

Review

Counter-current separations

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ABSTRACT

Development and state of the art of counter-current separation, in particular for liquids, with supercritical fluids, is reviewed, covering principles, early development, actual and possible applications, and counter-current separation as published in the Journal of Supercritical Fluids. A description of processes (continuous counter-current flow, mixer-settler principle, the role of co-solvents), necessary fundamentals, design procedure (including gas cycles), a summary of the methodical knowledge, and cost calculation are covered. A discussion and a comparison to competitive processes and an outlook on future perspectives conclude the review.

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1. Introduction and scope: principle of counter-current separation for liquids

Counter-current separation is applied to achieve a multistage treatment, in this context a separation, reduce the necessary amount of separation agent, increase concentration in product streams, and to carry out a continuously operated optimised process. Counter-current processing can be applied to solids as well as

liquids. For solids, a simulated counter-current process is preferred due to problems with moving solids in vessels. This type of process is useful for extraction from solids, using a few stages, and with packed bed chromatography applying many stages. In all cases, a continuous counter-current process will separate the feed mixture into two products, if not special features are applied in the process, like a side stream withdrawal, or using different stationary phases in chromatography. Supercritical fluids were proposed for this unit operation at least from the early 1970s on and developed first by the group of S. Peter at the University of Erlangen [1]. Using near-critical propane, a process for the separation of fish oil constituents was in operation in the 1940s and 1950s of last century [2].

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This paper is concentrating on the counter-current processing of liquid mixtures with supercritical or near-critical fluids. Nearly all processes or process proposals use carbon dioxide as solvent at supercritical conditions. If not, it will be specified. Furthermore, it concentrates on multistage counter-current separation. Multistage separations become necessary when the separation factor between components is in the order of 1–10. In such a counter-current separation process, the components distribute between the solvent (extract phase) and the liquid (raffinate phase) which counter-currently flow through the separation equipment. In most cases, a separation column is used, in which components' flow is caused by pressure drop and gravity. Applying the mixer-settler principle, these restrictions for the flow are eliminated.

Counter-current operation of a separation device reduces the amount of solvent necessary, increases throughput, and enables higher extract concentrations in the solvent and lower residual concentrations in the raffinate than does single-stage or multistage cross-current operation. Counter-current operation is therefore useful for separations with high separation factors, as, for example, the extractions from solid substrates. But counter-current operation is absolutely necessary for achieving a reasonable separation between two substances with a relatively low separation factor.

Counter-current processing with supercritical fluids extends the possibilities of separation processes like distillation, absorption and liquid–liquid extraction to the isolation and purification of components of low volatility. Furthermore, it enables separation of components with very similar properties if used in the counter-current mode. Process temperatures are determined by the critical temperature of the solvent and not, as is the case of distillation of any kind, by the liquid–vapor transition of the feed mixture. For an example, distillation of fatty acid esters (C14–C18) is carried out at pressures of about 3 mbar at temperatures around 200 °C. Using supercritical CO₂, this process can be achieved at temperatures between 40 and 70 °C, eliminating problems with thermal stability of the components.

As compared to liquid–liquid extraction, counter-current processing with supercritical fluids makes easily possible to operate a two cascade separation column, applying a stripping and an enriching section, enabling high purity of products at high yield. This often poses a problem in liquid–liquid extraction where a two-phase region often only can be achieved by applying a second solvent. Combined, these possibilities allow counter-current processing with supercritical fluids to be operated at very moderate temperatures and as a separation process for difficult separations. Again, as an example, azeotropes, like that in ethanol–water can be overcome with supercritical fluids processing.

2. Applications

A compilation of possible and actual applications may illustrate the scope of compounds involved. As a basis, the compounds and mixtures are taken, on which counter-current processing with supercritical fluids has been reported in *The Journal of Supercritical Fluids*. Although not being a comprehensive compilation of the published work, it should provide a sufficient insight into the type of compounds treated by counter-current separation processing with supercritical fluids.

2.1. Edible oil components, and derivatives

Olive oil: [3]; tocopherols from deodorizer condensates: [4]; oil deodorizer distillate (DOD) and tocopherols [5]; squalene from vegetable oil sources, squalene and fatty acid esters [6]; minor components of crude palm oil, purification of tocopherols

from edible oil [7], purification of raffinated rice oil from rice bran [8], separation of glyceride mixtures under supercritical fluid conditions [9], removal after an enzymatic reaction of an unreacted compound (ethyl ferulate) and an by-product (fatty acid ethyl esters) from a reaction mixture, leaving the cleaned product (feruloylated acylglycerols) [10], separation of different lipid-type materials [11], de-acidification of vegetable oils using supercritical CO₂: holdup and residence time experiments [12], removal of fatty acid esters from a reaction mixture [13], fractionation of fatty acid ethyl esters [14,15], fractionation of fish oil fatty acid ethyl esters in an automated pilot plant column [16], fractionation of fish oils using supercritical CO₂ and CO₂ + ethanol mixtures [17].

2.2. Citrus oil and components, and essential oils, flavours

Flavours from milk fat [18], counter-current deterpenation of citrus oils [19], optimal process and solvent cycle design for citrus peel oil deterpenation [20], fractionation of lemon oil in a batch process with an external reflux [21], fractionation of citrus oil in a counter-current extractor with side-stream withdrawal [22], supercritical deterpenation of lemon essential oil, simulation of the semi-continuous extraction process [23], semi-batch operation and counter-current extraction fractionation of lemon oil [24], deterpenation of mandarin (*Citrus reticulata*) peel oils [25], fractionation of Lavandin essential oil [26], review of supercritical fluid extraction and fractionation of essential oils and related products [27].

2.3. Extraction from aqueous solutions, ethanol–water

Supercritical fluid extraction of ethanol from aqueous solutions, near-critical separation of aqueous azeotropic mixtures: process synthesis and optimization, (simulation) [28,29], utilisation of excess wine, extraction of ethanol and aroma compounds out of wine [30], isolation of brandy aroma [31], spirits fractionation [32].

2.4. Mineral oil components

Paraffin wax fractionation: state of the art vs. supercritical fluid fractionation [33], oligomer fractionation with supercritical fluids [34].

Most investigations have been concerned with edible oils and their components. A number of specific separations are of interest: Removal of free fatty acids (de-acidification), separation of glycerides, e.g. purification of mono-acyl-glycerides used as emulsifiers, de-oiling of lecithin, removal of cholesterol, separation of squalene and tocopherols, removal of fatty acid esters, recovery of products from olive oil distillates, or palm oil distillates, as well as from the residues of the de-oiling process of the plant materials. Another interesting application is the separation of fatty acid esters for enrichment of physiological essential *n*-3 fatty acid esters, or for separation of C16- and C18-components in connection with bio-diesel, in order to reduce the palmitic acid (C16) concentration.

A third area is the essential oils, comprising e.g. terpenes and flavour components. The major application is the deterpenation of citrus oils (i.e. the removal of limonene). Counter-current processing with supercritical fluids is a powerful tool for increasing aroma and flavour components, as long as the initial concentration is not too low, approximately 0.5 wt.%. If that is the case, adsorption and desorption with sc fluids is preferable [25]. In connection with the citrus oil components, flavour compounds, ethanol and other very volatile components, become important, which are present in the so-called water-phase, produced by fruit juice concentration. After recovery from the aqueous solution, it can be added to fruit juices [29]. A related topic is the separation of alcohols and water, in particular ethanol–water. Using counter-current separation

with supercritical CO₂ from a fermentation broth of around 7 wt.% ethanol, a residue of less than 0.1 wt.% ethanol and an ethanol product of >99.8 wt.% ethanol, directly usable as fuel additive can be produced [29,35]. The application to mineral oil derived mixtures is related to components of very low volatility, e.g. paraffin waxes [33,34].

Other areas of application are rather scarce, e.g. a separation of disaccharide mixtures by supercritical CO₂ with ethanol as co-solvent, ethanol/water: 95/5 is reported [36]. An important application is the removal of caffeine from the aqueous solution in which the caffeine is absorbed after the extraction from the coffee beans. The removal of chlorinated compounds from iso-cyanates is a problem, which on one side proves that counter-current processing with supercritical fluids can well be applied to difficult to handle compounds, on the other hand has shown the limitation, that supercritical fluids do not primarily separate according to functionality but to volatility or solubility in the supercritical fluid [37].

3. Early proposals and development

Early proposals and development work began in the 1960s and 1970s of last century. Zhuze [38], Ellis [39], Zosel [40], Peter et al. [41] proposed processes implying counter-current separation. Zosel proposed quite a number of applications, also such using a counter-current multistage separation, but did not develop the process. First process development was carried out by the group of Peter at Erlangen in the 1970s on the special process modification using polar and volatile components as co-solvents in a pilot plant column of 50 mm diameter and 6 m effective height.

4. The counter current separation process [42]

In Fig. 1 the process scheme of a counter current process for the separation of two components (or a mixture of two fractions) into

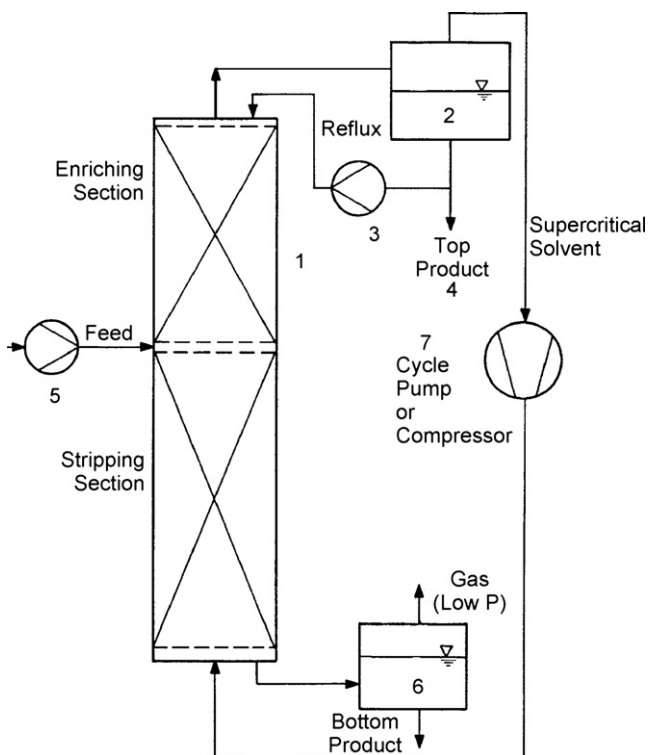


Fig. 1. Process scheme of a counter current process with a supercritical fluid for the separation of two components [42].

practically pure substances is shown. Process equipment consists of the separation column (1) where gaseous and liquid phases are contacted counter currently, a separator at the top for separating solvent and extract (2), devices for feeding reflux to the column (3), for recovering top product (4), for delivering feed to the column (5), for recovering product at the lower end of the column (6), and for recycling the solvent (7).

The separation column consists of two separation cascades. In the upper one (enriching section) the bottom product compounds are separated from the top product compounds and rejected to the lower section (stripping section). In the stripping section the top product compounds are separated from the bottom product compounds and transported to the enriching section.

At the top of the column the separator removes the extract from the solvent. From the extract a specified part is separated and introduced at the top of the column as reflux. The remaining part of the extract is the top product. The solvent is reconditioned (filtered, sometimes liquefied and again evaporated for removing trace substances, pressure and temperature are adjusted) and recycled by the cycle pump as the supercritical solvent at the bottom of the column. The feed is introduced at an intermediate location in the column by the feed pump; for a mixture of two components of about the same concentration, this location is at about the middle of the column.

The separation of two compounds into practically pure substances is possible with multistage counter current gas extraction. Two separation cascades are needed for this separation. A separation cascade is a sequence of separation steps. Gaseous or liquid streams enter or leave the cascade only at the ends. No side-streams or additional feed-streams are allowed. A separation of two components is specified by two values, e.g. the concentration of a compound at one end of the cascade and the amount recovered of this compound. In order to achieve this specified separation, two separation cascades are needed. The upper one serves to separate the bottom product compound from the top product, and the lower one serves to separate the top product compound from the bottom product. In multistage distillation the separation cascades are known as rectifying and stripping sections. In most cases the two cascades for one separation are unified in one separation column.

The separation of two components is the basic case. This case is not very common in practice, since multi-component mixtures prevail. But the main features of a multi-component separation can be clearly shown by a two-component separation. Therefore, it is common practice to try to reduce multi-component separations to two-component separations. For the separation of more than two components into pure substances two more cascades are needed for each additional compound. The same reasoning holds for cases where components are actually fractions of a multi-component or complex mixture.

5. Counter current multistage separation in a mixer-settler

There are several reasons for employing mixer-settler arrangements: the liquid phase being small, is not covering the mass transfer equipment, resulting in a reduced mass transfer rate. If flow rates for the liquid and gaseous phase are very different, it is difficult to maintain stable operation in columns. Substances with a relatively high viscosity of the liquid phase, even when a supercritical fluid is dissolved in the phase have a high value for a theoretical stage. Density difference between phases is often low, limiting the flow in a gravity driven column. These disadvantages can be avoided by a mixer-settler arrangement. Flows in each stage are driven by pumps, mixing and mass transfer is achieved mechanically, importance of the density difference is minor since

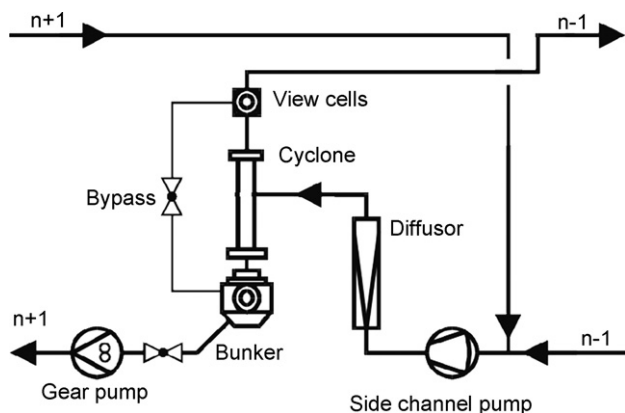


Fig. 2. Flow sheet of a mixer-settler unit [44,45].

phases can be separated in cyclones. On the other hand, for each theoretical stage at least one mixer-settler element is necessary. This limits the application to the mixer-settler principle to a relatively low number of stages. For example, a reasonable separation of C18/C20-methylesters requires about 50 theoretical stages. This is not suitable for a mixer-settler, while the above mentioned application, separation methyl esters from carotenes requires only a few number of stages and is therefore fitting to the mixer-settler principle.

A mixer-settler unit fulfils two tasks [44,45]. One of the tasks is to achieve mixing of the phases, i.e. the gaseous and the liquid phase in such a way that phase equilibrium is approached, and the other is the separation of the phases after mass transfer. Fig. 2 illustrates such a unit. Here the liquid phase is transported with a gear pump from the preceding stage to the mixing part, which is a side channel pump. The side-channel pump effectively mixes both phases, creates a large surface for mass transfer and transports the phases into the settler part, which consists of a cyclone and a buffer volume, from which the separated phases are transported to the appropriate next stage. Typically multiple stage mixer-settler units are utilized. The system, in addition to the mixer-settler units consists of a feed pump, product removal, and the CO₂-cycle.

6. Design considerations

The separation process of counter current gas extraction can be modeled using the common basic equations: Mass balance, energy balance, equilibrium distribution coefficients, and rate equations for mass transfer, for which solution methods are available from other counter-current processes like distillation and liquid-liquid extraction [42]. The difficulty remaining with modelling of counter-current processes with supercritical fluids is connected with the wide variability of properties of systems with supercritical compounds. The solution of these problems is split into three parts, for which fundamental information is needed to carry out modeling and design:

6.1. Determination of number of theoretical stages or number of transfer units and analysis of the separation

This part is related to phase equilibrium and is independent from any realization in separation equipment. Phase equilibrium data are determined, either experimentally and correlated with equations of state, and/or empirical equations or, in particular for screening purposes, by calculation. The extent of the two-phase region, equilibrium solubility in both phases, density of phases, equilibrium distribution coefficients of individual compo-

nents, and dependence of separation factors on concentration are determined.

A vast literature is available on calculation of phase equilibrium. For modeling of phase equilibrium, a number of commercial and free calculation programs are available, providing the ability of data-correlation and predictive calculations. The institute for Thermal and Separation Processes at the Hamburg University of Technology has provided a free research program, PE, which uses the more common equations of state and mixing rules [46].

These programs provide information about the extent of the two-phase region, essential for a counter-current two-phase process, the composition of the liquid and the gaseous phase, and yield data on separation factors. The composition of the liquid phase is essential, since the supercritical solvent dissolves in it in high concentrations. Separation factors, derived from the ratio of component concentration in the phases is much less accurate than concentrations. The latter may be around 1–3% (in real systems), while the separation factors comprise error ranges of 10–20%. For design purposes, experimentally determined separation factors are essential. Empirical solubility correlations are of very limited use, since essential data for the process cannot be calculated. On the type of systems mentioned above, and in connection with counter-current separation, in most of the publications, this type of thermodynamic modeling has been applied.

On the basis of mutual solubility and composition of the phases, a simplified determination of the number of theoretical plates can be carried out using well known Chemical Engineering methods like McCabe–Thiele or Ponchon–Savarit, see Fig. 3. This calculation is carried out on a quasi-binary system (key components) or with pseudo-components, and provides essential insight into the operation of the separation column or the separation machines.

The number of theoretical stages is calculated as a function of the reflux ratios, conditions of state, and separation factors. With systematic variation of parameters, a broad overview on number of theoretical stages and reflux ratio and solvent to feed ratio can be obtained from this separation analysis just from equilibrium data.

Examples for this type of analysis have been published for several separations. An example is shown for ethanol–water [29] and for tocopherol–sterol [7] in Fig. 4.

Simulation of the multi-component separation and determination of concentration profiles is carried out for a more detailed representation and analysis of the process, e.g. for optimization of number of stages. An example is shown for the separation of fatty acids, squalene, and fatty acid methyl esters in Fig. 5. These calculations have been carried out with a commercial simulation program, introducing Experimentally determined phase equilibrium data.

In the literature, modeling of the fractionation of liquids has been published, e.g. with a model based on the differential mass and energy balances over the height of the extractor, which are solved numerically [47], or with a non-isothermal dynamic model of a supercritical fluid extraction packed column [48], also including algebraic equations describing the thermodynamic phase equilibrium, mass transfer and the hydrodynamics of the two counter-current phases [49].

Modeling of the concentration profiles provides an overview on the performance of the counter-current separation. It reveals clearly the limits of a separation, first with the available number of theoretical stages, i.e. the height of an available column, or with the variation of the separation factor with changing concentration. In Fig. 5, right hand side, the concentration of squalene is limited at the top by the fact that fatty acids at low concentrations have a separation factor of >1 and tend to increase their concentration in the vapor phase (open symbols in Fig. 5).

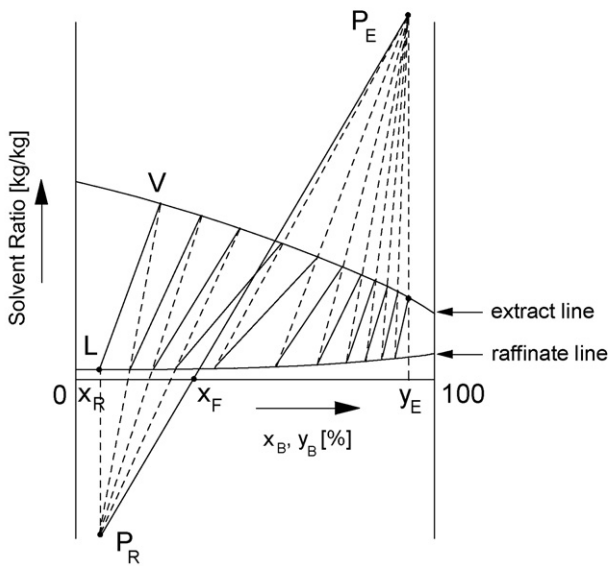
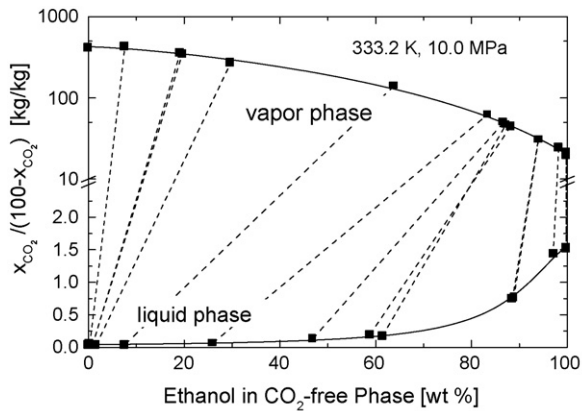


Fig. 3. Application of the short-cut method of Ponchon and Savarit in a Jänecke diagram on the basis of VLE data of CO₂ + ethanol + water [29].

Similar behaviour has been found in other multi-components systems.

6.2. Size and type of a separation device with respect to separation performance

For further design of a process, and in case of a separation column, height and diameter of the column have to be determined. The first part is related to mass transfer and depends strongly on the type of mass transfer equipment, the second part determines capacity or throughput. For counter-currently operated separation columns are height of theoretical stages (HETP) or height of transfer units (HTU) are determined, mostly by experiment or taken from literature on similar systems.

In the literature, mass transfer is reported in most cases for small columns, e.g. [3] on Raschig rings, Dixon rings, Fenske rings, and glass beads; [18] on 5-mm steel Raschig rings, for the extraction of flavours from milk fat an HTU of approximately 0.20 m. Compounds with a low viscosity like fatty acid esters, short chain alcohols, essential oil exhibit HETP or HTU of around 0.2–0.3 m. Compounds with a higher viscosity like edible oil free fatty acids and tocopherols have HETP and HTU-values of around 0.5–1 m. In aqueous systems, these values are up to 1 m for water rich mixtures and approach 0.25 m for the organic rich part. Mass transfer in counter-current columns, especially in packed columns, not

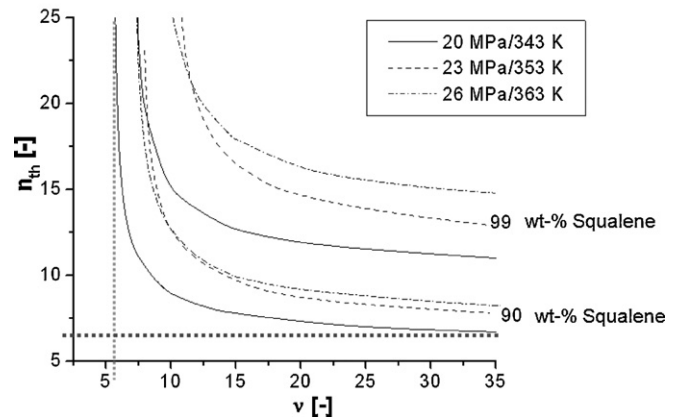
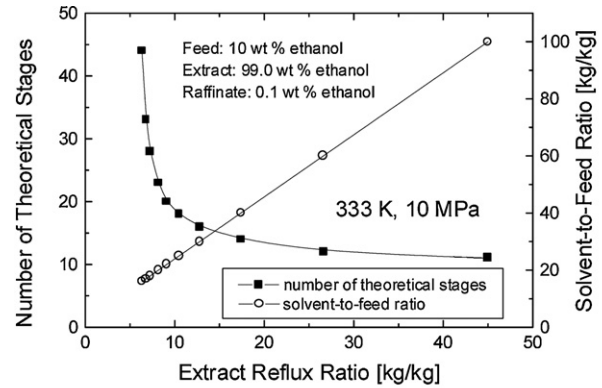


Fig. 4. Analysis of separation. Calculation of the theoretical number of stages as a function of reflux ratio and process conditions. Separation of ethanol-water (left) and squalene from a mixture of tocopherols and sterols (right).

only depends on viscosity, but also strongly on hydrodynamics. With higher throughput, the mass transfer is improved. Effective axial dispersion coefficients have been determined for packed beds [54], holdup and RTD experiments published for de-acidification of edible oils [12]. Conclusive correlations for mass transfer in supercritical separation column have not been developed so far.

Capacity or throughput is related to hydrodynamic behaviour in the separation equipment (flooding) and strongly depends on density difference of the phases, on the type of the internal equipment of the separation column and on the amounts of the counter currently flowing phases. Capacity limits for packing materials and the individual mixtures must be determined by measuring or calculating pressure drop and flooding points.

Hydrodynamic behaviour of counter-current columns at high pressure can be described with models developed for normal pressure if density of the gaseous phase is taken into account. This phase produces significant buoyancy which reduces the static head of the liquid. Dry pressure drop can be modeled with an Ergun-type equation. Liquid holdup below the loading point is correlated with one set of parameters of a two-parameter expression using the Reynolds and Froude number of the liquid phase. Falling film thickness can be described with Nusselt's equation. Flooding points could not be predicted in general with a mechanistic model of solid physical background. A modified empirical flooding diagram from Sherwood, Shipley and Holloway and the flooding equation proposed by Wallis [50] for vertical pipes are suitable to correlate the measured flooding points with sufficient accuracy, Eqs. (1) and (2) [51–53]:

$$J_G^* = \frac{1.1457}{(1 + 0.4222\sqrt{\Phi})^2} \quad (1)$$

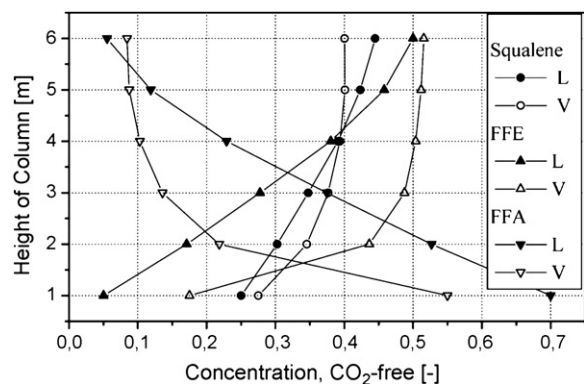
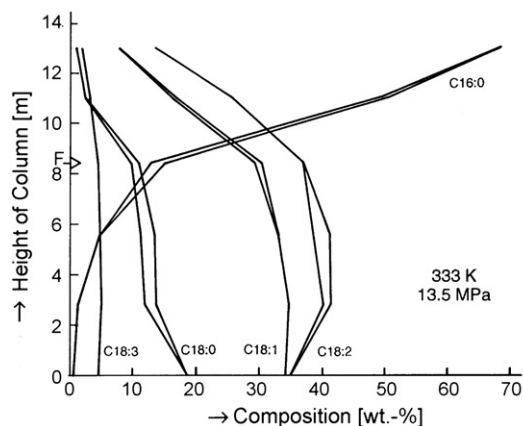


Fig. 5. (Left) Separation of C16-methyl esters from C18-methyl esters with supercritical CO₂. Separation of fatty acid esters (methyl and ethyl) from squalene and free fatty acids (right).

$$J_G^* = f(J_L^*) \quad \text{with} \quad J_G^* = \frac{u_G}{\varepsilon} \sqrt{\frac{\rho_G}{gd_H(\rho_L - \rho_G)}} \quad \text{and}$$

$$J_L^* = \frac{u_L}{\varepsilon} \sqrt{\frac{\rho_L}{gd_H(\rho_L - \rho_G)}} \quad (2)$$

Fig. 6 (left) demonstrates the regimes for loading of the mass transfer equipment. Gas phase loading is represented as parameter in the diagram, liquid loading on the abscissa. Below the line a–a, at low throughput, practically no mass transfer takes place, between lines a–a and b–b, gas flow interacts with the liquid flow, mass transfer is improved and gets higher with increased loading. Above line b–b, entrainment of the liquid phase increases rapidly until flooding occurs.

In case of a mixer-settler type construction, its selection is based on one or more of the facts that only a few theoretical stages are necessary, density difference of the phases is low, viscosity of the liquid phase is high, and gaseous and liquid phase flows are of very different size. Efficiency of the single mixer-settler stages is high and approach 100% [43]. Mixer-settler have been discussed in general [55], applied for concentration of minor components from palm oil [13,43], for enhancing concentration of tocopherols [56], and for effective removal of ethanol from aqueous solutions at low ethanol concentration [35].

The capacity of counter-current columns often is relatively high. Low viscous systems will allow a linear gas velocity of about 40 to 50 mm/s to be achieved at sufficient density differences of the phases. Capacity of commercial regular packing is in the range of 50,000–100,000 kg CO₂/(m² h). Relatively high quantities of supercritical CO₂ are needed for optimum mass transfer. A production rate of 400 t/a can be achieved in a 300 mm diameter column, for

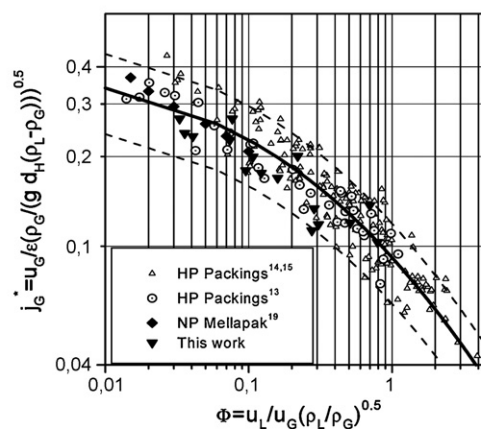
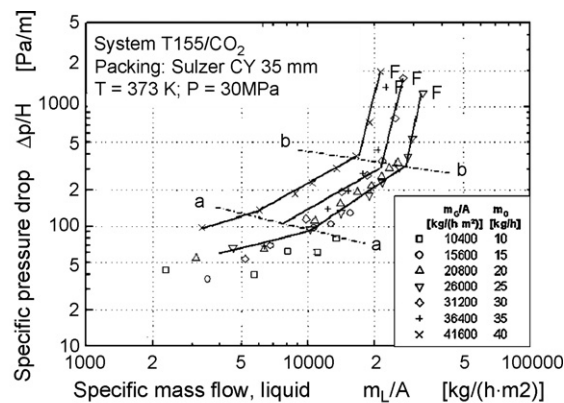


Fig. 6. (Left) Pressure drop in a counter-current column with regular packing (Sulzer CY), in a tocopherol-concentrate with CO₂. (Right) Flooding diagram. Thick line: correlation. Dashed lines: 30% interval. Empty triangles: structured and random packing at high pressures. Circles: structured packing at high pressures. Full diamond: Mellapak™ at normal pressure. Full triangles: falling film flooding at high pressures.

100,000 t/a a column diameter of about 2 m is sufficient. Nevertheless, a look at the characteristic data of the solvent cycle reveals the ratio of gas to liquid is in the range of 20–50, about the same range as the solvent to feed ratio. Both values emphasise the need for low cost solvent processing and make necessary a detailed analysis of the solvent cycle.

6.3. Design of the solvent cycle

For nearly all processes, the solvent, i.e. the supercritical fluid, must be recycled. This cycle of the supercritical solvent in counter-current processing determines costs of the process. Costs for the solvent cycle are determined by the solvent ratio (amount of supercritical solvent needed for a unit quantity of product) and the mode of carrying out the solvent cycle. The solvent ratio may be determined by thermodynamic properties or by operating parameters. Thermodynamic influence is exerted by changing pressure, temperature, and density. Solvents other than carbon dioxide, mixtures of gases may essentially change the equilibrium solubility and consequently the necessary solvent ratio. Operating parameters, not determined by thermodynamics, are essentially the reflux ratio, and for mixer-settler arrangements, the residence time in a stage. The reflux ratio can be varied within the limits of minimum reflux ratio and minimum number of theoretical stages. While residence time in a gravity driven counter current column is controlled by hydrodynamics, it can be varied in a mixer-settler by the volume of one mixer-settler stage.

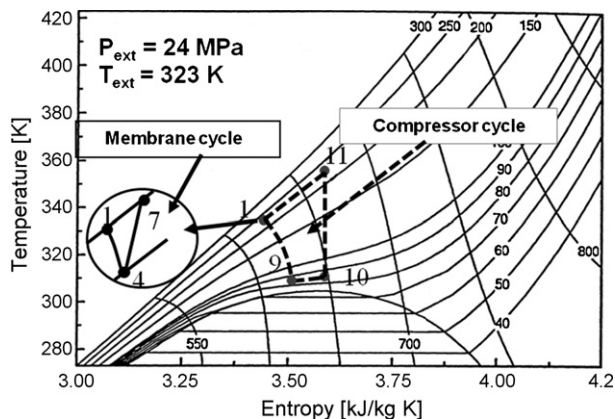


Fig. 7. Solvent cycle for a supercritical fluid solvent in a T,s -diagram. Comparison of a compressor cycle and a cycle for a product recovery at low pressure drop, e.g. a membrane cycle.

Recovery of the product is the most important step within the gas cycle. Different modes for separating solvent (supercritical fluid) and solute (extract) are possible. Recovery of product at constant pressure and only minor changes in temperature is the ideal cycling from a point of energy needed. Means for recovering the solute are separation by another solvent or solid (mass separating agent), including anti-solvents, membrane processes, and others. Different methods for regeneration were examined with respect to the ability of each to separate a solute-supercritical fluid mixture [57,58]: pressure and temperature change, adsorption, absorption, membranes and a new method called de-entrainment. Three different solutes were considered as examples to be separated from the supercritical fluid: caffeine, tocopherols, and triglycerides. The data base was used together to establish an evaluation system for the regeneration of supercritical fluids, using membership functions $m(x)$, known in fuzzy-sets, to establish the regeneration ability of a method for a certain parameter x (x : solute properties, thermodynamic conditions, operating parameters). The evaluation scheme provides basic insight in the possible procedures, but have to be evaluated further by detailed design.

In most cases the separation of solute from the solvent is achieved by reduced solvent power (lower density) caused by pressure reduction or temperature enhancement. In certain cases, temperature reduction causes also reduction of solvent power of the supercritical solvent. For reduction of pressure, different modes for carrying out the solvent cycle are possible, the compressor mode or the pumping mode. They are easily demonstrated using a T,s -diagram (see Fig. 7). Preference for a mode depends on the total amount of energy needed, but availability (and cost) of equipment and heat sinks are sometimes decisive.

The compressor cycle (dashed lines) in Fig. 7 represents the amount of thermodynamic work needed if the solute is separated by reduction of pressure. If this can be avoided, much less thermodynamic work is needed, as represented by the enlarged triangle (membrane cycle). In addition, in a cycle with substantial pressure changes, heat recovery must be applied for an optimised solvent cycle. Then, about 70–100 kJ/kg CO_2 have to be dissipated in the solvent cycle. If this figure is multiplied by the solvent to feed ratio, the necessity for reducing energy needed in the solvent cycle becomes even more clear than before.

Investigations on different solvent cycles have been published [59]. Cycles used are analyzed in detail with respect to energy requirements and exergy losses. The cycle proposed by de Swaan Arons [60] was found to provide very low exergy losses for a given change in extraction and separation density. Supercritical

region cycles can provide lower exergy losses than cycles operating between the two-phase and the supercritical region. For a high density difference, pump or compressor cycles can be competitive with the supercritical region cycles. For deterpenation of orange peel oil with carbon dioxide, Diaz et al. [27] used thermodynamic predictions and laboratory-scale separation values to evaluate different solvent cycle schemes. The compression cycle was found to be the optimal solvent recovery system in all cases.

Some advantages of the pump process are the lower investment cost for a pump than for a compressor, good control of solvent mass flow, less energy consumption than the compressor process at pressures higher than about 30 MPa. Disadvantages of the pump process include that heat exchangers and condensators are necessary and additional heat energy is needed at low extraction pressures.

Advantages of the compressor cycle include low heat energy consumption and that only one heat exchanger is necessary. Disadvantages of the compressor cycle include (1) mass flow control is more difficult than in the pump process, (2) higher consumption of electrical energy, (3) higher investment cost for the compressor and (4) higher energy consumption at pressures higher than about 30 MPa.

Recovery by adsorption has been demonstrated as effective for extract recovery from the solvent as first used to remove caffeine from the carbon dioxide solvent by activated char coal. It was replaced by absorption with water, since the caffeine could not be recovered from the adsorbent. A favourable case occurs when the adsorbate (adsorbent + adsorbed compounds) is a useful product, as it could be demonstrated for synthetic tocopherol acetate [61].

Separation of solute from CO_2 by a membrane is another possibility for reducing cycle costs due to a low pressure drop. An active multiple layer of poly-tetra-fluoro-ethylene supported by a ceramic or organic material proved to be applicable at high CO_2 -pressures (tested up to 35 MPa). The solute is retained, the supercritical CO_2 permeates through the membrane at high rates. An example is the separation of rice bran oil from supercritical CO_2 by means of Teflon AF2400-PEI membranes at pressures of 200 and 300 bar and temperatures between 40 and 60 °C for trans-membrane pressure differences ranging from 5 to 20 bar. Membrane modules, containing active membrane areas of up to 0.4 m were tested in pilot plants. Separation factors between 0.1 and 0.3 were achieved for specific permeate flow rates of up to 3000 mol/(m² h). Separation performance improves with increasing feed concentration. These results show that the regeneration of supercritical CO_2 by means of membranes is feasible on pilot plant scale [62–64]. Ultimately, a cost analysis must be carried out.

7. Cost calculation

Cost calculations must be carried out on the individual case and situation. The results are variable according to economic data and the assessment of risk. Common estimation methods yield results with an error of $\pm 30\%$, while even after a project has been completed, costs are difficult to be determined better than 5%. For cost comparison, equal situations must be selected. Processes with supercritical fluids have often been evaluated on a low throughput basis, with the result that relatively high investment costs have determined total costs. The results of some cases, of which at least two have been carried out to industrial development are reported and given below. It is obvious that the amount processed is by far the most prominent parameter.

Tocopherols from edible oil distillates:

Throughput: 10, 20 and 50 t/a.

Diameter of column: 0.07, 0.100 and 0.150 m.

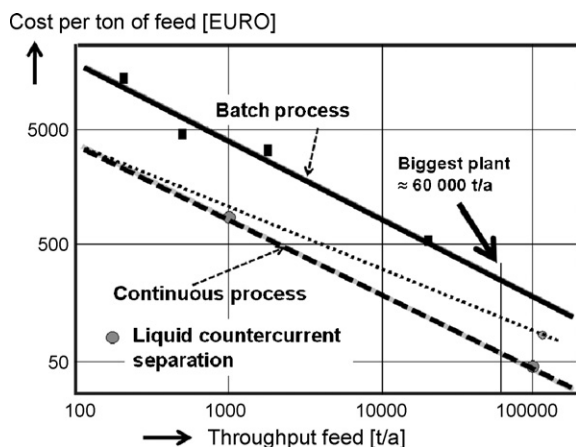


Fig. 8. Cost estimation for processes with supercritical fluids.

Separation costs: 70, 45 and 25 €/kg product.

Removal of free fatty acids from edible oils:

Throughput: 900 t/a.
Diameter of column: 0.4 m.
Separation costs: 1.4 €/kg product.

Purification of synthetic tocopherol acetate:

Throughput: 400 and 1100 t/a.
Diameter of column: 0.3 and 0.5 m.
Separation costs: 1.4 and 1.0 €/kg product.

Separation of C16/C18 fatty acid methyl esters:

Throughput: 105,000 t/a.
Diameter of column: 2.2 m.
Separation costs: 18–28.3 €/t of feed.

The trend is shown in Fig. 8, where the strong dependence of processing costs on throughput is clearly illustrated. Continuous operations are less costly than batch operations. This commonly accepted fact is disappointingly not holding for large throughputs of solids. The costs for introducing and removing large amounts of solids in a pressurized environment outweigh the advantage of continuous processing for high feed conditions, as indicated by the dotted line representing the cost result of a study on the extraction of oil from soja bean flakes.

The cost situation with respect to competitive processes has been discussed in the literature, e.g. by Nieuwoudt et al. [33] for paraffin waxes. Detailed cost analyses of short path distillation (SPD) showed that SPD is the cheaper fractionation process for light paraffin wax. However, supercritical fluid fractionation appears to be the more attractive option for the fractionation of medium to heavy paraffin waxes.

For purification of synthetic tocopherol acetate, the base case is high vacuum distillation (P about 1 mbar). Costs are twice as high with supercritical carbon dioxide and solvent recovery by pressure reduction. If propane is added, costs can be reduced to 20% of the base case. If the favourable case occurs that the solute can be adsorbed, and the adsorbate used as product, cycle costs are only 50% of the base case, even with pure carbon dioxide. If, in addition, propane is added, costs may be less than 10% of the base case.

The advantage of counter current processing with supercritical fluids is the low processing temperatures. All the high vacuum pro-

cesses are carried out at temperatures of about 200 °C. Products are not necessarily stable at these temperatures. Beside that operating cost for processes with supercritical fluids are markedly lower for such type of processes, i.e. due to the fact that to achieve a very low pressure at least two separate devices are necessary, the first removing the more volatile components to enable the low pressure necessary for the second step in which the actual processing takes place. For both devices the vacuum must be provided, which is energy intensive.

8. State of the art and future perspectives

Counter current processing for the separation and enrichment of compounds has been successfully demonstrated in various plants, e.g. on purification of ethanol [65], on the recovery of n-3 fatty acid esters [16], and for the purification of tocopherols [61]. Industrial plants have been erected for the de-oiling of lecithin with propane and for recovery of caffeine from water in a decaffeination cycle. Engineering and cost analysis has been carried out on many more separation problems, and the fact that in many cases conventional solutions have been preferred is not due to the inferiority of the process with a supercritical fluid. The technical means for designing and setting up such processes are available.

For the future perspective, several factors will influence the increasing application of counter-current processes with supercritical fluids. (I) Understanding of the process is spreading with a new generation of executives coming into positions, where decisions are made. (II) Product degradation through high processing temperatures will decreasingly be accepted by customers. (III) Rising costs for energy will make necessary a more thorough evaluation of operating costs, favoring supercritical fluid processing over high vacuum applications. (IV) Green processing, as provided with supercritical fluids, will be the way of processing in sustainable production.

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