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Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability

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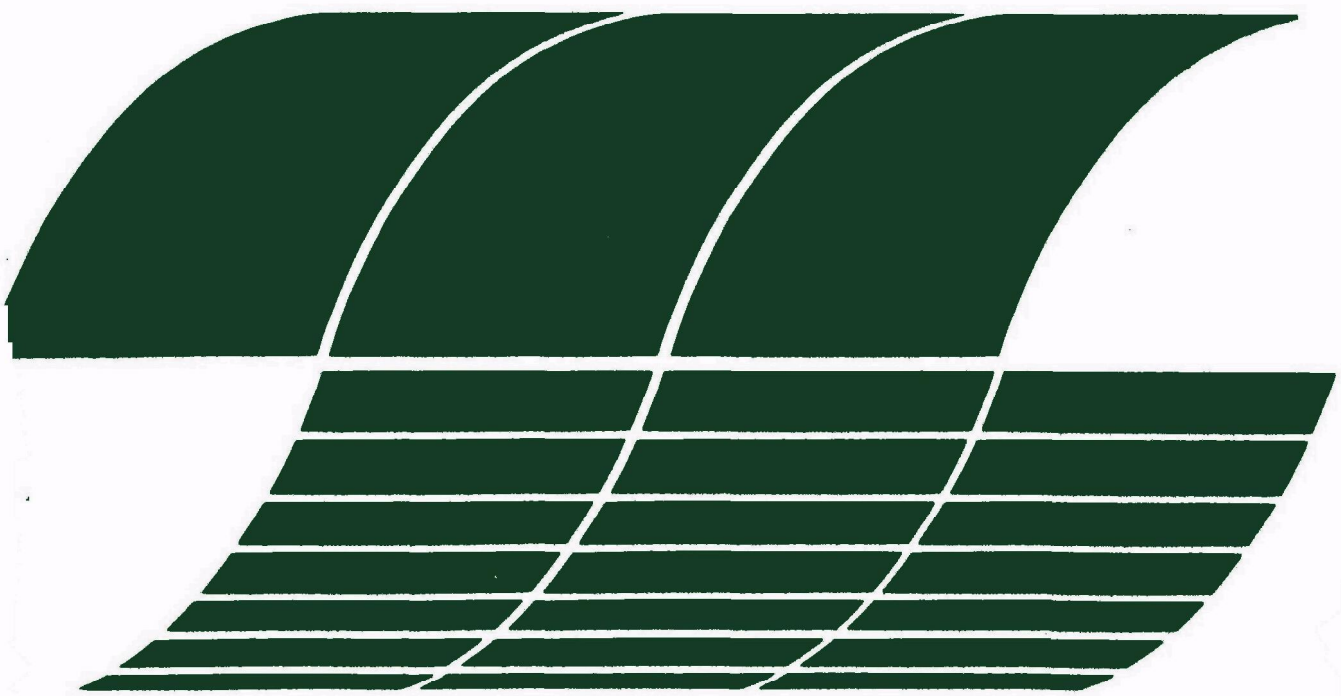

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Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability

by

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ABSTRACT

The objectives of this project are to assess the environmental impact of wastewater contaminants originating from the production of synthetic fuels from coal, and to evaluate, on a bench-scale, alternative wastewater treatment technologies for the control of these contaminants. This report presents the results of a survey aimed at determining the chemical characteristics of coal conversion wastewaters and at identifying specific organic contaminants which might be found in such wastewaters. The constituents have been identified by reviewing the published literature, visiting coal gasification and liquefaction research and development installations, and analyzing reports and project documents from a variety of coal conversion operations. A preliminary assessment of the aquatic impact of these wastewaters and of their biological treatability is also presented. The results indicate that approximately 60-80% of the total organic carbon is phenolic in nature, consisting of monohydric phenols, dihydric phenols, and polyphenols. The remainder of the organic material consists of mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, polynuclear aromatic hydrocarbons, and simple aliphatic acids. The composition of the wastewaters appears to be relatively uniform, especially with respect to the phenolic constituents, regardless of the specific process technology and type of feed coal employed.

At the concentrations reported, the discharge of these wastewaters would have an adverse impact on aquatic life and, as a result, a significant degree of wastewater treatment is necessary. While aerobic biological processes appear to be among the methods of choice for treating these wastewaters, additional information is required in order to assess the biological treatability of these coal conversion wastewaters and to develop suitable design and operating guidelines. An experimental program to provide such information is underway.

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CONTENTS

Abstract ii
Figures iv
Tables vi
Acknowledgements viii

1. Introduction 1
2. Conclusions 2
3. Background 3
4. Chemical Characteristics of Coal Conversion Wastewaters 7
5. Potential Aquatic Impact of Organic Constituents of Coal Conversion Wastewaters 24
   - Aquatic Pollution Problems: General Considerations . . . 24
   - Aquatic Toxicities of Organic Constituents of Coal Conversion Effluents 26
     - Phenols 32
     - Aliphatic Acids 35
     - Polynuclear Aromatic Hydrocarbons 35
     - Nitrogen- and Sulfur-Containing Compounds 39
   - Research Needs 41
   - References 43
6. Microbial Degradation of Organic Constituents in Coal Conversion Wastewaters 48
   - Literature Review 48
     - Phenol and Other Monoaromatic Hydrocarbons 48
     - Nitrogen-Containing Aromatic Compounds 69
     - Polynuclear Aromatic Hydrocarbons 77
     - Summary of Literature Findings 82
   - Experimental Biodegradability Studies: Preliminary Screening 84
   - References 89
7. Preliminary Biotreatability Studies 93
   - Introduction 93
   - Objectives 93
   - Composition of Synthetic Coal Conversion Wastewaters . . 94
   - Pilot Units for Acclimation and Biotreatability Studies 94
   - Experimental Approach 96
   - Respiration Studies 97
   - Future Directions 102

FIGURES

Number		Page
1	Initial Reactions in the Bacterial Degradation of Various Compounds that Converge on Catechol	50
2	Initial Reactions in the Bacterial Degradation of Various Compounds that Converge on Protocatechuate	51
3	Initial Reactions in the Bacterial Degradation of Various Compounds that Converge on Gentisic Acid	52
4	Example of an Aromatic Compound Possessing an Alkyl Side Chain which Remains Intact Prior to Ring Cleavage	54
5	Ortho and Meta Fission Pathways for the Dissimilation of Protocatechuate and Catechol	55
6	Bacterial Metabolism of Gentisic Acids	56
7	General Reaction Scheme for Bacterial Degradation of Substituted Phenols	65
8a	Oxidation of Dihydric Phenols	68
8b	Oxidation of Cresols and Other Methylphenol Derivatives	68
9	Pathway Proposed for the Microbial Degradation of 3,4-Dihydroxypyridine	71
10	Pathway Proposed for the Microbial Degradation of 2,5-Dihydroxypyridine	72
11	Pathway Proposed for the Degradation of Pyridine by Nocardia sp	73
12	Pathway Proposed for the Microbial Degradation of Pyridine by Bacillus sp	74
13	Pathway Proposed for the Microbial Degradation of Indole	76
14	Pathway Proposed for the Degradation of Naphthalene by a Species of Pseudomonas	78
15	Proposed Pathway for the Microbial Degradation of Phenanthrene	80

FIGURES (continued)

Number		Page
16	Proposed Pathway for the Microbial Degradation of Anthracene	81
17	Formation of cis-Dihydrodiols from the Microbial Metabolism of Benzo(a)pyrene and Benzo(a)anthracene .	83

TABLES

Number		Page
1	Water Quality Characteristics of Coal Conversion Wastewaters	4
2	Mass Spectrometric Analysis of Benzene-Soluble Tar	5
3	By-Product Water Analysis from Synthane Gasification of Various Coals	8
4	Percentage of COD Attributable to Phenol in Synthane Gasification	9
5	Some General Properties of Raw and Processed Wastewater from the Lurgi-Process Plant at Sasolburg, South Africa	10
6	Concentration of Organic Compounds in Raw and Processed Wastewater from the Lurgi-Process Plant at Sasolburg, South Africa	11
7	COD and TOC-Equivalents of Organic Constituents of Sasol Wastewater	12
8	Concentration of Organic Compounds, as COD and TOC, Found in the Raw and Processed Wastewater from the Lurgi-Process Plant at Sasolburg, South Africa	13
9	Percentages of Unidentified COD and TOC in Sasol Wastewater	14
10	Contaminants in Product Water from Synthane Gasification of Various Coals	15
11	Summary: Organic Constituents in Coal Conversion Wastewaters	16
12	Polynuclear Aromatic Hydrocarbons in SRC Raw Process Water	22
13	Summary of Environmental Behavior of Classes of Organic Coal Conversion Effluent Constituents	27
14	MATE and EPC Values in Water for Some Constituents of Coal Conversion Wastewaters Based on Human Health Considerations	28
15	MATE and EPC Values in Water for Some Constituents of Coal Conversion Wastewaters Based on Ecological Considerations	30

TABLES

Number		Page
16	Definitions of Subcategories of Estimated Permissible Concentrations (EPC's)	31
17	Acute Toxicity of Some Phenols to Fish	33
18	Threshold Concentrations of Various Phenolics to Lower Aquatic Organisms	34
19	Toxicities of Some Organic Acids to Aquatic Organisms	36
20	Toxicity of Some Polynuclear Aromatic Hydrocarbons to Marine and Aquatic Organisms	37
21	Toxicity of Some Nitrogen-Containing Compounds to Aquatic Organisms	40
22	Proposed Metabolic Pathways for the Microbial Degradation of Selected Phenolic Compounds	57
23	Oxidation and Removal of Various Phenolic Compounds by Phenol-Acclimated Bacteria	67
24	Initial Screening of Various Organic Compounds Found in Coal Conversion Effluents	85
25	Summary of Biodegradation Results for Compounds After 5 Days	88
26	Composition of Synthetic Coal Conversion Wastewater	95
27	Summary of Reactor Performance	98

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SECTION 1

INTRODUCTION

Several technologies for producing synthetic fuels from coal are under development. While most of the emphasis has centered upon development of efficient process technology to produce high energy, clean, synthetic fuels, little information is available with respect to the nature of the waste materials produced and the environmental impact of waste streams from the various gasification and liquefaction processes.

Most coal conversion technologies incorporate or project aerobic biological treatment as the principal means of removing phenol and the other organic impurities in the wastewater. However, since the nature and biodegradability of these other organic materials are not known, the extent to which these components can be removed by biological treatment cannot be reliably predicted. Synergisms and antagonisms due to the complex nature of real wastewaters are especially uncertain. Moreover, since even well-operated biological treatment processes typically remove only 85-95% of the influent BOD and a significant portion of the wastewater organics may not be biodegradable, it is doubtful that biological treatment alone can provide an environmentally-acceptable discharge.

In view of these considerations, a need exists to identify the nature and characteristics of aqueous discharges from coal conversion processes and to assess their environmental impact, and to develop satisfactory means for the treatment of these wastewaters in order that they may be disposed of in an environmentally-acceptable fashion. Accordingly, the purpose of this project is to assess the environmental impact of wastewater contaminants originating from the production of synthetic fuels from coal, and to evaluate, by bench-scale tests, alternative wastewater treatment technologies for the control of these contaminants.

This report presents the results of a literature review and a survey of facilities aimed at determining the chemical characteristics of coal conversion wastewaters and at identifying specific organic contaminants which might be found in such wastewaters. A preliminary assessment of the aquatic impact of these wastewaters and of their biological treatability is also presented.

SECTION 2

CONCLUSIONS

An attempt has been made to determine the chemical characteristics of wastewaters from coal gasification and coal liquefaction processes. Approximately 60-80% of the total organic carbon appears to be phenolic in nature, consisting of monohydric phenols, dihydric phenols, and polyphenols. The remainder of the organic material consists of mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, polynuclear aromatic hydrocarbons, and simple aliphatic acids. The composition of the wastewaters appears to be relatively uniform, especially with respect to the phenolic constituents, regardless of the specific process technology and type of feed coal employed. At the concentrations reported, the discharge of these wastewaters would have an adverse impact on aquatic life and, as a result, a significant degree of wastewater treatment is necessary.

With respect to the biodegradability of these constituents, there is a significant body of literature available concerning the microbial degradation of phenols, especially in pure cultures of microorganisms and in single-substrate systems. This is especially true for both mono- and dihydric phenols. Less information is available, however, with regard to the biodegradability of the more highly-substituted phenols, or of the other complex aromatic constituents of coal conversion wastewaters, such as the mono- and polycyclic nitrogen-containing aromatics, the oxygen- and sulfur-containing heterocyclics, and the polynuclear aromatic hydrocarbons. Furthermore, little information is available regarding the biodegradation of specific phenolic compounds in complex mixtures such as those characteristic of coal conversion wastewaters. Additionally, considering the needs from a wastewater treatment viewpoint, there is also little information available regarding the rate at which these compounds are microbially degraded in mixed cultures, and the concentrations at which these compounds become inhibitory to microbial degradation.

While aerobic biological processes appear to be among the methods of choice for treating these wastewaters, the following types of information are required in order to assess the biological treatability of these coal conversion wastewaters and to develop suitable design and operating guidelines: (a) more information on the biodegradability of the constituent compounds; (b) biokinetic information describing the rate at which degradation of the constituents takes place; (c) the concentration levels at which microbial degradation of the constituents is inhibited; and (d) how the constituents will behave in a composite mixture representative of coal conversion wastewaters. In view of the paucity of information available regarding the microbial degradation of many of the constituents identified in coal conversion wastewaters, an experimental program to provide such information has been developed and is now underway.

SECTION 3

BACKGROUND

Conversion of coal to synthetic gaseous and liquid fuels represents a plausible approach to meeting the nation's energy needs. Several technologies for producing synthetic fuels from coal are under development. While most of the emphasis has centered upon development of efficient process technology to produce high energy, clean, synthetic fuels at lowest process cost, little information is available with respect to the nature of the waste materials produced and the environmental impact of waste streams from the various gasification and liquefaction processes.

Wastewaters from coal conversion processes can originate from a variety of sources and can be widely variable in composition depending upon the specific process technology employed (operating temperature and pressure, mode of contact between coal and steam, process sequence, gas cleanup and separation technology, etc.). Additionally, the composition of the wastewater is also dependent upon the nature of the feed coal as shown in Table 1 (1)*. Many coal conversion technologies employ by-product recovery systems for phenol and ammonia, two of the major constituents of the wastewater as shown in the table. Phenol concentrations in the solvent-extracted liquor, however, may still be appreciable and further treatment of the waste streams may still be required.

Most coal conversion technologies incorporate or project aerobic biological waste treatment processes (e.g., activated sludge, aerated lagoons, etc.) as the principal means of treating the residual phenol and other organic impurities in the wastewater. However, the nature and biodegradability of these other organic materials which are included in Table 1 as part of the COD (chemical oxygen demand) are not known. Hence, the extent to which these other organic components can be removed by biological treatment cannot be predicted.

Table 2 shows the types of organics which have been identified in the tar from a coal gasification system. Many of the polynuclear aromatic hydrocarbons listed are known carcinogens. It can be anticipated that some of these contaminants will be found in the wastewaters from coal conversion facilities and may comprise part of the COD.

Since even well-operated biological treatment processes typically remove only 85-95% of the influent BOD (biochemical oxygen demand) and a significant portion of the wastewater organics may not even be biodegradable, it is doubtful that biological treatment alone can provide an environmentally-acceptable discharge. Furthermore, many inorganic materials of environmental concern may also be found in the wastewater. These include (see Table 1) cyanides, thiocyanates, ammonia (even after stripping), and heavy metals.

*References for each section appear at the end of that section.

TABLE 1. WATER QUALITY CHARACTERISTICS OF COAL CONVERSION WASTEWATERS.*
(ALL VALUES IN mg/1 EXCEPT pH.)

	Coke Plant	Illinois No. 6 Coal	Wyoming Subbituminous Coal	Illinois Char	North Dakota Lignite	Western Kentucky Coal	Pittsburgh Seam Coal
pH	9	8.6	8.7	7.9	9.2	8.9	9.3
Suspended Solids	50	600	140	24	64	55	23
Phenol	2,000	2,600	6,000	200	6,600	3,700	1,700
COD	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Thiocyanate	1,000	152	23	21	22	200	188
Cyanide	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3	5,000	8,100	9,520	2,500	7,200	10,000	11,000
Chloride	-	500	-	31	-	-	-
Carbonate	-	6,000	-	-	-	-	-
Bicarbonate	-	11,000	-	-	-	-	-
Total Sulfur	-	1,400	-	-	-	-	-

*After Forney, et al. (1).

TABLE 2. MASS SPECTROMETRIC ANALYSIS OF BENZENE-SOLUBLE TAR*

Structural type (includes alkyl) derivatives)	Percent, by Volume			
	Run HP-1 No. 92, Illinois No. 6 Coal	Run HPL No. 94, Lignite	Run HPM No. 111, Montana Subbituminous Coal	Run HP-118 No. 118, Pittsburgh Seam Coal
Benzenes	2.1	4.1	3.9	1.9
Indenes	8.6	1.5	2.6	6.1
Indans	1.9	3.5	4.9	2.1
Naphthalenes	11.6	19.0	15.3	16.5
Fluorenes	9.6	7.2	9.7	10.7
Acenaphthenes	13.5	12.0	11.1	15.8
3-ring aromatics	13.8	10.5	9.0	14.8
Phenylnaphthalenes	9.8	3.5	6.4	7.6
4-ring pericondensed	7.2	3.5	4.9	7.6
4-ring catacondensed	4.0	1.4	3.0	4.1
Phenols	2.8	13.7	5.5	3.0
Naphthols		9.7	9.6	
Indanols	.9	1.7	1.5	.7
Acenaphthenols	-	2.5	4.6	2.0
Phenanthrols	2.7	-	.9	-
Dibenzofurans	6.3	5.2	5.6	4.7
Dibenzothiophenes	3.5	1.0	1.5	2.4
Benzonaphthothiophenes	1.7	-	-	-
	(10.8)	(3.8)	(5.3)	(8.8)
Average molecular weight	212	173	230	202

*After Forney, et al (1).

In view of these considerations, a need exists to:

(a) identify the nature and characteristics of aqueous discharges from coal conversion processes and to assess their environmental impact; and

(b) develop satisfactory means for the treatment of these wastewaters in order that they may be disposed of in an environmentally-acceptable fashion.

Accordingly, the purpose of this project is to assess the environmental impact of wastewater contaminants originating from the production of synthetic fuels from coal, and to evaluate, by bench-scale tests, alternative wastewater treatment technologies for the control of these contaminants.

The project has been designed to be carried out in several phases over a five-year period. The first phase, for which preliminary results are presented in Section 4 of this report, consists of a review of the literature and a survey of pilot- and full-scale coal conversion facilities

to identify specific contaminants which might be found in coal conversion wastewaters. Concentration ranges for these contaminants are estimated and the potential effects of these contaminants on human health and aquatic life are to be assessed based upon a review of the literature and upon toxicity and water quality listings. A preliminary review of the aquatic impact of coal conversion wastewater constituents is presented in Section 5.

Phase 2 consists of a study of the biodegradability of selected model organic compounds from the classes of organics identified in phase 1. The investigation was designed to be conducted on a component basis since it was anticipated, a priori, that certain compounds and classes of organics would be common to all coal processing wastewaters even though the exact composition might vary depending upon the particular process scheme and cleanup and separation technology employed. (The results reported in Section 4 confirm this hypothesis.) Section 6 presents a comprehensive review of the literature on microbial degradation of the organic constituents which have been identified, and some preliminary results of long-term BOD tests on several component organics.

The remaining phases of the 5-year project involve:

(a) experimental evaluation of the biological treatability of coal conversion wastewater constituents, based in part on the biodegradability results developed in phase 2;

(b) experimental evaluation of alternative physical-chemical treatability techniques applied to the coal conversion wastewater constituents;

(c) aquatic bioassay studies to assess the impact of various constituents and composite samples on several forms of aquatic life;

(d) toxicological investigations to evaluate the potential health effects of various wastewater constituents and composites following treatment;

(e) composite treatability analyses of actual and synthetic coal conversion wastewaters, utilizing both biological and physical-chemical techniques; and

(f) development of design and operating criteria for the continuous treatment of coal conversion wastewaters.

REFERENCES

1. Forney, A. J., et al. 1974. Analysis of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process. U. S. Bureau of Mines Technical Progress Report 76, Pittsburgh Energy Research Center, Pittsburgh, Pa.

SECTION 4

CHEMICAL CHARACTERISTICS OF COAL CONVERSION WASTEWATERS

The first phase of this research investigation consisted of a review of the literature and a survey of pilot-scale coal conversion facilities. The purposes of these endeavors were to determine the chemical characteristics of coal conversion wastewaters and to identify the types of potential pollutants to be expected in wastewaters from such facilities. This analysis was necessary in order to be able to reasonably assess the aquatic impact of these wastewaters, and to develop an appropriate set of wastewater treatment methodologies.

The constituents of these wastewaters have been identified during this first phase of the project by reviewing the published literature, visiting coal gasification and liquefaction research and demonstration installations, and analyzing reports and project documents from a variety of coal conversion operations. Table 3 presents the results of an analysis of the condensate wastewater generated from the Synthane gasification of six different types of coal (1). The wastewater characteristics of the weak ammonia liquor from a coke plant are presented for purposes of comparison. The waste condensate streams appear to be somewhat alkaline and contain rather substantial concentrations of ammonia. The concentration of organic material, represented by the COD, consists for the most part of phenol. Table 4 indicates, however, that phenol accounts for only 21 to 46% of the COD in the condensate samples; the remaining 54 to 79% of the COD is apparently due to the presence of other organic components of the waste streams. Table 4 was developed by calculating the COD-equivalent of the phenol concentrations given in Table 3, using a stoichiometric factor of 2.38 gms. of COD per gm. of phenol from the equation:

$$\underset{\text{phenol}}{C_6H_5OH} + 7O_2 \rightarrow 6CO_2 + 3H_2O \qquad (1)$$

Bromel and Fleeker (2) examined some general properties of raw and processed wastewater from the Lurgi process plant at Sasolburg, South Africa. Table 5 shows that the raw Lurgi wastewater is similar to that from Synthane in terms of its alkaline pH and high ammonia and COD concentration. The raw wastewater consists of the condensate from the gasifier (gas liquor) after tar and oil separation. The processed wastewater refers to the gas liquor following phenol and ammonia extraction.

In order to determine the nature of the organic species comprising the COD and TOC (total organic carbon), Bromel and Fleeker conducted a series of chromatographic separations and identified and quantified the components reported in Table 6. It is apparent, that, of the specific organic compounds identified, phenol and its methyl substituents, the cresols (methylphenols) and xylenols (dimethylphenols), are the major organic components of the condensate. Polyhydric phenols were not determined. The other major classes identified are the fatty acids (aliphatic acids) and the aromatic amines consisting of aniline and the heterocycle pyridine and its methyl derivatives. Quinoline and alkyl

TABLE 3. BY-PRODUCT WATER ANALYSIS FROM SYNTHANE GASIFICATION OF VARIOUS COALS.* (ALL VALUES IN mg/l EXCEPT pH.)

	Coke Plant	Illinois No. 6 Coal	Wyoming Subbi-tumi-nous Coal	Illi-nois Char	North Dakota Lignite	Western Kentucky Coal	Pitts-burgh Seam Coal
pH	9	8.6	8.7	7.9	9.2	8.9	9.3
Suspended Solids	50	600	140	24	64	55	23
Phenol	2,000	2,600	6,000	200	6,600	3,700	1,700
COD	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Thiocyanate	1,000	152	23	21	22	200	188
Cyanide	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3	5,000	8,100	9,520	2,500	7,200	10,000	11,000
Chloride	-	500	-	31	-	-	-
Carbonate	-	6,000	-	-	-	-	-
Bicarbonate	-	11,000	-	-	-	-	-
Total Sulfur	-	1,400	-	-	-	-	-

*After Forney, et al. (1).

TABLE 4. PERCENTAGE OF COD ATTRIBUTABLE TO PHENOL IN SYNTHANE GASIFICATION BY-PRODUCT WATER.*

Component	Coke Plant	Illinois No. 6 Coal	Wyoming Subbi-tumi-nous Coal	Illi-nois Char	North Dakota Lignite	Western Kentucky Coal	Pitts-burgh Seam Coal
Chemical Oxygen Demand, mg.l	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Phenol, mg/l	2,000	2,600	6,000	200	6,600	3,700	1,700
Phenol, mg/l of equivalent COD	4,760	6,188	14,280	476	15,708	8,806	4,046
Phenol, % of COD	68.0	41.2	33.2	28.0	41.3	46.3	21.3

*Raw data from Forney, et al (1).

TABLE 5. SOME GENERAL PROPERTIES OF RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA*

Parameter	Values	
	Raw Waste Water	Processed Waste Water
Chemical Oxygen Demand (mg/1)	12,500	1,330
Organic Carbon (mg/1)	4,190	**
Total Dissolved Solids (mg/1)	2,460	596
pH	8.9	8.2
Ammonia (mg/1)	11,200	150

*After Bromel and Fleeker (2).
**not determined

amines were found in lesser amounts. It is apparent from the table that the phenol extraction step is relatively efficient in separating the monohydric phenols and even the aromatic amines from the gas liquor.

In order to determine what fraction of the COD and TOC reported in Table 5 for the Sasol wastewater could be accounted for by the specific organics identified in Table 6, a series of calculations was performed to determine the COD and TOC-equivalents of the specific compounds identifed. The basis for these calculations is shown in Table 7. The TOC and COD-equivalents of the identified organic constituents are listed in Table 8. The total COD of the raw wastewater attributable to these indicated constituents is 6738 mg/1, of which the monohydric phenols comprise 5915 mg/1. The monohydric phenols contribute 1866 mg/1 of TOC out of the total TOC of 2143 mg/1 accounted for by the indicated constituents. However, if the COD and TOC of these organic components are compared to the total concentrations reported in Table 5 for the same sample, it is shown (Table 9) that 46.1% of the COD and 48.9% of the TOC of the raw wastewater are not accounted for. Similarly, a very small percentage of the COD (and, also probably of the TOC) of the processed wastewater is attributable to the residual aliphatic acids following phenol extraction.

It should be noted that the data presented in Tables 5 and 6 by Bromel and Fleeker (2) were derived from single samples of the aqueous gas liquor and the phenol-extracted gas liquor. The age of the samples was not accurately known, but is believed to have been less than six months for the raw wastewater and less than one month for the processed wastewater. The analyses were completed within four months following receipt of the samples (2).

TABLE 6. CONCENTRATION OF ORGANIC COMPOUNDS FOUND IN RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA.*

Compound	Concentration (mg/l)	
	Raw Waste Water	Processed Waste Water
Fatty Acids		
Acetic Acid	171	123
Propanoic Acid	26	30
Butanoic Acid	13	16
2-Methylpropanoic Acid	2	5
Pentanoic Acid	12	7
3-Methylbutanoic Acid	1	5
Hexanoic Acid	1	8
Monohydric Phenols		
Phenol	1,250	3.2
2-Methylphenol	340	0.2
3-Methylphenol	360	0.2
4-Methylphenol	290	0.2
2,4-Dimethylphenol	120	**
3,5-Dimethylphenol	50	**
Aromatic Amines		
Pyridine	117	0.45
2-Methylpyridine	70	0.05
3-Methylpyridine	26	0.05
4-Methylpyridine	6	0.05
2,4-Dimethylpyridine	1	**
2,5-Dimethylpyridine	1	**
2,6-Dimethylpyridine	1	**
Aniline	12	**

*After Bromel and Fleeker (2)
**Not found

TABLE 7. COD AND TOC-EQUIVALENTS OF ORGANIC CONSTITUENTS OF SASOL WASTEWATER.

Reaction	Chemical Oxygen Demand, gm/gm	Total Organic Carbon, gm/gm
Phenol $C_6H_5OH + 7\ O_2 \rightarrow 6CO_2 + 3H_2O$	2.38	0.77
Methylphenol (cresol) $C_7H_8O + 8.5\ O_2 \rightarrow 7CO_2 + 4H_2O$	2.52	0.78
Dimethylphenol (xylenol) $C_8H_{10}O + 10\ O_2 \rightarrow 8CO_2 + 5H_2O$	2.62	0.79
Pyridine $C_5H_5N + 5.5\ O_2 \rightarrow 5CO_2 + H_2O + NH_3$	2.23	0.76
Methylpyridine $C_6H_7N + 7\ O_2 \rightarrow 6CO_2 + 2H_2O + NH_3$	2.41	0.77
Dimethylpyridine $C_7H_9N + 8.5\ O_2 \rightarrow 7CO_2 + 3H_2O + NH_3$	2.54	0.79
Aniline $C_6H_7N + 7\ O_2 \rightarrow 6CO_2 + 2H_2O + NH_3$	2.41	0.77
Acetic Acid $CH_3COOH + 2\ O_2 \rightarrow 2CO_2 + 2H_2O$	1.07	0.40
Propanoic Acid $CH_3CH_2COOH + 3.5\ O_2 \rightarrow 3CO_2 + 3H_2O$	1.51	0.49
Butanoic Acid $CH_3(CH_2)_2COOH + 5\ O_2 \rightarrow 4CO_2 + 4H_2O$	1.82	0.60
Methylpropanoic Acid $C_4H_9O_2 + 21/4\ O_2 \rightarrow 4CO_2 + 9/2\ H_2O$	1.89	0.54
Pentanoic Acid $C_5H_{10}O_2 + 6.5\ O_2 \rightarrow 5CO_2 + 5H_2O$	2.04	0.59
Methylbutanoic Acid $C_5H_{11}O_2 + 27/4\ O_2 = 5CO_2 + 11/2\ H_2O$	2.10	0.58
Hexanoic Acid $C_6H_{12}O_2 + 8\ O_2 = 6CO_2 + 6H_2O$	2.21	0.62

TABLE 8. CONCENTRATION OF ORGANIC COMPOUNDS, AS COD AND TOC, FOUND IN THE RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA.*

Compounds	Concentration, mg/l			
	Raw Wastewater		Processed Wastewater	
	COD	TOC	COD	TOC
Fatty Acids				
acetic acid	183	68.4	131.6	49.2
propanoic acid	39.3	12.7	45.3	14.7
butanoic acid	23.7	7.8	29.1	9.6
2-methylpropanoic acid	3.8	1.1	9.5	2.7
pentanoic acid	24.5	7.1	14.3	4.1
3-methylbutanoic acid	2.1	0.6	10.5	2.9
hexanoic acid	2.2	0.6	17.7	5.0
	278.6	98.3	258	88.2
Monohydric Phenols				
phenol	2975	963	7.6	2.5
2-methylphenol	857	265	<0.5	<0.2
3-methylphenol	907	277	<0.5	<0.2
4-methylphenol	731	226	<0.5	<0.2
2,4-dimethylphenol	314	95	-	-
3,5-dimethylphenol	<131	<39.5	-	-
	5915	1866	9.1	3.1
Aromatic Amines				
pyridine	261	88.9	1.0	0.34
2-methylpyridine	169	53.9	<0.12	<0.04
3-methylpyridine	62.7	20.0	<0.12	<0.04
4-methylpyridine	14.5	4.6	<0.12	<0.04
2,4-dimethylpyridine	<2.5	<0.8	-	-
2,5-dimethylpyridine	<2.5	<0.8	-	-
2,6-dimethylpyridine	<2.5	<0.8	-	-
aniline	28.9	9.2	-	-
	544	179	1.4	0.5
TOTAL	6738	2143	269	92

*Raw data from Bromel and Fleeker (2).

TABLE 9. PERCENTAGES OF UNIDENTIFIED COD AND TOC IN SASOL WASTEWATER*

Parameter	Raw Wastewater	Processed Wastewater
Total COD, mg/l	12,500	1,330
COD of Identified Constituents, mg/l	6,738	269
% of COD Unidentified	46.1	79.8
Total TOC, mg/l	4,190	-
TOC of Identified Constituents, mg/l	2,143	92
% of TOC Unidentified	48.9	-

*Raw data from Bromel and Fleeker (2).

It is apparent from Tables 4 and 9 that many other organic species are present in coal conversion wastewaters, and that a need exists for further identification and quantitation of these constituents. Along these lines, Schmidt, Sharkey and Friedel (3) have employed mass spectrometric methods to determine the nature of the organic contaminants in condensate waters from the Synthane gasification of coal. The Synthane process produces about 0.4-0.6 tons of condensate water per ton of coal gasified (1). The condensate waters from the gasification of six different coals were extracted with methylene chloride and were identified using high resolution mass spectrometry, combined gas chromatography-mass spectrometry, and low-voltage mass spectrometry. Table 10 summarizes the results of these spectrometric analyses for the six different coals gasified. Again, phenol appears to be the major organic component of the condensate waters and, along with the other monohydric phenols, dihydric phenols, and polyphenols, constitute approximately 60 to 80% of the methylene chloride extract. Several other classes of organics appear to be represented, including heterocyclic compounds such as the pyridines and furans, and polycyclic components such as indenols, indanols, naphthols, quinolines, and indoles. It is interesting to note that, regardless of the type of coal gasified, the composition of the condensate water, in terms of the component organics and their concentrations, is relatively uniform. It should also be noted that the constituents reported by Bromel and Fleeker (2) in Table 6 are consistent with the listing by Schmidt, Sharkey and Friedel (3) in Table 10.

Expanding on this effort to identify organic constituents in wastewaters from coal gasification and coal liquefaction operations from various different sources, Table 11 is a summary of information gathered from the several references cited. The organics have been grouped into various classes and include monohydric and dihydric phenols, polycyclic hydroxy compounds (polyphenols), monocyclic and polycyclic nitrogen-containing aromatics (including heterocyclic compounds such as the pyridines, quinolines, indoles, acridines and carbazoles, and the amino-benzenes), aliphatic acids, and a group of miscellaneous other compounds. The check (✓) marks indicate that the compound in question has been identified but not quantified. The notation (⇕) indicates that the concentrations given are for a group of compounds, but that the individual components within the group have not been quantified, e.g., 140-1170 mg/l in column 1 for the C_2-phenols include the isomers of xylenol

TABLE 10. CONTAMINANTS IN PRODUCT WATER FROM SYNTHANE GASIFICATION OF VARIOUS COALS.* (ALL CONCENTRATIONS IN mg/1.)

Component	Illinois No. 6 (HVBB)		Montana (Sub)	N. Dak. (Lig)	Wyo. (Sub)	W. Ky. (HVBB)	Pgh. (HVAB)
Phenol	3,400	2,660	3,160	2,790	4,050	2,040	1,880
Cresols	2,840	2,610	870	1,730	2,090	1,910	2,000
C_2-Phenols	1,090	780	240	450	440	620	760
C_3-Phenols	110	100	30	60	50	60	130
Dihydrics	250	540	130	70	530	280	130
Benzofuranols	70	100	80	60	100	50	70
Indanols							
Acetophenones	150	100	140	110	110	90	120
Hydroxy-Benzaldehyde / Benzoic Acid	60	110	-	-	60	50	80
Naphthols	160	110	160	140	80	160	170
Indenols	90	90	70	50	60	80	20
Benzofurans	-	-	10	10	-	-	110
Dibenzofurans	-	-	-	-	-	-	-
Biphenols	40	20	-	-	40	20	60
Benzothio-Phenols	110	60	-	10	20	70	20
Pyridines	-	60	270	220	120	30	540
Quinolines	-	-	20	10	-	-	10
Indoles	-	20	70	30	20	40	40

*After Schmidt, et al. (3).

TABLE 11. SUMMARY: ORGANIC CONSTITUENTS IN COAL CONVERSION WASTEWATERS
(ALL CONCENTRATIONS IN mg/1.)

	Synthane (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Lurgi-GRFERC (9)	Hydro-Carboniz. (10)	COED (11)
Monohydric Phenols											
Phenol	1000–4480	10	2100	2100	✓	1200–3100		1250	5647		
o-Cresol		30	670	650	✓	153–343	2209	340			
m-Cresol	530–3580				✓	170–422		360	1965		
p-Cresol		20	1800	1800	✓	160–302		290			
2,6-Xylenol			40	30	✓						
3,5-Xylenol			230	240	✓			50			
2,3-Xylenol			30	40					453		
2,5-Xylenol	140–1170		250	220	✓	100–393					
3,4-Xylenol			100	900			2185				
2,4-Xylenol			–	–	✓			120			
o-Ethylphenol			30	30	✓						
m-Ethylphenol					✓						
p-Ethylphenol					✓						
3-Methyl,6-Ethylphenol					✓						
2-Methyl,4-Ethylphenol					✓						
4-Methyl,2-Ethylphenol	20–150				✓						
5-Methyl,3-Ethylphenol					✓		66				
2,3,5-Trimethylphenol					✓						
o-Iospropylphenol	✓						40				
Dihydric Phenols											
Catechol	✓				✓	190–555				1700	✓
3-Methylcatechol					✓	30–394				11	✓
4-Methylcatechol					✓	110–385					✓
3,5-Dimethylcatechol						✓					
3,6-Dimethylcatechol						0–45					
Methylpyrocatechol	✓										
Resorcinol	✓				✓	176–272				2000	✓
5-Methylresorcinol					✓	40–64				2000	✓

(continued)

TABLE 11. (continued)

	Synthane (1)	Oil Shale (2)	Synthane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Synthane (7)	Lurgi-Sasol (8)	Lurgi-GRFERC (9)	Hydro-Carboniz. (10)	COED (11)
4-Methylresorcinol						0-36				2000	
2-Methylresorcinol					✓						
2,4-Dimethylresorcinol						✓					✓
Hydroquinone	✓										
Polycyclic Hydroxy Compounds											
γ-Naphthol			10								
β-Naphthol	30-290		30								
Methylnaphthol											
Indenol	20-110										
C_1-Indenol											
4-Indanol	40-150						66				
C_1-Indanol											
Biphenol	0-110										
Biphenyl									19		
Monocyclic N-Aromatics											
Pyridine								117			
Hydroxypyridine										10	
Methylhydroxypyridine										10	
Methylpyridine							✓	104			
Dimethylpyridine	30-580						5	<1			
Ethylpyridine										20	
C_3-Pyridine											
C_4-Pyridine											
Analine							21	12			
Methylaniline							9				
Dimethylaniline							11				
Polycyclic N-Aromatics											
Quinoline					✓		7				
Methylquinoline					✓		27				

(continued)

TABLE 11. (continued)

	Synthane (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Lurgi-GRFERC (9)	Hydro-Carboniz. (10)	COED (11)
Dimethylquinoline					✓						
Ethylquinoline	0-100				✓						
Benzoquinoline					✓						
Methylbenzoquinoline					✓						
Tetrahydroquinoline					✓						
Methyltetrahydroquinoline					✓						
Isoquinoline					✓						
Indole					✓		63				
Methylindole					✓						
Dimethylindole	0-110				✓						
Benzoindole					✓						
Methylbenzoindole					✓						
Carbazole					✓				9		
Methylcarbazole					✓					4	
Acridine					✓						
Methylacridine					✓						
Aliphatic Acids											
Acetic Acid		600	620	600				171			
Propanoic Acid		210	60	90				26			
n-Butanoic Acid		130	20	40				13			
2-Methylpropanoic Acid		-	-	-				2			
n-Pentanoic Acid		200	10	30				12			
3-Methylbutanoic Acid		-	-	-				1			
n-Hexanoic Acid		250	20	30				1			
n-Heptanoic Acid		260	-	-							
n-Octanoic Acid		250	-	-							
n-Nonanoic Acid		100	-	-							
n-Decanoic Acid		50	-	-							

(continued)

TABLE 11. (continued)

	Synthane (1)	Oil Shale (2)	Synthane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Synthane (7)	Lurgi-Sasol (8)	Lurgi-GRFERC (9)	Hydro-Carboniz. (10)	COED (11)
Others											
Benzofurans	10-110								74		
Benzofuranols	50-100										
Benzothiophenols	10-110										
Acetophenones	90-150										
Hydroxybenzaldehyde or Benzoic Acid	50-110										

(dimethylphenol) and ethylphenol. A range of values, e.g., 1000-4480 mg/l for phenol in column 1, indicates that several samples have been analyzed and the concentrations measured are within the given range.

Column 1 is derived from the previously-discussed mass spectrometric analysis of the methylene chloride extract by Schmidt, Sharkey and Friedel (3) for the condensate waters from the Synthane gasification of six different types of coal under different process conditions. Columns 2, 3 and 4 include data from Ho, Clark and Guerin (4) and were obtained by gas chromatography using Tenax columns and flame ionization detection. Identifications were made from comparisons of the chromatograms with retention time data for reagent grade compounds. Some identifications were confirmed by gas chromatography-mass spectrometry. Quantitation was made by integrating peak areas from the chromatogram and comparing with standards of known concentration. The oil shale by-product water (column 2) was obtained by centrifugation of an oil/water emulsion product from a simulated in-situ retort run at the Laramie (Wyoming) Energy Research Center. The gasification by-product water (column 3) was a sample of filtered condensate water from the Synthane process, provided by the Pittsburgh (Pennsylvania) Energy Research Center. The coal liquefaction by-product sample (column 4) was filtered water from the first-stage gas scrubber from the COED (Char Oil Energy Development) liquefaction process, provided by FMC Corporation, Princeton, New Jersey.

The information in column 5 results from a characterization by Fruchter et al. (5) of organics in coal-derived liquids from the Solvent Refined Coal Plant at Ft. Lewis, Washington. The constituents of the raw process water were separated into acidic, basic, neutral, and polyaromatic fractions and each fraction was separated further by gas chromatography. Gas chromatography/mass spectrometry was then employed to identify the components. The constituents indicated in column 5 were positively identified, but not quantified.

Column 6 contains data collected by Janes and Rhodes (6) from the Lurgi gasification facility in Westfield, Scotland. The data were obtained for tar water and oil water samples from old plant records, and the analytical and sample-handling procedures were not reported. Nevertheless, the constituents and the concentrations appear to be consistent with those in other reports.

Column 7, after Neufeld and Spinola (7), contains data for a condensate sample from the Synthane gasification of an Illinois No. 6 coal. The organic content was analyzed by direct gas chromatography of acidic and basic fractions and identification was based on relative retention time data.

The data in column 8 for the Lurgi facility in Sasolburg, South Africa are from the report by Bromel and Fleeker (2) discussed above in connection with Tables 5-9.

Column 9 contains the results of a mass spectrometric analysis of the soluble organic material in a composite sample of aqueous liquor from the slagging Lurgi gasifier at the Grand Forks (North Dakota)

Energy Research Center (8). Phenol, cresol, and xylenol accounted for approximately 80% of the organic constituents, while the remaining material consisted of heavier organic components, including polynuclear aromatic hydrocarbons, suspended and dissolved to some degree in the liquor.

The information in column 10 is from an analysis by Jolley, Pitt, and Thompson (9) of an aqueous stream from the product scrubber of a bench-scale hydrocarbonization coal liquefaction operation. The samples were analyzed by high performance liquid chromatography, and the separated constituents were identified by a multiple-analytical procedure involving gas chromatography and mass spectrometry.

Column 11 cites specific organics identified (10) in an aqueous sample from the product separator (2nd stage liquor) of the COED coal liquefaction pilot plant. The constituents were separated by high-resolution anion exchange chromatography, and a variety of different analytical techniques were employed for identification and quantitation.

With reference to the material contained in Table 11, it is important to note that the components identified and the concentrations reported are from single grab samples of process streams collected from the various facilities and locations cited. The fact that they are analyses of grab samples from processes still under development means that the concentrations may not be truly representative of on-line, commercial, steady-state coal gasification and liquefaction operations. Additionally, the number and type of organic compounds listed are limited, in part, by the analytical methodologies employed for extracting, separating, and identifying the constituents of the waste streams. Nevertheless, Table 11 reflects the present state of knowledge concerning the organic composition of coal conversion wastewaters.

While it might have been predicted, a priori, that the composition of wastewaters from coal conversion facilities would vary depending upon the specific process technology (operating temperature and pressure, mode of contact between coal and steam, process sequence, gas cleanup and separation technology, etc.) and type of feed coal employed, Table 11 suggests that the composition of coal gasification and liquefaction wastewaters is relatively uniform, especially with respect to the phenolic constituents. Less information is available regarding the presence of specific N-containing aromatics, other polycyclic and heterocyclic compounds, and polynuclear aromatic hydrocarbons. Table 12 lists some of the PAH's identified by Fruchter, et al. (5) in the raw process wastewater from the Solvent-Refined Coal facility in Ft. Lewis, Washington, but the quantitation and wide-spread occurrence of these PAH's in coal conversion wastewaters have not been established.

Additional high performance liquid chromatography and gas chromatography/mass spectrometry analyses of aqueous samples from a variety of coal conversion operations are being carried out at the present time by a number of research laboratories with which contact has been made during this first phase of our study. As more information regarding the composition of coal conversion wastewaters is collected, Tables 11 and 12 will be expanded.

TABLE 12. POLYNUCLEAR AROMATIC HYDROCARBONS IN SRC RAW PROCESS WATER*

PAH	Concentration (mg/l)	Identified But Not Yet Quantitated
Methylindane	15	Methylpyrene
Tetralin	0.1	Benzofluorene
Dimethyltetralin	0.5	C_2-Pyrene
Naphthalene	5	C_2-Fluoranthene
2-Methylnaphthalene	2	Tetrahydrochrysene
Dimethylnaphthalene	0.3-2	Chrysene
2-Isopropylnaphthalene	0.7	Methylbenzofluorene
1-Isopropylnaphthalene	2	C_3-Pyrene
Biphenyl	0.2	C_3-Fluoranthene
Acenaphthalene	0.1	Methylchrysene
Dimethylbiphenyl	0.2-0.5	Methylbenzanthracene
Dibenzofuran	0.6	Cholanthrene
Xanthene	0.1	Tetrahydrobenzofluoranthene
Dibenzothiophene	1.5	Tetrahydrobenzopyrene
Methyldibenzothiophene	0.1	Benzopyrene
Dimethyldibenzothiophene	0.05	Methylbenzopyrene
Thioxanthene	0.1	Methylbenzofluoranthene
Fluorene	0.3	Benzofluoranthene
9-Methylfluorene	0.3	
1-Methylfluorene	0.2	
Anthracene/Phenanthrene	1.1	
Methylphenanthrene	0.2-0.3	
C_2-Anthracene	0.05	
Fluoranthene	0.4	
Dihydropyrene	0.05	
Pyrene	0.6	

*After Fruchter, et al. (5)

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SECTION 5

POTENTIAL AQUATIC IMPACT OF ORGANIC CONSTITUENTS OF COAL CONVERSION WASTEWATERS

There is general agreement that most coal conversion processes will produce relatively contaminated wastewaters. However, little is known about the biological impact such wastes will have upon receiving waters. The lack of information reflects the fact that coal conversion technology has only recently emerged, and no commercial systems have yet been constructed in the U. S. While ultimate evaluation of the biological impact resulting from the discharge of wastewaters into aquatic ecosystems must await the construction and continuous operation of commercial scale conversion systems, interim predictive efforts are mandated by the number of highly toxic, mutagenic, and carcinogenic compounds known or anticipated to occur in coal conversion wastes. The objectives of this section are to: (a) identify potential problems expected from coal conversion wastewaters; (b) review the literature pertaining to toxic effects of constituents in the wastewater; and (c) discuss existing gaps in knowledge concerning the potential impact of coal conversion wastewater constituents on aquatic environments.

AQUATIC POLLUTION PROBLEMS: GENERAL CONSIDERATIONS

Currently, efforts to assess the impact of coal conversion wastewaters on aquatic environments are in a predictive rather than descriptive phase. The limited availability of coal conversion wastewaters precludes extensive experimental assessment. The impact such effluents will have can only be based on knowledge of effluents thought to be similar in composition, or from an analysis of existing toxicity data on waste constituents. Neither approach is wholly satisfactory. Comparisons with existing coal-related industrial effluents would perhaps provide the most meaningful appraisal, but such information is limited.

In Section 4, it was suggested that composition of coal conversion wastewaters will be similar to those from coking operations and petroleum refineries. Several authors have investigated the toxicity of coal-processing wastes to fish, but few generalizations can be derived from the available literature. Wastes from the production of "illuminating gas" by the destructive distillation of coal were demonstrated to be lethal to fish as early as 1917 (1), but the toxicity varied to such a degree that a general statement concerning its overall effects could not be made. Herbert (2) stated that the composition and volume of spent still liquors from coal carbonization will vary with the nature of the coal and with the design and operation of the plant, but that ammonia, sulfides, thiosulfates, and monohydric phenols constituted the most toxic components of the waste. Rainbow trout exposed to 2-10 ml/l of gas liquor died within 0.25-1.25 hrs. in laboratory tests. A 48-hr LC_{50} (concentration lethal to 50% of the test organisms in 48 hrs.) of 5.8 mg/l of gas liquor phenols has also been reported for rainbow trout (3). The only other reference dealing with coal carbonization effluents documented a massive fish kill caused by an intermediate oil from coke ovens (4). Other references exist, but are restricted to individual waste constituents

rather than combined effluent toxicity.

Since the constituents of fossil fuel wastes share common characteristics, certain generalizations about the toxicity of coal conversion wastes may be inferred from petroleum refinery wastewater toxicity data. Reliance on such data is necessary becuase parallel information from existing coal processing wastes is scant. The variable acute toxicity of refinery effluents is well known (5,6). Acute lethal toxicity is usually attributed to phenols, ammonia, and hydrogen sulfide, but assessment of effluent toxicity based solely on the chemical characteristics of these constituents may be misleading. Heavy metals and cyanides as well as a number of other inorganic and organic constituents may be present in such wastes. To what degree they interact with respect to toxicity is largely unknown.

The effects of petrochemical effluents on aquatic organisms were recently reviewed (7), and factors that affect pollutional characteristics of effluent components were listed. Included were the degree of waste treatment, water quality characteristics of the receiving stream, synergistic and antagonistic interactions, and microbial degradation of organic waste components. Bacterial activity has the positive effect of degrading oils and other organic compounds, but oxygen depletion may contribute additional pollution problems. Aquatic organisms require dissolved oxygen in order to survive. The discharge of wastes with large concentrations of biodegradable organics results in oxygen depletion, thereby making the receiving water unsuitable for aquatic biota. Additionally, when bacteria oxidize carbon compounds to carbon dioxide and water, the carbon dioxide may be assimilated by algae. Given sufficient amounts of inorganic nitrogen and phosphorus, more algal growth will occur in waters high in BOD than in low BOD siutations. Other organic components of petrochemical wastes may promote algal growth making such wastewaters potential contributors to eutrophication. Oxygen depletion may also inhibit microbial degradation of toxic organics, increasing their persistence in the aquatic environment. Additionally, most toxic substances become even more toxic at low dissolved oxygen levels. Thus, petrochemical wastes released in toxic concentrations can eliminate fish, either directly or through the destruction of lower organisms on which they feed.

Although acute toxicity of coal conversion effluents will certainly be a problem, chronic effects may be of equal or greater importance. Long-term bioassays of treated oil refinery wastes indicated that complex refineries produced effluents containing low-level toxins which caused cumulative deleterious effects (8). Constituents which produce chronic effects are not immediately lethal, but can have long-term significance for the survival of ecologically important species. Chemically-induced impairment of behavior of physiological functions can ultimately affect growth and reproduction. Oil and other organic pollutants may include carcinogenic and mutagenic compounds. From genetic studies in general, a large majority of mutations are known to be detrimental to the survival of young, and many are lethal.

Several organic components of complex organic wastes impart unpleasant tastes and odors to water, and produce tainted tastes in fish

and shellfish (7,9). Although tainted organisms apparently survive without ill effects, they may be rendered unfit for human consumption, adversely affecting economics of the fisheries industry. If undetected, consumption of contaminated water and seafood by humans may pose a potential hazard to public health. Furthermore, bioaccumulation of organic compounds through the aquatic food web may result in problems wholly unanticipated at present.

A general assessment of potential environmental problems created by coal conversion effluents was recently presented (10). A summary of the results is presented in Table 13. Five major classes of organic compounds were identified as being of particular concern. Each class was assessed according to: (a) concentration ranges anticipated in effluents; (b) removal efficiency by waste treatment systems; (c) acute toxicity; (d) chronic toxic effects on aquatic organisms; and (e) environmental transport and persistence. These findings suggest that while phenols and monoaromatic hydrocarbons are the major components of coal conversion wastewaters, their environmental impact may be far less detrimental than that of the polycyclic and heteroatomic compounds. Besides the five major classes of organic constituents addressed in the table, effluents will also include lesser concentrations of carboxylic acids, ethers, esters, furans, tetralins, aldehydes, organometallics, and other compounds.

Ambient level goals for a number of hazardous pollutants were recently calculated and compiled by Cleland and Kingsbury (11). They list minimum acute toxicity effluent values (MATE's) for water, defined as the concentration levels of contaminants in water that will not evoke significant harmful responses in exposed humans or to the ecology, provided the exposure is of limited duration. Similarly, estimated permissible concentrations (EPC's) are given, defined as the estimated level of a substance for continuous exposure that will not result in toxic effects to humans or to the ecology. MATE's and EPC's based upon health and ecological considerations relevant to coal conversion wastewaters are summarized in Tables 14 and 15, respectively. EPC's were calculated according to different criteria which are defined in Table 16.

In contrast to data for health considerations (Table 14), fewer data are currently available concerning the ecological effects of coal conversion wastewater constituents (Table 15). In nearly all cases, EPC's based on ecological considerations are derived from concentrations that produce tainting of fish flesh. With the exception of phenolic compounds, it is of interest to note that, where data are available, MATE's based on aquatic organisms are less than those calculated for humans. A comparison of the degree of sensitivity of fish and human beings to acute intoxiciation by pollutants (12) has shown that fish proved more sensitive in 97% of the cases. Therefore, it has been suggested (13,14) that standards to protect aquatic life would serve adequately to maintain public health.

AQUATIC TOXICITIES OF ORGANIC CONSTITUENTS OF COAL CONVERSION EFFLUENTS

The toxic chemicals considered in this section are based on the summary of organic constituents of coal conversion wastes from Section 4.

TABLE 13. SUMMARY OF ENVIRONMENTAL BEHAVIOR OF CLASSES OF ORGANIC COAL CONVERSION EFFLUENT CONSTITUENTS*

	Acute Toxicity	Chronic Effects	Wastewater Removal Efficiency	Microbial Degradation	Bioaccumulation Potential	Information Available
Phenols	High	Low	High	Rapid	Low	Much
Monoaromatics	Moderate	Low	Moderate	Moderate	Low	Moderate
Polycyclic Aromatics	High	High	Low	Slow	High	Moderate
Aromatic Amines	Moderate	High+	Low	Slow	Moderate+	Little
Thiophenes	Moderate	High+	Low+	Slow+	Moderate+	Little

*After Herbes, et al. (10).

+Insufficient information to support valid conclusions.

TABLE 14. MINIMUM ACUTE TOXICITY EFFLUENTS (MATE's) AND ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC's) IN WATER FOR SOME CONSTITUENTS OF COAL CONVERSION WASTEWATERS BASED ON HUMAN HEALTH CONSIDERATIONS*

Compound	MATE (µg/l)	Estimated Permissible Concentrations (µg/l)			
		EPC_{wh1}	EPC_{wh2}	EPC_{whs}	EPC_{ws}
Aldehydes					
benzaldehyde	8.8×10^5	1580	520	--	--
Ketones					
acetophenone	6.1×10^5	--	--	--	--
Carboxylic Acids					
acetic acid	3.8×10^5	900	345	--	--
benzoic acid	2.1×10^6	3700	1200	--	--
Amides					
acetamide	6.8×10^6	--	--	--	--
Phenols					
phenol+	5	675	210	1	--
cresols	5	780	304	1	--
ethylphenols	5	--	--	1	--
xylenols#	5	360	120	1	--
alkyl cresols	5	640	212	1	--
catechol	5	720	280	1	--
1,3-dihydroxybenzene	5	--	--	1	--
1,4-dihydroxybenzene	5	--	--	1	--
1,2,3-trihydroxybenzene	5	--	--	1	--
1-naphthol	5	--	--	1	--
2-naphthol	5	--	--	1	--
indanols	5	--	--	1	--
2-hydroxydibenzofuran	5	--	--	1	--
Substituted Benzene Compounds					
biphenyl	1.5×10^4	36	13.8	--	--
tetrahydronaphthalene	2.0×10^6	3480	1640	--	--
Fused Polycyclic Hydrocarbons					
naphthalene+	7.5×10^5	1785	690	--	2170
dimethylaphthalenes	3.46×10^6	--	--	--	--
acenaphthalene	--	--	--	--	--
anthracene+	8.45×10^5	--	--	--	1995
phenanthrene+	2.39×10^4	855	280	--	57
methylphenanthrene	4.6×10^5	--	--	--	--
chrysene+	3.33×10^4	--	--	--	79.4
methylchrysenes	2.69×10^4	--	--	--	64.5
pyrene	3.45×10^6	--	--	--	8333
dimethylpyrenes	--	--	--	--	--
benzo(a)pyrene++	0.3	61.5	20	--	7.5×10^{-4}
benzo(e)pyrene+	4.56×10^4	--	--	--	109
flourene**	--	--	--	--	--
1,2-benzoflourene	--	--	--	--	--
2,3-benzoflourene	--	--	--	--	--
flouranthene**	1.4×10^6	2430	800	--	--
benzo(k)flouranthene	1.6×10^3	--	--	--	--

(continued)

TABLE 14 (continued)

Compound	MATE (µg/l)	Estimated Permissible Concentrations (µg/l) EPC_{wh1}	EPC_{wh2}	EPC_{whs}	EPC_{ws}
benzo(e)flouranthene	$1.4x10^4$	--	--	--	--
benzo(j)flouranthene+	$9.8x10^4$	--	--	--	231
benzo(b)flouranthene+	$1.34x10^4$	--	--	--	31.5
3-methylcholanthrene++	56	--	--	--	0.14
Aromatic Amines					
aniline##	$3.5x10^5$	675	262	--	--
methyanilines#	$1.65x10^3$	780	304	--	4
dimethylanilines	$3.75x10^5$	900	345	--	--
Heterocyclic Nitrogen Compounds					
pyridine	$2.25x10^5$	535.5	207	--	--
picolines	$5.34x10^5$	960	316	--	--
collidines	$1.04x10^6$	1875	616	--	--
di & poly substituted pyridines	$4.1x10^5$	--	--	--	--
Fused 6 Member Heterocyclics					
quinoline/isoquinoline	$2.36x10^5$	28.4	140	--	--
2-methyl quinoline	$3.31x10^5$	1500	492	--	--
dimethyl quinoline	--	--	--	--	--
dimethyl isoquinoline	--	--	--	--	--
acridine	$1.35x10^6$	2430	800	--	--
Pyrrole and Fused Ring Derivatives					
pyrrole	$4.05x10^4$	75	24	--	--
indole+	$1.65x10^5$	1200	400	--	390
methylindoles	$6.8x10^5$	--	--	--	--
carbazole	$3.4x10^5$	615	200	--	--
methylcarbazoles	--	--	--	--	--
Heterocyclic Oxygen Compounds					
furan	--	--	--	--	--
benzofuran	--	--	--	--	--
hydroxybenzofuran	--	--	--	--	--
benzofuranol	--	--	--	--	--
Heterocyclic Sulfur Compounds					
thiophene	$6.75x10^4$	120	40	--	--
methylthiophenes	$3.4x10^5$	615	200	--	--
dimethylthiophenes	--	--	--	--	--

*After Cleland and Kingsbury (11).
+on NIOSH suspected carcinogen list
#insufficient evidence to rate carcinogenic potential, but has produced tumors in test animals
++active carcinogen
**not known to be carcinogenic alone, but associated with compounds that are
##not known to be carcinogenic, but derivatives are

TABLE 15. MINIMUM ACUTE TOXICITY EFFLUENTS (MATE's) AND ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC's) IN WATER FOR SOME CONSTITUENTS OF COAL CONVERSION WASTEWATERS BASED ON ECOLOGICAL CONSIDERATIONS*

Compound	MATE (µg/l)	Estimated Permissible Concentrations (µg/l)		
		EPC_{we1}	EPC_{we2}	EPC_{wes}
acetic acid	$1x10^3$	500	--	
Phenols				
phenol	500	500	1000	100 (as phenolics)
cresols	500	50	70	100 (as phenolics)
ethylphenol	500	--	--	100 (as phenolics)
xylenols	500	700	1000	100 (as phenolics)
alkyl cresols	500	--	--	100 (as phenolics)
catechol	500	--	800	100 (as phenolics)
1,3-dihydroxybenzene	500	--	--	100 (as phenolics)
1,4-dihydroxybenzene	500	--	--	100 (as phenolics)
1,2,3-trihydroxybenzene	500	--	--	100 (as phenolics)
1-naphthol	500	--	--	100 (as phenolics)
2-naphthol	500	--	--	100 (as phenolics)
indanols	500	--	--	100 (as phenolics)
2-hydroxydibenzofuran	500	--	--	100 (as phenolics)
Substituted Benzene Compounds				
tetrahydronaphthalene	$1x10^3$	500	--	--
Fused Polycyclic Hydrocarbons				
naphthalene	100	50	1000	--
Aromatic Amines				
aniline	$1x10^3$	500	--	--
Heterocyclic Nitrogen Compounds				
pyridine	$1x10^4$	5000	5000	--
collidines	$1x10^4$	5000	--	--
Fused 6 Member Ring Heterocyclics				
quinoline/isoquinoline	--	--	500	--

*After Cleland and Kingsbury (11).

TABLE 16. DEFINITIONS OF SUBCATEGORIES OF ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC's).

EPC_{wh1} - The EPC of a chemical in water derived from the assumption that a maximum daily safe dosage to humans results from a 24-hour exposure to air containing the chemical, and that the same dosage is permissible in the volume of drinking water consumed in 24 hours.

EPC_{wh2} - The EPC of a chemical in water based on human health considerations of the safe maximum body concentration and the biological half-life of the substance.

EPC_{whs} - The EPC of a chemical in water corresponding to the most stringent existing or proposed federal regulation or criteria prescribing a water concentration for the chemical based on human health considerations.

EPC_{wc} - The EPC of a chemical in water based on the potential carcinogenicity of the substance. The concentrations assume a minimal risk dosage rather than a no-effect level.

EPC_{we1} - The EPC of a chemical in water based on the lowest reported LC_{50} or TL_m (median tolerance limit) for sensitive aquatic species and assuming an application factor of 0.05.

EPC_{we2} - The EPC of a chemical in water based on the lowest concentration of the chemical reported to cause tainting in fish flesh.

EPC_{wes} - The EPC of a chemical substance corresponding to the most stringent existing or proposed federal water criteria established to protect aquatic life.

*After Cleland and Kingsbury (11).

Toxicity data for a number of compounds are scant or wholly lacking. For those compounds which have been studied, the majority of information is derived from acute lethal toxicity tests on fish conducted with pure compounds or simple mixtures. The potential impact of coal conversion wastewater constituents on aquatic biota may be inferred from these studies, but extrapolations to determine toxic effects of combined effluents may prove meaningless. Although synergistic and antagonistic interactions between components will certainly occur, to what extent they will affect toxicity cannot currently be predicted from available data.

Phenols

The toxicity of phenols to aquatic organisms was recently reviewed by the European Inland Fishery Advisory Commission (15). Phenol concentrations in the range of 4-56 mg/l are acutely toxic to fish, and concentrations of 1-2 mg/l may produce long-term damage. Cresols have been studied less than phenol, and, of the three isomers, m-cresol is the least toxic. Toxicity values reported for o- and p-cresol are inconsistent. Xylenols are the least studied of the monohydric phenols, and no work has been conducted on 2,3- or 2,6-xylenol. Few data exist for either dihydric or polyphenols. Hydroquinone and naphthols are more toxic than phenol (0.1-1.40 mg/l), but these compounds are usually found in much smaller concentrations in coal conversion wastes. Sublethal responses of fish exposed to phenols include weight loss, reduction of growth, decreased sexual activity, alteration of reflexes, and histopathological anomalies.

The acute toxicity of several phenols to fish are presented in Table 17. Threshold concentrations of various phenolics to lower organisms are summarized in Table 18. Generally, bacteria, algae, protozoa, crustaceans, and molluscs are 10-100 times more resistant to phenol than fish. The cladoceran, Daphnia, however, appears to be more sensitive than other aquatic invertebrates.

Several papers not considered in the E.I.F.A.C. review should be mentioned. Huang and Gloyna (18) studied the amount of chlorophyll destruction sustained to the green algal, Chlorella pyrenoidosa, exposed to a number of phenolic compounds. A 30 per cent reduction in chlorophyll was observed in the presence of 100 mg/l of phenol. Cresols were found to further the reduction in chlorophyll over that observed for phenol, but there were not significant differences among the cresol isomers. Xylenols generally exhibited higher "toxicities" than cresols, but the position of the substituent methyl groups did not significantly affect the relative chlorophyll concentration. None of the xylenols showed any damage to chlorophyll at concentrations less than 50 mg/l. "Phenol coefficients" (the ratio of the destructive effect of a compound to that of phenol) of o-cresol, m-cresol, p-cresol, catechol, resorcinol, and hydroquinone were listed as 1.48, 1.36, 1.57, 0.74, 0.41, and 1.30, respectively.

Oxygen consumption by the snail, Helisoma trivolvis, was significantly reduced by exposure to 2 mg/l of phenol (19). Similarly, life-long exposure to 2.8, 8.2, 11.2, 16.3, and 22.4 mg/l of phenol depressed oxygen

TABLE 17. ACUTE TOXICITY OF SOME PHENOLS TO FISH

Compound	Organism	Concentration (mg/l)	Response Tested	Reference
phenol	crucian carp	25	24-hr LC_{50}	15
	roach	15	24-hr LC_{50}	15
	tench	17	24-hr LC_{50}	15
	"trout" embryos	5	24-hr LC_{50}	15
	rainbow trout	4.2-5.0	threshold concentration	2
	rainbow trout	1.39	48-hr LC_{50}	3
	fathead minnow	33	72-hr LC_{50}	16
	fathead minnow	32	96-hr LC_{50}	16
o-cresol	crucian carp	30	24-hr LC_{50}	15
	roach	16	24-hr LC_{50}	15
	tench	15	24-hr LC_{50}	15
	"trout" embryos	2	24-hr LC_{50}	15
m-cresol	crucian carp	25	24-hr LC_{50}	15
	roach	23	24-hr LC_{50}	15
	tench	21	24-hr LC_{50}	15
	"trout" embryos	7	24-hr LC_{50}	15
p-cresol	crucian carp	25	24-hr LC_{50}	15
	roach	17	24-hr LC_{50}	15
	tench	16	24-hr LC_{50}	15
	"trout" embryos	4	24-hr LC_{50}	15
	fathead minnows	21	72-hr LC_{50}	16
	fathead minnows	19	96-hr LC_{50}	15
2,4-xylenol	crucian carp	30	24-hr LC_{50}	15
	tench	13	24-hr LC_{50}	15
	"trout" embryos	28	24-hr LC_{50}	15
2,5-xylenol	crucian carp	10	24-hr LC_{50}	15
	roach	10	24-hr LC_{50}	15
	tench	9	24-hr LC_{50}	15
	"trout" embryos	2	24-hr LC_{50}	15
3,4-xylenol	crucian carp	21	24-hr LC_{50}	15
	roach	16	24-hr LC_{50}	15
	tench	18	24-hr LC_{50}	15
	"trout" embryos	7	24-hr LC_{50}	15
	fathead minnows	14	72-96 hr LC_{50}	16
3,5-xylenol	crucian carp	53	24-hr LC_{50}	15
	tench	51	24-hr LC_{50}	15
	"trout" embryos	50	24-hr LC_{50}	15

TABLE 18. THRESHOLD CONCENTRATIONS OF VARIOUS PHENOLICS TO LOWER AQUATIC ORGANISMS (mg/l)*

Compound	Daphnia (microcrustacean)	Scenedesmus (alga)	Microregma (protozoan)	E. Coli (bacterium)
phenol	16.0	40.0	30.0	>1000
o-cresol	16.0	40.0	50.0	600
m-cresol	28.0	40.0	20.0	600
p-cresol	12.0	6.0	10.0	>1000
3,4-xylenol	16.0	40.0	10.0	500
2,4-xylenol	24.0	40.0	70.0	>100
2,5-xylenol	10.0	40.0	50.0	>100
resorcinol	0.8	60.0	40.0	>1000
hydroquinone	0.6	4.0	2.0	50
pyrocatechol	4.0	6.0	6.0	90
quinone	0.4	6.0	2.0	50

*After McKee and Wolf (17).

uptake by the aquatic midge larva, Chironomus attenuatus (20). These data suggest that sublethal effects of phenol on invertebrates can occur within the same concentration range that affect fish. Finally, a 48-hr. LC_{50} value of 1.28 mg/l of resorcinol was recently reported for Daphnia (21).

Aliphatic Acids

Information on the toxic effects of organic acids to aquatic organisms is limited. Acute toxicity tests have been conducted with several compounds, and results are summarized in Table 19. Although comparisons are difficult due to the paucity of data, Daphnia and the diatom, Nitzschia, appear to be more sensitive than the various fish species tested.

Mattson, et al. (16) recently conducted acute toxicity tests with fathead minnows, and reported 96-hr LC_{50}'s of 88 mg/l for acetic acid, 97 mg/l for adipic acid, 88 mg/l for caproic acid, 205 mg/l for oleic acid, and 77 mg/l for valeric acid. Sublethal responses of aquatic organisms to organic acids have not been well studied, although green sunfish were not repelled by 20 mg/l of glacial acetic acid in preference-avoidance trials (22).

Polynuclear Aromatic Hydrocarbons

Although polynuclear aromatic hydrocarbons (PAH's) will be present in coal conversion effluents, little is known about the toxicity of these compounds to aquatic organisms. Those data that are available have been obtained primarily from oil spill studies. Extrapolation of toxicity data from these studies to coal conversion effluents must be made cautiously.

The absence of data for specific polynuclear aromatic hydrocarbons necessitates some consideration of the toxic effects of water-soluble fractions of oils. A number of investigators have conducted toxicity tests on water-soluble fractions of crude oils which contain PAH's, but rarely have individual compounds within these fractions been characterized. In general, water-soluble fractions of refined oils are more toxic than water-soluble fractions of equivalent amounts of crude oils. The difference in toxicity has been attributed to the higher percentage of boiling point, low molecular weight aromatics found in refined oil. Naphthalenes, methylnaphthalenes, and dimethylnaphthalenes have been specifically implicated by several investigators (23-27). Soluble aromatic derivatives of crude oil, in concentrations from 1-100 mg/l, can be expected to be acutely lethal to most adult marine organisms. Larvae and juveniles are usually much more sensitive, and may be eliminated by concentrations as low as 0.1 mg/l (28).

Despite an abundance of literature dealing with soluble fractions of petroleum, the toxicity of specific PAH's are not well known. Acute toxicity data from some PAH's are presented in Table 20. From these data, it appears that algae are most resistant to acute poisoning, and crustaceans are more sensitive than fish. A number of physiological and behavioral responses of marine organisms exposed to oil and oil constituents

TABLE 19. TOXICITIES OF SOME ORGANIC ACIDS TO AQUATIC ORGANISMS*

Compound	Organism	Exposure Time	Concentration (mg/l)	Toxicity
Formic Acid	Sewage Microorganisms	24 hr	175	LC_{50}
	Lepomis macrochirus	5 day	550	TC_{50}
Acetic Acid	L. macrochirus	96 hr	75	LC_{50}
	L. macrochirus	24 hr	100-1000	LC_{50}
	L. macrochirus	96 hr	75	LC_{50}
	Ictalurus punctatus	72 hr	270 (by vol)	LC_{50}
	Carassius auratus	48 hr	100	"killed some"
	Semotilus atromaculatus	24 hr	100-200	critical range
	Gambusia affinis	96 hr	251	LC_{50}
	Carp, Perch	8 hr	4.7 (by vol)	lethal
	Daphnia magna	24 hr	47	LC_{50}
	Daphnia magna	24-72 hr	125	lethal
	Daphnia magna	32 hr	150	threshold of immobilization
	Culex sp., larvae	48 hr	1500	LC_{50}
	Nitzschia linearis	120 hr	74	LC_{50}
Propionic Acid	L. macrochirus	24 hr	188	LC_{50}
	D. magna	48 hr	50	LC_{50}
	Culex sp., larvae	48 hr	1000	LC_{50}
Butyric Acid	L. macrochirus	24 hr	200	LC_{50}
	D. magna	48 hr	61	LC_{50}

*After Smith (7).

TABLE 20. TOXICITY OF SOME POLYNUCLEAR AROMATIC HYDROCARBONS TO MARINE AND AQUATIC ORGANISMS

Compound	Organism	Concentration (mg/l)	Response	Reference
Naphthalene	Chlorella vulgaris	27	24-hr. LC_{50}	29
	Chlamydomonas angulosa	3.5	61% killed in 4 days (open flasks)	25
	Chlamydomonas angulosa	3.5	97% killed in 4 days (stoppered flasks)	25
	Paleomonetes pugio	2.6	24-hr. LC_{50}	30
	Penaeus aztecus	2.5	24-hr. LC_{50}	30
	Sheepshead Minnow	2.4	24-hr. LC_{50}	30
	Silver Salmon	1.8-3.2	72-hr. critical conc.	31
	Mosquito Fish	220	24-hr. LC_{50}	33
	Mosquito Fish	165	48-hr. LC_{50}	33
	Mosquito Fish	150	96-hr. LC_{50}	33
1-Methylnaphthalene	Sheepshead Minnow	3.4	24-hr. LC_{50}	30
	Fathead Minnow	9.0	96-hr. LC_{50}	16
2-Methylnaphthalene	Paleomonetes pugio	1.7	24-hr. LC_{50}	30
	Penaeus Aztecus	0.7	24-hr. LC_{50}	30
	Sheepshead Minnow	2.0	24-hr. LC_{50}	30
Dimethylnaphthalene	Paleomonetes pugio	0.7	24-hr. LC_{50}	30
	Penaeus aztecus	0.08	24-hr. LC_{50}	30
	Sheepshead Minnow	5.1	24-hr. LC_{50}	30
1,6-dimethylnaphthalene	Sea Lamprey	5	no effect*	32
Anthracene	Rainbow Trout	5	no effect*	32
	Bluegill	5	no effect*	32
	Sea Lamprey	5	no effect*	32
	Chinook & Coho Salmon	10	no effect*	34
Phenanthrene	Rainbow Trout	5	lethal in 5-hr.	32
	Bluegill	5	lethal in 5-hr.	32

(continued)

TABLE 20. (continued)

Compound	Organism	Concentration (mg/l)	Response	Reference
Chrysene	Rainbow Trout	5	no effect*	32
	Bluegill	5	no effect*	32
	Sea Lamprey	5	no effect*	32
	Chinook & Coho Salmon	10	no effect*	34
Flourene	Sea Lamprey	5	no effect*	32
Flouranthene	Sea Lamprey	5	no effect*	32
3-Methylcholanthrene	Chinook & Coho Salmon	10	no effect*	34
Pyrene	Chinook Salmon	10	loss of equilibrium in 5-9 hr., lethal in 9-13 hr.	34
	Coho Salmon	10	lethal in 13-17 hr.	34
3,4-Benzopyrene	Chinook & Coho Salmon	10	no effect*	34

*only concentration tested

have been documented, but the extent to which PAH's play a role is not clear. Various sublethal responses to petroleum products have been demonstrated including effects on respiration (35,36), feeding (37,38), molting (39), growth (40), carbon flux (41), locomotor activity (42,43), enzyme activity (44,45), chemotactic behavior (46,47), and histopathology (48,49).

A number of PAH's which have been identified or are anticipated to occur in coal conversion wastes will contribute to acute toxicity. Mixtures of various PAH's, and PAH's and other organic compounds, may prove to be more toxic than individual compounds since combined naphthalenes have been shown to be more toxic than either naphthalene, methylnaphthalene, or dimethylnaphthalene alone (27). PAH-induced acute toxicity is of concern, but a more serious threat to aquatic environments may be posed by the release of slightly soluble, high molecular weight, multi-ring compounds. Included in this group are a number of known carcinogenic and mutagenic compounds, such as benzopyrenes and methylcholanthrenes. Coal conversion wastes are expected to contain only minuted amounts of these compounds, but they do not appear to be readily biodegradable and may be difficult to remove by waste treatment. Consequently, they may bioaccumulate in a number of aquatic organisms (including edible fish and shellfish) and thereby become a source of carcinogens to man. The detection of carcinogenic substances in fish would almost certainly lead to a ban on both commercial and recreational fishing in affected areas.

While the production of PAH-induced cancers in aquatic organisms has not been experimentally verified, the occurrence of tumors and neoplasms has been associated with PAH's in several instances. Analysis of water samples from the Fox River in Illinois verified the presence of several aromatic compounds, including 0.01 mg/l benzanthracene, and 0.1 mg/l each of naphthalene, toluene, and benzene (50). The frequency of various neoplasms in fish collected from contaminated water was 4.38%, compared to 1.03% in fish from control waters. Papilliform tumors and other lethal malformations have been produced in planaria exposed to 3-methylcholanthrene and benzo(a)-pyrene (51). Uncontrolled growth of ovicells has been induced in the estuarine bryozoan, Schizoporella unicornis, by placing normal colonies near coal tar derivatives in an estuary. It was suggested that the growth was stimulated by several PAH's present in coal tar (1,2,5,6-dibenzanthracene, benzo(a)pyrene, and methylcholanthrene) (52). Although abnormal growths are usually associated with animals, multi-ring compounds have been implicated as the cause of cancer-like growths in algae as well (53,54).

Nitrogen- and Sulfur-Containing Compounds

Toxicity of the nitrogen- and sulfur-substituted aromatics were recently reviewed (55) and are the least understood constituents of coal conversion wastewaters. Aryl amines and thiophenes are more soluble in water than the PAH's, and may therefore occur at greater concentrations in coal conversion effluents. The potential for bioaccumulation and food chain magnification are marked, and the relative hazards to aquatic biota may equal or exceed those of the PAH's. A summary of acute toxicity data for several nitrogen containing compounds is given in Table 21. Similar data for sulfur substituted compounds are virtually non-existent. Thiophene

TABLE 21. TOXICITY OF NITROGEN CONTAINING COMPOUNDS TO AQUATIC ORGANISMS*

Compound	Organism	Concentration (mg/l)	Response
Aniline	Fathead Minnow	200	96-hr. LC_{50}
	Goldfish	1000	96-hr. LC_{50}
	Trout	100	96-hr. LC_{50}
	Sunfish	1020-1120	lethal in 1 hr.
	Fish	250	lethal
	Daphnia	279	lethal
	Daphnia	0.4	48-hr. LC_{50}
Indole	Trout	5.0	lethal in 10 hr.
	Bluegill	5.0	no effect in 24 hr.
	Sea Lamprey	5.0	no effect in 24 hr.
Isoquinoline	Sunfish	65	lethal in 1 hr.
	Perch	100	lethal in 1 hr.
Pyridine	Mosquito Fish	1300-1350	96-hr. LC_{50}
	Fish	1000	threshold effect
	Perch	1000	lethal
	Yearling Trout	400	toxic limit
	Perch	200	no effect
	Carp	200	threshold toxicity
	Bream	180	threshold toxicity
	Bleak	160	threshold toxicity
	Fish	100	threshold toxicity
	Daphnia	40	threshold toxicity
	Fish	15	toxic action on central nervous system
Quinaldine	Trout	5.0	lethal in 1 hr.
Quinoline	Sunfish	52-50	lethal in 1 hr.
	Perch	30-50	lethal in 1 hr.
	Perch	30	lethal
	Trout	5.0	lethal in 14 hr.
	Bluegill	5.0	lethal in 4 hr.
	Fish	7.5	lethal
	Trout Yearlings	7.5-10	lethal in 1 hr.
	Bleak	10	96-hr. LC_{50}
	Bream	10	96-hr. LC_{50}
	Carp	10	96-hr. LC_{50}
	Daphnia	52	at 23°C
	Ciliates	750	lethal
	Fathead Minnow**	46	24,48,72,96-hr. LC_{50}

*After Wilkes (55).
**From Mattson, *et al.* (16).

is approximately 33% more toxic to sunfish than is benzene, and thiophene and 2-methylthiophene are more toxic to mammals than their benzene analogs. From these correlations, it is assumed that the higher molecular weight thiophene compounds may also be more toxic than the corresponding PAH compounds. No information is available regarding the carcinogenic and mutagenic effects of heterocyclic compounds, potential interactions between heterocyclics and other classes of organic compounds, or chronic effects of trace levels of heterocyclics to aquatic organisms. However, the presence of nitrogen or sulfur heteroatoms in PAH structures has been noted to either intensify or lessen carcinogenicity. Several heterocyclic analogs of phenanthrene (acridine, carbazole, and thiophene derivatives) have also been proven to be carcinogenic to mammals.

RESEARCH NEEDS

More complete information about the aquatic impact of coal conversion effluents is needed in three major areas:

1. determination of acute lethal toxicity values for those compounds for which information is lacking;

2. analysis of interactions among organic compounds which occur together in coal conversion effluents; and

3. development of chronic toxicity data for coal conversion effluents and constituents in both laboratory and ecosystem populations.

Before research in the latter two areas can be conducted, however, basic acute toxicity data for the constituents must be accumulated. Particular attention should be given to those components which are not readily biodegradable and are not easily removed by waste treatment. Such components are likely to be persistent in aquatic systems.

If the entire aquatic community is to be protected, pollutant toxicity must be determined for at least three components of the aquatic food web. The most sensitive group of organisms must then be identified (56,57). The realization that the elimination of lower organisms may have serious environmental consequences has led to increased reliance on invertebrates and algae, as well as fish, for toxicity testing. Several aquatic species have become widely accepted as bioassay organisms, including the fathead minnow (Pimephales promelas), cladocerans (Daphnia magna and D. pulex), and an alga (Selenastrum capricornutum), and standard procedures for acute toxicity testing are available (58,59).

Although acute toxicity tests can identify specific pollutants of immediate concern and may be used to determine "safe" levels in receiving waters by appropriate application factors (9), it is impossible to predict safe limits for complex effluents. The degree of interaction that occurs in complex wastes is unknown. Further, the effluents of any two conversion plants may differ, and a compound common to both waste streams could exhibit different toxic behavior in each. Unfortunately, the limited availability of coal conversion effluents at present precludes research on the toxic

effects of composite effluents.

Therefore, in order to assess the aquatic impact of coal conversion wastewaters, the following approach has been adopted. Aquatic bioassay tests will be conducted to develop acute toxicity data for selected wastewater constituents on the three test organisms cited: Pimephales promelas, Daphnia pulex, and Selenastrum capricornutum. The constituents to be tested will be those which are non-biodegradable and would tend to persist in waters receiving biologically treated coal conversion wastewater. Following collection of such component toxicity data, treated effluents from both synthetic and real composite samples will be subjected to similar tests. The results of the component studies will be used to help interpret the results from the composite tests. While acute toxicity data for the organic components cannot be used to assess chronic effects of coal conversion wastes, such data should provide a reasonable preliminary assessment of toxicity problems anticipated from coal conversion wastewaters.

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SECTION 6

MICROBIAL DEGRADATION OF ORGANIC CONSTITUENTS IN COAL CONVERSION WASTEWATERS

In this section, a literature review of the biological degradability of constituents from coal conversion processes is presented, along with the results of some preliminary biodegradation experiments performed during this first phase of our study. The microbiological literature has been reviewed to determine microbial pathways by which phenols, N-containing aromatics, and polynuclear aromatic hydrocarbons are degraded. The majority of the research work on microbial degradation of these organic compounds and the identification of metabolic pathways has been done with pure cultures and single substrates, under highly-controlled laboratory conditions. The microbial cultures employed were often maintained and manipulated solely for the purpose of degrading a particular substrate. It is therefore important to recognize that the degradation of a compound under these conditions does not imply that it will be readily biodegradable under natural or waste treatment conditions.

Lack of information as to degradation patterns or pathways does not necessarily mean that the compound is not biodegradable, as many compounds identified in coal conversion wastewaters have not been studied. For some compounds which pose particular hazards to man, such as the carcinogenic polynuclear aromatic hydrocarbons, attention has been directed to mammalian metabolism rather than microbial degradation. Nevertheless, such a review does provide a starting point in evaluating the biodegradability of organic constituents under real, environmental conditions.

LITERATURE REVIEW

Phenol and Other Monoaromatic Hydrocarbons

Coal conversion effluents contain a large number and variety of organic components as discussed and illustrated previously in Section 5. Of the many compounds that have been reported as constituents of coal conversion effluents, the microbial degradation of only one class of these compounds, the phenolics, has been extensively investigated. However, review of this work provides information about the microbial degradation of aromatic compounds in general, since phenols are the major intermediates in the degradation of aromatics, i.e., they are the substrates for ring fission enzymes. Therefore, an understanding of the metabolism of phenols is basic to the study of the degradation of other aromatic compounds. Additionally, phenolic compounds comprise the major portion of the total organic carbon content of coal conversion effluents.

Microbial Pathway Studies--

Many bacteria and fungi can utilize aromatic hydrocarbons as a sole source of carbon and energy. Specialized metabolic pathways convert initial aromatic substrates to aliphatic cellular intermediary metabolites. Gibson (1) has recently confirmed that the initial reaction in the

bacterial oxidation of aromatic hydrocarbons is the formation of cis-dihydrodiols. These compounds then undergo further oxidation to yield dihydric phenols which are substrates for ring fission enzymes. This process has been demonstrated for compounds ranging in size from benzene to benzo(a)pyrene.

In general, the metabolism of benzenoid compounds is dependent on the presence of molecular oxygen. Oxidative ring cleavages, along with most oxidation steps in the initial sequences that converge on diphenols, are mediated by oxygenases not deoxygenases (2). While molecular oxygen acts as a terminal electron acceptor, it is also a specific reactant with those enzymes which catalyze the introduction of hydroxyl groups and the fission of suitably hydroxylated rings. Therefore, such pathways are strictly aerobic since, even though some substances such as nitrate may fulfill the role of electron acceptor, they are not reactive with oxygenases (3). Some exceptions to this general condition do exist. For example, some heterocyclic ring systems undergo hydroxylations in which water serves as the source of the hydroxyl group (4). Also, water supplies a hydroxyl group for the anaerobic photometabolism of benzoic acid by Rhodopseudomonas palustris (5).

Another general condition for microbial degradation of aromatics is that in order for ring cleavage to occur, the primary substrate must initially be converted to either an ortho or para dihydric phenol. Two of the most important of these compounds are catechol and protocatechuic acid, both ortho phenols. Figure 1 shows initial sequences for bacterial metabolism of various substrates that converge on catechol. Compounds related to catechol which also serve as intermediate ring fission substrates are 3-methylcatechol (7), 4-methylcatechol (8), and 1,2-dihydroxynaphthalene (9).

Initial metabolism of m- and p-cresols along with other benzenoid compounds may result in another ortho dihydric phenol, protocatechuic acid. Figure 2 illustrates the convergence of some aromatic hydrocarbons on this ring fission substrate. Another frequently encountered acidic fission substrate is 2,3-dihydroxybenzoic acid (10).

The third important ring cleavage substrate is gentisic acid. This is a para-dihydric phenol formed from such primary substrates as β-naphthol (see Figure 3). A less common para-dihydric phenol is hydroquinone (11).

The importance of the position of the two hydroxyl groups on the ring should not be overlooked. For example, in the metabolism of resorcinol, a meta-dihydric phenol, ring fission does not occur until the compound is hydroxylated to form a 1,2,4-trihydric phenol (12,13).

The modification of a substituent group may or may not occur before ring cleavage depending on bacterial species, nature of the primary substrate and position on the ring relative to other substituents. In the case of the methyl group, some species of bacteria hydroxylate the nucleus of cresols leaving the methyl group intact (8), while others oxidize the methyl group initially to a carboxyl group (14). In the former case the fission substrate is then a methyl-catechol, whereas in the latter case the intermediate formed is either gentisic or protocatechuic

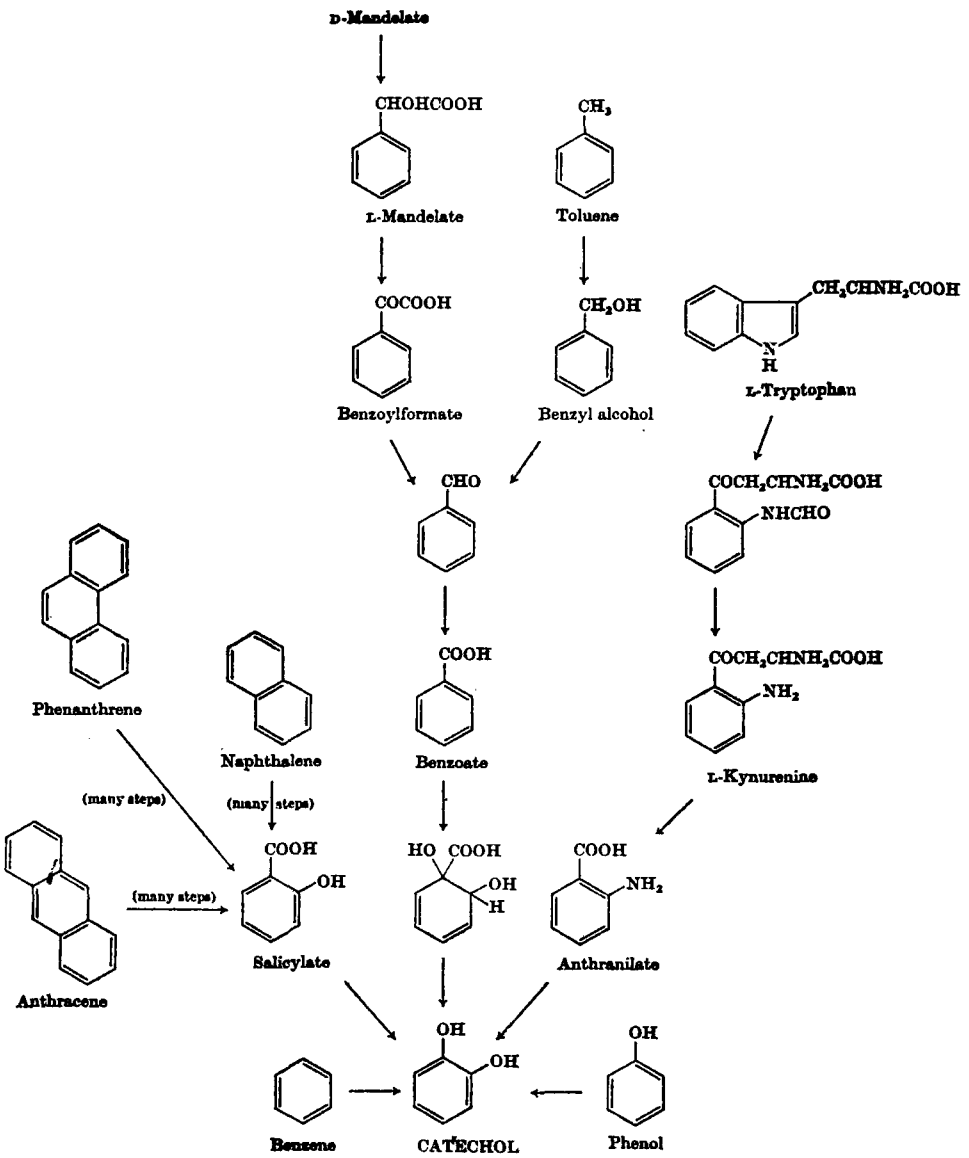


Figure 1. Initial reactions in the bacterial degradation of various compounds that converge on catechol. (From Stanier and Ornston (6).) Reproduced with permission from Advances in Microbial Physiology, Academic Press Inc. (London) Ltd.

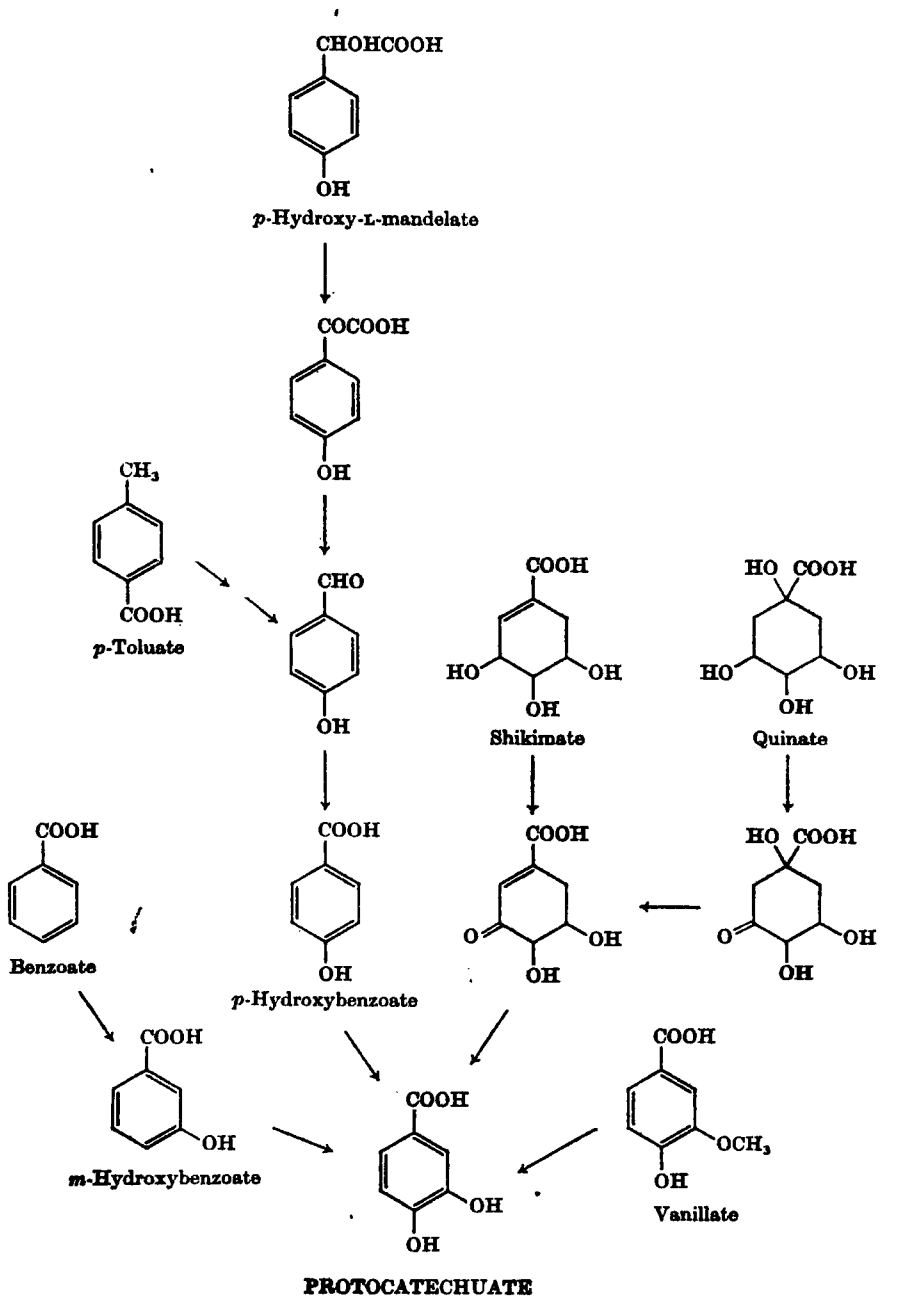


Figure 2. Initial reactions in the bacterial degradation of various compounds that converge on protocatechuate. (From Stanier and Ornston (6).) Reproduced with permission from Advances in Microbial Physiology, Academic Press Inc. (London) Ltd.

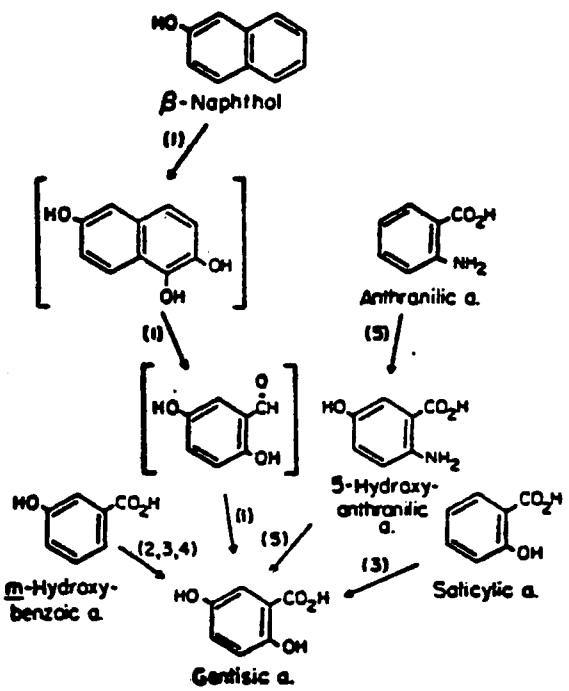


Figure 3. Initial reactions in the bacterial degradation of various compounds that converge on gentisic acid. (From Chapman (18).) Reproduced from Degradation of Synthetic Organic Molecules in the Biosphere (1972), Page 22, with the permission of the National Academy of Sciences, Washington, D.C.

acid. The dimethylphenols (xylenols) act similarly. Depending on the position of the methyl groups on the ring, metabolism results in either protocatechuic acid or a methylgentisic acid (14,15).

Alkyl side chains possessing two or more carbons may also undergo modification. Carboxylic acids are formed by the oxidation of the terminal methyl group. The larger carboxylic alkyl chains may then undergo β-oxidation, but sometimes may remain intact on the ring cleavage substrates as shown in Figure 4. Generally, carboxyl groups remain intact prior to ring cleavage, but they may be eliminated as in the metabolism of benzoic acid to catechol (17). Chapman (18) notes that alkoxyl groups are usually dealkylated initially to form an aldehyde and the parent phenol.

Once the primary substrate has been converted to one of the ring fission substrates, cleavage can then occur. Bacteria employ two different modes of enzymatic ring cleavage, known respectively as ortho and meta fission. Figure 5 shows both types of fission for catechol and protocatechuic acid. Ortho fission is the splitting of the bond between two carbon atoms bearing hydroxyl groups. This results in the formation of dicarboxylic acids. The other pathway, meta fission, leads to either an aldo-acid or keto-acid by cleavage of a carbon-carbon bond where only one carbon bears a hydroxyl group. Usually, a particular microbial species employs only one method of ring fission for a certain primary substrate (6). However, catechol is an exception. Some bacteria can metabolize catechol via both ortho and meta fission pathways (19). The method of ring fission varies with species, structure of the dihydric phenol, and the substrate upon which the microbial culture has been maintained. This last condition has been demonstrated by Hopper and Taylor (20) for the cresol isomers. When bacteria were grown on p-cresol, p-cresol was degraded by the ortho-fission pathway, but when the same culture had been maintained on m-cresol, p-cresol was degraded via meta-fission.

Figure 6 shows the fission pathway for gentisic acid. Fission occurs at the carbon-carbon bond where one carbon bears a hydroxyl group and the other carbon bears the carboxyl substituent.

The trihydric ring fission substrate, 1,2,4-trihydroxybenzene, found in the degradation of resorcinol, undergoes ortho-fission (11) with the ultimate products being acetic and formic acids. Other trihydric phenols undergo meta-fission.

If all of the information presented above is applied to the various phenolic compounds found in coal conversion wastewaters, certain patterns emerge. Table 22 presents the relevant metabolic pathways for selected phenolic constituents.

Figure 7 is a general scheme for the bacterial degradation of substituted phenols. The ultimate ring fission products of most phenolics undergo fatty acid metabolism or enter the tricarboxylic acid cycle of the microorganisms.

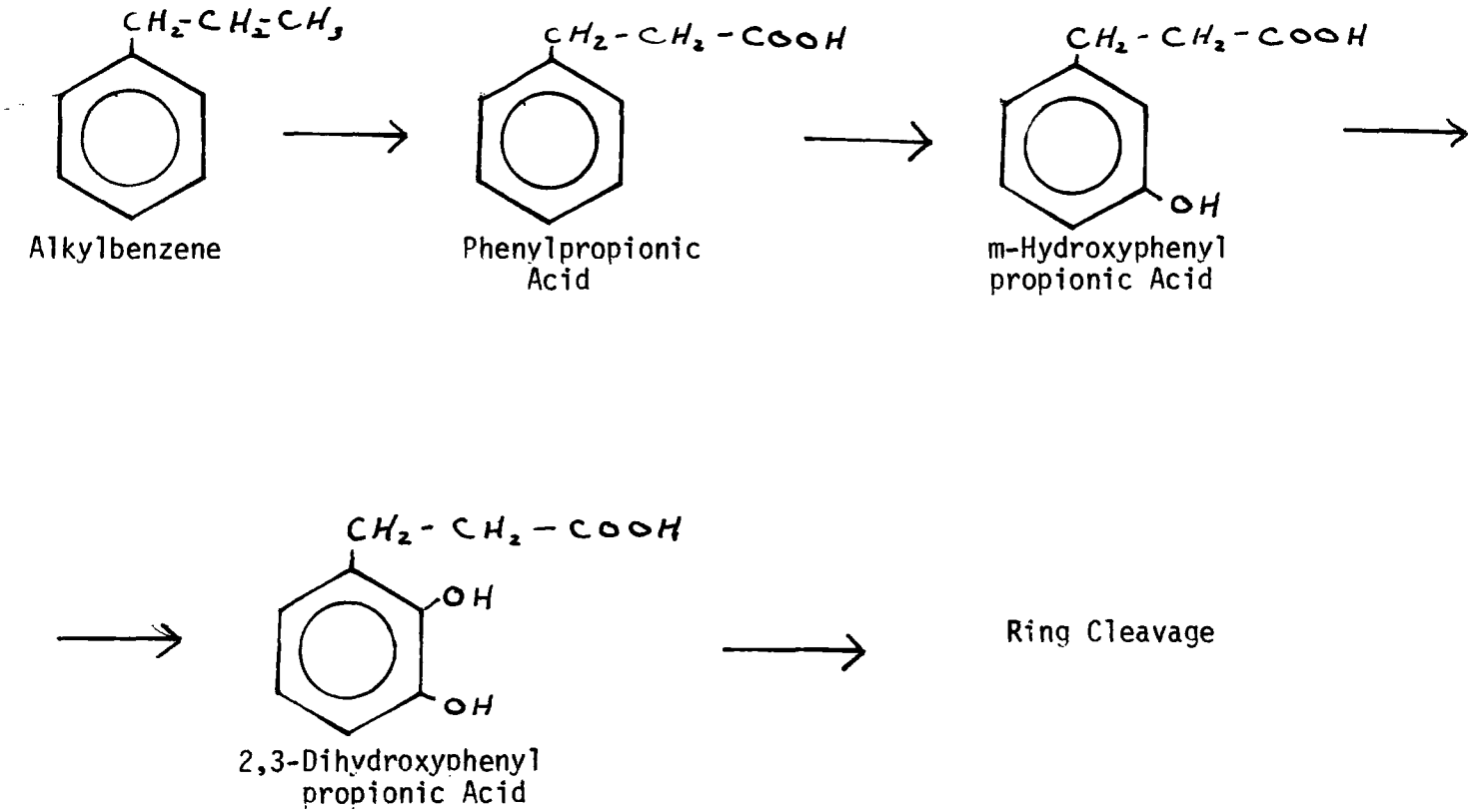


Figure 4. Example of an aromatic compound possessing an alkyl side chain which remains intact prior to ring cleavage. (From Van der Linden and Thijsse (16).)

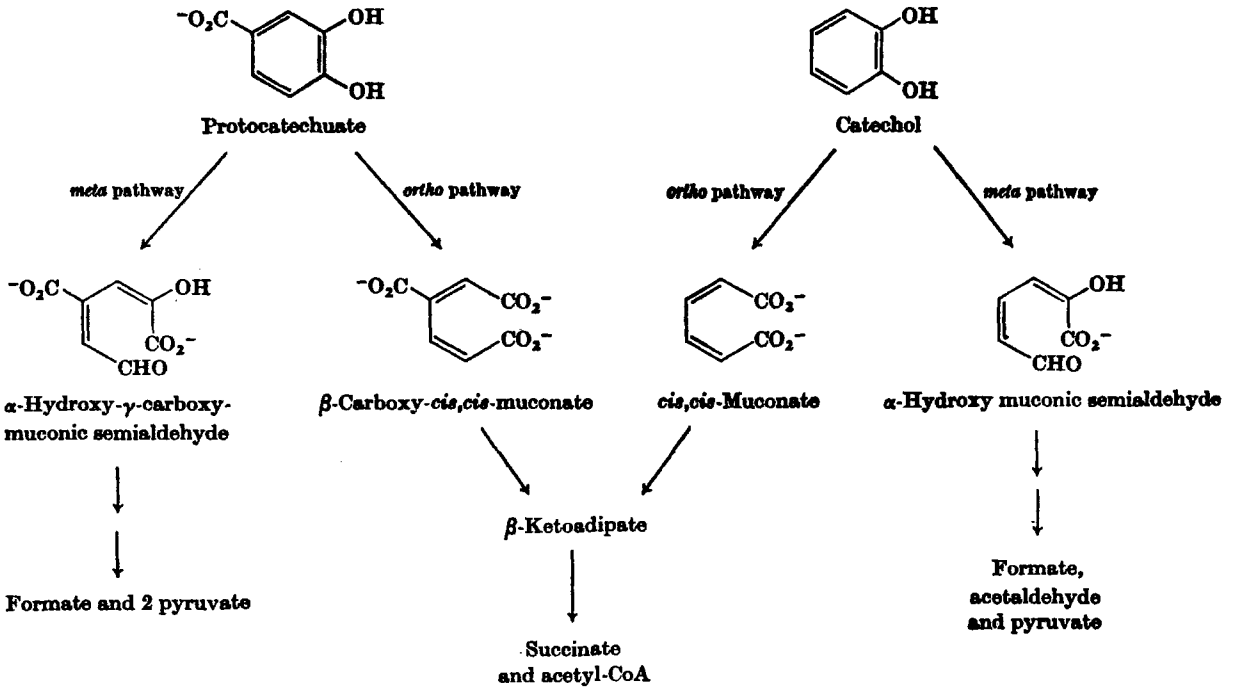


Figure 5. Ortho and meta fission pathways for the dissimilation of protocatechuate and catechol. (From Stanier and Ornston (6).) Reproduced with permission from Advances in Microbial Physiology, Academic Press Inc. (London) Ltd.

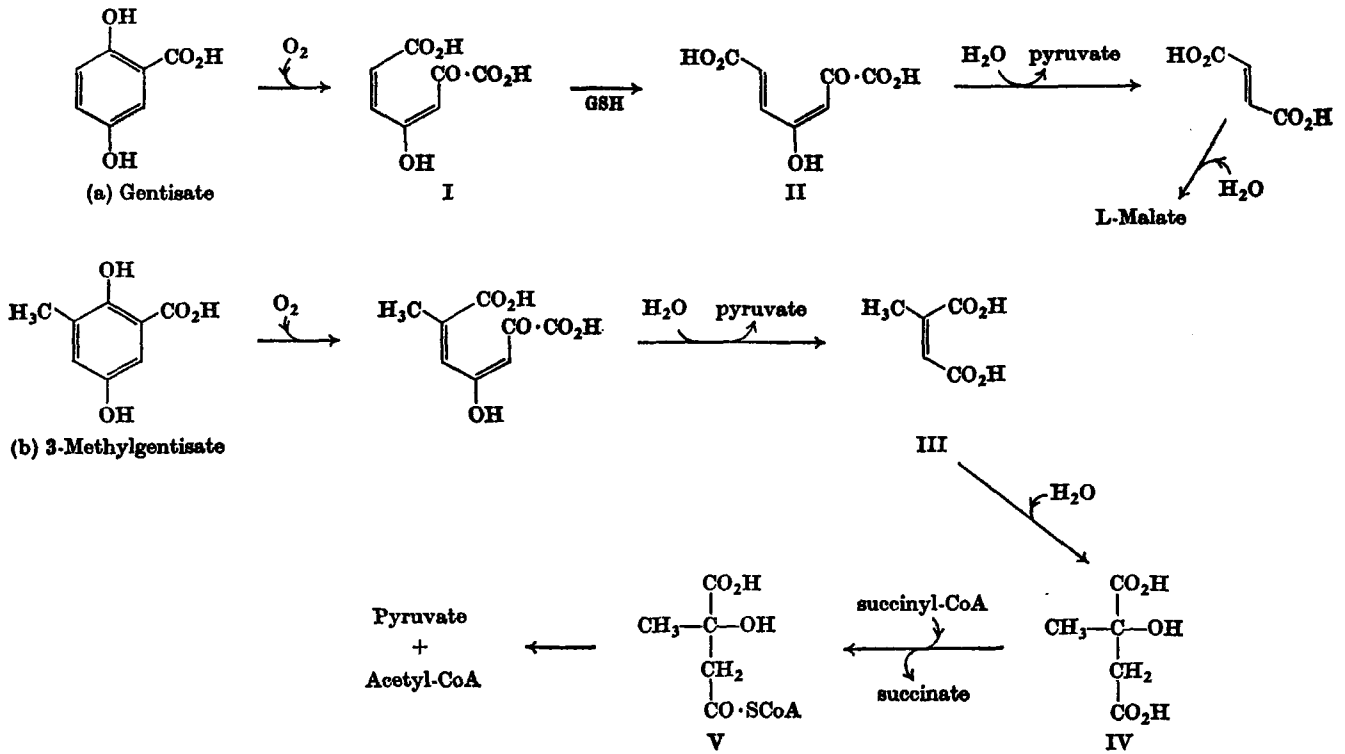
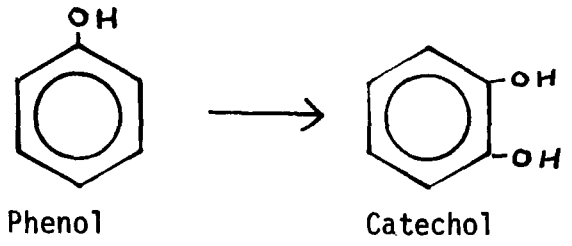
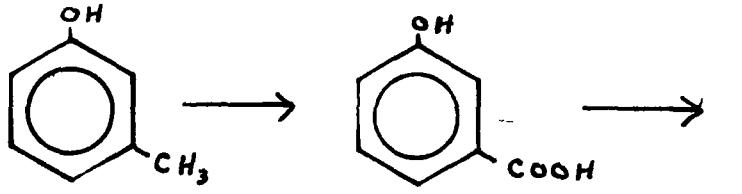


Figure 6. Bacterial metabolism of gentisic acids. (From Dagley (21).) Reproduced with permission from Advances in Microbial Physiology, Academic Press Inc. (London) Ltd.

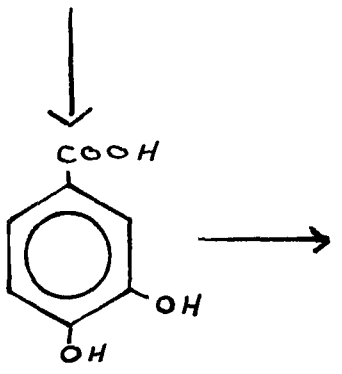
TABLE 22. PROPOSED METABOLIC PATHWAYS FOR THE MICROBIAL DEGRADATION OF SELECTED PHENOLIC COMPOUNDS.



Phenol Catechol Figure 5 "Ortho" fission



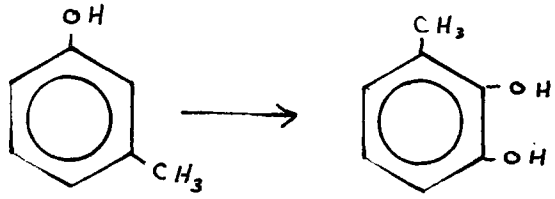
m-Cresol Gentisic Acid Figure 6



Protocatechuic Acid Figure 5 "Meta" fission

(continued)

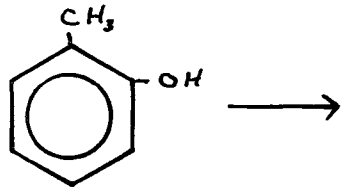
TABLE 22. (continued)



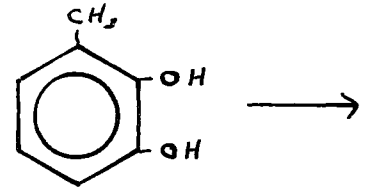
m-Cresol

3-Methylcatechol

Figure 5
"Meta" fission

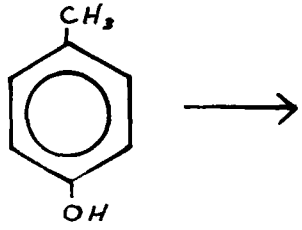


o-Cresol

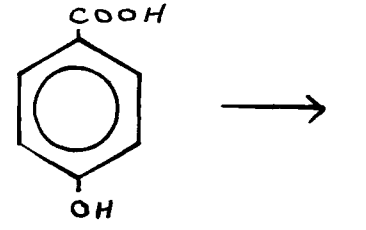


3-Methylcatechol

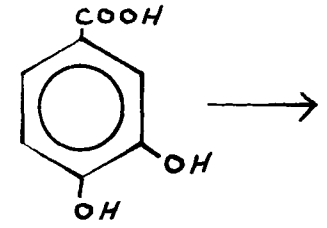
Figure 5
"Meta" fission



p-Cresol



p-Hydroxybenzoic Acid

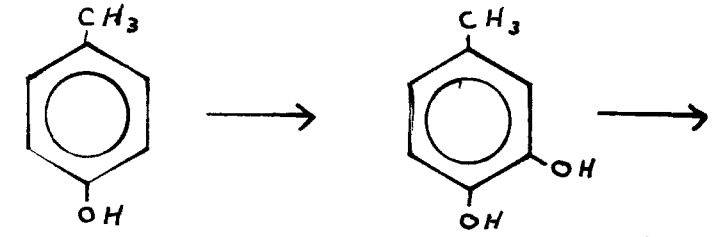


Protocatechuic Acid

Figure 5
"Ortho" fission

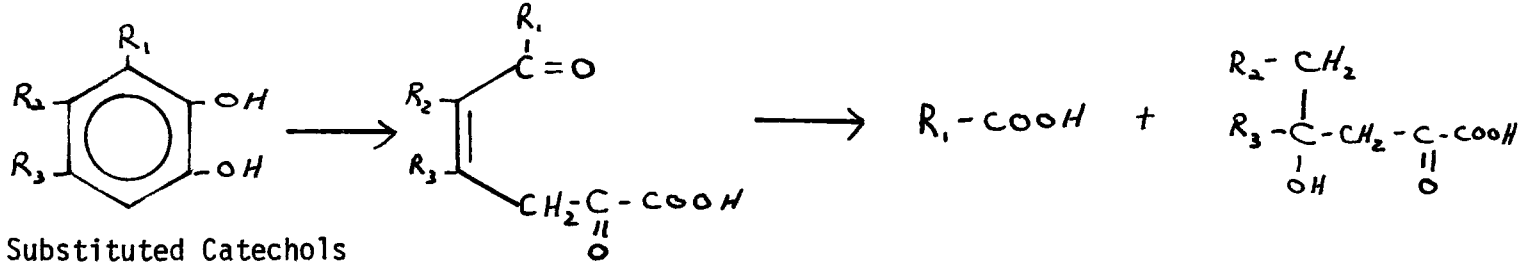
(continued)

TABLE 22. (continued)



p-Cresol 4-Methylcatechol

Figure 5
"Meta" fission



Substituted Catechols

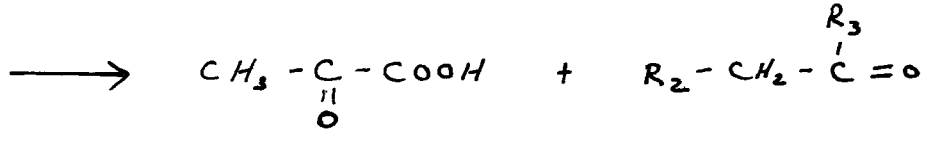


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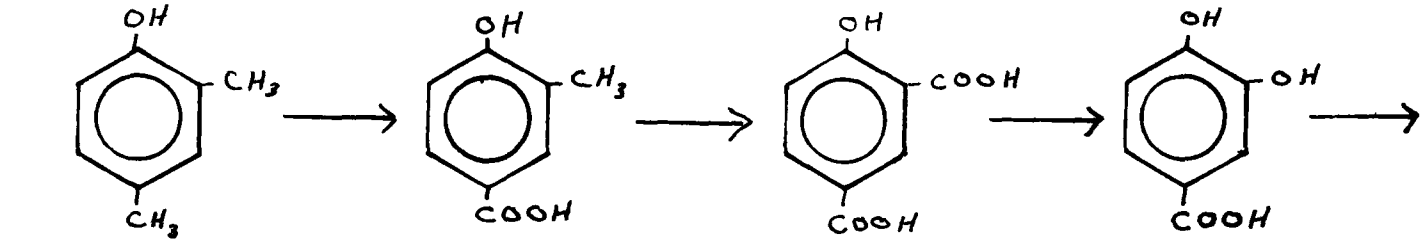
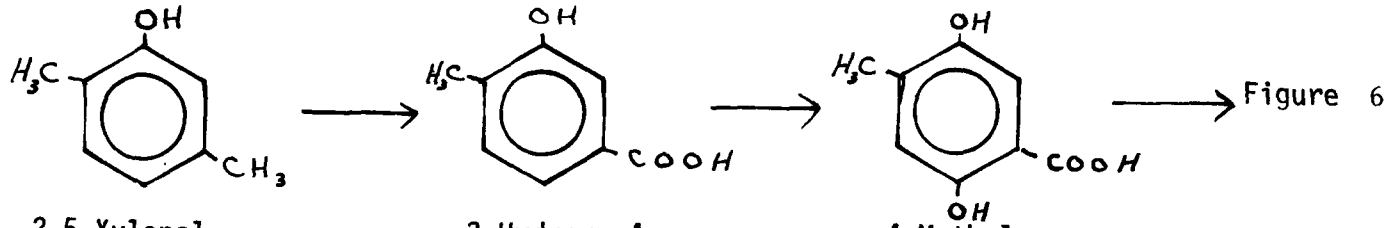
TABLE 22. (continued)



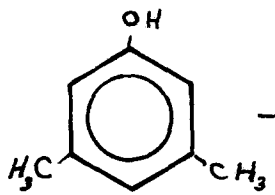
2,4-Xylenol → 4-Hydroxy-3-Methylbenzoate → 4-Hydroxyisophthalic Acid → Protocatechuic Acid Acid → Figure 5



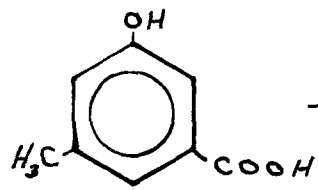
2,5-Xylenol → 3-Hydroxy-4-methylbenzoate → 4-Methylgentisic Acid → Figure 6

(continued)

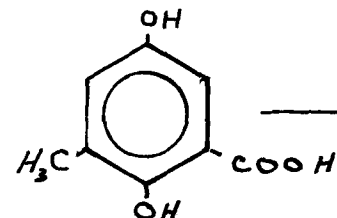
TABLE 22. (continued)



3,5-Xylenol

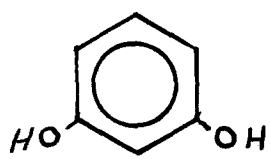


3-Hydroxy-5-Methylbenzoate

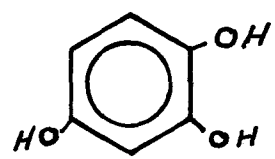


3-Methyl-gentisic Acid

Figure 6

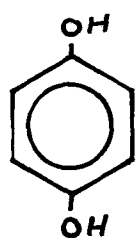


Resorcinol

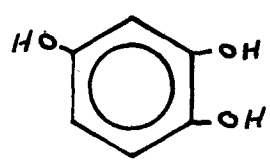


2-Hydroxyhydroquinone

Figure 5
"Meta" fission



Hydroquinone

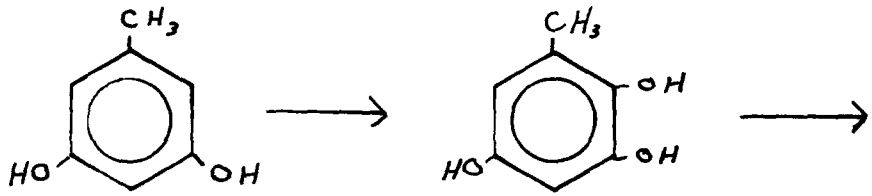


2-Hydroxyhydroquinone

Figure 5
"Meta" fission

(continued)

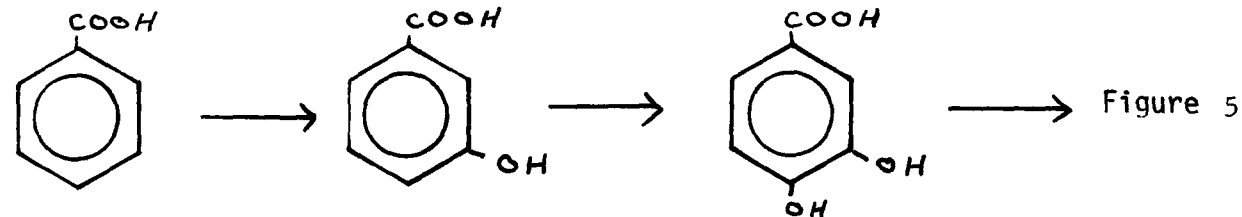
TABLE 22. (continued)



Orcinol

2,3,5-Trihydroxy-toluene

Figure 5
"Meta" fission



Benzoic Acid

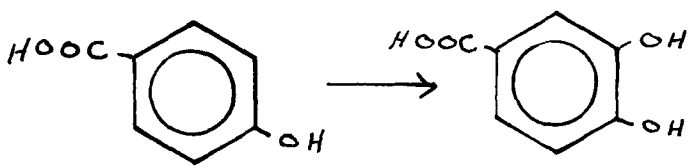
m-Hydroxy-benzoic Acid

Protocatechuic Acid

Figure 5

(continued)

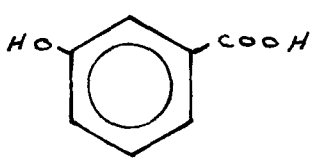
TABLE 22. (continued)



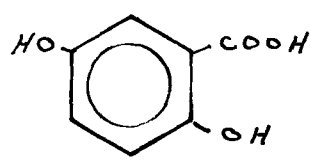
p-Hydroxybenzoic Acid

Protocatechuic Acid

Figure 5. "Ortho" fission



m-Hydroxybenzoic Acid



Gentisic Acid

Figure 6

(continued)

TABLE 22. (continued)

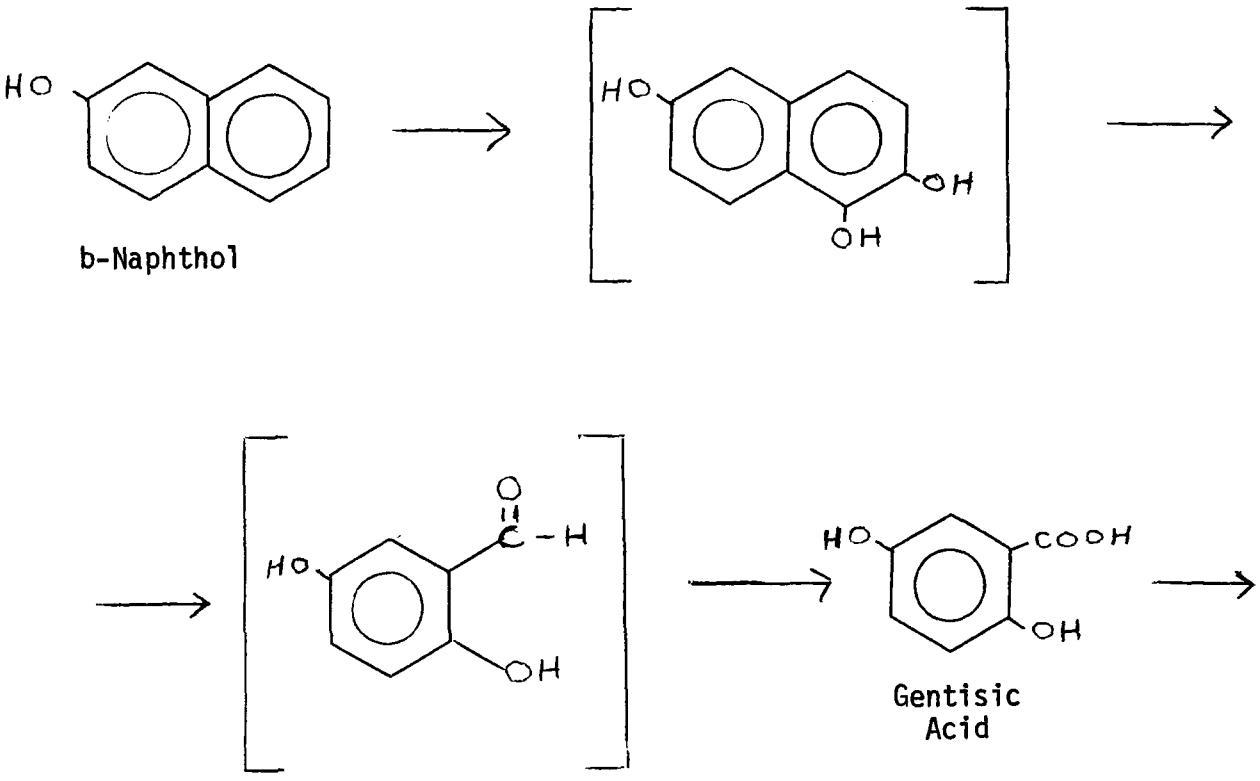
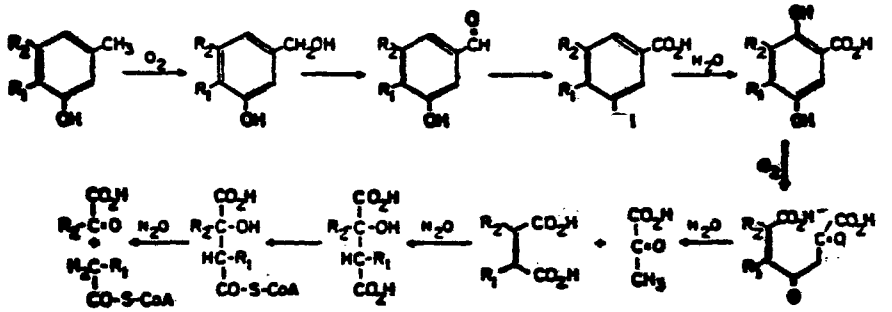


Figure 6



PHENOL	R_1	R_2
2,5-DIMETHYL-	CH_3	H
3,5-DIMETHYL-	H	CH_3
2,3,5-TRIMETHYL-	CH_3	CH_3
3-ETHYL-5-METHYL-	H	C_2H_5

Figure 7. General reaction scheme for bacterial degradation of substituted phenols. (From Chapman (18).) Reproduced from Degradation of Synthetic Organic Molecules in the Biosphere (1972), page 46, with the permission of the National Academy of Sciences, Washington, D.C.

Metabolism by Mixed Cultures--

The metabolic pathway studies described above were carried out with pure cultures of microorganisms under controlled laboratory conditions. For the most part, these studies were conducted in order to discover the enzymes and mechanism by which microorganisms metabolize aromatic compounds for energy and growth. However, with respect to biological treatment of wastewaters containing these compounds, it is necessary to focus attention on mixed microbial communities, such as soil, sewage and activated sludge. Furthermore, the rate at which the substrate is metabolized must be considered.

Many of the data that exist on the biodegradability of phenolics in mixed cultures in wastewaters are based on oxygen uptake measurements. Early investigators studying biodegradability used the standard BOD test. A summary of this type of data for a large number of pure organic compounds included many phenols (22). The majority of the studies were done with unacclimated sewage as seed. Under these conditions the data revealed that phenol at concentrations below 500 mg/l was readily degraded. Ortho and meta cresol were degraded at approximately the same rate as phenol, as were α- and β-naphthol. Para-cresol and 3,4-xylenol gave somewhat lower oxygen demands and the BOD's of hydroquinone and 3,5-xylenol were only one-half that of phenol after five days.

Respirometric studies with acclimated activated sludge demonstrate the similar behavior of compounds of similar chemical structures, and the ability of microorganisms adapted to a given substrate to oxidize related compounds. The data of McKinney, Tomlinson and Wilcox (23) show that organisms acclimated to phenol, o-cresol or m-cresol metabolized phenol, the three cresol isomers, benzoic acid and p-hydroxybenzoic acid to approximately 33% of their ThOD (theoretical oxygen demand) in twelve hours. However, the phenol-acclimated sludge oxidized catechol to only 13% of its ThOD, while o-cresol and m-cresol-acclimated sludges metabolized catechol to the same extent as the other compounds (33% of ThOD). In the phenol-acclimated system, cresols were oxidized to about the same extent as phenol. The 3,4- and 2,4- and 2,6 and 3,5-methyl substituted phenols showed progressively less oxidation than phenol, indicating the importance of substituent position on the ring.

These results were later verified by a major study of the decomposition of phenolic compounds by phenol-adapted bacteria (24). In addition to respiration measurements, chemical analysis for residual substrate was also performed. Some of the results of the study are presented in Table 23 and Figures 8a and 8b. The data indicate that phenol itself is immediately and rapidly degraded and that dihydric phenols are oxidized to the same extent as phenol. The presence of more than two hydroxyl groups on the ring (e.g., phloroglucinol) increases resistance to degradation. The addition of one methyl group (cresols) appeared to stimulate total oxygen uptake for ortho and meta cresol. Total oxygen uptake for p-cresol was the same as that for phenol although there was a rapid initial uptake. Again, the effect of position of substitution on the ring was illustrated by the dimethylphenols. Nitro-, chloro-substituted, and trihydric phenols were relatively resistant to oxidation.

TABLE 23. OXIDATION AND REMOVAL OF VARIOUS PHENOLIC COMPOUNDS BY PHENOL-ACCLIMATED BACTERIA. (AFTER TABAK, et al. (24).)

Test compound	Test concn		Amt of O_2 consumed* (endogenous corrected)
	Initial ppm	Loss ppm	
			μliters
Phenol	100	99	319
Phenol	80	79	252
Phenol	60	59	186
Catechol	100	97	255
Resorcinol	100	98	252
Quinol	100	86	149
Phloroglucinol	60	3	12
m-Chlorophenol	100	50	66
p-Chlorophenol	100	66	80
2,4-Dichlorophenol	60	18	46
2,6-Dichlorophenol	100	35	39
2,4,6-Trichlorophenol	100	70	56
o-Cresol	100	97	417
m-Cresol	100	97	457
p-Cresol	100	97	306
2,6-Dimethylphenol	100	69	40
3,5-Dimethylphenol	100	37	70
2,4-Dimethylphenol	100	81	126
3,4-Dimethylphenol	100	90	189
Orcinol	100	36	72
Thymol	100	44	48
6-Chloro-*m*-cresol	80	51	81
6-Chloro-2-methylphenol	80	37	66
4-Chloro-2-methylphenol	80	50	90
4-Chloro-3-methylphenol	60	46	113
o-Nitrophenol	100	49	48
m-Nitrophenol	100	39	65
p-Nitrophenol	100	32	54
2,4-Dinitrophenol	60	19	66
2,6-Dinitrophenol	60	8	51
2,4,6-Trinitrophenol	100	28	22
4,6-Dinitro-*o*-cresol	100	60	31
2,4,6-Trinitroresorcinol	60	13	6
2,4,6-Trinitro-*m*-cresol	60	8	14
4-Chloro-2-nitrophenol	100	64	123
2-Chloro-4-nitrophenol	60	7	51
2,6-Dichloro-4-nitrophenol	100	9	35
m-Dinitrobenzene	100	25	42
p-Dinitrobenzene	100	20	32
m-Nitroaniline	100	31	70
2,4-Dinitroaniline	100	39	53
m-Nitrobenzaldehyde	100	27	38
3,5-Dinitrobenzoic acid	100	13	48

* Based on 180 min results

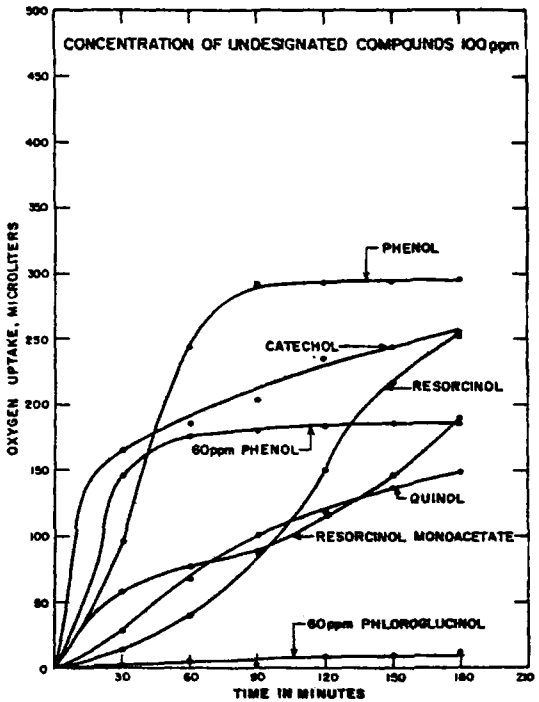


Figure 8a. Oxidation of dihydric phenols. (From Tabak, et al. (24).)

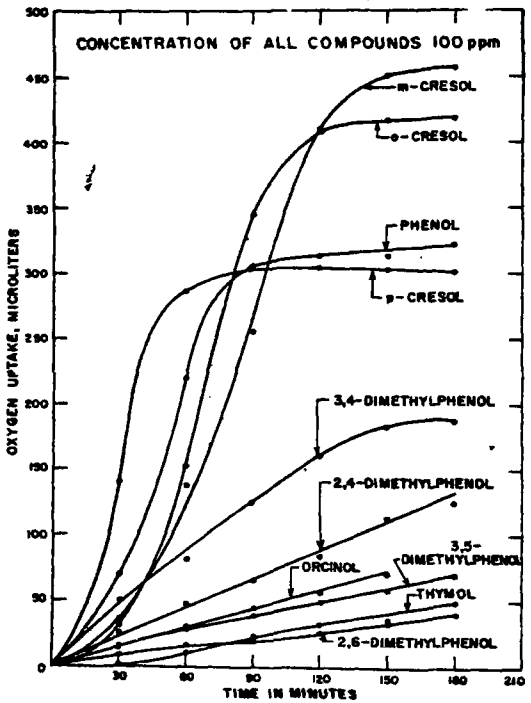


Figure 8b. Oxidation of cresols and other methylphenol derivatives. (From Tabak, et al. (24).)

By monitoring the disappearance of substituted benzenes, Alexander and Lustigman (25) observed the effect of chemical structure on biodegradability. Although a mixed population of soil microorganisms was used, results were similar to those obtained in the previous work with activated sludge. The presence of a chlorine atom in any position retarded degradation significantly. The amino group inhibited degradation only when in the meta position. Addition of one methyl group had no effect and the addition of a methoxy group to phenol inhibited degradation only when in the meta position.

Alexander and Lustigman (25) also noted that for some apparently resistant compounds, degradation could be enhanced by the addition of an available (supplemental) carbon source such as glucose. Some microorganisms are capable of degrading a compound which they are unable to utilize for growth. Such a situation was also encountered in a similar study of the biodegradation of phenols (26). This phenomenon, known as co-metabolism, has been observed frequently for a variety of species and substrates although it is often overlooked (27). Co-metabolism has been shown to occur not only in pure laboratory cultures, but also by naturally-occurring mixed populations (28). In degradation studies, the use of gas chromatography can detect products of co-metabolism as well as the disappearance of the compound of interest.

Summary--

As indicated in the above discussion, there is a significant body of literature available concerning the microbial degradation of phenols, especially in pure cultures of microorganisms and in single-substrate systems. This is especially true for both mono- and dihydric phenols. Less information is available, however, with regard to the biodegradability of the more highly substituted phenols, and the biodegradation of specific phenolic constituents in mixtures of phenolic compounds. Furthermore, little information is available regarding the level at which these phenolic compounds become inhibitory to microbial degradation, and the rates at which degradation takes place.

Nitrogen-Containing Aromatic Compounds

Microbial Pathway Studies--

The literature dealing with metabolic pathways for the degradation by microorganisms of nitrogen-containing substances such as pyridine, quinoline, and aniline is incomplete. Ultimate degradation has been assumed because such compounds are not found to accumulate to any degree in the soil. Microbial isolates from soil that can grow with pyridine as the sole source of carbon, nitrogen and energy are usually members of the actinomycetes. Other types of isolates from soil and sewage, grown on pyridine, include species of Agrobacterium, Achromobacter, Nocardia, Bacillus, and a possible Pseudomonas.

The nitrogen atom of the pyridine ring is electronegative in relation to the carbon atoms of the ring. This results in an asymmetric molecule with a degree of polarity quite different from the benzene ring. Pyridine is relatively electron deficient and will resist electrophilic substitutions especially at the 2, 4, and 6 carbon positions, making hydroxylations at

these positions unlikely. The nitrogen atom has the least influence on the C-3 position and chemical reactions of 3-hydroxypyridine resemble those of phenol (29). The presence of a hydroxyl group on the ring makes the ring more susceptible to further electrophilic attack, particularly in the sites ortho and para to the hydroxyl group. On the other hand, pyridines can become even more resistant to electrophilic attack in acidic aqueous solution. The nitrogen atom possesses a pair of electrons by which it can accept a proton to form the stable pyridinium ion. This results in the distribution of a positive charge over all the carbon atoms in the ring.

Quinolines and isoquinolines are the most common of the pyridines fused to benzene rings. These compounds show largely the same reactivity as pyridine (30).

While there is no single definitive pathway for the dissimilation of pyridine by all microorganisms, the appearance of the pyridine N-atom as NH_3 has been confirmed (29). The fate of the carbon-nitrogen skeleton and the nature of the initial metabolic reactions are less clear.

It has been reported that under certain conditions, the degradation of pyridine and its three monohydroxy isomers by microorganisms isolated from soil and sewage results in the accumulation of pyridine-diols (29). However, of these diols, only the 3,4-isomer was even slightly metabolized further. According to the sequential induction theory, this casts some doubt on the role of the diols as major intermediates in the degradation of pyridines. Later studies (31,32) have shown the degradation of 3,4- and 2,5-pyridine-diols by species of Agrobacterium and Achromobacter. Pyridine-3,4-diol is thought to be an intermediate in the degradation of 4-hydroxypyridine, and pyridine-2,5-diol is produced from both 2- and 3-hydroxypyridine. Watson et al. (31), proposed the pathway shown in Figure 9 for microbial degradation of 3,4-dihydroxypyridine. The proposed pathway for pyridine-2,5-diol (32) was based on the maleate pathway (33) and is shown in Figure 10.

More recently, Watson and Cain (34) proposed two distinct metabolic pathways for the microbial dissimilation of pyridine itself. Two microorganisms, one Nocardia and one Bacillus, were isolated from soil and were able to utilize pyridine as the sole source of carbon, nitrogen and energy. Analysis of culture filtrates showed no evidence that UV-absorbing products accumulated during degradation. This would indicate the lack of any stable aromatic product, such as a pyridine-diol. The N-atom was released as NH_3. Neither species, however, could utilize other pyridine compounds for growth. These other compounds included methyl-, amino-, ethyl-, dimethyl-, and hydroxy-pyridines, and pyridine carboxylic acids. Pathways proposed for each species are presented in Figures 11 and 12.

Another nitrogen-based compound identified in various coal conversion effluents is indole. Indole is a benzene-fused, five-membered heterocycle and its reactivity is determined by the heterocycle portion of the molecule. The molecule tends to be susceptible to electrophilic attack at the carbon atoms rather than at the N-atom. This is in contrast to the pyridines which are relatively resistant to electrophilic attack and

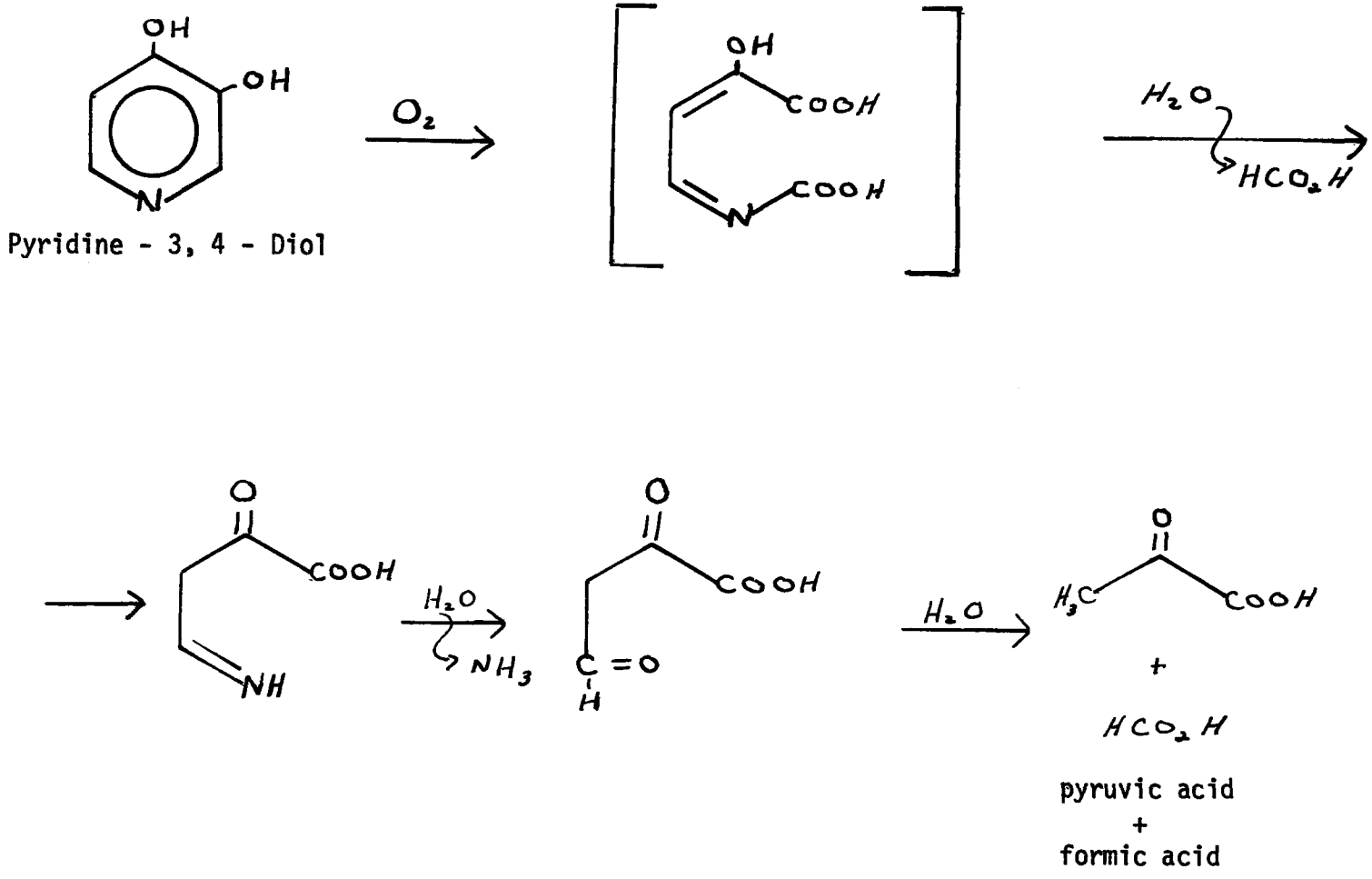


Figure 9. Pathway proposed by Watson et al. (31) for the microbial degradation of 3,4-dihydroxypyridine.

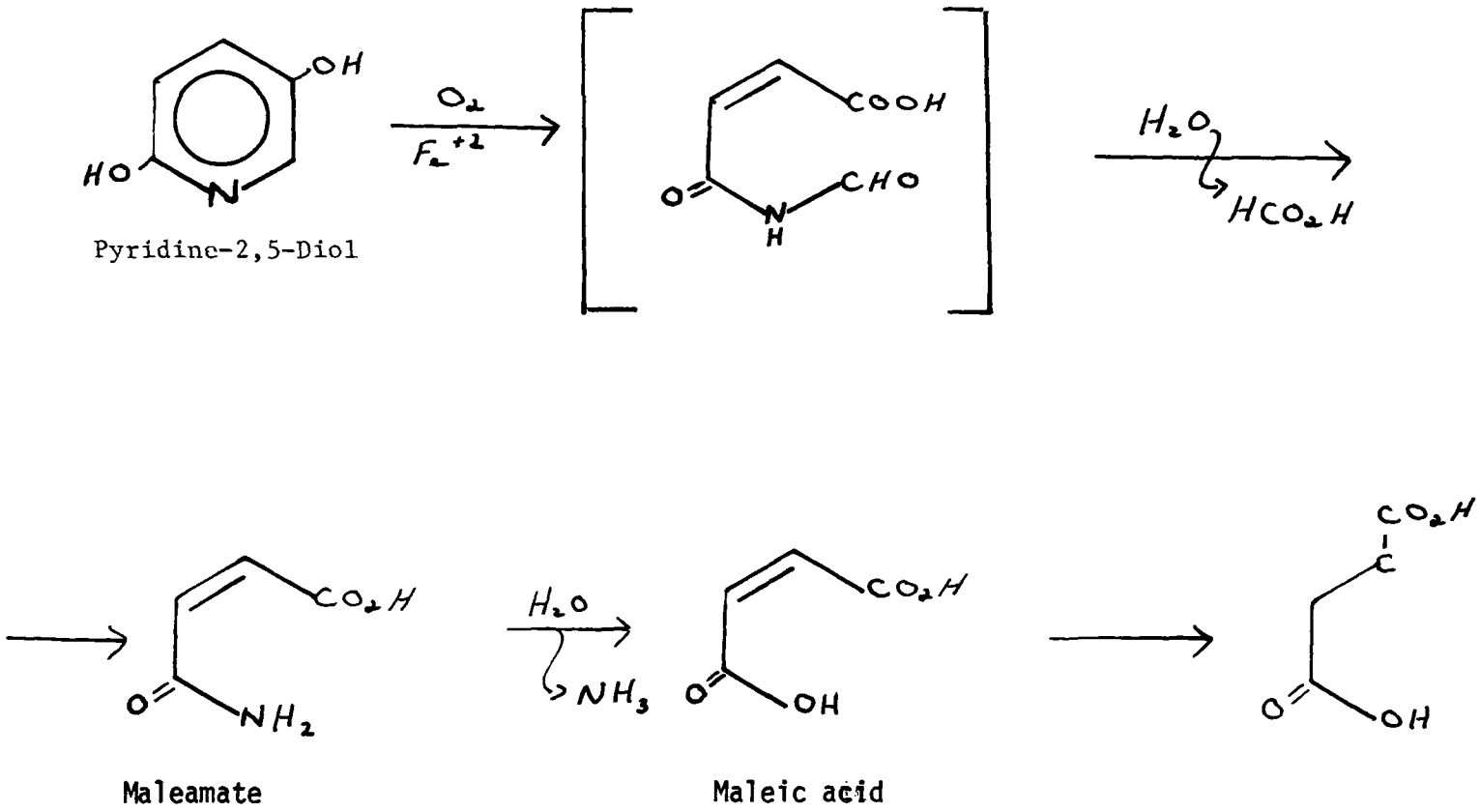


Figure 10. Pathway proposed by Cain et al. (32) for the microbial degradation of 2,5-dihydroxypyridine.

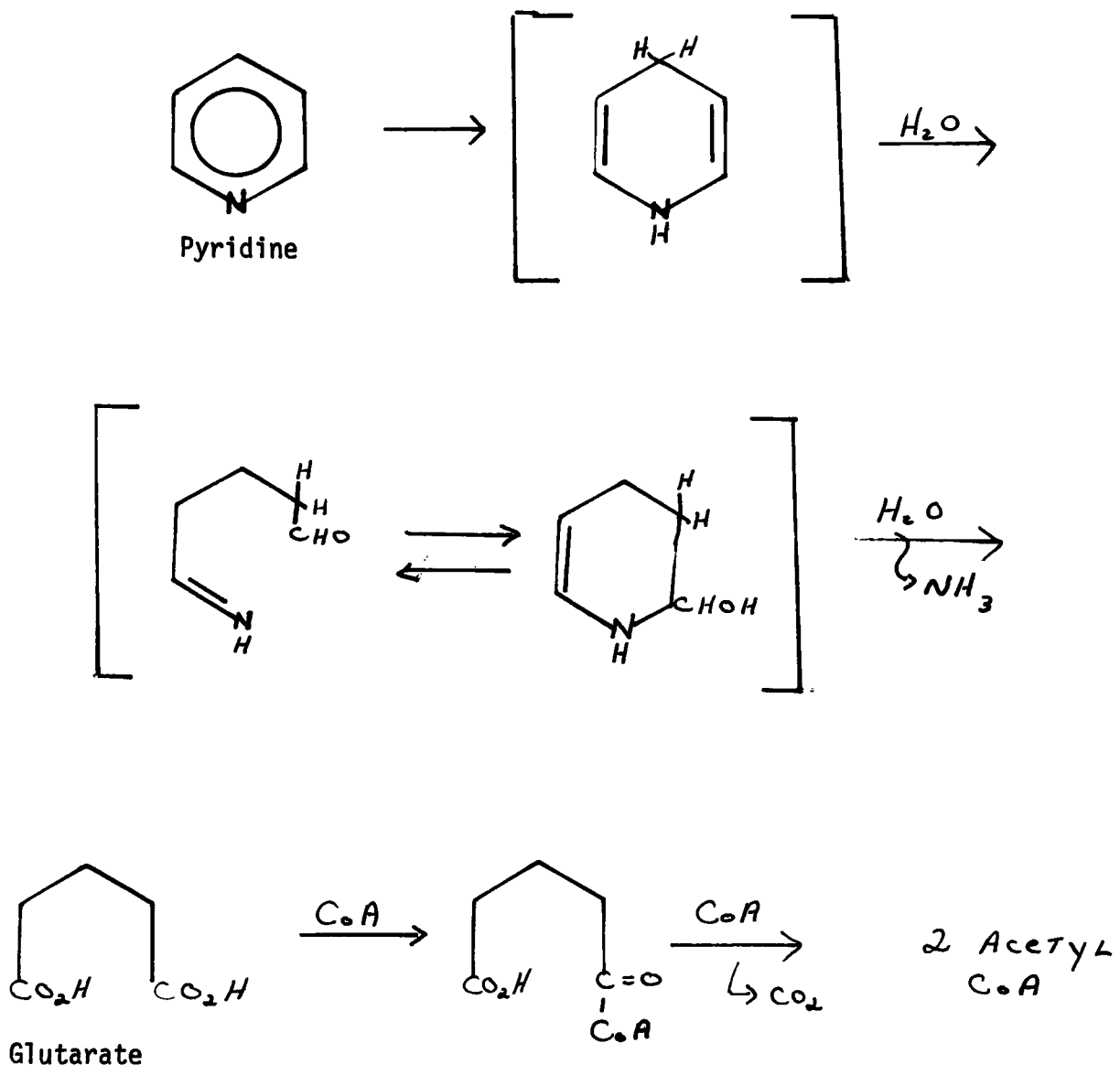


Figure 11. Pathway proposed by Watson and Cain (34) for the degradation of pyridine by Nocardia sp.

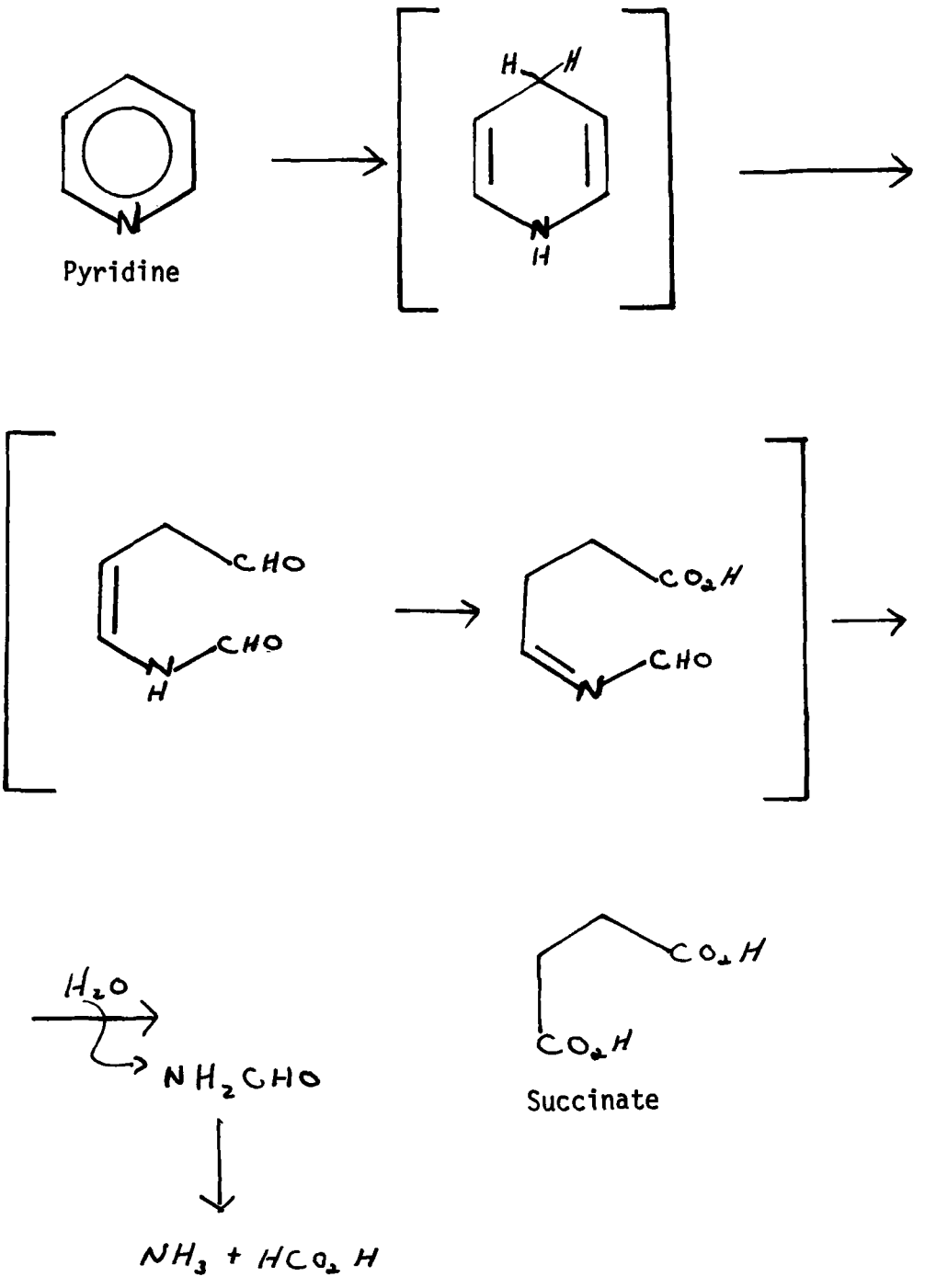


Figure 12. Pathway proposed by Watson and Cain (34) for the microbial degradation of pyridine by Bacillus sp.

subsequent oxidation. Reversion to the simpler aromatic ring occurs after electrophilic attack, resulting in substitution rather than addition. The β-position is the more reactive one since reaction at the α-position would disturb the benzene resonance. The microbial degradation of this compound seems to occur by hydroxylation of the five-membered ring. A gram positive coccus which utilizes indole as a sole source of carbon and nitrogen was isolated from the soil (35). When grown on indole, this microoganism could also degrade dihydroxyindole, anthranilic acid and catechol, indicating that these compounds are intermediates in metabolism. As in the case of pyridine, the N-atom is released as NH_3. It was also demonstrated that the conversion of dihydroxyindole to anthranilate and CO_2 is under the control of an inducible enzyme, termed dihydroxyindole oxygenase, for this microorganism. The pathway proposed by Fujioka and Hiroshi (35) is shown in Figure 13.

Biodegradability of anilines, toluidines and other aromatic-amino compounds depends on ring position and the presence and position of other substituents (25,36). The data indicate that aniline itself is readily degradable. Toluidines (methyl anilines) are oxidized as readily as aniline with the possible exception of o-toluidine. The addition of a second amino group (amino anilines or phenylenediamines) renders the compound less susceptible to oxidation. The m-isomer is the least susceptible. The nitroanilines are markedly resistant to degradation by both soil bacteria and aniline-acclimated activated sludge. Substitution of a carboxyl group ortho to the amino group does not increase resistance to degradation, but m- and p-aminobenzoic acids are relatively resistant, particularly the m-isomer. The presence of one or two carbon atoms between the ring and the nitrogen of aniline renders such a compound relatively resistant to oxidation, but resistance is less with increased length of carbon chain. Of the primary aliphatic amines, only methyl amine and n-hexylamine are not oxidized by aniline-acclimiated microorganisms. Phenol and pyridine were oxidized by aniline-adapted cultures only after a long period of acclimation.

Other nitrogen compounds that may be of concern are the amides. Many species of Pseudomonas can utilize acetamide as a carbon and energy source (37). Some species are also capable of utilizing propionamide and butyramide as growth substrates (38). Propionamide is utilized as readily as acetamide, but butyramide utilization is only 2% that of acetamide. Butyramide may act as an inducer for amidase synthesis. In some species it is an anti-inducer and will prevent induction by substrate (acetamide) and non-substrate inducers. In some strains, where amidase is constituitive, utilization of amides is severely repressed by butyramide.

Mutant strains of Pseudomonas that can utilize aromatic amides (phenylacetamide) as a nitrogen source have been isolated (39). Others have been isolated using phenylacetamide as a sole source of both carbon and nitrogen. A gram negative rod has been shown to degrade picolinamide (pyridine-2-carboxamide) to maleic and fumaric acids (33). In all cases, removal of the amide group appears to take place by means of a simple hydrolytic cleavage of the carbon-nitrogen bond of the amide group with the formation of a carboxyl group at that carbon.

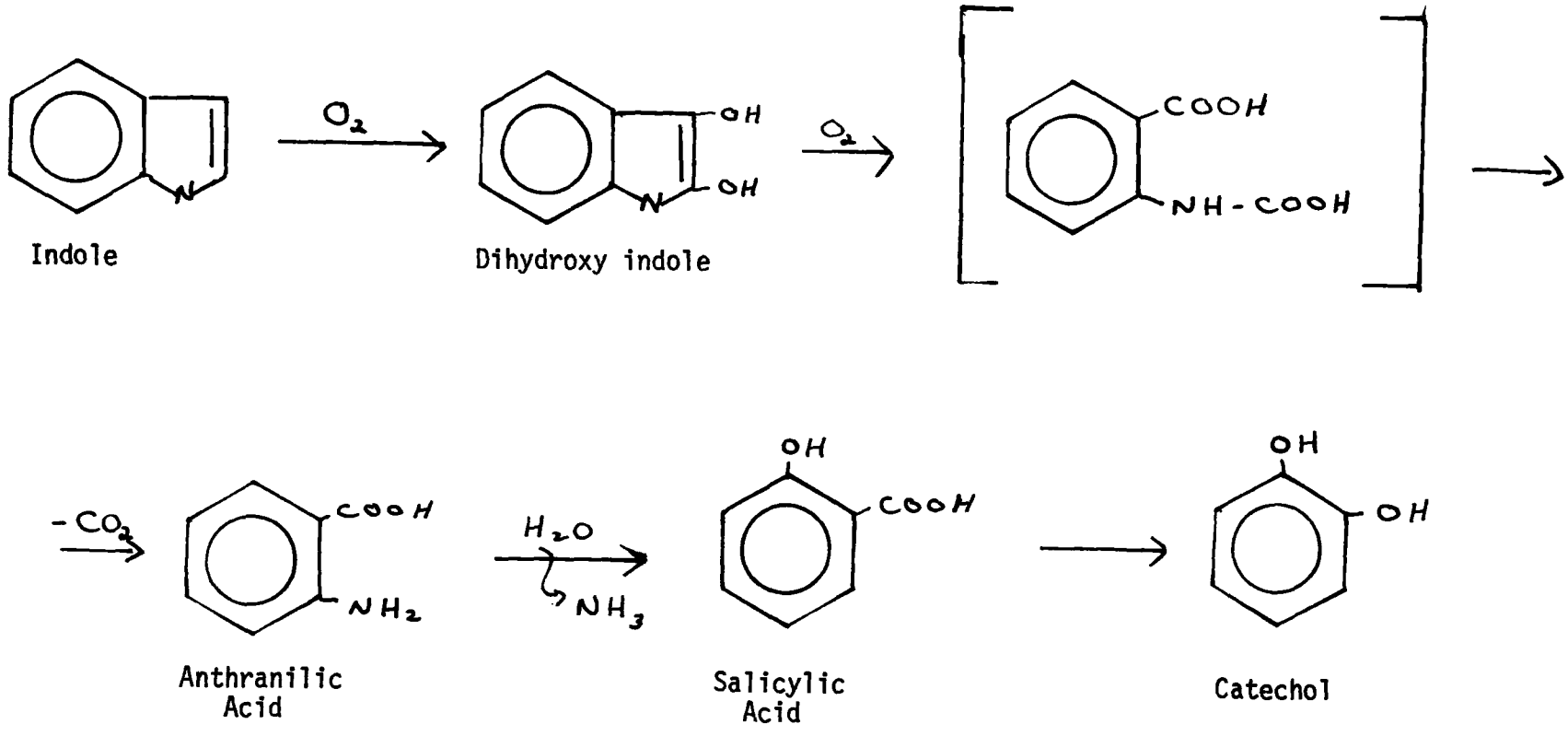


Figure 13. Pathway proposed by Fujioka and Hiroshi (35) for the microbial degradation of indole.

Summary--

Again, as in the case of the complex phenolic compounds, little information is available regarding the behavior of N-containing aromatic compounds, other than the fact that they are degradable as deduced from the metabolic pathway studies. The fact that they do not accumulate in soils suggests that they are degradable in natural environmental systems. However, the rate of such microbial degradation, and their behavior as part of a complex mixture at the concentrations found in coal conversion wastewaters is not known.

Polynuclear Aromatic Hydrocarbons

Microbial Pathway Studies--

Many of the polynuclear aromatic hydrocarbons (PAH's) are known or suspected carcinogens and, as a result, the oxidation of these aromatic hydrocarbons by mammalian systems has been extensively investigated. There is considerably less information, however, on the microbial dissimilation of these compounds. While a large volume of information is available concerning pathways and mechanisms utilized by microorganisms in degrading oxygenated aromatic compounds such as aromatic acids and phenols, the parent aromatic hydrocarbons have received much less attention. Van der Linden and Thijsse (16) attribute this to the difficulties encountered in working with such relatively insoluble substrates, the scarcity of high purity substrates, and the non-physiological nature of hydrocarbons. Gibson (40) also suggests that the shortage of studies on parent hydrocarbons is due to the fact that once oxygen is introduced into the substrate, the study becomes one of phenol or aromatic acid metabolism. Also, those enzymes responsible for the incorporation of oxygen into aromatic hydrocarbons are extremely labile and therefore have resisted detailed investigation.

Of all the PAH's, only the parent bi- and trinuclear compounds (naphthalene, anthracene and phenanthrene) have been studied in any detail. Although it had been reported (41) as early as 1947 that a broad spectrum of bacteria attack PAH's, it has only been in the last two decades that metabolic pathways have been determined for the three above-mentioned parent compounds.

Naphthalene-- A pathway for the degradation of naphthalene by a species of Pseudomonas was proposed by Davies and Evans (9) and is presented in Figure 14. It has been demonstrated that the initial reaction in the bacterial degradation of non-phenolic aromatic hydrocarbons is the incorporation of two atoms of oxygen into the molecule with the formation of cis-dihydrodiols (1,42). Once naphthalene has been oxygenated, subsequent ring fission produces pyruvate and salicylaldehyde. The latter compound is then degraded to salicylic acid and then to catechol. Catechol is the final ring-fission substrate and is ultimately degraded to carbon dioxide and water (see above). The by-product, 1,2-naphthoquinone, has been isolated but is not considered to be an intermediate metabolite because it cannot be oxidized by naphthalene-grown cultures. It has been postulated (16) that 1,2-naphthoquinone is formed from the dihydroxy compound by a non-enzymatic reaction.

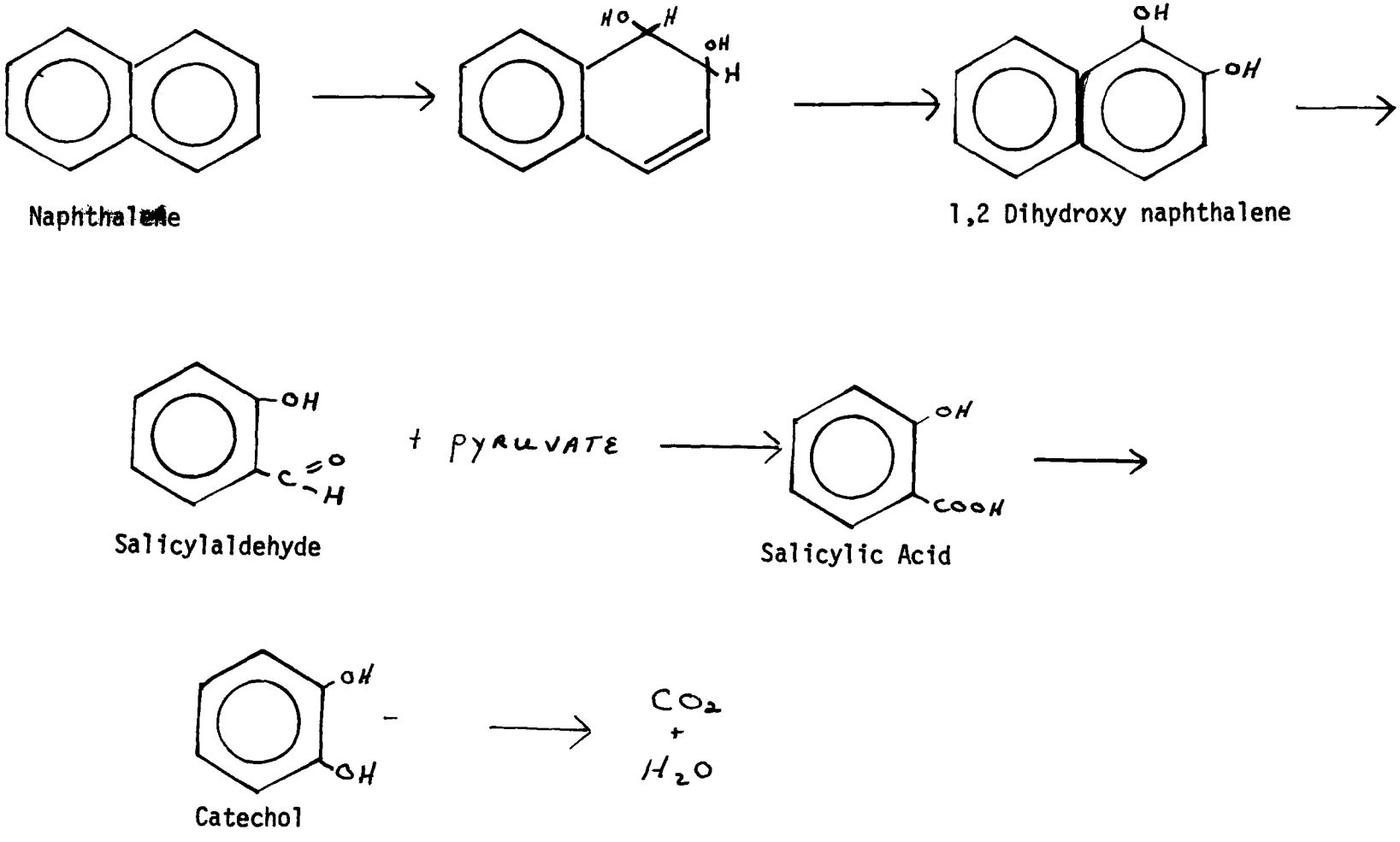


Figure 14. Pathway proposed by Davies and Evans (9) for the degradation of naphthalene by a species of Pseudomonas.

1-, and 2-methylnaphthalene have been shown to be degraded via 3- and 4-methylsalicylic acids, respectively (43). Degradation then proceeds by way of 3-, and 4-methylcatechol, respectively.

Phenanthrene and Anthracene-- Soil pseudomonads have been employed to study the metabolic pathways in the microbial degradation of phenanthrene and anthracene (44,45,46). The degradation pathway proposed for phenanthrene is shown in Figure 15. Ragoff and Wender (44) suggest that such a pathway is in line with the hypothesis of Pullman and Pullman (47) that polynuclear aromatic hydrocarbons bind to enzymes at the region of highest electron density (K region). The actual oxidation and ring-fission reactions take place at nearby bonds of secondary chemical reactivity. The actual bond that undergoes fission is determined by electronic and steric configuration of the resulting enzyme-substrate complex (45). The K region of phenanthrene is the 9-10 bond. Oxidation then occurs at the 5-6 bond or the 3-4 bond (they are equivalent in reactivity). Ultimate dissimilation is via salicylic acid and catechol.

Degradation of the linear, condensed polynuclear tri-aromatic hydrocarbon, anthracene, is similar to that of phenanthrene (45,48) except that the K region for anthracene is the 1-2 bond, as it is for naphthalene. Attachment of the enzyme is most likely to occur at this bond. Oxidation and ring-fission take place on the same ring as enzyme attachment. A proposed pathway for anthracene degradation is shown in Figure 16.

Ragoff (45) has suggested that there are two types of enzymes involved in the oxidation of PAH's. One attacks linearly condensed compounds, such as napththalene and anthracene, and splits the same ring that is attached to the enzyme. The other enzyme attacks angularly condensed compounds such as phenanthrene. This enzyme is induced to split a ring adjacent to the one attached to the enzyme.

Ragoff's work with methylphenanthrenes demonstrates the importance of substitutent position in the biodegradability of PAH's. Addition of a methyl group at the 9-carbon of phenanthrene blocked oxidation of the compound completely. Oxidation of 2-methylphenanthrene was similar to that of phenanthrene. Oxidation of 3-methylphenanthrene was intermediate between the two other isomers even though the methyl group was attached to a carbon involved in ring-fission. It was proposed that 9-methylphenanthrene was not metabolized due to blockage of the site of enzyme attachment by the methyl group. The 3-carbon is one of two possible sites of oxidation and ring-fission. Because only one of the two possible sites is blocked in 3-methylphenanthrene, oxidation proceeds, but at a lower rate than with 2-methylphenanthrenes.

Other PAH's-- While pathways for the dissimilation of naphthalene, anthracene and phenanthrene have been proposed, there is relatively little information on the microbial degradation of other larger PAH's. It has recently been reported (49) that a number of species of Pseudomonas are capable of metabolizing fluoranthene and, to a smaller extent, benzo(a)pyrene in the presence of succinate. Degradation was most rapid when cultures were in the stationary phase. Degradation was measured by monitoring the disappearance of the PAH by gas chromatography. All species capable of degrading fluoranthene could also utilize naphthalene

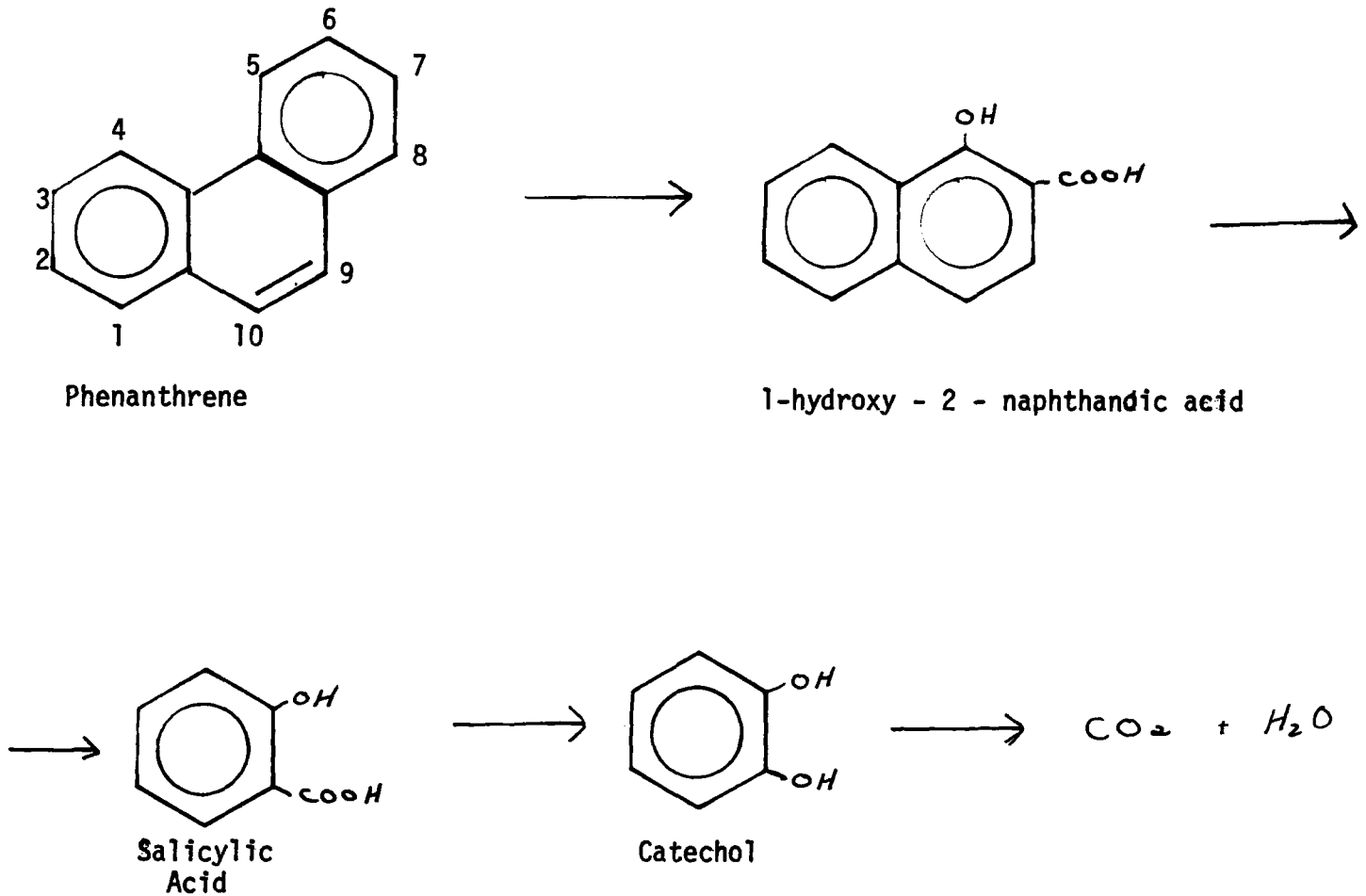


Figure 15. Proposed pathway for the microbial degradation of phenanthrene. (After Ragoff and Wender (44).)

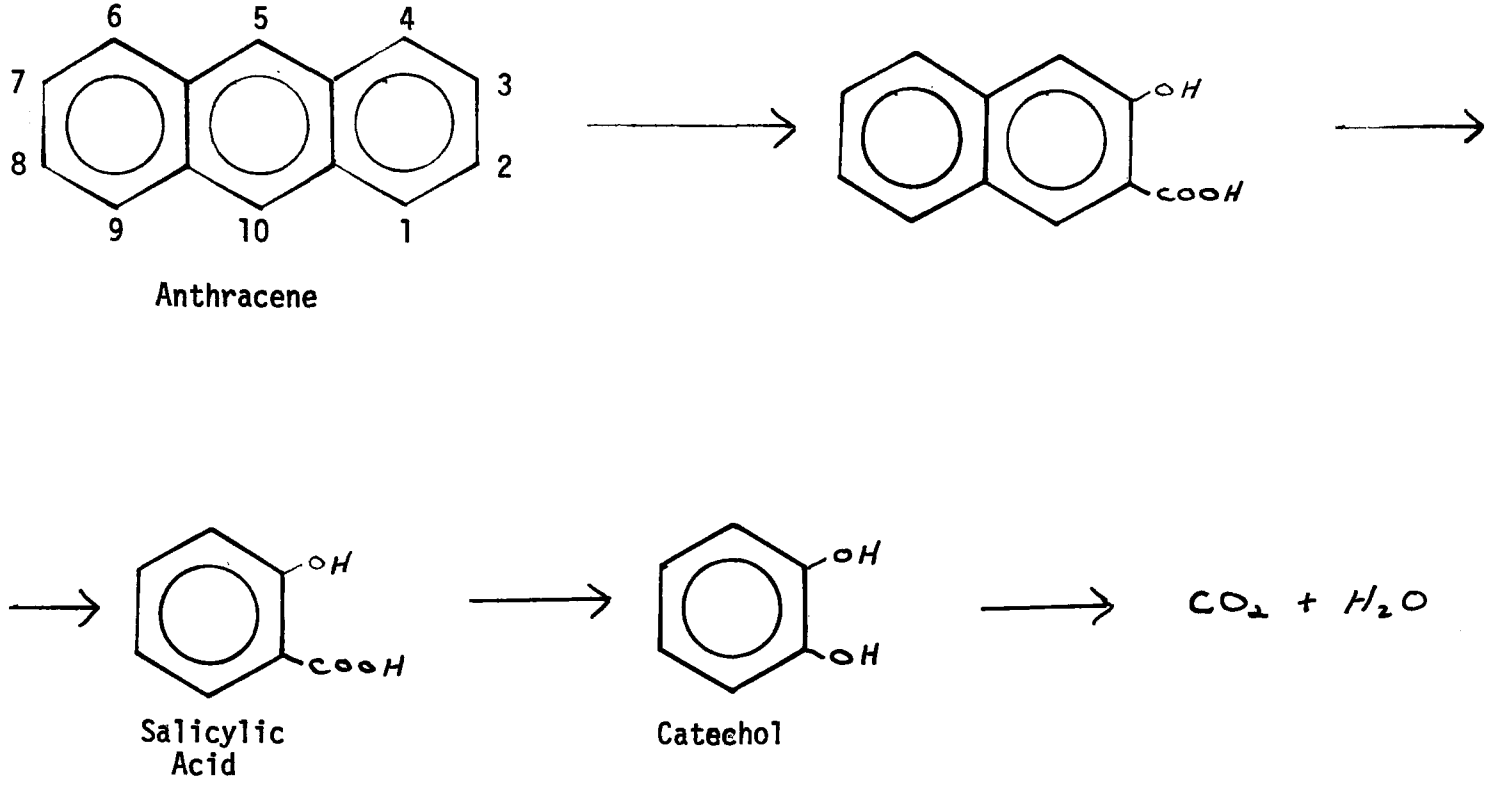


Figure 16. Proposed pathway for the microbial degradation of anthracene. (After Ragoff (41).)

as a sole source of carbon and energy. Those species which could not grow on naphthalene did not degrade fluoranthene. Those species metabolizing the PAH's did so at an average rate of 4 μmoles/hr. The mechanism by which the PAH was removed from solution seemed to be dependent on the presence of oxygen and the presence of a heat-labile substance, assumed to be a protein.

Although there are some reports of such bacteria which appear to metabolize the larger PAH's, the structures of the resulting metabolites have not been determined. It can be speculated that degradation proceeds via hydroxylation mechanisms similar to those reported for smaller molecules. Gibson et al. (41), have demonstrated the formation of cis-dihydrodiols from the metabolism of benzo(a)pyrene and benzo(a)anthracene. The microorganism employed was a strain of Beijerinckia isolated from a polluted stream and grown on succinate in the presence of biphenyl. The major dihydrodiol from benzo(a)pyrene was determined to be cis-9,10-dihydroxy-9,10-dihydrobenzo(a)pyrene. Benzo(a)anthracene was metabolized to four dihydrodiols, the major isomer being identified as cis-1,2-dihydroxy-1,2-dihydrobenzo(a)anthracene (see Figure 17).

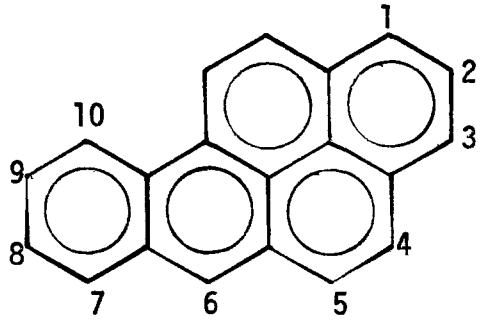
Subsequent metabolic pathways and the factors regulating these metabolic processes are not known. Some problems involved with the study of the larger PAH's are the instability of even sterile solutions, and the low solubility of the compounds.

Mixed Culture Studies--

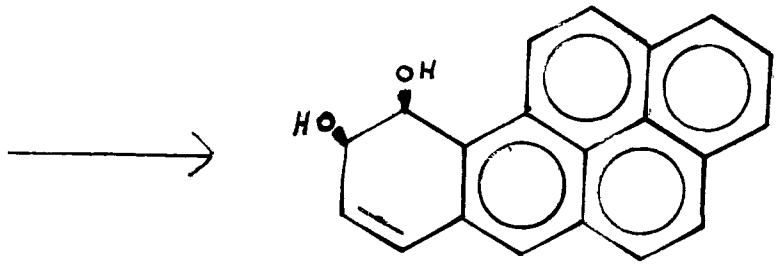
All of the above-mentioned metabolic pathway studies were conducted with pure cultures, under highly-controlled laboratory conditions. When exposed to various activated sludges, PAH's have been shown to be extremely resistant to biological oxidation (50). Even the smaller molecules, naphthalene, anthracene and phenanthrene, showed only very slow rates of oxidation. Furthermore, none of the sludges showed any significant ability to acclimate to these compounds. Such results would imply that removal of PAH's by biological waste treatment would not be signficant within normal retention times.

Summary of Literature Findings

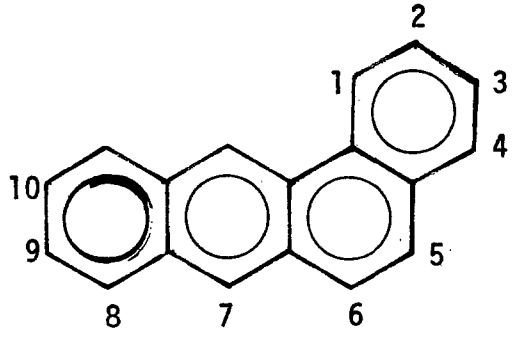
As described in the preceding section, information concerning the microbial degradation of the mono- and dihydric-phenols is plentiful. Less information is available regarding the biodegradability of the more highly substituted phenols. Of the polycyclic hydroxy compounds, some information is available on naphthol and biphenol degradation, but few data have been found concerning the indanols, indenols, and substituted naphthols. A need also exists for more information on the microbial degradation of the mono- and polycyclic nitrogen-containing aromatics. Limited information is available on the parent compounds pyridine, quinoline, indole, and aniline; biodegradability of the methyl and ethyl substituted isomers will also have to be examined. Information on the microbial dissimilation of the polynuclear aromatic hydrocarbons is mostly limited to naphthalene, anthracene, and phenanthrene. Very little is known about the degradation of the larger PAH's. In general, they seem to be quite resistant to biological oxidation, and will require further study.



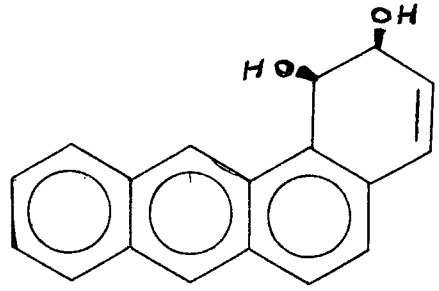
Benzo [a] pyrene



cis - 9,10 - Dihydroxy - 9,10 - dihydro - benzo [a] pyrene



Benzo [a] anthracene



cis - 1,2 - dihydroxy - 1,2 - Dihydro-benzo [a] anthracene

Figure 17. Formation of cis-dihydrodiols from the microbial metabolism of benzo(a)pyrene and benzo(a)anthracene. (After Gibson (41).)

EXPERIMENTAL BIODEGRADABILITY STUDIES: PRELIMINARY SCREENING

In order to assess the biological treatability of coal conversion wastewater and to develop suitable design and operating guidelines, the following types of preliminary information are required: (a) an assessment of the biodegradability of the constituent compounds, as reviewed in the preceding section; (b) biokinetic information describing the rate at which degradation of the constituents takes place; (c) the concentration levels at which microbial degradation of the constituents is inhibited (when the constituent becomes toxic to the microorganisms); and (d) how the constituents will behave in a composite mixture representative of coal conversion wastewaters. In view of the paucity of information available regarding the microbial degradation of many of the constituents identified in coal conversion wastewaters, an experimental program to provide such information is under development.

Before performing any extensive biodegradation studies on composite coal conversion wastewaters or their constituents, it was felt that some information on the approximate degree of microbial oxidation of each constituent compound would be valuable. Such a preliminary screening would provide useful comparative information for each of the constituents, and could save future time and effort. In order to obtain such preliminary information, initial screening experiments were conducted to obtain a gross qualitative assessment of the biodegradability of a number of specific compounds. This approach was intended to earmark potential "problem" compounds, i.e., those which are signifcantly resistant to microbial degradation, those which require a long lag period before oxidation, or those which show toxic effects (inhibit microbial activity) even at low concentrations. These data were intended to assist in the design of more extensive biodegradation studies and to supply some background information for the development of a synthetic waste and an acclimated seed culture for these more extensive biodegradation studies (see Section 7).

Individual compounds were added to duplicate, acid-washed, 300 ml BOD bottles at a concentration of approximately 5 mg/l. Dilution water was prepared from water which had been passed through activated carbon and ion exchange columns and then glass-distilled. Standard nutrients were added to the water as was 0.5 mg/l allylthiourea for control of nitrification. The dilution water was seeded with 1.5 mg/l of domestic sewage obtained from the Chapel Hill sewage treatment plant. The BOD bottles were filled, stoppered, and incubated in the dark at $65^{o}F$ for twenty days. Oxygen uptake was measured at various intervals over the twenty-day period by means of a Weston and Stack dissolved oxygen meter. This procedure was chosen for its simplicity, and the ability to incubate cultures over time periods long enough to observe potential problems with acclimation of the seed to the compound in question.

Results for the first forty-two compounds tested over the twenty-day period are presented in Table 24. The monohydric phenols were judged to be readily degraded, with the exception of 2,6- and 3,5-xylenol and 2,3,6- and 2,4,6-trimethylphenol. The dihydric phenols,

TABLE 24. INITIAL SCREENING OF VARIOUS ORGANIC COMPOUNDS FOUND IN COAL CONVERSION EFFLUENTS. (ALL COMPOUNDS WERE TESTED AT 5 mg/l. INITIAL OXYGEN CONCENTRATION WAS 7.6 mg/l.)

Compound	Per Cent O_2 Depletion* Days of Incubation at 65°F			
	5	10	15	20
Phenol	92	92	92	92
m-Cresol	92	92	92	92
o-Cresol	92	92	92	92
p-Cresol	92	92	92	92
2,5-Xylenol	4	6	86	86
2,3-Xylenol	91	91	91	91
2,6-Xylenol	0	1	1	11
3,4-Xylenol	79	80	80	84
3,5-Xylenol	0	42	48	52
2-Ethylphenol	86	86	86	86
3-Ethylphenol	85	85	85	85
4-Ethylphenol	86	86	86	86
2-Isopropylphenol	86	86	86	86
2,3,5-Trimethylphenol	56	75	79	80
2,3,6-Trimethylphenol	0	0	0	0
2,4,6-Trimethylphenol	**	**	**	**
Catechol	87	87	87	87
4-Methylcatechol	85	85	85	85
Resorcinol	80	80	80	80
4-Hydroxybenzaldehyde	3	3	27	50
3-Hydroxybenzaldehyde	74	74	77	80
1-Naphthol	35	35	35	51
2-Naphthol	86	86	86	86
o,o'-biphenol	4	7	33	50
p,p'-biphenol	0	0	0	0
Naphthalene	92	92	92	92
1-Methylnaphthalene	92	92	92	92
2,3-Dimethylnaphthalene	0	0	3	15
2,6-Dimethylnaphthalene	0	0	0	3
1,5-Dimethylnaphthalene	4	6	9	17
Thiophene	0	0	0	0
3-Methylthiophene	1	1	1	4
2-Ethylthiophene	0	1	8	17
3-Ethylthiophene	0	0	0	5
Pyridine	0	75	75	75
2-Ethylpyridine	**	**	**	**
4-Ethylpyridine	0	0	9	22
Indole	60	60	60	79
2-Methylindole	**	**	**	**
3-Methylindole	85	85	85	85
Indan	4	4	15	21

(continued)

TABLE 24. (continued)

Compound	Per Cent O_2 Depletion* Days of Incubation at 65°F 5	10	15	20
2-Indanol	5	5	6	12
5-Indanol	5	5	12	22
Quinoline	82	82	82	82
2-Methylquinoline	0	0	79	80
4-Methylquinoline	0	0	0	0
Gentisic Acid	51	51	52	65
Protocatechuic Acid	58	58	59	65
Succinic Acid	36	36	36	39
Glutaric Acid	49	49	49	68
Dibenzofuran	**	**	**	**

*Values of percent O_2 depletion have been corrected for endogenous respiration of the seed. Approximately 8% of the initial oxygen concentration had been depleted by the seed in 20 days.

**Oxygen depletion was less than that for the seed control alone indicating that the compound may have inhibited the growth of at least a portion of the seed population. All compounds having this designation were retested with phenol added as an alternative carbon source. In all instances, oxygen depletion increased with addition of phenol indicating that the primary substrate was not toxic to all microorganisms at 5 mg/l.

resorcinol, catechol, and 4-methylcatechol, were all readily degraded. The two naphthol isomers showed different oxygen uptakes: 2-naphthol showed both high total oxygen uptake and high initial uptake, while 1-naphthol showed only moderate total uptake and low initial uptake. The lower total uptake may have been due to the lower solubility of 1-naphthol. The problem and effect of solubility on these initial screening studies will be addressed and investigated in the later, more extensive set of experiments.

Biphenol degradation also was dependent on the particular isomer tested. 0,o'-biphenol showed moderate oxygen uptake while p,p'-biphenol exhibited a toxic response. Compounds were labeled as toxic when oxygen uptake for that compound was significantly less than oxygen uptake for the seed alone. The thiophenes were all relatively resistant to degradation. Indan and the indanols were only slightly oxidized, and even then only after a significant lag period. Quinoline was readily oxidized, but its methyl derivatives were more resistant. 2-Methylquinoline required a long lag period while 4-methylquinoline was toxic. Ring fission substrates along with acid degradation products were all readily oxidized.

Table 25 divides the compounds into 3 categories based on oxygen uptake in 5 days. The compounds are classified as resistant, moderately degraded, and readily degraded. Those compounds listed as moderately degraded or resistant will be studied more extensively with regard to their resistance using an acclimated culture (see Section 7). Those compounds which were readily degraded will also be studied further to determine concentrations at which their degradation is inhibited, and to determine the kinetics of oxygen uptake. The majority of this work will be done using Warburg respirometric techniques.

TABLE 25. SUMMARY OF BIODEGRADATION RESULTS FOR COMPOUNDS AFTER 5 DAYS

Readily Degraded	Moderately Degraded	Resistant
phenol	2,3,5-trimethylphenol	2,5-xylenol
m-cresol	4-hydroxybenzaldehyde	2,6-xylenol
o-cresol	1-naphthol	3,5-xylenol
p-cresol	o,o'-biphenol	2,3,6-trimethylphenol
2,3-xylenol	indole	2,4,6-trimethylphenol
3,4-xylenol		p,p'-biphenol
2-ethylphenol		dibenzofuran
3-ethylphenol		thiophene
4-ethylphenol		2-ethylthiophene
2-isopropylphenol		3-methylthiophene
catechol		3-ethylthiophene
4-methylcatechol		2-methylindole
resorcinol		indan
3-hydroxybenzaldehyde		2-indanol
2-naphthol		5-indanol
3-methylindole		2-methylquinoline
quinoline		4-methylquinoline
gentisic acid		pyridine
protocatechuic acid		2-ethylpyridine
succinic acid		4-ethylpyridine
glutaric acid		2,3-dimethylnaphthalene
naphthalene		2,6-dimethylnaphthalene
1-methylnaphthalene		1,5-dimethylnaphthalene

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SECTION 7

PRELIMINARY BIOTREATABILITY STUDIES

INTRODUCTION

The preliminary biodegradability screening analysis described in Section 6 served to identify which of the components of coal conversion wastewaters were readily biodegradable and which were nondegradable and would require further study using acclimatized organisms. It should be noted that in conventional biodegradability studies (using BOD bottles), very low concentrations (5-10 mg/l) of the test compound are often used. Although the test compound may be biodegradable under these circumstances, it could be toxic to microorganisms at the concentration level at which it is found in the actual wastewater. For example, phenol is known to be readily biodegradable at concentrations below 100 mg/l, but concentrations above 1000 mg/l may inhibit oyxgen uptake, even by acclimatized organisms. Since coal conversion wastewaters are relatively concentrated with respect to organic content, toxicity levels for the major constituents also need to be determined.

OBJECTIVES AND GENERAL APPROACH

This phase of the project has been undertaken in order to:

(a) provide a continuing supply of "seed" organisms for use in biodegradation studies;

(b) provide reproducible and acclimatized sludges for respiration studies to evaluate biodegradation and toxicity of wastewater components under conditions similar to those which would be encountered in practice; and

(c) develop preliminary information on biological treatability of the wastewater.

In order to carry out the appropriate oxygen uptake investigations, an acclimatized microbial culture must be used. Accordingly, a synthetic coal conversion wastewater was formulated to provide a mixture of organic compounds, at known concentrations, for acclimatization and maintenance of a microbial culture to be used in the subsequent biodegradation and biotreatability experiments. Ideally, a synthetic mixture should include all constituents present in coal conversion wastewaters at appropriate concentrations. From a practical standpoint, however, this is not possible because all of the constituents are not known, their concentrations vary depending on the source of the waste, and the mixture would be too complex to handle experimentally. It was decided, therefore, to formulate a synthetic coal conversion wastewater that would adequately mirror the real waste in general composition and concentrations, but would be simpler and better defined.

COMPOSITION OF SYNTHETIC COAL CONVERSION WASTEWATER

Several criteria were employed in choosing the specific compounds to be included in the synthetic wastewater, and their concentrations. Since it was desired to use this waste as a feed for microorganisms, most of the compounds included are biodegradable. However, not all constituents in the real wastewaters can be utilized by microbes. Accordingly, some slowly degraded or nondegradable materials as deduced from the experiments in Section 6 were included (e.g., 2-indanol, indene, 2-methylquinoline, 3,5-xylenol).

In order that the various compounds would be present in concentrations similar to those encountered in real wastewaters, reference was made to the summary of constituents found in coal conversion wastewaters (Table 11, Section 4) and the range, midrange, and median concentrations were determined for each constituent and for each class of compounds (e.g., cresols, xylenols, heterocyclic N compounds). From each class, one or several compounds were chosen to provide a synthetic waste reasonably representative of real wastes.

Specific chemicals chosen within each class were based on knowledge of the biodegradability of the compounds, both from the literature survey and from the preliminary biodegradation screening experiments (see Section 6). The choice was usually the compound reported at highest concentration within that class in the real wastes. Often, if a class contained many components or if differences in biodegradability were apparent, more than one representative from that class was chosen. The concentration selected was the midrange value reported for that compound in the real wastes, or the midrange of the class if only one compound from that class was picked. If concentration data for a specific compound were not available, the compound was included in the synthetic waste at the midrange concentration for its class.

Table 26 lists the composition of the wastewater formulated in the manner just described. Twenty-eight organic components are included, as well as inorganic nutrients and pH-buffering additives. The synthetic waste represents all the major classes of organics present in the real wastewaters for which data are available, and virtually all of the compounds that have been shown to be present at high concentrations. A microbial community acclimatized to this waste should be a useful starting point for many studies of the biodegradability of specific waste constituents, mixtures of pure compounds, and eventually complex mixtures of known chemicals.

PILOT UNITS FOR ACCLIMATION AND BIOTREATABILITY STUDIES

Four 25-liter biological treatment units were constructed, each consisting of a 7 1/2-in ID lucite tube, fitted at the bottom to a stainless steel funnel. Compressed air is introduced at the bottom point of the funnel at rates adequate to insure thorough mixing and aerobic conditions at all times. Each unit is fed from a reservoir of synthetic wastewater by a variable-speed peristaltic pump. An exhaust

TABLE 26. COMPOSITION OF SYNTHETIC COAL CONVERSION WASTEWATER

Compound	Concentration, mg/l
1. Phenol	2000
2. Resorcinol	1000
3. Catechol	1000
4. Acetic Acid	400
5. o-Cresol	400
6. p-Cresol	250
7. 3,4-Xylenol	250
8. 2,3-Xylenol	250
9. Pyridine	120
10. Benzoic Acid	100
11. 4-Ethylpyridine	100
12. 4-Methylcatechol	100
13. Acetophenone	50
14. 2-Indanol	50
15. Indene	50
16. Indole	50
17. 5-Methylresorcinol	50
18. 2-Naphthol	50
19. 2,3,5-Trimethylphenol	50
20. 2-Methylquinoline	40
21. 3,5-Xylenol	40
22. 3-Ethylphenol	30
23. Aniline	20
24. Hexanoic Acid	20
25. 1-Naphthol	20
26. Quinoline	10
27. Naphthalene	5
28. Anthracene	0.2
29. $MgSO_4 \cdot 7H_2O$	22.5
30. $CaCl_2$	27.5
31. FeNaEDTA	0.34
32. NH_4Cl	3820
33. Phosphate buffer:	
KH_2PO_4	170
K_2HPO_4	435
$Na_2HPO_4 \cdot 7H_2O$	668

system vents each unit to the outside of the building.

The reactors are fed continuously, or at one-half hour intervals through use of a time clock, and are allowed to overflow into separate effluent reservoirs. The amount of wastewater fed to each reactor is determined daily by measuring the amount of effluent discharged into each collection container.

EXPERIMENTAL APPROACH

All four units have been operated as "chemostats," with continuous and complete mixing, without accumulation of biological solids beyond levels produced by growth during retention of the wastewater in the unit, i.e., as CSTR's (continuously-stirred tank reactors) without recycle of biomass, such that solids retention time equals hydraulic retention time. One reactor has been operated at a 20-day detention time principally to produce seed organisms and sludge for use in the respirometric studies. The remaining three reactors have been operated at detention periods of 5, 10, and 20 days to develop biodegradation data on the synthetic waste. The reactors are checked at least once daily to insure that all systems are operating properly, and mixed liquor dissolved oxygen and pH are measured. Twice per week the mixed liquor is sampled to determine suspended solids concentration, as well as total soluble organic carbon, sludge volume index, and alkalinity.

Initially, the reactors were started using activated sludge from the Durham, North Carolina municipal wastewater treatment plant, and the feed of synthetic wastewater was gradually increased over a period of several days to allow time for acclimatization of the sludge to the wastewater. Initial studies were performed on full-strength synthetic wastewater. During the few weeks following startup, however, the units gradually failed. The five-day chemostat, failed first, followed by the ten- and twenty-day reactors.

The exact reason for failure is unknown, but several possibilities have been considered. Uncertain operation at early stages of the investigation made it possible for the dissolved oxygen occasionally to drop to zero. Also, the pH decreased to very low levels (approximately 4) and remained there for extended periods. Further, there is a possibility that some wastewater constituents could have exerted a toxic effect on the biological systems as concentrations of these components increased during the period following startup. The pattern of failure, i.e., in order of ascending reactor detention period, is consistent with this latter hypothesis.

Because of the possibility of toxic effects, and a desire to stabilize operations as quickly as possible, it was decided that the waste would be treated at one-quarter strength during initial investigations. At some later date, the question of toxicity at higher concentrations could be explored in more detail. Accordingly, the reactors were started again, using the same wastewater diluted to one-quarter strength.

The reactors have operated in this fashion without failure, at the same detention periods as indicated above, since the middle of March of

this year (1978). Operating data, as shown in Table 27, suggest that they are now approaching steady-state. Accordingly, intensive data collection is underway for this pattern of operation. Filtered samples of the contents of the chemostats are being analyzed for the following characteristics:

1. Total organic carbon
2. Biochemical oxygen demand
3. Chemical oxygen demand
4. Organic nitrogen
5. Ammonia nitrogen
6. Nitrite nitrogen
7. Nitrate nitrogen
8. Inorganic phosphorus
9. Total phosphorus

These analyses will be continued at intervals of two days over a period of two weeks. If the data indicate that steady-state has, in fact, been attained, intensive sampling will be discontinued and the units will be modified to operate at another series of appropriate detention times.

At two times during the period of intensive sampling, contents of the units will be sampled for more detailed analyses to determine specific effluent constituents. Chemostat contents will be filtered to remove the microorganisms and other suspended matter and twenty ml aliquots will be quick-frozen in tightly-capped 50 ml pyrex tubes. These will be subsequently analyzed for specific organic constituents using gas chromatography/mass spectrometry and high performance liquid chromatography.

RESPIRATION STUDIES

Equipment has been set up to conduct respiration studies of the reactor contents, and to evaluate the effects of various wastewater constituents on biological activity. This will be done by determining the endogenous respiration rate of mixed liquor from an operating reactor, and evaluating the effects of additives on the rate of oxygen consumption in the presence of the reactor contents. An increase in respiration rate may be interpreted as evidence that the additive is being utilized by the organisms in their metabolism. On the other hand, decreases in respiration rate indicate inhibition of biological activity by the additive in question.

The studies will be conducted by continuously recording the output of an electrode monitoring dissolved oxygen in a BOD bottle containing mixed liquor and the additive in question. The additives to be considered will be components of the synthetic wastewater itself, as well as other coal conversion wastewater constituents identified in Table 11. This will allow determination of (1) biodegradability of key wastewater constituents under conditions similar to those actually present in the reactors, and (2) acute toxicity effects which may be caused by various coal conversion wastewater constituents.

The studies will evaluate biochemical effects of the wastewater and its constituents in the presence of other wastewater constituents normally

TABLE 27. SUMMARY OF REACTOR PERFORMANCE

Reactor #1 5-Day Hydraulic Detention Time

Date	pH	MLSS* (mg/1)	MLVSS** (mg/1)	Effluent TOC (mg/1)	TOC Removal+ %	TOC Loading++ Factor	Sludge Volume Index
3-21-78	7.21	4250	-	30	-	-	-
4-11-78	7.31	1040	-	100	-	-	-
5-1-78	7.25	270	270	500	69	1.185	-
5-5-78	7.07	213	204	360	78	1.568	-
5-8-78	7.16	164	161	450	72	1.987	-
5-12-78	7.27	147	147	380	76	2.17	-
5-15-78	7.20	115	115	415	74	2.78	-
5-19-78	7.20	123	123	450	72	2.60	-
5-23-78	7.13	113	113	330	79	2.83	-
5-26-78	7.09	111	111	405	75	2.88	-
5-29-78	7.06	91	91	385	76	3.51	-
5-30-78	7.21	-	-	430	73	-	-

(continued)

TABLE 27. (continued)

Reactor #2 10-Day Hydraulic Detention Time

Date	pH	MLSS* (mg/l)	MLVSS** (mg/l)	Effluent TOC (mg/l)	TOC Removal+ %	TOC Loading Factor++	Sludge Volume Index
3-21-78	7.01	4500	-	30	-	-	-
4-11-78	4.60	1845	-	72	-	-	-
5-1-78	7.32	985	877	110	93	0.182	91
5-5-78	7.28	787	704	135	92	0.227	76
5-8-78	7.23	887	680	210	87	0.235	56
5-12-78	7.37	846	639	255	84	0.250	41
5-15-78	7.30	679	578	230	86	0.276	59
5-19-78	7.27	468	468	300	81	0.321	64
5-23-78	7.20	531	503	205	87	0.318	66
5-26-78	7.13	698	587	105	93	0.273	50
5-29-78	7.16	701	622	105	93	0.257	49
5-30-78	7.22	-	-	95	94	-	-

(continued)

TABLE 27. (continued)

Reactor #3 20-Day Hydraulic Detention Time

Date	pH	MLSS* (mg/l)	MLVSS** (mg/l)	Effluent TOC (mg/l)	TOC Removal+ %	TOC Loading Factor++	Sludge Volume Index
3-21-78	6.97	4250	-	30	-	-	-
4-11-78	5.89	1705	-	55	-	-	-
5-1-78	5.67	1250	1250	50	97	0.064	40
5-5-78	4.93	1476	1183	60	96	0.067	61
5-8-78	5.77	1198	1114	85	95	0.072	71
5-12-78	5.87	1274	1153	60	96	0.069	98
5-15-78	6.16	1508	1162	40	98	0.069	86
5-19-78	6.51	1231	1060	40	98	0.075	81
5-23-78	6.59	1156	1135	45	98	0.070	60
5-26-78	6.47	1192	1031	45	98	0.077	50
5-29-78	6.55	1169	1054	45	98	0.076	51
5-30-78	6.62	-	-	47	97	-	-

(continued)

TABLE 27. (continued)

Chemostat - 20-Day Hydraulic Detention Time

Date	pH	MLSS* (mg/l)	MLVSS** (mg/l)	Effluent TOC (mg/l)	TOC Removal+ %	TOC Loading Factor++	Sludge Volume Index
3-21-78	6.66	3000	-	154	-	-	-
4-11-78	7.09	1633	-	106	-	-	-
5-1-78	7.04	1290	1293	48	97	0.065	193
5-5-78	6.90	1470	1135	60	96	0.070	149
5-8-78	6.91	1289	1005	130	92	0.080	124
5-12-78	6.99	975	863	110	93	0.092	133
5-15-78	6.77	1210	961	60	96	0.083	91
5-19-78	-	802	802	50	97	0.099	93
5-23-78	6.95	790	790	45	98	0.101	63
5-26-78	6.86	953	825	45	98	0.096	47
5-29-78	6.89	743	743	50	97	0.109	47
5-30-78	7.10	-	-	57	96	-	-

*Mixed liquor suspended solids

**Mixed liquor volatile suspended solids

+TOC in feed = 1600 mg/l

++TOC loading factor = $\frac{\text{lb TOC in Feed}}{\text{lb MLVSS-DAY}}$

present in the reactors while treatment is underway. This differs from the Warburg studies described earlier (Section 6), in which biodegradability and toxicity of constituents are evaluated individually, without simultaneous presence of the other wastewater components.

FUTURE DIRECTIONS

The effluent from each of the biological reactors will be analyzed as to specific organic content in order to determine which components are resistant to biological treatment under the various treatment conditions. This information will be used to design physical-chemical treatability experiments involving such processes as adsorption on activated carbon and chemical oxidation. The physical-chemical experiments will be conducted on both a component bases (directed at those specific compounds resistant to biological treatment) and on a composite basis (directed at the composite effluent from the biological reactors).

In addition to specific organic analysis of the reactor effluents, the biological impacts of the treated effluents will also be analyzed. Aquatic bioassay, mammalian cytotoxicity, and mutagenicity tests will be conducted to determine the degree to which any negative biological impacts associated with these wastewaters can be alleviated by the various types of treatment.

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16. ABSTRACT The report gives results of the first phase of a project to assess the environmental impact of coal conversion wastewaters and to evaluate, by bench-scale tests, alternative treatment methods. Characteristics of coal conversion wastewaters were obtained from the literature and from information gathered during visits to facilities for coal conversion process development. For all these wastewaters, about 60-80% of total organic carbon is phenolic. Remaining organic material includes, nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, polynuclear aromatic hydrocarbons, and simple aliphatic acids. To test treatment methods, especially biological treatability, on these wastewaters, a synthetic wastewater was formulated which includes 28 organic compounds, inorganic nutrients, and pH buffering additives. For each class of compounds in real wastewaters, one or more representatives are in the synthetic wastewater at the appropriate mean concentrations. Experiments are underway using the synthetic wastewater at quarter strength in four 25-liter biological treatment units. These units are to test biodegradability as a function of retention time and produce acclimated microorganisms for use in respirometric studies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Aromatic Compounds	Pollution Control	13B	
Coal	Nitrogen	Stationary Sources	21D	07B
Conversion	Heterocyclic Compounds	Coal Conversion	14B	
Waste Water		Biological Treatability		
Assessments	Sulfur	Respirometrics		
Properties	Aromatic Polycyclic Hydrocarbons			
Phenols			07C	

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NORTH CAROLINA 27711

DATE: November 16, 1978

UBJECT: Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability

FROM: N. Dean Smith N. Dean Smith
Fuel Process Branch (MD-61)

TO: Distribution

Researchers at the University of North Carolina-Chapel Hill are well into their project to assess the environmental impact of coal conversion wastewaters and to evaluate, by bench-scale tests, alternative treatment methods. The attached report describes work during the first 1-1/2 years of the 5-year project. Characterization of coal conversion wastewaters and preliminary biotreatability experiments are described.

Based on the characterization of real coal conversion wastewaters, a synthetic wastewater has been formulated. It includes 28 organic compounds, at concentrations representative of mean values in real wastewaters. This synthetic wastewater is being used at quarter strength in 25-liter biological treatment units. Biodegradability data, as a function of retention time, and acclimated microorganisms are being produced.

Attachment

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