The Third French-MFU Seminar on "Aromatherapy and Spa"

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

สวทช
NSTDA
Northern Network

Organized by

French-Upper Mekong Sub-region Academic Cooperation Centre

School of Cosmetic Science; MFU

Supported by

French Embassy of Thailand

National Science and Technology Development Agency (NSTDA); Northern Network

Division of Research Services; MFU

December 13-14, 2007
Meeting Room 306, D1 Building
Mae Fah Luang University, Chiangrai
THAILAND

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Dr. Nattaya Lourith
School of Cosmetic Science
Mae Fah Luang University

Prof. Karim ALLAF

Director of LMTAI--Laboratory Mastering
of Technologies for Agro-Industry
at La Rochelle University, France

Equipement & Engineering for Industry
Innovating Industrial Technology

Extraction of essential oils by Instant Controlled Pressure DIC process

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Equipement & Engineering for Industry
Innovating Industrial Technology

How new processes of extraction may contribute to improve the quality of essential oil for pharmaceutic and cosmetic applications?

"Specific quality of essential oils extracted by Instant Controlled Pressure – Drop DIC process"

M. Kristiawan, C. Besombes, V. Sobolik, K. ALLAF

Presented by: Prof. Karim ALLAF
LMTAI, Avenue Michel Crepeau; 17042 La Rochelle Cedex 01
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Essential Oils EO's: End-Users Markets

Sectors	Segments	Essential oils
Perfumery & Cosmetic	Personal & Dental cares, Soap & detergent	Lemon, Peppermint, Orange, Patchouli, Rosewood, Mint, Spice, Eucalyptus & derivatives
Food	Softdrink, Chewing gum, Candy, Confectionery, Tobacco, Processed & canned food products	Citrus, Peppermint, Vanilla, Spice oleoresins, Flavour & floral oils, Oleoresins
Pharmaceutical	Homeopathy, Health-care products, Aromatheraphy	Orange, Citrus, Patchouli, Lavender, Geranium
Niche market	Natural Isolates of EO's : - Nutraceuticals / Functional Food - chemicals substitution	Exotic essential oils: Jasmine, Rose, Sandalwood, Cinnamon bark, Neroli, Bay, Caraway, Bergamot, Cardamom, Vetiver, Pimento leaf

Essential Oils (EO's) - The Facts

- Developing Countries account for 85% of EO's production.
- Developed Countries (EU, USA, Japan) occupy 72% of world consumption of EO's
- The challenges for entering EO's international market:
  - Consumer trend is towards health & well being
  - No quality standard exist for the authentication of therapeutic grade of EO's
  - More & more excessive & stringent regulations:
    Environmental, social, health & safety issues
    Green process & sustainable development

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Over-regulations

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Extraction Solvents Regulations

- "Hexane"
  - European Council Directive 88/344/EEC (June 1988)
    Max residu limit in the foodstuffs - flavour : 1 ppm
    - fat / oil / cocoa butter : 5 ppm
  - FDA Guidance for industry – Q3C Impurities : Residual solvents (Dec 1997)
    Class 2 solvent : Solvent to be limited; flammable, carcinogen
    Max Permitted Daily Exposure in pharmaceuticals : 2.9 mg / day
- "Ethanol"
  - FDA Guidance for industry - Q3C Impurities : Residual solvents (Dec 1997)
    Permitted in pharmacy & perfumery as Class 3 solvent
    Low toxic potential , Concentration limit : 5000 ppm
  - Proposition of European Chemical Bureau (Oct 2006)
    as Category 1 **CMR** substance (Carcinogenic, Mutagenic or Reproductive toxin)
- New European **"chemical"** policy: REACH is under the consideration.

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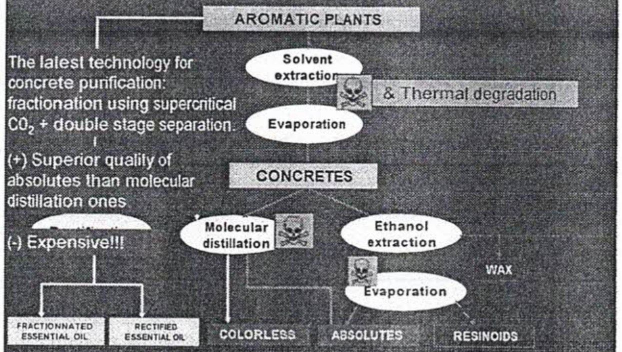
Current industrial extraction process



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Modern extraction techniques

- Examples
  - Supercritical fluid extraction (SFE) (1970's)
  - Solvent-free microwave extraction (SFME) (1990's)
  - Subcritical water extraction (SWE) (1990's)
    (T = 125 - 175°C, P = 2 – 5 MPa) [critical point = 374°C, 22.1 MPa]
- Advantages
  - Faster extraction (10 – 60 min vs 2 – 48 h in conventional processes)
  - High quality extract, no thermal degradation, no toxic residue (SFME & SWE)
  - For SFE and SWE, compounds selectivity depends on the processing parameters
- Drawbacks
  - **High investment cost** (SFE & SWE) connected to **Long time of treatment**
  - **Non selective process** → Needs second distillation stages...
  - **Non-homogeneity** of electromagnetic field (SFME) in industrial scale

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Innovative extraction technology

Instant Controlled Pressure Drop

(Détente Instantanée Contrôlée) DIC®

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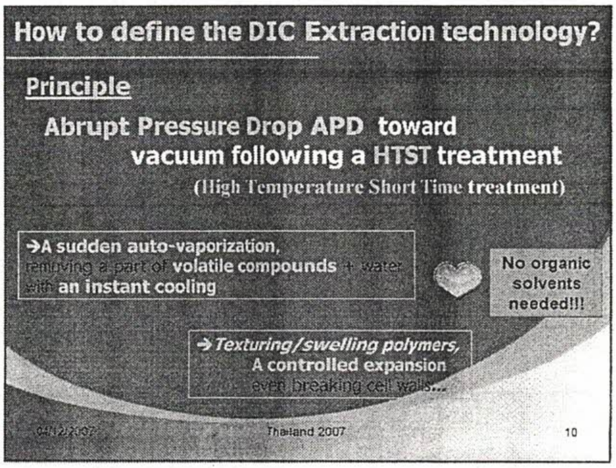
How to define the DIC Extraction technology?
Principle
Abrupt Pressure Drop APD toward vacuum following a HTST treatment
(High Temperature Short Time treatment)
→A sudden auto-vaporization, removing a part of volatile compounds + water with an instant cooling
No organic solvents needed!!!
→ Texturing/swelling polymers, A controlled expansion even breaking cell walls...
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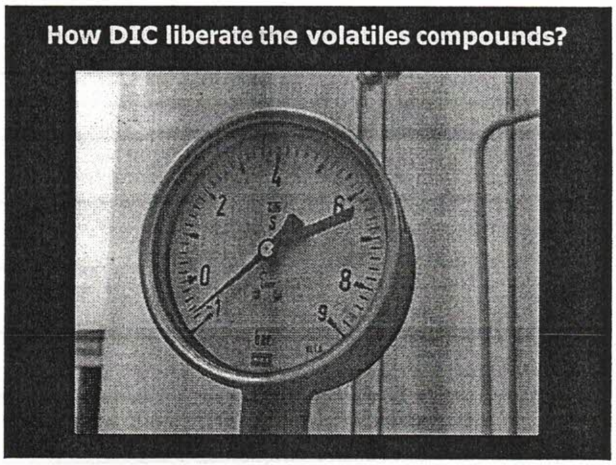
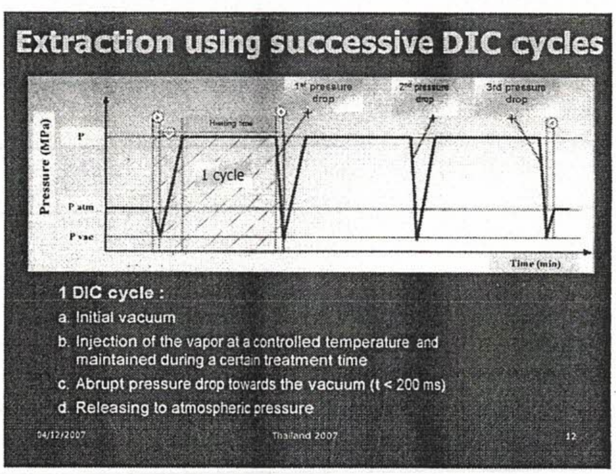

How DIC liberate the volatiles compounds?


Extraction using successive DIC cycles
1st pressure drop
2nd pressure drop
3rd pressure drop
Heating time
1 cycle
Pressure (MPa)
P
P atm
P vac
Time (min)
1 DIC cycle :
a. Initial vacuum
b. Injection of the vapor at a controlled temperature and maintained during a certain treatment time
c. Abrupt pressure drop towards the vacuum (t < 200 ms)
d. Releasing to atmospheric pressure
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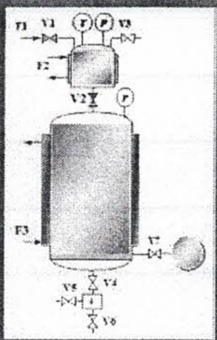
DIC Lab scale equipment



- **Treatment vessel (1)**
  - High temperature / Steam / Micro-Waves
  - High pressure / Steam / Air or inert gas
- **Vacuum system**
  - Vacuum pump (2) / Vacuum tank (3)
- **Instant valve (V2)**
  - With possibility to modify opening section
- **Condensation system (F3)**
  - Various condensation temperature
- **Heating system (F1, F2)**
  - Saturated steam / Micro-Waves

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DIC operating parameters

•Initial temperature	T_i	50°C	→	160°C
•Initial pressure	P_i	0.05 MPa	→	0.6 MPa
•Vacuum pressure	P_v	1 kPa	→	10 kPa
•Final pressure	P_f	f (Pi, Pv,v/V)	→	~13 kPa
•Equilibrium temperature	T_e	15°C	→	45°C
•Initial Moisture content	W	10%	→	90% WB
•Heating time	t	30 s	→	20 min
•Speed of pressure drop	$\Delta P/\Delta t$	0.04 MPa/s	→	2.5 MPa/s
•Number of cycles	N	1	→	~12

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Cananga oil

Raw Material

- *Cananga odorata forma macrophylla*
- Indonesian origin
- *Dry* mature flowers
  Moisture content : 10.2 % dm

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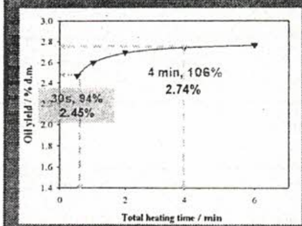
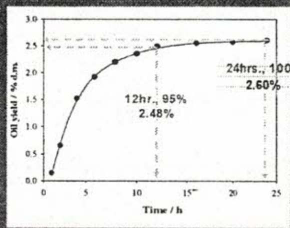
DIC vs. Steam Distillation

Oil yield

DIC: P = 0.6 MPa, 8 cycles



Steam Distillation (Lab)



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DIC vs. Steam Distillation

Oil composition

Grouped compounds	DIC 0.6 MPa 8 cycles in 4 min	Steam Distillation 24 h
Oxygenated monoterpenes (%)	5.6	4.5
Other light *oxygenated* compounds (%)	8.1	1.3
Sesquiterpenes hydrocarbons (%)	24.8	39.8
Oxygenated sesquiterpenes (%)	42.5	36.7
Other heavy *oxygenated* compounds (%)	17.6	16.7

Oxygenated compounds are more odoriferous & stables than terpenes hydrocarbons !!

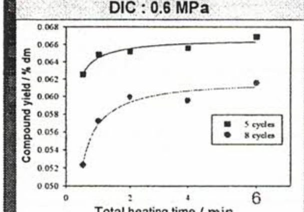
How DIC can preserve thermal sensible compounds?

Short duration (< 1 min) of heating which done in several cycles

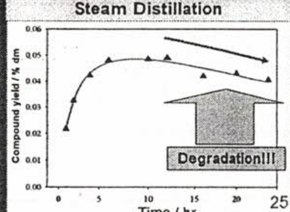
trans-Geraniol

(oxygenated monoterpene)

DIC : 0.6 MPa



Steam Distillation



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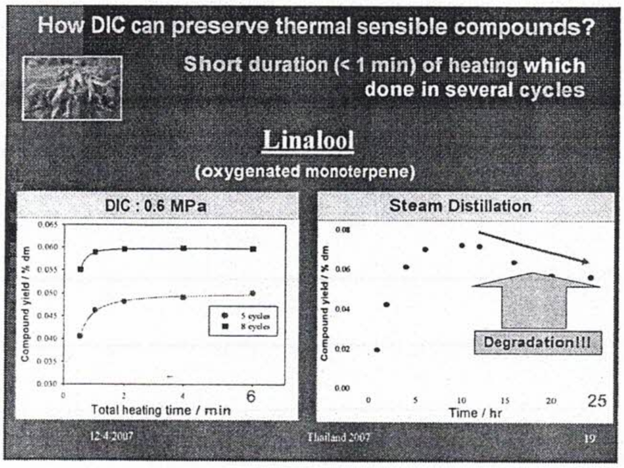
How DIC can preserve thermal sensible compounds?
Short duration (< 1 min) of heating which done in several cycles
Linalool
(oxygenated monoterpene)
DIC : 0.6 MPa
Compound yield / % dm
Total heating time / min
5 cycles
8 cycles
Steam Distillation
Compound yield / % dm
Degradation!!!
Time / hr
12.4.2007
Thailand 2007
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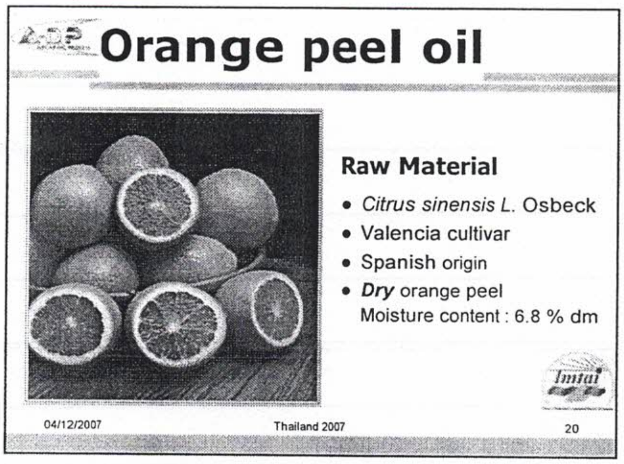
Orange peel oil
Raw Material
• Citrus sinensis L. Osbeck
• Valencia cultivar
• Spanish origin
• Dry orange peel
Moisture content : 6.8 % dm
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Thailand 2007
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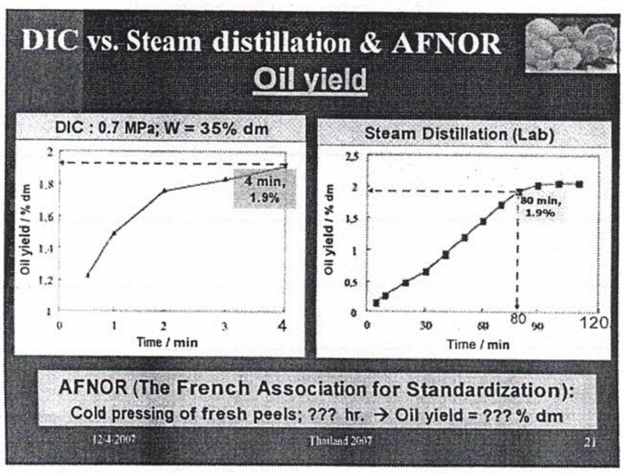
DIC vs. Steam distillation & AFNOR
Oil yield
DIC : 0.7 MPa; W = 35% dm
Oil yield / % dm
4 min, 1.9%
Time / min
Steam Distillation (Lab)
Oil yield / % dm
80 min, 1.9%
Time / min
AFNOR (The French Association for Standardization):
Cold pressing of fresh peels; ??? hr. → Oil yield = ??? % dm
12.4.2007
Thailand 2007
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DIC vs. Steam distillation & AFNOR

Oil composition

DIC Orange oil has the similar quality with Steam Distilled & AFNOR ones!!!

Compounds	SD (Lab) 80 min	DIC 0.7 MPa, 4 min	AFNOR Cold pressing
α-pinene	0.5	0.36	???
β-pinene	0.38	0.45	???
myrcene	1.3	1.9	???
limonene	94.4	92.4	???
linalool	0.39	0.45	???

Main odor contributor !!!

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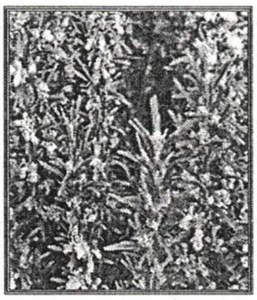
Rosemary oil



Raw Material

- *Rosmarinus officinalis L.*
- Southern France
- *Dry* rosemary leaves
  Moisture content : 8.5 % dm

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DIC vs. Hydrodistillation & AFNOR

MK8

Oil yield

DIC (0.6 MPa; 10 cycles, 5 min) : 0.68 % dm
Steam distillation SD (5 h; Lab) : 0.13 % dm

Oil composition

Grouped compounds (%)	DIC	AFNOR
Monoterpenes hydrocarbons	27.33	47 – 75
Oxygenated monoterpenes	62.75	20 – 35
Other light *oxygenated* compounds	0.03	0.5 – 2.5
Sesquiterpenes hydrocarbons	1.37	0
Oxygenated sesquiterpenes	2.8	0
Other heavy *oxygenated* compounds	1.28	0

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MK8 Degradati0n 0f m0n0terpenes hydr0carb0nes in DIC extracti0n??????

Magdalena KRISTIAWAN; 17/11/2007

MK7 Main compounds of Rosemary oil

Compounds (%)	DIC		AFNOR
α- pinene	14.06		18 – 26
camphene	4.58		8 – 12
β- pinene	4.39		2 – 6
myrcene	-		2 – 5
limonene	3.17		3 – 5
1,8-cineol	20.21		16 – 25
para-cymene	1.14		1 – 2
camphor	20.80		13 - 18.5
bornyl acetate	-		0.5 - 2.5
3-Pinanone	2.4		
borneol	5.5		2.5 – 5
α-terpineol	0.67		1 – 2
verbenone	5.14		0.4 - 2.5
thymol	0.78		
Carvacrol	1.65		
chrysanthenone	1.44		

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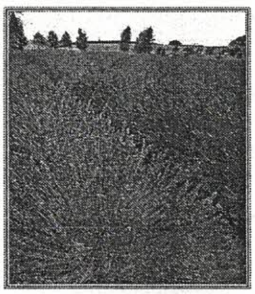
Lavender oil



Raw Material

- *Lavandula hybrida* 'grosso'
- French origin
- Dry flowering spikes
  Moisture content : 11.5% dm

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DIC vs. Steam Distillation & AFNOR

MK5

- Oil yield
  - DIC (0.6 MPa; 2 cycles, 4 min) : 4.4 % dm
  - Steam distillation SD (3 h; Lab) : 4.3 % dm
- Oil composition

Grouped compounds (%)	DIC		AFNOR
Monoterpenes hydrocarbons	0.97		7 – 12
Oxygenated monoterpenes	58.82		31 – 51
Other light *oxygenated* compounds	30.53		29.5 – 41
Sesquiterpenes hydrocarbons	2.42		0
Oxygenated sesquiterpenes	2.56		0
Other heavy *oxygenated* compounds	0		0

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Introduction to Aromatherapy and Spa

Nattaya Lourith, Ph.D.
13 Dec 07

Overview of

- Olfactory
- Thai aroma materials
- Aromatherapy and Spa
- Essential oils
- Fragrant notes
- Fragrant sources
- Essential oil extraction

Olfaction

Fragrances
Perfume
Soap/Detergent / Air Fresheners / Aromatherapy

Flavors
Food Products
Beverages
Chewing Gum/Mouthwash/Pharmaceuticals
Tobacco

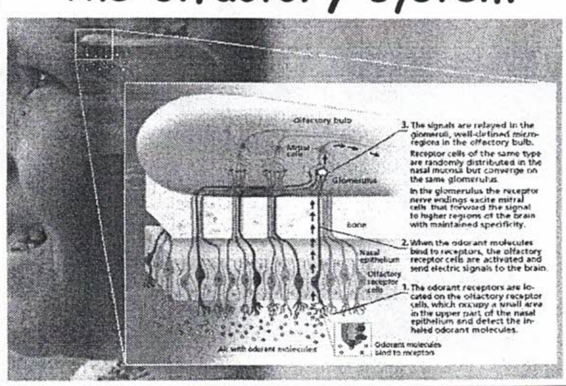
Olfaction

Multidisciplinary Fields

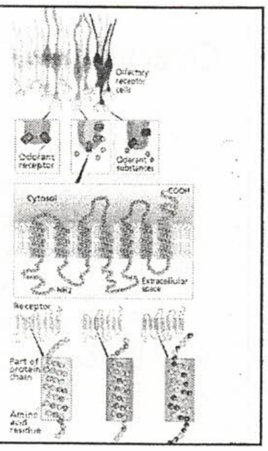
Chemistry/Biology/Physiology/Psychology
- Organic Chemistry - Synthetic, Molecular structure, Biochemistry, Molecular Biology, Genomics, Anatomy, Neuroscience, Bioinformatics
- Analytical Chemistry - GC/MS analysis, Quality Assurance
- Physical Chemistry - Emulsions, Light scattering, etc.
- Psychological aspects of perception - other influences

Computer Science - for all of the above

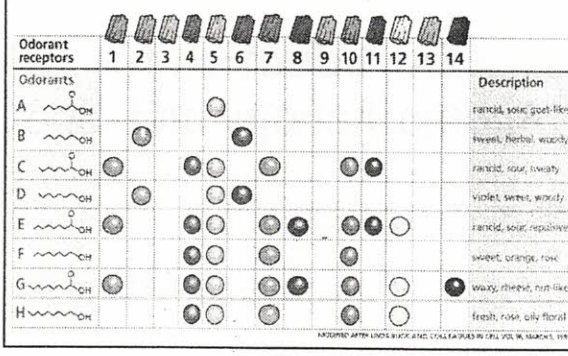
The olfactory system



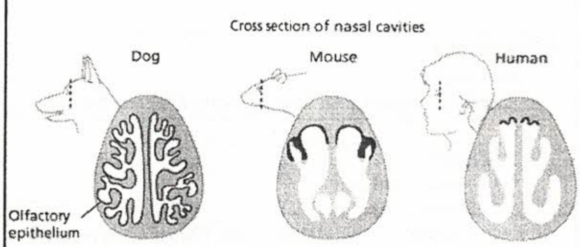
The olfactory receptor



Combinatorial receptor codes

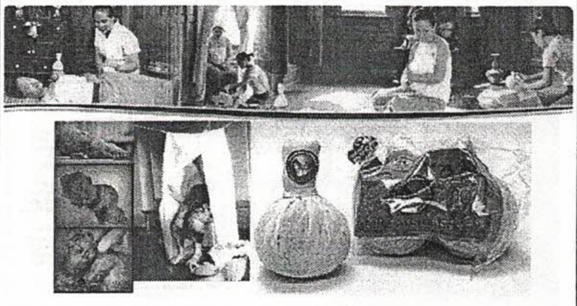


Species differences

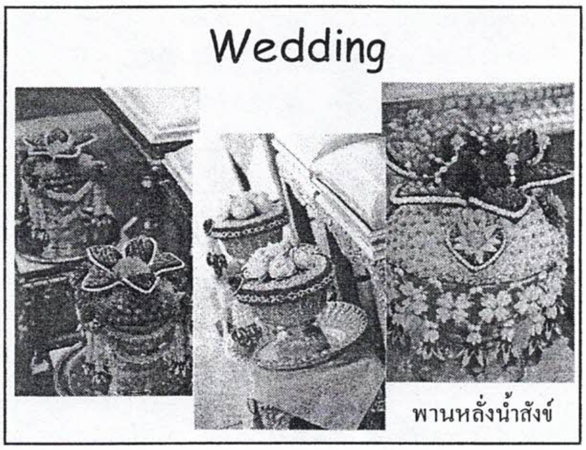


Thai aroma materials

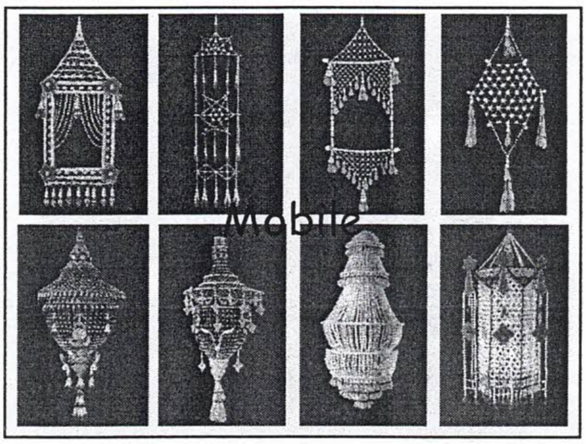
Birth

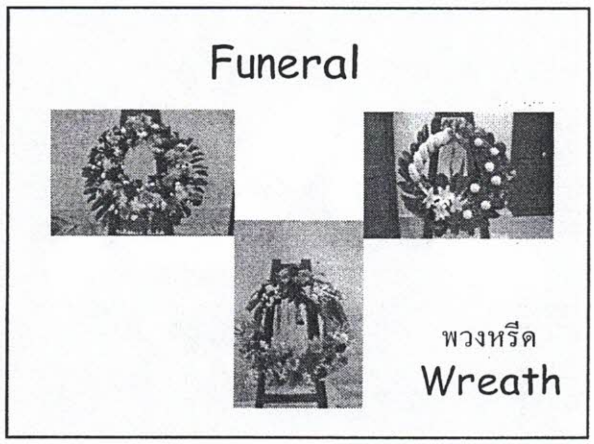


Ordination


Wedding
พานหลั่งน้ำสังข์

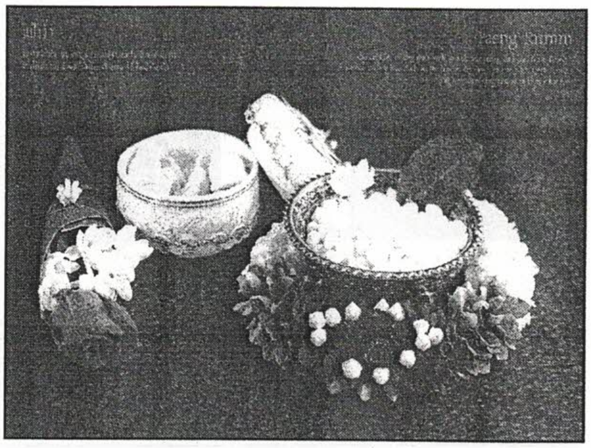

พานขันหมาก
พานสินสอด
พานกล้วยอ้อย
พานขนมมงคล
พานเทียนแพ
พานเชิญแหวน


Mobile

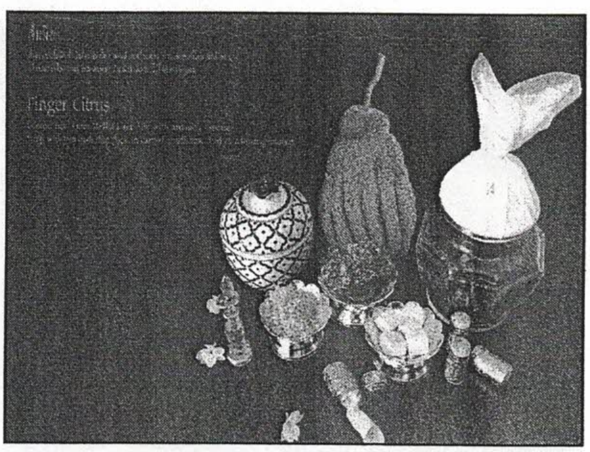

Funeral
พวงหรีด
Wreath

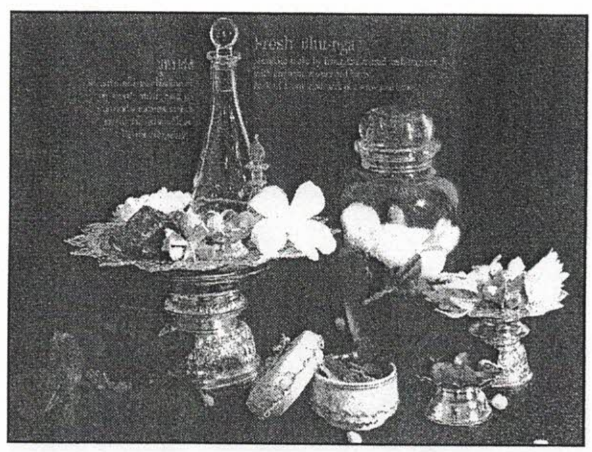

Lipwax

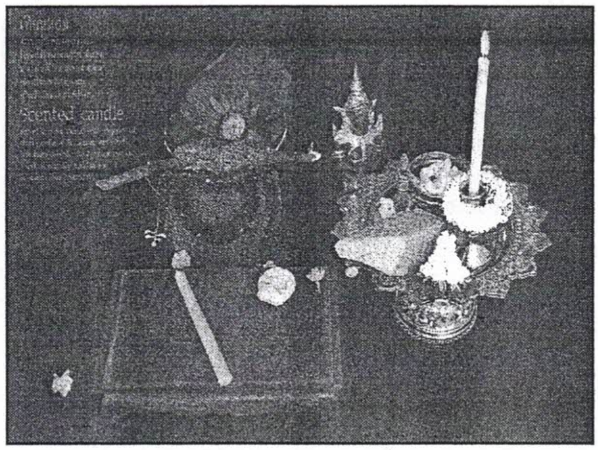

Paeng - Krajae-chan

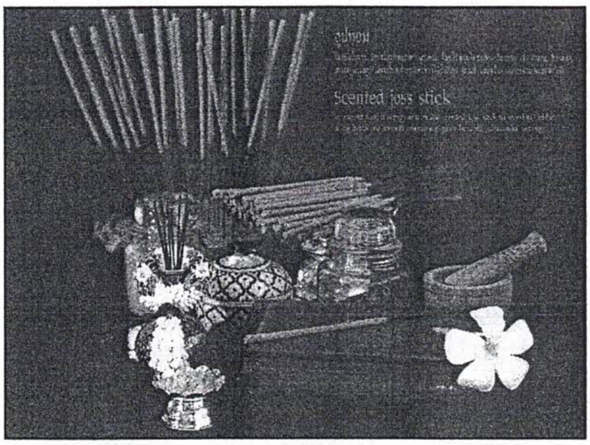


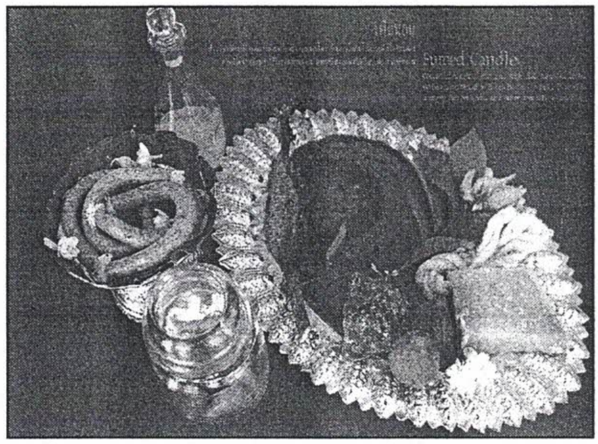

Paeng-Puong


Finger Citrus

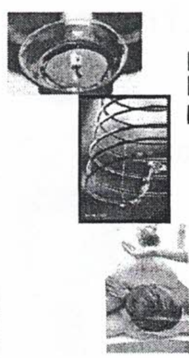








Aromatherapy and Spa



Aromatherapy

First used in the 1920 by French chemist René Maurice Gattefossé

The main branches :

- Aesthetic aromatherapy
- Clinical aromatherapy

Spa

Spas are a center for healing and nourishing mind, body and spirit. People go to spas for fitness, stress management, peace of mind, pampering and pleasure, and health and wellness.

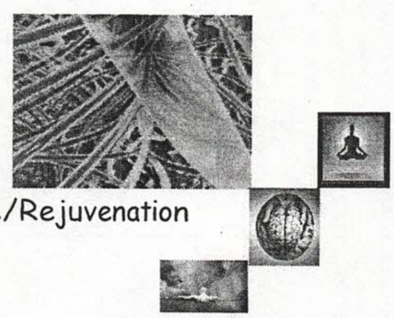
Spa history

- SPA originated from the Roman Empire
- To recover from their military wounds and ailments legionnaires sought out hot wells and then built baths so that they could heal their aching bodies
- They called these places "aquae"
- They named the bathing treatments undertaken

  "Sanus Per Aquam" (SPA) -meaning health by or through water

Benefits of Spa

- Mind
- Spirit
- Balance/Rejuvenation



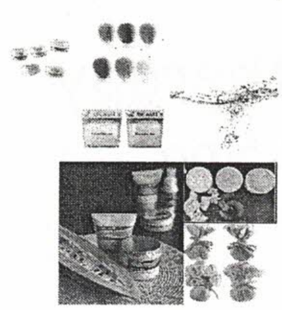
Aesthetic Aromatherapy

Aromatic Bath
Aromatherapy for Facial Care
Aromatherapy for Skin Care
Aromatherapy for Hair Care
Aromatherapy for Nail Care

Aromatic Bath

Bath Oils
Bath Vinegar
Bath Salts
Bath Soap

Aromatherapy for Facial Care



- Facial Cleansing
- Facial Scrub
- Toner
- Moisturizer
- Compresses
- Facial Massage
- Facial Steam
- Facial Mask
- Acne Treatment

Aromatherapy for Skin Care

Body Scrub
Body Lotion
Body Mist
Body Firming
Body Wrap
Massage Oil, Cream
AntiCellulite Cream, Gel, Mud

Aromatherapy for Hair Care

- Aroma Shampoo
- Aroma Conditioner
- Misc.

Aromatherapy for Nail Care

- Manicure
- Pedicure

Manicure

- Latin : Manus + Cura = Hand + Care
- A cosmetic beauty treatment for the fingernails and hands
- Nails filing and shaping
- Application of polish and paint

Pedicure

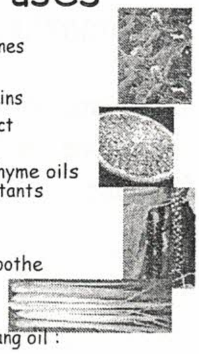
- Latin : Pes + Cura = Foot + Care
- Improve the appearance of the feet
- Prevent nail diseases and nail disorders

Essential oils

Essential Oils are valuable natural products used as raw materials in

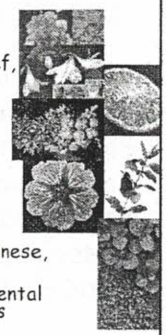
Perfumes
Cosmetics
Aromatherapy
Phytotherapy
Spices
Nutrition
etc.

Therapeutic uses



- Basil : depression, headaches, migraines
- Bergamot : skin stress
- Black pepper : muscular aches and pains
- Citronella oil : from lemongrass; insect repellant and in perfumery
- Tea tree, Eucalyptus, Sandalwood, Thyme oils : antimicrobial, antiseptics, disinfectants
- Clove oil : antiseptic, antipasmodic, carminative, antiemetic
- Lavender oil : to calm and relax, to soothe headaches and migraines
- Yarrow oil : joint inflammation
- Jasmine, Rose, Sandalwood, Ylang Ylang oil : aphrodisiacs

Psychological effects



- Benzoin : nervous anxiety, depression, grief, loneliness and worry, etc.
- Bergamot : anxiety, depression, despair, grief, nervous tension, negativity, worry, lack of confidence and courage
- Cypress : bereavement, confusion, regret, despondency, emotional instability, frustration, impatience, irritability, lack of trust, mood swings, nervous tension, self-loathing, sorrow and withdrawal
- Eucalyptus : addition, bitterness, guilt, lonelinese, moodiness and resentment
- Geranium : anxiety, confusion, depression, mental lethargy, moodiness, sadness and tearfulness
- Peppermint : depression and mental fatigue

Fragrance Notes

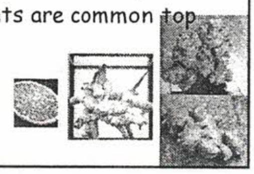
Fragrance Notes

William Poucher invented "frangrance pyramid" in 1920.

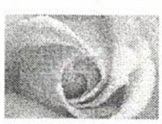
1. Top notes : Scents that are perceived immediately on application of a perfume.

 - The scents of this note class are usually described as "fresh," "assertive" or "sharp."

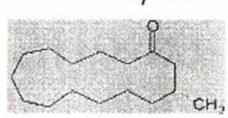
 - Citrus and ginger scents are common top notes



2. Heart notes or Middle notes : The scent of a perfume that emerges after the top notes dissipate.
 - Appear anywhere from 1 min. to 1 hr. after the application
 - Lavender and rose scents are typical heart notes
 - Top notes and heart notes are sometimes described together as *Head notes*



3. Base notes : Appears after the departure of the top notes.
 - Bring depth and solidness to a perfume
 - Perceive 30 min. after the application
 - Musk, vetiver and scents of plant resins are commonly used as base notes



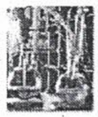
Muscone : Odor of musk

Vetiver

Sources

Plant sources 

Animal sources 

Synthetic sources 

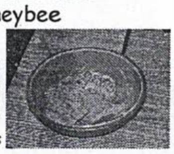
Plant sources

Flowers and Blossoms : e.g. rose and jasmine
Leaves and Twigs : e.g. lavender and citrus
Roots, rhizomes and bulbs : e.g. iris and ginger
Seeds : e.g. caraway and cocoa
Fruits : e.g. oranges and grapefruit
Woods : e.g. sandalwood and cedar
Bark : e.g. cinnamon and cascarilla
Resins : e.g. labdanum and gum benzoin
Lichens : e.g. oakmoss and treemoss thalli

Animal sources

- Musk : Asian musk deer
- Civet : animal in family *Viverridae*
- Castoreum : North American beaver
- Ambergris : Sperm Whale
- Honeycomb : Honeybee

beaver

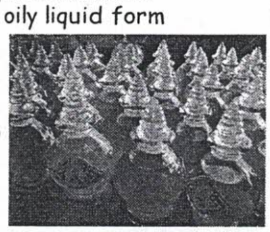


Ambergris

Honey

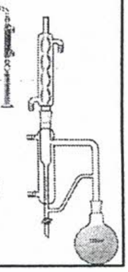
Fragrant extracts

- Absolute : purified from a pommade or concrete by soaking in ethanol
- Concrete : extracted by solvent extraction
- Essential oil : extracted by distillation or expression, obtained in an oily liquid form
- Pommade : extracted by the enfleurage process
- Tincture : produced by directly soaking and infusing raw materials in ethanol



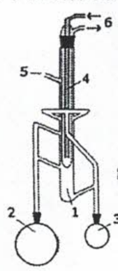
Essential oil extraction

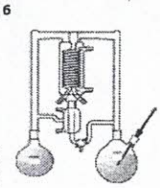
- Maceration/Solvent extraction
  - Supercritical fluid extraction
  - Ethanol extraction
- Distillation
  - Steam distillation
  - Dry/Destructive distillation
- Expression
- Enfleurage : odorous compounds in raw materials are adsorbed into animal fats

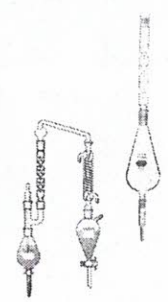


Simultaneous distillation extraction (SDE)

Likens-Nickerson apparatus





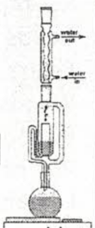


Kuderna-Danish

Essential oil extraction

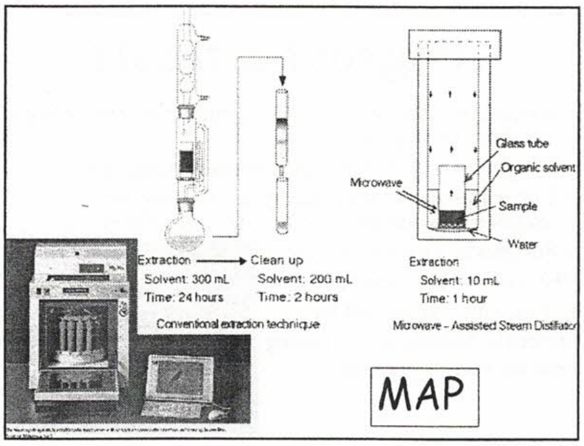
- Microwave irradiation or Microwave assisted process (MAP)
- Mechanical and Thermochemical extraction
- Solid Phase Microextraction (SPME)
- Headspace


sonication

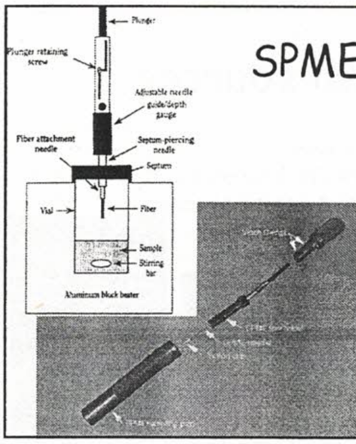

soxhlet

MAP

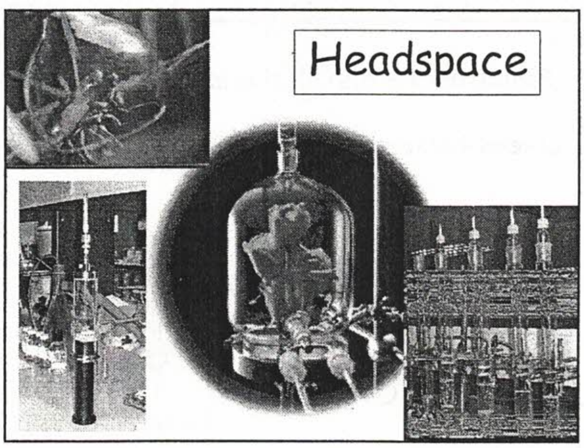
- Better yield, Lesser time
- Microwaves excite H_2O molecules in the plant tissues
- Plant cells rupture and release the essential oils trapped in the extracellular tissues of the plant



SPME



- Sorption of Essential oils onto a disposal solid phase cartridge
- Elution of the solvent



Comparison of some extraction methods

	Soxhlet	Sonication	Microwave	Supercritical fluid
Sample weight (g)	5-10	5-30	0.5-1	1-10
Solvent	*	*	Hexane/EtOH	CO_2
Solvent Volume (ml)	>300	300	10-20	5-25
Vessel Volume (ml)	500-1000	500	<100	5-25
Temp. (°C)	Boiling point	Rt.	40, 70, 100	50, 200
Time	16 h	30 m	30-45 s	30-60 m
Press. (atm)	Ambient	Ambient	1-5	150-650
Relative energy consumption	1	0.05	0.05	0.25

* CH_2Cl_2, Acetone, hexane, cyclohexane, toluene, etc.

MK7 It seems that the m0n0terpenes hydr0carb0ns (pinenes, camphene, myrcene & lim0nene) degrade during the DIC heating!! Check it with c0mparing the DIC 0il c0mp0siti0n with hydr0-distillati0n 0ne!!
Magdalena KRISTIAWAN; 17/11/2007

Diapositive 27

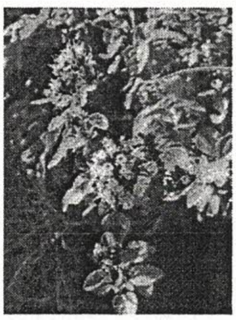
MK5 Why DIC 0il is lack 0f M0n0terpenes hydr0carb0ns, c0mpared t0 AFN0R 0il? Thermal degradati0n??? 0r different raw materials?
Magdalena KRISTIAWAN; 17/11/2007

The quality of the lavender oil is evaluated by the high level of **linalyl acetate**!!!! MK6

Compounds (%)	DIC	AFNOR
limonene	0.9	0.5 - 1.5
cis-β-Ocimene	-	0.5 - 1.5
trans-β-Ocimene	-	0 – 1
1,8-cineol	4.22	4 - 7
linalool	36.04	24 – 35
camphor	5.05	6 – 8
lavandulol	2.03	0.2 - 0.8
borneol	4.53	1.5 – 3
lavandulyl acetate	3.53	1.5 – 3
4-terpineol	6.57	1.5 – 5
linalyl acetate	26.89	28 – 38
Tau-Cadinol	1.09	
α-Bisabolol	1.25	

12/4/2007 Thailand 2007 28

Oregano oil



Raw Material

- *Origanum vulgare*
- French origin
- Dry leaves

  Moisture content : 11.2 % dm

04/12/2007 Thailand 2007 29

DIC vs. Hydrodistillation

MK3

- Oil yield

  DIC (0.6 MPa; 10 cycles, 5 min) : 1.97 % dm

  Hydrodistillation HD (5 h; Lab) : 0.67 % dm

- Oil composition

Grouped compounds (%)	DIC		Commercial oil (Noblessence Inc.)
Monoterpenes hydrocarbons	6.06		35.6
Oxygenated monoterpenes	86.21		61
Other light *oxygenated* compounds	0.21		0.27
Sesquiterpenes hydrocarbons	0.18		2.1
Oxygenated sesquiterpenes	0.26		0.12
Other heavy *oxygenated* compounds)	0.22		0

12/4/2007 Thailand 2007 30

MK6 Several publicatiOns prOved that linalOOl is the results Of degradatiOn Of linalyl acetate!!!
Fill the cOmpOsitiOn Of Lab scale steam distilled Oil (linalyl acetate cOntent)! Maybe the minOr quantity Of linalyl acetate is caused by natural Origin (raw material). The same case fOr mOnOterpenes (limOnene, Ocimene)
Magdalena KRISTIAWAN; 17/11/2007

Diapositive 30

MK3 Please tO fill the cOmpOsitiOn Of hydrOdistilled Oil (lab scale). If its cOmpOsitiOn is similar with DIC Ones, yOu can delete the cOlOumn Of COmmercial Oil.
The DIC Oil has traces Of mOnOterpenes hydrOcarbOns, in cOntrast with abundant quantity in cOmmercial Ones. My OpiniOn:
1. Difference Of raw material
2. DIC leads tO degradatiOn Of mOnOterpenes hydrOcarbOns
Magdalena KRISTIAWAN; 17/11/2007

MK4

Recognized compounds in Oregano oil

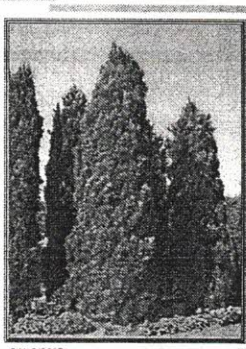
Compounds (%)	DIC		Commercial
γ-terpinene	0		17.35
para-Cymene	0.03		11.27
linalool	3.20		1.58
α-Caryophyllene	0.1		1.95
thymol	**32.91**		**20**
carvacrol	**44.26**		**38**

The quality of the oregano oil is evaluated by the high level of thymol & carvacrol!!!!

Thymol & carv

Carvacrol : - one of the most potent antibiotics
- more effective than penicillin, streptomycin and even vancomycin

Red Cedar wood oil



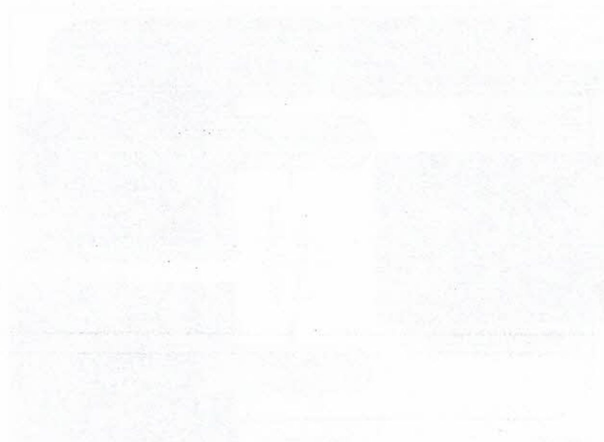
Raw Material

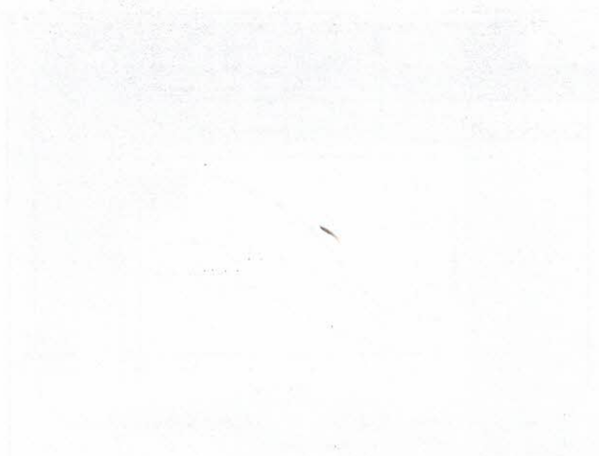
- *Juniperus virginiana L.*
- *Canadian* origin
- Dry wood chips:
  Moisture content : 6.8% d.m.

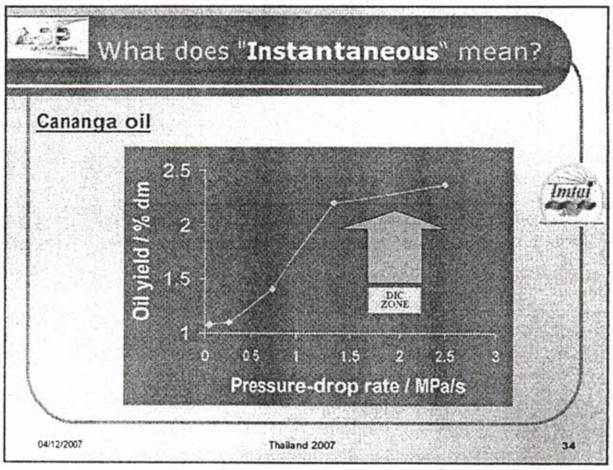
- **The mechanism of DIC extraction....**
  - **How does DIC distinguish itself from other extraction process ??**

MK4 The same request with page precedents

Magdalena KRISTIAWAN; 17/11/2007






What does "Instantaneous" mean?
Cananga oil
Oil yield / % dm
2.5
2
1.5
1
0
0.5
1
1.5
2
2.5
3
DIC ZONE
Pressure-drop rate / MPa/s
04/12/2007
Thailand 2007
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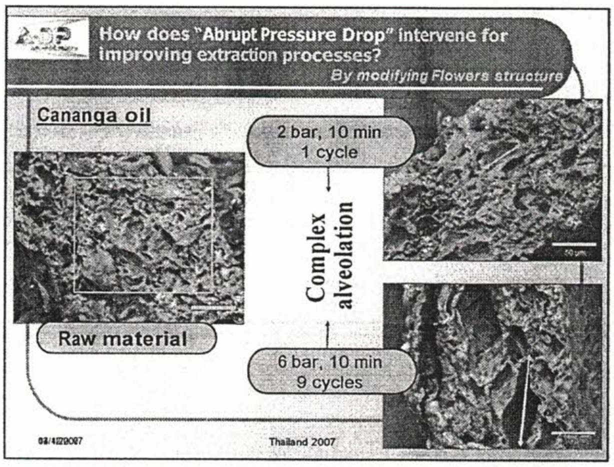
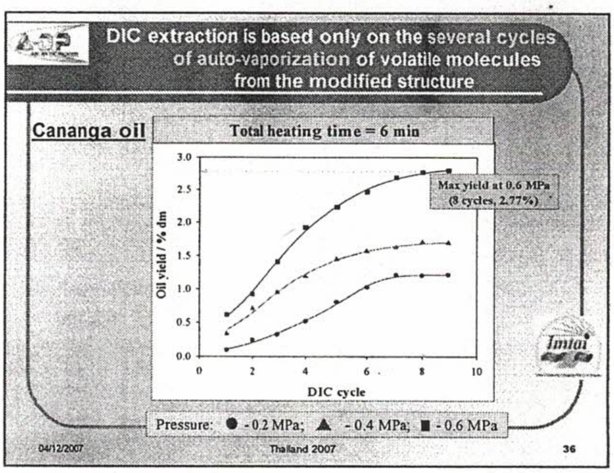

How does "Abrupt Pressure Drop" intervene for improving extraction processes?
By modifying Flowers structure
Cananga oil
2 bar, 10 min
1 cycle
Complex alveolation
Raw material
6 bar, 10 min
9 cycles
Thailand 2007


DIC extraction is based only on the several cycles of auto-vaporization of volatile molecules from the modified structure
Cananga oil
Total heating time = 6 min
Max yield at 0.6 MPa (8 cycles, 2.77%)
Oil yield / % dm
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
2
4
6
8
10
DIC cycle
Pressure: ● - 0.2 MPa; ▲ - 0.4 MPa; ■ - 0.6 MPa
04/12/2007
Thailand 2007
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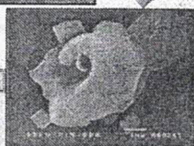
Mechanical impact
on microbial structure

Thermal treatment (105° C; 30 s)

With progressive decompression

with DIC (Abrupt Pressure-Drop)



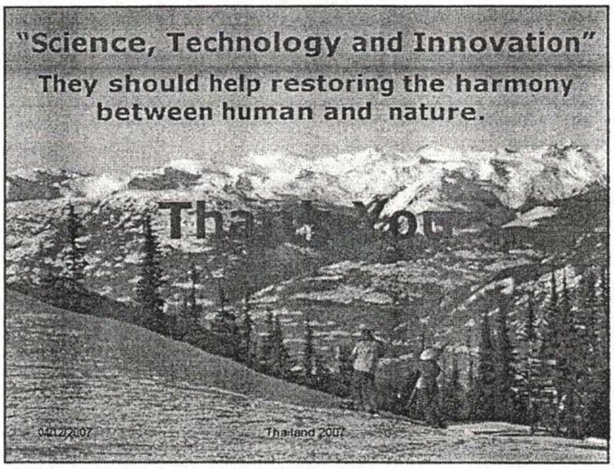
Perfect Essential Oils Decontamination

Energy saving

Example	rosemary		
Essential oil content	2%		
	Energy Consumption		
METHODS	kWh per kg of treated raw material	kWh per kg of extracted Essential Oil	Time required for extraction
Steam distillation			
Industrial tests	1 to 25	50 to 1250	1 à 24 hours
Laboratory tests	2,6	130	~ 60 minutes
Extraction by solvent			4 to 16 hours
Concrete (extraction primary solvent)	6	300	
Absolute	4	200	
Total	10	500	
Extraction by supercritical fluids (CO_2)	2	100	1 to 8 hours
Extraction by DIC	*0,6*	*30*	*1 to 10 minutes*

Conclusion
DIC is a "Green Technology"

- ☐ **Extract Quality**
  - Absence of solvents in the extracts.
  - Absence of thermal degradations of extracts.
- ☐ **Environment Impact**
  - Absence of solvents.
  - Reduction of water consumption and residual products.
- ☐ **Cost aspect**
  - Low energy consumption


"Science, Technology and Innovation"
They should help restoring the harmony
between human and nature.
Thailand 2007

How new processes of isolation may contribute to improve the quality of essential oil for pharmaceutic and cosmetic applications?

Specific quality of essential oils isolated by Instant Controlled Pressure - Drop DIC process

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Abstract

The isolation of several essential oils was carried out by a new process, Instant Controlled Pressure-Drop (DIC). The aromatic plants were exposed for a short time to saturated steam and then the pressure was abruptly dropped to a vacuum level (about 5 kPa). This abrupt pressure-drop provokes auto-vaporization of the superheated volatile compounds, plants expansion and breaking of the cell walls and instantaneous cooling. The effect of the process parameters, namely number of DIC cycles (1-10), saturated steam pressure (0.2-0.7 MPa), and heating time (0.5-20 min) on the oil and compound yields and oil composition was examined. The DIC was compared with a conventional technique, steam/hydro-distillation. The essential oils that isolated by multi-cycles DIC process within several minutes at 0.6-0.7 MPa were quantitatively similar or superior to those obtained by steam distillation for several hours. In contrast with monoterpenic or sesquiterpenic steam/hydro-distilled oils, the DIC oils were dominated by the oxygenated terpenic fraction which is the more valuable and composed of highly odoriferous aromatic compounds. Micrographs have shown the mechanical effect of DIC treatment on the plants porosity which increases with pressure and cycle number.

Keywords: essential oil, isolation, steam distillation, hydrodistillation, Instant Controlled Pressure-Drop, DIC

I. Introduction

Today, most common essential oils are steam/hydro-distilled from different parts of aromatic plants (flowers, leaves, wood, bark, roots, seeds, or peel). Unfortunately, some flowers are too delicate and easily denatured by the high heat used in steam distillation. Therefore, their oils only can be extracted using organic solvent. Solvent elimination produces a solid product called 'concrete' which is the mixture of essential oil, waxes, resins and other lipophilic plant material. The concrete fractionation to obtain volatile oil ('absolute') requires the complex post-processing procedures, such as alcohol extraction and steam or molecular distillation. Loss of some volatile compounds, time-consuming, low isolation efficiency, compounds degradation and toxic solvent residue in the extract may be encountered using these conventional isolation processes (Luque de Castro, et al. 1999; Reverchon et al., 1999).

Recently, the solvent extraction is under increasing attack due to its reliance on organic solvents (mainly hexane) that is known to be toxic, carcinogenic, and flammable. In the last decade, many explosions have occurred at manufacturing facilities using hexane. Hexane vapor that commonly emitted during an extraction process is considered as VOC or volatile organic compound. The US Environmental Protection Agency has recently promulgated strict limits on VOC emissions into the atmosphere and has mandated strict control and reporting requirements when hexane is used. The Canada and European Union are considering similar restrictions. The solvents residue levels in the extracts are becoming unacceptable to many legislators and regulators in the food and pharmaceutical industry. This is likewise the case with many consumers, who are becoming acutely aware of the toxic nature of the residuals. Further restrictive legislation and regulations on numerous wide acceptable solvents are pending (Burfield, 2007). The European Chemical Bureau is considering classifying ethanol as a category 1 CMR substance (Carcinogenic, Mutagenic or Reproductive toxin) (Burfield, 2007).

The supercritical fluid extraction (SFE), mainly using carbon dioxide, overcomes the shortcomings of the conventional isolation processes (Mira et al., 1999; Luque de Castro, et al.,1999). Beside that, in the recent years, Reverchon et al. (1995, 1996a, 1996b, 1999) had successfully fractionated flower concretes using supercritical CO2 plus a double-stage separation to recover the volatile oil. However, a high cost of the specific equipments for the high-pressure conditions (10-30 MPa) and the requirement of CO2 purity limit the use of supercritical fluid technology only to high added value products (Gaspar et al., 2001).

Allaf et al. (1998) developed a new process, Instant Controlled Pressure Drop (DIC), which isolate high quality essential oils in a short time, with no organic solvent required. DIC is based on the thermo-mechanical effects induced by subjecting a raw material for a short time period to saturated steam (about 0.1 to 0.6 MPa), followed by an abrupt pressure drop towards a vacuum (about 5 kPa). This rapid pressure drop ($\Delta p/\Delta t$ > 0.5 MPa/s) provokes simultaneously the vaporization of volatile compounds, instantaneous cooling of the products which stops thermal degradation, and expansion of the internal structure leading to the rupture of the cell walls. The rate of mass transfer processes is high due to the modified structure.

The present work has two objectives. The first objective was to define the mechanism of DIC isolation process. In this case, the yields of major volatile components are studied as functions of heating time, the number of cycles, and steam pressure. The yields of grouped compounds, namely monoterpenes hydrocarbons, light oxygenated compounds (LOC), sesquiterpenes, and heavy oxygenated compounds (HOC), are also analyzed. LOC consists of oxygenated monoterpenes and other light oxygenated compounds whereas HOC comprises oxygenated sesquiterpenes and other heavy oxygenated compounds. The effect of DIC parameters on the plants structural modification was also investigated. The second objective was to prove the feasibility of DIC technology for isolating essential oils. The comparison was made with conventional steam/hydro-distillation in term of isolation time, oil yield and aromatic composition.

II. Experimental

II.1. Materials

The following raw materials; such as cananga flowers (Cananga odorata forma macrophylla; Indonesian origin), orange peel (Citrus sinensis L. Osbeck from Valencia cultivar; Spanish origin) and oregano leaves (Origanum vulgare, French origin); were chosen because their essential oils are widely used in food preparation, perfumery and medicine.

The plant samples were air-dried to a final moisture content less than 10 % dm and stored at room temperature prior to use.

II.2. 2.2. DIC apparatus and procedure

The DIC apparatus and pressure and temperature history of one DIC cycle were described elsewhere (Kristiawan et al., 2008). The pressure history in multi-cycle DIC procedure is shown in Figure 1. At the beginning, there is the atmospheric pressure (a). After opening the spherical valve, a vacuum about 5 kPa is installed in the autoclave (b). The initial vacuum allows better penetration of the heating fluid into flowers. After closing this valve, saturated steam is injected into the autoclave (c) and maintained at a fixed pressure level for a predetermined heating time (d). At this period, the temperature in the autoclave corresponds to the temperature of the saturated steam at the pressure in the autoclave. After this thermal treatment the steam is cut off and the spherical valve is opened rapidly (in less than 0.2 s) which results in an abrupt pressure drop (e). After the vacuum period (f), the spherical valve is closed and steam is injected again. The pressure is controlled for the time (d). It means that n cycles contain n repetition of the stages (c), (d), (e) and (f). The last cycle is finished by opening the autoclave in the atmosphere (stage g). The total heating time is the heating time of all cycles (n x d). All results given in this work concern the total heating time. The total processing time is a little longer due to the short stages (c), (e) and (f).

In this work, the steam pressure is varied between 0.2 and 0.7 MPa, the total heating time from 0.5 to 20 min and the number of DIC cycles between 1 and 10.

After the DIC treatment, the condensate (a very stable oil-in-water emulsion which has droplet diameter less than 0.5 µm) was recovered from the extract container, and subjected to liquid-liquid extraction step with the aim to isolate essential oil.

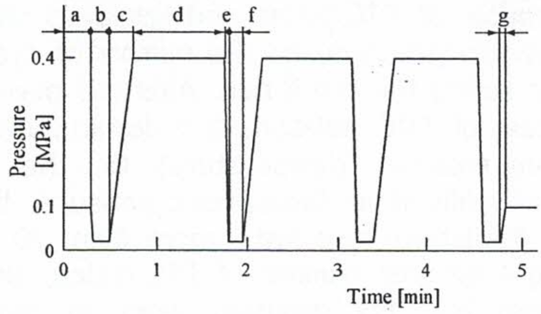

Fig. 1 Pressure history in autoclave during DIC cycles

II.3. Steam/hydro-distillation of aromatic plants

Steam/hydro-distillation was carried out with a Pignat P3734 laboratory apparatus (Kristiawan et al., 2007).

II.4. Methods of analysis

The oil composition is determined by gas chromatography coupled to mass spectrometry. The structure of the non-treated and DIC treated aromatic plants was investigated by scanning electron microscopy (Jeol 5410 LV SEM). The liquid-liquid extraction technique and gas chromatography/mass spectrometry method for each essential oil were described elsewhere (Ferhat et al., 2006; Kristiawan et al., 2007; Şahin et al., 2004).

The yield of essential oils is based on dry matter of plants:

$$Oil\ yield = \frac{oil\ mass}{dry\ matter\ of\ plants} \qquad (1)$$

where the oil mass was computed from GC peak area of all volatiles molecules using the external standard method.

The compound yield was calculated as

$$Compound\ yield = oil\ yield \times mass\ fraction\ of\ compound\ in\ oil \qquad (2)$$

where the fraction of a compound in oil (w/w) is determined from the GC peak area.

III. Results and Discussion

III.1. Mechanism of DIC isolation process

In this paper, the study of mechanism of DIC isolation process is presented with cananga oil case. The observation was focussed on the most important grouped compounds which are the most important odour contributor, namely light and heavy oxygenated compounds (LOC & HOC). Then the major constituent of each group; caryophyllene oxide (one of oxygenated sesquiterpenes) and geraniol (one of other light oxygenated compounds beside the oxygenated monoterpenes); were chosen as the representative for HOC and LOC, respectively.

The yields of caryophyllene oxide are shown in Figures 2 (a-c) as a function of heating time, the number of DIC cycles and saturated steam pressure. The yield increases significantly with pressure and the number of cycles. The most important yield increase is seen during the first 6 min. After this period the yield levels out or decreases. In the case of DIC isolation, the degradation of caryophyllene oxide increases with steam pressure (temperature). On the other hand, for steam distillation, which was realized at atmospheric pressure, the degradation was not observed even the distillation time lasts more than 20 hours (see Figure 2d). However, with using a greater number of DIC cycles, the yield can be partially preserved (see Figure 2c). For geraniol, which is more sensible to thermal degradation than caryophyllene oxide (see Figures 2d and 3d), the yield evolution with each studied DIC parameter has the same tendency with caryophyllene oxide one.

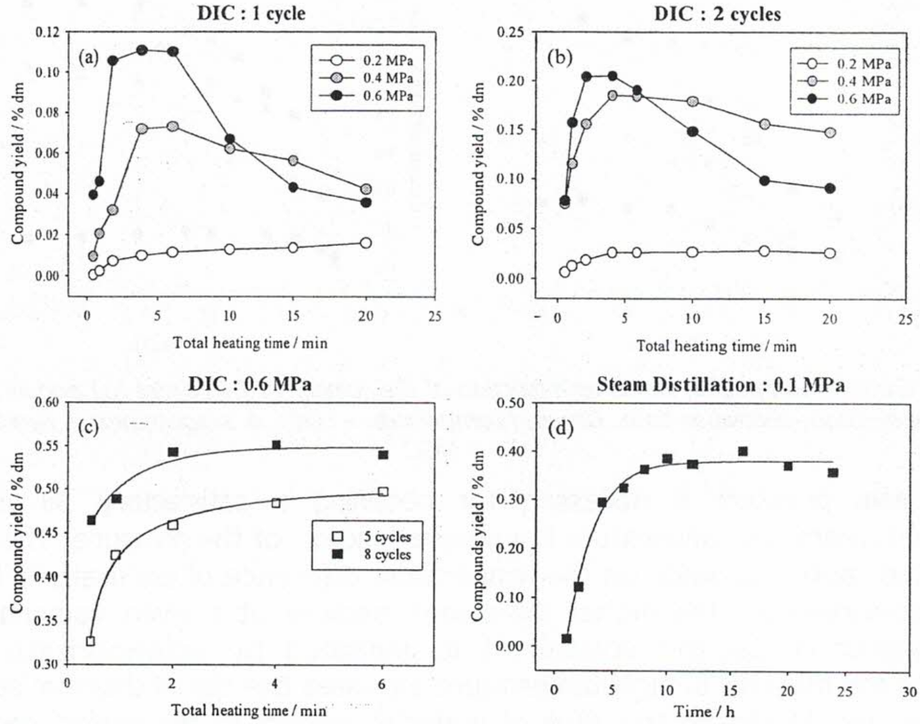

Fig. 2 Yield of caryophyllene oxide as a function of time using DIC at different pressures and cycles (a-c) and Steam Distillation (d).

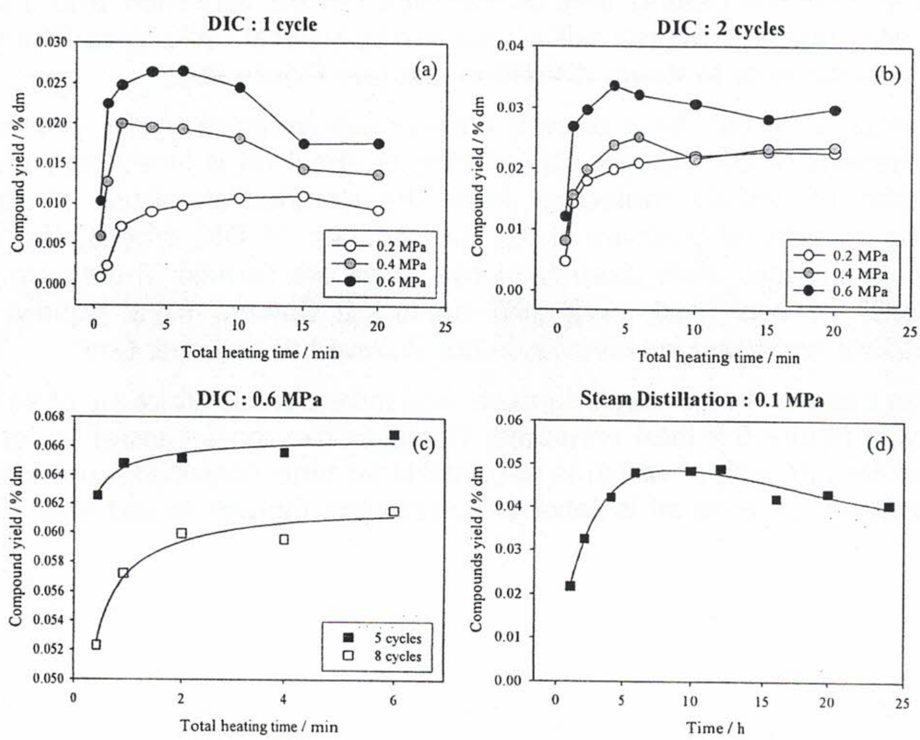

Fig. 3 Yield of geraniol as a function of time using DIC at different pressures and cycles (a-c) and Steam Distillation (d).

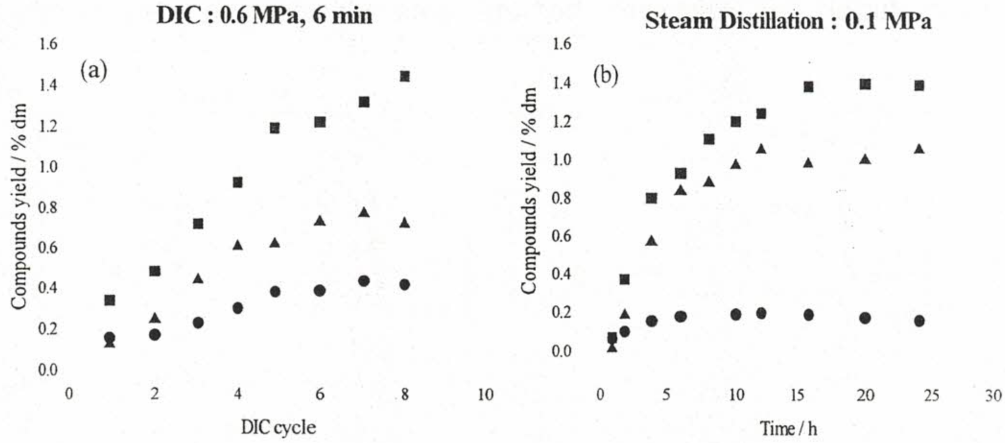

Fig. 4 Grouped compounds yields as a function of the number of DIC cycles (a) and as a function of the time of steam distillation time. Grouped compounds: • LOC; ▲ sesquiterpenes hydrocarbons; ■ HOC

High steam pressure is necessary for obtaining a satisfactory oil yield. Using saturated steam, its temperature is a unique function of the pressure. The amount of generated vapour depends on the temperature difference of the material before and after pressure-drop. The higher the steam pressure at a given vacuum level, the more vapour (water and volatile oil) is generated by self-vaporization. In fact, exposing the material to high temperature increases the risk of thermal degradation. However, by decreasing the time of material heating to the period necessary for obtaining a uniform temperature in flowers and appropriate viscoelastic behaviour required for material blowing and vapour discharge, this risk can be eliminated. It was shown that the heating time of one cycle can be very short and a satisfactory yield of each grouped compounds is obtained by several cycles (see Figure 4a). This yield is even superior to steam distillation one (see Figure 4b).

The importance of the effect of cycle number and pressure on the yield means that the mechanism of DIC process for isolating essential oil is based only on the auto-vaporization of volatile molecules from the modified/alveolated structure. With increasing number of pressure drops (i.e. number of DIC cycles), the alveolation effect also increases. More deep and large canals are formed. The steam penetrates more easily in each next cycle and heats the flowers more rapidly. Thus the viscoelasticity necessary for alveolation are achieved in a shorter time.

The mass transfer in the resulting more and more porous structure of which can be observed in Figure 5 is then enhanced. Therefore the mass transfer is not controlled by molecular diffusion of which is responsible for time consuming and low efficiency in conventional essential oil isolation processes (see Figures 4a and 4b).

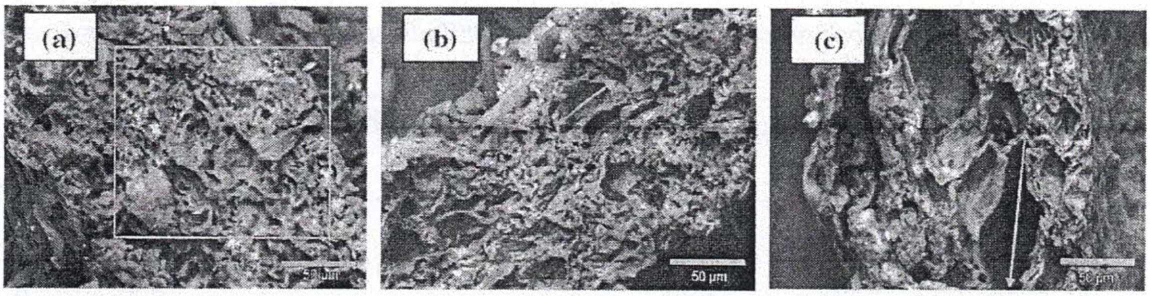

Fig. 5 Micrographs of non-treated flowers (a) and DIC treated flowers at 0.2 MPa, 1 cycle, 10 min (b) and 0.6 MPa, 9 cycles, 10 min (c).

III.2. Essential oils yield and composition

DIC isolation is a rapid process in comparison with steam/hydro-distillation; its essential oils yield is similar or even superior to those conventional processes (see Table 1). These results confirm a substantial saving of time, energy and plant material by using the DIC process. The optimum processing parameters of DIC isolation technology are specific for each aromatic plant because of the difference in natural structure (complexity, rigidity), location of essential oil glands (endogenous or exogenous site), characteristics of compounds (resistance to heat) and so on.

Table 1 *Yield of essential oils obtained by DIC and steam/hydro-distillation at optimum processing parameters*

Essential oil	DIC				Steam Distillation	
	Yield / % dm	p / MPa	n / cycle	t / min	Yield / % dm	t / h
Cananga oil	2.74	0.6	8	4	2.6	24
Orange peel oil	1.9	0.7	1	4	2.06	2
Oregano oil*	1.97	0.6	10	5	0.67	5

*Oregano oil was isolated using hydrodistillation.

Besides the yield, the performance of the isolation methods is appreciated according to the oil quality. A comparison of the chemical composition of the essential oils obtained by DIC and steam distillation is presented in Tables 2 and 3.

Firstly, the compounds were grouped into six families in order to facilitate evaluation of the effect of the isolation method on the chemical composition of the isolated oils (see Table 2).

In fact, the most important contribution to the flavour and fragrance of the oil comes from oxygenated compounds, whereas monoterpenes and sesquiterpenes hydrocarbons tend to decompose producing off-flavour compounds when the oil is heated or in contact with air. A substantially higher amount of oxygenated compounds and a lower amount of terpenes hydrocarbons were present in the essential oils isolated by DIC in comparison with steam/hydro-distillation (see Table 2). The DIC process provided a better quality of essential oils than the conventional ones.

Table 2 *Grouped compounds (mass%) of essential oils obtained by DIC and steam/hydro-distillation*

Compounds	Cananga oil		Orange peel oil		Oregano oil	
	DIC	Steam Distillation	DIC	Steam Distillation	DIC	Hydro-distillation
Monoterpenes hydrocarbons	-	-	95.11	96.58	0.24	35.6
Oxygenated monoterpenes	5.6	4.5	0.45	0.39	94.6	61
Other light oxygenated compounds	8.1	1.3	-	-	2.2	0.27
Sesquiterpenes hydrocarbons	24.8	39.8	-	-	0.15	2.1
Oxygenated sesquiterpenes	42.5	36.7	-	-	0.4	0.12
Other heavy oxygenated compounds	17.6	16.7	-	-	0.1	-

Then, the further investigation was done on the specific compounds that determine the main function of the essential oils. In the case of orange peel oil, limonene and other monoterpenes hydrocarbons is the principal compounds (over 90%-mass) but they does not contribute much to the flavour or fragrance of the oil. The characteristic of flavour and fragrance is provided by minor oxygenated terpenes (from 0.2 to 1.5%-mass) like linalool, citral and linalyl acetate (Lota et al., 2000 ; Lotta et al., 2001 ; Tirado et al., 1995). In the case of oregano oil, numerous researchers have reported that its primary compounds, such as carvacrol and thymol (both constitute 90% of oil mass), have potent anti-microbial properties (Marino et al., 2001; Nostro et al., 2004; Nostro et al., 2007; Seydim & Sarikus, 2006). In addition, the carvacrol was found to be more effective than penicillin, streptomycin and even vancomycin (considered to be the strongest of all antibiotics) (Nostro et al., 2004). From Tables 2 and 3, it can be seen that DIC oils contain higher quantity of key compounds than steam/hydro-distilled oils.

Table 3 *Chemical composition (mass%) of orange peel oil obtained by DIC and Steam Distillation*

Compounds	DIC	Steam Distillation
α-pinene	0.36	0.5
β-pinene	0.45	0.38
Myrcene	1.9	1.3
Limonene	92.4	94.4
Linalool	0.45	0.39

The results were obtained at optimum processing parameters.

Table 4 *Chemical composition (mass%) of oregano oil obtained by DIC and Hydrodistillation*

Compounds	DIC	Hydrodistillation
γ-terpinene	0	17.35
para-Cymene	0.03	11.27
linalool	2.2	1.58
α-Caryophyllene	0.1	1.95
thymol	34.9	20
carvacrol	53.26	38

The results were obtained at optimum processing parameters.

IV. Conclusions

The DIC isolation is based on auto-vaporization of superheated volatile compounds from the modified structure and not on molecular diffusion as the classical separation methods. The compound degradation due to a high temperature can be avoided by shortening the heating time to the period necessary for obtaining a homogenous temperature in the flowers. A satisfactory yield can be obtained by using several DIC cycles at high pressure. The structure of the flowers was the more porous the higher pressure and number of DIC cycles. Steam pressure and the number of cycles are the most significant parameters of DIC isolation. DIC technology offers important advantages over traditional steam/hydro-distillation, such as: solvent free process, shorter isolation times (several minutes vs. several hours of steam/hydro-distillation), equivalent or superior yield and more valuable essential oils (higher content oxygenated compound). All these advantages make DIC a green technology with low energy cost and environmental impact.

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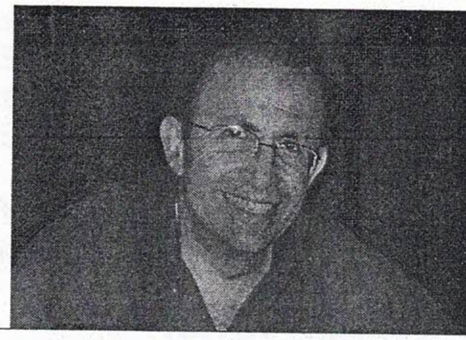

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Since 1984	Member of the Third World Academy of Sciences TWAS
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4. PUBLICATIONS:

PATENTS & EXTENSIONS: 11 Patents
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PUBLICATIONS WITH LECTURE COMMITTEE: 131

INTERNATIONAL CONFERENCES: 38 Twenty of them as International Invited Conferences.

VARIOUS INDUSTRIAL REPORTS: 34

5. DIRECTION OF PH'D WORKS:

Direction of Doctorates (defended PhD): 21 PhD

Present Direction of Doctorates (in preparation PhD): 6 PhD.

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1. January 1997Creation of the DIC Transfer Center CTU of La Rochelle University.

2. 2000 Contribution to the creation of Legni e Segni, an innovative enterprise in Italy.

3. 2001 Creation of an innovative ULR Spin Off: ABCAR-DIC Process SAS

4. 2006 Creation of FLORINNOV, Award of National Innovative Entreprises

5. 2006 Creation Project "2B-BOOSTER BARRE", award of 2006 France national prize of innovative enterprises.

6. Large activity of collaboration with French, European and international industries.