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Recent advances on supercritical fluid extraction of essential oils

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Supercritical fluid extraction (SFE) is one of the most commonly used extraction techniques in the course of analysis or preparation. It is environmentally friendly and has some advantages over other conventional extraction methods. This review covers the recent developments of SFE in the extraction of essential oils from the plant materials during the period 2005 to 2011, in particular some factors influencing SFE extraction yield, its characteristics and applications.

Key words: Supercritical fluid extraction, essential oils, review.

INTRODUCTION

Solvent extraction is one of the oldest methods of separation known. The science of solvent extraction has evolved over a long period of time and much progress has been made in the understanding of solvation and the properties of liquid mixtures used in extraction processes. Hannay and Hogarth's (1879) early observations on the dissolution of solutes in supercritical fluid (SCF) media introduced the possibility of a new solvent medium. However, it is recently (around 1960) that commercial process applications of supercritical fluid extraction have been extensively examined (Herrero et al., 2010).

In recent decades, the supercritical fluid extraction (SFE) has received special attention in the fields of solid material extraction and fractionation of liquid mixtures. Nowadays, the possibility of extracting and fractionating oils (plant and animal) receives widespread interest due to the direct applications in the food and pharmaceutical industries for the generation of high-value products (Danielski, 2007). Moreover, conventional methods are usually carried out at high temperatures, which can be responsible for the destruction of valuable substances. Additionally, the use of organic solvents can also lead to product contamination with solvent residues (Zaidul et al., 2006, 2007).SFE method is very advantageous and environmentally friendly over other conventional either solvent or enzyme extraction methods for recovering natural oil. Use of SFE technology that offers suitable extraction and fractionation appears to be promising for the food and pharmaceutical industries. There are many literatures about the natural materials extraction with SFE such as vetiver root (Talansier et al., 2008), sunflower (Salgin et al., 2006; Fiori, 2009), banana peel (Comim et al., 2010), jojoba seed (Salgin, 2007), grape seed (Fiori, 2007; Passos et al., 2009; Yilmaz et al., 2010) and sesame seed (Corso et al., 2010).

In recent years, there has been an increasing interest in essential oils extracted from various herbs and aromatic plants. This interest is to discover their multifunctional properties in addition to their classical roles as food additives and/or fragrances. Newly discovered properties of essential oils include antibacterial, antifungal, antioxidant and anti-inflammatory activities. The pharmacological properties of essential oils extracted from plants have been the focus of interest from both academia and the pharmaceutical industry. In addition, the insecticidal activities of essential oils are of interest to agricultural scientists and agri-businesses. Essential oils are now widely used as natural insecticides, cosmeceuticals, and aroma therapeutic agents.

SFE works have been the subject of several reviews

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(Reverchon and Demarco, 2006; Pourmortazavi and Hajimirsadeghi, 2007; Diaz and Brignole, 2009; Sahena et al., 2009; Herrero et al., 2010). Therefore, we will limit time interval of our analysis to the last several years (since 2005). In this paper, recent progresses on extraction methods of essential oils particularly SFE are reviewed.

ESSENTIAL OIL

Essential oils represent a small fraction of a plant's composition but confer the characteristic for which aromatic plants are used in the pharmaceutical, food and fragrance industries. Essential oils have a complex composition, containing from a few dozen to several hundred constituents, especially hydrocarbons and oxygenated compounds. Both hydrocarbons and oxygenated compounds are responsible for the characteristic odors and flavors (Pourmortazavi and Hajimirsadeghi, 2007). The proportion of individual compounds in the oil composition is different from trace levels to over 90% (δ-limonene in orange oil). The aroma's oil is the result of the combination of the aromas of all components. The components include two groups of distinct biosynthetical origin. The main group is composed of terpenes and terpenoids and the other of aromatic and aliphatic constituents, all characterized by low molecular weight. Trace components are important, since they give the oil a characteristic and natural odor. Thus, it is important that the natural proportion of the components is maintained during extraction of the essential oils from plants by any procedure (Anitescu et al., 1997).

Since the middle ages, essential oils have been widely used for bactericidal (Antonio et al., 2009; Lin et al., 2010), virucidal (Jackwood et al., 2010), fungicidal (Nguefack et al., 2009), acaricidal (Sertkaya et al., 2010), insecticidal (Pavela, 2005; Liu et al., 2006), medicinal and cosmetic applications (Bakkali et al., 2008), especially nowadays in pharmaceutical, sanitary, cosmetic, agricultural and food industries. Because of the mode of extraction, mostly by distillation from aromatic plants, they contain a variety of volatile molecules such as terpenes and terpenoids, phenol-derived aromatic components and aliphatic components. *In vitro* physicochemical assays characterize most of them as antioxidants. However, recent work shows that in eukaryotic cells, essential oils can act as prooxidants affecting inner cell membranes and organelles such as mitochondria. Depending on type and concentration, they exhibit cytotoxic effects on living cells, but are usually nongenotoxic. In some cases, changes in intracellular redox potential and mitochondrial dysfunction induced by essential oils can be associated with their capacity to exert antigenotoxic effects. These findings suggest that, at least in part, the encountered beneficial effects of essential oils are due to prooxidant effects on the cellular level (Bakkali et al., 2008).

Methods of essential oils extraction

A large number of plant species contain volatile chemical compounds which can be extracted as an essential oil. Different methods are used to separate these oils from the various plant materials. Although it seems relatively simple to isolate such oils, the composition of oil may vary to a large extent depending on the extraction method used. The advantages and disadvantages of some methods such as hydrodistillation (Cassel and Vargas, 2006; Cassel et al., 2009), solvent extraction (Chyau et al., 2007), simultaneous distillation-extraction, supercritical carbon dioxide extraction and the use of microwave ovens have been discussed in extension model of the extraction of essential oil (Cravotto et al., 2007; Chao et al., 2008; Bousbia et al., 2009).

Steam distillation and solvent-extraction

The steam distillation is a traditional technique for essential oils (Demorais et al., 2007; Smelcerovic et al., 2007; Telascrea et al., 2007; Di Leo Lira et al., 2009; Jeong et al., 2009). This is a very simple process, but suffers of many drawbacks: Thermal degradation, hydrolysis and solubilization in water of some compounds that alter the flavour and fragrance profile of many essential oils extracted by this technique.

Chyau et al. (2007) studied on the essential oil of *Glossogyne tenuifolia* using a simultaneous steam-distillation and solvent-extraction (SDE) apparatus for the first time. However hydro- and steam-distillation have several disadvantages, such as incomplete extraction of essential oils from plant materials, high operating temperatures with the consequent breakdown of thermally labile components, promotion of hydration reactions of chemical constituents, and require a post-extraction process to remove water. Solvent extraction overcomes the drawbacks of distillation, but has the major disadvantage of solvent residue in the extracts (Metherel et al., 2009).

Ideally, extraction procedures should be environment-tally friendly and should not create additional pollution. Steam extraction and solvent extraction do not meet these criteria because they generate large volumes of contaminated, hazardous solvents and emit toxic fumes. Recently clean techniques, such as SFE, microwave and ultrasound, for extracting essential oils from complex matrices, have been developed where they can be used routinely.

Ultrasound extraction

Ultrasound-assisted extraction (UAE) has been widely used

for the extraction of nutritional material, such as lipids (Metherelet al., 2009), proteins (Zhu et al., 2009), flavoring (Chen et al., 2007; Da Porto et al., 2009), essential oils (Kimbaris et al., 2006) and bioactive compounds (e.g., flavonoids (Ma et al., 2008), carotenoids (Sun et al., 2006; Yue et al., 2006) and polysaccharides (Iida et al., 2008; Chen et al., 2010; Wei et al., 2010; Yan et al., 2011). Compared with traditional solvent extraction methods, ultrasound extraction can improve extraction efficiency and extraction rate, reduce extraction temperature, and increase the selection ranges of the solvents (Vilkhu et al., 2008). Also the ultrasonic does not affect the composition of the almond oil, but the ultrasonic cavitating energy can cause structure breakage of the almond powder and greatly reduce the extraction time (Zhang et al., 2009). In view of its growing use for isolating organic compounds and its significant advantages, the future introduction and dissemination of ultrasound equipment seem to be assured for more essential oils extraction.

Microwave extraction

The use of microwaves for isolating essential oils has recently been reported (Deng et al., 2006; Bayramoglu et al., 2008). Microwave technology has allowed the development of rapid, safe, and cheap methods for extracting essential oil and does not require samples devoid of water (Chemat et al., 2006; Bousbia et al., 2009). Recently, extraction equipment that combines microwave energy with small volumes of solvent has appeared, resulting in the procedure known as microwave-assisted extraction (Li et al., 2006). Results from various types of biological samples obtained by this method are qualitatively and quantitatively compared to the steam distillation method (Ferhat et al., 2006; Bendahou et al., 2008; Sahraoui et al., 2008; Farhat et al., 2009, 2011). However, it still uses the organic solvent, not a green method.

Supercritical fluid extraction

Supercritical fluid extraction has been used for the extraction of flavors and fragrances from natural materials. The SFE is a separation technology that uses supercritical fluid as the solvent. Every fluid is characterized by a critical point, which is defined in terms of the critical temperature and critical pressure (Brunner, 1994). Fluids cannot be liquefied above the critical temperature regardless of the pressure applied, but may reach a density close to the liquid state. A substance is considered to be a supercritical fluid when it is above its critical temperature and critical pressure. Several compounds have been examined as SFE solvents. For example, hydrocarbons such as hexane, pentane and butane, nitrous oxide, sulphur hexafluoride and fluorinated hydrocarbons.

As will be seen throughout this paper, the main supercritical solvent used is carbon dioxide. Carbon dioxide (critical conditions = 30.9°C and 73.8 bar) is cheap, environmentally friendly and generally recognized as safe. Supercritical CO_2 (SC-CO_2) is also attractive because of its high diffusivity and its easily tuneable solvent strength. Another advantage is that CO_2 is gaseous at room temperature and ordinary pressure, which makes analyte recovery very simple and provides solvent-free analytes (Herreroet al., 2010). Also important for the sample preparation of food and natural products, is the ability of SFE using CO_2 to be operated at low temperatures using a non-oxidant medium, which allows the extraction of thermally labile or easily oxidized compounds. The main drawback of SC-CO_2 is its low polarity, problem that can be overcome employing polar modifiers (co-solvents) to change the polarity of the supercritical fluid and to increase its solvating power towards the analyte of interest. The compounds that are added to the primary fluid to enhance extraction efficiency are known as co-solvents. For example, the addition of 1 to 10% methanol or ethanol to CO_2 expands its extraction range to include more polar lipids. When the extraction is performed with SC-CO_2 containing 20% ethanol, more than 80% of the phospholipids are recovered from salmon roe (Tanaka et al., 2004). In a word, carbon dioxide is an ideal solvent for the extraction of natural products because it is non-toxic, non-explosive, readily available and easy to remove from the extracted product.

SC-CO_2 extraction has been an excellent alternative method for seed oil extraction to replace conventional industrial methods. It becomes the focus of attention due to its chemical and physical properties: Non-flammable, non-toxic, non-corrosive, etc. Furthermore, the extracted product has a good quality and scarcely needs any particular refining operation (Han et al., 2009). Thus, SC-CO_2 technology has been applied to the extraction of oil from a large number of materials. The supercritical CO_2 apparatus is showed in the Figure 1.

Effect of extraction parameters

One of the main aspects that should be considered in SFE is the extraction optimization. The use of the optimum values for the different variables influencing the SFE extractions could significantly enhance the recovery or extraction yield of a target compound.

Effect of temperature and pressure

The change of oil yield with the temperature is due to two kinds of effects. On one hand, the increasing of temperature results in the decrease of solvent density

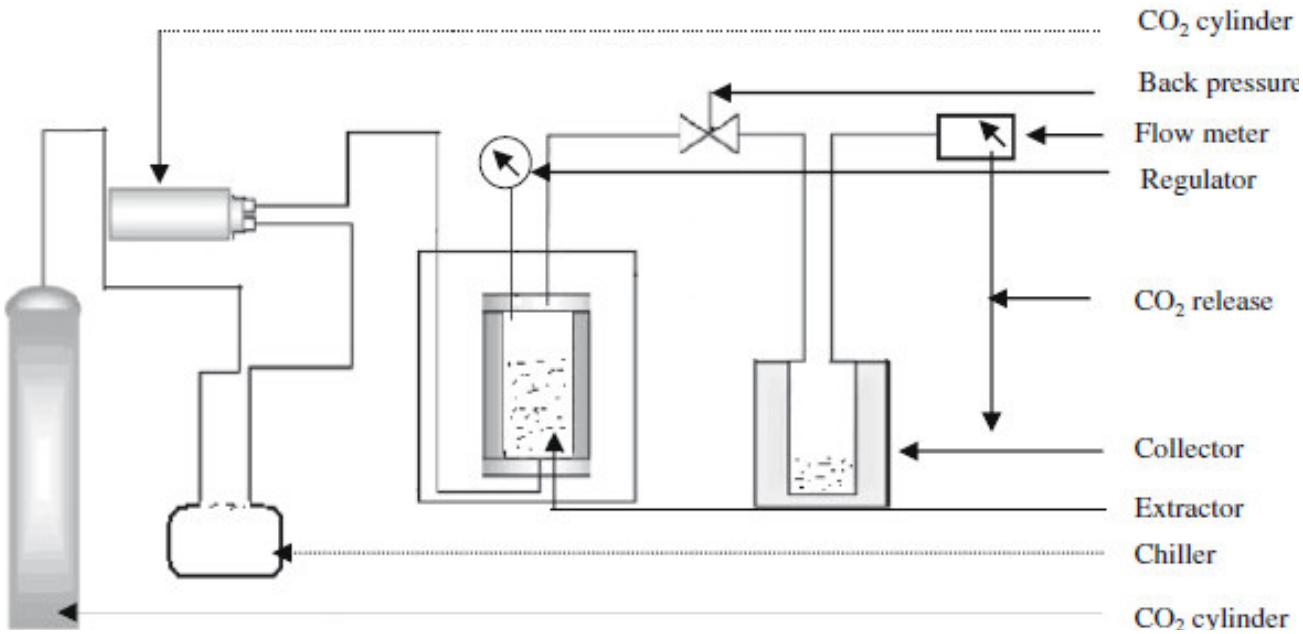

Figure 1. Supercritical CO_2 apparatus (Pradhan et al., 2010).

thus decreases the solubility of seed oil in supercritical fluid (SCF). However, high pressure is not always recommended due to increased repulsing solute-solvent interactions resulting from highly compressed CO_2 at high-pressure levels, which potentially induce complex extraction and difficult analysis. On the other hand, the saturation pressure of solute in SCF increases with the increase of temperature, which improves the solubility (Terada et al., 2010).

It is clear that with the increase of pressure, the oil yield increases. It is well known that with the increase of pressure, the density of SCF-CO_2 increases, and the solubility of solute increases. The extraction yield enhances significantly with the increase of pressure, due to the increase of the solubility of the oil components (Guan et al., 2007). This is attributed to the increase of the CO_2 density, which results in the increase of its dissolving ability.

Temperature seems to promote the rapid release of the monoterpene hydrocarbons from the plant matrix (Grosso et al., 2008), as could be observed after only 10 min. Su et al. (Zhang et al., 2010) studied supercritical fluid carbon dioxide of seed oil from yellow horn. The extraction pressure is the main parameter that influenced the extraction efficiency. It could be observed that the yield of oil significantly increases with the increase of pressure at a given temperature, especially at low pressure and temperature. If the given temperature is higher than a certain value (about 45℃), while pressure is rising, the oil yield increases at low-pressure levels. Once the pressure reaches high levels, the oil yield slightly decreases.

The influence of temperature on extraction is more difficult to predict than that of pressure, because of its two counter effects on the yield of oil. First, the temperature elevation decreases the density of CO_2, leading to a reduction in the solvent power to dissolve the solute. Second, the temperature rise increases the vapor pressure of the solutes, bringing about the elevation in the solubility of oils in SF-CO_2. Consequently, the solubility of the solute is likely to decrease, keep constant, or increase with rising temperatures at constant pressure, which depends on whether the solvent density or the solute vapor pressure is the predominant one.

Response surface methodology (RSM) was employed to optimize the conditions of supercritical CO_2 extraction of the whole berry oil from sea buckthorn (Xu et al., 2008). The pressure has a positive linear effect on oil yield at low-pressure levels. At high-pressure levels, however, the negative quadratic effect of pressure on the oil yield also becomes important. Temperature shows a negative linear effect, while the interaction between temperature and pressure has a positive effect on the oil yield. These two opposing effects are clearly seen in Figure 2. At low pressure levels, the oil yield decreases with the rise of temperature, most likely due to the reduced density of CO_2 at higher temperatures. At higher pressures, however, the oil yield increases with the rise of temperature. The crossover pressure, beyond which the effect of temperature on the oil yield begins to reverse, is about 30 MPa.

Claudia et al. (Passos et al., 2010) studied the SFE of grape seed (*Vitis vinifera* L.) oil, assessing the effect of pressure and temperature on the antioxidant capacity

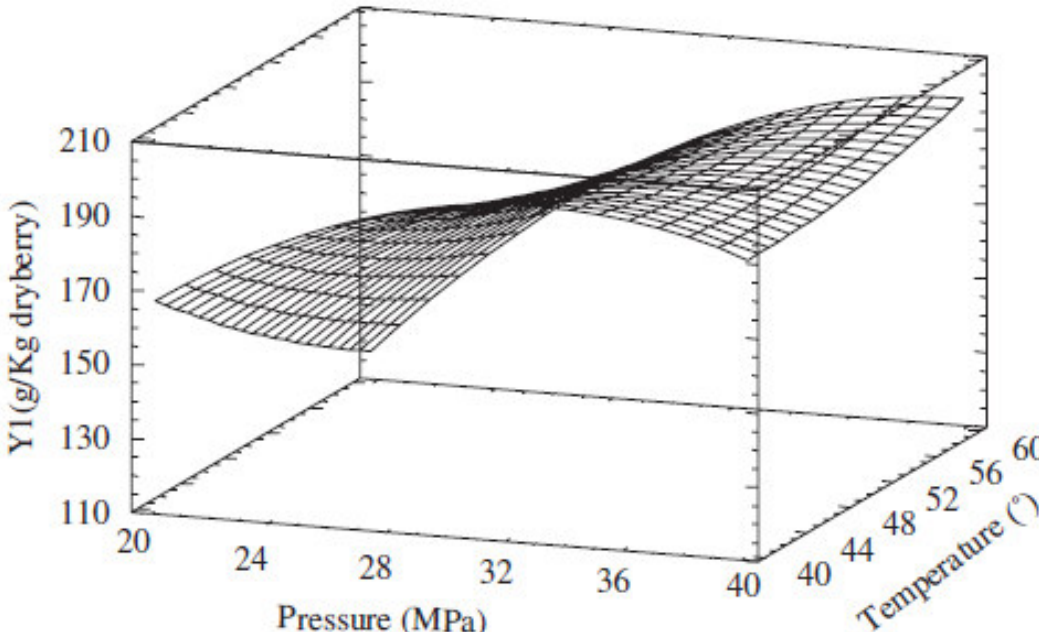

Figure 2. Surface plot of the oil yield (Y1) as a function of pressure and temperature at fixed CO_2 flow rate of 15 L/h and extraction time of 60 min (Xu et al., 2008).

(AOC). The results show that the AOC increases with the increase of pressure and/or temperature, although temperature imparts the strongest effect. Such results may be interpreted by the influence that pressure and temperature exert on solubility, more precisely upon CO_2 density and vapor pressure of the interested antioxidant molecules. The increasing pressure increases solvent density, which enhances solubility. On the contrary, when temperature raises, the density decreases inherently, while solute vapor pressure increases instead.

Similar crossover phenomena are also reported for the extraction of other oils by SC-CO_2 (Mitra et al., 2009; Silva et al., 2009; Wei et al., 2009).

Effect of pressure on supercritical carbon dioxide extraction from various seeds was studied (Machmudah et al., 2008). Three kinds of seeds (rosehip, loquat and physic nut) are used as materials. At constant temperature, the recovery of rose hip seed oil increases with the increase of pressure at short extraction time, but decreases over progressing extraction time. In the extraction of rosehip seed oil, the cross-over region of the pressure curves shift with increasing temperature. The recovery of loquat seed oil increases with the decrease of pressure at the higher temperatures, but at the lowest temperature (40°C) recovery of extract is independent on the pressure. For physic nut, the increasing pressure causes an increase in extraction recovery at constant temperature. Due to oil content in the physic nut seed is high, high recovery can be obtained, especially at high pressure. However, the SC-CO_2 cannot completely extract the oil from the seeds compared with hexane soxhlet extraction. For physic nut, extraction should be conducted at high pressures and temperatures to extract bio-diesel oil and remove toxic compounds from physic nuts for use as high-protein meal.

Effect of sample particle sizes and packed amount

Besides temperature and pressure, the particle size may have a critical impact on the extraction efficiency. As anticipated from basic physical considerations, the smaller the particles, the greater the effective fluid solid contact area, the higher the extraction rate. Moreover, the slope of first part of extraction curve of large particles is lower than that of small particles, indicating that the oil content is not saturated in the CO_2. That is probably because the quantity or surface area of easily accessible oil is not sufficient (Han et al., 2009).

Figure 3 shows two examples about the effect of substrate particle size on the extraction rate and yield of plant essential oils using SC-CO_2 for sesame seed oil (Figure 3A) and sage (Figure 3B). In both cases, the large improvements in extraction kinetics can be explained by the positive effect of a reduced particle size on the internal resistance to mass transfer in the solid matrix. Indeed, the extraction rate increased because of a shortening in the diffusion path. Furthermore, improvements in the grinding process leading to smaller particles caused increases in the specific surface area as well as a disruption of the cell walls and other inner barriers to mass transfer, thus leaving the essential oil more

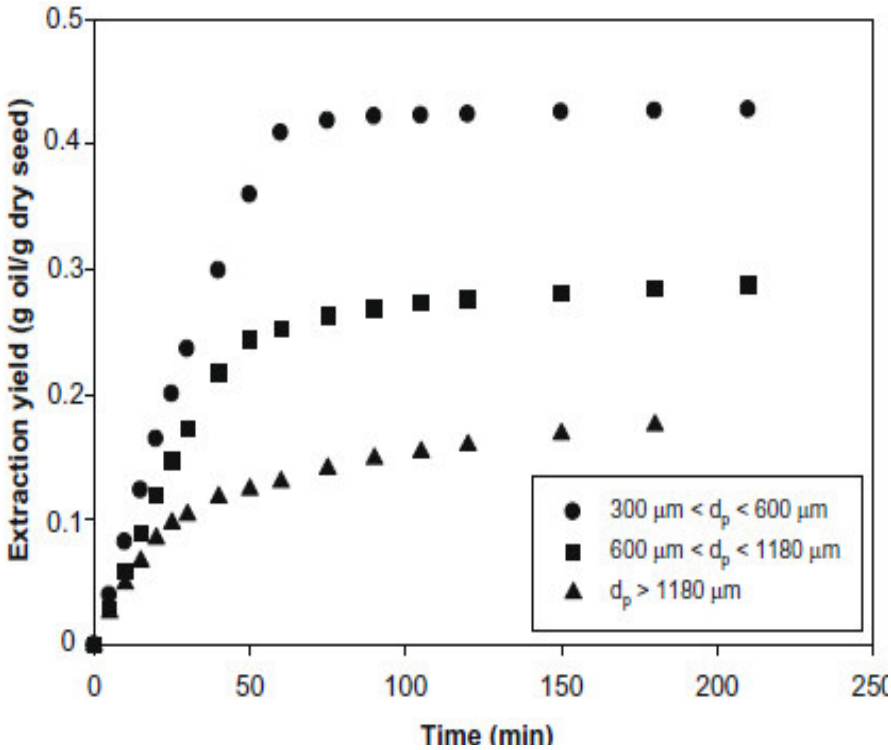

Figure 3A. Effect of particle size on the extraction yield of sesame oil with time at 50°C, 350 bar and 1.81 g CO_2/min (Dökeret al., 2010).

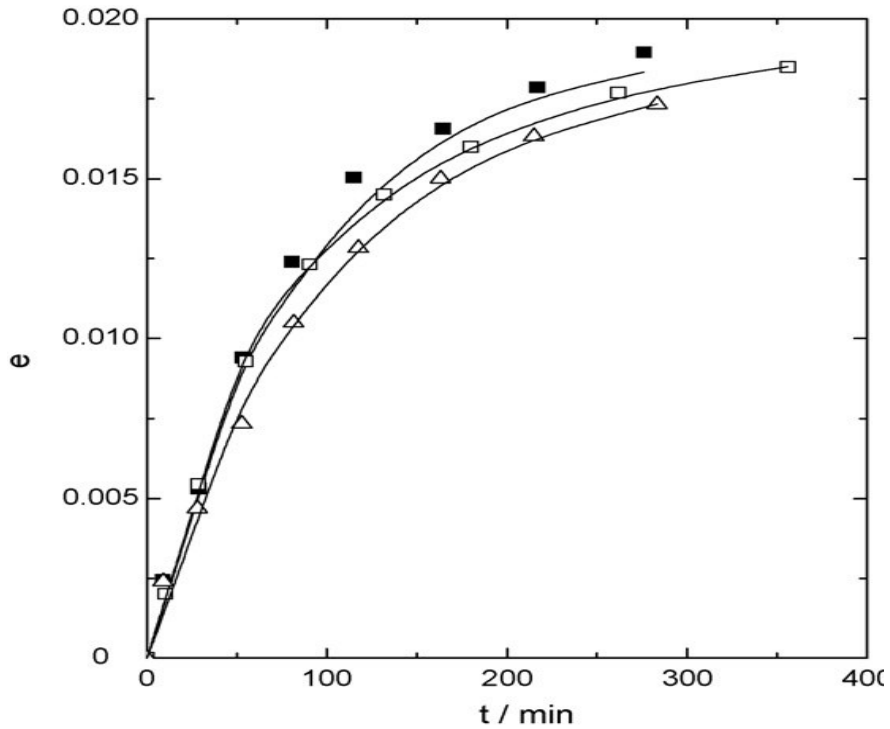

Figure 3B. Influence of plant mean particle diameter in the supercritical extraction of sage oil, e vs t (min), experiments 90 bar-40°C-1.32 kg/h-0.8mm, ■; 90 bar-40°C-1.32 kg/h-0.5 mm, □ ; 90 bar-40°C-1.32 kg/h-0.3 mm,▵; — Sovová's model (Langa et al., 2009)

accessible to the SC-CO_2 (Döker et al., 2010). Intraparticle diffusion resistance becomes smaller for small particle sizes because of the shorter diffusion path. Effect of intraparticle diffusion seems to gain importance for large particles causing appreciable decrease in the extraction. In that case, part of the oil is not extracted due to the very long diffusion times of the solvent in the vegetable seed particles. It means that the rate of extraction is also increased because with grinding more of the oil is freed from the cells and therefore more accessible. This effect may be stronger with smaller particle sizes. Hence, extraction yield increases with the decrease of the particle size, as noted in the literature (Yin et al., 2005; Salgin et al., 2006; Ozkal et al., 2005; Louli et al., 2004). According to previous investigations (Glisic et al., 2007; Sandra et al., 2007; Zizovic et al., 2007), we can also get a conclusion: Particle size has no influence on the extraction rate in two outermost cases: Fine milled material and coarsely ground plant material. The knowledge of secretory structure makes possible prediction of herbaceous material behavior during the SFE of essential oils. In the case of SFE of species with secretory ducts, it can be expected that particle size will have no influence on evolution of extraction yield, which is the fact of interest from the point of industrial scale SFE of essential oils. So researchers should make a specific investigation to determine whether sample particle sizes can influence extraction yields during the SFE process. Then a suitable particle size can be employed.

Effect of extraction time

The extraction process is composed of three stages: Rapid extraction of free solute, transitional stage of surface and internal diffusion and slow extraction mainly based on the internal diffusion. The time consumed in the first extraction stage depends both on the solute solubility in SCF-CO_2 and on the particle size. Yin et al. (2005) reported that most parts of seed oil were extracted in the first stage (about 90 to 100 min). Safaralie et al. (2010) extracted essential oil from valerian roots. The dynamic extraction time has a dual effect on the extraction of valerenic acids. However, the enhancement of dynamic time leads to an increase in the oil yield. That might be due to the drag of a part of the extracted volatile compounds by CO_2 from the collecting vessel and/or decomposition of desired constituents during this time.

Effect of SCF-CO2 flow rate

Liu et al. (2009) examined extraction of pomegranate seed oil by using supercritical carbon dioxide. The CO_2 flow rate exhibits a positive and significant effect on the pomegranate seed oil yield. It might be due to the decrease in the mass transfer resistance with increasing flow rate.

From the engineering point of view, the SFE mechanism contains three successive steps: Solute dissolution, intraparticle diffusion and external diffusion. The controlling step is changing gradually and slowly, not sharply (Forment, 1979). For example, in the initial stage of extraction ($t = 0$, $r = R_0$), the main resistance may come from the external diffusion or solute dissolution, so it will be external diffusion limited or solute dissolution limited; at this stage, the SCF-CO_2 flow rate may has significant influence on the extraction yield. With the dissolution progressing, the dissolution front is moving from the external surface to the center of particle gradually, and the intraparticle diffusion distance (R_0-r) is becoming bigger and bigger, the intraparticle diffusion resistance will increase accordingly (Forment, 1979). So eventually (at the later stage) the system will convert from external diffusion controlling or dissolution controlling into intra-particle diffusion controlling; at this stage, the SCF-CO_2 flow rate has no influence on the extraction yield (Forment, 1979). It is also confirmed by Perakis et al. (2010) whose research suggested that intraparticle diffusion resistance was dominant in the SFE process. Therefore, the controlling step is relative rather than absolute, and dynamic rather than static (Forment, 1979).

Effect of modifier

Due to the limited solubility of polar organic compounds in the supercritical carbon dioxide, quantitative extraction of these compounds with pure supercritical CO_2 is not possible. Firstly, the addition of a polar modifier to supercritical carbon dioxide decreases the efficiency of the extraction. Most of essential oil is non-polar component; therefore, because of decreasing their solubility in supercritical CO_2, the efficiency of extraction decreases. But by adding of more methanol as a modifier, due to an extraction of unwanted components such as free fatty acids, alcohols and waxes, the efficiency of the extraction increases (Ghasemi et al., 2007).

Zahedi et al (2010) investigated the effect of methanol on extraction of nimbin from neem seeds. When methanol is used as a co-solvent, there is no local equilibrium between the solid and the solvent at each time and enough time is necessary to reach equilibrium conditions. This needed time is referred to as delayed time and has been calculated using the experimental data. Some time should elapse to reach equilibrium and this time is delayed time. In addition, from a thermodynamic point of view, the equilibrium constant of nimbin between solid and solvent also have been changed, so the new equilibrium constant should be calculated.

The effects of every parameter of pressure, temperature

and SC-CO_2 density are interacted. The solubility of oil directly affects the extraction rate and it is controlled by a balance between the SC-CO_2 density and the oil vapor pressure. At high pressure, the influence of temperature on the solubility of oil is predominated by the oil vapor pressure effect, and then the solubility of oil increases with the increase of temperature. While at low pressure, SC-CO_2 density has a pronounced effect on the solubility of oil and the solubility decreases with the increase of temperature (Kiriamiti et al., 2002).

In 2010, Danh et al. (2010) investigated the effect of pressure, temperature and amounts of added ethanol on vetiver essential oil by using SCE. In short, ethanol-modified SCE performs at low temperature; low pressure and high concentration of ethanol have great application potential for producing high yields of vetiver oil with low pressure extraction apparatus.

NATURE PRODUCT APPLICATION

SFE has for long been used to extract bioactive compounds from plant materials in order to characterize compounds responsible for a specific functional activity. In Table 1, a summary of the recent works published on this topic is shown.

EXAMPLES OF SFE IN ESSENTIAL OILS

Probably, the most extended use of SFE is in the essential oil extraction. A high variety of samples, type of materials, target compounds and procedures have been published in the last years. A summary of some essential oils extraction studies using SC--CO_2 is presented in Table 2.

SFE has been successfully used to obtain oil from seeds of: apricot, palm, canola, rape, soybean, sunflower, jojoba, sesame, celery, parsley, neem, amaranth, borage, flax and grape. Oil has been also extracted from nuts such as acorn, walnut, almond and pistachio (Sánchez-Vicenteet al., 2009).

Comparison of SC-CO_2 extraction and solvent extraction

Solvent extraction is a common method of lipid extraction. The advantages of SFE over other conventional processes such as extraction by solvents and separation by distillation are automation, the reduction in operational steps, safe operation due to the use of nonorganic solvents and the use of moderate temperature in the critical range favorable for heat labile foods. The main advantage of SFE is the excellent quality of the resulting product. For example, SFE is more advantageous than the hydrodistillation for the extraction of oils from *Salvia mirzayanii* and *Nepeta persica* (Yamini et al., 2008; Khajeh et al., 2010), even grape seed by using enzymatically pre-treated (Passos et al., 2009). For the extraction of patchouli essential oil, supercritical carbon dioxide shows better results in terms of yield and oil quality than steam distillation, besides offering the advantage of not promoting the decomposition of possibly thermolabile compounds (Donelian et al., 2009).

A comparison of SFE and solvent extraction is shown in Table 3 (Sahena et al., 2009).

SFE effect on the activity

In contrast, hydrodistillation provides better results in terms of number of volatiles extracted, although the loss of these compounds in the depressurization step after SFE is a possibility to consider. By using the suitable extraction conditions, SFE is more selective than the conventional hydrodistillation method in the extraction of essential oil and the reservation of its quality (Ghasemi et al., 2007). The quality of safflower seed oil obtained by supercritical CO_2 extraction is superior to that of oil obtained by traditional methods (Han et al., 2009).

Glisic et al. (2011) reported the combination of ultrasound-assisted extraction followed by re-extraction of obtained extract with supercritical CO_2. It can be proposed that the best extraction procedure is the ultrasound pretreatment of plant material with distilled water and re-extraction of plant material (residue) using supercritical CO_2. That procedure gives two valuable products: The ultrasound extract which is rich in sugars and possess the immunomodulatory activity and supercritical extract which is rich in diterpenes and sesquiterpenes.

Orav et al. (2010) compared the yield and composition of the oil obtained by different methods (micro-distillation and extraction, SDE, and SFE) from various parts of juniper (berries, needles). The composition of the oil obtained by SFE with CO_2 at moderate conditions from fresh common juniper needles is to be similar to that obtained by SDE. The oil obtained by SFE from dried juniper berries contains more sesquiterpenes and high boiling compounds than that obtained by SDE.

SFE of essential oil from clove buds with CO_2 was explored (Guan et al., 2007). Essential oil of clove buds obtains by SFE, hydrodistillation, steam distillation and soxhlet extraction are further analyzed by gas chromatography/mass spectrometric detection to compare the extraction methods. Twenty three compounds in the clove oils have been identified, showing that the composition of the clove oil extracted by different methods is mostly similar, whereas relative concentration of the identified compounds is apparently different. General characteristics of the clove oils obtained by different methods are further compared, and SFE is considered as the optimum process among the

Table 1. Summary of the works published on the extraction of bioactive and interesting compounds from plants by SFE in the period 2008 to 2010.

Plant material	Compound of interest	Related functional activities	Extraction conditions	Analytical technique	Reference
Cynanchum paniculatum	Paeono	Anti-inflammatory, anti-diabetic, cardiovascular protective	CO_2 +methanol, 150 bar, 55 ℃, 20 min (static) + 90 min (dynamic)	HSCCC, HPLC-DAD	Sun et al., 2008
Ramulus cinnamoni Cassia tora L. seeds	Volatile oil	Antioxidant, antimicrobial	CO_2, 230-410 bar, 40-50℃ CO_2 + ethyl acetate (10%), 250 bar, 45 ℃	GC-MS	Liang et al., 2008
Cardamom	Voltiles, fatty acids, tocopherols	Antioxidant	CO_2, 300 bar, 35℃	GC-MS; HPLC-FD (ex: 295 nm, em: 330 nm);HPLC-DAD	Hamdan et al., 2008
Rhodiola rosea roots	Rosavin	Antioxidant, anti-stress, among others	CO_2 +water (10%), 200 bar, 80℃, 3 h	HPLC-UV (254 nm)	Iheozor-jioforandDey, 2009
Stevia rebaudiana	Glycosides	Anti-inflammatory, diuretic, among others	CO_2, 211 bar, 80℃,, 60 min	HPLC-UV (210 nm)	Erkucuk et al., 2009
Coriander (*Coriandrum sativum* L.)	Volatile oil		CO_2, 90 bar, 40℃, 100 min	GC-MS	Grossoet al,, 2008
Braccharis dracunculifolia	Phenolics	Antioxidant	CO_2, 400 bar, 60℃, 20 min	HPLC-UV (280 nm)	Piantino et al., 2008
Borago officinalis	Seed oil		CO_2, 200 bar, 50℃, 2.5 h (dynamic)	HPLC-DAD	Soto et al., 2008
Coriander (*Coriandrum sativum* L.)	Isocoumarins		CO_2, 80 bar, 35℃, 2 h (dynamic)	High-speedcounter-current chromatography (HSCCC)	Chen et al., 2009
Vitex agnus castus	Diterpenes, triterpenes, casticin		CO_2, 450 bar, 45℃, 4 h (dynamic)	TLC; GC; HPLC	Cossuta et al., 2008
Hyssop (*Hyssopus officinalis* L.)	Essential oil		CO_2, 90 bar, 40℃ (dynamic)	GC-MS	Langa et al., 2009
Eugenia uniflora fruits	Carotenoids	Antioxidant	CO_2, 250 bar, 60℃, 120 min (dynamic)	HPLC-DAD (450 nm)	Genival Filho et al., 2008
Garcinia mangostana	Xanthones	Antioxidant	CO2 + ethanol (4%), 200 bar, 40℃	HPLC-ESI-MS	Zarena and Udaya Sankar, 2009

Table 1. Contd.

Sunflower (*Hellianthus annuus*) leaves	Natural herbicide		CO_2, 500 bar, 50°C, 15 min	-	Casas et al., 2009
Pinus sp.	Flavonoids	Antioxidant activity	CO_2 + ethanol (3%, v/v), 200 bar, 40°C	HPLC-UV (280 nm)	Yesil-Celiktas et al., 2009
Rosehip (*Rosa canina*)	Carotenoids	Antioxidant	CO_2, 450 bar, 80°C, 150 min	HPLC-UV (450 nm)	Machmudah et al., 2008
Hibiscus cannabinus	Oil	Antioxidant	CO_2, 200 bar, 80°C, 150 min	-	Chan and Ismail, 2009
Eremanthus erythropappus	Bisabolol	Anti-inflammatory	CO_2, 150 bar, 40°C (dynamic)	-	de Souza et al., 2008
Vativeria zizanioides	Volatile oils		CO_2 + ethanol (5%)200 bar, 40°C,5 h	TLC; GC-FID	Talansier et al., 2008
Hippophae rhamnoides	Coagulation related compounds	Antithrombotic and antiaterogenic	CO_2, 450 bar, 60°C	GC-FID, HPLC-DAD	Upadhyay et al., 2009
Psidium guajava L.	phenolic fraction	Antioxidant activity	CO_2+EtOH(10%),0 MPa and 40°C	-	Castro-Vargas et al., 2010
Tomato juice	Lycopene	Antioxidant activity	CO_2 40°C and 350 bar	HPLC-UV （503nm）	Egydio et al., 2010
Salvia officinalis L.	Essential oil	Antioxidant activity	CO_2 , 30 MPa and 50°C	GC/FID , GC/MS	Glisicet al,, 2010
Mexican chia seed (*Salvia hispanica* L.)	Oil		CO_2 ,80°C, 450 bar and 300 min	Gas chromatography (GC)	Ixtaina et al., 2010
Evodia rutaecarpa fruit	evodiamine rutaecarpine		time 78 min, temperature 62°C, pressure 280 bar and co-solvent flow rate 0.4 ml/min	HPLC	Liu et al., 2010

Table 1. Contd.

Eugenia uniflora L.	Volatile phenolic compounds	antioxidant properties		GC/MS	Malaman et al., 2011
Kalahari melon and roselle seeds	tocopherol-enriched oils		melon seeds: 290 bar, 58°C and flow rate of carbon dioxide 20 ml/min		Nyam et al., 2010
Chrysobalanus icaco	essential oils	hypoglycemic	CO_2 20 kPa and 353.15 K	GC/DIC and GC/MS	Vargas et al., 2010

Table 2. Summary of some essential oils extraction studies using SC-CO_2 (2005-2010).

Sample	Analyte(s)	Pressure (MPa) / Temperature (°C)	References
Hippophae rhamnoides L.	Seed oil	25/40	Yinet al., 2005
Valeriana officinalis L. roots	Essential oil	24.3-25.0/37	Safaralieet al., 2010
Plant material	Essential oil		Araus et al., 2009
Yarrow flowers	Essential oil	10/ 40-60	BocevskaandSovová, 2007
Vetiveria zizanioides root	Essential oil	190 bar/50	Danh et al., 2009
Citrus reticulate peel	Oils	10.0/60	Danielski et al., 2008
Coffea Arabica beans	Green coffee oil	15.2/70	de Azevedo et al., 2008
Valeriana officinalis L. rhizomes	Essential oil	15.2-30.4/37-61	Safaralie et al., 2008
Peach seeds	seed oil	15.0-19.8/40-51	Sánchez-Vicente et al., 2009
Carqueja	Carqueja oil	100-300 bar /30-40	Silvaet al,, 2009
Chrysobalanus icaco	Essential oil	20 /85.15	Vargaset al,, 2010
Salvia mirzayanii	Essential oil	35.5 /35	Yamini et al., 2008
Patchouli	Essential oil	14/40	Donelian et al., 2009
Palm kernel	Palm kernel oil	20.7 -48.3/45.2-85.2	Zaidulet al,, 2007
Juniperus communis L.	Essential oil	11.8/45	Orav et al., 2010
Salvia lavandulifolia L.	Essential oil	90 bar/40	Langaet al,, 2009
Nepeta persica	Essential oil	20.3/45	Khajeh et al., 2010
Satureja hortensis	Essential oil	35.0/72.6	Khajeh, 2010
Artemisia sieberi	Essential oil	30.4/50	Ghasemiet al,, 2007
Carrot fruit	Essential oil	10/40	Glisic et al., 2007

Table 3. Comparison of SFE with solvent extraction.

No.	Solvent extraction	Supercritical extraction
1	Solvent presence is unavoidable. The residual level of the solvent depends on the type of solvent used	Is totally free of solvents and hence very pure
2	Heavy metal content is also unavoidable and depends on the solvent, the method of solvent recycling, the source of the raw material, and the material used to construct the contact parts of the machinery	Totally free of heavy metals since they are not extractable even if they are present in the raw material. No heavy metals are present in CO_2 or the equipment
3	Inorganic salt content cannot be avoided, using the same concept as above	Totally free of inorganic salts using the same explanation as above
4	Polar substances get dissolved along with the lipophilic substances from the raw material due to poor selectivity of the solvent. During solvent removal operations, these polar substances form polymers, which lead to discoloration of the extract and poor flow characteristics. All this causes the extract to look different from the basic components in the raw material and hence it is more of a ‘‘pseudo” natural extract	No such possibility exists since CO_2 is highly selective and no chance of polar substances forming polymers exists. In addition the operating temperature is only 40 to 80°C
5	Both polar and non-polar colours are extracted	Only non-polar colours get extracted
6	Solvent removal requires extra unit operations resulting in higher cost and lower recovery of useful material	No extra unit operations needed and yield of useful material is very high

four processes for obtaining clove oil with high quality.

According to Glisic et al. (2007), the qualitative and quantitative analyses of the supercritical extract, as well as of the essential oil obtained by hydrodistillation, were done by GC/FID and GC/MS methods. Antimicrobial properties of both samples are investigated against ten species of microorganisms. The main component of the supercritical extract, as well as of the essential oil is carotol. The supercritical extract is characterized by the presence of heavier molecular weight compounds, while some lighter compounds, e.g. pinenes, are not detected. The supercritical extract and the essential oil are the most effective against Gram-positive bacteria.

Conclusion

SFE has an enormous interest nowadays, with thousands of references dealing with SFE last five years (2005-2010). It is now a real option for product development, mainly those that will be used for human consumption, such as new foods, food ingredients/additives or pharmaceutical products. Moreover, SFE has also demonstrated some advantages in the environmental field; for example, to reduce solvent waste, to get new useful compounds from industrial by-products, and to allow quantification and/or removal of toxic compounds from the environment. This article summarizes research findings involving the supercritical fluid extraction of volatile components from plant materials. Emphasis is placed on optimization of extraction parameters (temperature, pressure, extraction time, modifier, etc.) for complete recovery of analytes from their matrices. Then we compare it with conventional extraction methods in terms of selectivity, rapidity, cleanliness and so on. So the future of SFE for the extraction of volatile components from plants looks bright based on a number of considerations. Firstly, SFE has a wide application area. It is capable of extracting a wide range of diverse compounds from variety of sample matrices. Secondly, supercritical fluids offer extraction selectivity unsurpassed by solvent polarity. Thirdly, the environmental friendliness of this technique can never be disputed. Readers are encouraged to treat the information provided as a tool to develop new processes at lab and pilot scale, to discover new ways for sample preparation, to learn how to deal with SFE optimization and, certainly, to be able to develop in the future emerging technologies able to fulfill the requirements of environmentally clean processes.

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