

# COMPOSITION AND BIODEGRADABILITY OF ORGANICS IN COAL CONVERSION WASTEWATERS

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## 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 byproduct waste streams from the various gasification and liquefaction processes.

Wastewaters from coal conversion processes can originate from a variety of sources depending upon the specific processes employed. The composition of the wastewater depends upon the process technology, operating conditions, and nature of the feed coal. Some characteristics of these wastewaters are shown in Table 1. Many coal conversion technologies employ byproduct 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, are still appreciable and further treatment of the waste streams is still 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 COD

components can be removed by biological treatment cannot be predicted.

Since even well-operated biological treatment processes typically remove only 85-95 percent 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.

In view of these considerations, a need exists:

- a. to identify the nature and characteristics of aqueous discharges from coal conversion processes and to assess their environmental impact, and
- b. to develop satisfactory means for the treatment of these wastewaters in order that they may be disposed of in an environmentally acceptable fashion.

Accordingly, this paper 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 demonstration 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.

## CHARACTERISTICS OF COAL CONVERSION WASTEWATERS

Table 1, presented earlier, shows the results of an analysis conducted by Forney, et al., (1974)<sup>1</sup> of the condensate wastewater generated from the Synthane gasification of six different types of coal. The wastewater characteristics of the weak ammonia liquor from a coke plant are also presented for purposes of comparison. The waste condensate streams appear to be somewhat alkaline and contain rather substantial amounts of ammonia. The concentration of organic material, represented by the chemical oxygen demand (COD), appears to consist, for the most part, of phenol.

TABLE 1

BYPRODUCT WATER ANALYSIS FROM SYNTHANE GASIFICATION  
OF VARIOUS COALS. (AFTER FORNEY ET AL. (1974).<sup>1</sup>)  
(ALL VALUES IN mg/l EXCEPT pH.)

	Coke Plant	Illinois		Wyoming		Illinois		North		Western		Pittsburgh	
		No. 6 Coal	Coal	Subbituminous Coal	Coal	Illinois Char	Dakota Lignite	Kentucky Coal	Coal	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 <sub>3</sub>	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	-	-	-	-	-						

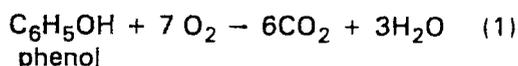
TABLE 2

PERCENTAGE OF COD ATTRIBUTABLE TO PHENOL IN SYNTHANE  
GASIFICATION BYPRODUCT WATER. (RAW DATA FROM FORNEY ET AL. (1974).<sup>1</sup>)

Component	Sample*						
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
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 equiv. of 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

\*Column 1 contains wastewater data from a coke plant; Columns 2-7 contain wastewater data from the gasification of several different types of coals (see Table 1).

Table 2 indicates, however, that phenol accounts for only 21 to 46 percent of the COD in the condensate samples; the remaining 54 to 79 percent of the COD is apparently due to the presence of other organic components of the waste streams. Table 2 was developed by calculating the COD-equivalent of the phenol concentrations given in Table 1, using a stoichiometric factor of 2.38 g of COD per g of phenol from the equation



Bromel and Fleeker (1976)<sup>2</sup> examined some general properties of raw and processed wastewater from the Lurgi process plant at Sasolburg, South Africa. Table 3 shows that the raw Lurgi wastewater is similar to that from Synthane in terms of its alkaline pH and high ammonia and COD concentrations. 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 total organic carbon (TOC), Bromel and Fleeker con-

ducted a series of chromatographic separations and identified and quantified the components reported in Table 4. 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 analyzed for. The other major classes identified are the fatty acids (aliphatic acids) and the aromatic amines consisting of pyridine and its methyl derivatives, and aniline. Quinoline and alkyl 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 3 could be accounted for by the specific organics identified in Table 4, a series of calculations was performed to determine the COD and TOC-equivalents of the compounds listed in Table 4. The basis for these calculations is shown in Table 5, and the TOC and COD-equivalents of the organic constituents are listed in Table 6. In the raw wastewater, the total COD of the constituents listed is 6738 mg/l of which the monohydric phenols comprise 5915 mg/l. The

**TABLE 3**  
**SOME GENERAL PROPERTIES OF RAW AND PROCESSED WASTEWATER**  
**FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA.**  
**(AFTER BROMEL AND FLEEKER (1976).<sup>2</sup>)**

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

<sup>AND</sup>, not determined.

TABLE 4

CONCENTRATION OF ORGANIC COMPOUNDS FOUND IN RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA. (AFTER BROMEL AND FLEEKER (1976)<sup>2</sup>.)

<u>Compound</u>	<u>Concentration (mg/l)</u>	
	<u>Raw Waste Water</u>	<u>Processed Waste Water</u>
<b>Fatty Acids</b>		
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
<b>Monohydric Phenols</b>		
Phenol	1,250	3.2
2-Methylphenol	340	<0.2
3-Methylphenol	360	<0.2
4-Methylphenol	290	<0.2
2, 4-Dimethylphenol	120	NF <sup>A</sup>
3, 5-Dimethylphenol	<50	NF
<b>Aromatic Amines</b>		
Pyridine	117	0.45
2-Methylpyridine	70	<0.05
3-Methylpyridine	26	<0.05
4-Methylpyridine	6	<0.05
2, 4-Dimethylpyridine	<1	NF
2, 5-Dimethylpyridine	<1	NF
2, 6-Dimethylpyridine	<1	NF
Aniline	12	NF

<sup>A</sup>NF, not found.

**TABLE 5**  
**COD AND TOC-EQUIVALENTS OF ORGANIC CONSTITUENTS**  
**OF SASOL WASTEWATER**

<u>Reaction</u>	<u>Chemical Oxygen Demand, gm O<sub>2</sub>/gm org.</u>	<u>Total Organic Carbon, gm C/gm org.</u>
Phenol $C_6H_5OH + 7 O_2 \rightarrow 6CO_2 + 3H_2O$	2.35	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

monohydric phenols contribute 1866 mg/l of TOC out of the total TOC of 2143 mg/l accounted for by the indicated constituents. However, if the COD and TOC of the identified organic components of the Sasol wastewater from Table 6 are compared to the total concentrations reported for the same sample in Table 3, Table 7 shows that 46.1 percent of the COD and 48.9 percent of the TOC of the raw

wastewater is 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 3 and 4 were derived from single samples of the aqueous gas liquor and the phenol-extracted gas liquor. The age of the

TABLE 6  
CONCENTRATION OF ORGANIC COMPOUNDS, AS COD AND TOC,  
FOUND IN THE RAW AND PROCESSED WASTEWATER FROM THE  
LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA.  
RAW DATA FROM BROMEL AND FLEEKER (1976)<sup>2</sup>.)

Compound	Concentration, mg/l			
	Raw Wastewater		Processed Wastewater	
	COD	TOC	COD	TOC
<b>Fatty Acids</b>				
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
	<u>278.6</u>	<u>98.3</u>	<u>258</u>	<u>88.2</u>
<b>Monohydric Phenols</b>				
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	-	-
	<u>5915</u>	<u>1866</u>	<u>9.1</u>	<u>3.1</u>
<b>Aromatic Amines</b>				
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	-	-
	<u>544</u>	<u>179</u>	<u>1.4</u>	<u>0.5</u>
<b>TOTAL</b>	<b>6738</b>	<b>2143</b>	<b>269</b>	<b>92</b>

**TABLE 7**  
**PERCENTAGES OF UNIDENTIFIED COD AND TOC IN SASOL**  
**WASTEWATER (RAW DATA FROM BROMEL AND FLEEKER (1976)<sup>2</sup>.)**

<u>Parameter</u>	<u>Raw Wastewater</u>	<u>Processed Wastewater</u>
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	-

samples was not accurately known, but is believed to have been less than 6 months for the raw wastewater and less than 1 month for the processed wastewater. The analyses were completed within 4 months following receipt of the samples (Bromel and Fleeker, 1976)<sup>2</sup>.

It is apparent from Tables 2 and 7 that many other organic species are present in coal conversion wastewaters, and that a need exists for further identification and quantification of these constituents.

Along these lines, Schmidt, Sharkey, and Friedel (1974)<sup>3</sup> 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 (Forney et al., 1974).<sup>1</sup>) 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 8 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, dihydric, and polyphenols, constitutes approximately 60 to 80 percent 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 (1976)<sup>2</sup> in Table 4 are consistent with the listing by Schmidt, Sharkey, and Friedel (1974)<sup>4</sup> in Table 8.

Expanding on this effort to identify organic constituents in wastewaters from coal gasification and coal liquefaction operations from various sources, Table 9 is a summary of information gathered from the eight different 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 aminobenzenes), 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 range 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 for column 1

TABLE 8

CONTAMINANTS IN PRODUCT WATER FROM SYNTHANE  
GASIFICATION OF VARIOUS COALS. (AFTER SCHMIDT ET AL. (1974).<sup>3</sup>)  
(ALL CONCENTRATIONS IN mg/l.)

	Illinois No. 6 (hvBb)	Montana (Sub)	N. Dak. (Lfg)	Wyo. (Sub)	W. Ky. (hvBb)	Pgh. (hvAb)
Phenol	3,400	3,160	2,790	4,050	2,040	1,880
Cresols	2,840	870	1,730	2,090	1,910	2,000
C <sub>2</sub> -Phenols	1,090	240	450	440	620	760
C <sub>3</sub> -Phenols	110	30	60	50	60	130
Dihydric	250	130	70	530	280	130
Benzofuranols	70	80	60	100	50	70
Indanols						
Acetophenones	150	140	110	110	90	120
Hydroxy-						
benzaldehyde	60	-	-	60	50	80
Benzoic Acids						
Naphthols	160	160	140	80	160	170
Indenols	90	70	50	60	80	20
Benzofurans	-	10	10	-	-	110
Dibenzofurans	-	-	-	-	-	-
Biphenols	40	-	-	40	20	60
Benzothio-						
phenols	110	-	10	20	70	20
Pyridines	-	270	220	120	30	540
Quinolines	-	20	10	-	-	10
Indoles	-	70	30	20	40	40

TABLE 9

SUMMARY: ORGANIC CONSTITUENTS IN COAL  
CONVERSION WASTEWATERS (ALL CONCENTRATIONS IN mg/l).

	SYNTHANE TPR-86 (1)	OIL SHALE (2)	SYN- THANE (3)	COED (4)	SRC (5)	LURGI- WESTFIELD (6)	SYN- THANE (7)	LURGI- SASOL (8)	HYDRO- CARBONIZ. (9)	COED (10)
<u>MONOHYDRIC PHENOLS</u>										
PHENOL	1000-4480	10	2100	2100	✓	1250-3100	↑	1250		
o-CRESOL		30	670	650	✓	153-343	2209	340		
m-CRESOL	530-3580	↑	1800	1800	✓	170-422	↑	360		
p-CRESOL		20	40	30	✓	160-302		290		
2, 6-XYLENOL			230	240	✓			50		
3, 5-XYLENOL			30	40	✓					
2, 3-XYLENOL			250	220	✓	100-393				
2, 5-XYLENOL	140-1170		100	900			2185			
3, 4-XYLENOL			-	-	✓			120		
2, 4-XYLENOL			30	30	✓					
o-ETHYLPHENOL					✓					
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-ISOPROPYLPHENOL					✓		40			
<u>DIHYDRIC PHENOLS</u>										
CATECHOL	✓									
3-METHYLCATECHOL					✓	190-555		1700		✓
4-METHYLCATECHOL					✓	30-394		11		✓
3, 5-DIMETHYLCATECHOL					✓	110-385		↓		✓
3, 6-DIMETHYLCATECHOL						0-45				
METHYLPYROCATECHOL	✓									
RESORCINOL	✓									
5-METHYLRESORCINOL					✓	176-272		2000		✓
4-METHYLRESORCINOL					✓	40-64		2000		✓
2-METHYLRESORCINOL					✓	0-36		2000		✓
2, 4-DIMETHYLRESORCINOL					✓			↓		✓
HYDROQUINONE	✓							4-7		
<u>POLYCYCLIC HYDROXY COMPOUNDS</u>										
γ-NAPHTHOL			10							
β-NAPHTHOL	30-290		30							
METHYLNAPHTHOL										
INDENOL	20-110									
C <sub>1</sub> -INDENOL										
4-INDANOL	40-150						66			
C <sub>1</sub> -INDANOL										
BIPHENOL	0-110									

TABLE 9 (Continued)

	SYNTHANE TPR-86 (1)	OIL SHALES (2)	SYN- THANE (3)	COED (4)	SRC (5)	LURGI- WESTFIELD (6)	SYN- THANE (7)	LURGI- SASOL (8)	HYDRO- CARBONIZ. (9)	COED (10)
<u>MONOCYCLIC N-AROMATICS</u>										
PYRIDINE	30-580							117		
HYDROXYPYRIDINE									10	
METHYLHYDROXYPYRIDINE									10	
METHYLPYRIDINE							✓	104		
DIMETHYLPYRIDINE							5	<1	7	
ETHYLPYRIDINE									20	
C <sub>3</sub> -PYRIDINE									1	
C <sub>4</sub> -PYRIDINE										
ANILINE							21	12		
METHYLANILINE							9			
DIPETHYLANILINE							11			
<u>POLYCYCLIC N-AROMATICS</u>										
QUINOLINE	0-100				✓		7			
METHYLQUINOLINE					✓		27			
DIMETHYLQUINOLINE					✓					
ETHYLQUINOLINE					✓					
BENZOQUINOLINE					✓					
METHYLBENZOQUINOLINE					✓					
TETRAHYDROQUINOLINE					✓					
METHYLTETRAHYDROQUINOLINE				✓						
ISOUINOLINE				✓						
INDOLE	0-110				✓		63			
METHYLINDOLE					✓					
DIMETHYLINDOLE					✓					
BENZOINDOLE					✓					
METHYLBENZOINDOLE					✓					
CARBAZOLE					✓					
METHYLCARBAZOLE					✓				4	
ACRIDINE				✓						
METHYLACRIDINE				✓						

TABLE 9 (Continued)

	<u>Synthane TPR-86 (1)</u>	<u>Oil Shale (2)</u>	<u>Syn- thane (3)</u>	<u>COED (4)</u>	<u>SRC (5)</u>	<u>Lurgi- Westfield (6)</u>	<u>Syn- thane (7)</u>	<u>Lurgi- Sasol (8)</u>	<u>Hydro- carboniz. (9)</u>	<u>COED (10)</u>
<u>Aliphatic Acids</u>										
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	-	-						
<u>Others</u>										
Benzofurans	10-110									
Benzofuranols	50-100									
Benzothiophenols	10-110									
Acetophenones	90-150									
Hydroxybenzaldehyde or Benzoic Acid	50-110									

for the C<sub>2</sub>-phenols which include the isomers of xlenol (dimethylphenol) and ethylphenol. Where a range of values is given, e.g., 1000-4480 mg/l for phenol in column 1, this indicates that several samples have been analyzed and the concentrations measured are within the given range.

Column 1 is derived from the previously discussed methylene-chloride, mass spectrometric analysis by Schmidt, Sharkey, and Friedel (1974)<sup>3</sup> 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 (1976)<sup>4</sup> 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 byproduct water (column 2) was obtained by centrifugation of an oil/water emulsion product from a simulated in-situ retort run made by the Laramie (Wyoming) Energy Research Center. The gasification byproduct 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 byproduct sample (column 4) was filtered water from the first-stage gas scrubber of the COED (Char Oil Energy Development) liquefaction process, provided by FMC Corporation, of Princeton, New Jersey.

The information in column 5 was obtained from a characterization of organics in coal-derived liquids from the Ft. Lewis, Washington Solvent Refined Coal Plant by Fruchter et al., (1977).<sup>5</sup> 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 have been positively identified, but not yet quantified.

Column 6 contains data collected by Janes and Rhodes (1977)<sup>6</sup> 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 the other reports.

Column 7 is derived from an M.S. thesis by Spinola (1976)<sup>7</sup> and 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 is from the report by Bromel and Fleeker (1976)<sup>2</sup> discussed above in connection with Tables 3-7.

The information in column 9 is from an analysis by Jolley, Pitt, and Thompson (1977)<sup>8</sup> of an aqueous stream from the product scrubber of a bench-scale hydrocarbonization coal liquefaction operation. The samples were analyzed by high pressure liquid chromatography, and the separated constituents were identified by a multiple analytical procedure involving gas chromatography and mass spectrometry.

Column 10 cites specific organics identified in an aqueous sample from the product separator (2nd stage liquor) of the COED coal liquefaction pilot plant (Shults, 1976).<sup>9</sup> The constituents were separated by high resolution anion exchange chromatography, and a variety of different analytical techniques were employed for identification and quantification.

With reference to the material contained in Table 9, it is important to note that the components identified and the concentrations reported are from grab samples of process streams collected from the various facilities and locations cited. The analyses are not complete, and 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 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.

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 9 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 10 lists some of the PAH's identified by Fruchter et al., (1977)<sup>5</sup> in the raw process wastewater from the Solvent-Refined Coal facility in Ft. Lewis, Washington, but the quantification and widespread occurrence of these PAH's in coal conversion wastewaters have not been established.

In any case, the similarity in composition of coal conversion wastewaters from different developing technologies suggests that the environmental impact of such wastewaters from

**TABLE 10**  
**POLYNUCLEAR AROMATIC HYDROCARBONS IN SRC RAW**  
**PROCESS WATER. (AFTER FRUCHTER ET AL. (1977).<sup>5</sup>)**

<u>PNA</u>	<u>CONCENTRATION</u> (mg/l)	<u>IDENTIFIED BUT NOT</u> <u>YET QUANTITATED</u>
METHYLINDANE	15	METHYLPYRENE
TETRALIN	<0.1	BENZOFLUORENE
DIMETHYLTETRALIN	0.5	C <sub>2</sub> -PYRENE
NAPHTHALENE	5	C <sub>2</sub> -FLUORANTHENE
2-NAPHTHALENE	2	TETRAHYDROCHRYSENE
DIMETHYLNAPHTHALENE	0.3-2	CHRYSENE
2-ISOPROPYLNAPHTHALENE	0.7	METHYLBENZOFLUORENE
1-ISOPROPYLNAPHTHALENE	2	C <sub>3</sub> -PYRENE
BIPHENYL	0.2	C <sub>3</sub> -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 <sub>2</sub> -ANTHRACENE	<0.05	
FLUORANTHENE	0.4	
DIHYDROPYRENE	<0.05	
PYRENE	0.6	

different sources, and the treatability of these wastewaters will be similar.

**AQUATIC IMPACT OF ORGANIC  
CONSTITUENTS OF COAL  
CONVERSION WASTEWATERS**

Although there is general agreement that most coal conversion processes will produce relatively contaminated wastewaters, little data are available concerning 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 United States. As such, efforts to assess the environmental impact of coal conversion wastewaters are in a predictive rather than descriptive stage. While ultimate evaluation of the environmental impact of these streams must await the construction and continuous operation of large scale conversion systems, interim predictive efforts are mandated by the number of highly toxic, carcinogenic, and mutagenic compounds known or anticipated to occur in coal conversion wastes.

Currently, prediction of the impact that coal conversion wastewaters will have on aquatic environments can only be based on a knowledge of the impact of effluents thought to be similar in composition to such wastewaters, or from an analysis of toxicity data on the constituents of the wastes. Towards this latter end, Table 11 shows threshold concentrations of various phenolic constituents of coal conversion wastewaters to selected lower aquatic organisms. If these threshold concentrations are compared to the wastewater concentrations shown in Table 9, it is obvious that a substantial level of wastewater treatment must be accomplished before the discharge can be considered acceptable from an aquatic impact point of view.

Estimated permissible concentrations for a number of hazardous pollutants were recently calculated and compiled by Cleland and Kingsbury (1977).<sup>11</sup> Ambient level goals (see Table 12) were calculated based upon estimated permissible concentrations in order to avoid detrimental health and ecological effects, and emission level goals (see Table 13) were computed based upon treatment technology and the ambient level goals. Several

**TABLE 11**  
**THRESHOLD CONCENTRATIONS OF VARIOUS PHENOLICS TO**  
**LOWER AQUATIC ORGANISMS (mg/l)**  
**(AFTER MCKEE AND WOLF (1963).<sup>10</sup>)**

<u>COMPOUND</u>	<u>DAPHNIA</u> <u>(MICROCRUSTACEAN)</u>	<u>MICROREGMA</u> <u>(PROTOZOAN)</u>	<u>SCENEDESMUS</u> <u>(ALGA)</u>	<u>E. COLI</u> <u>(BACTERIUM)</u>
PHENOL	16.0	30.0	40.0	>1000
o-CRESOL	16.0	50.0	40.0	600
m-CRESOL	28.0	20.0	40.0	600
p-CRESOL	12.0	10.0	6.0	>1000
3, 4-XYLENOL	16.0	10.0	40.0	500
2, 4-XYLENOL	24.0	70.0	40.0	>100
2, 5-XYLENOL	10.0	50.0	40.0	>100
RESORCINOL	0.8	40.0	60.0	>1000
HYDROQUINONE	0.6	2.0	4.0	50
PYROCATECHOL	4.0	6.0	6.0	90
QUINONE	0.4	2.0	6.0	50

TABLE 12

**AMBIENT LEVEL GOALS FOR KNOWN CONSTITUENTS OF COAL  
CONVERSION WASTEWATERS. CONCENTRATION IN  $\mu\text{g/l}$ .  
(AFTER CLEVELAND AND KINGSBURY, (1977.<sup>11</sup>))**

COMPOUND	CURRENT OR PROPOSED AMBIENT STANDARDS OR CRITERIA		TOXICITY BASED ESTIMATED PERMISSIBLE CONCENTRATION		ZERO THRESHOLD POLLUTANTS ESTIMATED PERMISSIBLE CONCENTRA- TION
	BASED ON HEALTH EFFECTS	BASED ON ECOLOGICAL EFFECTS	BASED ON HEALTH EFFECTS	BASED ON ECOLOGICAL EFFECTS	BASED ON HEALTH EFFECTS
PHENOL	1	100			
CRESOLS	1	1-100			
XYLENOLS	1	100			
ALKYL CRESOLS	1	100			
CATECHOL	1	100			
INDANOLS	1	100			
PYRIDINE		<5000	207		
METHYL PYRIDINES			316		
QUINOLINE		<500	14		
METHYL QUINOLINE			492		
ACRIDINE			800		
INDOLE			400		
CARBAZOLE			80		
ANILINE			69		
METHYL ANILINE			303.6		3.9
DIMETHYLANILINE			345		

known constituents of coal conversion wastewaters were included, as shown. The number of categories for which no data exist illustrates the limited amount of information available concerning health and ecological effects of coal conversion wastewater constituents. The few standards based upon ecological effects are limited to the phenolics; in all cases, these standards are derived from concentrations that produce tainting of fish flesh. The lack of information in Table 13 regarding best treatment technology reflects the fact that treatment standards are currently based on gross organic parameters such as BOD, COD, and TOC, and generally not on individual constituents even if these constituents are known or suspected aquatic toxicants or carcinogens. Additionally, the treatment stand-

ards have generally been developed for standard industrial categories and, to date, no such category has been established for coal conversion wastewaters.

The report by Cleland and Kingsbury is not complete, and is currently being expanded. Nevertheless, comparisons between the concentrations listed in Tables 12 and 13, and those reported in Table 9 again support the need for a relatively substantial degree of wastewater treatment in order to achieve an environmentally acceptable discharge.

In addition to the specific organic constituents of concern, as discussed above, it is significant to note the high concentrations of oxygen-demanding impurities (as implied by the high COD) associated with these wastewaters (see Tables 1 and 3). These

TABLE 13

EMISSION LEVEL GOALS FOR KNOWN CONSTITUENTS OF COAL  
CONVERSION WASTEWATERS. CONCENTRATIONS IN  $\mu\text{g/l}$ .  
(AFTER CLELAND AND KINGSBURY, (1977.<sup>11</sup>))

COMPOUND	BASED ON BEST TECHNOLOGY		BASED ON AMBIENT FACTORS
	EXISTING	DEVELOPING	AMBIENT LEVEL GOAL
	TECHNOLOGY	TECHNOLOGY	
	BPT	BAT	
PHENOL			1-100
CRESOLS			1
XYLENOLS			1-100
ALKYL CRESOLS			1-100
CATECHOL			1-100
INDANOLS			1-100
PYRIDINE			207
METHYL PYRIDINES			-
QUINOLINE			14-500
ISOQUINOLINE			-
METHYL QUINOLINE			-
ACRIDINE			3
INDOLE			-
CARBAZOLE			-
NAPHTHALENE			690-3800

oxygen-demanding impurities result in the depletion of dissolved oxygen in the receiving water, thereby making the water unsuitable for many types of aquatic organisms, including fish. From this standpoint alone, a significant degree of wastewater treatment is required.

BIODEGRADABILITY OF ORGANIC  
CONSTITUENTS OF COAL  
CONVERSION WASTEWATERS

In considering various alternatives for the treatment of coal conversion wastewaters, it is likely that aerobic biological treatment processes, such as activated sludge systems or aerated lagoons, will play a significant role in the overall treatment scheme. In order to assess the feasibility of using such biological processes for treating coal conversion wastewaters, it is first necessary to determine if the constituents of the wastewaters are biologically degradable and, if so, whether or not the

wastewater as a whole is biologically treatable, given the actual concentrations of the constituents. In conventional biodegradability studies, very low concentrations (5-10 mg/l) of the test compound are often used in order to avoid the problem of toxicity. While the test compound might prove to be biodegradable under these circumstances, the compound might be toxic to microorganisms at the concentration level at which it is found in the wastewater of interest.

Of the many compounds that are listed in Table 9 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 major intermediates in the degradation of aromatics. Therefore, an understanding of the metabolism of phenols is basic to the study of the degradation of other aromatic compounds. Additional-

ly, phenolic compounds comprise the major portion of the total organic carbon content of coal conversion effluents.

It is important to note, however, that the majority of the 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 in a natural or waste treatment situation. Also, lack of degradation or pathway information does not necessarily mean that the compound is not biodegradable, as many compounds identified in coal conversion wastewaters have not been studied.

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. The initial reaction in the bacterial oxidation of aromatic hydrocarbons is believed to be the formation of *cis*-dihydrodiols (Gibson, 1976).<sup>12</sup> 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.

It is generally recognized that metabolism of benzenoid compounds is dependent on the presence of molecular oxygen. While molecular oxygen acts as a terminal electron acceptor, it is also a specific substrate for those enzymes which catalyze the introduction of hydroxyl groups and the fission of suitably hydroxylated rings. Therefore, such pathways are strictly aerobic.

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* dihydric phenols. Figure 1 shows initial sequences for bacterial metabolism of various substrates that converge on catechol, including

phenol. The initial metabolism of *m*- and *p*-cresols along with other benzenoid compounds may result in the formation of protocatechuic acid. Figure 2 illustrates the convergence of some aromatic hydrocarbons on this ring fission substrate.

The third important ring cleavage substrate is gentisic acid. This is a *para*-dihydric phenol formed from such primary substrates as  $\beta$ -naphthol (see Figure 3).

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 first hydroxylated to form a 1, 2, 4-trihydric phenol (Ribbons and Chapman, 1968; Chapman and Ribbons, 1976).<sup>13,14</sup>

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 (Bayly et al., 1966),<sup>15</sup> while others oxidize the methyl group initially to a carboxyl group (Hopper and Chapman, 1971).<sup>16</sup> 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 acid. The dimethylphenols (xyleneols) act similarly. Depending on the position of the methyl groups on the ring, metabolism results in either protocatechuic acid or a methylgentisic acid (Hopper and Chapman, 1971; Chapman and Hopper, 1968).<sup>16,17</sup>

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  $\beta$ -oxidation, but sometimes may remain intact on the ring cleavage substrates. Generally, carboxyl groups remain intact prior to ring cleavage, but they may be eliminated as in the metabolism of benzoic acid to catechol (Reiner and Hegeman, 1971).<sup>18</sup>

Once the primary substrate has been converted to one of the ring fission substrates,

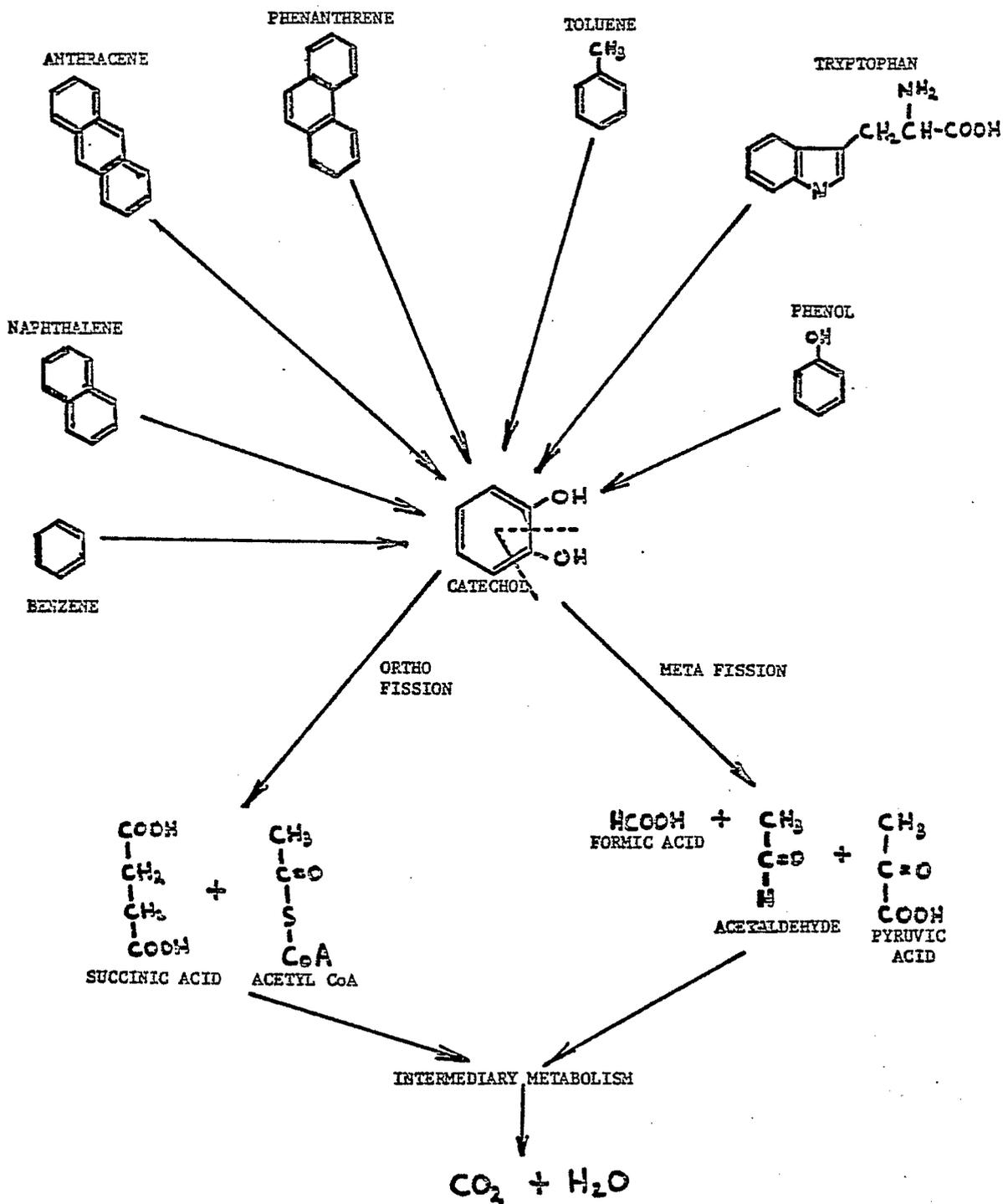


Figure 1. Schematic diagram illustrating catechol as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

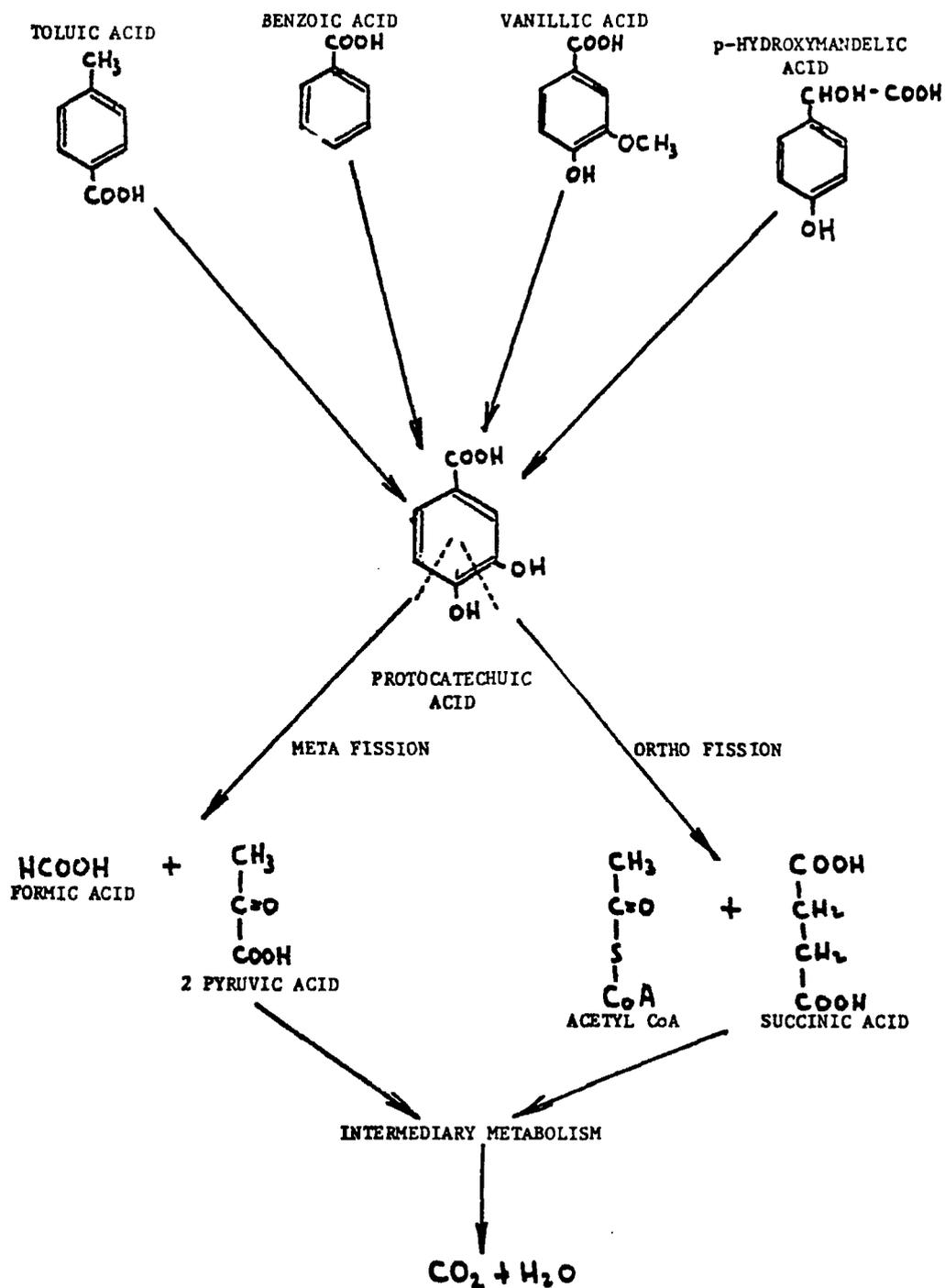


Figure 2. Schematic diagram illustrating protocatechuic acid as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

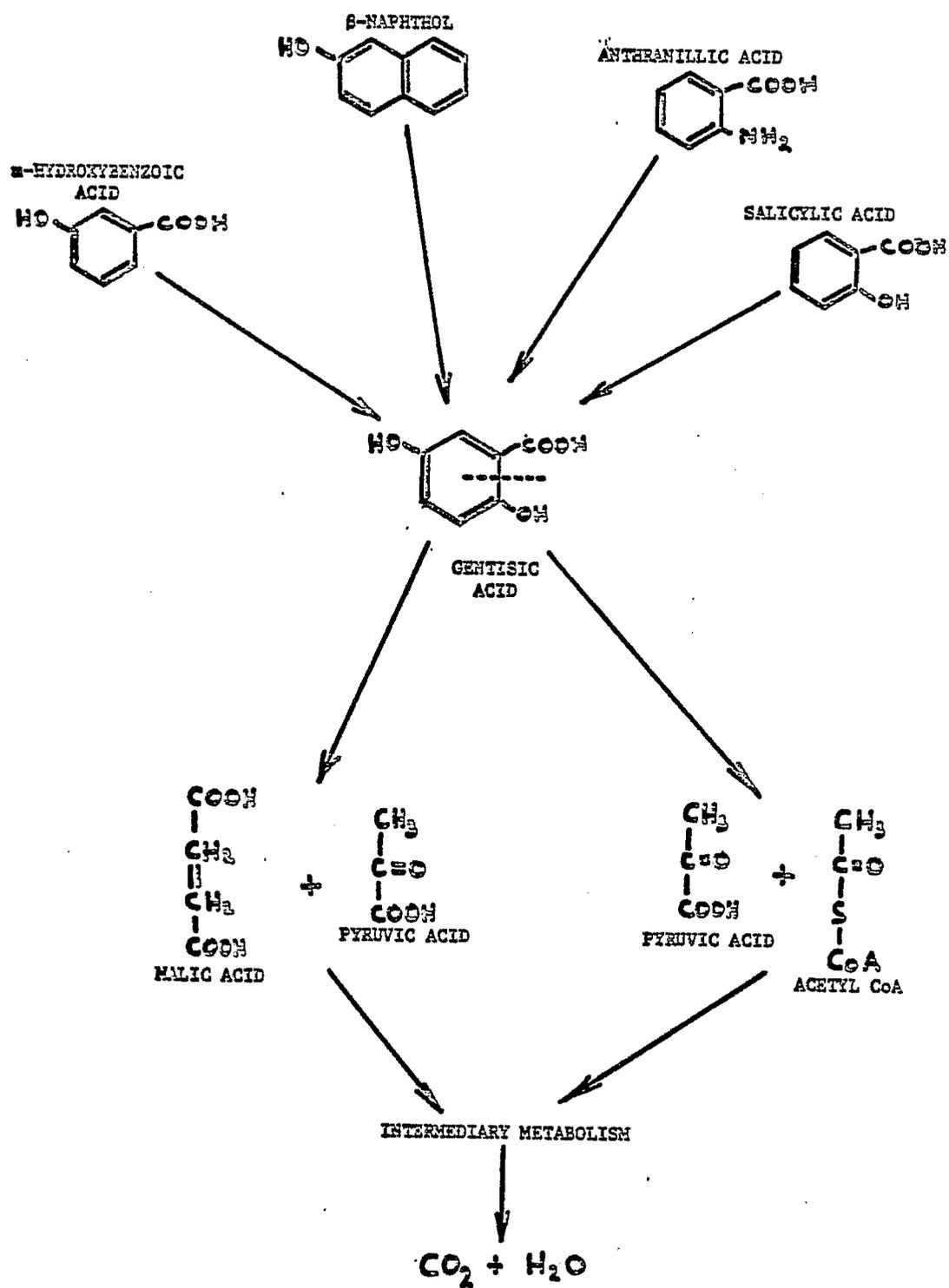


Figure 3. Schematic diagram illustrating gentisic acid as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

cleavage can then occur. Bacteria employ two different modes of enzymatic ring cleavage, known respectively as *ortho* and *meta* fission. Figures 1 and 2 show both types of fission for catechol and protocatechuic acid. *Ortho* fission is the splitting of the bond between the two carbon atoms bearing hydroxyl groups. This results in the formation of dicarboxylic acids. The other pathway, *meta* fission, leads to either an aldehyde-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. 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 (1975)<sup>19</sup> 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 3 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 (Larway and Evans, 1965)<sup>20</sup> with the ultimate products being acetic and formic acids. Other trihydric phenols undergo *meta*-fission.

The ultimate ring fission products of most phenolics undergo either fatty acid metabolism or enter the tricarboxylic acid cycle of the microorganisms.

As indicated above, these metabolic pathway studies 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 mechanisms by which microorganisms metabolize aromatic compounds for energy and growth. While pure culture work is important for a basic understanding of biodegradation, it is necessary in relation to biological treatment of wastewaters

containing these compounds, to focus attention on mixed microbial communities, such as soil, sewage, and activated sludge. Another concern that is usually not considered in metabolic pathway studies is the rate at which the substrate is metabolized.

Much of the data that exist on the biodegradability of phenolics in mixed cultures in wastewaters is based on oxygen uptake measurements. Early determinations of biodegradability were done by means of the standard biochemical oxygen demand (BOD) test. A summary of this type of data for a large number of pure organic compounds included many phenols (Heukelekian and Rand, 1955).<sup>21</sup> 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  $\alpha$ - and  $\beta$ -naphthol. *Para*-cresol and 3, 4-xyleneol gave somewhat lower oxygen demands and the BOD's of hydroquinone and 3, 5-xyleneol were only one-half that of phenol after five days.

Respirometric studies with acclimated activated sludge demonstrate the behavior of compounds of similar chemical structure, and the ability of microorganisms adapted to a given substrate to oxidize related compounds. The data of McKinney, Tomlinson, and Wilcox (1956)<sup>22</sup> 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 percent of their theoretical oxygen demand (ThOD) in 12 hours. However, the phenol-acclimated sludge oxidized catechol to only 13 percent of its ThOD, while the o-cresol and m-cresol-acclimated sludges metabolized catechol to the same extent as the other compounds (33 percent 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 in a major study of the decomposition of phenolic com-

TABLE 14  
 OXIDATION AND REMOVAL OF VARIOUS PHENOLIC  
 COMPOUNDS BY PHENOL-ACCLIMATED BACTERIA.  
 (AFTER TABAK ET AL. (1964.<sup>23</sup>))

Test compound	Test concn		Amt of O <sub>2</sub> consumed* (endogenous corrected)
	Initial ppm	Loss ppm	
			<i>μliters</i>
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
<i>m</i> -Chlorophenol.....	100	50	66
<i>p</i> -Chlorophenol.....	100	66	80
2,4-Dichlorophenol.....	60	18	46
2,6-Dichlorophenol.....	100	35	39
2,4,6-Trichlorophenol...	100	70	56
<i>o</i> -Cresol.....	100	97	417
<i>m</i> -Cresol.....	100	97	457
<i>p</i> -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- <i>m</i> -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
<i>o</i> -Nitrophenol.....	100	49	48
<i>m</i> -Nitrophenol.....	100	39	65
<i>p</i> -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- <i>o</i> -cresol....	100	60	31
2,4,6-Trinitroresorcinol.	60	13	6
2,4,6-Trinitro- <i>m</i> -cresol..	60	8	14
4-Chloro-2-nitrophenol..	100	64	123
2-Chloro-4-nitrophenol..	60	7	51
2,6-Dichloro-4-nitro- phenol.....	100	9	35
<i>m</i> -Dinitrobenzene.....	100	25	42
<i>p</i> -Dinitrobenzene.....	100	20	32
<i>m</i> -Nitroaniline.....	100	31	70
2,4-Dinitroaniline.....	100	39	53
<i>m</i> -Nitrobenzaldehyde....	100	27	38
3,5-Dinitrobenzoic acid.	100	13	48

\* Based on 180 min results

pounds by phenol-adapted bacteria (Tabak, Chambers, and Kabler, 1964).<sup>23</sup> In addition to respiration measurements, chemical analysis for residual substrate was also performed. Some of the results of the study are presented in Table 14 and Figures 4 and 5. 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.

#### Summary of Biodegradability Review

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, 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

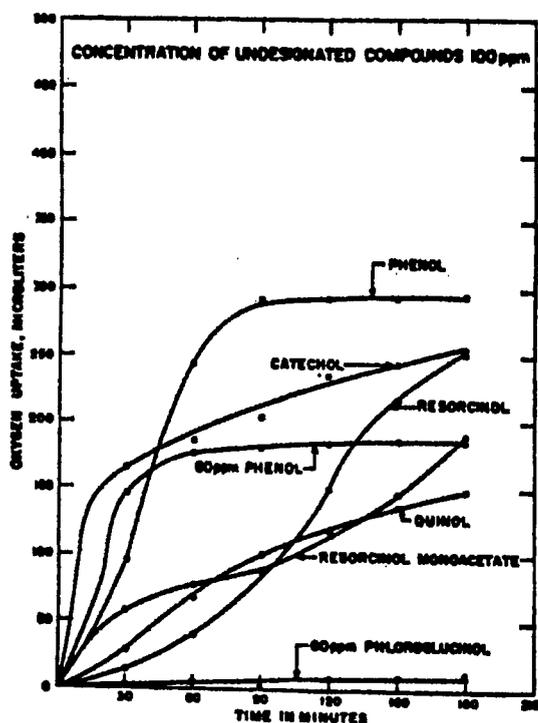


Figure 4. Oxidation of dihydric phenols. (From Tabak et al (1964).<sup>23</sup>)

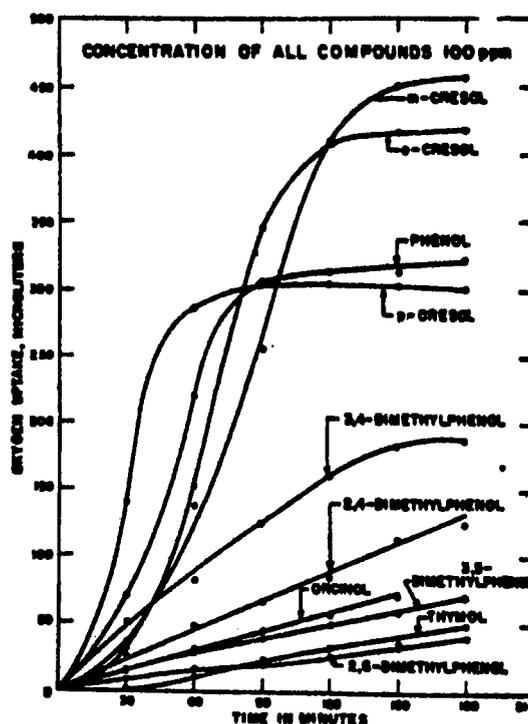


Figure 5. Oxidation of cresols and other methylphenol derivatives. (From Takak et al. (1964).<sup>23</sup>)

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.

### CONCLUSIONS

An attempt has been made to determine the chemical characteristics of byproduct wastewaters from coal gasification and coal liquefaction processes. Approximately 60-80 percent of the total organic carbon appears to be phenolic in nature, consisting of monohydric, dihydric, 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 appear 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, 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) an assessment of the biodegradability of the constituent compounds, as reviewed above; (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 consti-

tuents identified in coal conversion wastewaters, an experimental program to provide such information is underway.

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