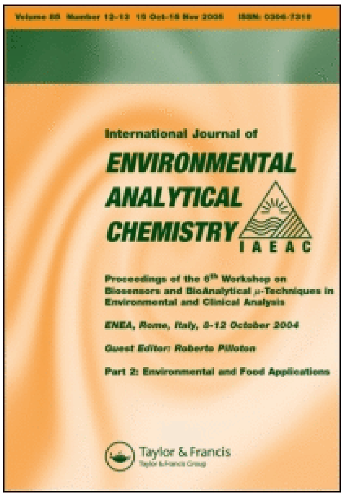

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Characterization of Major and Minor Organic Pollutants in Wastewaters from Coal Gasification Processes†

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In order to investigate the feasibility of anaerobic biological treatment for wastewaters generated from thermal gasification processes of coal, a characterization program was implemented whose major effort consisted in the elucidation of specific organic constituents contained in the wastewater. Solvent extraction in acid and base conditions followed by glass capillary gas chromatography in combination with several detectors (i.e., FID, NPD, and MS-DS) were employed for the investigation of major and minor "extractable" organic constituents. Direct aqueous injection on a polar glass capillary column (i.e., OV-351) was used for the major "nonsolvent extractable" organic constituents amenable to GC. The identity of 28 organic compounds was confirmed by comparison with pure standards. Phenol, the three cresol isomers, 5,5-dimethyl-hydantoin and 5-methyl,5-ethylhydantoin were identified as major wastewater constituents. Several substituted phenols (e.g., methyl, dimethyl,

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trimethyl, methylethyl, hydroxy and methoxy), pyridines, anilines, quinolines, PAHs, dibenzofuran and aldehydes were either confirmed or tentatively identified as minor wastewater constituents. Although the organics identified did not account for the total organic content, which implies the presence of still unidentified highly polar compounds, the information was utilized to set a data base for monitoring the biological treatment operations. Process monitoring data indicated that several organics (i.e., 5,5-dimethyl-hydantoin, 5-methyl,5-ethylhydantoin, o-cresol, m-cresol and p-cresol) were only partially removed by the treatment process employed.

KEY WORDS: Characterization of coal gasification wastewater, polar and non-polar WCOT, direct aqueous injection analysis.

INTRODUCTION

Technologies for producing synthetic fuels from coal have been the focus of major developments during the past years in an attempt to establish a competitive industry which could supplement or partially replace current energy sources. A number of pilot-scale coal gasification plants are being evaluated around the country to produce a raw gas that is then upgraded to yield a methane-rich product. Along with pilot plant coal gasification tests to improve process efficiency, environmental assessment studies are being conducted to establish the nature and extent of waste associated with such processes and consequently to assess the feasibility of current waste treatment operation that would better satisfy the economical as well as the environmental and health factors. A major source of concentrated waste in coal gasification plants occurs under the form of wastewaters generated from gas cooling and quenching steps and, therefore, one of the major efforts currently taking place in this area consist of the evaluation of biological and physico-chemical wastewater treatment processes.

Anaerobic Fluidized Activated Carbon Filters (AFACF) have attracted the attention of investigators as a potential treatment process for such wastewaters after a few studies demonstrated its feasibility for synthetic wastewaters of similar nature.[1–3] Currently this institution is evaluating lab scale AFACF for the treatment of wastewater generated from the gasification of Indian Head lignite coal in the pilot plant operated by the Grand Forks Energy Technology Center of North Dakota (U.S.A.). As a part of the overall study and in order to properly assess the treatment potential of AFACF, a detailed characterization program is being undertaken to elucidate major and minor specific organic constituents contained in the coal gasification wastewater. A number of studies have been reported on the nature of organic constituents in the aqueous by-products of fossil fuel conversion processes.[4–6] However, it has been found that the chemical composition of these wastes vary considerably depending on the type of coal, process employed, and operating conditions including the degree of recycle of the wastewater. Furthermore, since the biodegradability of different organic constituents varies markedly, the behavior of specific refractory organic compounds under the experimental conditions of AFACF would also provide information which could be utilized to assess their ultimate fate in the environment. In this study, conventional liquid-liquid solvent extraction in acid and alkaline conditions has been selected for separating the complex mixture of "extractable" organic constituents into acid base and neutral fractions before qualitative and quantitative analysis by High Resolution Gas Chromatography-Mass Spectrometry (HRGC-MS). An OV-351 Wall Coated Open Tubular (WCOT) column has been investigated for the analysis of major non-extractable organic constituents of the wastewater by Direct Aqueous Injection (DAI). The information thus far generated has been integrated in a reference data base of organic compounds present in coal gasification wastewater and used for monitoring the AFACF. As coal gasification pilot plants are upgraded to commercial large scale facilities, it is expected that a relatively simple analytical scheme and the availability of a data base of organic compounds present in waste streams, might be valuable in the pursuit of a competitive industry as well as in the preservation of the environment.

EXPERIMENTAL

Coal gasification wastewater

The wastewater used in this study was obtained from gasification of Indian Head lignite coal in the slugging fixed-bed pilot plant operated by the Grand Forks Energy Technology Center of North Dakota (U.S.A.). A description of the pilot-plant effluent flow distributions and test program are provided by Ellman, et al.[7] It is important to recognize that the pilot plant wastewater employed in this investigation is representative only in a qualitative fashion of quench water that may be produced in a larger-scale slugging fixed-bed coal gasification plant.

The wastewater was preserved by freezing and shipped in 1 gallon plastic containers via freezer truck. Details concerning procedures employed in wastewater collection and transport, and long term preservation studies were reported by Stamoudis, et al.[8] and Luthy, et al.,[9] respectively. A description of the AFACF investigated in this study and the gross characteristics of the wastewater were reported elsewhere.[10]

Analytical techniques

The organic solvents were all of "distilled in glass" grade as supplied by Burdick and Jackson Labs (Muskegon, MI, U.S.A.). All of the organic compounds used for identity confirmation were purchased from Aldrich (Milwaukee, WI, U.S.A.) and Fisher Scientific (Fair Law, NJ, U.S.A.) with purities ranging between 96% and 99% as specified in the manufacturer's literature. Deuterated organic compounds were obtained from Merck Sharp and Dohme (St. Louis, MO, U.S.A.). The extraction scheme used in this investigation is shown in Figure 1. The wastewater was filtered on a 0.45 μm filter before 500 ml or 200 ml aliquots were adjusted to pH = 2 and extracted with methylene chloride (50 × 50 × 50 m) in separatory funnel.

The methylene chloride solutions were concentrated to approximately 5 ml in a Kuderna–Danish apparatus and for the base fraction adjusted to 1 ml under a stream of nitrogen. A Hewlett–Packard 5830-A GC (Avondale, PA, U.S.A.) equipped with a split-splitless capillary injection system, a flame-ionization and a nitrogen-phosphorous detector was employed for the acid, base and neutral fractions, and DAI analyses. A Shimadzu GDM-1 glass drawing machine was used to draw glass capillaries (ca. 100 m × 0.3 mm I.D.) from soft-glass tubing (121 × 0.6 cm I.D.; Kimble, Toledo, OH, U.S.A.), which had been washed with a detergent solution and rinsed with "organic free" water and acetone. The glass capillaries were subsequently leached and deactivated according to the procedures

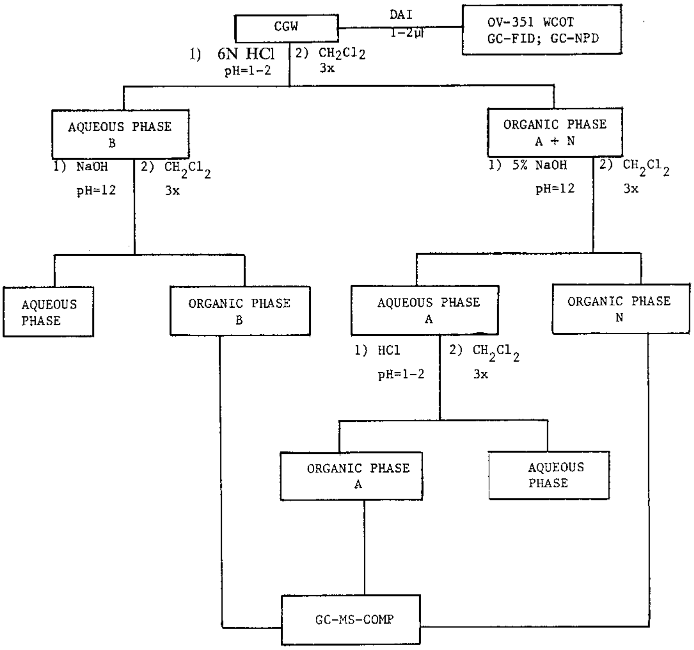

FIGURE 1 Analytical scheme adopted for characterization of coal gasification wastewater.

proposed by Grob.[11] These capillaries (ca. 30 m) were then coated by the static method[12] with SE-54 or SE-30 silicone gum-phases (ca. 0.2 µm film thickness). The OV-351 WCOT column was prepared by static coating of a fused silica capillary (ca. 30 m × 0.35 mm I.D.; SGE, Austin, TX, U.S.A.) or of a glass capillary which had been only leached. Tentative identification and confirmation was carried out by means of a Finnigan-Mat 4023 MS (San José, CA, U.S.A.), equipped with Data General NOVA 3 computer and Incos software package, and interfaced with a Hewlett–Packard 5830-A GC, as described elsewhere.[13] Fused silica tubing served as the sample transfer line between the column effluent and the ionization source. The MS conditions were as follows: ionization mode, electron impact; electron multiplier, 1500 V; electron energy, 70 eV; emission current, 0.5 mA; mass range, 45–450 a.m.u.; and scan rate, 0.95 sec/decade.

The MS was calibrated with perfluorotributyl amine, and a solution of decafluorotriphenylphosphine was subsequently injected on to the chromatograph to verify the calibration thus obtained. Tentative identification of the organic compounds was performed by computerized search against the National Burea of Standard library, consultation of the Registry of Mass Spectral Data,[14] and by considering the fragmentation of the organic compounds in mass spectrometry. Confirmation of the identity of selected compounds was performed by comparing the retention time data and mass spectrum of a standard solution of pure compound analyzed under identical GC-MS conditions.

RESULTS AND DISCUSSION

Reconstructed ion chromatograms (RIC) of the acid, base and neutral fractions obtained by liquid-liquid solvent extraction (see Figure 1) are presented in Figure 2. It should be pointed out that the organics in the acid and neutral fractions were concentrated by a factor of × 100 (i.e., 500 ml wastewater to 5 ml organic extract), whereas the base fraction was concentrated by a factor of × 500 (500 ml wastewater to 1 ml organic extract). Moreover, a split injection mode was used for the acid and neutral fractions versus a splitless mode for the base fraction. This explains the relatively higher GC-MS response of the base fraction (see Figure 2), although the actual concentration of the organic bases in the sample is smaller (see Table 1). Identities and estimated concentrations of the organic constituents in wastewater are summarized in Table I. It is important to point out that the estimated concentrations of each individual compound was calculated by assuming a uniform extraction efficiency and instrumental response. Since the primary scope of this characterization consisted of monitoring the performance of AFACF, the change in relative concentration values of influent versus effluent, rather than absolute concentration values, were considered satisfactory. However, labeled organic compounds (i.e., phenol-d_6, 1,4-dichlorobenzene-d_4, naphthalene-d_8 and perylene-d_{12}) were used for analytical control and added to the wastewater before starting the extraction procedures. It is planned to evaluate recovery efficiencies of each identified organic in coal gasification wastewater in future work.

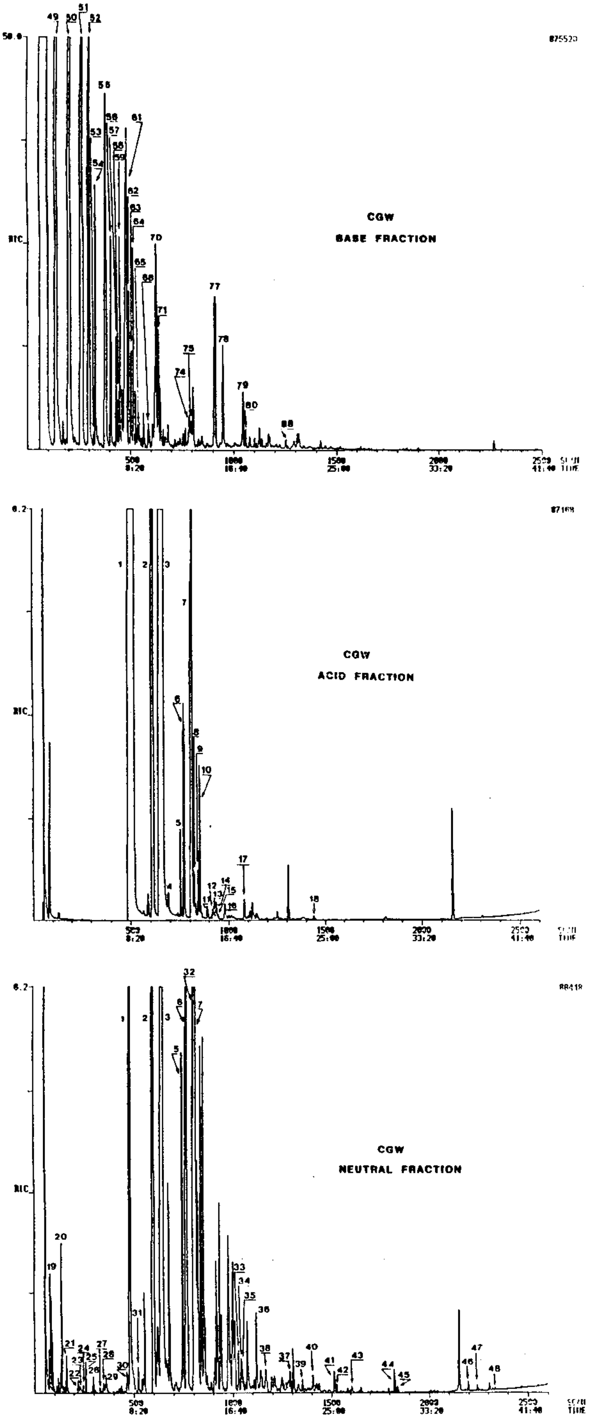

FIGURE 2 RIC traces of acid, base and neutral extracted fractions of coal gasification wastewater. SE-54 WCOT; 40° (3 min.)—290°C 5°C/min.; acid and neutral 1 μl split mode (split ratio ca. 50:1); base 1 μl splitless mode.

TABLE I

Organic compounds determined in watewater from gasification of Indian Head lignite

Peak no. (see Fig. 2)	Compound	Estimated concentration (mg/L)
	Acid Fraction	
1	Phenol[a]	5,600
2	o-Cresol[a]	640
3	m- + p-Cresol[a]	1,840
4	2,6-Dimethylphenol[a]	12
5	2-Ethylphenol[a]	50
6	2,4-Dimethylphenol[a] + 2,5-Dimethylphenol[a]	358
7	3,5-Dimethylphenol[a] + 3-Ethylphenol[a] + 4-Ethylphenol[a]	968
8	2,3-Dimethylphenol[a]	40
9	Dimethoxybenzene or C_2-Benzenediol	46
10	3,4-Dimethylphenol[a]	158
11	Unknown	
12	C_3-Phenol	10
13	C_3-Phenol	8
14	C_3-Phenol	20
15	C_3-Phenol	4
16	C_3-Phenol	24
17	C_3-Phenol	20
18	Naphthol	4
	Neutral Fraction	
19	Benezene	1.1
20	Toluene	1.4
21	Cyclopentanone	0.8
22	Aliphatic hydrocarbon	0.3
23	C_1-Cyclopentanone	0.3
24	Ethylbenzene	0.1
25	o-Xylene	0.5
26	m- and p-Xylene	0.3
27	Methoxybenzene	0.2
28	Benzonitrile	0.7
29	C_3-Benzene	0.6
30	C_1-Methoxybenzene	0.5
31	C_3-Benzene	2.0
32	Naphthalene	0.7
33	C_1-Naphthalene	2.1
34	Indole	1.0
35	C_1-Naphthalene	0.9
36	C_2-Benzaldehyde	2.2
37	Acenaphthylene	0.6
38	1,1'-Biphenyl	0.4
39	Dihydroacenaphthylene	0.3
40	Dibenzofuran	0.5
41	Fluorene	0.5
42	C_3-Naphthalene	0.1
43	C_1-Dibenzofuran	0.2
44	Phenanthrene	0.6
45	Anthracene	0.2
46	Fluoranthene	0.2
47	Pyrene	0.1
48	C_1-Pyrene	0.04

TABLE I (continued)

Peak no. (see Fig. 2)	Compound	Estimated concentration (mg/L)
	Base Fraction	
49	Pyridine[a]	4.62
50	2-Picoline[a]	3.71
51	3-Picoline + 4-Picoline[a]	2.53
52	C_2-Pyridine	1.4
53	Unknown	
54	C_2-Pyridine	0.29
55	C_2-Pyridine	1.06
56	C_2-Pyridine	0.32
57	C_2-Pyridine	0.12
58	C_2-Pyridine	0.04
59	Unknown	
60	C_2-Pyridine	0.07
61	Aniline	1.10
62	C_3-Pyridine	0.16
63	C_2-Pyridine	0.12
64	C_3-Pyridine	0.20
65	Unknown	
66	C_3-Pyridine	0.02
67	C_3-Pyridine	0.02
68	C_3-Pyridine	0.01
69	C_3-Pyridine	0.03
70	C_1-Aniline	0.53
71	C_1-Aniline	0.18
72	Unknown	
73	C_2-Aniline	0.01
74	C_3-Pyridine	0.06
75	C_2-Aniline	0.03
76	C_3-Pyridine	0.01
77	Quinoline	0.49
78	Isoquinoline	0.01
79	C_1-Quinoline	0.08
80	C_1-Quinoline	0.03
81	C_1-Quinoline	0.02
82	C_1-Quinoline + Unknown	
83	C_1-Quinoline	0.01
84	C_1-Isoquinoline or C_1-Quinoline	0.01
85	C_1-Quinoline	0.01
86	C_1-Isoquinoline	0.01
87	C_2-Quinoline	0.01
88	C_2-Quinoline	0.02
	DAI	
	5,5-Dimethylhydantoin	456
	5-Methyl,5-Ethylhydantoin	174
	Acetic acid	125
	Propionic acid	64

[a]Confirmed with Pure Standard.

Examination of Table I reveals that the constituents of the acid fraction are present in larger quantities than any one of the other two fractions. Identity confirmation of the major constituents and their chromatographic behavior on SE-54 and SE-30 WCOT columns was therefore pursued by analyzing standard solutions of several pure compounds. It was found that two cresols (i.e., meta and para) and two C_2-phenols (i.e., 2,5-dimethylphenol and 2,4-dimethylphenol) were coeluting. Other C_2-phenol isomers (i.e., 4-ethylphenol, 3,5-dimethylphenol and 3-ethylphenol) showed close but not identical retention behavior and, although separated under low column loading, they appeared as a broad single peak when present in high concentration (see Figure 2, peak No. 7). In the neutral fraction it is noteworthy the presence of several well known or potentially highly toxic organics (e.g., PAHs, dibenzofurans, etc.). However, most of their concentrations appear to be within the parts per billion (ppb) level range, except in the case of naphthalene and a few alkylated isomers. In this fraction are also noticeable several phenols which were carried over from the acid fraction during solvent extraction separation. This may be partially attributed to the high concentration that occurs in the wastewater. However, in the estimation of the concentration reported in Table I the amount observed in the neutral fraction was also taken into account. Pyridine, picoline isomers, a few C_2-alkylated pyridines and aniline were among the major constituents of the base fraction. Other organic compounds tentatively identified included quinoline, isoquinoline and several C_1-, C_2- and C_3-alkyl pyridines, anilines and quinolines.

Recently the investigation of major non-extractable constituents of a similar wastewater was pursued by Olson, et al.[15] by treating the wastewater, which had undergone the conventional solvent extraction scheme, with activated carbon and by desorbing the organics with boiling alcohol. Hydantoin and a number of alkylated isomers were identified by GC-MS. The high concentration level of a few of these constituents (i.e., parts per million level), led us to investigate a direct acqueous injection (DAI) method for their monitoring. A OV-351 WCOT column was found adequate for the separation of several hydantoins, particularly for 5,5-dimethylhydantoin and 5-methyl,5-ethylhydantoin which are the most abundant among this class of compounds in coal gasification wastewater (see Figure 3). Furthermore, this column showed a higher degree of flexibility in that it enabled the separation and DAI analysis of other classes of organic compounds present in coal gasification wastewater as shown in Figure 3. Phenols, fatty acids and hydantoins were adequately separated in less than thirty minutes under optimized GC oven temperature program conditions, although phenol and o-credol coeluted. It is noteworthy to point out the relative higher temperature stability of this stationary phase compared to similar WCOT columns (e.g., FFAP) as demonstrated by the low "bleeding" experienced up to 250°C. Furthermore, the selectivity of the alkali flame ionization detector for nitrogen containing compounds was successfully exploited for the specific determination of hydantoins as shown in Figure 4.

The data obtained during the characterization study was used to generate a reference data base for the wastewater organic constituents thus far identified. A monitoring program of the AFACF is presently undergoing to assess the feasibility of this treatment in the removal and/or transformation of refractory and potentially toxic organic constituents of the wastewater. Preliminary results on the behavior of specific organic constituents were very useful in pointing out the successes and shortcomings of the AFACF. As shown in Figures 5 and 6, although the major part of the organic compounds appeared to be removed or biologically transformed, several wastewater constituents persisted in the AFACF effluent (i.e., o-cresol, m-cresol, p-cresol, 5,5-dimethylhydantoin and 5-methyl, 5-ethylhydantoin). Investigations are currently being pursued to establish a better understanding of their behavior under the operational conditions of the AFACF.

CONCLUSIONS

The characterization of coal gasification wastewaters by conventional liquid-liquid solvent extraction and GC-MS, and by direct aqueous injection resulted in the identification of various classes of organic compounds. Phenol, the three cresol isomers, several dimethylphenol isomers, two alkylatedhydantoin isomers and free fatty acids were the major organic constituents thus far identified. In addition, several other minor organic constituents were

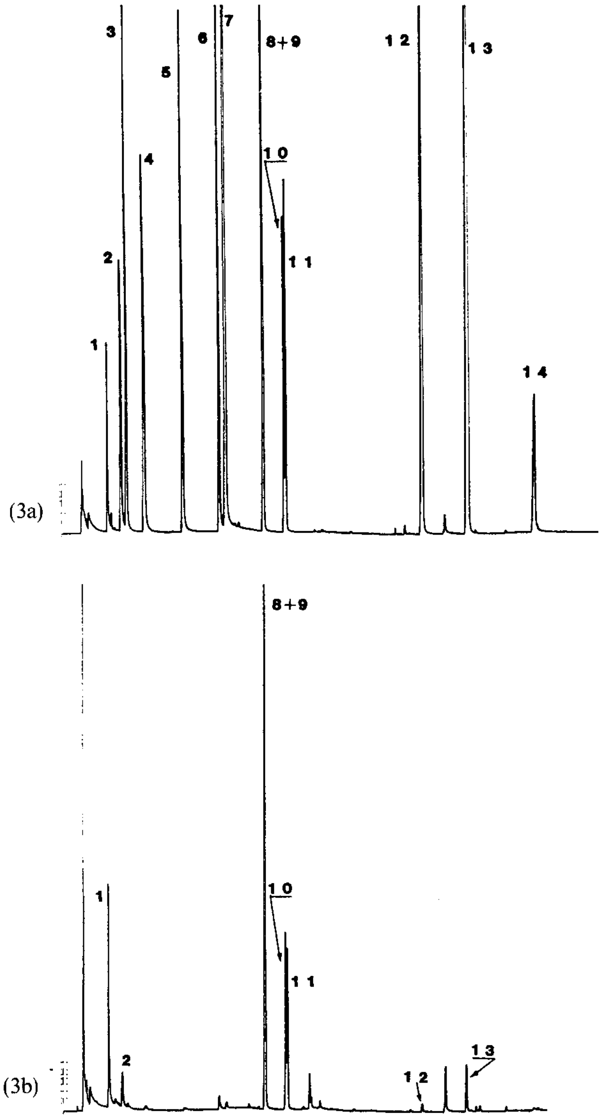

FIGURE 3 GC-FID traces of selected compound synthetic aqueous mixture (3*a*) and coal gasification wastewater (3*b*). OV-351 WCOT; 100°C (5 min.)—250°C (5 min.) 7°C/min.; 1 μl split mode (split ratio ca. 30:1).

1. Acetic acid
2. Propionic acid
3. Isobutyric acid
4. Butyric acid
5. Valeric acid
6. Caproic acid
7. Benzyl alcohol (I.S.)
8. Phenol
9. o-Cresol
10. p-Cresol
11. m-Cresol
12. Methylhydantoin
13. 5,5-Dimethylhydantoin
14. Hydantoin

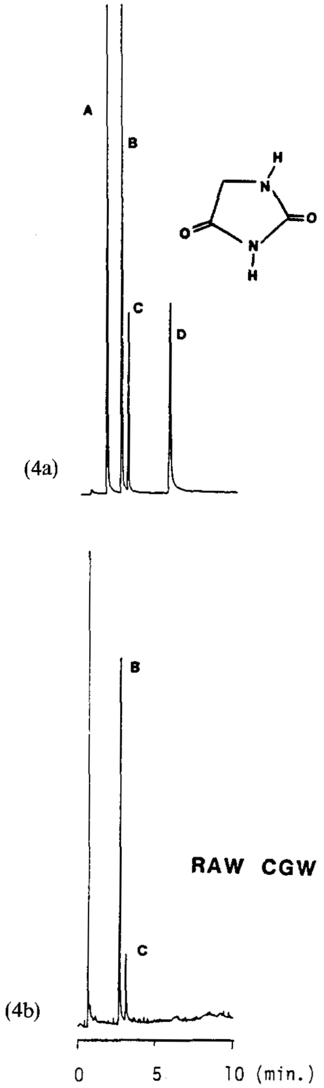

FIGURE 4 GC-NPD traces of aqueous solutions of selected hydantoins (4*a*) and coal gasification wastewater (4*b*). OV-351 WCOT; 200°C (0.5 min.)—215°C 2°C/min.

A. 1-Methylhydantoin
B. 5,5-Dimethylhydantoin
C. 5-Methyl,5-Ethylhydantoin
D. Hydantoin

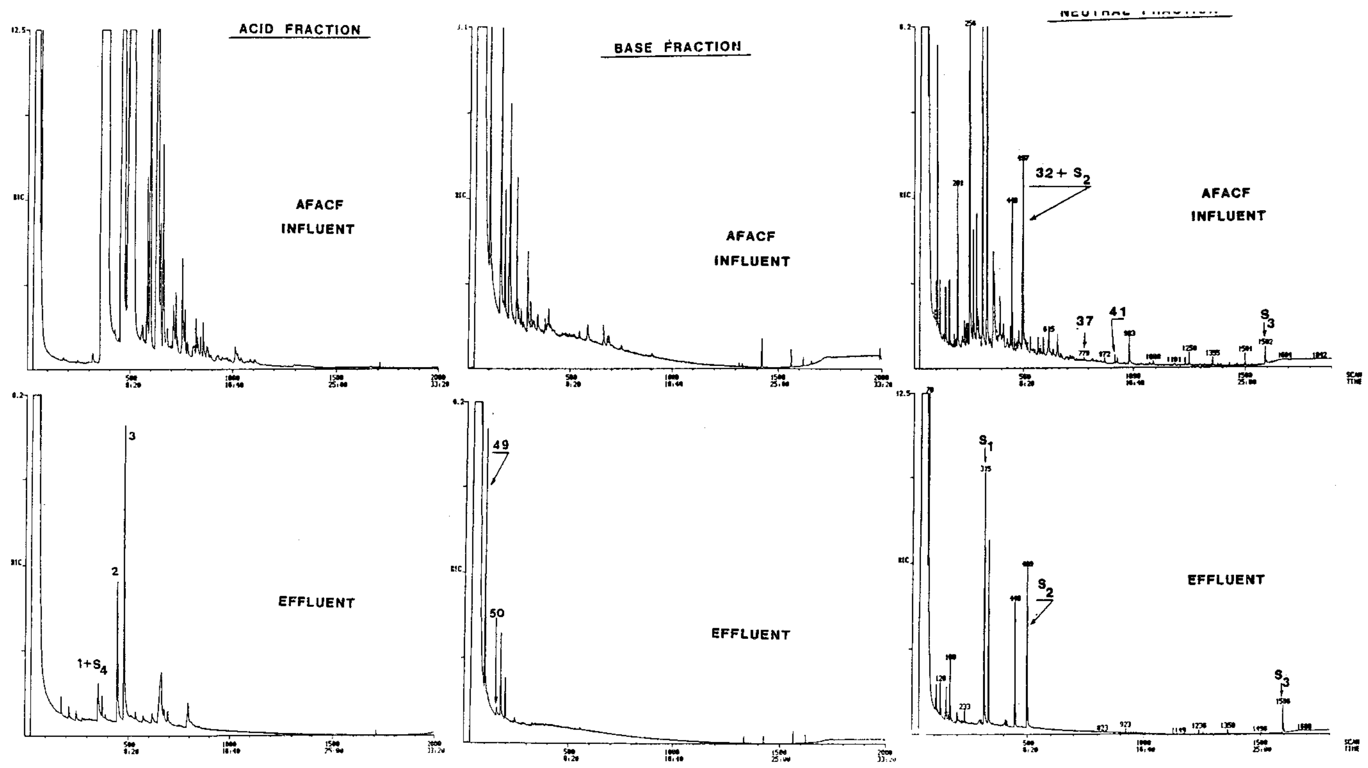

FIGURE 5 RIC of acid, base and neutral fractions of influent and effluent from AFACF. SE-30 WCOT; 40° (2 min.)—290° 10°C/min. S_1, 1,4-dichlorobenzene-d_4; S_2, naphthalene-d_8; S_3, perylene-d_{12}, S_4, phenol-d_6.

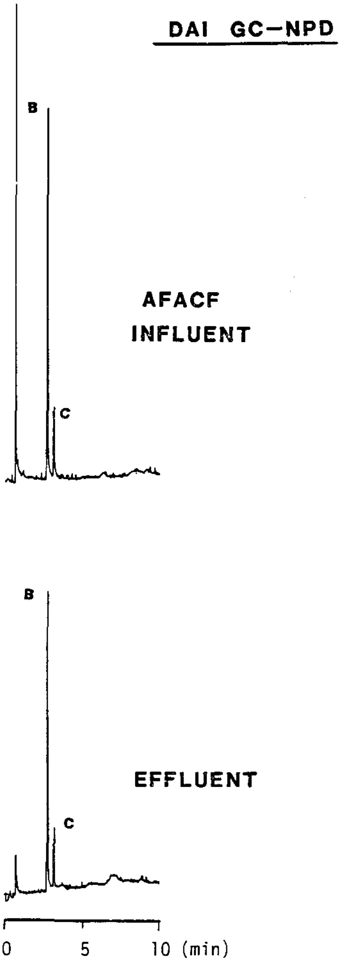

FIGURE 6 GC-NPD traces of influent and effluent of AFACF.

tentatively identified in the base, neutral and acid organic fractions including PAHs, dibenzofurans, indoles, ketones, pyridines, quinolines and anilines. These results compared favorably with previously reported list of tentatively identified organic constituents of similar wastewaters.[15,16] The use of a OV-351 WCOT column proved to be very effective in the separation and analysis of the major organic constituents in less than thirty minutes by DAI.

The use of the analytical scheme was implemented in the monitoring program of an anaerobic fluidized activated carbon filter for wastewater treatment. This resulted in useful information on the effectiveness of such treatment in the removal and/or biotransformation of specific organic compounds. Furthermore, it pointed out the shortcomings of the anaerobic biological treatment under certain operational conditions toward several refractory and potentially toxic organic constituents. It must be recognized, however, that the analytical scheme investigated in this study was not able to account for all the organic carbon present in the wastewater. This appears to indicate that other organic compounds more polar or hydrophilic in nature, need still to be elucidate. In addition, the complex nature of the coal gasification wastewater suggest the need for a fractionation scheme which would separate the organic compounds with similar behavior. Current efforts are therefore directed toward pursuing more comprehensive analytical schemes (e.g., Leenheer, et al.,[17] Giabbai, et al.[18]) which would provide a "complete" information to better assess economical as well as environmental and health factors involved in the establishment of a new industry.

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