

New Method for Supercritical Fluid Regeneration

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Entrainers have the potential of enhancing the solubility of a solute in a supercritical gas. Removing the entrainer from the supercritical gas, on the other hand, reduces the solubility. This effect may be used for separating solutes from a supercritical solvent. It will be shown, for example, that for the system CO₂ and ethanol, it is advantageous to extract the ethanol in a countercurrent extraction with water, leading to a reduction in the solvent power of the gaseous phase. This was tested using a deodorizer condensate of soybean oil containing more than 55 wt % tocochromanols.

Keywords: phase equilibria, regeneration, entrainer, supercritical fluid, tocochromanols

INTRODUCTION

In a closed-circuit supercritical-fluid extraction the normal way of regenerating the fluid is reducing its density. From an exergetic point of view these processes are not optimal. To ensure a high degree of regeneration most of the applications decompress the fluid to pressures close to the critical pressure. When using CO₂, this means pressure differences of more than 20 MPa. Isobaric processes such as adsorption and absorption are much less energy-consuming. But unfortunately, the knowledge about these processes is still quite low compared to decompression. Gähns¹ published the idea of adding an additional gas such as nitrogen to reduce the solubility of the solute in the fluid phase, but this process must deal with the problem of separating the nitrogen from the fluid phase after the regeneration step. Brunner and Peter² published the concept of a two-column isobaric process that uses entrainers to change the phase behavior of a quasi-ternary system. This is done by a temperature change between the extraction column and the regeneration column. This temperature change causes a change of the miscibility gap from a Type I to a Type II in ternary diagram and a splitting of the fluid phase into a nearly pure CO₂ phase and a solute-entrainer phase. The new method of regeneration that is described in this paper contains features of these concepts.

THEORETICAL BACKGROUND

Several authors³ have shown that the addition of an entrainer with a vapor pressure between the vapor pressure of the solute and the solvent can enhance the solubility of the solute. The basic idea of a new method is as follows: if the fraction of the entrainer in the fluid phase is reduced,

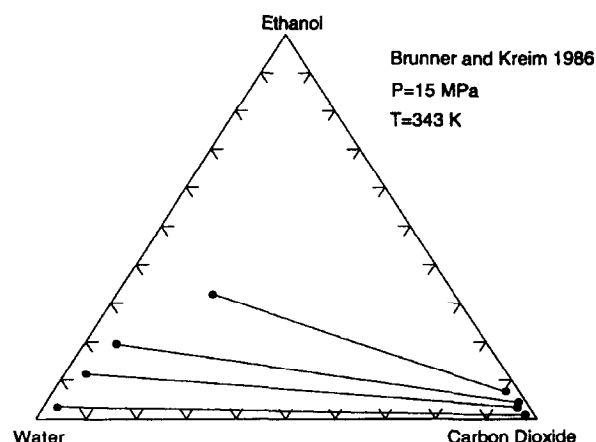


Figure 1. Ternary system ethanol–water–CO₂ at $P = 15$ MPa and $T = 343$ K.

then the solubility of the solute will be reduced as well. The problem is how to use this technique without changing temperature, pressure, or adding a new substance to the regenerated supercritical fluid. One of the most interesting entrainers is ethanol because of its usability in the food processing industry. The ternary system ethanol–CO₂–water, which was measured by several authors (e.g., Brunner and Kreim,⁴ Yao⁵ see Figure 1) provides the key to the problem. This system forms two phases: the supercritical CO₂ phase and the water phase. Ethanol is more concentrated in the water phase. If an ethanol–CO₂ stream loaded with solute is mixed with a water stream, the ethanol will be extracted from the fluid phase into the liquid phase. Therefore, the solubility of the solute in the remaining gaseous phase should decline, if the solute does

TABLE I
Feed Mixture Composition

Component	Wt %
Low boiling substances	9.3
C16 fatty acids	2.6
Squalene	7.8
α -Tocopherol	4.7
β -Tocopherol	34.4
δ -Tocopherol	16.6
Sterols	9.0
Sterolic compounds	14.4
Diglycerides	1.2

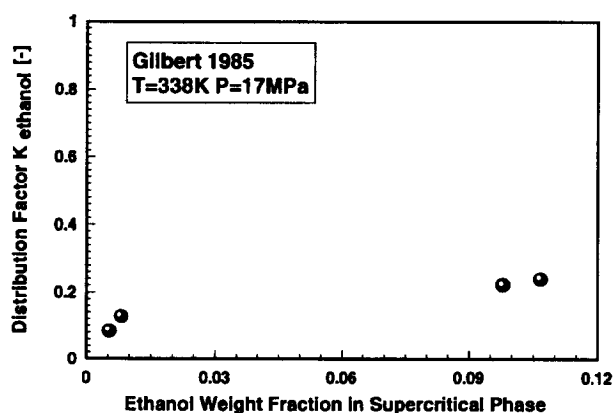


Figure 2. Distribution factor K of ethanol in the system ethanol-water- CO_2 .

not change the basic phase behavior of the ternary system ethanol- CO_2 -water. To prove this, phase equilibrium measurements were carried out. As an example for this new way of regenerating a supercritical solvent, a mixture of tocochromanols (Table I) with squalene and sterols was contacted with supercritical ethanol- CO_2 mixture at $P = 17$ MPa and $T = 343$ K. Gilbert⁶ has measured the ternary system ethanol- CO_2 -water at $P = 17$ MPa and $T = 338$ K. The distribution factor K of ethanol is displayed in Figure 2. Note that K for ethanol is smaller than 1.

EXPERIMENTS

In the first part of the experimental work, phase equilibria were determined with a static analytical method and an apparatus that has been described in more detail elsewhere.⁷ This apparatus (produced in the workshop of Technical University Hamburg-Harburg) contains a pressure vessel of 1000 cm³ and is capable of detecting three different phases. For the experiments, a deodorizer condensate of soybean oil (T155, Henkel, FRG) was chosen that contains about 55 wt % tocochromanols (Table I). In a first experiment series, the solubility of tocochromanols in a mixture of CO_2 (99.9% Kohlensäurewerke, FRG) and ethanol (pa. Merck, Darmstadt, FRG) was measured at $P = 17$ MPa and $T = 343$ K. The results are displayed in

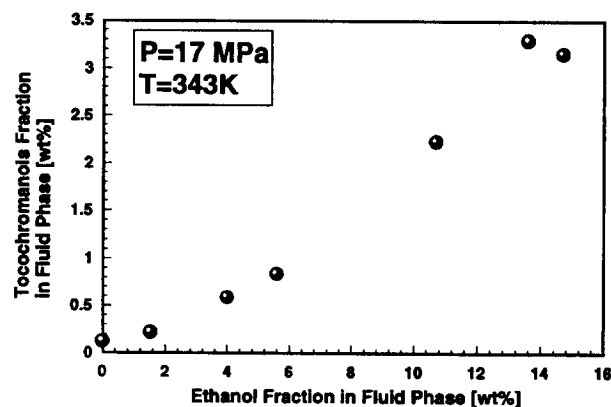


Figure 3. Solubility of tocochromanol in supercritical fluid phase as function of ethanol weight fraction.

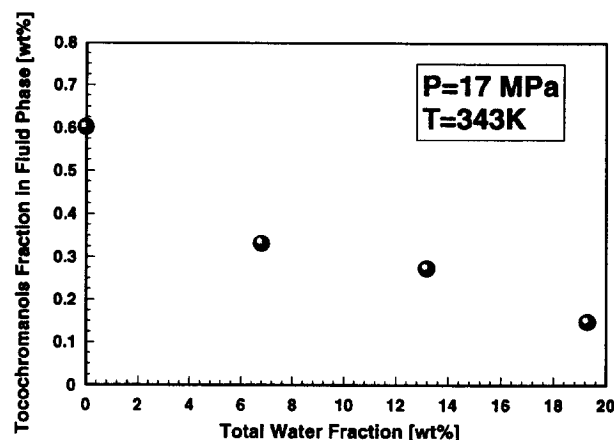


Figure 4. Solubility of tocochromanol in supercritical fluid phase as a function of total water weight fraction.

Figure 3 as a function of ethanol weight fraction. The solubility of tocochromanols in supercritical CO_2 is enhanced by adding ethanol.

In the next stage of the experiments, water was added to the ternary system ethanol-tocochromanol- CO_2 with the ethanol-tocochromanol ratio remaining constant. Before water was added to the system, the tocochromanol solubility at the above conditions was 0.60 wt % having an ethanol weight fraction in the liquid phase of 5.7 wt %. The results are displayed as weight fractions in Table II. Adding 55 mL water led most likely to the existence of a third phase, which was not detected. Still the weight fraction of the total tocochromanols was reduced to 0.331 wt %. By adding another 55 mL water, corresponding to a weight fraction of 13.2 wt % water in the cell, a detectable third phase was formed containing most of the water and the major part of the ethanol. The weight fraction of ethanol in the supercritical-fluid phase is reduced from 4.04 to 2.44 wt %, and subsequently, the solubility of tocochromanols in the supercritical phase is reduced to 0.27 wt %. Increasing the water weight fraction in the cell to 19.3 wt % leads to a weight fraction of 1.7 % ethanol and 0.15 wt % total tocochromanols in the vapor

TABLE II
Results of the Phase Equilibrium Experiments with the Static Cell
(in Wt %)

Point	Substance	SCF	Liquid 1 (T155-rich)	Liquid 2 (water-rich)	Total content (g)
1	T155	1.21	74.6		389,0
	hereof Tocochr.	0.60	40.4		
	ethanol	4.04	5.7		98,2
	carbon dioxide	94.75	19.8		297, 9
	water	no water			0
2	T155	0.69	70.2		388,9
	hereof Tocochr.	0.331	38.0		
	ethanol	2.66	5.1		98, 1
	carbon dioxide	96.2	22.6		265, 9
	water	0.56	2.0		55,0
3	T155	0.57	71.2	0.0	388,8
	hereof Tocochr.	0.27	38.5		
	ethanol	2.44	5.9	19.3	98, 0
	carbon dioxide	96.4	20.7	4.9	233, 9
	water	0.56	2.2	75.8	110, 0
4	T155	0.31	74.4	0.0	388, 7
	hereof Tocochr.	0.15	40.0		
	ethanol	1.7	1.4	11.6	98,0
	carbon dioxide	97.8	22.0	5.4	201,9
	water	0.6	2.2	83.0	165,0

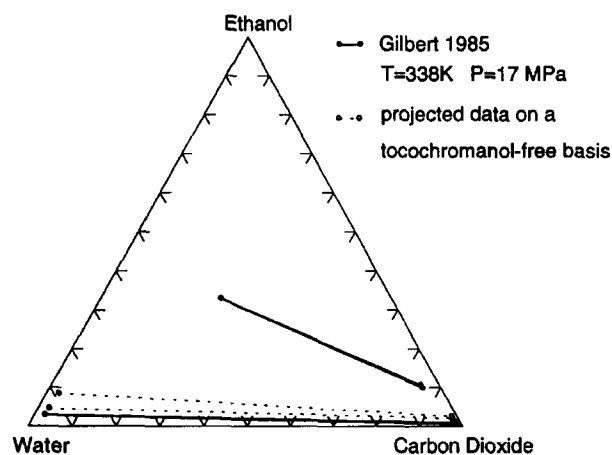


Figure 5. Ternary system ethanol–water–CO₂ at $P = 17$ MPa and $T = 338$ K.

phase, corresponding to a reduction of 75% for the tocochromanols (Figure 4). If the three-phase data points are projected on a solute-free ternary system, they fit well into the ternary system ethanol–water–CO₂ at $P = 17$ MPa and $T = 338$ K, as shown in Figure 5. This experiment shows, that the general phase behavior of ethanol is not altered by the presence of a third tocochromanol-rich phase. To test this method for the regeneration of a supercritical fluid, a closed-circuit apparatus as shown in

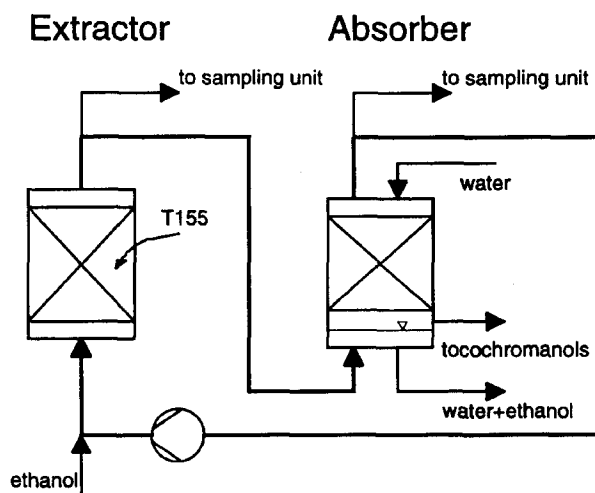


Figure 6. Flow scheme of the absorber cycle.

Figure 6 was used. The extractor (Nova Swiss, Effretikon, Switzerland) has a volume of 4000 cm³ that was half-filled with the mixture listed in Table I. Spiral packing was used to ensure good mass transfer. The absorber for separating the ethanol can be assumed to be one theoretical stage. The absorber has a volume of 1000 cm³ and was filled with spiral packing. In the experiment the solvent ratio, defined as the ratio between the mass flow

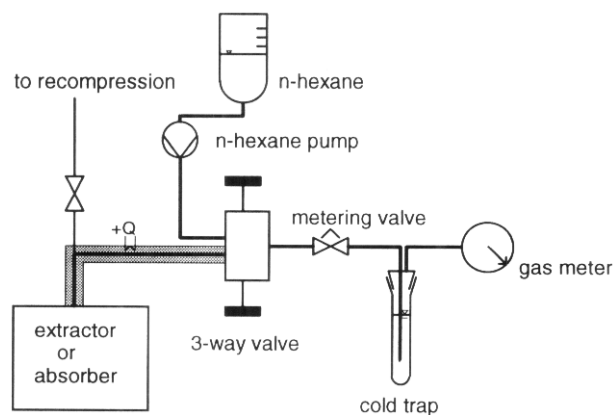


Figure 7. Flow scheme of sampling unit.

of the water and the mass flow of the fluid phase, was varied.

The weight fractions of the tocopherols in the fluid phase were measured before and after the absorber by sampling, using a metering valve in combination with a cold trap as shown in Figure 7. 1000 cm³ of CO₂ (STP) were passed through the cold trap. The major part of the extract in the gas precipitated right beyond the point of pressure reduction in the metering valve. The valve and the following capillary were cleaned afterwards with *n*-hexane (99.8% Merck, Darmstadt, FRG) to remove the precipitated compounds. Three experiments at a pressure of 17 MPa were carried out (Table III).

The results are displayed in Figure 8, and show that the results from the phase-equilibria experiments can be transferred to the extraction plant. The weight fraction of the tocopherols in the fluid phase is reduced from about 1.4 to 0.45 %. The fractions of ethanol and water in the supercritical fluid were only determined for the third data point. Here, the ethanol weight fraction is reduced to 1.9% after the absorber while the water weight fraction was 0.25%.

DISCUSSION AND CONCLUSIONS

The described method is a way to separate solute and entrainer from supercritical solvents without pressure reduction. It is a suitable method for processes where the remaining loading of the regenerated fluid does not have to be very low or as the first step of regeneration. This is

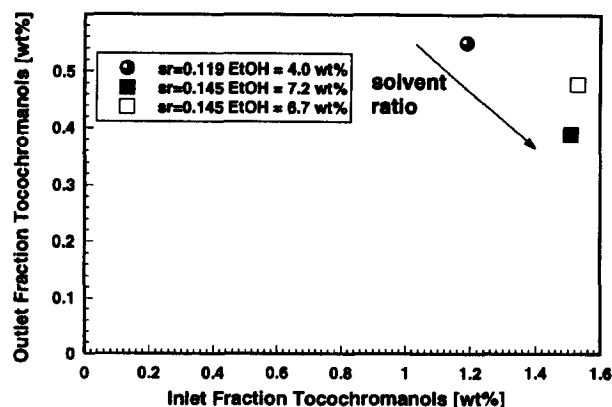


Figure 8. Results from the absorber experiments.

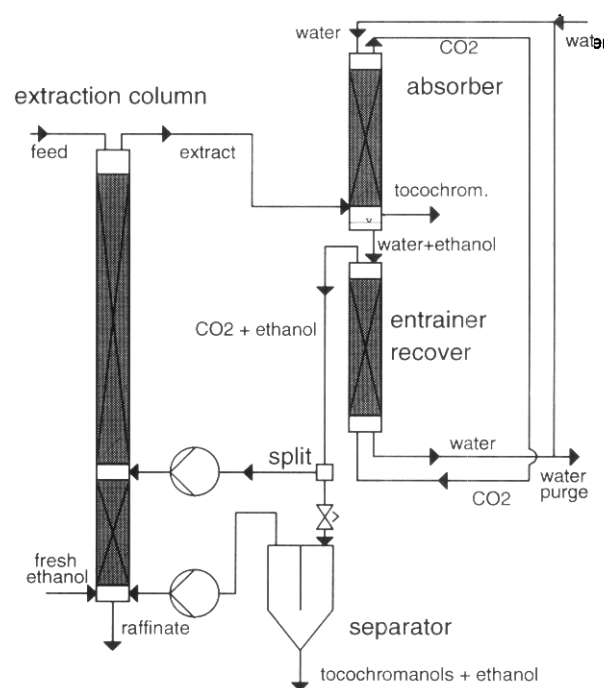


Figure 9. Flow scheme of a possible application of the new regeneration method.

the case for an extraction column with two different solvent feed streams as shown in Figure 9. The major part of the fluid is regenerated in the absorber and recycled after compression into the column at about 1/4th of the total

TABLE III
Conditions of the Experiments Using the Closed Cycle Apparatus

Experiment	Solvent ratio	wEthanol CO ₂ (kg h ⁻¹)	Mass flow ethanol (kg h ⁻¹)	Mass flow water (kg h ⁻¹)	Mass flow temperature	Absorber
1	0.119	3.1%	8.5	0.35	1.05	339 K
2	0.145	6.8%	6.5	0.51	1.02	341 K
3	0.151	7.3%	6.2	0.44	1.0	341 K

height of the column. In the lowest part of the column a further purification of the raffinate is done by countercurrent flow with CO₂ in higher purity. This solvent purity is achieved by a second regeneration step for the minor part of the solvent using a pressure reduction valve and a precipitator. Also shown in Figure 6 is a possible regeneration of the ethanol from the water-ethanol phase. This is done by a countercurrent extraction where the ethanol is separated from the water.⁸ The ethanol is extracted by the upstreaming supercritical solvent while the almost ethanol-free water is led to the top of the absorber column. This results in a good recovery of the entrainer and no further need of separation for the water cycle. The CO₂ will be saturated with water throughout the complete cycle (approx. 0.5 wt %). Of course, the losses of ethanol have to be replaced and the water cycle must be purged.

A positive side effect of the method is that the tocochromanol phase leaving the absorber contains less ethanol compared to a pressure-reducing process because the ethanol is dissolved in the water phase. The process might also enhance the selectivity for solute components

if the regeneration is done with a two-stage process. This will be investigated in the future.

It is likely that this method works for other water soluble entrainers as well.

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