor. Solvent extraction followed by biological oxidation or PAC/AS combines the advantages of both processes.

Literature reports show that extraction with diisopropyl ether (DIPE) removed only 46 to 89% of the COD, although all of the phenols and other identified compounds were removed. The compounds which remain after DIPE extraction are more polar and hydrophilic than phenol.

Activated-sludge processes also failed to remove a substantial fraction of the COD, although all of the phenols and other identified compounds were removed. The compounds in the effluent from these processes were difficult to adsorb on activated carbon. Solvent extraction followed by PAC/AS removed 95 to 98% of the COD in three reports.

From the above data it is apparent that there are polar organic compounds in condensate waters which are not identified with common analytical techniques, have low distribution coefficients into common solvents, and are resistant to biological oxidation. The toxicity of these compounds has not been characterized, and they are an important treatment problem.

A reversed-phase HPLC technique was employed to analyze four samples of condensate water from the Grand Forks Energy Technology Center (GFETC) slagging fixed-bed gasifier. This technique allows direct injection of aqueous samples and avoids the loss of polar compounds due to incomplete extraction. A novel sample-preparation procedure was developed to allow GC-MS identification of individual compounds eluting from the HPLC. This technique consisted of an azeotropic distillation with isopropanol. The primary advantage of this technique is that the solute, which may be very polar, does not have to be extracted from an aqueous phase into an organic phase.

With these techniques four groups of compounds were measured which accounted for 69 to 84% of the COD in four samples. This is an improvement over most published analyses. These groups of compounds included phenol and alkylated phenols, dihydroxy benzenes, hydantoins, and a fourth group consisting of methanol, acetonitrile, and acetone. The phenols accounted for 59 to 76% of the COD. The precision of ±5% in this work is an improvement over previous analyses.

The dihydroxy benzenes accounted for 0.02% to 9.5% of the COD in four samples. The differences between the samples was probably due to changes in the operation of the coal gasifier. Dihydroxy benzenes have a low recovery in the methylene chloride/GC-MS technique. It is important to have an accurate analysis of these compounds because a DIPE extraction designed to remove phenol would only remove a small fraction of the dihydroxy benzenes. Methyl isobutyl ketone (MIBK) has much higher distribution coefficients (K_D) for dihydroxy benzenes than does DIPE. Therefore, the presence of these compounds in condensate waters provides a strong incentive to use MIBK as the solvent in an extraction process.

Another communication from this work was the first report of hydantoins, primarily 5,5-dimethyl hydantoin, in condensate waters. The identification of this compound has subsequently been verified in other samples. This compound is very polar and has low K_D's into many solvents. One solvent, tributyl phosphate (TBP) was found to have a K_D of 2.6 for this compound. A study from the literature showed that dimethyl hydantoin was not removed from a condensate water by DIPE extraction, was not oxidized in a biologically active cooling tower, and accumulatated to a concentration of nearly 2% in the cooling-tower blowdown.

The analysis of hydantoins in condensate waters is important because these compounds are difficult to remove by biolgical oxidation or solvent extraction. Also, their toxicity is not known. These compounds may have been present in other condensate waters, but they may not be detected by the methylene chloride/GC-MS technique.

Methanol, acetonitrile, and acetone accounted for 15% of the COD in one sample. The presence of these volatile compounds may complicate the design of a stripping process to remove ammonia. Acetone may react with ammonia, carbon dioxide, and hydrogen cyanide to form dimethyl hydantoin via the Bucherer-Bergs reaction.

Generic analyses such as the COD and organic nitrogen were employed to obtain physical property information about the solutes and to estimate the performance of solvent extraction processes. MIBK extraction removed 86% to 96% of the COD from four condensate waters under various conditions. MIBK extraction removed only a small fraction of the hydantoins, probably a small fraction of the methanol, and nearly all of the other identified components.

Evidence was presented which shows that chemical reactions occurred during storage of condensate-water samples even though the samples were stored at 4°C in the absence of light and air. The products of these reactions had lower K_D values into MIBK. Many investigations of condensate-water treatment processes have been performed with an aged sample that had been exposed to air. It is probable that chemical reactions during storage of the sample had a large effect on the results of those studies.

MIBK extraction can probably remove about 90% of the COD at an economically reasonable solvent-to-water ratio. However, approximately 10% of the COD has a K_D of nearly zero into MIBK. These compounds probably also have low values of K_D into DIPE since MIBK is a more polar solvent and generally has higher K_D values. The K_D values of these compounds are so low that they could not be removed by either of these solvents under any economically feasible conditions. The majority of these compounds have not yet been identified. However, some physical-property information has been obtained for these solutes. The removal of these compounds was not improved by extraction at either low pH or high pH. This suggests that these solutes may be amphoteric and ionized over a wide range of pH. These solutes contain a high concentration of organic nitrogen and have molecular weights less than 1,000 as determined by ultrafiltration. In addition, some of these compounds are sufficiently volatile with respect to water that they would be stripped out of a cooling tower.

Extraction with TBP increased the COD removal as compared to MIBK for two samples. This suggests that some of the solutes may be Lewis acids because TBP is a stronger Lewis base than MIBK. However, a substantial fraction of the COD remained in the raffinate.

A solvent mixture of 25% w/w trioctyl phosphine oxide (TOPO) in MIBK was compared to MIBK alone. The TOPO solvent removed more of the COD in one sample and the same amount in another. This also suggests that some of the solutes may be Lewis acids since TOPO is a strong Lewis base. Solvents containing TOPO have very high values of K_D for phenol and dihydroxy benzenes. However, the K_D for these solutes is a function of concentration, and the K_D decreases substantially when the concentration of phenols in the organic phase is high. Both TBP and TOPO have low volatilities, and they may be difficult to regenerate in a continuous extraction process.

In conclusion, it appears to be generally true that a substantial fraction of the COD in condensate waters is unidentified, difficult to extract, and resistant to biological oxidation. Analyical techniques have been described which are an improvement over the standard methylene chloride/GC-MS technique because polar compounds are not lost in a preliminary solvent extraction step. Dimethyl hydantoin and related compounds have been identified in condensate waters. These compounds are an important treatment problem because they are difficult to extract, resistant to biological oxidation, and their toxicity is not known. MIBK has several advantages over DIPE, especially for the dihydroxy benzenes. However, a substantial fraction of the COD has such low K_D values that these solutes could not be removed by either solvent at any feasible solvent-to-water ratio. Among the literature reports summarized, the most effective condensate-water treatment was obtained with MIBK extraction followed by activated sludge treatment with powdered activated carbon added to the biological reactor.

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