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Fractionation technologies for liquid mixtures using dense carbon dioxide.

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- Main fractionation applications include lipid mixtures, essential oils, and alcoholic beverages
- Fractionation in packed columns is the most common technology for all applications
- The manuscript characterizes packed column facilities in leading institutions
- The manuscript also discusses mixer-settlers, membrane contactors, and spray processes
- Some physicochemical properties (*e.g.*, interfacial tension) affect all technologies

Abstract

Supercritical fluid extraction of liquid mixtures with dense CO₂ is an end-of-line process that is typically used to fractionate materials extracted by conventional methods. Because continuous countercurrent packed columns are the devices most commonly applied to fractionate liquid mixtures (lipid mixtures, essential oils, and alcoholic beverages), this review offers general background on the use of countercurrent Supercritical Fluid Fractionation (SFF) in packed columns. Additionally, the manuscript characterizes in detail packed column facilities in leading institutions, and describes different modes of operation of countercurrent packed columns. The manuscript also discusses less common SFF technologies for liquid mixtures such as membrane contactors, mixer-settler arrangements, and spray processes. When appropriate, the review includes extensions of these topics (*e.g.*, special uses of static mixers in SFF of liquid mixtures). In all cases, applications, future perspectives, and developments are included. Main fractionation applications include lipid mixtures, essential oils, and alcoholic beverages. Available phase equilibrium data and relevant physical properties of mixtures that are common to all technologies are also discussed. Even though a comparison between technologies is not straightforward, considerable effort has been made to identify the characteristics that make a technology more suitable for each application. In general, mixtures with low separation factors are associated with packed columns. Mixer-settler arrangements are limited to mixtures with high separation factors and when a small number of stages (≤ 5) are required for separation. An immobile interface at the pores mouth makes aqueous systems ideal for membrane contactors, and spray processes are used when handling with high viscosity mixtures.

Keywords

CO₂, Membrane contactors, Mixer-settler, Review, Spray processes, Supercritical fractionation.

1. Introduction

Supercritical fluids are substances under temperature and pressure conditions above their respective critical values and where distinct liquid and gas phases do not exist. Supercritical Fluid Extraction (SFE) is a process that uses gases at high pressures as solvents to extract valuable materials. SFE has been studied to take advantage of the hybrid transport and solvent properties between gases and liquids of supercritical fluids. The most commonly used solvent in SFE is carbon dioxide (CO₂), mainly because it has a near-ambient critical temperature (T_c , 31.1 °C), it is innocuous, and it is completely removable from the extract and treated substrate by simple decompression. These characteristics coupled with the selectivity of CO₂ towards high-value compounds in biological

matrices, make it an ideal solvent to extract bioactive and/or temperature-sensitive solutes for use in foods, cosmetics, and pharmaceuticals.

In contrast to SFE from solid matrices, in which the compounds of interest are directly extracted from its natural source, the SFE from liquid mixtures is considered as an end-of-line process, known as Supercritical Fluid Fractionation (SFF). SFF is typically used to fractionate materials extracted by conventional methods [1], and is frequently carried out in the countercurrent mode. Early developments of the SFF technology and its advantageous characteristics were first described in the late 1970's [2–5]. However, the number of applications of SFF nowadays is limited because the process has to be designed for each application, and the required know-how is not universally shared by all members of the chemical engineering community [6]. Continuous CounterCurrent (CC) SFF in packed columns is more commonly applied than other methods of fractionation and considerable information regarding this process is available in scientific literature.

In general, among SFF applications, it is possible to identify two broad categories (fractionation of non-aqueous and aqueous mixtures) and three major areas of intense scientific research (lipids, essential oils, and alcoholic beverages). In the first category, the fractionation of edible oil components and derivatives is perhaps the furthestmost explored area followed by the deterpenation of essential oils. In the second category, the removal of ethanol and separation of the aromas from alcoholic beverages is the most studied application.

In non-aqueous mixtures, there is plenty of information available regarding edible oil components and derivatives (Table 1), specifically on fractionation and concentration of sterols, tocopherols, fatty acids, and carotenoids from pepper oleoresin [49], olive oils [12,17,22,26,28], and other vegetable oils such as those of palm [18,19], sunflower [20], and soybean [7,9,23,50–53]. Another important application is the fractionation of fish oil fatty acid alkyl esters [42–47,54–58] where the main issues that remain to be addressed are the appropriate representation of the phase behaviour for more complex or real mixtures, and the process scale-up [59]. Further information on separation of fish oil constituents using supercritical fluids can be consulted in Staby & Mollerup [60] and Shahena *et al.* [61].

A second area of intense research for non-aqueous mixtures is the deterpenation (removal of monoterpenes) from essential oils (Table 2). Monoterpenes hydrocarbons are associated with off-flavours and decomposition of essential oils. The most important contribution to the flavour of the essential oil comes from oxygenated compounds from which the monoterpenes hydrocarbons are partially removed. Citrus fruits essential oils [67,75–78], and plants essential oils like lavender [72] and oregano [79,80] are the most studied systems for fractionation in countercurrent and semi-batch packed columns.

The third area of active research, in the aqueous mixture category, is the dealcoholization of alcoholic beverages (Table 3) and, to a more limited extent, the recovery of their aromas [87,89–91,98,99]. The recovery of aromas from other liquid mixtures as juices is even more limited [85,86]. Tables 1–3 list the type of technology used, the operational conditions under study, and the objective of the work in an extensive compilation of references. For more detailed and comprehensive information regarding continuous countercurrent packed columns, their applications, and process design please refer to the reviews of Brunner [100–102].

This work reviews less common technologies than CC-SFF in packed columns, and their applications for fractionation of liquid mixtures using dense CO₂ or SuperCritical CO₂ (SC-CO₂). The technologies examined in this review are membrane contactors, devices based on the mixer settler principle, and spray processes. Aspects of the use of static mixers and nozzles are also briefly included. However, because of the importance of CC-SFF, this contribution includes a description of fundamental engineering topics of packed columns, their different modes of operation, and available equipment and installations in leading research groups around the world. This work also

covers subjects transversal to all technologies such as phase equilibrium and relevant physicochemical properties like diffusivity, density, and surface tension.

1 2. Continuous CC-SFF fundamentals, research groups, and applications

This section includes a description of fundamental engineering topics regarding CC-SFF, specifically how mass transfer and other column operational issues as pressure drop and flooding points are approached in the literature. Even though CC-SFF has been extensively reviewed in the past, this work contributes with a detailed list (Table 4) of packed column facilities in leading research institutions and companies around the world. Additionally, this section includes a description of different modes of operation of packed columns. Table 4 contains dimensions, operating pressures, column-packing, type of equipment used to compress CO₂, and research areas of the leading institutions.

1.1 2.1 Fundamentals

Basically, CC-SFF is a mass transfer operation that can be considered as a stripping process, and is usually developed in a packed column. In an ordinary stripping process, the liquid-gas contact in a packed column is continuous and non-staged, unlike in plate or other types of columns. The solute of interest is transferred from a descending liquid stream to an ascending dense gas stream. In the particular case of CC-SFF, due the liquid-like density of the dense gas, its velocity through the packing conduits can be about 100 times lower (around cm·s⁻¹ instead of m·s⁻¹) than in distillation [146]. In order to achieve the separation it is essential that operational conditions warrant the presence of a two-phase region inside the column. Therefore, phase equilibrium, interfacial tension, and differences in density between phases, are of great importance to ensure the partial immiscibility and separation of the contacting streams.

In general, for the design of packed columns, the separation is treated as a staged process, and uses the packed bed Height Equivalent to a Theoretical Plate (HETP) to convert the required number of ideal stages to a packing height. The basic model for the mass transfer performance of a packed column in distillation or absorption/stripping processes is often expressed by the HETP. According to the double-film theory the relationship between HETP and the Height of the mass-Transfer Unit for the gas phase (HTU_G) and for the liquid phase (HTU_L) is given by the following equations [147]:

$$(1a) \text{HETP} = \frac{Z}{N}, \text{ and}$$

$$(1b) \text{HETP} = \frac{\ln(\lambda)}{\lambda - 1} \cdot (\text{HTU}_G + \text{HTU}_L),$$

where Z is the height of packing, N is the number of theoretical stages, and λ is the stripping factor defined as the ratio between the slope of the equilibrium line and that of the operating line (mass balance equation). Combining Eq. (1b) with the definitions of HTU_G and HTU_L [148], the expression becomes:

$$(2) \text{HETP} = \frac{\ln(\lambda)}{\lambda - 1} \cdot \frac{G_m}{k_G \cdot a_e} + \lambda \cdot \frac{L_m}{k_L \cdot a_e},$$

where G_m and L_m are the molar flow rates per unit cross sectional area of the gas and liquid phase, respectively; k_G and k_L are the corresponding gas and liquid phase mass-transfer coefficients; and a_e is the effective interfacial area for mass transfer provided by the packing. It is simple to perceive that Eq. (2) will be accurate if the correlations used to predict the basic parameters are accurate. When assuming binary or pseudo-binary systems, low concentrations of the solute, straight equilibrium and operation lines (generally true in CC-SFF), and constant molar overflow

throughout the column, Eq. (1a) and Eq. (2) can be solved using conventional methods. The number of stages can be estimated using graphical methods such as those of McCabe-Thiele or Ponchon-Savarit as described by Brunner [100,101,149], or using numerical integration of traditional expressions for the Number of Transfer Units (NTU) [148]. For multicomponent separations a more complex approach, based on the Stefan-Maxwell equation to estimate multicomponent diffusivities, is necessary. Literature reporting diffusion coefficients in multicomponent mixtures at elevated pressures is scarce and this topic is beyond the scope of this work. However, studies of multicomponent diffusion using the Stefan-Maxwell approach under high pressure for the ternary system (CO₂ + methanol + water) can be found in the work of Unsulu & Sunol [150,151]. Recent improvements to the HETP model are also reported by Hanley & Chen [152].

In general, the mathematical description of CC-SFF considers only axial dispersion and the mass fluxes in terms of overall mass-transfer coefficients for the solutes into the dense gas ($K_{i,SC}$) and of the SC-CO₂ into the liquid phase ($K_{CO_2,L}$, non-negligible in non-aqueous systems).

Due to back mixing effects, a correction factor dependent on the densities of both phases (ρ_{SC} , ρ_L) and the corresponding superficial velocities (u_{SC} , u_L) is usually introduced in the expression for the mass fluxes, Eq. (3a) and Eq. (3b), to take into account the buoyancy effects produced by the slight density difference between the SC-CO₂ and the liquid phase [153].

$$(3a) J_i = K_{i,SC} \cdot \rho_{SC} \sqrt{\frac{\rho_{SC}}{\rho_L - \rho_{SC}}} \cdot \frac{u_{SC}}{u_L} \cdot (y_i^* - y_i)$$

$$(3b) J_{CO_2} = K_{CO_2,L} \cdot \rho_L \sqrt{\frac{\rho_{SC}}{\rho_L - \rho_{SC}}} \cdot \frac{u_{SC}}{u_L} \cdot (x_{CO_2}^* - x_{CO_2})$$

From Eq. (2), Eq. (3a), and Eq. (3b) it is seen that phase equilibrium mole fractions (y_i^* , $x_{CO_2}^*$) are essential in the description of the process. Comprehensive reviews on correlations for estimating basic parameters, *i.e.*, mass-transfer coefficients of both phases, and effective interfacial area for different types of packing can be found in literature [146,147,154]. Several mass-transfer and hydrodynamics studies, along with CC-SFF process modelling and simulation, can be found in literature, mainly for non-aqueous systems and very few applications related with aqueous systems. Hydrodynamics of countercurrent packed columns consists of studying dry and wet pressure drops, liquid holdups, and flooding points. The work of Stockfleth & Brunner [155–157] demonstrated that the hydrodynamic behaviour of countercurrent columns at high pressure could be described with models developed for normal pressure operation if specific peculiarities, such as the real mixture properties of miscible systems at the relevant conditions of high-pressure operation, are appropriately addressed. Becker and Heydrich [158] contributed greatly to clarify the fluid dynamic dispersion of the mixture (CO₂ + ethanol + water). The authors studied the separation efficiency and hydrodynamics of two types of packing, wiremesh and Sulzer BX. They found lower separation efficiencies and very irregular flow patterns for the wiremesh packing. The authors also predicted axial dispersion coefficients using a conventional liquid/liquid model and found that experimental data obtained for the wiremesh packing did not follow the general trend. In general, as it can be seen from Table 1, the fractionation of edible oil components and derivatives has been relatively well studied. Much less is known about hydrodynamics of aqueous systems, other than ethanol + water, in contact with dense gases, and experimental investigation of these systems is more challenging.

Availability of information regarding phase equilibrium, interfacial tension, and other physicochemical properties, transversal and relevant to all fractionation technologies will be described in Section 4.

2.2 Modes of operation of packed columns and applications

As mentioned before, CC-SFF in packed columns is the type of technology more commonly used in SFF. It is possible to identify three different modes of operation in CC-SFF in packed columns: stripping mode, reflux mode, and batch or semi-batch modes. Because the applications of CC-SFF in packed columns have been reviewed in the past by Brunner [100–102], in this section we will

describe the applications and mode of operation used by the first six institutions listed in Table 4. The applications mentioned in this section are listed along with the applications of the other fractionation technologies described in this work, classified according to the three major areas of research; edible oil components and derivatives (Table 1), essential oils (Table 2), and alcoholic beverages (Table 3). As it can be understood, the equipment listed in Table 4 can be used also for other applications that may not fall in the defined areas of research, and/or use other solvents such as ethane and propane. These studies are very scarce in literature, and therefore were only included in Table 4 and not listed in Tables 1 to 3.

Research groups in Table 4 are organized according to number of publications associated with the equipment found in the literature. Considerable effort was devoted to make Table 4 as complete and actualized as possible, and to include all equipment available at the research groups. However, some installations may have been modified, discarded, or upgraded, and are no longer operational.

2.2.1 Stripping mode

The stripping mode of operation is achieved when the liquid mixture is fed from the top of the column and the dense gas is fed at the bottom of the column causing the countercurrent flow (Fig. 1A). The extract is recovered by the expansion of the loaded CO₂ in the separator. In this type of operation there is no partial reflux of the extract.

Slight variations of the stripping mode are found in the investigations of the *Instituto de Investigación en Ciencias de la Alimentación* (CIAL) from the *Universidad Autónoma de Madrid* (UAM) and the *Consejo Superior de Investigaciones Científicas* (CSIC) (CIAL-UAM-CSIC). The feed point of liquid phase can be in different positions of the column (upper, middle and low). The extract is obtained in two separators where cascade decompression takes place. No reflux of the extract is used in this way of operation. CIAL-UAM-CSIC research group has developed investigations in two areas of research. Regarding edible oil components and derivatives, it has studied the removal of free fatty acids [28,47], recovery and concentration of minor lipids such as tocopherols, phytosterols, phytosterol esters, carotenoids, and squalene from olive oil and other lipids [1,17,20,22,23,26,53,159]. It has also studied the fractionation of alcoholic beverages [87–89], and isolation of antioxidants from orange juice [85,86].

The research group of Portugal at the *Laboratório Associado para a Química Verde – Tecnologias e Processos Limpos* (REQUIMTE) has operated their columns in both the stripping, and reflux mode of operation. REQUIMTE research is related mainly to edible oil components and derivatives: fractionation and de-acidification of olive oil deodorized distillates [12,44] and separation of squalene from methyl oleate [16]. Additionally, they have reported one work on wine must aroma [90] and have contributed with mass-transfer studies in packed columns [62,160], dynamic simulation of coupled mass and energy balances [109,153,161,162], and the use of Computer Fluid Dynamics (CFD) for pressure drop calculations [163,164].

Another group that applies a slight variation of the stripping mode is the one at the Northern United States Department of Agriculture (USDA). The column is divided into different sections and the liquid is fed in the first section of the column, just above the bottom feed of CO₂, in order to achieve the countercurrent flow. Northern USDA research group also applies an ascending temperature gradient from the bottom to the top of the column. The increase in temperature decreases CO₂ density allowing the higher vapor-pressure compounds to concentrate at the top of the column. The main area of research of the Northern USDA is the edible oil components and derivatives; fractionation of mixtures composed of mono-, di-, and tri-acylglycerols [11,24,25,31], removal of free fatty acids from vegetable oils [13,29], enrichment of phytosterol esters of rice bran oil [14], and removal of the organic solvent from an hexane-extract of soybean oil [35].

The research group of Cornell University applies the stripping mode with no variations, *i.e.*, no extract reflux and liquid feed on top of the column. The main applications of this group are related to non-aqueous solutions: refining palm oil [10], and anhydrous milk fat fractionation [36–40].

2.2.2 Reflux mode

In the reflux mode of operation the liquid feed is introduced in the middle section of the column and the extract is partially returned to the top of the column to achieve the countercurrent flow. The

partial reflux of the extract is done in order to obtain an extract richer in light components (Fig. 1B). Other possibility is to partially reflux the raffinate to the feed supply in order to increase extraction yield but at the expense of lower product volumes at the bottom of the column.

Perhaps the world leader research group in supercritical fluid technology is that of the *Technische Universität Hamburg-Harburg* (TUHH). Researchers at TUHH operate their available columns in the reflux mode (as a distillation column) and they have developed research in the three main areas of application described in this work. This group has influenced the way in which supercritical fractionation is addressed. The approach of the TUHH research group can be divided in four important steps: (i) phase equilibrium measurements; (ii) pilot scale experiments in order to adjust velocities, solvent-to-feed ratio, and measure real compositions of extract and raffinate samples; (iii) determination of hydrodynamic characteristics such as dry and wet pressure drops, flooding points, and liquid holdups; and, (iv) graphical or computer-aided determination of NTU and HTU or HETP. Detailed information on the steps of the approach followed by the TUHH group and their applications are described in detail in the reviews of Brunner [100–102] and the work of Brunner & Machado [103].

A less common technique is the semi-batch mode of operation. Particularly the research group of Kumamoto University has applied this mode of operation for the deterpenation of citrus oils.

2.2.3 Semi-batch contacting equipment

Semi-batch contacting can be achieved in columns with continuous flow of CO₂ through a quiescent portion of liquid held in the bottom of the column. The extract is recovered by pressure reduction in a separator at controlled temperature and pressure as depicted in Fig. 1C. This mode of operation is a much less common technique than the stripping and reflux modes of operation. The infrastructure needed for this type of operation is simpler than for the stripping and reflux modes, and the same equipment used for SFE of solids may be used for SFF of liquid mixtures using laboratory-size equipment. Phase equilibrium, extraction kinetic curves, and derived information can be obtained with this kind of arrangement.

For the reasons exposed above, only for this mode of operation a detailed description of the applications found in literature is given below. A few comparisons with the stripping and reflux modes were carried out by the research group of Kumamoto University and are described below. Rincón *et al.* [30] studied the separation of triglycerides from the unwanted polar fraction in used frying oil using liquid and supercritical ethane. In order to determine the best conditions for the separation, preliminary semi-batch experiments were performed in a 940-cm³ vessel packed with an irregular steel material. Rincón *et al.* [30] performed the same separation by CC-SFF using the best pressure and temperature conditions found in the semi-batch experiments (24.5 MPa and 298.2 K). By the use of CC-SFF, the authors recovered 85% of the triglycerides in the used frying oil, and the content of polar compounds decreased from 29.9 to 11.2%, close to the value of the fresh sunflower oil (7.3%). The CC-SFF with ethane showed better separation efficiencies than obtained by CC-SFF with CO₂ in a previous work [48]. In the work of Chen *et al.* [15] on de-acidification of rice bran oil, the removal of free fatty acids reached 97.8% in a 75-cm packed column operated in the semi-batch mode.

Regarding essential oils, Jaubert *et al.* [70] modelled accurately the extraction profiles of citrus oil components with SC-CO₂. The authors applied a theoretical model to the separation of limonene and citral in a 40-cm vessel operated in the semi-batch mode packed with glass beads. Gañán & Brignole [74] studied the fractionation of essential oils from plants (*Salvia officinalis*, *Tagetes minuta*, and *Mentha piperita*) with biocidal activity. The experimental set up used in this study was a conventional screening unit with a 50-cm³ vessel where a small quantity of oil (1.0 to 1.5 cm³) was embedded in 80-mesh glass beads. After two hours of approaching equilibrium, CO₂ was allowed to flow through the column and extracts were collected for analysis. Solubility of main components of different fractions of essential oil in CO₂ were determined and correlated using the Group Contribution Equation of State (GC-EoS). The study concluded that the active biocidal fraction of *Tagetes minuta* oil could be extracted in a semi-continuous or countercurrent column without external reflux.

The research group of Kumamoto University has studied the deterpenation of essential oils of lemon and other citrus fruits on larger columns. Researchers from this group observed that when performing continuous fractionation, the selectivity was not significantly influenced by the use of an external reflux (reflux mode). On the other hand, they found that the solvent-to-feed ratio, and feed-inlet position were important variables in the fractionation of citrus fruit essential oils [63–65,67,68,71,73]. In fact, better results were obtained operating the column in the stripping mode [66].

A countercurrent flow in the semi-batch mode can be obtained by applying a temperature gradient on the column. Sato *et al.* [64] studied the effect of the operation of the column under isothermal and linear temperature gradient conditions on the selectivity in the extraction of terpenes (limonene) *versus* oxygenated terpenes (linalool). An internal reflux was induced by a temperature gradient, from 313 K at the bottom to 333 K at the top of the column. Under these conditions selectivity increased significantly because physical properties such as solubility, density, and viscosity changed remarkably. Kondo *et al.* [71] compared the continuous countercurrent operation of the column with semi-batch experiments for the fractionation of lemon essential oil (with and without temperature gradient). The continuous operation of the column at higher solvent-to-feed ratios increased the selectivity between limonene and citral, and the highest value was obtained with the column working at 8.8 MPa under the temperature gradient from 313 K at the bottom to 333 K at the top.

An application that stands out from the three outlined areas is the recovery of aroma compounds from non-alcoholic beverages such as fruit juices or essences. Early researchers of the Western Regional Research Laboratory of the USDA (California) applied the semi-batch mode of operation. In the work developed by Schultz *et al.* [83] and Schultz & Randall [81], aqueous apple juice essence was dispersed into liquid CO₂. After ~3.3 cycles of aqueous essence passing through the column, the concentration went from 150-fold to 10,000-fold although steady-state was not achieved. The authors also compared different gases as solvents for the extraction; CO₂ showed good recovery of the major essence constituents. Later, Schultz *et al.* [82] built a pilot plant for continuous liquid-liquid extraction of fruit aroma in order to reach steady-state conditions. Very limited applications of this methodology were found in literature. All experiments using the semi-batch mode of operation were made using laboratory-size equipment (from 0.4–2.4 m of column height) and model mixtures were considered.

3. Membrane contactors

This section describes the use of membrane contactors to fractionate liquid mixtures using dense CO₂ along with its main applications (Table 3). Liquid fractionation with supercritical fluids in a separation device containing a porous membrane is characterized by a two-phase immobilized phase interface. As shown in Fig. 2, one fluid phase (phase 2, usually the dense gas) is on one side of the membrane occupying the pores, and an immiscible fluid phase (phase 1, usually aqueous) is on the other side of the membrane. The pressure of the fluid phase 1 (P_1) must be equal to or greater than the pressure of the second fluid phase (P_2) in order to immobilize the immiscible phase interface at the pore mouth. However, the pressure difference ($P_1 - P_2$) should not exceed a critical value (ΔP_{crit}); otherwise the fluid phase 1 will be forced through the pores and disperse into the fluid phase 2 as drops or bubbles. As no drops or bubbles are formed in either phase, the process becomes an equilibrium-based separation, and the separation device is generally called membrane contactor [165]. Other membrane technologies and their applications can be consulted in the work of Sarrade *et al.* [166].

Most of literature regarding applications of membrane contactors deals with the separation of different organic solvents from aqueous solutions, probably because water solutions have favourable wetting behaviour for membrane contactors and an immobile interphase is better achieved. Bothun *et al.* [92] used a model solution of fermentation products, acetone and ethanol, to separate them from water in a Hollow Fiber Membrane Contactor (HFMC) with three different dense gases: CO₂, ethane, and propane.

Gabelman & Hwang [94] made a comparison between the predictions of a mathematical model and the experimental results for the separation of various solutes (caffeine, ethanol, dimethylformamide, 1,2-dichloroethane, and ethyl acetate) from aqueous solutions into dense CO₂ and propane. A previous work [95] presented the mathematical model that described the HFMC process for the separation of isopropanol and acetone from water into dense CO₂. When applying the model to the new aqueous solutions, it predicted the steady-state fluid velocities and solute concentrations, and it estimated mass transfer coefficients. The mass transfer predictions made in both works agreed with experimental results.

Another interesting study made by Gabelman & Hwang [96] compared sieve and spray towers, and packed columns with HFMC. The authors simulated HFMC using experimental information reported by others on the fractionation of isopropanol and ethanol from water. The comparison was made in terms of the HETP. The simulated HETP was compared with the experimental data reported in the literature. The experimental data was obtained in sieve-tray columns, spray columns, and columns packed with Sulzer and Raschig rings of 0.5 to 4 m of active height. In some cases, the simulated HETP was significantly lower than compared with sieve tray, packed (Sulzer and Raschig rings), and spray columns. Consequently, Gabelman & Hwang [96] claimed that HFMC technology is more efficient in most cases.

Perhaps the most common alcoholic beverage in the world is wine and its ethanol content and aroma profile is of great interest to producers. Thus, separation of organic solvents such as ethanol or isopropanol from aqueous solutions by HFMC can be used as an alternative to dealcoholize alcoholic beverages. Diban *et al.* [167] tested the validity of HFMC to partially dealcoholize wine without compromising the aroma profile. They used model solutions with typical compositions of real wines and found that the technology was feasible to reduce ethanol to 2% (v/v) without perceptible loss of quality of the product. However, they observed that prolonged retention times of the mixture into the HFMC caused adsorption of highly hydrophobic flavours in the membrane with almost complete disappearance of aroma from the feed solution.

Simulation and mathematical modelling of the process is an intensive area of research. Simulation for the separation of organic solvents (ethanol and acetone), sulphur aroma components, and caffeine from aqueous matrices by single and multiple fiber modules is available in literature [93,97,168,169]. In general, the mass transfer of the process was described by a resistance-in-series model, taking in consideration four steps for solute transport: (i) the solute flows through the aqueous boundary layer, from the bulk phase to the interface; (ii) the solute goes across the aqueous/solvent interface; (iii) the solute diffuses in the pore filled with the solvent phase; and, (iv) the solute flows through the solvent boundary layer. More recent advances are the application of CFD to model the separation of ethanol and acetone from water in a HFMC with dense CO₂ [168] and the simulation and optimization of an industrial scale HFMC to separate organic solvents such as ethanol, methanol, and acetone from water [170].

Examples of SFF with membrane contactors and other membrane technologies that use dense CO₂ to fractionate liquid mixtures are relatively recent. More complex or real mixtures need to be studied to improve the knowledge of the process and scale it up to industrial size. Application of this technology is limited to one equilibrium stage and to aqueous systems mainly because fractionation for non-aqueous systems would probably lead to a mobile interphase in the pores causing the liquid phase to break into the CO₂ as drops or bubbles. Additionally, care must be taken to not exceed ΔP_{crit} especially when the HFMC is operated in countercurrent mode. Typical values of ΔP_{crit} are in the range of 0.1 to 0.5 MPa.

In membrane contactors, the main function of membranes is increasing interfacial area for mass transfer. However, membranes can be used for other purposes. For example, they can be coupled to CC-SFF for enhanced separation of the extract at the top of the column for CO₂ recycling. Ruivo *et al.* [27] carried out a comparison of six different membranes for the separation of squalene from oleic acid with CO₂. Polydimethyl siloxane and polyamide membranes gave significant enrichment of squalene in the permeate side. The authors suggested that this technology could be used as an additional reflux step in a SFF packed column where the less-pure extract stream from the packed

column would be diverted to the membrane cell. The permeate side, which has a higher squalene content, would be partially refluxed to the top of the SFF column, increasing the squalene content of the “enrichment section” of the column. A similar approach was studied by Carlson *et al.* [171] who compared four different commercial membranes (one nano-filtration and three reverse osmosis) to separate limonene from a solution with CO₂. They found that the best was a thin film polyamide reverse osmosis membrane achieving a limonene retention factor as high as 0.94.

4. Mixer-settler process and components

This section describes devices that take advantage of mixer-settler and the spray extraction processes to fractionate liquid mixtures. The role of the mixing devices (*e.g.*, static mixers and nozzles) is discussed, and in each case a discussion of the main applications, findings, developments, and future directions is provided.

Several mixer-settler equipment and configurations exist. Nevertheless, they work based on the same principle, a separation process that consists of two steps: the first mixes the solvent and the solution with the solute(s) of interest, that together follow to a second step where a quiescent settling takes place allowing phases to separate by gravity. The use of mixer-settler arrangements in SFF is desirable when (i) the liquid phase flow is low and does not cover all the mass transfer equipment, causing a limited mass transfer rate; (ii) the viscosity of substances in the liquid phase is high, even with dissolved supercritical fluids; (iii) the flow differences between liquid and gaseous phases are large, compromising stable operation of the column; and, (iv) there are small density differences between phases causing limited flow in columns driven by gravity. Using a mixer-settler arrangement circumvents these problems. The main drawback of this technology is its limitation to mixtures that require a relative small number of stages for a reasonable separation [101].

The mixer-settler arrangement must accomplish two purposes: provide the adequate mixing of the liquid and gaseous phase, so as to approach phase equilibrium, and allow separation of phases after mass transfer has occurred in the mixing device. Typically, multiple mixer-settler units are used for a multistage process; this is achieved by driving the separated liquid phase to the mixing device of the next stage, and the gaseous phase to the preceding stage as shown in Fig 3. Each stage requires at least one mixing device, and one separator. Usually, for fast and intense phase contact and segregation, side channel pumps with a diffusor or static mixers are used as mixing devices in order to approach equilibrium. At high pressures, quiescent phase separation is not practical and induced vortexes in cyclonic separators are typically used to speed up phase separation.

It is well known that static mixers, also known as motionless mixers, are engineered devices for continuous mixing of fluid materials, that show significant advantages over conventional mixers for both turbulent and laminar flow. A typical design of a static mixer consists of a series of inserts commonly called elements, which can be contained in pipes, columns, or reactors. The purpose of the elements is to redistribute the fluid direction tangentially and radially to the main flow. In both laminar and turbulent flow, static mixers can significantly improve heat and mass transfer due to enhanced turbulence and fast and intense mixing even near walls [172].

There are few studies regarding mixer-settler arrangements. Chuang & Brunner [19] used a pilot scale five-stage mixer-settler device to study the fractionation of minor components (tocochromanols, sterols, β -carotene, and squalene) in crude palm oil. Each stage used a side-channel pump as mixing device and a cyclone for separation. The authors estimated four theoretical stages for the mixer-settler arrangement. After the third stage, tocochromanols were concentrated from 600 to 60,000 ppm, β -carotene from 550 to 105,000 ppm, squalene from 400 to 33,000 ppm, and sterols from 300 to 30,000 ppm. Thus, the enrichment of carotenoids (200-fold) was higher than that of tocochromanols (90-fold), and because β -carotene is the least volatile of the minor components in crude palm oil it has the largest concentration factor.

The results obtained by Chuang & Brunner [19] are consistent with the findings of other authors [21,44] for olive oil deodorizer distillate systems suggesting that the separation of carotenes from fatty acid methyl esters is suitable for the mixer-settler systems. For mixtures that need a larger number of theoretical stages like C18/C20-methyl esters, a reasonable separation of these fractions

can be achieved in a countercurrent packed column and the mixer-settler principle is not suitable. Most of the works reported are based in known phase behaviour of the mixtures and use model systems in experiments.

Schaffner & Trepp [8] modified a conventional countercurrent column, to address the lack of longitudinal mixing and of packing wetting, by installing a mixer-settler device, composed of a pump and a cyclone, between the stripping and enrichment sections of the column. The authors used a synthetic model solution in the range of 51 to 55% by weight of α -tocopherol and α -tocopherol acetate and evaluated the Murphee Efficiency, the separation efficiency of the cyclone, and the performance of the pump as mixing device. Schaffner & Trepp [8] reported Murphee Efficiencies in the range of 81 to 96%. The separator was a homemade cyclone and achieved separation efficiencies from 92 to 99%. The authors also found that the separation efficiency could be improved significantly by entraining a fraction of the gas phase into the liquid phase. Regarding the performance of the mixing device (pump), the mixing performance was evaluated by studying the hydrodynamics and particle size distribution generated by the pump. Schaffner & Trepp [8] correlated the specific surface area with the Reynolds number obtaining a maximum surface area of $3,000 \text{ m}^2 \cdot \text{m}^{-3}$.

As an alternative to using a pump as mixer, a Kenics-type static mixer was evaluated in the separation of the system (caffeine + water + CO_2) by Pietsch & Eggers [84]. The authors used a single stage mixer-settler arrangement and compared the performance of an empty tube and a tube with a static mixer in its interior. Separation efficiencies were found to be higher at low gas-to-liquid phase flow and at high temperatures (353 K), and the Kenics static mixer increased significantly the efficiencies of the empty tube. Moreover, there were no significant differences observed when replacing the static mixer with wire-mesh packing. The separation efficiencies achieved were around 65% for a phase ratio in the range of 10:20 $\text{kg} \cdot \text{kg}^{-1} \text{ CO}_2$ -to- H_2O . Additionally, Pietsch & Eggers [84] made pressure drop calculations across the static mixer concluding that the later can be neglected in supercritical fluid processes.

As the use of the mixer-settler principle avoids some of the disadvantages of conventional columns, Catchpole *et al.* [44] compared the use of a single stage co-current mixer-settler arrangement with a countercurrent packed column for the fractionation of shark liver oil (SLO) and olive oil deodorizer distillate (OODD). The objective of the work was to evaluate squalene recovery from SLO and OODD. Experiments were made in a pilot and laboratory column and using a static mixer. Results indicated that CC-SFF pilot and laboratory columns were more efficient than the static mixer for the fractionation of SLO, but equally efficient for the fractionation of OODD. Catchpole *et al.* [44] suggested using multiple stages to obtain high-purity squalene due to the very low separation factor of squalene in OODD. Additionally, mass transfer coefficients and pressure drop in the static mixer were correlated to Reynolds and Schmidt dimensionless numbers. Another study leading to similar results was developed by Ruivo *et al.* [21]. The comparison between a CC-SFF column and a Kenics static mixer on the selective fractionation of squalene from methyl oleate was carried out with a model mixture representing OODD. Hydrodynamics and mass transfer of the static mixer was studied and the conclusion was that even though the static mixer showed higher extraction efficiency per transfer unit, the packed column presented higher yield of extraction. The later can be explained by the fact that the countercurrent packed column had a higher number of transfer units than the static mixer.

Due to the design characteristics of static mixers, it is common finding them in heat or mass transfer operations related to SFF or SFE. Regarding mass transfer, Catchpole *et al.* [44] as well as Pietsch & Eggers [84] suggested that static mixers could be used for phase equilibrium measurements as done by Fonseca *et al.* [173]. Regarding enhanced heat transfer, Simões *et al.* [174] studied their performance with satisfactory results compared with the traditional tube-in-tube heat exchanger. Additionally, Lisboa *et al.* [175] performed CFD simulations to analyse the use of a Kenics static mixer as heat exchanger in supercritical processes. The authors proved that static mixers had thermal efficiencies three times greater than conventional heat exchangers. Static mixers and nozzles are also of interest in spray extraction with supercritical fluids.

5. Spray processes

High-pressure spray processes are a group of five similar technologies that have in common the atomization of the mixture (liquid + CO₂) or suspension in an empty column or recipient. Fig. 4 shows a simplified schematic flow diagram of the five processes: (i) Rapid Expansion of Supercritical Solutions (RESS); (ii) Particles from Gas-Saturated Solutions (PGSS); (iii) Spray drying of gas loaded liquids; (iv) CC Spray Extraction (SE); and, (v) Two-Phase (TP) SE.

Supercritical fluids have been intensively applied in spray processes in many diverse configurations derived from those listed above, mainly to produce solid particles. Several applications of particle formation methods are available in the literature and are not extensively reviewed here. However, some examples of precipitation of flavonoids from green tea and *Ginkgo biloba* leaf extracts can be found in Meterc *et al.* [176] and Miao *et al.* [177]. Additionally, recent works on precipitation of rosemary antioxidants can be reviewed in Visentín *et al.* [178,179]. Comprehensive reviews on different methods to produce solid particles and liposomes can be found elsewhere [180,181]. Additionally, high-pressure micronization and product formulation using supercritical fluids for food and pharmaceutical applications can be found in the excellent reviews of Weidner [182] and Knez *et al.* [183].

This work focuses in less common spray extraction processes like CC-SE (Fig. 4D) and TP-SE (Fig. 4E). As the other spray processes, CC-SE and TP-SE are suitable for mixtures with high separation factors because only one equilibrium stage can be achieved. Additionally, CC-SE and TP-SE are carried out in empty columns. Therefore, in contrast to CC-SFF in packed columns, there is no external element that provides high specific surface. Compared to the other spray processes, CC-SE and TP-SE offer the advantage that the prevailing process conditions have a positive effect on the spraying of the liquid phase. The solubility of the gas in the liquid, which increases significantly under pressure, leads to a considerable reduction in liquid viscosity allowing it to disperse into droplets more easily. However, particularly the reduction of interfacial tension causes small drops to form, leading to a high specific surface for mass transfer.

Eggers & Wagner [32] used a TP-SE column to deoil soy lecithin proposing this technology as an alternative to batch SC-CO₂ processes, and conventional processes using organics solvents. The device can solve problems such as agglomeration when processing viscous solutions and avoid inefficiencies of batch operations. The technology is based on jet extraction (dispersion of a thin string of lecithin with a CO₂-jet) and the authors remarked the importance of the mixing device, responsible for the highly turbulent two-phase flow. The experiments were carried out in a semi-industrial scale apparatus, producing a powdery and well-deoiled product as the raffinate. Best deoiling results were obtained with a lecithin-to-CO₂ mass flow ratio of 1:40 kg·kg⁻¹, at 7.5 MPa and temperatures >373 K. Nevertheless, the authors pointed out that the problem of collecting continuously a raffinate stream still persisted.

Later, Wagner & Eggers [33] optimized the geometry of the mixing device employing different designs. Fundamental formulations for particle formation in atomizers, the fluid dynamics, and the mass transfer in turbulent two-phase flows were successfully modified to match the problem of SFE. The process was patented by Eggers *et al.* [34].

Regarding the phenomenology of spraying of liquids in dense gases, Czerwonatis & Eggers [184] studied and characterized the disintegration of liquid jets and the size distribution of the drops in jets of water or vegetable oil pressurized with CO₂ or N₂. The authors observed the same shapes of disintegrating jets as those at atmospheric pressure (Rayleigh breakup, sinuous wave break up, and atomization). However, the empirical classification by dimensionless analysis (Ohnesorge number) applied only for atmospheric pressure. The authors modified the Ohnesorge number in order to take into account the density of the gas phase. Results showed that an additional correction for the viscosity of the dense gas was needed in order to describe the regimes of jet disintegration in one unified diagram (modified Ohnesorge *versus* Reynolds number) appropriately. With this approach, the authors were able to determine the range boundaries that describe the disintegration of jets in pressurized gases. The main conclusions of Czerwonatis & Eggers [184] were that, compared to the disintegration of liquid jets at atmospheric pressure, the regime of atomization in pressurized gases

is reached at lower nozzle outlet velocities, and lower liquid flows are necessary to reach atomization. As long as the generated drops maintain a spherical shape these were found to move faster than hard spheres because of the induced inner circulation flow.

A known application of CC-SE is the striping of caffeine from CO₂ with water using a high-pressure washing tower [4]. To the best of the authors' knowledge, there are no other applications of CC-SE and TP-SE.

Particle size, size distribution, and morphology are characteristics that are highly dependent on process parameters that must be optimized based on an exhaustive knowledge of phase equilibria and thermodynamic behavior of the system [183]. Additionally, relevant physicochemical properties such as density, viscosity, and interfacial tension play also a key role in fluid dynamics and mass transfer. Moreover, these properties are of the utmost importance to achieve optimum separation efficiencies for all the technologies described in sections 2 to 4.

6. Phase equilibrium and relevant physicochemical properties

As mentioned above, the requirement of knowledge of phase equilibria is transversal to all technologies because they are essentially separation processes. Separation processes are based on phase equilibrium of adjacent fluid or fluid-solid phases. Consequently, the presence of an interphase is essential for mass transfer of the desired solute. However, the rate of mass transfer is dependent on both, equilibrium and hydrodynamic conditions. Physicochemical properties such as density, viscosity, and Interfacial Tension (IFT) are relevant parameters used to characterize the hydrodynamics of the phases inside any separation equipment.

6.1 Phase equilibrium

Table 5 lists selected experimental phase equilibrium data relevant to the fractionation technologies and areas of application described in this work. The information listed in Table 5 includes the systems studied, experimental temperatures and pressures, and type of data. The information presented is limited to the three main areas of research described in this work: fractionation of edible oil components and derivatives, deterpenation of essential oils, and fractionation of alcoholic beverages. Thereby, only phase equilibrium measurements of ternary or more complex mixtures (real systems) are listed in Table 5. Comprehensive information of binary or other mixtures can be found in specific high-pressure phase equilibria reviews [215–219].

Phase equilibrium of edible oil components and derivatives is an extensive field. However, the respective experimental data and available correlations for more than three components or real mixtures are scarce. Usually, the approach is to define pseudo-binary mixtures based on the predominant components of the real mixture. Experimental data of model mixtures containing valuable vegetable oil components such as methyl oleate, α -tocopherol, and triolein, among other components of edible oil plus CO₂ can be found in Gast *et al.* [18], Bharath *et al.* [185], Fang *et al.* [189,221], and Inomata *et al.* [220]. Partition coefficients and phase equilibrium of fish oil components can be found in Nilsson *et al.* [186], Catchpole *et al.* [187], and Riha & Brunner [188]. Comprehensive information on the separation of constituents of fish oil using supercritical fluids, including experimental solubility and extraction studies can be consulted in Staby & Mollerup [60]. In the case of essential oils, information is available mainly for citrus fruits oil and some effort has been done to study the phase behaviour of complex mixtures, at least ternary systems such as model mixtures of (CO₂ + limonene + linalool) and (CO₂ + limonene + citral) at 323 K and pressures <11 MPa [173,200,201,204]. Binary systems composed of typical citrus terpenes with CO₂ have been reported by Fonseca *et al.* [173].

The phase behaviour, concerning the fractionation of alcoholic beverages, is relatively well studied. Nevertheless, mainly simple and model systems have been considered. The phase equilibrium of the binary system (CO₂ + ethanol) and other higher chain and substituted alcohols is readily accessible in literature [215–219]. Information on more complex systems like the ternary (CO₂ + ethanol + water) are presented by Fornari *et al.* [206]. Recent works focus on the thermodynamic modelling for the removal of ethanol from alcoholic beverages (brandy, wine, and cider) using predictive Equations of State (EoS) [91,108].

In particular, the GC-EoS showed reasonable good results when applied to simulate the countercurrent SC-CO₂ dealcoholization of model systems representing wine, brandy, and cider [91]. Ruiz-Rodríguez et al. [91] used experimental data of the (CO₂ + ethanol) and (CO₂ + water) binary mixtures, and the (CO₂ + ethanol + water) ternary mixture, and readjusted the interaction parameter of H₂O-CH₂OH in order to achieve good modeling results. With the model developed by Ruiz-Rodríguez et al. [91] the authors were able to estimate process conditions to achieve an ethanol content reduction from 10 wt% to values lower than 1 wt%. Additionally, Ruiz-Rodríguez et al. [108] used the model to develop a two-step process for the production of a low-alcohol beverage from wine, but maintaining the aroma and the antioxidant activity similar to that of the original wine.

There is limited information regarding experimental data on equilibrium of odorant compounds of non-alcoholic beverages plus CO₂ at elevated pressures. The main challenge in phase behaviour is to study and model complex multicomponent mixtures in order to come closer to real mixtures, which is difficult from both the experimental and the mathematical standpoint. Phase equilibrium measurements are very time-consuming and complicated tasks, especially for heterogeneous and multicomponent mixtures at elevated pressures. Complex EoS models are needed to describe and predict these systems appropriately. Usually experimental data are obtained for a particular application in a relatively narrow range of pressures and temperatures.

In view of the difficulty in obtaining reliable phase equilibrium data and versatile models applicable to a wide range of mixtures and conditions, a common strategy in modelling CC-SFF and membrane contactors, is to use empirical correlations or a simple or a predictive EoS, such as the Peng-Robinson EoS or the GC-EoS.

Besides phase equilibrium, the hydrodynamics of the phases inside the separation equipment is decisive for obtaining high separation efficiencies by improving mass transfer rates. In order to characterize the hydrodynamics, it is important to study relevant physical properties such as density, viscosity, and IFT.

6.2 Density and viscosity

The density and viscosity of loaded supercritical fluids and expanded liquid phases in the three areas of research described in this work is scarce. Densities and viscosities of coexisting phases of lipid-type mixtures with CO₂ such as Anhydrous Milk Fat (AMF) fatty acids and derivatives [222–225], cocoa butter [226], fish oil fatty acid ethyl esters [227], minor components of edible oils such as α -tocopherol and β -carotene [228,229], and capsaicin [230] are predominant. Experimental data on the volumetric behaviour of essential oil constituents and aqueous systems with CO₂ or other gases were not found in the literature. Few studies reporting experimental data of binary mixtures of alcohols or acetone with CO₂ are reported in the literature [231–234]. Indeed, most studies reporting experimental values of the volumetric behaviour of mixtures with CO₂ or other gases at high pressures relate to hydrocarbons [235–242]. Fluid densities can also be obtained from phase equilibrium modelling by use of an appropriate EoS.

Peter & Jakob [223] reported that the viscosity and density of binary mixtures of pelargonic, oleic, linoleic, and valeric acid with CO₂ and ethane (C₂H₆) were similar. The authors found that the viscosity of the coexisting gas phase increases with increasing pressure whereas the viscosity of the liquid phase decreases. Additionally, the authors showed that the density of the liquid phase of systems containing C₂H₆ decreases with increasing pressure (increasing gas content) while that of systems containing CO₂ increases. Dilatant flow behaviour was observed for the systems (CO₂ + pelargonic acid) and (C₂H₆ + pelargonic acid). The other binary systems showed Newtonian flow behaviour.

A similar work carried out by Kashulines *et al.* [222] and Yener *et al.* [224] evaluated applicability of two viscosity models developed for liquid mixtures (Arrhenius and Grunberg equations) to SC-CO₂ / liquid mixtures. The authors measured the viscosity of several types of lipids saturated with SC-CO₂ such as oleic and linoleic acid, its methyl esters, and the complex mixture of AMF. The authors found that the viscosity of the fatty acid methyl esters saturated with SC-CO₂, decreased 5 to 10 times as pressure increased from 0.1 to 8.0 MPa. Similar behaviour was observed for the fatty

acids and the AMF. At constant pressure, the viscosity of the fatty acids and AMF decreased with increasing temperature, whereas the viscosity of the fatty acid methyl esters increased with increasing temperature.

Results of the modelling reported by Kashulines *et al.* [222] and Yener *et al.* [224] showed that if only pure component viscosities and mixture compositions are used, errors using the Arrhenius equation were 52% for the fatty acids, 10% for the fatty acid methyl esters, and 111% for the AMF. These large errors were partially attributed to the large difference in viscosity between the mixture components. By the introduction of an experimentally determined adjustable parameter (Grunberg equation) the model errors were reduced to 8% for the fatty acids, 10% for the fatty acid methyl esters, and 5% for AMF. The authors also showed that all the mixtures had Newtonian behaviour. Tuan *et al.* [225] measured the viscosity of binary (CO_2 + methyl oleate) and (CO_2 + AMF) systems and evaluated the applicability of a modified Ely and Hanely's corresponding state model (addition of an adjustable parameter in energy shape term) in order to improve the prediction capability of the purely correlative Grunberg and Nissan models. With this approach the authors described well the viscosity of both the fluid and liquid phases with an average absolute deviation of 3 to 6%. Staby & Mollerup [227] reported the density of the liquid phase along with experimental solubility of fish oil fatty acid ethyl esters in SC-CO_2 . They showed that the densities of the liquid phases were almost constant when the CO_2 content of the liquid phase (x_{CO_2}) was $< 80\%$ and that the highest densities occurred at the lowest temperature. The authors also observed that at $x_{\text{CO}_2} > 80\%$ the density suddenly decreased as the supercritical region was approached, and that at x_{CO_2} in the range of 90 to 95% the density curves cross over.

For minor components of edible oil, Pecar & Doleck [228,229] reported experimental density data of β -carotene and α -tocopherol in SC-CO_2 at various concentrations within wide intervals of temperature (308 to 333 K) and pressure (10 to 40 MPa). The data obtained for α -tocopherol was successfully correlated with the Peng-Robinson EoS and the Panagiotopoulos-Reid mixing rule.

6.3 Interfacial tension and contact angle

Besides the important effect of density and viscosity of the coexisting phases in the operation of separation equipment, their sizing further needs to account for apparent interfacial effects. These are IFT and contact angles on the technical surfaces involved in the process. IFT is a key property, especially when drops are formed. In spray columns (and other processes which make use of the large exchange area of small liquid drops) knowledge of the IFT of the employed liquids is crucial. This property defines the area-to-volume ratio of a liquid embedded in another fluid and thus, the drop size distribution [243].

The idea of employing structured and random packing columns is to enlarge the exchange area and in this way to increase the efficiency of the process. In packed columns, the property that controls the extent of the exchange area is called wettability, which is characterized by the so-called three-phase contact angle and influenced by the IFT. An appropriate wettability enhances mass transfer rates and, in consequence, improves the separation efficiency of the process. Other applications where the IFT is an important parameter are nucleation and bubble formation in polymer melts [244,245], reservoir systems and CO_2 storage [246–248], ionic liquids [249], and the use of modern EoS based on the Statistical Association Fluid Theory (SAFT) for modelling and prediction of IFT and other interfacial properties [250–253]. However, the work of Niño-Amézquita *et al.* [252] and Hu *et al.* [253] contribute to the understanding of the interfacial phenomena of aqueous systems. The authors used the van der Waals density gradient theory in combination with the Perturbed Chain Polar (PCP-SAFT) and the First-order Mean Spherical Approximation (FMSA-SAFT) EoS to overcome the challenge correctly describe water, due to strong hydrogen bonding. Aqueous systems are involved in the fractionation of alcoholic beverages and removal of acetone from water. Table 6 lists selected IFT datasets that provide relevant information regarding the main application areas in this work (edible oil components and derivatives, essential oils and alcoholic beverages). It is well known that the IFT of a liquid in dense CO_2 declines with increasing pressure. In general, as pressure increases the surrounding CO_2 dissolves into the liquid decreasing the IFT of the liquid.

The behaviour of the IFT of several edible oils with temperature and pressure are relatively well known specially for CC-SFF of fish oil constituents [262], vegetable oil constituents [254–256,258], vegetable oils such as walnut, wheat, olive, palm, and un- and refined corn oils [257,259–261], and lemon essential oil [257], and coffee oil [257].

In order to understand the transport phenomena that occurs at the interface of a fluid/liquid separation process, Jaeger *et al.* [257] reported and compared the IFT data of different oils in contact with CO₂ (walnut, wheat, lemon, and coffee) and investigated the mass transport into pendant oil drops simultaneously. The authors observed the decreasing tendency of the IFT with increasing pressure due to increased adsorption of the compressed fluid at the interface.

Additionally, the authors studied IFT at various conditions of pressure and temperature and as a function of time showing that in the case of considerable mutual solubility, IFT further decreases with time as mass transfer into the bulk phase proceeds. Similarly, Simões *et al.* [259] used Portuguese extra virgin olive oil, enriched with oleic acid to a known amount of free fatty acids (7.6% w/w), to compare the IFT data with those of other edible oils. They found that triglycerides (walnut and wheat) with low content of volatiles behaved similarly to the extra virgin olive oil. The behaviour of coffee and lemon oil was different because of their strong IFT decrease at moderate pressures resulting in a vanishing interfacial tension at the point of complete miscibility [257].

A similar work was carried out by Dittmar *et al.* [260] who modelled and compared for the first time the IFT and the mixture density of triglycerides in contact with CO₂ and N₂. The authors found that IFT of the triglyceride mixtures (corn, germ, palm, wheat, and olive oils) were similar.

Additionally, the IFT in contact with CO₂ and N₂ decreased with increasing pressure. The modelling of the IFT of triglycerides in contact with CO₂ or N₂ using the density gradient theory and an EoS was successful. Nevertheless, the authors suggested that it is essential to choose the appropriate EoS for modelling the IFT in systems of CO₂ at high pressure. Additionally, for complex systems, *e.g.*, for triglyceride mixtures, it is indispensable to check the EoS by means of experimental equilibrium data (*e.g.*, density, volume, or mole fraction). Dittmar *et al.* [261] studied the IFT behaviour of refined (Mazola®) and unrefined corn germ oil in contact with CO₂ at lower temperatures (263 to 295 K). The authors found that the unrefined corn germ oil showed lower IFT, possibly caused by the presence of minor components lost in the refining process, and the addition of vitamin E to the refined oil.

Regarding aqueous systems, available data on IFT and contact angles are limited to pure water in dense CO₂ [266,267,269,271,272] and (ethanol + water) solutions in dense CO₂ [243,263,270]. Enders & Kahl [273] measured and modelled IFT for (ethanol + water) and (1-butanol + water) solutions at atmospheric pressure. Other sources of IFT data of pure water in contact with different gases, other than CO₂, can be consulted in Dittmar *et al.* [268]. Information regarding IFT data for ethanol in CO₂ and N₂, are also available in Oei *et al.* [264] and Dittmar *et al.* [268]. No data for other aqueous mixtures in contact with CO₂ at elevated pressures were found in the literature. Sutjiadi-Sia *et al.* [243] studied the interfacial phenomena of aqueous systems in dense CO₂. The authors used the pendant drop method to measure IFT, and the sessile drop method to estimate contact angles of pure water and the system (water + ethanol) surrounded by CO₂ at 313 K and pressures ≤ 27 MPa. Wetting was studied on three different materials commonly found in industry: PTFE, steel, and glass. Sutjiadi-Sia *et al.* [243] observed the same decreasing tendency of the IFT as pressure increased as in the oily systems. The authors showed that the change in the IFT with increasing pressure is closely related to the mass transfer between the bulk phases, *i.e.*, in systems composed of water, ethanol, and CO₂ the IFT of a drop changes until ternary equilibrium is reached. Sutjiadi-Sia *et al.* [243] also reported drop phenomena such as kicking of the drop, upward motion of the continuous phase around the drop, rising bubbles in the drop phase, and intense stirring in the drop during mass transfer. Additionally, the authors demonstrated that a precise estimation of the IFT requires the values of the instantaneous, mean densities of both phases which sometimes are unavailable. Regarding the contact angles, Sutjiadi-Sia *et al.* [243] observed increasing values at higher pressures, and the water mixtures showed better wettability (lower contact angles) on glass than on the other materials.

Based on these observations, Sutjiadi-Sia *et al.* [243] concluded that when aqueous drops are desired in a spray column, it is advantageous to work with higher CO₂ pressures because the wetting becomes poorer (formation of small drops due to lower IFT). However, for such systems less liquid hold up is expected. The authors also concluded that when a wide covering film is expected for an optimal mass transfer between the phases, high CO₂ pressure may be disadvantageous in spite of the decreasing IFT, which should rather promote wetting. As a consequence, interfacial phenomena at high pressure need to be precisely characterized and accounted for in order to decide whether a packed or a spray column will achieve better separation results.

A comparison of available data on IFT of water in CO₂ at high pressures from different sources is shown in Figure 5. As it can be seen there are significant discrepancies between the data, especially at higher pressures. Moreover, as shown by Sutjiadi-Sia *et al.* [243], the effect of the density of the phases used in the calculation of IFT is significant. From the discussion above it becomes clear that, although IFT is an essential requirement for several processes, so far there is an important lack of relevant data for aqueous systems at elevated pressures.

As described at the beginning of the section, IFT and contact angles are key properties that define the separation efficiency of the separation process. Poor or imprecise knowledge of these properties may lead to errors in the design of high-pressure extraction columns, and to obtain separation efficiencies far from the optimum.

The IFT of the liquid phase plays an important role in the break-through pressure in membrane contactors. However, experimental studies of IFT and wetting behaviour in membrane contactors are non-existent. The wetting of the membrane in membrane contactors is a non-desirable event because CO₂ absorption can cause long-term operational concerns and mass transfer efficiency may decrease. A detailed discussion of the wetting phenomenon, as well as different methods to avoid membrane wetting, along with their advantages and disadvantages can be found in Mosadegh-Sedghi *et al.* [274].

7. Concluding remarks

This manuscript describes in detail liquid fractionation technologies with SC-CO₂. Main applications are fractionation of lipids, detarpenation of essential oils, and fractionation of alcoholic beverages. Isolated applications also found in literature include fractionation of polymer mixtures and removal of organic solvents from water. The furthest explored technology is CC-SFF. Different types of operation were identified and described. Operating the column with an external reflux at the top (reflux mode) adds an extra equilibrium stage compared with the other modes of operation (stripping and semi-batch). The review overviews comprehensively countercurrent packed columns in leading public research groups and some private institutions. Several random and structured packing materials have been tested. Internal column diameter ranges from 9 mm to 12.6 cm and the height ranges from 40 cm to 13.6 m, however, a standard height seems to be 3 m. Less common technologies like membrane contactors are limited to aqueous solutions because they achieve a better immobile interphase. Care must be taken to not exceed ΔP_{crit} specially when operating a HFMC in the countercurrent mode. Fractionation of non-aqueous systems would probably lead to a mobile interphase in the pores causing the liquid phase to break into the CO₂ as drops or bubbles. In a single stage mixer-settler arrangement, as well as in a single HFMC module, only one equilibrium stage can be achieved. Therefore, these technologies are limited to mixtures that require a relatively small number of stages for a reasonable separation.

Columns without packing material are used in countercurrent and two-phase spray extractions. The absence of packing material (high specific surface for mass transfer) is overcome by generating very fine droplets by atomization. Therefore, the study and characterization of disintegration of liquid jets and atomization regimes at high pressures, where IFT plays a key role, are of great importance. Countercurrent and two-phase spray extractions are limited to mixtures with high separation factors (relatively small number of stages for a reasonable separation). Formation of particles using SC-CO₂ in spray processes is a vast field of research and was not covered in this work. However, relevant references in this topic were provided to the interested reader.

Due to their design characteristics, static mixers are commonly used as mixing devices in mixer-settler arrangements as well as spray processes. Additionally, literature informs some successful attempts to use static mixers for equilibrium measurements and fractionation purposes. It is surprising that there are few comparisons between different technologies for a common application in literature.

This review provides a general overview of fundamental equilibrium data and physicochemical properties of mixtures relevant to all the described applications and technologies. Densities and viscosities are commonly estimated from equilibrium data and are relevant to understand the hydrodynamics of the phases inside the separation equipment. IFT and contact angles of diverse aqueous mixtures surrounded by CO₂ at high pressures need to be studied in detail to improve the knowledge and application of CC-SFF for complex aqueous systems. Knowledge of IFT and contact angles of edible oil mixtures in contact with dense CO₂ is well studied. No wetting behavior studies were found for membrane contactors.

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Fig. 1 Modes of operation of countercurrent packed columns

Fig. 2 Immobilized phase interface in a membrane contactor.

Fig. 3 Schematic flow diagram of a mixer-settler arrangement of (k+1) stages.

Fig. 4 Simplified schematic flow diagram of high-pressure spray processes.

Fig. 5 Interfacial tension (IFT) at various pressures (*P*) for pure Water in contact with CO₂. (*), [271] at 314 K; (), [269] at 308 K; (), [263] at 311 K; (↘), [265] at 313 K; (↘), [272] at 313 K; (↘), [266] at 318 K; (⊗), [267] at 318 (+), [243] at 313 K.

Table 1 Edible oil components and derivatives fractionation applications, associated technology, equipment, or type of experimental set up, temperature and pressure conditions, and main objective of the work of selected references.

Technology / Equipment / Experimental set up	Extraction Temperature / K	Extraction Pressure / MPa	Objective	Reference
Countercurrent packed column	343	13.0–25.0	Enrich tocopherols from oil deodorizer distillates. Favourable conditions for separation. Phase equilibrium measurement and separation behaviour.	[7]
Column-mixer-settler: pump and cyclone between stripping and enrichment sections.	323–343	17.0–20.0	Fractionate a (α-tocopherol + α-tocopherol acetate) mixture. Improve the longitudinal mixing of the column and wetting of the packing.	[8]
Countercurrent packed column	323–353	13.0–25.0	Refine vegetables oils. Describe and predict fluid dynamics and mass transfer. Obtain a high concentration of tocopherols and sterols in the extract.	[9]
Countercurrent packed column	323; 333	10.7–27.4	Fractionate crude and refined palm oil by CC-SFF with SC-CO ₂ . Effect of pressure, temperature, and co-solvent on free fatty acids and carotenes content of extract and raffinate.	[10]
Countercurrent packed column	323–353	13.0–25.0	Fractionate glyceride mixtures. Investigate the effects of process parameters in the separation efficiencies and yields of mono, di and triacylglycerols.	[11]

Countercurrent packed column	353; 359	26.0–31.0	Deacidify olive oil. Study the technical feasibility for deacidification of olive oil. [12]
Countercurrent packed column	313–363	13.6–25.0	Deacidify crude rice bran oil. Study the effect of isothermal and temperature gradient operation of the column on the composition of rice bran oil. [13]
Countercurrent packed column	318–353	13.8–27.5	Phytosterol ester fortification in rice bran oil. Isothermal CC-SFF of rice bran oil for enrichment of oryzanol and phytosterol fatty acid esters. [14]
Semi-batch screening unit	343; 353; 363	20.0; 20.5; 30.0	Deacidify rice bran oil. Study of pressure and CO ₂ consumption on free fatty acids removal, and triglycerides retention. [15]
Countercurrent packed column	313	11.5	Fractionate edible oil mixtures. Separate squalene and methyl oleate from deodorizer distillates. Hydrodynamics and mass transfer behaviour. [16]
Countercurrent packed column	313	20	Separate sterols and tocopherols from olive oil. Evaluate the efficiency of different random packing materials on the selectivity of sterols and tocopherols. [17]
Countercurrent packed column	308–323	7.5–20.0	Fractionate a raw extract of olive leaves in hexane. Separate waxes, hydrocarbons, squalene, β -carotene, triglycerides, α -tocopherol, β -sitosterol, and alcohols. Process parameter influence on selectivity [1]
Countercurrent packed column	340; 370	20.0–30.0	Purify tocochromanols from edible oil. Enrich of vitamin E from crude palm oil and a soy oil deodorizer distillate. Phase equilibrium measurements theoretical description of the separation. [18]
Five stage mixer-settler (pump-cyclone) device	333	14.0	Enrich minor constituents from crude palm oil. Enrich carotenoids and tocochromanols, in a pilot-scale mixer-settler apparatus. [19]
Countercurrent packed column	338	15.0–23.0	Fractionate sunflower oil deodorizer distillates. Influence of the feed composition in the extraction process. Analysis of the tocopherol and phytosterol yields and enrichment factors obtained. [20]
Mixer-settler (static mixer-gravimetric phase separator).	313–343	11.0–24.0	Selective fractionation of squalene from methyl oleate. Hydrodynamics and mass transfer study of a Kenics-type static mixer. Pressure drop and overall mass transfer coefficient calculations. [21]
Countercurrent packed column	343	15.0–23.0	Recover squalene from olive oil deodorizer distillates. Simulate the separation process and find optimal process conditions with the GC EoS. [22]
Countercurrent packed column	318–328	20.0–28.0	Separate phytosterol esters from soybean oil deodorizer distillates. Study the CC-SFF of an enzymatically modified soybean oil deodorizer distillate for concentration of phytosterol esters. [23]

Countercurrent packed column	298	8.3	Purify 1,2-diacylglycerols from vegetable oils. Compare molecular distillation and CC-SFF in terms of the removal of the fatty acid propyl ester by-products while reducing the migration of the 1,2-diacylglycerols to 1,3-diacylglycerols.	[24]
Countercurrent packed column	296–298	11.0	Purify a model crude reaction mixture from the enzymatic synthesis of SoyScreen™. Use of liquid CO ₂ for the fractionation of a model mixture of ethylferrulate, fatty acid ethyl esters and, soybean oil triacylglycerides. Study the effect of column length and S/F ratio.	[25]
Countercurrent packed column	313	18.0; 234; 250	Recover squalene, tocopherols and phytosterols from oil deodorizer distillates. Use of GC EoS to simulate the separation process, phase equilibrium, and find optimal process conditions.	[26]
Membrane module apparatus (small flat sheet membrane test cell)	313	18.0	Fractionate squalene from oleic acid. Compare membrane performance to separate squalene from a model mixture. Feasibility of coupling membrane separation with SC-CO ₂ extraction.	[27]
Countercurrent packed column	313	18.0; 234; 250	Deacify olive oil. Use of GC EoS to simulate the separation process, representing the oil as a simple pseudo-binary oleic acid + triolein mixture.	[28]
Countercurrent packed column	298	8.3	Fractionate of partially deacylated sunflower oil. Remove by-product fatty acid propyl esters of partial deacylated sunflower oil using liquid CO ₂ . Study the effect of S/F ratio to optimize separation.	[29]
Semi-batch screening unit / Countercurrent packed column	298; 313; 353	14.7; 19.6; 24.5	Fractionate triglycerides from the unwanted polar fraction present in used frying oil using liquid and supercritical ethane and CO ₂ .	[30]
Countercurrent packed column	298	8.62	Purify 2-monoacylglycerols. Use of liquid CO ₂ to remove fatty acid ethyl esters and diacylglycerols from 2-monoacylglycerols from the enzymatic alcoholysis of triolein with ethanol.	[31]
Two phase flow spray column	373	75	Present new device of deoiling of soy lecithin based on jet extraction with SC-CO ₂ . Viscosity and surface tension determination.	[32]
Two phase flow spray column	373; 393; 413	48.0; 60.0; 70.0	Deoil lecithin and extraction of liposomes. Mathematical modelling and optimization of mixing and extraction zones. Measurement of viscosity and surface tension.	[33,34]
Countercurrent packed column	298	9.3	Remove hexane from soybean oil. Investigate the use of liquid CO ₂ in place of SC-CO ₂ to remove hexane from soybean oil.	[35]
Countercurrent	313	24.1	Fractionate anhydrous milk fat. Study the mass	[36]

nt packed column			transfer rates for low, medium, and high -melting triglycerides of anhydrous milk fat.	
Countercurrent packed column	313–348	3.4–24.1	Fractionate anhydrous milk fat. Determine physicochemical properties of anhydrous milk fat. Observe the effects of operating conditions on fatty acids, triglycerides and cholesterol distribution in anhydrous milk fat and its fractions.	[37]
Countercurrent packed column	313–348	3.4–24.1	Fractionate anhydrous milk fat. Pilot-scale fractionation of anhydrous milk fat. Studies for scale-up of larger plants. Compare physicochemical properties obtained by different methods.	[38]
Countercurrent packed column	313	24.1	Fractionate anhydrous milk fat. Develop a mathematical model for continuous extraction of multicomponent mixture anhydrous milk fat.	[39]
Countercurrent packed column	323–333	2.4–24.1	Fractionate anhydrous milk fat. Study the conjugated linoleic acid, and carotenes content of various fractions from milk fat, obtained in cascade separators.	[40]
Countercurrent packed column	321; 333	8.9–18.6	Fractionate fatty acid ethyl esters from butter oil. Obtain highly concentrated fractions of short- and long- chain fatty acids for use as starting material for the production of highly valuable functional lipids for nutritional applications.	[41]
Countercurrent packed column	333–353	14.5–19.5	Fractionate fatty acid ethyl esters from fish oil. Study the influence of the size of the column on separation efficiency and yield.	[42]
Countercurrent packed column	323–353	13.0–25.0	Fractionate acid ethyl esters from fish oil. Separate between low-molecular-weight components (C14 to C18) and (C20 and C22).	[43]
Static mixer and packed column.	333	25.0	Squalene recovery from shark liver oil and olive oil deodorizer distillate. Compare the performance of a static mixer and countercurrent packed column for the fractionation of shark liver oil.	[44,45]
Countercurrent packed column	333–353	6.0	Fractionate deep-sea shark liver oil. Study the effects of temperature, S/F, and squalene separation from oleic acid in model mixtures and two shark liver oils using R134a as solvent.	[46]
Countercurrent packed column	313; 323; 338	14.0–18.0	Fractionate non esterified alkoxyglycerols obtained from shark liver oil	[47]
Countercurrent packed column	363; 353–368	2.9	Determine the best processing conditions to fractionate used lubricant oil for the formulation of new lubricants by means of SFF with supercritical ethane.	[48]

Table 2 Essential oil fractionation and other deterpenation applications, associated technology, equipment, or type of experimental set up, temperature and pressure conditions, and main objective of the work of selected references.

Technology / Equipment / Experimental set up	Extraction Temperature / K	Extraction Pressure / MPa	Objective	Reference
Countercurrent packed column	313; 318	7.7–9.0	Separate a mixture of (δ -limonene and 1,8-cineole) SFF. Mass transfer study and feasibility of application to the purification of eucalyptus oil.	[62]
Semi-continuous packed column	313; 333; 313–333	8.8–11.8	Citrus oil deterpenation. Study the effect of an internal reflux induced by a temperature gradient on the separation behaviour of a model mixture of linalool, limonene and citral. Compare with isothermal operation.	[63]
Semi-continuous packed column	313; 313–343	8.8	Citrus oil deterpenation. Study the selectivity of terpenes vs. oxygenated terpenes (limonene vs. linalool) at isothermal and temperature gradient conditions.	[64]
Semi-continuous packed column	333	8.8; 9.8	Orange oil deterpenation. Observe the effects of pressure and (S/F) ratio on the separation selectivity for a model mixture (limonene + linalool) and raw orange oil.	[65]
Semi-continuous packed column	313; 313–333	8.8	Citrus oil deterpenation. Study of limiting operation conditions. Study the effect of reflux on separation selectivity. Total reflux and with internal and external reflux.	[66]
Semi-continuous packed column	313–353	7.8–10.8	Bergamot oil deterpenation. Phase equilibrium measurement and fractionation by semi-batch operation. Internal reflux fractionation by temperature gradient. Study the effect of temperature profile, S/F ratio on composition of extracts.	[67]
Semi-continuous packed column	313; 333; 353; 313–373	8.8–34.3	Bergamot oil deterpenation. Study the effects of feed composition, feed inlet position, reflux ratio, and stage number on extraction ratio of limonene, separation, selectivity, and recovery of linalyl acetate. Isothermal and temperature gradient operation.	[68]
Countercurrent packed column	323–343	8.0–13.0	Orange peel oil deterpenation. Phase equilibrium measurements and limit of separation and flooding-point calculations.	[69]
Screening unit	313–326	8.1–9.5	Citrus essential oil deterpenation. Simulate extraction process with PR-EoS for a model mixture of limonene and citral. Compare experiments with simulation results, and assess the model prediction capability.	[70]
Semi-continuous packed column	313; 313–343	8.8	Lemon oil deterpenation. Compare with countercurrent continuous contacting.	[71]
Countercurrent packed column	313; 323; 333	7.5; 9; 11	Fractionate Lavandin essential oil. Experiment and modelling of the separation of linalool and linalyl acetate. Study of the influence of process	[72]

			parameters and optimum conditions for the process.	
Semi-continuous packed column	313–373	8.8–20.0	Yuzu oil deterpenation. Study the effect of temperature, and pressure on the extraction yield, extract composition, and recovery factor of aroma components of Yuzu cold pressed oil.	[73]
Semi-batch screening unit	313–323	6.0–12.0	Fractionation of essential oils with biocidal activity. Equilibrium distribution and selectivity of monoterpenes, oxygenated terpenes and sesquiterpenes of <i>Salvia officinalis</i> , <i>Mentha piperita</i> and <i>Tagetes minuta</i> oil.	[74]

Table 3 fractionation of alcoholic beverages and other aqueous mixtures applications, associated technology, equipment, or type of experimental set up, temperature and pressure conditions, and main objective of the work of selected references.

Technology / Equipment / Experimental set up	Extraction n	Extraction Temperature / K	Extraction Pressure / MPa	Objective	Reference
Semi-continuous column	298		6.3	Fractionate volatile compounds from fruit essences. Extraction experiments to obtain highly concentrated fruit aroma using liquid CO ₂ .	[81–83]
Mixer-settler (static mixer-gravimetric phase separator).	333–353		28	Regenerate caffeine-loaded CO ₂ . Investigate the performance of the mixer–settler principle in application with a Kenics-type static mixer	[84]
Countercurrent packed column	313		16.0	Extract antioxidants from orange juice. Study the effect of the solvent-to-feed ratio (S/F) on the content of antioxidant compounds.	[85]
Countercurrent packed column	313		16.0	Extract antioxidants from orange juice. Analysis of antioxidants from orange juice obtained by CC-SFF with micellar electro-kinetic chromatography (MEKC) technique.	[86]
Countercurrent packed column	303–353		7.0–30.0	Fractionate alcoholic beverages. Optimization of process variables (extraction temperature and pressure, and liquid feed flow) for isolation of brandy aroma.	[87]
Countercurrent packed column	313		20.0	Fractionate of alcoholic beverages. Optimize the separation conditions for fractionation of spirits.	[88]
Countercurrent packed column	313		10.0; 20.0; 30.0	Fractionate alcoholic beverages. Selective extract aromatic components of brandy flavour. Study the effect of flow, temperature and extraction pressure on flavour quality.	[89]
Countercurrent packed column	313		10.9–18.0	Fractionate alcoholic beverages. Recover wine must aroma. Study the influence of process parameters (S/F and density) on the aromatic fraction of <i>Muscatel</i> wine, and <i>Muscatel</i> must wine.	[90]
Countercurrent	308		9.5;	Fractionate alcoholic beverages. Use of GC-EoS	[91]

nt packed column	13.0; 18.0	model to simulate the dealcoholization of red and white wines.	
Single hollow fiber membrane contactor	298 6.9; 6.9; 3.45	Extraction of fermentation products (acetone and ethanol). Study of the feasibility of extracting aqueous ethanol and acetone with dense CO ₂ .	[92]
Hollow fiber contactor	298 6.9; 3.45	Extract organic solvents and sulphur aroma compounds from aqueous solutions. Modelling extraction, in series mass transfer resistance theory.	[93]
Three module hollow fiber membrane contactor	294–298 9.0–27.6	Extract isopropanol or acetone from water. Experimental results and mathematical modelling, validation with data of extraction of caffeine, ethanol, dimethyl formamide.	[94]
Three module hollow fiber membrane contactor	294–298 9.0–27.6	Extract isopropanol or acetone from water. Experimental results and mathematical model development. Validate experimental results with dimensionless numbers.	[95]
Two module hollow fiber membrane contactor	305 13.5	Extract of acetone from water. Study mass transfer as function of membrane geometry and operating parameters.	[96]
Single and three module hollow fiber contactor	296–298 3.45; 9.6; 20.7;	Extract acetone or caffeine from water. Simulate membrane characteristics and operating parameters.	[97]

Table 4 Research lines of leading research groups and countercurrent packed columns dimensions and characteristics. Height (H), Inside diameter (ID), Operating pressures (P), Type of packing, Equipment used to compress CO₂, and Field of application for selected references.

Research group	Column dimensions and characteristics			Column packing	Equipment used to compress CO ₂	Mode of operation
	H / m	ID / mm	P / MPa			
TUHH	3.0	17.5	6.5–50.0	Sulzer Mellapak 500.X® (ε: 0.975 <i>a</i> : 500 m ⁻¹); Sulzer EX; Sulzer EX-Laboratory; Sulzer BX (ε: 0.97 <i>a</i> : 492 m ⁻¹); 6 mm random wire mesh (ε: 0.9 <i>a</i> : 820 m ⁻¹); 3 x 3 mm SS spirals - Teflon rings for liquid distribution; Shott Durapak (ε: 0.7 <i>a</i> : 280 m ⁻¹).	Pump / Compressor.	Continuous reflux mode / middle liquid feed / partial extract reflux.
	4.0 [†]	17.5				
		25.0 [†]				
	6.0	17.5				
	7.0	17.5				
	7.5	40.0				
CIAL-UAM-CSIC	1.5	30.0	15.0–30.0	3 mm Raschig rings (ε: 0.46), Fenske rings (ε: 0.76), Dixon rings (ε: 0.83), Glass beads (ε: 0.39), 2 mm and 5 mm (i.d) 316 SS balls.	Pump.	Continuous stripping mode / no reflux / upper, middle and bottom liquid feed
	1.0 [†]	10.0				
	3.0 [†]	17.6				
	2.8 [†]	29.7				
	4.0 [†]	40.0				
REQUIMTE	1.0	24.0	7.7–18.0	24 mm Sulzer EX (ε: 0.86 <i>a</i> : 1,710 m ⁻¹); 24 mm Sulzer CY	High-pressure membrane pump	Continuous stripping mode / partial extract
	2.5 [†]	24.0				

	4.0 [†]	40.0		1,710 m ⁻¹); 24 mm Sulzer CY (ϵ : 0.90 a : 890 m ⁻¹).	/ Gas compressor.	reflux with upper liquid feed.
Northern USDA	0.6 1.2 1.7 1.8 2.5	17.5 17.5 14.3 44.5 102 (O.D) 14.3	8.3–35.0	4 mm Pro-Pak protruded metal (ϵ : 0.94).	Gas booster pump.	Continuous stripp mode / no reflux / upper, middle, and bottom liquid feed temperature gradi (internal reflux).
Kumamoto Univ.	1.0 2.4	9.0 20.0	7.8–11.8	2 mm and 3 mm Dixon packing	High-pressure pump	Semi-batch mode linear temperature gradient (internal reflux).
Cornell Univ.	0.6 1.8	17.5 49.0	2.4–24.1	SS 304 Goodloe knitted mesh (ϵ : 0.95 a : 1,920 m ⁻¹).	High-pressure positive- displacement pump.	Continuous Stripp mode.
Industrial Research Limited	1.2 1.9 2.5	24.3 20.3 56.0	6.0–30.0	SS wire wool; 6 mm and 8.5 mm glass Raschig rings; 4 mm glass Fenske helices.	High-pressure compressor / Triplex diaphragm pump.	Continuous stripp mode and reflux m / upper and middl liquid feed.
University of Stellenbosch	4.3	29.0	8.7–30.0	Sulzer DX.	Positive displacement pump / compressor.	Continuous stripp and reflux mode / upper, middle, and bottom liquid feed
Univ. degli Studi di Roma “La Sapienza”	1.9	20.0	84.0–10.5	Sulzer EX.	Volumetric compressor.	Semi-batch mode
Univ. of Technology Graz	2.0	35.4	7.5–18.0	10x10x0.3 mm ³ Pall® Raschig rings; Sulzer DX.	High-pressure diaphragm pump.	Continuous stripp and Semi-batch m no reflux.
Lund Univ.	1.1	25.0	15.0; 20.0	SS Sulzer; 6x6 mm Raschig	High-pressure	Continuous stripp

	1.0	14.0	15	rings		diaphragm pump.	mode / no reflux.
NOAA's National Marine Fisheries Service	1.8	17.5	11.0–17.29	304 SS ball bearings and 4 mm 316 SS Propak.		Diaphragm compressor	Semi-batch mode
Univ. of Texas at Austin	1.2 2.2	25.4 98.8	8.2–15.2	Sieve trays; 12.7 mm ceramic Raschig rings; 6.4 mm ceramic Raschig rings ($a: 722 \text{ m}^{-1}$); Intalox saddles N° 15.		Positive displacement pump.	Continuous stripping mode.
Univ. di Salerno	1.9	17.5	70.0	5 mm Steel berl ($\epsilon: 0.9 a: 1600 \text{ m}^{-1}$); 5 mm Raschig rings ($\epsilon: 0.66 a: 1050 \text{ m}^{-1}$).		High-pressure diaphragm pump.	Continuous reflux mode / upper, middle and bottom liquid feed.
Bogazici Univ.	1.5	9.0	7.0; 8.5	1.5 mm Dixon wire mesh ($\epsilon: 0.8$); 5 mm glass beads.		Diaphragm pump.	Semi-batch mode
Clemson Univ.	2.0	18.0	3.5–8.4	4 mm Pro-Pak protruded metal.		Two-piston reciprocating pump.	Continuous stripping and Semi-batch mode
Delft Univ. of Technology	1.0	35.0	10.0–20.0	Sulzer BX Gauze Packing ($\epsilon: 0.90 a: 890 \text{ m}^{-1}$); 5-mm metal Raschig ring.		Membrane pump.	reflux finger. Continuous stripping mode / no reflux.
Univ. de Castilla-La Mancha	1.7	20.0	2.9–24.5	3 mm Pall® Raschig rings ($\epsilon: 0.46 a: 1185 \text{ m}^{-1}$); 3 mm irregular steel packing ($\epsilon: 0.85 a: 195 \text{ m}^{-1}$).		Membrane pump.	Continuous stripping mode / Semi-batch mode.
Univ. of Birmingham	1.5	11.5	10.0–20.0	Glass beads		Piston pump	Continuous stripping mode isothermal with temperature gradient (internal reflux).
Beijing Univ. of Chemical Technology	3.3	25.0	20	3.2 mm θ ring ($\epsilon: 0.93 a: 2400 \text{ m}^{-1}$); 2 mm triangle ($\epsilon: 0.84 a: 2700 \text{ m}^{-1}$)		Diaphragm compressor.	Continuous stripping mode / Middle liquid feed with temperature gradient (internal reflux).
Ehime Univ.	1.0	12.7 (O.D)	15.0–30.0	3.0 mm Dixon.		High-pressure pump.	Continuous stripping mode
Institut National	0.4	23.0	8.0–9.5	5 mm glass beads		High-pressure pump.	Semi-batch mode

Polytechnique de Lorraine							
Isfahan Univ. of Technology	0.5	9.0 10.0 22.0 ^(*)	10.0–14.0	Glass beads.		Reciprocating pump.	Bottom liquid feed with temperature gradient (internal reflux).
Korea Inst Sci & Technol	1.5	31.7	9.1–112.2	31.5x100 mm knit mesh (ϵ : 0.95 a : 1400 m ⁻¹).		High-pressure metering pump.	Continuous stripping mode / no reflux.
National Chung Hsing Univ.	0.8	22.0	20.0–30.0	θ type SS.		Syringe pump.	Semi-batch mode
Univ. of Udine	4.5	30.0	10	Sulzer EX.		High-pressure pump.	Continuous stripping mode.
Univ. of Alberta	3.1	17.5	20.0; 25.0	4.1 mm SS Propak.		Syringe pump.	Bottom liquid feed with temperature gradient (internal reflux).
Fachhochschule Lübeck	2.4 [†]	40.0	50	10 mm VFF Interpack®		Membrane pump.	Continuous stripping mode / no reflux.
FAU-Erlangen-Nuremberg	7.5 [†] 8.0	67.0 33.0	16.0	Sulzer CY, BX.		Compressor.	Continuous reflux mode / middle liquid feed / partial extra reflux.
VTT Chem. Technol.	2.0	35.0	40.0	Oldshue-Rushton column: flat-blade paddle-type impeller.		Compressor.	Continuous stripping mode / no reflux.
LAEPSI, INSA	2.0 1.0	100.0 62.0	1.0–1.3	6.4 mm Beryl Saddles, Raschig rings, Sulzer Mellapack 250Y	n.a.		Continuous stripping mode / no reflux.
Aix-Marseille Univ.	2.0	19.0	35.0	VFF Interpack®.		High-pressure pump.	Continuous stripping mode / no reflux.
SSEA-Univ. of Reggio Calabria	3.0	30.0	8.0	Raschig rings		High-pressure membrane pump.	Continuous stripping mode / no reflux.
EXTRALIANS	4.0 [†]	45	30.0	(n.a)		High-pressure pump.	(n.a)
Plataform	8.0 [†]	126	35.0				
Solvay Specialty Polymers,	1.1	38	30.0	Sulzer CY		High-capacity metering diaphragm	Continuous stripping mode / no reflux.

R&D Center. Muller extract Co.	3.0	30.0	8.0–30.0	10 mm x10 mm SS Raschig rings.	pump. High-pressure pump.	Continuous stripping mode / Upper, middle and, bottom liquid feed with temperature gradient (internal reflux).
FLAVEX Naturextrakte	3.0	46.0	30	SS spirals.	(n.a.)	(n.a.)
F. Hoffmann- La Roche AG	13.6	35.0	14.5–19.5	Sulzer CY.	Membrane pump.	Continuous reflux mode / middle liquid feed / partial extra reflux.

(ϵ), void fraction

(a), specific surface $\text{m}^2 \cdot \text{m}^{-3}$

(n.a.), Not available on scientific literature

(SS), Stainless steel

(†), Actually active, personal communication

(*), The same column has three sections of different internal diameters.

Table 5 Phase equilibrium. Studied system, temperature and pressure ranges, and type of equilibrium data of selected references.

System	Temperature / K	Pressure / MPa	Type of data	Reference
Edible oil and derivatives				
(CO ₂ + oleic acid + triolein)	313; 323; 333; 253	20.0; 25.0; 30.0;	Pxy and partition coefficients of triglyceride groups.	[185]
(CO ₂ + kernel oil)		6.0– 33.0		
(CO ₂ + sesame oil)		12.5		
(CO ₂ + ethyl esters of menhaden oil)	333		Partition coefficients of ethyl esters in SC-CO ₂ and SC-CO ₂ with 5%wt ethanol.	[186].
(CO ₂ + ethyl esters of menhaden oil + Ethanol)				
(CO ₂ + cod liver oil)	313; 323; 333	10.0– 30.0	Pxy: Solubility of Squalene, Orange Roughy oil, Spiny Dogfish liver oil, Cod liver oil and Vitamin A Palmitate in SC-CO ₂ and solubility of CO ₂ in liquid phase.	[187]
(CO ₂ + vitamin A palmitate + spiny dogfish liver oil)				
(CO ₂ + squalene + orange roughy oil + spiny dogfish liver oil + cod liver oil + ethanol)				
(CO ₂ + ethyl ester mixtures from sardine oil)	313; 333; 343; 353	9.0– 25.0	Pxy: mass fraction ethyl esters (C14–C22) in both, gas and liquid phases. Peng-Robinson EoS correlation of ternary mixtures.	[188]
(CO ₂ + methyl oleate + α -tocopherol)	313; 333; 353	10.0; 20.0; 29.0	xy: mol fraction of methyl oleate and α -tocopherol in both, gas and liquid phases.	[189]
(CO ₂ + Crude palm oil)	310; 340;	20.0–	Pxy; mol fraction of crude palm oil	[18]

oil)	370	30.0	and SODD in both, gas and liquid phases. Partition coefficients of minor components.	
(CO ₂ + SODD)	343; 353; 363			
(CO ₂ + olive husk oil + methanol)	328; 338	30.0; 35.0	Solubility of olive husk oil in SC-CO ₂ with (1 and 5)% v/v of methanol and ethanol. Chrastil correlation.	[190]
(CO ₂ + olive husk oil + ethanol)				
(CO ₂ + β -carotene + ethanol)	303; 313; 323; 333;	3.0– 12.0	Bubble and dew points: Synthetic method. β -carotene concentrations from (0.10 to 0.34) g·L ⁻¹ . Peng-Roninson EoS correlation.	[191]
(CO ₂ + β -carotene + ethyl acetate)	343			
(CO ₂ + caffeine + ethanol)	313	15.0	Solubilities of caffeine in CO ₂ + ethanol at various ethanol concentrations	[192]
(CO ₂ + oleic acid + squalene)	313; 323; 333	14.0– 22.0	Vapor and liquid phase compositions at various squalene global mass fractions (0.25, 0.50 and, 0.75).	[193]
(CO ₂ + ethanol + sunflower oil)	313; 333	13.0; 20.0	LL and LSC phase compositions. GC-EoS modelling and prediction.	[194]
(CO ₂ + propane + sunflower oil)	308	2.8–6.2	LL and LLV phase compositions. GC-EoS modelling and prediction.	[195]
(CO ₂ + carnosic acid + ethanol)	313; 323; 333	28.0– 40.0	Solubility of solid carnosic acid in SC-CO ₂ with 0.7 to 10% of ethanol.	[196]
Essential oils				
(Ethane + orange peel oil)	282–363	1.0– 10.0	Bubble, dew and critical points: synthetic method. Peng-Robinson EoS correlation.	[197]
(CO ₂ + orange peel oil)	303; 333; 343	4.0– 13.0	Compositions of both phases at equilibrium	[69,77,198]
(CO ₂ + lemon oil)	298–313	0.4–8.8	Solubility of lemon oil in SC-CO ₂ and ethane. Soave-Redlich-Kwong EoS correlation. Molar densities of saturated liquid phase.	[199]
(Ethane + lemon oil)				
(CO ₂ + limonene + linalool)	333	7.5; 8.1; 8.8; 8.9	xy; compositions of both phases at equilibrium (tie lines). Selectivity between limonene and linalool in CO ₂ .	[200]
(CO ₂ + limonene + linalool)	318; 328	7.0– 11.0	xy: compositions of both phases of mixtures of global compositions (40:60% wt) limonene:linalool and (60:40% wt) linalool:limonene. Selectivity between limonene and linalool in CO ₂ .	[201]
(CO ₂ + limonene + linalool)	293–363	3.0– 14.0	Bubble dew and critical points: synthetic method. Liquid-liquid-vapor equilibrium.	[202,203]
(Ethane + limonene + linalool)				
(CO ₂ + limonene + citral)	315	8.4; 9.0	xy; compositions of both phases at equilibrium (tie lines)	[204]
(CO ₂ + propane +	304–384	2.4–	Bubble and dew points of the	[205]

camphor)		15.0	mixture: synthetic method. Peng-Robinson EoS correlation.	
Aqueous systems				
(CO ₂ + ethanol + water)	271–280, 313; 323; 328; 333; 343.	1.3–30.0 21.0; 29.8.	Bubble points (synthetic method), xy data GC-EoS, PR-EoS modelling. Hydrate dissociation pressures and temperatures.	[206–209]
(CO ₂ + 1-butanol + water)	297	5.9–6.4	LL equilibrium. Cloud-point data	[210]
(CO ₂ + wine)	308; 313;	9.7–	xy; compositions of both phases at	[206]
(CO ₂ + whiskey)	318; 328	29.8	equilibrium (tie lines), GC-EoS modelling pseudo ternary mixtures.	
(CO ₂ + acetone + water)	314; 353; 395	0.1–10.0	Solubility of CO ₂ in acetone water solutions, Henry's constants and	[211] [212]
	270–279	0.8–3.5	UNIQUAQ modelling. Hydrate dissociation pressures	
(CO ₂ + caffeine + water)	313	15.0	Solubility of caffeine in (CO ₂ + water) and (CO ₂ + ethanol+ water) at various water and ethanol concentrations.	[192]
(CO ₂ + caffeine + ethanol+ water)				
(Propane + 2-propanol + water)	272–282	0.2–1.3	Hydrate dissociation pressures and temperatures.	[209,213]
(Propane + ethanol + water)				
(Ethane + 2-propanol + water)				
(Ethane + ethanol + water)				
(CO ₂ + ethanol + p-coumaric acid + water)	313	15.0; 20.0	VL equilibrium. Separation factors of phenolic compounds between gaseous and liquid phases.	[214]
(CO ₂ + ethanol + resveratrol + water)				
(CO ₂ + ethanol + quercetin-3-glucoside + water)				
(CO ₂ + ethanol + catechin + water)				
(CO ₂ + ethanol + boldine + water)	313; 323; 333; 343	5.1–17.0	Bubble-point pressures, xy data; Synthetic method.	[207]
(CO ₂ + ethanol + catechin + water)				
(CO ₂ + ethanol + boldine + catechin + water)				
(CO ₂ + ethanol + boldo leaf tincture + water)				

LL, (liquid + liquid)

VL, (vapor + liquid)

LSC, (liquid + SuperCritical)

LLV, (liquid + liquid + vapor)
SODD, Soybean oil deodorizer distillate

Table 6 Interfacial tension (IFT) datasets from selected references, system under study, experimental temperatures and pressures, and IFT measurement method.

System	Temperature / K	Pressure / MPa	Method	Reference
Edible oil and derivatives				
Binary mixtures of pelargonic and linoleic acid + ethane and CO ₂	313; 333; 353	0.1–25.0	CR / DNR	[254]
Binary mixtures of pelargonic acid + N ₂ , Ar, He, and H ₂	313–393	0.1–25.0	PD-DSA	[255]
Binary mixtures of stearic acid + CO ₂ , ethane, He and H ₂				
Binary mixtures of methyl myristate, methyl palmitate and, pelargonic and oleic acid + CO ₂	313; 323; 333	0.1–17.5	CR	[256]
Methyl myristate + Methyl palmitate + CO ₂				
Binary mixtures of coffee, walnut, wheat and olive oil + CO ₂	313–393	0.1–50.0	PD-DSA	[257]
α -Tocopherol + CO ₂	313–402	0.1–37.0	PD-SP	[258]
Olive oil + oleic acid + CO ₂	313; 353	0.1–40.0	PD-DSA	[259]
Binary mixtures of vegetable oil + N ₂ and CO ₂	343; 353	0.1–30.0	PD-DSA	[184]
Binary mixtures of commercial corn germ oil, and wheat, palm and olive oil + CO ₂ and N ₂	313–393	0.1–50.0	PD-DSA	[260]
Refined (Mazola®) and unrefined corn germ oil + CO ₂			PD-DSA	[261]
Fish oil triglycerides + CO ₂	313; 328;	0.1–25.0	PD-DSA	[262]
Fatty acids ethyl esters + CO ₂	343			
Corn germ oil + CO ₂	313	0.1–27.0	PD-DSA	[243]
Essential oils				
Lemon oil + CO ₂	313–393	0.1–50.0	PD-DSA	[257]
Ethanol and Aqueous systems				
(Ethanol + water) + CO ₂	278–344	0.1–18.6	CR	[263]
Binary mixtures of water + N ₂ and CO ₂	343; 353	0.1–30.0	PD-DSA	[184]
Binary mixtures of ethanol and water + CO ₂	293–355	0.1–27.5	PD-DSA	[264,265]
Water + CO ₂	278–333	0.1–20.0	PD-DSA	[266,267]
Ethanol + N ₂	296; 314; 355	0.1–20.0	PD-DSA	[268]
Water + CO ₂ and brine + CO ₂	308–383	5.0–45.0	PD-DSA	[269]
Ethanol and water + CO ₂ and (Ethanol + water) + CO ₂	313	0.1–27.0	PD-DSA	[243]
IFT on solid materials of binary mixtures of	313	0.1–27.0	DSA	[270]

water and ethanol + CO ₂ and binary mixtures of water, formamide, ethanediol, and toluene + N ₂				
Water + CO ₂ and brine + CO ₂	293–393	2.0–27.0	PD- DSA	[271]
Binary mixtures of (carbon dioxide + n-alkane) and (carbon dioxide + water)	298–443	0.1–60.0	PD- DSA	[247]
Water + CO ₂	298–374	1.0–60.0	PD- DSA	[272]

PD=Pendant drop, CR= Capillary rise, DNR= Du Nouy Ring method, DSA=Drop shape analysis, SP= Selected plane.

2 Nomenclature

2.1 Acronyms

AMF	Anhydrous Milk Fat
CC	CounterCurrent
CC-SE	CounterCurrent Spray Extraction
CC-SFF	CounterCurrent Supercritical Fluid Fractionation
CFD	Computer Fluid Dynamics
CIAL	<i>Instituto de Investigación en Ciencias de la Alimentación</i>
CR	Capillary Rise
CSIC	<i>Consejo Superior de Investigaciones Científicas</i>
DNR	Du Nouy Ring
DSA	Drop Shape Analysis
EoS	Equation of State
FMSA	First-order Mean Spherical Approximation
GC	Group Contribution
HETP	Height Equivalent to a Theoretical Plate
HFMC	Hollow Fiber Membrane Contactor
HTU	Height of the mass-Transfer Unit
HTU _G	Height of the mass-Transfer Unit for the gas phase
HTU _L	Height of the mass-Transfer Unit for the liquid phase
IFT	Interfacial Tension

LL	Liquid + Liquid
LLV	Liquid + Liquid + Vapor
LSC	Liquid + SuperCritical
NTU	Number of transfer Units
OODD	Olive Oil Deodorizer Distillate
PCP	Perturbed Chain Polar
PD	Pendant Drop
PGSS	Particles from Gas Saturated Solutions
REQUIMTE	<i>Laboratório Associado para a Química Verde – Tecnologias e Processos Limpos</i>
RESS	Rapid Expansion of Saturated Solutions
SAFT	Statistical Association Fluid Theory
SC-CO ₂	Supercritical CO ₂
SFE	Supercritical Fluid Extraction
SFF	Supercritical Fluid Fractionation
SLO	Shark Liver Oil
SODD	Soybean Oil Deodorizer Distillate
SP	Selected Plane
SS	Stainless Steel
TP-SE	Two-Phase Spray Extraction
TUHH	<i>Technische Universität Hamburg-Harburg</i>
UAM	<i>Universidad Autónoma de Madrid</i>
USDA	United States Department of Agriculture
VL	Vapor + Liquid

2.2 Variables and parameters

a	Packing specific surface [m^{-1}]
a_e	Effective specific interfacial area [m^{-1}]
ΔP_{crit}	Critical pressure difference between fluids phases in membrane contactors [MPa]

G_m	Gas phase molar flow rate per unit cross sectional area [$\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
J_i	Mass flux of solute i [$\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
J_{CO_2}	Mass flux of CO_2 [$\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
$K_{\text{CO}_2,\text{L}}$	SC- CO_2 liquid phase overall mass-transfer coefficient [$\text{m}\cdot\text{s}^{-1}$]
k_G	Gas phase mass-transfer coefficient [$\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
$K_{i,\text{SC}}$	Solute i SuperCritical phase overall mass-transfer coefficient [$\text{m}\cdot\text{s}^{-1}$]
k_L	Liquid phase mass-transfer coefficient [$\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
L_m	Liquid phase molar flow rate per unit cross sectional area [$\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$]
N	Number of theoretical stages [-]
P_1	Pressure of fluid phase 1 in membrane contactors [MPa]
P_2	Pressure of fluid phase 2 in membrane contactors [MPa]
u_L	Liquid phase superficial velocity [$\text{m}\cdot\text{s}^{-1}$]
u_{SC}	SuperCritical phase superficial velocity [$\text{m}\cdot\text{s}^{-1}$]
x_{CO_2}	CO_2 liquid phase mole fraction [$\text{mol}\cdot\text{mol}^{-1}$]
$x_{\text{CO}_2}^*$	CO_2 liquid phase equilibrium mole fraction [$\text{mol}\cdot\text{mol}^{-1}$]
x_i^*	Solute i liquid phase equilibrium mole fraction [$\text{mol}\cdot\text{mol}^{-1}$]
y_i	Solute i gas phase mole fraction [$\text{mol}\cdot\text{mol}^{-1}$]
y_i^*	Solute i gas phase equilibrium mole fraction [$\text{mol}\cdot\text{mol}^{-1}$]
Z	Height of packing [m]

2.3 Greek symbols

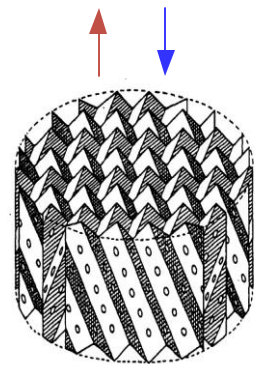
ε	Void fraction [-]
λ	Stripping factor [-]
ρ_L	Density of the Liquid phase [$\text{kg}\cdot\text{m}^{-3}$]
ρ_{SC}	Density of the SuperCritical phase [$\text{kg}\cdot\text{m}^{-3}$]

Liquid mixtures

Non-aqueous
Lipids
Essential oils

Aqueous
Alcoholic
beverages

Aqueous
mixtures



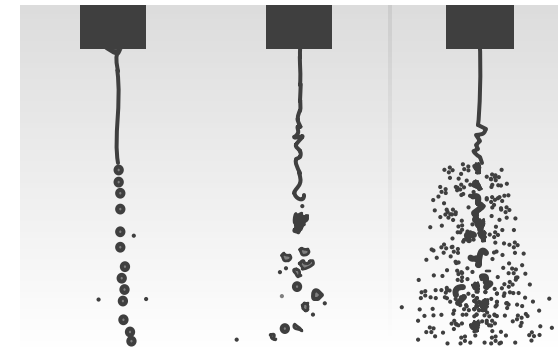
Low separation
factors

Packed columns

High separation
factors

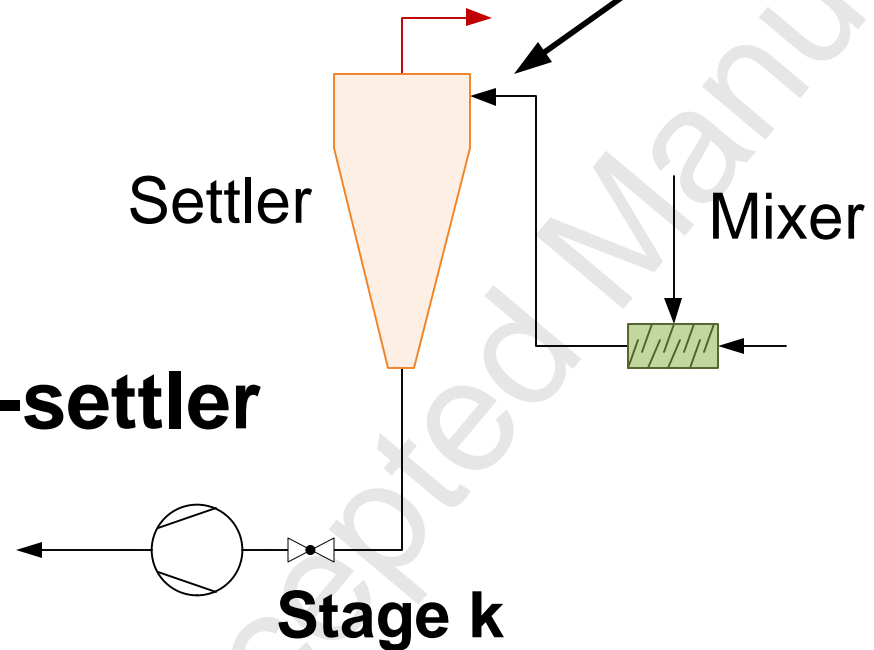
Membrane contactors

High viscosity mixtures



Spray processes

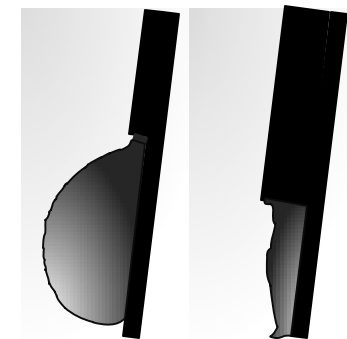
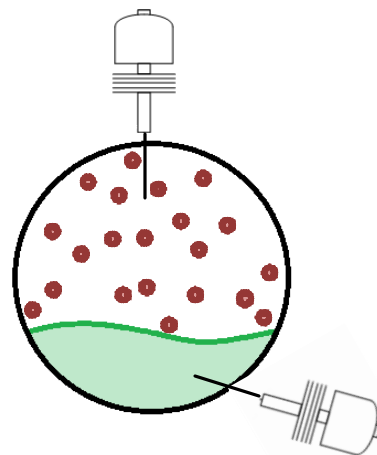
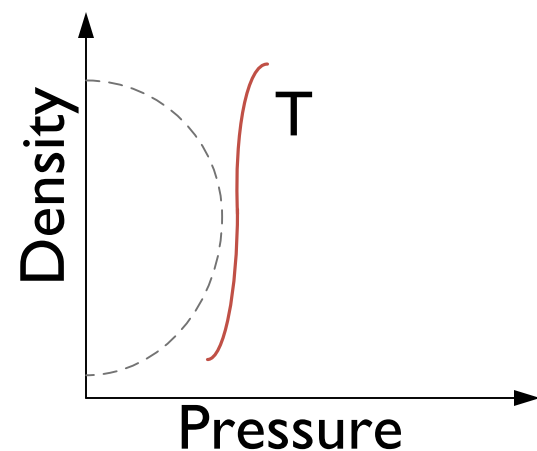
Mixer-settler



Density / viscosity

Phase equilibria

Interfacial properties

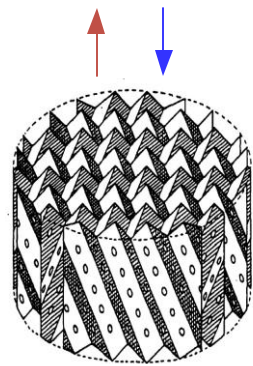


Liquid mixtures

Non-aqueous
Lipids
Essential oils

Aqueous
Alcoholic
beverages

Aqueous
mixtures



Low separation
factors

Packed columns

High separation
factors

Membrane contactors

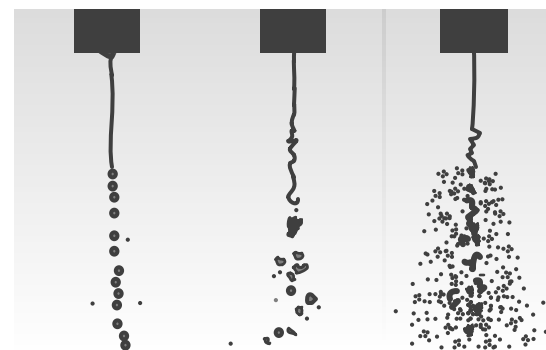
High viscosity mixtures

Settler

Mixer

Mixer-settler

Stage k

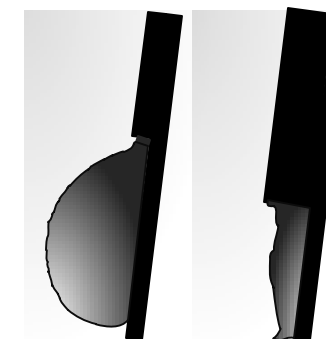
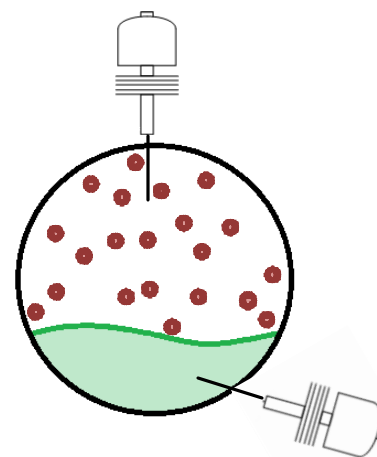
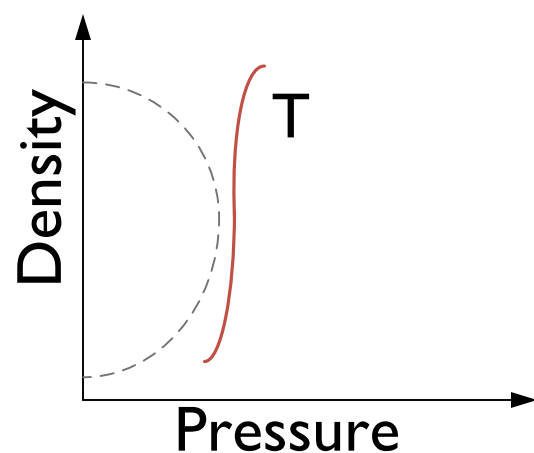


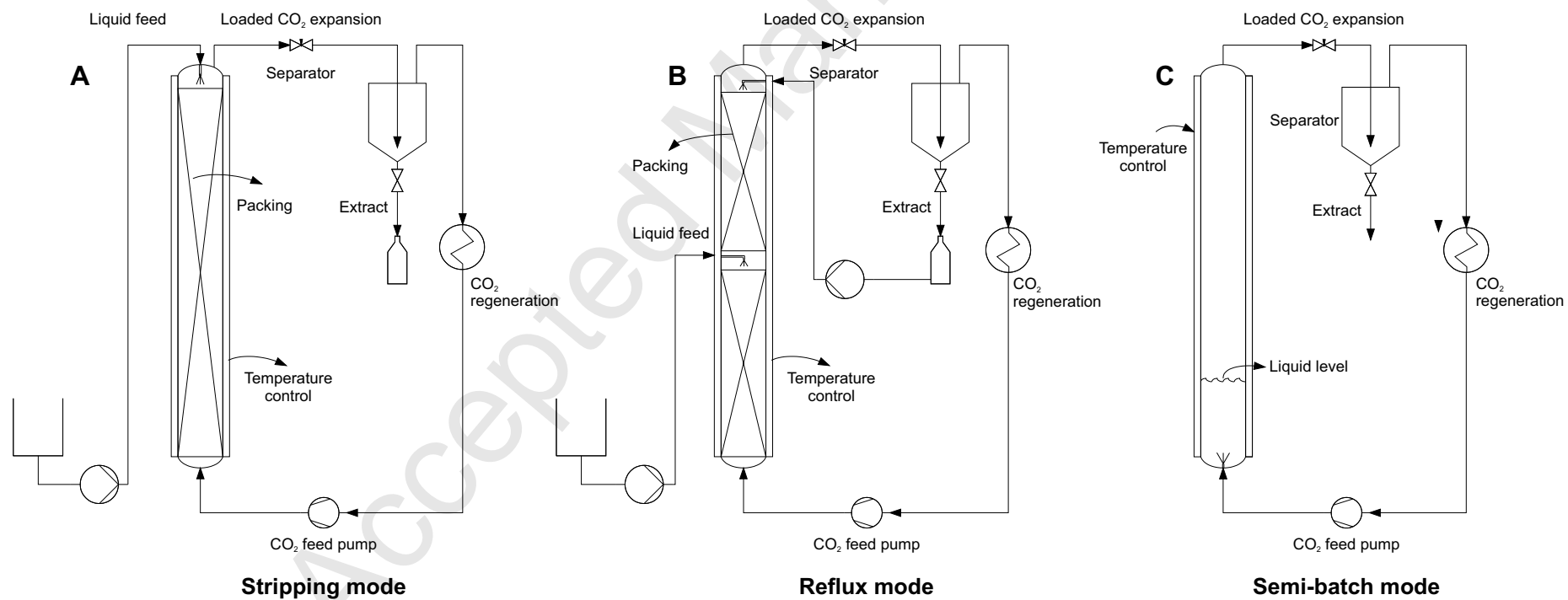
Spray processes

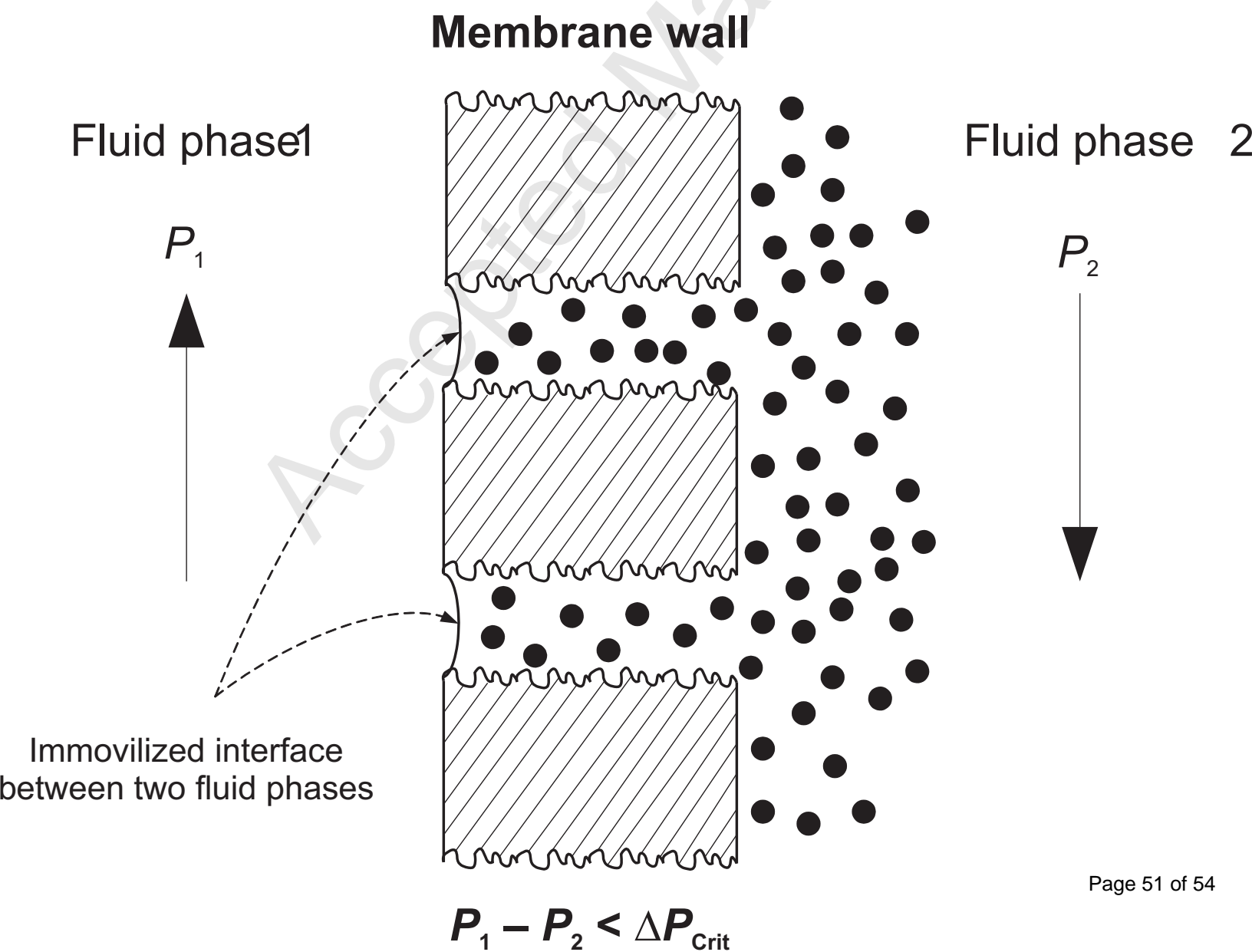
Density / viscosity

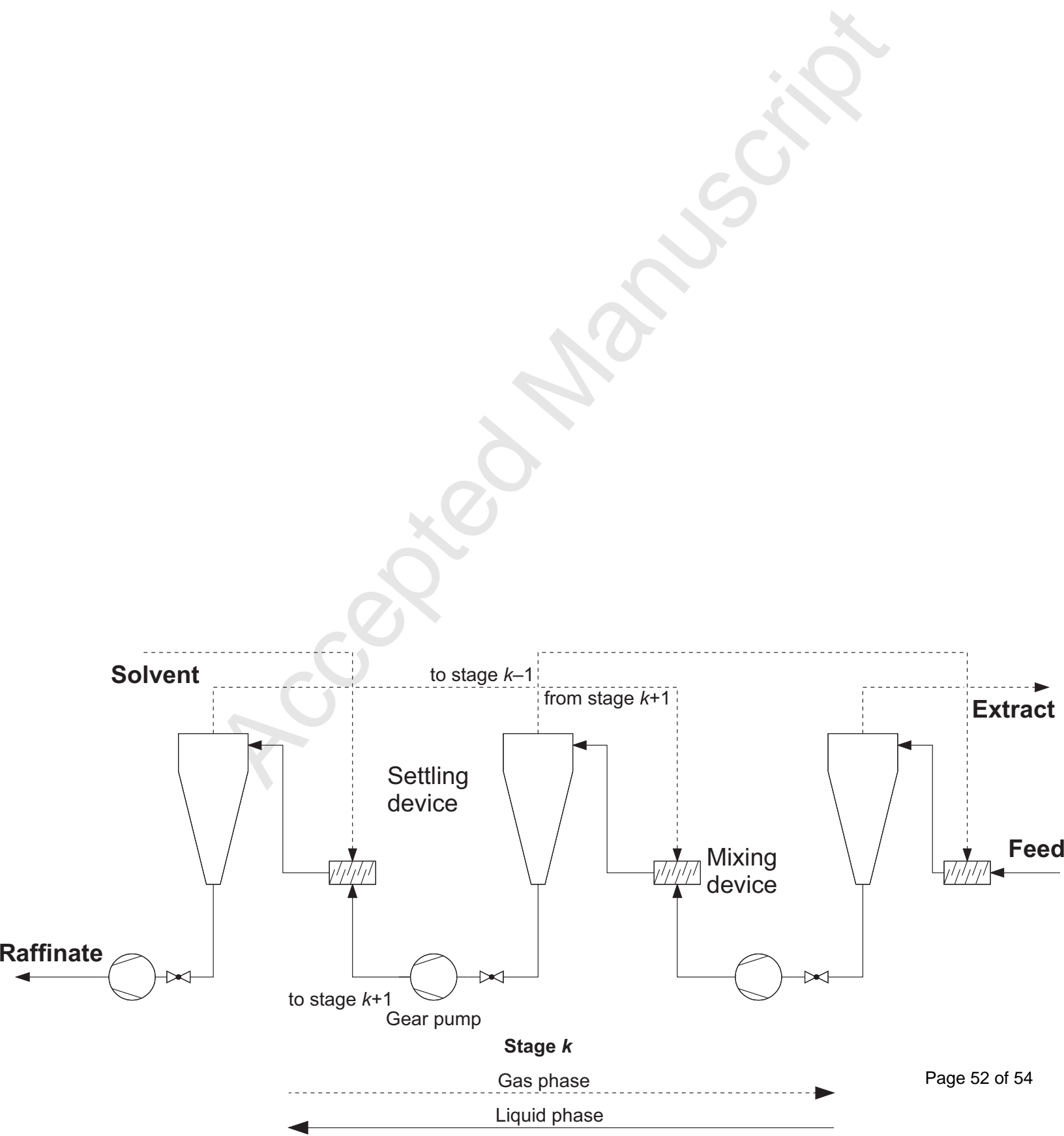
Phase equilibria

Interfacial properties

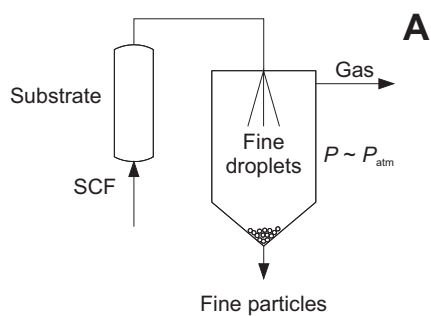




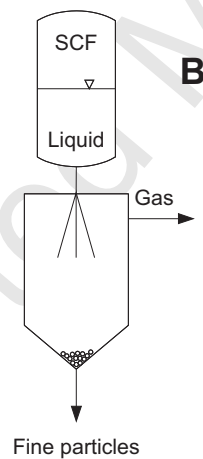




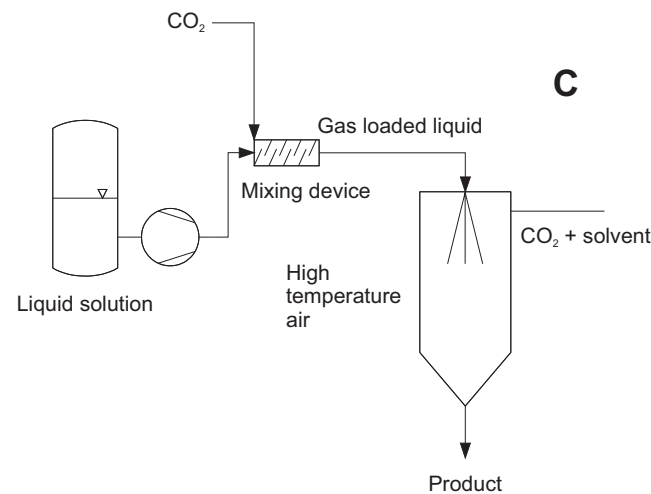
Rapid Expansion of Supercritical Solutions (RESS)



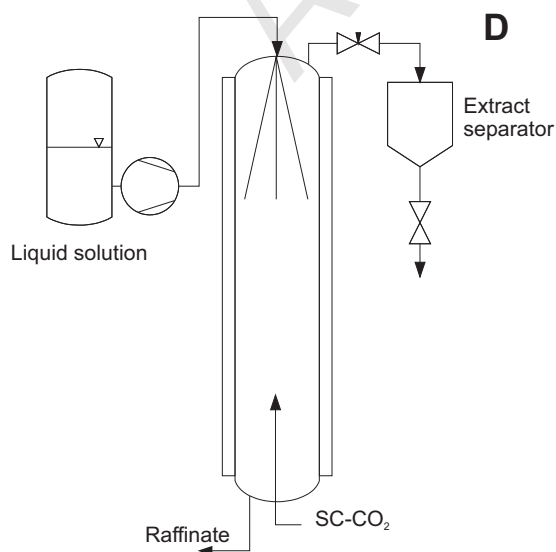
Particles from Gas-Saturated Solutions (PGSS)



Spray drying of gas loaded liquids



CC-spray extraction



Two phase spray extraction

