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Publication Date

1981-12-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

Submitted to Environmental Science and Technology

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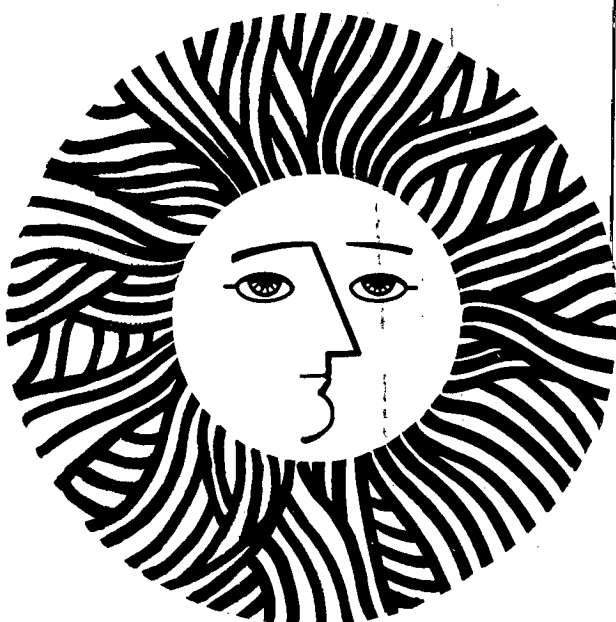
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IDENTIFICATION OF THE PRINCIPAL ORGANIC
COMPOUNDS IN REACTOR CONDENSATE WATER FROM
A COAL-GASIFICATION PROCESS

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This work was supported by the Assistant Secretary for Environmental
Protection, Safety and Emergency Preparedness, Environmental and
Safety Engineering Division of the U.S. Department of Energy under
Contract No. W-7405-ENG-48.

Abstract

Solvent extraction, GC-MS, and HPLC techniques were used to characterize the principal organic solutes in coal conversion condensate waters. Results of previous studies showed that a significant fraction of the Chemical Oxygen Demand (COD) in many condensate waters does not respond to standard GC-MS analysis. Many of these uncharacterized compounds are difficult to treat by biological oxidation or solvent extraction. Solvent extraction results indicated that a significant fraction of the COD is more polar than dihydric phenols. A novel solvent-change sample-preparation technique was developed which allows qualitative analysis of very hydrophilic compounds by GC-MS. A reversed-phase HPLC technique was used to characterize 70-83% of the COD in three condensate water samples. Dimethyl hydantoin and related compounds, previously unreported in condensate waters, were shown to represent 1-11% of the COD in these three samples. Chemical changes were observed during storage for one condensate water sample.

Introduction

Coal-conversion processes produce large amounts of reactor-effluent condensate water. It has been projected that a 250×10^6 SCF/day Lurgi-type gasification plant will generate about 1×10^6 lb/hr of process condensates (1). Proper management of this water is necessary because of its high content of organic solutes, ammonia, carbon dioxide, and other substances. Furthermore, many coal conversion plants will probably be located in areas where water is scarce. Water management, processing, and recycle are therefore important for both environmental and economic reasons. Coal-conversion condensate management and processing alternatives have been discussed elsewhere (1 - 4). Design and evaluation of water-handling systems are facilitated by a knowledge of the chemical compositions of the water streams.

It is generally recognized that the compounds composing a substantial fraction of the organic loading in the more concentrated coal-conversion condensate waters have not been identified. A useful way to examine this point is to compare the measured Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC) with the theoretical COD or TOC represented by the aggregate of the measured concentrations of the identified compounds. If the measured TOC is greater, then organic substances are present which have not been identified.

Phenols are important organic constituents of condensate waters from coal-liquefaction and low-temperature coal-gasification processes. Singer, et al. (5) report the concentration of phenols, as measured by the standard, generic colorimetric technique, for condensate waters produced from various coals by the Synthane gasification process. If the total measured phenols are taken as phenol itself for calculation of their contribution to the COD, then they constitute between 21 and 46% of the measured COD.

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

Stamoudis, et al. (8) report recoveries from distilled water solutions of 65% for o-xylene and 82% for phenol using the MC/GC-MS method. Such low recoveries represent a limitation on the quantitative precision of the method. Furthermore, the recoveries of compounds more polar and hydrophilic

than phenol should be still less, and may be so low that they would escape detection.

The data in Table II show that 4 to 38% of the TOC or COD in various condensate waters was not amenable to treatment by biological oxidation. These levels of TOC/COD in the effluent are significant due to the high organic concentrations in the water feeds. These treatment processes typically removed almost all of the identified compounds in the feed, including over 99% of the phenols. Therefore, most of the compounds which are difficult to remove by biological oxidation are not identified by MC/GC-MS analysis.

Bombaugh, et al. (15) 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. (5) report that a Phenosolvan process removed 89% of the COD and 99.7% of the phenol from another Lurgi condensate water. The results of laboratory solvent-extraction studies, discussed subsequently, show that commercial solvent extraction processes using diisopropyl ether (Phenosolvan process) or methylisobutyl ketone would leave behind a significant fraction of the TOC. Extraction with these solvents removes nearly all of the phenols and other compounds which are identified by MC/GC-MS analyses. Compounds not removed by extraction with these solvents should be much more polar and hydrophilic than phenol.

Combining the information in Tables I and II and the foregoing discussion, it is apparent that the compounds composing a substantial fraction of the organics loading in coal-conversion condensate waters have not been identified. Many of the unidentified compounds are also difficult to remove by biological treatment or conventional solvent extraction processes. Future research to improve the performance of condensate water treatment processes would be facilitated by a better understanding of the compositions of these streams. The work reported here utilized high performance liquid chromatography (HPLC), GC-MS, and chemical characterization by solvent extraction to improve understanding of coal-conversion condensate water chemistry.

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. One-half of each sample was acidified to pH 2 with H_2SO_4 . The samples were collected under nitrogen, and were stored at 4°C in the absence of light.

Inadvertent exposure of the sample to even small amounts of oxygen resulted in gross changes in the appearance of the condensate water. Oxygen contamination resulted in a color change from light yellow to dark brown and caused tars to precipitate. Oxygen was excluded from the condensate waters

throughout this work by carrying out storage and all handling steps under a nitrogen atmosphere.

The COD of each sample was measured, as described elsewhere (14), without further pH change. The COD of solvent-extracted samples was measured after removal of residual dissolved solvent. This was accomplished by stripping the solution with a 5:1 ($N_2:H_2O$) mole ratio of water-saturated nitrogen at 25°C. MIBK was removed from the test solution to a concentration of less than 100 ppm COD.

An 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 the loss of polar compounds or decrease in precision associated with insignificant or incomplete extraction with methylene chloride or other solvents.

Condensate water samples were prepared for HPLC analysis by slow addition of concentrated H_2SO_4 to reach pH 3. A precipitate formed upon acidification; it was found to represent less than 2% of the COD. This solution (5 ml) was filtered through a Waters Associates Sep Pak which contained a C_{18} reversed-phase liquid chromatography packing. The Sep Pak was then washed with 5 ml of dilute aqueous phosphate buffer (pH 3) and 5 ml of methanol. All of the eluent from the Sep Pak was combined for subsequent analysis. The purpose of this procedure was to remove compounds which might contaminate the HPLC

column. Tests with synthetic solutions verified that this procedure recovered the identified compounds in an essentially quantitative fashion.

A Spectra-Physics model 8000-B HPLC was used as the basic analytical apparatus. A C_{18} μ -Bondapack 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 (0.05 M phosphate buffer) 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. Diethyl hydantoin and methyl, ethyl hydantoin were eluted in a water-methanol gradient and were detected at 240 nm. Quantitative information was obtained by calibrating the detector with solutions of known compounds which were chromatographed in the same manner as the condensate-water samples.

Qualitative identification of compounds eluting from the HPLC 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; co-chromatography was used as an additional check. The second method used GC-MS (Finnigan model 4000). However, as has been noted, methylene chloride extraction followed by GC-MS analysis may not detect

the most polar compounds of interest due to inadequate initial extraction. Direct injection of aqueous samples is not practical with GC-MS. Therefore, a GC-MS sample-preparation procedure was developed which recovers even the most hydrophilic and difficult-to-extract compounds for qualitative analysis.

An aqueous solution (typically 5 ml) containing one or more compounds to be identified was mixed with about 50 ml of high purity isopropanol (Burdick & Jackson Co.) to form a single phase. In this solution water is more volatile than isopropanol. The volume of the mixture was reduced to about 1 ml in a rotary evaporator. More isopropanol (10 ml) was added and evaporation was carried out to a final volume of approximately 0.1 ml. The resulting solution was a water-free isopropanol concentrate which was suitable for GC-MS analysis.

In order to obtain qualitative identification by this solvent-change approach, the solute concentration in the final isopropanol solution must be greater than the detection limit of the GC-MS. The solute must be less volatile than isopropanol. However, moderately volatile compounds can be concentrated by this technique even though the total solute recovery may be quite low. The solute must be soluble in isopropanol, and the isopropanol must be free of non-volatile impurities.

The principal advantage of the solvent-change approach is that the solute, which may be very hydrophilic, does not have

to partition between an aqueous phase and an organic phase. This technique was applied to condensate-water raffinates from solvent extraction experiments and to various fractions of the aqueous effluent from the liquid chromatograph.

Results and Discussion

Table III presents the results of the chemical characterization of condensate waters by solvent extraction. This information can also be used to estimate the performance of a commercial-scale solvent extraction process utilizing the same solvent(s) under the same conditions.

The ethers are weak Lewis bases, which will effectively remove phenol and alkylphenols. On the basis of equilibrium distribution coefficients reported by Greminger, et al. (16), one would expect non-alkylated dihydric phenols (pyrocatechol, etc.) to be poorly removed by the ethers. Methylisobutyl ketone (MIBK) is a stronger Lewis base, which should be effective in removing dihydric phenols (16). Trioctyl phosphine oxide (TOPO) is a still stronger Lewis base extractant, which is known to complex strongly with phenols (17). The extractions at pH 2 and pH 12 were designed to suppress the ionization of strong acids and strong bases, respectively. Methylene chloride (MC) is a Lewis-acid solvent which is effective for removing nitrogen-containing organic bases, and weakly or moderately polar organic solutes in general.

The results show that less than 70% of the TOC was removed from a Lurgi-type gasification condensate water by extraction with diisopropyl ether (DIPE). Suppression of the ionization of strong acids and strong bases removed an additional 2% of the TOC.

DIPE extraction removed 65% of the TOC from a Chapman gasifier condensate water. Suppression of the ionization of strong acids and strong bases removed an additional 15% of the TOC in this case. Butyl Acetate extraction of a different condensate water sample from the same process removed 68% of the TOC.

The remainder of the data in Table III were obtained from four condensate water samples from the GFETC slagging fixed-bed gasifier. MIBK extraction removed 80 and 88% of the COD for two of the GFETC samples. 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. Extraction with MIBK followed by MIBK extraction at low pH removed 86 to 93% of the COD in three of the GFETC samples. This suggests that about 5% of the COD in the GFETC condensate waters may be strongly acidic. The case of a second extraction with MC compared with the case of a second extraction with MIBK shows that less than 2% of the COD is strongly basic for one GFETC condensate water.

TOPO, a strong Lewis-base extractant, removed an additional 5% of the COD when compared with MIBK extraction for one GFETC condensate water. Yet another 8% of the COD was removed by TOPO at low pH. This also suggests the presence of strong acids.

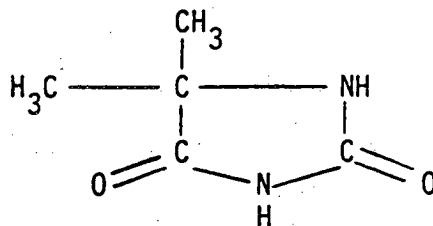
All of the extractions in Table III remove essentially all of the phenol and alkyl monohydric phenols. The extractions with MIBK and the TOPO-MIBK mixture should remove nearly all of the dihydric phenols. It is therefore apparent that a substantial portion of the TOC in these condensate waters is even more polar and hydrophilic than dihydric phenols.

Finally, a time dependence was found for the degree of COD removed by solvent extraction for one condensate water sample (GFETC run RA-106). After the sample aged from 1.7 to 24 days, an additional 4.4% of the COD remained in the raffinate after MIBK extraction. All of the results from this work were averages of two or more duplicate measurements which could be repeated within 0.5% of the original condensate water COD. Therefore, the observed time dependence is statistically significant. This time dependence is important because most treatability studies are performed on condensate water samples which have aged many days since collection. This result is an additional illustration of the complexity of condensate water chemistry.

Table IV gives the results of a chemical analysis of three samples of condensate water from the GFETC slagging fixed-bed gasifier. Corresponding HPLC chromatograms are shown in Figures 1 and 2. Compounds 1 to 5 account for 60 to 69% of the COD and consist mostly of monohydric phenols and other moderately polar compounds.

Compounds 6-9 in Table IV are dihydric phenols. These compounds represent a significant portion (5 to 10%) of the COD, except for the sample from run RA-106, 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 (16).

The third group of compounds in Table IV is composed of 5,5-dimethyl hydantoin



and related compounds. These components represent 1 to 11% of the COD and have not been reported previously in condensate waters from coal-conversion processes. These compounds are

very hydrophilic. Preliminary measurements indicate that dimethyl hydantoin has very low distribution coefficients into MIBK and several other solvents.

The concentration of dimethyl hydantoin was found to increase during storage for the condensate water from run RA-106 which was stored at 4°C without pH adjustment. This time dependence was statistically significant because the precision of the HPLC results was about 3% for baseline resolved compounds. None of the other results changed with time beyond the sample age reported in the table (up to 120 days for the RA-97 sample and up to 500 days for the RA-78 sample). When a portion of the acid-stored sample from run RA-78 was adjusted to the original pH by additions of Na_2CO_3 and NaOH, the concentration of dimethyl hydantoin increased from 655 to about 1800 mg/l after storage for two weeks. Acidification of the run RA-78 sample which has been stored without pH change produced no change in the dimethyl hydantoin concentration.

From these observations it appears that dimethyl hydantoin is formed in the GFETC condensate waters by a chemical reaction which proceeds over a period of many days at 4°C storage until a final concentration is reached. The difference in the final concentration between different condensate water samples is probably due to differences in the operation of the coal-gasification process. It also appears that acidification of the sample stops or greatly slows the

reaction (compare results at 1.7 and 38 days for the acidified RA-106 sample). Therefore, the concentration of dimethyl hydantoin in the acid-stored samples may represent the actual concentration at the sampling point in the process. The differences between different acid-stored condensate water samples are probably attributable to differences in the operation of the gasification process, including differences in the length of time that the condensate water was recycled in the process.

The increase in dimethyl hydantoin concentration occurred during the same time interval as the change in solvent extraction behavior noted previously for the same condensate water sample. Although dimethyl hydantoin does not represent enough of the COD by itself to account for the change in solvent extraction behavior, the combination of these results is strong evidence that chemical changes can occur in these condensate water samples during storage.

The fraction of the COD (70 to 83%) which has been characterized in this study is a considerable improvement when compared with the MC/GC-MS studies presented in Table I. However, a significant fraction of the COD in the GFETC samples remains unidentified after HPLC analysis. Nearly all of the UV absorbing compounds which eluted from the HPLC have been identified and reported in Table IV. The first two peaks in Figure 2 are probably inorganic compounds. A refractive-index

detector was employed to show that there were no significant concentrations of compounds in the isocratic HPLC eluent which were not detected in the UV at 192 nm. The HPLC sample-preparation procedure should have had minimal losses for any compound which would elute from the HPLC under the conditions utilized in this study. It is probable that some of the uncharacterized COD is composed of compounds which will not elute from a reversed-phase HPLC column.

Conclusions

Proper management and treatment of condensate waters from coal-conversion processes is environmentally and economically important. Design of wastewater treatment systems and interpretation of experimental treatability studies are facilitated by knowledge of the condensate water composition. It is generally recognized that a large portion of the organic compounds in these condensate waters has not been characterized by standard GC-MS analysis. Many of these uncharacterized compounds are difficult to treat by biological oxidation or by solvent extraction processes. Chemical characterization by solvent extraction shows that a substantial fraction of the COD in many condensate waters is more polar, hydrophilic and difficult to extract than dihydric phenols.

A novel solvent-change sample-preparation procedure has been developed to allow qualitative identification by GC-MS of hydrophilic compounds which may be too polar to be recovered by methylene chloride extraction.

Reversed-phase HPLC was employed to provide qualitative and precise quantitative analysis of organic compounds of widely differing polarity. The reported analyses identified 70 to 83% of the COD in three condensate water samples. Dimethyl hydantoin and related compounds, previously unreported in coal-conversion condensate-waters, were shown to represent 1 to 11% of the COD in these three samples. The fraction of the COD removed by one solvent extraction procedure was found to decrease with time, and the concentration of dimethyl hydantoin increased with time for one condensate water sample.

Acknowledgements

The authors would like to thank Lee Paulson of the Grand Forks Energy Technology Center for supplying the wastewater samples. This work was supported by the U. S. Department of Energy, Assistant Secretary for Environmental Protection, Safety and Emergency Preparedness, Environmental and Safety Engineering Division, under Contract #W-7405-ENG-48.

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

| Compound Class/ Compound | Fraction of Measured TOC | | | |
|--------------------------------------|---------------------------|---------------------------|-----------------------------|---------------------------|
| | Lurgi (a) Gasifier (5) | Lurgi (b) Gasifier (6) | Chapman (c) Gasifier (6) | GFETC (d) Gasifier (7) |
| Phenols: | 0.445 | | | |
| Phenol | | 0.206 | 0.119 | 0.214 |
| Cresols | | 0.174 | 0.127 | 0.065 |
| C ₂ -Phenols | | 0.090 | 0.090 | 0.020 |
| All Others: | | | | 0.014 |
| C ₂ -C ₆ Acids | 0.023 | | | |
| Aromatic Amines | 0.043 | | | |
| Total fraction of TOC Identified: | 0.511 | 0.470 | 0.336 | 0.313 |

- a) Lurgi gasifier, Sasolburg, South Africa.
b) Lurgi gasifier, lignite coal, Kosovo, Yugoslavia.
c) Chapman fixed-bed gasifier, bituminous coal, Kingsport, TN.
d) Grand Forks Energy Technology Center slagging fixed-bed gasifier, Indian Head lignite, Grand Forks, ND.

Table II. Effectiveness of Biological Treatment for Coal Conversion Condensate Waters

| Coal Conversion Process | Treatment Method (Ref.) | Fraction Removal of | |
|--------------------------------|---|---------------------|------|
| | | TOC | COD |
| GFETC ^(a) run RA-52 | Activated Sludge <u>(8)</u> | --- | 0.81 |
| GFETC ^(a) run RA-52 | MIBK Extraction Followed by Activated Sludge <u>(7)</u> | 0.95 | 0.96 |
| Hygas ^(b) run 64 | Activated Sludge <u>(8)</u> | --- | 0.81 |
| Hygas ^(b) run 72 | n- Butyl Acetate Extraction Followed by Activated Sludge <u>(9)</u> | --- | 0.94 |
| Hygas ^(b) run 79 | Activated Sludge <u>(9)</u> | --- | 0.90 |
| Chapman ^(c) | Activated Sludge <u>(10)</u> | 0.67 ^(d) | 0.62 |
| Synthane ^(e) | Activated Sludge <u>(11)</u> | 0.88 | --- |
| METC ^(f) run 95 | Activated Sludge <u>(12)</u> | 0.88 | 0.85 |
| SRC ^(g) | Activated Sludge <u>(13)</u> | 0.85 | 0.86 |

- a) Grand Forks Energy Technology Center slagging fixed-bed gasifier, Indian Head lignite, Grand Forks, ND.
 b) Hygas gasifier, Illinois #6 bituminous coal, Chicago, IL.
 c) Chapman fixed-bed gasifier, bituminous coal, Kingsport, TN.
 d) Effluent was toxic to Daphnia, Fathead Minnow and Chinese Hamster Ovary Cells.
 e) Synthane fluidized bed gasifier, Montana Rosebud coal, Pittsburgh, PA.
 f) Morgantown Energy Technology Center fixed-bed gasifier, Arkwright bituminous coal, Morgantown, WV.
 g) Solvent Refined Coal (SRC I) liquefaction process, Kentucky #9 coal, Ft. Lewis, WA.

Table III. Removal of TOC and COD from Coal-Gasification Condensate Waters by Various Solvent Extraction Procedures

| Coal Gasification Process | Water Age (days) | Ref. | Solvent (b) | Solvent/ Water Phase Ratio, V/V | Number of Sequential Batch Extractions | Fractional Removal of | |
|---------------------------|------------------|-------|------------------------------------|------------------------------------|--|-----------------------|---------|
| | | | | | | TOC (a) | COD (a) |
| Lurgi (c) | --- | 6 | DIPE | 0.33 | 3 | 0.690 | 0.755 |
| | --- | 6 | { DIPE MC (pH 12) DEE (pH 2) | 0.33 | 3 | 0.708 | 0.789 |
| | --- | | | 0.33 | | | |
| | --- | | | 0.33 | | | |
| Chapman (d) | --- | 6 | DIPE | 0.33 | 3 | 0.651 | 0.456 |
| | --- | 6 | { DIPE MC (pH 12) DEE (pH 2) | 0.33 | 3 | 0.806 | 0.746 |
| | --- | | | 0.33 | | | |
| | --- | | | 0.33 | | | |
| --- | 10 | BA | 0.10 | 3 | 0.681 | 0.665 | |
| GFETC (e) Run RA-52 | --- | 7 | MIBK | 0.067 | 5 | 0.824 | 0.878 |
| GFETC (e) Run RA-78 | 140 | (f) | MIBK | 1.00 | 1 | --- | 0.796 |
| | 140 | { (f) | MIBK | 1.00 | 2 | --- | 0.810 |
| | 140 | { (f) | { MIBK MIBK (pH 2) | 1.00 | 1 | --- | 0.861 |
| | 140 | (f) | { MIBK MC (pH 12) | 1.00 | 2 | --- | 0.833 |
| | 140 | (f) | 25% w/w TOPO in MIBK | 1.00 | 1 | --- | 0.842 |
| | 140 | (f) | same | 1.00 | 2 | --- | 0.843 |
| | 140 | (f) | { same same (pH 2) | 1.00 | 1 | --- | 0.921 |
| | 140 | (f) | { same same (pH 2) | 1.00 | 1 | --- | 0.921 |

Table III. (Cont'd)

| Coal Gasification Process | Water Age (days) | Ref. | Solvent (b) | Solvent/ Water Phase Ratio, V/V | Sequential Batch Extractions | Fractional Removal of | |
|---------------------------|------------------|------|--------------------------|------------------------------------|------------------------------|-----------------------|---------|
| | | | | | | TOC (a) | COD (a) |
| GFETC (e) Run RA-97 | 130 | (f) | { MIBK MIBK (pH 3) | 1.00 | 1 } 1 } | --- | 0.885 |
| | | | | 1.00 | | | |
| GFETC (e) Run RA-106 | 1.7 | (f) | { MIBK MIBK (pH 3) | 1.00 | 1 } 1 } | --- | 0.930 |
| | | | | 1.00 | | | |
| | 24 | (f) | { MIBK MIBK (pH 3) | 1.00 | 1 } 1 } | --- | 0.886 |
| | | | | 1.00 | | | |

- a) Residual dissolved solvent removed by inert gas stripping prior to analysis.
b) Solvents: DIPE - Diisopropyl ether, MC - Methylene chloride, DEE - Diethyl ether, BA - n-Butyl acetate, MIBK - Methylisobutyl ketone, TOPO - Trioctyl phosphine oxide.
c) Lurgi gasifier, lignite coal, Kosovo, Yugoslavia.
d) Chapman fixed-bed gasifier, bituminous coal, Kingsport, TN.
e) Grand Forks Energy Technology Center slagging fixed-bed gasifier, Indian Head lignite, Grand Forks, ND.
f) Present work.

Table IV. Analysis of GFETC Slagging Fixed-Bed Gasifier Condensate Waters^{a,d}

| Run # | RA-106 | RA-106 | RA-106 | RA-106 | RA-97 | RA-97 | RA-78 | RA-78 |
|--|---------|---------|---------|---------|---------|---------|---------|---------|
| Date of Sample | 9/30/81 | 9/30/81 | 9/30/81 | 9/30/81 | 6/10/81 | 6/10/81 | 6/20/80 | 6/20/80 |
| Sample Age (days) | 1.7 | 1.7 | 38 | 38 | 40 | 40 | 200 | 400 |
| Sample Acidified at Collection | NO | YES | NO | YES | NO | YES | NO | YES |
| 1) phenol | 3530 | 3645 | 3530 | 3645 | 7405 | 7415 | 5030 | 4460 |
| 2) cresols | 2420 | 2495 | 2420 | 2495 | 4265 | 4330 | 3240 | 2930 |
| 3) xylenols (b) | 435 | 430 | 435 | 430 | 475 | 435 | 455 | 245 |
| 4) o-methoxy phenol (b) | 165 | 170 | 165 | 170 | 450 | 440 | 260 | 220 |
| 5) p-hydroxy acetophenone (b) | 3 | 5 | 3 | 5 | 35 | 20 | 50 | 40 |
| 6) pyrocatechol | 40 | 50 | 40 | 50 | 850 | 895 | 975 | 985 |
| 7) 4-methyl pyrocatechol | 20 | 30 | 20 | 30 | 500 | 490 | 615 | 605 |
| 8) resorcinol | 2 | 2 | 2 | 2 | 30 | (e) | 60 | 55 |
| 9) hydroquinone | 1 | 1 | 1 | 1 | 25 | 20 | 35 | 35 |
| 10) 5,5- dimethyl hydantoin (b,c) | 295 | 235 | 455 | 235 | 295 | 150 | 1755 | 655 |
| 11) 5-methyl, 5-ethyl hydantoin (c) | (e) | (e) | (e) | (e) | (e) | (e) | 365 | (e) |
| 12) 5,5 diethyl hydantoin (c) | (e) | (e) | (e) | (e) | (e) | (e) | 270 | (e) |
| 13) 5-methyl hydantoic acid (c) | ND | ND | ND | ND | 125 | 85 | 100 | 50 |
| 14) 5-methyl hydantoin(c) | ND | ND | ND | ND | 40 | 20 | 135 | 135 |
| COD | 23,510 | 23,890 | 23,510 | 23,870 | 46,650 | 47,050 | 35,810 | 32,350 |
| Fraction of COD contributed by compounds 1-5 | 0.685 | 0.694 | 0.685 | 0.694 | 0.661 | 0.656 | 0.621 | 0.597 |
| Fraction of COD contributed by compounds 6-9 | 0.005 | 0.007 | 0.005 | 0.007 | 0.059 | 0.058 | 0.092 | 0.102 |
| Fraction of COD contributed by compounds 10-14 | 0.019 | 0.015 | 0.029 | 0.015 | 0.014 | 0.007 | 0.112 | 0.037 |
| Total fraction of COD which has been characterized | 0.709 | 0.716 | 0.719 | 0.716 | 0.734 | 0.721 | 0.825 | 0.736 |

- a) Qualitative identification was verified for all measurements by matching HPLC retention times.
- b) Qualitative identification by GC-MS
- c) Qualitative identification by HPLC co-chromatography.
- d) All concentrations in mg/l
- e) No relevant data
- ND none detected

Figure 1. HPLC chromatogram of condensate water from GFETC run RA-97. Peak numbers refer to compounds identified in Table IV. Mobile phase: linear gradient from 100% pH 3 H₂O (0 ml elution volume) to 33% pH 3 H₂O and 67% methanol (40 ml elution volume). Flow rate: 1.00 ml/min. Stationary phase: μ -bondapak C₁₈ in a Waters Assoc. Radial Compression Module. Sample Volume: 10 μ l.

Figure 2. HPLC chromatogram of condensate water from GFETC run RA-97. Peak numbers refer to compounds identified in Table IV. Mobile phase: 100% pH 3 H₂O, isocratic. Flow rate: 1.00 ml/min. Stationary phase: μ -bondapak C₁₈ in a Waters Assoc. Radial Compression Module. Sample Volume: 10 μ l.

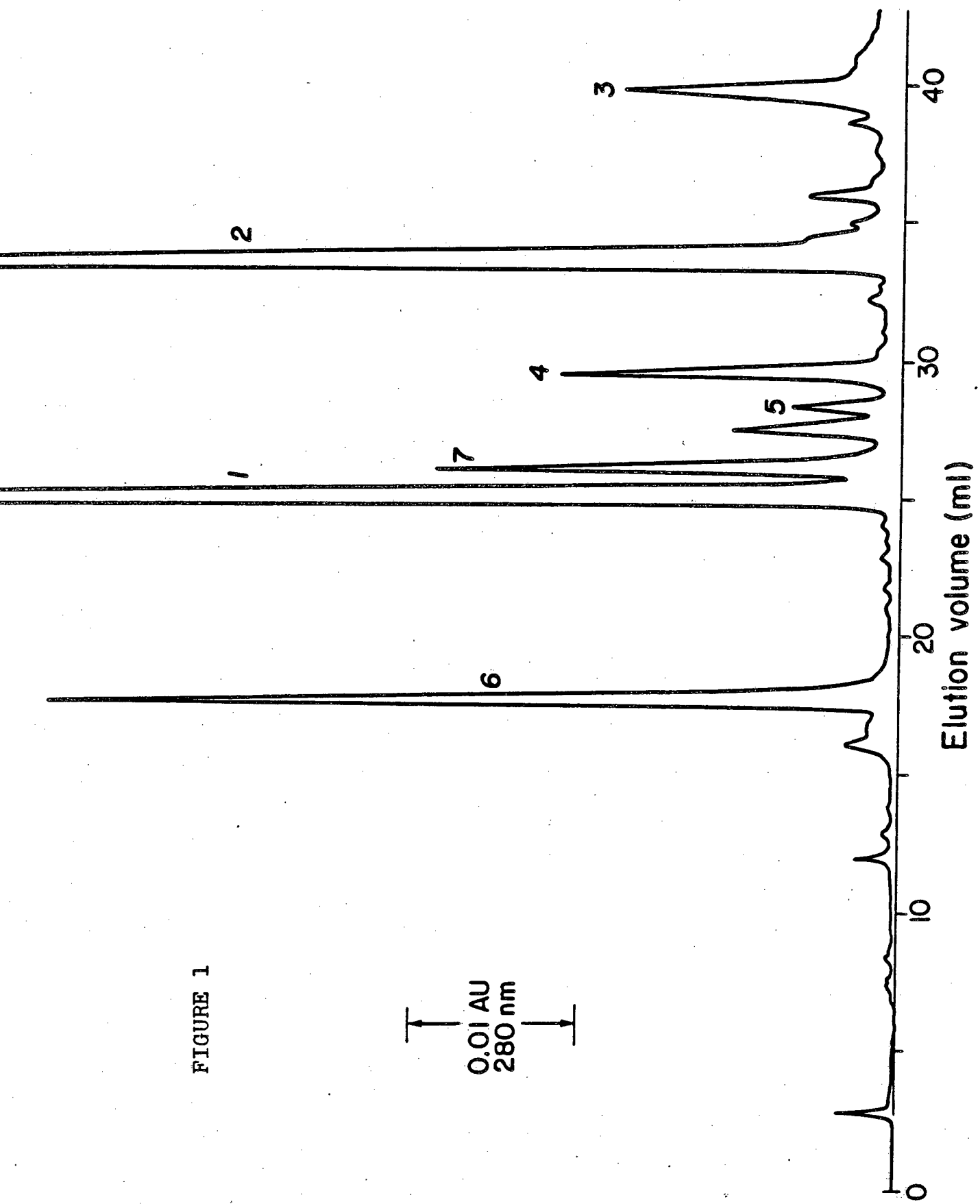
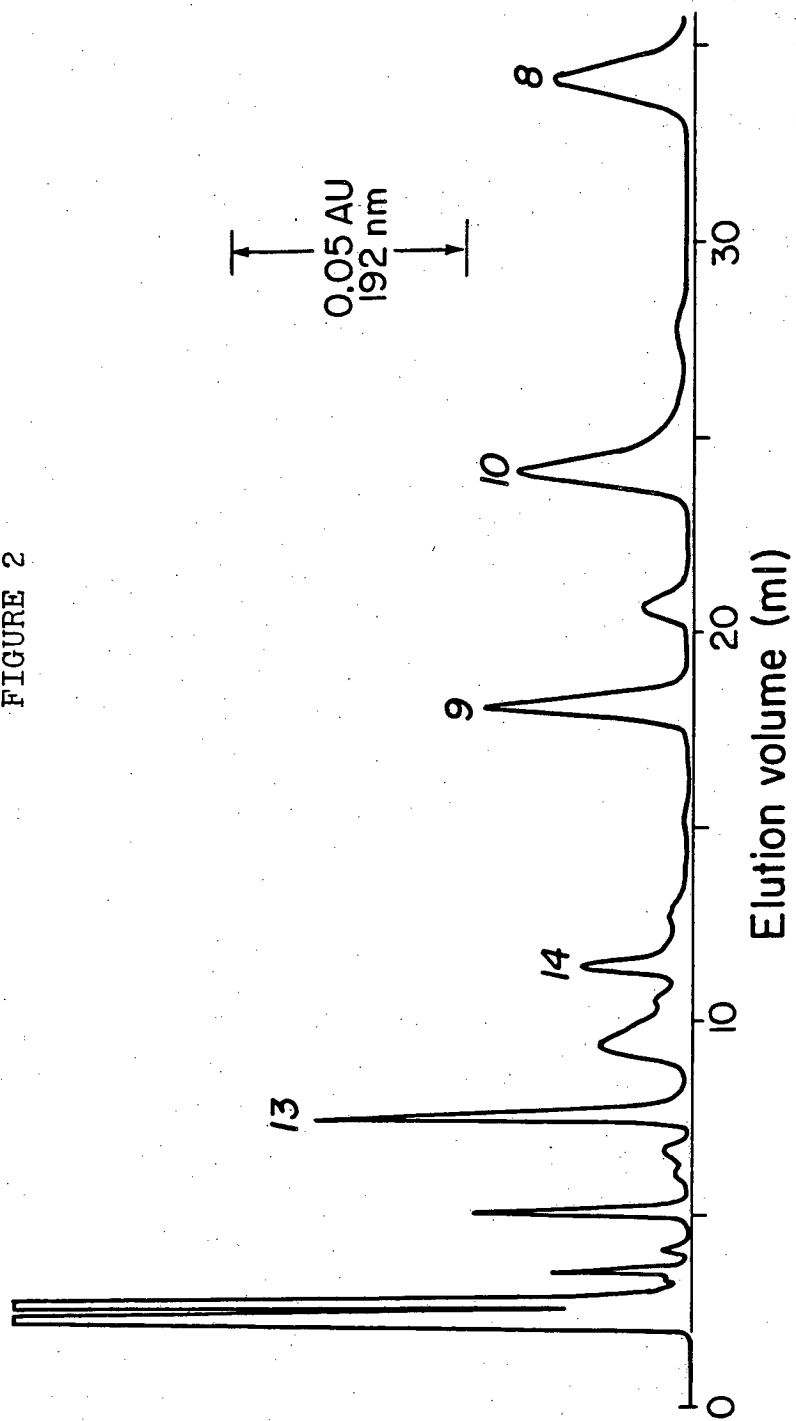


FIGURE 1

FIGURE 2



XBL 8112-1666

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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