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# Supercritical Fluid Extraction of Alcohols from Water

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Carbon dioxide is the most studied solvent for high-pressure recovery of alcohols. The present analysis shows, however, that using carbon dioxide does not lead to significant energy savings or to completely dehydrate alcohols. Light hydrocarbons such as propane and butanes exhibit two important properties which may be exploited in alcohol-water separation: high-pressure extracting capability and water entrainment effect. Such solvents are termed *dual-effect solvents*. Cyclic processes, where both of the above properties are exploited, have been synthesized for the recovery of pure alcohols from even dilute aqueous mixtures. The main elements of the cyclic processes are a high-pressure extractor, which also acts as a water entrainer, and a solvent recovery column. For ethanol recovery, propane is suggested as a solvent, for 2-propanol and isobutane. In both cases, an energy savings of a factor of 3 is achieved compared with conventional azeotropic distillation using, e.g., benzene as an entrainer.

The application of near critical fluid (NCF) extraction to the recovery of alcohols from aqueous solutions has several attractive features: very high selectivity, low solubility of the nonpolar NCF in the aqueous phase, ease of separation of the NCF from the extract, low heat of vaporization of the NCF solvent.

The main difficulty of the separation is the relatively great affinity between alcohols and water. The equilibrium distribution of an alcohol between the water phase and the NCF phase is defined by the distribution coefficient  $m_1$

$$m_1 = y_1/x_1 \quad (1)$$

where  $y_1$  and  $x_1$  are the mole fractions of the alcohol in the NCF and the aqueous phase, respectively. The value of the distribution coefficient greatly influences the economic feasibility of the extraction process.

The best studied solvent for the recovery of alcohols from water is CO<sub>2</sub>. However, in the case of ethanol recovery, the results of Kuk and Montagna (1983) and Kreim (1983), using CO<sub>2</sub> at supercritical conditions, and of Moses et al. (1982), with liquid CO<sub>2</sub>, indicate that even though there is a high ethanol-water selectivity in this process, it is not possible to break the azeotropic composition by means of a simple CO<sub>2</sub> extraction cycle. The maximum ethanol concentrations obtained in the pilot plant studies of Moses et al. were between 84 and 91 wt %. Another problem is the rather low distribution coefficient of ethanol in compressed or liquid CO<sub>2</sub>. When liquid CO<sub>2</sub> is used to extract ethanol from a 10 wt % ethanol-water mixture, 100 mol of CO<sub>2</sub> is circulated in the process for each mole of ethanol recovered.

Moses et al. (1982) reported a consumption of energy of 3167 kJ/kg of ethanol. This energy requirement is based on the use of a NCF extraction cycle (Figure 1) with vapor recompression.

In comparison it is possible to obtain by ordinary distillation 85 wt % ethanol in water using 3400 kJ/kg of ethanol (Maiorella, 1982) or 91 wt % ethanol with 3900 kJ/kg.

## Phase Equilibria and NCF Extraction

As demonstrated in detail by Brignole et al. (1985), it is possible to quantitatively predict phase equilibria in mixtures of alcohols (primary, secondary, and tertiary), water, and alkanes or CO<sub>2</sub> by using the Group-Contribution Equation of State, GC-EOS (Skjold-Jørgensen, 1984).

The predictions, which as far as possible are compared with experimental data, verify that it is not possible to break the ethanol-water azeotrope by extraction with CO<sub>2</sub> except at subambient temperatures.

One of the limitations of CO<sub>2</sub> as a NCF solvent is, thus, its relatively low critical temperature, which confines the extraction temperature to values close to or below ambient temperatures. The same limitation holds for ethane and ethylene. The use of solvents of higher critical temperature, like propane or butanes, will allow operation at higher temperatures with fluids of liquid-like densities.

Predicted distribution coefficients for ethanol in propane are shown at 43 and 75 bar in Figure 2. The distribution coefficients of ethanol between propane and water,  $m_1$ , increase monotonically with temperature when the pressure is above the critical pressure of propane. This illustrates the favorable effect of using a NCF solvent of greater critical temperature than those of CO<sub>2</sub> or ethane.

## Solvent Properties and NCF Extraction: Dual-Effect Solvents

An important factor in any extraction process is the product concentration in the extract (solvent free basis). This concentration is shown in Figure 3 for the extraction of ethanol with propane and with *n*-butane. The operation at greater temperature decreases the selectivity of the solvent. Therefore, a product less rich in ethanol is obtained. However, this loss can be regained if the NCF solvent exhibits a water *entrainment* effect, under the

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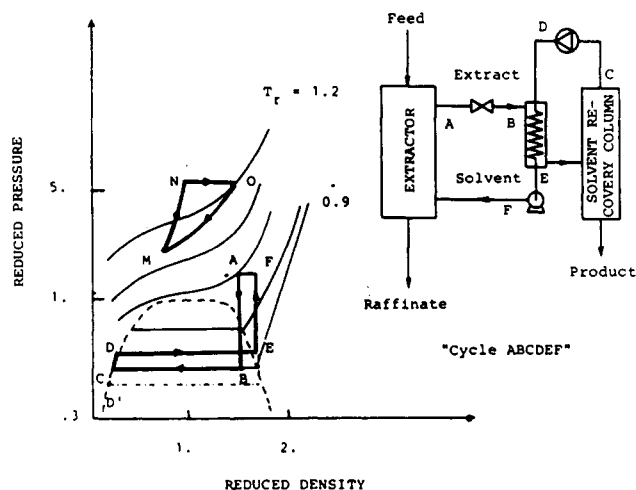


Figure 1. Supercritical fluid extraction cycles.

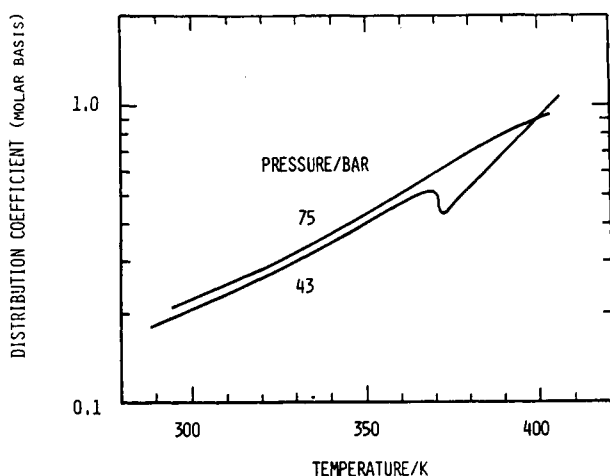


Figure 2. Ethanol distribution coefficient between water and propane. Ethanol concentration in the aqueous solution is 10 wt % (propane-free basis).

conditions of the solvent recovery column. By the entrainment effect, the NCF solvent will remove the water from the liquid phase, and absolute ethanol can thus be obtained as the bottoms product from this column. We term solvents that exhibit both extracting and entraining capabilities as *dual-effect solvents*.

To obtain the desired entrainment effect, it is required that the relative volatility of water with respect to the solvent should be greater than one in the solvent recovery column. It is not sufficient for the water to be more volatile than ethanol in this column. If the solvent is removed first, then the ethanol-water mixture composition ends up at the binary azeotropic point. While propane and butane exhibit entrainment effects on ethanol-water mixtures, CO<sub>2</sub> and ethane do not (Brignole, 1985).

Increasing the operating temperature of the extractor reduces the solvent requirements, but at the same time the amount of water in the extract increases and could lead to condensation of water in the solvent recovery column and the formation of a heterogeneous azeotrope. For a binary water-hydrocarbon mixture, the saturation conditions correspond to the liquid-liquid-vapor equilibrium line. The water-vapor-phase saturation value (Kobayashi and Katz, 1953; Tsonopoulos and Wilson, 1983) increases considerably with the system pressure. The need to increase the concentration of water in the vapor phase, and at the same time avoid the condensation problem, usually determines the operating pressure of the solvent recovery column. In the case of propane, the required pressure is

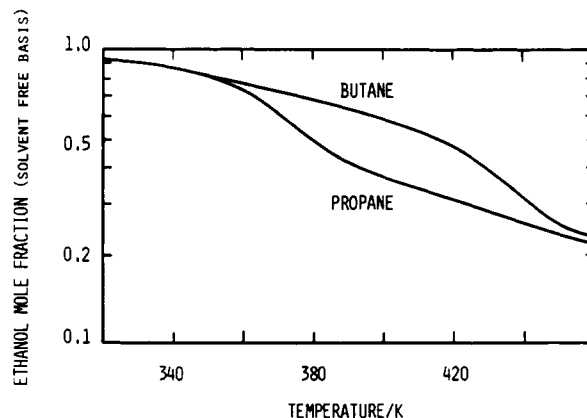


Figure 3. Ethanol extract concentration in NCF extraction with light hydrocarbons. Ethanol concentration in the aqueous feed to the extractor is 10 wt %. Extraction pressure: 50 bar.

around 25 bar and for the butanes around 10 bar. The separation between the NCF and the alcohol should be complete; alcohol and the NCF solvent should not form a binary azeotrope under the conditions of the solvent recovery column. No azeotrope can be expected in mixtures of ethanol or 2-propanol with propane or of 2-propanol with isobutane. However, the formation of azeotropes of ethanol with *n*-butane and isobutane is possible. Higher boiling alcohols like *n*-propanols and the butanols will not form binary azeotropes with propane or the butanes.

Finally, the following solvent selection is made, taking into consideration (a) the water entrainment property, (b) the critical temperature well above ambient, and (c) no formation of azeotropes: (i) *propane is the only suitable paraffinic solvent for ethanol extraction*, (ii) *propane or isobutane can be used for 2-propanol*, and (iii) *for the extraction of higher boiling alcohols like n-propanol or butanols, it is possible to use propane, n-butane, or mixtures of butanes*.

Even though light paraffins are the only dual-effect solvents discussed in the present work, for alcohol recovery and dehydration by NCF extraction, it is likely that the dual-effect-solvent property can also be found with other solvents, propylene, for example. The requisites for a dual-effect solvent are nonpolar or slightly polar, boiling point around 280 K or below, critical temperatures above 350 K, and chemically stable and very low solubility in water.

### NCF Extraction Cycles

In SCF or NCF extraction, the separation of the desired product from an extract stream can be achieved in different ways. One alternative is to precipitate the solute from the extract by reduction of the solvent density. This can be accomplished by pressure reduction (isothermal cycle), temperature increase (isobaric cycle), or mixing the extract with atmospheric gases (Gärs, 1984). When the feed to the process is a volatile liquid mixture, the process is usually continuous. The feed is contacted countercurrently in a multiple-stage extractor with the SCF solvent. In this case regeneration of the SCF solvent requires some type of fractionation due to the solubility of the SCF in the liquid product and to the relatively high vapor pressure of the product.

The path of the SCF in typical extraction cycles, based on pressure reduction and solvent recovery by fractionation, is shown in Figure 1. Cycle I (ABCDEF) corresponds to gases like CO<sub>2</sub>, propane, or butane that can be liquified at moderate pressures and are compressed as a liquid to

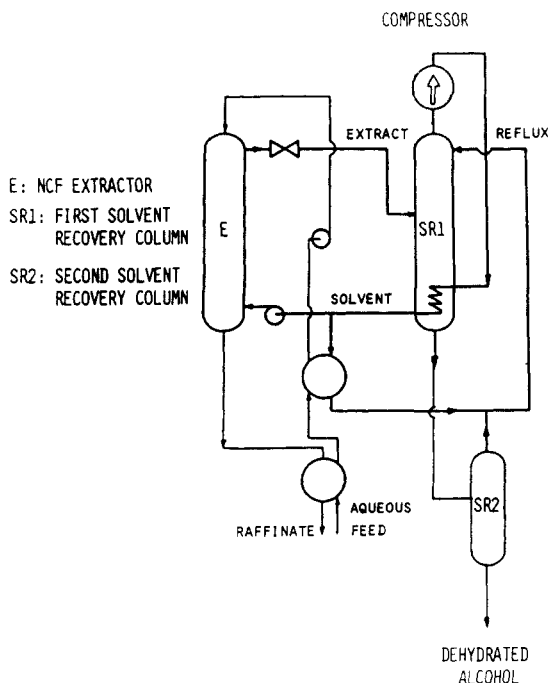


Figure 4. NCF extraction cycle with vapor recompression.

the extractor pressure. The condition of extraction is represented by point AB which corresponds to the conditions after the pressure reduction valve and point C to the outlet of the solvent recovery column. At this point the gas is compressed to a pressure high enough (D) for its condensation in the column reboiler (vapor recompression). In another alternative (without vapor recompression), from point C the fluid is condensed at a somewhat lower pressure (D') using external cooling and then pumped back to the extractor. In this case external heating is required to vaporize the solvent from the extracted product (from B to C). Cycle II (OMN) corresponds to gases such as ethane, ethylene, or even  $\text{CO}_2$  that, after pressure reduction to precipitate the solute, are directly recompressed to the extractor conditions. Extraction processes that use this type of cycle usually operate at reduced pressures of the supercritical fluid that are much greater than one. In comparison, processes corresponding to type I cycles, with vapor recompression, are highly energy efficient with low compression duty and almost no requirements of external heating or cooling.

**Vapor Recompression Cycle (Figure 4).** A typical NCF extraction cycle with vapor recompression (cycle I, Figure 1) is shown in Figure 4. The feed (dilute alcohol-water mixture), previously heat exchanged with the raffinate, is sent to the top of the high-pressure extractor, where it is contacted countercurrently with the solvent at near critical conditions. The extract, containing most of the alcohol and a certain amount of water, is (after pressure reduction) sent to a distillation column for solvent recovery, where the final alcohol dehydration also takes place. This column operates under pressure to increase the concentration of water in the vapor phase. In this column, water and the solvent are obtained as overhead products, and a mixture of alcohol and solvent is withdrawn as bottoms. The overhead vapor is (after compression) condensed in the column condenser/reboiler. Complete separation between the alcohol and the solvent takes place in a second column, which can be operated at a lower pressure. The reason behind the two-column system for solvent recovery is to optimize the energy consumption in the process. The energy consumption is

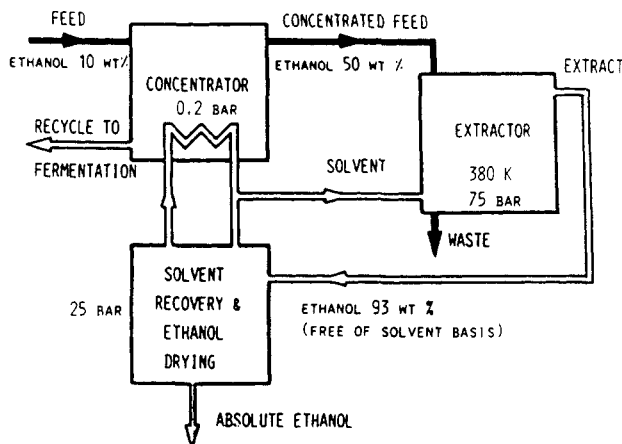


Figure 5. NCF extraction cycle with feed preconcentration.

mainly determined by the work of compression of the overhead vapor of the first solvent recovery column. When a rather high concentration of NCF solvent is kept in the bottoms of this column, a low temperature difference between top and bottoms is achieved. This gives a low-energy consumption for vapor recompression at the expense of some additional energy consumption by conventional heating, in the second solvent recovery column.

**NCF Extraction Cycle with Feed Preconcentration (Figure 5).** The recovery of ethanol and other alcohols from a dilute fermentation broth or aqueous solution can be made with low-energy consumption by ordinary distillation, if the separation goal is only the complete removal of the alcohol from the solution, but not to obtain a concentration of alcohol close to the azeotropic value in the distillate. This is due to the high relative volatilities of alcohols with respect to water at low alcohol liquid-phase concentrations. This property makes it possible to increase the alcohol concentration by a factor of 5–6 over the original concentration in the feed by using a simple stripping column without reflux (preconcentrator).

The enriched alcohol-water mixture is then fed to the NCF extractor where it is contacted with the hot solvent. The extract product is dehydrated and the solvent recovered by distillation, as has been described before. However, in the preconcentrator cycle no vapor recompression is used. Instead the vapor from the distillation column is used as the heating source for the preconcentrator. If the heating loads of both columns are balanced, then dehydrated alcohol can be obtained with the low-energy requirement of the preconcentration step.

In this cycle we can visualize three stages: (1) enrichment of the feed by alcohol stripping (preconcentrator), (2) separation of alcohol from water by selective NCF extraction, and (3) dehydration of alcohol (water entrainment effect) in the solvent recovery column.

**Modeling of NCF Extraction.** The modeling of the supercritical and NCF extraction cycles has been done with the SEPSIM flow-sheeting system developed by Andersen (1986). SEPSIM is among others interfaced with the GC-EOS thermodynamics. The unit operation library of the flow-sheeting system has rigorous models for simulation of the main units of the NCF extraction cycle: the high-pressure extraction and distillation columns. These models are based on an efficient implementation of a full multivariate Newton method with analytically generated Jacobians.

The flow-sheeting system has a modular structure but uses an equation-oriented method for simultaneous solution of the heat and material balance equations and design equations. This structure allows great flexibility in the

**Table I. Examples of Modeling and Design Problems for NCF Extraction**

given	design variables	design specifications
feed stream (composition and flow rate), solvent flow rate, no. of stages, and column pressure	column operating temp	alcohol recovery
feed stream (composition and flow rate), no. of stages, and column pressure	column operating temp and solvent flow rate	alcohol recovery and process selectivity

**Table II. Simulation of the Extraction of a 10 wt % Ethanol in Water Feed<sup>a</sup>**

temp, K	pressure, bar	extract		
		ethanol, kmol/h	water, kmol/h	propane, kmol/h
360	80	21.63	7.67	1238.0
380	80	21.63	11.4	884.0
388	80	21.63	13.3	780.0
400	80	21.63	17.0	643.0

<sup>a</sup>Basis: 10 000 kg/h of feed; 10 theoretical extraction stages; 99.5% ethanol recovery.

formulation of modeling and design problems, as indicated in Table I.

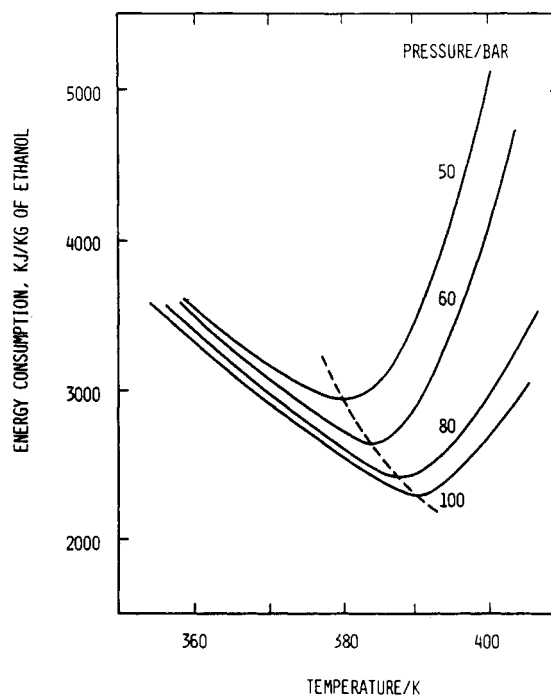
### Design and Evaluation of NCF Extraction Cycles for Ethanol Recovery from Aqueous Solutions Using Propane

Two cycles are considered for this separation problem: (a) vapor recompression and (b) preconcentrator.

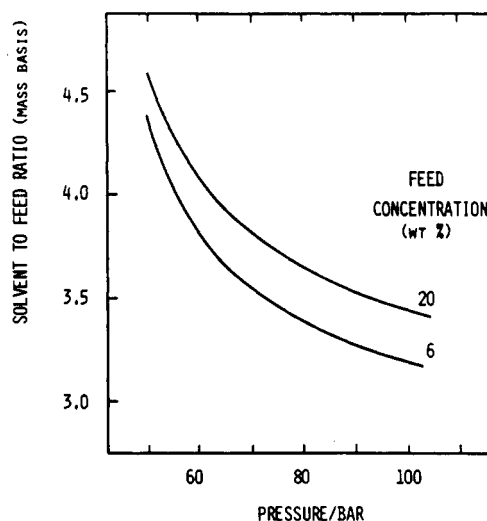
**Vapor Recompression Cycle (Figure 4).** Rigorous design of the extractor was carried out for the following specifications: 99.5% ethanol recovery and 10 theoretical stages at a given pressure and temperature. The results of the computations were solvent flow rate requirements, extract and raffinate flow rates, and compositions. The pressure was varied between 50 and 100 bar and the temperature between 350 and 420 K. The conditions during the extraction process were assumed isothermal. As an example, results of extractor simulations, corresponding to a 10 wt % ethanol in water feed, are given in Table II.

In a vapor recompression cycle, the conditions chosen for the high-pressure extractor have a large influence on the design of the solvent recovery system and therefore on the process energy consumption. The main contribution to the energy consumption in this cycle is the compression work required for vapor recompression in the first column of the solvent recovery system. This depends directly on the solvent flow rate to the extractor. The solvent flow rate requirements, as can be seen in Table II, decrease with increasing temperature, and therefore, the same can be said of the energy consumption. However, if the composition of the water in the vapor phase of the solvent recovery column reaches the saturation value, at the given column pressure, it is necessary to increase the vapor flow rate in the column to avoid the formation of a second liquid phase. In this situation the vapor flow rate in the column is increased to keep the water composition in the vapor phase below the saturation value.

It is possible to estimate the process energy consumption based solely on the results obtained by the rigorous simulation of the NCF extraction process and, on the basis of the minimum energy consumption, to determine optimum extraction conditions. The details of such computations are given by Brignole (1985). As an example, the resulting energy consumptions corresponding to a feed of 10 wt % ethanol in water are given in Figure 6. It can be seen that at each operating pressure there is an optimum operating temperature leading to a minimum in the energy consumption curve. It is also shown that the minimum energy consumption corresponds to the extraction conditions that lead to the water saturation value



**Figure 6.** Energy consumption of a NCF extraction cycle based on propane and using a vapor recompression cycle. Ethanol recovery, 99.5%. Ethanol concentration in the feed 10 wt %. (---) Extraction conditions that give the water saturation value in the vapor phase of the solvent recovery column.



**Figure 7.** Energy consumption at optimum extraction temperatures as a function of extractor pressure and ethanol concentration in the aqueous feed. The ethanol recovery in the extractor is 99.5%.

(dashed line) in the vapor phase of the solvent recovery column.

On the basis of this result, the optimum operating conditions can be directly determined by using the SEP-SIM flow-sheeting system, adding the specification of the water concentration in the extract corresponding to the saturation condition. In this case, the pressure is given and the program determines solvent requirements for the specified ethanol recovery, operating temperature, and all

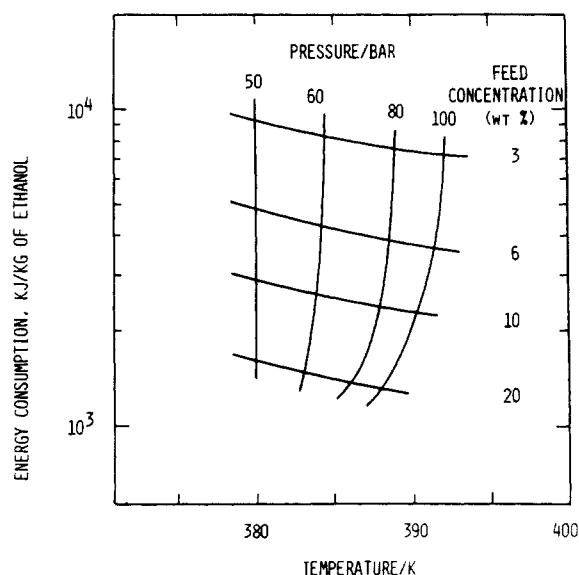


Figure 8. Solvent-to-feed ratio (mass basis) at optimum operating conditions as a function of extraction pressure and ethanol feed concentration.

Table III. Extraction Conditions for the Solvent Recovery System Simulations<sup>a</sup>

extraction variables	case I	case II
temp, K	380	380
pressure, bar	70	60
solvent/feed (mass ratio)	3.52	3.96
extract		
ethanol, kmol/h	21.4	21.6
water, kmol/h	10.8	12.96
propane, kmol/h	800.0	900.0

<sup>a</sup> Feed to the extractor, 10 wt % ethanol in water solution (10 000 kg/h)

other streams compositions and flow rates. The energy consumptions for the optimum extraction conditions are given in Figure 7 as a function of the ethanol concentration in the aqueous feed to the NCF extractor. The solvent requirements at the optimum conditions are shown in Figure 8. The energy consumption decreases only slightly with pressure in the range from 60 to 100 bar. At 50 and 60 bar, the optimum operating temperatures are almost independent of feed concentration. The results indicate that the optimum conditions for the operation of the extraction process of ethanol recovery with propane are as follows: temperature, 380–385 K; pressure, 60–70 bar, and solvent-to-feed ratio (mass basis), 3–4, in the case of a vapor recompression cycle.

After the optimum extractor operating conditions have been determined, rigorous simulation of the columns of the solvent recovery system is carried out to obtain improved estimates of the energy consumption and to establish the number of stages and reflux requirements, operating pressures, stream compositions, flow rates, and temperatures. The simulations are also useful to study the removal of water from the alcohol in the solvent recovery column (entrainment effect) and to confirm if complete recovery of ethanol in the bottoms is possible.

The solvent recovery system is studied for extract feeds obtained under near-optimum extraction conditions. The simulations were carried out for two different feeds (Table III). The distillation column design parameters obtained for both feeds were very similar. Therefore, only the results for case I are reported in this work. The composition of ethanol in the bottoms of the first column of the solvent recovery system is fixed at 0.25 fraction, in accordance with

Table IV. Simulation Results of the First Solvent Recovery Column<sup>a</sup>

component	feed, kmol/h	distillate, kmol/h	bottoms, kmol/h
water	10.8	10.76	0.04
ethanol	21.4	0.095	21.30
solvent	800.0	736.1	63.9
temp, K		340.6	352.0

the results of a bottoms composition optimization (Brignole, 1985). The simulations of this column are carried out at 20 and 25 bar to study the effect of column pressure on the total energy consumption. The operating pressure of the second column is fixed at 12.5 bar to obtain a condenser temperature of 309 K, which allows the use of cooling water in the condenser. The composition of the feed to this column is fixed at 0.25 mole fraction ethanol. Therefore the operation of this column is the same irrespective of the extractor conditions. The degree of vaporization of the feed is assumed to be 10% for the first column and 40% for the second. The ethanol recovery for both columns is set higher than 99.5%, and the same degree of separation is set for the water removal in the first column.

The following design parameters are determined by rigorous modeling of the first solvent recovery column on the basis of the given specifications: pressure, 25 bar; reflux ratio, 0.55; stages, 22 (ideal); feed stage, 4 (counting from the bottom). The stream compositions, temperatures, and energy consumption for the above conditions are given in Table IV. A pressure of 25 bar is chosen, because the maximum mole fraction of water in the vapor phase at 20 bar is greater than the saturation value. The water saturation value increases with pressure and reaches a maximum value of 0.013 mole fraction at a pressure close to 35 bar (Kobayashi and Katz, 1953).

The energy consumption in the solvent recovery system for optimum conditions is 2730 kJ/kg of ethanol. The total cycle energy consumption, taking into account feed preheating requirements, is 3350 kJ/kg. In comparison, 6400 kJ/kg is required to concentrate ethanol from 10 to 95 wt %, by conventional distillation, and the azeotropic distillation step (Busche, 1983) requires an additional 3340 kJ/kg.

The main drawbacks of this NCF extraction cycle are the need of vapor recompression and the rather large solvent volumetric flow rates required in the high-pressure extractor.

**NCF Extraction with Feed Preconcentration.** The pressure of the preconcentrator was fixed at 0.18 bar. At this pressure, the bottoms temperature is 330.5 K, and from the previous modeling of the solvent recovery unit, it is known that the temperature of the overhead vapor from this column is 340.6 K. This temperature difference allows reasonable heat integration between the two columns. In the preconcentrator, a distillate/feed ratio of 0.15 gave complete ethanol recovery, when the feed is a 10 wt % ethanol (or less) in water solution. This gives an energy consumption of 3400 kJ/kg for the 10 wt % feed. The feed flow rate to the NCF extractor is reduced to one-fifth of the original value by the use of the preconcentrator. The extraction conditions for the preconcentrated feeds were selected in accordance with the previous results. Table V shows some typical results of the extraction of preconcentrated feeds corresponding to 3, 6, and 10 wt % feeds to the ethanol stripper. The flow rates are based on a feed flow rate of 10 000 kg/h. It was found that the solvent flow rate requirements increase with feed concentration. The results of the simulation of the solvent recovery column

**Table V. Simulation of the Extraction of Preconcentrated Ethanol Feeds<sup>a</sup>**

original feed concn, wt %	T, K	P, bar	feed/solvent ratio mass basis	extract			$m_1$
				ethanol, kmol/h	water, kmol/h	propane, kmol/h	
10	380	75	6.02	21.5	4.06	280	0.27
6	380	75	4.88	12.9	2.9	200	0.37
3	380	75	3.8	6.4	1.9	140	0.55

<sup>a</sup> Basis: 10 000 kg/h of original feed; 10 theoretical states. Preconcentrated feed to the extractor: 80 kmol/h.

**Table VI. Results of the Simulation of the Solvent Recovery Column of a Preconcentrator Cycle<sup>a</sup>**

component	feed, kmol/h	distillate, kmol/h	bottoms, kmol/h
water	4.06	3.86	0.20
ethanol	21.5	0.17	21.33
solvent	280.0	279.9	0.10
temp, K		336.6	460.5

<sup>a</sup> System: water-ethanol-propane. Specifications: pressure, 23 bar; stages, 20; feed stage, 5; reflux, 0.4; vapor fraction in the feed, 0.4; energy consumption, 3500 kJ/kg.

for the case of 10 wt % feed are shown in Table VI. The energy consumption of this column is similar to the one of the preconcentrator for the same initial feed concentration. If the thermal loads of both columns are properly integrated, it is possible to obtain dehydrated alcohols, from dilute feeds with the rather low energy consumption of the preconcentration step.

The energy costs of the preconcentrator and vapor recompression cycles are similar. However, the preconcentrator cycle requires less capital investment because no compressor is needed, and the extractor and high-pressure distillation columns are of much smaller size. These factors make the capital investment of the preconcentrator cycle comparable with the ones of ordinary distillation processes coupled with azeotropic distillation.

### Application of NCF Extraction to 2-Propanol Recovery

2-Propanol is one of the most widely used solvents in the chemical industry. Therefore, its recovery from aqueous solutions is a problem of great interest. The conventional method of separation is distillation. However, this method consumes a large amount of energy, and the separation is limited by the existence of an 2-propanol-water azeotrope.

Moses et al. (1982) have shown, by pilot plant experiments, that it is possible to recover 2-propanol from aqueous solutions by extraction with liquid CO<sub>2</sub> at 66 bar and 298 K. Kuk and Montagna (1983), Radosz (1984), and Paulaitis et al. (1984) have reported additional data on phase equilibria for the system 2-propanol-water-CO<sub>2</sub>. The solubility of 2-propanol in near critical or liquid CO<sub>2</sub> is, under similar pressures and temperatures, greater than the solubility of ethanol. Besides, it is possible by extraction with liquid CO<sub>2</sub> to obtain a concentration of 2-propanol in water above the azeotropic composition. However, the production of dehydrated 2-propanol is not possible, due to the lack of water entrainment effect by CO<sub>2</sub> in the solvent recovery column. The concentration of 2-propanol obtained by liquid CO<sub>2</sub> extraction is 85 mol % (CO<sub>2</sub>-free basis). In principle, this mixture can be distilled, giving pure 2-propanol as the bottoms product and a distillate close to the azeotrope composition, which could be recycled to the extraction process. However, the energy consumption of this distillation process is high because the relative volatility between 2-propanol and water is close to one in this concentration range, and there is a need to recirculate 1 mol of alcohol for each mole

produced. These combined effects give rise to an energy consumption of 4800 kJ/kg for this distillation process. In addition, the energy requirement of the liquid CO<sub>2</sub> extraction cycle is 1520 kJ/kg of 2-propanol, for a 10 wt % 2-propanol-water feed. Therefore, the total energy requirement to obtain dehydrated 2-propanol using liquid CO<sub>2</sub> is 6320 kJ/kg. This energy consumption is higher than the one of a well-integrated ordinary distillation process coupled with azeotropic distillation.

The separation of 2-propanol-water mixtures by NCF extraction with light hydrocarbons is based on the same principles as applied to ethanol-water separations: extraction with "hot" solvent, water entrainment by the solvent, and no azeotrope between the alcohol and the solvent.

The conditions of critical temperature well above ambient (hot solvent) and no azeotrope formation limit the solvent choice among light hydrocarbons to propane and isobutane. Isobutane is chosen in this work.

There are many possibilities regarding the source of the 2-propanol-water mixture to be separated. Therefore, mixtures are considered from the dilute range up to 50 wt % 2-propanol in aqueous solutions. The basic process scheme is similar to the one described earlier for ethanol. However, the rather large values of the 2-propanol distribution coefficients open the possibility of using conventional heating in the reboiler of the solvent recovery column. A preconcentration cycle as described before is used only when this simple approach is not competitive with ordinary distillation. The vapor recompression scheme is not considered as an alternative for this separation problem. Therefore, only thermal energy is required for running the processing alternatives to be discussed.

**NCF Extraction of 2-Propanol with Isobutane.** Isobutane has a critical temperature higher than propane. Therefore, it is possible to operate the extraction process at higher temperatures than with propane, without a significant loss in selectivity. Another advantage of isobutane is that the water vapor-phase saturation values in water-isobutane mixtures for liquid-liquid-vapor equilibria are greater than the saturation values in water-propane mixtures at the same temperature. However, the separation between 2-propanol and isobutane in the solvent recovery column is more difficult, and the possibility of azeotrope formation when distilling 2-propanol and isobutane at high pressures cannot be completely ruled out a priori.

The best extraction conditions were determined by using the water vapor-phase saturation limit as a criterion for finding the optimum extracting temperature at a given pressure. The results of energy consumption are shown in Figure 9. Results from the extractor simulations for solvent-feed ratios that give a recovery of 2-propanol greater than 99% at near optimum pressures and temperatures are given in Table VII. Results from simulation of the distillation of the extract corresponding to case 5 (Table VII) are shown in Table VIII. In this case, the distillation pressure is set at 11 bar to avoid water condensation problems in the column.

The energy requirements of NCF extraction of 2-propanol from water using isobutane are shown as a

**Table VII. Extraction Simulation Results for the Recovery of 2-Propanol from Aqueous Solutions<sup>a</sup>**

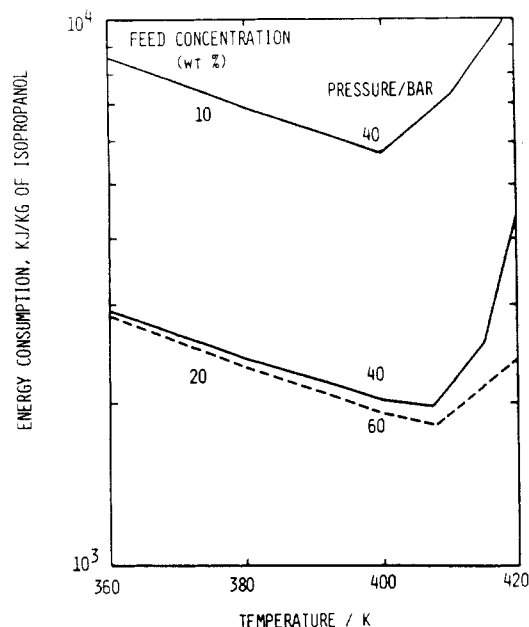
case	IPA concn in feed, wt %	temp, K	pressure, bar	solvent/feed, mass basis	extract			
					IPA, kmol/h	water, kmol/h	isobutane, kmol/h	affinate IPA, kmol/h
1	10	400	40	1.45	16.475	7.677	250.0	0.065
2	10	380	40	1.74	16.46	4.325	300.0	0.080
3	25	380	40	1.74	41.263	5.65	300.0	0.058
4	25	400	40	1.34	41.235	8.63	230.0	0.087
5	50	380	40	1.39	83.106	7.69	240.0	0.044

<sup>a</sup>Solvent: isobutane. Extraction stages: 10. Feed: 10 000 kg/h of 2-propanol (IPA) aqueous solution.

**Table VIII. Results of the Simulation of the Solvent Recovery Column of a Preconcentrator Cycle<sup>a</sup>**

component	feed, kmol/h	distillate, kmol/h	bottoms, kmol/h
water	7.67	7.66	0.01
2-propanol	83.11	0.11	83.00
isobutane	240.0	237.2	2.8
temp, K		342.6	422.8

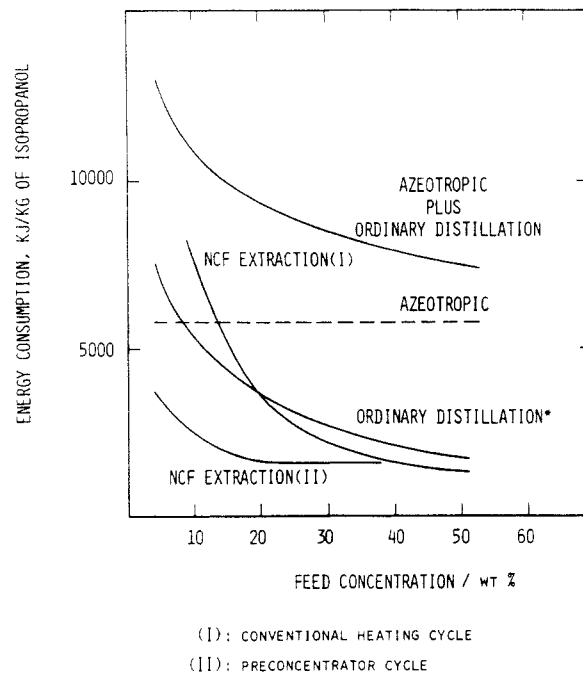
<sup>a</sup>System: water-2-propanol-isobutane. Feed corresponding to case 5 (Table VII). Specifications: pressure, 11 bar; stages, 22; feed plate, 6; reflux, 0.90; vapor feed fraction, 0.1; energy consumption, 1470 kJ/kg.

**Figure 9.** Optimization of extraction temperature for the recovery of 2-propanol with isobutane.

function of feed concentration in Figure 10. In this figure, the energy requirements of ordinary distillation and azeotropic distillation are also shown. It can be seen that the azeotropic distillation is the most energy-consuming step for feed concentrations greater than 8 wt %. Therefore, in this concentration range the energy consumption of azeotropic distillation can be considered to be the minimum energy consumption, even when the ordinary and azeotropic distillation steps are thermally integrated. For feed concentrations below 15 wt %, NCF extraction with conventional heating is no longer competitive with conventional distillation. In this concentration range, the use of a preconcentrator cycle, as was discussed for ethanol extraction, may be considered (Brignole, 1985).

## Conclusions

Phase equilibrium predictions of alcohol-water-light hydrocarbon systems using the GC-EOS model have shown that "hot" hydrocarbons have reasonable solvent properties

**Figure 10.** Comparison of energy consumption of NCF extraction cycles with distillation for the recovery and dehydration of 2-propanol from aqueous solutions. (\*) The concentration obtained by ordinary distillation is 0.66 mole fraction of 2-propanol.

for recovery of alcohols from water and that they exhibit a water entrainment effect under the conditions of the solvent recovery column. These properties lead to the identification of light hydrocarbons as dual-effect solvents (extraction and entrainment) for this separation.

A selection of dual-effect solvents among light paraffins shows that propane is the only candidate for ethanol recovery: it has a relatively high critical temperature, does not form an azeotrope with ethanol, and shows adequate solvency, selectivity, and water entrainment properties. In the case of 2-propanol recovery, isobutane is a more attractive solvent than propane.

Three NCF extraction cycles were evaluated: (i) conventional heating, (ii) vapor recompression, and (iii) preconcentrator cycles. In the case of ethanol recovery, the most promising alternative is the preconcentrator cycle. For the recovery of 2-propanol, it is highly competitive to use a conventional heating cycle. However, at low alcohol feed concentrations, the preconcentrator cycle may be more attractive.

A criterion for the optimization of the energy consumption in NCF extraction cycles based on dual-effect solvents is formulated on the basis of the water vapor-phase saturation value in the solvent recovery column.

The separation concepts developed in this work can be easily extended to other separation problems involving the recovery of organic oxygenated compounds from water.

Finally, it should be emphasized that in order to further verify the results of this work, additional phase equilibrium



data on alcohol-water-solvent mixtures are needed.

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**Registry No.**  $\text{H}_3\text{CCH}_2\text{OH}$ , 64-17-5;  $(\text{H}_3\text{C})_2\text{CHOH}$ , 67-63-0;  $\text{H}_3\text{CCH}_2\text{CH}_3$ , 74-98-6;  $(\text{H}_3\text{C})_2\text{CHCH}_3$ , 75-28-5.

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## Supercritical Extraction of Toxic Organics from Soils

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Supercritical fluid (SCF) extraction of organic hazardous waste from contaminated soils is a promising new technique for hazardous waste-site cleanup. The ability of SCFs to solubilize heavy molecular weight organics is well-documented. In this investigation, supercritical carbon dioxide ( $\text{SC-CO}_2$ ) was used to extract polychlorinated biphenyls (PCBs), 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT), and toxaphene from contaminated topsoils and subsoils. An attractive feature of this process is that the  $\text{CO}_2$ , being virtually inert, leaves no solvent residue on the processed soil. Supercritical  $\text{CO}_2$  at 100 atm and 40 °C was continuously passed through a fixed bed of 10 g of soil. Approximately 70% of the DDT and 75% of the toxaphene can be leached from a topsoil contaminated with 1000 ppm DDT and 400 ppm toxaphene in under 10 min by using  $\text{SC-CO}_2$  at a rate of 0.7 g/s. The extraction of contaminated (with 1000 ppm PCBs) subsoil proved to be even more promising, with over 90% PCB extraction in under 1 min at the same  $\text{CO}_2$  rate.

Supercritical fluid (SCF) extraction of organic hazardous waste from contaminated soils is a promising new technique for hazardous waste-site cleanup. The ability of SCFs to solubilize heavy molecular weight organics is well-documented (Paulaitis et al., 1982; Groves et al., 1985). In this investigation, supercritical carbon dioxide ( $\text{SC-CO}_2$ ) was used to extract PCBs, DDT, and toxaphene from contaminated topsoils and subsoils. An attractive feature of this process is that the  $\text{CO}_2$ , being virtually inert, leaves no solvent residue on the processed soil. Furthermore, the ease of separation of the extracted solute from  $\text{SC-CO}_2$  results in the creation of a small waste volume of the now concentrated organic, improving the efficiency of subsequent treatment processes such as combustion.

Typically in SCF extraction, a simple solvent gas, such as  $\text{CO}_2$ , is contacted with a solid or liquid phase at high pressure and moderate temperature. Slight changes in the temperature or pressure of the system can cause large changes in the density of the solvent and consequently in its ability to solubilize heavy nonvolatile waste compounds from the solid or liquid phase. For example, by manipulation of the system pressure, a nonvolatile can be extracted. Following a pressure letdown, generally to below

the system's critical conditions, this same material can be completely precipitated from the solvent. Thus, the SCF phenomenon offers a unique opportunity for separation and recovery of "difficult to separate" materials in one processing stage.

Supercritical fluid densities compare to liquid densities; however, their viscosities and diffusivities are intermediate to typical liquid and gas values of these properties. Thus, SCFs have the solvent power of liquids with better mass-transfer characteristics than typical liquids. Consequently, separation efficiencies for SCF extractions can be much higher than for liquid solvent extractions.

In order to explain the application of SCF to the extraction of organics from soils, this paper is divided into four sections. The first section discusses the phase equilibria expected from both a  $\text{CO}_2$ -PCB and a  $\text{CO}_2$ -DDT mixture. The thermodynamic equations used to develop these semiquantitative phase diagrams are reviewed. The second section reviews the rate process of desorption from porous media, such as soils, into a supercritical phase. In the third section, the results of an experimental design employed to determine the effectiveness of  $\text{SC-CO}_2$  extraction are presented. Finally, a lumped parameter model