

Chapter 2

Essential Oils: From Conventional to Green Extraction

Abstract This chapter reviews the development of extraction techniques for essential oils (EOs). The conventional extraction techniques and their intensifications are summarized in terms of their principles, benefits and disadvantages. The green extractions with innovative techniques are also elaborated for future optimization and improvement of traditional EOs' productions.

Keywords Essential oils · Extraction techniques · Optimization · Innovation

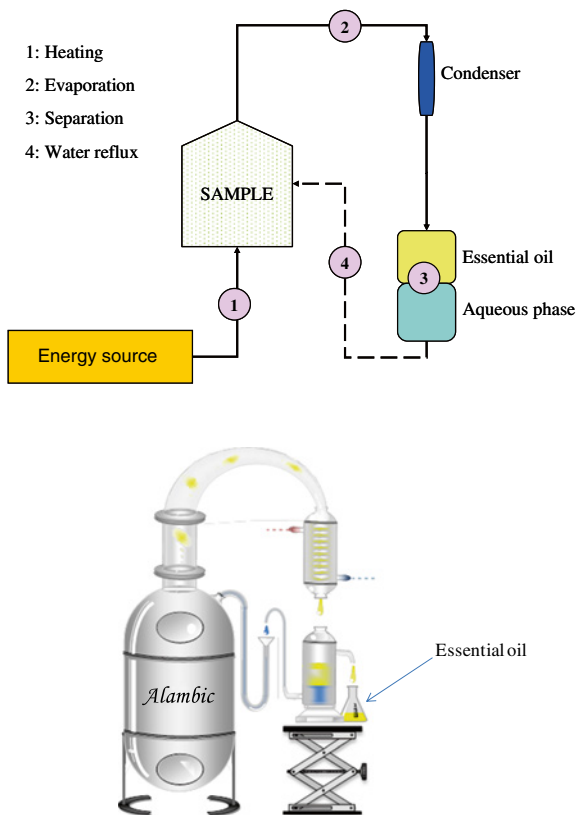
2.1 Conventional Extraction

As previously described, EOs are defined as products extracted from natural plants by physical means only such as distillation, cold press and dry distillation. However, the loss of some components and the degradation of some unsaturated compounds by thermal effects or by hydrolysis can be generated by these conventional extraction techniques. These disadvantages have attracted the recent research attention and stimulated the intensification, optimization and improvement of existing and novel “green” extraction techniques. All these techniques are appropriately applied with a careful consideration of plant organs and the quality of final products. Moreover, the analytical composition of EOs extracted from the same plant organ may be quite different with respect to the techniques used. These conventional extraction techniques could typically extract EOs from plants ranging from 0.005 to 10 %, which are influenced by the distillation duration, the temperature, the operating pressure, and most importantly, the type and quality of raw plant materials.

2.1.1 Steam Distillation

Steam distillation is one of ancient and official approved methods for isolation of EOs from plant materials. The plant materials charged in the alembic are subjected to the steam without maceration in water. The injected steam passes through the

Fig. 2.1 A schematic representation of conventional recovery of essential oils



plants from the base of the alembic to the top. The vapour laden with essential oils flows through a “swan-neck” column and is then condensed before decantation and collection in a Florentine flask (Fig. 2.1). EOs that are lighter or heavier than water form two immiscible phases and can be easily separated. The principle of this technique is that the combined vapour pressure equals the ambient pressure at about 100 °C so that the volatile components with the boiling points ranging from 150 to 300 °C can be evaporated at a temperature close to that of water. Furthermore, this technique can be also carried out under pressure depending on the EOs’ extraction difficulty.

2.1.2 *Hydro-diffusion*

Unlike steam distillation, the steam injected in this system is from the top of the alembic to the bottom. The vapour mixture with EOs is directly condensed below the plant support through a perforated tray. The way of separating EOs is the same as that in other distillation methods. This method can reduce the steam

consumption and the distillation time, meanwhile, a better yield can be obtained in comparison with steam distillation.

2.1.3 Hydro-distillation

Hydro-distillation (HD) is a variant of steam distillation, which is recommended by the French Pharmacopoeia for the extraction of EOs from dried spices and the quality control of EOs in the laboratory. Instead of the steam input, the plant materials in HD are directly immersed in water. This solid-liquid mixture is then heated until boiling under atmospheric pressure in an alembic, where the heat allows the release of odorous molecules in plant cells. These volatile aroma compounds and water form an azeotropic mixture, which can be evaporated together at the same pressure and then condensed and separated in a Florentine flask due to their immiscibility and density difference. Moreover, a cohobation system can recycle the distilled water through a siphon so as to improve the yield and quality of EOs. It is important to mention that the recovered EOs are different from the original essence due to the long treatment duration.

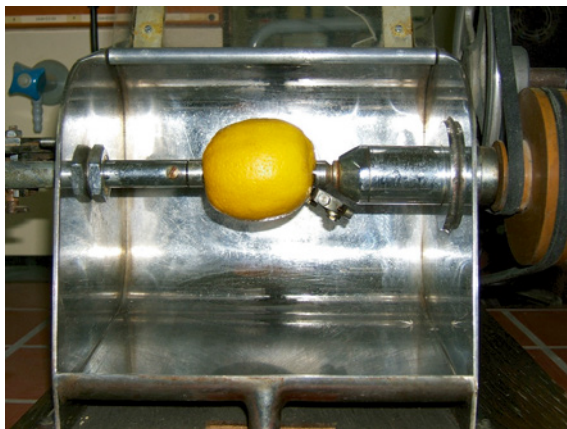
2.1.4 Destructive Distillation

This technique is only applied on birch (*Betula lenta* or *Betula alba*) and cade (*Juniperus oxycedrus*). The toughest parts of these woods (e.g. barks, boughs, roots, etc.) are exposed to dry distillation through a tar after undergoing a destructive process under intense heat. A typical, leathery and empyreumatic oil is then obtained after condensation, decantation and separation.

2.1.5 Cold Expression

This technique is an extraction without heating for EOs of citrus family (Fig. 2.2). The principle of this mechanic process is based on machine squeezing the citrus pericarps at room temperature for the release of EOs, which are washed in cold running water. The essence is then isolated by decantation or centrifugation. Although this method retains a high value of citrus odour, the high consumption of water can affect EOs' quality as the result of the hydrolysis, the dissolution of oxygenated compounds and the transport of microorganism. Several new physical processes appear more popular for the reason of avoiding such deteriorations. The oleaginous cavities on the peel are pressed to burst by two horizontal ribbed rollers (*sfumatrice*) or a slow-moving Archimedian screw coupling to an abrasive shell (*pelatrice*) thus EOs are bent to release. The oil-water emulsion is separated after

Fig. 2.2 Schematic of cold expression



rinse off with a fine spray of water. Besides, the machines which treat citrus peels only after removal of juices and pulps are known as *sfumatrici*, while those which process the whole citrus fruit are called *pelatrici* (Guenther 1948).

2.2 Green Extraction with Innovative Techniques

Since economy, competitiveness, eco-friendly, sustainability, high efficiency and good quality become keywords of the modern industrial production, the development of EOs' extraction techniques has never been interrupted. Strictly speaking, conventional techniques are not the only way for the extraction of EOs. Novel techniques abided by green extraction concept and principles have constantly emerged in recent years for obtaining natural extracts with a similar or better quality to that of official methods while reducing operation units, energy consumption, CO₂ emission and harmful co-extracts in specific cases. The principles of green extraction can be generalized as the discovery and the design of extraction processes which could reduce the energy consumption, allow the use of alternative solvents and renewable/innovatory plant resources so as to eliminate petroleum-based solvents and ensure safe and high quality extracts or products (Chemat 2012).

2.2.1 Turbo Distillation

This technique is developed to reduce energy and water consumption during boiling and cooling in hydro-distillation. The turbo extraction allows a considerable agitation and mixing with a shearing and destructive effect on plant materials so as to shorten distillation time by a factor of 2 or 3. Furthermore, it is an alternative for extraction of EOs from spices or woods, which are relatively difficult to distill.

Besides, an eco-evaporator prototype could be added with aspect of the recovery and the reuse of the transferred energy during condensation for heating water into steam (Chemat 2010).

2.2.2 Ultrasound-Assisted Extraction

With the aim of higher extraction yields and lower energy consumption, ultrasound-assisted extraction has developed to improve the efficiency and reduce the extraction time in the meanwhile. The collapse of cavitation bubbles generated during ultrasonication gives rise to micro-jets to destroy EOs' glands so as to facilitate the mass transfer and the release of plant EOs. This cavitation effect is strongly dependent to the operating parameters (e.g. ultrasonic frequency and intensity, temperature, treatment time, etc.) which are crucial in an efficient design and operation of sono-reactors. In addition to the yield improvement, the EOs obtained by Ultrasound-Assisted Extraction (UAE) showed less thermal degradation with a high quality and a good flavor (Porto et al. 2009; Asfaw et al. 2005). However, the choice of sonotrode should be careful as the result of the metallic contamination which may accelerate oxidation and subsequently reduce EOs' stability (Pingret et al. 2013). This technique has already proved its potency to scale up, which shows 44 % of increment on extraction yield of EOs from Japanese citrus compared to the traditional methods (Mason et al. 2011).

2.2.3 Microwave-Assisted Extraction

Microwave is a non-contact heat source which can achieve a more effective and selective heating. With the help of microwave, distillation can now be completed in minutes instead of hours with various advantages that are in line with the green chemistry and extraction principles. In this method, plant materials are extracted in a microwave reactor with or without organic solvents or water under different conditions depending on the experimental protocol. The first Microwave-Assisted Extraction (MAE) of EOs was proposed as compressed air microwave distillation (CAMD) (Craveiro et al. 1989). Based on the principle of steam distillation, the compressed air is continuously injected into the extractor where vegetable matrices are immersed in water and heated by microwave. The water and EOs are condensed and separated outside the microwave reactor. The CAMD can be completed in just 5 min and there is no difference in quantitative and qualitative results between extracts of CAMD and 90 min conventional extraction using steam distillation. In order to obtain high quality EOs, vacuum microwave hydro-distillation (VMHD) was designed to avoid hydrolysis (Mengal et al. 1993). Fresh plant materials have been exposed to microwave irradiation so as to release the extracts; reducing the pressure to 100–200 mbar enables evaporation of the azeotropic water-oil mixture at a temperature lower than 100 °C. This operation can be repeated in a stepwise way with a constant microwave power, which is contingent on the desired yield.

The VMHD, which is 5–10 times faster than classic HD, showed comparable yield and composition to HD extracts. The EOs have organoleptic properties very close to the origin natural materials. Moreover, the occurrence of thermal degradation reduces because of the low extraction temperature. Beyond that, in fact, there exist a couple of modern techniques assisted by microwave such as microwave turbo hydro-distillation and simultaneous microwave distillation, which are impressive for short treatment time and less solvent used (Ferhat et al. 2007; Périno-Issartier et al. 2010).

On account of growing concern for the impact of petroleum-based solvents on the environment and the human body, several greener processes without solvent have sprung up in the last decade. Solvent-free microwave extraction (SFME) was developed with considerable success in consistent with the same principles as MAE (Li et al. 2013). Apart from the benefits mentioned before, the SFME simplifies the manipulation and cleaning procedures so as to reduce labor, pollution and handling costs. The SFME apparatus allows the internal heating of the in situ water within plant materials, which distends the plant cells thus leads to the rupture of oleiferous glands.

A cooling system outside the microwave oven allows the continuous condensation of the evaporated water-oil mixture at atmospheric pressure. The excessive water is refluxed to the reactor in order to maintain the appropriate humidity of plant materials. It is interesting to note that the easy-controlled operating parameters need to be optimized for maximization of the yield and final quality. The potential of using SFME at laboratory and industrial scale has been proved on familiar plant materials with a considerable efficiency compared to conventional techniques (Filly et al. 2014). Inspired by SFME, a number of its derivatives have emerged, which offer significant advantages like shorter extraction time, higher efficiency, cleaner feature, similar or better sensory property under optimized conditions (Michel et al. 2011; Sahraoui et al. 2008, 2011; Wang et al. 2006; Farhat et al. 2011). In 2008, a novel, green technique namely microwave hydro-diffusion and gravity (MHG) has been originally designed (Fig. 2.3). This technique is a microwave-induced hydro-diffusion of plant materials at atmospheric pressure, which all extracts including EOs and water drop out of the microwave reactor under gravity into a continuous condensation system through a perforated Pyrex support. It is worth mentioning that the MHG is neither a modified MAE that uses organic solvents, nor an improved HD that are high energy and water consumption, nor a SFME which evaporates the EOs with the in situ water only. In addition, MHG derivants such as vacuum MHG and microwave dry-diffusion and gravity (MDG) has developed later with the consideration of energy saving, purity of end-products and post-treatment of wastewater (Farhat et al. 2010; Zill-e-Huma et al. 2011).

2.2.4 Instantaneous Controlled Pressure Drop Technology

The DIC process is a direct extraction-separation technique, which is not like the molecular diffusion in conventional techniques. It allows volatile compounds to be removed by both evaporation for a short time at high temperature (180 °C) and high



Fig. 2.3 Solvent free microwave extraction at laboratorial and industrial scale

Table 2.1 Innovative techniques for extraction of essential oils

Name	Brief introduction	Advantages (A) and drawbacks (D)	Main influencing parameters	References
Simultaneous distillation extraction (SDE)	Either HD or steam distillation is combined with solvent extraction, which is frequently used for the isolation of volatile compounds from EOs bearing plants. Solvent used should be insoluble in water and of high purity. SDE has been modified into several variants with the consideration of efficiency, scale and quality of end-products	A: less solvents, elimination of excessive thermal degradation and dilution of extract with water D: artefact production, loss of hydrophilic compounds	Treatment time Solvent Oxygen	Jayatilaka et al. (1995) Blanch et al. (1996) Chaintreau (2001) Altun and Goren (2007) Teixeira et al. (2007)
Pulsed electric field assisted extraction (PEF)	This technique applies short pulses at high voltage in order to create electro compression, which causes plant cells to be ripped open and perforated. The treatment chamber in PEF consists of at least two electrodes with an insulating region in between, where the treatment of plant materials happens	A: preserved fresh character, low heating impact and energy consumption D: only for pumpable materials, restricted by viscosity and particle size of products, high cost	Flow rate Pulse frequency Electric field strength Preheating	Jeyamkondan et al. (1999) Barbosa-Canovas et al. (2000) Fincan et al. (2004)
Supercritical fluid extraction	The plant material is placed in an extractor with the flow of supercritical CO ₂ . In the supercritical state (above 74 bar and 31 °C), CO ₂ is characterized as lipophilic solvent with the high diffusivity, which gives itself a good capacity for diffusion, and a high density ranging from gas-like to liquid-like endows the capacity of transport and major extraction. The fluids carrying extracts pass through the gas phase. The extracts are then separated and collected in a separator	A: inexpensive CO ₂ , nontoxic, high diffusion, rapidity, selectivity and no denaturation of sensitive molecules D: expensive equipment investment, high energy consumption for pressure and temperature establishment	Treatment time Pressure Flow rate of CO ₂	Mira et al. (1996) Reverchon (1997) Caredda et al. (2002) Marongiu et al. (2003) Donelian et al. (2009)

(continued)

Table 2.1 (continued)

Name	Brief introduction	Advantages (A) and drawbacks (D)	Main influencing parameters	References
Subcritical water extraction	<p>The hot water is used at temperatures between boiling (100 °C) and critical point (374.1 °C) of water. Water is maintained in its liquid form under the effect of high pressure.</p> <p>Under these conditions, the polarity of water decreases, which allows the extraction of medium polar and nonpolar molecules without using organic solvents</p>	<p>A: clean, low cost, simple, safe, rapidity, adjustable water polarity, high ratio of oxygenated compounds</p> <p>D: expensive equipment investment, high energy consumption, thermal degradation</p>	<p>Temperature</p> <p>Pressure</p> <p>Water flow rate</p> <p>Solid particle size</p>	<p>Jiménez-Carmona et al. (1999)</p> <p>Ayala and Luque de Castro (2001)</p> <p>Smith (2002)</p> <p>Eikani et al. (2007)</p> <p>Giray et al. (2008)</p>

pressure (10 bar) and auto-vaporization from alveolated plant structures resulting from multi-cycle instantaneous pressure drop (Rezzoug et al. 2005; Besombes et al. 2010). This solvent-free process presents a significant improvement whether in efficiency or in energy consumption and a very short heating time in each DIC cycle eliminate the thermal degradation. Moreover, the DIC obtained the same or even higher yield of EOs with a higher quality than conventional methods regarding to their more oxygenated compounds and lower sesquiterpene hydrocarbons. In addition, heating time and cycle number in particular, have an influence on the extraction efficiency of DIC for all aromatic herbs and spices (Allaf et al. 2013a, b).

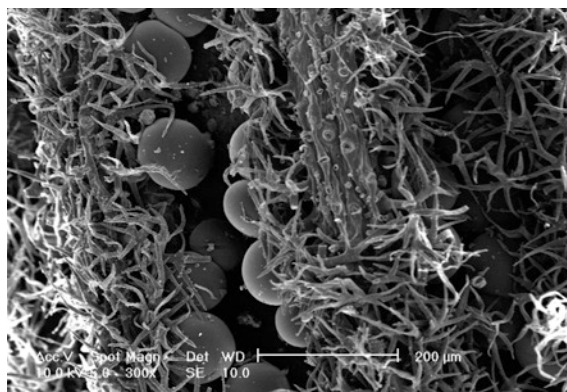
2.2.5 Other Emerging Green Extraction Techniques

With the exception of above-described techniques, there are other emerging techniques for EOs extraction which are well established in the early time of the innovation. Table 2.1 summarizes these techniques in terms of their fundamentals, influencing parameters, advantages and draw-backs. It is hard to ignore that all these techniques have been successfully applied at an industrial scale.

2.3 Conclusions

An overview of extraction technique has been presented here for obtaining EOs, which covers a range from conventional to up-to-date methods. The new techniques have been proved to obtain extracts with higher quality in a shorter time compared to traditional techniques. Nevertheless, from a regulatory point of view, these so-called EOs of innovative techniques are not listed in norms due to the restrictive definition of EOs which is only based on the conventional extraction methods. As the consequence of this, the amendment or reestablishment of industry standards in a broader sense becomes more important than ever.

A scanning electron micrograph of untreated lavender



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<http://www.springer.com/978-3-319-08448-0>

Essential Oils as Reagents in Green Chemistry

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2014, X, 71 p. 28 illus., 19 illus. in color., Softcover

ISBN: 978-3-319-08448-0