Assessment of Solvent Extraction for Treatment of Coal Gasifier Wastewater

Progress Report

MASTER

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Abstract

A preliminary study has been completed for the assessment of solvent extraction for coal gasifier wastewater treatment. This study shows very favorable economics; wastewater contaminants have a market value of about \$45.00 per 1000 gallons of water to be treated while treatment costs are about \$1.25 to \$2.50 per 1000 gallons.

Measurements of distribution coefficients between water and various solvents has been completed for m-dihydroxy benzene (resorcinol) and is in progress for o- and p-dihydroxy benzene, pyridine, o-cresol and naphthol. A very high distribution coefficient of 40 was found for m-dihydroxy benzene between water and octanone -2 (methyl heptyl ketone).

1. Introduction

The objective of the work in this proposal is to evaluate the feasibility of solvent extraction for the removal of contaminants from coal gasifier wastewater. The tasks outlined were:

- A. To perform preliminary economic evaluation of solvent extraction for removal of coal gasifier wastewater contaminants;
- B. To measure distribution coefficients of 8 to 10 of the principal constituents in wastewater from coal gasification processes in 10 to 12 solvents.
- C. To utilize data and correlations of data to produce a design for a solvent extraction process together with economic evaluations.

2. Research Progress (to May 30, 1977)

A. Process Design and Evaluation

As provided in the proposal, a report entitled "Assessment of Solvent Extraction for Treatment of Coal Gasifier Wastewater: Preliminary Cost Evaluations" was prepared and sent for review in January 1977. A revised version of this report is included as Appendix I of this report.

B. Evaluation of Distribution Coefficients

B1. Equipment

Solutions for measurement of distribution coefficients were prepared by equilibrating 50 ml of H_2O containing a known concentration of solute with 50 ml of solvent. Equilibration was achieved by vigorous shaking of the two-phase mixture in a 300 ml separatory funnel. Using phenol with an isopropyl ether-water mixture, it was established that equilibrium is achieved in less than 20 sec. of vigorous shaking (Figure 1) but a standard shaking time of one minute was retained in the analytical procedure.

Analyses were made on a Model 1520 Varian Gas Chromatograph using a flame ionization detection system. For a series of calibration experiments using phenol as the solute, a stainless steel column (5ft. by 3/16 inches OD) was packed with 9% FFAP on 60/80 mesh Chromosorb W-AM-DMCS. Nitrogen was used as the carrier gas at a flow rate of approximately 20 ml/min. The flame ionization detector used hydrogen at 25 ml/min. and air at 250-400 ml/min. Direct analysis was made of the aqueous phase at column temperatures of 170°C. Injector and detector temperatures were 230°C and a 5 µl. sample was used.

B2. Calibration with Phenol and Isopropyl ether

An extensive series of experiments were performed to evaluate overall precision and accuracy of the procedures by comparison with values from the literature. The results of this study (Table 1 and Figure 2) showed a standard deviation of about 13% in measured values of individual activity coefficients. Thus multiple measurements will be necessary to achieve the 10% accuracy level projected in the proposal. This constitutes no change in the experimental method; it had been expected that replication would be required.

The average distribution coefficient measured in these experiments is within 5% than that found for equivalent conditions in the literature.

B3. Measurements on Resorcinol (m-dihydroxy benzene)

In the original proposal, it was projected that measurements of higher boiling compounds, such as resorcinol would be made using silylation reagents. These are compounds that esterify hydroxyl groups and the resulting esters have a much higher volatility and can be measured in gas chromatographs with greater ease. We found, however, that the silylation reaction procedure is very exacting and time consuming. Several months of experimental efforts

yielded very few results.

A much more practical approach proved to be direct measurement of the compound using a column design and substrate with which resorcinol exhibits a suitable retention time. For resorcinol, a satisfactory contribution was a four foot by 3/16" OD stainless steel column packed with 80/100 mesh chromosorb W AW/DHCS coated with 1% SP-1000. Carrier gas flow rates of 40 ml/min. of N_2 with a column temperature of 195°C. Ten μ l samples were used with the injector at 225°C and the detector at 260°C; 25 ml/min. of H_2 and 250 ml/min. of air were used in the flame ionization detector. Preliminary experiments indicate that this combination is useful for hydroquinine and catechol. We plan to use the direct analytical approach for all compounds if at all possible.

One persistent problem with direct analysis is the question of sensitivity at low concentrations (Figure 3). We have found it necessary to evaporate and concentrate the more dilute solutions in order to achieve satisfactory base line performance on the chromatograph. A commercial thin-film evaporator designed to do this job would increase accuracy of analyses in this important concentration region; therefore \$800 has been added to the budget for purchase of one of these items.

The distribution coefficients of resorcinol were measured in di-isopropyl ether, n-butyl acetate, octanone-2, octanol, chloroform and hexane (Table 2 and Figures 3 to 6). Resorcinol is almost insoluble in both hexane and chloroform although the latter is a quite polar solvent. Obviously strong hydrogen bonding through the hydroxyl group occurs in solutions of resorcinol.

The values for the distribution coefficients in n-butyl acetate were about 15% less than reported in the literature. If the straight line shown on Figure 3 is taken as correct, the standard deviation of the measurements

is 3.0 and the standard error of the mean is 0.097. Daily calibrations were used to eliminate systematic error.

The only other distribution coefficient for resorcinol found in the literature is a value of 15.2 given for methyl isobutyl ketone. We found a much higher value of about 40 for methyl heptyl ketone (octanone-2). It will be interesting to try to rationalize the influence of structure that causes this large an effect on the distribution coefficient. The results of this series of measurements exemplify that very highly efficient solvents for this extraction process may be found; much will depend on the results found using this on similar solvents for other solutes.

3. Budget

The principal investigator spent approximately 20% of his time during the academic year (9 months) and 83% of his time during the summer (3 months) on this project. In the future is projected that approximately the same fractions of time will be spent.

Funds were also requested last year to support a graduate assistant. For the future, funds for part-time support of a technical assistant in addition to the graduate assistant are requested.

4. Future Work

We are hopeful of attaining the principal goals of this research with respect to the analyses and prediction of activity coefficients. Economic analyses of overall extraction process designs will be further developed and improved. We can see the need for future studies:

- (a) Enhancement of separation by pH control;
- (b) Enhancement of separation by use of other additives;
- (c) Chemical and economic problems in separation of recovered pollutants.

Figure 1 - Distribution coefficients for phenol between water and di-isopropyl ether as a function of equilibration time. Final concentration 225 mg/l of phenol in H_2O ; temp. = 25°C.

2.

Figure 2 - Distribution coefficients for phenol between water and di-isopropyl ether (25°C).

Figure 3 - Distribution coefficients for Resorcinol between water and n-butyl acetate (25°C). Literature value for K_{ow} = 9.9.

K_D FOR RESORCINOL IN n-BUTYL ACETATE

Figure 4 - Distribution coefficient for Resorcinol between water and diisopropyl ether (25°C).

K_D FOR RESORCINOL IN ISOPROPYL ETHER

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Figure 5 - Distribution coefficient for Resorcinol between water and 2-octanone (25°C).

K_D FOR RESORCINOL IN 2-OCTANONE

Figure 6 - Distribution coefficient for Resorcinol between water and octanol (25°C).

K_D FOR RESORCINOL IN OCTANOL

Table I - Distribution Coefficients Measured for Phenol
between Di-isopropyl Ether and Water (25 C),
Calibration Experiments

Initial Aqueous Conc mg/l	Final Aqueous Conc mg/l	Distribution Co- efficient K_D (weight)
5000	237	29.1
5000	215	32.1
5000	225	30.7
5000	205	33.6
5000	228	30.2
5000	227	30.4
5000	218	31.6
5000	203	34.0
5000	235	29.3
5000	240	28.7
5000	233	29.6
5000	236	29.2
5000	213	32.4
5000	220	31.3
250	12.5	27.6
250	8.8	34.2
250	12.5	27.6
250	13.8	25.0
250	11.2	30.8
250	9.3	37.1
250	9.0	38.3
250	10.7	32.2
250	11.4	30.2
5000	214	32.2
5000	205	33.6
5000	207	33.3
5000	204	33.8
5000	211	32.7
5000	212	32.5
250	11	31.3
250	10	34.5
250	10	34.5
250	12	28.7

Table 2 - Distribution Coefficient Data For Resorcinol And Various Solvents

Solvent	Initial Conc mg/l	Final Conc mg/l	K_D weight ratio
n-butyl acetate	5048	680	7.38
	5048	760	6.48
	2382	320	7.40
	5048	630	8.05
	2382	270	8.99
	837	97	8.77
	359	46	7.82
	5048	660	7.64
	2382	290	8.29
	837	96	8.87
	359	53	6.64
	5048	630	8.06
	2382	275	8.80
	837	103	8.18
	359	47	7.63
di-isopropyl ether	116	35	3.16
	116	40	2.60
	1612	635	2.11
	905	380	1.89
	590	245	1.93
	2576	1010	2.12
	2576	1000	2.16
	590	235	2.07
	590	220	2.30
	336	125	2.32
	336	120	2.47
	2576	1100	1.83
	1612	645	2.06
	905	380	1.89
	336	116	2.60
	1612	650	2.03
	905	370	1.99
	590	220	2.30
2-octanone	8475	400	24.3
	8475	370	26.4
	5725	190	35.1
	5725	270	24.3
	8475	360	27.1
	5725	260	25.3
	2410	80	35.1
	5725	230	28.8
	2410	77	36.5
	2652	79	37.9
octanal	2250	310	7.54
	2250	305	7.60
	952	155	6.19
	952	150	6.43
hexane	350	360	0
	350	365	0

Table 2 (cont.)

Solvent	Initial Conc mg/l	Final Conc mg/l	K_D weight ratio
chloroform	10075	9992*	.008
*organic layer analyzed			
cyclohexane	500	505	0

Appendix I: Assessment of Solvent Extraction for Treatment of Coal Gasifier Wastewater

This report was prepared as part of the tasks outlined in the proposal. Originally submitted in January, 1977, it has been extensively revised for the present work. Nonetheless, the report is still not in final form, there are a number of design configurations that must be investigated.

Assessment of Solvent Extraction
for Treatment of Coal Gasifier Wastewater

Preliminary Cost Evaluations

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Abstract

Coal gasification plants pose a serious environmental problem with waste water that is contaminated with mono- and poly-substituted phenols cresols, naphthols and with pyridines and indenols. The toxic nature of these materials causes difficulties in biological removal processes. Solvent extraction has promise of being an economic abatement alternative which also allows recovery of the contaminants which are valuable chemicals.

An optimal economic process design requires accurate distribution coefficient data not only for the design itself but also to allow selection of the most propitious solvent. The contaminants are polar and associative, however, and form very non-ideal solutions in almost all solvents. There is a need for experimental activity coefficient data for these compounds particularly in a variety of solvents as would be utilized for process evaluations.

A dual solvent extraction process has been described (Earhart, et al, 1976) that is very effective in the recovery of phenol, cresols and xylenols. The processing cost, including capital costs, is \$2.50/1000 gal of effluent water while the market value of these pollutants in a typical coal gasifier wastewater is in excess of \$25.00/1000 gal of effluent.

Other pollutants that are present have a value in excess of \$20.00/1000 gal. If the proper solvents can be found, it is evident that solvent extraction of these materials is also economically feasible.

Introduction

The construction and operation of large coal gasification plants poses a serious environmental challenge in the form of contaminated wastewater. In the Bureau of Mines Synthene process, for example, condensate water from a laboratory scale gasifier has been found to be heavily polluted by aromatic hydrocarbons (Schmidt, Sharkey and Friedel, 1974). Since the volume of this stream is so large, about 120 gallons per ton of coal gasified (Forney et al, 1974), a full-scale gasification process may easily produce a million gallons per day of wastewater contaminated by phenol, cresols, dihydroxy-phenols, indenols, pyridines, naphthols, and other pollutants.

The Bureau of Mines has quantitatively analyzed these contaminants as they occur in the condensate during the gasification of a variety of coals. The maximum concentrations of the various components found in gasifier wastewaters is given in Table 1.

Removal Methods

The principal techniques that are being employed to control dissolved organics may be divided into two groups -- those that degrade the pollutants into substances suitable for the environment and those that permit the recovery of the valuable wastes as products or for recycle. The former include biological oxidation and destructive chemical oxidation; in the latter category are adsorption processes and solvent extraction.

a. Chemical Oxidation

The destructive chemical oxidation of organic contaminants in wastewater is a relatively uncommon treatment scheme because of generally unfavorable economics. Among the many oxidizing agents available (such as ozone, potassium permanganate, and assorted forms of chlorine) ozone

TABLE 1 Pollutants in Coal Gasifier Wastewater

phenol,	4480 mg/l;
cresols,	3580 mg/l;
xlenols,	1170 mg/l;
pyridines,	580 mg/l;
dihydroxy benzenes,	540 mg/l;
naphthols,	290 mg/l;
indenols,	110 mg/l.

appears to be superior for the oxidation of dissolved organics. It may be readily generated at any location, it is an extremely powerful oxidant, and it leaves no permanent residual in the treated water. However, consideration of the quantity of ozone required indicates that minimal costs would be \$20-25 per 1000 gal. for oxidation of phenol alone. This figure could increase drastically when the solubility and kinetics of the oxidation reaction were considered. Potassium permanganate treatment is reported to cost \$0.05 to 0.15 per mg/l phenol per 1000 gal of wastewater so that treatment of these wastes would cost \$225/1000 gal. While chlorine treatment is cheaper, the residual products are both distasteful and potentially harmful (Rosfjord et al, 1976). For these reasons, destructive chemical oxidation processes will not be considered any further in this report.

b. Biological Oxidation

Biological oxidation is often the least expensive treatment process in an operational context, by which dissolved organics can be reduced to the required levels. Certain toxicity problems can arise from these contaminants however, that make it difficult to maintain an active bacterial sludge. McKinney, Tomlinson, and Wilcox (1956) found that activated sludge acclimated to phenol was able to metabolize phenol, o-cresol, m-cresol, p-cresol, benzoic acid, p-hydroxybenzoic acid, and benzaldehyde successfully, but was unable to similarly metabolize catechol. Under other substrate conditions, Warburg studies revealed that sludges acclimated to phenol or benzoic acid were unable to metabolize hydroquinone. No investigations were made of cases in which the concentration of phenolics exceeded 500 mg/l.

There are several other operational problems that hinder the application of biological oxidation to wastewaters contaminated by phenolic

derivatives. The more severe of these include loading fluctuations, the bacterial production of organic acids (which must be neutralized), the maintenance of highly efficient oxygen transfer, and the maintenance of the proper balance of essential nutrients such as phosphorus. Nonetheless, the very possibility of so inexpensive a process as biological oxidation dictates that costs associated with any other treatment must be kept very low. One distinct mode of operation would be a pretreatment by a recovery process followed by a polishing step of biological oxidation to reduce pollutants to low levels.

c. Adsorption

Among the recovery processes, adsorption has been used for some time to deal with dissolved organics. The basis for such separations relies upon the affinity of the organic solute for the solid surface at the liquid-solid interface. Traditional adsorbents such as activated carbon provide reversible physical adsorption for which the driving forces are electrochemical or are derived from the hydrophobic character of the organic molecule.

In the adsorption of dissolved organic materials, the rate-limiting step is either film or pore diffusion, depending primarily upon the hydrodynamic regime in which the adsorption is to take place. Typical rate constants predicted by Dedrick and Beckman (1967) for the adsorption of 2-4-dichlorophenoxyacetic acid on activated carbon is in the range of 0.02 to 0.06 hr^{-1} . Thus, to attain 70 - 90% of equilibrium, contact time would have to be on the order of 100 hours or more which would require formidable investment.

A number of studies of adsorption processes are available which do, however, show apparent feasibility (e.g., Baker et al, 1973; Crook, Mc-

Donnell and McHulty, 1975; Smith, Hiltgen and Juhola, 1959; Juntgen et al, 1974). Adsorption processes can generate sizeable credit for recovery of the organic contaminants but one important problem is frequently that the effluent problem is not wholly abated.

Solvent extraction becomes a preferred recovery process at higher concentrations of pollutants since flows and equipment size for extraction processes are relatively constant over a wide range of loading. This is in contrast with adsorption operating costs which increase along with investment costs with higher loadings since frequent regenerations become necessary. In addition, at moderate loadings, extraction may recover a wider range of products since many adsorption agents (such as resins) are specific for one, or perhaps a few, compounds. Nonetheless, physical adsorption remains a competitive alternative to solvent extraction as a recovery process.

d. Solvent Extraction

Solvent extraction operations have a long history in the coal and coke industries. Weak ammonia liquors in coke plants have been dephenolized by extraction with benzene since the early part of the twentieth century in this country (Crawford, 1926). In some German coke plants, tri-o-cresyl phosphate (or "triphos") has been used as a solvent for the extraction of phenolic compounds (Wilson and Wells, 1950). Coal gasification plants being considered for a New Mexico site by the El Paso Natural Gas Company will use the Lurgi Phenosolvan extraction process to remove phenolic compounds from gasifier condensate (Beychok, 1974). This process was developed about 40 years ago for dephenolization in coke plants; the solvent is isopropyl ether. On a weight basis, isopropyl ether provides a distribution coefficient for the solvent-phenol-water system of about 27.

Eddinger, et al. (1965) have suggested the possible use of butyl acetate as a solvent for the extraction and recovery of phenolic compounds produced by the COED process. The FHC performance report indicates that the recovery of the aromatics could have a beneficial effect upon process economics. In contrast with other available technologies, solvent extraction offers the possibility of the abatement of polluting discharges along with the recovery of valuable by-products from coal gasification.

Economic Factors

For economic operation of any solvent extraction process, regeneration and recycle of the solvent is essential. Recycle solvent processing equipment and energy requirements represent important cost elements for the extraction process so that solvent circulation volume must be minimized. The importance of the distribution coefficient in solvent extraction operations may be very roughly assessed using a method described by Sawyer and McCarty (1967). To attain a decontamination factor of 10^4 , the equation

$$10^4 = \frac{1}{\left(\frac{KS}{W} + 1\right)^n} \quad (1)$$

must approximately hold true. In this expression, W is the volume of wastewater per extraction stage, S is the volume of fresh solvent used in each consecutive extraction, K is the constant distribution coefficient, and n is the number of extractions required. It is apparent that a large distribution coefficient is necessary to minimize the solvent-to-wastewater ratio while maintaining high extraction efficiency.

Another source of substantial expense in solvent extraction processes is the dissolved solvent remaining in the wastewater after treatment. This loss can become particularly important in a process for coal gasifier

wastewater since in general relatively polar solvents are most effective for the type of pollutants present. These same polar solvents tend to have relatively high water solubility.

It is possible to recover much of the solvent dissolved in wastewater by stripping. However if gas stripping is used, a relatively expensive process for condensation of the solvent from the gas stream is required. With steam stripping a large cost for heating the wastewater is incurred. If the solvent is highly volatile with the process perhaps operating at some moderately small pressure, then a low residual level of solvent in wastewater may be expected. A highly volatile solvent is also advantageous in the separation of solvent from the solutes (recovered pollutants) since this reduces the need for reflux in a separation column thereby minimizing energy requirements. A low heat of vaporization is, of course, also advantageous in the solvent recovery-for-recycle process. Both low solubility and low heats of vaporization could be expected of non-polar solvents.

The Dual Extraction Process

The conflicting requirements of the solvent needing a high affinity for polar pollutants but a low residual solubility in water have prompted design of dual solvent extraction process (Earhart, et al, 1976). In this process, shown in Figure 1, the wastewater is first contacted countercurrently with a polar solvent and then in a second countercurrent extractor with a volatile non-polar solvent. The solvent streams leaving both extractors are sent to separate distillation columns, with pollutants being recovered and the separated solvents being recycled to the appropriate extractors.

The key to economical operation of this scheme is that in addition to having a good pollutant-to-solvent distribution coefficient for the polar solvent, and good thermal and water solubility properties of the non-polar solvent, the distribution coefficient for the polar solvent in the non-polar solvent must also be high. Fortunately there are a number of sets of solvent pairs meeting this latter criteria.

The feasibility of the sequential extraction process was demonstrated on a tube-oil wastewater containing phenolic pollutants (Earhart, 1975; Earhart, et al, 1974). The polar solvent was n-butyl acetate and the non-polar was isobutylene. The data shown in Table 2 demonstrates that at 0.1 solvent-to wastewater ratio (for each solvent), 99+% of the phenol and o-cresol was recovered and about 70% of methylethyl ketone. By increasing the S/W ratio for n-butyl acetate, the recovery of methyl ethyl ketone was increased to 88%. Note that n-butyl acetate losses were very low. Isobutylene losses are also low since its solubility in water is 0.053% (Earhart, 1975); the loss is about 3¢ per 1000 gal.

Economic Analysis of Dual Extraction

A detailed study of investment and operating costs associated with the dual extraction process was made by Earhart (1975). With some modifications his design programs were adopted here to evaluate economic process feasibility.

It is apparent from Table 1 that a whole gamut of impurities rather than a single substance must be removed from the waste water. This complicates economic design consideration; a process or solvent that is optimal for one component may be far from optimal for another. Furthermore the process is relatively complex and is amenable to a number of modifications that can have important effects on the economics. For example, large quantities of steam are used in the distillation for solvent recovery. Distillation

TABLE 2 SEQUENTIAL EXTRACTION OF WASTEWATER FROM LUBE-OIL REFINING USING BUTYL ACETATE (S/W = 0.100 and 0.30) AND ISOBUTYLENE (S/W = 0.101); RDC EXTRACTOR (Earhart et al, 1976)

Component	K_D	<u>Butyl-Acetate Extraction</u>			K_D	<u>Isobutylene Extraction</u>			Overall % Removal
		<u>Concentration (ppm)</u>		% Removal		<u>Concentration (ppm)</u>		% Removal	
		<u>Feed</u>	<u>Product</u>			<u>Feed</u>	<u>Product</u>		
<u>A. S/W for Butyl-Acetate Extraction = 0.100</u>									
Methylethyl Ketone	4.6	12,200	5900	52	2.5	5600	3600	36	69
Phenol	65	8,800	104	98.8	0.7	310	230	26	99.1
o-Cresol		890	6.5	99.3	4.8	24	2.3	91	99.9
n-Butyl Acetate		0	7100	--	168	7100	11.0	99.8	--
TOD		52,900	--	--		--	9350	--	82
COD		54,500	--	--		--	8570	--	84
<u>B. B/W for Butyl-Acetate Extraction = 0.30</u>									
Methylethyl Ketone	4.6	12,200	2500	82	2.5	2800	1890	33	88
Phenol	65	8,800	77	99.1	0.7	230	190	17	99.3
o-Cresol		890	4.3	99.5	4.8	18.0	2.8	84	99.9
n-Butyl Acetate		0	6800	--	168	6800	15.2	99.8	--
TOD		52,900	--	--		--	5110	--	90
COD		54,500	--	--		--	4690	--	91

columns can be designed with feed preheaters or side stream boilers so that most of this heat is supplied with low pressure steam rather than the more expensive high pressure steam in a reboiler. Other opportunities abound for energy conservation using heat exchange between various process streams.

The process must first of all be efficient in the recovery of the principal pollutant - phenol. We consider here design of a process for removal of 99% of the phenol. If the other pollutants are to be recovered also, a solvent or combination of solvents must be found that has a distribution as favorable as that for phenol. Alternatively a third extraction step could be introduced.

It was not possible at this stage of development to explore these many avenues of design. In fact, any final design depends greatly on the particular installation. Is excess low pressure, low cost steam available? What are temperature limits of cooling water? If the wastewater is to be reused, what temperature range must it be in (or may it be used for cooling water)?

We present here, however, evaluation of a relatively straight-forward design for removal of phenol. It will be seen that the economics are so overwhelmingly favorable when the value of recovered pollutants is considered that further detailed study of process alternatives is easily justified.

Capital Investment and Operating Costs

A schematic flowsheet is shown in Figure 1. The cost of the rotating disc contactors (RDC's) proposed for the extraction steps depends on many factors. The physical design parameters of the RDC must be optimized. These include column diameter, disc and stator diameters and rpm of the discs. Important physical properties of the solvent include boiling point and heat of vaporization which govern solvent recovery costs. In the extraction, properties such as density, viscosity and interfacial tension govern extraction

efficiency. However the most important single property is the solution distribution coefficient for the solute.

The variation of total capital investment as a function of scale and distribution coefficient is indicated in Table 3 and Figure 2. For these calculations the effect of changing the distribution coefficient was compensated by changes in the number of extractor stages only. In more detailed calculations, changes could be partially compensated by changes in the solvent-to-waste-water flow ratio and in operating characteristics of the RDC. It is to be noted that total investment cost for a process treating 1000 gpm is of the order of one-half million dollars and that the scale-up exponent factor is about 0.4.

Operating costs as a function of scale and distribution coefficient are given in Table 4 and Figure 3. Since the plant to handle 1000 gpm costs only about 2.5 times the plant designed for 100 gpm, charges associated with capital equipment are much less, proportionately, for the larger plant. Labor and laboratory charges are also much less per gpm for the larger plant. It was assumed $\frac{1}{2}$ man per shift could operate the smaller plant and $\frac{1}{2}$ man per shift would be needed for operation of the larger plant. Thus the operating cost and operating cost plus return for the larger plant is less than $\frac{1}{2}$ that of the smaller plant on a per gpm basis. Nonetheless even the total cost of \$1.35/1000 is quite a bit higher than the \$0.15/1000 gal. that is about average for a biological oxidation process. If only economic factors are considered, it is clear that a sizeable credit for recovered pollutants is necessary to justify the solvent extraction process.

	$KD_1 = 300$		$KD_1 = 55$		$KD_1 = 35$		$KD_1 = 25$	
	100 gpm	1000 gpm	100 gpm	1000 gpm	100 gpm	1000 gpm	100 gpm	1000 gpm
EXTRACTORS (2)	50	182	58	212	97	272	135	320
DISTILLATION (2)	48	134	48	134	48	134	48	134
HEAT EXCHANG (5)	41	128	41	128	41	128	41	128
PUMPS (8)	14	28	14	28	14	28	14	28
TANKS (2)	15	57	15	57	15	57	15	57
TOTAL (\$1000)	168	400	176	430	215	480	253	528

TABLE 3 Total capital investment for dual extraction processes. Major equipment costs include installation, associated piping, instrumentation, etc. (\$1000)

	$KD_1 = 300$		$KD_1 = 55$		$KD_1 = 35$		$KD_1 = 25$	
	100 gpm	1000 gpm	100 gpm	1000 gpm	100 gpm	1000 gpm	100 gpm	1000 gpm
Chemicals	18	180	18	180	18	180	18	180
Utilities	15	150	15	150	15	150	15	150
Capital Equip.	44	104	46	111	56	124	66	137
Labor, lab, etc.	40	80	40	80	40	80	40	80
Total (\$1000/yr)	117	514	119	521	129	534	139	547
\$/1000 gal	2.44	1.07	2.48	1.09	2.69	1.11	2.90	1.14
charges in \$/1000 gal for 25% return on investment	0.61	0.27	0.62	0.27	0.67	0.28	0.72	0.29

TABLE 4 Annual operating costs and cost/1000 gal. for dual extraction process (8000 hr/yr)

Justification of Extraction Processes

The high operational costs of the solvent extraction process must be offset by the value of recovered pollutants. The current values (Chemical Marketing Reporter, Dec. 1976) of pollutants in the previously cited coal gasifier wastewater are tabulated in Table 5. It was suggested by Earhart et al; 1976, that the value of recovered pollutants be taken at one-half market price to allow for purification costs and other associated expenses. (Also market values may be adversely affected by the availability of these recovered materials). Even so, it is evident that the recovery values far exceed previously discussed operating costs including a generous allowance for return on investment.

Previous studies have developed solvents and processes for extraction of phenol, cresols and xylenols (Beychok, 1974; Earhart, et al 1975; Wilson & Wells, 1950). Table 5 implies that the economics of these processes are very favorable.

Only meager information is available about distribution coefficients between water and organic solvents for the last five pollutants listed in Table 5. Yet it is clear that there is substantial economic motivation for recovery of these materials. Thus there is strong justification of a research project to develop solubility and activity coefficient data for these solutes in a variety of solvents.

Several options exist for recovery processes for these materials which can be explored further when the basic physical data becomes available:

- (1) A new solvent pair may be found which is efficient in extraction of all compounds listed.

Table 5.

Major Components of Coal Gasifier Wastewater
(Values taken for lowest purity reported in Dec. 1976
Chemical Marketing Reporter)

<u>Pollutant</u>	<u>Concentration</u>	<u>Value</u>	
		<u>\$/lb. pollutant</u>	<u>\$/1000 gal.</u>
Phenol	4480	0.26	9.71
Cresols	3580	0.41	12.24
Xylenols	1170	0.42	4.10
Pyridines	580	2.66	12.87
Dihydroxy Benzenes	540	1.10	4.95
Napthols	290	0.75	1.81
Indenol	110	1.00 (Est.)	0.92
			<u>\$46.60</u>

- (2) A solvent pair that is efficient for phenol, cresols and xlenols may have low effectiveness for the other solutes. In this case sufficient economic justification exists to consider a three stage extraction process. The third solvent could provide sufficient flexibility to recover all products. A third unit would add about another 50% to the costs listed in Table 3.
- (3) Another possibility is to find a chemical agent to improve solubility relationships in solvent systems. For example it has been reported (Beychok, 1967) that pyridines form a loose combination with phenols that results in a very favorable distribution ratio between water and benzene. Thus recovery of the pyridines may be simpler than would be suggested by distribution coefficients of pure materials alone.

Similarly the recovery of some of the other pollutants may also be enhanced by an agent that alters distribution ratios. It is desirable that such additives be cheaper and less of a pollution problem than the pyridines. Furthermore subsequent separation costs of the recovered materials may be increased by this procedure.

Conclusion

These studies indicate that the serious problem of pollution abatement of this wastewater can be solved with an extraction processing scheme that is profitable to operate. A full process design that would determine more precise economics as well as determine whether complete abatement standards can be achieved depends upon experimental definition of solubility equilibrium constants. However, it would appear that even in the case of incomplete abatement, a profitable recovery process could reduce interfering compounds to a level where bio-oxidation could complete the clean-up.

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Figure 1 Dual Solvent Process (Separate Solvent Cycles)

FIGURE 3 OPERATING COSTS OF DUAL EXTRACTION PROCESS INCLUDING 25% RETURN ON INVESTMENT (BEFORE TAXES)

FIGURE 2 INVESTMENT COST OF DUAL EXTRACTION PROCESS

FIGURE 3 OPERATING COSTS OF DUAL EXTRACTION PROCESS INCLUDING 25% RETURN ON INVESTMENT (BEFORE TAXES)