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To be presented at the American Institute of Chemical
Engineering Conference, Philadelphia, PA, June 8-12, 1980

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February 1980

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Solvent Extraction of Phenols from Water

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Abstract

Methyl isobutyl ketone (MIBK) and diisopropyl ether (DIPE) have been evaluated as solvents for extraction of phenols, at high dilution, from water. Equilibrium distribution coefficients (K_D) have been measured for phenol, dihydroxybenzenes and trihydroxybenzenes in both solvents as a function of pH. Particularly for the multihydric phenols, MIBK gives substantially higher values of K_D than does DIPE. The effect of pH can be described quantitatively through a simple ionization model, using published values of dissociation constants for the various phenols.

Some method for removal of residual dissolved solvent must ordinarily be included in any extraction process for phenols. Possibilities include atmospheric-steam or inert-gas stripping, vacuum-steam stripping, and extraction with a second solvent. Vacuum-steam stripping is a particularly attractive choice for removal of MIBK; this reinforces the utility of MIBK as a solvent. The optimal temperature for vacuum stripping is generally the temperature of the extraction operation, which in turn is related to the effect of temperature on K_D . Values of K_D for phenol-water-MIBK were determined at 30°, 50°, and 75°C, and were found to decrease with increasing temperature at all concentrations.

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- Presented at Philadelphia meeting, American Institute of Chemical Engineering, June 1980.

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Introduction

Phenols appear in aqueous streams from many industrial processes, including petroleum refining and petrochemical manufacture (Earhart, et al, 1977) and coking (Würm, 1968). Phenols are also the principal organic constituents in condensate waters formed during coal gasification and liquefaction (Ho, et al, 1976; Singer, et al, 1977). Often the concentration of phenols in such streams is high enough to warrant recovery, as opposed to degradation. Also, a high and fluctuating concentration of phenols can make treatment by biological treatment difficult.

Among recovery processes, solvent extraction is generally preferable over steam stripping for removal of phenols, since the phenol-water system forms an azeotrope at 9.2 wt. % phenol. Benzene, tricresyl phosphate and butyl acetate have been used as solvents for extraction in the past, but the most common solvent at present is diisopropyl ether (DIPE), which is used in the Phenosolvan process (Würm, 1968; Beychock, 1974). Another recent process (Laurer, et al, 1969; Mulligan & Fox, 1976), licensed by Chem-Pro Equipment Corp., appears to use methyl isobutyl ketone (MIBK) as solvent.

Dihydric phenols (dihydroxybenzenes) appear in concentrations of hundreds or even thousands of ppm in condensate waters from coal-conversion processes (Singer, et al, 1977; Exxon Research & Engineering Co., 1976; Lowenstein-Lom, et al 1947) and probably are present in other phenolic waters, as well. However, until recently most analyses of phenolic waters have not reported these substances specifically, because the colorimetric generic test for phenols does not identify them separately and because they are difficult to pass through a gas chromatograph. Trihydric phenols would also be expected, but are still more difficult to analyze. Using reversed-phase HPLC, Greminger and King (1979) found 600 ppm of a trihydric phenol, phloroglucinol, in an aged condensate water from the SRC (Solvent-Refined Coal) liquefaction process. The polyhydric phenols are more difficult to extract because of their increased affinity for water. Many also

form strong color bodies, when exposed to air at the high pH of most condensate waters. Furthermore, the trihydric phenols are extremely resistant to biological oxidation (Chambers, et al, 1963).

Coal-conversion process condensates contain a large amount of dissolved ammonia and carbon dioxide, by virtue of which the pH typically lies between 8 and 9.8. The waters are also highly buffered. At such high values of pH a significant fraction of phenols can be ionized, further discouraging extraction. Treybal (1963) gives a simple model for a weak acid distributing between organic and aqueous phases, with dissociation occurring in the aqueous phase:

$$K_{D, \text{ apparent}} = \frac{K_{D, \text{ low pH}}}{\frac{K_a}{[H^+]} + 1} \quad (1)$$

Here K_D is the equilibrium distribution coefficient (wt. fraction in organic phase/wt. fraction in aqueous phase), K_a is the acidic dissociation constant, and $[H^+]$ is the molar hydrogen ion concentration. Values of K_a , taken from the work of Körtum, et al (1961), are shown in Table 1.

Common polar solvents have an appreciable solubility in water--of order 1%--and must somehow be removed and recovered. Stripping with steam at atmospheric pressure is expensive. The Phenosolvan process uses a complex, three-tower, inert-gas stripping system, and Earhart, et al (1977) have proposed using a volatile hydrocarbon solvent to extract residual polar solvent. Rasquin, et al (1978) have shown that vacuum steam stripping can be attractive for removal of organic substances which fall within certain ranges of volatility and solubility.

The objective of the present work was to measure equilibrium distribution coefficients for di- and tri-hydric phenols from water into DIPE and MIBK, to measure the effects of temperature and pH upon K_D , and to assess the attractiveness of vacuum steam stripping for recovery of residual solvents from water. The results lead strongly toward the use of MIBK as a preferred solvent, with recovery of residual MIBK by vacuum steam stripping.

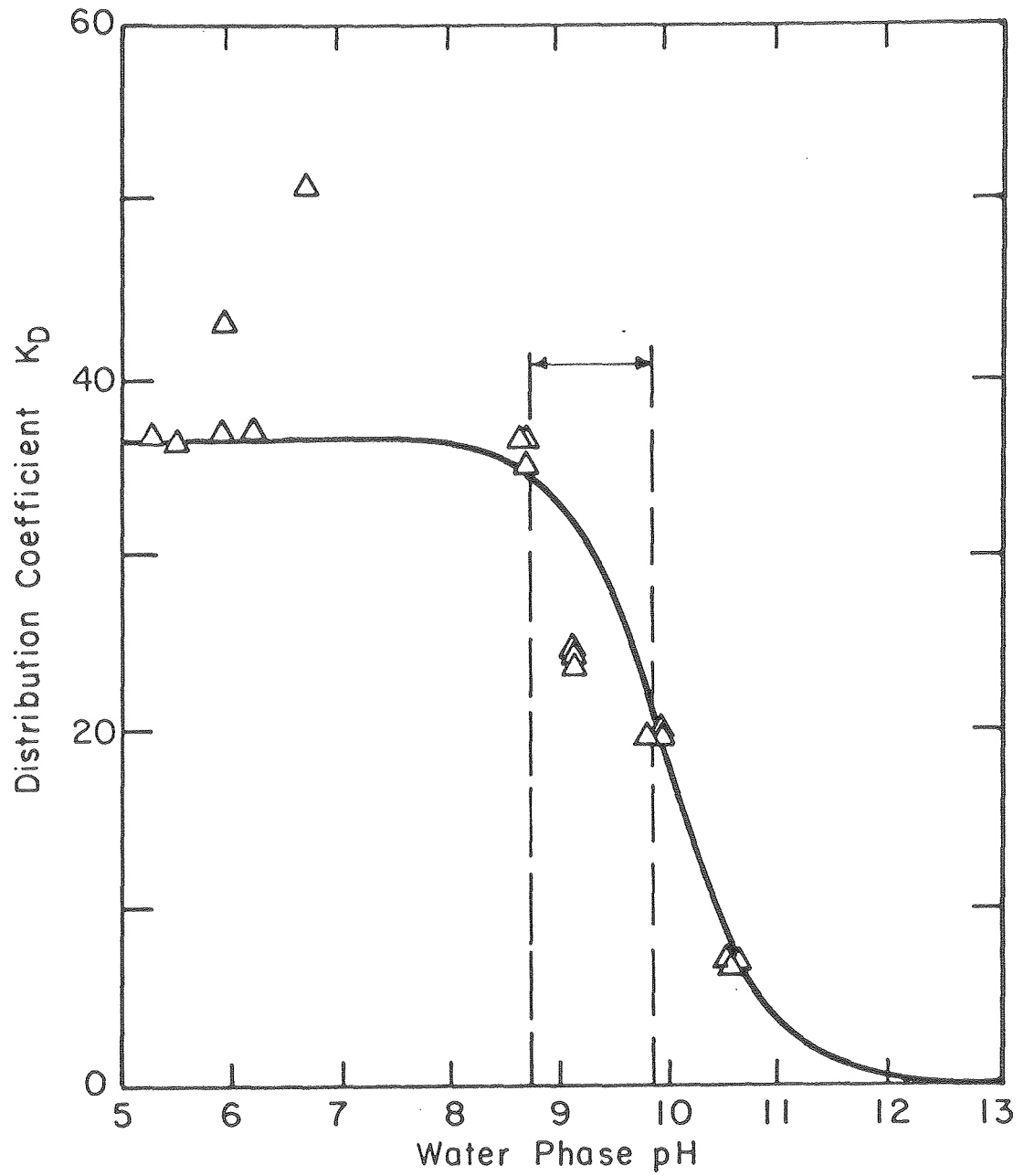
Experimental

Apparatus and Procedure

Batch extractions of the phenols were performed under nitrogen in a constant-temperature bath. The single-component feed solutions were sparged with nitrogen to strip out oxygen, which oxidizes phenols rapidly in basic solution. The pH was adjusted by the addition of KOH, and was monitored with a Corning Model 10 pH meter. Phenol solutions were analyzed with a Varian Model 1740 gas chromatograph equipped with a flame-ionization detector and a 3.18 mm x 2.4 m stainless steel column packed with Porapak Q (Waters Associates), operated at 240°C. Solutions of polyhydric phenols were analyzed with an isocratic liquid chromatograph consisting of a Spectra Physics Model 740 pump, a Waters Associates Model 440 UV absorbance detector operated at 254 nm, and a Waters Associates Model 27324 reverse-phase μ Bondapak C₁₈ column. The mobile phase used was 25 vol. % methanol in water, buffered to pH 3 by the H₃PO₄/KH₂PO₄ system. Additional details are described elsewhere (Greminger and King, 1979).

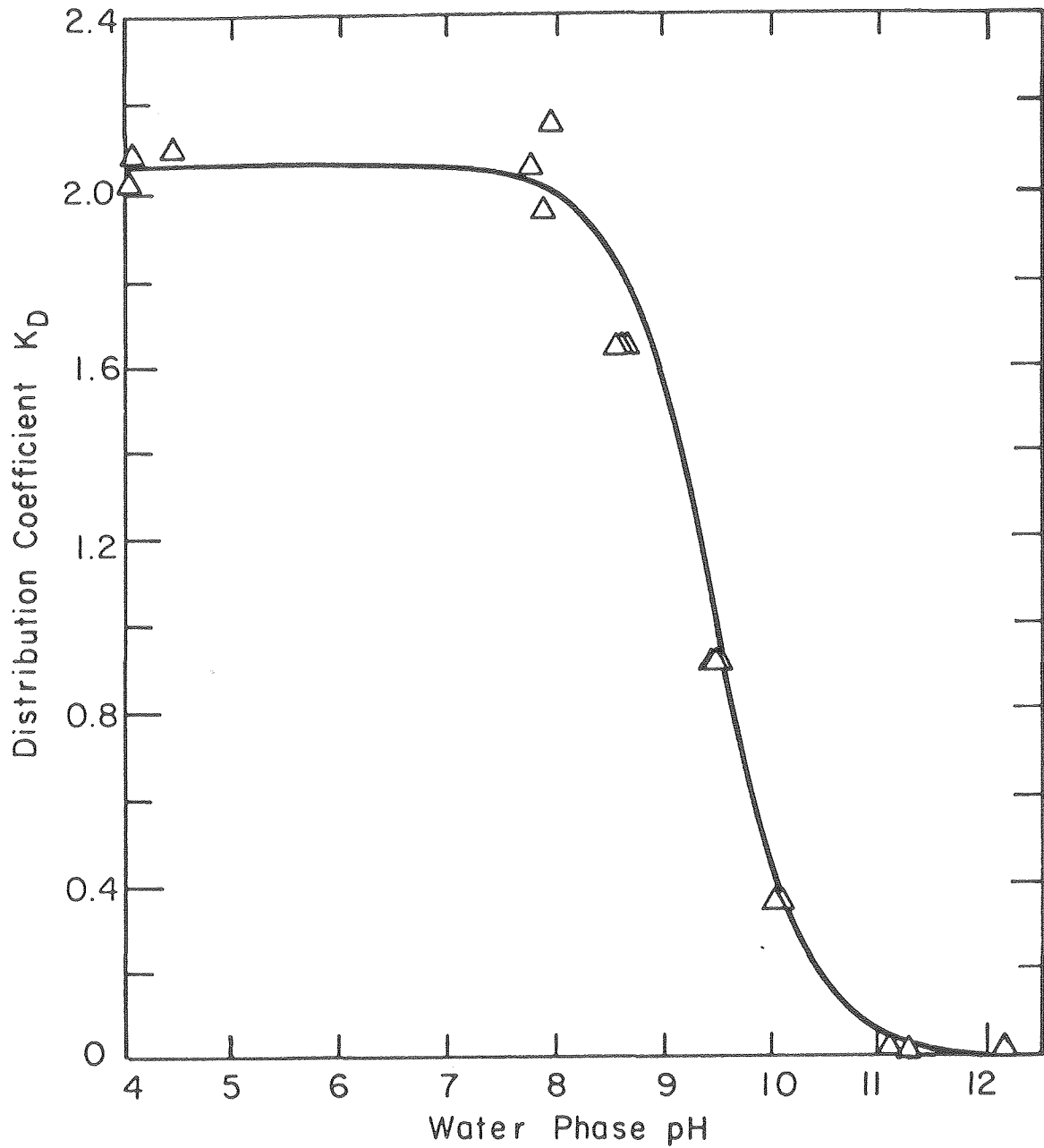
Effect of pH

Figures 1 and 2 show the experimentally measured distribution coefficients as a function of water-phase pH for phenol and resorcinol, respectively, distributing between DIPE and water. The curves are calculated from the model given by Equation 1, using the value of K_D measured at low pH as a single adjustable parameter, along with the values of K_a listed in Table 1. The model fits the data well. Effects of concentration and ionic strength on activity coefficients are ignored in the model, and the analytical methods used are not precise enough to detect these small effects experimentally.



XBL 795-6298

Figure 1. Distribution Coefficient for Phenol Between Diisopropyl Ether and Water as a Function of pH at 298°K. Curve from Equation 1 with $K_D = 36.5$, $K_a = 1.05 \times 10^{-10}$.



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Figure 2. Distribution Coefficient for Resorcinol Between Diisopropyl Ether and Water as a Function of pH at 298°K. Curve from Equation 1 with $K_D = 2.06$, $K_a = 3.36 \times 10^{-10}$.

K_D Values for Polyhydric Phenols

Measured values of K_D at low pH are presented in Table 1 for phenol, the three dihydric phenols, and the three trihydric phenols, extracted into both DIPE and MIBK. Aqueous solute concentrations were in the range 1500-3000 ppm. Fuller details are presented elsewhere (Greminger & King, 1979).

From the results it can be seen that MIBK gives much higher values of K_D than DIPE, especially for the polyhydric phenols. If we use $K_D S/W \geq 1.4$ as a criterion for effective removal (King, 1980), a solvent-to-water mass flow ratio, S/W , ≥ 0.39 would be required for removal of trihydric phenols with MIBK at low pH, while $S/W \geq 0.14$ would suffice for dihydric phenols. For DIPE, on the other hand, $S/W \geq 1.4$ would be required to remove dihydric phenols effectively, and $S/W \geq 8$ or more would be required for trihydric phenols. These differences in solvent flow would have a large effect on process economics.

At high pH the solvent flows needed would be even larger, and can be obtained from values of K_D' apparent given by Equation 1, using the information given in Table 1. At high pH, phloroglucinol will be the most difficult phenol to remove of those listed, because of its lower value of pK_a .

Results from the present work are compared with those of previous investigators for phenol and the dihydric phenols, in Table 2.

It is also instructive to examine the K_D values in terms of the activity coefficients in the two phases. On the basis of measured solubilities (Walker, et al, 1931; Korman & La Mer, 1936), Tsonopoulos (1970) gives activity coefficients of 1.90, 0.61 and 4.3 (average value) for pyrocatechol, resorcinol and hydroquinone, respectively, at high dilution in water at 298K. Tsonopoulos and Prausnitz (1971) indicate that the best fit of reported vapor-liquid equilibrium data gives an activity coefficient of 64 for phenol at high dilution in water at 298K. The equilibrium distribution coefficient in terms of mole fractions, K_X , is simply the ratio of

the activity coefficient in the aqueous phase (γ_w^∞) to that in the organic phase (γ_s^∞). Since $K_D = K_X(M_w)/(M_s)$ at high dilution where M_s and M_w are molecular weights of solvent and water respectively, we have

$$\gamma_s^\infty = \frac{\gamma_w^\infty M_w}{K_D M_s} \quad (2)$$

Table 3 gives values of γ_s computed in this way for phenol and the dihydric phenols in the two solvents. The activity coefficients are all less than unity, indicating strong negative deviations from ideality. This results from the ability of the phenolic hydroxyl group to hydrogen-bond with the oxygen of the ether and the carbonyl group of the ketone. The hydrogen bond with the carbonyl oxygen is stronger, making MIBK the more effective solvent. Presumably the difference among dihydric phenols in γ_s^∞ within a given solvent results from steric factors.

Effect of Temperature

Since MIBK was shown to be the preferred solvent, the effect of temperature on K_D for phenol in this solvent was studied. The values of distribution coefficient found at 30°C, 50°C, and 75°C are shown in Figure 3 as a function of weight fraction phenol in the organic phase. The values of K_D are uniformly high, but are highest at low temperature, indicating that extraction at low temperature is desirable. Figure 3 also shows that K_D is highly satisfactory, e.g. $K_D=60$ at 30°C, even at phenol concentrations in the organic phase of 20% by weight. Values of K_D at higher phenol concentrations were not investigated since it is unlikely that such concentration levels would be achieved in the solvent, even for waste streams relatively rich in phenol. The solvent-to-water ratios required for satisfactory removal of di- and trihydric compounds, which would also be likely contaminants, would be such that concentration levels of phenol in the solvent would be relatively low. In addition, high levels of phenol concentration in the organic phase would probably induce increased water solubility. The water would ultimately have to be removed from the phenol and would increase the energy load of the process.

Data were also taken at the same temperatures to determine the mutual solubility of MIBK and water. The values obtained for weight fraction of MIBK in water are 0.0182, 0.0146, and 0.0137, and for weight fraction water in MIBK are 0.0204, 0.0244 and 0.0284 at temperatures of 30°C, 50°C and 75°C respectively. These values are in good agreement with the results of Gross, et al. (1939), Ginnings, et al. (1940), and Narasimhan et al. (1962). The values most important to the process are the solubilities of MIBK in water, which should be as low as possible in order to keep energy loads associated with solvent-recovery low. These data would appear to indicate that higher extraction temperatures are desirable. However, the effect is small and would be completely outweighed by the increase in solvent flow necessitated by the diminished K_D for phenol at higher extraction temperatures; energy loads stemming from the separation of the additional solvent from the phenol would be greatly increased. In sum, the extraction should be performed at low temperatures.

Vacuum Steam Stripping

Solvent recovery following the extraction operation can be achieved in different ways. The Phenosolvan process utilizes inert gas stripping followed by reabsorption of the stripped solvent by phenol and subsequent distillation of the mixture. The Chem-Pro process utilizes steam stripping at atmospheric pressure. The Phenosolvan process is low in operating costs but complex, the Chem-Pro process is relatively high in operating costs because of the energy supplied to the stripper, but is simpler.

If the steam stripping is more closely examined, it is apparent that the energy requirements can be held down by heat exchange of the bottom product, the stripped water stream, with the feed. A significant portion of the energy inevitably goes into heating the bottom product to the boiling point of water at column pressure, and this energy can be partially recovered in the exchanger. The energy finally lost in heating the water stream is thus essentially independent of the column pressure used, corresponding only to the temperature approach used in the exchanger. However, as column pressure is lowered sufficiently, say to the vapor pressure of water at feed temperature, the heat exchanger becomes unnecessary, and no energy is lost in this way. The water stream is heated only through

the temperature difference between the top and the bottom of the column. Since the feed to the stripper is coming from the extractor, and it is advantageous to operate the extractor at relatively low temperatures, the stripper must usually be operated under vacuum. Vacuum operation would normally require large column diameters to accommodate the vapor flow, but the vapor requirements of the strippers considered here are small, of the order of 0.02 moles/mole of feed. Under these conditions, the column size is determined by the liquid flow, and large column diameters are not necessary.

If, as occurs in many processes, the temperature of the wastewater stream is of the order of 70 to 80°C, the amount of low-grade energy available from the sensible heat of this stream is more than adequate for recovery of the dissolved solvent in the water stream leaving the extractor. Again, for efficient use of this energy, the solvent stripper must be operated under vacuum. The incoming waste water stream can then be used to reboil the stripper, and the energy load associated with solvent recovery can be reduced essentially to zero.

However, if vacuum operation is to be used effectively, a solvent having certain physical properties must be chosen. A practical lower limit on stripper pressure arises from the necessity to condense the overhead vapor from the stripper with cooling water. The condensed vapor will split into two liquid phases, water and solvent, and the condensate will exhibit the vapor pressure of a pseudo-azeotrope, or essentially the sum of the vapor pressures of water and solvent at cooling water temperature. If the vapor pressure of solvent is too high at this temperature, it will force the use of higher column pressure and will reduce the possible use of waste energy in reboiling the column. Di-isopropyl ether has an undesirably high vapor pressure whereas MIBK is a desirable solvent from this standpoint. In general, the solvent should have a boiling point of approximately 100°C, or somewhat higher.

Too high a solvent boiling point reduces the volatility of the solvent in the stripper. However, this is largely offset by the high activity coefficient for the solvent in the aqueous phase, a concomitant of low solvent solubility. Again, MIBK is satisfactory from this standpoint. Detailed calculations of a vacuum steam stripper

by Burns et al. (1979), show that the concentration of MIBK in water can be readily reduced from 15,000 ppm to 20 ppm in a packed tower six meters high operated at 72 torr (9.56 kN/m^2), with a steam flow of only 0.023 moles/mole of feed. Moderate increase in height would allow almost any degree of stripping at essentially the same steam flow.

Complete designs for the treatment of 115,000 kg/hr of a quench stream containing 15,800 ppm of phenol have been given by Burns et al. (1979) for the Phenosolvan, Chem-Pro, and MIBK extraction-vacuum stripping processes. Capital costs are comparable, $\$3.7 \text{ M}^2$, $\$3.0 \text{ M}^2$, and 3.3 M^2 respectively. Annual operating costs are also comparable, $\$1.8 \text{ M}^2$, $\$2.0 \text{ M}^2$, and $\$1.6 \text{ M}^2$ respectively, but clearly show the benefit obtained from use of the waste energy of the process stream to accomplish solvent recovery.

Acknowledgement

One of the authors (D.C. Greminger) received partial support from a Domestic Mining, Mineral Resource and Mineral Fuel Conservation Fellowship from the U. S. Department of Health, Education and Welfare. This work was also supported by the U. S. Department of Energy under Contract W-7405-ENG-48.

Table 1. Extraction of Phenols from Water, 298K

Solute	pK_a^*	into DIPE		into MIBK	
		pH	K_D	pH	K_D
Phenol	9.98	5.56	36.5	ND	~ 100 (303K)
Pyrocatechol (1,2-dihydroxybenzene)	9.48**	5.88	4.86	4.18	18.7
Resorcinol (1,3-dihydroxybenzene)	9.47**	4.16	2.06	4.21	17.9
Hydroquinone (1,4-dihydroxybenzene)	10.1**	5.17	1.03	3.88	9.92
Pyrogallol (1,2,3-trihydroxybenzene)	9.01	ND	ND	4.52	3.58
Hydroxyquinol (1,2,4-trihydroxybenzene)	NA	4.64	0.181	4.24	5.01
Phloroglucinol (1,3,5-trihydroxybenzene)	8.44	ND	ND	4.53	3.92

* - $\text{pK}_a = \log_{10} (\text{K}_a)^{-1}$. pK_a is also the value of pH at which the solute is half ionized.

** - interpolated from data at other temperatures.

ND - Not determined

NA - Not available

Table 2. Comparison of Values of K_D at Low pH and High Dilution for Phenol and Dihydric Phenols.

(Temperature = 298K, unless noted otherwise)

	<u>Phenol</u>	<u>Pyrocatechol</u>	<u>Resorcinol</u>	<u>Hydroquinone</u>
<u>Solvent = DIPE</u>				
Present Work	36.5	4.86	2.06	1.03
Korenman (1972)	40*	5.8*	2.6*	2.2*
Won & Prausnitz (1975)	33	-	-	-
Luecke (1979)	42	16.0	2.1	0.81
Kiezyk & Mackay (1971)	40	-	-	-
Pollio, et al (1967)	13.9	-	-	-
Lowenstein-Lom, et al (1947)	45*	16*	-	-
<u>Solvent = MIBK</u>				
Present Work	~100**	18.7	17.9	9.92
Won & Prausnitz (1975)	110	20.3	15.2	-
Lowenstein-Lom, et al (1947)	59*	18.6*	-	-

* - 293K

** - 303K

Table 3. Computed Values of γ_S^∞

<u>Solute</u>	<u>γ_S^∞</u>	
	<u>DIPE</u>	<u>MIBK</u>
Phenol	0.31	0.105
Pyrocatechol	0.069	0.018
Resorcinol	0.052	0.0061
Hydroquinone	0.74	0.078

References

- Beychok, M.R., "Coal Gasification and the Phenosolvan Process," pres. at 168th Natl. Mtg., American Chemical Society, Atlantic City NJ, September 1974.
- Burns, G.P., S. Lynn, and D.N. Hanson, "Energy Reduction in Phenol Recovery Systems," Report No. LBL 9176, Lawrence Berkeley Laboratory, December 1979.
- Chambers, C.W., H.H. Tabak and P.W. Kabler, "Degradation of Aromatic Compounds by Phenol-Adapted Bacteria," J. Water Pollution Control Fed., 35, 1517 (1963).
- Earhart, J.P., K.W. Won, H.Y. Wong, J.M. Prausnitz and C.J. King, "Recovery of Organic Pollutants via Solvent Extraction," Chem. Eng. Prog., 73(5), 67 (1977).
- Exxon Research & Engineering Co., "EDS Liquefaction Process Development, Phase IIIA," Quarterly Technical Progress Report, p. 153, July 1 - September 30, 1976.
- Ginnings, P.M., Plonk, D., and Carter, E., J. Am. Chem. Soc., 62, 1923 (1940).
- Greminger, D.C. and C.J. King, "Extraction of Phenols from Coal Conversion Process Condensate Waters," Report No. LBL 9177. Lawrence Berkeley Laboratory, June 1979.
- Gross, P.M., Rintelen, J.C., and Saylor, J.H., J. Phys. Chem., 43, 197 (1939).
- Ho, C.H., B.R. Clark and M.R. Guerin, "Direct Analysis of Organic Compounds in Aqueous By-Products from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification and COED Coal Liquefaction," J. Environ. Sci. Health, All, 481-489 (1976).
- Kiezyk, P.R. and D. Mackay, "Waste Water Treatment by Solvent Extraction," Canadian J. Chem. Eng., 49, 747-752 (1971).
- King, C.J., "Separation Processes," 2nd ed., p. 367, McGraw-Hill Book Co., Inc., New York, 1980.
- Korenman, Y.I., "Extraction of Dihydric Phenols," Zh. Prikl. Khim., 45, 2031-2034 (1972).
- Korman, S. and V.K. La Mer, "Deuterium Exchange Equilibria in Solution and the Quinhydrone Electrode," J. Am. Chem. Soc., 58, 1396-1403 (1936).
- Kortüm, G., W. Vogel and K. Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solution," Pure & Appl. Chem., 1 (2-3), 190-536 (1961).

Laurer, F.C., E.J. Littlewood and J.J. Butler, "Solvent Extraction Process for Phenols Recovery from Coke Plant Aqueous Wastes," Iron & Steel Engr., 99-102 (May 1969).

Lowenstein-Lom, V., B. Schnabel and V. Kejla, "The Phenosolvan Process," Petroleum, X(4), 82-84 (1947).

Luecke, R.H., "Assessment of Solvent Extraction for Treatment of Coal Gasifier Wastewater," in C.J. King, S. Lynn, D.N. Hanson and D.H. Mohr, eds., Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale and Biomass to Synfuels, Report in press, ECT/PECO/ASEV, U.S. Dept. of Energy, 1980.

Mulligan, T.J. and R.D. Fox, "Treatment of Industrial Wastewaters," Chem. Eng., 83(22), 49-66 (October 18, 1976).

Narasimhan, K.S., Reddy, C.C., and Chari, K.S., J. Chem. and Eng. Data, 7, No. 4, 457 (1962).

Pollio, F.X., R. Kunin and A.F. Preuss, "Extraction of Phenol from Water with a Liquid Anion Exchanger," Environ. Sci. & Technol., 1, 495-498 (1967).

Rasquin, E.A., S. Lynn and D.N. Hanson, "Vacuum Steam Stripping of Volatile, Sparingly Soluble Organic Compounds from Water," Ind. Eng. Chem. Fundamentals, 13, 170 (1978).

Singer, P.C., F.K. Pfaender, J. Chinchilli and J.C. Lamb III, "Composition and Biodegradability of Organics in Coal-Conversion Wastewaters," in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, III, Report No. EPA-600/7-78-063, U.S. Environmental Protection Agency, 461-486 (1978).

Tsonopoulos, C., Ph.D. dissertation in Chemical Engineering, University of California, Berkeley, 1970.

Tsonopoulos, C. and J.M. Prausnitz, "Activity Coefficients of Aromatic Solutes in Dilute Aqueous Solutions," Ind. Eng. Chem. Fundamentals, 10, 593-600 (1971).

Walker, W.H., A.R. Collett and C.L. Lazzell, "The Solubility Relations of the Isomeric Dihydroxybenzenes," J. Phys. Chem., 35, 3259-3271 (1931).

⑤ Won, K.W. and J.M. Prausnitz, "Distribution of Phenolic Solutes between Water and Polar Organic Solvents," J. Chem. Thermodynamics, 7, 661-670 (1975).

Wurm, H.J., "Recovery of Phenols from Coker Gas Liquor by the Phenosolvan Process," Glückauf, 104, 517-523 (1968).

