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Review

Research Progress on Extraction, Separation, and Purification Methods of Plant Essential Oils

Weiwei Zhou [1], Jun Li [1], Xuefeng Wang [1], Ling Liu [1], Yun Li [2], Rui Song [2], Mengxue Zhang [2] and Xiumei Li [1,*]

[1] Institute of Feed Research of Chinese Academy of Agricultural Sciences, Beijing 100081, China; zhouweiwei@caas.cn (W.Z.); lijun08@caas.cn (J.L.); wangxuefeng199810@163.com (X.W.); liuling20231998@163.com (L.L.)
[2] Shijiazhuang Livestock Products and Veterinary Drug Feed Quality Testing Centre, Shijiazhuang 050041, China; liyun_361029@163.com (Y.L.); songrui_911@163.com (R.S.); zhangmengxue3077@163.com (M.Z.)
* Correspondence: lixiumei@caas.cn

Abstract: Essential oils (EOs), also called liquid gold, are known for their wide range of applications and biological activities. The modern use of EOs has received increasing attention for more than 60 years. The precious EOs have been refined from plant raw materials using a variety of methods. Since the extraction, separation, and purification methods determine the type, quantity, and stereochemical structure of EO molecules as well as the final yield and quality of EOs, the selection of an appropriate method is crucial. The traditional and emerging extraction methods (hydrodistillation, steam distillation, organic solvent extraction, etc.), as well as separation and purification methods (chromatography, macroporous resin, chemical reaction, etc.), of plant EOs and their main volatile compounds were shown. Our review focused on the principles, processes, characteristics, and applications of these methods, so as to better understand the preparation of pure plant EOs and further guide their large-scale use.

Keywords: essential oil; extraction; separation; purification

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1. Introduction

Essential oils (EOs) are volatile substances initially obtained from the flowers, leaves, stems, roots, or fruits of aromatic plants by simple squeezing [1]. EOs, usually of complex composition, are composed of secondary metabolites of plants [2]. At room temperature, the pure EOs from natural plants are volatile oily liquids, normally soluble in organic solvents and lipids [3–5]. Upon contacting with air, EOs can quickly evaporate for their strong volatility. To the naked eye, some EOs are colorless, while more common ones are yellow or orange (*Citri reticulatae pericarpium* oil and lemon oil) [6,7]; some are even indigo (*Matricaria chamomilla* oil) or green (*Artemisiae argyi folium* oil) [8,9]. Most EOs sits on top of water because they are less dense, such as citronella oil, lime oil, or orange oil, while there are some heavier than water, such as cinnamon oil, clove oil, or garlic oil [10]. The first recorded use of EOs abroad was in ancient Egypt, India, and Persia [11].

Dated 2551–2528 B.C., EOs were discovered for beauty treatments, spiritual rituals, preservation of some mummies, and medical use purposes in ancient Egypt. The Egyptians extracted EOs by soaking plants in fatty substances and then boiling them consequently, so that the aroma fixed in the fat would evaporate out. Dated around 1000 B.C., Arabs first distilled rose EO using distillation technology, heralding the emergence of liquid EO. In modern times, Rene-Maurice Gattefossé discovered, for the first time, the healing effect of lavender EO on wounds and, thus, began his research on EOs, writing the book "*Aromatherapy*". As early as 2700 B.C., China used plants for medicinal purposes [12]. According to *Shen Nong's Herbal Classic*, the usage guidelines for 365 plants were described, among them many belonged to aromatic plants [13]. Furthermore, almost all citrus EOs such as

sweet orange (*Citrus sinensis*), bitter orange (*Citrus aurantium*), neroli (*Citrus aurantium*), etc., originated from China [14]. Another representative aromatic plant that originated in China was the camphor tree, which has many applications in the fields of perfume medicine and architecture stretching going back thousands of years [15].

Currently, the diversified plants provide various important EOs with good smells for the fragrance industry, used to produce shampoos, makeup, and other products [16]. In food manufacturing, EOs are served as food preservatives. The significant biological activity of EO components also provides good efficacy that renders them outstanding for medical use in the fields of antimicrobial, sedative, analgesic, and anti-inflammatory drugs, spasmolytic agents, and local anesthetics [17]. Additionally, EOs and their components are also used for aromatherapy [18]. Although EOs have various biological activities, medicinal and food value, and aromatic properties, only 10% out of the 3000 known EOs have been developed and utilized. The reason for the low utilization rate of EOs is due to their complex composition as well as the low extracted yield and quality [19]. Numerous studies have shown that all of them mainly depend on the selected extraction, separation, purification methods, and conditions [20,21]. However, previous research has focused more on the extraction methods of EOs, with less attention paid to separation and purification methods [1,17].

Therefore, this review not only focused on the principles, processes, characteristics, and applications of traditional and emerging extraction methods (hydrodistillation, steam distillation, organic solvent extraction, etc.) but also the separation and purification methods (chromatography, macroporous resin, chemical reaction, etc.) to improve the efficiency of extraction, separation, and purification, and provide reference for expanding the application of plant EOs.

2. Extraction

Hydrodistillation, steam distillation, organic solvent, cold pressing, and supercritical fluid extraction are the main conventional methods to acquire EOs. To shorten the extraction time and improve the extraction efficiency, various advanced forms of extraction technologies gained a lot of interest, such as ultrasound-assisted and microwave-assisted extraction and solid-phase microextraction, as shown in Table 1 and Figure 1. Certainly, the joint applications of these methods are more welcomed by people, such as microwave-assisted hydrodistillation concatenated liquid–liquid extraction and ionic liquid-based microwave-assisted extraction [22,23].

2.1. Hydrodistillation (HD) and Steam Distillation (SD)

HD is one of the conventional extraction methods for recovering plant EO processes by heating a plant matrix [24]. During the distillation process, volatile materials in the plants are carried out from the dregs with solvent steam or water and then condensed into a liquid in a condensing device and removed easily based on density differences. The HD method specified in the *Chinese Pharmacopoeia* is the most extensively used for extracting EOs components with boiling points mostly above 100 °C, immiscible with or only slightly soluble in water [25]. The principle of SD used for EOs extraction is similar to that of HD, but the plant material is not in contact with water and yet entrained by water steam [26]. Both HD and SD are characterized as follows: low cost, non-poisonous, high reproducibility, harmless, simple operating; thus, they are becoming the most extensively choice for researchers to extract EOs.

In previous studies, various plant EOs with significant biological activity were extracted by distillation, such as *Teucrium ramosissimum* EOs with anti-acanthamoeba effect [27], EOs from the leaves of *Alseodaphne perakensis* (Gamble) Kosterm [28], and *Malaysian horsfieldia* EOs [29]. *Boswellia sacra* EOs, prepared from *Boswellia* sp. gum resins through hydrodistillation at 78 or 100 °C for 12 h, had a therapeutic effect on advanced breast cancer. It induced breast-cancer-cell-specific cytotoxicity, suppressed cellular network formation and disrupted spheroid development [30]. Additionally, it had been verified that the

determination of distillation time could not only be used to optimize the production of EOs but also affect the composition of EOs. Jurevičiūtė R et al. [31] isolated lemon thyme EOs via HD at different distillation times and detected them using GC/MS analytical methods. The results showed that, with the distillation time increased, the percentage of EOs content did not uniformly increase but led to the changes in content, such as a decrease in monoterpene and an increase in sesquiterpenes content. The above research results indicated that distillation for too long is useless and the specific process conditions suitable for a certain EO need to be continuously optimized.

2.2. Organic Solvent Extraction (OSE)

OSE is also a common chemical purification and separation method. It can extract plant EOs that are easily soluble in organic solvents. Using a solvent (methanol, ethanol, or ethyl acetate) at boiling temperature, EOs from plants can be extracted using a Soxhlet extractor for 5 to 6 h; its maximum yield is achieved when the solvent extract is concentrated using a rotary evaporator at reduced pressure [32].

People often compare the yield and composition of EOs obtained via different extraction methods. Some researchers discovered that the organic solvent extraction gave higher yield than HD during the extraction of EOs of rose-scented geranium, and the composition was also different [33]. Nevertheless, organic reagents are difficult to completely separate from solutes and fully recycle and reuse, even bringing negative effects on human health. Furthermore, solvent removal using a rotary evaporator might result in the loss of EO during evaporation. As a result, better separation and purification methods are introduced in the "Separation and Purification section" below. Additionally, a series of solvent-free extraction methods gain full exploitation and application [34].

2.3. Cold Pressing (CP)

CP is a traditional method for extracting seed and peel oil with high content [35,36]. The method uses mechanical pressure to compress plants, causing the oil glands to rupture and releasing the EOs components. After washing and oil–water separation, impurities are removed. The pressing method has a simpler process, lower energy consumption, and less environmental pollution than the solvent extraction [37]. The biggest advantage of this method is that it can be operated at room temperature, retaining the original aroma and more benefits of the EOs.

Belsito E L et al. [38] isolated bergamot oil via cold pressing and discovered that the aroma components were similar to that furnished by vacuum distillation. Li G et al. [39] showed that lemon EOs had good antioxidant effects and that obtained via CP had a better antioxidant effect than HD as it retained more active non-volatile substances. However, the CP extraction method has a low yield. Furthermore, the pectin contained in the fruit peel precipitated during the pressing and crushing process, causing emulsification and making it difficult to separate oil and water. Additionally, EOs obtained through pressing may also be turbid and impure, as they contain many non-volatile components, chlorophyll, and impurities such as cellular tissue.

2.4. Supercritical Fluid Extraction (SFE)

As one of green extraction and separation technologies, SFE has attracted much attention during last decades [40]. For separation purposes, SFE uses supercritical fluids, especially CO_2 as extracting agents to extract desired components from natural plants, in a thermodynamic state where the temperature is above the critical temperature (*Tc* of 31.1 °C) and the pressure is above the critical pressure (*Pc* of 73.8 bar) [41]. Its temperature close to the environment makes it particularly suitable for extracting heat-resistant components, like EOs. The principle of supercritical carbon dioxide (SC-CO_2) extraction and separation is to utilize the special dissolution effect of SC-CO_2 on natural plant EOs.

Compared to conventional organic solvent extraction techniques, SC-CO_2 extraction has faster extraction speed, higher extraction yield, and less loss of active ingredients [42].

It can extract heat-resistant compounds and maintain their natural proportion under mild conditions, due to its relatively low critical temperature and pressure. What is more important, CO_2 can be removed from the extracted material by simply reducing pressure to a suitable collection device, leaving no residue or pollution in EOs, as it is a colorless, odorless, inert, non-explosive, inexpensive, and environmentally friendly gas under environmental conditions [43]. Additionally, in the extraction process, parameters such as temperature, pressure, static and dynamic time, and flow rate can be controlled and regulated [44]. Rai A et al. [40] obtained the maximum yield (54.37 wt%) for sunflower oil at an extraction temperature of 80 °C, extraction pressure of 400 bar, 0.75 mm particle, and 10 g/min solvent flow using 5% co-solvent. By applying the orthogonal test design using a L9 (34) matrix, Zhang J et al. [42] obtained the maximum extraction yield (92.07 ± 0.76%) for red radish seed oil under the conditions of 35 MPa, 45 °C, 0.45 kg/min, for 80 min. By performing a response surface analysis based on a Box–Behnken design with three levels and four independent variables, Lin G et al. [43] discovered that extraction pressure is the most critical one among the factors affecting *Origanum vulgare* L. EO yield. The optimized extraction conditions (217 bar, 54 °C, 2 h, and 14% modifier concentration) can achieve the EO yield of 1.136%, with the content of thymol and carvacrol reaching 53.172 and 41.785 mg/g, respectively. Hence, on account of the superiority characteristic of the solvent and the high selectivity of its extraction conditions, SC-CO_2 extraction is a better alternative to replace other conventional methods. However, the related high-pressure equipment is expensive and poses a potential safety hazard, so it requires more careful control and operation.

Currently, SC-CO_2 extraction is widely used as a solvent for EOs from natural plants [45]. To further increase the final yield of the oil and reduce energy consumption, the ultrasonic-assisted static extraction was integrated with CO_2 dynamic extraction. Wei M C et al. [46] reported that the supercritical carbon dioxide extraction using ultrasound assistance (USC-CO_2) improved the yield of clove oil and α-humulene from clove buds and shortened extraction time.

There are also a number of shortcomings during the use of the conventional extracting method as follows: long extraction process, high temperature, open system, easy to cause damage and volatile loss of thermal unstable, and easily oxidized components. It is worth noting that the method needs high-level equipment and it is difficult to control the final concentration of EOs because the extract also contains non-volatile lipophilic constituents.

2.5. Ultrasound-Assisted Extraction (UAE)

Like the developed new extractions technologies, UAE also achieves the goal of green extraction [47]. Ultrasound is a mechanical wave with an effective frequency generally ranging from 20 to 50 kHz, which can generate the comprehensive effects of cavitation, vibration, crushing, and stirring [48]. As a source of energy, it can break plant cells to release oil, and can also disperse organic phases in water [49].

At present, some innovative technologies, such as ultrasound-assisted soxhlet extraction, ultrasound-assisted distillation, microwave–ultrasonic assisted hydrodistillation (MUAHD) and other combination ultrasound technologies, have developed rapidly and have been applied to the extraction of EOs, which is achieved by using ultrasound to break the cell wall to release intracellular components [50,51]. MUAHD is a method of distilling EOs from plants with the joint help of microwave and ultrasonic waves. Shehadeh M et al. [52] extracted EOs of wild *Origanum syriacum* samples from four different geographical areas using MUAHD, which further proved to be one of the rapid, cost-effective, and organic solvent-free methods. To fully leverage the advantages of these two extraction methods, UAE and optimized ultrasound-assisted emulsification microextraction (USAEME) were applied to extract and preconcentrate the EOs of *Elettaria cardamomum* Maton. together. The results demonstrated that α-terpenyl acetate was the most abundant with 46.0%; the 1, 8-cineole and linalool were 27.7% and 5.3%, respectively [53]. Due to the high product yield,

low organic solvents, short processing time, and low maintenance costs, the application of UAE has a growing trend in obtaining EOs in the laboratory [54] and industry [55].

2.6. Microwave-Assisted Extraction (MAE)

The microwave refers to electromagnetic waves with wavelengths from 0.01 to 1 m and frequencies from 0.3 to 300 GHz, which have strong thermal effects and penetrating power [56,57]. Because microwave has mutually perpendicular electric and magnetic fields, it can easily penetrate materials, rapidly increase the temperature inside and outside the tissue, promote cell rupture, and diffuse the components inside the cell into the extraction solution [58]. The heating method of using microwaves is unique and efficient. In the process of extracting EOs, the heat is transferred from the outside of the medicinal material to the inside, some is transferred from the inside of the medicinal material to the outside, consistent with the mass transfer direction of the volatile oil components. Its synergistic effect of heat and mass can improve the extraction efficiency of EOs [59].

Recently, the MAE has attracted wide attention and been used to extract bioactive chemicals from various plant materials, such as *Citrus* limon (*Lisbon variety*) peel, Humulus lupulus, *Thymus vulgaris* L., and so on [60]. It has been proven that using MAHD for 30 min yields has an extraction effect equivalent to eight times that of HD [61]. The microwave time has the greatest impact on the EOs yield, followed by solid–liquid ratio and microwave power [62]. The yield of Eos was also improved rapidly and significantly while reducing CO_2 emissions and increasing the MAHD power. But, it is worth noting that higher microwave power may alter the chemical content of EOs [63]. Additionally, to further pursue more effective heating, fast energy transfer, time savings, low operating costs, and being environment friendly, the solvent-free microwave extraction (SFME) method has been developed. As one of the promising techniques for EOs extraction, SFME depends on microwave heating and dry distillation without the addition of water or organic solvents. Researchers compared SFME and the conventional techniques with respect to the extraction, antioxidant, and antimicrobial activities of *Thymus mastichina* EOs. The results showed that 1, 8-cineole (eucalyptol) was the main constituent of the volatile oil and SFME provided a higher yield and a shorter extraction time to achieve the same pharmacological activity [64].

In summary, the MAE technologies for plant EOs have many advantages, including high utilization of energy, high extraction rate, and short extraction time, thus avoiding the chemical modification of the oil components and preserving the natural quality of EOs.

2.7. Solid-Phase Microextraction (SPME)

SPME technology is a novel sample pretreatment and enrichment technology first developed and studied by professor Pawliszyn's research team in the 1990s [65]. As a solvent-free selective extraction method, SPME are used as a prior sample pretreatment stage that integrates sampling, extraction, concentration, and injection [66]. SPME has three basic extraction modes: direct extraction SPME, headspace SPME, and membrane protected SPME.

Compared to the traditional solid-phase extraction technology, the unique features of SPME are simpler, lower cost, more selective and flexible when paired with appropriate detectors [67–69]. In addition, it overcomes the shortcomings of solid-phase extraction, including low recovery rate and easy blockage of adsorbent pores. Now, it has become one of the widespread used methods for analyzing volatile component in various plants, food, beverage and natural product matrices, and biological and environmental samples [70,71]. However, SPME does not perform detailed extraction, which is necessary for calibration using spiked blank samples [72].

Table 1. Extraction methods of EOs.

Method	Abbreviation	Principle	Pros	Cons	Sample
Hydrodistillation/steam distillation	HD/SD	Heating reflux using water or steam	Low cost, non-poisonous, high reproducibility, harmless, and simple operating	Long heating time and high aroma loss	Chinese Pharmacopoeia [25], *Teucrium ramosissimum* [27], *Alseodaphne perakensis* (Gamble) Kosterm [28], *Malaysian horsfieldia* [29], *Boswellia sacra* [30], and Lemon thyme [31]
Organic solvent extraction	OSE	Similar solubility	Higher yield but difficult to completely separate from solutes and fully recycle and reuse, even bringing negative effects on human health	Difficult to completely separate from solutes and fully recycle and reuse, even bringing negative effects on human health	*Lantana camara* leaf [32] and *Pelargonium graveolens* L'Hérit. (Geraniaceae) [33]
Cold pressing	CP	Mechanical pressure	Simpler process, lower energy consumption, less environmental pollution; operating at room temperature retains the original aroma and more benefits of the EOs; turbid and impure	Turbid and impure	*Moringa oleifera* seed [35], *Citrus* [36], Rapeseed (*Brassica napus*) [37], Bergamot [38], and Lemon [39]
Supercritical fluid extraction	SFE	Special dissolution effect of supercritical fluids	Faster extraction speed, higher extraction yield, less loss of active ingredients, and low critical temperature and pressure; expensive and difficult to control the final concentration; poses a potential safety hazard	Expensive, difficult to control the final concentration; poses a potential safety hazard	Sunflower oil [40], Red radish seeds [41], *Origanum vulgare* L. [42], Hemp (*Cannabis sativa*) [43], Chlorella pyrenoidosa [44], and Clove [45]
Ultrasound-assisted extraction	UAE	Mechanical wave with an effective frequency generally ranging from 20 to 50 kHz	High product yield, low organic solvents, short processing time, and low maintenance costs	High equipment requirements and costs; not suitable for industrial large-scale production	Papaya seed [49], *Origanum syriacum* [52], *Elettaria cardamomum* Maton [53], and Pomegranate seed [54]
Microwave-assisted extraction	MAE	Electromagnetic waves with wavelengths from 0.01 to 1 m and frequencies from 0.3 to 300 GHz	High utilization of energy, high extraction rate, and short extraction time, avoiding the chemical modification of the oil components	High equipment requirements and costs; not suitable for industrial large-scale production	*Citrus* limon (*Lisbon variety*) peel [59], Humulus lupulus [60], *Thymus vulgaris* L. [61], Lavender [62], Peppermint [63], *Thymus mastichina* [64]
Solid-phase microextraction (SPME)	SPME	Similar solubility	No solvent; simpler, lower cost, more selective and flexible when paired with appropriate detectors GC, LC, and CE	Perform no detailed extraction	Brazilian virgin oil [70], *Mentha pulegium* L. (*Lamiaceae*) [71]

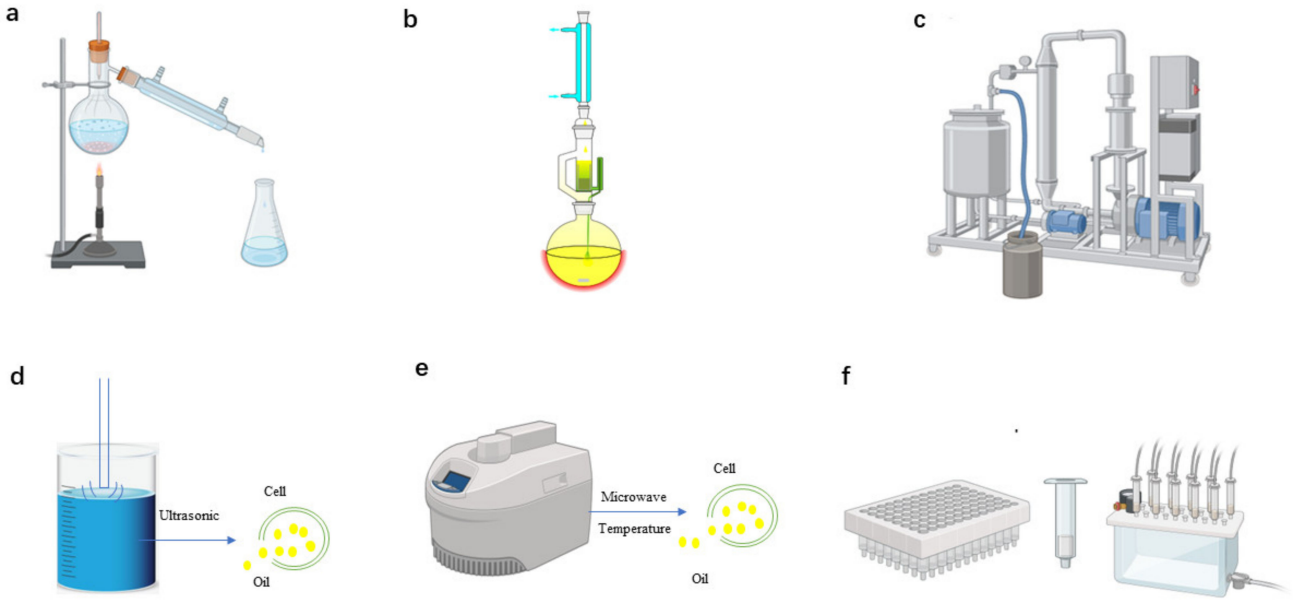

Figure 1. The schematic diagram for the extraction method: (**a**) HD/SD; (**b**) OSE; (**c**) SFE; (**d**) UAE; (**e**) MAE; (**f**) SPME.

3. Separation and Purification

In the preparation process of EOs, two main aspects deserve attention: yield and quality. They are not only closely related to extraction methods but are also greatly influenced by separation and purification methods. If the extracted crude EOs contain moisture, some components will become chemically unstable and prone to hydrolysis, or bacterial growth occurs, that will have a negative impact on the yield and quality of EOs [73]. Therefore, we summarized the commonly used separation and purification methods of EOs in this review, as shown in Table 2 and Figure 2.

3.1. Chromatography

Chromatography is a method of separation and analysis based on the different physical, chemical, and biological characteristics of the separated substances, which move at different speeds in a certain matrix. Its advantage lies in its high separation efficiency for substances with very similar properties.

Plenty of research shows that the chromatography can be used not only for the analysis and identification of substances but also for the separation and purification of substances. Moein M R et al. [74] extracted and fractionated EOs of *Trachyspermum ammi* (L.) Sprague. seeds using column chromatography (CC) and then analyzed all fractions via gas chromatography/mass spectrometry (GC-MS). As a result, γ-terpene (48.07%), ρ-cymene (33.73%), and thymol (17.41%) were identified as its main antimicrobial components. To elucidate more unknown volatile components, Dong G et al. [75] analyzed lavender EOs via GC-MS provided with three capillary columns of different polarities. Nineteen monomers were separated and detected using CC and improved preparative gas chromatography (pGC). Among them, fifteen compounds obtained the first detection in lavender EOs. To further achieve bioassay-guided isolation, researchers attempted to combine multiple chromatographic methods, including silica gel CC, thin layer chromatography (TLC), high-performance liquid chromatography (HPLC), and preparative chromatography (PC). Wu C C et al. [76] performed the separation via silica gel CC with gradient elution using n-hexane and polar-increased ethyl acetate and then separated michelia formosana leaf EOs into 11 fractions using (TLC). Ultimately, the pure compounds with the inhibition effect against wood-rotting fungi such as guaiol, bulnesol, and β-elemol were obtained from the active components using a HPLC with a preparative chromatographic column.

Compared to traditional CC, countercurrent chromatography (CCC) is a full liquid chromatography method without solid phase support [77]. Its principle is based on the distribution effect of the sample between two immiscible solvents, where each component in the solute can be separated during passing through the two solvent phases due to different distribution coefficients [78]. Some researchers found that application of selective reagents such as polysaccharides, transitional metal ions, anionic surface active, etc., in the biphasic solvent system could improve the peak resolution of target components [79]. Referencing the results of partially purifying *Curcumae rhizoma* EOs using silica-gel CC, Lu M et al. [80] used silver nitrate as a selective reagent, further enriching the antitumor constituent β-elemene from fractions based on the formation of coordination complexes by CCC. The recovery of β-elemene was successfully increased from 46.1% to 63.6%.

The special advantages of CCC include no irreversible adsorption and high recovery. In collaboration with other extraction methods, the CCC has become a powerful technique for the isolation and purification of nonpolar bioactive compounds from natural plant EOs, such as *Flaveria bidentis* (L.) Kuntze [81], *Cuminum cyminum* L. [82], *Curcuma wenyujin* [83], *Alpinia oxyphylla* Miquel [84], *Pimenta pseudocaryophyllus* leaf [85], and *Ligusticum chuanxiong* Hort. [86].

3.2. Macroporous Resin (MR)

Macroporous resin (MR) is a type of organic material with good adsorption performance developed in the late 1970s, which has the advantages of the large specific surface area with ideal pore structure and various functional groups [87]. MR mainly adsorbs molecules through the production of van der Waals gravity or the formation of hydrogen bonds, so it is easily regenerated and has relatively low-cost. On the other hand, when compounds in different molecular sizes pass through resin columns, resin also has a certain degree of molecular-sieve effect [88]. Based on the surface properties of the resin, MR can be divided into non-polar, medium-polar, and polar.

Currently, MR has been successfully applied for the separation and purification of crude EOs. Combining the solvent extraction and the MR purification flexibly, Pang J et al. [89] proposed a strategy to prepare *Houttuynia cordata* Thunb. (*H. cordata*) EOs (HEOs) safely and effectively and then encapsulated it using microemulsion. The results demonstrated that D101 resin and microemulsion encapsulation improved the safety and activity of pure HEO significantly. Using various separation methods such as MR and chromatography, Wang X et al. [90] evaluated the components of *Atractylodis macrocephalae rhizoma* (AMR) that were responsible for its expectorant and tocolytic effects; the identified volatile oils were the key components that contributed to the usage change of AMR in both ancient and current time. The above research indicated that MR would be a promising approach for industrial application.

3.3. Chemical Reaction (CR) and Chemical Separation (CS)

Chemical reaction (CR), a method through which a single volatile component is obtained through synthesis via chemical reaction. Millar J G et al. [91] found that with sesquiterpene hydrocarbon zingiberene, dienophile 4-phenyl-1, 2, 4-triazoline-3, and 5-dione formed a Diels–Alder adduct, which was then purified via flash chromatography and hydrolyzed to recover zingiberene. They attained a good yield and >99% purity. Although the CR method can obtain high-purity volatiles, it needs multiple steps, long time, high cost, and also has difficulty in industrial production. So, essentially, more chemical separation methods are used for separating and purifying crude EOs.

Chemical separation (CS) is a method of treating each component one by one using a series of chemical methods such as precipitation, extraction, and fractionation to achieve the separation goal of each component, on the basis of the structure or unique functional groups of each component in EOs. Usually, in order to obtain components with strong acidity, EOs is directly extracted using a 5% sodium bicarbonate solution. Then, the alkaline solution is separated and acidified using dilute acid and subsequently extracted with ether

before volatilization. To obtain phenolic or other weakly acidic components, the EO is usually extracted using a 2% sodium hydroxide solution and an alkaline water layer is separated. After acidification, it is extracted using ether before volatilizing. Applying the latter method, Elbestawy M K M et al. [92,93] successfully obtained the pure eugenol as a light-yellow oil from clove EO and discovered its antibacterial, antibiofilm, and anti-inflammatory activities.

In short, there are various chemical separation methods for separating and purifying EOs, and suitable methods should be selected based on the principles of science, safety, and simplicity. Especially, it should be noted that obtaining a single component is difficult and requires a comprehensive application of multiple chemical methods, now that the separation and purification process of EOs is relatively complex.

3.4. Melt Crystallization (MC) and Three-Phase Crystallization (TPC)

Melt crystallization (MC) is a typical separation method that includes suspension crystallization and layer crystallization, mainly for purifying organic compounds and enantiomeric mixtures [94,95]. One of the advantages is that it does not require any solvents, whereas it is difficult to isolate crystals subsequently from the melt during downstream processing. Moreover, MC can produce high-purity products with a purity of 99.9% or even 99.99%, while the purity processed via distillation and recrystallization is around 99% [96]. Certainly, low cost is another advantage, as the low-temperature operation process is simple and safe without high equipment investment. Additionally, MC is environmentally friendly and energy-saving, the energy consumption of which is only 10% -30% of distillation [97]. Therefore, it can meet the high requirements for separating and purifying pharmaceutical products, food additives, spices, biochemical products, and reagent products [98]. However, a solid solution rich in major components may sometimes be formed for certain systems in MC, when obtaining pure crystals of major components. A solid solution refers to a solid mixture containing secondary components uniformly distributed in the lattice of the main components, which has never been reported to occur in the three-phase crystallization (TPC) process.

Combining the MC method and vaporization, Shiau LD and his colleagues developed a new separation and purification technology called TPC for the separation of the mixtures with close boiling temperatures [99]. By reducing temperature and pressure, it produces desired crystalline products from liquid mixtures with the unwanted components evaporated through three-phase conversion. Thus, there is no need for solid/liquid separation and crystal cleaning throughout the process.

To avoid considering the formation of solid solutions, TPC was also applied in an attempt to separate and purify menthol. Menthol has been developed as a medicine, seasoning, and fragrance due to its cooling effect and special pungent odor. Actually, it is a mixture separated from peppermint oil and can also be artificially synthesized [100]. To merely bio-catalytically resolve L-menthol with an analgesic effect from the menthol enantiomer, Hsu Y C et al. [101] applied the TPC method and determined the conditions for the liquid menthol enantiomer mixtures based on the thermodynamic calculations. It turned out that L-menthol was isolated from the mixtures successfully and the experimental purity of the final product was consistent with that predicted by the model proposed based on the mass and energy balances, although the experimental yield was slightly lower than that of the model [102].

3.5. Pervaporation (PV)

The PV is also addressed as an innovative and economical emerging process for the separation of EOs components. It can substitute conventional methods, such as liquid-liquid extraction and distillation, which are difficult or costly in the purification of mixtures [103]. The PV process mainly depends on the use of a membrane with high potential for purifying substances that degrade/decompose at high temperatures, downstream of which a pressure gradient (vacuum) is applied to promote the diffusion and transfer of substances [104–106].

The crucial part is the presence of a specific membrane with selectivity towards one (or some) component, that will promote a permeate flow of substances more related to the membrane and ultimately determine the separation mode and process efficiency [107–109].

According to the types and separation modes of the membrane, PV can be divided into three categories: hydrophilic pervaporation, hydrophilic organic pervaporation, and target hydrophilic organic pervaporation [110,111]. Castro-Muñoz R et al. [112,113] clearly discovered the potential of PV technology for recovering aroma and flavor compounds from food systems. The task was studied using common hydrophobic/organophilic membranes [114]. Other novel membrane materials are also assessed or explored to overcome the limitations of the selectivity and permeation relationship. She M et al. [115] concentrated three flavor compounds (benzaldehyde, ethyl butyrate, and trans-2-hexenal) from dilute aqueous solutions via PV experiments with flat-sheet PDMS–PVDF composite membranes at ambient temperature (20~22 °C).

To date, the applicability of PV in reference to aroma recovery from EOs, fruit, beverages, and nutritional products has evoked more and more attention, because it meets the needs of lower energy consumption and high efficiency. The PV may be able to substitute other methods, although it is necessary to further investigate the mass transfer process and optimize operating parameters as well as evaluating the economic aspects of the process [116,117].

3.6. Molecular Distillation (MD)

In recent years, MD is an emerging separation and purification technology, mainly utilizing the differences in average free path and volatility of molecules from different substances to achieve efficient separation. This technology is carried out at temperatures far below the boiling point in high vacuum, the heating time of the material is short, and the separation effect is good. In fact, most components in EOs are heat-sensitive compounds that are susceptible to oxidation or degradation due to factors such as light and heat. So, MD is particularly suitable for concentration, purification, or separation of EOs with poor thermal stability.

In previous study, Martins P F et al. [118] extracted and enriched methyl chavez alcohol from basil EO, and its concentration was increased from 83.81% to 89.79% using the MD method. MD was also used to separate fractions from oregano EOs with greater antioxidant activity. The results showed that with higher concentrations of thymol and carvacrol and terpinen-4-ol and γ-terpinene in residue fractions, free radical scavenging capacity (RSC) was increased [119]. As Xu Y et al. [120] reported, different fractions of lavender EOs separated via MD could ameliorate sleep disorders induced by the combination of anxiety and caffeine in mice. The light fraction performed better at sleep maintenance, while the heavy fraction contributed more to sleep initiations owing to affection on GABAergic system, cholinergic system, histaminergic system, and monoamines in the limbic system.

Recent studies have further revealed that the antioxidant activity of the residue fractions obtained via short path MD from rosemary EOs was greater than either the distillate fractions or original EOs and could be developed as natural antioxidants of sunflower oil [121]. In addition, MD has been combined with supercritical CO_2 fluid extraction (SFE) to purify ginger EOs. The results indicate that the method is not only green and environmentally friendly but can also improve the extraction rate of EOs [122].

3.7. Ultrasound-Assisted Purification (UAP)

In addition to being used for extracting EOs, ultrasound can also be used to remove residual solvents from fragrant oil after organic solvent extraction. Liu H M et al. [123] obtained the fragrant oil of red pepper seed via subcritical propane extraction and removed the residual solvent via ultrasound-assisted methods. The results showed that the typical aroma of the oil had no obvious loss, whereas the oil was more suitable for cooking due to the good oxidation stability and quality after ultrasonic desolventizing. It can be seen that

the current widespread application of ultrasound has been applied throughout extraction, separation, and purification of EOs.

Table 2. Separation and purification methods of EOs.

Method	Abbreviation	Principle	Pros	Cons	Sample
Column chromatography	CC	Substances move at different speeds in a certain matrix	High separation efficiency for substances with very similar properties	Long time; require relatively large quantities of solvents	*Trachyspermum ammi* (L.) Sprague. seeds [74], Lavender [75], Michelia formosana leaf [76]
Countercurrent chromatography	CCC	Distribution effect of the sample between two immiscible solvents	No irreversible adsorption; high recovery	Lack of mature theoretical guidance; not suitable for industrial large-scale production	*Curcumae rhizoma* [80], *Flaveria bidentis* (L.) Kuntze [81], *Cuminum cyminum* L. [82], *Curcuma wenyujin* [83], Fruits of *Alpinia oxyphylla* Miquel [84], *Pimenta pseudocaryophyllus* leaf [85], *Ligusticum chuanxiong* Hort. [86]
Macroporous resin	MR	Organic material with good adsorption performance	Easily regenerated and relatively low-cost	Strict pre-treatment and regeneration requirements	*Houttuynia cordata* Thunb. [89], *Atractylodis macrocephalae rhizoma* [90]
Chemical reaction	CR	Synthesis via chemical reaction	High purity; multiple steps, long time, and high cost	Multiple steps, long time, and high cost	Ginger [91]
Chemical separation	CS	Treating each component one by one using a series of chemical methods based on the structure or unique functional groups of each component	Simple, fast, and diverse solvent types	Complex; difficult to obtain a single component	Eugenol clove [92] and Eugenol [93]
Melt crystallization	MC	Crystallization	No solvents; high purity, low cost, and low temperature; simple and safe without high equipment investment, environmentally friendly, and energy-saving	Complex relatively; possible formation of solid solution	Ethylene glycol [95]
Three-phase crystallization	TPC	Crystallization and vaporization	No solvents; high purity, low cost, and low temperature; simple and safe without high equipment investment, environmentally friendly, and energy-saving; no need for solid/liquid separation and crystal cleaning; no solid solution formation	Complicated process	Menthol [100] and L-menthol [101,102]

Table 2. *Cont.*

Method	Abbreviation	Principle	Pros	Cons	Sample
Pervaporation	PV	A membrane with high potential for purifying substances that degrade/decompose at high temperatures	Low energy consumption and high efficiency	Expensive; high demands for membrane and equipment	Strawberry aroma [113,114]
Molecular distillation	MD	Utilizing the differences in average free path and volatility of molecules from different substances	Short heating time and good separation effect	High demands for equipment, high production costs	Basil [118], Oregano [119], Lavender [120], Rosemary [121], and Ginger [122]
Ultrasound-assisted purification	UAP	Mechanical wave with an effective frequency generally ranging from 20 to 50 kHz with the comprehensive effects of cavitation, vibration, crushing, and stirring	High product yield, low organic solvents, short processing time, low maintenance costs, and low aroma loss	High demands for equipment; not suitable for industrial large-scale production	Red pepper seed [123]

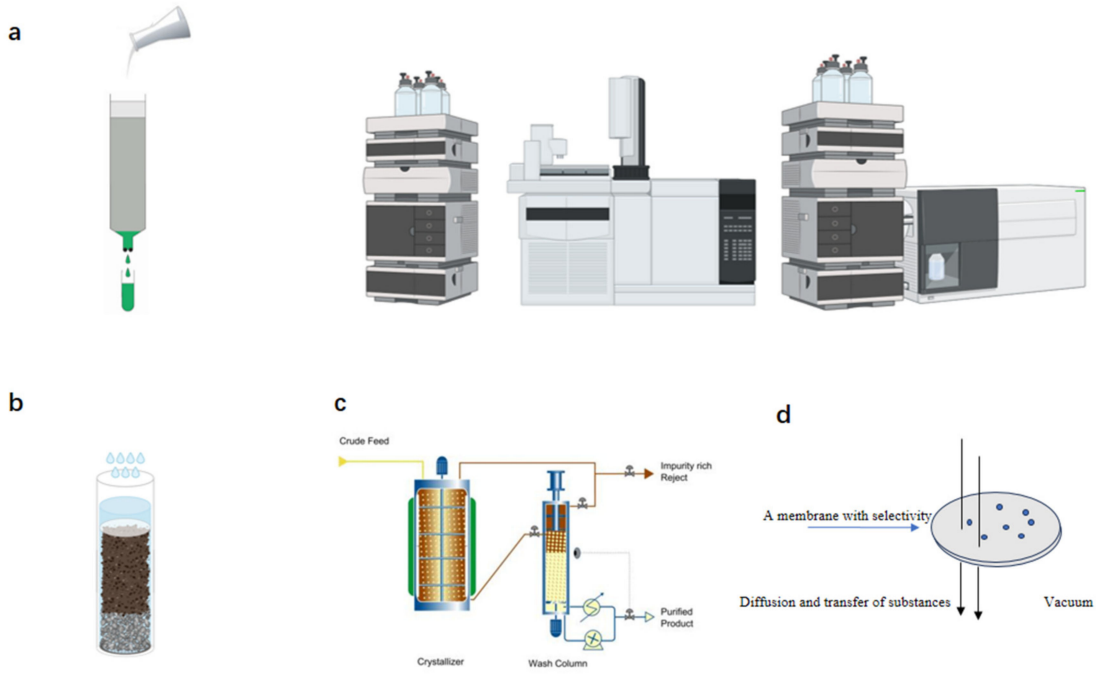

Figure 2. The schematic diagram for separation and purification method: (**a**) CC HPLC, GC-MS, and LC-MS; (**b**) MR; (**c**) MC; (**d**) PV.

4. Conclusions

The use of the aromatic plants has a long and rich history. Their main active ingredient EOs, called liquid gold, can be traced back to the ancient Egyptian era for beauty treatments, spiritual rituals, preservation of some mummies, and medical use purposes. Currently, the diversified plants provide various precious EOs with good smells for the fragrance industry, food manufacturing, medical use, and aromatherapy. But, only a few types of EOs have been developed and utilized due to their complex composition, low yield, and quality. Numerous studies have shown that all of them mainly depend on the appropriately selected methods and conditions for extraction, separation, and purification of natural plant EOs. Due to the advantages and disadvantages of these traditional and novel methods, some

only stay in the laboratory trial stage, while others have gradually adapted to industrial production. In fact, the combined use of multiple technologies is gradually becoming a mainstream choice for researchers or manufacturers because the three processes of extraction, separation, and purification are sometimes inseparable. Based on optimizing the processing parameters, the composition of EOs is gradually clear, the quality is controllable, and the yield is increased subsequently. Together with effective market promotion, the industrial application of natural plant EOs will be vigorously developed.

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