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"Use of essential oil constituents in technical products"

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Abstract

The aim of this literature work was to provide an overview of the areas in which the use of essential oils is also possible in addition to their use in cosmetics, the perfume industry, aromatherapy and medicine. The main focus was on the use in technical products.

EOs are used because of their pleasant smell and taste, but they have also a bactericidal, antifungal, insecticidal and virucidal effect. The use of EOs is generally recognized as safe for humans and vertebrates. This results in a broad spectrum of application possibilities in the technical field.

Synopsis

Das Ziel dieser Literaturarbeit war es, einen Überblick zu schaffen, in welchen Bereichen der Einsatz ätherischer Öle, neben der Anwendung in der Kosmetik, Parfumindustrie, Aromatherapie und Medizin, noch möglich ist. Hauptaugenmerk lag dabei auf dem Einsatz in technischen Produkten.

ÄÖ werden auf Grund ihres angenehmen Geruches und Geschmackes eingesetzt, weisen aber auch eine bakterizide, antifugale, insektizide und viruzide Wirkung auf. Der Einsatz von ÄÖ gilt für den Menschen und Wirbeltiere grundsätzlich als sicher. Daraus ergibt sich ein breites Spektrum an Anwendungsmöglichkeiten im technischen Bereich.

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1.1 Definition

Essential oils (Aetherolea, ethereal oils, EOs) are mixtures of liquid, volatile, lipophilic secondary substances formed by intact plants and stored by them in special depots. They can be isolated from plants by physical processes. Mostly they have the typical smell of the plant from which they were extracted. The composition of a plant's EO depends on genetic and environmental factors and often varies from organ to organ. EOs are soluble in ethanol, fatty oils and other lipophilic solvents. Their solubility in water is low. (Teuscher et al., 2012)

EOs, freshly distilled, represent colourless liquids; a few are brown, red, green or blue, e.g. clove oil (reddish brown), chamomile oil (blue). Their density is usually lower than that of water, some such as cinnamon oil, clove oil and allyl mustard oil are specifically heavier. (Sticher et al., 2015)

Their boiling points are between 150 and 300 °C. (Teuscher et al., 2012)

To date, more than 5000 chemical compounds have been isolated from EOs. An EO obtained from a plant usually contains more than 100 compounds. Of these components, only a few often determine the odour of the EO. (Teuscher et al., 2012)

The majority of the components of EOs are compounds with aliphatic, monocyclic or polycyclic monoterpene or sesquiterpene bases, including mostly unsaturated hydrocarbons, aldehydes, alcohols, ketones, esters or epoxides. Phenylpropane derivatives are also found in some EOs. Rarely do they also contain aliphatic compounds, polyins and hydroxide derivatives of benzaldehyde or benzyl alcohol in larger quantities. (Teuscher et al., 2012)

EOs are produced in gland cells of plants. They are either stored in the cells that produce them or they are excreted in secretion spaces between the cells or, in the case of glandular cells on the surface, from the cells under the cuticle. (Teuscher et al., 2012)

EOs are used especially in the food industry, the cosmetics industry, then in aromatherapy and in technical products.

1.2 Sources

EOs occur in significant quantities in about 30% of all plant species studied. Especially rich in EOs are Apiaceae, Asteraceae, Cupressaceae, Lamiaceae, Lauraceae, Myrtaceae, Pinaceae, Piperaceae, Rutaceae and Zingiberaceae. For the commercial production of EOs they are especially used: Representatives of Apiaceae (16 species), Asteraceae (20 species), Cupressaceae (7 species), Fabaceae (11 species), Lamiaceae (16 species), Lauraceae (9 species), Myrtaceae (5 species), Pinaceae (6 species), Rutaceae (10 species) and Zingiberaceae (5 species). Particularly large quantities of turpentine oil, orange peel oil, mint oil, peppermint oil, lemon oil, clove oil, citronella oil, cedar wood oil, spearmint oil and eucalyptus oil are obtained. (Teuscher et al., 2012)

1.3. Extraction

EOs are usually obtained by steam distillation (carrier steam distillation). In most cases, fresh, wilted, or dried plants, whole or cut, are mixed with water, which is heated to boiling point, or steam flows through them. (Teuscher et al., 2012)

Steam distillation: The EO is obtained by treating the plant source material with steam in a suitable apparatus. The water vapour may come from an external source and be introduced from the outside or be produced by boiling water below the starting material or boiling water in which the starting material is immersed. The water and oil vapours condense. Water and EO are separated by decantation. (European Pharmacopoeia 10.0, 2020)

Dry distillation: The EO is obtained by heating the stems or barks at elevated temperatures in suitable apparatus without the addition of water or steam. (European Pharmacopoeia 10.0, 2020)

Mechanical treatment: The so-called "cold pressed" EO is obtained by mechanical processes without heating. This mechanical treatment is mainly used for fruits of the genus *Citrus* to extract the oil from the fruit peel and the

separation is then done by physical methods. (European Pharmacopoeia 10.0, 2020)

Steam distillation is the cheapest, but not the gentlest method of extraction. (Teuscher et al., 2012)

1.4. Effects

Most EOs, when used in appropriate concentrations, can damage microorganisms: antibacterial, antifungal and virucidal effects are known. All EOs have an irritant effect on chemoreceptors, which means they stimulate the chemical senses, the sense of smell and taste. Therefore, preparations with EOs are extensively used as odour and taste corrigences and to conceal unpleasant odours in rooms.

Chemoreceptor stimuli can trigger mood changes; some can have a calming effect, others can have a mood-enhancing effect. (Sticher et al., 2015)

1.5. Use of essential oils

EOs have become an integral part of everyday life. They are used in a great variety of ways: as food flavourings, as feed additives, as flavouring agents by the cigarette industry, and in the compounding of cosmetics and perfumes. Furthermore, they are used in air fresheners and deodorizers as well as in all branches of medicine such as in pharmacy, balneology, massage, and homeopathy. A more specialized area will be in the fields of aromatherapy and aromachology. In recent years, the importance of EOs as biocides and insect repellents has led to a more detailed study of their antimicrobial potential. EOs are also good natural sources of substances with commercial potential as starting materials for chemical synthesis. (Schmidt, 2016)

EOs show radical scavenging activity, which qualifies them as natural antioxidans. When compared with synthetic ones, EOs show fewer toxic sideeffects, which make them an important substitution in food preservation. (Aidi Wannes et al., 2010; Bassolé and Juliani, 2012; Miguel, 2010; Mimica-Dukic et al., 2010)

2. Use of essential oil constituents in technical products

Volatile compounds like EOs and terpenes have mainly been used in perfumery and fragrance industry for the impact on our sense of smelling. (Karlsen, 2016)

Due to their antimicrobial, antifungal, insecticidal and antioxidant effects, as well as their good odour and properties as an environmentally friendly solvent, EOs are also used in technical products.

Components of EOs are used in soaps, detergents, cleaning agents, fragrance pastilles for laundry, air fresheners because of their antibacterial effect and pleasant smell. In shoe pastes and furniture polishes the unpleasant odour of the products should be covered.

Liquid, surfactant-containing compositions have become an indispensable part of everyday life. On the one hand, these are body care products such as shampoos, shower gels or bubble baths. But also washing or cleaning agents, such as household cleaners, fabric softeners, laundry detergents, floor care products, all-purpose cleaners, manual dishwashing detergents, machine dishwashing detergents or all-purpose detergents. (Sunder et al., 2019)

Such products contain fragrances. The smell of a fragrance is perceived by most people as pleasant and often corresponds to the smell of flowers, fruits, spices, bark, resin, leaves, grasses, mosses and roots. Fragrances can also be used to overlay unpleasant odours or to give a non-smelling substance a desired odour. Both synthetic fragrance compounds and EOs of plant origin can be used as fragrances. (Sunder et al., 2019)

When using detergents and cleaning agents, the consumer not only wants to wash, clean or care for the objects, but also wants the treated objects, such as textiles, to smell pleasant e.g., after laundry. For this reason, in particular, most commercially available detergents and cleaning agents contain fragrances. (Holderbaum et al., 2019)

Often fragrances in the form of fragrance particles are either used as an integral part of a detergent or cleaning agent or dosed into the washing drum

in a separate form (so-called fragrance pastilles) directly at the beginning of a washing cycle. In this way, the consumer can control the scent of the laundry to be washed by individual dosing. (Holderbaum et al., 2019)

Mixtures of different fragrances are preferred, which together produce an appealing fragrance. Such a mixture of fragrances can also be called perfume or perfume oil. Such perfume oils can also contain natural fragrance mixtures, such as those available from plant sources. (Sunder et al., 2019)

The fragrances of vegetable origin include EOs such as angelica root oil, aniseed oil, arnica flower oil, basil oil, citrus oil, noble fir oil, noble fir cone oil, eucalyptus oil, fennel oil, spruce needle oil, geranium oil, ginger grass oil, guaiac wood oil, ginger oil, iris oil, jasmine oil, cajeput oil, calamus oil, camomile oil, camphor oil, cardamom oil, cassia oil, pine needle oil, coriander oil, spearmint oil, cumin oil, lavender oil, lemongrass oil, lime blossom oil, lime oil, mandarin oil, lemon balm oil, mint oil, musk seed oil, muscatel oil, myrrh oil, neroli oil, niaouli oil, orange blossom oil, orange peel oil, origanum oil, palmarosa oil, patchouli oil, Peru balsam oil, peppermint oil, pimento oil, pine oil, rose oil, rosemary oil, sage oil, sandalwood oil, spiked oil, star anise oil, turpentine oil, thuja oil, thyme oil, verbena oil, vetiver oil, juniper berry oil, wintergreen oil, ylang-ylang oil, hyssop oil, cinnamon oil, cinnamon leaf oil, citronella oil, lemon oil, cypress oil and mixtures thereof. (Sunder et al., 2019)

2.1 Detergent for hand washing and food contact surface cleaning

EOs have the potential to kill bacteria. Since they are lipophilic themselves, they can pass through the membrane of cells and cause cytotoxicity (Bakkali et al., 2008). On the one hand they inhibit the respiration and increase the permeability of bacterial cytoplasmic membranes, and on the other hand they cause potassium leakage (Ibrahim et al., 2008). According to Burt (2004), other mechanisms that cause the bactericidal effects are depletion of proton motive force, damage to membrane proteins as well as to the cytoplasmic membrane and degradation of the cell wall, for example, the EO of *Cymbopogon densiflorus* (Poaceae), whose main compounds are limonene,

cymenene, p-cymene, carveol and carvone, were active against Gramnegative as well as Gram-positive bacteria. (Ibrahim et al., 2008)

Another EO with effect against bacteria is that of *Eucalyptus sp.* (Myrtaceae), which mostly contains 1,8-cineole, linalool, citronellal and limonene (Batish et al., 2008). The EO of *Calamintha nepeta* (Lamiaceae), which contains limonene, menthone and pulegone, showed high activity against Salmonella. Also, the EOs of *Foeniculum vulgare* (Apiaceae) – mostly sweet fennel – *Rosmarinus officinalis* (Lamiaceae) and *Thymus vugaris* (Lamiaceae) showed high activity against bacteria. (Buchbauer & Hemetsberger, 2016)

An example of an EO as an antimicrobial additive to detergent for hand washing and food contact surface cleaning is the EO of oregano. (Rhoades et al., 2013)

The hands are continually in contact with the environment and therefore can be contaminated by a very wide range of bacterial species, which may then be transferred to foods or food contact surfaces. A study of the hands of 204 homemakers (nonworking parents of preschool children) found 48 different species of Gram-negative bacteria and 12 species of coagulase-negative staphylococci. Most prevalent species were *Pseudomonas fluorescens/putida*, *Staphylococcus warneri*, *Klebsiella pneumoniae*, *Staphylococcus aureus and Enterobacter cloacae*, while the mean mesophilic aerobic count per hand was 57 log CFU. (Aiello et al., 2003).

A study of 50 delicatessen food handlers by Lues and van Tonder (2007) found aerobic plate counts ranging from 'negligible' up to 88 CFU cm² on the palms (the latter figure equates to roughly 45 log CFU per hand).

As bacteria on the hands can potentially contaminate foods and food preparation surfaces, it is desirable to have available an effective antimicrobial soap for hand washing in a domestic and catering environment. Several are available on the market; one example, used as a comparison in these experiments, is Dettol® antibacterial hand soap, which contains chloroxylenol as a biocidal agent. This compound can cause contact allergies in some individuals and is toxic if inhaled or ingested. (Magee, 1998; Aronson, 2006) Another commonly used antimicrobial, triclosan, may be implicated in the development of antibiotic resistance in bacteria. (Aiello et al., 2007)

An alternative antimicrobial ingredient for soap would therefore be beneficial, especially for individuals who are sensitive to other commonly used compounds. Oregano EO, more specifically its main active component carvacrol, has a well-established antimicrobial activity and has been tested in a variety of foods as a preservative and to control pathogenic bacteria. (Tajkarimi et al., 2010)

Baydar et al. (2004) tested oregano EO *in vitro* for inhibitory activity against a total of 15 different bacteria (Gram-positive and Gram-negative) and observed inhibition against all 15 when the oregano EO concentration was 2 % v/v and against 12 of the 15 strains at 1 % v/v concentration. Minimum inhibitory concentrations vary according to several factors, but are of the order of 0.02-0.5 % v/v in clean buffer systems according to a review by Burt (2004).

Alcohol-based hand rubs have been shown to have their antimicrobial activity enhanced by the addition of various EOs, which can act synergistically with other antimicrobial components in the product (United States Patent number US 6,884,763 BT Willard et al., 2005; Shintre et al., 2006). However, although these are hand cleansing products and are designed to kill the microbial flora of the skin, they are not soap based and are designed to be used without water and are therefore somewhat different to the soap product being examined in the current work. (Rhoades et al., 2013)

Bacteria on the hands, together with those from other sources, can also contaminate food preparation surfaces such as worktops and chopping boards. Food-borne pathogenic bacteria may remain viable on surfaces for several days and can be transferred from surfaces to foods or from one surface to another via cleaning sponges. (Kusumaningrum et al., 2003) The ease with which bacteria can be removed and/or killed depends on, among other things, the bacterium itself, the surface properties (Gough and Dodd, 1998), extent and type of soiling with organic residues (Kuda et al., 2008), the time for which the bacterium has been present on the surface and the maturity of the biofilms formed (Nguyen and Yuk, 2013; Stojicic and Haapasalo, 2013), environmental

conditions (Nguyen and Yuk, 2013) and the sanitizing method used. (Bae et al., 2012; Koo et al., 2013)

These experiments have demonstrated that oregano EO is a potentially useful antimicrobial additive for hand soaps and could be an alternative to triclosan and chloroxylenol. It is also effective in food contact surface decontaminating solutions. (Rhoades et al., 2013)

2.2 Handkerchiefs

EOs are also used in handkerchiefs, e.g., in Tempo® handkerchiefs from the company Essity Hygiene and Health AB or in Feh® handkerchiefs from the company Essity Austria GmbH.

Eucalyptus oil is used in Tempo® handkerchiefs. The EO is inhaled by the use of this product.

Eucalyptus oil (*Eucalypti aetheroleum* Ph. Eur.) is obtained by steam distillation and subsequent rectification from the fresh leaves or the fresh twig tips of various 1,8-cineole-rich eucalyptus species (Myrtaceae). Eucalyptol (1,8-cineole) is obtained from oils containing cineole by freezing with a cold mixture or by fractional distillation. (Sticher et al., 2015)

Rectified eucalyptus oils mainly contain eucalyptol (70-85 %) besides α pinene, limonene and other mono- and sesquiterpenes. (Sticher et al., 2015)

Eucalyptus oil and eucalyptol have antiseptic benefits. They also have a secretolytic and anti-inflammatory effect. (Sticher et al., 2015)

Also, in Feh® handkerchiefs eucalyptus oil is used. Additionally, menthol and lemon oil are also included.

(-)-Menthol is a major component of the EOs of *Mentha x piperita* and *Mentha arvensis var. piperascens* (Lamiaceae); besides, it is also found in other mint oils. It has a pleasant typical minty odour and taste. (Jäger & Höferl, 2016) Menthol is one of the rare naturally occurring monocyclic monoterpene alcohols that have not only various physiological properties, such as sedative,

anaesthetic, antiseptic, gastric, and antipruritic, but also characteristic fragrance. (Bauer et al., 1990)

Lemon oil (*Limonis aetheroleum* Ph. Eur.) is obtained by suitable mechanical processes, without heating (!), from the fresh fruit peel of lemon, *Citrus x limon* (Rutaceae). Main components are limonene, β -pinenes and γ -terpinenes, odour carriers are geranial and neral (citral a and citral b). It is used almost exclusively as a flavour correction. (Teuscher et al., 2012)

2.3 Shoe Industry

Further application possibilities due to the antibacterial and antifungal effect of EOs can be found in the shoe industry. (Sánchez-Navarro et al., 2015)

The new strategies for the development of innovative products addressed to users are based on products created to satisfy a user's emotional and functional needs, expectations and preferences, apart from considering the product's basic functionalities. Therefore, materials with scent properties open a new dimension for marketing based on the olfactory sense, which could offer new opportunities in high-added-value product development. Scent microencapsulation is a common practice in several industrial fields such as cosmetics, food, pharmaceuticals, etc. (Benita, 1996, Kumar Gosh, 2006) The advantages that microencapsulation offers with respect to conventional processes can be summarised as the protection and masking of the encapsulated substance against unstable or hostile media for subsequent gradual release. (Sánchez-Navarro et al., 2015)

Encapsulation of EOs can give a dry free-flowing powder easily incorporated into consumer products. Lowering the volatility can also allow incorporating these compounds into textiles, surface films and aerosols for spraying. (Karlsen, 2016)

In the footwear industry, the incorporation of microencapsulated substances into materials or components allows the concept of active shoes to be realized, which contributes to improve the welfare of users, satisfying their needs and expectations. Fragrances applied to footwear, both directly and through packaging, cover one of the main consumers demands regarding the solution of bad odours generated during footwear use. Along the same lines, in shoe packaging, microencapsulation allows the development of active issues with different purposes: trapping undesirable odours or incorporation of antimicrobial agents to be released over time in order to improve the useful life of the packed shoe or, as in the present study, the incorporation of controlled-released scents to avoid their degradation and to improve the durability of the aroma. (Sánchez-Navarro et al., 2015)

An example of an EO that - as mentioned above - can be used in microcapsules for use in shoes, is tea tree oil. (Sánchez-Navarro, 2011)

Microencapsulation presents a new option for the shoe industry as its application can transform traditionally used materials or products into smart materials or products capable of interacting with feet. For instance, they can improve quality of life by incorporating products for foot care such as properly dosed EOs. The microencapsulation of active substances to be incorporated in different footwear components in order to obtain an "active shoe" presents an opening up of a new way of innovation. (Sánchez-Navarro, 2011)

In recent years, interest in natural medicinal products, EOs and other botanicals, has grown in response to the ever-increasing incidence of adverse side effects associated with conventional drugs, and the emergence of resistance to antibiotics, synthetic disinfectants and germicides. Particularly, there has been resurgence of interest in Australian Tea Tree Oil (TTO) which has been employed for its germicidal activity since 1925. (Sánchez-Navarro, 2011)

This oil is obtained by steam distillation of the leaves of *Melaleuca alternifolia* (Myrtaceae) and contains almost 100 components (Brophy et al., 1989), which are mostly terpene hydrocarbons, mainly monoterpenes, sesquiterpenes and related alcohols; it was used early the last century to treat various ailments with demonstrated activity against bacteria, fungi and viruses. (Satchell et al., 2002)

In the study "Scent properties by natural fragrance microencapsulation for footwear applications" by Sánchez-Navarro et al., (2011) a series of melamine-formaldehyde (MF) microcapsules containing TTO was prepared by in situ polymerization (O/W) method to be applied to footwear materials (lining, insoles, etc...) as antimicrobial agent and their physicochemical properties have been characterized by different experimental techniques. (Sánchez-Navarro, 2011)

Previously to the microencapsulation process, the antimicrobial activity of TTO against different microorganisms typically found in used footwear (*Escherichia coli* SG13009 (QIAGEN), *Bacillus subtilis* 168 ATCC 23857, *Klebsiella pneumoniae* CECT 141 and *Staphylococcus aureus* CECT 239) was analysed. (Sánchez-Navarro, 2011)

Melaleuca alternifolia oil showed suitable antimicrobial activity against different microorganisms found in foot skin and worn shoes, to be used as a natural biocide for footwear applications. (Sánchez-Navarro, 2011)

The results from the incorporation of microcapsules in leather and fabrics obtained have demonstrated the feasibility of this technology for use in shoes to achieve the concept of "active shoe". (Sánchez-Navarro, 2011)

2.4 Leather Industry

Hide or skin is a natural product which begins to putrefy vigorously after flaying due to an action of microorganisms. The leather produced from the hide or skin is markedly resistant against the mentioned action, but many species of microorganisms can successfully live on a surface of the leather. When human body has contact with leather it gets moisture and warm, and conditions for the bacteria growth become more and more convenient. (Gao et al., 2008; Lim et al., 2004)

Usually, the microorganisms present on leather cannot injury healthy person, but they are very dangerous for immuno-compromised individuals, such as the elderly, people with diabetes or infants. The quality of leather can be decreased by the action of microorganisms when the leather is stored for long time in the environment characterised by high humidity at relatively high temperature. (Jucyte et al., 2016)

Since the biocides currently used as antimicrobial agents are dangerous to human health and the environment (Annamalai et al., 1997), it necessitates to search for the new and more safe materials for the preservation of leather. In this case, EOs can be proposed as antimicrobial agents. (Jucyte et al., 2016)

Bairamoglu et al. reported that *Origanum onites* EO (Lamiaceae) used in fatliquoring process significantly eliminates the release of free formaldehyde in leather (Bairamoglu et al., 2013). *Coridothymus capitatus* (Lamiaceae), *Olea europaea* (Oleaceae), *Corylus avellana* (Betulaceae), and *Juglans regia* (Juglandaceae) extracts, which were used during the retanning stage of leather manufacturing, significantly reduced chromium (VI) formation in the leather (Bayramoglu et al., 2012). Gu et al. investigated the possibilities of EOs extracted from traditional Chinese medicinal materials as leather fungicides. (Gu et al., 2011)

Unfortunately, the main challenge in such an application of environmentally friendly materials is selection of the suitable method for qualitative incorporation of EO into derma structure. The simple daubing of EO is just not efficient and leads to leather quality decrease because its surface becomes "fat". (Sirvaityte et al., 2011, 2012)

The results of the present study have shown that the commercial EOs of *Eucalyptus globulus* (Myrtaceae) and *Lavandulae angustifolia* (Lamiaceae) can be mixed with technical fatliquoring materials resulting in formation of stable fatliquoring emulsions, which can be disintegrated by adding electrolytes. The stability of the emulsion depends on the sort of EO and technical fatliquoring material. (Jucyte et al., 2016)

Also, the EO of *Thymus vulgaris* (Lamiaceae) could be used as a preservation agent in the leather tanning industry. Analyses have shown differences between commercial and pure EOs of thyme. The composition of EOs influences their antibacterial activity. Gram-positive bacteria were more sensitive to the EOs of thyme compared to Gram-negative bacteria.

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Pseudomonas aeruginosa was the least sensitive to the action of all selected EOs. If EOs are used as a preservative for chromed leather, their amount should not be less than 3% of the wet-blue mass. (Sirvaityte et al., 2012)

Antimicrobial properties of the EOs of thyme depend mostly on their phenolic constituents. The quantitatively most important compounds are the phenols thymol and carvacrol. Two different monoterpene phenols with similar properties are isomeric molecules. It is known that these two phenolic compounds have strong antimicrobial properties. (Panizi et al., 1993) High antimicrobial activity of the EOs of thyme is also characterized by a high content of monoterpenes, such as hydrocarbons γ -terpinene and β -cymene. (Sivropoulou et al., 1996)

The EOs of thyme can be used as a preservative in a mixture with a synthetic biocide. In this case the amount of the necessary synthetic biocide can be reduced from 0.2 % to 0.05 % of the wet-blue mass. In the effectual mixture the amount of the biocide should be 0.05 % and that of the EO of thyme 3.75 % of the wet-blue mass. The authors supposed that application of a mixture of EO and synthetic preservative could solve two problems at once: first, decrease the amount of the synthetic preservative for leather treatment and thus reduce an irritant effect to customers, and second, decrease the amount of EO, which is fairly expensive. (Sirvaityte et al., 2012)

Treatment of leather with the EO of thyme simultaneously with fatliquoring has an influence on the strength properties of the leather. Addition of EO into the fatliquoring emulsion changes the stability of the fatliquoring emulsion and the tensile strength of the leather becomes lower. On the other hand, such addition of the EO of T. vulgaris into fatliquoring emulsion does not change the chemical quality indexes of leather. (Sirvaityte et al., 2012)

The addition of EO for leather fatliquoring has negligible influence on tanned leather quality indexes. The high content of matter soluble in dichloromethane does not warrant qualitative distribution of fatty materials in leather when the fatliquoring is carried out using compositions containing EOs. (Jucyte et al., 2016)

2.5 Antioxidants in the Metal Industry

Due to the antioxidative characteristics of EOs, there is another possible application as an eco-friendly, green corrosion inhibitor.

Antioxidant activity is defined as a property of antioxidants to neutralize any free radicals. Generally speaking of antioxidants, their activity is required to act as a hydrogen donor. On the other hand, the aromatic ring plays a significant role and especially phenolic hydroxyl groups enhance the inhibition of oxidation. (Gülcin, 2011)

Many studies assess the antioxidant activity of the EO to be used as a natural source of antioxidants. Single compounds of EOs donate protons to highly reactive radicals, inactivate it and prevent possible damage. (Buchbauer & Erkic, 2016)

An example of an EO that is used as a green corrosion inhibitor due to its antioxidant effect is the EO of rosemary.

The investigated naturally compounds called green or eco-friendly corrosion inhibitors offer interesting possibilities for corrosion inhibition. Moreover, these components have a particular interest because of their safe use with various mixtures of molecules containing electronegative atoms such as nitrogen, sulphur, and oxygen; such of these compounds should be good corrosion inhibitors. (El Ouariachi et al., 2010)

There are environmental issues associated with the application of most inhibitors as some are toxic to the ecosystem. Plants extracts are eco-friendly and have been found to contain phytochemical constituents with similar characteristics to organic corrosion inhibitor; hence, their applicability as inhibitors has been reported. The use of wastes from plants as corrosion inhibitors can be another way of extending the beneficial use of these plants and so enhance municipal waste management. (Challouf et al., 2016)

Natural inhibitors constitute a source of cheap and environmentally safe substances. The scientific and technical corrosion literature has descriptions and lists of numerous compounds that exhibit inhibitive properties for steel. Several natural compounds as plant extracts, EOs or purified compounds were investigated as green inhibitors for steel in acidic solutions. For example, thyme extract, henna, ginger extract, cedar oil, artemisia oil, jojoba oil, menthol oil, eugenol and acetyleugenol, pulegone, etc. have been investigated. (El Ouariachi et al., 2010)

Rosmarinus officinalis (Lamiaceae) is a small evergreen perennial plant growing wild in Mediterranean bassin. The main producers of *R. officinalis* oil are Italy, Spain, Greece, Turkey, Egypt, France, Portugal and North Africa. It is an almost colourless to pale yellow liquid with a characteristic, refreshing and pleasant odour. (El Ouariachi et al., 2010)

The corrosion inhibition is generally explained by adsorption of the inhibitor at the metal/solution interface. The EO was dominated by oxygenated monoterpenes amounting to 77 % of the total composition. The main compounds were 1,8-cineole (54.1 %), camphor (14 %), α -pinene (9.6 %), α -terpineol (4.8 %), β -pinene (3.4 %) and borneol (2.9 %). Other components were found in less quantity (<2 %). Oxygenated monoterpenes, particularly 1,8-cineole acted on the corrosion of steel in acid solution. (El Ouariachi et al., 2010)

The results obtained from the experimental data show that *R. officinalis* oil can be used as an inhibitor for the corrosion of steel in 0.5 M H₂SO₄. Inhibition efficiency increases with increase of inhibitor concentration but does not change with temperature rise. The natural oil acts on steel surface as cathodic inhibitor. Chemical analysis shows 1,8-cineole can be the major component of *R. officinalis* oil. Inhibition efficiency on C38 steel may occur by action of 1,8-cineole. (El Ouariachi et al., 2010)

Another work examined the potential of *Origanum majorana* (Lamiaceae) to be used as an eco-friendly corrosion inhibitor.

O. majorana is a somewhat cold-sensitive perennial herb or undershrub with sweet pine and citrus flavours. In some Middle Eastern countries, marjoram is synonymous with oregano, and there the names sweet marjoram and knotted marjoram are used to distinguish it from other plants of the genus Origanum. It is also called pot marjoram, although this name is also used for other cultivated species of Origanum. (Challouf et al., 2016)

From the present study, it was found that the extract of *O. majorana* (OM) leaves can be used as an inhibitor for mild steel corrosion. The optimization of the extraction parameters using chemiometric approach method gave the optimal extract of OM. The inhibition efficiency measured by means of polarisation curves can attain about 90%. The presence of the extract increased the activation energy which can be attributed to the physical adsorption of the OM molecules on the surface of steel. Thermodynamic adsorption parameters show that OM is adsorbed on steel surface by an exothermic process. (Challouf et al., 2016)

Another work is concerned with the microbiologically influenced corrosion. For this purpose, a *Salvia officinalis* (Lamiaceae) extract was used as green corrosion inhibitor. (Lekbach et al., 2019)

Microbiologically influenced corrosion (MIC) is known as an electrochemical process in which microorganisms adhere to the surfaces of metals or other materials. This can induce or accelerate corrosion reactions of these materials through the interfacial interaction with the metabolic activities of these microorganisms. (Xu et al., 2016) Microbial corrosion occurs for metals exposed to fresh water, seawater, soils, gas and oil fluids. (Javaherdashti, 1999)

In the marine environment, many types of microorganisms can initiate and/or induce corrosion of materials including bacteria, fungi and archaea. (Li et al., 2018) Among these microorganisms, a pioneer bacterium for biofilm formation in seawater environment, *Pseudomonas aeruginosa*, can form a biofilm on different types of metals and their alloys. (Khan et al., 2019)

P. aeruginosa is a ubiquitous bacterium associated with nosocomial infections to biocorrosion, and even biofouling (Klevens et al., 2008). Many previous studies have reported the corrosive effects of *P. aeruginosa* on metals and alloys (Jia et al., 2017)

Several possible mechanisms have been published to explain the corrosion induced by *P. aeruginosa* under aerobic conditions. Yuan et al. (2008) suggested that creation of differential aeration cells by *P. aeruginosa* biofilm led to the initiation of pit formation on the 304 stainless steel (SS) surfaces.

This mechanism was confirmed by Hamzah et al. (2013). Furthermore, a recent study by Huang et al. (2018) explained the corrosion influenced by this bacterium at the genetic level. They found that phenazine-1-carboxamide, which is a water-soluble electron mediator encoded by the gene PhzH, was responsible for the accelerate corrosion of 2205 duplex stainless steel by facilitating the extracellular electron transfer (EET) between the bacterial cells and the metal.

Since stainless steel is widely employed in various industries, many studies have been carried out to study the corrosion and biofouling of these materials (Skovhus, 2017). 304L SS is known for its good mechanical properties, and corrosion resistance due to the formation of a thin, but dense protective film that covers the surface. (Soltani et al., 2014)

Several mitigation techniques have been proposed to address MIC problems, including chemical, biological and physical methods (Xia et al., 2015). Among these techniques, the use of biocides as chemical treatment is in the forefront for mitigation of MIC. (Skovhus et al., 2017)

However, as a result of the increasing awareness of environmental risks caused by biocides, there is a need to seek cheap, eco-friendly and highly efficient MIC inhibitors. (Little et al., 2007) Natural products, such as aromatic and medicinal plants, present an enormous source of environmentally benign organic compounds which are readily available and renewable. Aromatic and medicinal plants have many secondary metabolic pathways that secrete active compounds, such as phenols, flavonoids, alkaloids, tannins, terpenes, etc., which are known for their antimicrobial, antioxidant, antifouling and anticorrosion activities. (Karagöz et al., 2015)

The ability of these active molecules to inhibit corrosion is due to their molecular structures which are similar to the conventional organic corrosion inhibitors. It is well known that plant extracts contain organic compounds such as heterocyclic compounds which contain polar functional groups like OH, C=O, C-O, C-C, C=N, N-H (EI Hamdani et al., 2015). These compounds possess the ability to adsorb on metal surfaces and to form a protective layer that protects them from corrosion. (Díaz-Cardenas et al., 2017)

Seeking eco-friendly and non-toxic natural compounds that could be used for MIC protection of 304L SS, a *Salvia officinalis* extract was selected for the present study.

S. officinalis belongs to the family of Lamiaceae and it is widely used in medicine preparation, cosmetic formulations, food flavouring and insecticides. (Kamatou et al., 2008) Many previous studies reported the richness of *S. officinalis* plant in phenolic compounds which makes it a suitable source of potential inhibitors for MIC mitigation (Martins et al., 2014).

Furthermore, lemon grass was also examined regarding to an anti-corrosion effect. (Antimicrobial action and anti-corrosion effect against sulfate reducing bacteria by lemongrass. (Korenblum et al., 2013)

Hydrocarbons in petroleum may serve as electron donors for sulfate reducing bacteria (SRB), which use sulfate as the terminal electron acceptor for respiration, resulting in sulfide production. The biogenic sulfide production results in metal biocorrosion and reservoir souring, and SRB are typically the main bacterial group involved in these harmful processes in petroleum industries. The biogenic hydrogen sulfide production causes the acidulation and plugging of petroleum reservoirs and biocorrosion of metal surfaces of pipelines and tanks (Nemati et al., 2001a). Moreover, the sulfide is explosive in high concentrations. SRB may grow in pipes and tanks forming biofilms, leading to the biodegradation of the metal surface (Zuo, 2007). Finally, the accumulation of SRB biomass causes reduced oil recovery (Muyzer and Stams 2008; Nemati et al., 2001b).

Therefore, in petroleum industries, it is mandatory to control and inhibit SRB growth, which is usually done by biocide dosage. (Korenblum et al., 2010; Videla, 2002)

Biofilms are an agglomeration of microbial cells that adhere to a surface and are imbibed in a polymeric matrix built by the microorganisms themselves. (Costerton, 1999)

Regardless of the effectiveness of these biocides, antimicrobial resistance often occurs, particularly in biocide treated biofilms. (Fraise, 2002; Stewart and

Costerton, 2001) In addition, the residual concentration, toxicity and persistence of biocides in industrial effluents is of high environmental concern. Hence, alternatives for SRB control are of great interest to the petroleum industry. (Nemati et al., 2001b; Stewart, 2002)

Citral, the principal compound of lemongrass (*Cymbopogon citratus* (DC.) Stapf, Poaceae) EO (LEO), is valued as an antimicrobial compound against several important medical and food bacteria, such as *Campylobacter jejuni*, *Escherichia coli* O157, *Listeria monocytogenes*, *Bacillus cereus* and *Staphylococcus aureus* (Fisher and Phillips, 2006). The citral is found at 65-85 % of total compounds in LEO as two evenly distributed isomers, neral and geranial. (Moore-Neibel et al., 2012)

In the study of Korenblum et al., (2013) for the first time, the use of LEO or citral are being proposed for application by the petroleum industry to control and/or remove SRB biofilm formation and sulfide induced corrosion of metal surfaces, such as in pipes and tanks. (Korenblum et al., 2013)

Lemongrass EO (LEO) and its major constituent – citral were tested against a SRB strain (*D. alaskensis* NCIMB 13491) in planktonic and sessile growth stages. The MIC of either LEO or citral was established at 0.17 mg ml-1 according to the spectrophotometric assay result, while the real time PCR of dsrA gene indicated a MIC of 0.085 mg/ml. Thus, citral was evinced to be responsible for the antimicrobial effect in LEO, as no inhibition difference was observed between the EO and its main component. (Korenblum et al., 2013)

Cytoplasm leakage was observed in many cells suggesting loss of cell constituents and lysis caused by LEO treatment. Even though a few treated cells presented a cytoplasmatic appearance similar to the control, unusual electron-dense granules near the cell membrane could be observed. The indication of cell morphology alterations after the LEO treatment, especially lysis, corroborates its bactericidal effect. *D. alaskensis* biofilm removal and sessile growth inhibition by LEO was observed when testing biofilm formation on glass coupons. (Korenblum et al., 2013)

The EO was a highly effective biofilm inhibitor. The black corrosion precipitates could be observed in the control carbon steel coupons, while the treated

coupons were preserved from biofilm formation and therefore from SRBinduced biocorrosion processes. There was a slight corrosion detected on conditioned coupons, it was very similar to the corrosion observed on blank coupons (p=0.54), which was considered as chemical corrosion. Weight loss of the untreated coupons was significantly higher than on conditioned coupons when blank coupons corrosion rate was subtracted. Then, there was no biocorrosion on conditioned coupons, while a high biocorrosion rate was detected on untreated ones (1.06 (\pm 0.1) 107 mm year-1, p<0.01). (Korenblum et al., 2013)

The findings showed that the EO of lemongrass has antimicrobial activity against SRB and anti-biocorrosion effect on carbon steel metal. Besides that, the main component of LEO, citral, which is an oxygenated terpene, has shown an active inhibition of SRB growth (Korenblum et al., 2013) and other bacteria. (Reichling et al., 2009; Solórzano-Santos and Miranda-Novales, 2012)

In petroleum industries, LEO and citral may be used in formulations in the same manner as synthetic biocides; and may be formulated in water, methanol or isopropanol. (Korenblum et al., 2013)

2.6 Agriculture

2.6.1 Essential oils as antipests

EOs play a major role in nature for the plants that produce them in order to protect the plants against bacteria, fungi and viruses as well as against herbivores and pests. (Bakkali et al., 2008)

Since pollution of our environment and intoxication of mammalians with pesticides and herbicides is a severe problem all over the world, it is necessary to look for healthier alternatives. Especially natural products such as EOs offer an enormous potential for agricultural usage since most of them are nontoxic to vertebrates and do not harm our ambience. Even though there are so many advantages of EOs, some disadvantages must also be mentioned, like the slow action and short duration of effectiveness as well as the high quantities needed. (Buchbauer & Hemetsberger, 2016)

Crop protection has always been an important topic in agriculture. Due to the herbicidal, pesticidal, and antimicrobial activity of EOs, they can be used in agriculture. (Buchbauer & Hemetsberger, 2016)

Examples of EO used as antipests: (Buchbauer & Hemetsberger, 2016)

- Rosmarinus officinalis (Lamiaceae)
- Thymus sp. (Lamiaceae)
- Eucalyptus sp. (Myrtaceae)
- Satureja sp. (Lamiaceae)
- Ocimum sp. (Lamiaceae)
- Origanum sp. (Lamiacea)
- Artemisia sp. (Asteraceae)
- Mentha sp. (Lamiacea)
- Cinnamomum sp. (Lauraceae)
- Foeniculum vulgare (Apiaceae)
- Lavandula sp. (Lamiaceae)

EOs are natural products, which are excellent alternatives to synthetic products. (Koul et al., 2008) Even though there are a lot of botanical insecticides available, from 1980 to 2000, only one single product was registered in the United States and Europe, which is called neem. It is obtained by the seeds of the Indian tree *Azadirachta indica* (Meliaceae). (Buchbauer & Hemetsberger, 2016)

Insects form the largest population in the animal kingdom and many of them are harmful toward human beings, since they act as pathogenic vectors and devastate crops. That is why pesticides bear a huge market potential, which can be seen in the regular growth of 7 % - 10 % per year. But due to the massive use of oil-based synthetic molecules as pesticides since the middle of the twentieth century, there have also been negative side effects reported, such as environmental pollution, toxicity toward mammalians, and increased insect resistance (Regnault-Roger, 1997). Every year million tons of pesticides are used and harm our environment, because of that it is important to find alternatives that do not damage our environment. (Koul et al., 2008)

In static water eugenol appears to be 1,500 times less toxic than pyrethrum, which is also a botanical insecticide, and not more than 15,000 times less toxic than the organophophate insecticide azinphosmethyl. Moreover, eugenol is volatile, which means that its half time is extremely short. After about 2 days there will be no eugenol left, which also avoids rare side effects of EOs. (Isman, 2000)

Also, the tobacco cutworm, which is a severe problem to vegetable and tobacco crops in Asia, can be killed by compounds of EOs (thymol, carvacrol, pulegone, eugenol, and trans-anethole) even though it is quite resistant (Hummelbrunner and Isman, 2001). Many monoterpenes like (+)-limonene, pinene, and Δ 3-carene show acaricidal activity. Carvomenthenol and terpinen-4-ol proved to cause the highest toxicity against mites. (Ibrahim et al., 2008)

Eucalyptus EO was tested on several parasites, such as *Varroa destructor* (Varroa mite), *Tetranychus urticae*, *Phytoseiulus persimilis*, and *Boophilus microplus*. The studies concluded that several Eucalyptus sp. (Myrtaceae) EOs can be used as acaricides (Batish et al., 2008). *T. urticae* can be killed by EOs obtained from *Satureja hortensis* (Lamiaceae), *Ocimum basilicum* (Lamiaceae) and *Thymus vulgaris* (Lamiaceae). (Aslan et al., 2004)

EOs do not only act as deterrents but also as attractants toward insects. Ethanolic extracts of *Rosmarinus officinalis* (Lamiaceae) EO attracted the moth *Lobesia botrana*, a pest of grape berries. (Katerinopoulos et al., 2005)

EOs are neurotoxic to some pests as some of them interfere with neuromodulator octopamine and others with γ -aminobutyric acid (GABA)-gated chloride channel (Isman, 2006). Interrupting the function of Octopamine results in total breakdown of the nervous system in insects (Tripathi et al., 2009)

It was previously proposed that EOs exerted their activity by different modes of action:

- (a) act on insect respiration like a fumigant
- (b) act by contact or ingestion
- (c) prevent reproduction (also affecting fecundity or causing sterilization)
- (d) have an antifeedant effect
- (e) have a repulsive effect or alter insect behaviour
- (f) have a combination of the modes of action mentioned above (Shaaya et al., 1997)

The exact mode of action of repellents still could not be explained completely. (Buchbauer & Hemetsberger, 2016)

Even though single compounds of EOs can be isolated and tested for their repellent activity, it has been reported that the synergistic effect of the whole EO is more effective (Nerio et al., 2010)

The world food production is adversely affected by insect pests during crop growth, post-harvest and storage. Insects associated with raw grain and processed food cause quantitative and qualitative losses which are estimated at 5 - 10 % in the temperate zone and 20 - 30 % or more in the tropical and subtropical regions. (Phillips and Throne, 2010; Rajendran and Sriranjini, 2008) Losses caused by insects include the direct consumption of kernels and the accumulation of remains such as chemical excretions or silk, exuviae, body fragments and dead insects. (Shankar and Abrol, 2012)

The Indian meal moth, *Plodia interpunctella* (Hübner), is a cosmopolitan major economic insect pest of stored products (Rees, 2004). The larvae prefer to feed on broken grains and especially on milled products such as flour, breakfast foods, stored cereal products, dried vegetables and fruits, processed foods and meals. (Veena et al., 2005)

Generally, the control of this insect pest in storage systems depend on synthetic insecticides (organophosphates and pyrethroids) and fumigants (such as methyl bromide or phosphine) (Kim et al., 2014; Mbata and Shapiro-Ilana, 2010). Applications of insecticide had led to resistance in some *P. Inter-*

punctella populations and the accumulation of chemical residues in food, as well as human exposure to pesticides. (Arthur and Phillips, 2003; Attia, 1977; Phillips and Throne, 2010) Moreover, methyl bromide, a high toxic product, has been declared an ozone-depleting substance and therefore is being phased out completely. (Rajendran and Sriranjini, 2008) In Argentine the most used insecticides to control *P. interpunctella* are organophosphates (DDVP, pirimiphos-methyl), pyrethroids (lambdacyhalothrin and deltamethrin) and phosphine. (Jesser et al., 2017)

The use of plant materials (extracts, EOs and their components) as traditional protectants of stored products is an old practice used all over the world. (Rajendran and Sriranjini, 2008; Tripathi and Dubey, 2004)

EOs have shown toxic, repellent and antifeedant effects on stored product insects (Isman, 2006; Regnault-Roger, 1997; Regnault-Roger et al., 2012). Toxicity tests conducted with EOs and their components have largely focused on Coleopteran pests such as *Acanthoscelides obtectus* Say, *Tribolium castaneum* Herbst, *Rhyzopherta dominica* Fabricius, *Sitophilus oryzae* L. and *Sitophilus zeamais* Motsch. (Benzi et al., 2009; Papachristos et al., 2004; Singh et al., 2012; Stefanazzi et al., 2011)

It was reported that the EO from *Zingiber officinale* Roscoe (Zingiberaceae) and *Satureja hortensis* (Lamiaceae) produces fumigant and contact toxicity on larvae and repellent activity on adults of *P. interpunctella* (Maedeh et al., 2013, 2012). The EOs from *Allium sativum* (Amaryllidaceae), *Betula lenta* (Betulaceae), *Cinnamonum verum* (Lauraceae) and *Pimpinella anisum* (Apiaceae) cause fumigant toxicity on eggs and the EO from *Armoracia rusticana* (Brassicaceae), on different life stages of *P. interpunctella*. (Chen et al., 2011; Işıkber et al., 2009)

The following study dealt with the efficacy of EOs to control the Indian meal moth, *Plodia interpunctella* (Hübner) (Lepidoptera: Pyralidae). (Jesser et al., 2017)

This work investigated the chemical constituents and bioactivity of six EOs namely lavender (*Lavandula angustifolia*, Lamiaceae), peppermint (*Mentha x*

piperita, Lamiaceae), geranium (*Geranium maculatum*, Geraniaceae), palmarosa (*Cymbopogon martinii*, Poaceae), eucalyptus (*Eucalyptus globulus*, Myrtaceae) and bergamot (*Citrus bergamia*, Rutaceae) against adults of the Indian meal moth, *Plodia interpunctella*, a cosmopolitan pest that infests a wide range of stored products. (Jesser et al., 2017)

Analysis by gas chromatography coupled to mass spectrometry (GC–MS) revealed the presence of several compounds, mainly mono- and sesquiterpenes. The contact toxicity assay showed that the EO from palmarosa was the most toxic with a LD₅₀ value of 22.8 μ g cm⁻². The toxicity order was palmarosa > geranium > peppermint > lavender > bergamot > eucalyptus. In fumigant toxicity assay, the greatest effect was found with the EO from eucalyptus with a KT50 value of 8.34 min. The toxicity order was eucalyptus > peppermint > geranium =lavender > bergamot > palmarosa. The EO from palmarosa showed the highest residual activity when the insects were exposed to its volatile's constituents. Finally, all EOs produce sublethal activity promoting effects in the fecundity. In conclusion, the EOs could be used as potential biopesticides for *P. interpunctella* control. (Jesser et al., 2017)

For bergamot EO, the principal components found were linalyl acetate and limonene. For geranium EO, the major compounds were citronellol, geraniol, linalool, menthone and citronellyl formate. For peppermint EO the major compounds were isomenthone and menthone while for palmarosa EO, geranyl acetate and caryophyllene. The EO from lavender showed linalool and caryophyllene as the main compounds. Finally, eucalyptus EO presented 1,8-cineole as the major constituents. (Jesser et al., 2017)

EOs in general have attracted attention in recent years as potential pest control agents (Dimetry, 2014). The EOs are characterized by rapid degradation, selectivity, low mammalian toxicity, and minimal impacts on the environment. (Cloyd et al., 2004)

The EOs, which are complex mixtures of non-polar or minimally polar substances, can cross the insect cuticle after contact and diffuse vertically and horizontally. By diffusing vertically, the substances cross from the cuticle to the epidermis, enter the organism and are distributed by the haemolymph either

dissolved in lipids or bound to proteins; by diffusing horizontally, they reach the tracheae system, where they continue diffusing to the rest of the tissues in the organism and therefore reach their site or sites of action. (Tarelli et al., 2009)

The partition coefficient of components of EOs may affect their penetration through the lipophilic portion of the cuticle, the interaction with hydrophobic compartments, the degradation of the EO component, movement of the compound to the target site (Rice and Coats, 1994), and the ability of the insect to excrete the compound. (O'Donnell, 2008)

Fumigants are pesticides acting in the vapor or gaseous phase on the target pest. (Kedia et al., 2015) The most common method used to control stored product pests is fumigation because it is effective against most species, allows the insecticide to easily reach the insect inside the grain, and leaves little residues. (Phillips and Throne, 2010) Previous reports demonstrated that the EO from *Armoracia rusticana* (Brassicaceae) (Chen et al., 2011), *Zingiber officinale* (Zingiberaceae) (Maedeh et al., 2012) and *Satureja hortensis* (Lamiaceae) (Maedeh et al., 2013) produced fumigant toxicity in the Indian meal moth.

The main access to the organism in a fumigation method is airborne: the volatile substance enters through the spiracles as part of the respiratory process. The substances are transported to different tissues through the network of tracheas and tracheoles, thus reaching their site of action. (Sfara et al., 2009)

EO components with high vapor pressures can volatilize easily and are generally more toxic than those with low vapour pressures. (Toloza et al., 2006) The EO from eucalyptus (the most effective with a KT50 value of 8.34 min) had 1,8-cineole as the major compound, which has the highest vapor pressure value. (Jesser et al., 2017)

Previously, the fumigant toxicity of 1,8-cineole was shown determined for *S. oryzae*, *T. castaneum* and *R. dominica* (Lee et al., 2004a, 2004b). In concordance with this observation, eucalyptus EO had not contact toxicity effects; probably, 1,8 cineole (the compound with biological activity of this oil) would be lost from the mixture during the evaporation time. On the other hand, the

EO from palmarosa showed the lowest fumigant activity which could be attributable to the low vapour pressure of EO compounds. (Jesser et al., 2017)

It is known that EOs tend to degrade by action of sunlight, air and moisture and by detoxification enzymes, hence they present less persistence and reduced risks to non-target organisms. (Guleria and Tiku, 2009) More frequent applications and precise timings are therefore needed. (Grdiša and Gršić, 2013)

Regarding residual activity of the EOs, the property physicochemical related to residual activity is the boiling point. A compound with a low boiling point evaporates more rapidly than a compound with a high boiling point, which would make it less available for interaction with the insect. In the study, the palmarosa EO compounds showed the highest boiling points while eucalyptus had the lowest ones. Palmarosa EO compounds could therefore likely remain in the substrate for a longer period inducing a higher residual activity than the other ones. (Jesser et al., 2017)

The EOs can cause lethal and sublethal effects on insect biology. (Werdin-González et al., 2013) Sublethal effects are defined as those (either physio-logical or behavioural) which occur on individuals that survive exposure to a pesticide (the pesticide dose/concentration can be sublethal or lethal). (Desneux et al., 2007)

EOs from lavender, peppermint, geranium, palmarosa and bergamot produced sublethal activity promoting effects in the fecundity and decreasing the number of eggs laid. It is known that the EO components can modify the insect behaviour. (Mauchline et al., 2005; Regnault-Roger, 1997)

The reduction in fecundity could be due to the direct effect of the EO on adults, to a disruption of reproductive behaviour by compounds present in the EO, or a combination of the two process. Plant products/ EOs can alter gametogenesis (Alves et al., 2014; Lemenith and Teketay, 2005; Quilici et al., 2013), thus reducing fecundity.

Another study shows the use of plant EOs as Arrestants and Repellents for Neonate Larvae of the Codling Moth (Lepidoptera: Tortricidae). (Landolt et al., 1999)

The codling moth, *Cydia pomonella*, is a cosmopolitan pest of apples and other fruits. In many areas it is the principal cause of damage to fruit of apple; *Malus x domestica Borkh*. (Rosaceae); and pear, *Pyrus communis L*. (Rosaceae)) (Beers et al., 1993), and control of this insect is key to any integrated pest management (IPM) system.

The codling moth adult lays most eggs on host foliage, and larvae generally must find fruit on which to feed. (Jackson, 1978) Neonate codling moth larvae are attracted to the odours of apple fruit. (Sutherland, 1972, Landolt et al., 1998) This behaviour provides an opportunity to prevent newly hatched larvae from reaching and infesting fruit.

Nonhost chemicals may be useful for controlling insect pests of crop plants by interfering with orientation to, and selection of, host plants. EOs of 27 plant species were tested for evidence of arrest and repellence of neonate larvae of the codling moth, *Cydia pomonella*. In an olfactometer in which larval upwind movement toward apples was assessed, greatest arrest was achieved with oils of lavender, *Lavandula angustifolia* (Lamiaceae); pennyroyal, *Mentha pulegium* (Lamiaceae); and cypress, *Cupressus sempervirens* (Cupressaceae). Oil of lavender was most effective in preventing larvae from moving upwind in the olfactometer.

In a barrier assay, essential plant oils were applied to the distal ends of a glass rod (15 cm long) on which larvae were placed. Larvae crossed the barrier to reach apples impaled on each end of the glass rod. The most effective repellents in this barrier assay were rue, *Ruta graveolens* (Rutaceae); garlic, *Allium sativum* (Amaryllidaceae); patchouly, *Pogostemom cablin* (Lamiaceae); and tansy, *Tanacetum vulgare* (Asteraceae), oils. These 4 plant EOs were most effecttive in causing larvae to turn away at the oil barrier. These materials, or their active ingredients, may be useful in protecting fruit from attack by codling moth larvae by preventing larvae from orienting to and arriving at fruit. (Landolt et al., 1999)

The results of these experiments indicate that several plant EOs are promising as arrestants and repellents against larval codling moth. (Landolt et al., 1999)

Conceivably, plant oils may be applied directly to apple foliage and near fruit to confuse, arrest, or repel codling moth. Dispensers releasing volatile plant odorants may be used to protect trees or individual fruit.

In another paper the effect of selected single compounds from EOs of the group's monoterpenes (carvacrol, thymol, linalool, 4-terpineol), phenyl-propanoids (eugenol) and salicylates (methyl salicylate, salicylaldehyde) was tested on two polyphagous pest species, *Frankliniella occidentalis* Pergande and *Thrips tabaci* Lindeman (Thysanoptera: Thripidae). (Riefler et al., 2009)

A model catalogue of behavioural patterns was developed for both thrips species and the behavioural change induced by exposure to single chemical compounds, applied onto host plants, described. Bean (*Phaseolus vulgaris* (Fabaceae)) and cucumber (*Cucumis sativus* (Cucurbitaceae)) were used in experiments with *F. occidentalis*, leek (*Allium porrum* (Amaryllidaceae)) and cucumber for *T. tabaci*. The chemicals methyl salicylate and carvacrol appeared specifically effective against *F. occidentalis* as well as linalool and eugenol against *T. tabaci*. The behavioural manipulations may be included in various pest management strategies. However, the effect varies between plant species. (Riefler et al., 2009)

In addition to the comparatively high costs (Steward & Weatherstone, 2002), the strong volatility of the substances is a problem due to their low molecular weight structure, since the effect only lasts for shorter periods of time. (Tunç & Erler, 2003) The solution here is a question of the appropriate formulation. Mixtures of different components may affect desensitization (habituation) or associative learning processes of pests to a particular fragrance. (Isman, 2002; Erler & Tunç, 2005) The phytotoxicity of some EOs and their components in the plant protection is also problematic. This risk could be reduced by small but effective concentrations. (Erler & Tunç, 2005)

The prospect of using EOs or their components as plant protection products is promising. Due to their mostly sublethal effect, they are not potent enough to sufficiently control mass reproduction of pests, but they show their potential as repellents, phago- and oviposition deterrents and also as attractants and development inhibitors, in combination with other plant protection measures. (Renault-Rogner, 1997; Cook, 2007; Koschier, 2008)

Due to the "relatively slow action" variable efficacy, lack of persistence and inconsistent availability" of natural products, they still cannot compete against synthetic pesticides. (Buchbauer & Hemetsberger, 2016)

Natural pesticides can be mixed with synthetic products that could lessen the needed quantities of pesticides and improve the environmental problems that are caused by excessive use of synthetic pesticides. (Buchbauer & Hemetsberger, 2016)

2.6.2 Essential oils as acaricides

EOs could also be used as acaricides. (Ebadollahi et al., 2014) Acaricide is a pesticide designed to control harmful species of mites (Acari). (Dejan et al., 2011)

Spider mites belong to the family Tetranychidae and are named because many members of this family produce silk webbing on the host plants. Two-spotted spider mite, *Tetranychus urticae* Koch, is widely distributed globally and a common pest of many plant species in greenhouses, orchards and field crops. *T. urticae* feeding causes greying or yellowing of the leaves and necrotic spots occur in advanced stages of leaf damage. Mite damage to the open flower causes a browning and withering of the petals that resembles spray burn. In addition, small chlorate spots can be formed at feeding sites as the mesophyll tissue collapses due to the destruction of 18–22 cells per minute. (Isman et al., 2011) The importance of this mite pest is not only due to direct damage to plants but also due to indirect damage to plants which decreases photosynthesis and transpiration. (Brandenburg et al., 1987) Because of their high reproductive rates, its management can be difficult. When mites begin to feed on a plant, they produce webbing that can protect both motile and egg stages from the acaricide. (Brandenburg et al., 1987)

Synthetic acaricides have been used as the main strategy for Tetranychus species resulting in an increased cost for production and environmental impacts as well as resistance development to even the newly synthesized molecules such abamectin (Isman et al., 2011; Ramasubramanian et al., 2005). In addition, control methods based on the use of synthetic acaricides sometimes fail to keep the number of spider mites below economic threshold levels. (Tirello et al., 2012) It is therefore necessary to find alternatives that can minimize negative effects of synthetic acaricides.

In the present study, anethole, limonene, α -fenchone, and carvone were the major compounds of EO of *Foeniculum vulgare* (Apiaceae) while linalool, 1,8-cineole, 1-borneol and camphor were the main compounds of EO of *Lavandula angustifolia* (Lamiaceae). (Ebadollahi et al., 2014)

In the study of Chowdhury et al. (2009), anethole (58.5 % in seed oil and 51.1 % in leaf oil) and limonene (22.9 % in leaf oil and 19.6 % in seed oil) determined as main components of the seeds and leaves of *F. vulgare*. In the other study, borneol, α -terpinene, linolool, and geranyl proprionate were found as major constituents in the *L. angustifolia* EO. The variations could be due to differences in location, elevation, and genetic makeup of the plant or due to an adaptive process to particular ecological conditions. (Facundo et al., 2008)

In the contact toxicity, lethal concentration 50 % mite mortality (LC₅₀) was 0.557 % and 0.792 % with *F. vulgare* and *L. angustifolia*, respectively, with *F. vulgare* EO being the most toxic the adult females of *T. urticae*. On the other hand, fumigant toxicity was 1.876 and 1.971 μ L/L air for *F. vulgare* and *L. angustifolia* EOs, respectively. (Ebadollahi et al., 2014)

Another study is about the acaricidal activity of *Cymbopogon citratus* (Poaceae) and *Azadirachta indica* (Meliaceae) against house dust mites. (Hanifah et al., 2011)

Dermatophagoides farinae and *Dermatophagoides pteronyssinus* are important pyroglyphid mites because of their cosmopolitan occurrence and abundance in homes, major sources of multiple potent allergens and their causal association with sudden infant death syndrome. (Heimerdinger et al., 2006) Various natural bioactive products with acaricidal activity (botanical and microbial pesticides, EOs, horticultural spray oils, mycopesticides) have become important alternatives to synthesize acaricides. (Copping et al., 2007; Faria et al., 2007)

Naturally existent acaricidal compounds against house dust mites include Oanisaldehyde citronellal and perillaldehyde derived from perilla oil (Watanabe et al., 1989), as well as isosericenine, aryophyllene oxide and α -cadinol from EO of the leaves from *Neolitsea sericea* (Lauraceae). (Furuno et al., 1994)

The findings of this survey demonstrated that lemongrass has the potential to be a chemical control agent of dust mites. (Hanifah et al., 2011)

The neem tree produces highly active pesticides mainly in the seeds. (Schroer et al., 2001) A commercial neem seed extract known as Tre-san, is available for the control of dust mites. (Schmahl et al., 2010)

The finding in this study shows that an ethanol-extract of the neem leaf is toxic against the 2 species of dust mite. (Hanifah et al., 2011)

2.6.3 Essential oils as herbicides

Weed control in agriculture is very important as a high percentage of weed causes a high crop reduction, even more than pests. While in ancient times people were dependent on removing weed by hand, today's weed control is managed by synthetic and natural substances. (Buchbauer & Hemetsberger, 2016)

Since synthetic substances for weed control cause the same environmental and health problems as synthetic substances for pest control, natural substances such as EOs seem to be highly preferable. (Dayan et al., 2009) Examples of EOs in weed control:

- Thymus vulgaris (Lamiaceae)
- Mentha sp. (Lamiaceae)
- Cymbopogon sp. (Poaceae)

Besides its mosquito-repellent action, lemongrass oil can also be used as herbicide and *Cymbopogon citratus* (Poaceae) as weed control and antipest. It is used as contact herbicide, since limonene is able to "remove the waxy cuticular layer from leaves" that leads to death by dehydration. Limonene can be used as pesticide as well as herbicide. (Dayan et al., 2009) The effect of *C. citratus* EO was also proved by Dudai et al. The EO proves to be one of the most effective ones, as it is able to inhibit germination sooner (0 % germination at 80 nL/mL) than most other EOs tested. (Dudai et al., 1999)

- *Eucalyptus sp.* (Myrtaceae), such as *Eucalyptus citriodora* and *Eucalyptus tereticornis*, can be used for weed control, because they could reduce growth and chlorophyll and water content when used as fumigant. Moreover, the EO of *E. citriodora* can also inhibit its seed germination. The suspected mode of action is the inhibition of mitosis. (Sing et al., 2005) The EO obtained from *E. tereticornis* showed a higher toxicity than that of *E. citriodora*, because of a slightly different composition of the EO.
- Lavandula sp. (Lamiaceae)
- Origanum sp. (Lamiaceae)

Phytotoxicity means the harmful impact of chemical substances on plants that can be seen in many different ways: their parts can appear to be burned; they can suffer from chlorosis, which colours the leaves yellow; or they can also result in a lack of growth or even an excessive growth. (Buchbauer & Hemetsberger, 2016) When phytotoxicity of various components of EOs was tested, pulegone was least and (+)-carvone most phytotoxic to maize plants. (+)-limonene appeared most toxic to sugar beet seedlings. Limonene showed toxicity toward strawberry seedlings in preliminary screenings as well as toward cabbage and carrot seedlings. (Ibrahim et al., 2008) De Almeida et al. (2010) found out that EOs of balm, caraway, hyssop, thyme and vervain showed a 100 % inhibition of germination of *Lepidium sativum* (Brassicaceae). Raphanus sativus' (Brassicaceae) germination was inhibited by 100 % by vervain oil at all concentrations. At low concentrations anise and basil EOs promoted the germination and radicle growth, while caraway, sage, marjoram EOs inhibited the of vervain and growth radish. Lactuca sativa's (Asteraceae) growth was inhibited by thyme EO. Vervain, balm and caraway also had the ability to suppress the growth of lettuce.

Generally said, a high level of oxygenated monoterpenes is most harmful toward weed. When it comes to inhibit the seed germination and subsequent growth, ketones and alcohol showed the highest activity followed by aldehydes and phenols. (De Almeida et al., 2010)

Plants especially from the Lamiaceae family can inhibit the growth of several weeds by releasing phytotoxic monoterpenes (α -pinene, β -pinene, camphene, limonene, α -phellandrene, *p*-cymene, 1,8-cineole, borneol, pulegone and camphor). (Angelini et al., 2003) The herbicide effect of 1,4-cineole and 1,8-cineole is also described by Dayan et al. (2012) Plants that are exposed to EOs often metabolize them and when citral was added geraniol, nerol and their acids appeared. When citronellal metabolization was tested, citronellol and citronellic acid were formed and with pulegone (iso)-menthone, isopulegol and menthofuran were found. (Dudai et al., 2000)

It was also reported that EOs lead to accumulation of H₂O₂ in other plants. That way they increase oxidative stress, which leads to "disruption of metabolic activities in the cell." Another cause for phytotoxicity is that EO destroys the cell membrane of plants and inhibits their enzymes (Mutlu et al., 2010).

Organic weed control's problem is the huge quantities that must be applied to harm the weed. This may also cause a large negative impact on the environment and the microbes in the soil. Also, the volatility is a problem of EOs, on account of which they also have to be applied very often, which could be avoided by using microencapsulation of EOs because it will decrease their volatility. The third problem is that EOs can also harm the desired crop and lead to a partly destruction of the culture. Altogether, organic weed control using EOs does not seem too promising as a future replacement of synthetic products. (Dayan et al., 2009)

2.6.4 Essential oils for inhibiting and inducing sprouting

EOs can be used in agriculture not only as pesticides and herbicides, but also as natural and alternate methods for inhibiting and inducing the sprouting of potato tubers. (Shukla et al., 2019)

Potato (Solanum tuberosum (Solanaceae)) is one of the most important and ubiquitous food crops used across the globe. (Saraiva & Rodrigues, 2011) Potato tubers are nutritionally high and easy to cultivate hence they occupy a special space in meals of humankind. The yield of potato crop is many times compromised due to delay in sprouting and breaking of dormancy of potato tubers which shows an adverse effect on the quality of tubers during storage. (Teper-Bamnolker et al., 2010) To meet the growing demand, potatoes are grown on a large area but suffer downfalls, due to post-harvest losses. The occurrence of losses due to sprouting of tubers during storage causing loss of water, remobilisation of starch and proteins and shrinking of tubers losing their quality (Sonnewald, 2001) causing significant economic losses. To overcome these losses is a challenge and opens new avenues for research since sprouts restrict the usage of tubers. After the harvest, tubers enter the state of growth suspension i.e., dormancy but with the change in physiological and environmental conditions, this stage of dormancy is broken (Campbell et al., 2008) and tubers start sprouting. Physical as well as chemical methods are utilized for the management of sprouting, but each of them has their limitations.

One of the methodologies adopted to delay sprout development is by means of the cold storage method; low temperature during storage $(3-7^{\circ}C)$ delays sprout development, but it results in undesirable tissue sweetening. (Alamar et al., 2017) The chemical method uses compounds like maleic hydrazide, and CIPC (isopropyl N-(3-chlorophenyl) carbamate, chlorpropham), etc., to control sprouts. Amongst them CIPC is the most commonly used compound for more than four decades (Sorce et al., 2005), helping in long-term storage.

However, excessive and frequent use of chemical may cause problems to the environment, non-targeted flora and also in case it enters the food chain may cause adverse health effects (Kleinkopf et al., 2003). CIPC is reported as highly toxic pollutant, carcinogenic in nature, exhibit cytolytic effects, and cause reduction in ATP synthesis by cell permeability modifications. (Balaji et al., 2006; Mohammed et al., 2015; Smith & Bucher, 2012)

Due to this reason the chemical usage is facing restrictions from regulators of various countries. (Teper-Bamnolker et al., 2010) Hence, the development of a method using natural compounds is the need of the hour to overcome these post-harvest losses. Finger et al. (2018) reported that some natural component like eugenol, menthol can also reduce the number of sprouts in refrigerated conditions. Eucalyptus and coriander EO also inhibit the sprouting of potato tuber in storage condition 25°C for 10 days. (Gomez-Castillo et al., 2013) Previously (+)-carvone also has been reported to inhibit sprouting in storage condition (4°C) for 90 days. (Xie et al., 2018)

The current study of Shukla et al., focuses on the alternative method using EOs from different plants to delay and induce sprouting. Induction of sprouting leading to growth promotion of potato using EOs for improvement in tubers yield was also evaluated in the present study. Inadequate quantities of good quality seed among growers are another major problem adversely affecting the expansion of potato production in several developing countries. The major constraint for production of quality potato seed is extended dormancy which leads to delayed sprouting and planting leading to poor tuber productivity. To delays, some chemical enhancers overcome these like ethylene. chlorohydrins, 1,2-dichloroethane and carbon tetrachloride are used extensively by the seed producers to break potato seed tuber dormancy to promote sprouting. (Sharma, 2012) Chemicals are though effective but are very toxic and environment-unfriendly and harmful to human health. Hence, the current study also focuses on alternate EO based combinations to enhance the sprout quality and potato yields.

The study of Shukla et al., (2019) reports the screening of four EOs from the library of 20 EOs from medicinal and aromatic plants for sprouting and anti-

sprouting activity in potato tubers at normal room temperature $(25 \pm 2^{\circ}C)$ storage. Overall, lemon grass (LG) and clove oil (CL) found to most effective for sprout induction whereas palmarosa (PR) and ajwain (AZ) oils inhibited the sprouting. (Shukla et al., 2019)

Selected EOs (LG, CL, PR, AZ) could induce/inhibit the sprouting process by altering the accumulation of reducing sugars, ethylene production and expression of key genes known to be involved in sprouting process of potato tubers. Interestingly AZ treatment inhibited sprouting for 30 days which was mediated via damaging of the apical meristem. CL and LG EOs are able to enhance the sprouting numbers and produced enhanced yield under field condition. (Shukla et al., 2019)

Present work clearly demonstrates that the use of selected EOs can be a promising eco-friendly approach for inducing/inhibiting the sprouting of potato tubers during potato storage and use of these EOs (PR and AZ) can replace the presently used approaches such as use of harmful chemicals such as CIPC and expensive cold storage practices. Also, the study, recommends the use of CL and LG oils to improve the sprouting and potato yield. (Shukla et al., 2019)

2.7 E-cigarettes

Use of electronic cigarettes (aka e-cigarettes, electronic nicotine delivery systems and ENDS) is expanding rapidly, with global sales estimated at US \$ 1.5 billion in 2012 and US \$ 3.5 billion in 2013. (Tierney et al., 2015)

Electronic cigarettes have several attractions for cigarette smokers. E-cigarettes are promoted as an alternative to cessation, as a means to smoke where smoking is not allowed (Etter, 2010), as a safer alternative or adjunct to traditional cigarettes (Berg et al., 2015; Klein et al., 2016) and for use in social settings where smoking might be objectionable. (Richardson, 2014) E-cigarettes are perceived to be less harmful to health, less addictive and more socially acceptable than most other types of tobacco products. (Pearson, 2012) The result is that the trend towards adoption of e-cigarettes by smokers has been increasing in recent years. (King et al., 2010-2013; Pearson, 2012)

Several characteristics of e-cigarettes may be involved in smokers trying and adopting e-cigarettes. Among these characteristics are flavours. Farsalinos et al. (2013) conducted an online survey of over 4000 e-cigarette users. Their results indicated that flavours, and particularly the variety of flavours, were an important factor in the use and maintenance of e-cigarettes by current and former smokers. Interestingly, their results indicated that smokers tended to start with tobacco-flavoured e-cigarettes, and then would switch to multiple flavours as they transitioned from dual use to complete (or almost complete) substitution of e-cigarettes for their usual cigarettes. (Litt et al., 2016)

Several reports suggest that sweet or fruity flavours are particularly attractive, especially to young people. (Cheney et al., 2016; Goldenson et al., 2016) Menthol may also play a role in smokers' initiating and maintaining e-cigarette use. In one study, Rosbrook and Green (2016) exposed adult cigarette smokers to aerosolised e-liquids containing different concentrations of nicotine and menthol and measured liking and harshness. Among the findings were that nicotine tended to enhance rather than suppress sensations of coolness from menthol, and menthol tended to slightly increase liking independently of nicotine concentration. The authors concluded that menthol potentially improves the appeal of e-cigarettes by its cooling properties and minty flavour, as well as by reducing the harshness of high concentrations of nicotine. (Litt et al., 2016)

Menthol may be an attractive flavour for cigarettes, it also appears to be the most effective suppressor of cigarette smoking when used in e-cigarettes. (Litt et al., 2016)

(-)-Menthol is a major component of the EOs of *Mentha x piperita* (Lamiaceae) and *Mentha arvensis var. piperascens* (Lamiaceae); besides, it is also found in other mint oils. It has a pleasant typical minty odour and taste and is widely used to flavouring liqueurs and confectionary, in perfumery, tobacco industry, toiletries, oral hygiene products, lotions and hair tonics. (Jäger & Höferl, 2016)

Besides menthol also the EO from *Chrysanthemum x morifolium* (Asteraceae) is used as cigarette flavour. (Chun-Ping et al., 2015)

There are a lot of flavour components in the *C. morifolium* EO, such as (E)- β -farnesene, (Z)- β -farnesene, zingiberene, nerolidol and caryophyllene oxide with floral flavour (Chun-Ping, 2015), benzeneacetaldehyde and β -sesquiphellandrene with fruity flavours, isophorone with tobacco flavour (Li et al., 2012), endobornyl acetate with woody flavour. (Chun-Ping, 2015)

2.8 Ventilation systems

Numerous studies (Bluyssen et al., 2002; Flückiger, 1999) have shown that in mechanical ventilation systems, many germs, bacteria, fungi and moulds can be found, which therefore can affect the entire shell of the building.

These airborne microorganisms can cause health problems for the persons present. This problem is particularly acute in hospitals, where the patients react more sensitive to microbiological contamination. (Bardana and Anthony, 1996) A recommended method of significantly reducing microorganisms in ventilation systems is to design the system accordingly and to keep all parts absolutely clean during construction and use. (Bluyssen et al., 2002) However, this rarely happens, so that the dirt on the surface parts of the mechanical ventilation systems and microorganisms can subsequently settle there. (Pibiri et al., 2006)

The spread of microbes can be prevented, among other things, using EOs. In contrast to most antimicrobial substances currently used for air disinfection, EOs have a low toxicity. (Pibiri et al., 2006)

In indoor spaces, the controlled penetration of strictly selected EOs in volatile form could bring the following advantages: (Pibiri et al., 2006)

- 1. prevention of microbial contamination
- 2. microbiological hygienisation of ventilation systems and disinfection if required
- 3. promoting the health, well-being and productivity of persons, because, in

addition to air temperature and humidity, odours and fragrances also influence the general perception of indoor air quality

More than 60 EOs were examined in advance for their bactericidal features using aromatograms and microatmospheric methods. A highly phenolic EO (carvacrol 47 %, thymol 2 %), the mountain savory (*Satureja montana*, (Lamiaceae)) was chosen. (Pibiri et al., 2006)

The protocol in this study was applied to one of the most active EO, mountain savory, and to the 40 % formaldehyde solution formol, a chemical disinfectant used in clinics. The study has proven that the gaseous phase of the EO from the savory kills the *Staphylococcus aureus* bacterium and almost the same reduction in the number of bacteria is achieved as with total disinfection with evaporated formol. (Pibiri et al., 2006)

Thanks to the pleasant scent they may even have a positive effect on human well-being. Furthermore, the potential condensation on the surfaces of a ventilation system may have a bacteriostatic and bactericidal effect. (Pibiri et al., 2006)

2.9 Room diffuser/ Airwasher

Airborne microbes are still an underestimated cause of risk for human health, as they surround us 24 hours a day. Various airborne microbes have the potential to cause infections and, dropping down on foods, the microbes grow up there and foods become spoiled. (Krist, 2011)

Today, mainly formaldehyde, glutaraldehyde and phenol derivatives such as cresol are used as disinfectants (Hegna, 1977). An application of these chemical compounds for decreasing airborne microbes is not optimal because of their toxicity and their unpleasant smell. (Moore & Kaczmarek, 1990; Clark, 1983; Coldiron et al., 1983)

The antimicrobial (antibacterial and antifungal) potential of volatile compounds and EOs is well known and scientifically tested. (Prashar et al., 2003; Lis-Balchin & Hart, 1999; Kim et al., 1995; Morris et al., 1979) In the study "Antimicrobial effect of vapours of terpineol, (R)-(-)-linalool, carvacrol, (S)-(-)-perillaldehyde and 1,8-cineole on airborne microbes using a room diffuser" (Krist, 2011) the antimicrobial activities of five volatiles, which represent main compounds of several EOs, were tested. Terpineol, (R)-(-)-linalool carvacrol, (S)-(-)-perillaldehyde and 1,8-cineole were evaluated for their influence on airborne microbes when vaporized with a room diffuser. In the present investigation terpineol and (S)-(-)-perillaldehyde showed highest antimicrobial activities. The average reduction of germ count was 59.4 % and 42.3 %, respectively after five hours of spreading in a testing room. (Krist, 2011)

In the study "Antimicrobial effect of vapours of geraniol, (R)-(-)-linalool, terpineol, γ -terpinene and 1,8-cineole on airborne microbes using an airwasher" (Krist, 2011) five selected compounds, geraniol, (R)-(-)-linalool, terpineol, γ -terpinene and 1,8-cineole were tested for their influence on airborne microbes when vaporized with an air washer. Terpineol and 1,8-cineole showed highest antibacterial activities. The average reduction of germ count was 68 % and 64 %, respectively. (Krist, 2011)

In consideration of the fact that commonly used disinfectants like glutaraldehyde or phenol derivatives are not optimal to decrease airborne microbes due to their human toxicity, possible mucosa irritations and unpleasant smell, volatile compounds and EOs with antimicrobial activity possibly represent a suitable alternative. (Krist, 2011)

The small amounts of volatiles used in this study are generally recognised as not being harmful when inhaled. (Pappas et al., 2000) Therefore, people could stay in the room when volatile compounds are spread for reducing germ number. The convenient safe method presented in this study is considered to improve environmental health at places where people gather, such as lecture halls, theatres, stations or airports. (Krist, 2011)

2.10 Aroma plasters

Patent: SELG Christian, 2019, Duftputze, Deutschland, DE202016008605 (U1), 2019-05-09

Plaster has been used for a long time in the interior construction of buildings. Under the term "plaster" is to be understood a covering mass, which is suitable to be applied on surfaces, in particular on brickwork or concrete on surfaces at walls as well as ceilings. In the past, plasters became more and more popular as an individual design element, and in this context so-called aroma plasters were developed, which can give off a certain aroma to room air. (Selg, 2019)

Such aroma plasters, however, have different weaknesses, for example that they often mean a restriction of colour or that the aroma they exude becomes weaker over time. In addition, the aromas used in aromatic plasters are not suitable for all types of buildings. For example, a coffee-based aroma plaster might be suitable for a coffee house, but not for the wellness area of a hotel. (Selg, 2019)

It is the task of the invention to eliminate or at least mitigate the disadvantages of the aforementioned state of the art. In particular, it is the task of the invention to create a possibility to individually scent rooms with plaster. (Selg, 2019)

The task is solved by a scented water for use in plasters. The scented water contains water, an emulsifier and a perfume. The perfume contains an EO. EOs are extracts soluble in organic solvents or the organic phase of steam distillates from plants or parts of plants which have a strong odour characteristic of the plant of origin. (Selg, 2019)

The invention is based on the knowledge that such EOs are particularly suitable for use in plasters that are supposed to fragrance the air in a room. In particular, it is possible to mix the scented water with a plaster base mixture before applying it to a wall surface, so that an already scented plaster is applied to the wall surface. This plaster holds the smell of the EO then for a certain time. In addition, the scented water can also be used to reinforce a scent already present on the wall surface, especially by spraying the plaster with the scented water. (Selg, 2019)

In an advantageous design, the fragrance water is characterized, that the water makes up 92 to 96 % vol, preferably 93 to 95 % vol, particularly preferably about 94.34 % vol of the fragrance water, and the emulsifier 2 to 8 % vol, preferably 3 to 6 % vol, particularly preferably about 4.72 % vol of the scented water. The EO should make up 0.3 to 3 % vol, preferably 0.5 to 2 % vol, particularly preferably about 0.94 % vol of the scented water. The inventor has found that such mixing ratios are particularly advantageous because they provide good workability and durability as well as a fragrance intensity adapted to the intended use. Alternatively, however, other mixing ratios are possible. For example, the water content can be significantly reduced so that a kind of scented water concentrate is available. The term "about" is to be understood in the sense of "+/- 1 %". (Selg, 2019)

The fragrance is produced as follows: First a basic mixture is produced which consists of one part (e.g. 5 ml) of EO (a single oil or oil mixture) and five parts (e.g. 25 ml) of an emulsifier. The EO can, for example, be a 100 % natural EO in organic quality. The emulsifier is a nonionic surfactant from vegetable raw materials for low viscosity emulsions, which contains for example lauric acid. (Selg, 2019)

The EO is first mixed with the emulsifier for at least 2 minutes using a magnetic stirrer so that the basic mixture is formed. Then 30 parts of the basic mixture (e.g. 30 ml) and 500 parts (e.g. 500 ml) of spring water are added while the stirrer is still running. This mixture is then stirred for at least 5 minutes to produce the fragrance. (Selg, 2019)

Since the EOs typically evaporate after a few days from the surface of a plaster, the fragrance water can be filled into spray bottles, e.g. in sizes of 30 ml. With this scent water the plaster surface can be sprayed as desired and the scents can be reactivated. This ensures that exactly the same fragrance can always be applied to the corresponding surface. (Selg, 2019)

In an advantageous design, the scent area comprises several individual scent areas, whereby each individual scent area preferably comprises a plaster and/or a plaster base mixture. This has the advantage that each of the individual scent surfaces can be equipped with different scent water, so that scent mixtures can be produced. The individual scent surfaces are advantageously separated from each other by at least one, preferably several, separating surfaces. Such separating surfaces have the advantage that it is possible to fragrance the individual surface purposefully again. (Selg, 2019)

In an advantageous design, the scent surface is an interactive scent panel. The interactive scent panel is suitable to be sprayed simultaneously or staggered with different scents, preferably a scented water according to the invention. The interactive scent panel is portable and/or comprises a carrying device and/or a device for attachment to a wall and/or ceiling. The interactive scent panel is firmly integrated and/or inseparably connected to the surface of a room wall or ceiling. (Selg, 2019)

In an advantageous design, the fragrance area comprises a fragrance storage medium. Such a fragrance storage medium has the advantage that the fragrance and/or the EO is kept longer in the fragrance area, so that the area needs to be re-scented less often. The fragrance storage medium comprises a textile, preferably a non-woven fabric. Surprisingly, tests have shown that nonwovens are particularly suitable for storing fragrance water with EO. However, other fragrance storage media can also be used, for example microcapsules. (Selg, 2019)

Possible uses for the inventive scent surfaces can be found in aromatherapy, in waiting rooms, in massage rooms, in relaxation rooms, in wellness hotels and of course in private houses. (Selg, 2019)

2.11 Mould-resistant building materials

Patent: Henkel KGAA, WEIDE Mirko, 2006, Schimmel-beständige Baustoffe, Deutschland, WO2006056266 (A1), 2006-06-01

The presented invention concerns mould-resistant building materials and auxiliary building materials which are characterised by the fact that they contain an azole, optionally in combination with a sporulation inhibitor and/or with a substance anti-adhesive to micro-organisms. Silicone, acrylate and other joint sealants, especially when used in damp areas, such as bathrooms in the household, shower cubicles, etc., often show mildew-related discolorations. These mostly black or coloured coverings are difficult or often impossible to remove. Normally, these affected sealing compounds must then be mechanically removed and replaced. The same applies to other materials such as filter media, textiles, furs, paper, or leather that are exposed to moisture and inadequately ventilated. (Weide, 2006)

Joint sealants are normally treated with fungicides to prevent such mould deposits in the cured compounds. For example, DCOIT (Dichloroctyliso-thiazolinon) is used as a fungicide. However, the use of fungicides such as DCOIT is not sufficient to keep the joint sealants permanently free of mould discoloration. The biocides used are washed out after a relatively short time and moulds can grow on the surface of the joint sealant. A general problem here is that effective fungicides are washed out after a relatively short time, whereas less easily washed-out fungicides do not have sufficient activity. (Weide, 2006)

Azol compounds in high concentrations are able to keep the mentioned materials free from mildew-related discolorations over a longer period of time. Furthermore, it was found that by combining an azole compound with a sporulation inhibitor and/or with a substance anti-adhesive to microorganisms, a further improvement can be achieved in terms of mould-free time or discolouration-free time. (Weide, 2006)

A sporulation inhibitor is a substance which is capable of preventing or at least significantly reducing the asexual reproduction of fungi, in particular moulds, whereby the reduction in asexual reproduction is not attributable to a microbicidal or fungicidal effect. By the use of a sporulation-inhibitor instead of a microbicide, one bypasses the problem of the resistance-formation. (Weide, 2006)

An anti-adhesive substance is a substance capable of reducing the adhesion of microorganisms, in particular fungi, especially moulds, whereby the antiadhesive effect is preferably not due to a microbicidal or fungicidal effect. The sporulation inhibitor is preferably selected from plant extracts, propolis extracts and algae extracts. (Weide, 2006)

Fragrance alcohols with one or two free hydroxyl groups are particularly preferred. From the large group of fragrance alcohols to which terpene alcohols also belong, preferred representatives with at least one free hydroxyl group can be named. (Weide, 2006)

Terpenes are all-natural substances and derivatives composed of isoprene units. Farnesol, patchouli alcohol and geraniol are preferred. Monoterpenes such as α - or β -ocimene, linalool, linalyl acetate, carene, terpineole, nerol, nerolenic acid, geraniol, geranium acid, α - or β -phellandrene and/or thujone, in particular geraniol, linalool and/or thujone, are preferred. Geranylgeraniol (3,7,11,15-tetramethyl-2,6,10,14-hexadecatetraen-1-ol) as well as its isomers and derivatives may be mentioned here as an example for the diterpenes. Plant extracts containing mono-, sesqui- and/or diterpenes (e.g. geranium oil, rose oil, orange blossom oil, lavender oil, jasmine oil, basil oil, citronella oil, cypress oil, cedar leaf oil, coriander oil, rosewood oil, pimento oil, ginger oil or clove oil) may also be preferred. (Weide, 2006)

The concentration of sporulation inhibitors can be varied by the expert in a wide range, depending on the conditions of use of the agents. (Weide, 2006)

The sporulation inhibitor is preferably used in an amount of 0.00001 to 1 % by weight, especially preferred in an amount of 0.0001 to 0.1 % by weight, especially in an amount of 0.001 to 0.05 % by weight. (Weide, 2006)

2.12 Solar technology – Photovoltaic

Photon upconversion (UC), which is a process that converts low-energy photons to higher ones, has the potential to break the thermodynamic efficiency limit of solar technologies such as photovoltaics and photocatalytic reactions. (Ma et al., 2019)

The TTA-UC triplet-triplet annihilation upconversion (TTA-UC) process typically employs organic and metalloorganic chromophores that are only

soluble in organic solvents, and the contact among the chromophores is essential for the transfer and annihilation of triplet excitons. Consequently, numerous common organic solvents, such as toluene, chloroform and tetrahydrofuran, have been widely used in the TTA-UC systems for the last few decades. Moreover, to avoid triplet-state quenching by the dissolved oxygen molecules, anaerobic environments are needed, which requires time consuming, multi-step and high-cost deoxygenating processes by bubbling inert gases or by repeated freeze–pump–thaw cycles. To simplify the operating process, researchers have been searching for innovative media with the aim of maximizing the efficiency, air stability and biosafety of the TTA-UC method. (Ma et al., 2019)

Generally, the existing toxic co-solvents are difficult to remove completely, which cannot assure biosafety in biological applications; moreover, the low UC efficiency limited by high viscosity is still a big issue. Accordingly, the straightforward approach for solving the oxygen quenching problem is to find a suitable solvent that can achieve air-stable, high-performance and biosafe TTA-UC applied in fields ranging from energy conversion to biology. (Ma et al., 2019)

In this study, inspired by nature, a type of natural solvent, terpenes, which can be used as a green solvent for operating air-stable and highly efficient TTA-UC is demonstrated. In nature, terpenes represent a class of cheap and abundant nonpolar substances with enormous potential for green chemistry. One of the typical "green" constituents, namely, (+)-limonene is abundantly present in the rind of oranges and related fruits and it is recognized as a safe chemical by the U.S. Food and Drug Administration (FDA). Besides, non-polar (+)-limonene has similar molecular weight and chemical structure to substituted toluene; therefore, it possibly has the potential to replace toluene, which is commonly used as a TTA-UC solvent. (Ma et al., 2019)

Because of its low polarity, low viscosity and optical transparency, (+)limonene is considered as the only bio-solvent capable of replacing nonpolar traditional solvents. The result suggests that (+)-limonene has a unique advantage in the cases where high concentrations of dyes are required to ensure high absorption and a consequent stimulated observable emission at the excitation wavelength. (Ma et al., 2019)

2.13 Eco-friendly solvent

Polymer nanofibers have been largely used in applications ranging from biomedical applications such as in tissue engineering, regenerative medicine, and anti-infective membranes to military and food industries. Moreover, they can be used to encapsulate and deliver natural antimicrobial active substances such as EOs and phytoconstituents to replace synthetic ones, therefore, being of great interest to pharmaceutical and food products. (Miranda et al., 2019)

Orange oil is a by-product of the citrus juice industry produced in large quantities, as orange is the most produced and consumed fruit in the world. Orange oil has been used in food, cosmetics, and pharmaceutical industries due to its flavour, fragrance, and antimicrobial activity. According to the European Commission, a variety of EO components has been used as flavour-ings in food since they possess no risk to human health. Among them is limonene which is generally recognized as safe for its nontoxic potential (LD₅₀ > 5 g kg⁻¹). (Miranda et al., 2019)

In this sense, limonene can be used to reduce effects of long-term exposure to solvents such as toluene that can damage the central nervous and reproductive systems, causing respiratory diseases and cancer. This is especially true in polymer processing industries where toluene is largely used as a solvent for paints, resins, and adhesives. (Miranda et al., 2019)

Terpenes have been used as green solvents to polystyrene (PS), especially limonene and cymene due to their capacity to dissolve PS and their high potential as substitute of petrochemical solvents, including n-hexane, ethyl ketone, acetone, toluene, and glycol ethers. Limonene has been used to produce PS nanofibers by electrospinning, but this is the first time it has been used by solution blow spinning, an alternative to other fibre-forming technique, including electrospinning, to produce microfiber and nanofiber of polymers and ceramics due to advantages such as larger production rates and reduced costs. (Miranda et al., 2019)

GC–MS analysis of orange oil shows six major compounds. (+)-limonene being the major compound (97.06 %), and the minor being β -myrcene (1.33 %), (I)- α -pinene (0.76 %), (I)- β -pinene (0.35 %), δ -3-carene (0.33 %), and citronellal (0.18 %). (Miranda et al., 2019)

While PS nanofibrous mats spun from toluene did not show any microbial inhibition, mats spun from orange oil had an antimicrobial activity when in direct contact with the culture medium due to the presence of (+)-limonene and other minor compounds. (Miranda et al., 2019)

Orange oil was successfully used as an alternative green solvent to replace toluene to produce SBS fibers of PS. The effect of green solvent on rheological behavior of PS solutions was evaluated and associated with changes in nanofiber morphology. The average diameters of PS fibers increased with polymer concentration and were dependent of the polymer evaporation rate more than on the rheological behaviour of the starting solutions. Residual limonene in spun mats acted as a plasticizer, reducing glass-transition temperature as compared to the ones spun from toluene solutions. Furthermore, these fibers containing residual orange oil had antimicrobial properties inhibiting *A. alternata* growth. Slightly lower CAs were found for the mats spun from orange oil as compared to toluene. These results suggest that the eco-friendly nanofibrous mats spun from PS/orange oil can be used in applications such as wound healing and active food packaging. (Miranda et al., 2019)

3. Conclusio

EOs can be used in many different ways in technical products due to their diverse properties.

Components of EO are used in soaps, detergents, cleaning agents, fragrance pastilles for laundry and air fresheners because of their antibacterial effect and pleasant smell. In shoe pastes and furniture polishes the unpleasant odour of the products should be covered.

Due to the antioxidative characteristics of EOs, there is another possible application as an eco-friendly, green corrosion inhibitor.

Excessive and frequent use of chemicals in the agricultural sector may cause problems to the environment and in case it enters the food chain it may cause adverse health effects. Therefore, natural substances such as EOs seem to be a highly preferable alternative. The prospect of EOs or their components as plant protection products is very promising, e.g., as antipests, acaricides, herbicides or for inhibiting and inducing sprouting.

Because of its low polarity, low viscosity and optical transparency, (+)limonene is considered as the only bio-solvent capable of replacing nonpolar traditional solvents. (+)-limonene has a similar molecular weight and chemical structure to substituted toluene. Therefore (+)-limonene can be used as a green solvent in solar technologies such as photovoltaics and photocatalytic reactions.

EOs are considered as safe for humans, animals and the environment. Due to their diverse characteristics, more studies on possible further applications should follow.

Fazit

Ätherische Öle können aufgrund ihrer vielfältigen Eigenschaften in technischen Produkten auf unterschiedlichste Weise eingesetzt werden.

Bestandteile von ätherischen Ölen werden aufgrund ihrer antibakteriellen Wirkung und ihres angenehmen Geruchs in Seifen, Wasch- und Reinigungsmitteln, Duftpastillen für Wäsche und Lufterfrischer eingesetzt. In Schuhpasten und Möbelpolituren soll der unangenehme Geruch der Produkte überdeckt werden.

Aufgrund der antioxidativen Eigenschaften von ätherischen Ölen ergibt sich eine weitere Anwendungsmöglichkeit als umweltfreundlicher, grüner Korrosionsschutz.

Der übermäßige und häufige Einsatz von Chemikalien in der Landwirtschaft kann zu Umweltproblemen führen und falls diese Chemikalien in die Nahrungskette gelangen, zu gesundheitlichen Beeinträchtigungen führen. Daher scheinen natürliche Substanzen wie ätherische Öle eine höchst wünschenswerte Alternative zu sein. Die Aussicht auf den Einsatz von ätherischen Ölen oder ihrer Komponenten als Pflanzenschutzmittel ist sehr vielversprechend, z.B. als Schädlingsbekämpfungsmittel, Akarizide, Herbizide oder zur Hemmung und Förderung des Austriebs.

Aufgrund seiner geringen Polarität, niedrigen Viskosität und optischen Transparenz wird (+)-Limonen als einziges Bio-Lösungsmittel angesehen, das unpolare traditionelle Lösungsmittel ersetzen kann. (+)-Limonen hat ein ähnliches Molekulargewicht und eine ähnliche chemische Struktur wie das zu substituierende Toluol. Daher kann (+)-Limonen als grünes Lösungsmittel in Solartechnologien, wie der Photovoltaik und photokatalytischen Reaktionen, verwendet werden.

Ätherische Öle gelten als sicher für Menschen, Tiere und die Umwelt. Aufgrund ihrer vielfältigen Eigenschaften sollten weitere Studien zu möglichen, zusätzlichen Anwendungsmöglichkeiten folgen.

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