Chapter 2

Sustainable extraction of perfumery plant

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1. Introduction

Since ancient times, combinations of natural ingredients, mainly of plant origin have been used in order to produce perfumes. Traces of scented products were found in almost all ancient civilizations including Egyptian, Persian, Greek, Arab and Roman civilizations.[1] One key step for producing natural perfume ingredients is extraction from plant raw material. Traditional extraction techniques, such as cold-pressing, solvent extraction, hydrodistillation and more modern techniques such as supercritical CO_2 extraction are, as detailed in chapter 1, currently used in the perfume industry. Some techniques present drawbacks. For example, hydrodistillation results in a large energy consumption due to high distillation temperature (100°C) and long processing times. Solvent

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extraction requires large amounts of solvents, generally produced from fossil resources and leading to residual traces of solvents remain in the extract.

Sustainable-minded consumers became aware of the environmental drawbacks of chemical processes in general and in conventional extraction techniques, which led to distrust of ingredients with safety and ecological issues. This led, along with concepts of green chemistry and eco-extraction emerging, to the research and development of alternative and sustainable extraction techniques. The development of such alternative techniques aimed at proposing eco-conceived new fragrant ingredients are mainly studied along two lines: i) using alternative solvents that are safer and sustainable and produced from renewable biomass together and ii) developing innovative extraction intensification techniques.

In this chapter, will be reported concepts and principles of green chemistry and eco-extraction will first be introduced in this chapter. Then, innovative sustainable extraction techniques will be detailed. Finally, a case study taken from one of our works and dealing with extraction of volatile compounds from *Rosa centifolia* using biobased solvents.

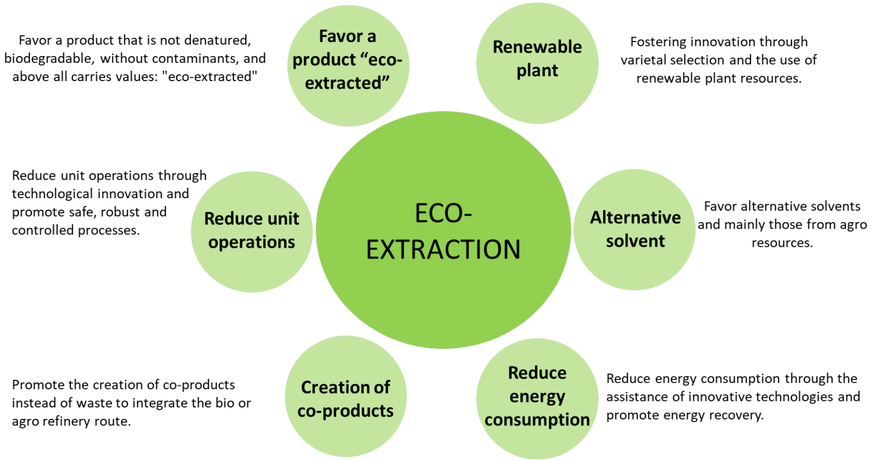
2. Green Chemistry and Eco-extraction

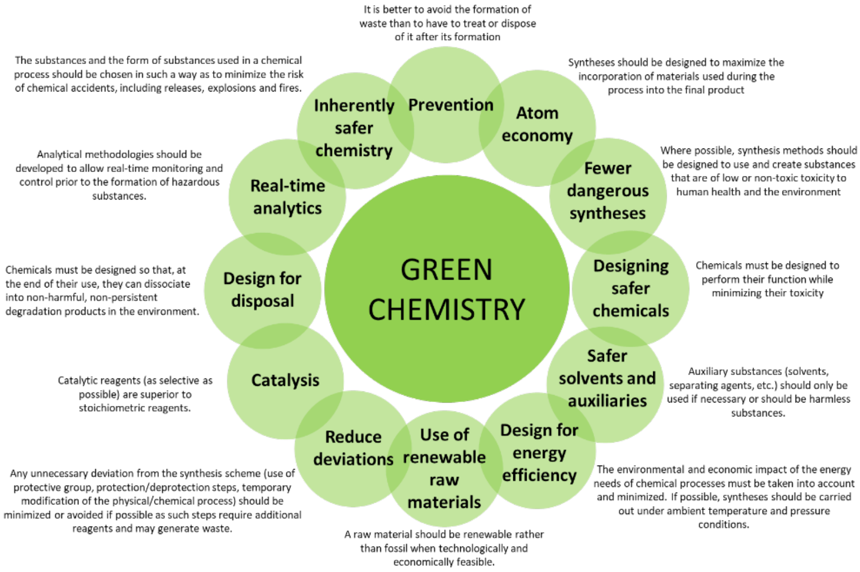
The amount and of chemical products created, distributed, and released in the environment has reached 220 billion tonnes of chemicals were released in 2017 including 20% of greenhouse emissions.[2] This amount of released compounds, along with their extremely large diversity in structure and properties, is nowadays responsible for serious environmental and health issues.[3] In the 90's, as an answer to this ever growing environmental footprint of chemistry, a new concept of so-called green chemistry emerged.[4] It was proposed together with 12 principles, paving the way to developing alternative, sustainable and environment friendly chemistry processes. Later on, this concept was extended to plant extraction by the creation of eco-extraction principles.[5]

In the fragrance industry, a shift towards more sustainable processes started in the early 1980s when regulatory entities restricted, and even prohibited petroleum-based solvents in plant extraction processes, for health, safety, and ecological reasons.[6]

2.1. Green Chemistry

Green chemistry is a general concept that was first defined by Anastas and Williamson in 1996.[4] As stated in their "Green principles" milestone book "*Green chemistry is a set of techniques and methodology to reduce or eliminate the use or production of raw materials, products, co-products, solvents, reagents... that are harmful to human health and the environment*" [4]. This definition was further detailed in 1998 by Anastas and Warner with the introduction of twelve principles of green chemistry, as detailed *Figure* ,[7] acting as a general framework for the development of new sustainable chemical processes, taking into account all aspects of a process life cycle.





It is better to avoid the formation of waste than to have to treat or dispose of it after its formation

Syntheses should be designed to maximize the incorporation of materials used during the process into the final product

Where possible, synthesis methods should be designed to use and create substances that are of low or non-toxic toxicity to human health and the environment

Chemicals must be designed to perform their function while minimizing their toxicity

Auxiliary substances (solvents, separating agents, etc.) should only be used if necessary or should be harmless substances.

The environmental and economic impact of the energy needs of chemical processes must be taken into account and minimized. If possible, syntheses should be carried out under ambient temperature and pressure conditions.

A raw material should be renewable rather than fossil when technologically and economically feasible.

Any unnecessary deviation from the synthesis scheme (use of protective group, protection/deprotection steps, temporary modification of the physical/chemical process) should be minimized or avoided if possible as such steps require additional reagents and may generate waste.

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Chemicals must be designed so that, at the end of their use, they can dissociate into non-harmful, non-persistent degradation products in the environment.

Analytical methodologies should be developed to allow real-time monitoring and control prior to the formation of hazardous substances.

The substances and the form of substances used in a chemical process should be chosen in such a way as to minimize the risk of chemical accidents, including releases, explosions and fires.

Figure 1: The twelve principles of green chemistry. Figure adapted from [7].

Green chemistry, or sustainable chemistry, emphasizes on the reduction of chemistry environmental impact through optimization of the energetic consumption of processes, recycling of both raw materials and by-products created, waste reduction and lowering of health and environmental impacts of such processes, as well as reducing or eliminating use and generation of hazardous substances.[8]

2.2 Eco-extraction

Soon after the proposition of a new concept of green chemistry, the latter has been applied to a wide range of industrial sectors. Obviously, depending on the chemistry field it is supposed to be applied to, such as plant extraction, some of the twelve principles of green chemistry are not adequate, or out of the topic. For example, the 9th principle of green chemistry, dealing with catalytic reagent, has been written for synthetic chemistry processes.[7]

As an extension of green chemistry to plant extraction, concept and principles of eco-extraction were defined by a group of researchers and professionals gathered in Grasse in January 2010. A very general definition was adopted: "*Eco-extraction is based on the discovery and design of extraction processes in order to reduce energy consumption, but also the use of alternative solvents and renewable plant resources, while guaranteeing a safe and quality product/extract*". Six principles of eco-extraction were then proposed (Figure 2). These principles have not been identified as rules but rather as examples of innovation to follow.[5,9] They are listed here below:

1) Encourage a reasonable use of plant renewable resources without over-exploitation to prevent plant extinction because of overutilization.

2) Ask researchers and industries to favour the use of solvents produced from renewable sources rather than petroleum-based ones.

3) Reduction of energy consumption that can be achieved, for example by recovering heat released during solvent vapour condensation or by using activation methods such as ultrasounds.

4) Promote creation of by-products instead of waste during the extraction process, in order to integrate further on a bio- or agro-refinery route.

5) Encourage the use of more robust and controlled processes considering more compact production units and a reduced number of unit operations, energy and raw material savings, process safety control, reduction in waste and ecological footprint.

6) Favour the production of non-denatured and biodegradable extract without contaminants such as pesticides.[5]

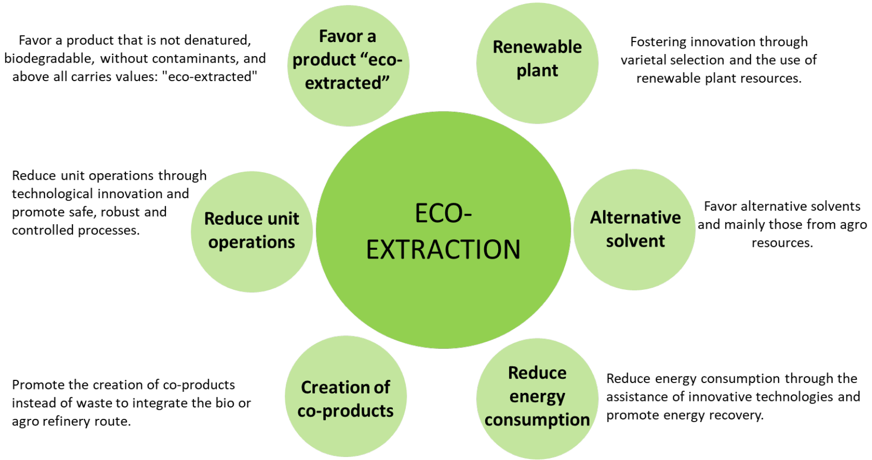


Figure 2: The six principles of eco-extraction. Figure adapted from [9]

Principles of green chemistry and eco-extraction are nowadays strong guidelines for the development of sustainable extraction processes.

3. Innovative Techniques for Green Extraction

Alternative innovative processes were progressively developed in order to satisfy to criteria of green chemistry and eco-extraction and in particular yield higher efficiency, reduce solvent consumption, and lower environmental and health impacts. Applied on traditional raw materials, such innovative processes also represent opportunities to create new products, with their own fragrances and qualities.[10]

Several paths of innovation can be considered to improve the sustainability of extraction processes. For instance, the 5th and 7th principles of green chemistry together with the 2nd principle of eco-extraction encourage the use of safer solvents produced from renewable resources. In the light of the 6th principle of green chemistry for energy efficiency and the 3rd principle of eco-extraction for reduction of energy consumption, new extraction techniques, called intensification techniques, were developed to improve extraction processes.

3.1 New solvents

The efficiency of solid-liquid extraction is mainly conditioned by the nature of the solvent used: it should be selective, inert regarding the compounds to extract and volatile enough to be easily and safely removed at the end of the process.[10]

As stated in the chapter 1, volatile organic solvents and in particular hexane and ethanol are very often used in perfumery plant extraction processes. The use of hexane and more generally of non-polar petroleum-based solvents is in contradiction with the 7th principle of green chemistry and the 2nd principle of eco-extraction as they are produced from fossil resources. Therefore, alternatives solvents produced from biomass resources have been developed. Three kinds of alternative solvents would be introduced in this chapter: biobased solvents (BioSol), deep eutectic solvents (DES) and ionic liquids (IL). The first kind of alternative solvents, BioSol, are solvents produced from biomass resources, for example through fermentation process in the case of ethanol and 1-butanol or chemical transformation of biomass derivatives in the case of 2-methyltetrahydrofuran (MeTHF) or cyclopentyl methylether (CPME). DES are a second family of alternative solvents and are a mixture of at least two compounds exhibiting a significant decrease in the melting point of the mixture compared to the pure substances which makes its use as an extraction solvent possible. The last family of alternative solvent considered is the one of ionic liquids. ILs are salts composed with an organic cation and an organic or inorganic anions and exhibiting a low melting point, typically below 100°C.

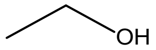
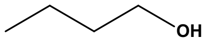
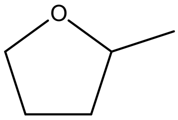
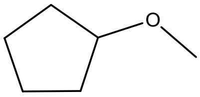
On the one hand, BioSol, DES and ILs can be considered as more sustainable than organic solvents because their production from renewable bioresources comply with the 7th principle of green chemistry and the 2nd principle of eco-extraction. But on the other hand, there is several other criteria that a solvent must meet to be classified as “green” or sustainable. There is no clear definition of a “green” solvent, but several methods were studied previously in order to evaluate the sustainability of a solvent. In 2013, Gu and Jérôme proposed twelve criteria to be met by a solvent to be qualified of ‘green’.[11] Several environmental, health, and safety (EHS) assessments of solvents were previously proposed by pharmaceutical companies Pfizer [12], Sanofi [13], and GlaxoSmithKline (GSK).[14] A guide, proposed by GSK, is nowadays one of the more important and complete method for solvent EHS assessment of a solvent adopting a life cycle approach.[15].

3.1.1 Biobased solvents

As alternative to solvents produced from petroleum resources, several BioSol were developed and among them ethanol, 1-butanol, 2-methyltetrahydrofuran (MeTHF), cyclopentyl methyl ether (CPME), cyrene, γ-valerolactone.[16] However, the constraints of extracting odorous compounds reduce the list of BioSol used in the perfumery field. Solvents generally useful for perfumery are apolar and volatile to be remove after plant extraction.[10]

In this section selected BioSol used in perfumery will be introduced, namely ethanol, 1-butanol, 2-methyltetrahydrofuran (MeTHF) and cyclopentyl methyl ether (CPME). These solvents are moderately polar to non-polar solvents and exhibit boiling point relatively low to be remove by evaporation after extraction. Names, structure, production method and hydrophobicity in terms of octanol water partition coefficient for these solvents are presented in *Table 1*.

Table 1: Names, structure, production method and hydrophobicity of some biobased solvents

Name	Structure	Octanol-water partition LogP	Production method
Ethanol		-0.31 [17]	Sugars fermentation
1-Butanol		0.88 [17]	Sugars fermentation
2-Méthyltetrahydrofuran (MeTHF)		1.01 [18]	Hydrogenation of furfural from lignocellulosic biomass
Cyclopentyl methyl ether (CPME)		1.65 [19]	Furfural rearrangement

Ethanol

Ethanol is one of the most popular solvents that could be produced from biomass. In 2022, the amount of ethanol produced worldwide reached 107 billion litres.[20] In addition, ethanol can be used to produce apolar solvents such as benzene, toluene, and xylene by acid-catalyzed oligomerization.[21]

In one process, ethanol is prepared through an acid-catalysed reaction of hydration of ethylene, a petrochemical compound.[22] Alternatively, ethanol is produced through biomass fermentation. Resulting ethanol is often called bioethanol. Feedstocks used for this fermentation are either rich in saccharides such as sugarcane, sugar beets, corn, molasses, potatoes or rich in starch such as wheat, barley, oat or rice. Ethanol can also be produced from lignocellulosic materials such as agricultural wastes and woody materials.[23] Pretreatment of biomass prior to fermentation is crucial, and differs from one biomass to the other. Such processes are presented in Figure 3.

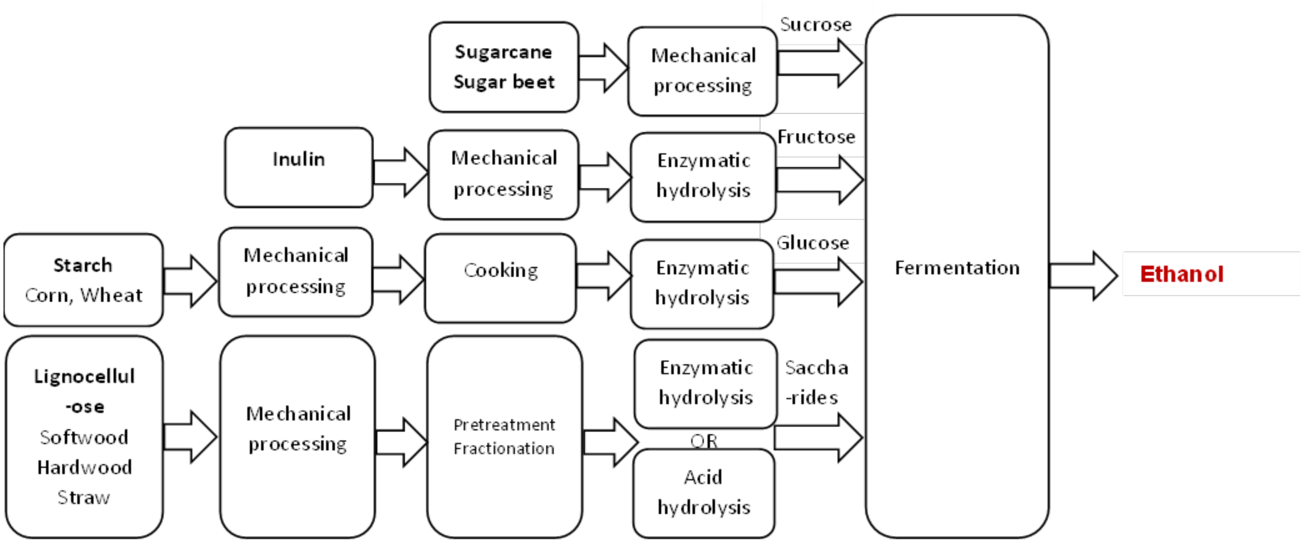


Figure 3: Differents processes for ethanol according to the biomass used. Figure adapted from [23].

Production of bioethanol using microorganisms requires fermentable sugars typically 6-carbon sugars which can be converted into ethanol. Therefore, biomass containing high level of glucose such as sugarcane or sugar beet are most interesting for ethanol conversion. Sugarcane represents the most widely used resource for bioethanol production. However, using such biomass for ethanol production is generally expensive and competes with human food chain.[24] It was estimated that the agricultural sources of crops used in order to produce bioethanol could feed up to 200 million people.[25]

Starch is another biomass commonly used for ethanol production. Corn, wheat, potato, sweet potato and cassava are starchy materials commonly used around the world for ethanol production. Starch is made up of long chains of glucose molecules which must be broken before fermentation. For that reason, starch is commonly mixed with water, stirred and heated followed by the addition of amylase enzymes in order to hydrolyse starch into glucose units.[24] However, as from glucose-rich biomass, such production of ethanol from starch compete with the human food chain. In 2007, 375,000 square kilometres of corn were planted in the US and one-third of it was used to produce ethanol. This led to increases in corn price up to 73% at the end of year 2010.[26]

Alternatively, lignocellulosic materials, obtained from agricultural and forestry by-products can be used as an abundant source of carbohydrates. Lignocellulose is composed of cellulose, hemicellulose which are

polymers of saccharides, and of lignin, a hydrophobic polymer that is very resistant to chemical or biological degradation. Before fermentation, lignocellulose must be hydrolysed in fermentable saccharides. That is achieved mostly using two methods: Acid or enzymatic hydrolysis.[23]
After the pretreatment of biomass, baker's yeast *S. cerevisiae* is the most widely used organism for industrial production of ethanol. *S. cerevisiae* presents many advantages: it grows both under aerobic and anaerobic conditions and tolerates a wide range of pH, temperatures up to around 40°C and high concentrations of sugar and ethanol.[23]

In perfumery, ethanol has been largely use for a long time for the purification of concretes, leading to so-called absolutes.[10] Ethanol is also used to extract dry raw materials such as balsams, oleo gum resins, oleo resins, and resinous products to obtain resinoids. For example, ethanol is use to produce for ginger oleoresin, myrrh resinoid, olibanum resinoid or vanilla oleoresin.[27] Ethanol has recently been used in order to extract fresh perfumery plants such as jasmine (*Jasminum grandiflorum, Jasminum sambac*) or orange blossom (*Citrus aurantium* L. var.amara flowers). But ethanol generally extracts, together with volatile fragrance compounds, some undesirable compounds such as water and sugars that must be removed to obtain a "clearer" fragrance extract. Ethanolic extracts must therefore often be refined. In 2013, Sophie Lavoine-Hanneguelle from Charabot patented a process using supercritical CO_2, in order to obtain flower extracts comparable to traditional absolutes.[28,29] This process has been very little diffused and remains very little used today.

2-Methyltetrahydrofuran

MeTHF is a low polar solvent with very interesting physicochemical properties, such as low miscibility with water, low boiling point, and improved stability compared to tetrahydrofuran. 2-Methyltetrahydrofuran shows properties similar to those of toluene and dichloromethane and have numerous applications, such as solvent for synthesis.[16]
MeTHF can be produced from furfural. Furfural is prepared from carbohydrates derived from lignocellulose-based biomass, such as polysaccharide hemicellulose, present in many plant materials.[30] Pentose carbohydrates are obtained from pentosan contained in hemicellulose through hydrolysis reaction. As shown in Figure 4, furfural can then be obtained from pentose carbohydrates by dehydration reaction

in acidic conditions using sulfuric or phosphoric acid as catalysts.[31] From furfural, MeTHF can finally be obtained by successive hydrogenation reactions using Ni-Cu, Fe-Cu, Cu-Zn, or Cu-Cr alloy catalysts.[30]

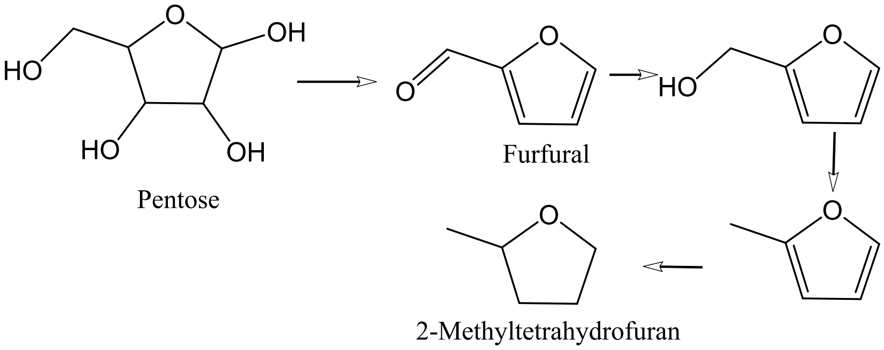


Figure 4: Preparation of 2-Methyltetrahydrofuran from pentose [30].

In January 2023, MeTHF has been authorized as extraction solvent in the food industry. Applications include fractionation of fats, oils or cocoa butter, the preparation of defatted protein products, flours, cereal germs and flavouring with limits with a residual solvent limit varying from 1 to 30 mg/kg of final product.[32]

MeTHF is a promising solvent for the extraction of fragrance compounds. For example, blackcurrant buds (*Ribes nigrum* L) volatile compounds were extracted using several alternatives solvents, namely α-pinene, MeTHF, ethyl acetate, methyl acetate, ethyl lactate, butanol, isopropanol, ethanol and CO_2 supercritical fluid, with the perspective of finding a substitute for hexane traditionally used. MeTHF was found to be the most promising alternative for n-hexane substitution with good yield and selectivity of volatile compounds.[33]

1-Butanol

1-Butanol is a four carbon-alcohol relatively low polar used as solvent and intermediate in synthesis such as butyl acetate synthesis.[16]

1-Butanol could be produced from biological or chemical routes. In 1861, the first route discovered for producing butanol was a fermentation process called ABE (Acetone Butanol Ethanol). The process produced butanol through fermentation of sugars using *Clostridium* species. This process remained the main source of butanol until the 1950s. Later, favoured by cheap oil, a petrochemical process was developed to produce butanol. The fermentation route was then abandoned. More recently, rise in price of oil has revived the fermentation process. Butanol can thus be produced through fermentation of sugar, glycerol, or lignocellulose feedstock in the presence of different micro-organisms from the *Clostridiaceae* family. In 2006, BP company BP launched a production plant capable of producing annually 420 million liters of butanol per year through fermentation.[34]

1-Butanol has been previously used to extract fragrance compounds from peppermint (*Mentha piperita*), lavender and orange peels. 1-Butanol extracts have a comparable odor profile to ethanol extracts but with much higher yields. Compared with hexane and ethanol, 1-butanol gave higher concentrations of fragrance and flavor molecules. Despite a high boiling point of 117°C which makes it difficult to eliminate, this demonstrate biobutanol's potential applicability as an effective alternative solvent.[35]

CPME

Cyclopentyl methyl ether or CPME is an aprotic solvent employed in organic chemistry. Compared to other ethers, CPME is safer with its relatively high boiling point (106 °C) and low tendency to generate peroxides.[16] Nevertheless its high boiling point also represents a strong limit for the extraction of odorants due to the difficulty of eliminating CPME.

Nowadays, CPME is exclusively produced using petrochemical compounds even if some production processes starting from bioresources are considered. In particular, a synthesis route using furfural, through cyclopentanone or cyclopentanol intermediates, is currently studied.[36] Furthermore, it has been recently reported that cyclopentanone could be obtained from a rearrangement of furfural, using water as solvent under hydrogen atmosphere and a heterogeneous metal catalyst (Figure 5).[37] As furfural could be obtained from carbohydrates derived from lignocelluloses' biomass[30], this reaction allows synthesis of CPME from bioresources.

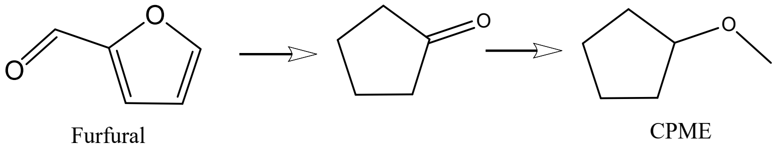


Figure 5: Preparation of CPME from furfural [37].

CPME can be a possible solvent for extraction of volatile compounds. CPME has been compared with a variety of green solvents in comparison with hexane for extraction of limonene from orange peels. Extraction yield for limonene obtained using CPME was found to be 80 % higher than that obtained using hexane. Using MeTHF, extraction yield of limonene was found to be 40 % higher than that of hexane.[38] Beyond this study on the limonene model compound, it would be necessary to evaluate the impact of the use of CPME on the olfactory profile of the resulting extract. To the best of our knowledge, no study has evaluated the olfactory profiles of extracts produced using CPME. Moreover, the use of CPME in perfumery could be limited by the relatively high boiling point of this solvent as explained above.

3.1.2 Deep eutectic solvents

A DES can be described as a mixture of hydrogen bond acceptor (HBA) and hydrogen bond donors (HBD) compounds, exhibiting a significant decrease in the melting point of the mixture compared to that of each pure substance. Such a mixture is called a eutectic mixture. This is related to the occurrence of unexpected interactions between components within mixture.[39] Deep eutectic solvent is "deep" when the melting point of a DES is much lower than the ideal one calculated for a mixture according to the colligative properties of a mixture.[40]

The concept of eutectic was first observed in 1884 and was limited to metallic mixtures. Mixtures of bismuth with either lead, tin, cadmium or zinc were found to exhibit melting points lower than that of each pure metal, or than that obtained using an ideal mixing rule.[41] The use of inorganic salts in order to form eutectic solvents was reported by Abbott et al in 2001.[42] The authors demonstrated the ability of quaternary ammonium salts to form eutectic mixtures when mixed with zinc and or tin chloride and observed that choline chloride (ChCl) led to mixtures with unexpectedly low melting points.[42] These unexpectedly high decrease in freezing point values for such mixtures led to the definition of "deep eutectic solvents", unlike ideal eutectic mixtures detailed above.

DES could be classified in five class depending on their chemical structure. Abbott et al. proposed first in 2014 a classification of DESs in four class.[43] This classification is proposed in Table 2. For plant extraction the main types of DES used are *type III* and *type V* DES. In *type*

III, the HBA Cat^+X^- is in principle any ammonium, phosphonium, or sulfonium cation and X^- a Lewis's base generally a halide anion. The more practical and classically studied HBA compound is choline chloride. The HBD is typically an organic molecular component such as an amide, carboxylic acid, or polyol. *Type V* DES is a non-ionic type of DES, proposed recently by Coutinho et al. This latter type of DES consists of mixtures of non-ionic hydrogen bond acceptor and donor molecules.[40]

Table 2: The five types of DES

Type	General formula	Examples	References
Type I	$Cat^+X^- zMCl_x$	$ChCl:ZnCl_2$	[44]
Type II	$Cat^+X^- zMCl_x yH_2O$	$ChCl:CuCl_2{\cdot}2H_2O$	[45]
Type III	$Cat^+X^- zHBD$	ChCl:Urea	[46]
Type IV	$MCl_x (yH_2O) zHBD$	$FeCl_3$:Acetamide	[47]
Type V	yHBA zHBD	Thymol:Menthol	[40]

Some DES are produced by a mixture of natural compounds. The resulting DES is then called NaDES for Natural DES.

For example, NaDES of type V were used to extract vanillin from vanilla pods.[48] DES were found to exhibit a higher extraction capacity for vanillin than ethanol, while most gave similar or slightly higher yields than methanol. Best extractions yields were obtained with DES composed with lactic acid and 1,2-propanediol or lactic acid and fructose, respectively. Unfortunately, due to high viscosity and low volatility, these DES cannot be removed by evaporation after extraction. Nevertheless, as these DES are composed with chemicals safe in high doses and that have received the "Generally Recognized As Safe" (GRAS) certification (e.g. FG and FGS), these extracts can therefore be included directly in food products without requiring any removal of DES.[48]

Using a different approach, the non-volatility of DES may become an advantage making their use possible as co-solvent during hydrodistillation. Type III DES oxalic acid/choline chloride was used in mixture with 50% of water in a microwave-assisted hydrodistillation of *Litsea cubeba* (Lour.) Pers. Fruits. After 30 min of microwave-assisted hydrodistillation in presence of DES, extraction yield of essential oil was found to be nearly twice as high as that of hydrodistialltion without any DES added to water. This result was explained by the capacity of DES to destroy peel and tissue of plant fruits and therefore accelerate the outflow of volatile compounds.[49]

Currently, despite their interesting solvent capacities, high viscosity and very low volatility found in most DES make their removal from an extract at the end of an extraction process tedious, when not impossible.[10]

3.1.3 Ionic liquids

ILs are salts exhibiting low melting point. A limit for defining a salt as an ionic liquid has been set arbitrarily to a value of 100°C.[50] In addition, most ILs reported in the literature are so-called room-temperature ionic liquids, namely ionic liquids being liquid at or near room-temperature.

ILs are considered as sustainable solvents considering their numerous advantages particularly for process safety and the environment. ILs present high thermal, chemical, and electrochemical stability, non-flammability, and negligible volatility. In addition, ILs can solubilized a wide range of compounds and materials specially those produced naturally.[51] Nevertheless their non-volatility represents a strong limit for the extraction of odorants due to the impossibility of eliminating ILs by evaporation after extraction. The use of ILs requires the development of alternative processes to recover the volatile compounds extracted.

ILs can be formed using both organic and/or inorganic ions and may contain more than one cation or anion.[50] Most ions are monovalent, and at least one of them, generally the cation, exhibits both an ionic head, typically a saturated or unsaturated heterocycle and one or several side chains. Together with unsymmetrical ion shapes, this lead to steric hindrances and oppositions between short-range and coulombic long-range interactions and a significant decrease in the melting point of the ionic structure.[52]

First IL was observed in 1877 during Friedel–Crafts reactions. Over the course of this reaction, formation of a red liquid phase was observed.[53] The structure of these Friedel–Crafts complexes, given in Figure 6, was confirmed in 1952 as heptachlorodialuminate salts.[54]

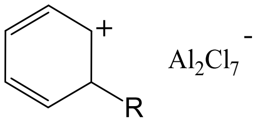


Figure 6: Structure of heptachlorodialuminate salts form during Friedel–Crafts reactions [54].

The first ILs were developed in 1914 by Paul Walden and consisted of alkylammonium nitrates salts being liquid at low temperatures. In particular, ethylammonium nitrate has a melting temperature of 12 °C.[55] ILs became then the subject of intense research activities[56–58] and in 1999 commercially available ILs in high qualities and at accessible prices appeared.[59] In 2002 Swatloski et al., first reported the ability of 1-butyl-3-methylimidazolium chloride IL to dissolve cellulose[60], paving the way for the use of ILs for the treatment of biomass.

Among many applications of ionic liquids, the latter were used as solvent for extraction of essential oil of orange peels.[61] In a first step, orange peels were dissolved in imidazolium-based ionic liquids such as 1-methyl-3-ethylimidazolium acetate ([C_2MIM][AcO]). In a second step, distillation of orange peels straightforward from [C_2MIM][AcO] was carried out. Due to the extremely low vapour pressure of ionic liquids, a volatile extract without any ionic liquid was recovered. Finally, recycling of the ionic liquid was achieved by washing with water and charcoal, hence removing biopolymers solubilized within. In this process, the specific properties of ILs allowed a dissolution of plant matrix, allowing an efficient release of fragrance molecules and a straightforward and mild distillation of these molecules from the IL. This yielded an increase in yield and improved energy efficiency but this study does not provide informations on the olfactory properties of these extracts[61]

'Greenness' of ILs was questioned due to poor biodegradability and toxicity of some ionic liquids. Furthermore, their high viscosities and the steps required in order to synthesize them has hindered up to now large-scale industrial applications.[53]

3.1.4 Conclusion

Greener alternatives to petroleum-based solvents exist, but their sustainability should be carefully considered through a life cycle assessment approach. However, these solvents have some drawbacks in particular higher boiling points which makes their elimination difficult and prevents access to all odorous compounds. The ultimate alternatives are the development of solvent-free extraction methods. These methods would avoid the use of large volumes of solvent which is safer and cheaper and give a resulting extract of higher purity with no traces of residual solvent.[10] This is possible by an intensification technique, called solvent-free microwave extraction.[62]

3.2 Processes' Intensification Technologies

As stated in the chapter 1, conventional extraction techniques, such as hydrodistillation, is energy consuming. To minimize this energy consumption, in accordance with the 6th principle of green chemistry and the 3rd principle of eco-extraction, intensification technologies have been developed. These intensification techniques include microwave assisted extraction (MAE), ultrasound assisted extraction (UAE), pressurized fluid extraction (PFE), enzyme assisted extraction (EAE) and other intensification techniques.[10] Particularly microwaves, enable the development of solvent-free processes[62], an even more advantageous and greener alternative extraction.

3.2.1 Microwave-Assisted Extraction (MAE)

Microwaves are electromagnetic waves with a period typically ranging between 1 m and 1 mm, that is, frequencies ranging between 300 MHz to 300 GHz.

Microwaves interact with molecule dipoles. Submitted to an electric field, a molecule rotates so as to align its dipole with the electric field. Because the latter is oscillating, dipolar molecules irradiated by such microwaves will continuously move upside down. This movement, due to friction with neighbors molecules causes a strong and homogeneous heating effect.[63] Therefore, microwave heating is homogeneous throughout the solution and selective to only dielectric materials as well as solvents with permanent dipoles. In the case where a plant cell is submitted to such electromagnetic field, unlike conventional heating, heat transfer occurs from the inside of the plant cell to the outside (see figure 7).

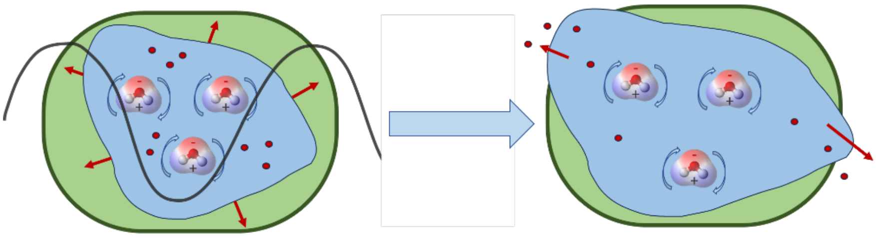


Figure 7: Mechanism of microwave extraction of natural compounds (red dots) from a plant cell based on dielectric heating.

Use of microwave for extraction of natural compounds was first proposed in 1986[64] for the extraction of crude fat, antinutritives i.e. chemical compounds that prevent the absorption of nutrients and organophosphate pesticides from soya bean, cottonseed, walnut and fava beans. The microwave assisted extraction appeared to be more effective than conventional methods with savings in energy and time.[64] afterwards, microwave assisted extractions was used to extract various compounds from plant material including fats and oils[65], antioxidants and food colors[66] essential oils and aromas.[67]

For essential oils and aromas extractions several microwaves assisted extraction methods were developed.[67] These techniques are summerized in Table 3.

Table 3: Microwaves assisted extraction methods for extraction of essential oils and aromas with example of biomass extracted and characteristics of the extracts obtained using these techniques.

Technique	Example of biomass extracted	Extract characteristics	Ref
Compressed Air Microwave Distillation	*Lippia sidoides* Cham	Composition similar to conventional extract with reduced extraction time	[68]
Microwave Hydrodistillation	Boldo leaves	Olfactive profile similar, slightly improved compared to conventional extract	[69]
Solvent-Free Microwave Extraction	*Rosmarinus officinalis* L.	More odoriferous than conventional extract with reduced extraction time	[70]
Microwave Hydrodiffusion and Gravity	*Rosmarinus officinalis* L.	Superior olfactive properties better reproducing the smell of rosemary leaves compared to conventional extract	[71]

Advantages and drawbacks of MAE are presented in Table 4.

Table 4: Advantages and drawbacks of microwave-assisted extraction (MAE)

Advantages	Drawback
- energy and time savings[64] -possibility to perform solvent-free extraction[72]	-higher cost of microwave assisted extractor[73] -promote certain chemical reactions[74]

Compressed Air Microwave Distillation (CAMD)

Compressed Air Microwave Distillation (CAMD) is known as the first microwave assisted method for extraction of essential oil. It has been developed in 1989 by Craveiro et al.[68] This technique is similar to steam distillation except that compressed air is injected instead of steam. A scheme for the experimental setup is shown in Figure 8. A flask containing the plant material is heated in a microwave oven while a compressor injects a flow of compressed air within the flask. The steam produced from the microwave heating of raw material becomes saturated in volatile molecules and is then driven to a recovery vessel immersed in a refrigeration system situated outside the microwave oven. This technique has been applied to the extraction of essential oil from *Lippia sidoides* Cham. The essential oil obtained using CAMD has a composition similar to the one obtained by conventional steam distillation while CAMD significantly reduce the extraction time.[68] Unfortunately the authors did not give information on the olfactory properties of these extracts.

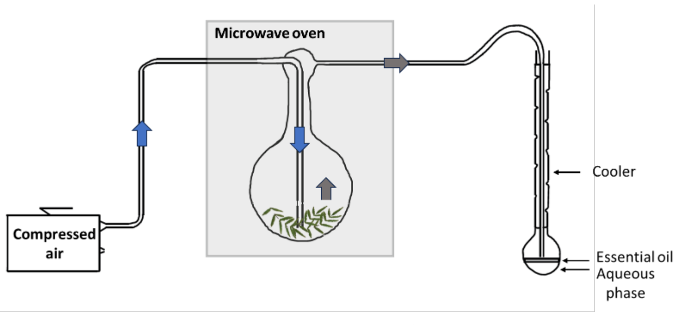


Figure 8: Compressed air microwave distillation apparatus.

Microwave Hydrodistillation (MWHD)

Microwave assisted hydrodistillation (MWHD) was developed by Stashenko et al. in 2004.[75] This method is based on a conventional hydrodistillation apparatus except the heat is provided by a microwave oven. A scheme of the MWHD apparatus is presented in Figure 9. This technique was applied to the extraction of colombian *X. aromatica* fruit essential oils.[75] Hydrodistillation and MWHD gave essential oils with similar compositions in which the compounds responsible for the different olfactory notes of these fruits are found without providing an olfactory analysis of the extracts. For obtaining the same amount of essential oil, time needed using MWHD was four times shorter than using conventional hydrodistillation.[75]

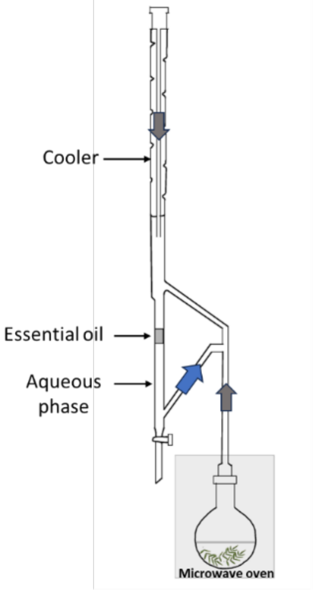


Figure 9: Microwave hydrodistillation apparatus.

In 2014 Petigny et al.[69] studied MWHD of Boldo leaves. The author observed that the essentials oils obtain by MWHD or conventional hydrodistillation technique contain the same major compounds but in different relative proportions. The authors then investigate the sensorial properties of these extracts. The results are presented in Figure 10.

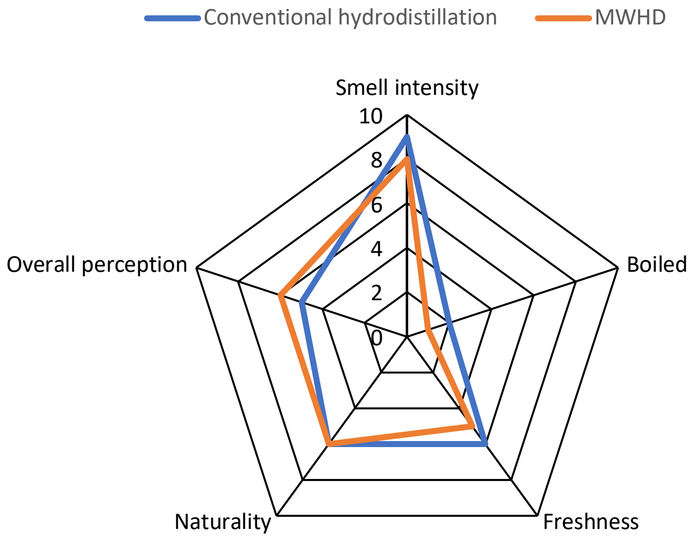


Figure 10: Sensorial analysis of essential oils produced by conventional hydrodistillation or MWHD. Figure adapted from [69]

It can be observed that the two different essential oils have similar olfactive profile with a slightly better overall perception for the MWHD. The use of MWDH reduce the boiled smell and an improved the quality of the essential oil.[69]

A modification of this technique was proposed in 2007 by Flamini et al. which introduce an *in situ* microwave heating through an insulated microwave coaxial antenna placed inside the glass flask.[76] Another improvement was proposed by Sahraoui et al. in 2008. This innovation is based on the principle of steam distillation with a steam generator placed outside the extraction reactor which is irradiated with microwaves.[77]

Solvent-Free Microwave Extraction (SFME)

Solvent-free microwave-assisted extraction (SFME) was developed and patented in 2004 by Chemat et al.[72] In this process, also called microwave-assisted dry distillation, a fresh plant matrix is placed in a microwave reactor without any water or organic solvent added. Heating of the water constituting the raw material yields a breaking of cell walls containing essential oil releasing the essential oil, the latter distillating with the steam produced from matrix water.[72] This method has been applied to several fresh and dry plants, such as spices (ajowan, cumin and star anise), aromatic herbs (basil, mint and thyme) and citrus fruits. For extractions of essential oils, SFME has revealed a more efficient and quicker method than conventional hydrodistillation. Also, essential oil produced using SFME was found to contain more oxygenated compound which are more odoriferous than monoterpene hydrocarbons.[70]

Microwave Hydrodiffusion and Gravity (MHG)

Microwave hydrodiffusion and gravity (MHG) extraction was patented by Chemat et al. in 2008.[78] As in the previous subsection, microwaves induce warming of the water contained in a plant matrix, yielding a destruction of cells containing essential oil. A cooling system is placed outside the microwave below the plant for condensing the distillate.[71] This technique combines microwaves for hydrodiffusion of volatile compounds from the inside to the exterior of biological material and earth gravity to improve collection and separation of the extract. It is important to note that the extract obtained cannot be called "essential oil" because the technique does not correspond to the techniques for the definition of an essential oil described in the ISO 9235 standard.[79] In addition, non-volatile compounds can be solubilized in the extracted mixture. A scheme for the experimental setup is shown in Figure 11. This technique was applied to pearmint (*Mentha spicata* L.) and pennyroyal (*Mentha pulegium* L.). MHG for 15min allowed to extract quantitatively (yield) and qualitatively extracts similar to conventional hydrodistillation for 90min. Therefore, the MHG method is advantageous in terms of time and energy.[80]

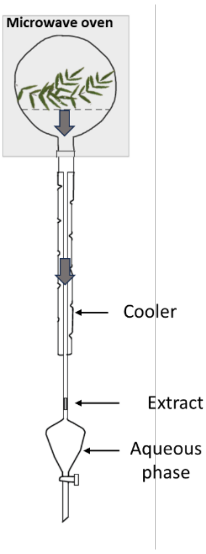


Figure 11: Microwave hydrodiffusion and gravity apparatus.

In 2009, Bousbia et al.[71] compared hydrodistillation and MHG for the extraction of volatile compounds from Rosmary leaves. The used of MHG improved the composition of the extract with a higher amount of oxygenated compounds. In addition, the extract produced with MHG presented superior olfactive properties better reproducing the smell of rosemary leaves.[71]

3.2.2 Ultrasound-Assisted Extraction (UAE)

Low frequency ultrasounds are sonic waves with frequencies ranging from 16 kHz to 100 kHz and are used for extraction and processing of biomass. Ultrasounds irradiating a liquid phase lead to a cavitation phenomenon. This corresponding to the formation in the solvent of microscopic air bubbles/cavities which size and shape oscillate in response to the successive compression/relaxation cycles according to the wavelength of the sonic wave. These cavities always reach an unstable size and implode in such a way that pression and temperature during the implosion can reach locally, where the cavitation bubble implodes, several hundreds of atmospheres and thousands kelvins, respectively.[81] This results in a disruption the biological cell membranes.[82] A schematic representation of the effect of ultrasounds is proposed in Figure 12.

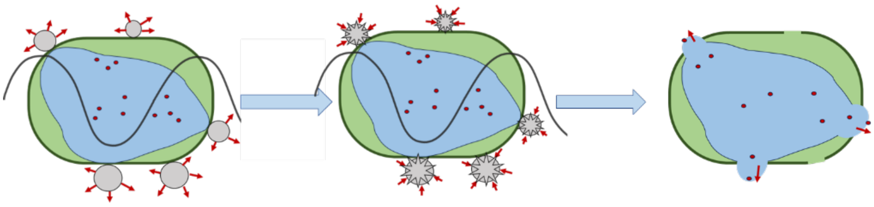


Figure 12: Mechanism of ultrasound extraction of natural compounds (red dots) from a plant cell based on cavitation (grey circles).

UAE is mainly used at the industrial scale in the aroma sector as this technique is known to cause lesser damage to thermal-sensitive molecules than conventional techniques. For example, fresh garlic (*Allium sativum*) cloves were extracted using UAE and conventional hydrodistillation.[83] Variation among sulfur containing molecules, which are thermo-sensitive compounds, were observed. Polysulfides concentration decreased whereas that of vinyl dithiin isomers increased when the isolation techniques were changed from conventional hydrodistillation to UAE. Therefore, UAE appears to be a promising approach in order to preserve and extract the compounds responsible for the characteristic odor and taste of freshly chopped garlic. [83]

UAE was also used in combination with other techniques. UAE were used coupled with supercritical fluid to extract oil from adlay seeds. Ultrasounds led to an increase of the extraction yield and a significant decrease in the extraction time.[84] Ultrasounds were also used combined with hydrodistillation in order to enhance the extraction of essential oil of Celery Seeds (*Apium graveolens* L.).[85] Grounded celery seeds were sonicated prior to the hydrodistillation process. Sonication accelerates water absorption leading to a faster swelling of plant material and an increase in pore size on the cell walls, thus facilitating recovery of essential oil during hydrodistillation process. With the help of ultrasounds, extraction yield increased by 48% compared to conventional hydrodistillation, while chemical composition was similar using both methods.[85] Nevertheless, even though there are several applications of UAE in the aroma industry are quite numerous, there is little use in the fragrance industry.[10] Advantages and drawbacks of UAE are presented in Table 5.

Table 5: Advantages and drawbacks of ultrasound-assisted extraction (UAE)

Advantages	Drawback
- cause lesser damage to thermal-sensitive molecules[83] - energy and time savings[84] - comparing with other activation techniques, ultrasound equipment is economical [86]	-in an ultrasound bath, waves vary depending on position, ultrasound probes are more efficient[86] -scale up difficult[87]

3.2.3 Pressurized fluid extraction (PFE)

Pression is another interesting parameter in order to intensify extraction processes. Pressurized fluid extraction methods can be divided in four classes:
i) Supercritical fluid extraction (SFE) already presented in the chapter 1 for supercritical CO_2.
ii) Pressurized Solvent Extraction (PSE) also known as Accelerated Solvent extraction, Pressurized Liquid Extraction, or Subcritical Solvent Extraction (SSE), accordingly.
iii) Pressurized Low Polarity Water extraction (PLPW), also known as subcritical water extraction, pressurized hot water extraction or superheated water extraction.[10]
iv) Pressurized gas extraction (PGE)[88]

In PSE and PLPW, elevated temperatures increase the extraction efficiency whereas elevated pressure keeps the solvent in a liquid state above its boiling point. High pressures also improve the diffusion of solvents to regions of the plant matrix that could not be reached at atmospheric pressure. However, one must keep in mind that high temperatures are incompatible with extraction of fragile raw material and heat-sensitive compounds.[10] In 2008, Giray et al.[89] studied the extraction of *Lavandula stoechas* flowers using PLPW. The author observed the appearance of thermal degradation with burning smell and the blackening of extracts when the temperature was increase in particular at 150 °C.[89]
PSE was investigated for the extraction of volatile compounds of *Thymus vulgaris* L.[90] Maximum extraction efficiency was obtained using hexane as an extraction solvent, an extraction time of 10 min, an extraction pressure of 30 bar and a temperature of 100°C. PSE was compared with

steam distillation, Soxhlet extraction, supercritical CO_2 extraction and solid phase microextraction. PSE was the most efficient and the most appropriate sample preparation method in determining volatile compounds from thyme herb. Even if the authors did not provide information on the olfactive profile of their extract, they highlighted several advantages of PSE such as high yields and short extraction time but this method present the disadvantage of co-extracting non-volatile component together with volatile compounds.[90] In addition PSE equipment have high cost due to because the materials constituting this equipment must withstand high pressures and temperatures.[91]

PLPW extraction, using pressurized hot water as a solvent, can be consider as an even more sustainable version of PSE as no organic solvents are used in this method. Water is a polar solvent but when heated at 200°C, its dielectric constant drops from 79 to 35, displaying a polarity similar to that of acetonitrile.[92] PLPW was applied to extraction of extraction of fragrance compounds from *Rosa canina*. The author showed that the best extraction conditions are 100 °C with 2 ml/min water flow rate and 50 bar pressure for 2 h. This method was compared with Soxhlet extraction using hexane for 12h. Under these condition PLPW and Soxhlet extraction gave similar yields of benzyl alcohol and phenylethyl alcohol while tetrahydroional, eicosane and 2,6,11-trimethyl dodecane are much better extracted with PLPW. In addition, some fragrance compounds, namely benzaldehyde, α- pinene and limonene were found only in the PLPW extract. The PLPW method is therefore quicker, more environmentally friendly and more efficient than Soxhlet but no information on the olfactory profile of these extracts were provided.[93] In 2013 Miyashita and Hideo[94] showed that PLPW improves the aroma profile of green-tea extracts. Green tea leaves were extracted by PLPW at 30 bar and 130°C for 1 min. The resulting extract had higher catechins extraction yields together with less bitterness and astringency than the conventional sample extracted at 90°C for 10 min. The author explain this result by the improved capacity of PLPW in extracting arginine and water-soluble pectin, which mask the bitterness and astringency of green tea.[94] Advantages and drawbacks of PFE are presented in Table 6.

Table 6: Advantages and drawbacks of pressurized fluid extraction (PFE)

Advantages	Drawback

- energy and time savings[95] -extraction of apolar compounds with water by decreasing, water dielectric constant[92]	-high temperatures are incompatible with extraction of heat-sensitive compounds.[10] - high equipment cost [91]

In PGE, a gas is used under pressure but below its critical point to extract natural compounds from plants. The use of a gaseous solvent allows the production of extracts at low temperatures, to preserve heat-sensitive compounds, and moderate extraction pressures. The use of a gaseous solvents simplifies the elimination of the extraction solvent which can be removed by simple depressurization to obtain an extract without solvent traces.[88] PGE has been used for the extraction volatile compounds from several plant species particularly using halogenated gas such as 1,1,1,2-tetrafluoroethane (freon R134a),[96] or hydrocarbon gas such as n-butane.[97] In 2011 Nenov et al.[98] studied the low temperature extraction of cinnamon barks (*Cinnamomum zeylanicum* Nees) with 1,1,1,2-tetrafluoroethane. The author observed that extracts produce with this technique have odors, tastes and physico-chemical properties comparable with those of cinnamon essential oil.[98] In 2017 Rapinel et al.[97] studied the extraction of lipophilic compounds from sunflower seeds, carrots chips and caraway seeds using pressurized n-butane. The authors observed that the chemical compositions of extracts were unchanged when the reference solvent, hexane, was substituted with n-butane but the extraction yields were reduced. The author attributed reduced extraction yields to a slow mass transfer inside the solvent due to the lack of stirring.[97] Unfortunately, the authors did not provide information on the sensory properties of their extracts. In 2021 Dobreva et al.[96] used pressurized 1,1,1,2-tetrafluoroethane extraction to compare volatile compounds present in four rose species namely, *Rosa gallica* L., *Rosa damascena* Mill., *Rosa alba* L. and *Rosa centifolia* L. The chemical compositions obtained were close to those of the traditional rose oils and absolutes but no information on olfactive profiles were provided in this study.[96] Advantages and drawbacks of PGE are presented in Table 7.

Table 7: Advantages and drawbacks of pressurized gas extraction (PGE)

Advantages	Drawback
- moderate extraction pressures[88] -solvent removed by simple depressurization[88]	-environmental concerns around halogenated gas[96] -reduction of extraction yield due to slow mass transfer[97]

-extracts without solvent traces[88]	

3.2.4 Enzyme-assisted extraction (EAE)

In a plant matrix, compounds of interest are contained within plant cells. The presence of large amounts of various polysaccharides such as hemicelluloses, starch, pectin and of lipid bilayers composing cell walls reduces extraction efficiency using conventional extraction methods. Enzymes, proteins with specific hydrolytic properties, are able to degrade the plant matrix and therefore gain access to active components. A schematic representation of the effect of enzymes is proposed in Figure 13. Enzymes are classified according to the target molecule it hydrolyzes.[99] Cellulases enzymes (such as endoglucanases, cellobiohydrolases, β-glucosidases) hydrolyze celluloses, hemicellulases (such as endoxylanases and β-xylosidases) hydrolyze hemicelluloses and pectinases (such as pectintranseliminase, polygalacturonase, and pectinesterase) hydrolyze pectin. Very often, cooperative effects of multiple enzymes are necessary to increase degradation of cell walls, resulting in higher extraction yields. Therefore, commercially available multiple enzyme blends were developed.[100]

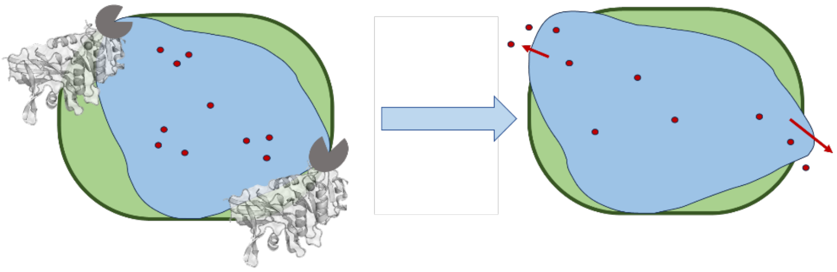


Figure 13: Mechanism of enzyme assisted extraction of natural compounds (red dots) from a plant cell based on enzyme hydrolysis (grey).

EAE was used in order to extract essential oil from black pepper and cardamom.[101] A mixture of enzymes, called Lumicellulae and composed of cellulase, β-glucanase, pectinase, and xylanase, was used for the pre-treatment of black pepper and cardamom. After enzymatic pretreatment, essential oils were recovered by hydrodistillation. Compared with conventional hydrodistillation, EAE increased the extraction yields from 0.9 to 1.8% in black pepper and 1.9 to 2.5% in cardamom. Also, compared to conventional hydrodistillation, mass fraction of major active compounds in spices, such as β-caryophyllene in black pepper and α-terpenyl acetate in cardamom, increased from 15.03 to 25.58 and 38.91 to 48.6%, respectively. EAE was therefore found to improve extraction yield and quality of essential oils by increasing fractions of major active compounds.[101] Unfortunately the author did not provided description of the olfactive profile of their extracts. Enzymes are already used in various domains including food industry for texturing, lactose removal, or flavoring.[102] But today, to the best of our knowledge, enzymes have no industrial applications for aroma or perfume extraction. Advantages and drawbacks of EAE are presented in Table 8.

Table 8: Advantages and drawbacks of enzyme-assisted extraction (EAE)

Advantages	Drawback
- energy and time savings [83] - higher extraction yields [101]	-enzymes are pH and temperature sensitive [83] -enzymes' incorporation into products is regulated[103]

3.2.5 Other intensification techniques

Other intensifications techniques were developed at a laboratory scale for intensifying plant extraction processes, with limited industrial applications.

Instant Controlled Pressure Drop (ICPD)

Instant Controlled Pressure Drop (ICPD) is a technique used at industrial scale for drying, decontamination and texturing of materials applications. ICPD is a two-step technique. First the raw material is submitted to a rapid (usually between 5 and 60 s) thermal treatment with high-pressure saturated steam, typically between 0.1 to 0.7 MPa. This stage is followed by an instant pressure drop towards a vacuum at about 5kPa. This provokes an autovaporization of a part of the water in the product, an instantaneous cooling of the products together and a mechanical effect breaking the cell walls.

This technique has been applied to the extraction of essential oils from Algerian myrtle leaves.[104] ICDP improved the essential oil extraction yield by 10% compared to conventional hydrodistillation, in a shorter time extraction time of 2 min compared with 180 min.[104]

Pulsed electric field (PEF)

Under the effect of PEF at low electric fields, a biological membrane is electrically pierced and becomes permeable. This phenomenon is called electroporation. PEF has been first used for killing microorganisms.[105] Later, PEF was found to be useful for extraction of compounds from plants. For example, PEF was applied to the extraction of functional compounds from cinnamon. Plant powder, mixed with ethanol as a solvent, was placed between electrodes. In order to perform extraction, a pulse generator was used with voltage from 2 to 6 kV/cm and number of 40–60 pulses. The PEF assisted extraction was applied to the extraction of aroma compounds from aromatic plant and food by-product. The use of PEF improved the extraction yield of vanillin from vanilla pods by 14% theobromine and caffeine from cocoa bean shells by respectively 25 and 34%, linalool from vermouth mixture by 114%, and limonene from orange peels by 33%, as compared with untreated samples.[106]

3.2.6 Conclusion

Intensification techniques present several advantages, such as a reduction of time and energy consumption compared with conventional method. Furthermore, innovative technologies are expected to yield ingredients with properties and olfactory profile different from those obtained conventional methods. Such original ingredients can be very valuable for specific sectors, such as niche perfumery. Nevertheless, some limitations, such as regulation or higher extraction equipment costs, hinder the widespread of these techniques.

4. A case study: Sustainable extraction of fragrances from Rosa centifolia.

Rosa centifolia L. belongs to the genus *Rosa* in the Rosaceae family. Until our days, roses are one of the most important groups of ornamental and perfumery plants. Nowadays, about 1000 genotypes of roses are known.[107] *Rosa centifolia* L. is an ancient rose formed by a complex hybridation of *R. gallica, R. moschata, R. canina*, and *R.damascena.*[108] In the perfumery field, the fragrance of *R centifolia* L. cannot be extracted by hydrodistillation, because essential oil yields are too low. Therefore, extraction of R *centifolia* L. is therefore obtained by solvent extraction, producing concrete and absolute. [107]

Figure 14: Pictures of Rosa centifolia L. taken in the garden of the international perfume museum in Grasse (France).

Production of rose concrete is until currently obtained using hexane, a petroleum-based solvent. MeTHF and CPME, two alternative sustainable solvents produced from bioresources, were evaluated as hexane substitutes for obtaining rose concretes and absolutes. These two solvents were selected as low polar bio-based solvents. Also, these solvents exhibit boiling point relatively low to be remove by evaporation after extraction.

Rosa centifolia flowers (Figure 14) were collected from the garden of the international perfume museum in Grasse (France) and extracted by solid-liquid extraction using hexane, MeTHF or CPME for 2h at room temperature under constant magnetic stirring. Compositions of resulting extracts were determined using gas chromatography flame ionization detector coupled with mass spectroscopy (GC-FID/MS). For comparison reasons, an additional extraction using hexane, the solvent industrially used for rose extraction, was carried out. Extraction yields were evaluated using GC-FID with predicted response factor[109] by summing the amount of each compounds identified and reported in Figure 15.

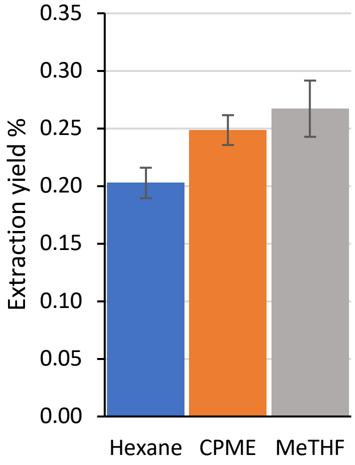


Figure 15: Rose petals extraction yields as function of different solvents used during maceration.

With hexane a yield of 0.20 % was obtained. Using CPME and MeTHF as alternative solvents led to extraction yields improvements to 0.25% and 0.27%, respectively. This corresponds to increases by 25 and 35% respectively.

Then, chemical compositions of these extracts were investigated. In all extracts, major compounds identified using GC-MS were 2-phenylethanol, nonadecane, geraniol and citronellol. Compound structures are presented in Figure 16. These compounds correspond to those previously reported in *Rosa centifolia* extracted through hexanoic solvent extraction.[110] But in rose extracts some minor compounds present at traces levels also contribute to the rose smell. These compounds include citronellol acetate, rose oxides, nerol oxides, farnesol and damascenone.[111] Traces of rose oxides were found only in MeTHF extracts which should have some influence on the scent of this extract. The other compounds were not detected in these three extracts. These compounds are either absent of the extracts or present at concentration below the limit of detection of GC-MS.

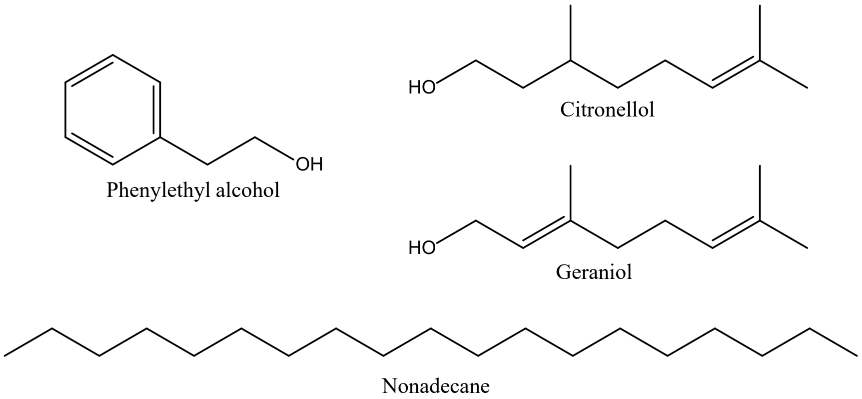


Figure 16: Structure of major compounds identified in rose petal extracts.

The major compounds extracted were quantified in GC-FID using external calibration curves. Results are presented in Figure 17.

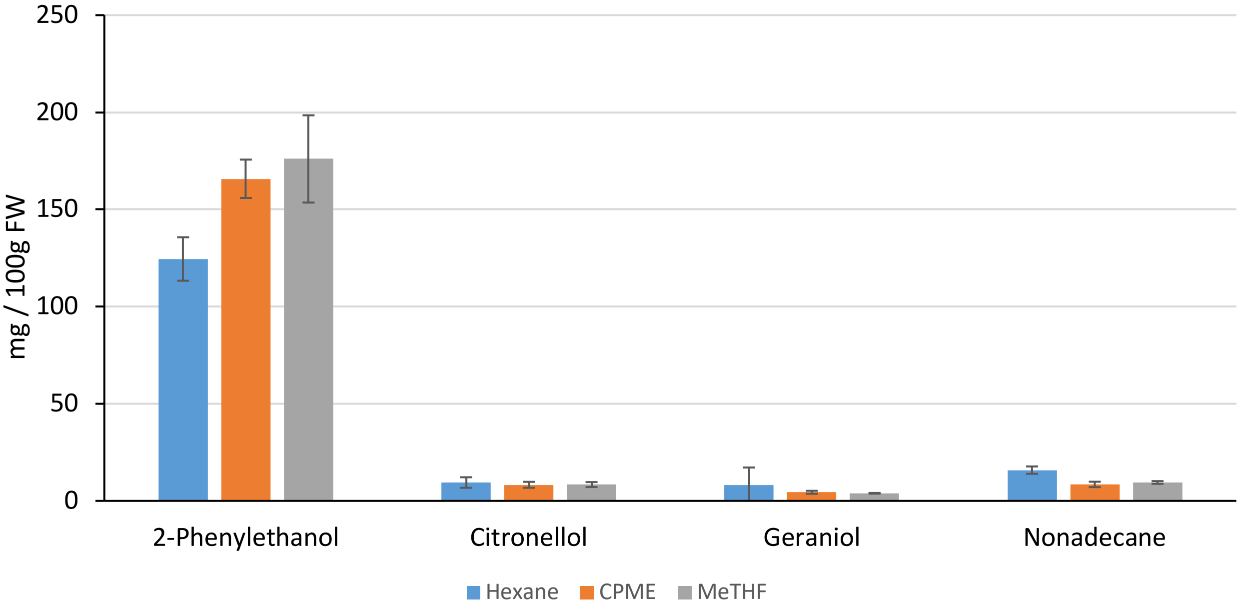


Figure 17: Composition of rose extracts obtained using different solvents. Blue: Hexane. Orange: CPME. Gray: MeTHF. Only major compounds are shown.

Compared to hexane, CPME and MeTHF improved extraction of 2-phenylethanol from 124 mg/g of fresh weight (FW) of flower to 166 and 176 mg/g FW, respectively. On the contrary, there was no significant difference in extraction yield for citronellol or geraniol. Finally, use of

CPME and MeTHF decreased the extraction of nonadecane from 16 mg/g FW to 8 and 9 mg/g FW respectively. Differences in polarity between hexane and CPME or MeTHF explain our results. Hexane is the least polar of all three solvents, exhibiting a value for its octanol-water partition coefficient (logP) of 3.90[17], compared to 1.01 [18] and 1.65 [19] for MeTHF and CPME, respectively. 2-phenylethanol, exhibiting a logP value of 1.36[17], close to that of MeTHF and CPME, is therefore expected to be better extracted using tese two solvents than hexane. On the contrary, nonadecane exhibiting a logP value of 10.39[112] is better extracted in hexane.

CPME and MeTHF therefore appear to be promising alternatives to hexane for extraction of volatile compounds from *Rosa centifolia*. Nevertheless, use of such solvents significantly changes the composition of an extract. Impact of these changes on olfactive profiles were therefore evaluated with the help of a perfumist. Because CPME and MeTHF are volatile, volatile compounds were first separated from solvent by rotary evaporation. Resulting concrete was then mixed with warm ethanol. Upon cooling down the ethanolic solution in a freezer, non-volatile compounds including waxes and fatty acids precipitate. An absolute, shown in Figure 18, is then obtained after filtration and evaporation of ethanol.[10]

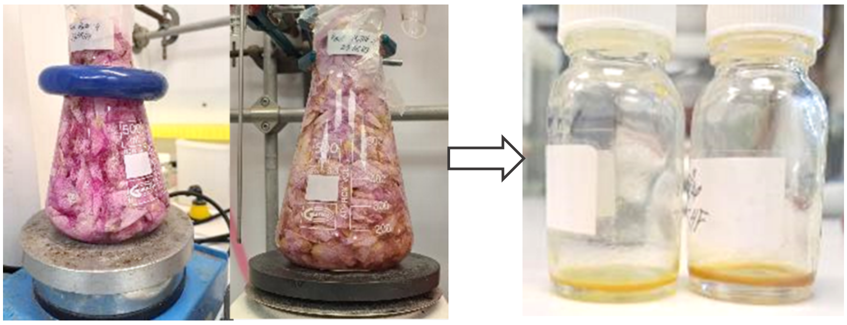


Figure 18: Picture of Rosa centifolia petals maceration and absolute produced with hexane (left) or MeTHF (right)

This procedure was performed for extracts obtained with MeTHF and hexane. CPME was excluded because of its high boiling point (106°C). Evaporating CPME leads to the loss of a non-negligible fraction of volatile compounds. Olfactive notes from absolutes obtained from hexane or MeTHF extraction were determined by a perfumiest[‡] and rated on a scale

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[‡] Virginie Armand fragrance artist, InnovaGrasse, Grasse, France

of 0 to 5. 0 corresponds to an absence of this note in the extracts and 5 a strong presence of this note. For clarity reasons, olfactive notes are presented on a radar chart presented in Figure 19.

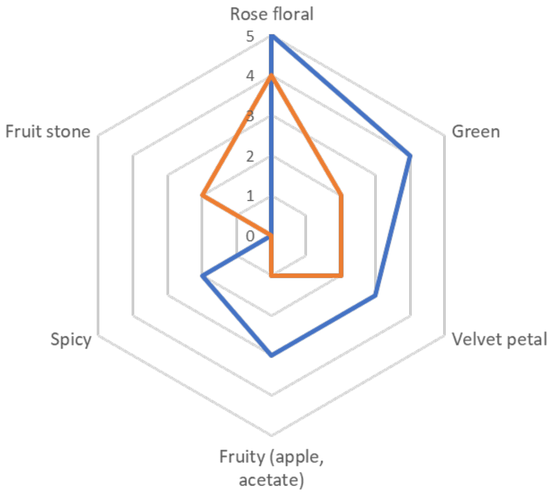

Figure 19: Odor description graphs for Rosa centifolia petals absolutes Blue: concrete extracted with hexane, orange: concrete extracted with MeTHF

Olfactive profiles for hexane and MeTHF absolutes are significantly different. Both absolutes share a common characteristic rose floral note. But the one obtained from MeTHF is less spicy and green. Also, a new fruit stone note appeared. MeTHF is therefore able to extract the characteristic rose floral note from *Rosa centifolia* and complete it with additional notes do not present in the conventional absolute obtained from hexane. Use of MeTHF allow to produce a new type of rose extract that will be evaluated in a perfume composition to confirm the applicability of this new rose absolute.

5. Conclusion

This chapter shows that numerous innovative technologies are currently developed in order to create more sustainable natural ingredients in agreement with the principles of green chemistry and eco-extraction as well as nowaday's consumers concerns. Nevertheless, proposing sustainable alternatives to conventional ingredients, and integrate these new ingredients into a perfumer's palette will require much effort. Today the vast majority of the favor and fragrances ingredients are manufactured by traditional methods presented in chapter 1. There are a certain number of obstacles to the industrialization of processes using alternative solvents and/or modern activation techniques. In particular, the high cost or the absence of large-scale equipment on the market make a certain number of projects economically unrealistic. There are also several regulatory limits that prevent further developments and widespread of these techniques at industrial scale. Finally, because any modification in the extraction process leads to a modification of the extract composition and its sensorial profile and for all the reasons mentioned above it is unlikely to see in a near future such modern technologies and green solvents replacing conventional methods currently used in the fragrance sector.

But because niche perfumery looks for new and innovating fragrance extracts, and because volumes of extracts required in this niche field remain quite restricted, such alternative techniques might have good opportunities to invest such a sector.

Finally, considering a regulatory environment constantly evolving towards more environmentally friendly processes and safer ingredients, current non sustainable ingredients or extraction techniques will eventually be prohibited or restricted. Eco-extracts obtained from sustainable processes. are in line with the general movement of chemistry towards safer and greener process and products and represent a valuable alternative to current ingredients.

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