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Removal of Organic Constituents in a Coal Gasification Process Wastewater by Activated Sludge Treatment

by

V. C. Stamoudis, R. G. Luthy, and W. Harrison

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ENERGY AND ENVIRONMENTAL SYSTEMS DIVISION

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WATER RESOURCES RESEARCH PROGRAM

REMOVAL OF ORGANIC CONSTITUENTS IN A COAL GASIFICATION PROCESS WASTEWATER BY ACTIVATED SLUDGE TREATMENT

by

Vassilis C. Stamoudis, Richard G. Luthy,*
and W. Harrison

Energy and Environmental Systems Division

June 1979

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ABSTRACT

Removal of organics by activated sludge treatment of wastewater from an experimental coal gasification plant was estimated by capillary-column gas chromatography/mass spectrometry (GC/MS) of extracts of wastewater sampled before and after processing by bench-scale, activated sludge units. The wastewater sample characterized for organic constituents was obtained from a stable, representative pilot-scale HYGAS run. Wastewater was pretreated to reduce ammonia and alkalinity and was then processed in an activated sludge reactor at a hydraulic residence time of two days with a bacterial mean cell residence time of 15 days and a COD removal rate of 0.86 per day.

Organic constituents were isolated from biological reactor influent and effluent samples and separated into acidic, basic, and neutral fractions using a methylene chloride extraction procedure. Capillary-column GC/MS was used to semiquantify the organics, and analysis of the results indicates that activated sludge treatment removed the bulk of the extractable and chromatographable organic constituents. The influent acidic fraction, composed mainly of phenol and alkylated phenols, constituted 98.5% of the total organics identified; these were removed almost completely. Organics of the basic fraction, composed mainly of alkylated pyridines and anilines, were removed effectively, with the exception of certain alkylated pyridines. In the case of the organics in the neutral fraction, which constituted less than 0.75% of the total organics in the influent, certain heterocyclics and compounds containing heteroatoms were removed effectively. For aromatic hydrocarbons, the more aliphatic the substitution or alicyclic the content, the less the removal. Alicyclic hydrocarbons and alkylated benzenes generally were removed poorly or very poorly.

Wastewater sample strength, gasifier operating conditions, and biological reactor operating conditions are reviewed with reference to operation of a projected commercial-scale activated sludge plant. The study concludes by comparing the bench-scale organics removal data with data for the removal of similar organic constituents from a petroleum refinery wastewater by activated sludge at full scale.

1 *INTRODUCTION*

1.1 *PROGRAM OBJECTIVE*

The long-range objective of this study is to establish the efficiency of activated sludge treatment for the removal of various classes of organic contaminants present in raw process wastewater from coal gasification plants. Present efforts are directed toward study of removal efficiencies attained by bench-scale, activated sludge units, since there are at present no full-scale activated sludge plants treating coal gasification plant wastewaters. Results are being compared with Argonne data on the removal of organic constituents from petroleum refinery wastewater as treated by activated sludge at full scale.

1.2 *RESEARCH STRATEGY*

As one part of a cooperative program between the Institute of Gas Technology (IGT), Argonne National Laboratory (ANL), and Carnegie-Mellon University (C-MU), representative samples of pilot-scale, HYGAS process wastewater were collected by IGT, processed in bench-scale, activated sludge treatment equipment by C-MU, and delivered to ANL for extraction and analysis. Analysis was performed on acidic, basic, and neutral fractions of samples using capillary-column GC/MS techniques. Percentage removals for various organic compounds and classes of organic compounds were estimated by comparing GC/MS data for raw influent and treated effluent.

1.3 *REVIEW OF PREVIOUS WORK*

The authors are unaware of any published results for removal by activated sludge treatment of trace organic constituents from coal gasification wastewaters. Singer, and others (1978) have recently summarized the available literature on characterization of organics in coal-conversion wastewaters, and have presented preliminary biotreatability data on synthetic, coal-conversion wastewater. Characterization data for organics in HYGAS wastewaters were not among those presented in their report.

Raphaelian and Harrison (1978) recently completed a study of organic compounds across the wastewater treatment system of a Class B petroleum refinery. Their study involved estimation of the removal of organics by the refinery's full-scale, activated sludge unit and by add-on, mixed-media filtration and granular activated carbon at pilot scale. Experience gained in their study has been used in the present effort.

2 FIELD AND LABORATORY PROCEDURES

Coordinated efforts on the part of the three organizations involved in the program, both in the field and the laboratory, were required to generate and insure the reliability of the results presented in this report. Procedures employed in the selection, collection, processing, and analysis of an appropriate coal gasification aqueous condensate for this study are summarized below. Further details and discussions are available in the literature and/or in appendices to this report as noted.

2.1 WASTEWATER SELECTION, COLLECTION, AND CHARACTERIZATION

HYGAS wastewater was selected for this study for a number of reasons. Among these are: (1) the HYGAS process is a major DOE/GRI-sponsored coal gasification system in an advanced state of development, (2) it is a process that currently produces a product oil and therefore can be expected to produce an aqueous condensate containing a broad distribution of organic components, (3) it is a process presently under intensive environmental study by DOE, (4) it is currently the subject of a range of DOE-sponsored ANL investigations of the biological and chemical characteristics of coal gasification-generated organics, and (5) it has been the focus of a joint experimental investigation of the treatability characteristics of gasification wastewaters by C-MU and IGT during the past two years.

Details regarding the procedures employed by C-MU and IGT in the collection of the HYGAS wastewater sample used in the present investigation are well documented by Luthy and Tallon (1978a and b); significant aspects are noted here. Raw wastewater was collected in two batches during stable operating periods of HYGAS pilot-plant runs 62 and 64 and later were used for acclimatization and steady-state performance testing of treatment systems, respectively. Each of these batches was immediately transported by truck to C-MU (Pittsburgh) where they were blended and frozen in 5-gallon allotments for preservation, to be thawed for use as needed. Although no studies of the stability of the organics in these samples were conducted at the time of their collection, a recent ANL investigation of the stability of HYGAS quench water by Raphaelian and Harrison (1979) suggests that a high degree of sample stability could be expected (see also Sec. 3.3.1).

Bulk chemical characteristics of the raw and pretreated HYGAS wastewaters are summarized in Table 2.1* and reflect a high pressure (1000 psig) gasification of an Illinois No. 6 bituminous coal with a steam-to-coal ratio of 1.81. Extensive discussion of bulk wastewater sample characteristics is provided in a separate report by Luthy & Tallon (1978b). Several points must be noted, however, regarding the interpretation of these data and the organic data reported later in the present report. Although the majority of organic and inorganic species observed in pilot-scale HYGAS wastewaters might be expected to exist in a subsequent commercial version of the HYGAS process, their relative quantities and concentrations are likely to be

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*Data cited on lime addition and ammonia stripping are discussed in Appendix A (Sec. A.1) of this report.

Table 2.1. Representative HYGAS Wastewater Sample Characteristics

	Parameter, mg/L								
Specification	COD	Phenol	NH_3-N	CN-	SCN^-	$S^=$	$SO_4^=$	Alkalinity as $CaCO_3$	pH (units)
Raw Wastewater	4050	710	3690	0.32	28	138	184	12,600	7.8
Lime Pretreatment	3830	660	3200	0.36	28	96	241	1,210[a]	10.1
Ammonia Stripped	3700	660	133	0.45	24	15	236	1,060[a]	10.0
Net change (%) between raw and stripped wastewater	-8.6	-7.0	-96	-	-14	-89	+28	-92	-

[a] Alkalinity measured after pH adjustment to 7.3.

different. Factors that contribute to this situation include: (1) different degrees of coal pretreatment in pilot-scale operations than are anticipated for commercial-scale operations (affecting both the quantity and concentrations of aqueous species); (2) different steam-to-coal ratios in the pilot-scale operation (affecting the concentrations of aqueous species); (3) different gasifier geometry and operating conditions in the pilot-scale operation (affecting both the quantity and concentrations of aqueous species); and (4) a different raw product as quench system than that anticipated for a commercial-scale operation (affecting the distribution of species between the gas and liquid phase).

Where direct scaling of pilot-scale observations to the analysis of commercial-scale characteristics is envisioned, each factor cited above must be addressed carefully and its effects accounted for. However, in the context of the present investigation, issues of scaling are intentionally less demanding. The primary objective here has been to secure a representative sample of HYGAS pilot-scale wastewater that reasonably can be expected to contain the spectrum of species that might exist in a commercial-scale plant. The fate of this spectrum of species during wastewater treatment, particularly activated-sludge processing, has then been determined. In this context, the emphasis is on the spectrum of species present and their relative changes during treatment rather than upon their absolute concentrations.

2.2 *BENCH-SCALE WASTEWATER TREATMENT*

Pilot plants (including HYGAS) do not as a rule operate scalable wastewater treatment systems. C-MU and IGT have, therefore, assembled a series of scalable wastewater pretreatment and treatment unit operations to simulate and study the treatment of HYGAS wastewaters. This bench-scale system is described briefly for the reader in Appendix A and discussed in detail in a separate report by Luthy & Tallon (1978b).

Wastewater samples used in the present organics study were subjected to two stages of pretreatment, lime addition for the removal of excess alkalinity ($CaCO_3$ precipitation), and air stripping for the removal of excess ammonia. Pretreated wastewater was then fed to a carefully acclimatized 6-L bench-scale activated sludge reactor for biological treatment.

The reactor was operated at dissolved oxygen levels greater than 3.0 mg/L and in the pH range of 7.0 to 7.5. The reactor was managed on the basis of a 15-day, mean bacterial cell residence time and approximately two-day hydraulic residence time. The attainment of steady-state operation was defined as that interval (balance period) necessary to achieve three complete solid wasting cycles. For this reactor, steady-state operation occurred 45 days after the reactor was acclimatized to HYGAS wastewater. The reactor was then run for an additional seven weeks to obtain sufficient steady-state performance data. Basic operating conditions and performance characteristics of the activated sludge reactor during influent and effluent sampling for the present organics study are presented in Table 2.2. Samples utilized in the present study represent a composite collected over a three-week period of steady-state reactor operation at the conditions cited.

Table 2.2. Basic Operating and Performance Characteristics of Activated Sludge Reactor during Sampling for ANL Organics Study

Parameter[a]	Average Value[b]	
Mean Cell Res. Time, days	15	
Hydraulic Res. Time, days	2.05	
COD Rem. Rate, day^{-1}	0.86	
Mixed Liquor Suspended Solids (MLSS)	2000	
Mixed Liquor Volatile Suspended Solids (MLVSS)	1820	
O_2 Util. Rate, mgO_2/mg MLVSS-day	0.28	
Zone Set. Vel., ft/hr	24	
Sludge Volume Index, mL/g	54	
	Inf.	Eff.
COD	3710	700
Phenolics	625	0.3[c]
NH_3-N	148	101
Org-N	10	7
CN^-	0.4	0.4
SCN^-	12	2
Alkalinity, mg/L as $CaCO_3$	710	260
Conductivity, µmhos/cm	4500	5900

[a] All parameters mg/L except as noted.

[b] Average values measured during the seven-week steady-state operating period. This period was preceded by 45 days of operation prior to onset of steady state.

[c] Average effluent phenolic concentration during the period of sample collection for trace organic analysis was <0.05 mg/L.

2.3 *EXTRACTION PROCEDURES*

The extraction scheme used in this study is shown in Fig. 2.1. This scheme follows generally accepted protocol and has been used previously for characterization of organics in petroleum refinery wastewater (Raphaelian and Harrison, 1978).

Influent and effluent wastewater samples were extracted concurrently and in exactly the same fashion. One liter of sample was transferred to a 2-L separatory funnel and sufficient 6N HCl was added to bring the pH of the mixture to a value of 1 to 2. The pH of the influent samples was 9-10 and that of the effluent was about 8. Approximately 125 mL of methylene chloride were added and the mixture was shaken thoroughly and left standing for 1-2 hr for the layers to separate. Severe emulsion problems were encountered. The methylene chloride layer originally consisted of tiny droplets, which later formed larger globules surrounded by debris that may have been organic material. Most of the globules coalesced to form a clear red-yellow bottom layer when the separatory funnel was carefully tilted back and forth. This layer was collected into an Erlenmeyer flask having a ground-joint glass stopper, and it was observed that its color in the influent sample was more intense. The emulsion layer that remained in the separatory funnel was minimized in volume by repeating a process of collecting the layer that formed in the funnel into a beaker,* transferring the beaker's contents back into a separatory funnel, and after performing the tilting operation draining the clear bottom layer into an Erlenmeyer flask; the process was continued until the emulsion layer was minimized to a desired volume of a few mL.

Finally, the aqueous and the remaining emulsion layers were transferred back to the original aqueous phase (in the 2-L separatory funnel). The whole process was then repreated twice using 80 mL methylene chloride. The combined methylene chloride extract was named fraction A+N.

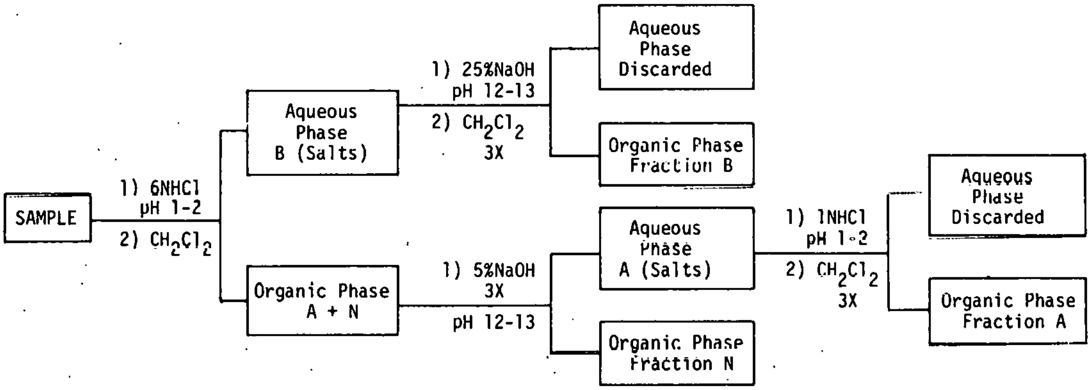

Fig. 2.1. Extraction Scheme for HYGAS Wastewater Samples

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*At this stage in each repetition, considerable further coalescence of methylene chloride globules and droplets usually occurred.

Next, the pH of the aqueous layer was adjusted to a value of 11-12 with 25% NaOH, and the mixture was extracted with methylene chloride. Since emulsions were encountered, the above described procedure was followed. The combined methylene chloride extract was named Fraction B (Fig. 2.1) and was dried overnight with ∿20 g of anhydrous sodium sulfate.

Fraction A+N was transferred to a separatory funnel and then extracted three times with 60 mL of 5% NaOH. No emulsions were encountered this time. The methylene chloride layer was called Fraction N, and it was dried overnight with ∿20 g of precleaned anhydrous sodium sulfate. The pH of the combined aqueous layer was adjusted to 1-2 with 1N HCl, and the mixture was extracted three times with methylene chloride (1 × 100 mL, 2 × 75 mL). The aqueous phase was discarded. The methylene chloride layer was named Fraction A, and it was dried overnight with ∿20 g of anhydrous sodium sulfate.

The dried methylene chloride extract (Fractions A, B, N) was transferred into a Kuderna-Danish type concentrator using a Snyder column and Kontes tube. The column and concentrator were wrapped with aluminum foil. Each Erlenmeyer flask was rinsed twice with 10-15 mL of methylene chloride. The concentrator was placed in a steam bath and the solvent evaporated until a volume of 1-2 mL was left. The Snyder column and concentrator were rinsed with 3-4 mL of methylene chloride. The samples were then sealed in vials with Teflon-lined caps and stored in a freezer at ∿-20°C.

The basic fraction of the influent contained phenols in relatively high concentration levels, making the GC/MS analysis of the basic compounds difficult. The original basic fraction was worked up for the removal of phenols as follows. The influent basic fraction was diluted to 50 mL with methylene chloride, and the mixture was washed three times with 25 mL in NaOH and then with 25 mL water. The methylene chloride layer was then dried with sodium sulfate and concentrated to a 1 mL volume (new basic fraction).

2.4 PROCEDURE FOR TESTING EXTRACTION EFFICIENCY

One mL of a standard solution containing a series of acidic and neutral organic standard compounds (250 μg/mL) was added to 1000 mL distilled water and the mixture was extracted as described above (Sec. 2.3). For a blank, 1000 mL of distilled water was also extracted in exactly the same way.

2.5 GC/MS ANALYSIS OF SAMPLE EXTRACTS

Analysis of the organics in all fractions was performed on a Hewlett-Packard 5982A GC/MS equipped with a Hewlett-Packard 5934A Data System. The data system consisted of a 21MX Computer with 32K, 16-bit-word core memory, 7900A Dual Disc Drive with 2.5 M bytes/disc memory, 5948B Data Subsystem (A/D and D/A Converters), and a Tektronix 4012 Display Terminal. A 5830 Hewlett-Packard GC was used in place of the 5700 series Hewlett-Packard GC normally delivered with the 5982A GC/MS.

Due to the complexity of the samples, glass-capillary, wall-coated open-tubular (WCOT) columns were used. The temperature was programmed from 20°C to 240°C at 2°/min, with a 2-min hold at 20°C. The column used was a Perkin-Elmer, 0.25 mm ID, 50-m long OV-101.

The identification of the compounds was based on mass spectra and known retention times. For compounds that were not resolved, the percent removal was done by single-ion monitoring. Calculation of the recovery of the organics in the spiked water extracts was also done by single-ion monitoring.

To estimate percent removal of individual compounds the total-ion (TI) chromatograms of both the influent and effluent were plotted and the total ions of the peaks corresponding to the compounds were determined. The assumptions made for this were that

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,

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 found in the effluent, it is 100% removed. To substantiate the second assumption one has to determine the total-ion (or single-ion) area vs concentration for each compound or for a few compounds serving as models for the others. Table 2.3 and Fig. 2.2 show the results of such a study involving benzonitrile. This compound gave surprisingly good linearity over a concentration range of 1-100 ng/μL. Benzonitrile was chosen as a compromise model for neutral compounds because (1) its mass spectrum is typical of an unsubstituted or singly substituted aromatic compound, (2) it has a medium polarity, and (3) it is abundant in the influent neutral fraction (see Table 3.3, Peak No. 45 in Section 3). Since it could not be assumed that what is true for benzonitrile will necessarily be true for the other compounds, any attempt to quantify the latter based on the former might involve large errors. However, for estimating percent removal (comparing total ions for the same compound), compounds with mass spectra similar to benzonitrile would possibly behave similarly.

The assumption of uniform extraction yields is probably the least substantiated. Limited ANL recovery studies on selected standard compounds in distilled water are shown in Table 2.4. These data show that extraction efficiencies even in distilled water are variable. Furthermore, it is known that concentration levels (Warner, 1976), matrix effects, and the extent of emulsion in extraction affect solvent extraction yields. Recoveries of the organics extracted from spiked water vary considerably, from 32% to 133%, with an average recovery of 61% for the 8 compounds. These results are not unexpected since variability in extraction yields is a very common phenomenon. The reported yields are based on GC/MS data (single-ion counts). Of course, recoveries of organics from distilled water solutions do not imply similar recoveries from complicated samples. However, since the scope of this study was only to estimate percent removals of organic constituents using a quick and convenient tool, the assumption of uniform extraction yield was followed.

Table 2.3. Total-Ion and Single-Ion (Mass 103) Counts for Different Concentrations of Benzonitrile

Conc. of Benzonitrile in ng/μL	Total Thousand ions	Mass 103 Thousand ions
1	0.93	0.52
5	7.5	4.0
10	11.3	6.4
25	21.9	12.8
50	63.5	36.2
83	98.0	58.0
100	135.7	73.9
500	985	581

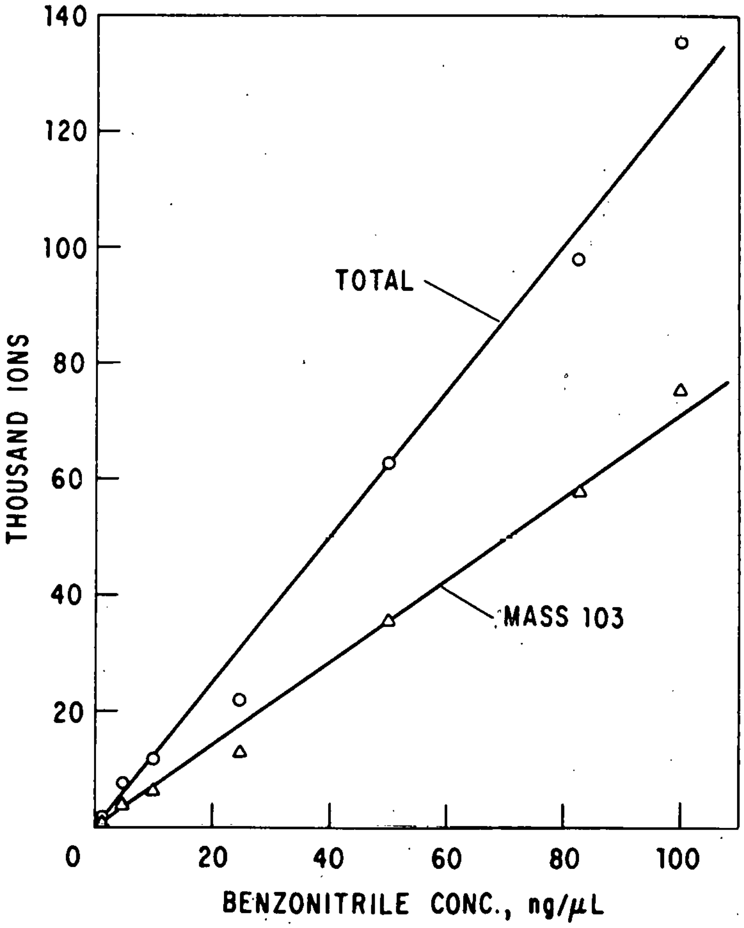

Fig. 2.2. Plot of Total-Ion and Single-Ion (Mass 103) Areas vs Concentration for Benzonitrile

Table 2.4. Percent Recoveries of Organics Extracted from Spiked Distilled Water

Compound Name	% Recovery
O-Xylene	42
3-Octanone	71
1-Heptanol	70
n-Butylbenzene	32
Phenol	61
Cresol	75
o-Ethylphenol	105
d_{10}-Anthracene	133

3 RESULTS AND DISCUSSION

3.1 WASTEWATER CHARACTERIZATION AND BIOLOGICAL REACTOR OPERATING CONDITIONS

Typical analyses of the quench and cyclone condensates used in the biological treatability study are provided in Luthy and Tallon (1978b). Average concentrations of raw pilot HYGAS plant wastewater characteristics after blending and following pretreatment were presented in Table 2.1. Raw wastewater had COD values of about 4000 mg/L and phenolic constituents of approximately 700 mg/L. Gas chromatographic analysis of one sample that had a COD of 4400 mg/L showed phenol equal to 800 mg/L, o-cresol equal to 64 mg/L, and (m+p)-cresol equal to 210 mg/L. Colorimetric phenol analysis of the same sample gave phenolic concentration of 980 mg/L. The colorimetric procedure does not report para-substituted phenols if the substituted group is a methyl radical, as is the case with para-cresol; thus it is not unexpected that the colorimetric procedure reports slightly lower total phenol concentration than the gas chromatographic determination. Approximately 60% of raw wastewater COD may be accounted for as phenol and cresol. Raw wastewater after blending had approximately 3700 mg/L ammonia (0.26 m/L) and approximately 13,000 mg/L of alkalinity as $CaCO_3$ (0.26 eqv/L). Thus, essentially all of the ammonia contained in raw HYGAS wastewater is present, in theory, as so-called free ammonia.

Table 2.2 summarized general operating parameters and performance characteristics for the reactor used in the organics study. These data are based on average values presented in Appendices V and XII of Luthy and Tallon (1978b). Data presented in Table 2.2 show that the reactor gave good removal efficiencies for COD, phenolics, and thiocyanate. The reactor possessed typical steady-state values of MLVSS and demonstrated good sludge settling properties. The reactor's operating conditions resulted in a COD removal rate of 0.86 day^{-1}. These performance factors are similar to those envisioned for a commercial activated sludge facility, although a commercial facility may be designed for a lower COD removal rate, depending on the degree of conservatism desired.

It is recognized that questions may be raised concerning sample storage in plastic containers. Out of necessity, raw wastewater samples collected at the pilot-plant facility were shipped and stored in plastic containers because of the large quantity of wastewater being handled and because it was believed that freezing offered the best alternative for long-term storage. The activated sludge effluent sample was collected in a plastic container and frozen because the biological oxidation experiments preceded the trace organic characterization studies by several months. Subsequent work performed at ANL on activated sludge treatment of wastewater from a coal gasification plant has used fresh samples of biological reactor effluent not stored in plastic containers.

3.2 CHEMICAL CHARACTERISTICS AND REMOVAL EFFICIENCIES OF ORGANIC CONSTITUENTS

Visual comparison of the total-ion chromatograms (Figs. 3.1-3.3) of all fractions reveals that the C-MU activated sludge process removed the

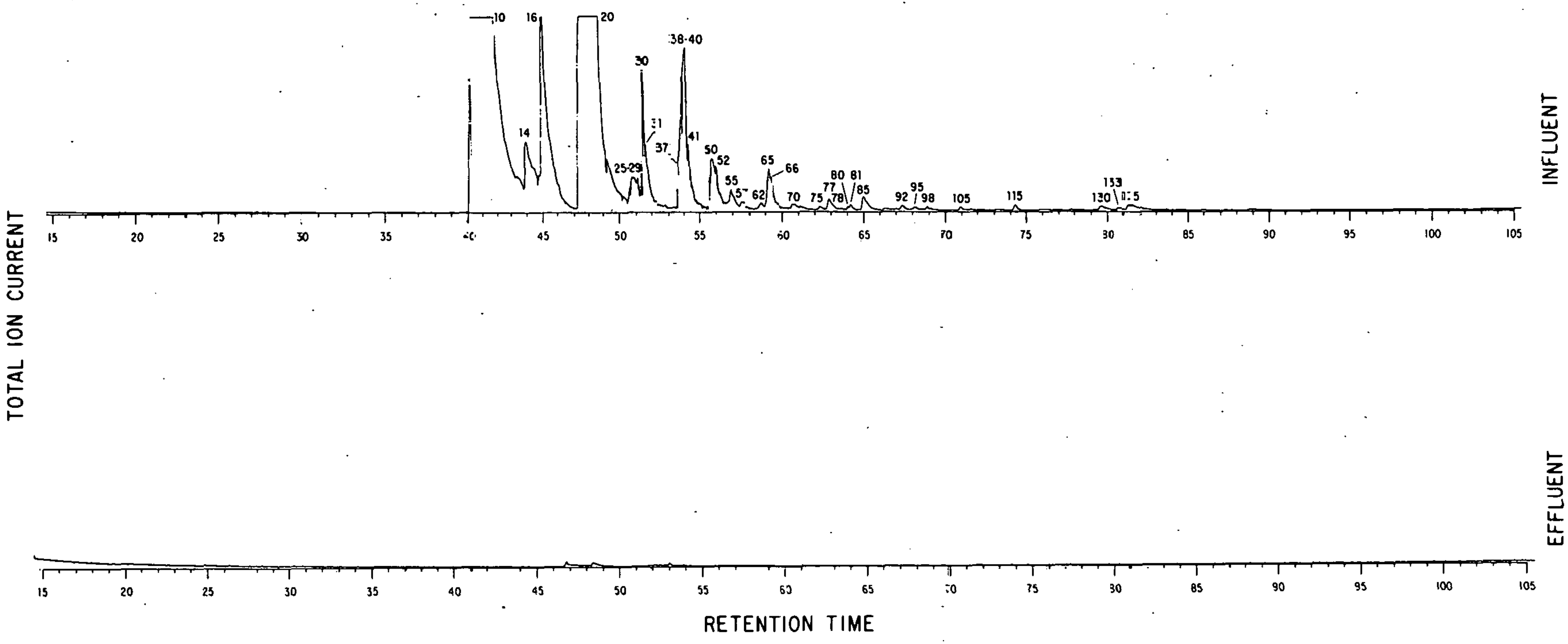

Fig. 3.1. Total Ion Chromatograms of Acidic Fraction Extracts of HYGAS Wastewater Treated by C-MU Reactor V. (The volume of the effluent extract was 20 times less than that of the influent extract.)

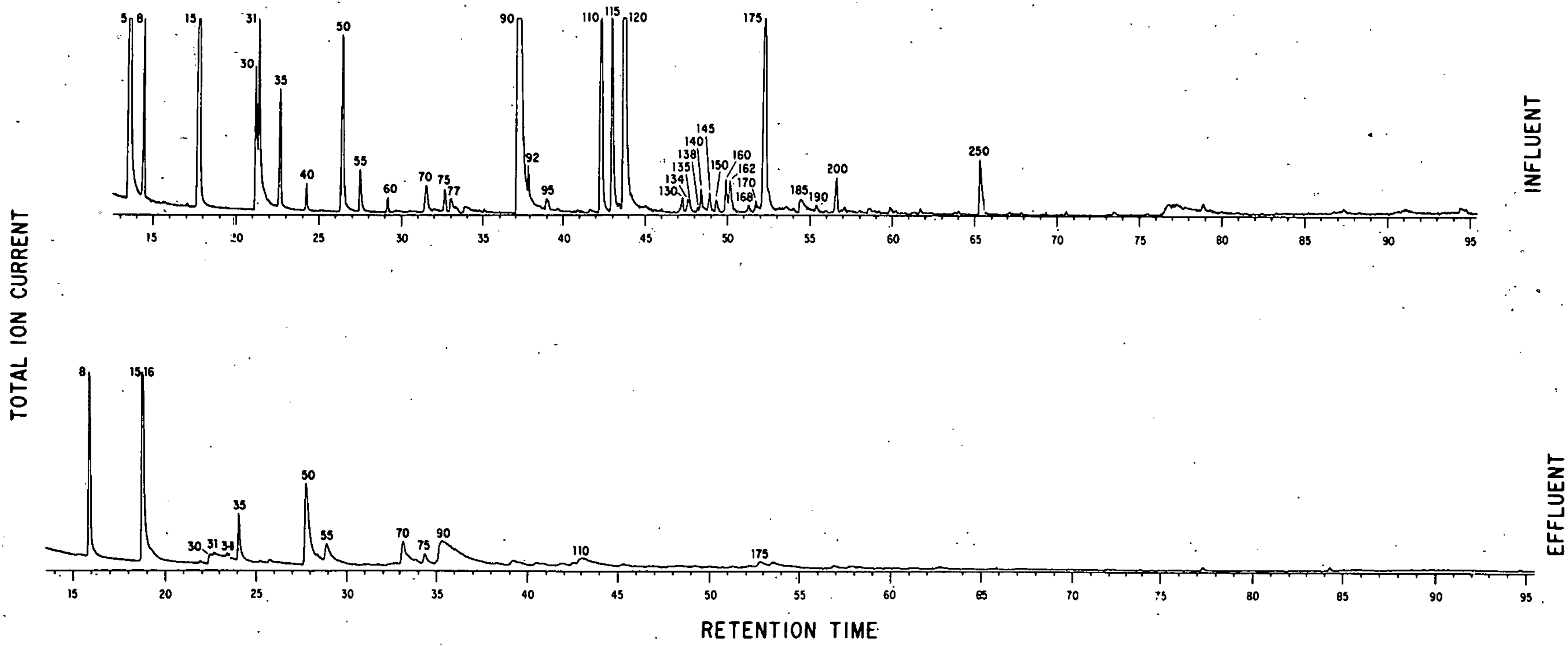

Fig. 3.2. Total Ion Chromatograms of Basic Fraction Extracts of HYGAS Wastewater Treated by C-MU Reactor V. (The volume of the effluent extract was 3 times less than that of the influent extract. Extracts were run using different columns of the same type, but different resolutions were employed.)

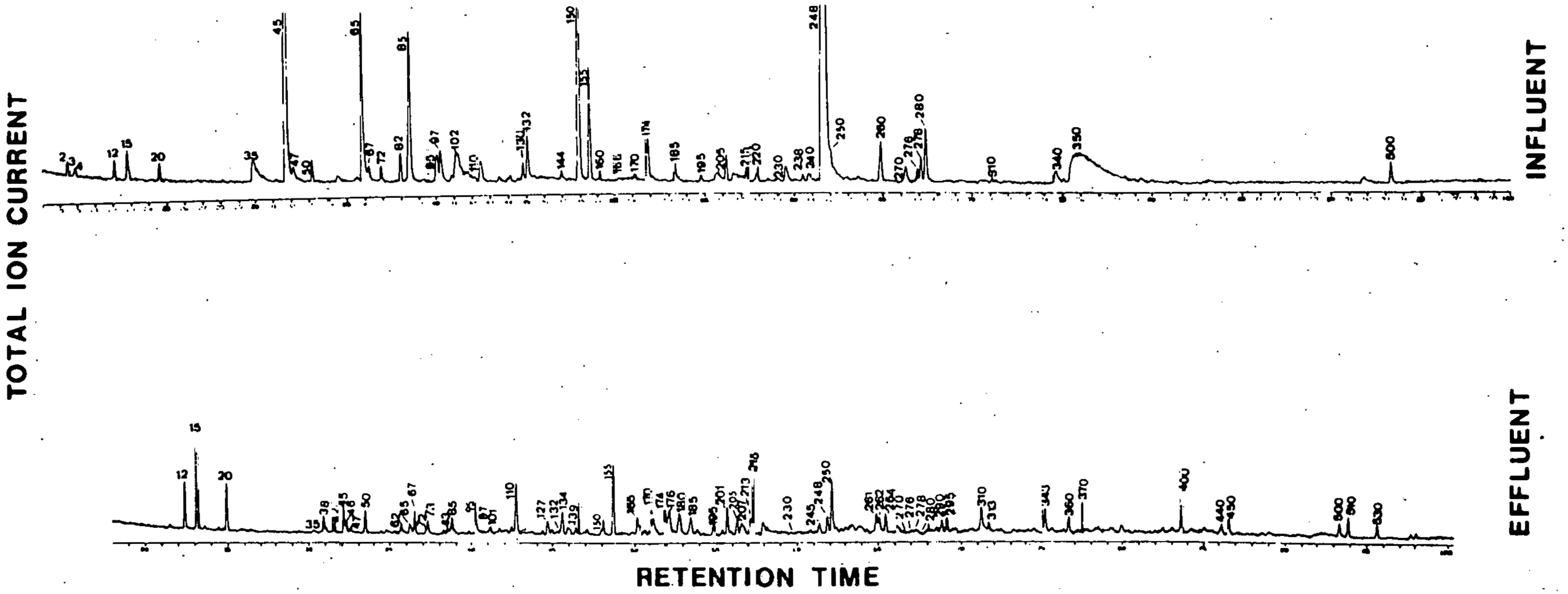

Fig. 3.3. Total Ion Chromatograms of Neutral Fraction Extracts of HYGAS Wastewater Treated by C-MU Reactor V. (The finer structure of the total ion chromatogram for the effluent extract is due to the fact that the volume of the effluent extract is 10 times less than that of the influent extract.)

bulk of the organic constituents. Results of extractable and chromatographable organics identified in the acidic, basic, and neutral fractions are presented in Tables 3.1, 3.2, and 3.3, respectively, on an estimated influent concentration basis together with an estimated percentage of activated sludge removal efficiency. Total ion peak areas served as the primary basis for the estimation of concentrations. For the neutral fraction, the concentration levels were estimated based on the benzonitrile study discussed in Section 2.5. For the acidic and basic fractions, additional information was obtained from several runs of standard compounds. Note that for practical purposes, however, reported concentration levels are only semiquantitative estimates, not only because of the nature of the GC/MS method used, but also because of possible losses due to extraction or separation procedures. Thus, instead of giving single-value concentration numbers (Tables 3.1-3.3), it was decided to assign ranges in concentration levels that allowed for a factor of variability of 2 to 3.

As shown in Table 3.1, the acidic fraction of raw wastewater influent consists almost exclusively of single-ring substituted phenolic compounds, all of which are virtually removed by activated-sludge treatment. Consistent with previous C-MU analyses (Luthy and Tallon, 1978b) and the screening studies of the Institute of Gas Technology, phenol and cresols constitute by far the largest fraction of organics observed. Despite the abundance of these compounds in the influent, no trace of phenol and only a trace of cresol was detected in the effluent.

Tables 3.2 and 3.3 present organics found in the basic and neutral fractions, respectively. The reader is cautioned to note that the total of extractable and chromatographable organics in the acidic influent fraction is two orders of magnitude larger than that reported for the basic fraction. As for the neutral organics, the total amount is slightly less than that of the basic fraction. The acidic fraction represented more than 98.5% of the identified compounds on a mass basis.

As shown in Table 3.2, organics in the basic fraction were primarily nitrogen heterocyclics (pyridine, quinoline, indole) and aniline and their alkylated derivatives. Most of the basic compounds were removed either completely or quite effectively, with the exception of certain substituted pyridines, e.g., dimethyl pyridine. In general, aliphatic substitutions resulted in lower percentage removal for derivatives of pyridine: compare pyridine versus picoline, and C_2- and C_3-pyridines. The results also show a certain selectivity of efficiencies of removal toward isomers of C_2- and C_3-pyridines. It has to be noted here that in the extraction procedure, certain basic compounds (indazole or benzimidazole, carbazole) ended up in the neutral fraction where their removal was complete (see Table 3.3, Peak Nos. 230 and 500).

As in the case of the basic fraction, organic concentrations in the neutral fraction of the influent wastewater sample are very low (Table 3.3). The extent of removal of neutral fraction organics by the bench-scale, activated-sludge process is very dependent on the chemical structure of the particular compound. The general trend is that heterocyclics and compounds containing heteroatoms are usually removed effectively. Examples are benzonitrile (peak No. 45), acetylthiophene (peak No. 97), isopropylthiophene (peak No. 101), methycyanobenzene (peak No. 132), benzothiophene (peak No. 155),

Table 3.1. Concentration in Reactor Influent and Effluent and Percent removal of Acidic Fraction Organics in HYGAS Plant Wastewater by Activated Sludge at Pilot Scale

Peak No.	Compound Name	Estimated Influent Conc. (μg/L)	Estimated Effluent Conc. (μg/L)	Estimated Percent Removal
10	Phenol	250,000	NT	100
14	Cresol	13,000	NT	100
16	Cresol	40,000	NT	100
20	Cresol	180,000	3	99.99+
25 - 29	C_2-Phenols	5,000	NT	100
30	C_2-Phenol	15,000	NT	100
31	C_2-Phenol	1,500	NT	100
37 - 41	C_2-Phenols	14,000	NT	100
50	C_2-Phenol	7,500	NT	100
52	C_3-Phenol	5,000	NT	100
55	C_3-Phenol	2,500	NT	100
57	C_3-Phenol	800	NT	100
62	C_3-Phenol	800	NT	100
65 + 66	C_3-Phenols	7,500	NT	100
70	C_3-Phenol	750	NT	100
75	C_4-Phenol	350	NT	100
77	Allyphenol or Methylvinylphenol or Hydroxyindan	1,100	NT	100
78	Methyldihydroxybenzene	500	NT	100
80	C_4-Phenol	300	NT	100
81	C_4-Phenol	500	NT	100
85	Allylphenol or Hydroxyindan or Methylvinylphenol	3,500	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

NT, not detected

Table 3.2. Concentration in Reactor Influent and Effluent and Percent Removal of Basic Organics in HYGAS Plant Wastewater by Activated Sludge at Pilot Scale

Peak Number	Compound Name	Estimated Influent Conc. (μg/L)	Estimated Effluent Conc. (μg/L)	Estimated Percent Removal
5	Pyridine	540	NT	100
8	Toluene	--	--	--
15	Picoline	310	160	48
30+31	Picolines	290	25	92
35	Ethylpyridine	75	32	57
40	C_2-Pyridine	14	NT	100
50	C_2-Pyridine	150	95	37
55	C_2-Pyridine	31	28	10
60	C_3-Pyridine	9	NT	100
70	C_3-Pyridine	30	28	7
75	C_3-Pyridine	15	8	47
77	Acetylenylpyridine	14	NT	100
90	Aniline	2,000	105	95
92	C_4-Pyridine	8	NT	100
110	Methylaniline	250	28	89
115	Methylaniline	180	NT	100
120	Methylaniline	510	NT	100
134+135	C_2-Aniline & C_4-Pyridine	15	NT	100
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	9	97
185	Isoquinoline	24	NT	100
200	Methylquinoline	28	3	90
205	Indole	60	NT	100

NT, not detected.

Table 3.3. Concentration in Reactor Influent and Effluent and Percent Removal of Neutral Fraction Organics in HYGAS Plant Wastewater by Activated Sludge at Pilot Scale.

Peak Number	Compound Name	Estimated[a] Influent Conc. (μg/L)	Estimated[a] Effluent Conc. (μg/L)	Estimated Percent Removal
12	Ethylbenzene	15	18	0.0[b]
15	m- & p-Xylene	30	5	0.0[b]
20	o- Xylene	14	18	0.0[b]
35	Cycloalkene?	66	10	85
38	n-Propylbenzene	ND	7	ND/PR[c]
42	Isopropylbenzene	ND	4	ND/PR[c]
45	Benzonitrile	800	12	98.5
46	Ethylmethylbenzene	ND	5	ND/PR[c]
47	Cycloalkene	8	2	75
50	Trimethylbenzene	16	10	37
62	Trimethylbenzene	6	5	17
65	C_2-Cyclohexene or C_3-Cyclopentene	208	6	97
67	Indan or Methylstyrene	18	8	53
72	Indene	12	3	70+[d]
82	Acetylcyclohexene or C_3-Cyclohexene	29	11	62
85	Acetophenone	190	13	93
95	Acetylcyclohexene or C_3-Cyclohexene or C_2-Cyclohexenone	47	23	51
97	Acetylthiophene or (C_3-Thiophene)	47	trace	99+
99	Methylindan	ND	9	ND/PR[c]
101	Isopropylthiophene	4	NT	100[e]
105	Methylindan or C_2-Styrene	ND	trace	ND/PR[c]
109	Methylindan or C_2-Styrene	ND	trace	ND/PR[c]
110	C_3-Cyclohexenone or Methylacetylcyclohexene	37	17	50+[f]
118	C_4-Benzene & C_3-Cyclohexene	ND	10	ND/PR[c]
125	C_4-Benzene	ND	12	ND/PR[c]
127	C_3-Cyclohexane?	ND	16	ND/PR[c]
130	C_4-Thiophene	17	8	53
132	Methylcyanobenzene?	47	NT	100
134	C_4-Thiophene & Methylindan or C_2-Styrene	ND	13	ND/PR[c]
135	Methylindene	ND	11	ND/PR[c]

Table 3.3. (Contd.)

Peak Number	Compound Name	Estimated[a] Influent Conc. (μg/L)	Estimated[a] Effluent Conc. (μg/L)	Estimated Percent Removal
136	Methylindene & C_4-Benzene	ND	11	ND/PR[c]
139	Methyl benzyl sulfide?	ND	12	ND/PR[c]
144	C_4-Benzene [1-(2-methylpropyl) benzene]	ND	11	ND/PR[c]
150	Naphthalene	405	9	98
155	Benzothiophene	111	35	68
160	C_4-Cyclohexadiene (terpenoid) or Phenyl isopropyl ether	ND	12	ND/PR[c]
165	C_4-Cyanobenzene	ND	6	ND/PR[c]
166	Dimethoxybenzene	ND	6	ND/PR[c]
174	Quinoline (80+) and Ethylmethoxybenzene or C_4-Cyclohexadiene	57	20	65 (combined)
176	C_4-Cyclohexadiene	ND	19	ND/PR[c]
180	C_4-Cyclohexadiene	ND	15	ND/PR[c]
185	C_4-Benzene and C_2-Methoxybenzene or C_4-Cyclohexadiene	24	14	42 (combined)
195	1-Indanone	ND	7	++[g]
201	Methylbenzothiophene	ND	11	ND/PR[c]
205	2-Methylnaphthalene	23	9	61
207	C_5-Cyclohexadiene	ND	trace	ND/PR[c]
213	Methylbenzothiophene	ND	22	ND/PR[c]
215	1-Methylnaphthalene	ND	24	ND/PR[c]
219	Isopropylmethoxybenzene or C_5-Cyclohexadiene	16	9	44
220	C_3-Methoxybenzene	ND	trace	ND/PR[c]
230	Indazole or Benzimidazole	29	NT	100
238	n-Propylmethoxybenzene or C_5-Cyclohexadiene	5	trace	99+
240	C_3-Methoxybenzene or C_5-Cyclohexadiene	trace	6	99+
245	Ethyl benzoate	ND	6	++[g]
248	Indole	1,980	10	99.5
250	Biphenyl	22	trace	99+
260	Methylindole	50	NT	100
261	C_2-Naphthalene	ND	10	ND/PR[c]
262	C_2-Naphthalene	ND	7	ND/PR[c]

Table 3.3. (Contd.)

Peak Number	Compound Name	Estimated[a] Influent Conc. (μg/L)	Estimated[a] Effluent Conc. (μg/L)	Estimated Percent Removal
264	Methylbiphenyl	ND	9	ND/PR[c]
270	Methylindole	26	trace	98+
276	Methylindole	15	NT	100
278	Methylindole	25	NT	100
280	Methylindole	65	NT	100
290	Acenaphthene	ND	7	ND/PR[c]
295	Methylbiphenyl	ND	7	ND/PR[c]
310	C_6-Thiophene & Methylbiphenyl	ND	8	ND/PR[c]
311	Bibenzyl	ND	7	ND/PR[c]
313	C_6-Thiophene	ND	4	ND/PR[c]
340	n-Propylnaphthalene	7	trace	98+
343	Fluorene	ND	17	ND/PR[c]
350-355	Cyanophenyl benzoate (?), & ?	68	NT	100
370	Plasticizer	--	--	++[g]
400	Aliphatic hydrocarbon	ND	6	ND/PR[c]
450	Anthracene or Phenanthrene	ND	6	ND/PR[c]
500	Carbazole	32	15	53
510	Aliphatic hydrocarbon	ND	10	ND/PR[c]
530	Plasticizer	--	--	++[g]
550	Plasticizer	--	--	++[g]

[a] ND, not determinable; NT, not detected.

[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. So, all told, 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 strictly appears only in the effluent.

C_3-methoxybenzenes (peak Nos. 260, 270, 276, 278, 280). In the case of aromatic hydrocarbons, the more aliphatic the substitution or alicyclic the content, the less the removal. Examples are substituted benzenes (peak Nos. 12, 15, 20, 50, 62), cycloalkanes or cycloalkenes (peak Nos. 35, 47, 67). Also most of the compounds with the labels ND/PR (see Table 3.3, note C, and discussion below) fall in this category. Polynuclear aromatics were only partially removed, depending again on the amount of substitution. Examples are napthalene (peak No. 150) vs substituted napthalenes (peak Nos. 205, 215, 261, 262), acenaphthene (peak No. 290), fluorene (peak No. 343), bibenzyl (peak No. 311) methylbiphenyl (peak No. 295) and anthracene of phenanthrene (peak No. 450). It is noted that all of the neutral fraction organics identified in the biological reactor effluent were found to be present at very low concentrations, e.g., less than several μg/L.

Compounds that were at very low concentrations in the influent neutral fraction were obscured or in the "noise" level in the influent chromatogram. It was very difficult or 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 3.3 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 influent, were poorly removed.

Some compounds like ethyl benzoate (No. 245) and plasticizers (Nos. 370, 530, 550) in Table 3.3 show up strictly only in the effluent. Ethyl benzoate can be either a contaminant or an artifact. As for plasticizers (primarily phthalates), they are ubiquitous trace contaminants. Also, plastic containers were used during sampling and pretreatment of the wastewater.

3.3 FACTORS PERTAINING TO INTERPRETATION OF RESULTS

This study used wastewater from HYGAS pilot plant Run Number 64. To evaluate the utility of the study results for projecting to commercial-scale, activated sludge performance, it is necessary to comment on the representativeness of the raw wastewater used and the relevance of the bench-scale tests and pilot-plant operating conditions. Important issues are wastewater sample strength, gasifier operating conditions, and biological reactor operating conditions.

3.3.1 Wastewater Sample Strength and Stability

The purpose of this study was to assess the fate of organic species in activated sludge treatment of a coal gasification wastewater. In this respect, the HYGAS wastewater contained the spectrum of organics that might be present in a commercial-plant effluent. However, for reasons discussed below little can be concluded about absolute concentration levels.

The wastewater used in the treatability study comprised a 1:1 blend of cyclone and quench condensates. This blending procedure ensured that all pilot-plant wastewater organic species were represented in the sample. However, because make-up water was introduced into the pilot plant's cyclone separator, the blend of cyclone and quench condensates may have been diluted as much as 30 to 50%. The steam-to-carbon ratio during the pilot-plant run was 1.82. Presently conceived commercial-scale designs call for a steam-to-carbon ratio approaching 1.0. This suggests that the pilot-plant product gas contained excess unreacted steam, and for this reason the effluents may have been more dilute. Other factors that may have tended to make the pilot-plant effluents of lesser strength are that organics may be adsorbed on overhead fines and may be removed by extraction from the aqueous phase and enters into the recirculating-coal-feed slurry oil.

With regard to the stability of the wastewater samples during transport, storage, and the bench-scale tests, a recent study (Raphaelian and Harrison, 1979) showed no detectable compositional changes for HYGAS quench-water samples stored at refrigerator temperatures (2-4°C) for a 60-day period or at an incubator temperature (37°C) for a 7-day period. The extractable organic constituents examined by Raphaelian and Harrison were of the same type as investigated in the present study and were isolated and analyzed in exactly the same way. Because the wastewater samples of this study were subject to conditions milder than the 37°C condition, it is probable that little or no detectable changes in the extractable and chromatographable organics took place.

3.3.2 Gasifier Operating Conditions

It is important to note that anticipated changes in commercial-scale gasifier operating conditions may offset the effects on sample strength described above. All of the above effects suggest that the pilot-plant wastewater used in this study may be relatively weak by comparison with predicted commercial-scale effluents. Potentially countering this aggregate effect is the fact that the low temperature reactor (LTR) in the commercial plant is designed (D.K. Fleming, IGT, written communication, 1979) to operate at higher temperatures, higher hydrogen partial pressure, and longer gas residence time than has been true at the pilot plant. Available data are contradictory as to the precise effects of gasifier operating conditions on organics production; however, it is anticipated that as the LTR temperature and the gas-phase residence time increases, decomposition reactions are possible. Decomposition reactions in a commercial facility may be enhanced further over those achieved at pilot scale by improved gas-solids contacting.

A commercial HYGAS facility is envisioned to process bituminous coal at about 90% carbon conversion. The wastewater characterized in this study was formed from pilot-plant processing of bituminous coal; however, carbon conversion was only 72%. This factor may also affect the relative strength of pilot-plant vs commercial-plant wastewater. Differences in raw product gas quench configuration between pilot plant and commercial plant would affect the distribution of organic species between gaseous and liquid effluents.

Appendix B presents additional information on the process conditions for HYGAS Run 64, including gasifier conversion and temperature data, and plant water balance.

3.3.3 Biological Reactor Operating Conditions

The bench-scale biological reactor was fed lime-pretreated, ammonia-stripped wastewater. Wastewater treatment in the commercial facility may incorporate phenol extraction and recovery prior to ammonia stripping if wastewater phenol loadings are sufficiently high. The addition of phenol extraction could affect the performance of a commercial biological wastewater treatment plant.

Lime pretreatment may have removed some raw wastewater organic bases and other material by precipitation. Commercial-scale wastewater treatment designs call for free and fixed-leg ammonia stripping prior to biological oxidation. Similar organic precipitation and adsorption reactions may occur in the fixed leg of an ammonia still, as in the lime pretreatment operation used in this study, if lime is added to the fixed leg. These conditions may not occur if caustic is used in fixed-leg stripping instead of lime. The extent to which bench-scale, lime-pretreatment ammonia stripping and free and fixed-leg ammonia stripping are identical with respect to the fate of organic constituents requires further evaluation.

The biological reactor selected for analysis of influent and effluent organic compounds was operated under conditions similar to those that would be expected in a commercial facility. A commercial facility may be designed for somewhat lower rates of COD removal than those that were employed with the reactor selected for the organics study; approximately 0.50 day^{-1} versus 0.86 day^{-1}, depending on the amount of conservatism desired. The reactor's performance showed good sludge settling properties and good removal efficiencies for COD, phenolics, and thiocyanate.

3.4 COMPARISON WITH OTHER STUDIES

It would be useful if the organics removal data obtained at bench scale in this study could be compared with data for similar kinds of organic constituents removed from an industrial process wastewater by activated sludge at full scale. One would expect that studies of organics removal by wastewater treatment systems of petroleum refineries or coking plants could provide data that would permit a rough measure of the reliability of trace organics removal estimates when going from bench scale to full scale. A careful search of the literature has been made, but the only study found that adequately treats the removal of a broad spectrum of organic constituents by activated sludge at full scale is Argonne's study of organics variation across the wastewater treatment system of a Class-B petroleum refinery. The study is described in detail in Raphaelian and Harrison (1978) and only those results that are pertinent to the present study are repeated here.

Wastewater samples were collected at SOHIO's Toledo refinery every four hours for four days. Influent to the activated sludge plant was collected from the dissolved-air-flotation (DAF) unit. Effluent from the activated-sludge plant was collected from the final clarifier (FC). The same methods of organics extraction, GC/MS sample analysis, and compound identification and quantitation procedures were used in the present study as were used in the refinery wastewater study.

A total of 304 compounds were identified in the neutral fraction of the DAF effluent. Only a very few of these compounds could be identified directly by their mass spectra. By using massgrams, however, identification of a majority of compounds was achieved. Concentrations of specific organic compounds identified in the DAF and FC effluents must be considered to represent order-of-magnitude estimates whose main value is for evaluation of the performance of the activated-sludge process. Used in this context, these data are the best available for defining performance of a full-scale, biological treatment plant for removing a great variety of specific organic compounds.

Over 400 specific organic compounds were found in the SOHIO wastewater before biological treatment. Data collected at the SOHIO refinery disclose an extremely high removal of specific neutral-fraction organic compounds in the activated-sludge unit, with the lowest removal demonstrated being 99.3%. This finding compares well with the neutral-fraction organics removal data of the present study only for those compounds initially at high concentrations in the influent (Table 3.3). In general, however, aromatic compounds were seldom as effectively removed from the gasification wastewater as from the refinery wastewater. The data correlate much better in the case of organics in the acidic fraction where the activated sludge removal efficiencies for phenolic compounds are excellent in both the coal gasification and refinery studies. The same good correlation exists with the organics in the basic fraction, where the removal efficiencies, in both cases, are generally good with the exception of certain alkylated pyridines.

It can be speculated that much of the organic material remaining in an activated sludge effluent, for either a bench-scale, coal gasification or a full-scale, petroleum-refinery wastewater will consist of compounds that are by-products of biological processes. The concentrations of specific organic compounds that originate in coal gasification and petroleum refining processes may be expected to be extremely low (in the parts per billion range) after conventional activated sludge treatment of process wastewaters.

The above expectation will be valid only for a properly designed and operated activated-sludge plant. It will not hold for operational upsets or shock loadings to the biological system. For this reason additional treatment systems may be needed to supplement activated sludge treatment. Harrison et al. (1979), for example, have recently recommended standby powdered activated carbon treatment systems for control of trace organics that could be emitted during subnormal operation of activated sludge systems used to treat petroleum-refinery wastewaters. The potential frequency and magnitude of upsets in activated sludge plants projected for commercial-scale, coal gasification plant will be addressed in later phases of the present program.

4 CONCLUSIONS

In this study it was found that over 98.5% of extractable and chromatographable organic material, on a mass basis, was represented in the acidic fraction of a coal-gasification process wastewater. The remaining material was composed largely of basic and neutral organic compounds with the latter being present at levels somewhat less than those in the basic fraction. Activated sludge processing removed most of the identifiable organic constituents. Compounds of the acidic fractions were removed almost completely. High removal efficiencies were also observed for compounds in the basic fraction, with the exception of certain substituted pyridines. The extent of removal of compounds in the neutral fraction was dependent on chemical structure. Aromatic hydrocarbons containing aliphatic substitutions and polynuclear aromatic compounds were only partially or poorly removed. Basic and neutral fraction organics in the biological reactor effluent were found in concentration levels of only several μg/L, with an overall removal of about 90%. Considering all the organics, the overall removal was 99.8%.

Analytical data presented in this study for organic characterizations are at best semiquantitative estimates. In future studies, it is planned to address some of the unresolved questions regarding quantification of organic compounds in complex wastewater. This work will include evaluation of extraction efficiencies for selected organic compounds from coal-gasification process effluents.

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APPENDIX A

PROCEDURES EMPLOYED FOR WASTEWATER PRETREATMENT AND ACTIVATED-SLUDGE PROCESSING

A.1 WASTEWATER PRETREATMENT PROCEDURES

Wastewater pretreatment consisted of:

a. Blending cyclone and quench condensates,

b. Removing excess alkalinity by treatment with lime, and

c. Removing excess ammonia by air stripping.

As shown in Fig. A.1, not all of the wastewater was subjected to ammonia removal because it was desired to reserve some for studies of biological oxidation at high ammonia levels. All wastewater was pretreated with lime because it was found that the excessively high values of alkalinity caused biological reactor pH to fluctuate upward uncontrollably. This activity was a result of carbon dioxide being stripped from solution during aeration at a rate greater than that which acid was being produced by the biological degradation reactions.

Alkalinity removal was achieved in this study by adding lime to the raw wastewater, which precipitated alkalinity as a calcium carbonate sludge. Lime addition was carefully controlled by experimental design so as to leave approximately 1000 mg/L residual alkalinity in the ammonia stripped wastewater after adjustment to a pH value of 7.3. It was found that this value of alkalinity provided sufficient buffering capacity to prevent downward pH changes as a result of the acid-producing reactions accompanying biological oxidation. This strategy eliminated the need for automatic pH control units on the biological reactors, and it permitted biological reactor pH to be monitored only on a daily basis. It was found that small additions of acid or base were required to prevent pH drift, and that pH value could be maintained within desired limits by daily chemical additions.

The purpose of the ammonia stripping process was to prepare influent to the biological reactors by reducing raw wastewater ammonia concentration to acceptable level. These levels were achieved by air stripping lime-pretreated wastewater at a pH of approximately 10. At this pH, ammonia equilibrium shifts to favor ammonia over ammonium ion and permits dissolved ammonia to be liberated from solution by contacting with air. The stripping process reduced raw wastewater ammonia concentration from an average level of 3200 mg/L to between 100 and 150 mg/L. A diagram of the ammonia stripping column is shown in Fig. A.2. Average characteristics for raw, lime treated, and ammonia stripped wastewater, and percentage change through ammonia stripping are presented in Table 2.1.

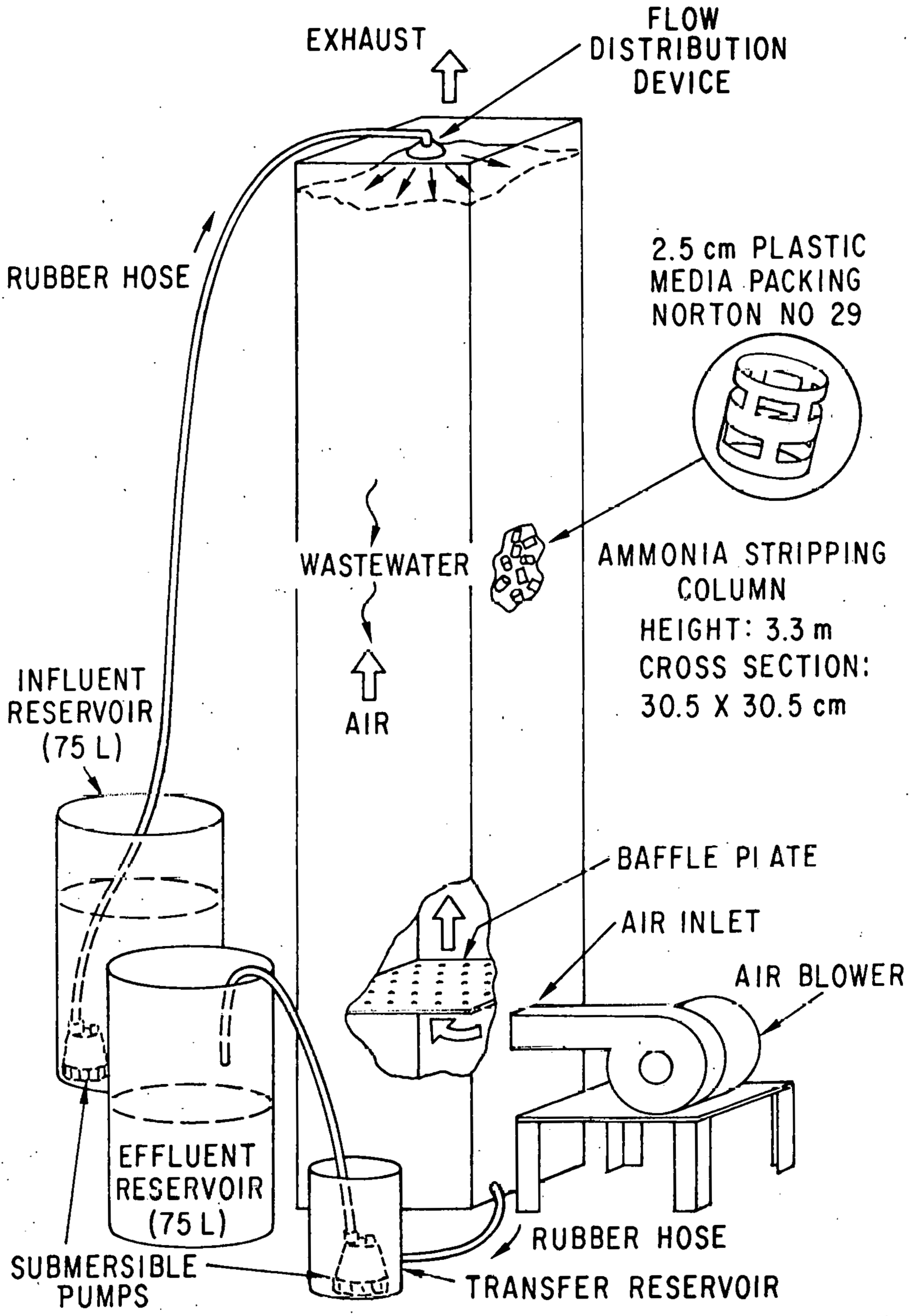

Fig. A.1. Schematic of Wastewater Pretreatment by Ammonia Stripping

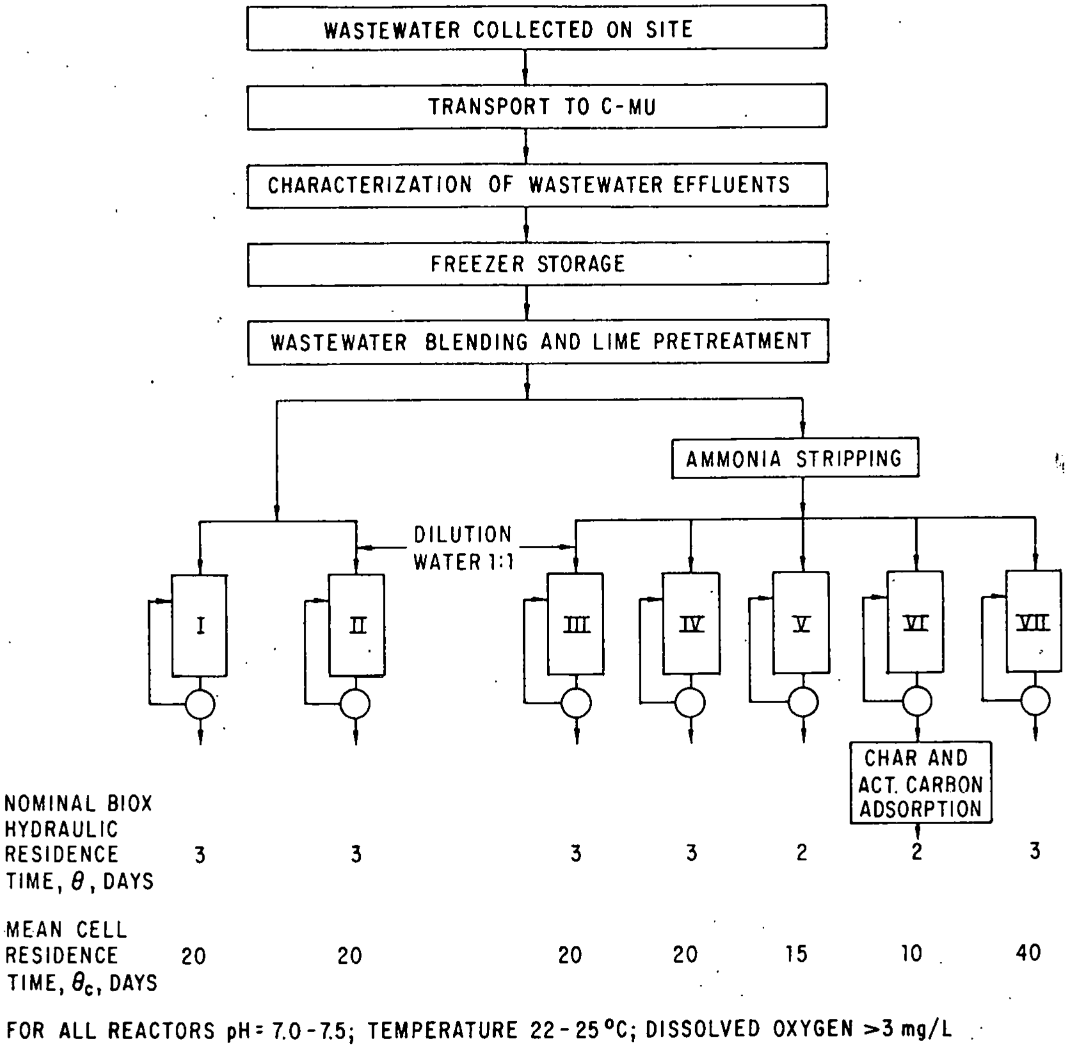

Fig. A.2. Experimental Design for Biological Oxidation Studies on HYGAS Pilot Plant Wastewater

A.2 EXPERIMENTAL DESIGN

The purpose of the biological treatability study was to define activated sludge performance characteristics with HYGAS wastewater and to address some of the basic questions identified with regard to biological treatment of coal conversion effluents. Figure A.2 shows a schematic of the general experimental design to meet the objectives of the treatability study. Results from that study are presented in a report by Luthy and Tallon (1978b).

The present report presents results of identification and removal of trace organic compounds. For the purpose of this study, GC/MS analysis of organic constituents was performed only on samples of influent and effluent from Reactor V (Fig. A.2). This reactor was selected for analysis of influent and effluent organic compounds because it was representative of the midrange of processing conditions employed in the biological oxidation study.

A.3 BIOLOGICAL OXIDATION EXPERIMENTAL PROCEDURES

A.3.1 EXPERIMENTAL APPARATUS

The biological oxidation unit consisted of complete-mix, continuous-flow, stirred-tank reactors. Figure A.3 shows a side view of the reactor used for the biological treatment studies. Each reactor was made of glass; the body was cylindrical with the bottom of the reactor being cone-shaped. Each reactor had a total volume of 6 liters. The reactors were equipped with semicircular plexiglass internal clarifiers; these were secured to the side of the reactors with silicone glue. The remaining portion of the reactor volume (5.15-5.40 L) served as the aeration chamber. The lower part of the clarifier was cut diagonally and partially covered with plexiglass to prevent air bubbles from entering the clarifier. This modification permitted treated effluent to rise and mixed-liquor suspended solids to settle back into the aeration chamber. Outlet taps were constructed through the side of the reactors at the supernate levels of the clarifiers, thereby allowing the effluent to gravity drain into collection reservoirs. Aquarium pumps provided air to the units; the air was evenly dispersed by use of diffusing stones located at the base of the aeration chambers. The conical design of the base of the aeration chamber prevented incomplete mixing. Though biological floc-mixing was satisfied by aeration, aeration alone was found ineffective in handling problems arising from bacterial floc-clumping. Aeration also caused the wastewater to foam. Electric stirrers were mounted above the reactors and set at 60 rpm. This setup remedied problems associated with bacterial floc-clumping and controlled foaming problems to a certain extent by helping to reentrain solids that tended to accumulate on the surface of the reactor. Stirring did not effectively solve foaming problems, and so it was necessary to apply antifoaming agent (Calgon C-37) sparingly to the surface of the aerator on a daily basis during most of the study.

The general layout of the experimental apparatus is shown in Fig. A.4. Influent flow rate was controlled with variable speed peristaltic finger pumps. The influent flowed from refrigerated storage tanks kept at a height of about 20 cm above the reactors. The height differential provided a positive pressure head to the finger pumps and reduced flow fluctuations caused by influent line clogging owing to the relatively low flows that were

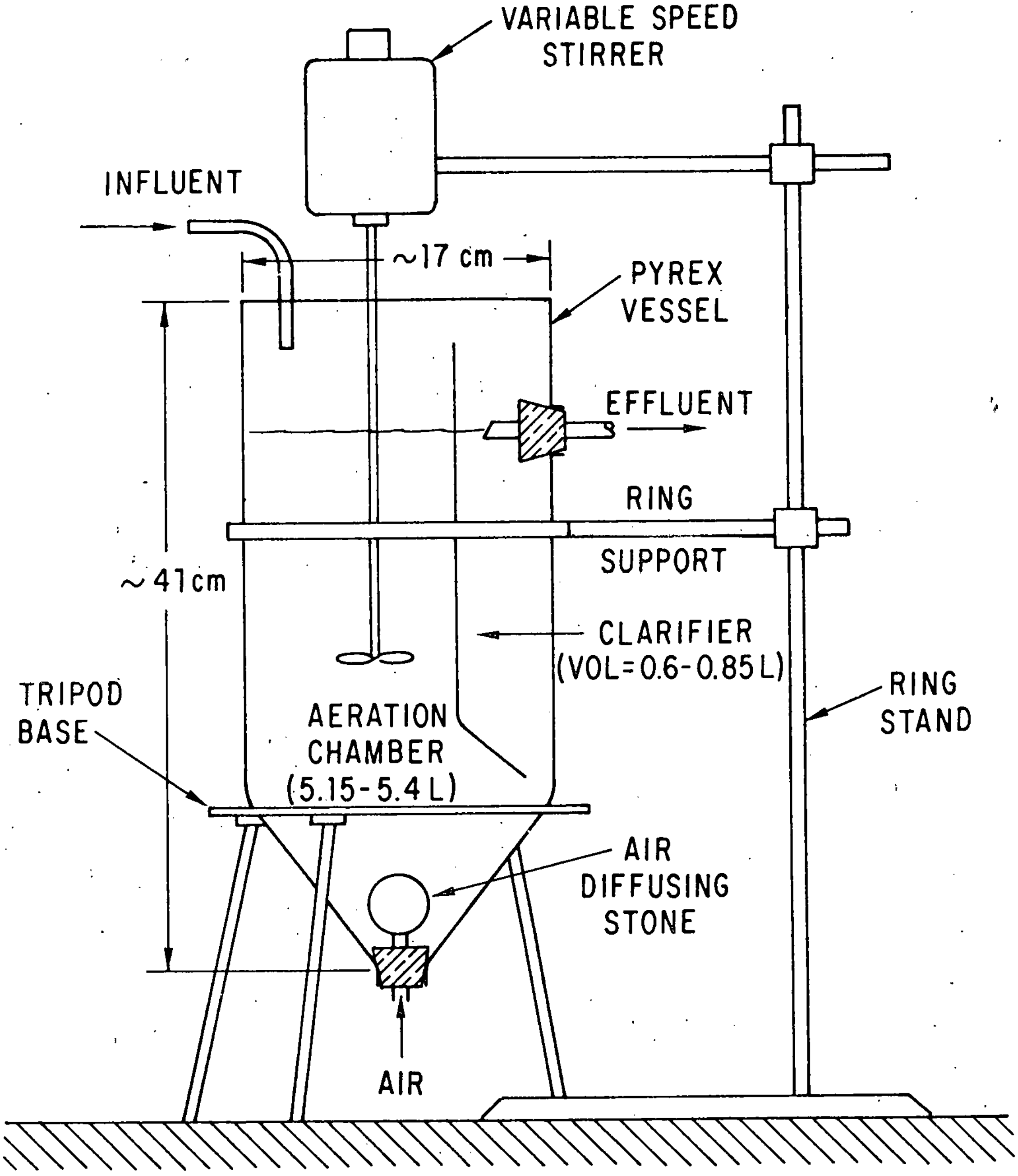

Fig. A.3. General View of Continuous Stirred-Tank Reactor for Biological Oxidation Kinetic Studies

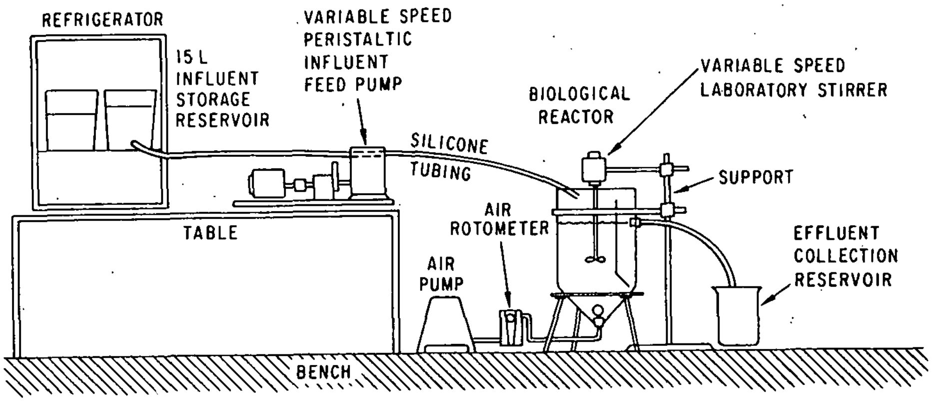

Fig. A.4. General Layout of Biological Oxidation Experimental Apparatus

maintained. Reactor temperature was not controlled and varied in the range of 22 to 25°C. Influent to the biological units was refrigerated in order to minimize sample degradation. Effluent samples were analyzed and/or composited daily. Composite samples were preserved and stored in a refrigerator.

A.3.2 SAMPLING, ANALYSIS, AND OPERATING SCHEDULE

The biological reactors were monitored daily for flow, pH, MLSS, and sludge wasting. The following parameters were held as experimental constants: influent COD, D.O., pH, hydraulic residence time, and mean cell residence time. Reactor D.O. was maintained greater than 3 mg/L. Reactor pH was maintained in the range of 7.0-7.5 by the residual alkalinity in the pretreated wastewater and by small daily pH adjustments to the influent and/or to the mixed liquor. Consistency of influent COD was assured as well as may be achieved by the wastewater storage and blending procedures.

The reactor was managed on the basis of mean cell residence time. It was therefore necessary to compute the quantity of sludge to be wasted daily. This computation was made according to the following formula:

$$\text{mL of sludge wasted per day} = \frac{\left(\frac{1}{\theta_c} V X_1 - F X_2\right) 1000}{X_1}$$

where:

θ_c = desired mean cell residence time, days

V = reactor volume, L

X_1 = MLVSS, mg/L

X_2 = effluent VSS, mg/L

F = daily flow, L/d

The procedure ensured that cell wasting calculations took into account the amount of volatile suspended solids carried out with the effluent.

Sludge was wasted by syphoning off the desired volume of mixed liquor, dewatering the sludge on a vacuum filter, and returning the filtrate to the reactor. This methodology allowed independent control of hydraulic and mean cell residence times. Hydraulic residence time was calculated by dividing reactor volume minus clarifier volume by effluent flow volume collected over twenty-four hours.

An abbreviated sampling schedule was employed during acclimatization and the balance period. The balance period, the time required for the reactor to attain steady-state operation, was defined as being equal to three complete solid wasting cycles, i.e., three times θ_c. During steady-state operation, the reactor performance was characterized according to a set of standard wastewater parameters and sludge properties.

A.3.3 ACCLIMATIZATION

Activated sludge was obtained from a local coke plant treating weak ammonia liquor. The sludge was used to seed the biological reactors. Prior to receipt of HYGAS wastewater, the reactors were fed weak ammonia liquor for several weeks. Upon arrival, the HYGAS wastewater was blended, pretreated, and diluted to 50% strength; feed strength was gradually increased to 100% strength over a period of three weeks.

Reactor performance and stability during acclimatization were evaluated on the basis of COD, thiocyanate, and phenol removal. Oxygen uptake, sludge volume index, and microbial activity were used as indicators of sludge viability. During startup, feed strength was increased by 10-25% whenever COD and phenol removals approached 75 and 99%, respectively.

An estimate of nutrient requirements showed that phosphorus was the only apparent serious nutrient deficiency. Hence the wastewater was supplemented with phosphorus.

Boron was present at approximately 100 mg/L in HYGAS wastewater. This concentration of boron may not be severely toxic to the acclimatized bacteria that removes carbonaceous substrates. However, nitrification was inhibited in these studies, and one of the suspected causes was high boron levels. Boron was also suspected of inhibiting bacterial growth.

A.4 BIOLOGICAL OXIDATION STUDIES

A.4.1 REACTOR OPERATING CONDITIONS

The biological reactors were operated at dissolved oxygen (DO) levels greater than 3 mg/L, and dissolved oxygen generally fluctuated in the range of 4 to 6 mg/L. At this concentration DO is not limiting to bacterial stabilization reactions, including nitrification.

Reactor pH was maintained in the range of 7.0-7.5. That pH range represented a compromise between selection of appropriate pH conditions for minimizing potential HNO_2 and NH_3 toxicity to nitrifying bacteria while encompassing the pH range recommended as being suitable for thiocyanate oxidizing organisms.

Reactor mean cell residence time was selected on the basis of literature review recommendations and on laboratory experimentation. The literature review indicated that a sludge wastage rate of about 5% per day may be suitable for treatment of related wastewaters. This wastage rate corresponds to a mean cell residence time of 20 days, a value that was selected as a point from which to perform parametric studies to determine a range of suitable mean cell residence times. When one of the reactors was operated with a sludge age of approximately 60 days, the sludge demonstrated very poor settling characteristics. When managed on a sludge age of 40 days, settling characteristics improved to the point where effluent suspended solids were not excessive. It was concluded that a sludge age of 40 days represented an upper bound beyond which operational problems may be encountered. It was also found in this study that a sludge age of about 10 days was the lowest permissible mean cell residence time that could be sustained during prolonged steady-state testing. For these reasons the biological kinetic study employed mean cell residence times varying from 10-40 days.

Hydraulic residence time was selected initially on the basis of conservative estimates of kinetic growth constants. Assumed values of yield coefficient and organism decay coefficient were used to correlate estimates of COD removal efficiency, mixed liquor volatile suspended solids (MLVSS), and mean cell residence time. Hydraulic residence times were then selected that gave flexibility in steady-state MLVSS values. It was desired that under steady-state conditions reactor MLVSS should fall within a normal operating range of 1000-8000 mg/L. Experimental results showed in fact that MLVSS varied from 1000-3000 mg/L for the test conditions shown in Fig. A.1.

The attainment of steady-state operation was defined as that interval (balance period) necessary to achieve three complete solid wasting cycles. The reactors were then run from 7-14 weeks to obtain sufficient steady-state performance data.

A.4.2 BIOLOGICAL OXIDATION OF UNDILUTED STRIPPED WASTEWATER

The main series of biological oxidation experiments consisted of a study to determine biological oxidation kinetics with undiluted stripped wastewater as represented by Reactors IV, V, VI, and VII on Fig. A.1. In these experiments, mean cell residence time, hydraulic residence time, and influent COD were maintained as experimental constants, while effluent COD and MLVSS were system variables. There was no variability in mean cell residence time, which was imposed by the solids wasting schedule. Held reasonably stable by the wastewater storage procedure, influent COD had a coefficient of variation of 11-16% during the time that the reactors were at steady-state operation. Hydraulic residence time was maintained as constant as was feasible by use of peristaltic feed pumps.

Table 2.2 in the main body of this report showed general operating parameters and performance characteristics for Reactor number V, and these are based on average values presented in Appendices V and XII of Luthy and Tallon (1979*b*). Influent and effluent samples were collected from the reactor for characterization of trace organic species. The samples were composited over a three-week period during steady state and were preserved prior to shipment to Argonne by freezing in plastic containers. The samples were thawed and one-gallon aliquots of influent and effluent were shipped by air on June 7, 1978 from C-MU to Argonne, where they were stored at 2-4°C until prepared for GC/MS analysis.

APPENDIX B

PROCESS REVIEW OF OPERATING CONDITIONS

The wastewater samples analyzed in this report consisted of a composite of condensates from Runs 62 and 64 at the HYGAS pilot plant. C-MU's biological-reactor system was acclimated on Run 62 wastewater. The biological-system treatability data, however, were obtained from Run 64 wastewater. The coal for both runs was Illinois No. 6 bituminous coal from the Peabody No. 10 mine.

Pilot plant operating conditions were reviewed with respect to comparable conditions given in Revision No. 2 of the commercial concept design prepared by PROCON Inc. for the HYGAS process. Operating variables evaluated were gasifier conversion, gasifier temperatures, and plant water balance.

B.1 GASIFIER CONVERSION

Gasifier conversion is a measure of the relative amount of coal or carbon gasified and is based on the amount of coal fed down into the gasifier. This feed rate is called the net feed rate and is equal to the total feed less the overhead dust. Net feed rate is a better measure of gasifier performance, since the overhead dust does not have an opportunity to be gasified. Because the level of pretreatment in the pilot plant is comparable to that of the commercial-plant design, the amount of volatile materials able to be gasified is comparable.

Conversion can be calculated either by an ash balance method or by weight balance. The ash balance assumes that the overhead dust has the same ash content as the feed coal. The weight balance method makes no such assumptions and uses an overall weight balance. The following equations are used in the ash-balance method of computation:

$$\%\ \text{carbon gasified} = 100 \times \quad 1 - \frac{A_F C_{SC}}{A_{SC} C_F} \qquad \text{(B.1)}$$

$$\%\ \text{coal gasified} = 100 \times \quad 1 - \frac{A_F (1 - A_{SC})}{A_{SC} (1 - A_F)} \qquad \text{(B.2)}$$

where:

A_F = ash content of feed
A_{SC} = ash content of spent char
C_F = carbon content of feed
C_{SC} = carbon content of spent char.

The equations used in the weight balance method are as follows:

$$\% \text{ carbon gasified} = 100 \times \quad 1 - \frac{W_{SC}C_{SC}}{W_FC_F-W_DC_D} \qquad (B.3)$$

$$\% \text{ coal gasified} = 100 \times \frac{W_F(1-A_F)-W_D(1-A_D)-W_{SC}(1-A_{SC})}{W_F(1-A_F)-W_D(1-A_D)} \qquad (B.4)$$

where:

W_F = lb/hr coal feed
W_{SC} = lb/hr spent char
W_D = lb/hr overhead dust
A_D = ash content of overhead dust
C_D = carbon content of overhead dust.

The relative values for these conversions compared to the commercial plant design are shown below. The values were calculated from a report by the Institute of Gas Technology (1978). The commercial-plant design values were calculated from flows shown on PROCON process flow diagram 2174-02.00-12.10-D, dated 3/31/78. The overall values are based on the total coal feed, not the net feed.

	% Carbon Gasified			% Coal Gasified		
	Ash Balance	Wt. Balance	Overall	Ash Balance	Wt. Balance	Overall
HYGAS Run 64	72.8	74.6	59.5	77.4	79.4	64.7
Commercial Plant	90.1	90.1	83.3	91.1	91.1	84.3

During the period of Run 64, the ash content of the overhead dust (12.29%) was near that for the feed (12.63%). Thus, the close agreement between ash and weight-balance conversion for the pilot plant. The commercial-plant conversions are close because ash contents are nearly equal (21.9 for dust, 20.9 for pretreated char), conversion is high, and the rate of overhead dust loss is low.

It is important to note that the lower gasifier conversions do not necessarily mean that the process is incapable of higher conversions. Each pilot-plant run is planned to demonstrate the interrelationships among specific process variables, like feed rate, conversion, bed temperatures, steam rate, etc. In this particular run, lower conversions were noted as a result of run-specific goals. The effects of the lower conversions on gasifier yields are not totally clear and can best be discussed as they are related to gasifier temperatures.

B.2 GASIFIER TEMPERATURES

A comparison of gasifier temperatures for Run 64 is given below. Note that the low temperature reactor (LTR) and high temperature reactor (HTR) are cooler than called for in the commercial-plant design. Steam-Oxygen Gasifier (SOG) bed temperature is up to design. Again, these temperatures as tabulated here are specific to the goals of the run and do not directly reflect upon process capabilities.

	Commercial Design	Temperatures of Run 64 8/23/77 to 8/24/77
Slurry Drying Bed	600	639
LTR	1432	1148
HTR	1700	1468
SOG	1800	1819

The main effect of these lower temperatures is to decrease reactor conversion. The resulting effect on gasifier product composition requires a more complicated evaluation. In addition to the synthetic gas components, oils, phenols, and other heavy organics are produced during coal devolatilization and gasification in the LTR. Some of these condensible organics are soluble in water and are eventually present in the plant wastewater. The quantity of chemically oxidizable components in the wastewater is the Chemical Oxygen Demand, or COD.

Only gaseous components are produced in the HTR and SOG because of the high temperatures and configuration of these reactors. Therefore, changes in conversion and gasifier temperature can affect only the production of heavy organics as they occur in the LTR.

The real question of the effect on product gas composition of raising LTR temperatures from this pilot-plant run to the commercial-design level cannot be fully determined at this time. First, no hard data exist for bituminous gasification from the IGT bench-scale reactor that simulates the LTR. Second, the data available for lignite and sub-bituminous devolatilization and gasification, as reported in Johnson (1973-1975), are somewhat contradictory. Some results indicate that the LTR would continue to produce a slightly increasing quantity of COD components as temperature increased from 1100-1500°F. Other data indicate that no such increase could be expected. At most, the increased production would only be about 10-15%.

Another interesting, and as yet unquantified, occurrence in the LTR that could affect the composition of the organics produced is dealkylation and dehydroxylation of the more complex components in the LTR. Dealkylation and dehydroxylation reactions remove respectively alkyl and hydroxyl groups from aromatic compounds. The resulting effects are a decrease in compounds such as alkylbenzenes and higher phenolics and an increase in the quantity of benzene that is produced.

Data on peat gasification in an LTR type unit, and other kinetic studies conducted by IGT and others, reportedly indicate that higher LTR temperatures greatly promote dealkylation. A similar relationship is expected for dehydroxylation. Depending on the reactions involved, dealkylation conversions as high as 90% have been reported. These results cannot as yet be applied to coal gasification in the pilot plant, but they do indicate that higher commercial-plant design temperatures could change treatability requirements; a shift from phenol recovery to biological, or to other forms of chemical treatment, could become cost effective because of the presence of fewer refractory organics in the wastewater.

B.3 PLANT WATER BALANCE

In both the pilot-plant and the commercial design, water is required to remove entrained char and to quench the raw gas from the gasifier. In the pilot plant it is discharged directly and is not treated for reuse. Additional make-up water is required to replace the higher blowdown, which results in dilution of the organics that are present relative to those expected in a commercial plant.

Also, as shown below, steam use in the pilot plant is higher than that expected in the commercial-plant design. The additional steam required is used to maintain fluidization velocities and to reduce the relative quantity of oxygen in the SOG to inhibit clinkering. In the commercial plant, the SOG would be resized to achieve the desired velocities without the higher steam requirements. The feasibility of this possibility has been demonstrated during recent runs at lower gasifier pressures, as indicated below.

	# Steam/# Coal Feed	# Steam/# Carbon (net)
HYGAS Run 64	1.73	3.12
Commercial Design	1.13	1.94

B.4 RESULTS

Based on the process review, it is felt that the pilot-plant wastewater should, in general, be comparable to untreated commercial-plant wastewater. That is, the same general types of compounds should be present in both streams. The review also indicates that pilot-plant effluent water should be more dilute in wastes requiring treatment than would be the wastewater from a commercial plant. If the LTR temperature is increased to the level specified in the commercial design, the quantity of COD-producing organics will probably remain constant, within ±10%. There may, however, be a shift from substituted aromatics to benzene, as a result of dealkylation and dehydroxylation. This effect could be significant and should be confirmed by laboratory testing. Final confirmation will not occur until a demonstration plant is constructed.

B.5 REFERENCES

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