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Deterpenation of Citrus Peel Oils with Supercritical Carbon Dioxide – A Review

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ABSTRACT

Citrus oils are used worldwide as raw materials for the food, flavor, cosmetic, pharmaceutical and chemical industries. Basically, citrus oils are a mixture of oxygenated, high-volatile and low-volatile compounds. The high-volatile fraction is mostly composed of terpenes, whereas the most important contribution to the oil's distinct flavor and fragrance comes from oxygenated compounds. Since terpenes can degrade and produce undesirable off-flavors, they must be removed in order to stabilize the final product by a process called deterpenation. Traditionally, the removal of terpenes is by distillation. In order to avoid the drawbacks presented by the conventional processes, including high operational temperatures, supercritical extraction techniques have been extensively investigated in the last few decades. This present review focuses on the deterpenation of citrus peel oils using supercritical carbon dioxide (SC-CO_2) as solvent. To date, two different deterpenation techniques employing SC-CO_2 have gained relevance: supercritical ad-/desorption and countercurrent multistage fractionation. An overview of these processes is presented. In general, both processes have shown the capacity of concentrating oxygenated compounds from citrus oils at relatively mild temperatures (not higher than 70°C). Deterpenation in a countercurrent column has proved to be more suitable for obtaining folded extracts, whereas supercritical ad-/desorption are more appropriate when higher purification is required.

Keywords: countercurrent multistage fractionation, desorption, supercritical fluids, terpenes

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INTRODUCTION

The supercritical state

A pure substance is considered to be in a supercritical state when pressure and temperature are beyond their respective critical values, denoted as Pc and Tc, respectively. The critical point of a substance can be defined as the end point of the vapor-pressure curve, as illustrated in **Fig. 1**. At the critical point and beyond it, the distinction between liquid and vapor phases can not be ob-served (McHugh and Krukonis 1986; Brunner 1994). Besides, supercritical fluids (SCF) can easily vary their properties from low to high densities without phase transitions. The thermodynamic and transport properties can change drastically only by manipulating the operational process conditions (pressure and temperature), which consequently affect the solubility of substances identified in the supercritical phase (Brunner 1994). The transition from gas-phase boundary to the supercritical phase can be considered smooth. Therefore, models and basic considerations originally applied to conventional separation processes, such as adsorption, desorption, solvent extraction, striping, distillation and rectification, can be applied to supercritical fluid extraction processes (McHugh and Krukonis 1986).

Table 1 presents the characteristic values for liquid, gaseous and supercritical states. SCFs present liquid-like densities, gas-like viscosities and diffusion coefficients about two orders of magnitude higher than those presented by liquids. Due to these unique and advantageous features, namely high solvent power associated with gas-like transport properties, supercritical fluids have been chosen for several engineering applications, especially for the extraction and fractionation of natural products for the food and pharmaceutical industries (Stahl *et al*. 1987; Brunner 1994).

Regarding the supercritical separation processes in general, the driving potentials for mass and heat transfers are determined by the deviations from the equilibrium state. The equilibrium state provides valuable information about the solvent capacity of a supercritical fluid (thermodynamic

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Invited Review

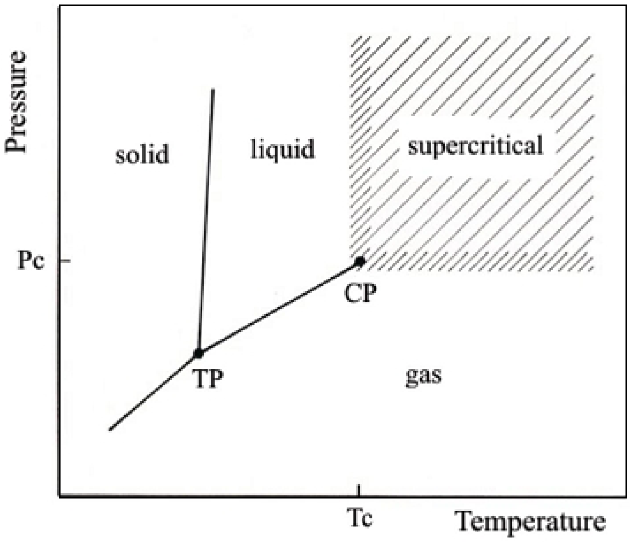

Fig. 1 Pressure-temperature diagram of a pure substance. Based on Brunner (1994). (TP=Triple Point; CP=Critical Point)

Table 1 Physical properties of different fluids. Data from Stahl *et al.* (1987).

Fluid	**P/ T (MPa)/(°C)**	**Density (kg/m^3)**	**Diffusion coefficient (cm^2/s)**	**Viscosity (g/cm·s)**
Gas	0.1/25	0.6-2.0	0.1-0.4	(1-3) × 10^{-4}
SCF	Pc/Tc	200-500	0.7 × 10^{-3}	(1-3) × 10^{-4}
Liquid	0.1/25	600-1600	2 × 10^{-6}-2 × 10^{-5}	(0.2-3) × 10^{-2}

Table 2 Critical data for pure substances. Data from Brunner (1994).

Component	**Tc (°C)**	**Pc (MPa)**
Nitrogen	-146.9	3.39
Carbon monoxide	-140.2	3.50
Nitric oxide (NO)	-93.0	6.48
Methane	-82.7	4.60
Carbon tetrafluoride	-45.6	3.74
Ethylene	9.2	5.04
Trifluoromethane	26.1	4.86
Carbon dioxide	31.1	7.38
Ethane	32.2	4.88
Nitrous oxide (N_2O)	36.5	7.24
Propane	96.6	4.25
n-Hexane	234.3	3.01
Acetone	234.9	4.70
Methanol	239.4	8.09
Ethanol	240.7	6.14
Toluene	318.6	4.10
Water	374.1	22.12

solubility), the amount of gas dissolved in the liquid or solid phase and the equilibrium composition between the phases involved, the solvent selectivity (the ability to dissolve one or more substances, usually expressed by the separation factor), and the dependence on the operational temperature and pressure conditions (McHugh and Krukonis 1986; Brunner 1994).

Several pure substances may be used as SCF. Special attention is given to carbon dioxide (CO_2), the most commonly used SCF worldwide. In comparison to other substances (as presented in **Table 2**), CO_2 presents a critical temperature (Tc) of 31.1°C, relatively close to the ambient temperature, and a relative low critical pressure (Pc = 7.38 MPa), which is interesting when considering the energy requirements for the solvent delivery at the operational pressure. Besides, it is abundant, relatively inexpensive, inert, can be used in high purity, is non-flammable, non-toxic and non-explosive; all properties that are in agreement with the environmental and health organizations' restrictions (McHugh and Krukonis 1986). Since CO_2 is a non-polar solvent, the addition of small percentages of modifiers or entrainers (liquids like ethanol and other alcohols) or co-solvents (substances in gaseous phase, like ethane and propane) can be employed in order to increase the efficiency of the process through the enhancement of the solvent's polarity (Brunner 1994). However, their separation from the final products may pose a problem, especially when a high purity is required, since they remain as solvent residues at the end of the process.

As presented by Brunner (2005), the solvent power of supercritical CO_2 (SC-CO_2) can be stated according to the following: (i) CO_2 presents high affinity with oxygenated organic substances of medium molecular weights and dissolves non-polar or slightly polar substances; (ii) the solvent power for low molecular weight substances is high, decreasing with increasing molecular weights; (iii) free fatty acids and their respective glycerides present low solubilities; (iv) pigments are less soluble and proteins, polysaccharides, sugars and mineral salts are not soluble; (v) water presents a low solubility at temperatures below 100°C; and (vi) SC-CO_2 is capable of separating less volatile substances as pressure increases.

Citrus peel oils processing – general considerations

Following the juice extraction, the remaining residues are composed basically of peels and other solids, accounting to approximately 50% (weight) of the fruits. The remaining peel oil can be extracted and recovered from the aqueous phase after juice expression (Blanco-Tirado *et al.* 1995; Braddock 1999). Citrus peel oils are usually extracted by means of steam distillation or cold-pressing and the yields may vary from 0.20 to 0.70% of the total weight of a fruit (Blanco-Tirado *et al.* 1995). Steam distillation is one of the most used extraction methods and is based on the different solubilities of the high valued citrus oil components in the steam stream. This method is employed mostly due to its simplicity and to the economical aspects, since significant amounts of raw material can be processed simultaneously. On the other hand, the main disadvantage of steam distillation extraction resides in the high operational temperatures used, which in some instances are responsible for the degradation of valuable components. In despite this cold-pressing has become the most used method for citrus peel oils extraction, since it is carried out at low temperatures, resulting in higher extraction yields (Budich 1999; Atti dos Santos *et al.* 2003).

Once the oil is extracted, it must be purified to make it proper for human consumption. The deterpenation process consists on the removal of terpenes from the oil, especially monoterpenes, like limonene and terpinene. Limonene is the major citrus oil component, achieving up to 99% of the total oil amount. As other monoterpenes (such as pinene, sabinene and myrcene) are more volatile than limonene, they can be separated earlier or at the same time, thus improving the final quality of the oil, i.e., producing folded aroma concentrated mixtures. Depending on the amount of terpenes present in the oil, it is possible to concentrate the aroma fraction up to 20-fold or even achieve terpeneless concentrates (Braddock 1999; Budich 1999). Due to the presence of several thermolabile components, fractionation of the oil is generally carried out at low temperatures. Since aroma components present very similar chemical and physical properties, multistage processes are employed in order to provide good separation. Conventional deterpenation methods include chromatographic procedures, adsorption/desorption, solvent extraction and vacuum distillation, among others (Reverchon 1997a; Braddock 1999). Recent investigations on the use of one ionic liquid (1-ethyl-3-methylimidazolium ethylsulfate, namely [emim][$EtSO_4$]) as solvent for citrus oil deterpenation through liquid–liquid extractions are available in the literature (Arce *et al.* 2007). These methods will not be further presented and discussed since they are considered beyond the scope of this review.

ADSORPTION/DESORPTION PROCESSING

Adsorption occurs whenever a solid surface is exposed to a gas or a liquid. It is basically defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface (Sattler 1995). Under certain conditions, highly porous and very fine media are preferred as the adsorbent, since they provide larger specific surface areas. The usual examples are activated carbon, silica gel, clays, zeolites and aluminophosphates, among others (Perry *et al.* 1984; Rouquerol *et al.* 1999).

Adsorption is a very important process in the industry: some adsorbents are used in large amounts as desiccants, catalysts or catalysts supports; others are used for the separation of gases, liquid purification and pollution control. Additionally, adsorption processes play an important role in solid state reactions and biological mechanisms (Perry *et al.* 1984; Rouquerol *et al.* 1999). The reverse process to adsorption is called desorption. The substance of interest (solute or adsorptive) is initially present in the fluid phase and afterwards accumulated on the adsorbent as adsorbate. Adsorption at a surface or interface is caused largely by binding forces between the individual atoms, ions, or molecules and the adsorbent's surface. Physical adsorption is mainly the result of van der Waals and electrostatic forces between adsorbate molecules and the atoms that compose the adsorbent surface. Due to the small energy range of these forces, the adsorbent and adsorbate are bond loosely and can generally be easily released (Rouquerol *et al.* 1999). Several factors influence the adsorption of a certain compound to an adsorptive. For the adsorptive, they include the molecular weight and size, structure, polarity, and its affinity to the fluid phase. For the adsorbent, the chemical composition of the surface, pore size distribution and their configuration, as well as the size and form of the particles, determine the adsorption properties. Furthermore system conditions, such as pH, temperature, and pressure may affect adsorption (Sattler 1995; Rouquerol *et al.* 1999).

Desorption of the adsorbed solute from the adsorbent is accomplished by one or two general methods. The first method consists of changing the physical operational conditions in order to decrease the equilibrium interactions between the adsorbent and the solute (adsorptive). It could be performed by passing a different feed stream through the adsorbent or by decreasing the pressure of the system. The second method corresponds to the modification of the nature of the adsorbed material by carrying out chemical reactions. Then, the adsorbed material can be desorbed and removed from the system readily. This method ranges from passing a feed solution, which reacts with the adsorbed material, to thermal type regenerations at high temperatures where under a controlled gaseous atmosphere, preferred chemical reactions occur with the adsorbed components (Rouquerol *et al.* 1999).

Adsorption/desorption of citrus oils with SC-CO$_2$

The adsorption/desorption with SCF is carried out following the same principles and operational procedures of the conventional supercritical extractions from solid particles, as highlighted by several textbooks (McHugh and Krukonis 1986; Brunner 1994). The supercritical adsorption/desorption process generally employs silica gel as adsorbent, but several other adsorbents, such as aluminium oxide, activated carbon and bentonite, may be used. Oxygenated aroma compounds can be selectively adsorbed on the adsorbent's polar sites due to their chemical structures (polar compounds), providing a good possibility to perform fractional desorptions only by manipulating the operational pressures. Hydrocarbon terpenes (high-volatile compounds like limonene, pinene and myrcene) can be firstly desorbed, operating at low CO$_2$ densities, i.e., at lower pressures, and the oxygenated compounds, the so-called "aroma" fraction, can be desorbed by increasing operational pressures under isothermal conditions (Danielski 2007).

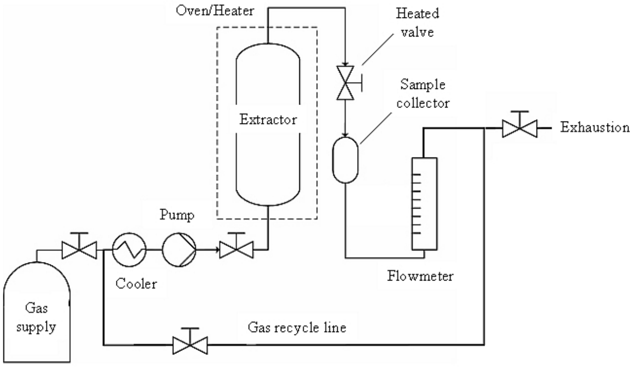

Fig. 2 Simplified flowsheet of the apparatus used for the deterpenation of citrus peel oils by means of adsorption/desorption with SC-CO$_2$. Adapted from Danielski (2007).

The extraction is carried out through the continuous contact between the loaded adsorbent (solid matrix) and CO$_2$ at high pressures. Most of the published studies present the adsorbent loading only through mixing the adsorbent with the citrus peel oils prior to the beginning of the process. The solid substrate (adsorbent+adsorbate) is then loaded into the extractor and forms a fixed bed of particles. Once the fixed bed is formed, CO$_2$ is fed at the desired pressure and temperature conditions, flowing through the loaded extractor. The compounds of interest are selectively and continuously extracted by the supercritical phase until its complete desorption from the solid phase. The loaded (or even saturated) solvent flows to one separator vessel in order to perform the separation solute/solvent by means of an increase in temperature or a drastic pressure reduction.

The process typically uses extractors from 0.1 to 2 dm^3 on the laboratory scale and from 2 to 50 dm^3 on the pilot scale (Reverchon 1997a). If the extraction process is conducted at laboratory or pilot scales, the regenerated gas phase can be released to the atmosphere. Otherwise, if larger extractors are used, i.e., the CO$_2$ consumption is high, or if another SCF is used and considered flammable, explosive or toxic, the solvent can be recycled and fed once more into the extractor, closing the solvent cycle and avoiding the discharge of the solvent into the atmosphere.

Fig. 2 presents a simplified flowsheet of the apparatus generally used for the deterpenation of citrus peel oils by means of adsorption/desorption with SC-CO$_2$. The set-up basically consists of an oven or heated/jacketed medium, in which the extractor is placed. The lower portion is connected to the inlet valve where the solvent flows through and the upper part is connected to the outlet valve, where the solvent flow rate is controlled and the extract collected. The system pressure is reduced to atmospheric pressure during sampling and the total solvent flow rate can be measured by different methods (usually rotameters). Based on the process scale, the possibility of solvent recycling after the extract separation may be considered (Danielski 2007).

Adsorption and desorption processes in the field of citrus oil deterpenation by means of SCF have been extensively investigated for approximately two decades. Reverchon (1997a) have reviewed the work of several authors on selective adsorption/desorption with different citrus peel oils. **Table 3** summarizes some of these studies and also presents the process conditions employed.

In 1990, Cully *et al.* published the first patent of a citrus peel oil deterpenation process with SC-CO$_2$. Different adsorbents were employed (silica gel, aluminium oxide, cellulose, bentonite, among others) at temperatures varying from 50 to 70°C and pressures from 7.0 to 9.0 MPa. Up to 95% terpene removal was achieved, highlighting the major advantages of the process, such as high selectivity, production of special fractions of oxygenated compounds and the possibility to obtain products free of phototoxic and other high volatile components. Since the process can selectively

Table 3 Papers on selective desorption and pressure swing adsorption of citrus peel oils and corresponding model mixtures with SC-CO_2.

Peel oil	**Selective Desorption**				**References**
	Terpene desorption		**'Aroma' desorption**		
	P (MPa)	**T (°C)**	**P (MPa)**	**T (°C)**	
Bergamot	7.5	40	10.0	40	Chouchi *et al.* 1995
Bigarade	7.7	40	12.0	40	Chouchi *et al.* 1996
Citrus, general	7-9	50-70	20.0-30.0	30-70	Cully *et al.* 1990
Lemon	7.4	40	8.7	40	Barth *et al.* 1994
	12.2	40	40.5	60	Dugo *et al.* 1995
	10.0	40	20.0	40	Yamauchi and Saito 1990
Distilled Lime	7.5	40	8.5-12.0	40	Della Porta *et al.* 1995
Mandarin	7.5	40	8.5-12.0	40	Della Porta *et al.* 1995
	7.5-10.0	35-40	15.0-24.0	35-40	Schwänke 2006; Danielski 2007; Danielski *et al.* 2008
Model mixtures	7.5	40	20.0	40	Reverchon 1997b
Sweet orange	12.2	40	40.5	60	Dugo *et al.* 1995
Orange	13.1	35-45	13.1	35-45	Shen *et al.* 2002
Peel oil	**Pressure Swing Adsorption**				**References**
	Adsorption		**'Aroma' desorption**		
	P (MPa)	**T (°C)**	**P (MPa)**	**T (°C)**	
Citrus, general	8.8	40	19.4	40	Goto *et al.* 1997
Orange	8.8	40	19.4	40	Sato *et al.* 1998a
Bergamot	8.8	40	24.8	40	Goto *et al.* 2002

fractionate products of high purity with very compact equipment, supercritical adsorption followed by desorption is one of the best alternatives for the deterpenation of citrus oils. The method is also highly recommended when low quantities of raw materials have to be fractionated into products of high market value.

Yamauchi and Saito (1990) reported the fractionation of lemon peel oil using supercritical fluid chromatography on silica gel at 40°C with two pressure steps of 10 and 20 MPa. Ethanol was added as a modifier to remove the oxygenated aromatic components. Four fractions were obtained and were mainly composed by terpenes, oxygenated terpenes, oxygenated terpenes removed only by the addition of ethanol and high molecular weight compounds, such as waxes and hydrocarbons. Additionally, they have observed that the amount of water present in the oil considerably reduced the activity of the adsorbent. It was concluded that the removal of water must be previously performed.

The work of Barth *et al.* (1994) investigated the separation of the terpene fraction and the low-volatile compounds, such as coumarins, psoralens (phototoxic compounds) and waxes from lemon peel oil by different pressure levels with SC-CO_2. Silica gel was used as adsorbent and the experiments were conducted at 40°C. Desorbed fractions were precipitated in two high-performance thermostatized cyclonic separators operated in series. These separators allowed the analysis of the precipitates during the desorption process, since it was possible to discharge the product at fixed time intervals from the bottom of the separators. Monoterpene hydrocarbons were obtained at the lowest pressure level (7.5 MPa, CO_2 density of 220 kg/m^3). A deterpenated and psoralen-free fraction was obtained at 8.5 MPa (CO_2 density of 400 kg/m^3). Desorption of waxes was obtained at about 12.0 MPa (CO_2 density of 700 kg/m^3), whereas coumarins and psoralens were removed from the adsorbent by washing the column with warm ethanol. The extract profiles obtained by gas chromatography-mass spectrometry (GC-MS) analysis of the products are presented in **Fig. 3**, where: (A) shows the raw oil profile and (B) the deterpenated fractions, while waxes and other high molecular weight compounds remained adsorbed after the process (residue) are shown in (C). As a final result, the authors found that the enrichment of oxygenated compounds in the deterpenated fraction was about 20-fold and approximately 10% oxygenated compounds were lost with waxes as residues, while 3% was lost during the terpene fractionation.

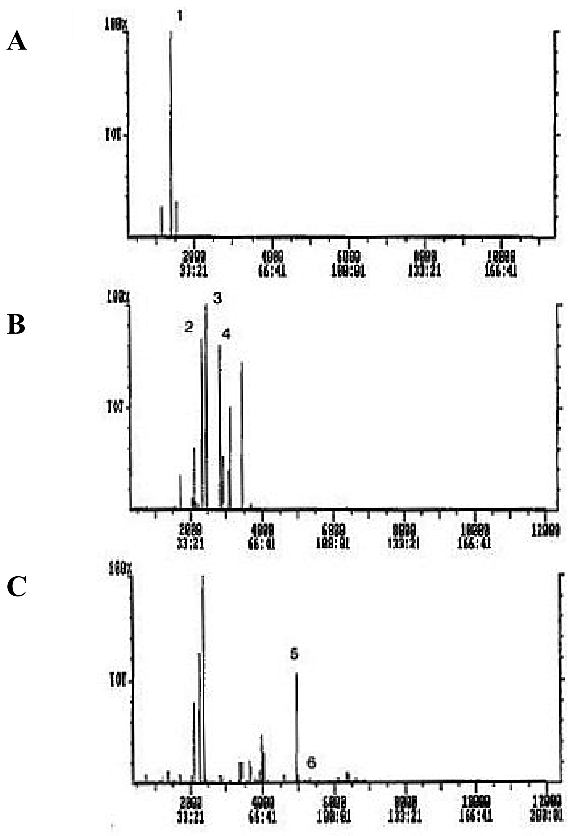

Fig. 3 Gas chromatograms illustrating lemon peel oil desorption with SC-CO_2. (**A**) Raw oil; (**B**) Deterpenated fraction; (**C**) Residue. Peak compounds are listed as: (1) limonene; (2) neral; (3) geranial; (4) neryl acetate; (5) citropten; (6) bergapten (Barth *et al.* 1994).

Dugo *et al.* (1995) investigated the supercritical deterpenation of sweet orange and lemon peel oils with SC-CO_2. Several adsorbents were tested, including sand, magnesium and calcium sulphates, celite, and silica gel. The results indicated that sand and magnesium sulphate produced no fractionation of the studied oils. Also, celite was found very selective for aldehydes. Additionally, linalool was almost completely co-extracted during the removal of terpenes. Calcium sulphate was very effective, but the results depended strongly on the water content of the adsorbent, presenting a very low reproducibility of the desorption step. Silica gel was confirmed as the best adsorbent for the task. The process was performed in two steps: 12.2 MPa and 40°C for 20 min and 40.5 MPa and 60°C for 100 min, using a microscale extraction apparatus. Most hydrocarbons were desorbed during the first step. The fraction desorbed at higher CO_2 density still contained 20-30% hydrocarbon terpenes.

Table 4 Results obtained for the bigarade peel oil desorption with SC-CO_2. Adapted from Chouchi *et al.* (1996).

Compounds	Raw oil (%)	Terpenic fraction (%)	Deterpenated fraction (%)	Residue (%)
Hydrocarbon terpenes	92.41	99.41	45.84	5.00
Oxygenated terpenes	7.59	0.59	49.87	23.77
Sesquiterpenes	-	-	1.82	-
Oxygenated sesquiterpenes	-	-	2.47	6.17
Waxes/Methyl esthers	-	-	-	1.18
Coumarins/psoralens	-	-	-	59.56
Polymethoxyflavones	-	-	-	1.18
Low volatile compounds	-	-	-	3.24

The product obtained by supercritical desorption was compared to the deterpenated oils produced by vacuum distillation and the authors concluded that the traditional deterpenation technique produced losses of the more volatile aliphatic aldehydes.

Following the same process considerations presented by Barth *et al.* (1994), the desorption of bigarade peel oil from a polar adsorbent was performed with SC-CO_2 in order to improve the oil quality through the selective elimination of hydrocarbon terpenes and coumarins (Chouchi *et al.* 1996). The oil fractions obtained at 40°C were analyzed by GC-MS. **Table 4** presents the concentration profiles obtained for bigarade peel oil. Three fractions were characterized: the terpenic fraction desorbed at 7.7 MPa, the deterpenated fraction obtained at 12 MPa, and the remaining residue. It is clear that the first fraction was practically composed of only terpenes and that content of oxygenated compounds in the deterpenated fraction was 6.6 times higher than that in the raw oil, confirming that fractionation was successfully achieved. Coumarins, psoralens, polymethoxyflavones, waxes and other low-volatile compounds contained in the starting material were recovered and identified in the residue fraction.

Reverchon (1997b) employed SC-CO_2 in order to desorb limonene, linalool and their mixtures (50 and 80% limonene) from silica gel to simulate the deterpenation of citrus peel oils. The influence of pressure, temperature, solvent flow rate and solute loading was studied. Maximum selectivity was obtained by operating at 40°C and 0.1 kg/kg loading. The optimal desorption conditions were obtained when two successive pressure steps were used: the first step performed at 7.5 MPa promoted the selective desorption of limonene and the second one, assured the fast desorption of linalool at 20 MPa. Adittionally, a Langmuir-like equation provided the best representation of the experimental data for each single component and for the mixtures. The desorption process was successfully modeled for the single components and also for limonene-linalool mixtures, with fairly well fitted data.

An alternative to charging the peel oil onto the adsorbent at ambient conditions (normal mixing), involves dissolving the oil in SC-CO_2 first. In this way, undesired heavy-weight compounds are removed as they are much less soluble in CO_2 and will remain in the mixing vessel. Then the loaded CO_2 is charged on the adsorbent and the oxygenated fraction is preferably adsorbed. In a second step, this product fraction is desorbed with pure CO_2 at higher pressures. This process, called pressure-swing-adsorption (PSA), can be carried out continuously when at least two adsorbers (extractor vessels) are used. The oil is continuously fed because one of the adsorbers is always in adsorption mode, while the other one is desorbed at reversed flow direction. Although the feed flow is continuous and thus much easier to automate, the aroma and terpene fractions do not accrue uniformly over the half-cycle. In order to increase the selectivity of the process, the bed can be rinsed with pure CO_2 at adsorption conditions before increasing the pressure (Goto *et al.* 1997; Sato *et al.* 1998a). Thus, most of the terpenes that were adsorbed along with the aroma fraction will be desorbed, similar to the first step in selective desorption. Besides PSA, it is also possible to perform a chromatographic separation after dissolving the oil in SC-CO_2, as presented by Pitol-Filho (1999) and Pitol-Filho *et al.* (1999).

Reverchon *et al.* (1998) and Subra *et al.* (1998) have investigated the adsorption of a mixture composed by 13 terpenes (α- and β-pinenes, myrcene, limonene, γ-terpinene, β-caryophyllene, citronellyl- and geranyl acetates, linalyl acetate+geraniol, linalool, citronellal and citral) on silica gel with CO_2 with the aim of simulating the essential oil fractionation. These components have been divided into four pseudocomponents according to the similarity of their behavior during the adsorption process. An equilibrium model was developed and the breakthrough time and the maximum concentration of the four pseudocomponents were satisfactorily well modeled. Additionally, they observed that the selectivity increased at low temperatures, as the differences in adsorption capacities of several components increase with decreasing temperature. Subra *et al.* (1998) obtained adsorption isotherms at 37 and 47°C for isochoric conditions of a CO_2 density of 750 kg/m^3. The equilibrium loadings, measured at individual solute concentration from 0.9 to 8 mg solute/g solvent were of the same order of magnitude for hydrocarbon and oxygenated terpenes. The adsorbed quantities were low, and in the range of 10 mg solute/g adsorbent. Measurements of CO_2 adsorptive capacities for several mixtures showed that this solvent is indeed competent for adsorption. Due to the complex behavior of the multi-component mixtures, the capacity data of the solutes were regressed according to an empirical Langmuir-like equation instead of a Langmuir model.

During adsorption and desorption processes, residues of heavy compounds can remain on the silica gel polar sites. The regeneration of the adsorbent can be performed by washing it with warm ethanol (Barth *et al.* 1994). When PSA is applied, most waxes do not reach the column and a steady-state is reached. This was observed after 13 half-cycles for bergamot oil deterpenation (Goto *et al.* 2002).

The deterpenation and bergaptene removal from bergamot essential oil have also been performed by Araújo and Farias (2003). These authors showed that limonene was firstly desorbed from silica gel at 40°C and 7.7 MPa. In the second step, bergaptene was separated (92.7%) from the other oxygenated components at 50°C and 15.1 MPa. The final concentrations of linalool and ethyl acetate obtained were approximately 52 and 69%, respectively.

The recent works of Schwänke (2006), Danielski (2007) and Danielski *et al.* (2008) dealt with the supercritical deterpenation of two different mandarin peel oils originating from Spain and Brazil (the so-called red and green oils, respectively) using CO_2 as solvent and silica gel as adsorbent. The raw mandarin peel oils presented a total terpene content of 99.13 and 96.39% for the Spanish and the Brazilian oils, respectively. By performing chromatographic analysis, the Brazilian raw oil presented the richest aroma profile, composed mainly by methyl-*N*-methyl-anthranilate (MNMA), decanal and sinensal. On the other hand, the aroma fraction of the Spanish oil was represented by linalool and decanal, the only oxygenated compounds detected by GC analysis. The experiments were carried out at pressures ranging from 7.5 to 24.0 MPa at 35 and 40°C, using different loading levels. The compounds evaluated were analyzed and the best fractionation results were obtained at 40°C, 25% oil loading (corresponding to 25% of the total mass of adsor-

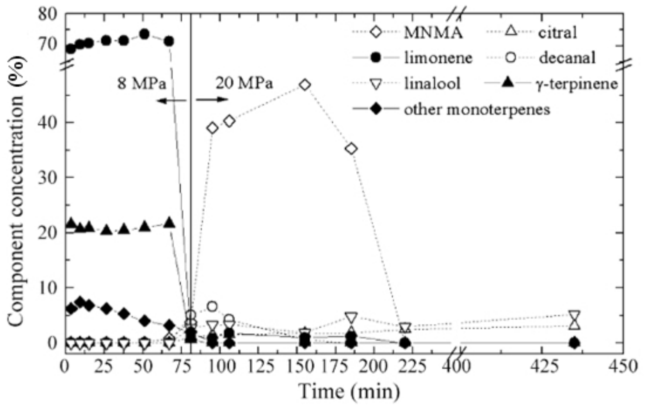

Fig. 4 Desorption curves of the most representative Brazilian green mandarin oil compounds at 40°C. Based on Danielski (2007) and Danielski *et al.* (2008).

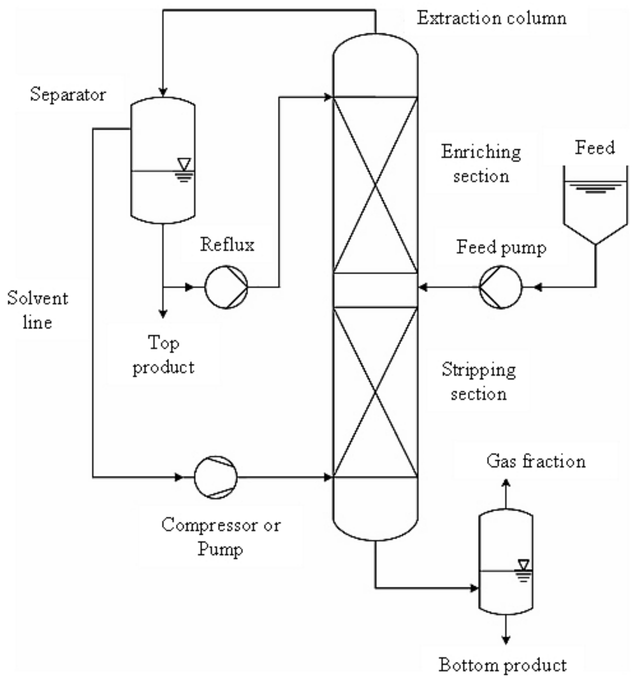

Fig. 5 Simplified process scheme of a countercurrent multistage extraction apparatus. Adapted from Brunner (1994).

bent used) in two sequential pressure steps for both raw samples. Initially, terpenes were completely desorbed at 8.0 MPa and, at 20.0 MPa, a selective fractionation of important aroma compounds was observed for both raw materials.

The extract recovery of a Brazilian green mandarin oil, carried out at 40°C and 25% loading, is presented in **Fig. 4** (Danielski 2007; Danielski *et al.* 2008). After 80 minutes desorption, monoterpenes were practically totally desorbed and the pressure could be increased up to 20.0 MPa. Decanal, citral, linalool and especially MNMA, were desorbed in relatively longer times. MNMA, decanal and linalool reached maximum concentrations at different desorption times, achieving approximately 47, 7 and 5% of their respective samples. At the end of the extraction, citral and linalool were the only identified aroma compounds. In order to investigate the process scale-up, experiments with the Brazilian and the Spanish mandarin peel oils were carried out with good results, using an up-scale factor of 4.0.

Additionally, the works on mandarin peel oil have shown the possibility of reusing the adsorbent by washing it with warm ethanol (Barth *et al.* 1994). The silica gel could be then reused in up to six subsequent assays using the Brazilian green oil. This must be taken into account when evaluating the process costs. Further analyses of all samples were performed and the obtained concentrations were very similar to the ones from previous experiments using new adsorbent charges (Schwänke 2006; Danielski 2007; Danielski *et al.* 2008).

COUNTERCURRENT MULTISTAGE FRACTIONATION WITH SC-CO$_2$

If the yield or the selectivity of an extraction using a simple one-stage apparatus are not sufficient, the liquid feed and supercritical solvent can be inserted countercurrently into one separation apparatus, in most cases a separation column. Such a countercurrent column enables multiple equilibrium stages through the enhancement of the mass-transfer area between gas and liquid phases by using structured packings, consequently improving the process efficiency (McHugh and Krukonis 1986). The countercurrent operation of a separation process reduces the amount of solvent needed, increases throughput, and provides higher extract concentrations in the solvent and consequently lower residual concentrations in the liquid phase in comparison to simple-stage processes. Therefore, countercurrent processing may be useful for separations with high separation factors between the selected main components (which are called key-components), but it is considered extremely necessary for achieving a reasonable separation between substances with relatively low separation factors, such as in the deterpenation of citrus peel oils (Brunner 1994).

A simplified flowsheet of a countercurrent multistage extraction process is presented in **Fig. 5**. The equipment is generally composed of a packed separation column where gaseous and liquid phases are in contact countercurrently, a separator vessel responsible for the solvent-extract separation through pressure reduction (and consequently expansion of the two-phase flow), feed and reflux pumps, a solvent pump or compressor (depending on the physical state of the solvent), and auxiliary devices for recovering top and bottom products (extract and raffinate fractions, respectively). The fractionation columns described in the literature are composed of stainless steel tubes with maximum heights of 7 m and with internal diameters up to 25 mm. They are filled with stainless steel mesh packings and usually heated by means of electrical heating tapes. Sapphire visualization windows can be placed at different sections of the column (enriching and stripping sections) and in the separator vessels in order to observe the level of the liquid phases (Goto *et al.* 1997; Sato *et al.* 1998b; Budich 1999; Budich and Brunner 1999). The process is comparable in many aspects to rectification and it can be operated with or without extract reflux. Reflux must be employed in order to provide the enrichment of the most volatile components in the extract fractions (top product). When employing extract reflux, a stripping section will be localized below the liquid phase feed inlet, where the top products (high volatile components) are separated from the bottom products and then transported to the enriching section. The enriching section is located between the liquid feed and extract reflux inlet points, where the bottom products (low volatile components) are separated from the top product components and transported to the lower section of the column (stripping section).

In order to evaluate the process efficiency for design purposes, the number of components to be fractionated must be carefully analyzed. By means of countercurrent processes, the separation of two components into practically pure substances is possible. In fact, this case is very unusual in practice, since multicomponent complex mixtures (like citrus peel and vegetable oils) are often separated with multistage countercurrent gas extraction. When several desired components with similar properties are present in the feed material, they can be treated as a single pseudocomponent, considering then the feed-mixture as a quasi-binary system (the system is reduced to a mixture of the oil and solvent). Alternatively to the pseudocomponent approach, the solute can be represented by two key-components, preferable the hardest to separate, i.e., reducing the system to a ternary one, formed by the solvent and the key-components. Consequently, the separation of the components is assumed to take place simultaneously (Danielski 2007).

Phase equilibria

Knowledge of the solubility of the extractable and the undesirable compounds in the supercritical solvent is fundamental for understanding supercritical processes. This information allows the selection of the range of operational pressures and temperatures for a specific separation task. It also provides some indication of the separation conditions, particularly when multistage separation procedures are employed (Brunner 1994; Reverchon 1997a).

Countercurrent supercritical fractionation, as well as other separation processes, is an equilibrium-determined process with the supercritical solvent as mass separating agent. In practical terms, countercurrent gas extraction is carried out near phase equilibrium conditions mainly due to low linear flow velocities (long residence time), low viscosity and high transport coefficients. For the total separation of two or more components in a countercurrent column, a two-phase flow up to the end of the column is necessary. Additionally, in order to characterize the phase compositions, it is useful to distinguish between the distribution of the solvent, to determine the extent of the two-phase area and the distribution of the solute components. This consideration is taken into account when modeling phase equilibrium of different systems, what is extremely important for the accurate economical evaluation of the separation process. Reduction of the amount of solvent and energy requirements is necessary at pre-determined operational conditions (McHugh and Krukonis 1986; Brunner 1994).

Vapor-liquid equilibrium (VLE) data of binary systems comprising SC-CO_2 and a pure oil component or SC-CO_2 and the multicomponent mixture (raw citrus oil) have been extensively investigated by different methods. VLE data of ternary systems have also been investigated, since they are necessary for deterpenation processes and provide the knowledge on the phase behavior of some volatile aroma compounds that must be separated from the most abundant terpenes. Although the discussion of the methods for VLE determination is beyond the scope of this review, **Table 5** summarizes VLE experimental data at different temperatures and pressures for different citrus oils, including binary and ternary systems.

The large number of publications on the CO_2+limonene system demonstrate the importance of evaluating its phase behavior, since mutual solubilities and critical pressures of CO_2+raw citrus oils can be estimated directly from CO_2+limonene VLE data, especially for citrus oils with a limonene content higher than 95%. In general, the measurements were performed between 40 and 70°C and from 5 MPa to pressures close to the one-phase region. The solubility of citrus peel oil components in SC-CO_2 was obtained below 8 MPa for the studied conditions. This could be expected, since the same behavior was observed for the binary CO_2+ limonene. Smaller mutual solubilities were obtained at 50°C and pressures lower than 8 MPa.

Budich (1999) compared the quasi-binary VLE data for different orange oil mixtures with raw orange peel oil. VLE data of a terpene rich fraction (0.15% aroma components) and a 5-fold concentrate fraction (8.01% aroma components) were determined at 50, 60 and 70°C. The influence of composition on mutual solubility is presented in **Fig. 6**. As illustrated, mutual solubility data for CO_2+orange peel oil lies between both fractions, presenting smaller deviations in comparison with the enriched terpene fraction (CO_2 +terpenes, 99.85%). It is also clear that the mutual solubility decreases with increasing concentrations of high-boiling (high molecular weight) aroma components in the liquid phase, such as waxes, which are practically insoluble in CO_2.

In order to design a countercurrent deterpenation process, the relation between loading (g extract/kg CO_2) and selectivity must be taken into account. The optimal conditions for a separation task are achieved when high loading is combined with high selectivity. Since the process is conducted under isothermal conditions, separation factors (the relationship between the concentrations of the chosen key-components in the gas and liquid phases) tend to decrease at higher loadings. When the critical point of the mixture is reached, no separation is possible (homogeneous mixture), i.e., the separation factor tends to unity. Budich (1999) showed that the tendencies of the separation factors at near-

Table 5 VLE data for diverse citrus peel oil systems at different conditions.

System	T(°C) / P(MPa)	References
CO_2+limonene	34-76 / 7.7-14.1	Tufeu *et al.* 1993
	40-60 / 5.1-12.6	Iwai *et al.* 1996
	40-60 / 1.0-11.0	Suzuki and Nagahama 1996
	50-70 / 5.1-12.6	Bertucco *et al.* 1997
	50-70 / 5.1-10.6	Vieira de Melo 1997
	40-60 / 6.0-13.0	Akgün *et al.* 1999
	45 / 6.9-11.1	Berna *et al.* 2000
	42 / 3.0-10.0	Benvenuti and Gironi 2001
CO_2+α-pinene	40-60 / 6.0-13.0	Akgün *et al.* 1999
CO_2+citral	42 / 3.0-10.0	Benvenuti and Gironi 2001
CO_2+fenchone	40-60 / 6.0-13.0	Akgün *et al.* 1999
CO_2+linalool	40-60 / 4.0-11.0	Iwai *et al.* 1994
	50 / 7.5-8.4	Vieira de Melo 1997
	45-55 / 6.9-11.1	Berna *et al.* 2000
CO_2+lemon oil	50-80 / 9.8-10.4	Cabral *et al.* 1993
	40-70 / 7.0-8.5	Perre *et al.* 1994
	40-70 / max. 19.0	Franceschi *et al.* 2004
CO_2+bergamot peel oil	40-70 / max. 19.0	Franceschi *et al.* 2004
CO_2+orange peel oil	40-70 / 8.3-12.4	Temelli 1987
	50-70 / 7.0-13.0	Budich 1999; Budich and Brunner 1999
	50-70 / 7.0-13.5	Stuart *et al.* 2000
	40-70 / up to ca. 14.0	Araújo *et al.* 2002
CO_2+limonene+linalool	40-70 / 8.3-12.4	Temelli *et al.* 1990
	40 / 7.5-8.9	Vieira de Melo 1997
	40-70 / 4.0-11.0	Vieira de Melo *et al.* 1999
	42 / 6.3-8.7	Bertucco *et al.* 1997
	40-50 / 6.9-10.0	Morotomi *et al.* 1999
	45-55 / 7.0-11.0	Cháfer *et al.* 2001
	20-76 / 5.0-14.0	Raeissi and Peters 2005b
CO_2+limonene+citral	42 / 8.4 and 9.0	Benvenuti and Gironi 2001

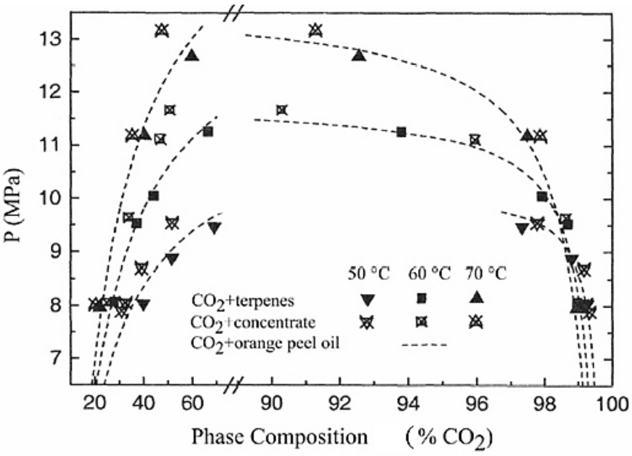

Fig. 6 Influence of product composition on mutual solubility. Adapted from Budich (1999).

critical conditions are in good agreement with critical values for the binary system CO_2+limonene, which suggests once more that VLE data for the multi-component system CO_2+orange peel oil can be estimated from the equilibrium data available for this pseudo-binary system.

Ternary mixtures, composed by CO_2+limonene+one representative aroma component, are also usually treated as model mixtures for VLE measurements of raw citrus oils. Therefore, the phase behavior of a ternary mixture can represent, with better accuracy, the behavior of a real multi-component mixture. This was observed in several works comparing the behavior of the ternary systems CO_2+limonene+linalool with the binary CO_2+citrus oils, especially when orange peel oil is considered (Temelli *et al.* 1990; Vieira de Melo 1997; Bertucco *et al.* 1997; Vieira de Melo *et al.* 1999; Budich 1999; Morotomi *et al.* 1999; Budich and Brunner 1999; Cháfer *et al.* 2001; Raeissi and Peters 2005b).

In order to investigate the use of other supercritical solvents in the deterpenation of citrus oils over a wide range of conditions, ethane has been suggested as a possible alternative to replace CO_2. VLE data of binary systems composed by ethane+limonene and ethane+linalool have been published in the last few years (Raeissi and Peters 2002; Raeissi *et al.* 2002), as well as ternary systems composed by ethane+limonene+linalool (Raeissi and Peters 2005a), which can represent with good accuracy the pseudo-binary system ethane+orange peel oil (Sampaio de Sousa *et al.* 2004, Raeissi and Peters 2004).

Countercurrent multi-stage fractionation

In order to avoid partial removal of volatile oxygenated components with the terpene fraction, during adsorption/desorption processes, a multi-stage countercurrent process may be employed. It is well known that the separation of terpenes (especially monoterpenes) from low volatile oxygenated components can be easily achieved, but multistage countercurrent processes produce interesting results when very high concentrated raw materials are used. Citrus oils are one example of these complex mixtures, with total terpene concentrations up to 99%. Therefore, investigations of the operational parameters on the recovery of determined components and improvement of product purity must be performed (Brunner 1994).

Once the geometrical characteristics of the process are defined, namely determination of column height, inner diameter and type of packing material to be used, the best operational conditions, like temperature, pressure, solvent-to-feed and reflux ratios, liquid and vapor cross section capacities must be defined. These conditions can be chosen through analysis of the equilibrium data available for each specific system (McHugh and Krukonis 1986; Brunner 1994). The determination of the number of equilibrium stages for one separation process can be established and its economic evaluation can be performed. **Table 6** summarizes relevant literature for the countercurrent multi-stage fractionation of citrus oils or even model mixtures composed of their most representative compounds with SC-CO_2.

Gerard (1984) was one of the first researchers to investigate the applicability of countercurrent deterpenation of citrus oils employing SC-CO_2. Internal reflux was proposed, once the column was heated with different temperature gradients, in order to increase the terpene concentrations in the extract stream. Internal reflux is applicable for laboratory scale columns of small diameter (maximum solubility differences caused by isobaric vapor-phase behavior), but the process can be better controlled when using external reflux, which is limited only by economical aspects. As expected, the bottom products (raffinate) were composed mainly by carotenoids and low volatile components (oxygenated aroma compounds). One suggestion proposed to improve the separation of the components, with very similar vapor pressures, was the change of the polarity of the solvent by adding water as an entrainer. In this case, the chosen components were anethole and caryophyllene, which present different solubilities in CO_2 only when saturated with water, enabling then the separation of sesquiterpenes from oxygenated compounds.

Stahl *et al.* (1987) treated sweet and bitter orange peel oils at 8.0 MPa. The starting feed material presented 90% hydrocarbon terpenes. By applying different axial temperature gradients, i.e., inducing internal reflux, they intended to achieve smaller losses during the deterpenation process. The column displayed the highest temperature in its middle, 85°C, while the temperatures were fixed at 75 and 60°C at the top and bottom of the apparatus, respectively. The lowest CO_2 density (166.7 kg/m^3) was obtained at the top, and provided a better separation between terpenes and oxygenated compounds: less than 1% oxygenated aroma compounds were obtained as top product, while the concentration of hydrocarbons at the bottom reached 42%.

The mass transfer efficiency in the fractionation of a model mixture of two terpenes (21.2% limonene and 78.8% 1,8-cineole) through countercurrent fractionation with CO_2 was investigated by Simões *et al.* (1995) at 40 and 45°C and pressures up to 9.0 MPa. The overall mass transfer coefficient was predicted by employing different mathematical models. The values obtained were relatively high in comparison to the experimental data, obtained. Separation factors were close to 1, a value that is not acceptable in a good process separation. It is also important to mention that the column employed was only 1 m height. As a final conclusion, the separation was not economically feasible due to the low selectivities obtained at the conditions investigated.

Table 6 Published studies on multistage fractionation of citrus oils with SC-CO_2.

Systems investigated	Operational conditions	References
Different citrus oils	7.0-9.0 MPa; 55-75°C	Gerard 1984
Bitter/sweet orange peel oils	8.0 MPa; temperature gradients; 60, 75 and 85°C	Stahl *et al.* 1987
Eucalyptus essential oil (system limonene-1,8 cineole)	Up to 9.0 MPa; 40 and 45°C	Simões *et al.* 1995
Model mixtures	8.8-11.8 MPa; 40-60°C	Sato *et al.* 1995
	8.8 MPa; 40-60°C; modeling	Sato *et al.* 1996
	7.5-8.0 MPa; 40-80°C	Reverchon *et al.* 1997
	Mathematical modeling	Espinosa *et al.* 2000
Orange oil + model mixture 80% limonene, 20% linalool	8.8 and 9.8 MPa; 50°C	Goto *et al.* 1997
Orange peel oil	8.8 MPa; 60°C; temperature gradients (40-60°C)	Sato *et al.* 1998b
	8.0-13.0 MPa; 50-70°C	Budich 1999; Budich and Brunner 1999; Budich *et al.* 1999
	Determination of optimal conditions (programming model)	Diaz *et al.* 2005
Bergamot oil	7.8-10.8 MPa; 40-80°C	Kondo *et al.* 2000
	8.8 MPa; 60°C; simulations	Kondo *et al.* 2002
	Up to 9.0 MPa; different temperature gradients	Poiana *et al.* 2003
Lemon oil and model mixtures	8.4-10.5 MPa; 42, 50, 60°C	Gironi and Maschietti 2005
	8.7-11.2 MPa; 50-70°C	Gironi and Maschietti 2008
Mandarin peel oil	8.0 to 11.5 MPa; 50, 60 and 70°C	Schwänke 2006; Danielski 2007; Danielski *et al.* 2008

Sato *et al.* (1995) studied the fractional extraction with supercritical carbon dioxide for the preparation of terpeneless citrus oil using a 9 mm internal diameter and 1.0 m long packed column with an axial temperature gradient of 20°C. The authors considered the separation of one citrus oil model mixture, which consisted of limonene, linalool and citral, and investigated various column temperature distributions (40-60°C), pressures of 8.8-11.8 MPa, and CO_2 flow rates between 0.091 and 0.512 g/s. Selective separation was performed due to the internal reflux in the column induced by an axial temperature gradient. The increase in pressure or CO_2 flow rate accelerated the extraction rate without decreasing the selectivity. Additionally, raw orange oil was successfully processed at a temperature gradient of 20°C, from 40°C at the bottom to 60°C at the top of the column, and a pressure of 8.8 MPa. One year later, Sato *et al.* (1996) investigated the fractionation of a mixture of limonene and linalool. The experiments were carried out with and without internal reflux. The semi-batch extraction with internal reflux induced by a temperature gradient (20°C) increased the separation selectivity. The temperatures employed were the same as presented by Sato *et al.* (1995) and the pressure was fixed at 8.8 MPa. The internal reflux ratio was calculated by the measurement of the extraction rates at the top and bottom of the column as 7.6.

A model mixture composed by 60% limonene, 10% γ-terpinene, 20% linalool, 10% linalyl acetate was employed by Reverchon *et al.* (1997) as feed material in the countercurrent fractionation with SC-CO_2. The investigated operational conditions ranged from 7.5 to 8.0 MPa and 40 to 80°C. Limonene separation was slightly improved when the reflux ratio was very high and tending to infinity. Without reflux, γ-terpinene was identified in the extract stream, mainly because it presents lower volatility than limonene. On the other hand, its separation from limonene was successfully achieved when applying total reflux. At 8.0 MPa and total extract reflux, the extract concentrations were maximized when the temperatures were increased from 70 to 80°C, reaching higher solubility conditions. In conclusion, the countercurrent deterpenation provided very interesting results when performed at higher temperatures, since the thermal stability of the products is not affected.

Cold-pressed orange oil from Brazil and a model mixture of 80% limonene and 20% linalyl acetate were investigated through total reflux and continuous countercurrent operations by Sato *et al.* (1998b). For a total reflux operation, a higher CO_2 flow rate was important to remove the terpene fractions. The increase of solvent flow rate or solvent-to-feed ratio produced a higher selectivity between terpenes and oxygenated compounds. When orange oil was used as feed material, the selectivity increase was smaller than that of the model mixture. For a continuous operation with temperature gradients from 40 to 60°C at 8.8 MPa, the authors found that terpenes were enriched at the top and the aroma fraction and waxes were better separated at the bottom and in the side stream, respectively. The side stream was used in order to avoid a higher concentration of waxes in the raffinate fraction that could cause further purification problems in the separation from the desired oxygenated aroma compounds.

The work of Budich (1999), Budich and Brunner (1999), and Budich *et al.* (1999) reported the countercurrent deterpenation of orange peel oils using SC-CO_2. In order to provide a complete understanding of the system behavior, phase equilibria measurements, countercurrent column experiments and flooding point measurements were carried out. The experimental conditions ranged from 50 to 70°C and from 8.0 to 13.0 MPa. Separation factors for the two groups of oil components, terpenes and aroma, were obtained for the system CO_2-orange peel oil at different temperatures and pressures. A short-cut stage calculation method based on the Jänecke diagram was applied to evaluate equilibrium data. **Fig. 7** shows that the required solvent-to-feed ratio decreases with increasing pressure up to a minimum value for two different extract compositions and different number of stages at 60°C. This is because the increase in loading with pressure has a more significant impact on the separation process than the decrease in selectivity. By performing the calculations, the height of a theoretical stage was found to be 0.5 m. At 60°C, 10.7 MPa and a solvent-to-feed ratio of 100, 18 theoretical stages (9 m height column) and a reflux ratio of 2.5 were required to produce a 20-fold concentrate containing 69% terpenes from a feed material concentration of 98% terpenes. With a feed flow of 100 kg/h, the authors found that the minimum inner diameter of the column from the flooding point data would be 0.4 m, proving that the production of flavor fractions of a high market value by supercritical countercurrent deterpenation can be a very competitive process.

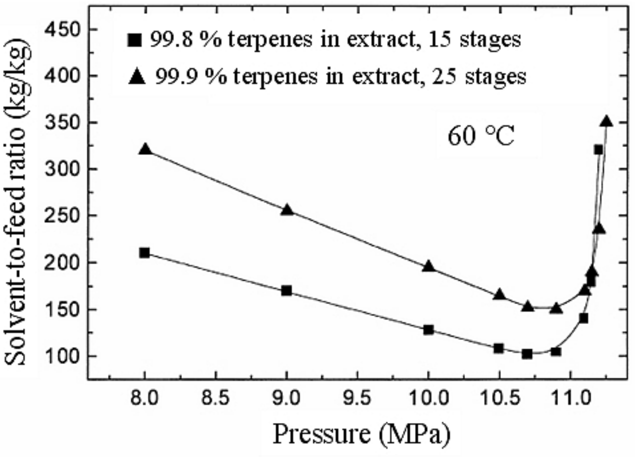

Fig. 7 Results presented by Budich (1999) and Budich *et al.* (1999) for the influence of pressure on operating conditions for a countercurrent deterpenation process producing a ten-fold concentrate.

Optimal schemes and operating conditions for the deterpenation of citrus peel oils with SC-CO_2 by means of mathematical simulations have been investigated by several researchers (Espinosa *et al.* 2000; Kondo *et al.* 2002; Diaz *et al.* 2005; Gironi and Maschietti 2008). The problem proposed was, in general, formulated as a mathematical programming model using a group contribution equation of state for rigorous phase equilibria predictions. Both thermodynamic predictions and simulation results were in most cases found to be in agreement with available experimental studies. Simulations of the countercurrent deterpenation process are necessary, since optimization results provide insights into improved accuracy of the experimental values obtained.

Diaz *et al.* (2005) determined optimal schemes and operating conditions through the formulation of a nonlinear programming model including thermodynamic predictions with a group contribution equation of state and unit models applied to the supercritical deterpenation of orange peel oil with carbon dioxide. A detailed comparison of binary and ternary equilibrium predictions with available experimental data was reported and the simulation results were in agreement with previous laboratory-scale separation data. By including different solvent cycle schemes in the mathematical model, the net profit was maximized taking into account capital and operating costs associated with the complete deterpenation process. Numerical results showed that a compression cycle was the optimal solvent recovery system. Furthermore, optimal operating conditions have been determined for the production of a five-fold concentrate and a high purity aroma composition as raffinate.

Kondo *et al.* (2002) developed a process flow diagram for citrus oil processing with SC-CO_2, employing an extraction column with and without reflux in order to evaluate the separation performance of a model mixture composed of limonene (20 to 80%) and linalyl acetate. For the calculation using the simulator SIMSCI PRO/II at 60°C and 8.8 MPa, the effects of operating conditions on extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate were observed as a function of the solvent-to-feed ratio. They concluded that extract reflux was not a rewarding technology for this case. The performance was improved with increases in the stage number at higher solvent-to-feed ratios.

The efficiency of the separation of bergamot essential oil carried out in a countercurrent column filled with Raschig rings and using SC-CO_2 as solvent was performed by Poiana *et al.* (2003). In this study, the effect of CO_2 density and the solvent-to-feed ratios were investigated in terms of product quality. The conditions that produced extracts with a similar volatile fraction composition of starting material, composed mainly by limonene (32.1%), linalool (12.1%) and linalyl acetate (29.7%), with a high yield (more than 80% recovery) were those with a low solvent-to-feed ratio. The lowest bergaptene content was obtained at low solvent density or at high solvent-to-feed ratio. Temperature gradients were used in order to achieve internal reflux. The best result was obtained at a CO_2 density of 206 kg/m^3 (8 MPa and a temperature gradient of 46-50-54°C) and a solvent-to-feed ratio of about 9.5; in this separation a bergaptene content lower than 0.01% could be measured in the extract stream. Following the same procedures, the deterpenation of bergamot oil was also carried out in a semibatch operation and a continuous countercurrent operation from 40 to 70°C and from 7.8 to 10.8 MPa. It was concluded that internal reflux, induced by the temperature gradient along the column, improved the separation selectivity (Kondo *et al.* 2000).

The deterpenation of two different cold-pressed mandarin peel oils with SC-CO_2 originating from Spain and Brazil was investigated by Schwänke (2006), Danielski (2007) and Danielski *et al.* (2008). The countercurrent experiments were carried out at pressures ranging from 8.0 to 11.5 MPa and at 50, 60 and 70°C. The evaluation of the separation was performed by analyzing solvent-to-feed ($kg_{solvent}/kg_{feed}$) and folding ratios ($kg_{feed}/kg_{raffinate}$) for each experimental condition. Additionally, the separation performance for the Spanish red oil was evaluated by the overall separation between the key-components limonene and linalool and between total terpene and aroma compounds. When performing the countercurrent fractionation of the Brazilian green mandarin peel oil, the overall separation was evaluated through the concentrations obtained of the key-components terpinolene and linalool as top and bottom products. Overall separation values between the terpene and aroma fractions were approximately two times higher for the Brazilian green oil due mainly to its higher concentration of aroma compounds in the starting raw material. The effectiveness of the separation could additionally be verified by analyzing the color of the samples and the GC-MS results obtained for experiments carried out at the same conditions (10.0 MPa and 60°C). **Fig. 8** shows comparisons between the colors obtained for both raw oils, extract and raffinate samples, according to Schwänke (2006). In **Fig. 9**, the GC-MS profiles obtained only for Spanish oil samples, namely the raw material, the extract and the raffinate, are presented (Danielski 2007; Danielski *et al.* 2008). Following the evaluation of the complete deterpenation process, the following was the design of the fractionation column based on VLE data presented by Budich (1999). **Fig. 10** presents a Jänecke diagram obtained by the authors for one experiment carried out at 10 MPa and 60°C with the Spanish red mandarin peel oil (Schwänke 2006; Danielski 2007; Danielski *et al.* 2008). The figure shows that one or two stages were determined for the stripping section and five stages for the enriching section. In the end, the authors suggested that a combination of multistage gas extraction with adsorption/desorption using SC-CO_2 as solvent may depend on the quality of the

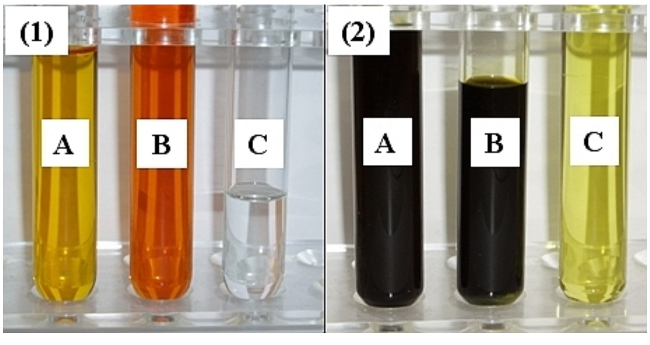

Fig. 8 Comparison between different mandarin peel oil samples. (**1**) Spanish red oil; (**2**) Brazilian green oil. (**A**), (**B**) and (**C**) correspond to the raw oil, raffinate and extract samples, respectively (Schwänke 2006).

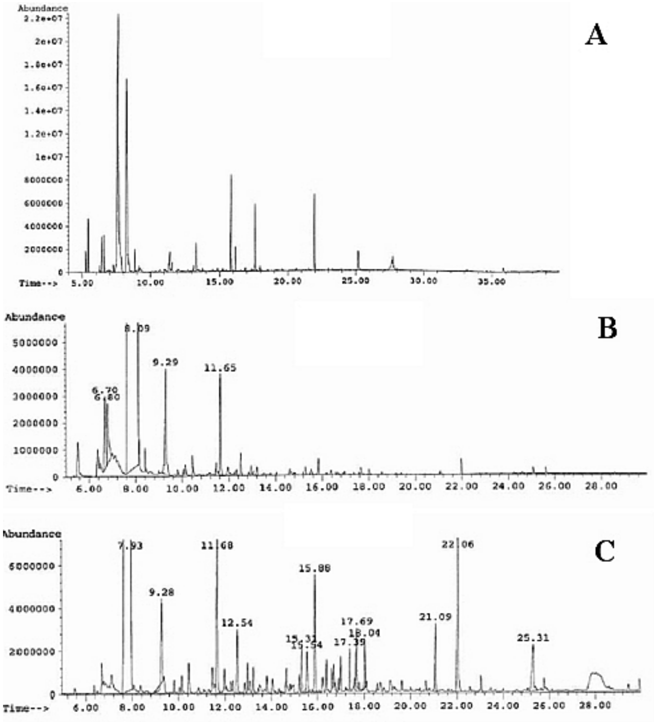

Fig. 9 GC-MS profiles obtained for different Spanish mandarin oil samples. (**A**) Raw material; (**B**) Extract sample; (**C**) Raffinate sample. Terpenes' peaks present retention times lower than 11 minutes. From Danielski (2007).

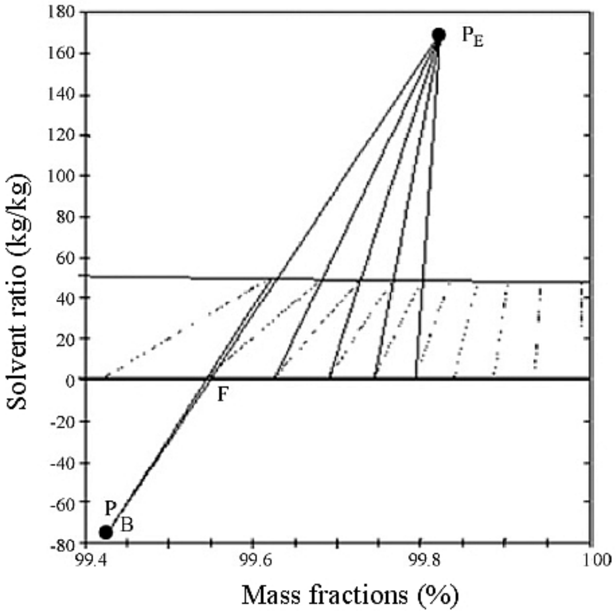

Fig. 10 Jänecke diagram obtained for the countercurrent deterpenation of Spanish mandarin oil at 10.0 MPa and 60°C. Based on Schwänke (2006), Danielski (2007) and Danielski *et al.* (2008).

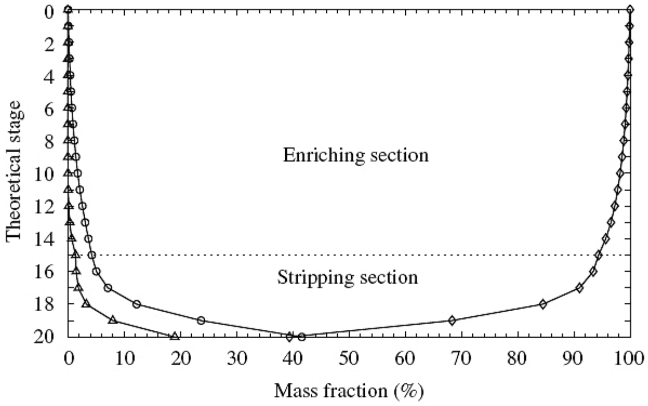

Fig. 11 Mass fraction profiles of monoterpenes, oxygenated compounds and sesquiterpenes in the liquid phase along the column according to Gironi and Maschietti (2008). *N* = 0 stands for the distillate. Feed inlet position: *N* = 15 (◊: monoterpenes; ○: oxygenated compounds; Δ: sesquiterpenes).

products to be generated.

The recent work of Gironi and Maschietti (2008) dealt with the development of a thermodynamic model based on the Peng–Robinson equation of state in order to perform high-pressure phase equilibria calculations for the system CO$_2$–lemon essential oil. The multi-component natural oil was simulated by a mixture of three key-components, one for each relevant class of compounds. Monoterpenes (93.9% of the total lemon oil amount) were represented by limonene (53.5%), monoterpene oxygenated compounds (4.2%) were represented by citral (2.6%), and sesquiterpenes (1.9%) were represented by β-caryophyllene (0.4%). Initially, the proposed model was validated on semi-batch experimental data and then used to simulate the behavior of a continuously operated countercurrent column. Experiments on the deterpenation process using a 20 mm internal diameter packed column (Sulzer EX packings, packed bed height of 1155 mm), operating as a stripping section, were carried out at a temperature range from 50 to 70°C and pressure range from 8.7 to 11.2 MPa. The comparison between experimental results and process simulation demonstrated that the proposed model was capable of reliable predictions of the behavior of the countercurrent continuous deterpenation process. Furthermore, an average height equivalent to a theoretical plate of about 0.40 m was estimated for the stated packing and operating conditions. A case study for the production of 10-fold high quality oil, with strict specifications for the recovery of oxygenated compounds (99%), was investigated by simulations of a continuous countercurrent process with an external reflux. The linkage between the number of theoretical stages, the reflux and the solvent-to-feed ratios was investigated using the previously mentioned pressure and temperature ranges. Operating conditions at higher pressure and temperature proved to be more effective, as presented when operating a 20 theoretical stage column at 70°C and 11.2 MPa, where it was possible to attain process specifications with a solvent-to-feed ratio of approximately 63. **Fig. 11** shows the concentration profiles obtained under these operational conditions along the column. The feed inlet position was performed at stage number (*N*) 15. In this case, a 10-fold deterpenated oil (oxygenated compounds concentration of 41.6%) was obtained using a reflux ratio of 0.92.

Although the countercurrent deterpenation of citrus oils with SC-CO$_2$ is considered a good alternative for the conventional processes with reliable results, the use of high-pressurized ethane as solvent in the deterpenation of orange peel oil has been recently investigated (Raeissi *et al.* 2008). In order to compare the separation performances of ethane and carbon dioxide as solvents for orange oil deterpenation, VLE data were predicted and the separation between the terpene and aroma fractions was evaluated and compared for both solvents. Although solvent selectivity is a determining factor in many extraction tasks, this is not entirely valid in the case of citrus peel oil deterpenation. When performing deterpenation tasks, obtaining a highly purified (terpeneless) product is not necessarily the main goal. Generally, it is simply desirable to partially remove the terpenes and to concentrate the oil from about 1% aroma constituents to around 5%. The authors showed that compared to CO$_2$, ethane is the better solvent for citrus constituents, presenting a higher solvent power and resulting in a decreased solvent/feed mass ratio for ethane when the processes are compared at the same reduced pressure. Additionally, since the critical pressure of ethane is lower (4.88 MPa), the ethane-operated column requires lower operational pressures (a factor of 0.7 can be employed), as well as lower energy requirements when recycling the solvent. On the other hand, problems related to safety during the operation of an ethane-based separation plant must be taken into account.

CONCLUDING REMARKS

We reviewed the main aspects related to the deterpenation of citrus peel oils with supercritical carbon dioxide. Two methods, namely adsorption/desorption and countercurrent multistage fractionation, are highlighted by several published works in the last two decades. Deterpenation processes by adsorption/desorption may be used when highly purified or even terpeneless extracts are desired. However, the plant capacities will be smaller than those using the continuous countercurrent fractionation. In general, the removal of terpenes from citrus peel oils by means of desorption has been successfully achieved by employing silica gel as adsorbent. The process may be carried out at low CO$_2$ densities (from 200 to 500 kg/m^3), with pressures ranging from 7.0 to 11.0 MPa and temperatures from 35 to 50°C. Since the oxygenated aroma compounds present polar characteristics, they can selectively desorb from the silica polar sites by applying higher CO$_2$ densities at pressures of 20.0 MPa at 40°C (CO$_2$ density of 840 kg/m^3). The continuous countercurrent multistage fractionation has been investigated by using columns with structured packings. Extended and reliable solubility data are required for the deterpenation of essential oil compounds, since the partition factors between the fluid and vapor phases are needed. Several authors have simulated the countercurrent process and successfully compared the results with available experimental data. The deterpenation process has given better results when applyied to external extract reflux and when internal reflux is induced (column operated under temperature gradients). Most of the works reported temperatures between 40 and 70°C and pressures ranging from 7.0 to 12.0 MPa as the best operational conditions for the removal of terpenes from citrus peel oils using SC-CO$_2$ as solvent. The use of gases with low critical properties as solvent (like ethane, Tc = 32.3°C and Pc = 4.88 MPa) in the deterpenation of citrus oils may be applicable when economical, environmental and safety aspects are considered.

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