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Essential Oils for Pest Control

Leo M.L. Nollet, Hamir Singh Rathore

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Valentina Aristizábal Marulanda, Christian David Botero Gutiérrez, Carlos Ariel Cardona Alzate
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8.1 Citronella: Overview

Cymbopogon (Poaceae) is a genus of aromatic plants that includes about 140 species distributed across all continents. A tentative distribution of these plants is mentioned in [1]. The vast majority of these aromatic plants are in Africa, with 52 reported species, followed by 45 in India. Australia and South America have six species each, Europe hosts four species, and North America two. The remaining species are located in South Asia. Genus *Cymbopogon* dates to 1815, when Sprengel named it for the first time. Years later, a group of taxonomists concluded that this plant was a subgenus of *Andropogon*, a convention that was accepted for a few years. In 1906, Stapf stated that *Cymbopogon* should again be considered a genus, as it is known today [1].

The great importance of this genus of aromatic plants lies in its commercial power, because the essential oils extracted from the plants are used in various chemical syntheses. Industries such as the perfume, pesticide, and pharmaceutical industries have the greatest demand for essential oils, especially the genus *Cymbopogon*. Some of the active compounds with higher concentrations in the genus *Cymbopogon* are citronellol, geraniol, citronellal, and linalool. These compounds are used for the production of fragrances and as food additives [1].

According to taxonomy, species of *Cymbopogon* are classified into three groups: "Schoenathi," "Rusae," and "Citrati." The difference between these groups lies in the physiological characteristics of their leaves. For "Schoenathi," the leaves are laminations; in "Rusae," the leaves are heart shaped (subcordate); and "Citrati" has broad leaves at the bottom, but with a sharp point (lanceolate). A clear classification of *Cymbopogon* has been very difficult to carry out due to the large number of species and varieties of this genus and the constant appearance of transitional forms that are generated by hybridization [1]. Table 8.1 shows some of the species and varieties of *Cymbopogon*.

Experimentally, the *Cymbopogon* species can be classified according to their morphology and chemotypical characteristics, although in many cases the distinction is confusing [2].

In this genus, *C. martinii* var. Sofia and *C. martinii* var. Motia present similar morphological characteristics, not distinguishable to the eye, although they have different chemical composition. On the other hand, *C. flexuosus* and *C. citratus* have similar chemotypical features but different morphology [1]. The different chemical compositions that exist between some species and even with plants of the same species may be the work of human intervention, geography, and weather conditions where the plant is [1]. Hybridization can also play an important role in the chemical composition of essential oils, since it can develop plants with morphological and chemotypical intermediate characteristics that cannot be defined taxonomically [1]. At the time, studies performed to discern the extent of genetic

TABLE 8.1

Some Species and Varieties of *Cymbopogon*

C. ambiguus A. Camus.	*C. annamensis* A. Camus.
C. arabicus Nees ex Steud.	*C. arundinaceus* Schult.
C. bassacensis A. Camus.	*C. bhutanicus* Noltie
C. bombycinus var. townsvillensis Domin.	*C. bracteatus* Hitchcock
C. calcicola C.E. Hubb.	*C. chevalieri* A. Camus
C. citratus Stapf	*C. citriodorus* Link
C. densiflorus Stapf	*C. divaricatus* Stapf
C. elegans Spreng.	*C. excavatus* Stapf
C. flexuosus Stapf	*C. floccosus* Stapf
C. giganteus Chiov.	*C. gratus* Domin.
C. iwarancusa Schult.	*C. khasianus* (Hackel) Stapf ex Bor
C. lividus (Thwaites) Willis	*C. martinii* Stapf
C. nardus (L.) Rendle	*C. nyassae* Pilg.
C. polyneuros Stapf	*C. princeps* Stapf
C. winterianus Jowitt	*C. virgatus* Stapf ex Bor

variation between species are presented, aiming at a more accurate classification of the species in this genus [2].

The aim of this chapter is to show the potential of citronella oil given its ovicidal, antimicrobial, fungicidal, and insecticidal ability, as an alternative to synthetic products of this type. This work also presents the chemical composition of citronella oil according to different authors, characteristics, uses, and methods of extraction. Finally, a technoeconomic and environmental analysis of citronella oil extraction is performed with the most relevant extraction technologies, such as solvents, supercritical fluids, and steam distillation.

8.2 Citronella Oils: *Cymbopogon winterianus* (Java) and *Cymbopogon nardus* (Ceylon)

The *Cymbopogon* genus belongs to the family Poaceae (Gramineae), and some species produce essential oils that are a valuable source for the flavor industry, as the case of *C. winterianus* and *C. nardus* [3,4]. The famous citronella oil is derived from *C. nardus* and *C. winterianus*. *C. nardus* (L.) Rendle is also called Ceylon citronella oil or Lanabatu oil, and *C. winterianus* Jowitt is also called Java citronella. Between these oils, there are some differences, such as morphology by length, shape of its leaves, and the chemical composition of its essential oil. The characteristics, uses, and production of citronella essential oil are shown in the following subsections.

8.2.1 Characteristics

Java citronella oil is grown in tropical and subtropical countries of Asia, America, and Africa, among which Haiti, Honduras, Taiwan, Guatemala, China, and Brazil are the most recognized [4]. Citronella Java is an aromatic herbal plant native of southeastern Asia [3] that is of

great importance for both the industry and the Aborigine cultures of the countries where it grows. In India, one of the countries with higher commerce of citronella oil, this plant was introduced in 1959 [5]. In America, the plant was incorporated in Brazil, around the eighteenth century [3]. Citronella Java (*C. winterianus*) comes from citronella Ceylon (*C. nardus*) [5]. At the beginning of the last century, the latter was the largest-producing species of citronella oil, but because citronella Java has higher yields of essential oil, it gradually replaced citronella Ceylon in the market. Currently, Brazil is the largest producer of citronella oil in the Americas [6]. Figure 8.1 shows a picture of citronella Java (*C. winterianus*) [7].

Citronella Java is known for its long leaves, which can grow to be more than 100 cm long and 4 cm wide. Leaves have the highest concentration of oil, which is rich in citronellol, geraniol, and citronellal, ranging from 1% to 1.2% of these compounds [8]. Ceylon-type oil contains phenolic derivatives (methyl eugenol and methyl isoeugenol)—the most significant difference between it and Java-type oil. Both types contain similar amounts of geraniol, although the Java type presents a high quantity of citronellol and citronellal. Also, it contains tricyclene, eugenol, and 1-borneol and small amounts of monoterpene hydrocarbons, such as limonene [4]. Citronella oil comprises about 30–40 compounds extracted from the stem and leaves, among which aromatic compounds like monoterpenes, which are approximately 80%, and sesquiterpenes can be highlighted [9]. Table 8.2 shows the composition of the essential citronella oil Java and the compounds with a higher percentage content (citronellol, citronellal, and geraniol) [10]. These active compounds are highly sought in the chemical industry because they are raw materials for various chemical syntheses [5].

Citronella oil production is affected by factors such as weather conditions and geographical location of plants [8]. Citronella Java generates good yields in warm and high-humidity locations. It is calculated that annual rain precipitations of 200–250 cm are necessary in the crop area [8]. Citronella Java, as well as almost all the plants in the *Cymbopogon* genus, is tolerant to alkalinity and soil salinity [8], but this aromatic plant is very susceptible to flooding in the sown area, so it is necessary to take account of the weather conditions [9]. The necessary conditions for the plant to provide the most oil yield have been studied, and it has been shown that fertile sandy soils are ideal for growing *C. winterianus* [4]. The high concentration of nitrogen in the soil and the plant can generate a high amount of biomass but a low yield of essential oil [4]. Similarly, agricultural factors such as amount of light,

FIGURE 8.1
Citronella Java (*C. winterianus*). (From Singh, N. K. et al., *Parasitol. Res*., 113(1), 341–350, 2014.)

TABLE 8.2

Composition of the Citronella Oil Java (*C. Winterianus*)

Compounds	%
Limonene	1.58
(Z)-Ocimene	0.19
(E)-Ocimene	0.09
Bergamal	0.10
NI	0.25
Linalool	0.88
Isopulegol	0.60
Citronellal	27.44
iso-Isopulegol	0.20
NI	0.09
NI	0.16
n-Decanal	0.41
NI	0.07
Citronellol	10.45
Neral(-citral)	6.02
Geraniol	40.06
Geranial(-citral)	8.05
Citronellyl acetate	0.79
Geranyl acetate	1.77
Caryophyllene	0.55
Cardinene	0.23
Total identified	99.41

Source: Souza, T. et al., *Phytomedicine*, 15(8), 619–624, 2008.
Note: NI, not identified.

humidity, and time of seeding alter oil composition significantly [4]. The supply of light provided by the environment for the plant is a priority for its growth, and low temperatures and moderate relative humidity generate high yields of oil [4].

C. winterianus oil is sold at a higher cost than that of *C. nardus* because geraniol and citronellal are precursors of various chemical synthesis, so consumers prefer high concentrations of these compounds to be fractionated and used in different industrial applications [5].

Due to its benefit, citronella Java has been moved to different countries, and because of problems such as low germination percentage, different researchers have modified its DNA, seeking to reduce these problems and get more oil yield from the plant [11]. Essential oils obtained from genetically modified plants may vary the concentration of some compounds compared with Java oil from unmodified plants, generating advantages for crops that are modified, because they theoretically have higher yields, improved adaptability to the environment, and increased composition of value-added compounds in the produced essential oil.

8.2.2 Uses

Citronella essential oils are used in Chinese and Brazilian medicine. Chinese medicine implements this oil to provide massages and treat rheumatoid problems. It is also used as a painkiller and treatment for women with menstrual problems [12]. Citronella oil has been used for the treatment of parasites so that they can be expelled from the body, to treat muscle

TABLE 8.3

Chemical and Physical Characteristics of Citronella Oil

Guideline 151B-17	Characteristics/Description
Color	Light yellow/yellowish-brown
Physical state	Liquid
Odor	Sweet–floral/grassy/camphoraceous
Melting point	Not applicable
Boiling point	170°C
Density	0.891–0.901 (at 25°C)
Solubility	Very soluble in water at 20°C
Vapor pressure (major components)	Camphene 3.0/limonene 1.4/geraniol 0.02 Citronellal 0.23/citronellol 0.015
Flammability	Flash point at 170°C (TCC)[a]
Storage stability	Stable under normal conditions
Viscosity	Not known
Miscibility	Not to be diluted with petroleum solvents
Corrosion characteristic	Noncorrosive
Octanol–water partition coefficient	Very large, because of high solubility in octanol

[a] U.S. Environmental Protection Agency, "Re-registration eligibility decision oil of citronella list C case 3105."

spasms, and as a diuretic in people with liquid retention [13]. Similarly, Brazilian medicine has employed it as an anxiolytic and analgesic, but its greatest application is as an anticonvulsant [10]. The fact that some people do not respond to conventional treatments with drugs obtained by chemical synthesis, and knowing that, in many cases, these drugs cause serious side effects, prompted natural medicine doctors to test the infusion of the leaves of citronella Java for the treatment of epileptic patients [10]. This treatment resulted in eyelid ptosis, ataxia, analgesic sedation, and reduction of motor activity. With this purpose, the depressant action of the active compounds of the essential oil on the central nervous system of the individual was demonstrated, by improving chronic conditions of the disease in the patient [10]. Because of its high amount of monoterpenes, citronella essential oil has antitumor activity, which can be used for the treatment of cancerous tumors in their stages of initiation and promotion or progression. It can also be used in patients with advanced stages of this disease. Citronella oil has geraniol among its main components, which is highly used in the food industry. Although this substance is needed in low amounts (45 ppm) [12], it is used as a flavoring component of black currant, melon, red apple, orange, lemon, pineapple, watermelon, and blueberry [9]. Geraniol has a smell of roses and is colorless; on the other hand, citronellal also has a pleasant smell, although it is less refined than the aroma of geraniol. Therefore, geraniol has gained a strategic position in the synthesis of fragrances for the perfume industry in the world [9]. For its sweet aromas, it is also used in soap, candles, and even the cosmetics and pharmaceuticals industry [10]. Citronella oil has a repellence property, so it is used in the pesticide industry, but this will be shown in more detail in the next section. Table 8.3 shows the chemical and physical characteristics of citronella oil.

8.2.3 Market

Information on citronella oil, such as its production, cultivated area, price, and market, is not easily available. Indonesia and China are the major producers of citronella oil, with more

TABLE 8.4

U.S. Imports and Prices of Citronella Oil, 2013

Country	Tonnes	USD/kg
Indonesia	197.2	18
China	63.8	15
France	15.3	21
Sri Lanka	11.6	15
Spain	3.8	30
India	3	12
United Kingdom	1.2	28
Taiwan	3.1	10
Total	298.9	18.5

Source: Adapted from Market Insider, Essential oils and oleoresins, 2014.

than 40% of the world's production. Other producers are Taiwan, Guatemala, Sri Lanka, Argentina, Honduras, Ecuador, Jamaica, Madagascar, Mexico, and Brazil. The leading exporters of citronella oil are Indonesia and China, followed by Sri Lanka, India, Taiwan, and European countries such as France and the United Kingdom [4]. The United States is the world's largest importer of citronella oil, and Table 8.4 indicates the reported values of the imports and prices in 2013. Other countries, such as France, the United Kingdom, Germany, the Netherlands, Japan, and Hong Kong, are also importers. European countries prefer Java-type oil due to the presence of the world-famous perfumery industry [4,14].

8.3 Citronella Oil Used as a Pesticide

Rural areas are in constant search for solutions to control pests in crops and animals, becoming a firsthand necessity. Thus, synthetic pesticide consumption has increased in recent years to avoid the loss of products; however, excessive use generates resistance to the plague. About 2.5 million tonnes of pesticides are used worldwide on crops each year, causing great damage to soils. These damages are associated with high toxicity and low biodegradability [15]. Also, synthetic pesticides and plagues can be the cause of environmental problems and the deterioration of human health [13,16]. These reasons have forced the pesticides industry to look for environmentally friendly alternatives, and that is how "green pesticides" were born [15,17]. The concept refers to all types of plant materials that contribute to reducing pests and increasing the sustainability of crops. They are safe for application and consumption. Substances such as plant extracts, toxins of organic origin, hormones, and pheromones are considered green pesticides, and their properties are comparable to, or even better than, those of synthetics [17]. For example, essential oil repellents tend to have an effective short life that depends on volatility [17].

Essential oils are a complex mixture of volatile organic compounds and by-products of plant metabolism (secondary metabolites) that have strong aromatic compounds, and odor and flavor characteristics. Essential oils are contained in the cavities of the plant cell wall (leaves, roots, fruits, stem, etc.) in the form of liquid droplets, and the presence of these compounds in the plants allows their use as defense materials, and in attracting or repelling insects.

For example, the U.S. Environmental Protection Agency (USEPA) has registered citronella, lemon and eucalyptus oils as insect repellent ingredients for application on the skin. These oils have the characteristics of relatively low toxicity and comparable efficacy [17]. Citronella (*C. nardus*) essential oil has been used for more than 50 years as an insect repellent. The larvicidal activity of citronella oil has been mainly attributed to the high content of bioactive compounds such as citronellal, citronellol, and geraniol [15]. Some applications of citronella oil as a pesticide are shown in the following sections.

8.3.1 Ovicidal Potential

There has been research on citronella oil (*C. nardus*) applied for the biological control of mosquitoes, such as *Aedes aegypti* Linn, *Culex quinquefasciatus* Say, and *Helicoverpa armigera* Hubner [18–20]. According to Warikoo et al. [18], 1% of pure oil diluted in water has the capacity to avoid 100% the deposition of eggs in places where it has been applied, and the appearance of larvae is zero. Mosquitoes can perceive different chemical signals through the sensory receptors present on their antennas and select or reject specific oviposition sites. The full deterrent that applying citronella oil against mosquitoes offers is a major improvement over new prospects for pest and vector management. In this sense, citronella oil interrupts the cycle life, since it inhibits mosquito breeding and promotes the control of pests. According to Ramar et al. [19], citronella oil was tested for ovicidal activity against *C. quinquefasciatus* Say (commonly known as the southern house mosquito) at two different concentrations, 12.5 and 200 ppm, with the oil registering 30% and 83.75% of ovicidal activity, respectively. The dose-dependent oviposition activity of citronella oil against *C. quinquefasciatus* is 7.7% and 79.6% at 12.5 and 200 ppm, respectively. Setiawati et al. [20] reported that a 4000 ppm concentration of citronella oil reduced egg laying of *H. armigera* by 53%–66% on chili peppers.

8.3.2 Repellent Potential

Cymbopogon has been traditionally used in tropical regions as a repellent of mosquitoes. Extracts and essential oils of these plants have presented a good repellent effect against different kinds of arthropods [17]. *C. winterianus* oil, mixed with 5% vanillin, gave 100% protection for 6 h against *Ae. aegypti*, *C. quinquefasciatus*, and *Anopheles dirus*, compared with the results observed for 25% DEET (*N*,*N*-diethyl-3-methylbenzanmide) [21]. *C. citratus* has been formulated successfully in a liquid paraffin solution [22].

Citronella oil is marketed in different concentrations and presentations to be used as a natural repellent. Oil has been researched as an excellent repellent of mosquitoes through impregnation on skin, candles, or incense, producing an insecticidal effect against some arthropods [23–25]. The mechanism of repellency for citronella oil against arthropods is not clearly known [23]. Some authors report that citronella oil is harmless, but others have published that it can cause allergic reactions on the skin (irritancy) and has problems due to its rapid volatility [25,26]. Some examples of the repellent effect of citronella oil are

- *Triatoma rubida* (Uhler), *Triatoma protracta* (Uhler), and *Triatoma recurva* (Stal) are hematophagous insects that produce severe allergic reactions and possess the potential to transmit the blood parasite *Trypanosoma cruzi* [23]. Zamora et al. [23] evaluated the main components of citronella oil (geraniol, citronellol, limonene, and citronellal) and found them to be an excellent deterrent of the feeding of *T. rubida* on a restrained mouse. They determined that all components have some

inhibition of feeding (from a mild inhibition in the case of limonene to a considerable inhibition in the case of geraniol and citronellol).

- As a volatile repellent, the effect is achieved through lighting a candle when an uncontrolled release of oil is given in the environment, generating concentration gradients. This method is not the most suitable, because in the majority of cases, it does not reach the concentration in which the oil produces repellency. Otherwise, if the candle releases high amounts of oil, the repellency effect lasts a short time [16].

The storage of agricultural products is an important stage in their production and commercialization. Insects and pests changing the properties of products, such as nutritional value, weight, quality, and hygiene, can affect this stage. Thus, the products lose economic value in the market. Citronella oil is presented as an alternative to end this type of problem. For example, the oil has repellent action against *Callosobruchus maculatus*, considered the most important plague for the cowpea. At a concentration of 622 ppm of *C. winterianus*, a 100% reduction of *C. maculatus* in cowpea grains is achieved [27]. However, the addition of botanical oils can change the organoleptic properties of products. At this point, the quality and toxicity of essential oil play an important role.

8.3.3 Insecticidal Activity

In tropical countries, the livestock sector faces problems related to the proliferation of ticks in the animals, causing weight loss and thus economic losses. The use of synthetic insecticides has caused some species of ticks to generate immunity to the conventional chemicals and also the contamination of meat and dairy products, affecting human health [28]. Citronella oil has insecticidal effects for some species of ticks [7,28]. According to Singh et al. [7], the aqueous and ethanolic extracts of leaves of *C. winterianus* are assessed for their acaricidal activity against the larvae of deltamethrin (synthetic acaricidal)-resistant *Hyalomma anatolicum*. As a result, this work obtained that "the ethanolic extracts produced a concentration dependent increase in larval tick mortality, whereas the aqueous extracts exhibited a much lower mortality. The highest mortality (93.7 ± 0.66%) was observed at the 5.0% concentration of ethanolic extract of leaves of *C. winterianus*" [28]. Also, Singh et al. [28] reported that "the acaricidal activity of aqueous and ethanolic extracts of leaves of *C. winterianus* against the SP resistant engorged females of *Rhipicephalus* (*Boophilus*) *microplus* is evaluated. A high activity was found with the ethanolic extract of leaves of *C. winterianus* with LC_{50} (95%CL) values of 0.46% (0.35– 0.59%). The results of this study indicate that the extract can be used for the control of SP resistant ticks" [7]. Torres et al. (2012) show a work where "the influence of *C. winterianus* fractionation on acaricidal activity against the cattle tick *R. (B.) microplus* is studied. The oil is fractionated by vacuum distillation yielding fractions. The obtained results indicate that fractions 4 (100°C–125°C) and 5 (>125°C) of the *C. winterianus* essential oil are the most active, showing LC_{50} values of 1.20 and 1.34 µl/ml, respectively. The LC_{50} of the total oil is 3.30 µl/ml, while the effect of fractions 1–3 is less pronounced, with LC_{50} values of 4.37, 4.24 and 3.49 µl/ml, respectively" [29].

8.3.4 Antifungal Activity

The necessity to avoid the fungal contamination of industrial and agricultural products has generated the search for alternatives to conventional processes such as temperature control, ultraviolet irradiation, and dehumidification. These alternatives are focused to

develop nontoxic, environmentally friendly, and natural fungicides. For example, the antifungal activity of citronella oil on *Aspergillus niger* conidia is determined, and the experimental results indicate that "the citronella oil has strong antifungal activity: 0.125 (v/v) and 0.25% (v/v) citronella oil inhibited the growth of 5×10^5 spore/ml conidia separately for 7 and 28 days, while 0.5% (v/v) citronella oil could completely kill the conidia of 5×10^5 spore/ml. Moreover, the fungicidal kinetic curves revealed that more than 90% of the conidia (initial concentration is 5×10^5 spore/ml) was killed in all the treatments with 0.125 to 2% citronella oil after 24 h" [30]. Billerbeck et al. [31]) reported that essential oil of *C. nardus* at a concentration of 400 mg/L caused growth inhibition of 80% after 4 days of incubation of *A. niger*. Chen et al. [32] studied the antifungal activity of citronella oil against postharvest *Alternaria alternata* in cherry tomato. "The results indicate that citronella oil possesses strong antifungal activity against *A. alternata* in vitro and in vivo. For in vivo culture, the most effective dosage of the oil was 1.5 µl/ml, with 52% reduction, and the oil had no negative effect on fruit quality. Citronella oil could be a promising natural product for use as an anti-*A. alternata* agent to control black rot in cherry tomato" [32].

8.3.5 Antimicrobial Activity

Some works report studies where the antimicrobial activity of citronella oil is analyzed. Thus, Oussalah et al. [33] indicated that *C. nardus* and *C. winterianus* (herb grass) showed a high antimicrobial activity at concentrations of 4 and >8 mg/ml respectively, against *Pseudomonas putida* CRDAV 372 isolated from fresh beef [33]. According to Wei and Wee [34], "the antimicrobial activity values of the *C. nardus* ranged from 0.244 µg/ml to 0.977 µg/ml when tested against *Edwardsiella* spp., *Vibrio* spp., *Aeromonas* spp., *Escherichia coli*, *Salmonella* spp., *Flavobacterium* spp., *Pseudomonas* spp. and *Streptococcus* spp. isolated from internal organs of aquatic animals" [34]. Luangnarumitchai et al. [35] presents for "*C. nardus* a value of antibacterial activity of approximately 18 mm, represented as inhibition zone, against strains of *Propionibacterium acnes* that plays an important role in the pathogenesis of acne inflammation" [35].

8.4 Citronella Oil Composition

The experimental analysis of citronella oil is generally carried out by methods such as gas chromatography (GC) coupled to mass spectrometry (MS) [3,6,9,10,12,27,34,36], gas–liquid chromatography (GLC) [1], and gas chromatography [37]. Some authors report the chemical composition of citronella oil as indicated in Table 8.5.

8.5 Toxicity

8.5.1 Mammalian Toxicity

Table 8.6 shows the results for a toxicological analysis of Ceylon- and Java-type oils applied to mammals, supported in the Registration Eligibility Decision (RED) test [38]. According

TABLE 8.5

Chemical Composition of Citronella Oil

Component (%)	Java [39]	Java [3]	Java [12]	Ceylon [12]	Ceylon [34]	Java [6]	Java [27]	Java [10]	Java [9]	Java [37]	Java [36]
Limonene	8.02	2.2	1.3	9.7	2.7	3.0	3.90	1.58	3.41	2.6	2.15
Citronellyl acetate	10.22	2.5	3.0	1.9	–	3.5	2.51	0.79	4.58	4.5	4.41
Citronellal	11.05	26.5	32.7	5.2	29.6	36.1	35.47	27.44	40.23	28.8	35.28
Citronellol	14.61	7.3	15.9	8.4	4.8	–	10.94	10.45	13.39	9.4	10.93
Geraniol	15.40	16.2	23.9	18.0	–	19.9	21.83	40.06	17.70	17.6	21.99
Linalool	18.55	0.7	1.5	1.2	–	0.1	1.15	0.88	0.97	0.7	1.61
Geranial	19.48	0.7	–	–	–	0.6	0.50	8.05	1.13	–	1.22
Isopulegol	24.13	–	–	–	–	0.1	1.22	0.60	–	–	–
Neryl acetate	24.90	0.1	–	0.3	–	–	0.03	–	–	–	–
Myrcene	–	3.3	–	–	–	0.1	0.07	–	–	–	–
(E)-β-Ocimene	–	0.7	–	–	–	–	–	0.09	–	–	–
allo-Ocimene	–	0.2	–	–	–	–	–	–	–	–	–
(E)-Isocitral	–	0.2	–	–	–	–	–	–	–	–	–
Nerol	–	0.4	7.7	0.9	–	0.3	–	–	–	0.3	–
Neral	–	0.5	–	–	–	0.4	0.33	6.02	–	–	–
Geranyl acetate	–	3.4	–	–	–	3.8	–	1.77	4.67	6.3	4.52
β-Elemene	–	4.4	–	–	3.3	1.6	1.67	–	2.71	–	2.83
β-Ylangene	–	0.3	–	–	–	–	–	–	–	–	–
β-Gurjunene	–	0.2	–	–	–	–	–	–	–	–	–
Aromadendrene	–	0.1	–	–	–	–	–	–	–	–	–
Neryl Propanoate	–	0.1	–	–	–	–	–	–	–	–	–
α-Humulene	–	0.1	–	–	–	0.1	0.11	–	–	–	–
cis-Cadina 1,(6),4-diene	–	0.1	–	–	–	–	0.05	–	–	–	–
cis-Muurola-4,(14),5-diene	–	0.1	–	–	–	–	–	–	–	–	–
ɣ-Muurolene	–	0.1	–	–	–	–	0.14	–	–	–	–
Germacrene D	–	1.1	–	–	2.3	2.6	1.93	–	–	–	–
trans-Muurola-4,(14),5-diene	–	0.1	–	–	–	–	0.05	–	–	–	–
Viridiflorene	–	0.1	–	–	–	–	–	–	–	–	–

(*Continued*)

TABLE 8.5 (CONTINUED)

Chemical Composition of Citronella Oil

Component (%)	Java [39]	Java [3]	Java [12]	Ceylon [12]	Ceylon [34]	Java [6]	Java [27]	Java [10]	Java [9]	Java [37]	Java [36]
ɣ-Cardinene	–	0.4	–	–	–	–	–	–	–	–	–
α-Muurolene	–	0.4	–	–	–	0.4	0.45	–	–	–	–
δ-Cadinene	–	2.5	–	–	1.8	1.9	–	–	2.87	–	2.80
Zonarene	–	0.1	–	–	–	–	–	–	–	–	–
α-Cadinene	–	0.1	–	–	–	–	0.08	–	–	–	–
Elemol	–	14.5	6.0	1.7	–	5.8	3.73	–	4.77	12.3	4.62
10-*epi*-ɣ-Eudesmol	–	0.1	–	–	–	0.2	0.07	–	–	–	–
1-*epi*-Cubenol	–	0.1	–	–	–	–	0.05	–	–	–	–
ɣ-Eudesmol	–	0.8	–	–	–	–	0.58	–	–	–	–
epi-α-Cadinol	–	0.5	–	–	–	–	–	–	–	–	–
epi-α-Muurolol	–	0.7	–	–	–	1.0	0.86	–	–	–	–
β-Eudesmol	–	0.2	–	–	–	–	0.33	–	–	–	–
α-Eudesmol	–	0.2	–	–	–	1.6	–	–	–	–	–
α-Cadinol	–	2.7	–	–	–	–	1.61	–	–	–	–
(2E,6Z)-Farnesol	–	0.2	–	–	–	–	–	–	–	–	–
Methyl heptenone	–	–	Traces	0.2	–	–	0.06	–	–	–	–
Bourbonene	–	–	Traces	1.0	–	–	–	–	–	–	–
Linalyl acetate	–	–	2.0	0.8	–	–	–	–	–	0.3	–
β-Caryophyllene	–	–	2.1	3.2	–	0.1	0.11	–	–	1.0	–
Geranyl formate	–	–	2.5	4.2	–	–	–	–	–	1.5	–
Citronellol butyrate	–	–	Traces	Traces	–	–	–	–	–	–	–
Methyl eugenol	–	–	Traces	1.7	–	–	–	–	–	–	–
Methyl isoeugenol	–	–	2.3	7.2	–	–	–	–	–	–	–
Farnesol	–	–	0.6	Traces	–	0.2	–	–	–	–	–
Tricyclene	–	–	–	1.6	–	–	–	–	–	–	–
α-Pinene	–	–	–	2.6	–	–	0.01	–	–	–	–
Camphene	–	–	–	8.0	–	–	–	–	–	–	–
β-Pinene	–	–	–	Traces	–	–	–	–	–	–	–

(*Continued*)

TABLE 8.5 (CONTINUED)

Chemical Composition of Citronella Oil

Component (%)	Java [39]	Java [3]	Java [12]	Ceylon [12]	Ceylon [34]	Java [6]	Java [27]	Java [10]	Java [9]	Java [37]	Java [36]
Sabinene	–	–	–	Traces	–	–	–	–	–	–	–
Car-3-ene	–	–	–	Traces	–	–	–	–	–	–	–
α-Phellandrene	–	–	–	0.8	–	–	0.02	–	–	–	–
cis-Ocimene	–	–	–	1.4	–	–	–	–	–	–	–
trans-Ocimene	–	–	–	1.8	–	–	–	–	–	–	–
p-Cymene	–	–	–	Traces	–	–	–	–	–	–	–
Terpinolene	–	–	–	0.7	–	0.1	0.07	–	–	–	–
1-Hexanol	–	–	–	0.1	–	–	–	–	–	–	–
Camphor	–	–	–	0.5	–	–	–	–	–	–	–
α-Terpineol	–	–	–	Traces	–	0.1	0.06	–	–	–	–
4-Terpineol	–	–	–	Traces	–	0.1	0.06	–	–	–	–
Menthol	–	–	–	Traces	–	–	0.21	–	–	–	–
1-Borneol	–	–	Traces	6.6	–	–	–	–	–	–	–
Geranyl butyrate	–	–	–	1.5	–	–	–	–	–	–	–
Nerolidol	–	–	–	0.3	–	–	–	–	–	–	–
2,6-Octadienal, 3,7-dimethyl-, (E)-	–	–	–	–	11	–	–	–	–	–	–
cis-2,6-Dimethyl-2,6-octadiene	–	–	–	–	6.9	–	–	–	–	–	–
Propanoic acid, 2-methyl-, 3,7-dimethyl-2,6-octadienyl ester, (E)-	–	–	–	–	6.9	–	–	–	–	–	–
Caryophyllene	–	–	–	–	6.5	–	0.55	–	–	–	–
Phenol, 2-methoxy-3-(2-propenyl)-	–	–	–	–	4.5	–	–	–	–	–	–
2,6-Octadien-1-ol, 3,7-dimethyl-, (E)-	–	–	–	–	2.4	–	–	–	–	–	–
2,6-Octadiene, 2,6-dimethyl-	–	–	–	–	1.6	–	–	–	–	–	–
Eugenol	–	–	–	–	1.5	–	0.82	–	–	–	–
3,7-Cyclodecadiene-1-methanol, α, α,4,8-tetramethyl-, [s-(z,z)]	–	–	–	–	1.3	–	–	–	–	–	–
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis (1-methylethenyl)-,[1S-(1α,2α,4α)]-	–	–	–	–	1.3	–	–	–	–	–	–

(*Continued*)

TABLE 8.5 (CONTINUED)

Chemical Composition of Citronella Oil

Component (%)	Java [39]	Java [3]	Java [12]	Ceylon [12]	Ceylon [34]	Java [6]	Java [27]	Java [10]	Java [9]	Java [37]	Java [36]
Cyclohexanemethanol, 4-ethenyl-α,α,4-trimethyl-3-(1-methylethenyl)-,[1R-(1α,3α,4α)]-	–	–	–	–	1.3	–	–	–	–	–	–
2,6-Octadien-1-ol,3,7-dimethyl-,acetate,(E)-	–	–	–	–	1.2	–	–	–	–	–	–
α-Caryophyllene	–	–	–	–	0.3	–	–	–	–	–	–
Naphthalene, 1,2,4α,5,6,8α-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1α,4αα,8αα)-	–	–	–	–	1.1	–	–	–	–	–	–
Naphthalene, 1,2,3,4,4α,5,6,8α-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-, (1α, 4αα, 8aa)-	–	–	–	–	0.6	–	–	–	–	–	–
2-Furanmethanol,5-ethenyltetrahydro-α,α-5-trimethyl-, *cis*-	–	–	–	–	0.2	–	–	–	–	–	–
β-Phellandrene	–	–	–	–	–	0.1	–	–	–	–	–
Decanal	–	–	–	–	–	0.1	0.08	–	–	–	–
β-Citronellol	–	–	–	–	–	9.9	–	–	–	–	–
β-Bourbonene	–	–	–	–	–	0.2	–	–	–	–	–
ɣ-Cadinene	–	–	–	–	–	0.4	0.36	0.23	–	–	–
Germacrene D-4-ol	–	–	–	–	–	1.7	0.45	–	–	–	1.48
O-Cymene	–	–	–	–	–	–	0.02	–	–	–	–
(Z)-β-Ocymene	–	–	–	–	–	–	–	–	–	–	–
Bergamal	–	–	–	–	–	–	0.05	0.10	–	–	–
ɣ-Terpinene	–	–	–	–	–	–	0.02	–	–	–	–
(Z)-Rose oxide	–	–	–	–	–	–	0.03	–	–	–	–
(E)-Rose oxide	–	–	–	–	–	–	0.01	–	–	–	–
Menthone (iso)	–	–	–	–	–	–	0.03	–	–	–	–
Isopelugol (neoiso)	–	–	–	–	–	–	0.08	–	–	–	–
Methyl chavicol	–	–	–	–	–	–	0.04	–	–	–	–
(E)-Anethole	–	–	–	–	–	–	0.72	–	–	–	–
Thymol	–	–	–	–	–	–	0.03	–	–	–	–

(*Continued*)

TABLE 8.5 (CONTINUED)

Chemical Composition of Citronella Oil

Component (%)	Java [39]	Java [3]	Java [12]	Ceylon [12]	Ceylon [34]	Java [6]	Java [27]	Java [10]	Java [9]	Java [37]	Java [36]
α-Copaene	–	–	–	–	–	–	0.02	–	–	–	–
Geranil acetate	–	–	–	–	–	–	3.15	–	–	–	–
β-Copaene	–	–	–	–	–	–	0.03	–	–	–	–
Muurola-3,5-diene	–	–	–	–	–	–	0.03	–	–	–	–
Dauca-5,8-diene	–	–	–	–	–	–	0.03	–	–	–	–
β-Selinene	–	–	–	–	–	–	0.06	–	–	–	–
Cubebol	–	–	–	–	–	–	0.13	–	–	–	–
Germacrene-A	–	–	–	–	–	–	0.38	–	1.75	–	–
Cadina-1,4-diene	–	–	–	–	–	–	0.05	–	–	–	–
Eudesmol (5-epi-7-epi-α)	–	–	–	–	–	–	0.03	–	–	–	–
α-Muurulol	–	–	–	–	–	–	0.15	–	–	–	–
Bulnesol	–	–	–	–	–	–	0.16	–	–	–	–
-(Z)-Ocimene	–	–	–	–	–	–	–	0.19	–	–	–
iso-Isopulegol	–	–	–	–	–	–	–	0.20	–	–	–
n-Decanal	–	–	–	–	–	–	–	0.41	–	–	–
1,6-Germacradien-ol	–	–	–	–	–	–	–	–	1.8	–	–
Cedrenus	–	–	–	–	–	–	–	–	–	–	0.76

TABLE 8.6

Report of Acute Mammalian Toxicity for Citronella Oil

Guideline	Test Material	Results	Toxicity Category
152B-10: Acute oral tox. (rat)	Citronella oil 100% (Ceylon)	LD_{50} > 5000 mg/kg	IV
	Citronella oil 100% (Java)	LD_{50} > 4380 mg/kg	III
152B-11: Acute dermal tox. (rabbit)	Citronella oil 100% (Ceylon)	LD_{50} > 2000 mg/kg	III
	Citronella oil 100% (Java)	LD_{50} > 2000 mg/kg	III
152B-12: Acute inhalation (rat)	Citronella oil 100% (Ceylon)	LC_{50} > 5000 mg/kg	IV
	Citronella oil 100% (Java)	4 h exposure LC_{50} > 3.1 mg/L	IV
152B-13: Primary eye irritation (rabbit)	Citronella oil 100% (Ceylon)	Irritation cleared in 72 h	III
	Citronella oil 100% (Java)	Irritation cleared within 7 days	III
152B-14: Primary dermal irritation (rabbit)	Citronella oil 100% (Ceylon)	Irritation present at 21 days	II
	Citronella oil 100% (Java)	All irritation resolved by 48 h Citronella mild irritant	III
152B-15: Dermal sensitization (guinea pig)	Citronella oil 100% (Ceylon)	Sensitizer (Buehler test)	Not applicable
	Citronella oil 100% (Java)	Nonsensitizer (Buehler test)	Not applicable
152-16: Hypersensitivity	All products	All incidents must be reported to the agency	

Source: Adapted from USEPA, Registration eligibility decision—Oil of citronella, USEPA, Washington, DC, 1992; USEPA, R.E.D. FACTS oil of citronella, USEPA, Washington, DC, 1997.

Note: Categories: I, very highly or highly toxic; II, moderately toxic; III, slightly toxic; IV, practically nontoxic. LC_{50}, median lethal concentration. A statistically derived concentration of a substance that can be expected to cause death in 50% of test animals. It is usually expressed as the weight of substance per weight or volume of water, air, or feed (e.g., mg/L, mg/kg, or ppm). LD_{50}, median lethal dose. A statistically derived single dose that can be expected to cause death in 50% of the test animals when administered by the indicated route (oral, dermal, or inhalation). It is expressed as a weight of substance per unit weight of animal (e.g., mg/kg).

to the USEPA, the Ceylon-type oil is most appropriate to be qualified in toxicity category III due to dermal irritation, and therefore the products that contain citronella oil must be labeled with precautions [26]. For Java-type oil, there is no presence of dermal irritation in the animals when the test is carried out, as shown in Table 8.5. In the primary eye irritation for both oils, the results are similar (toxicity category III—all irritation cleared within 7 days). As part of the RED test, the oils are reevaluated for the studies of dermal sensitization. The Ceylon-type oil is a sensitizer and Java-type oil is a non-sensitizer. Thus, the USEPA requires additional precautions for Ceylon-type oil about dermal sensitization [26].

8.5.2 Ecological Toxicity

Table 8.7 shows the ecological toxicity data of citronella oil to perform an assessment of the environmental effects for the use of oil. Applications such as lotion, candle, and spray

TABLE 8.7

Report of Ecological Toxicity for Citronella Oil

Guideline	Study	Results
154B-6	Avian acute oral (bobwhite quail)	LC_{50} > 2250 mg/kg; practically nontoxic; NOEL 1350 mg/kg
154B-7	Avian subacute dietary	Waived because of low avian acute toxicity and no mortality observed at upper test limits
154B-8	Fish toxicity (rainbow trout)	LC_{50} > 17.3 mg/L (based on nominal concentration); slightly toxic; minimal exposure to aquatic sources
154B-9	Invertebrate toxicity (*Daphnia magna*)	EC_{50} > 24.6 mg/L (based on nominal concentration); slightly toxic; minimal exposure to aquatic invertebrate species
154B-10	Nontarget plants	Waived because exposure to nontarget plants will be minimal
154B-11	Nontarget insects	Waived because exposure to nontarget insects will be minimal

Source: Adapted from USEPA, Registration eligibility decision—Oil of citronella, USEPA, Washington, DC, 1992.
Note: NOEL, no observed effect level.

do not represent dangerous exposure situations for avian, aquatic, and nontarget species. For ornamental and dump uses, the citronella oil presents a major exposure potential. Table 8.7 indicates that for avian, aquatic, or insect species, adverse effects are not likely. The USEPA reported that the effectiveness of citronella oil diminishes over time as insect repellent; the reasonable effectiveness lasts for 1–2 h [26].

8.6 Extraction of Citronella Oil

Essential oils can be extracted from different parts of a plant, such as peels, flowers, seeds, leaves, and bark. Different extraction methods are used according to botanical use and the state and form of material. The quality of an essential oil depends on the extraction method. The extraction can be carried out by various methods, such as extraction with solvent and distillation; for example, the steam distillation technique has been a method widely used for industrial-scale production. The use of an inappropriate procedure can damage or alter the action of the chemical composition of essential oil, affecting its bioactivity and natural characteristics. Also, the oil can present physical changes, such as discoloration, loss of odor and flavor, and increase of viscosity [40]. These changes are due to loss of components or the presence of solvent residues, and they can affect the economic value of the product in the market.

A brief description of extraction methods is presented in the next sections.

8.6.1 Solvent Extraction

8.6.1.1 Conventional Solvents

This method is used for extraction of delicate components that are not tolerant to heat. Various solvents can be used, depending on the plant material and interesting compounds. Ethanol, hexane, water, methanol, and acetone, among others, can be used as extraction solvents [41]. To achieve a good efficiency, the extraction technique should consider parameters such as particle size, solvent-to-feed ratio, solvent characteristics,

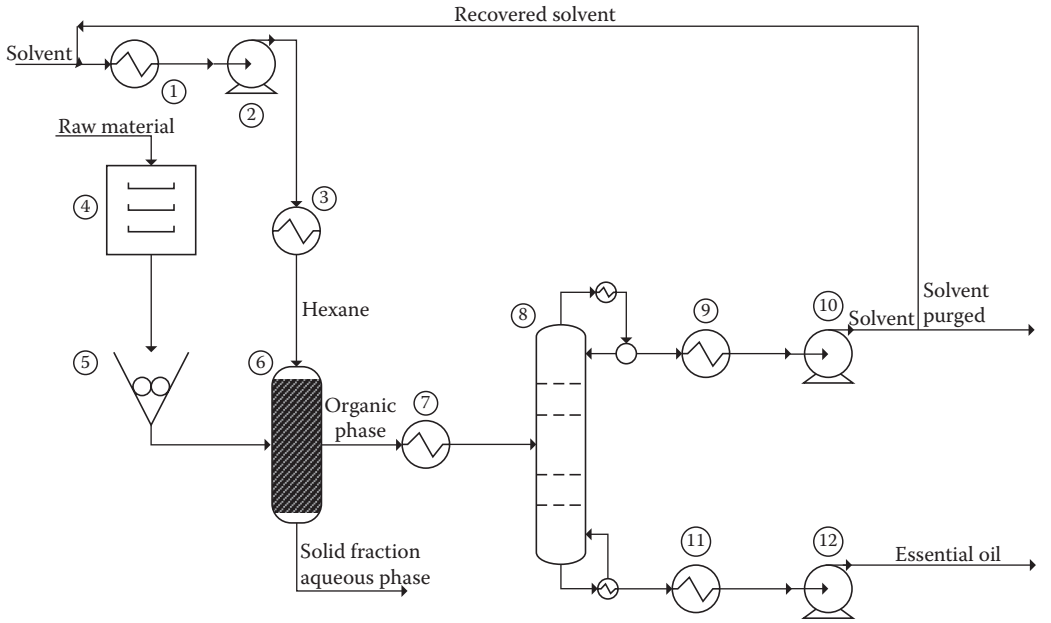

FIGURE 8.2
Flowsheet of solvent extraction. 1, heat exchanger; 2, pump; 3, heat exchanger; 4, dryer; 5, grinder; 6, contact container; 7, cooler; 8, recovery column; 9 and 11, heat exchanger; 10 and 12; pump.

and temperature. The method consists of mixing the material with solvent, heating up to extract the essential oil, and filtering to separate the solid from the liquid phase. The liquid contains the organic phase and essential oil. This is concentrated, and the solvent is recovered by evaporation. The obtained resin (waxy mass) is diluted in alcohol (ethanol) to purify the essential oil and remove the unwanted material by distillation at low temperature to avoid the thermal degradation of oil. Figure 8.2 shows the process scheme of solvent extraction (SE). This technique has the disadvantages of requiring a long time in comparison with other methods, the presence of solvent traces in oil that can be toxic, the cost of solvents, and that it might be unfriendly to the environment [40–43].

8.6.1.2 Supercritical Carbon Dioxide

Supercritical fluid extraction (SFE) is presented as a novel, environmentally benign, and green technology to obtain natural extracts. This technique is carried out at mild temperatures in the absence of air, avoiding thermal and oxidative degradation of thermolabile components, and therefore, it can be successfully used for the recovery of volatile compounds. The technique consists in taking the CO_2 to supercritical conditions and contacting it with the plant material. A stream rich in essential oil mixed with supercritical CO_2 is obtained. Then, it is slowly depressurized to prevent loss of product of interest. Figure 8.3 shows the process scheme of SFE. SFE is presented as an alternative to conventional techniques to correct some problems linked to low efficiency, high processing time, and energy consumption. For example, supercritical fluid extraction is more economically viable than steam distillation due to the lower yield and the higher energy consumption that

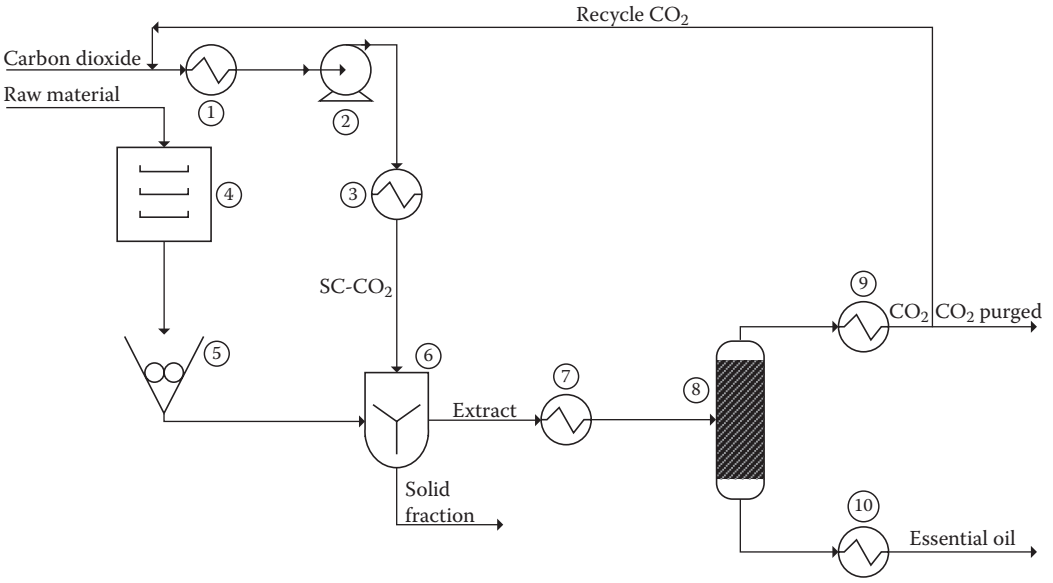

FIGURE 8.3
Flowsheet of supercritical fluid extraction. 1, heat exchanger; 2, pump; 3, heat exchanger; 4, dryer; 5, grinder; 6, extraction chamber; 7, heat exchanger; 8, container; 9 and 10, heat exchanger.

the second technique presents [44]. Hydrodistillation (HD) cannot recover some organic compounds that SFE can obtain [40].

Carbon dioxide is the most commonly used supercritical fluid for extraction because it has nontoxic and nonflammable characteristics, and it is an inexpensive solvent [44–46]. CO_2 is converted into liquid under high-pressure conditions, and thus generates a safe medium to extract aromatic components from plant material. In the final product, there are no residues of solvent because at ambient temperature and atmospheric pressure, it is gas and evaporates. The extraction efficiency depends on the solubility between interesting products and supercritical fluid. Therefore, the extraction efficiency is low for polar compounds because CO_2 is a nonpolar solvent and cannot be solubilized. The solubility of natural compounds in supercritical CO_2 is improved through the variation of temperature and pressure of extraction and the addition of polar cosolvents. In supercritical CO_2 extraction, ethanol is commonly used as a cosolvent due to its properties of high miscibility in CO_2 and low toxicity [4,40,44–47].

8.6.1.3 Subcritical Water

This method of extraction is also known as pressurized hot water or superheated water (subcritical water extraction [SWE]), and it is a technique based on using water as an extracting agent at certain temperature and pressure conditions (100°C–374°C, high pressure) to maintain it in the liquid state. Figure 8.4 indicates the flowsheet of subcritical water extraction. SWE is presented as a powerful alternative of extraction by features such as rapid extraction, use of low temperatures, low cost in terms of energy and material, and favorable environmental impact. Subcritical water extraction is a method of high efficiency because, compared with hydrodistillation, it consumes less time and obtains high-quality

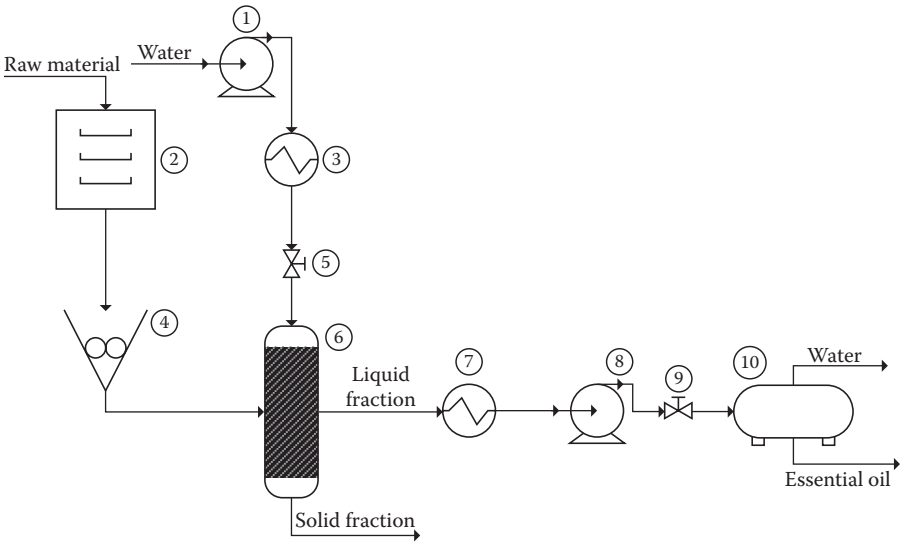

FIGURE 8.4
Flowsheet of subcritical water extraction. 1, pump; 2, dryer; 3, heat exchanger; 4, grinder; 5, valve; 6, contact container; 7, heat exchanger; 8, pump; 9, valve; 10, decanter.

and terpene-free essential oils. The work at low temperatures avoids the degradation or loss of volatile and thermolabile compounds [40,48,49].

8.6.2 Solvent-Free Microwaves

The conventional methods to extract essential oil have some failures, such as low extraction efficiency, loss of some volatiles, long extraction times, and thermal degradation of compounds. These factors have led to consideration of the use of other techniques, such as solvent-free microwave extraction (SFME), which is based on the combination of microwave heating and dry distillation, and is carried out at atmospheric pressure. The method consists in putting the vegetal material in a microwave reactor. If the plant material is fresh, do not add any water or solvent. Otherwise, the sample must be rehydrated by soaking in water for some time, and then the water excess is drained off. The internal heating of the *in situ* water within the material distends the plant cells and leads to rupture of the glands, releasing the essential oil that is evaporated by the *in situ* water of the material. The distillate is condensed with a cooling system outside the microwave oven and is collected in a receiving vessel. Figure 8.5 indicates the flowsheet of solvent-free microwave extraction. SFME has advantages involving shorter time and higher yields and selectivity, and it is environmentally friendly [40,50–52].

8.6.3 Distillation

8.6.3.1 Steam Distillation

The essential oil extraction by steam distillation is the most widely used method for commercial-scale production, although in some cases, the high costs of installation and use of steam can be limiting. The steam distillation method has advantages over other

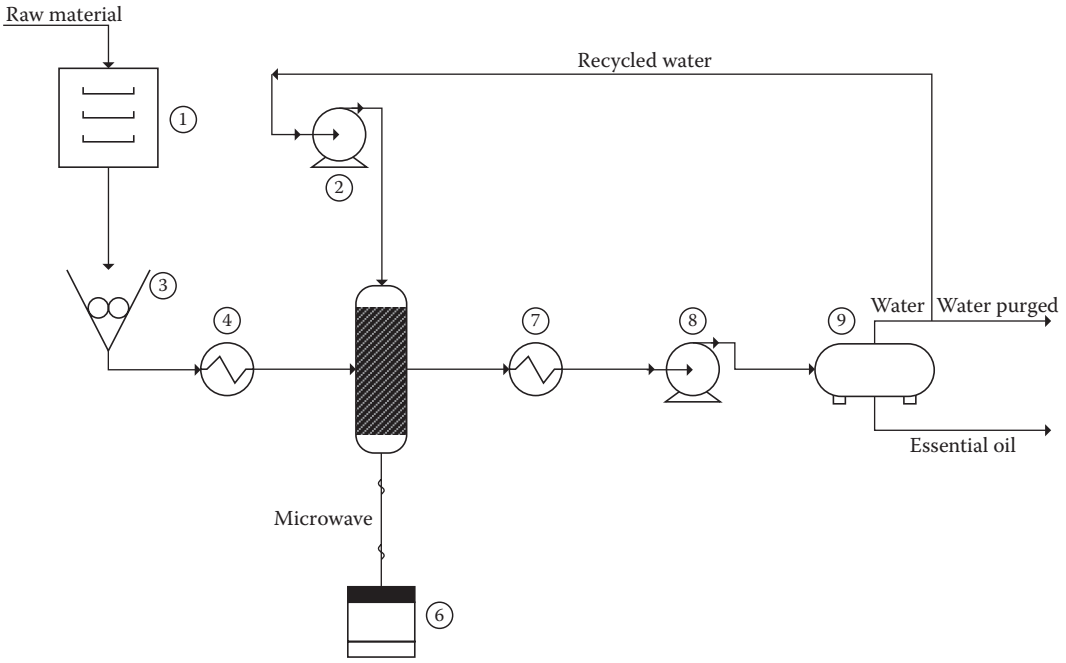

FIGURE 8.5
Flowsheet of solvent-free microwave extraction. 1, dryer; 2, pump; 3, grinder; 4, heat exchanger; 5 and 6, microwave reactor; 7, heat exchanger; 8, pump; 9, decanter.

methods; for example, it is relatively fast to operate at a basic level, and the properties of oil are not altered if there is good temperature control. The proportion of essential oils extracted by steam distillation is 93%, and the remaining 7% is extracted by other methods [40,53]. Steam distillation is a special type of separation process that considers the sensitivity of materials to the temperature and their low water solubility (e.g., oil and hydrocarbons). Figure 8.6 shows the process diagram for steam distillation extraction. The method consists in drying the material and reducing particle size to promote high contact between the raw material and steam. Then, the plant sample gets in contact with boiling water or steam, where the hot solvent breaks the cell structure of material, and the aromatic compounds and essential oils are released. The heat supply must be sufficient to break the plant material and vaporize the oil present, but not so high that it can destroy the plant or burn the oil. After the extraction process, steam containing essential oil is rapidly cooled to form two liquid fractions, rich in oil and rich in water, which are separated in a decanter [40,43,53,54]. Masango [53] reported a method to reduce the loss of compounds in wastewater and increase oil yield. "The system is composed of a packed bed of material that is located above the steam source and only steam passes through it and the boiling water is not mixed with material. Therefore, the process requires the minimum amount of steam and the amount of water in the distillate is reduced" [53].

8.6.3.2 Hydrodiffusion

The hydrodiffusion method consists in putting the steam in contact with plant material, as described in the steam distillation technique, but the difference is that the steam

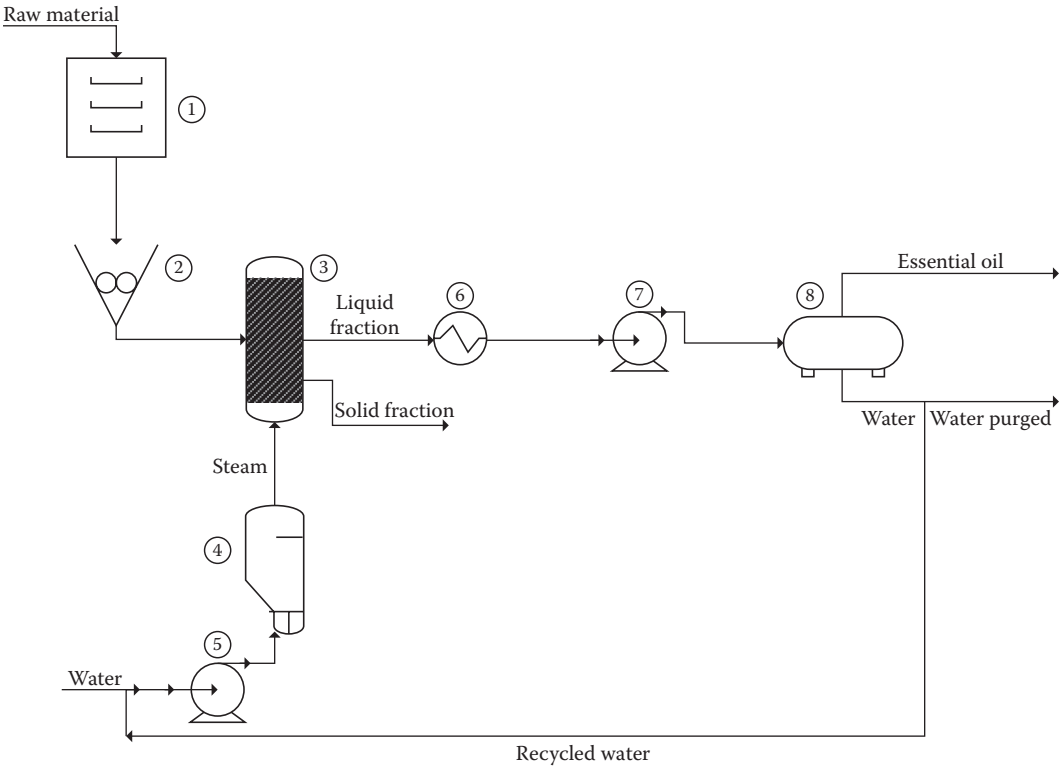

FIGURE 8.6
Flowsheet of steam distillation extraction. 1, dryer; 2, grinder; 3, contact container; 4, heat exchanger; 5, pump; 6, cooler; 7, pump; 8, decanter.

inlet is at the top of the container. The technique can operate to low pressure or vacuum, and Figure 8.7 shows the process scheme. This method is used when the material is not degraded at boiling temperature and has been dried and crushed [55]. The hydrodiffusion method has advantages over steam distillation due to a shorter processing time and less steam used, with a higher oil yield [40].

8.6.3.3 Hydrodistillation

Also called water distillation, hydrodistillation consists in the complete immersion of the material in water, followed by boiling and condensation in an aqueous fraction of the steam and essential oil vapor. Figure 8.8 shows the flowsheet of the hydrodistillation process. Direct contact, steam jackets, coils, and electric resistances can carry out the heat transfer to a material–water mixture. The material is constantly stirred to avoid deposits on the bottom of the container, and it has a thermal degradation. The material size is considered, in order to generate good contact between material and water and obtain essential oil of quality.

The extraction of essential oils considered in the hydrodistillation technique has become a standard method that is often used to isolate non-water-soluble natural products with a high boiling point [40]. This method has advantages, such as protection against overheating of the extracted oil by the barrier exerted by the surrounding water, that the required

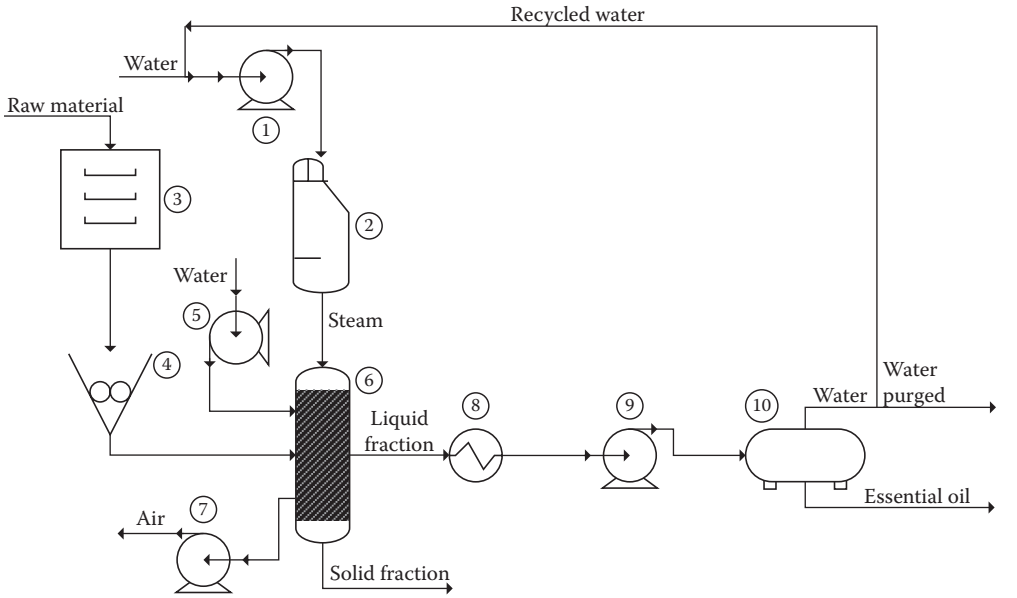

FIGURE 8.7
Flowsheet of hydrodiffusion method. 1, pump; 2, heat exchanger; 3, dryer; 4, grinder; 5, pump; 6, contact container; 7, vacuum pump; 8, cooler; 9, pump; 10, decanter.

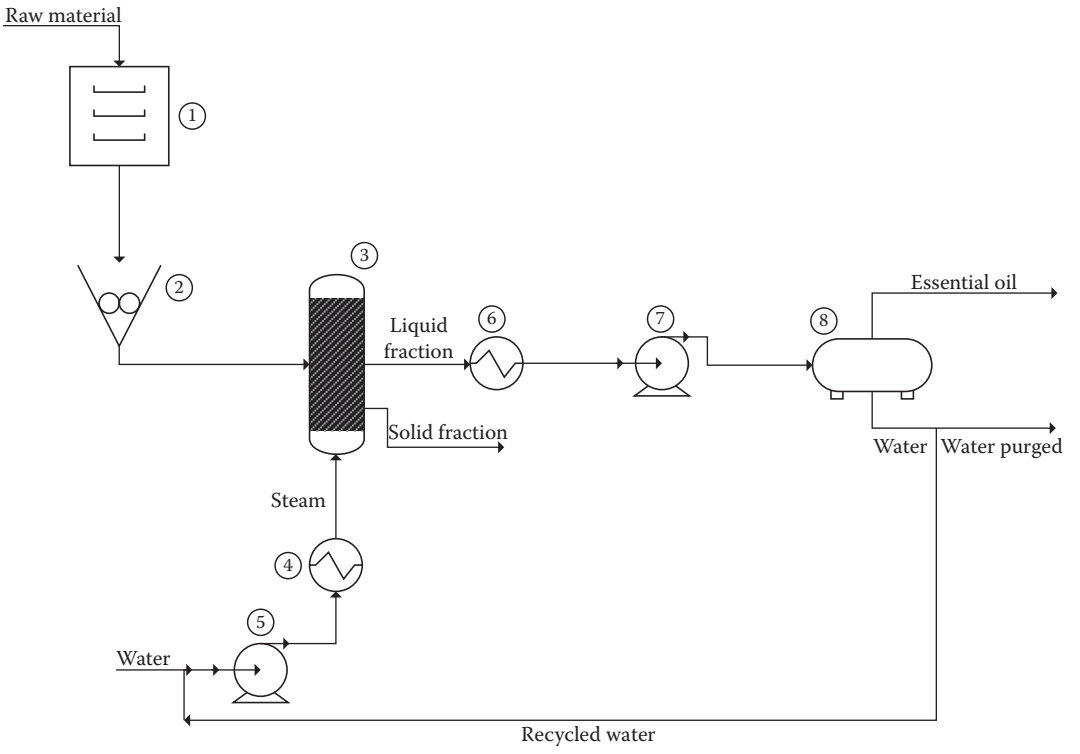

FIGURE 8.8
Flowsheet of hydrodistillation process. 1, dryer; 2, grinder; 3, contact container; 4, pump; 5 and 6, heat exchanger; 7, pump; 8, decanter.

material can be distilled below 100°C, and a moderate demand of capital costs. Some problems that the technique presents are the formation of hydrolyzed compounds, the polymerization of aldehydes, and the extraction time [40,45,56].

8.7 Analysis of the Citronella Oil Production

The objective of this section is to analyze as an example the feasibility of three extraction technologies of citronella oil cropped in Colombia from technical, economic, and environmental perspectives.

8.7.1 Methodology

8.7.1.1 Raw Material

Citronella (*C. winterianus*) is obtained from a farm placed in Chinchiná town, located in the department of Caldas (west center of Colombia), with an average temperature of 21°C and an altitude of 1368 m above sea level.

8.7.1.2 Experimental Extraction of Citronella Essential Oil

An experimental analysis is proposed to determine the chemical characterization of the essential oil and to use this information as a starting point to feed a simulation procedure.

The steps considered in the experimental analysis are (1) drying at 30°C until reaching 10% of moisture, (2) grinding for particle size reduction below 500 μm, (3) extraction by water distillation (2 h), (4) condensation and separation, and (5) storage and sample preparation.

8.7.1.3 Analysis of Essential Oil

Ten microliters of essential oil obtained from citronella is diluted in 1.5 ml of chromatographic-grade hexane and added to a test tube. This mixture is analyzed by mass spectra (Electron Impact [IE] I, 70 eV) obtained with a gas chromatograph (Agilent Technologies 6850 Series II) equipped with a mass-selective detector (MSD 5975B). The injector temperature is operated at 260°C. The chromatographic separation is performed using a HP-INNOWAX capillary column (30 m length, 0.25 mm internal diameter). Helium (99.99%) is used as the carrier gas (split ratio 30:1). The GC oven temperature is programmed from 50°C for 2 min, temperature ramp of 7°C/min to 85°C for 5 min, temperature ramp of 10°C/min to 130°C for 5 min, temperature ramp of 10°C/min to 200°C for 3 min, temperature ramp of 10°C/min to 250°C for 3 min.

8.7.1.4 Process Description

The technologies included in the technoeconomic and environmental assessment of the extraction of essential oil from *Citronella* are supercritical fluid extraction with carbon dioxide, solvent extraction with n-hexane, and extraction by hydrodistillation. The description of each technology is presented in the following sections.

8.7.1.5 Supercritical Fluid Extraction

The process to extract essential oil using supercritical fluids begins with the reception of the raw material. First, the material is cut to an average particle size of 5 cm, and subsequently dried at 30°C in order to reach a moisture content of 10% in weight. After this, the solid is grinded to a particle size below 500 μm in order to expose the oily fraction, allowing a proper extraction condition. Subsequently, the reduced size solid is directed to the extraction vessel to pack it. Once the last procedure is done, the carbon dioxide must be prepared to the supercritical conditions, which begins with a cooling process to approximately −30°C in order to avoid pump cavitation in the compression stage. The cooling fluid used for this stage is an ethylene glycol–water mixture (70:30). After this, the CO_2 is compressed to 200 bars, and its temperature is increased to 35°C, reaching the supercritical conditions [57]. Later, the supercritical fluid is passed through the extraction vessel previously packed with the solid material. It is very important to consider that temperature and pressure should be kept constant during the extraction stage, because a little perturbation on these variables will notoriously affect the carbon dioxide density and viscosity, and therefore the extraction yield. After the extraction process, two streams are obtained: one including the exhausted solid and another with the essential oil diluted in supercritical CO_2. Considering that the extract is obtained at high pressure, it is necessary to depressurize the stream and separate the CO_2 from the essential oil. The depressurization is done in two stages, reducing the pressure to 50 bars and gasifying the carbon dioxide at 25°C and 35°C, respectively. The ratio of grams of essential oil per kilogram of CO_2 is 29.03. Besides, up to 97.95% of CO_2 can be recovered and recycled. However, it is first cooled to −30°C and then pressurized to 200 bars. The power required to compress the carbon dioxide is 21.71 MJ/t of CO_2.

8.7.1.6 Solvent Extraction

In the case of extraction using solvents, the process begins with the reception of the raw material. First, the material is cut to an average particle size of 5 cm, and subsequently dried at 30°C, in order to reach a moisture content of 10% in weight. After this, the solids are ground to a particle size below 500 μm in order to expose the oily fraction, allowing a proper extraction condition, and then the solid is sent to the extraction column. It is very important to take into account that important conditions should be met to conduct a proper extraction process, such as particle size, solvent-to-feed ratio, and temperature. The solvent-to-feed ratio (dry basis) was kept at 4:1, while the extraction temperature was kept at 50°C; therefore, the extracting solvent is prepared to the extraction conditions. Hexane was selected as a solvent because of its selectivity to extract organic compounds [58]. On the other hand, after the extraction process, two streams are obtained: one stream including the solid and the aqueous phase, and a second stream containing the organic phase, which is rich in hexane and essential oil. After the essential oil extraction, the solvent is recovered in a vacuum distillation column with a solvent-rich top stream and a bottom stream rich in essential oil.

8.7.1.7 Hydrodistillation

The process includes the reception, material cutting to an average particle size of 5 cm, drying at 30°C in order to reach a moisture content of 10% in weight, and grinding to a particle size below 500 μm in order to expose the oily fraction, allowing a proper extraction condition to pack the solid in the extraction column. After this, steam is generated in a boiler to pass subsequently through the packed column. The water-to-feed ratio is 5:1 (dry

basis). In the case of water distillation, the energy required to generate steam uses low-pressure steam (3 bars) and cools water for the other units. After the extraction process, steam containing essential oil is rapidly cooled to form two liquid fractions: an oily rich one and a water-rich one, which are separated in a decanter.

8.7.1.8 Simulation Procedure

Simulations of the extraction of essential oil from citronella are carried out using Aspen Plus v8.0. The simulations considered a plant capacity to process 200 kg/h of fresh feedstock. The physical property data for components missing in the Aspen Plus databases, and required in the simulations, are estimated by correlating data available from the National Institute of Standards and Technology (NIST) to the Aspen properties, and missing properties are estimated using the method reported by Marrero and Gani [59], which is suitable for complex molecules. Additional data are obtained from the work of Wooley and Putsche [60] (i.e., hemicellulose and lignin). The Unifac–Dortmund thermodynamic model is used to calculate the activity coefficients in the liquid phase, and the Hayden–O'Connell equation of state is used to model the vapor phase.

8.7.1.9 Technoeconomic Assessment

In the economic assessment, the capital and operating costs are calculated using the software Aspen Economic Analyzer (Aspen Technologies, Inc.). However, specific parameters regarding some Colombian conditions, such as raw material costs, income tax (33%), labor salaries, and interest rate (16.02%), among others, are incorporated in order to calculate the production costs per unit of essential oil at the Colombian conditions. The above-mentioned software estimates the capital costs of process units, as well as the operating costs, among other valuable data. This software uses the design information provided by Aspen Plus and data introduced by the user for specific conditions, for instance, project location. Equipment calculations are performed following the Aspen Economic Analyzer v8.0 user guide. Utilities, civil works, pipelines, person-hours, and many different parameters are estimated using the same software. Table 8.8 shows prices used in the economic evaluation.

TABLE 8.8

Prices/Costs Used in the Economic Assessment

Item	Value	Unit
Citronella[a]	18	USD/ton
Citronella oil[b]	10	USD/kg
CO_2[b]	1.55	USD/kg
Hexane[b]	0.31	USD/L
Water[c]	1.252	USD/m^3
Electricity[c]	0.1	USD/kWh
Operator[c]	2.14	USD/h
Supervisor[c]	4.29	USD/h

[a] Price due to transport charges and average market. Average traveled distance, 100 km; type of truck, 10 t truck; diesel price, 4.11 USD/gal.

[b] Prices based on ICIS pricing indicatives [61].

[c] Colombian national average.

8.7.1.10 Environmental Assessment

The waste reduction algorithm (WAR), developed by the National Risk Management Research Laboratory from the USEPA, was used as the method for the calculation of the potential environmental impact (PEI). This method proposes to add a conservation reaction over the PEI, based on the impact of input and output flow rates from the process. The PEI for a given mass or energy quantity could be defined as the effect that those (energy and mass) would have on the environment if they were arbitrarily discharged. The environmental impact is a quantity that cannot be directly measured. However, it can be calculated from different measurable indicators [62,63]. The WAR includes eight categories: human toxicity by ingestion (HTPI), human toxicity by dermal exposition or inhalation (HTPE), terrestrial toxicity potential (TTP), aquatic toxicity potential (ATP), global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP). The weighted sum of all impacts ends in the final impact per mass of products. It is very important to clarify that this environmental assessment only corresponds to the possible impact generated in the processing stage.

8.7.2 Results and Discussion

8.7.2.1 Experimental Analysis

In the experimental extraction, a yield of 8.27 g of essential oil per kilogram of citronella is obtained. The relative density of the citronella extract is 0.898 at 25°C, the refraction index is 1.466 at 20°C, and the solubility in ethanol at 80% and 20°C is 1:2 (v/v). The main compounds identified in the citronella essential oil are (mass percentage): citronellal (54.16%), d-limonene (6.49%), citronellyl acetate (3.29%), β-bourbonene (5.60%), β-cubebene (4.54%), β-elemene (2.41%), α-bergamotene (2.19%), β-caryophyllene (2.34%), β-gurjunene (2.85%) and α-selinene (2.02%).

8.7.2.2 Process Simulation

The analysis of process simulation for the extraction of essential oil from citronella is focused on the processing yield, which is defined as kilogram of essential oil per tonne of fresh raw material. In this sense, the extraction yield depends on the technology. The moisture content of citronella is around 60%–70%. Yields for citronella correspond to 10.16, 9.97, and 8.75 kg/t for SFE, SE, and HD, respectively. SFE technology led to a high processing yield, which can affect the energy consumption and total production cost. However, there is not a big difference between SFE and SE. SFE yield is only 1.92% higher than SE, while SFE is 13.88% higher than HD. The yields obtained in simulations are in concordance with typical values reported in literature [57,64,65].

The energy consumption corresponds to 280.33, 244.76, and 303.76 MJ/tonne of fresh citronella, for SFE, SE, and HD, respectively. The technology with the highest energy consumption is HD, because of the energy required to produce the steam required for the extraction. In the case of SFE, the required energy is mainly due to the compression and depressurization process for adapting and separating the carbon dioxide, respectively. In the case of SE, most of the required energy is due to the recovery process of the solvent. It can be inferred that each process has a specific unit that consumes most of the energy.

8.7.2.3 Economic Evaluation

The economic evaluation is presented for each technology in Table 8.9. The production costs obtained for SFE, SE, and HD are 7.93, 8.77, and 8.19 USD/kg, respectively. SE technology presents the higher cost due to the energy demand to heat and recover the solvent. In all extraction methods, raw material costs and utilities contribute to the majority of the total costs. Considering the production cost, it is possible to calculate the economic margin for each technology. Thus, values of 20.7%, 12.3%, and 18.1% are obtained for SFE, SE, and HD, respectively. At this point, it is also very important to note that all technologies can be feasible. In this sense, this could serve as a basis to draw recommendations on the selection of technologies to extract essential oils. Furthermore, this selection should consider different aspects, such as the environmental impact. This is significantly relevant since all technologies should be seen not only from the economics perspective, but also from the environmental one. The environmental assessment is presented next.

8.7.2.4 Environmental Evaluation

The environmental assessment is based on the criteria of the impacts named in the methodology, which includes the analysis for the different technologies. The results of the potential environmental impact per kilogram of product (essential oil) are presented in Figure 8.9. The results show that the friendliest configuration is SFE, followed by HD. The analysis is very similar to the one presented in the economic evaluation. In this sense, it can be inferred that energy consumption affects the environmental impact, as it directly affects the economics. On the other hand, it is shown that the SE technology shows the highest impact. This is due to the solvent selected for the extraction, because the hexane purge affects impacts such as ATP and PCOP in a most dramatic way compared with technologies using CO_2 and water. The toxicity of hexane and its harmful effects significantly

TABLE 8.9

Citronella Essential Oil Production Using SFE, SE, and HD as Technologies

Item	Cost (USD/kg) and Share (%)	SFE	SE	HD
Raw materials	Cost	2.54	2.23	2.06
	Share	32.09	25.54	25.08
Operating labor	Cost	0.95	1.27	1.10
	Share	12.02	14.50	13.44
Utilities	Cost	2.60	2.72	3.30
	Share	32.89	31.10	40.25
Operating charges, plant overhead, maintenance	Cost	0.65	0.95	0.64
	Share	8.26	10.84	7.85
General and administrative cost	Cost	0.31	0.37	0.34
	Share	3.87	4.25	4.15
Depreciation of capital	Cost	0.86	1.20	0.76
	Share	10.87	13.77	9.23
Total	Cost	7.91	8.74	8.20
	Share	100.00	100.00	100.00
Total production cost (USD/kg)		7.93	8.77	8.19

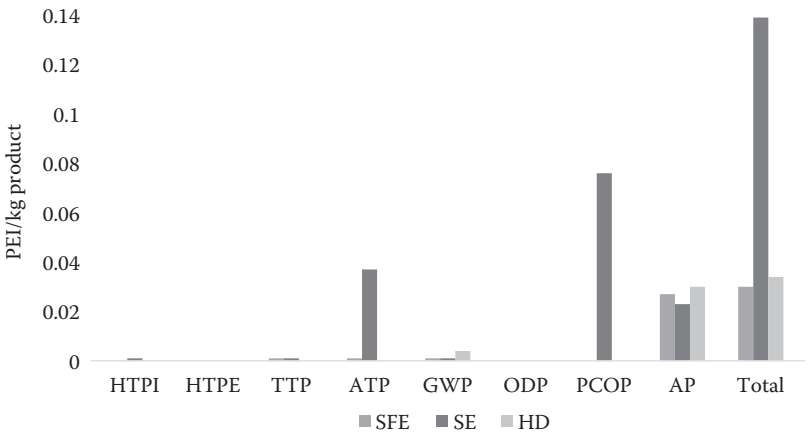

FIGURE 8.9
Potential environmental impact of extraction technologies.

increase the impact if it is not properly handled at the processing level. Therefore, it can be inferred that the potentials affected by energy are the GWP and the AP. At this point, it is very important to take into account that total environmental impact is the result of the weighted sum of all categories, and as mentioned in methodology, WAR is used to compare different process configurations.

SFE can be considered a promising technology due to its similarity to HD. Another important aspect to consider in the selection of technologies is the possible impact of traces on the final product. In the case of SFE, the essential oil can be completely separated from the CO_2 at normal conditions. The HD leads to a very small amount of water in the final product because of the insolubility of the oil in an aqueous phase. In addition, the water is not considered a substance with high environmental potential impact at normal conditions. Against this, a technology using solvents would lead to traces in the final composition of the essential oil, which can certainly affect the quality of product. In this way, greener solvents should be proposed, or newer technologies following the green engineering and green chemistry rules [66,67], for instance, the use of ionic liquids as green solvents [68].

8.8 Conclusions

Citronella oil is considered a good option as an alternative to synthetic pesticides. The chemical composition of oil gives representative characteristics like ovicidal and repellent potential and insecticidal, antifungal, and antimicrobial activity.

When the production of citronella oil is evaluated, the three technologies taken into account from the technoeconomic perspective are feasible. Based on a potential environmental perspective, the most harmful technology is solvent extraction using hexane because of its high toxicity. From both perspectives, the most promising technology is the extraction by supercritical fluids.

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