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MASTER

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report
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by

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I. INTRODUCTION

This report summarizes the work performed during the period from October 1, 1981 through December 30, 1981 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward the continued acclimation of two anaerobic treatment systems, start up of a third anaerobic treatment system, GC/MS characterization of the coal gasification wastewater, data acquisition for determination of distribution coefficients for the extraction of phenol from the wastewater using MIBK, and preliminary design of a solvent extraction system for wastewater pretreatment. The progress of these efforts are depicted in the Gantt Chart (Figure 1) along with project expenditures for the above contract, (Figure 2) and are presented in detail in the following sections.

Projected Expenditures for DOE Contract
No. DE-AC18-81FC10297

Figure 2

II. ANAEROBIC TREATMENT SYSTEMS

A. Systems I and II

1. Operation and Acclimation

System I and II have been initially operated in an identical fashion for a period of 70 days. Diluted wastewater containing glucose, phosphates and vitamin extract (Table I) was pumped through the columns at a flow rate of 10 ml/min. At the end of 25 days the addition of vitamin extract to the dilution water was discontinued. At the end of 50 days the glucose supplement was discontinued. After an additional ten days of operation the activity within the reactors was decreasing as evidenced by both reduced gas production and a decrease in total volatile acids within the systems. It was decided to supplement the feed to one system with a low level of glucose. Therefore, on day 60 of operation, glucose, equivalent to 300 mg/l TOC, was added to the feed of System II. Simultaneously the flow rate to the Rashig Ring columns of both systems was reduced to 6.7 ml/min. The effluent from the Rashig Ring column was combined with an additional flow of 3.3 ml/min of final effluent from an anaerobic system being operated on phenol prior to being pumped through the granular activated carbon columns. This anaerobic effluent contains only a low residual COD of 40 mg/l, zero phenol and active methanogenic organisms. The results of these changes in operation will allow for the evaluation of two means of acclimation; that is acclimation by supplementation with an easily degraded substrate versus acclimation using diluted raw wastewater alone.

2. Volatile Acid Production

Both systems are producing volatile acids with the overall concentrations being similar in both systems (Figures 3 and 4). The concentration of acids in the final effluent of System I is higher which is also reflected by a lower gas production in System I, indicating that an active methane producing population of microorganisms has not been established in System I.

TABLE I. Feed Solution For System I and II

<u>Days of Operation</u>	<u>Feed Solution</u>
0-25	Raw Wastewater (500 ppm TOC), Glucose (500 ppm TOC), Phosphates, Vitamin Extract
25-50	Raw Wastewater (500 ppm TOC), Glucose (500 ppm TOC), Phosphates
50-70	Raw Wastewater (800 ppm TOC), Phosphates
70-75	System I - Raw Wastewater (800 ppm TOC), Phosphates System II- Raw Wastewater (700 ppm TOC), Glucose (300 ppm TOC), Phosphates
75-present	Same as days 70-75 except diluted wastewater flow rate was reduced to 6.7 ml/min and an additional 3.3 ml/min of effluent from an operating phenol degradation unit was pumped through the GAC column

Concentrations of volatile acids in the effluent from the Raschig Ring Columns in both systems are increasing indicating that viable acid forming populations of microorganisms are being established in the Raschig Ring Columns of both systems.

3. Gas Production

Both System I and II are producing measurable quantities of methane rich gas (Figure 5). Average methane content is 60 to 70%. As can be seen by Figure 5 both systems were producing at a relatively constant rates until shortly after the glucose supplement was discontinued (day 50 of operation). The gas production rate then decreased rather markedly, therefore, one system received an additional glucose supplement at a level of 300 mg TOC glucose to ascertain if this process would shorten the required acclimation time for the system. As can be seen in Figure 5 the addition of glucose has markedly increased the gas production rate in System II. The increase in the quantity of gas produced is more than can be accounted for by complete conversion of the added glucose to methane and carbon dioxide. Therefore, it is concluded that the system is anaerobically converting some of the organic compounds in the raw wastewater to methane and carbon dioxide. The bulk of the gas currently being produced in System II is being produced in the GAC column.

System I is still producing measurable quantities of gas in both the Rashig Ring and GAC columns but at a much lower rate than System II.

4. Phenol Removal

Phenol removal is occurring in both systems (Figure 6 and 7). Increases in phenol concentration in the final effluent are indicative of saturation of the GAC with incomplete biodegradation of the phenol occurring at this time. Phenol removal efficiencies should improve as acclimation proceeds.

5. COD and TOC removals

Influent COD and TOC (Figures 8,9,10,11) values are becoming more uniform indicating improvements in method of substrate preparation. Overall removals are similar in both systems at this time and are expected to improve as acclimation proceeds.

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

B. System III

1. Start Up

The third system was assembled and seeded in the same fashion as Systems I and II and began operation on December 22, 1981. Substrate containing wastewater (500 ppm TOC), glucose (500 ppm TOC) and phosphates is being used for acclimation of this system. Performance of this system will be monitored and the results will appear in succeeding reports.

III. GC/MS ANALYSIS

A. Introduction

A coal gasification wastewater sample from the Grand Forks Energy Technology Center was investigated for the identification of specific organic components. Two aliquots of the sample were solvent extracted by steam distillation vapour phase and stir-bar liquid-liquid techniques, fractionated by means of gel permeation chromatography (GPC) and submitted to HRGC-MS-DS analysis. The compounds identified and an estimate of their relative amounts are reported along with the general search computer report and reconstructed ion chromatograms.

B. Experimental Procedures

1 liter and 500 ml samples were subjected to steam distillation vapour phase and stir-bar liquid-liquid solvent extraction, respectively. Distilled in glass methylene chloride was used as solvent and the extraction was carried out in acidic (pH=2) and basic (pH=12) conditions. Concentration of the methylene chloride solution was achieved by Kuderna-Danish flask equipped with Snyder column. The GPC was carried out on Bio-Beads SX-2 (BioRAD Lab) gel that was slurry packed in a glass column 1 meter long and 1 cm internal diameter. A low pressure pump (Milton-Roy) was employed for solvent delivery and a micro sampling valve was used for sample injection. Pentane-methylene chloride (1:1) was used as solvent system. A Hewlett-Packard 5830A GC was interfaced with a Finnigan 4000 MS equipped with Nova 3 data system and Incos software package. The chromatography was carried out on a 30 m x 0.25 mm I.D. glass capillary column deactivated according to the persilylation method (Grob, 1980) and coated by the static method (Giabbai, 1978) with SE-54 gum phase. The sample transfer line between the GC and the ionization source consisted of approximately 40 cm long x 0.1 mm I.D. fused silica tubing. The experimental conditions were as follows:

GC	Splitless injection mode (30")
	Temperature program 40°(3 min)-290°C at 4°C/min
	Injector temperature 250°C

MS Electron Impact Ionization mode
 Electron Energy 70 eV
 Electron Multiplier 1500 V
 Preamp Sensitivity 10^{-7} Amp/V
 Emission Current 0.5 mAmp
 Mass range 46-450 a.m.u.
 Scan rate 1 scan/sec

The data were processed by a software program designated "Auto GC" developed at Finnigan Application Laboratory. The National Bureau of Standards mass spectra library, capable of approximately 25,000 mass spectra, was the reference basis for the tentative identification of the organic compounds.

C. Results

Figure 12 and 13 represent the reconstructed ion chromatogram of the samples extracted by steam distillation vapour phase under acidic and basic conditions, respectively. It is evident that the ionization source was overloaded by the presence of at least three major components. After further dilution of the extract it was possible to introduce an adequate amount for these three compounds and obtain proper ionization conditions. The three major peaks were identified as phenol, a cresol isomer and the third peak was the combination of the other two cresol isomers that were not resolved under the mentioned chromatographic conditions (Figure 14). Taking into consideration that 1) the compounds analyzed represent only the ones that are solvent extractable from water, 2) among the extractables only the ones directly amenable to GC were detected, 3) the MS response factors for all the compounds is considered the same, it is possible to roughly estimate that the sum of the amounts of phenol and cresols is at least 30 times higher than the sum of all the rest of the compounds detected. The amount of phenol itself is approximately 5 times higher than the amount of each cresol isomer. All the other components tentatively identified by the software program are reported in Figures 15 and 16.

RIC
10/29/81 13:26:00
SAMPLE: COAL GASIFICATION WASTEWATER V.P.E. (72-1)+IS

DATA: CGU721 #1
CALI: CALGAS #5

SCANS 1 TO 1500

RIC
10/29/81 13:26:00
SAMPLE: COAL GASIFICATION WASTEWATER V.P.E. (72-1)+IS

DATA: UGW/21 #1
CALI: CALGAS #5

SCANS 1500 TO 3000

INTEN
50000.
1.

Figure 12 (continued)

RIC

-20-

RIC
10/29/81 14:58:00
SAMPLE: COAL GASIFICATION WASTEWATER V.P.E. (72-2)+IS

DATA: CGU722 #1
CALI: CALGAS #5

SCANS 1 TO 1200

Figure 13

INTEN
50000.
1.

RIC

-21-

200
3:20

400
6:40

600
10:00

800
13:20

1000
16:40

1200 SCAN
20:00 TIME

RIC
10/29/81 14:58:00
SAMPLE: COAL GASIFICATION WASTEWATER V.P.E. (72-2)+IS

DATA: CGV722 #1
CALI: CALGAS #5

SCANS 1200 TO 3000

Figure 13 (continued)

INTEN
50000.
1.

RIC

-22-

1400 1600 1800 2000 2200 2400 2600 2800 3000
23:20 26:40 30:00 33:20 36:40 40:00 43:20 46:40 50:00
SCAN TIME

RIC
12/01/81 13:15:00
SAMPLE: COAL GAS. WU(72-1) 0.5MCL IN 0.5ML

DATA: CGU721A #1
CALI: CALGAS #7

SCANS 1 TO 1200

Figure 14

RIC
12/01/81 13:15:00
SAMPLE: COAL GAS. WU(72-1) 0.5MCL IN 0.5ML

DATA: CGU721A #1
CALI: CALGAS #7

SCANS 1 TO 1200

INTEN
10000.
1.

RIC

-23-

200
3:20

400
6:40

600
10:00

800
13:20

1000
16:40

1200
20:00 TIME

DATA: CGU721.TI

10/29/81 13:26:00

SAMPLE: COAL GASIFICATION WASTEWATER V.P.E. (7) IS

CONDS.: SE54 30M, #84, 40(3) SBU 4/M, SPL 10, LESS 11

FORMULA: - INSTRUMENT: CHINN

SUBMITTED BY: MFG ANALYST: MFG

NO.:

Figure 15

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

NO	NAME	SCAN	FIT	PURITY	LIBRARY ENTRY	AREA	AMOUNT	%TOT
1	BENZOFURAN, 2,3-DIHYDRO-	1207	976	836	NB 2474	69615.	45.917	5.79
2	PHENOL, 4-(1-METHYLETHYL)-	1231	956	820	NB 861	39120.	25.800	3.26
3	PHENOL, 2-ETHYL-5-METHYL-	1243	960	871	NB 5449	122386.	80.725	10.19
4	UNKNOWN	1246	940	660	NB 6076			
5	5-ISOBENZOFURAN CARBOXYLIC ACID, 1,3-DIHYDRO-1,3-DIOXO-	1258	675	511	NB 2839	1599.	1.055	0.13
6	PHENOL, 4-ETHYL-2-METHYL-	1281	930	802	NB 6076	151610.	100.000	12.62
7	PHENOL, 2,3,5-TRIMETHYL-	1295	866	665	NB 3908	53783.	35.474	4.48
8	ETHANONE, 1-(2,4-DIHYDROXYPHENYL)-	1300	988	747	NB 583	35886.	23.670	2.99
9	1H-INDOLE	1320	998	829	NB 1488	45739.	30.169	3.81
10	DECANE, 3-BROMO-	1326	759	523	NB 16274	9907.	6.534	0.82
11	PROPANOIC ACID, 2,2-DIMETHYL-, 2-(1,1-DIMETHYLETHYL)PHENYLESTER	1331	666	368	NB 20924	4820.	3.179	0.40
12	NONANOIC ACID	1334	984	702	NB 1362	18618.	12.280	1.55
13	PHENOL, 2,3,5-TRIMETHYL-	1337	987	784	NB 3908	14127.	9.318	1.18
14	BENZENEMETHANOL, AR-ETHENYL-	1343	795	660	NB 16282	1806.	1.244	0.16
15	1,3-BENZENEDIOL, 4,5-DIMETHYL-	1351	881	568	NB 2678	7871.	5.192	0.66
16	1,4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1355	953	506	NB 15415	11847.	7.814	0.99
17	BENZENEMETHANOL, AR-ETHENYL-	1362	969	761	NB 16282	42614.	28.108	3.55
18	2H-1-BENZOPYRAN-2-ONE, 3,4-DIHYDRO-	1370	769	538	NB 1470	2298.	1.516	0.19
19	UNKNOWN	1374	698	467	NB 2974			
20	PHENOL, 2-(1-METHYLPROPYL)-	1378	758	660	NB 575	2449.	1.616	0.20
21	2-PROPENAL, 3-PHENYL-	1384	980	818	NB 1006	14596.	9.627	1.21
22	BENZOFURAN, 7-METHYL-	1388	981	874	NB 11795	14629.	9.649	1.22
23	BENZENE, 1-ETHYL-2,4,5-TRIMETHYL-	1400	880	706	NB 12129	95745.	63.152	7.97
24	UNKNOWN	1404	826	431	NB 6740			
25	1,4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1417	989	824	NB 15415	34774.	22.936	2.89
26	UNKNOWN	1420	780	466	NB 17899			
27	2-PROPENAL, 3-PHENYL-	1421	978	784	NB 1006	37618.	24.812	3.13
28	2-PROPENAL, 3-PHENYL-	1422	981	754	NB 1006	37783.	24.921	3.14
29	BENZENEPROPANOL, 2-HYDROXY-	1430	728	405	NB 5168	5803.	3.308	0.42
30	BENZENEMETHANOL, .ALPHA.-ETHYL-4-METHOXY-	1438	822	571	NB 8409	9519.	6.279	0.79
31	1,9-NONANEDIOL, DIMETHANESULFONATE	1451	726	397	NB 7695	2460.	1.622	0.20
32	DECANOIC ACID	1462	881	680	NB 2029	6580.	4.287	0.54
33	1-NAPHTHALENOL, 1,2,3,4-TETRAHYDRO-	1466	769	519	NB 2692	11564.	7.627	0.96
34	1H-INDOLE, 3-METHYL-	1467	974	598	NB 490	9363.	6.176	0.78
35	BENZENE, 2-(METHYLSULFINYL)ETHENYL-	1472	721	436	NB 9726	13146.	8.671	1.09
36	2-PROPYN-1-OL, 3-P-TOLYL-	1485	697	357	NB 11341	3298.	2.176	0.27
37	1,4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1504	979	792	NB 15415	18401.	6.860	0.87
38	BENZENE, 1,3-DIMETHYL-5-(1-METHYLETHYL)-	1512	887	423	NB 8007	4375.	2.886	0.36
39	BENZENE, 2,4-DIMETHYL-1-(1-METHYLETHYL)-	1517	777	580	NB 8006	5004.	3.360	0.42
40	BENZENE, (1,1-DIMETHYLETHYL)METHYL-	1531	804	471	NB 15328	1807.	1.192	0.15
41	BENZENE, HEXAMETHYL-	1538	767	554	NB 549	14698.	9.695	1.22
42	1H-INDOLE-1,2-DIOL, 2,3-DIHYDRO-1-METHYL-, CIS-	1539	815	450	NB 24305	18990.	7.249	0.91
43	2-PROPYN-1-OL, 3-P-TOLYL-	1549	834	663	NB 11341	5381.	3.549	0.45
44	BIPHENYLENE	1553	978	937	NB 1888	9814.	5.945	0.75
45	BENZENE, HEXAMETHYL-	1563	992	854	NB 549	66497.	43.861	5.53
46	TEREPHTHALALDEHYDE, 2,5-DIMETHYL-	1577	959	771	NB 9337	9584.	6.322	0.80
47	2-PROPYN-1-OL, 3-P-TOLYL-	1583	900	657	NB 11341	14062.	9.275	1.17
48	BENZENE, HEXAMETHYL-	1584	680	558	NB 549	9082.	5.938	0.75
49	ACENAPHTHYLENE, 1,2-DIHYDRO-	1610	951	800	NB 488	3169.	2.090	0.26
50	TEREPHTHALALDEHYDE, 2,5-DIMETHYL-	1628	890	572	NB 9337	2266.	1.494	0.19
51	TEREPHTHALALDEHYDE, 2,5-DIMETHYL-	1644	833	635	NB 9337	2905.	1.916	0.24
52	2-NAPHTHALENOL	1662	992	690	NB 1678	17945.	11.836	1.49
53	2-NAPHTHALENOL	1675	988	834	NB 1678	21025.	13.868	1.75
54	1-NAPHTHALENOL, 3-METHYL-	1739	928	802	NB 10488	1796.	1.185	0.15
55	1H-PHENALENE	1764	939	823	NB 1836	5589.	3.687	0.47
56	1-NAPHTHALENOL, 3-METHYL-	1822	973	889	NB 10488	7255.	4.785	0.60
57	1-NAPHTHALENOL, 3-METHYL-	1837	829	749	NB 10488	4479.	2.955	0.37
58	DIBENZOFURAN, 4-METHYL-	1850	893	708	NB 9509	1863.	0.701	0.09
59	1H-PYRAZOLE, 3-METHYL-5-PHENYL-	1868	732	614	NB 7024	2009.	1.325	0.17
60	PHENANTHRENE	2067	967	927	NB 518	5442.	3.589	0.45
61	PHOSPHINE, BIS(PENTAFLUOROPHENYL)PHENYL-	2209	845	785	NB 8245	1766.	1.165	0.15
62	BENZENETETRACARBOXYLLIC ACID TETRAMETHYLESTER	2643	022	744	NB 25414	31691.	20.903	2.64

Figure 16

SAMPLE: LUAL GASTRICATION ANALYSIS, 11/11/72
 CONDS.: SE54 30M, 40(3)300 4/M, SPLITLESS INCL
 FORMULA: PH12 INSTRUMENT: FINN DE UNIT: 0.008
 SUBMITTED BY: MFG ANALYST: MFG ACCT. NO.:

AMOUNT-AREA * REF. AMNT / (REF. AREA * RESP. FACT)

NO	NAME	SCAN	FIT	PURITY	LIBRARY ENTRY	AREA	AMOUNT	%TOT
1	ACETAMIDE, 2, 2, 2-TRIFLUORO-N-METHYL-	1078	703	409	NB 4125	10232.	4.490	0.82
2	1H-1, 2, 3-TRIAZOLE-4-CARBOXYLIC ACID, 4, 5-DIHYDRO-1-PHENYL-	1095	765	615	NB 21120	7747.	3.400	0.62
3	5-(4H)-INDANONE, TETRAHYDRO-, TRANS-	1097	696	519	NB 7985	11346.	4.979	0.91
4	AZETIDINE, 2-PHENYL-	1100	577	341	NB 13929	730.	0.324	0.06
5	1H-IMIDAZOLE, 2-ETHYL-	1114	763	514	NB 4676	11886.	4.865	0.89
6	3-PENTEN-2-ONE, 3-ETHYL-4-METHYL-	1121	920	737	NB 13789	9249.	4.059	0.75
7	PHENOL, 2, 4-DIMETHYL-	1131	873	734	NB 1045	5003.	2.231	0.41
8	CYCLOPENTANE, NITRO-	1137	880	530	NB 6465	1705.	0.748	0.14
9	4-PENTEN-1-OL	1141	731	360	NB 4151	3968.	1.741	0.32
10	BORANAMINE, N, N, 1-TRIMETHYL-1-PHENYL-	1153	733	660	NB 7186	2613.	1.147	0.21
11	PHENOL, 3-ETHYL-	1159	983	903	NB 3417	61273.	26.891	4.94
12	UNKNOWN	1162	978	802	NB 3417			
13	CYCLOHEXENE, 1-METHYL-4-(1-METHYLETHYL)-, (+)-	1180	751	564	NB 4952	2022.	0.888	0.16
14	PHENOL, 2, 5-DIMETHYL-	1194	980	888	NB 735	53967.	23.684	4.35
15	PHENOL, 3, 4-DIMETHYL-	1198	996	900	NB 726	59471.	26.100	4.79
16	CYCLOHEXANE, 1, 1'-(OXYD1-2, 1-ETHANEDIYL) BIS-4-METHYL-	1209	794	345	NB 21604	1084.	0.476	0.09
17	BENZOFURAN, 2, 3-DIHYDRO-	1223	975	830	NB 2474	51433.	22.572	4.15
18	PHENOL, 4-METHOXY-	1237	963	725	NB 1708	2906.	1.275	0.23
19	ISOQUINOLINE	1254	998	940	NB 1467	105308.	46.251	8.50
20	QUINOLINE	1259	983	915	NB 623	32501.	14.263	2.62
21	NICOTINONITRILE, 1, 4-DIHYDRO-1-METHYL-4-OXO-	1279	932	658	NB 4052	9239.	4.055	0.74
22	ISOQUINOLINE	1292	989	894	NB 1467	20674.	9.073	1.67
23	1, 3-CYCLOHEXADIENE, 1, 2, 6, 6-TETRAMETHYL-	1299	755	408	NB 2614	2772.	1.216	0.22
24	BENZENE, (3-METHOXY-1-PROPENYL)-	1300	789	387	NB 11453	2415.	1.060	0.19
25	1H-INDEN-1-ONE, 2, 3-DIHYDRO-	1314	933	828	NB 489	1643.	0.721	0.13
26	2-PROPENITRILE	1328	975	545	NB 1111	5088.	2.584	0.47
27	UNKNOWN	1335	992	744	NB 1488			
28	1H-INDOLE	1338	904	932	NB 1488	10627.	8.175	1.50
29	1, 3-BENZENEDIOL, 4-ETHYL-	1344	816	368	NB 6734	2400.	1.053	0.19
30	1, 3-BENZENEDIOL, 4, 5-DIMETHYL-	1353	820	704	NB 2678	2375.	1.042	0.19
31	ISOQUINOLINE, 3-METHYL-	1370	946	848	NB 4820	19221.	8.435	1.55
32	BENZENEMETHANOL, AR-ETHENYL-	1376	970	744	NB 16282	29177.	12.805	2.35
33	2, 5-CYCLOHEXADIENE-1, 4-DIONE, 2, 3, 5, 6-TETRAMETHYL-	1384	892	852	NB 2675	6041.	2.651	0.49
34	UNKNOWN	1386	842	550	NB 2675			
35	BENZENEETHANOL, 3-HYDROXY-	1391	759	588	NB 10375	7357.	3.229	0.59
36	FORMAMIDE, N-PHENYL-	1394	874	788	NB 977	8970.	3.937	0.72
37	2-PROPENAL, 3-PHENYL-	1401	983	792	NB 1006	29286.	12.853	2.36
38	BENZENEMETHANOL, AR-ETHENYL-	1413	959	800	NB 16282	82798.	36.338	6.67
39	BENZOFURAN, 7-METHYL-	1422	947	540	NB 11795	11420.	5.012	0.92
40	BENZOFURAN, 7-METHYL-	1437	977	697	NB 11795	24237.	10.637	1.95
41	QUINOLINE, 3-METHYL-	1444	930	831	NB 3331	2664.	1.169	0.21
42	QUINOLINE, 5-METHYL-	1453	879	553	NB 9695	1090.	0.478	0.09
43	QUINOLINE, 4-METHYL-	1471	968	865	NB 2446	3036.	1.333	0.24
44	BENZENECARBOXYMIDYLCHLORIDE, N-METHYL-	1489	876	616	NB 19082	8458.	3.712	0.68
45	ETHANONE, 1-PHENYL-, OXIME	1516	872	668	NB 3346	227859.	100.000	18.37
46	1, 4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1525	933	887	NB 15415	9664.	4.241	0.78
47	1, 4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1540	992	822	NB 15415	7197.	3.159	0.58
48	1, 4-BENZENEDICARBOXYALDEHYDE, 2-METHYL-	1547	925	776	NB 15415	2366.	1.038	0.19
49	2-PROPYN-1-OL, 3-P-TOLYL-	1563	917	746	NB 11341	5083.	2.231	0.41
50	NAPHTHALENE, 1, 2, 3, 4-TETRAHYDRO-1-METHYL-	1569	830	694	NB 5249	8601.	3.810	0.70
51	BENZENE, HEXAMETHYL-	1585	992	881	NB 549	89901.	39.455	7.25
52	1H-PYRROLO[2, 3-B]PYRIDINE	1597	912	542	NB 1889	6863.	3.012	0.55
53	2-PROPYN-1-OL, 3-P-TOLYL-	1604	927	717	NB 11341	16915.	7.423	1.36
54	AZETIDINE, 2-PHENYL-	1632	835	783	NB 13929	22633.	9.933	1.82
55	ETHANOL, 2-(1-PHENYLHYDRAZINO)-	1639	816	617	NB 19496	4489.	1.970	0.36
56	BENZENEETHANAMINE, N-(PHENYL METHYLENE)-	1648	713	564	NB 6950	33343.	14.633	2.69
57	2-PENTEN-1-ONE, 1-(2-HYDROXY-5-METHYLPHENYL)-	1667	668	411	NB 19996	2121.	0.931	0.17
58	TEREPHTHALALDEHYDE, 2, 5-DIMETHYL-	1683	891	735	NB 9337	1135.	0.498	0.09
59	2-NAPHTHALENOL	1696	908	809	NB 1678	19300.	8.505	1.56
60	BENZOB[THIOPHENE, 2, 7-DIMETHYL-	1716	732	489	NB 11555	859.	0.377	0.07
61	BENZENEETHANAMINE, N-(PHENYL METHYLENE)-	1723	777	466	NB 6950	894.	0.393	0.07
62	1H-BENZIMIDAZOLE-2-CARBOXYALDEHYDE	1772	630	482	NB 7000	2061.	0.904	0.17
63	ETHANONE, 1-PHENYL-, OXIME	1777	829	513	NB 3346	3041.	1.334	0.25
64	1-NAPHTHALENOL, 3-METHYL-	1851	959	833	NB 10408	3495.	1.534	0.28
65	1-NAPHTHALENOL, 3-METHYL-	1861	810	704	NB 10408	2653.	1.164	0.21
66	1, 4-NAPHTHALENE DIONE, 2, 3-DIMETHYL-	1877	933	801	NB 6035	1059.	0.465	0.09
67	1-NAPHTHALENOL, 3-METHYL-	1893	800	707	NB 10408	2677.	1.175	0.22
68	ISOQUINOLINE, 1-ETHYL-	2077	740	402	NB 9699	2909.	1.277	0.23
69	BENZENETETRACARBOXYLLIC ACID TETRAMETHYLESTER	2671	824	746	NB 25414	29708.	13.038	2.39

IV. SOLVENT EXTRACTION

A. Experimental Procedure

Organic free water was spiked with concentrations of phenol ranging from 0.1 to 1,000 mg/l. 200 ml aliquots of the spiked phenol were then extracted with 50 ml of methyl isobutyl ketone. The two phases were separated the organic phase was reduced in volume and analyzed for phenol by capillary column gas chromatography. The aqueous phase was acidified to pH 2 and extracted with three 25 ml portions of methylene chloride. The methylene chloride was dried and concentrated to a small volume and analyzed for phenol using capillary column gas chromatography

The results from the above analysis were used to calculate the distribution coefficient for phenol.

To obtain data which would be more representative of actual wastewater extraction the above procedure was repeated using solvent extracted (MIBK) wastewater in the place of the organic free water. The solvent extracted wastewater was prepared by extracting raw wastewater with 5 portions of MIBK.

B. Results

Distribution coefficients obtained from using spiked organic free water had values ranging from 88 to 95 with an average of 91. These values agree well with those reported in the literature. However, the results using extracted wastewater as the diluent were inconclusive. The methylene chloride back extraction of the acidified wastewater tended to concentrate the acid species which were not extracted by the MIBK. These species severely interfered with the gas chromatographic analysis for phenol and reliable data could not be obtained.

Extraction recovery data for known samples was quite good with phenol recoveries averaging 113% with an average aeration of 21%.

C. Extractor Design

Using the preliminary data from the organic free water extractions the design for the staged continuous laboratory extractor is given in Figure 17 and the overall extraction process unit is illustrated in Figure 18. The extractor will be constructed of three inch galvanized pipe and fitting. Each section will be 6 inches long giving a volume of approximately 700 ml per section. A five stage unit would therefore have an overall volume of 3.5 liters.

Operation of the unit would involve charging the unit with wastewater and solvent and then: 1) opening valves A and C and allowing approximately 550 ml of wastewater to flow through the system and close valve A and C; 2) allow the mixed system to phase separate; 3) open valves B and D and allow approximately 150 ml of solvent to flow through the system and then close valves B and D; 4) allow the mixed system to phase separate; and 5) repeat steps 1 through 4 until the desired volume of wastewater has been treated.

V. FUTURE WORK

Acclimation of Systems I, II and III will continue until one system is at psuedo-steady state. At that time the acclimated system will be used for the initial loading studies as outlined in the project proposal while the other two systems continue to acclimate. Additional efforts will be made to assure that all systems are receiving raw wastewater of identical composition.

Construction of the solvent extractor will begin and efforts will be made to obtain K_d values using raw wastewater as the diluent by first extracting the raw wastewater with methylene chloride at pH 2 to remove those species interfering with the phenol analysis. The CH_2Cl_2 extracted raw wastewater will then be neutralized to pH 7 to 8 and used as the diluent.

Literature surveys pertaining to the nitrification system will be completed.

Figure 17

Figure 18

The nitrification systems will be assembled and initial operation of these systems will begin.

Analysis for inorganic species will be incorporated into the process monitoring and development of ion chromatographic procedures will begin.

GC/MS work will focus on better estimates of the concentration level of phenol, cresols and other major identified components by updating the response factors of the MS with standard solutions of the aforementioned compounds. Further, the confirmation of the identity of other major and minor components will be pursued by chemical ionization techniques, pure compounds analysis under the same experimental conditions and eventually by fractionating the extracts by a preliminary separation by high performance liquid chromatography.