# الإهـــــــــــــــــداء

**إلى من جرع الكأس فارغاً ليسقيني قطرة حب**

**إلى مـــــن كلّت أنامله لـــــــيقدم لنـــــا لحظة سعادة**

**إلى من حصد الأشواك عن دربي ليمهد لي طريق العلم**

**والـــــــدي العزيز**

**إلى مـــــــن أرضعتني الحب والحنان**

**إلى رمـــــــــــز الحب وبلسم الشفـــــــــــــــاء**

**إلى القلب الناصع بالبياض والدتي الحبيبة**

إلى القلوب الطاهرة الرقيقة والنفوس البريئة إلى رياحين حياتي إخوتي

إلى الأجساد التي سكنت تحت تراب الوطن الحبيب المعفرة بدماء الشهادة

الآن تفتح الأشرعة وترفع المرساة لتنطلق السفينة في عرض بحر واسع مظلم هو بحر الحياة وفي هذه الظلمة لا يضيء إلا قنديل الذكريات ذكريات الأخوة البعيدة إلى الذين أحببتهم وأحبوني

أصدقائي

إلى الذين بذلوا كل جهدٍ وعطاء لكي أصل إلى هذه اللحظة أساتذتي الكرام ولا سيما الدكتور

الفاضل **حسن محمد لعيبي**

إليكم جميعاً أهدي هذا العمل

# ﴿شكر وتقدير﴾

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من الحق والوفاء وأنا أنتهي من إعداد هذه الدراسة ، أن أتقدم بأسمى آيات الشكر والتقدير والامتنان إلى أستاذي الفاضل الدكتور **حسن محمد لعيبي**، لجهوده العلمية القيمة ورعايته المخلصة لانجاز هذه الدراسة. وأرى من الوفاء أن أهدي شكري وتقديري إلى الأساتذة الأفاضل رئيس وأعضاء لجنة المناقشة لقبولهم مناقشة البحث.

ويلزمني الواجب أن ابدي خالص امتناني وعرفاني بالجميل إلى أساتذتي في كلية العلوم /جامعة القادسية / لما قدموا من مجهود وتوصيات دلت على دقة علمهم وكرم أخلاقهم وأتمنى لهم الموفقية والصحة الدائمة.

وشكرا وعذرا لكل من نساه قلمي ولم ينسه قلبي وفكري من أصدقائي وزملائي وإخوتي أينما كانوا . . .

# AIM OF STUDY

1- the learing for wright of research .

2-study of new techniqui which is

supercritical fluid Extraction and

Application its, such as Extraction of

volatile oils

**Abstract:**
This review will cover the application of supercritical of
fluid extraction (SFE) for obtaining
volatile oils (VOs) from aromatic, spice and medicinal plants.

Abrief discussion of advantages and
disadvantages of SFE for obtaining these very complex mixtures of substances will be presented. The

chemical profile of volatiles oils obtained by SFE will be comp ared with that obtained by the

conventional process, that is, steam distillation. Applications of SFE to obtain clove and chamomile

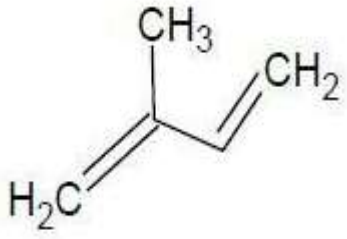
volatiles oils based on the LASEFI´s experience will also be consider ed. Finally

## 1-1 INTRODUCTION

Essential or volatile oils (VOs) are a mixture of compounds belonging to the ter penoid family ; .these are compounds containing an isoprene unit (C5, see Fig. (1)). The most
common structures found in
VOs are the monoterpenes (C10) and sesquiterpenes (C15) as well as their oxy genated forms. In general,
these structures possess a characteristic aroma with a very low threshold, thus , they can be detected even
when present at very low concentration. The terpenoid structures are a result of the plant secondary
metabolism, that is, the substances produced by the defense mechanism. The s ources of VOs are the
aromatic, spice, and medicinal plants. VOs can be a simple mixture, as for insta nce, clove bud oil that is
formed by 4 compounds [1]: eugenol (64.3%), ß-caryophyllene (19.6%), eugen

ol acetate (13.8%), and
humulene (2.3%) or as complex as the fennel oil (anethole , fenchone, limonen e, methyl chavicol,
myrcene, □-pinene, □-terpinene) [2]. The amount of VOs in plants vary widely, depending of the variety
of clove buds the amount of VOs can be up to 24% [3]; or, as low as 0.04% for roses [4].

**Fig. (1). Isoprene unit**



assisted and ultrasound assisted extraction the reader is referred to Takeuchi et al [7]; a in depth discussion of applications of supercritical fluids can be found in Pereira and Meireles [8].

The supercritical carbon dioxide will extract both the waxes and the essential oils that make up the concrete. Subsequent processing with liquid carbon dioxide, achieved in the same extractor by merely lowering the extraction temperature, will separate the waxes from the essential oils.

1-1 SUPERCRITICAL FLUID EXTRACTION (SFE)

Several fluids have been used in supercritical fluids (SCF) applications. And, lately, several novel applications of SCF from particle design [9],[10] to reaction [11], encapsulation [12] and microelectronics [13] have been reported in literature.

SFE is a process that takes advantage of the increase in the solvation power of fluids near or above their critical points. The phenomenon of increasing the density of fluids as they approach their critical point was first reported by Hannay and Hogarth [14]. In spite of the possibility of using different SCF, carbon dioxide is the solvent usually used in applications related to the cosmetic, food and pharmaceutical industries. $CO_2$ has a low critical temperature (304 K) and a mild critical pressure (7.8MPa); it is non-toxic, relatively inert to several mediums, and, can be obtained at high purity at a reasonable cost. Francis [15] reported the solubility of about 200 substances in subcritical carbon dioxide.

In some cases, the solubility of compounds in subcritical or supercritical $CO_2$ is not good. This can be overcome by the addition of cosolvent, usually a polar solvent such as water, ethanol, methanol, etc. to the sub or supercritical solvent; this affects the properties of the fluid phase because of the strong interactions among the solute, the solvent, and the cosolvent [16].

Fig. (1-2) shows a flow diagram for a SFE unit. The raw material (comminuted plant with moisture content bellow 20% if $CO_2$ is the solvent) is accommodated inside the extractor vessels forming a fixed bed. SCF flows through the fixed bed, the solute is carried by the SCF and the solvent/ solute mixture is separated in the flash tank. Heating and cooling are required in various step of the process. In industrial practice, the SCF from the separator vessel is recirculated. Thus, only a small amount of the SCF is lost;

in general, the lost is approximately 2%.

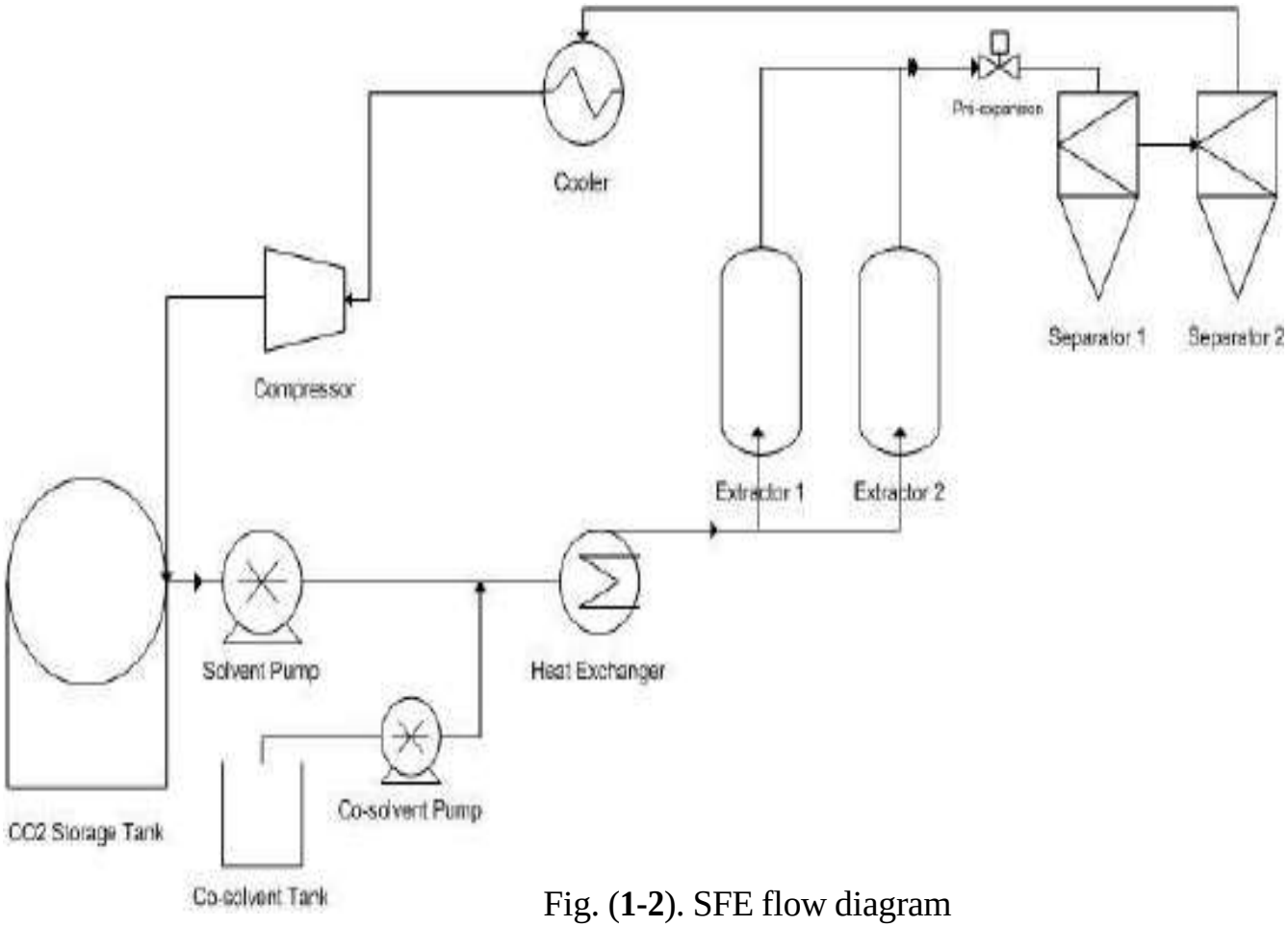



Fig. (**1-2**). SFE flow diagram

**1-3 OBTAINING VOs BY SFE**

SFE has been considered one of the most potentially useful emerging methods of sample preparation in pharmaceutical and food processing industry. To avoid chemical alteration of volatiles and exploiting the other advantages of liquid or compressed gases such as carbon dioxide, extraction of different VOs sources have been successfully performed under different conditions.

Some extracts from aromatic, spice, and medicinal plants obtained by SFE should not be referred only as VOs since besides the terpenoids they also contain non-volatile substances; for instance, the SFE extract from fennel seeds contains besides the terpenoidic fraction several fatty acids (linoleic, linolenic, oleic acid, palmitic, palmitoleic, and stearic acids) [2]. Ginger oleoresin produced by SFE possesses in addition to the VO fraction a gingerols-rich fraction, the substances associated with antioxidant activity of the oleoresin [17]; other examples of VOs extraction by SFE can be found elsewhere [18]-[22].

One exception to this behavior is clove bud oil; both the VO as well as the SFE extract have the same compositions. Nonetheless, the process yields are quite different. In the SD process an emulsion of VO and water is formed; thus, in the separation process part of the VO is lost in the water rich phase.

Therefore, to produce VOs by SFE one of two techniques may be employed: (1) fractional extraction and/or (2) separator cascade. In the first case, a mild extraction conditions can be used to obtain the VOs; then, the operating temperature and pressure are increased and/or cosolvent is added and the heavier

compounds are extracted. In the second case, a cascade consisting of 3 or more separator vessels is used;
the pressure and temperature decrease from the first to the last separator; the VOs are obtained in the
separators which are operating at the lower pressure and temperature [18].
Another exception is chamomile flowerheads oil; qualitatively, the profile of the SFE extract is
similar to that of the SD extract. However, there is significant quantitative difference between them.
Kotnik et al. [23] demonstrated that the extract obtained by SFE presents better quality than that obtained
by traditional SD: SFE extracts mainly contained matricine while the amount of chamazulene, the thermal
degradation product of matricine, was much lower than in the extract obtained by steam distillation. In
terms of extraction yield the yield obtained by SFE after 30-min extraction was 4.4 times higher than that
produced by steam distillation performed for 4 h [24]. Analogous to produce VOs by SFE from clove bud
there are two techniques: (1) extraction at low operating temperature and pressure and/or (2) extraction
with separators. In the first case, only the essential oil is extracted due to its high solubility in the
supercritical fluid. In the second case, the extracts are separated into cuticular wax (heavier fraction) and
essential oil using fractional separation [25],[26].

**1-4RECENT PATENTS IN OBTAINING VOS BY SFE**

A search done in the ISI Web of Knowledge taking into account the period since 1963 using the
following topic (supercritical fluid* and essential oil*) resulted in 37 records. Restricting the search to the
topic (supercritical fluid* extraction and essential oil*) returned 22 records.
In order to compare records between surveys involving SFE to SD a second search was done
using the topic (steam distillation extraction and essential oil*) resulting in 60 records.
**Fig. (3)** presents an analysis of the patent evolution over time involving extraction of VOs by SD
and SFE. It was verified that the first patent involving the use of SD method to extract essential oils was

granted in 1966 while that involving the use of SFE method was granted in 19 93. Also it was observed
that very few process developments have been described in the patents involvi ng SD to extract VOs; most
of the recent patents (last 5 years) are associated to the application of the VOs extracted by SD into novel
products/compositions with pharmaceutical [27]-[32], herbicide [33], cosme tic [34] properties, among

others.

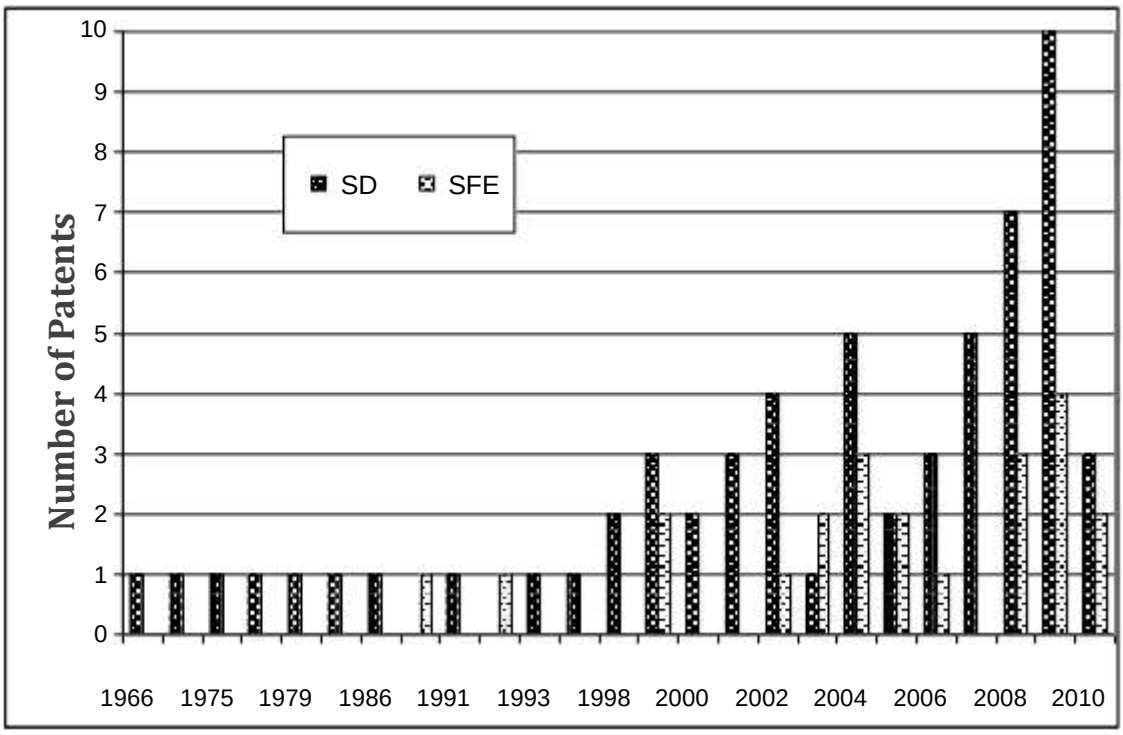



Fig. (**1-15**). Analysis of the patent evolution over time involving extraction of VOs by S D and SFE

Analogously, most of the recent patents (last 5 years) involving SFE to obtain VOs are also
associated to the application of these VOs into novel products/compositions wit h different properties
(Table **1**). Indeed, it is verified that patent developments using SFE showed an increa sing interest in this
technique to produce VOs to be incorporated in specific products.

**Table 1.** Recent patents involving the use of VOs extracted by SFE into novel prod ucts/compositions.with different properties

| | | | | | |
|---|---|---|---|---|---|
| essential oil, chloroxylenol, and additives | | vaginal environment (keep the normal pH value) | fungicide | | |
| Natural soap, comprising an VO and additives | $CO_2$ | As natural soap | Not related | 2009 | [38] |
| Cherry soft capsule, comprising VOs from traditional Chinese medicine plants, vitamin E, vitamin C, among others additives | Not related | As cherry soft capsule | Not related | 2009 | [39] |
| Du Liang compound Chinese medicine soft capsule, comprising VOs from angelica dahurica and rhizoma ligustici wallichii | $CO_2$ | As Du Liang compound Chinese medicine soft capsule | Therapeutic | 2008 | [40] |
| Peony essential oil | $CO_2$ | Added to tobacco | Cigarette aromatizing | 2008 | [41] |
| Purified extract of roots from Ligusticum species, comprising VO rich in ligustilide, fatty acids and glycerides | Not related | Added to food items or nutritional supplements | Nutraceutical | 2006 | [42] |

On the other hand, a significant number of patents involving SFE to extract VO s are associated
to the process development. From 22 records 12 deal with process developme nt. In general, these patents
describe the SFE conditions used to obtain and/or purify VOs from different so urces.
In the first patent, granted in 1993, involving the use of SFE method to obtain VOs, Bethuel et
al. [43] described a process using preferred carbon dioxide for extracting diff erent constituents such as
essential oils, perfumes, flavours, colouring agents, alkaloids, pharmaceutic al ingredients, etc. from
vegetables, flowers, etc. The process is similar to the conventional SFE descri bed before; differing only
that the fluid discharged from the extractor is treated to separate the extracted constituents. The
discharged fluid is expanded through a pressure reducing valve so that the less volatile constituents can be
separated as liquid from the fluid in gaseous phase. This gaseous phase is then liquefied and the liquid is
rectified in a vertical column in order to concentrate the constituents in the li

quid phase. The column is

topped with a condenser so that the gas exhausted by the column can be wash ed with condensed fluid.
In 1999, HASEGAWA CO LTD [44] presented a novel process to extract natural essential oil.
The process uses a chromatography column filled with a porous polymerisat ion resin for fractionating
psoralens in the natural essential oil. The psoralens content of the natural es sential oil is provided in a

fluid state in CO2 of subcritical or supercritical state.

HAUSMANN SA [45], also in 1999, developed a method to produce natural antioxidants. The

method comprises in purifying antioxidant compounds by extraction with carbon dioxide under

supercritical conditions after prior treatments, including enzymatic treatm ent of the aromatic plants
leaves.

Webster and Sarna [46] in 2002 patented a preparation method to produce cannabis extracts.
These extracts can be used in several products for treating symptoms as p ain, nausea, AIDS related
weight loss or wasting, etc. This preparation method was the first to men tion the use of other SCF
different from CO2 for obtaining VOs. It comprises 4 steps: (a) harvesting cann abis comprising seed and
chaff; (b) extracting the chaff with solvent that can be subcritical water or su percritical carbon dioxide
with or without cosolvent; (c) passing the extract over a chromatographic column to fractionate at least
one cannabinoid, cannflavin or essential oil and (d) collecting the fractions la cking these ingredients to
produce a hemp extract and at least one purified cannabinoid, cannflavin or es sential oil.

In 2005, Nakamura et al. [47] proposed a different VOs continuous extracti on method using
carbon dioxide in the supercritical and/or subcritical state. The method com prises: (a) an essential oil-
containing plant raw material is extracted in water and/or hydrophilic solvent, to prepare a plant essential-
oil liquid sample; (b) the plant essential-oil liquid sample is contacted/ saturated with carbon dioxide fluid
under stirred in the supercritical and/or subcritical state, to obtain plant essential oil. Recycling is
performed after carbon dioxide fluid contact, and then continuous processi ng of the plant essential oil
liquid sample is performed.
Other recent patents have been focused on the advantages of the SFE method to obtain essential
oils from sources not yet studied using this extraction method. Some inventors name the SFE method as
“new method” enlightening the advantages of this process. Among these adva ntages are: no need of any
solvent treatment process [48], possible reuse of the CO2, high VOs rec overing [49] and possible
immediate purification of VOs [41],[42]. Other patent publications have been f ocused on the advantages
of the supercritical extracts, which are extracts with different quantitative c hemical profiles, called by
some inventors by “new extracts” [50]-[52].

**1-5 CURRENT & FUTURE DEVELOPMENTS**

The conventional extraction of VOs by the steam distillation (SD) method clearly presents
drawbacks that lead to loss or degradation of volatile components in the extract. Supercritical fluid
extraction (SFE) is a well established technique that presented good results for VOs extraction. SFE from
clove bud and chamomile flowerheads produced higher extraction yields than the SD method, similar or
even better extracts using one of the two most commom techniques: (1) extraction at low operating
temperature and pressure and/or (2) extraction with separators.

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