

ANALYSIS OF VOLATILE POLAR ORGANICS IN UNTREATED BY-PRODUCT
WATERS FROM COAL CONVERSION PROCESSES

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INTRODUCTION

Analysis of by-product waters from coal conversion processes is important because the need for constructing large-scale coal liquefaction and gasification plants is increasing. Coal liquefaction and gasification technologies will use or produce water which must be made environmentally acceptable before discharge from the plant. However, some gasification processes plan to recirculate a major portion of the process water within the plant. It is therefore necessary to obtain qualitative and quantitative data concerning the trace organic constituents present in these process waters in order that effective water treatment technologies can be developed and evaluated. This knowledge would also provide insight into the potential environmental impact of coal conversion processes.

Interest in trace organic constituents present in waters from coal conversion processes is not new. Schmidt, Sharkey and Friedel (1) identified a large number of organic components in SYNTHANE (2) gasifier condensate waters, using extraction techniques followed by analysis via combined gas chromatography-mass spectrometry (GC-MS) and high resolution mass spectrometry (HRMS). Ho, Clark and Guerin (3) have used direct aqueous injection gas chromatography to quantitate sixteen organic compounds present in by-product waters from two coal conversion processes. Ellman, Johnson, Schoubert, Paulson and Fegley (4) have recently used mass spectrometry to investigate the nature of water-soluble organics in water from a modified Lurgi slagging fixed-bed gasification process. Kavan and Basyrova (5) have determined by gas chromatography (GC) the ketone content of waste water from the "pressure gasification" of coal.

The present investigation was undertaken to more fully define the nature of the trace volatile polar organics in by-product waters from four coal conversion process development units, in order to provide input for water treatment process design and to develop rapid analytical techniques to monitor the effectiveness of various water treatments. The samples investigated included by-product waters from two gasification processes, SYNTHANE (2) and a modified Lurgi slagging fixed-bed gasification process (4), and two liquefaction processes, SYNTHOIL (6) and Project Lignite (7). A variety of analytical techniques were used, including direct aqueous injection GC-MS, GC-MS of extracts from these waters, and direct aqueous injection GC employing flame ionization and flame photometric detection.

EXPERIMENTAL

The combined GC-MS analyses were performed using a Varian* 1700 gas chromatograph equipped with a flame ionization detector interfaced to a DuPont 490 mass spectrometer. Mass spectrometric data reduction and storage was accomplished by a Hewlett-Packard 2100A computer. The mass spectrometer was operated at a resolution of one part in 600 and an ionizing voltage of 70 eV. The ion source, jet separator and glass line connecting the chromatograph to the spectrometer were held at 275° C.

*Use of brand names facilitates understanding and does not necessarily imply endorsement by the Department of Energy.

The chromatographic effluent was continuously scanned at a rate of four seconds per decade of mass by the mass spectrometer.

In most cases, the gas chromatographic separations were effected using a 20 ft. x 1/8 in. glass column packed with 60/80 mesh Tenax GC with a helium flow rate of 15 cc per minute. The column was held at 30^o C for 6 minutes and then temperature programmed at 2 C^o per minute to 300^o C.

Where possible the combined GC-MS analyses were performed by direct injection of the aqueous samples (8). In cases where the amounts of individual components present were insufficient to obtain usable mass spectrometric data, the waters were extracted using methylene chloride (1) and the resulting extracts were subjected to GC-MS analysis using conditions identical to those used during direct aqueous injection.

In general, identification of specific compounds was made on the basis of mass spectral data and in most cases was subsequently confirmed by co-chromatographic experiments in which pure compounds were spiked into the by-product waters. In a few cases, this was not done because standard compounds, such as certain alkyl furans and C₃-phenols, were not available.

Gas chromatographic analysis of the volatile sulfur constituents of SYNTHANE condensate water was performed using a Tracor 550 gas chromatograph equipped with a dual flame ionization detector and a flame photometric detector specific for sulfur. The sulfur components were chromatographed using a 10 ft. x 1/8 in. glass column packed with 60/80 mesh Tenax GC.

Identification of specific sulfur compounds using flame photometric detection was achieved solely on the basis of co-chromatographic experiments using by-product water spiked with authentic sulfur compounds. In addition, the mass spectrum of carbon disulfide was observed in a number of GC-MS experiments where the untreated by-product waters were injected directly into the GC-MS system.

Gas chromatographic results were quantitated by determining peak areas from chromatographic profiles obtained from direct aqueous injection of the by-product waters. In order to obtain specific response factors for individual compounds, a standard solution was injected and separated using chromatographic conditions identical to those under which the sample was analyzed.

RESULTS AND DISCUSSIONS

Figure 1 shows gas chromatographic profiles obtained by direct aqueous injection of by-product waters from four different coal conversion processes: 1. end-of-run liquor from a slagging fixed-bed gasifier (4); 2. by-product water from Project Lignite (7); 3. SYNTHANE (2) gasifier condensate water; and 4. SYNTHOIL (6) process development unit scrubber water. The numbered chromatographic peaks are identified in Table 1. The chromatographic profile of SYNTHANE condensate water, obtained using sulfur specific flame photometric detection, appears in Figure 2, and the numbered peaks are identified in Table 2.

The data presented in Table 2, obtained with the use of a flame photometric detector, are preliminary but illustrate the potential applicability of element-specific gas chromatographic detectors to the analysis of coal conversion products. The sulfur compounds identified in Table 2 have not been quantitated.

Table 1. Organic constituents in untreated by-product waters from coal conversion process development units.^{a/}

| Peak # | Compound | Concentration in mg. per liter | | | |
|--------|--------------------------------------|--------------------------------|-----------------|----------|----------|
| | | Slagging gasifier | Project Lignite | SYNTHANE | SYNTHOIL |
| 1 | methanol | 900 | 5000 | 140 | 80 |
| 2 | ethanol | <10 | 320 | <10 | 10 |
| 3 | acetonitrile | 500 | 320 | 210 | 40 |
| 4 | isopropanol | -- | { 5600 | -- | 30 |
| 5 | acetone | 540 | { | 950 | 200 |
| 6 | carbon disulfide | { 400 | { 10,200 | { 1400 | 40 |
| 7 | acetic acid | { | { | { | -- |
| 8 | propionitrile | 60 | 30 | 40 | <10 |
| 9 | 2-butanone | 100 | 1100 | 230 | 100 |
| 10 | propionic acid | 30 | 3400 | 30 | -- |
| 11 | 3-methyl-2-butanone | 30 | 50 | 80 | <10 |
| 12 | butyronitrile | 10 | <10 | <10 | <10 |
| 13 | 2-pentanone | 30 | { 130 | { 20 | 20 |
| 14 | i-butyric acid | -- | { | { | -- |
| 15 | n-butyric acid | <10 | 630 | <10 | -- |
| 16 | valeronitrile | 10 | 20 | <10 | <10 |
| 17 | cyclopentanone | { 30 | { 160 | { 40 | 20 |
| 18 | i-valeric acid | { | { | { | -- |
| 19 | n-valeric acid | 20 | 200 | <10 | -- |
| 20 | methylcyclopentanone | 20 | 50 | 10 | 20 |
| 21 | n-caproic acid | 50 | 60 | 70 | -- |
| 22 | phenol | 2700 | 4700 | 3100 | 3300 |
| 23 | C ₂ -furan ^{b/} | 80 | 100 | 70 | -- |
| 24 | aniline | 40 | -- | 30 | 140 |
| 25 | o-cresol | 550 | 980 | 560 | 1300 |
| 26 | m- and p-cresols | 1100 | 1800 | 1100 | 1900 |
| 27 | C ₄ -furan ^{b/} | 90 | -- | 40 | -- |
| 28 | 2,6-xylenol | 30 | 30 | 30 | 110 |
| 29 | o-ethylphenol | 40 | 80 | 50 | 160 |
| 30 | 2,4- and 2,5-xylenols | 130 | 210 | 130 | 280 |
| 31 | 3,5-xylenol and p-ethylphenol | 140 | 280 | 160 | 300 |
| 32 | 2,3-xylenol | 50 | 60 | 50 | <10 |
| 33 | 3,4-xylenol | c/ | { | { | -- |
| 34 | 2-isopropylphenol | { 60 | { 90 | { 50 | <10 |
| 35 | C ₅ -furan ^{b/} | { | { | { | -- |
| 36 | C ₃ -phenol ^{b/} | 10 | -- | -- | 20 |

Table 1. Organic constituents in untreated by-product waters from coal conversion process development units.^{a/} (Continued)

| Peak # | Compound | Concentration in mg. per liter | | | |
|--------|--|--------------------------------|-----------------|----------|----------|
| | | Slagging gasifier | Project Lignite | SYNTHANE | SYNTHOIL |
| 37 | C ₃ -phenol* | 10 | -- | -- | 10 |
| 38 | C ₃ -phenol and naphthalene | -- | 70 | 20 | -- |
| 39 | 3-ethyl-5-methylphenol | { <10 | { 30 | { 10 | { 20 |
| 40 | catechol | | | | |
| 41 | 2,3,5-trimethylphenol _{b/} | <10 | 20 | 10 | <10 |
| 42 | resorcinol, C ₃ ^{b/} phenol ^{b/} and C ₄ -phenol ^{b/} | -- | 50 | 10 | 30 |

^aThe data obtained on SYNTHANE and SYNTHOIL by-product waters are similar to results obtained on many other water samples from these processes. The results obtained on Project Lignite and fixed-bed slagging gasification by-product waters represent the analysis of a single sample from each process.

^bRefers to the number of alkyl carbons. These compounds were identified on the basis of mass spectrometric data only. All other compounds listed were identified on the basis of mass spectrometric data and confirmed by chromatographic experiments.

^cIncludes 3, 4-xylene and C₅-furan, while 2-isopropylphenol was not detected.

Table 2. Organic sulfur constituents identified in an untreated by-product water from the SYNTHANE process development unit.

| <u>Peak No.</u> | <u>Compound</u> |
|-----------------|--------------------------------|
| 1 | carbon disulfide ^{a/} |
| 2 | thiophene |
| 3 | 2-methylthiophene |
| 4 | benzothiophene |

^aCompounds were identified on the basis of co-chromatographic experiments.

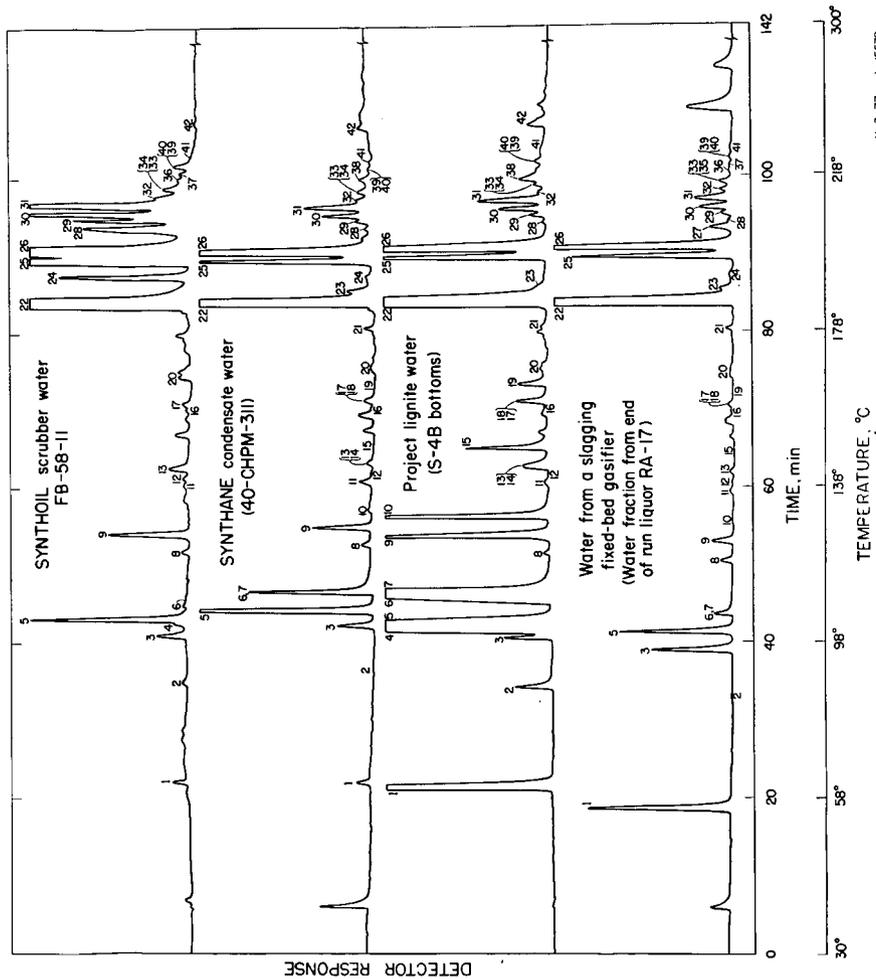


Figure 1. Chromatographic profile of by-product waters from coal conversion processes. The numbered compounds are identified in Table 1.

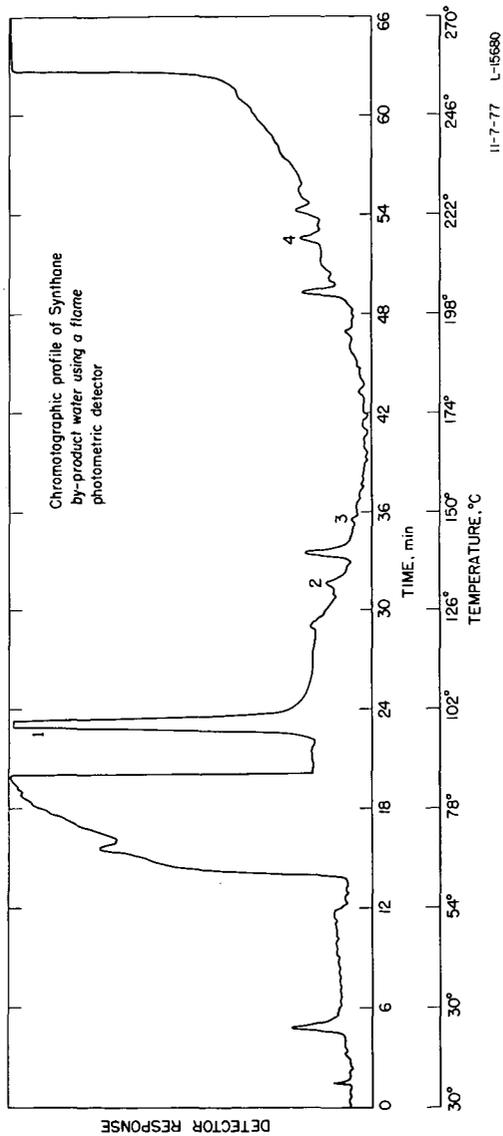


Figure 2. Chromatographic profile of a SYNTHANE by-product water using a sulfur specific flame photometric detector. The numbered compounds are identified in Table 2. These compounds were identified on the basis of co-chromatographic experiments only.

While monitoring the trace volatile polar organics in SYNTHOIL and SYNTHANE by-product waters, it was determined that the same compounds are present irrespective of minor changes in process conditions; however, the concentrations in which components are present can change significantly with changes in plant operating conditions.

The results of this study agree reasonably well with those reported by other investigators. In particular the chromatographic profile of SYNTHANE condensate water and overall results obtained by Ho, et al. (3) are very similar to that shown here. Many of the compounds identified earlier by Schmidt (1) have also been observed in this investigation. Although the mass spectrometric data obtained by Ellman (4) and co-workers on the organic content of by-product water from a fixed-bed slagging gasifier indicated many relatively non-volatile compounds, the results of that investigation support our findings that phenol and cresols are the major components. Further, Kavan and Basyrova (5) have identified ketones and an alcohol in by-product water from the "pressure gasification" of coal and these results are in agreement with those reported here.

The detection of alcohols and nitriles in these by-product waters is interesting. To our knowledge, this is the first report in which nitriles have been positively identified and quantitated in products formed during the hydroliquefaction or gasification of coal. Although alcohols have been previously reported in gasification products (5), they have not, to our knowledge, been positively identified and quantitated in products formed during the hydroliquefaction of coal. The origin of alcohols in the by-product waters is unknown; however, three routes to their formation are reasonable. Alcohols could be: 1. the pyrolysis or hydrogenolysis products of coal or lignite; 2. formed by catalytic reaction of synthesis gas (CO and H₂); or 3. formed by secondary reactions occurring in the aqueous phase. Alcohols are present in highest concentration in the by-product water from Project Lignite. In this process, lignite is solvent-refined in the presence of CO and H₂, using the naturally occurring mineral constituents of lignite as catalysts. CO and H₂ are known to react in the presence of some catalysts to form methanol as well as other products (9, 10). Alcohols are known to be products formed during the Fischer-Tropsch reaction. It is conceivable that at least some of the alcohols detected in by-product water from Project Lignite were formed by catalytic conversion. The SYNTHOIL process does not use CO, and therefore the small amounts of alcohols in SYNTHOIL by-product water were probably formed by routes 1 and/or 3. The alcohols detected in by-product waters from SYNTHANE and the slagging fixed-bed gasification process may have been formed from any one or a combination of the three suggested routes.

The presence of naphthalene, which was found in some of these by-product waters, is significant and indicates that higher homologs of polynuclear aromatic hydrocarbons (PAH's) may be present. This is particularly true in light of the recent mass spectrometric results of Ellman, et al. (4) who detected PAH's in by-product water from the slagging fixed-bed gasifier. Because many PAH's are known or suspected carcinogens, it is important to determine their exact nature and level in these waters. The analytical techniques used in this investigation employing Tenax GC are not effective in the analysis of higher homologs of PAH's.

Several homologous series of organic compounds have been detected, including alcohols, nitriles, ketones, carboxylic acids, furans, and phenols. In general, the first member of each homologous series is present in highest concentration. This is probably due to the higher water solubility of the lower homologs.

Gas chromatography using direct aqueous injection on Tenax GC is an excellent technique for rapidly and reproducibly monitoring the trace volatile polar organics in by-product waters from coal conversion processes. The gas chromatographic analysis can be completed in less than two hours and may be entirely automated and computerized using an autosampler and chromatographic data system. Further, little sample preparation time is required, and no prior concentration of components is needed. These characteristics of the analysis suggest that the gas chromatographic techniques employed in this research could be used online within a coal conversion plant to monitor trace volatile polar organic constituents of by-product waters.

The overall trace volatile polar organic contents of the four by-product waters investigated are very similar although a few significant differences exist. This study implies that, since the volatile polar organic contents of the waters from four different coal conversion processes are very similar, it may be possible to develop a single waste water treatment technology that is effective in treating the by-product waters from more than one coal conversion process.

It should be emphasized that the by-product waters investigated were untreated. The present investigation not only provides detailed quantitative analytical data for by-product waters from selected coal conversion process development units, but also provides an indication of the types of materials that may be present in waters from larger scale-up units.

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