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Application of Supercritical Fluid Extraction in Industrial Waste Treatment: Thermodynamic Modeling and Design

CHRISTOS BOUKOUVALAS, KOSTIS MAGOULAS*,
and DIMITRIOS TASSIOS
LABORATORY OF THERMODYNAMICS AND TRANSPORT PHENOMENA
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TECHNICAL UNIVERSITY OF ATHENS
9, HEROON POLYTECHNIOU STR, ZOGRAPHOU CAMPUS, 15780 ATHENS, GREECE

ABSTRACT

The use of supercritical fluid extraction (SFE) as a separation process for the treatment of industrial wastewater is examined. The performance of the LCVM EoS/G^E model in thermodynamic modeling of the systems CO_2/H_2O/organic pollutant (aromatics, phenol, cresol), including the presence of a cosolvent, is evaluated. The design of a unit that processes the water/phenol system with carbon dioxide, with and without a cosolvent, is also examined. The use of a cosolvent is a very important parameter for the SFE process since it can cause a significant decrease in the total cost of the unit. Application of the process appears limited due to the lack of predictive models and the high cost of equipment.

INTRODUCTION

Supercritical fluid extraction (SFE) is a separation process that has attracted much attention lately in fields where the usual methods, e.g. distillation, extraction, desortpion, etc., either fail or are very expensive. As solvent, SFE utilizes gases such as carbon dioxide, ethane, and propane in supercritical conditions, i.e., an operating temperature just above the critical temperature and a pressure above the critical pressure. In such conditions the density of these fluids and their dissolving ability are similar

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* To whom correspondence should be addressed.

to the ones of the liquids, while at the same time they maintain a high diffusivity, a low viscosity, and a low surface tension similar to those of gases. As a result, their use as solvents makes SFE a much more efficient separation process than liquid–liquid extraction.

SFE has now found many applications in different fields such as polymers, aromatics and essential oils, fats, natural products, soil decontamination, chromatography, etc., and several production units are operated in the agro-food (e.g., separation of caffeine from coffee) and the pharmaceutical industries (1–3). Furthermore, its application to environmental problems, such as the removal of dangerous toxic organic compounds from wastewater or polluted soils, has been considered (4). As reported by the Environmental Protection Agency (EPA), there are at least 26,000 noncontrolled areas for the disposal of wastes currently in the United States (4). The characteristic feature of such areas is the pollution of water due to the transportation of dangerous organic compounds from the soil to the water, carried by rain water. Therefore, the removal of these compounds from the wastes has attracted much attention.

The methods applied so far for the treatment of polluted soil are burial and incineration. Burial is cheap and easy, but due the strict environmental rules it is no longer a solution. Incineration is technologically simple, but the large energy consumption, the disposal of ashes, the possibility of air pollution with dangerous compounds, and the significant amounts of carbon dioxide produced are very important handicaps.

The methods that have been applied to wastewater treatment are, apart from incineration, distillation and liquid extraction. The problems with incineration were previously mentioned. Distillation, especially of dilute aqueous solutions, demands a large amount of energy and is thus considered unattractive. Finally, liquid extraction is a good method to deal with the problem, but its application is limited because there are strict environmental rules for the concentration of many compounds, considered to be solvents, in water, and the recovery of solvents is a very energy-consuming process.

SFE can be applied to both these limitations because it utilizes nontoxic solvents that can be easily removed from the final product, and its energy consumption is low due to the relatively low operating temperatures employed. However, the few reliable experimental data that are available, the insufficient modeling, and the need for high-pressure equipment have not allowed for a broader application of the method.

Thermodynamic modeling of CO_2/H_2O/organic pollutant (aromatics, phenol, cresol) systems, including the presence of a cosolvent, is evaluated in this study. The results are then applied to the design of a unit for the treatment of an aqueous waste stream containing phenol.

THERMODYNAMIC MODELS

Equations of states (EoS) with conventional mixing rules and the recently developed EoS/excess Gibbs energy (EoS/G^E) models have been successfully used for the thermodynamic modeling of SFE. The main advantage of EoS/G^E is that the use of a group contribution G^E model, such as UNIFAC, transforms the developed model to a completely predictive tool. Of the latter, the LCVM model (5) is used in this work to evaluate its ability to predict and describe the equilibrium of solvent/(cosolvent)/water/pollutant systems.

For comparison, the conventional mixing rule developed by Panagiotopoulos and Reid, and applied in systems of interest in this study (6), is also considered.

The two models used in this study are briefly presented in the followings subsections.

The LCVM Model

The LCVM model is a recently developed EoS/G^E one [Boukouvalas et al. (5)], that couples the t-mPR EoS (translated and modified Peng–Robinson) [Magoulas and Tassios (7)] with the original UNIFAC G^E model [Hansen et al. (8)]. The EoS parameter b is given by the conventional linear mixing rule, while the parameter $\alpha (= a/bRT)$ is a *l*inear *c*ombination of the *V*idal and *M*ichelsen (LCVM) mixing rules, given by:

$$\alpha = \sum_i x_i \alpha_i + \left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M}\right)\frac{G^E}{RT} + \frac{1-\lambda}{A_M}\sum_i x_i \ln\left(\frac{b}{b_i}\right) \qquad (1)$$

with $\lambda = 0.36$, $A_V = -0.623$ and $A_M = -0.52$. A detailed description of the model development was presented by Boukouvalas et al. (5).

The LCVM model has been applied successfully to:

- VLE in systems containing polar compounds at high and low pressures (5)
- VLE in systems containing gases (CO_2, CH_4, C_2H_6, N_2, O_2, H_2S, CO, C_2H_4) with other compounds (gases, *n*-alkanes, aromatics, alcohols, etc.) (5, 9, 10, 11)
- VLE in synthetic gas condensates and oils (11)
- Henry constants (10)
- Infinite dilution activity coefficients (9)
- Solubilities of liquids and solids in supercritical fluids (9–12)

A thorough comparison between LCVM and the other EoS/G^E models [MHV2, Dahl et al. (13); PSRK, Holderbaum and Gmehling (14) and K.

Fischer (15); WS, Wong and Sandler (16)] was presented by Voutsas et al. (11). They showed that LCVM provides a successful vapor–liquid equilibrium (VLE) prediction of systems containing components with considerable size differences, where the other models fail, while it matches the performance of the latter ones in predicting the VLE behavior of (polar and nonpolar) systems with components of similar size at low and high pressures. In the same publication the updated interaction parameter table for use with LCVM is also presented.

The Panagiotopoulos–Reid Model (R–P)

For comparison, a model based on an EoS with a conventional mixing rule is also examined in this study: the Peng–Robinson EoS (PR EoS) with the modification of the mixing rule proposed by Panagiotopoulos and Reid (6). The normally used single interaction parameter K_{ij} in the energy parameter a is replaced by a linear function with the composition shown below:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

with

$$a_{ij} = (1 - K_{ij}) \sqrt{a_i a_j}$$

where

$$K_{ij} = (k_{ji} - k_{ij})x_i + k_{ij}$$

A significant improvement was observed in the representation of binary and ternary phase equilibrium data for highly polar and asymmetric systems. The results are presented for binary and ternary systems with water and supercritical fluids at high pressures, as well as for low-pressure nonideal systems (6).

DATA BASE

For the thermodynamic modeling of these systems, experimental data obtained from recent publications have been used. The references for binary system data have been presented in previous publications (5, 9–11). The references for the data of ternary and quaternary systems are presented in Table 1.

The data of Roop and Akgerman (2) have been published in a diagram. The accuracy of the numbers read from this diagram is not quite reliable. Therefore, they have not been used in the parameter estimation but only

TABLE 1
Data Base for Ternary and Quaternary Systems[a]

No.	CO_2/H_2O and A	B	C	D	E	F	Number of isotherms	T (K)	P (bar)	References
1	+						1	318	80–101	(17)
2		+					1	318	79–108	(17)
3			+				1	318	81–100	(17)
4				+			2	313, 323	97–172	(1)
5					+		2	313, 323	97–165	(1)
6	+						2	313, 323	97–165	(1)
7				+			2	298, 323	73–306	(2)
8	+			+			2	298	173, 276	(2)
9				+		+	2	298	173, 276	(2)

[a] A = benzene, B = toluene, C = naphthalene, D = phenol, E = *m*-cresol, F = methanol.

for comparison with the prediction results. The 323 K isotherm has not been studied in these data because the scattering in the diagram is significant and the values obtained are in disagreement with the data of Ghonasgi et al. (1).

THERMODYNAMIC MODELING

Binary Systems (parameters and results)

Interaction parameters for the original UNIFAC model used in LCVM are those reported by Hansen et al. (8). The CO_2 (group i)/group j interaction parameters needed in this study are available from previous publications (5, 9–12) and are of the form

$$\Psi_{ij} = \exp\left[-\frac{A_{ij} + B_{ij}(T - 298.15)}{T}\right] \tag{3}$$

with T in K. Values for A_{ij} and B_{ij} are presented in Table 2, and their performance for the corresponding binary system is summarized in Table 3 ($\Delta P\%$: average percent error in bubble-point pressure, Δy: average absolute error in vapor-phase concentration).

In order to use the R–P model in the prediction of the ternary equilibrium, the necessary interaction parameters for this model have also been calculated and are presented, along with the corresponding results, in

TABLE 2
Interaction Parameter Values for Use With LCVM Model (9)

i	j	A_{ij} (K)	B_{ij}	A_{ji} (K)	B_{ji}
CO_2	CH_2	110.60	0.5003	116.70	−0.9106
CO_2	H_2O	1120.07	−4.8883	249.48	2.3350
CO_2	ACH	−26.80	−1.2348	187.00	1.0982
CO_2	$ACCH_2$	175.70	−2.9577	87.40	0.3087
CO_2	ACOH	572.23	4.2682	128.02	−0.8018

Table 4. Notice that the results obtained, along with the parameters that are specific to each binary system, are no better than those obtained with LCVM where group interaction parameters are used.

Prediction of Ternary Equilibria

Flash calculations have been performed for prediction of the ternary equilibria. Only interaction parameters from binary data have been used in these calculations. The results for the two models are presented in Table 5 in terms of the absolute % errors in the predicted equilibrium ratios K of the pollutant in the ternary system, along with the results of PSRK, the successful EoS/G^E model.

The behavior of all three models is not satisfactory. Both EoS/G^E models (LCVM and PSRK) constantly underestimate the K values of the

TABLE 3
Performance of The LCVM Model with Binary Systems of Interest to This Study

CO_2 with	T range (K)	P range (bar)	$\Delta P\%$	$\Delta y \times 100$	Compounds
Alkanes	253–583	2–188	4.3	0.7	Alkanes from C_3 up to nC_{44}
Aromatics	273–423	6.2–154	4.2	1.8	Benzene, naphthalene, phenanthrene, pyrene, biphenyl
Alkyl-aromatics	311–423	3.3–221	6.6	0.5	Toluene, ethylbenzene, *o*-xylene, tetralin, *p*-xylene, *o*-xylene, *m*-xylene, 1-methylnaphthalene, 2-Methylnaphthalene
Phenols	308–473	10–240	3.7	—	1-Naphthol, 2-naphthol, *m*-cresol, catechol, phenol
Water	304–478	2–1500	6.2	0.2	Water

TABLE 4
Correlation Results and Parameter Values Obtained with the R–P Model.

i	j	k_{ij}	k_{ji}	T range (K)	P range [bar]	$\Delta P\%$	$\Delta y \times 100$
CO_2	Benzene	0.1136	0.0754	273–414	8.3–153.9	2.9	2.2
CO_2	*m*-Cresol	0.1322	0.0861	308–328	20.0–240.0	3.0	0.1
CO_2	Naphthalene	0.1890	−0.1913	373–473	10.1–104.5	20.0	0.7
CO_2	Phenol	0.0863	0.0541	348–398	10.1–50.6	2.3	0.1
CO_2	Toluene	0.0985	0.0840	311–422	3.1–152.9	4.4	0.5
CO_2	H_2O	0.0502	0.0195	473–623	100–1500	12.1	1.4
H_2O	Phenol	−0.0612	−0.0481	318–455	0.01–1.00	4.5	0.9
H_2O	Cresol	−0.0612	−0.0481[a]				
H_2O	Benzene	0.2600	−0.0240[b]				
H_2O	Toluene	0.2600	−0.1060[b]				
H_2O	Naphthalene	0.4000	−0.1100[b]				

[a] Data not available; parameters from H_2O phenol.
[b] Data not available; parameters from Yeo and Akgerman (17).

pollutant, while the R–P model usually gives extreme over predictions with errors greater than 100%. For the system CO_2/H_2O/phenol, however, the results with the R–P model are quite good for the data of Ghonasgi et al. (1), but this is not so with the data of Roop and Agkerman (2) where the model fails (error in K about 300%).

TABLE 5
Prediction Results with the LCVM, PSRK, and R-P Models

CO_2/H_2O and	Ref.	Data points	T (K)	P range (bar)	% Error in K LCVM	PSRK	R–P
Benzene	(1)	6	313	96.5–165.4	93.8	92.9	>100
	(17)	3	318	79.8–100.6	95.3	94.3	>100
	(1)	6	323	96.5–165.4	90.7	89.7	>100
Toluene	(17)	3	318	79.1–107.6	92.9	88.7	>100
Naphthalene	(17)	3	318	81.3–99.9	55.3	51.4	>100
Phenol	(1)	5	313	96.5–172.3	85.7	77.8	12.6
	(1)	5	323	96.5–172.3	85.5	76.5	36.7
m-Cresol	(1)	6	313	96.5–165.4	81.5	58.6	>100
	(1)	5	323	96.5–151.6	89.2	78.1	>100

Correlation of the Ternary and Quaternary Data

To overcome this problem, the ternary and the quaternary data were correlated by adjusting the H_2O interaction parameters. For the quaternary system containing methanol, the interaction parameters used for CO_2/methanol were obtained by Voutsas et al. (9), and for methanol/water and methanol/ACOH the parameters were presented by Hansen et al. (8).

The correlated parameters for LCVM are presented in Table 6. They are temperature independent since the temperature range of the available data is very narrow (313–323 K). The R–P model interaction parameters obtained are also presented in the same table.

The ternary results of the two models are presented in Table 7. The performance of the R–P model is examined with two sets of parameters: the one obtained in this study and the one proposed by Yeo and Agkerman (17) and Roop and Agkerman (2). Both models behave similarly, and this can be also observed in Fig. 1 and 2, while the second set of interaction parameters for R–P gives rather poor results.

The results for the system CO_2/H_2O/benzene at 313 K are presented in Fig. 1. The LCVM model performs better than R–P one. The system CO_2/H_2O/phenol at 298 K from Roop and Agkerman (2) is shown in Fig. 2. The performance of both models is satisfactory, with a slight advantage for the R–P model.

The Cosolvent Effect

As mentioned before, SFE has not been extensively applied as a separation process in the past because the use of high pressures increases the cost of such a unit. The efficiency of SFE can be substantially improved

TABLE 6
Interaction Parameters Obtained with Correlation of Ternary Data with the LCVM and R–P Models

	For LCVM			For R–P	
H_2O (i) with j	A_{ij} (K)	A_{ji} (K)	H_2O (i) with j	k_{ij}	k_{ji}
CO_2	250.74	1610.46	Benzene	0.2600	−0.067
ACH	852.96	573.80	Toluene	−0.4012	−0.1086
AC	−974.36	−688.94	Phenol	0.6630	−0.0571
$ACCH_2$	2282.01	−327.81	*m*-Cresol	−0.3800	−0.1220
ACOH	949.26	−706.40	Naphthalene	0.1150	−0.1651

TABLE 7
Correlation Results with the LCVM and R–P Models

CO_2/H_2O and	Ref.	Data points	*T* (K)	*P* range (bar)	% Error in *K* LCVM	R–P	R–P[a]
Benzene	(1)	6	313	96.5–165.4	12.6	66.3	11.3
	(17)	3	318	79.8–100.6	21.1	23.2	>100.
	(1)	6	323	96.5–165.4	7.4	42.3	45.9
Toluene	(17)	3	318	79.1–107.6	12.5	11.6	27.1
Naphthalene	(17)	3	318	81.3–99.9	31.2	19.1	21.2
Phenol	(1)	5	313	96.5–172.3	29.5	18.3	64.9
	(1)	5	323	96.5–172.3	21.8	22.1	71.7
m-Cresol	(1)	6	313	96.5–165.4	15.2	20.2	n.a.[b]
	(1)	5	323	96.5–151.6	33.1	52.8	

[a] Parameter set given by Roop and Agkerman (2) and Yeo and Agkerman (17).
[b] Parameters not available

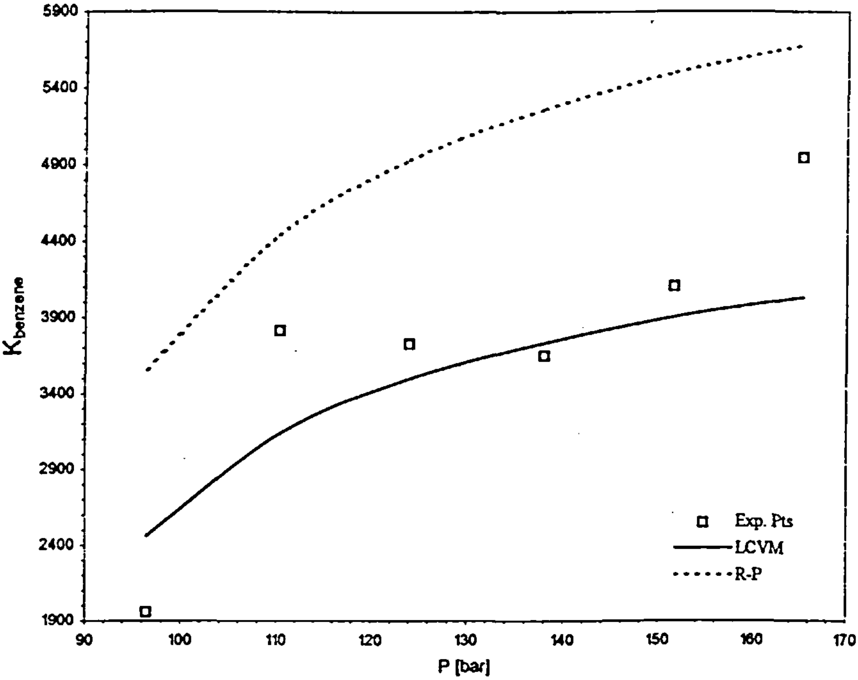


FIG. 1 Equilibrium ratios of benzene in system CO_2/H_2O/benzene at 313 K [data from Ghonasgi et al. (1)].

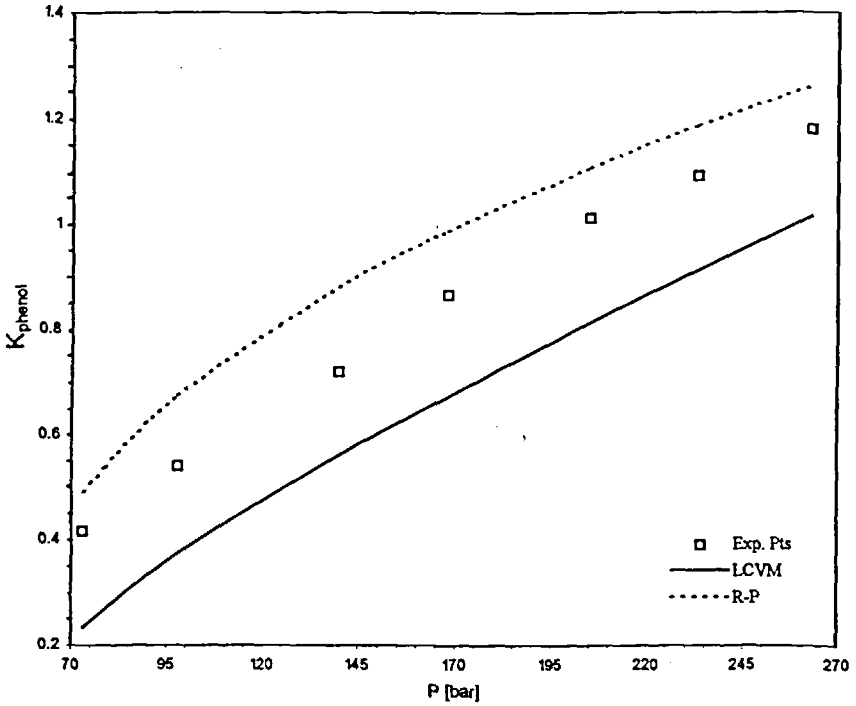


FIG. 2 Equilibrium ratios of phenol in system CO_2/H_2O/phenol at 298 K [data from Roop and Agkerman (2)].

by the use of an appropriate cosolvent. The cosolvent is a compound that will increase the solubility of a certain component in the supercritical solvent, and thus will reduce the necessary size of the unit and, of course, the cost.

In this work the system CO_2/water/phenol with benzene and methanol as cosolvents was studied with the use of the LCVM model as it was previously developed. The results are presented in Fig. 3. The experimental data are taken from values given by Roop and Agkerman (2). The LCVM results are satisfactory, qualitatively and quantitatively. Methanol is not a good cosolvent because its addition does not increase the solubility of the pollutant (phenol) in the solvent (CO_2). On the other hand, benzene can be used as a cosolvent since it almost doubles the solubility of phenol in CO_2 when added in a 6% mole concentration. It seems that methanol, a polar compound which is infinitely soluble in water, remains in the

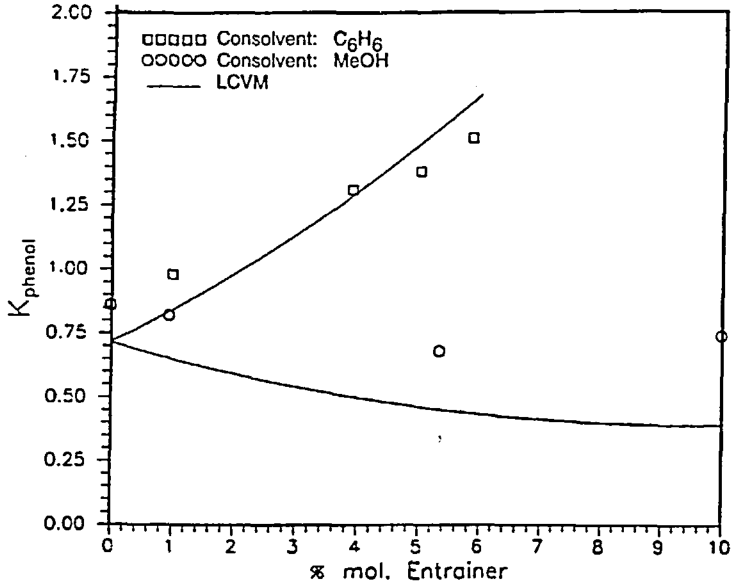


FIG. 3 Equilibrium ratios of phenol in system CO_2/H_2O/phenol/cosolvent at 298 K and 173 bar [data from Roop and Agkerman (2)].

aqueous phase holding phenol (a polar compound) there also, while a nonpolar compound (such as benzene), which is highly soluble in the supercritical phase, helps phenol to move in to the supercritical phase also.

The use of a cosolvent in SFE is thus so important that a fast and reliable screening of possible cosolvents must be done in every case. However, such experiments are expensive and very time consuming. Therefore, a reliable and predictive thermodynamic model, like LCVM, is necessary.

Conclusions

The performance of the LCVM EoS/G^E model for thermodynamic modeling of the SFE process is studied in this work. The prediction of the behavior of the supercritical fluid/water/pollutant system was not possible with the available interaction parameters. A constant underprediction of the *K* value of the pollutant was observed with both the EoS/G^E models examined in this work (LCVM and PSRK). For comparative purposes, a model with a conventional mixing rule was also examined (R–P model), but it presented similar problems (overprediction of the pollutant K value). However, the description of these systems was successful for adjusting some of the interaction parameters of the LCVM and R–P models. The description of quaternary equilibrium resulting from the addition of a cosolvent was also successful. Thus, the LCVM model with these adjusted interaction parameters can be used as a thermodynamic simulator in the plant design of the SFE process as described in the following section.

PLANT DESIGN

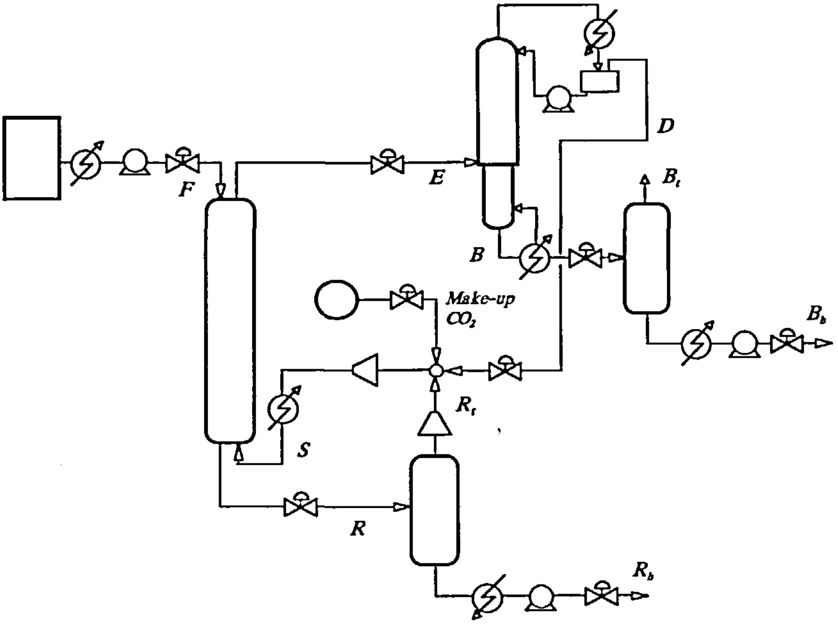
The design of a unit to treat 20 m^3/h aqueous waste containing a high concentration of phenol (6 wt%) is studied here. According to Greek regulations concerning the discharge of industrial effluents in the sea, the specifications of the treated water are:

- $T = 35°C$
- Phenols = 0.5 mg/L
- Aromatics = 0.2 mg/L

The unit design includes:

1. Calculation of the optimum operating parameters in order to achieve the desired separation. The Kremser equation (18) was used for the calculation of the extraction column stages. The Fenske–Underwood–Gilliland (18, 19) method was used for the calculation of the distillation column stages. The thermodynamic properties needed were obtained via the LCVM model.
2. Calculation of the size of the equipment (height, diameter, and wall thickness of vessels, surface of heat exchangers, power of pumps and compressors) was made through methods found in literature (18–21).
3. Estimation of the annual cost of the unit (in 1995 US) takes into account:
   - The investment: equipment free-on-board cost (columns, vessels, exchangers, pumps, compressors, piping), buildings, control, etc. (21, 22)
   - The capital cost: 10 years straight-line depreciation of the investment, insurance, taxes, and maintenance (21)
   - The operating cost: labor, energy consumption, raw and auxiliary materials (21).

It must be noted that all the costs are indicative and useful only for the comparison and optimization of various alternative schemes during the basic design of the unit.



Stream	T	P	Flow rate	CO_2	Phenol	Water
	[K]	[bar]	[Kg/hr]			
F	313	140	20000	0	1200	18800
S	313	140	86482	86400	≈0	82
E	313	20	86481	85086	1200	195
D	293	20	85101	85061	≈0	40
B	315	20	1380	25	1200	155
B_t	315	1	22	22	≈0	≈0
B_b	333	1	1258	3	1200	155
R	313	1	20001	1314	≈0	18687
R_t	360	20	1338	1296	≈0	42
R_b	313	1	18663	19	≈0	18644
Make-up CO_2	205	20	43	43	0	0

FIG. 4 Flow-sheet diagram of an SFE unit for aqueous industrial waste treatment.

No Cosolvent

Figure 4 presents a unit that processes aqueous wastes with SFE without cosolvent. The preheated feed (F) is pumped into the extraction column. The solvent (S) enters the column countercurrently. The extract (E) enters the distillation column where a phenol/water mixture moves to the bottom (B) while the top product (D) (almost pure CO_2) is recycled. The bottom product (B) is then flashed to atmospheric pressure and the gases produced (B_t) are burned. The refined water (R) is also flashed to atmospheric pressure. The top product (R_t) is recycled, while the treated water (R_b) can be discharged into the sea. The table included as the bottom part of Fig. 4 presents the conditions (T and P), the flow rates, and the compositions which resulted for every stream of the unit as a result of the process simulator developed in this work.

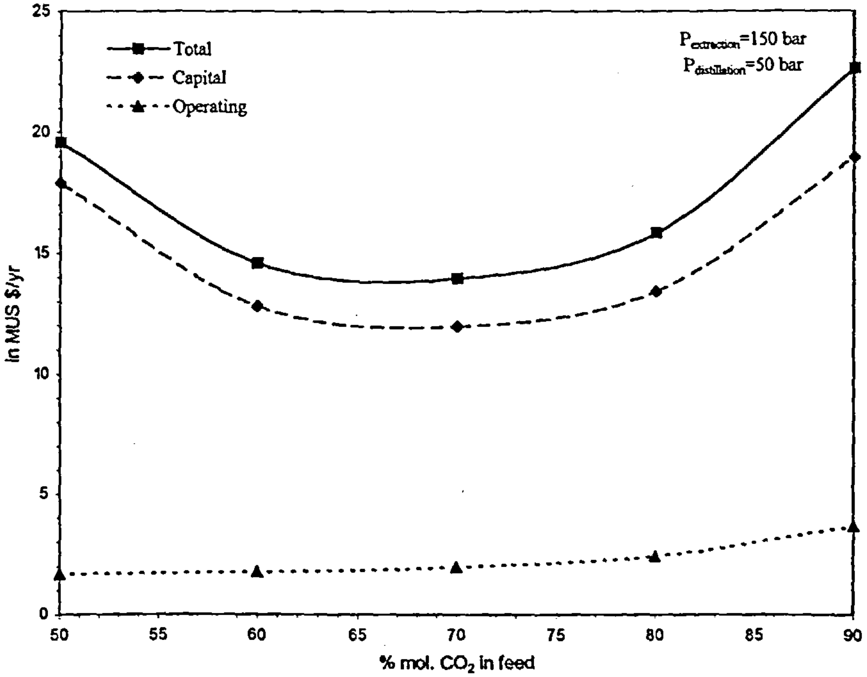


FIG. 5 Cost vs concentration of CO_2 in extractor.

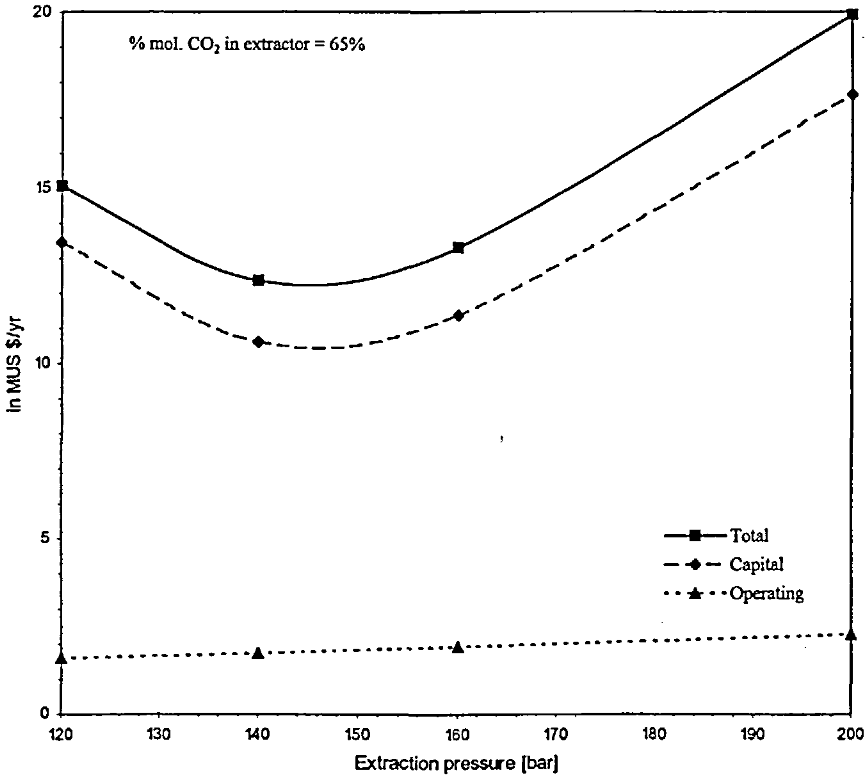


FIG. 6 Cost vs extraction pressure.

Optimization of Operating Parameters

The SFE is an expensive process due to the high operating pressures. Therefore, the optimization of some parameters is essential in order to decrease the total cost. The most important operating parameters are the amount of CO_2 used in feed and the operating pressures of the columns.

In order to estimate the optimum values of these operating parameters, the following procedure was applied. All operating parameters were given some initial values typical for such processes. The effect of each parameter on the total cost and the optimum value were obtained by changing the value of this parameter while keeping all the other constant to the initial values (the first step) or the optimum value (the next steps). In this way a

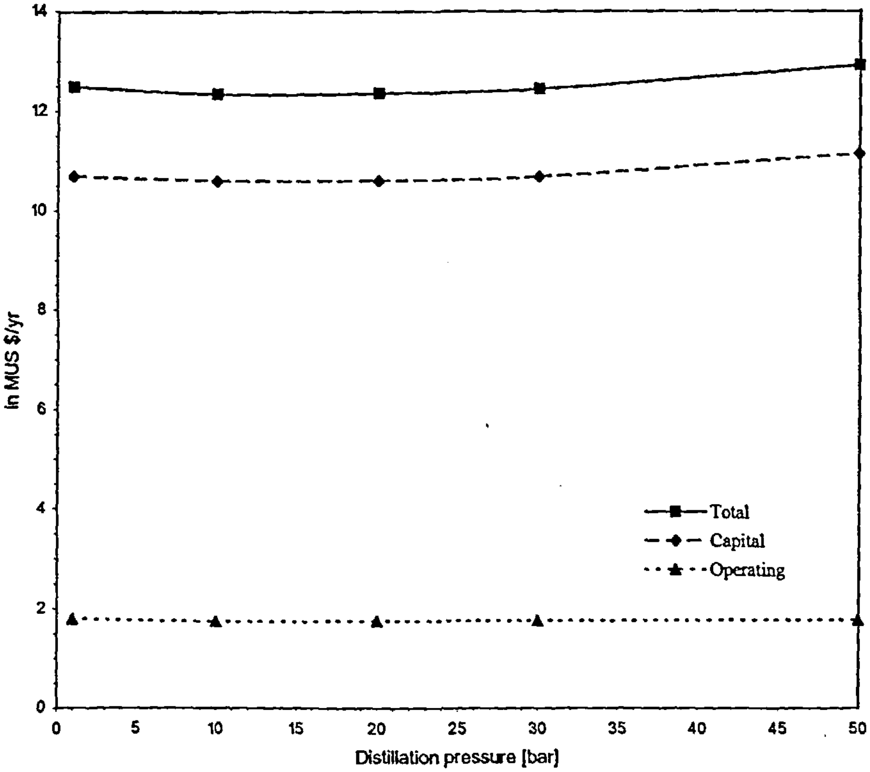


FIG. 7 Cost vs distillation pressure.

sensitivity analysis of the total cost was performed and the most important parameters were defined, along with their optimum values.

The parameters studied were the CO_2 in the feed and the pressures of the extraction and the distillation columns.

a. CO_2 in the Feed. The operating pressure for the extraction column was set at 150 bar and for the distillation column at 50 bar. The feed concentration of the phenol in water was 6 wt%.

The cost (total, equipment, and operating) vs the amount of CO_2 in the feed is presented in Fig. 5. A concentration of 60–70 mol% CO_2 in the feed seems to be optimum. Larger amounts, although they decrease the number of stages necessary, increase the size of the unit (diameters, exchangers, compressors, etc.), which results in higher equipment costs.

On the other hand, smaller amounts lead to a larger number of theoretical stages and to a unrealistic height for the extractive column.

b. Pressure of the Extraction and the Distillation Column. The amount of CO_2 in the feed of the extraction column was 65 mol% and the pressure of the distillation column was 50 bar. The feed concentration of phenol in the water was 6 wt%.

The cost vs the operating pressure of the column is presented in Fig. 6. The operating pressure for the extraction columns has an optimum of 140 bar. Although larger operating pressures can decrease the number of theoretical stages, the need for equipment with thicker shells increases the cost considerably. Pressure reduction leads to an increase of the number of the theoretical stages, and, consequently, of the cost.

For an operating pressure of the distillation column of 140 bar the amount of CO_2 in the feed of the extraction column was 65 mol%. The feed concentration of the phenol in water was 6 wt%. The operating pressure has little effect on the total cost, as shown in Fig. 7, since the cost

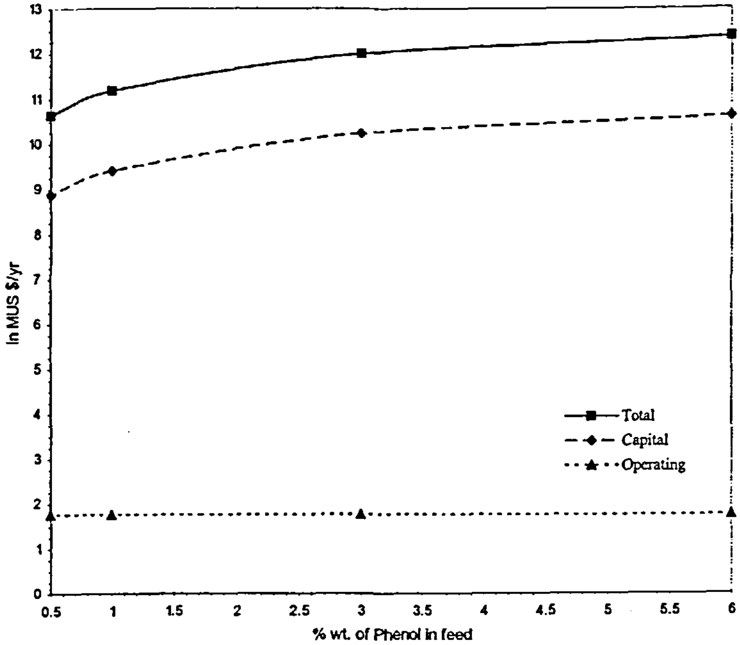


FIG. 8 Cost vs concentration of phenol in feed.

of the distillation column is much less than the cost of the extraction column.

Thus, the optimum operating parameters are:

- Extraction column pressure: 140 bar
- Distillation column pressure: 20 bar
- Amount of CO_2 in feed: 65 mol%

Effect on Phenol Concentration in Feed

The optimum operating parameters obtained previously were used again. From Fig. 8 it is obvious that the total cost of the unit is not strongly dependent on the concentration of phenol in the aqueous waste. Variations of feed concentration within the examined range caused a 5-tray variation in the number of trays needed. A slight decrease in the cost was observed, as expected, in the lower concentrations, and this decrease become more important at much lower concentrations of phenol in the feed. This does

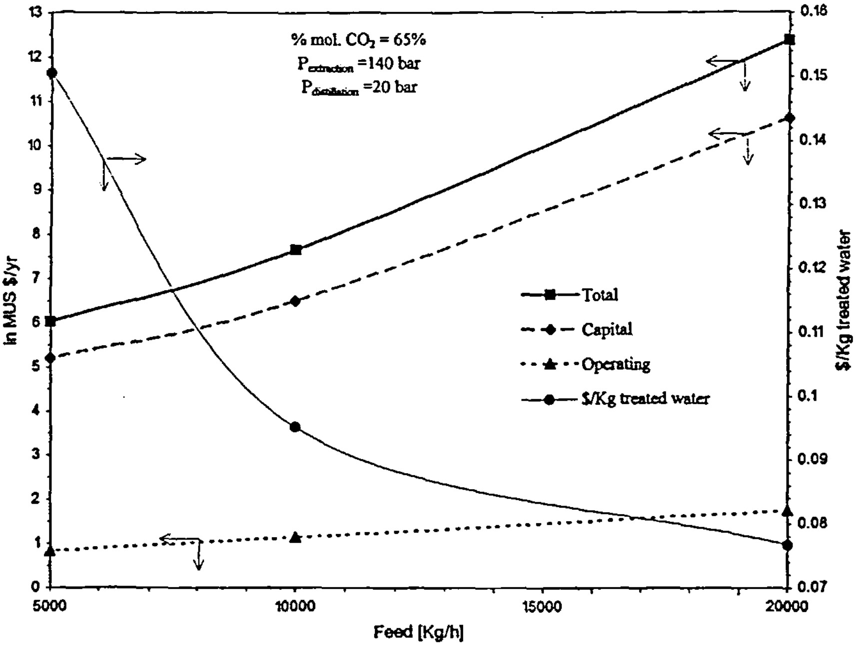
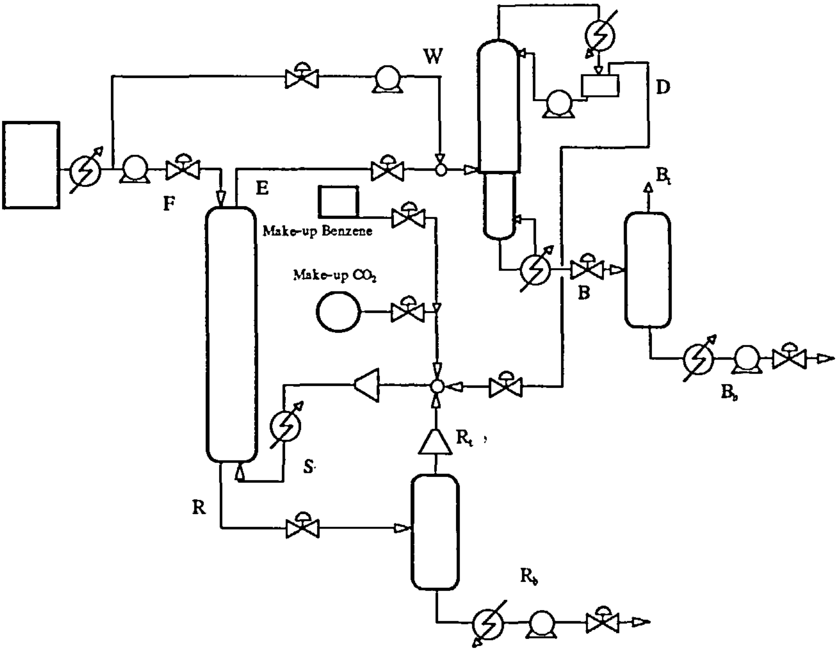


FIG. 9 Cost vs size of the unit.



Stream	T [K]	P [bar]	Flow rate	CO_2	Phenol [Kg/hr]	Water	Benzene
F	313	80	20000	0	1200	18800	0
W	313	20	1000	0	60	940	0
S	313	80	101587	93300	≈0	41	8246
E	313	80	101813	92176	1200	192	8245
D	293	20	100386	92138	≈0	5	8243
B	320	20	2427	38	1260	11237	2
B_t	320	1	33	30	≈0	2	1
B_b	333	1	2395	8	1260	1126	1
R	313	80	19774	1124	≈0	18649	1
R_t	360	20	1143	1106	≈0	36	1
R_b	313	1	18631	18	≈0	18613	≈0
Make-up Benz.	205	20	2	0	0	0	2
Make-up CO_2	205	20	56	56	0	0	0

FIG. 10 Flow-sheet diagram of an SFE unit for the aqueous industrial waste treatment that utilizes a cosolvent.

not significantly affect the cost of the extraction column as compared to the operating pressure.

The Size of the Unit

The optimum operating parameters obtained previously were used again. As expected, the size of the unit has a considerable effect on the cost. A decrease in size results in a decrease of the total cost (Fig. 9). However, the cost per kg of treated water increases significantly.

Cosolvent

As mentioned before, a very important factor for decreasing the cost is the use of a cosolvent. In this case, benzene was used as the cosolvent. Although benzene is toxic, the concentration of benzene used in the treated water was below the toxic specifications (0.2 ppm). Other com-

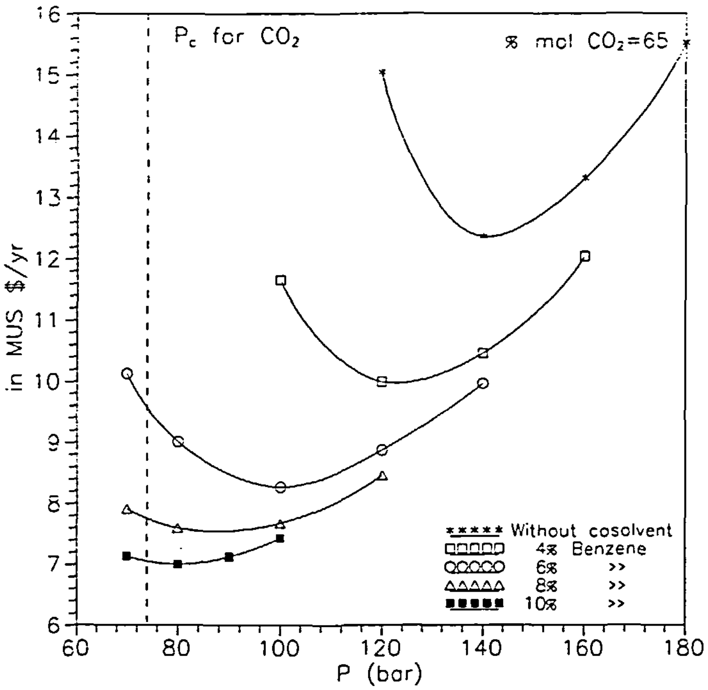


FIG. 11 Total cost vs extraction pressure for different concentrations of cosolvent.

pounds may be appropriate cosolvents. [Roop and Akgerman (2) suggest alkanes, 1-pentene, toluene, chloroalkanes, chlorobenzene, etc.]

In Fig. 10 the unit of SFE with a cosolvent is presented. A small amount of water was added in the distillation column feed in order to increase the *K* value of benzene and to achieve the desired concentration of benzene (<0.2 ppm) in the treated water.

The parameters considered here are the amount of cosolvent and the operating pressure. The amount of CO_2 in the feed was kept at 65 mol%, the pressure in the distillation column was 20 bar, and the feed concentration of phenol in the water was 6 wt%. In Fig. 11 the total cost of the unit is plotted vs the operating pressure for different concentrations of cosolvent in the feed. As can be observed from this figure, the use of the cosolvent is very important. As the amount of cosolvent increases, the optimum operating pressure of the extraction column decreases, and therefore also the total cost. Increasing the cosolvent over 10 mol% does

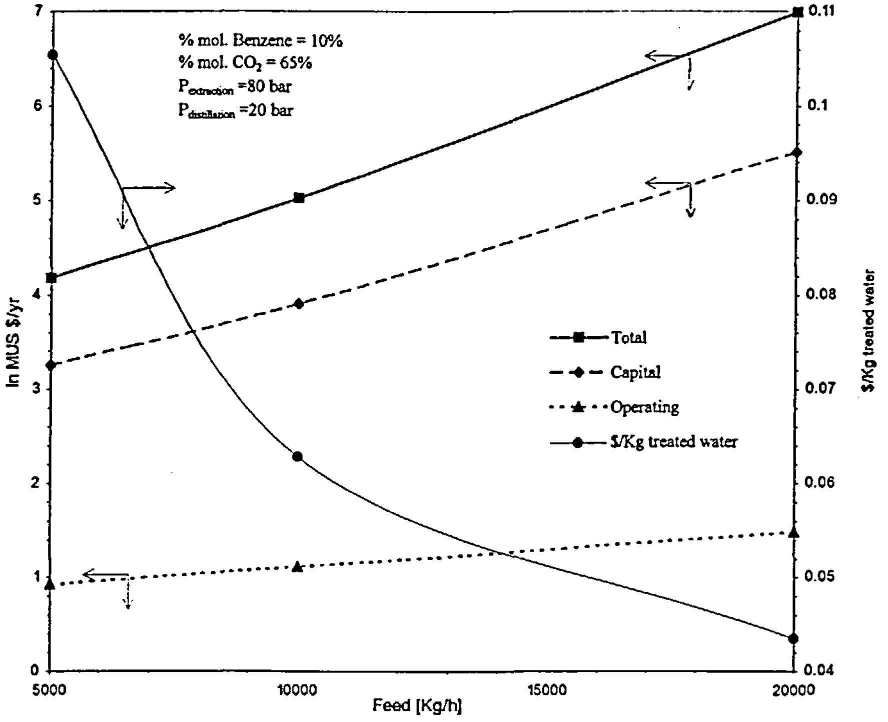


FIG. 12 Cost vs. size of the unit.

not significantly decrease the cost, while at the same time the optimum pressure tends to be subcritical and may cause elimination of the supercritical phenomenon.

Thus, the operating parameters that are obtained from this process are:

- Concentration of cosolvent: 10% mol
- Operating pressure of the extraction column: 80 bar

using:

- Operating pressure of the distillation column: 20 bar
- CO_2 concentration in feed: 65%

The concentration of phenol in the aqueous waste does not affect the total cost significantly. The total cost vs the size of the unit, plotted in Fig. 12, is significantly depressed to almost one-half of what is was without the use of a cosolvent (Fig. 9).

Conclusions

The application of SFE for the treatment of aqueous waste was studied. The LCVM was used for thermodynamic modeling of the EoS/G^E model process.

The design and optimization of an SFE plant shows that the application of SFE in the treatment of aqueous waste is feasible but the need for high pressures is a handicap because it increases the cost considerably.

The use of an appropriate cosolvent seems to be the solution to this problem. It is shown that a small amount of an appropriate cosolvent increases the equilibrium coefficients K of the pollutant, thus lowering the pressures required and resulting in a considerable decrease in cost (40%).

NOMENCLATURE

a	EoS attractive term (cohesion) parameter
A	mixing rule constant
A_{ij}, B_{ij}	coefficients defined in Eq. (3)
b	EoS covolume parameter
G^E	excess Gibbs free energy
k_{ij}	binary interaction parameters in Eq. (2)
K_{ij}	binary interaction parameter defined in Eq. (2)
K	equilibrium ratio
R	gas constant

T temperature, K
x mole fraction for both phases

Greek Symbols

α EoS parameter, $\alpha = a/bRT$
λ parameter of LCVM model as defined in Eq. (1)
Ψ_{ij} interaction energy parameter in UNIFAC

Subscripts

i component i
M Michelsen mixing rule
V Vidal mixing rule

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