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CONDENSATE WATERS

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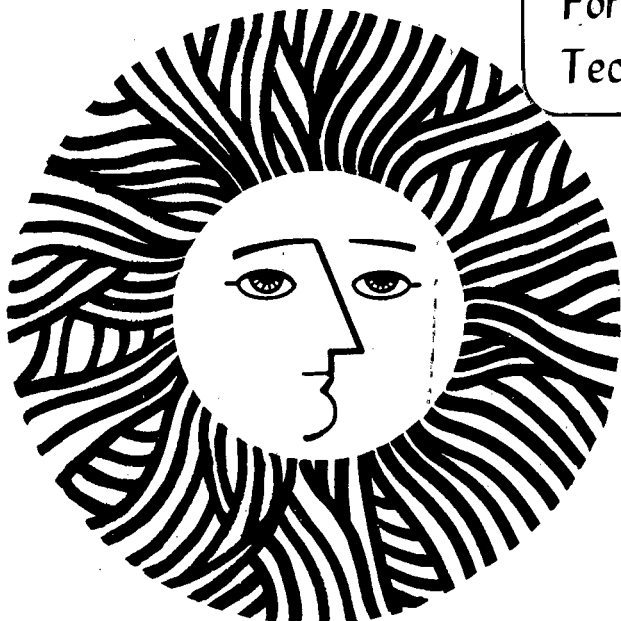
IDENTIFICATION AND REMOVAL OF THE ORGANIC COMPOUNDS  
IN COAL-CONVERSION CONDENSATE WATERS

Donald H. Mohr, Jr. and C. Judson King

November 1981

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Identification and Removal of the Organic  
Compounds in Coal-Conversion Condensate Waters

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Abstract

The purpose of this investigation is to design a physical-chemical treatment process to achieve bulk Chemical Oxygen Demand (COD) removal from coal-conversion condensate waters. It is anticipated that combinations of steam stripping and solvent extraction will economically meet most treatment goals.

However, there is a large amount of evidence in the literature which suggests that a significant fraction of the COD in many condensate waters is composed of compounds which are more polar than phenol. This presents two problems. First, these compounds have very low distribution coefficients into common industrial solvents such as diisopropyl ether (Phenosolvan process) or methylisobutyl ketone (Chem-Pro process). Second, these compounds are not extracted by methylene chloride, so they do not respond to the GC/MS analytical techniques which are currently used to study these water streams.

In this work the literature has been reviewed, and solvent extraction studies have been performed. These studies show that a large fraction of the COD can be economically removed with solvent extraction and steam stripping. The fraction of the COD which remains is significant and is composed of very polar compounds. A high-performance liquid chromatography technique has been developed which provides qualitative and quantitative information about these compounds, as well as phenolics. This technique uses an evaporative solvent change from water to isopropanol, which allows identification by GC/MS. Dimethyl hydantoin and related compounds have been identified in a coal gasification condensate water for the first time. However, the levels of these compounds appear to be affected by sample age and storage conditions. This behavior is presently being further investigated.

In future work other condensate water samples will be tested to assess the frequency of occurrence of hydantoins and related compounds. The analytical work will continue in order to account quantitatively for the COD. Further experimental studies will be carried out to define the capabilities of solvent extraction and steam stripping. Finally, these results will be used to facilitate the design of a treatment process.

Introduction

The purpose of this project is to develop and evaluate physical-chemical treatment processes to achieve bulk COD removal from coal-conversion condensate waters. It is anticipated that combinations of steam stripping and solvent extraction will economically meet most treatment goals.

Previous Analyses of Condensate Waters

Design and evaluation of water-handling systems is facilitated by a knowledge of the chemical compositions of the water streams. This information is also necessary to interpret experimental studies of wastewater treatment systems. It is generally

recognized that a substantial fraction of the organic compounds in the more concentrated condensate waters remains unidentified.

A useful way to examine this point is to compare the measured COD or TOC (Total Organic Carbon) with the theoretical COD or TOC represented by the identified compounds. Singer et al. (1) report that phenols (measured by the standard, generic colorimetric technique) constitute between 21 and 46% of the measured COD for condensate waters produced from various coals by the Synthane gasification process. It is apparent that a more incisive analytical technique is required before treatment processes can be designed in a compound-specific manner.

Table 1 contains reported analyses of condensate waters from various low-temperature coal gasification processes where the standard methylene chloride extraction, gas-chromatography, mass spectrometric (MC/GC-MS) technique was employed. In these cases only 31 to 51% of the measured TOC has been characterized. The MC/GC-MS technique has been used with similar results in many published analyses. The measured COD is frequently not reported. When it is reported, a similarly large fraction of the measured COD is not characterized.

#### Extraction Characteristics of Condensate Waters

Further information on the chemical character of the organic solutes in condensate waters can be obtained by measuring the fraction of the COD or TOC which is removed by various solvent extraction procedures. This information also relates closely to the effectiveness of an industrial solvent extraction process operating with the same solvent(s) under similar conditions. Table 2 shows the TOC and COD removal accomplished by batch solvent-extraction experiments for various condensate waters. The extractions at pH = 2 and pH = 12 were designed to suppress the ionization of strong acids and strong bases, respectively. In each case an exhaustive stripping procedure was used to remove residual dissolved solvent before the TOC or COD analysis.

Less than 70% of the TOC was removed from two condensate waters by extraction with the weak Lewis-base DIPE without pH change. DIPE is an effective solvent for phenol; however, Greminger, et al. (4) report that DIPE exhibits poor distribution coefficients for dihydric phenols.

MIBK is a stronger Lewis-base which has high distribution coefficients for dihydric phenols (4). MIBK removed 76 and 88% of the COD in two condensate waters. The relative lack of improvement from repeated extractions with the same solvent indicates that the unextracted solutes have quite low partition coefficients into that solvent.

The stronger Lewis-base, TOPO, removed an additional 5 to 7% of the COD, when compared to MIBK alone for one condensate water. Yet another 6 to 9% of the COD was removed by TOPO after the pH was lowered to 2. The COD removal obtained with TOPO does not necessarily represent a basis for an economical treatment process. TOPO is an expensive extractant (about \$7/lb) which may be difficult to regenerate to the full extent necessary. Also, addition of H<sub>2</sub>SO<sub>4</sub> to lower the pH of the highly buffered condensate waters would be expensive.

Methylene chloride is a Lewis-acid solvent which is effective for removing ketones, ethers, esters, nitrogen-containing organic bases, and low or moderately polar organic solutes in general. The information in Table 2, unreported results from the present work, and other studies indicate that no more than 1-2% of the COD has a strongly basic character.

Combining the results in Tables 1 and 2 and the foregoing discussion, it appears

that the main constituents of the unidentified TOC are polar compounds which have low distribution coefficients into the solvents which are commonly used in chemical analytical procedures and in industrial solvent extraction processes. The work reported here was directed toward determining the identities and concentrations of those substances.

### Experimental Procedure

Samples of condensate water were obtained from the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) of the U. S. Department of Energy. The feed coal to the gasifier at the time the samples were taken was Indian Head lignite. The samples were collected and handled under nitrogen, and were stored at 4°C in the dark.

The COD values of the samples were measured after lowering the pH to 2 with H<sub>2</sub>SO<sub>4</sub> and centrifuging the mixture. This step removes sulfide as H<sub>2</sub>S, thiosulfate as elemental sulfur and SO<sub>2</sub>, and a small amount of organic material.

A High-Performance Liquid-Chromatography (HPLC) technique was applied to separate and detect solutes having a wide range of polarity. This technique allows direct injection of aqueous samples and thereby avoids loss of polar compounds due to insignificant or incomplete extraction with methylene chloride or other solvents. Also, the precision of the technique is improved by this procedure.

A Spectra-Physics System 8000-B was used as the basic HPLC apparatus. A C<sub>18</sub>  $\mu$ -Bondapak stationary phase was utilized in a Waters Associates Radial Compression Module. A variable-wavelength UV absorption detector was employed (Perkin Elmer Model LC-75).

The most polar solutes were eluted isocratically in pH 3 water and were detected at 192 nm. Phenol and other moderately polar compounds were eluted in a gradient from water to methanol and were detected at 280 nm.

Qualitative identification of compounds eluting from the liquid chromatograph was obtained in two ways. The first method was to match the retention time of the unknown with that of a known compound under identical chromatographic conditions. The second method used GC-MS (Finnigan model 4000). However, as has been noted, methylene chloride extraction followed by GC-MS analysis cannot detect the most polar compounds of interest, possibly due to inadequate initial extraction. Direct injection of aqueous samples is not useful with GC-MS. Therefore, a technique was developed where the aqueous solution of one or more compounds to be identified was mixed with high-purity isopropanol (Burdick & Jackson Co.) to form a single phase. At the isopropanol/water ratios used, water was more volatile than isopropanol. Batch evaporation was then carried out in a rotary evaporator with repeated additions of isopropanol, up until the point where a water-free isopropanol concentrate was obtained, suitable for injection into the GC-MS system.

There are three principal requirements which must be met in order for this solvent-change approach to work. There must be a large enough quantity of the compound in the original aqueous solution. Second, the compound must be soluble in isopropanol. Finally, the compound must be sufficiently less volatile than isopropanol in order for it to be concentrated during the evaporation. The use of high-purity isopropanol is important, since non-volatile impurities will collect in the concentrate.

The solvent-change technique was applied to the entire wastewater mixture and to various fractions of the aqueous effluent from the liquid chromatograph.

## Results and Discussion

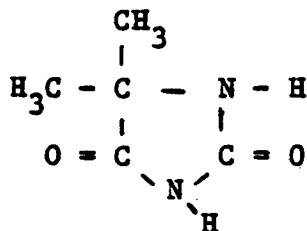
Table 3 gives the results of a chemical analysis of two condensate water samples from the GFETC slagging fixed bed gasifier. Each sample was stored at two different pH values. The 6/80 samples aged six months before analysis, whereas the 6/81 samples aged six weeks. Comparison of the different samples and different storage conditions is a useful method of detecting chemical reactions which may occur during storage.

The first group of compounds (#1-7) account for 60-68% of the measured COD and consist mostly of phenols and other moderately polar compounds. These compounds are easily detected by MC/GC-MS techniques.

The compounds in the second group in Table 3 (#8-11) are dihydric phenols. These compounds represent a significant portion (6-10%) of the COD, and they are frequently not reported by investigators using MC/GC-MS techniques. It is important to have an accurate analysis for these compounds because they are much more difficult to extract than phenol (4).

Concentrations of compounds 1-11 were measured immediately upon receipt of the first sample, and no change in their concentrations was detected during storage. The differences in the concentrations of these compounds between pH 8.5 and pH < 2 storage were probably a result of inadequate chromatographic resolution, and are not statistically significant.

The third group is composed of 5,5-dimethyl hydantoin and related compounds. These components account for 1-11% of the COD in the samples studied and have not been reported previously in condensate waters from coal conversion processes. These compounds are very hydrophilic. For example, the structure of 5,5-dimethyl hydantoin is:



Preliminary measurements indicate that these compounds have quite low distribution coefficients into MIBK.

The concentration of dimethyl hydantoin is much lower in the second sample, and it is lower for both samples for storage at pH < 2 than for storage at pH 8.5. Two possible explanations are consistent with the observations. Dimethyl hydantoin could be formed during storage at pH 8.5 by a reaction which is slowed or stopped by storage at pH < 2. The second possibility is that dimethyl hydantoin degrades during pH < 2 storage, and that changes in process conditions caused the difference between the two samples.

It is apparent that there is uncertainty concerning the formation and stability of dimethyl hydantoin and related compounds in condensate waters. The reactants and products involved in the chemical reactions leading to these compounds could also be very polar, hydrophilic compounds.

The information presented here is one illustration that polar compounds which do not respond to MC/GC-MS analytical techniques represent a significant gap in the understanding of condensate water chemistry.

## Conclusions

A large fraction of the COD in condensate waters from low-temperature coal gasification processes can be economically removed by solvent extraction with MIBK. A significant fraction of the COD in these condensates is composed of compounds which are more polar than phenol. Apparently, most of these compounds are not detected by MC/GC-MS analytical techniques, and a substantial portion of them cannot be extracted with solvents such as DIPE and MIBK. A HPLC technique has been developed which provides qualitative and quantitative information about these compounds. This method uses a solvent change from water to isopropanol, so that the resulting concentrate can be subjected to GC-MS analysis. Dimethyl hydantoin and related compounds have been detected in a coal-gasification condensate water for the first time. The levels of at least some of these compounds appear to be affected by aging and storage conditions.

## Acknowledgements

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Table 1. Reported Analyses of Condensate Waters From Coal-Gasification Processes, and Comparison with Measured Values of Total Organic Carbon (TOC).

<u>Compound Class/ Compound</u>	<u>Fraction of Measured TOC</u>			
	<u>Lurgi Process (1)</u>	<u>Lurgi Process (2)</u>	<u>Chapman Process (2)</u>	<u>GFETC Slagging Fixed-Bed Gasifier (3)</u>
Phenols:	0.445			
Phenol		0.206	0.119	0.214
Cresols		0.174	0.127	0.065
C <sub>2</sub> -Phenols		0.090	0.090	0.020
All Other:				
C <sub>2</sub> -C <sub>6</sub> Acids	0.023			
Aromatic Amines	0.043			
Total Fraction of TOC Identified:	0.511	0.470	0.336	0.313

Table 2. Removals of TOC and COD from Coal-Gasification Condensate Waters by Various Extraction Procedures, followed by Exhaustive Stripping for Removal of Residual Dissolved Solvent.

Water Source (Ref.)	Solvent**	Solvent/Water Phase Ratio, v/v	Number of Sequential Batch Extractions	Fraction Removal of	
				TOC	COD
Lurgi Gasifier (2)	DIPE	0.33	3	0.69	-
-same- (2)	{ DIPE MC (pH=12) DEE (pH=2)	{ 0.33 0.33 0.33	{ 3 3 3	0.708	-
Chapman Gasifier (2)	DIPE	0.33	3	0.651	-
-same- (2)	{ DIPE MC (pH=12) DEE (pH=2)	{ 0.33 0.33 0.33	{ 3 3 3	0.806	-
GFETC Slagging Fixed Bed Gasifier (3)	MIBK	0.067	5	0.824	0.878
-same- (*)	MIBK	1.00	1	-	0.760
-same- (*)	MIBK	1.00	2	-	0.777
-same- (*)	{ MIBK MIBK (pH=2)	{ 1.00 1.00	{ 1 1	-	0.836
-same- (*)	25% w/w TOPO in MIBK	1.00	1	-	0.812
-same- (*)	same	1.00	2	-	0.814
-same- (*)	{ same same (pH=2)	{ 1.00 1.00	{ 1 1	-	0.905

\* - Present work

\*\* - Solvents: DIPE - Diisopropyl ether  
 MC - Methylene chloride  
 DEE - Diethyl ether  
 MIBK - Methyl isobutyl ketone  
 TOPO - Trioctyl phosphine oxide

Table 3. Analysis of GFETC Slagging Fixed-Bed Gasifier Condensate Waters.

Date of Sample	6/80	6/80	6/10/81	6/10/81
Sample Age at Analysis	6 months	6 months	6 weeks	6 weeks
<u>pH of Sample Storage</u>	<u>8.5</u>	<u>&lt; 2</u>	<u>8.5</u>	<u>&lt; 2</u>
1) phenol	4,460	4,460	7,415	7,415
2) C <sub>1</sub> monohydric phenols	3,255	2,930	4,450	4,330
3) C <sub>2</sub> monohydric phenols (2)	425	244	520	435
4) O-methoxy phenol (2)	260	220	495	440
5) P-hydroxy acetophenone (2)	40	40	35	20
6) acetophenone	20	(5)	(5)	(5)
7) 2-naphthol	20	(5)	(5)	(5)
8) catechol	1,010	985	903	895
9) 4-methyl catechol (2,3)	625	605	535	490
10) resorcinol	60	57	28	(5)
11) hydroquinone	30	33	25	22
12) 5,5-dimethyl hydantoin (2,3)	1,700	650	300	150
13) 5-methyl, 5-ethyl hydantoin (3)	365	(5)	(5)	(5)
14) 5,5-diethyl hydantoin (3)	270	(5)	(5)	(5)
15) 5-methyl hydantoic acid (3)	90	85	130	85
16) 5-methyl hydantoin (3)	120	135	42	20
<b>COD</b>	<b>34,400</b>	<b>32,300</b>	<b>46,650</b>	<b>47,050</b>
Fraction of COD contributed by compounds 1-7	0.605	0.598	0.676	0.656
Fraction of COD contributed by compounds 8-11	0.098	0.102	0.063	0.058
Fraction of COD contributed by compounds 12-16	0.114	0.038	0.014	0.007
<b>Total fraction of COD which has been characterized</b>	<b>0.817</b>	<b>0.738</b>	<b>0.753</b>	<b>0.721</b>

Notes for Table 3

- 1) Qualitative identification was verified for all measurements by matching HPLC retention times.
- 2) Qualitative identification by GC-MS.
- 3) Qualitative identification by HPLC co-chromatography.
- 4) All concentrations in mg/l.
- 5) No relevant data.

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