

Antero Laitinen

Supercritical fluid extraction of organic compounds from solids and aqueous solutions



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Abstract

In this thesis, the extraction of organic compounds from solid and liquid matrices using supercritical carbon dioxide as a solvent was studied.

Dense carbon dioxide is a very good solvent for the cyclic amide, 6-caprolactam. 6-caprolactam exhibits relatively high solubilities, i.e. up to around 17 wt% at ambient temperatures, and at pressures below 220 bar. Carbon dioxide can be used to dissolve and extract 6-caprolactam from solid and liquid matrices.

The remediation of contaminated soil by carbon dioxide extraction was studied. The effect of extraction pressure, temperature, soil moisture content, pH, carbon dioxide mass flow rate, and extraction time on the residual pollutant concentration in the soil after extraction was systematically studied. The selected pollutants were phenanthrene, 2,3,4,6-tetrachlorophenol and pentachlorophenol. The results indicate that at least 80–90 % of the initial amount of pollutant can be removed at moderate temperatures even in the most difficult cases, and in many cases over 99 % of the initial amount of pollutant can be removed from the soil. Supercritical extraction is best suited to sand or silt type soils, which have a low adsorption capacity. The extraction results are found to be case-dependent, and soil remediation at moderate temperatures is observed to be difficult if the pollutant binds strongly to the soil or if the acceptable level of residual concentration is very low.

A novel mechanically agitated countercurrent continuous extraction column was introduced by extracting ethanol and 1-butanol from aqueous solutions in the rotating disk column and in the Oldshue-Rushton column. Column efficiencies were measured as a function of solvent-to-feed ratio and rotor speed. Generally, the values of the height equivalent to a theoretical stage HETS were in the range of 0.4–0.8 m. Mechanical agitation enhanced the extraction only at relatively

high solvent-to-feed ratios. Column capacities for both types of column were measured, and the total throughput calculated as the feed plus solvent flow rate divided by the smallest cross-sectional area was 50–80 m³h⁻¹m⁻². A mechanically agitated column successfully combines the high capacity of supercritical spray columns and the high efficiency of supercritical packed columns.

Preface

The research described in this thesis was carried out at the Chemical laboratory of the Technical Research Centre of Finland (VTT) during the years 1993–1998. I would like to thank VTT Chemical Technology for the excellent working facilities and for providing me with the opportunity to test my ideas. Financial assistance from Tekes is gratefully acknowledged.

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I warmly thank my friends and colleagues at VTT for helping me in so many ways during the project and for creating such a good working atmosphere. In particular, I would like to thank my co-authors, Matti Jäntti and Juha Kaunisto, and my colleagues, Martti Alkio and Markku Rantakylä, for their support and advices. My sincere appreciation is due to Mr. Richard Walker for revising the language of this thesis.

My most sincere thanks are due to my parents, my sister and my brother, and my friends for their unselfish support during this work.

Espoo, February 3rd, 1999

Antero Laitinen

List of publications

The thesis is based on the following publications, which are referred to by Roman numerals:

- I Laitinen, A., Jäntti, M. Solubility of 6-Caprolactam in Supercritical Carbon Dioxide. *J. Chem. Eng. Data*, 41(1996), pp. 1418–1420.
- II Laitinen, A., Michaux, A., Aaltonen O. Soil Cleaning by Carbon Dioxide Extraction: A Review. *Environ. Tech.*, 15(1994), pp. 715–727.
- III Laitinen, A. Soil Cleaning by Carbon Dioxide Extraction. In: *Advances in Environmental Control Technology, Ecological Issues and Environmental Impact assessment*. P. N. Cheremisinoff, (ed.). Gulf Publishing Co., Houston, Texas, 1997. Pp. 217–236.
- IV Laitinen, A. Remediation of Contaminated Soil by Carbon Dioxide Extraction. *Plant Design Report Series*, No. 53, Helsinki University of Technology, Espoo 1999. 20 p.
- V Laitinen, A., Kaunisto, J. Hydrodynamics and Mass Transfer in a Rotating Disk Supercritical Extraction Column. *Ind. Eng. Chem. Res.*, 37(1998), pp. 2529–2534.
- VI Laitinen, A., Kaunisto, J. Oldshue-Rushton Column in Supercritical Fluid Extraction. *Sep. Sci. Tech.*, 34(1999), pp. 1859–1872.
- VII Laitinen, A., Kaunisto, J. Supercritical Fluid Extraction of 1-Butanol from Aqueous Solutions. *J. Supercritical Fluids.*, 15(1999), pp. 245–252.

The author's contribution

The author has had an active role in all stages of the work reported in this thesis, including the design and construction of the experimental equipment, experimental design, the development of the working procedures, the carrying out of the experiments reported in publications, the interpretation the results, and the writing of the papers.

Matti Jäntti did the modeling work in Paper I. Olli Aaltonen contributed significantly to the writing of Paper II. The work of Martti Alkio in designing and constructing the apparatus used in the soil extraction experiments is acknowledged. A lot of the practical work in Papers V, VI and VII was carried out by Juha Kaunisto.

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(<http://www.inf.vtt.fi/pdf/publications/1999/>)***

Abbreviations

a	interfacial area, m^2/m^3
C	pollutant concentration in the soil, mg/kg
D	column diameter, m
E	extraction coefficient = mS/F
F	flow rate of feed, kg/h
h	holdup
HETS	height equivalent to a theoretical stage, m
HTU_{od}	height of a transfer unit based on the dispersed phase, m
K_{od}	overall mass transfer coefficient based on the dispersed phase, 1/s
m	distribution coefficient (concentration in solvent phase/concentration in feed phase)
NTU_{od}	number of transfer units based on the dispersed phase
p	pressure, bar
S	flow rate of the solvent, kg/h
t	extraction time, min
T	temperature, $^{\circ}\text{C}$
y	weight fraction of solute in the dispersed phase, mole fraction in section 4
V	superficial velocity, m/s
w	water content in the soil, wt%
V_s	slip velocity, m/s
Z	total agitated height of the column, m
ρ	density, g/ml

Subscripts

1	at the top of the column
2	at the bottom of the column
c	critical value, continuous phase in section 6
d	dispersed phase
f	final
i	initial

Superscripts

*	equilibrium value
–	through smallest cross-sectional area

1. Introduction

In recent years, the use of supercritical fluid extraction for the removal of organic compounds from different liquid and solid matrices has attracted much attention. This technique has some advantages over more conventional separation techniques, largely due to the unique physical properties of supercritical fluids. Supercritical fluids exhibit a liquid-like density, while their viscosity and diffusivity remain between gas-like and liquid-like values. Also, the recovery of a supercritical solvent after extraction can be carried out relatively simply by reducing the pressure and evaporating the solvent, because a supercritical solvent is usually a gas at NTP. There are several applications in the food processing, pharmaceutical and chemical industries, notably in the decaffeination of coffee beans and the production of polyethylene [1].

Another application now under development is the clean-up of contaminated soil and hazardous waste sites. Incineration, washing, biodegradation, isolation, solidification and solvent extraction are potential methods for the remediation of contaminated soil. In solvent extraction treatment technologies, the contaminated soil is first mixed with a suitable solvent. The contaminant dissolves into the solvent and is thereby removed from the cleaned soil. The spent solvent is then evaporated to get the contaminant into a very concentrated form. The isolated contaminant is transferred to an appropriate end treatment, such as an incineration plant, or, if the contaminant is valuable, a recovery process. The pure solvent that is evaporated from the spent extraction solution is recycled back to the soil extraction apparatus. Conventional extraction or leaching processes use organic, liquid solvents as the extraction medium.

In general, distillation is used in the chemical industry to separate organic products or wastes from concentrated aqueous solutions. However, the distillation of dilute aqueous solutions is energy intensive, and the formation of azeotropes can prevent the use of ordinary distillation. Other separation techniques, such as liquid-liquid extraction, could provide an appropriate solution if ordinary distillation is not applicable. In ternary liquid-liquid extraction, a liquid feed consisting of a carrier and solute is contacted with a solvent, which is practically immiscible with the carrier, but at the same time, a good solvent for the solute. Thus, the solute is transferred from the carrier to the solvent. The solute can be separated from the solvent by, for example,

distillation; the solvent is then recycled. Extraction processes are applied in the petroleum industry to separate close-boiling hydrocarbon mixtures (e.g. the BTX -process), in the pharmaceutical industry to separate heat-sensitive antibiotics, and in the chemical industry to separate, for example, caprolactam from aqueous feed. Supercritical fluids have been tested as solvents in several extraction applications, such as the extraction of ethanol or acetic acid from aqueous solutions [1].

This thesis focuses on the supercritical fluid extraction of organic compounds from solids and aqueous solutions. The aim of this work is to study the engineering fundamentals, which would allow the technically and economically successful exploitation of supercritical extraction technology to solve the practical separation problems

Before successful supercritical extraction operations can be started, it is necessary to understand the solvent behavior of compressed gases. Therefore, firstly, the solubility of ϵ -caprolactam was measured and the Peng-Robinson equation of state was used to model the solubility of ϵ -caprolactam in supercritical carbon dioxide [I]. Secondly, the possibility of using the compressed carbon dioxide at a supercritical state instead of a liquid solvent to extract organic compounds from contaminated soils was studied [II–IV]. Selected organic compounds including polycyclic aromatic hydrocarbons (PAHs) and chlorophenols were extracted from spiked and real contaminated samples. Thirdly, a high-pressure mechanically agitated continuous countercurrent extraction column was introduced, and the extraction of ethanol and 1-butanol from aqueous solutions in this column was studied [V–VII].

2. Supercritical fluids

A substance is at the supercritical state, i.e. a supercritical fluid, when its temperature and pressure are simultaneously higher than the critical values. A supercritical fluid exists in a single fluid phase possessing characteristics between those of gases and liquids. Figure 1 illustrates a pressure-temperature diagram in the critical region of pure carbon dioxide.

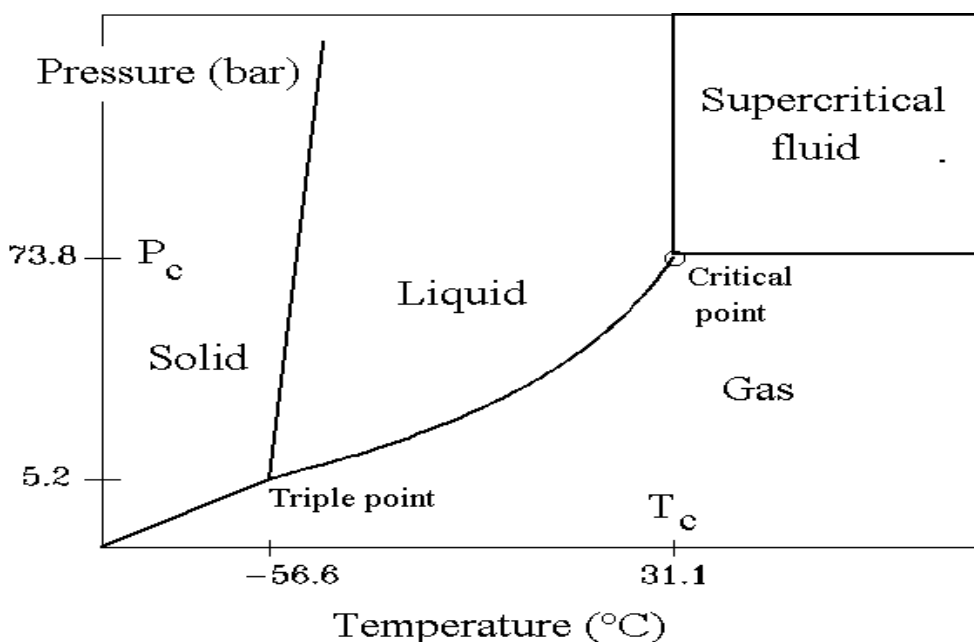


Figure 1. The phase diagram of carbon dioxide.

Above the critical temperature a liquid phase will not appear regardless of how much the pressure is increased. The critical pressure is the pressure, which causes the gas to become a liquid at the critical temperature. The density of a compound at the critical point is called the critical density. The critical temperatures, pressures and densities of some common solvents are listed in Table 1.

Table 1. Critical properties of selected solvents [1, 3].

SOLVENT	T _c (°C)	P _c (bar)	ρ _c (g /ml)
Ammonia	132.5	113.5	0.24
Benzene	289.0	48.9	0.30
n-Butane	152.0	38.0	0.23
Carbon dioxide	31.1	73.8	0.45
Chlorotrifluoromethane	28.8	39.5	0.58
Dichlorodifluoromethane	111.7	39.9	0.56
Ethane	32.2	48.9	0.20
Ethanol	243.4	63.8	0.28
Ethylene	9.3	50.4	0.22
Isopropanol	235.3	47.6	0.27
Methanol	240.5	79.9	0.27
Nitrous oxide	36.5	72.3	0.46
n-Propane	96.8	42.6	0.22
Propylene	91.9	46.2	0.23
Toluene	318.6	41.1	0.29
Water	374.2	221.2	0.34

The compressibility of a supercritical fluid just above the critical temperature is large compared to the compressibility of ordinary liquids. A small change in the pressure or temperature of a supercritical fluid generally causes a large change in its density. A commonly accepted opinion is that the solvent power of a supercritical fluid is mainly related to its density in the critical point region [2]. A high density generally implies a strong solvating capacity. The unique property of a supercritical fluid is, that its solvating power can be tuned by changing either its temperature or pressure.

A significant cost factor for many conventional liquid-liquid extraction processes is the recovery of the spent extraction solvent. The separation of the solvent from the solute is usually done by distillation, which can sometimes be very energy-consuming. If a supercritical solvent is applied, the solute can be separated from the mixture by e.g. lowering the pressure of the mixture. One

should remember, that to recycle the supercritical solvent, it must be compressed again. This can be a significant cost factor, if the difference between the pressure in the extraction vessel and the pressure in the separator is relatively large.

Even though the density of a supercritical fluid increases with pressure and becomes liquid-like, the viscosity and diffusivity remain between liquid-like and gas-like values [4]. Additionally, supercritical fluids exhibit almost zero surface tension, which allows facile penetration into microporous materials. As a result of the advantageous combination of physicochemical properties, the extraction process can often be carried out more efficiently with a supercritical solvent than it can with an organic liquid one. A comparison of selected physicochemical properties of liquids, gases and supercritical fluids is presented in Table 2.

Table 2. Selected physicochemical properties of liquids, gases and supercritical fluids [1].

Properties	Liquid	Supercritical fluid	Gas
Density (kg/m ³)	1 000	200–800	1
Viscosity (mPas)	0.5–1.0	0.05–0.1	0.01
Diffusivity (cm ² /s)	10 ⁻⁵	10 ⁻⁴ –10 ⁻³	0.1

The critical temperature (T_c) of the compound depends on the polarity of the compound. As seen in Table 1, the critical temperatures of non-polar gases, such as carbon dioxide or ethane, are below 50 °C, whereas for polar compounds, such as methanol or water, the critical temperature is well above 200 °C. In practice, especially in food-related industries, it is usually desirable that the critical temperature of the solvent is below 100 °C. Therefore, the solvents commonly used for supercritical operations are low molecular weight gases, such as carbon dioxide, ethane and propane.

Carbon dioxide is the most commonly used solvent in industrial practice for several reasons. Carbon dioxide has a technically convenient critical pressure and temperature of 73.8 bar and 31.1 °C, respectively. It is non-toxic, non-

flammable, non-reactive, non-corrosive, and abundant. Furthermore, it is the second least expensive solvent after water [5], and it does not leave any solvent residue after extraction.

Carbon dioxide is a relatively good solvent for hydrocarbons and non-polar solids. However, owing to the unique properties of supercritical solvents and to the rather large quadrupole moment of carbon dioxide in particular, supercritical carbon dioxide will dissolve many relatively volatile polar compounds. This explains why methanol and DMSO, for example, are miscible with supercritical carbon dioxide at 400 bar and 40 °C [1]. Adding small amounts of polar co-solvents, called entrainers, to the bulk carbon dioxide can enhance the solubility of polar, non-volatile solutes in supercritical carbon dioxide. Water and short-chain alcohols are efficient and usually the most acceptable co-solvents in industrial practice. Only the organic, non-polar or volatile compounds are expected to be effectively extracted from soils and aqueous matrices. An excellent review of solid solubilities in supercritical carbon dioxide is offered by Bartle et al. [6].

3. Applications of supercritical fluid extraction

3.1 Historical background

In 1879 Hannay and Hogard [7] reported that changes in pressure caused inorganic salts like cobalt chloride to dissolve in or precipitate from ethanol at a temperature above the critical temperature of ethanol. Later, Villard [8] demonstrated that gases such as methane, ethylene, carbon dioxide and nitrous oxide dissolve a number of liquid or solid compounds, such as camphor, stearic acid or paraffin wax. Since then, several authors have described the ability of a supercritical fluid to dissolve solid materials. The solubility of naphthalene in supercritical ethylene was studied by Diepen and Scheffer in 1948 [9], followed by several other studies [10–15] in which the solubility of naphthalene in a variety of supercritical solvents was examined. In 1954 Francis [16] presented a study, where he reported phase diagrams for 464 ternary systems containing liquid carbon dioxide, and measured the solubility of 261 organic compounds in near critical liquid carbon dioxide. Even though supercritical carbon dioxide was not applied in the study, the data can be used to assess the solvent power of supercritical carbon dioxide, because a compound which is soluble in liquid carbon dioxide is usually also soluble in supercritical carbon dioxide.

The ability of near critical or supercritical solvents to dissolve organic compounds was utilized in industrial operations in the middle of the twentieth century. A process for deasphalting lube oils using subcritical propane introduced by Wilson et al. [17] in 1936 is still used today. This process takes advantage of the possibility of changing the density of propane in the vicinity of its critical point. Since the solvent characteristics of propane can be changed dramatically by changing the pressure or temperature, this single solvent can be used to separate various fractions, including paraffin wax, asphalt, heavy ends, naphthalenes, color bodies, and purified light oil. The Solexol Process developed by Dickinson and Meyers [18] for the separation and purification of vegetable and fish oils uses propane as a solvent. The purpose of this process is to concentrate the polyunsaturated triglycerides and to extract vitamin A from the fish oils. The commercialized ROSE Process (Residuum Oil Supercritical Extraction) uses subcritical butane or pentane to fractionate residuum oil [19].

3.2 Food processing applications

Food processing is the most widely investigated industrial application of supercritical fluid technology. Carbon dioxide is a particularly suitable solvent for food processing applications, because its moderate critical temperature ($T_C = 31.1\text{ }^\circ\text{C}$) enables the extraction of thermally labile food compounds. Additionally, it is non-toxic, environmentally acceptable, and relatively inexpensive. Compared with conventional solvents such as hexane, carbon dioxide does not leave any harmful solvent residue after extraction. The food material to be extracted is often solid, and therefore semi-batch extraction is frequently used. A schematic picture of a semi-batch supercritical fluid extraction system is presented in Figure 2.

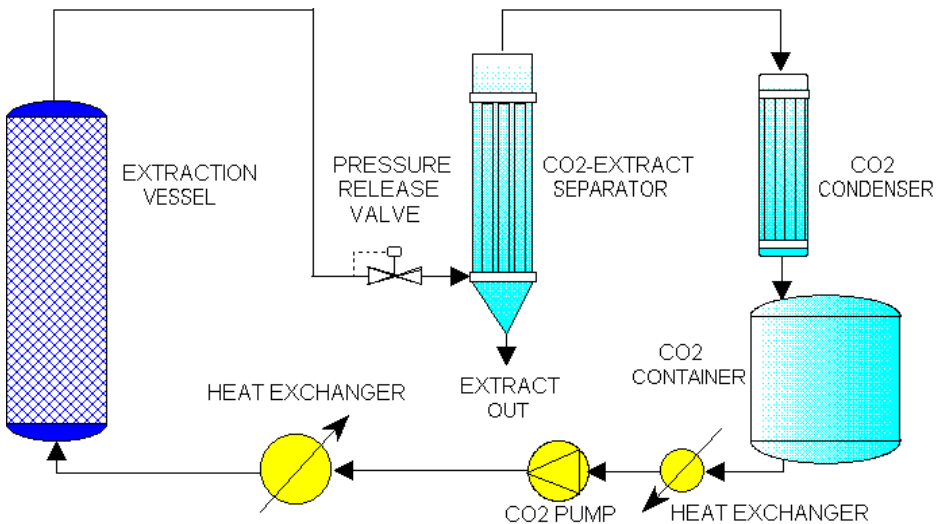


Figure 2. Operating principle of a semi-batch supercritical fluid extraction system.

Liquid carbon dioxide from the container is pressurized by the pump and heated to the extraction temperature by the heat exchanger. Pressurized carbon dioxide flows through the extraction vessel and dissolves the soluble extract. Carbon dioxide loaded with the extract is then flashed in the pressure release valve and carbon dioxide, now in the vapor and liquid phase, flows into the separator, where the liquid fraction is vaporized by heating. The extract is not soluble in

carbon dioxide vapor and can be removed from the bottom of the separator. Carbon dioxide vapor is condensed and returned to the container. A heat pump system can be installed to transfer heat from the condenser to the separator.

Supercritical carbon dioxide is industrially used to extract caffeine from green moist coffee beans and to produce pharmaceuticals, natural products, and specialty chemicals. The largest plants use batch extraction vessels with volumes up to tens of cubic meters. The flow rate of carbon dioxide in the largest plants are several tons per hour and the operating pressures are usually within 200–300 bars. Recently, Maxwell House Division of General Foods employed a 25 000 000 kg/a coffee decaffeination supercritical extraction process in Houston [1]. The semi-continuous high pressure extraction column is estimated to be around 23 m high.

3.3 Reactions in supercritical media

Polyethylene can be produced by polymerizing supercritical ethylene. In the case of radical polymerization, an ethylene pressure of 1 200–3 000 bar is required at 150–300 °C to produce polyethylene with a sufficient high molecular weight. Oxygen or organic peroxides are used as initiators [20]. The fact that the solvent power of a supercritical fluid can be changed by changing its pressure can be utilized to fractionate polymers such as polyethylene, ethylene-based copolymers, and polysiloxane [1]. In principle, the synthetic polymer can first be dissolved in a supercritical fluid solvent at high pressure. The pressure is then slightly reduced in a pressure reduction valve. Because the density of the supercritical fluid is also reduced, the highest molecular weight polymer fraction is no longer soluble in the solvent. This fraction is precipitates into the separator vessel. The pressure of the mixture which leaves the first separation vessel is then reduced again, causing the next highest molecular weight polymer fraction to precipitate.

Supercritical fluids serve as a reaction medium for the reactants, catalysts and products, or they can be a solvent and a reactant at the same time, as in polyethylene-free radical polymerization. Additionally, the properties of supercritical fluids may be utilized to separate the product from the reactants or catalyst by reducing the pressure of the reaction mixture. In the mid 1980s it was

discovered that enzymes are active in supercritical carbon dioxide [21, 22]. Since then, several supercritical fluid research groups have investigated enzymatic reactions, and more than 200 papers have been published. The basic motivation is to replace the hazardous organic solvents with environmentally acceptable carbon dioxide. Also, enzymes are more stable in the non-aqueous supercritical reaction environment than in the conventional aqueous environment. Review articles concerning enzymatic catalysis in supercritical fluids are available [23–25].

Supercritical water oxidation introduced by Modell [26] is used to destroy organic wastes. This technique benefits from the fact that supercritical water ($T_c = 374\text{ }^\circ\text{C}$, $p_c = 221\text{ bar}$) behaves like a non-polar solvent, showing complete miscibility for organics like toluene and for gases like oxygen and hydrogen. Under supercritical conditions ($T > 374\text{ }^\circ\text{C}$) organics such as chlorinated hydrocarbons are quickly oxidized into carbon monoxide, water and hydrochloric acid. Corrosion can be a severe problem in supercritical water oxidation reactors, especially if halogen-containing organics are oxidized. Furthermore, supercritical water does not dissolve salts, and depositions of salts can block the pipes and valves.

Several other reactions, such as oxygenation [27], hydroformulation [28], alkylation [29] and hydrogenation [30, 31] have been studied in supercritical fluids. Hydrogenation is a particularly interesting application. Supercritical fluids are almost completely miscible with hydrogen gas. This property means that hydrogenation rates in supercritical media are presumably much faster than in the conventional liquid-phase hydrogenations because of the high hydrogen concentration in the reaction mixture and on the catalyst surface. By applying a supercritical solvent, the external mass transfer resistance can be neglected.

3.4 Particle production

Supercritical fluids can be used as particle formation media [32, 33]. Two techniques have been used to make particles from supercritical fluids. Rapid expansion from supercritical solutions (RESS) is used to form fine particles of substances which are soluble in a supercritical solvent. In the RESS technique the substance is first dissolved in a supercritical solvent, after which the pressure

is rapidly decreased in a specifically designed nozzle, resulting in supersaturation of the substance in the supercritical solvent and leading to the formation of small particles with a narrow particle size distribution. Gas anti-solvent recrystallization (GAS) is used for substances, which are not soluble in a supercritical solvent. The substance is dissolved in a liquid solvent such as methanol, and a supercritical solvent acts as an anti-solvent to rapidly precipitate the substance in a nozzle.

3.5 Environmental applications

The remediation of contaminated soil by carbon dioxide extraction is considered to be a promising technique, and it has received a great deal of interest over the past ten years. Several authors [34–40] have extracted on a bench scale PAHs such as naphthalene, fluoranthene, pyrene, benzo[a]-anthracene, benzo[a]-pyrene and perylene, diesel oil containing C13-C22 hydrocarbons, PCBs, chlorophenols such as 2-chlorophenol and 2,4,6-trichlorophenol, and dioxins and furans from spiked and real contaminated soil. According to these experiments, the extraction result mainly depends on the soil type, extraction conditions, and type of contaminant. Sand is usually the best matrix for extraction, whereas mud is considered to be a difficult matrix. The success of the extraction operation depends on the soil-pollutant interaction, which is difficult to predict because there are so many types of soil. Contaminants which do not bind strongly to the soil are therefore the extraction targets with the most potential. It should be remembered that it is easier to extract pollutants from spiked soil than from real contaminated soil.

The operating principle of the supercritical carbon dioxide extraction of soil is described in Papers II [p. 717] and III [p. 219]. Furthermore, equipment for soil remediation is presented in Paper III [pp. 228–231]. The extraction vessels are usually operated batch-wise. The solids handling in high-capacity, high-pressure batch processes is a notable disadvantage, and an efficient method of moving the soil into the high-pressure extractor would be a significant advancement.

3.6 Separations in continuously operated columns

Supercritical Fluid Chromatography (SFC) with pure carbon dioxide eluent is applicable to the separation of relatively non-polar compounds, i.e. compounds which are soluble in toluene, hexane, freons and chlorinated solvents. A distinctive characteristic of SFC is that ion-ion interactions between eluted compounds and silica are practically absent. For example, compounds which contain primary or secondary amine groups are selectively fractionated with SFC. These compounds are generally impossible to separate by HPLC-silica systems due to severe peak tailing. The benefits of SFC are the increased separation rates due to high molecular diffusion in supercritical fluids, low operating costs because of low energy consumption in recycling pressurized carbon dioxide, non-toxicity and non-flammability of the carbon dioxide eluent, and simple recovery of products from the eluent by pressure reduction. An industrial-scale supercritical fluid chromatography plant for the purification of cyclosporin is presented by Aaltonen et al. [41].

A supercritical fluid can be applied as a separation agent in the same way as other solvents are applied in other separation processes, such as continuous countercurrent liquid-liquid extraction or gas absorption. Instead of using a liquid solvent supercritical fluid is used as a solvent for separation. Because the feed is liquid, it is possible to use the continuous mode of operation, which is much more suitable for high-pressure processes than the semi-batch mode. A two-cascade column containing a stripping and an enriching section can be continuously operated with relative ease. The same kind of equipment is needed to carry out continuous countercurrent supercritical fluid extraction, as in the semi-batch system presented in Figure 2, except that the extraction vessel in Figure 2 is replaced by a column in which the feed liquid is continuously pumped. A continuously operated raffinate valve is also needed at the bottom of the column, so that the liquid feed can be removed from the column, and the phase boundary inside the column is kept constant. This valve can be operated manually or automatically, for example by using an optical sensor to control the phase boundary.

According to Brunner [42], a general field of applications for countercurrent supercritical fluid extraction include fine chemicals such as free fatty acids, tococromanols, carotinoids, squalane, squalene, iso-cyanides, lecithin,

glycerides, hydrocarbons, citrus oils, organic compounds from aqueous extracts, and others.

The separation of organics from aqueous solutions by applying supercritical extraction has been studied by several research groups. Applications include the purification of industrial waste waters [43, 44], the separation of azeotropic mixtures [45], the enrichment of flavor fractions from wine or juice [46–49], and the separation of organics from fermentation processes [50].

Tiegs et al. [51] have used countercurrent a packed extraction column equipped with reflux to extract fatty acid ethyl esters from fish oil. Simões et al. [52] reported mass transfer results for the separation of a mixture of two terpenes of similar volatilities. Carmelo et al. [53] have designed a column for the extraction of free fatty acids (FFA) from olive oil.

The extraction of alcohols, such as ethanol, propanol or phenol, from aqueous solution has been tested intensively [54–59]. The separation of acetic acid from a dilute aqueous solution has been tried [1], but the distribution coefficient of acetic acid in a CO₂/acetic acid/water system is only about 0.03 (weight basis), which means that this application is not technically feasible. A partial list of other organics tested includes dioxane, acetone, formamide, N,N-dimethyl formamide, and ethylene glycol [1]. One possibility is to utilize the acidic property of carbon dioxide, and to use it as a solvent to extract weakly basic organics like pyridine from an aqueous solution [60].

Several other potential applications have undergone development. These applications include the regeneration of activated carbon, the swelling of polymers, and the separation of hydrocarbon and oil mixtures [1].

4. Solubility measurements

In the first paper of this thesis [I], the solubility of 6-caprolactam in supercritical carbon dioxide was reported. The ability of dense carbon dioxide to dissolve 6-caprolactam could possibly be utilized in the industry related to nylon production. Carbon dioxide could be used as a solvent to separate 6-caprolactam from various solid or liquid feeds in applications related to production, the recycling of used nylon or the purification of waste streams containing 6-caprolactam.

4.1 Experimental

The solubility of 6-caprolactam in supercritical carbon dioxide was measured in the static view cell apparatus [I]. The apparatus is equipped with a sapphire window, which allows visual observation of high-pressure phase behavior. A schematic diagram of the apparatus used in the experiments is shown in Figure 3.

Solubility measurements were carried out by first charging a desired amount of solid to the cell, after which the cell was slowly pressurized by pumping in carbon dioxide. A carbon dioxide pump control unit was used to calculate the amount of carbon dioxide pumped to the cell. The unit showed how much the volume of the pump cylinder changed during the pressure vessel loading while the piston was adjusted to maintain constant pressure. After loading, the pressure in the closed cell was slowly increased by moving the piston inside the cell until complete miscibility of the solid and the solvent was reached. After this, the pressure was slowly reduced until a second phase appeared. These phase changes were recorded on video tape for later examinations. The solubility of the solid is calculated from the masses of the solid and carbon dioxide. Details of the procedure have been reported in Paper I.

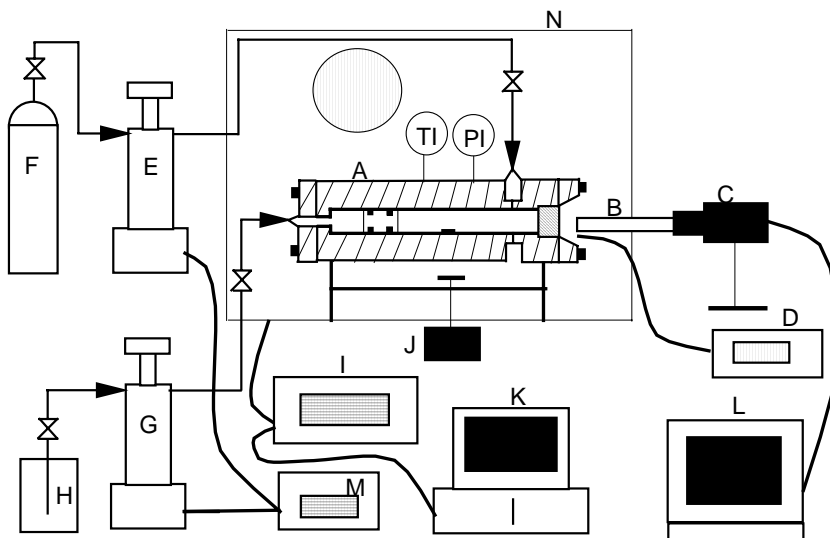


Figure 3. Apparatus used in solubility measurements.

A, variable volume view cell; B, Boroscope; C, camera; D, light source; E, carbon dioxide pump; F, carbon dioxide container; G, hydraulic oil pump; H, oil container; I, data acquisition and control unit; J, magnetic stirrer, K, computer; L, monitor; M, pump control unit; N, air bath.

4.2. Solubility results

6-Caprolactam was found to exhibit relatively high solubility in supercritical carbon dioxide, i.e. up to around 17 wt% in Figure 4. This was expected, since 6-caprolactam is very soluble in most common organic solvents [61]. The shape of the isotherms was relatively similar at all three temperatures, and the solubility curves increase steeply with pressure. The system temperature usually has a significant effect on the solid solubility in supercritical fluids, because it influences the solid vapor pressure, solvent density and solute-solvent interactions. In these experiments the temperature range was relatively narrow, and there were no significant temperature effects. The solubility was mostly affected by the solvent density, as seen in Table 3.

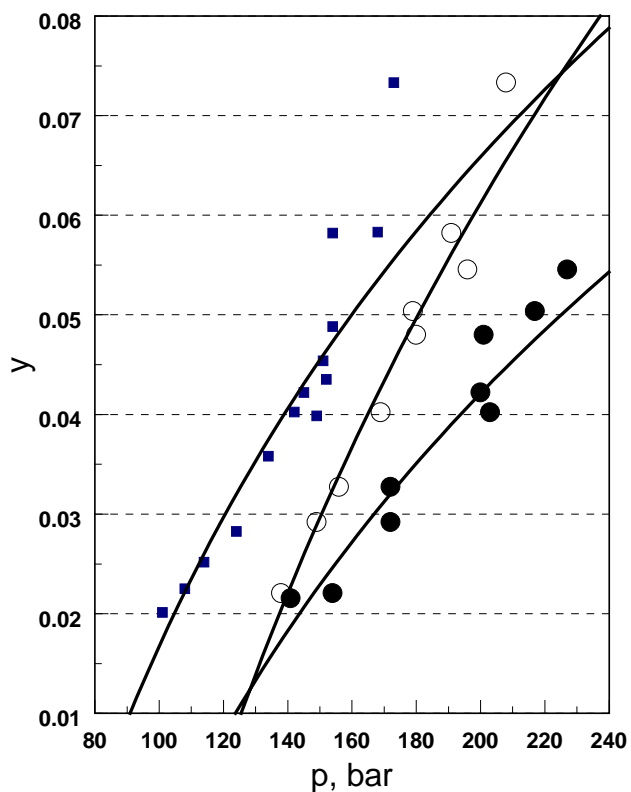


Figure 4. Mole fraction solubility of 6-caprolactam in supercritical carbon dioxide as a function of pressure: (■) 307 K; (○) 314 K; (●) 324 K; (—) calculated with PR-EOS [1].

Table 3. Mole fraction solubility of 6-caprolactam in supercritical carbon dioxide [I, Table 2].

T = 307 K			T = 314 K			T = 324 K		
p	ρ_{CO_2}	$10^3 y$	p	ρ_{CO_2}	$10^3 y$	p	ρ_{CO_2}	$10^3 y$
bar	kg m^{-3}	-	bar	kg m^{-3}	-	bar	kg m^{-3}	-
101	730.1	20.1	138	752.2	22.1	141	666.5	21.5
108	750.2	22.5	149	772.2	29.2	154	701.9	22.1
114	764.3	25.2	156	783.2	32.7	172	738.2	29.2
124	784.2	28.3	169	801.2	40.2	172	738.2	32.7
134	800.7	35.8	179	813.5	50.4	200	779.3	42.2
142	812.1	40.2	180	814.7	48.0	201	780.5	48.0
145	816.1	42.2	191	826.4	58.2	203	783.0	40.2
149	821.2	39.9	196	831.4	54.6	217	799.0	50.4
151	823.7	45.4	208	842.7	73.3	227	809.3	54.6
152	824.9	43.5						
154	827.3	48.8						
154	827.3	58.2						
168	842.6	58.3						
173	847.6	73.3						

The Peng-Robinson equation of state was used to model the solubility of 6-caprolactam into supercritical carbon dioxide. Two adjustable parameters were fitted to the experimental data by the Simplex search method as described in Paper I. The first parameter is a mixture parameter describing the intermolecular interaction between the unlike molecules, and the second parameter stands for the effect of the different size and structure of unlike components. No crossover pressure, i.e. the pressure at which two isotherms intersect, was found under the experimental conditions, although according to the Peng-Robinson model, isotherms at 314 K and 324 K seem to cross at 130 bar. The Peng-Robinson model with two adjustable parameters fitted to the experimental data relatively well at lower pressures, whereas at high pressures there seemed to be a deviation, especially at 307 K.

5. Soil extraction measurements

Prior to the experimental work, a literature review concerning the removal of organic pollutants from soil was written [II]. The primary purpose of the soil extraction work was to study the extraction of selected pollutants from soil-water slurries. The basic idea was to avoid the technically cumbersome semi-batch extraction process by first slurring the soil with water, and then continuously pumping the soil-water slurry to the extractor, where the pollutants were removed from the soil.

5.1 Experimental

The characterization and preparation of the soil samples as well as the extraction apparatus and working procedures are briefly described in this section.

5.1.1 Soil characterization and preparation

EURO-soils 5 and 6 were chosen as standardized soils. These soils had been dried in an air-conditioned laboratory for 3 to 4 months, sieved, homogenized, and sterilized by radiation. They were received from the EEC Joint Research Center (Ispra, Italy). Table 4 shows the main pedological parameters of the soils.

Table 4. Main pedological parameters of EURO-soils 5 and 6 [IV].

Pedological characterization	EURO-soil 5	EURO-soil 6
Sand / %	81.5	1.7
Silt / %	12.5	82.3
Clay / %	6.0	16.0
pH in water	4.5	8.3
Organic carbon / %	9.23	0.25
Organic matter / %	15.92	0.78

The EURO-soil samples were spiked using the following procedure. Approximately 300 g of EURO-soil was weighed and put into a 1000 ml flask. Because the soil samples were completely dry, 8–10 wt-% water was first added to the soils. The flask was then rotated in a rotavapor (Heidolph VV 2000) for at least 12 hours, in order to homogenize the soil moisture. The soil was then spiked with trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol (Fluga AG, tech.) and phenanthrene (Fluka AG, purum). The desired amount of these compounds were weighed and dissolved into 200 ml dichloromethane (Fluga AG, purum). The mixture was decanted into the flask containing the soil. The soil slurry was then rotated for at least 12 hours, after which dichloromethane was evaporated slowly to dryness at room temperature. The spiked soil was then kept in the fume hood for 24 hours to assure that there was no dichloromethane residue in the soil. Soil samples taken from contaminated soil areas were not characterized.

5.1.2 Soil extraction apparatus and procedure

Extractions were performed using the laboratory-built extraction apparatus presented in Figure 5. Compressed carbon dioxide flows through the extraction vessel (100 ml) and through the spiked soil (typically 20 g). The vessel is heated to the extraction temperature in the air bath. Carbon dioxide leaving the extraction vessel and containing the dissolved solids is expanded in a cold trap. A heated micrometering valve is used to regulate the carbon dioxide flow-rate (± 50 g/h). The exhaust carbon dioxide is vented to the atmosphere after passing through silica and activated carbon beds, a rotameter and a dry gas meter. The pressure is controlled manually from the compressor (± 5 bar) and the temperature is controlled by the air bath regulator (± 1 °C).

The residual concentrations of polycyclic aromatic hydrocarbons (PAHs) and chlorophenols in the soil were analyzed after each extraction. PAHs were analyzed with a HP 5890 gas chromatograph (GC) equipped with a 30 m DB-1301 fused silica (J&W) capillary column. The detector was a HP 5970 Mass Selective Detector (MSD). The detection and quantification were performed in SIM-mode (Electron Ionization). The chlorophenol analysis was performed with a HP 5890 gas chromatograph equipped with Electron Capture Detectors (ECD) and two columns, 30 m \times 0.25 mm ID coated with 0.25 μ m films of SPB-5 and

SPB-35 (Supelco). More details concerning the analytic procedure are given in Paper [IV].

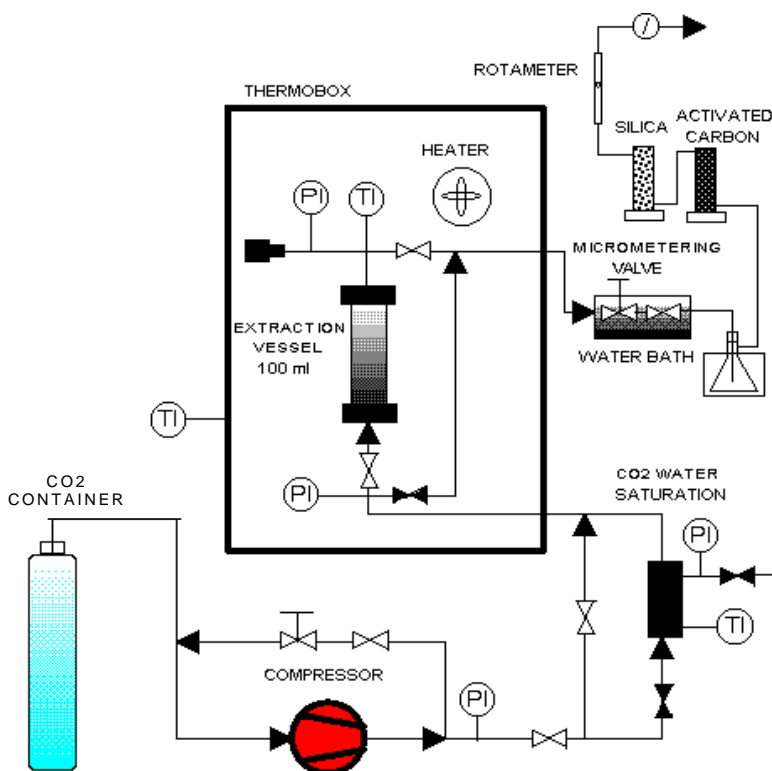


Figure 5. Soil extraction apparatus.

5.2. Soil extraction results

In Papers III and IV the extraction studies were carried out using either standardized soil, which was spiked with known amounts of pollutants before extraction, or by using soil samples taken from contaminated soil areas originally containing pollutants.

5.2.1 Extraction from spiked soil

The effect of soil moisture content on the residual pollutant concentration in the soil after extraction was the most important factor to be studied [IV]. The effect of extraction pressure, temperature, pH, carbon dioxide mass-flow rate, and extraction time on the residual pollutant concentration in the soil after extraction was also studied systematically [III, IV]. The experimental parameters and results are presented in Paper IV (Tables 3 and 4). Table 5 illustrates the best results and the set of extraction parameters with which these results were obtained.

Table 5. The best extraction results and parameters.

Pollutants: (1) phenanthrene, (2) 2,3,4,6-tetrachlorophenol, (3) pentachlorophenol. T is the extraction temperature, p is the extraction pressure, w is the soil moisture content, pH is the soil acidity, S is the carbon dioxide solvent flow rate, t is the extraction time, C_f is the final pollutant concentration in the soil after extraction, C_i is the initial pollutant concentration in the soil before extraction.

Soil	Pollutant	T (°C)	p (bar)	w (wt%-H ₂ O)	pH	S (kg/h)	t (min)	C _f (mg/kg)	C _i (mg/kg)
5	1	64	295	7.2	4.5	1.4	20	81	1 760
	2	64	295	7.2	4.5	1.4	20	101	1 870
	3	64	295	7.2	4.5	1.4	20	43	550
6	1	50	200	7.9	5.9	3	45	35	2 490
	2	64	295	14.0	6.7	1.5	20	8.5	940
	3	64	295	14.0	6.7	1.5	20	6.8	510

The selected pollutants were phenanthrene, 2,3,4,6-tetrachlorophenol and pentachlorophenol, and the selected soil matrices were standardized EURO-soils 5 and 6. According to Finnish recommendations [62], soil containing over 40 mg/kg phenanthrene, or over 4 mg/kg 2,3,4,6-tetrachlorophenol or pentachloro-

phenol is regarded as contaminated soil. In most extractions the final pollutant concentrations in the soil after extraction were not below the recommended values.

The initial water content in the soil tested in the experiments was 7–40 wt%. The experiments were carried out at relatively low temperatures (25–65 °C), and the extraction pressure range was 100–300 bar. The soil pH was changed by adding a weak aqueous solution of either H₂SO₄ or K₂CO₃ to the soil. By using a relatively high solvent flow rate (0.6–3 kg/h), it was possible to keep the extraction time relatively short (20–45 min).

The effect of soil moisture content on the pollutant concentration in the soil after extraction was dominant in all of the soil extraction experiments. Generally, the extraction of pollutants from soil-water slurries was not successful. Yeo and Akgerman [63] have affirmed this conclusion by extracting phenol and naphthalene from soil-water slurries at 47 °C and 175 bar. They were able to extract only 15 % of the initial amount of naphthalene and 60% of the initial amount of phenol from the soil.

It was found, that in order to reach the level of acceptable residual pollutant concentrations in the soil, it was necessary to keep the soil moisture content below approximately 10 wt%. It is possible that slurring the soil with water reinforces the adsorption between the soil and the hydrophobic pollutant, and the extraction result weakens. According to Andrews [64], the addition of small amounts of polar modifiers like water or methanol dramatically reduces PAH adsorption, indicating competition for polar adsorption sites on the soil. The highly polar aqueous environment deactivates the polar adsorption sites, leaving weak inductive, dispersive, and hydrophobic interactions as the only mechanism for sorption. However, non-ionic and nonpolar PAHs interact primarily with organic soil matter. Due to the negligible solubility of PAHs in water, adsorption onto the soil is highly favored in soil-water slurries [64]. It also seems reasonable to assume that water forms an extra mass transfer barrier, filling the soil pores, and carbon dioxide is not able to contact and dissolve the pollutant. A third possibility is that carbon dioxide saturated with water is no longer a good solvent for non-polar pollutants.

The effect of other parameters on the residual pollutant concentration in the soil was moderate compared with the effect of soil moisture content, even though it was noticed that the highest extraction pressure and temperature were favorable. This result is obvious, because a higher extraction temperature typically increases the pollutant desorption from the soil. Also, increasing the extraction pressure raises the solvent density and therefore increases the solubility of the pollutant in the supercritical carbon dioxide solvent.

It proved to be more difficult to remove 2,3,4,6-tetrachlorophenol and pentachlorophenol from soil 5 than from soil 6. This is due to the fact that EURO-soil 5 contains more organic matter than EURO-soil 6. Chlorophenols tend to bind strongly to organic matter. Reducing the pollutant sorption onto organic soil matter seems to be a key factor in soil extraction. One way to reduce the pollutant sorption is to increase the extraction temperature. It should be noted that increasing the extraction temperature, while keeping the pressure constant, reduces the carbon dioxide density, which usually reduces the pollutant solubility in the carbon dioxide. Therefore, the extraction pressure must be increased simultaneously to enhance the extraction.

5.2.2 Extraction from contaminated soil

Polycyclic aromatic hydrocarbons (PAHs) and chlorophenols were extracted from two different soil samples collected from polluted soil areas. In particular, the effect of soil moisture content on extraction efficiency was studied.

Polycyclic aromatic hydrocarbons (PAHs) were extracted from railway yard soil [IV]. The soil initially contained 50 mg/kg of PAHs. The soil was extracted with supercritical carbon dioxide at 200 bar and 40 °C. In the first experiment, the soil moisture content was 10 wt%. In this case the residual concentration of PAHs in the soil after extraction was 7 mg/kg. In the second experiment, the soil was slurried in water, and the soil moisture content was 50 wt%. This experiment was clearly worse. The residual concentration of PAHs in the soil after extraction was 30 mg/kg. The concentration of PAHs in the soil as a function of time is presented in Figure 6. Obviously, the presence of a relatively large amount of water (50 wt%) did make the efficient extraction of PAHs from the soil more difficult.

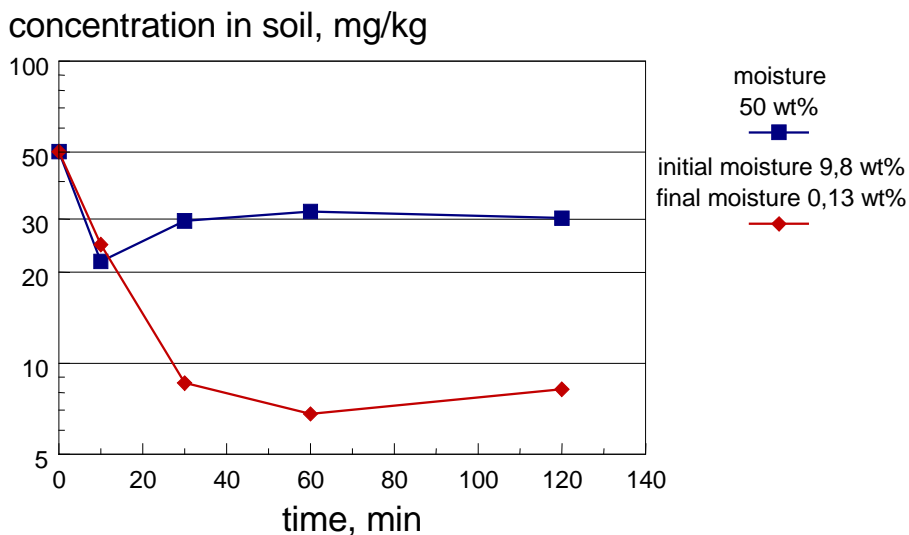


Figure 6. Extraction of PAHs from railway yard soil with supercritical carbon dioxide at 200 bar and 40 °C.

Chlorophenols were extracted from sawmill soil [IV]. The soil contained initially 62 mg/kg of 2,4,6-trichlorophenol, 3440 mg/kg of 2,3,4,6-tetrachlorophenol, and 800 mg/kg of pentachlorophenol. In the first experiment, the soil moisture content was 10 wt%. In this case the residual concentrations of the three chlorophenols in the soil after extraction were 0.5 mg/kg for 2,4,6-trichlorophenol, 23 mg/kg for 2,3,4,6-tetrachlorophenol, and 24 mg/kg for pentachlorophenol. The concentration of 2,4,6-trichlorophenol in the soil as a function of extraction time is presented in Figure 7.

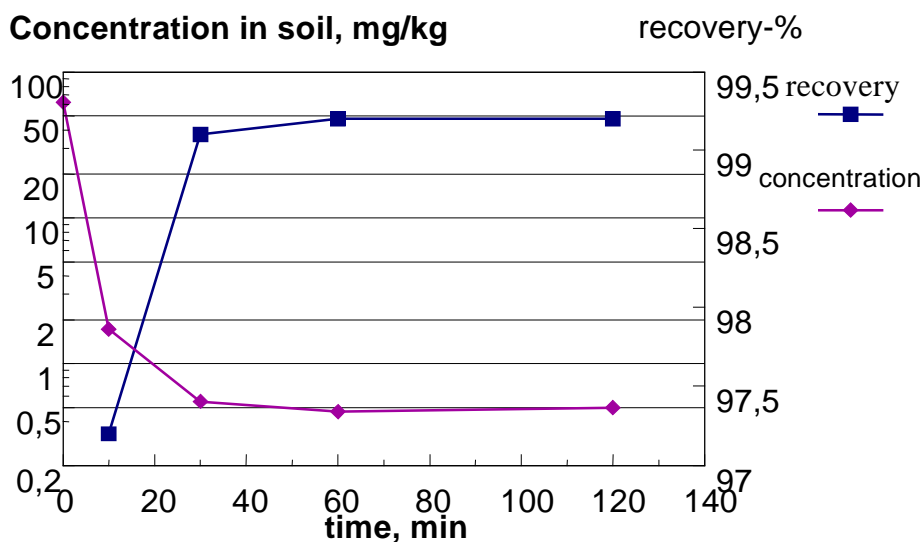


Figure 7. Extraction of 2,4,6-trichlorophenol from saw mill soil with supercritical carbon dioxide at 200 bar and 40 °C. Moisture content 10 wt%.

In the second experiment, the soil was slurred in water, and the soil moisture content was 50 wt%. As in the case of the extraction of PAHs from the railway yard soil, the second experiment was worse. The residual concentrations of the three chlorophenols in the soil after extraction were 3.1 mg/kg, 320 mg/kg, and 230 mg/kg, respectively.

6. Continuous column extractions

In Papers V, VI and VII a mechanically agitated high-pressure column was designed and tested by extracting organic compounds from aqueous solutions using dense carbon dioxide as a solvent. In Paper V a mechanically agitated continuous countercurrent rotating disk extraction column (RDC) was introduced by extracting ethanol from an aqueous solution. In Paper VI an Oldshue-Rushton type column was tested in the same application. In Paper VII the extraction of 1-butanol from an aqueous solution was studied using supercritical carbon dioxide solvent in an Oldshue-Rushton column.

6.1 Experimental

The equipment, working procedures and calculation methods that were used in Papers V–VII are presented in this section.

6.1.1. Equipment

A schematic view of the bench-scale experimental apparatus used in the experiments [V, VI, VII] is presented in Figure 8. The extraction column (Chematur Ecoplanning Co.) has a 35 mm internal diameter, is 2 m in height, and can be used up to 40 MPa. A special pressure compensating sealing system was developed to lead the electrically driven agitator shaft through the column head. The maximum rotating speed in this construction is around 400 rpm. The windows in the middle and at both ends of the column allowed observation of the liquid level and fluid hydraulics. The column is equipped with a heating jacket, in which water is circulated by a thermostat (Lauda C6 CS).

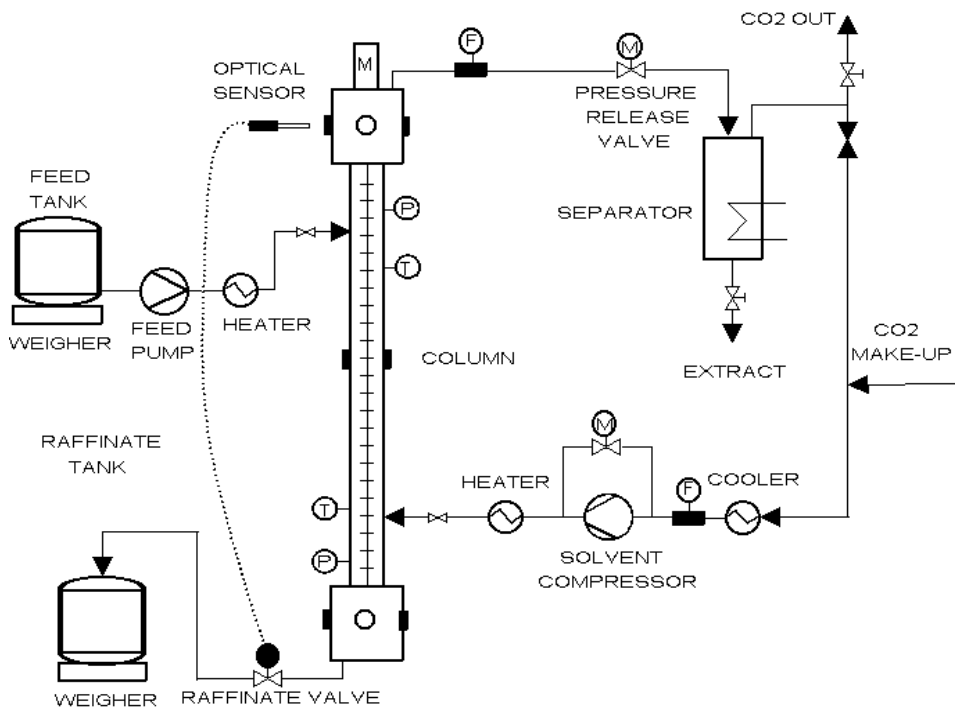


Figure 8. Column extraction installation.

The column's internal design consists of removable parts that allow the use of different agitator geometries or even different types of columns. The characteristics of the RDC- and Oldshue-Rushton columns which were used in the experiments [V, VI, VII] are summarized in Table 6.

Table 6. Rotating disk and Oldshue-Rushton column characteristics.

Character	RDC	Oldshue-Rushton
Height of the column, mm	2 000	2 000
Total agitated height of the column, mm	1 400	1 400
Column diameter, mm	35	35
Compartment height, mm	20	20
Stator plate opening diameter, mm	24	24
Smallest cross-sectional area, mm ²	452	452
Number of compartments	99	99
Impeller or disk diameter, mm	20	20
Impeller or disk height, mm	4	1
Number of flat blades	4	-

A commercial high-pressure extraction unit (Nova Werke AG) was used to feed carbon dioxide to the column. Carbon dioxide flow-rates were measured by two high-pressure turbine flow meters (EG&G Flow Technology) in the solvent and extract streams. No dispersers or other similar devices were used to create the drops. The liquid feed stream was pumped to the top of the column by a high-pressure piston pump (Lewa AG). The liquid feed and carbon dioxide solvent streams were preheated to the extraction temperature by means of constant temperature water baths.

The optical sensor (SITEC–Sieber Engineering AG) controlling the interface was focused on the phase boundary seen through the window at the top of the column. The sensor sends signals to the control unit, which pneumatically opens the needle valve placed in the raffinate stream. An alternative method of controlling the interface is to use a manually operated needle valve placed in the raffinate stream. The carbon dioxide flow rate was controlled by a micrometering valve placed in the extract stream. This valve was operated manually. The pressure inside the column was regulated by an automatically controlled micrometering valve placed in the carbon dioxide solvent stream.

6.1.2 Column extraction procedure

An aqueous solution containing ethanol [V, VI] or 1-butanol [VII] was used as a continuous phase and carbon dioxide as a dispersed phase in all of the experiments. Prior to each run, the column was heated to the operating temperature. The system was then pressurized to approximately 50 bars with carbon dioxide, after which the aqueous solution was pumped to the top of the column until the phase boundary was seen in the window at the top of the column. The carbon dioxide compressor (Nova AG) was then turned on, the system was pressurized to the extraction pressure, and the extract stream valve was opened to let carbon dioxide flow through the continuous liquid phase. The feed pump was then turned on again and the optical sensor controlling the liquid level was activated. A tachometer was used to measure the speed of the rotor.

All of the experiments were carried out at 100 bar and 40 °C. Each extraction experiment lasted approximately 4 hours. Fresh carbon dioxide from the container was used in all of the experiments to avoid using a preloaded solvent. During the run the feed and raffinate tanks were weighed, and the carbon

dioxide flow rates were measured every 20 minutes. After running for 2 hours, the samples were taken from the feed, raffinate and extract streams once every 20 minutes. The extract from the separator was continuously collected. The ethanol concentration in all of the samples was analyzed by GC. More details concerning the sampling and material balance deviation are presented in the Papers V, VI and VII.

The method described by Rathkamp et al. [59] was used to measure the dispersed phase holdup. The data was obtained by shutting the feed pump and carbon dioxide compressor off at steady state conditions, and measuring the time required for the carbon dioxide drops that entered the bottom of the column to rise to the top of the column. This information combined with the flow rate of the dispersed phase was used to calculate the volume of the dispersed phase in the column, and the holdup for the run was calculated. The raising drops were recorded at various flow rates and rotor speeds by a video-camera looking through the window in the middle of the column. The average diameter of the drop was calculated for each experiment from a video freeze-frame.

It was not possible to measure flooding points with the optical sensor construction, because the optical sensor opened the raffinate stream valve at the bottom of the column when the liquid level started to rise. However, when the solvent and feed flow rates reached certain values, the raffinate stream valve was open to such an extent that most of the solvent flow came out of the column with the raffinate stream. At this point the column was no longer operable. This point was used to describe the capacity of the column.

6.1.3 Calculation of column efficiency

Because both RDC- and Oldshue-Rushton columns are continuously operating columns, the HTU/NTU concept was used to estimate the column efficiency and to calculate the mass transfer coefficients. According to the two-film theory, the resistance in the solvent phase controls the mass transfer, provided that the distribution coefficient is relatively small [65]. Therefore the calculation was based on the dispersed carbon dioxide phase. For dilute solutions, an immiscible solvent and a linear equilibrium line, the number of transfer units (NTU_{od}), the height of a transfer unit (HTU_{od}), and the overall mass transfer coefficient K_{od} for the dispersed phase can be written as

$$NTU_{od} = \int_{y_2}^{y_1} \frac{dy}{y^* - y} \quad (1)$$

$$HTU_{od} = \frac{Z}{NTU_{od}} \quad (2)$$

$$K_{od}a = \frac{V_d}{HTU_{od}} \quad (3)$$

where y is the weight fraction of solute in the dispersed phase, y^* is the equilibrium value, V_d is the superficial velocity of the dispersed phase, and a is the interfacial area. The concentration of solute in the extract stream was calculated by the overall material balance, and this value was used when $K_{od}a$ - and HETS -values were calculated.

According to Treybal [65] the relationship between the height equivalent to a theoretical stage (HETS) and the height of a transfer unit (HTU_{od}) is given by

$$HETS = \frac{\ln E}{E - 1} HTU_{od} \quad (4)$$

where E is the extraction coefficient. The slip velocity through the smallest cross-sectional area of the column V_s describes the relative velocity of the phases, and is defined as

$$\bar{V}_s = \frac{\bar{V}_d}{h} + \frac{\bar{V}_c}{1-h} \quad (5)$$

where \bar{V}_d and \bar{V}_c are the relative velocities of the dispersed and continuous phases through the smallest cross-sectional area, and h is the dispersed phase holdup.

6.2 Column extraction results

6.2.1 Column efficiency

In Table 7 the values of the overall mass transfer coefficient K_{oda} and the height equivalent to a theoretical stage HETS are compiled [V, VI, VII]. The extraction efficiencies in RDC- and Oldshue-Rushton columns are relatively similar to each other. The measured K_{oda} values for the extraction of ethanol from water in the RDC-column range from 0.006 s^{-1} to 0.015 s^{-1} , and in the Oldshue-Rushton column the values range from 0.009 s^{-1} to 0.012 s^{-1} . The measured HETS values are between 0.8 m and 0.37 m. Slightly lower K_{oda} values were measured for 1-butanol extraction than in ethanol extraction. In the case of 1-butanol extraction, the measured K_{oda} values are $0.002\text{--}0.003 \text{ s}^{-1}$, and the HETS values are 0.4–0.5 m in the Oldshue-Rushton column.

In the literature the values of the overall mass transfer coefficient K_{oda} measured for spray and packed continuous countercurrent supercritical fluid extraction columns generally range from 0.006 s^{-1} to 0.04 s^{-1} , depending on the type of column, packing and solvent-to-feed ratio [57, 59]. Values of the height equivalent to a theoretical stage HETS for small-scale spray, packed and sieve tray supercritical fluid extraction columns have been measured by other authors [54, 56, 57, 59]. The reported HETS values for the supercritical spray, packed and sieve tray columns are typically in the range of 0.2–0.5 m.

It can be concluded that the K_{oda} and HETS values measured in Papers V, VI and VII for the RDC- and Oldshue-Rushton columns are of the same order of magnitude as those presented for small-scale supercritical spray and packed columns in the literature.

Table 7. Mass transfer efficiencies in mechanically agitated columns [V, VI, VII].

No.	S/F	Rotor speed (rpm)	Concentration in the feed stream (wt%)	Concentration in the raffinate stream (wt%)	Concentration in the extract (wt%)	K_{oda} ($s^{-1} \times 10^3$)	HETS (m)
Extraction of ethanol in the RDC-column							
1	13/1	0	10	2.59	78	6.0	0.80
2		50		2.17	82	7.2	0.67
3		158		0.97	84	9.7	0.46
4		223		0.78	86	12.7	0.37
5		301		0.84	80	11.1	0.41
6		388		0.95	81	10.3	0.44
7	13/1.5	0	10	2.30	84	13.0	0.44
8		104		2.69	91	12.3	0.49
9		207		2.75	89	11.0	0.53
10		312		2.52	89	11.8	0.49
11	13/2	0	10	3.76	89	11.6	0.58
12		103		3.39	89	13.0	0.50
13		204		3.70	89	13.1	0.52
14		303		3.32	84	14.8	0.45
Extraction of ethanol in the Oldshue-Rushton column							
1	14/1	0	10	1.27	90	8.7	0.55
2		45		1.15	85	9.8	0.50
3		120		0.87	87	10.9	0.44
4		227		0.92	91	10.6	0.45
5		324		1.03	86	10.0	0.48
6	14/1.5	0	10	2.47	84	11.5	0.53
7		100		2.55	82	11.9	0.52
8		199		2.56	85	11.0	0.55
9		303		2.56	86	11.3	0.54
10	14/2	0	10	4.00	90	9.7	0.72
11		103		4.13	91	10.6	0.68
12		201		4.19	86	9.8	0.74
13		311		3.98	90	10.3	0.69

Extraction of 1-butanol in the Oldshue-Rushton column

1	4.3/6	0	5	0.65	90	3.3	0.46
2		72		0.70	89	3.2	0.48
3		138		0.63	85	3.2	0.47
4		238		0.66	88	3.1	0.50
5	5.2/4.5	0	5	0.24	79	2.8	0.52
6		75		0.23	89	2.9	0.49
7		142		0.16	89	3.4	0.42
8		232		0.23	90	3.2	0.46
9	5.3/2	0	5	0.020	80	1.9	0.46
10		75		0.015	84	2.1	0.44
11		145		0.021	85	1.9	0.46
12		210		0.014	86	2.2	0.41

Mechanical agitation enhanced the column efficiency only at relatively high solvent-to-feed ratios. At solvent-to-feed ratio $S/F = 13$, mechanical agitation increased the Koda value from 0.006 s^{-1} to 0.013 s^{-1} , and reduced the HETS value from 0.8 m to 0.37 m for the RDC -column. On the other hand, agitation did not enhance the extraction at lower solvent-to-feed ratios. The same kind of behavior was noticed when the Oldshue-Rushton column was tested at solvent-to-feed ratio $S/F = 14$. Mechanical agitation slightly increased the Koda value from 0.009 s^{-1} to 0.011 s^{-1} , and reduced the HETS value from 0.55 m to 0.44 m in the case of the Oldshue-Rushton column. Mechanical agitation did not enhance the column efficiency when 1-butanol was extracted from water, presumably because the solvent-to-feed ratios used in this application were relatively low, i.e. $S/F = 0.9\text{--}2.7$.

The effect of agitation on the values of the overall mass transfer coefficient K_{oda} and the height equivalent to a theoretical stage HETS at the highest experimental solvent-to-feed ratios are presented in Figures 9 and 10.

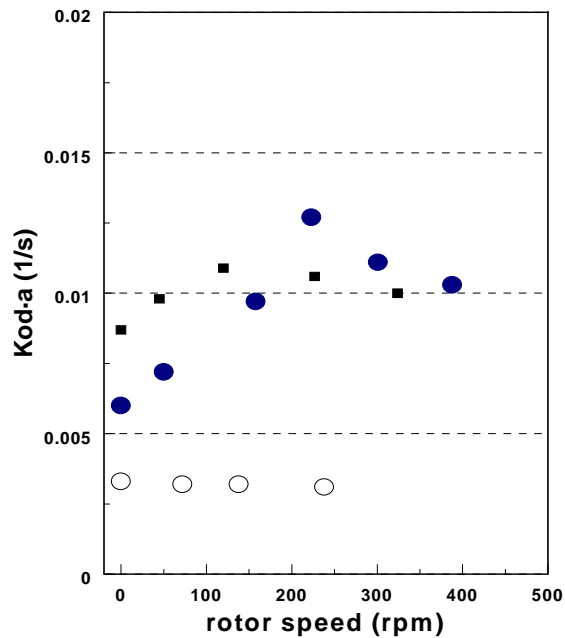


Figure 9. Effect of agitation on K_{oda} [V,VI,VII].

- (○) extraction of 1-butanol in Oldshue-Rushton column, $S/F=4.3/6$;
- (■) extraction of ethanol in Oldshue-Rushton column, $S/F=14/1$;
- (●) extraction of ethanol in RDC-column, $S/F=13/1$.

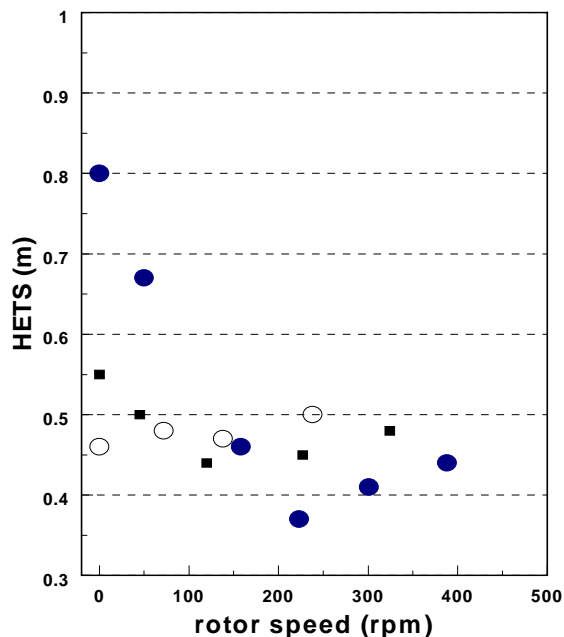


Figure 10. Effect of agitation on HETS [V,VI,VII].

- (○) extraction of 1-butanol in Oldshue-Rushton column, $S/F= 4.3/6$;
- (■) extraction of ethanol in Oldshue-Rushton column, $S/F=14/1$;
- (●) extraction of ethanol in RDC -column, $S/F=13/1$.

An efficiency optimum is seen in Figures 9 and 10 when ethanol is extracted at solvent-to-feed ratios $S/F = 13$ and $S/F = 14$. The optimum rotor speed is approximately 200 rpm. The same kind of behavior is known to occur in conventional liquid-liquid RDC -columns. According to Robbins and Cusack [66], the value of HETS becomes smaller with increased rotor speed but passes through a minimum. Obviously, mechanical agitation reduces the dispersed phase drop size and increases the dispersed phase holdup and interfacial area for mass transfer. In addition, higher rotor speeds increase the axial mixing of each phase. The two main factors of the axial mixing process are eddy diffusion or backmixing, which is most pronounced at the highest speeds, and channeling, which is specific in the forward direction [67]. Axial mixing, when present in both phases, causes a reduction in the concentration driving force between the phases. Therefore, the increased mass transfer rate caused by high rotor speed is

offset by increased axial mixing, resulting in an optimum rotor speed for each operating condition.

Mechanical agitation seems to have an effect on column efficiency only at relatively high solvent-to-feed ratios, e.g. $S/F = 13$ or $S/F = 14$. One possible explanation is that at relatively low solvent-to-feed ratios, equilibrium is approached in the column and mechanical agitation can no longer enhance the extraction.

6.2.2 Column capacity

The total throughput of the RDC- and Oldshue-Rushton columns calculated as the volumetric feed plus solvent flow rate divided by the smallest cross-sectional area of the column is presented in Figure 11. The total throughput of the RDC-column was approximately $80 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ without agitation. Agitation slightly lowered the value to $74 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ when the rotor speed was 300 rpm. Without agitation the total throughput of the Oldshue-Rushton column was approximately $70 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$, whereas at 300 rpm the total throughput was approximately $50 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$.

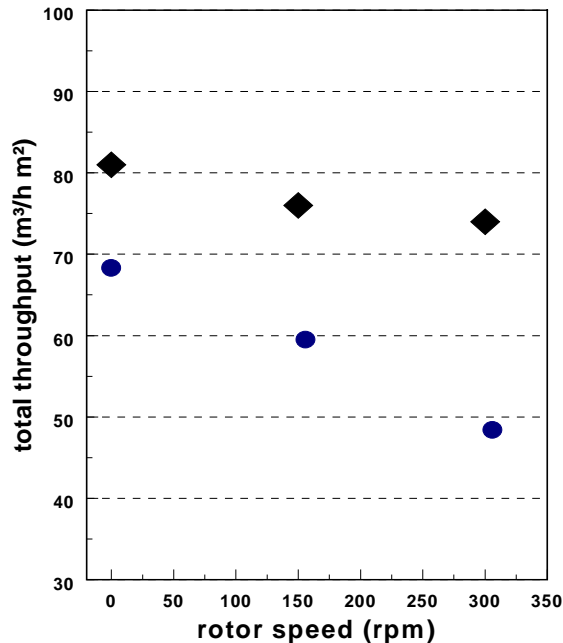


Figure 11. Effect of agitation on column capacity at $40 \text{ }^\circ\text{C}$ and 100 bar. (●) Oldshue-Rushton column; (◆) RDC -column.

Without agitation the capacities of the RDC- and Oldshue-Rushton columns are relatively similar. The relative deviation of the values is approximately 12 %. At 300 rpm the capacity of the RDC -column is almost the same as without agitation, whereas the capacity of the Oldshue-Rushton column is reduced significantly at 300 rpm. One possible explanation is that the Oldshue-Rushton type impeller provided more intense agitation than the relatively small-diameter RDC -disk. When the agitation power input is increased, the drop diameter decreases, and consequently the slip velocity and the column capacity decrease as well. At relatively low power inputs this effect is rather small, but at higher power inputs the drop size reduction reaches the point at which it becomes so large that the slip velocity and the capacity are substantially reduced.

The capacity of mechanically agitated supercritical extraction columns is significantly higher than that of the packed supercritical fluid extraction column, and is approximately equal to the capacity of a supercritical spray column. Flooding velocities for a 25.4 mm diameter column spray and packed column operated under supercritical conditions for a carbon dioxide/2-propanol/water system have been measured by Rathkamp et al. [59]. According to the authors, the packed column flooded when the superficial velocity of the continuous phase was $V_c = 0.4$ mm/s and the superficial velocity of the dispersed phase was $V_d = 3.0$ mm/s, whereas the spray column reached flooding at $V_c = 0.4$ mm/s and $V_d = 20.3$ mm/s. In this work, the capacity of the Oldshue-Rushton column without agitation was approximately $V_c = 5.0$ mm/s and $V_d = 14.0$ mm/s, and at 150 rpm, the capacity was approximately $V_c = 4.9$ mm/s and $V_d = 11.6$ mm/s. The RDC -column was operable at approximately $V_c = 5.3$ mm/s and $V_d = 15.6$ mm/s.

Compared with conventional extraction systems, the capacity of continuous countercurrent supercritical fluid extraction columns is higher most probably due to the larger density difference of the phases in supercritical fluid extraction. For example, the toluene/water system flooded in the mechanically agitated (200 rpm) Oldshue-Rushton column at approximately $V_c = 5.0$ mm/s and $V_d = 4.5$ mm/s [68].

The dispersed phase holdup and slip velocities were also measured in the RDC- and Oldshue-Rushton columns. The results are presented in Table 8.

Table 8. Dispersed phase holdup and slip velocities in the RDC- and Oldshue-Rushton columns.

S/F	Speed of agitation (rpm)	Holdup	Slip velocity (mm/s)
RDC -column			
3.2/1.6	0	0.026	0.136
	150	0.035	0.101
	300	0.038	0.093
12/1.6	0	0.089	0.138
	150	0.123	0.098
	300	0.132	0.09
16/1.6	0	0.122	0.134
	150	0.153	0.11
	300	0.21	0.078
Oldshue-Rushton column			
14/2	0	0.126	0.113
	150	0.145	0.098
	300	0.160	0.09
14/1.5	0	0.117	0.123
	150	0.133	0.107
	300	0.143	0.01
14/1	0	0.120	0.119
	150	0.130	0.110
	300	0.133	0.107

The measured dispersed phase holdup values are in the 0.03–0.20 range. As expected, all of the holdup values increase with increasing rotor speed. All of the slip velocity values decrease with increasing rotor speed because of increasing holdup.

7. Concluding remarks

Considering that there is a common need among chemical engineers to find environmentally benign solvents, the use of relatively inexpensive carbon dioxide solvent should increase in the future, provided that carbon dioxide proves to be a technically feasible and economically competitive solvent in selected industrial applications. In this thesis, the extraction of organic compounds from solid and liquid matrices using supercritical carbon dioxide as a solvent was studied.

Dense carbon dioxide is a very good solvent for the cyclic amide, 6-caprolactam, and can be used to dissolve and extract it from solid and liquid matrices. The ability of dense carbon dioxide to dissolve 6-caprolactam could possibly be utilized in the industry producing nylon.

Certain criteria must be fulfilled before solvent extraction can be considered for soil remediation [69]. The first criterion is that the process must be capable of yielding uncontaminated residual material. The results of this thesis indicate that at least 80-90 % of the initial amount of pollutant can be removed at moderate temperatures even in the most difficult cases, and in many cases over 99 % of the initial amount of pollutant can be removed from soil. Supercritical extraction is best suited to sand or silt type soils, which have a low adsorption capacity. The extraction results are found to be case-dependent and soil remediation at moderate temperatures is observed to be difficult if the pollutant binds strongly to the soil or if the acceptable level of residual concentration is very low. To verify technical feasibility, a commercial-scale extraction system will have to be successfully operated over an extended period. Only one such system is reported to have been installed in Port Arthur, Texas [69]. Generally, there is plenty of evidence in industry, e.g. the extraction of caffeine from coffee beans, that high-pressure extraction is a viable technology. The solids handling in high-capacity, high-pressure batch processes is a notable disadvantage, and an efficient method of moving the soil into the high-pressure extractor would be a significant advancement.

In this thesis a novel mechanically agitated countercurrent continuous extraction column was introduced and tested by extracting ethanol and 1-butanol from aqueous solutions in the rotating disk column and in the Oldshue-Rushton

column. A special pressure-compensating sealing system was used to lead the electrically driven agitator shaft through the column head. The capacity of a mechanically agitated supercritical extraction column is typically higher than that of a conventional liquid-liquid extraction column due to the fact that the density difference of the phases in supercritical extraction columns is larger than in conventional extraction processes. A mechanically agitated column successfully combines the high capacity of supercritical spray extraction columns and the high efficiency of packed supercritical extraction columns.

The extraction of ethanol from water is technically not a very feasible application due to the low distribution coefficient of ethanol in the carbon dioxide/ethanol/water system. The extraction of high molecular weight alcohols like 1-butanol from water is much more feasible than the extraction of ethanol, because in this case the distribution coefficients are higher than in case of ethanol extraction. Other potential applications include the extraction of phenolics or pyridine from water, and all industrial separations in which the feed is viscous or the extraction is mass transfer limited, and effective agitation is needed.

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Author(s) Laitinen, Antero			
Title Supercritical fluid extraction of organic compounds from solids and aqueous solutions			
Abstract <p>In this thesis, the extraction of organic compounds from solid and liquid matrices using supercritical carbon dioxide as a solvent was studied.</p> <p>Dense carbon dioxide is a very good solvent for the cyclic amide, 6-caprolactam. 6-caprolactam exhibits relatively high solubilities, i.e. up to around 17 wt% at ambient temperatures, and at pressures below 220 bar. Carbon dioxide can be used to dissolve and extract 6-caprolactam from solid and liquid matrices.</p> <p>The remediation of contaminated soil by carbon dioxide extraction was studied. The effect of extraction pressure, temperature, soil moisture content, pH, carbon dioxide mass flow rate, and extraction time on the residual pollutant concentration in the soil after extraction was systematically studied. The selected pollutants were phenanthrene, 2,3,4,6-tetrachlorophenol and pentachlorophenol. The results indicate that at least 80–90 % of the initial amount of pollutant can be removed at moderate temperatures even in the most difficult cases, and in many cases over 99 % of the initial amount of pollutant can be removed from the soil. Supercritical extraction is best suited to sand or silt type soils, which have a low adsorption capacity. The extraction results are found to be case-dependent, and soil remediation at moderate temperatures is observed to be difficult if the pollutant binds strongly to the soil or if the acceptable level of residual concentration is very low.</p> <p>A novel mechanically agitated countercurrent continuous extraction column was introduced by extracting ethanol and 1-butanol from aqueous solutions in the rotating disk column and in the Oldshue-Rushton column. Column efficiencies were measured as a function of solvent-to-feed ratio and rotor speed. Generally, the values of the height equivalent to a theoretical stage HETS were in the range of 0.4–0.8 m. Mechanical agitation enhanced the extraction only at relatively high solvent-to-feed ratios. Column capacities for both types of column were measured, and the total throughput calculated as the feed plus solvent flow rate divided by the smallest cross-sectional area was 50–80 m³h⁻¹m⁻². A mechanically agitated column successfully combines the high capacity of supercritical spray columns and the high efficiency of supercritical packed columns.</p>			
Keywords organic compounds, extraction, solids, aqueous solutions, supercritical gases, supercritical fluids, carbon dioxide, amides, lactams, solubility			
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