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Biological Removal of Organic Constituents in Quench Waters from High-Btu Coal-Gasification Pilot Plants

V. C. Stamoudis and R. G. Luthy

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BIOLOGICAL REMOVAL OF ORGANIC CONSTITUENTS IN QUENCH WATERS FROM HIGH-BTU COAL-GASIFICATION PILOT PLANTS

by

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ABSTRACT

Studies were initiated to assess the efficiency of bench-scale, activated-sludge treatment for removal of organic constituents from coal-gasification process effluents. Samples of pilot-plant, raw-gas quench waters were obtained from the HYGAS process of the Institute of Gas Technology and from the slagging, fixed-bed (SFB) process of the Grand Forks Energy Technology Center. The types of coal employed were Bituminous Illinois No. 6 for the HYGAS and Indian Head lignite for the SFB process. These pilot-plant quench waters, while not strictly representative of commercial condensates, were considered useful to evaluate the efficiency of biological oxidation for the removal of organics.

Biological-reactor influent and effluent samples were extracted using a methylene chloride pH-fractionation method into acid, base, and neutral fractions, which were analyzed by capillary-column gas-chromatography/mass-spectrometry. Influent acid fractions of both HYGAS and SFB condensates showed that nearly 99% of extractable and chromatographable organic material comprised phenol and alkylated phenols. Activated-sludge treatment removed these compounds almost completely. Removal efficiency of base-fraction organics was generally good, except for certain alkylated pyridines. Removal of neutral-fraction organics was also good, except for certain alkylated benzenes, certain polycyclic aromatic hydrocarbons, and certain cycloalkanes and cycloalkenes, especially at low influent concentrations.

1 INTRODUCTION

Diminishing supplies of petroleum and natural gas have stimulated interest in processes that convert coal into synthetic liquid and gaseous products. High-Btu coal gasification entails the reaction of coal, steam, and oxygen at elevated temperature and pressure to produce a raw gas that can be upgraded to yield a methane-rich product. A number of pilot-plant coal-gasification tests are in progress to evaluate improved process efficiencies and to perform environmental assessment studies in conjunction with process development research. The purpose of this investigation is to characterize and to assess removal efficiencies for organic constituents from the biologically treated raw-gas quench condensates of two high-Btu coal-gasification pilot plants. This investigation will aid environmental assessment of coal conversion processes, as a review of the available

literature (Singer et al., 1978; Stamoudis, Luthy, and Harrison, 1979; White and Schmidt, 1978) has shown that very limited studies have been performed with actual pilot-plant or process condensates to address issues relevant to removal of trace organic constituents.

2 EXPERIMENTAL APPROACH

The quench waters selected for study were obtained from the HYGAS steam-oxygen pilot plant, operated by the Institute of Gas Technology of Chicago, Illinois, and from the slagging, fixed-bed (SFB) pilot plant operated by the Grand Forks Energy Technology Center (GFETC) of North Dakota. Descriptions of the pilot-plant effluent flow distributions and pilot-plant test program are provided by Jonardi et al. (1979) and Ellman et al. (1979) for the pilot-plant runs from which quench waters were obtained for the HYGAS and SFB processes, respectively. Quench waters from these processes were selected for study because: (1) they represent major DOE-sponsored coal gasification systems in an advanced state of development, (2) they are contaminated with organic pollutants, and (3) they have the biologically treatable characteristics that have been the subject of recent experimental investigations (Luthy and Tallon, 1978; Luthy et al., 1979)

2.1 SAMPLE REPRESENTATIVENESS

It is important to recognize that the pilot-plant quench waters used in this study are not representative in a quantitative sense of wastewaters that would be expected in a demonstration or commercial scale HYGAS or SFB coal-gasification plant. This is due to a number of critical factors that differ between pilot and conceptual larger scale facilities. These factors include gasifier operating conditions, raw gas-quenching design and efficiency, and differences in flow rates and combinations of various aqueous waste and process streams. The pilot-plant quench water samples used, however, are qualitatively representative of the types of trace organic contaminants that could be present in larger scale coal-gasification plant wastewaters. Given this perspective, it should be clear that the quench water concentrations reported here (biological-reactor influents and effluents) are not necessarily directly related to expected larger scale plant wastewaters and that comparisons of HYGAS and SFB quench water samples are only meaningful in the context of bench-scale biological reactor performance.

2.2 QUENCH WATER COLLECTION AND STORAGE

Details regarding procedures employed in quench water collection and transport are documented in reports by Stamoudis, Luthy, and Harrison (1979) and Stamoudis and Luthy (1979). Raw quench water was collected during HYGAS pilot-plant runs 62 and 64 and represented gasification of Illinois No. 6 bituminous coal. Quench water was collected in approximately 300- to 350-gal quantities from each run with effluent from run 64 being used primarily during the steady-state period of biological reactor testing. The slagging fixed-bed effluent was generated during gasifier run RA-52 with Indian Head lignite. Approximately 250 gal of decanted quench water was shipped to Carnegie-Mellon

University via freezer truck. It was necessary to provide means for storage of quench water samples because of the long-term duration of the biological treatability studies. In these investigations quench water storage was achieved by freezing until needed as feed for the biological reactors.

Raw quench water samples collected at the pilot-plant facilities were stored and shipped in plastic containers because of the large quantities of quench water being handled. Biological reactor effluent from the HYGAS study, also stored in a plastic container, was frozen because the biological oxidation experiment preceded by several months the trace-organics characterization studies. Biological reactor effluent from the SFB study was collected fresh and not stored in plastic containers. Although no studies were performed to assess the stability of trace organics in frozen samples, a recent Argonne National Laboratory (ANL) investigation of the stability of HYGAS quench water suggests that a high degree of stability for the extractable/chromatographable components could be expected (Raphaelian and Harrison, 1979).

2.3 QUENCH WATER PRETREATMENT

Representative raw quench water characteristics for the samples used in this investigation are given in Table 1. Raw quench water was pretreated to reduce excess alkalinity and ammonia concentrations by lime addition and air stripping. This pretreatment simulated the free and fixed-leg ammonia removal that would be expected in a commerical treatment train. It was found that ammonia-stripped HYGAS quench water could be processed through a biological reactor at full strength without dilution. However, a series of sequential and parallel tests with stripped SFB effluent in which feed strength and loading were varied independently showed that this wastewater could not be processed at full strength. Stable biological reactor performance was achieved by diluting to 33% strength with tap water. (Trace-organics characterization data reported later in Tables 4, 5, and 6 for treatment of SFB quench water were adjusted by a factor of three in order to express results on an equivalent undiluted basis.)

2.4 BIOLOGICAL OXIDATION

The biological reactors employed in this study were complete-mix, single-stage, air-activated sludge reactors with internal clarifiers. These reactors were operated under conditions whereby hydraulic residence time, mean bacterial-cell residence time, and feed strength were held as experimental constants. Dependent variables were steady-state values of mixed-liquor volatile suspended solids (MLVSS) and effluent substrate concentration. The biological reactors were acclimatized to the quench waters over a sufficiently long period of time that the reactors were subjected to three complete bacterial sludge wasting cycles prior to the collection of steady-state performance data. Reactors were then operated for 7-8 weeks during which a 2-3-week composite sample was collected for trace-organics analysis.

Table 1. Representative Raw Quench Water Characteristics during Biological Oxidation Studies[a]

Parameter[b]	HYGAS[c,d] (Run 64)	SFB[d,e] (Run RA-52)
COD	4,050	25,400
Phenolics	710	5,100
NH_3-N	3,700	5,200
NO_3	<2	<2
Organic-N	10	90
CN^-_{tot}	0.3	12
SCN^-	28	140
S^{2-}	140	150
SO_4^{2-}	180	150
P	1	13
Alkalinity (as $CaCO_3$)	12,600	18,400
Total Acidity (as $CaCO_3$)	--	24,000
Total Oil & Grease	--	300
Soluble Oil & Grease	--	190
Conductivity (μmhos/cm)	19,000	20,000
pH (units)	7.8	8.4

[a] Refer to section on sample representativeness for limitations on data interpretation.

[b] All units in mg/L except as noted.

[c] Quench water comprised a 1:1 mixture of cyclone and quench condensates.

[d] HYGAS data from Luthy and Tallon (1978); SFB data from Luthy, Sekel, and Tallon (1979).

[e] Double-decanted gasifier quench condensate.

2.5 ANALYTICAL TECHNIQUES

Organic constituents were extracted by methylene chloride, using generally accepted techniques, into acid, base, and neutral fractions. The extraction scheme used in this investigation is shown in Fig. 1. Emulsion problems were minimized by manipulating the sample to enhance phase separation (Stamoudis et al., 1979; Stamoudis and Luthy, 1979).

Organics in acid, base, and neutral fractions were analyzed via gas-chromatography/mass-spectrometry (GC/MS) using a Hewlett-Packard 5984A GC/MS equipped with a Hewlett-Packard 5934A Data System. A 5830 Hewlett-Packard GC was used in place of the 5700-series Hewlett-Packard GC normally delivered with the 5982A GC/MS. Glass capillary, wall-coated, open-tubular columns were used (Perkin-Elmer, 0.25-mm ID, 50-m-long, OV-101). The temperature was programmed from 20 to 240°C at 2°/min, with a 2-min hold at 20°C. Compound identification was based on mass spectra and known retention times.

The percentage removal of individual compounds was estimated by obtaining the total-ion chromatograms of both influent and effluent and comparing the total-ion counts of the various peaks. The assumptions employed were:

a. Each compound found in the influent also could be present in the effluent (with the same chromatographability),

b. The concentration levels of the compounds are in the optimum range of linearity in a total-ion (or single-ion) vs concentration plot, and

c. The extraction yields for individual compounds in the influent and effluent are the same.

The first assumption is a plausible one and a corollary to this is that, if a compound is not detectable in the effluent, it is 100% removed. In order to substantiate the second assumption it would be necessary to determine the total-ion (or single-ion) area as a function of concentration for each compound or for a few compounds serving as models for the others. Figure 2 shows the results of such a study involving benzonitrile, which gave good linearity over a concentration range 1-100 ng/μ L. The scope of this investigation did not permit the evaluation of total-ion and single-ion areas as a function of concentration for a large number of compounds, hence model species were used to estimate concentration values. Benzonitrile is an example of a neutral-fraction compromise-model compound; its mass spectrum is typical of unsubstituted or singly substituted aromatic compounds, it has medium polarity, and it is present in the influent fractions. Limited studies were done on other organic compounds, used as models for purposes of estimation of concentration levels, with phenol, cresol, xylene, trimethylpyridine, ethylphenol, naphthalene, anthracene, acridine, and carbazole. Since removal efficiencies were estimated by comparing total ions of the same compound, removal efficiencies are reported with greater confidence than concentration values.

The assumption of uniform extraction efficiency is probably the least substantiated. Recovery studies for 16 standard compounds from distilled

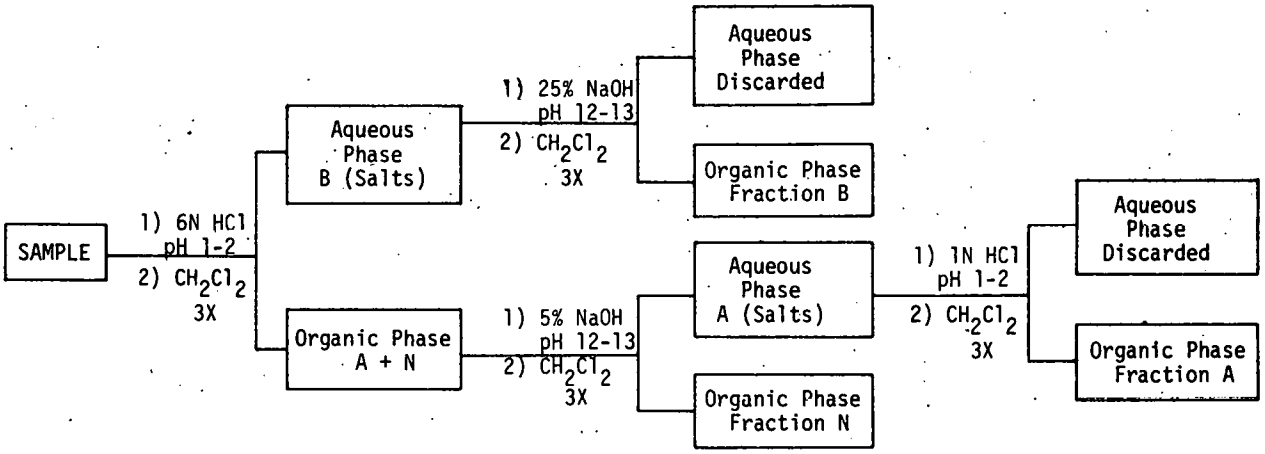

Fig. 1. Extraction Scheme for Biological Reactor Influent and Effluents Samples

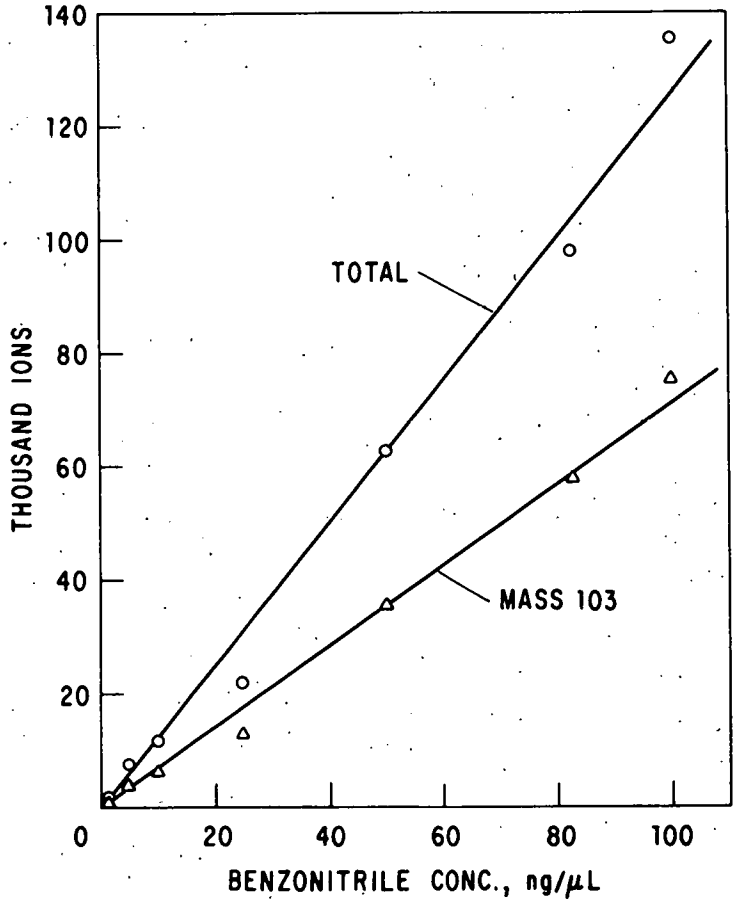

Fig. 2. Plot of Total-Ion and Single-Ion (Mass 103) Areas vs Concentration for Benzonitrile

Table 2. Percent Recoveries of Organics Extracted from Spiked Distilled Water Based on GC Analysis

Compound	% Recovery
o-Xylene	65
Mesitylene	65
3-Octanone	85
1-Heptanol	86
n-Butylbenzene	56
Trimethylpyridine	54
Phenol	82
o-Cresol	95
o-Ethylphenol	105
Naphthalene	68
Dimethylnapthalene	91
Anthracene	99
d_{10}-Anthracene	102
Acridine	78
Carbazole	101
Pyrene	105
Average for 16 compounds	84

water are presented in Table 2. These data show that recoveries of the organics varied considerably, from 54 to 105%, with an average value of 84%. Furthermore, it is known that concentration levels (Warner, 1976), matrix effects, and the extent of emulsion in extraction affect solvent extraction yields. Nonetheless, since the scope of this study was to estimate only percent removals of organic constituents, the assumption of uniform extraction yield was followed, using a convenient procedure. It is planned to evaluate recovery efficiencies of organics in coal-gasification quench water samples in future work.

3 EXPERIMENTAL RESULTS

3.1 BIOLOGICAL REACTOR CHARACTERISTICS

Table 3 summarizes general operating parameter and performance characteristics for the biological reactors employed for evaluation of the removal efficiencies of organic constituents.

Results for the HYGAS study show that the reactor used gave good removal efficiencies for COD, phenolics, and thiocyanate. The reactor possessed typical values of MLVSS and demonstrated good sludge settling propeties. The reactor operating conditions resulted in a COD removal rate of 0.86 day^{-1}. These parameters are similar to those that may be envisioned for a commercial facility, although a commercial facility may be designed for a lower COD-removal rate, depending on the degree of conservatism.

Comparison of operating parameters for treatment of 33%-strength SFB quench water shows similar values of mean-cell residence time and steady-state value of MLVSS as employed in the HYGAS study. However, the SFB reactor was operated at longer hydraulic residence time, which resulted in a lower COD removal rate, 0.37 $date^{-1}$. Data in Table 3 show excellent removal efficiencies for primary constituents and illustrate that a high degree of nitrification was achieved. The average concentration of SFB-effluent phenolic compounds was 1 mg/L or less as measured by the 4-amino-antipyrine colorimetric procedure. As shown below, GC/MS analysis of a composite sample of SFB biological reactor effluent gave a lower average concentration of specific phenolic compounds. Refer to Luthy and Tallon (1978) and Luthy et al. (1979) for additional information on operating characteristics of biological reactors.

3.2 REMOVAL EFFICIENCY OF ORGANIC COMPOUNDS

Total-ion chromatograms of the acid, base, and neutral fractions of the HYGAS and SFB biological reactor influent and effluent are presented in Figs. 3 to 5. Visual comparison of the chromatograms reveals that activated-sludge treatment removed the bulk of the organic constituents.

Estimated influent and effluent concentrations and percentage removal of major extractable and chromatographable organic compounds identified in the acid, base, and neutral fractions are presented in Tables 4 to 6. Since concentration levels were estimated on the basis of total-ion peak areas referenced to several standard compounds, and because of possible losses due to extraction and separation procedures, it is believed that reported concentration levels are only semiquantitative estimates (±33-50%). Percent removal values are considered more accurate than concentration values because these estimates are based on comparison of total ion counts assuming similar extraction efficiencies for reactor influent and effluent.

4 DISCUSSION

4.1 ACID FRACTIONS

As shown in Table 4, the acid fractions of both the HYGAS and SFB quench water influents were composed almost exclusively of phenol and single-ring alkylated phenolic compounds. Phenol and cresols constituted the largest fraction of observed organics. The acid influent fraction represented more than 98.5% of total identified organics on a mass basis for the HYGAS sample, and more than 99.3% for the SFB sample. Despite the abundance of these compounds in the influent, only traces of a cresol were detected in the HYGAS

Table 3. Average Biological Reactor Performance Data for Evaluation of Removal of Trace Organic Compounds[a]

Parameter[b]	HYGAS[c] Wastewater		SFB[d] Wastewater	
Mean Cell Residence Time, days	15		15	
Hydraulic Residence Time, days	2.05		9.2	
COD Removal Rate, $days^{-1}$	0.86		0.37	
Mixed Liquor Suspended Solids, MLSS	2000		1870	
Mixed Liquor Volatile Sus. Solids, MLVSS	1820		1500	
O_2 Util. Rate, mg O_2/mg MLVSS-day	0.28		0.33	
Zone Settling Velocity, ft/hr	24		15	
Sludge Volume Index, mL/g MLSS	54		39	
	Inf	Eff	Inf[c]	Eff[c]
COD	3710	710	6780	1260
Phenolics	625	0.3[e]	1510	1
NH_3-N	148	101	157	17
NO_3-N	--	2	<2	160
Org-N	10	7	43	21
CN^-_{tot}	0.4	0.4	0.5	0.9
SCN^-	12	2	16	2
S^{2-}	<10	<6	4	<3
Suspended Oil and Grease	--	--	<10	<10
Alkalinity (as $CaCO_3$)	710	260	1240	560
Conductivity (μmhos/cm)	4500	5900	3740	4520

[a] Refer to Section 2.1 for limitations on data interpretation.

[b] All units in mg/L except as noted.

[c] Ammonia stripped wastewater. Data source: Luthy and Tallon (1978).

[d] 33%-strength ammonia stripped wastewater. Data source: Luthy, Sekel and Tallon (1979).

[e] Average value during the period of sample collection for trace organic analysis was <0.05 mg/L.

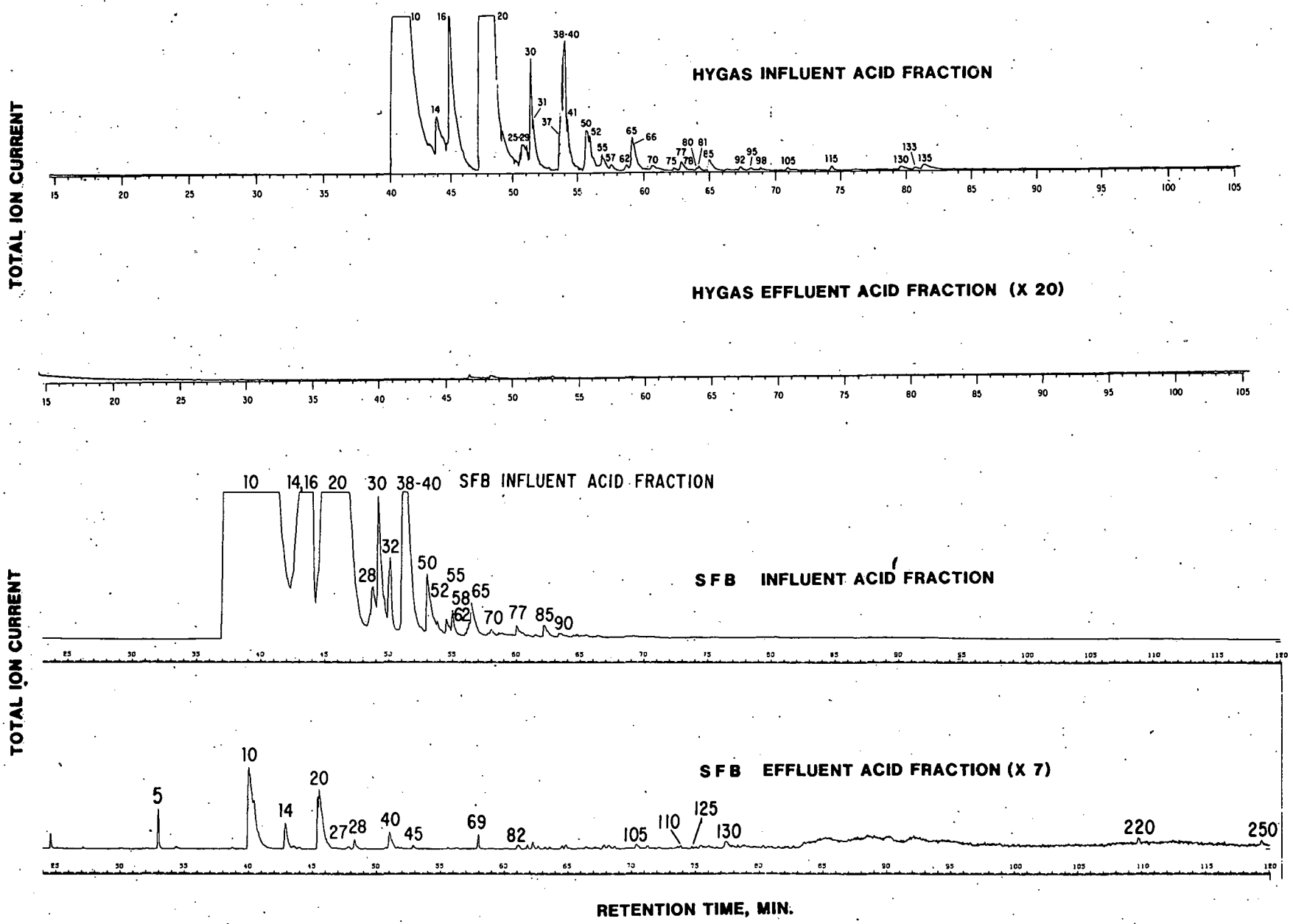

Fig. 3. Total-Ion Chromatograms of Influent and Effluent Acid-Fraction Extracts of Biologically Treated HYGAS and SFB Quench Waters

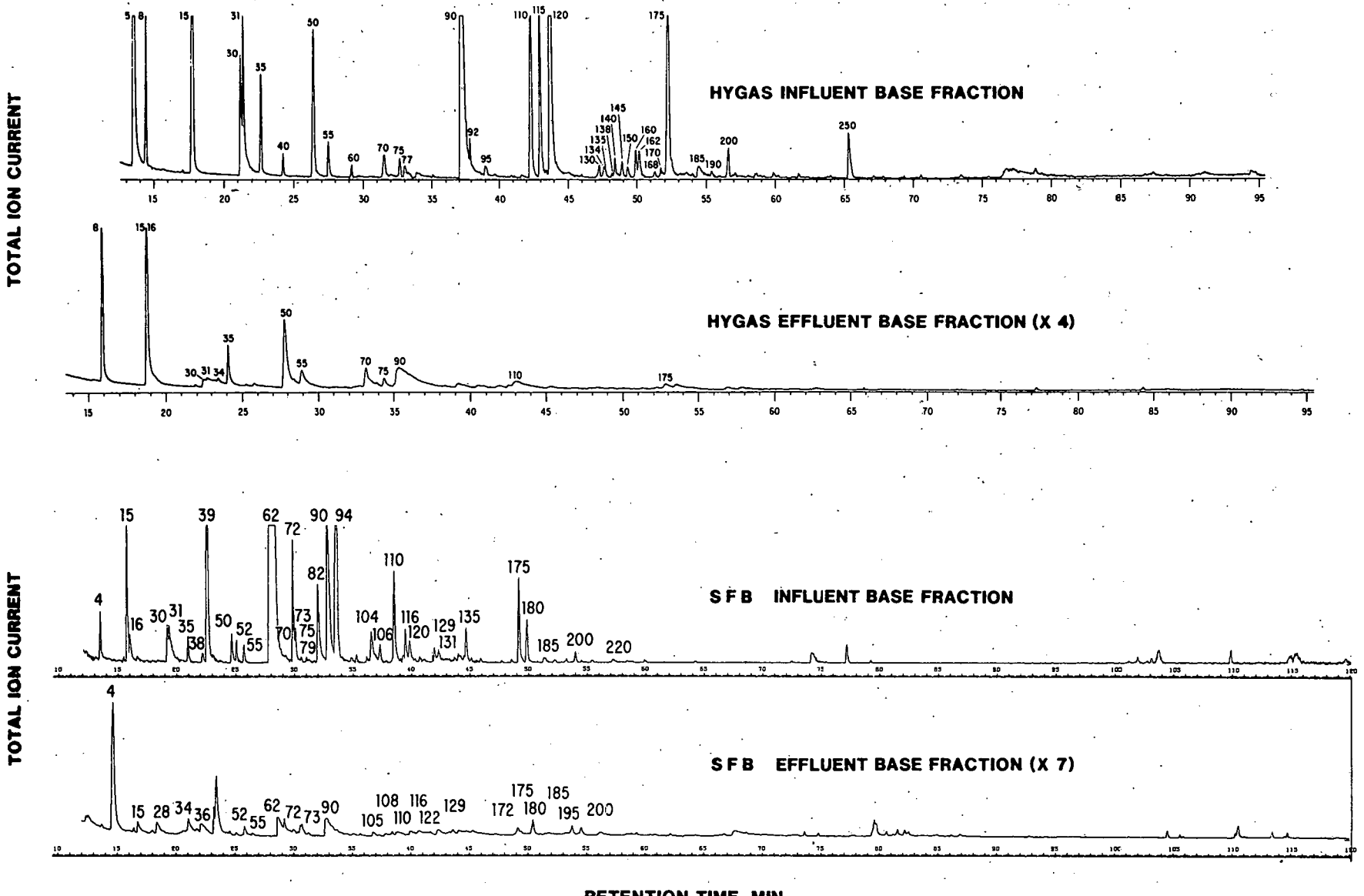

Fig. 4. Total-Ion Chromatograms of Influent and Effluent Base-Fraction Extracts of Biologically Treated HYGAS and SFB Quench Waters

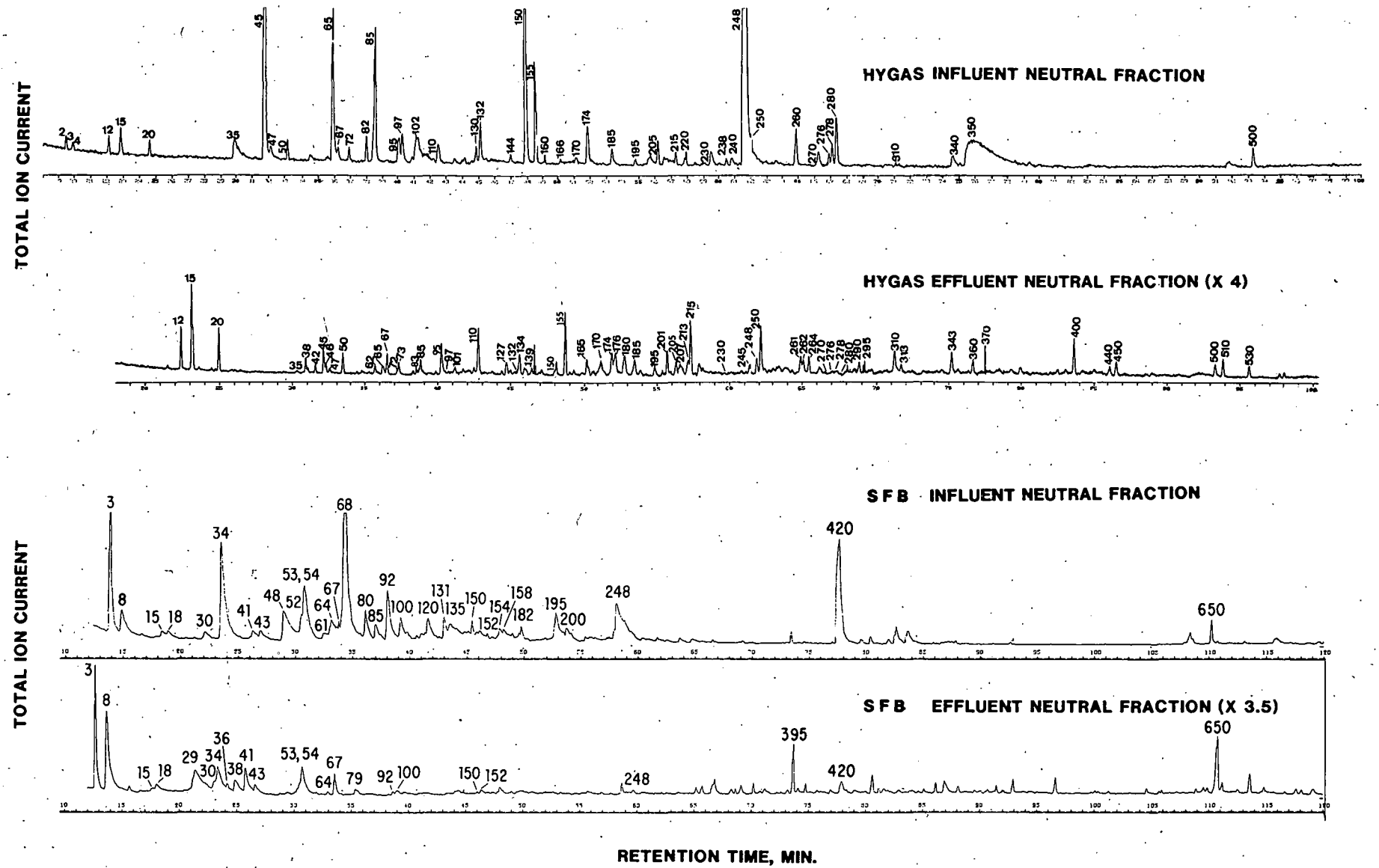

Fig. 5. Total-Ion Chromatograms of Influent and Effluent Neutral-Fraction Extracts of Biologically Treated HYGAS and SFB Quench Waters

Table 4. Concentration of Acid-Fraction Organic Constituents in Influent and Effluent Quench Waters by Activated-Sludge at Bench Scale, Together with the Percent Removal Values[a]

Peak Number	Compound Name	Estimated Influent Conc.[b] µg/L		Estimated Effluent Conc.[b] µg/L		Estimated Percent Removal	
		HYGAS	SFB[c]	HYGAS	SFB[d]	HYGAS	SFB
10	Phenol	>250,000	>500,000	NT	60	100	99.99
14&16	Cresols	53,000	30,000	NT	12	100	99.96
20	Cresol	>180,000	>150,000	3	45	99.99+	99.97
25-29	C_2-Phenols	5,000	870	NT	4	100	99.54
30&31	Dimethylphenols	16,500	4,500	NT	NT	100	100
32	Methyl-methoxyphenol	-	1,700	-	NT	-	100
37-41	C_2-Phenols	14,000	12,500	NT	7	100	99.94
50	Dimethylphenol	7,500	2,500	NT	1	100	99.96
52	C_3-Phenol	5,000	70	NT	NT	100	100
55-57	C_3-Phenols	3,300	400	NT	NT	100	100
58	C_2-Methoxyphenol	-	430	-	NT	-	100
62-66	C_3-Phenol	8,300	1,500	NT	NT	100	100
70	C_3-Phenol	750	150	NT	NT	100	100
75	C_4-Phenol	350	-	NT	-	100	-
77	Allyphenol or Hydroxyindan or Methyl-vinylphenol	1,100	-	NT	-	100	-
78	Methyl-dihydroxybenzene	500	-	NT	-	100	-
80	C_4-Phenol	300	-	NT	-	100	-
81	C_4-Phenol	500	-	NT	-	100	-
85	Allyphenol or Hydroxyindan or Methyl-vinylphenol	3,500	400	NT	NT	100	100
90	Hydroxyindene or Methyl-acetylenylphenol	-	120	-	NT	-	100
92	C_2-Dihydroxybenzene	500	-	NT	-	100	-
105	C_2-Dihydroxybenzene	400	-	NT	-	100	-
115	Hydroxybiphenyl	650	-	NT	-	100	-
130	Naphthol	650	-	NT	-	100	-
133	C_4-Phenol	450	-	NT	-	100	-
135	C_4-Phenol	2,500	-	NT	-	100	-

[a] Refer to section on sample representativeness for limitation on data interpretation.

[b] NT, not detected. 100% removal means that the compound was below detection limits.

[c] Undiluted ammonia-stripped quench-water concentrations reported here for comparative purposes. This sample was diluted to 33% strength for efficient biological treatment.

[d] Actual biological reactor effluent concentrations were multiplied by 3 as reported here to factor our apparent removal owing to dilution. Thus all SFB effluent concentrations are normalized to an undiluted basis.

Table 5. Concentration of Base-Fraction Organic Constituents in Influent and Effluent Quench Waters by Activated-Sludge at Bench Scale, Together with the Percent Removal Values[a]

Peak Number	Compound Name	Estimated Influent Conc.[b] µg/L		Estimated Effluent Conc.[b] µg/L		Estimated Percent Removal[e]	
		HYGAS	SFB[c]	HYGAS	SFB[d]	HYGAS	SFB
4	Methyl tetrazole?	--	21	--	20	--	5
5	Pyridine	540	--	NT	--	100	--
15	Picoline	310	76	160	2	48	97
16	Methyldiazine	--	20	--	NT	--	100
30&31	Picolines	290	65	25	NT	92	100
34	C_2-Imidazole or C_2-Pyrazole	--	ND	--	3	--	ND/PR
35	Ethylpyridine	75	14	32	NT	57	100
36	C_2-Imidazole or C_2-Pyrazole	--	ND	--	3.5	--	ND/PR
38	C_2-Diazine	--	7	--	2	--	71
39	Ethylimidazole or Ethylpyrazole	--	185	--	10	--	95
40	Dimethylpyridine	14	--	NT	--	100	--
50	C_2-Pyridine	150	16	95	NT	37	100
52	C_3-Imidazole or C_3-Pyrazole	--	10	--	0.9	--	91
55	C_2-Pyridine	31	9	28	NT	10	100
60	C_3-Pyridine	9	--	NT	--	100	--
62	C_1-Aminopyrrole	--	1,050	--	5	--	99.5
70	C_3-Pyridine	30	--	28	--	7	--
72	C_3-Imidazole or C_3-Pyrazole	--	64	--	1	--	98.5
73	C_3-Imidazole or D_3-Pyrazole	--	19	--	1	--	95
75	C_3-Pyridine	15	--	8	--	47	--
77	Acetylenylpyridine	14	--	NT	--	100	--
82	C_3-Imidazole or C_3-Pyrazole or C_2-Aminopyrrole	--	68	--	<1	--	98.5
90	Aniline	2,000	180	105	10	95	94.5
92	C_4-Pyridine	<10	--	NT	--	100	--
94	C_3-Imidazole or C_3-Pyrazole or C_2-Aminopyrrole	--	270	--	<0.5	--	99.8
104	C_3-Imidazole or C_3-Pyrazole or C_2-Aminopyrrole	--	34	--	NT	--	100
105	Methoxyaniline	--	ND	--	<1	--	ND/PR
106	C_4-Imidazole or C_4-Pyrazole or C_3-Aminopyrrole	--	10	--	NT	--	100
110	Methylaniline	250	58	28	0.5	89	99+
112	Methoxyaniline	--	ND	--	0.5	--	ND/PR
115	Methylaniline	180	--	NT	--	100	--
116	Methoxyaniline	--	22	--	1	--	95
120	Methylaniline	510	21	NT	NT	100	100

Table 5 (Contd.)

Peak Number	Compound Name	Estimated Influent Conc. µg/L HYGAS	Estimated Influent Conc. µg/L SFB	Estimated Effluent Conc. µg/L HYGAS	Estimated Effluent Conc. µg/L SFB	Estimated Percent Removal HYGAS	Estimated Percent Removal SFB
129	Methoxyaniline	--	10	--	1.5	--	85
134&135	C_2-Aniline & C_4-Pyridine	15	--	NT	--	100	--
135	C_4-Pyridine	--	26	--	0.4	--	98.5
140	C_2-Aniline	15	--	NT	--	100	--
145	C_2-Aniline	12	--	NT	--	100	--
150	C_2-Aniline	11	--	NT	--	100	--
160	C_2-Aniline	28	--	NT	--	100	--
162	C_2-Aniline	31	--	NT	--	100	--
168	C_2-Aniline	9	--	NT	--	100	--
170	C_2-Aniline	10	--	NT	--	100	--
175	Quinoline	280	57	9	NT	97	100
180	C_5-Pyridine	--	25	--	2	--	92
185	Isoquinoline	24	6	NT	NT	100	100
200	Methylquinoline	28	7	3	1	90	83
205	Indole	60	--	NT	--	100	--

[a] See notes under Table 4.
[b] ND/PR, not determinable/poorly removed. See note under Table 6.

effluent and only very small amounts of phenol and cresols were detected in the SFB effluent. The SFB effluent chromatogram (Fig. 3) showed a series of fine structure peaks in the retention time range of 55-80 min, corresponding to either alkylated phenols or alkylated hydroxyindans with olefinic substitutions.

4.2 BASE FRACTIONS

Table 5 shows that organics in the HYGAS basic influent fraction were primarily nitrogen heterocyclics (pyridine, quinoline, indole), as well as aniline and its alkylated derivatives. Most of the basic compounds were removed either completely or quite effectively, with the exception of certain alkylated pyridines.

The basic influent fraction of the SFB sample consisted largely of aniline, methoxyanilines, alkylated anilines, and a series of nitrogen heterocyclic compounds (viz., alkylated aminopyrroles, imidazoles and/or pyrazoles, and diazines), as well as the other compounds mentioned above. In general, removal efficiencies for these compounds were very good. The overall removal efficiency for base-fraction organics was over 90% in the HYGAS sample and over 96% in the SFB sample.

Table 6. Concentration of Neutral-Fraction Organic Constituents in Influent and Effluent Quench Waters by Activated-Sludge at Bench Scale, Together with the Percent Removal Values[a]

Peak Number	Compound Name	Estimated[a] Influent Conc. µg/L		Estimated[a] Effluent Conc. µg/L		Estimated Percent Removal	
		HYGAS	SFB	HYGAS	SFB	HYGAS	SFB
8	Cyclohexane	--	76	--	67	--	12
12	Ethylbenzene	15	--	18	--	0.0[b]	--
15	m- + p-Xylene	30	--	5	--	0.0[b]	--
16	C_2-Cyclopentane or Methylcyclohexane	--	19	--	2.4	--	87
18	C_2-Cyclopentane or Methylcyclohexane	--	17	--	6	--	65
20	o-Xylene	14	--	18	--	0.0[b]	--
30	C_2-Cyclopentane or Methylcyclohexane	--	31	--	4	--	87
34	Methylcyclopentenone	--	385	--	42	--	89
35	Cycloalkene?	66	--	10	--	85	--
38	n-Propylbenzene	ND	--	7	--	ND/PR[c]	--
41	C_3-Cyclopentene or C_2-Cyclohexene	--	27	--	16	--	41
42	Isopropylbenzene	ND	--	4	--	ND/PR	--
43	C_3-Cyclopentene or C_2-Cyclohexene	--	26	--	5	--	83
45	Benzonitrile	800	--	12	--	98.5	--
46	Ethyl-methylbenzene	ND	--	5	--	ND/PR	--
47	Cycloalkene	8	--	2	--	75	--
48	Dimethylfuran	--	204	--	NT	--	100
50	Trimethylbenzene	16	--	10	--	38	--
51	C_4-Cyclopentene or C_3-Cyclohexene	--	290	--	33	--	89 (combined)
52&53	Benzonitrile + C_3-Cyclopentene or C_2-Cyclohexene						
62	Trimethylbenzene	6	--	5	--	17	--
64&65	C_3-Cyclopentene or C_2-Cyclohexene	208	57	6	1.3	97	98
67	Indan or Methylstyrene	18	--	8	--	56	--
68	C_3-Cyclopentene or C_2-Cyclohexene	--	690	--	NT	--	100
72	Indene	12	--	3	--	75[d]	--
80	C_4-Cyclopentene or C_3-Cyclohexene	--	71	--	NT	--	--
82	Acetylcyclohexene or C_3-Cyclohexene	29	--	11	--	62	--
85	Acetophenone	190	43	13	NT	93	100
92	C_4-Cyclopentene or C_3-Cyclohexene	--	162	--	1.5	--	99
95	Acetylcyclohexene or C_3-Cyclohexene or C_2-Cyclohexenone	47	--	23	--	51	--
97	Acetylthiophene or C_3-Thiophene	47	--	ND	--	99+	--

Table 6 (Contd.)

Peak Number	Compound Name	Estimated Influent Conc. µg/L HYGAS	Estimated Influent Conc. µg/L SFB	Estimated Effluent Conc. µg/L HYGAS	Estimated Effluent Conc. µg/L SFB	Estimated Percent Removal HYGAS	Estimated Percent Removal SFB
99	Methylindan	ND	--	9	--	ND/PR	--
100	C_4-Cyclopentene or C_3-Cyclohexene	--	48	--	1.1	--	98
101	Isopropylthiophene	4	--	ND	--	100[e]	--
105	Methylindan or C_2-Styrene	ND	--	trace	--	ND/PR	--
109	Methylindan or C_2-Styrene	ND	--	trace	--	ND/PR	--
110	C_3-Cyclohexenone or Methyl-acetylcyclohexene	37	--	17	--	54[f]	--
118	C_4-Benzene + C_3-Cyclohexene	ND	--	10	--	ND/PR	--
120	C_4-Cyclopentene or C_3-Cyclohexene	--	44	--	NT	--	100
125	C_4-Benzene	ND	--	12	--	ND/PR	--
127	C_3-Cyclohexane?	ND	--	16	--	ND/PR	--
130	C_4-Thiophene	17	--	8	--	53	--
131	C_3-Cyclopentene or C_2-Cyclohexene + C_4-Cyclopentene or C_3-Cyclohexene	--	54	--	NT	--	100
132	Methyl-cyanobenzene	47	--	NT	--	100	--
134	C_4-Thiophene + Methylindan or C_2-Styrene	ND	--	13	--	ND/PR	--
135	Methylindene	ND	--	11	--	ND/PR	--
136	Methylindene + C_4-Benzene	ND	--	11	--	ND/PR	--
139	Methylbenzyl sulfide?	ND	--	12	--	ND/PR	--
144	C_4-Benzene [1-(2-methylpropyl)-benzene]	ND	--	11	--	ND/PR	--
150	Naphthalene	405	18	9	NT	98	100
152	C_5-Benzene	--	10	--	2	--	80
155	Benzothiophene	111	--	35	--	68	--
160	C_4-Cyclohexadiene (terpenoid) Phenyl isopropyl ether	ND	--	12	--	ND/PR	--
164	C_5-Cyclopentadiene or C_4-Cyclohexadiene	--	28	--	NT	--	100
165	C_4-Cyanobenzene	ND	--	6	--	ND/PR	--
166	Dimethoxybenzene	ND	--	6	--	ND/PR	--
168	C_5-Cyclopentadiene or C_4-Cyclohexadiene	--	29	--	NT	--	100
174	Quinoline (80+) & Ethyl methoxy-benzene or C_4-Cyclohexadiene	57	--	20	--	65	--
176	C_4-Cyclohexadiene	ND	--	19	--	ND/PR	--
180	C_4-Cyclohexadiene	ND	--	15	--	ND/PR	--
182	C_6-Cyclopentene or C_5-Cyclohexene	--	20	--	NT	--	100
185	C_4-Benzene + C_2-Methoxybenzene or C_4-Cyclohexadiene	24	--	14	--	42	--

Table 6 (Contd.)

Peak Number	Compound Name	Estimated Influent Conc. µg/L HYGAS	Estimated Influent Conc. µg/L SFB	Estimated Effluent Conc. µg/L HYGAS	Estimated Effluent Conc. µg/L SFB	Estimated Percent Removal HYGAS	Estimated Percent Removal SFB
194	C_6-Cyclopentadiene or C_5-Cyclohexadiene	--	100	--	NT	--	100
195	Indanone	ND	--	7	--	ND/PR	--
200	C_6-Cyclopentadiene or C_5-Cyclohexadiene	--	29	--	NT	--	100
201	Methyl-benzothiophene	ND	--	11	--	ND/PR	--
205	2-Methylnaphthalene	23	--	9	--	61	--
207	C_5-Cyclohexadiene	ND	--	trace	--	ND/PR	--
213	Methyl-benzothiophene	ND	--	22	--	ND/PR	--
215	1-Methylnaphthalene	ND	--	24	--	ND/PR	--
219	Isopropyl-methoxybenzene or C_5-Cyclohexadiene	16	--	9	--	44	--
220	C_3-Methoxybenzene	ND	--	NT	--	ND/PR	--
230	Indazole or Benzimidazole	29	--	NT	--	100	--
238	n-propyl-methoxybenzene or C_5-Cyclohexadiene	5	--	trace	--	99+	--
240	C_3-Methoxybenzene or C_5-Cyclohexadiene	6	--	trace	--	99+	--
245	Ethyl benzoate	--	--	6	--	++[g]	--
248	Indole	1,980	270	8	2	99.5	99.3
250	Biphenyl	10	--	3	--	70	--
260	Methylindole	50	--	NT	--	100	--
261	C_2-Naphthalene	ND	--	10	--	ND/PR	--
262	C_2-Naphthalene	ND	--	7	--	ND/PR	--
264	Methylbiphenyl	ND	--	9	--	ND/PR	--
270	Methylindole	26	--	trace	--	99+	--
276	Methylindole	15	--	NT	--	100	--
278	Methylindole	25	--	NT	--	100	--
280	Methylindole	65	--	NT	--	100	--
290	Acenaphthene	ND	--	7	--	ND/PR	--
295	Methylbiphenyl	ND	--	7	--	ND/PR	--
310	C_6-Theophene + Methylbiphenyl	ND	--	8	--	ND/PR	--
311	Bibenzyl	ND	--	7	--	ND/PR	--
313	C_6-Thiophene	ND	--	4	--	ND/PR	--
340	n-Propylnaphthalene	7	--	NT	--	98+	--
343	Fluorene	ND	--	17	--	ND/PR	--
350-355	Cyanophenyl benzoate ? & ?	68	--	NT	--	100	--
370	Plasticizer	--	--		--	++[g]	--
400	Aliphatic Hydrocarbon	ND	--	6	--	ND/PR	--
420	Unknown	--	440	--	NT	--	100

Table 6 (Contd.)

Peak Number	Compound Name	Estimated Influent Conc. µg/L HYGAS	Estimated Influent Conc. µg/L SFB	Estimated Effluent Conc. µg/L HYGAS	Estimated Effluent Conc. µg/L SFB	Estimated Percent Removal HYGAS	Estimated Percent Removal SFB
450	Anthracene or Phenanthrene	ND	--	6	NT	ND/PR	--
500	Carbazole	32	--	15	--	53	--
510	Aliphatic Hydrocarbon	ND	--	10	--	ND/PR	--
530	Plasticizer	--	--	--	--	++[g]	--
550	Plasticizer	--	--	--	--	++[g]	--

[a] ND, not determinable; NT, not detected. See notes a-d under Table 4.

[b] The effluent shows a larger peak. The influent extract possibly was dried when methylene chloride was evaporated, so the more volatile xylenes escaped.

[c] ND/PR stands for not determinable/poorly removed. Due to the fact that the effluent contained fewer organics of lower concentration levels, the final extract volume had to be concentrated to a volume much smaller than that of the influent. Certain peaks, corresponding to compounds that were in very low concentration level in the influent were then easier to identify in the effluent, but were obscured or in the "noise" level in the influent. Thus, the symbol ND/PR indicates that the percent removal for a particular compound could not be determined (ND) but is probably poorly removed (PR).

[d] Shoulder peak in effluent.

[e] The peak in the effluent corresponds to another compound.

[f] A dominant part of the peak in the influent corresponds to methylindoline.

[g] The symbol ++ means that the compound appears only in the effluent.

4.3 NEUTRAL FRACTIONS

Table 6 shows that neutral-fraction organics in the HYGAS sample cover a wide range of typical aromatic compounds, such as alkylated benzenes, indans, indenes, thiophenes, naphthalenes, benzothiophenes, biphenyls, fluorene, acenaphthene, and anthracene or phenanthrene. Alkylated cycloalkanes, cycloalkenes, benzonitriles, indoles, acetophenone, and carbazole were also present. The SFB influent neutral-fraction lacked the variety of compounds observed in the HYGAS sample, as many of the common aromatic hydrocarbons were not observed. Principal species in the SFB neutral fraction were toluene, benzonitrile, acetophenone, naphthalene, indole, and alkylated cycloalkanes and cycloalkenes. Removal efficiency for SFB neutral-fraction organics was generally high except for certain alkylated cycloalkanes.

It was observed that for the HYGAS sample the removal of neutral-fraction organics was dependent on the chemical structure of the particular compound. The general trend was that heterocyclics and compounds containing heteratoms were usually removed effectively. Examples from the HYGAS sample (Table 4) are benzonitrile (peak No. 45), acetylthiophene (peak No. 97), isopropylthiophene (peak No. 101), methyl-cyanobenzene (peak No. 132), and methyl indoles (peak Nos. 260, 270, 276, 278, 280). In the case of aromatic hydrocarbons, a trend of less efficient removal for compounds with more alicylcic content was observed. Examples are substituted benzenes (peak Nos. 12, 15, 20, 50, 62), cycloalkanes, and cycloalkenes (peak Nos. 35, 47, 67).

Also, most of the compounds with the labels ND/PR (see Table 6, note C, and discussion below) fall into this category. Polynuclear aromatics were only partially removed, depending again on the amount of substitution. Examples are naphthalene (peak No. 150) vs substituted naphthalenes (peak Nos. 205, 215, 261, 262), acenaphthene (peak No. 290), fluorene (peak No. 343), bibenzyl (peak No. 311), and anthracene or phenanthrene (peak No. 450).

Compounds that were at very low concentrations in the influent fraction were obscured or in the "noise" level in the influent chromatogram. It was very difficult, if not impossible, therefore, to determine percent removal values for these compounds, even though it was easier to identify them in the effluent fraction, due to the fact that the effluent fraction was concentrated to a smaller volume (0.5 mL) than that of the influent (5 mL). Such compounds are identified in Table 6 with the symbol ND/PR (not determinable/poorly removed) under the estimated-percent-removal column. The facts strongly suggest that these compounds, although in very low concentrations in the effluent, were poorly removed. This was also observed in the case of the base fraction of the SFB sample (Table 5). Some compounds such as ethyl benzoate (No. 245) and plasticizers (Nos. 370, 530, 550) in Table 5 show up only in the effluent. Ethyl benzoate can be either a contaminant or an artifact; the presence of plasticizers probably reflects contamination from containers used for raw quench water storage and pretreatment. The SFB effluent chromatogram (Fig. 5) showed a series of peaks in the retention time range of 65-120 min. Most of these peaks could not be identified with certainty — some of them are attributed to plasticizers. In general, the overall removal of organics from the neutral fraction was over 86% efficient for the HYGAS sample and over 93% efficient for the SFB sample.

5 CONCLUSIONS

Quench waters from HYGAS and SFB pilot-plant, coal-gasification processes were treated biologically and samples of reactor influent and effluent were fractionated and analyzed for organic constituents. It was found that approximately 99% of extractable and chromatographable organic material, on a mass basis, was represented in the acid fraction of the influent coal-gasification process waters from HYGAS and SFB. Activated-sludge processing removed most of these organic constituents. Compounds of the acid fractions were removed almost completely. Marked compositional differences were found between the HYGAS and the SFB base and neutral fractions. These differences may be attributable to differences in coal type, gasifier operating conditions, and other process variables. High removal efficiencies were observed for compounds in the base fractions, with the exception of certain alkylated pyridines. The extent of removal of compounds in the neutral fractions was dependent on chemical structure. Most major components were removed effectively. Some aromatic hydrocarbons containing aliphatic substitutions and polynuclear aromatic compounds were only partially or poorly removed.

6 RECOMMENDATIONS

Analytical data presented in this study for organic characterizations are at best semiquantitative estimates. In future work it is necesary to

address some of the unresolved questions regarding quantification of organic compounds in complex wastewaters. This work should include evaluation of extraction efficiencies for selected organic compounds from coal gasification process effluents. It is also recommended that special studies be performed for evaluation of removal efficiencies of polynuclear aromatic hydrocarbons. Finally, the fate of trace organic compounds during pretreatment also should be evaluated and a search should be made for improved removal efficiencies of refractory organics by various combinations of physicochemical and biological processes.

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