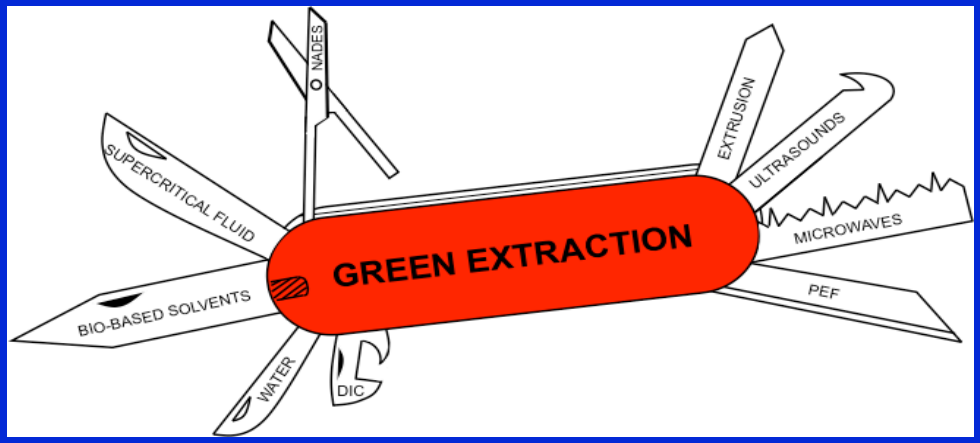
Pr. Farid CHEMAT

www.GREEN.univ-avignon.fr

Groupe de Recherche en Eco-Extraction de produits Naturels

Innovative Techniques and Alternative Solvents as Tools for Green Extraction of Natural Products



GREEN Extraction Team
Avignon University, France

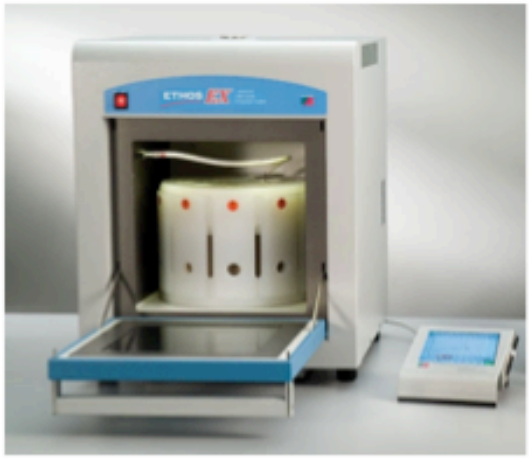
Solvants Alternatifs : Simulation par ab-initio utilisant Cosmos-RS

Procédés : Innovantion & Outils d'aide à la décision

Fonctionnalisation des extraits : Hémi-synthèse, encapsulation...

Micro-ondes

Version laboratoire

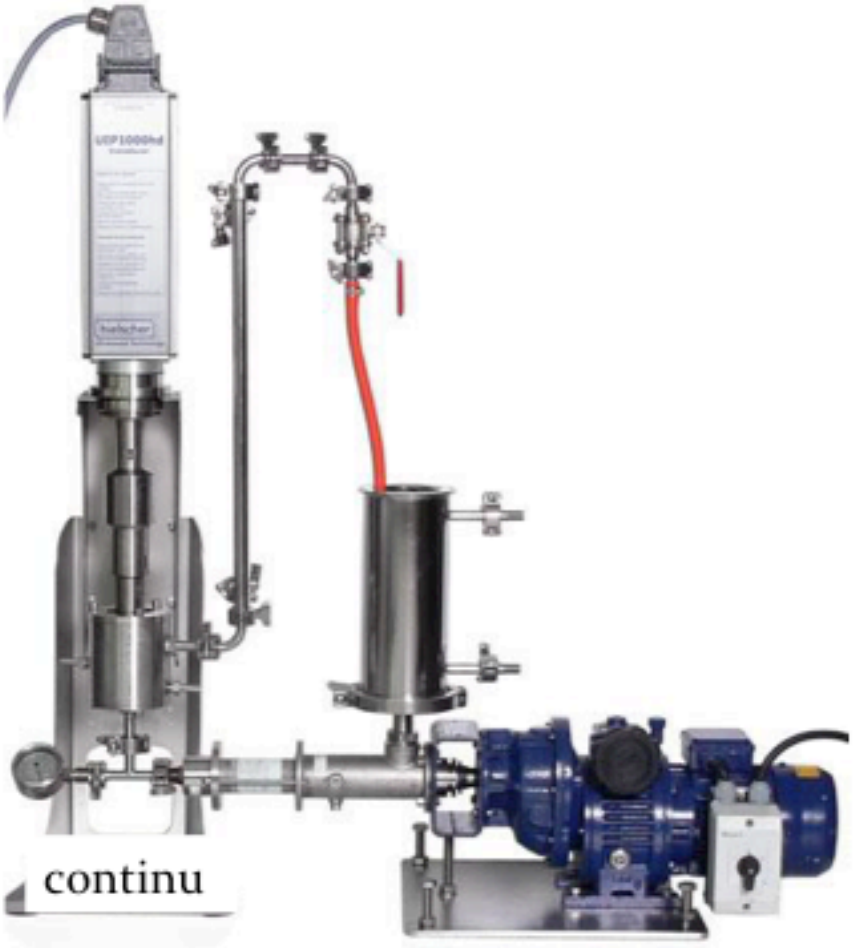


Version pilote

Réacteur Ultrasons

Version Labo/pilote
Hielscher UIP 1000 (20kHz, 1000W)

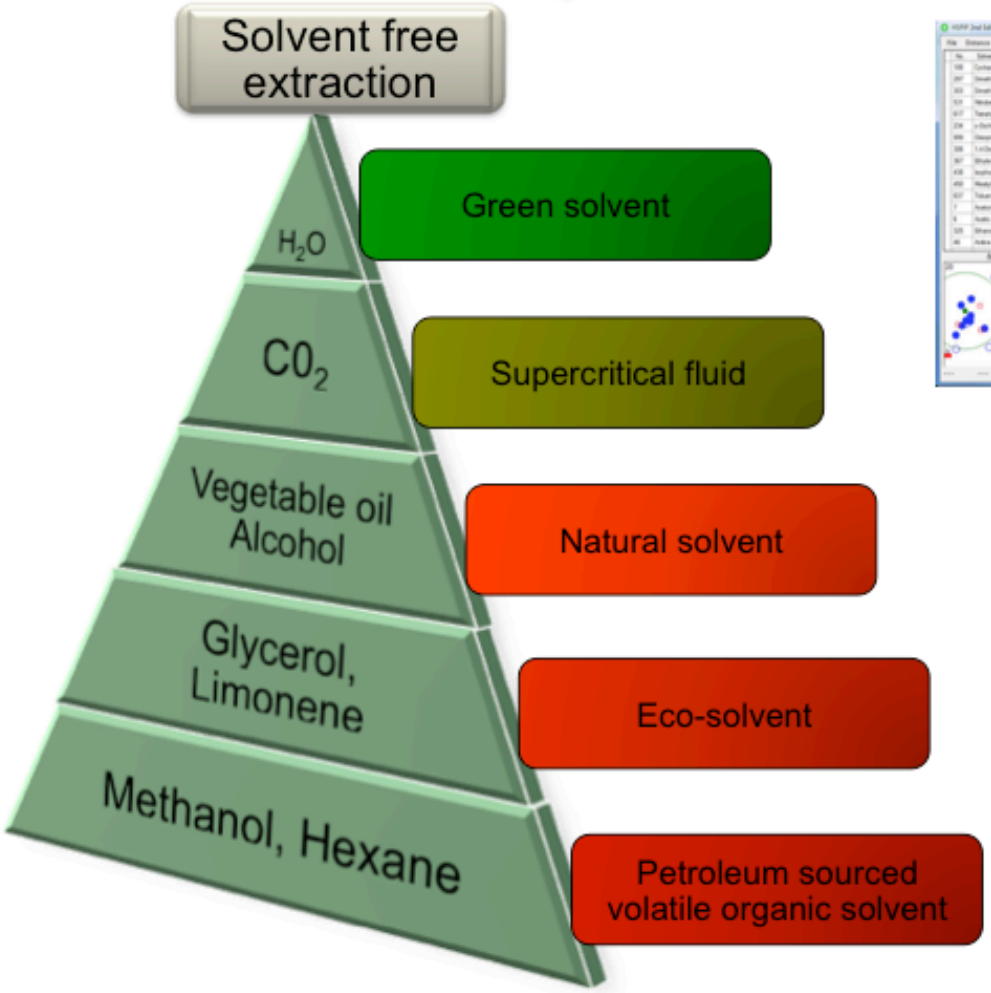
batch

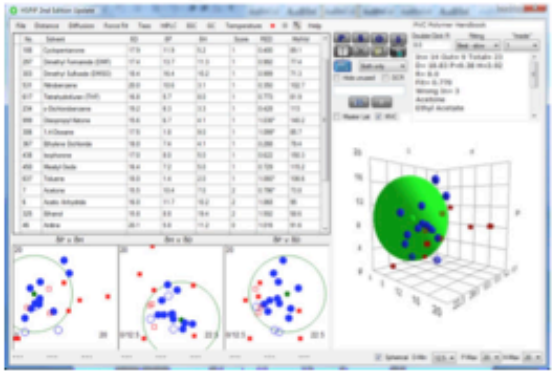


continu

Version Industrielle
Hielscher UIP 4000 (20kHz, 4000W)

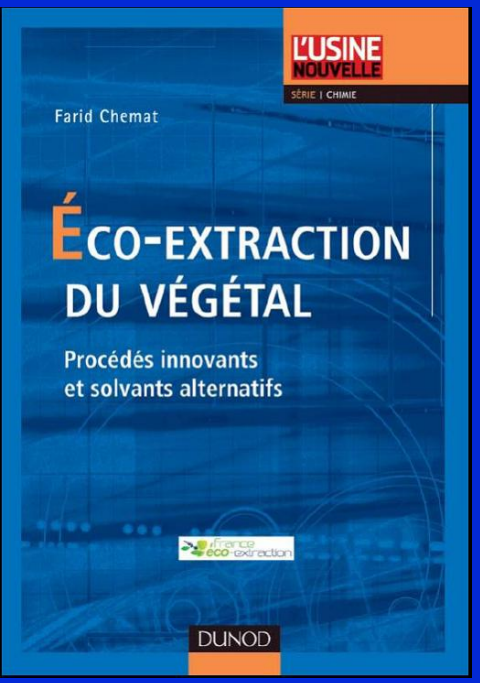
Solvants alternatifs

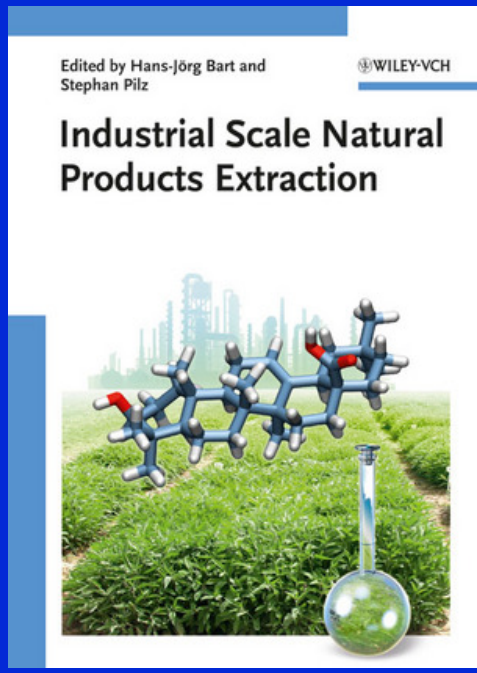




france éco-extraction

PROCESSNET
EINE INITIATIVE VON DECHEMA UND VDI-GVC





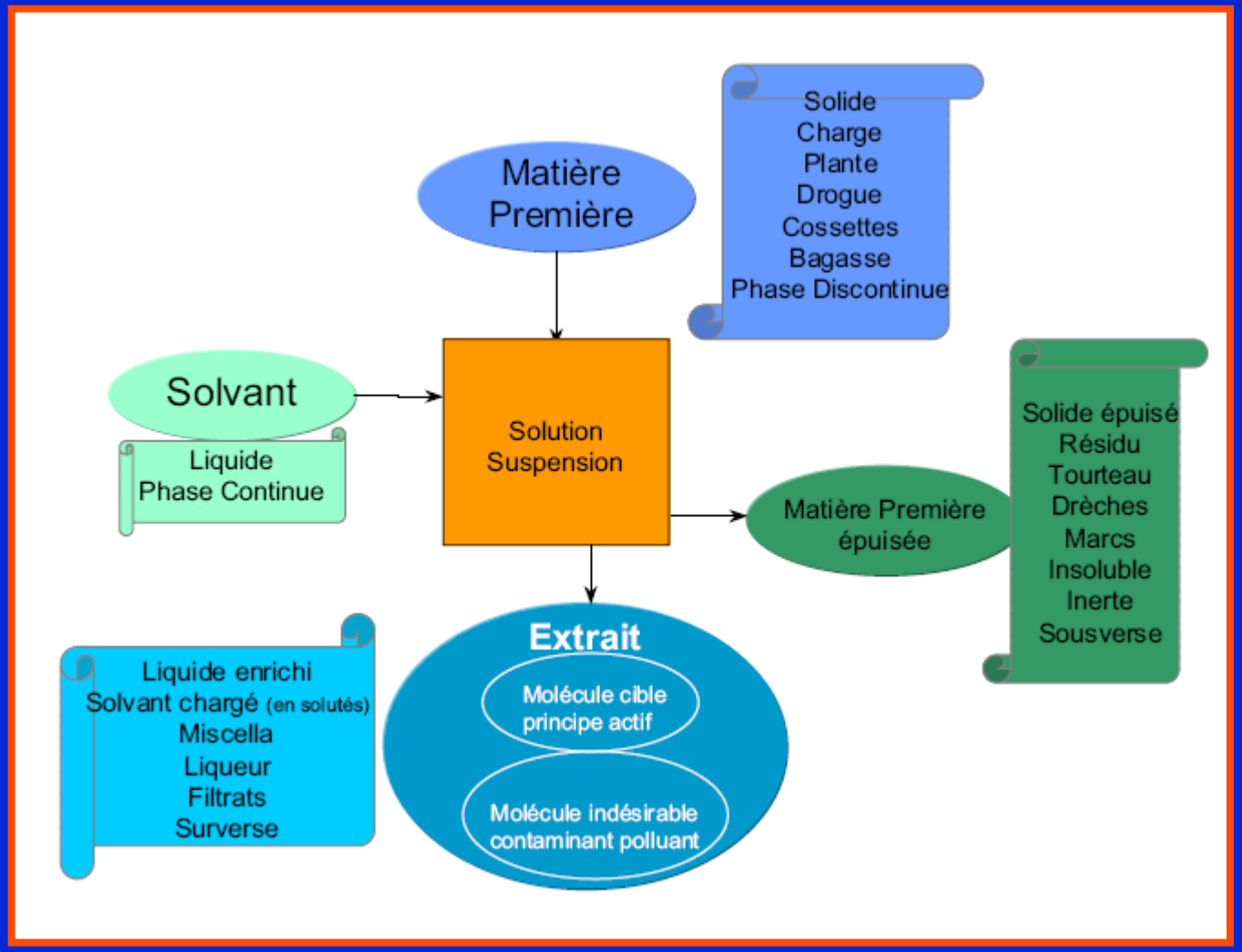
Innovative
Alternative

Techniques
Solvents

Drying
Grinding
Extraction
Separation
Purification

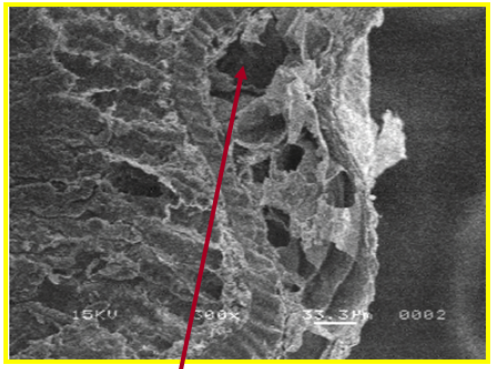
Solid-Liq

Extraction Process

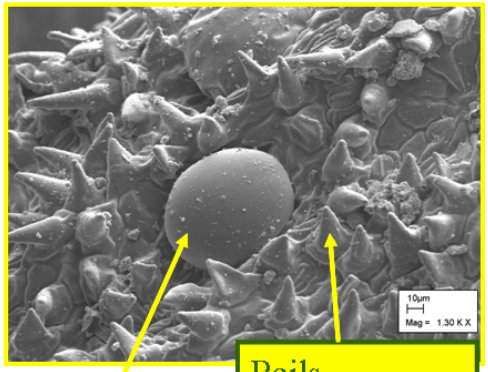


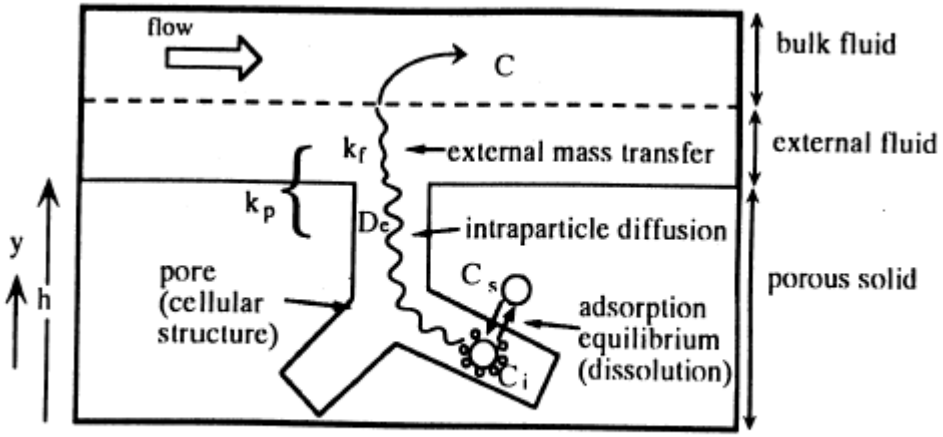
Extraction mechanism
Of primary and secondary metabolites
Essential oils,colors, antioxydants, principes actifs…

↳ Cas de la cardamome



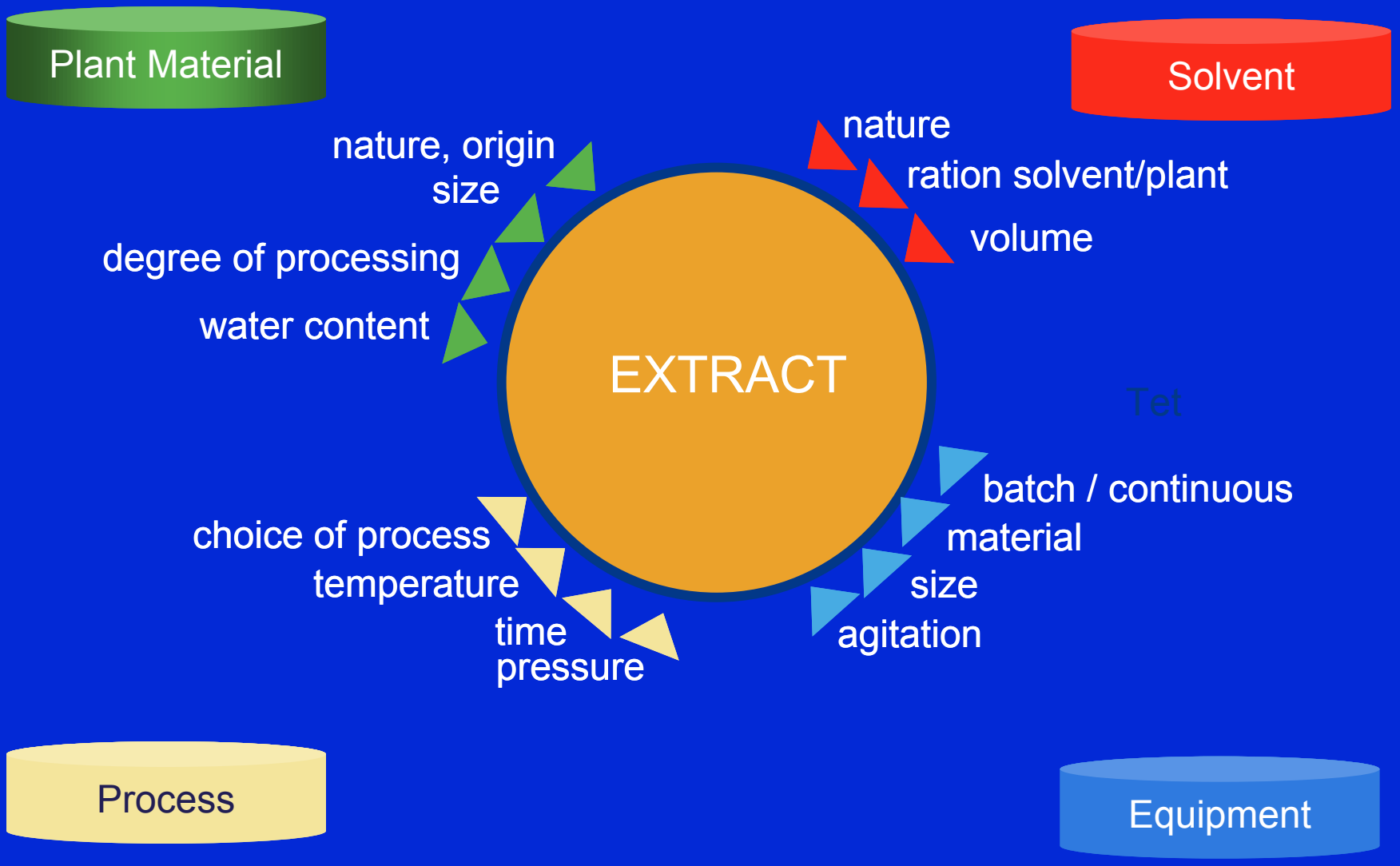
↳ Cas du thym





J. Chem. Eng. Japan, **26** (4), 401-407 (1993).

Extraction parameters

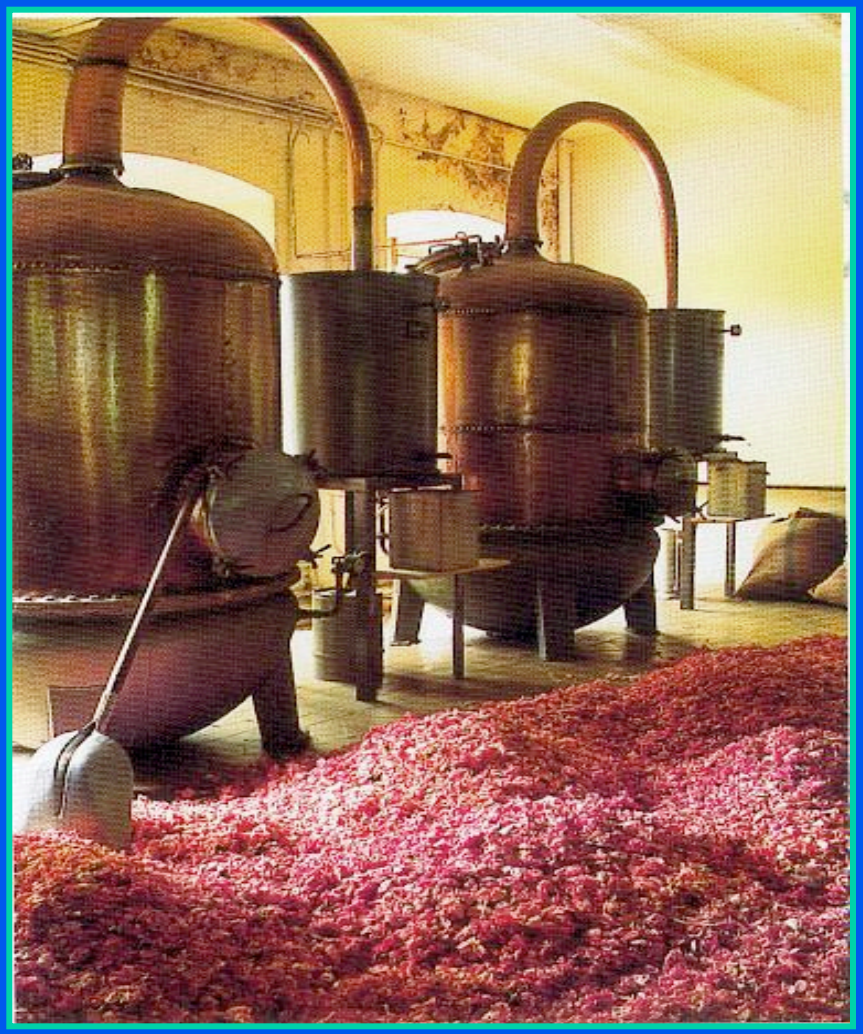


Extraction Techniques

Solvent extraction

Obtention d' extraits végétaux ou de macérats

Distillation de pétales de roses à Grasse



Distillation dans un atelier indien

Why GREEN EXTRACTION

ECO - EXTRACTION

ECOLOGIC

ECONOMIC

Extraction of Natural Products : Industry Problems

Extraction time : hours or days

Energy cost

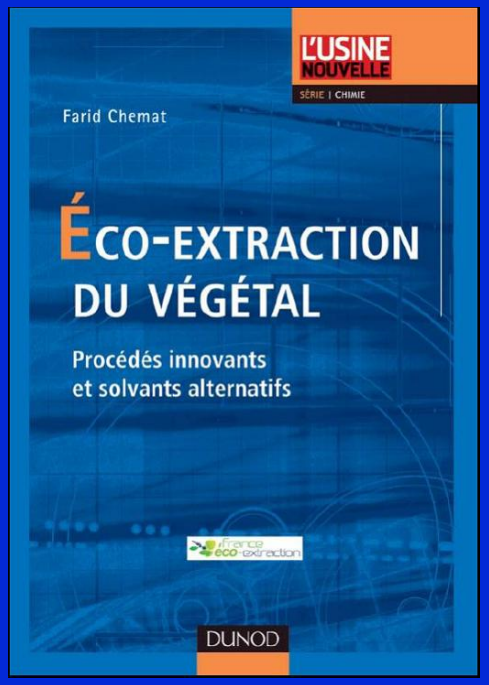
Extraction by batch

Problems of degradation

Use of « bio » solvants – Green chemistry

Reduction of waste: solid and liquid

Need of new products



Ask from Industry : Rapid, Cold extraction, without solvent, without water to eliminate wastes, continuous process, and competitif in price and quality.

Green Extraction of Natural Products
Concept and Principles

Int. J. Mol. Sci. **2012**, *13*, 8615-8627; doi:10.3390/ijms13078615

OPEN ACCESS
International Journal of
Molecular Sciences
ISSN 1422-0067
www.mdpi.com/journal/ijms

Review

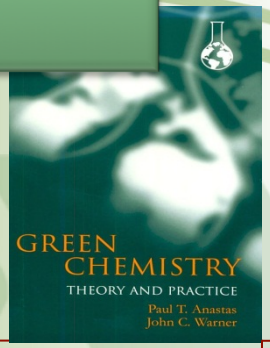
Green Extraction of Natural Products: Concept and Principles

Farid Chemat [1,*], Maryline Abert Vian [1] and Giancarlo Cravotto [2]

"Green Extraction is based on the discovery and design of extraction processes which will reduce energy consumption, allows use of alternative solvents and renewable natural products, and ensure a safe and high quality extract/product".

Principles of Green Extraction

12 Principles of Green Chemistry



1. Prevent Waste
2. Maximize Atom Economy
3. Design less Hazardous Chemical Syntheses
4. Design safer Chemicals and Products
5. Use safer Solvents and Reaction conditions
6. Increase Energy Efficiency
7. Use Renewable Feedstocks
8. Avoid Chemical Derivatives
9. Use Catalysts, not Stoichiometric Reagents
10. Design Chemicals and Products that Degrade
11. Analyze in Real time to Prevent Pollution
12. Minimize the Potential for Accidents

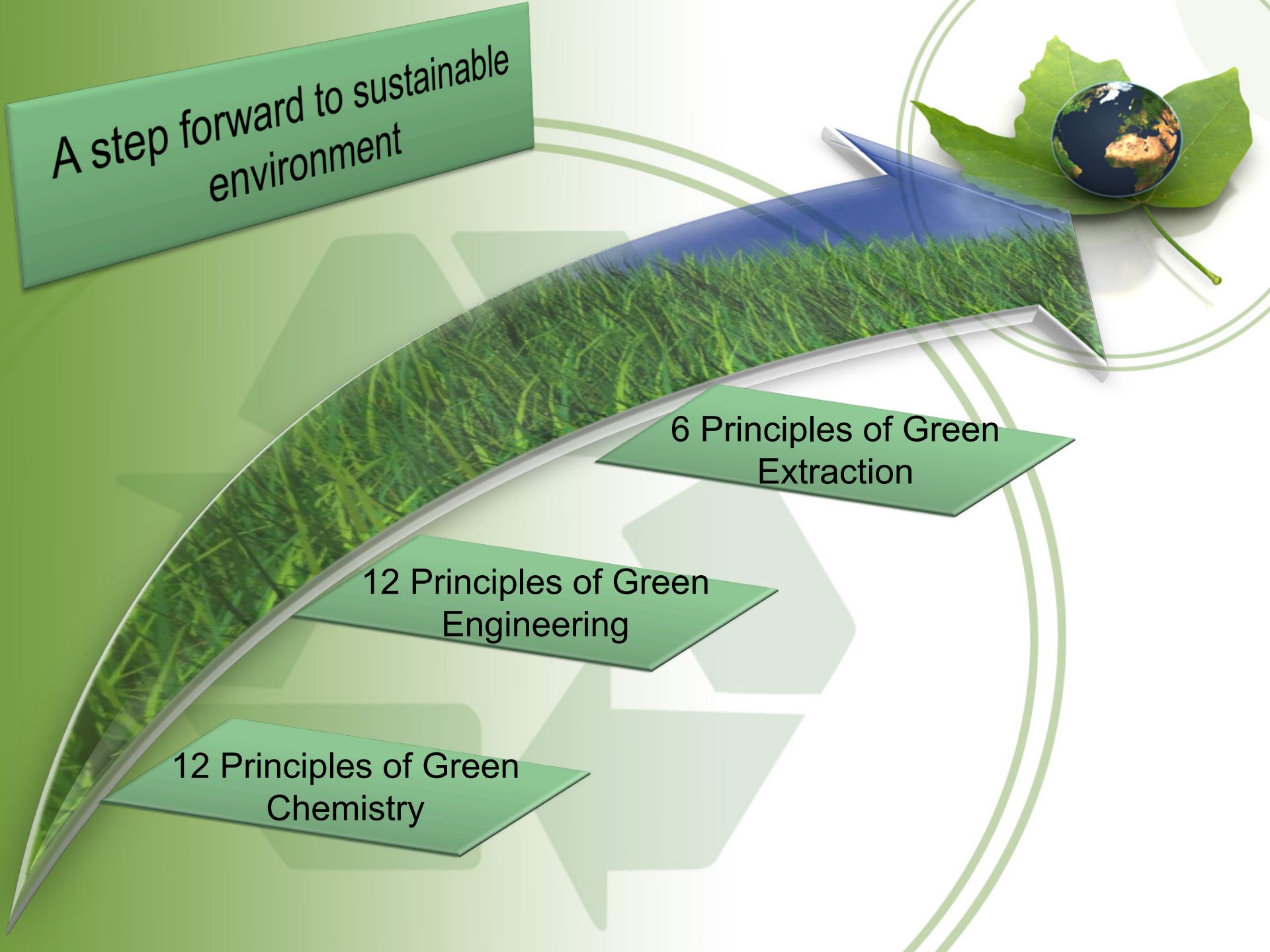
* **Anastas, Paul T.; Warner, John C. *Green Chemistry Theory and Practice;* Oxford University Press: New York, 1998**

12 Principles of Green Engineering

1. Inherent Rather Than Circumstantial
2. Prevention Instead of Treatment
3. Design for economize Separation processes
4. Maximize Efficiency
5. Output-Pulled Versus Input-Pushed
6. Conserve Complexity
7. Durability Rather Than Immortality
8. Meet Need, Minimize Excess
9. Minimize Material Diversity
10. Integrate Material and Energy Flows
11. Design for Commercial "Afterlife“
12. Renewable Rather Than Depleting

* **Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering“.**

A step forward to sustainable environment



6 Principles of Green Extraction

12 Principles of Green Engineering

12 Principles of Green Chemistry

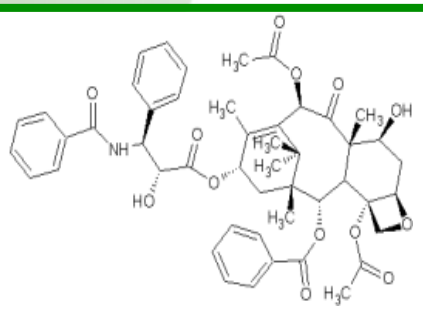
Principle1.

Principle 1: Innovation by the selection of varieties and the use of renewable plant resources.

Plant

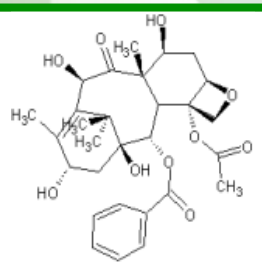
Renewable

Ecorce d'if
(*Taxus brevifolia*)

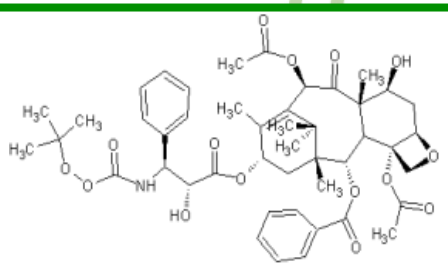


Paclitaxel ou Taxol®

Aiguilles d'if
(*Taxus baccata*)



10-désacétylbaccatine III

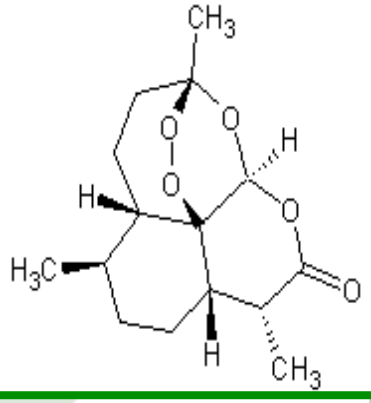


Docétaxel ou Taxotère®

Principle1.

Plant

Varietal selection



Artemisinin,
Artemisia Annua L.
Malaria

0.01% → **>1%**

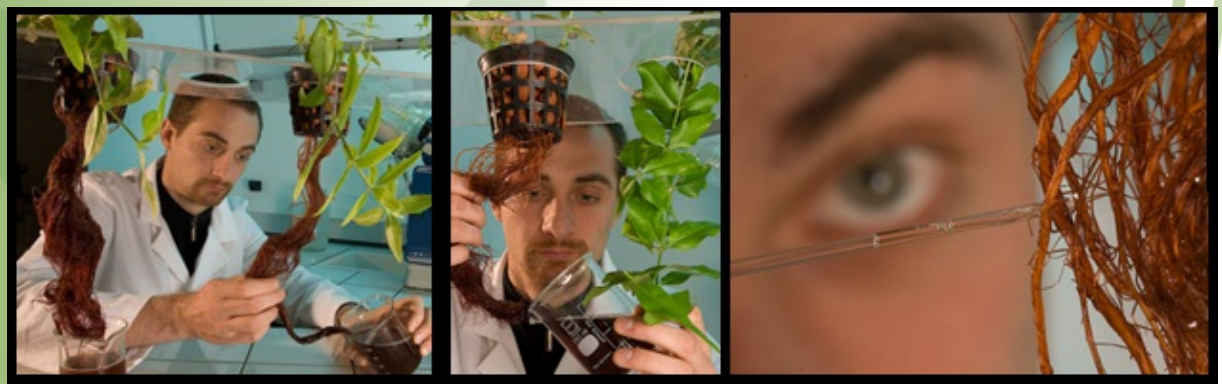
Principle1.

Plant

INNOVATION

Plant milking technology

Nepenthes sp.



Principle 2.

Principle 2 : Reduce energy consumption by using innovative technologies and favour energy recovery

Energy

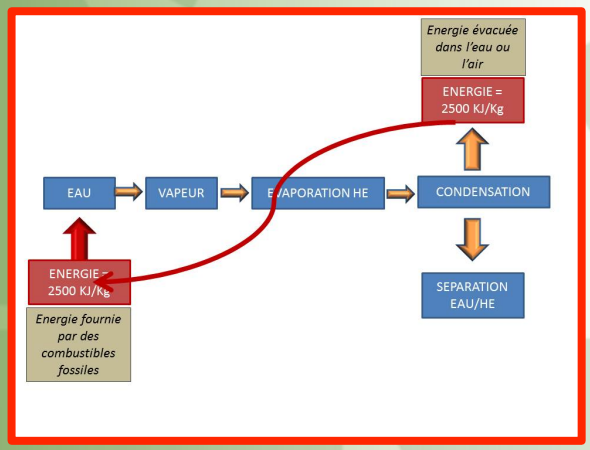
Optimisation of existing technologies

Alambics under 5 bars pressure
5000 Litres (Tournaire SA)

Principle 2.

Energy

Energy Recovery



Eco-VAPORATEUR - CRIEPPAM
(Centre Régionalisé Interprofessionnel d'Expérimentation en Plantes à Parfum, Aromatiques et Médicinales)

Principle 2.

Energy

Innovation

COLD EXTRACTION

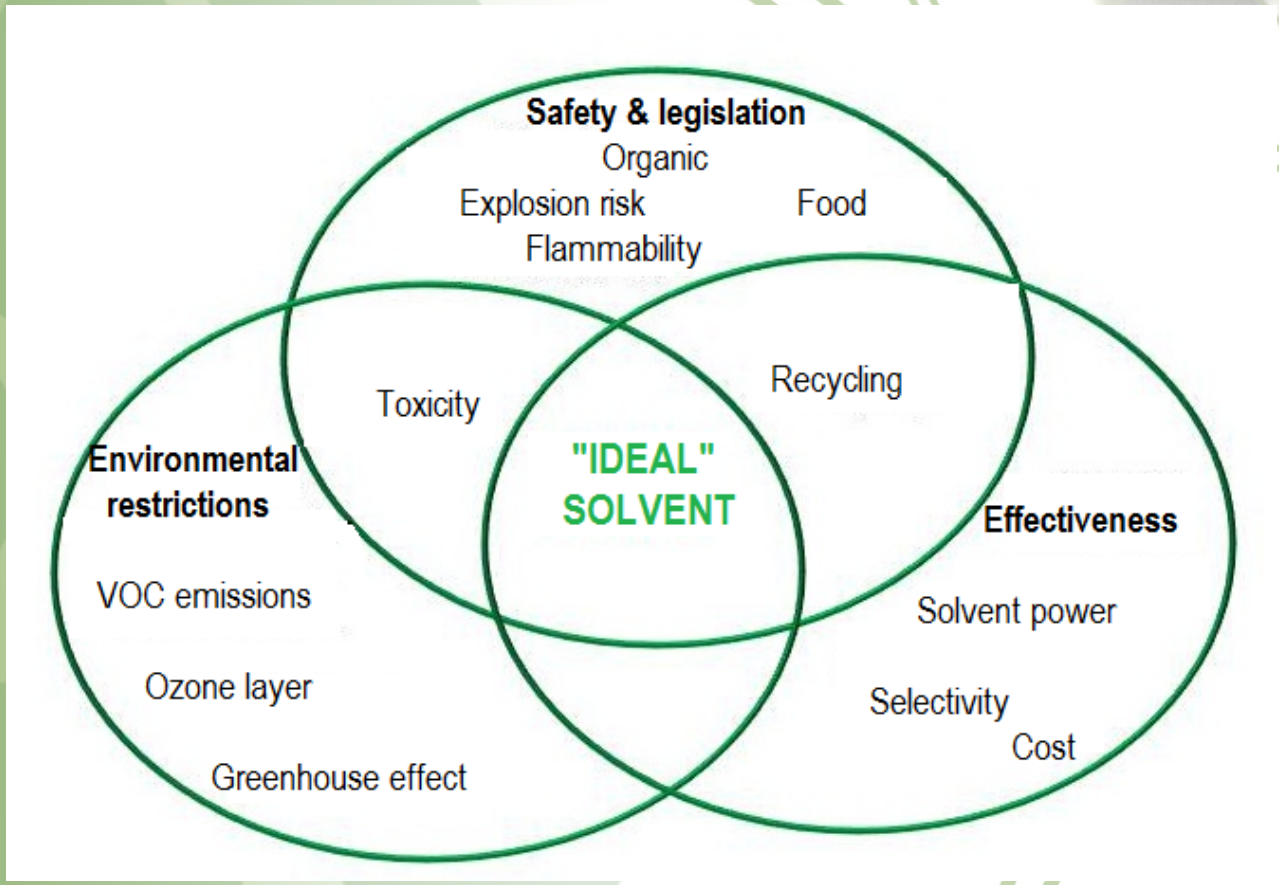
Pulsed electric field

Microwave Hydrodiffusion and Gravity
Under reduced pressure

Principle 3.

Principe 3 : Use alternative solvents and principally those from agricultural resources.

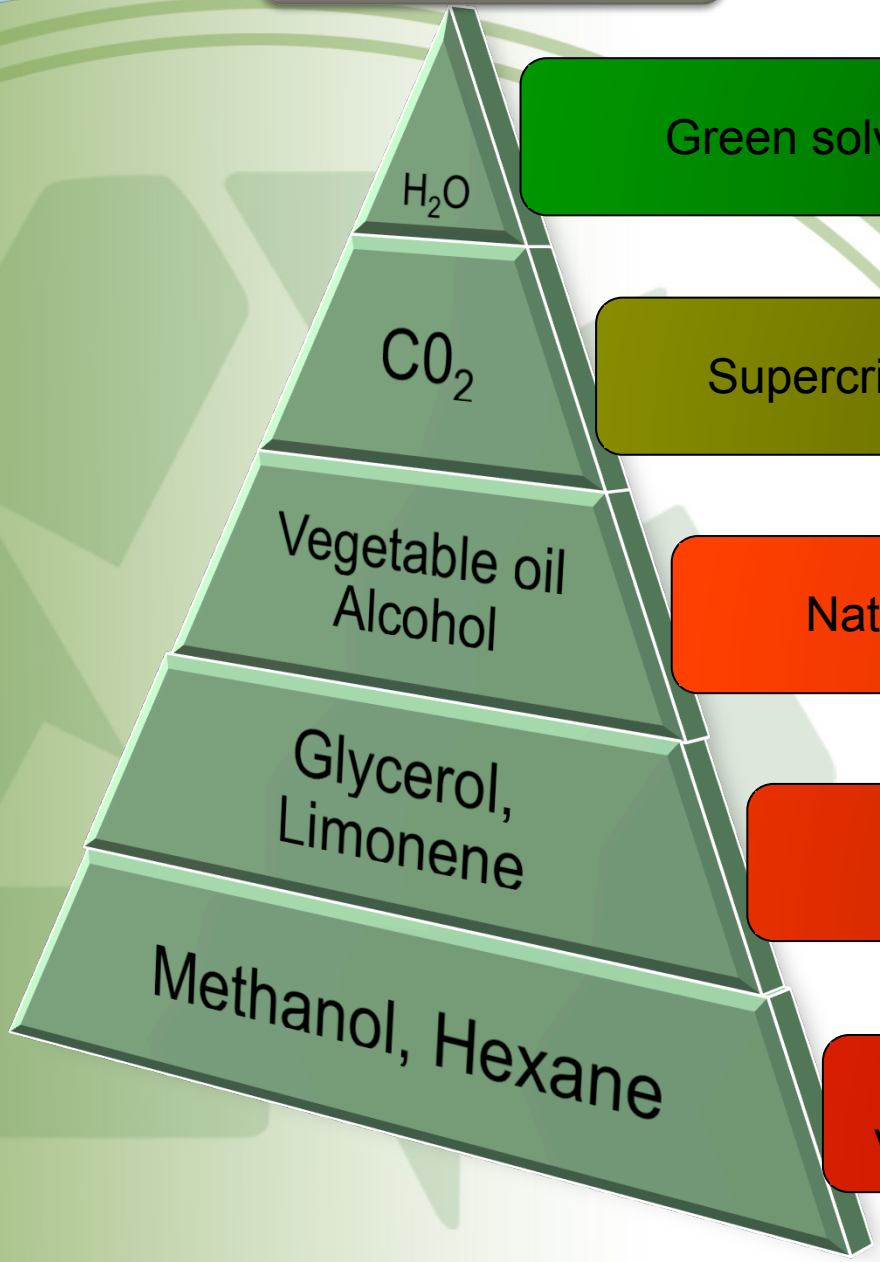
Solvent



Principle 3.

Solvent

Solvent free extraction



Green solvent

Supercritical fluid

Natural solvent

Eco-solvent

Petroleum sourced volatile organic solvent

Principle 4.

Principle 4 : Reduce unit operations through technical innovation and favour safe, robust and controlled processes

Process

One step

Simple & control

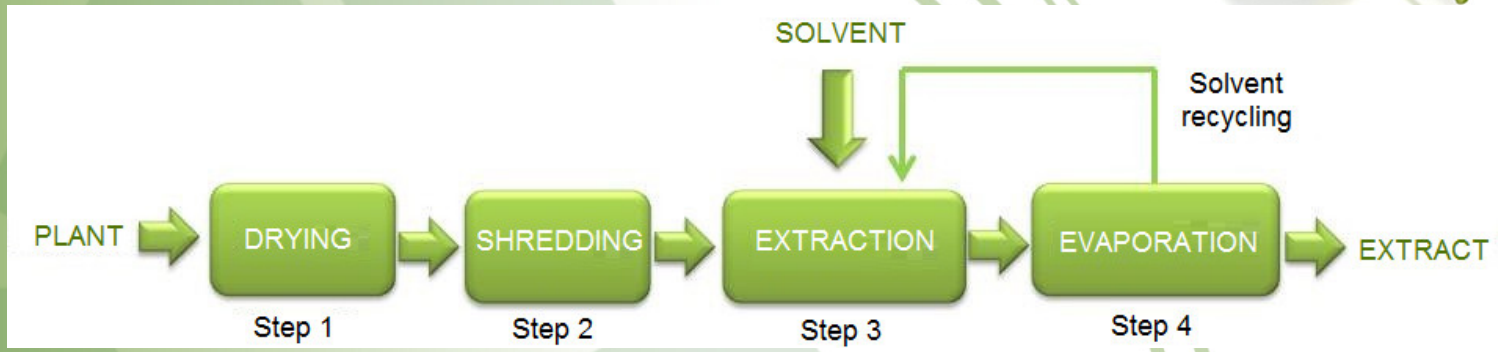
Efficient & Effective

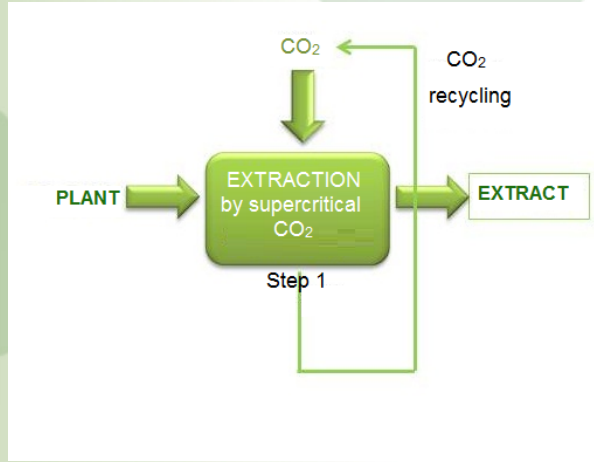
Suitable for by-products

Secure & Hazard free

Principle 4.

Process





Principle 5.

Principe 5 : Production of by-products instead of waste to include the bio- or agro-refining industry.

By-product

- **Definition of waste:**

"Generally, waste is any material that an industrial producer wants to get rid of or eliminate (waste disposal centre, incineration, landfill, etc.)",

- **Definition of by-product:**

"A by-product is a residual product that appears during the manufacture or distribution of a finished product. It is unintentional and unpredictable, and is accidental. It can be used directly or be an ingredient in another production process to manufacture another finished product",

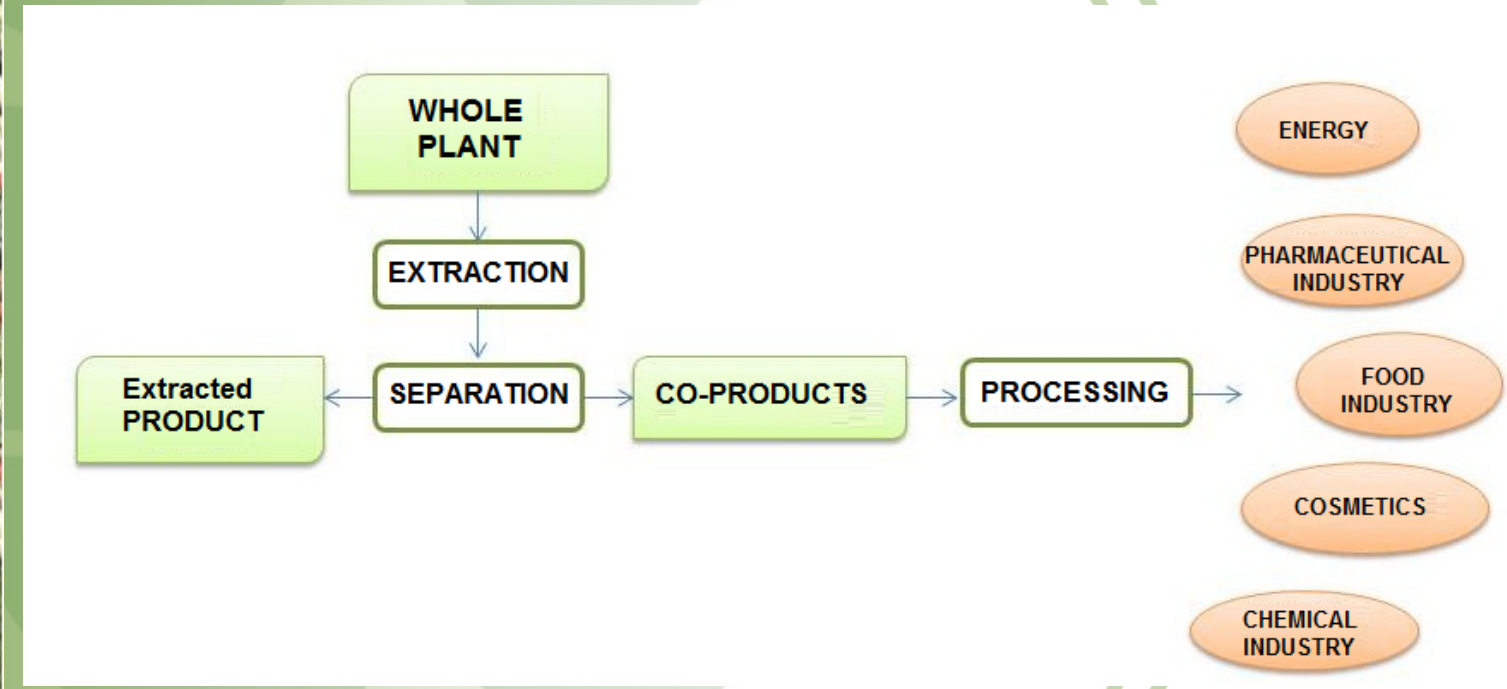
- **Definition of co-product:**

"A co-product is a material, intentional and inevitable, created during a single manufacturing process and at the same time as the main product.
The main final product and the co-product must always meet specifications for their characteristics, and each may be used directly for a particular application." Co-products also have economic value: a specific market for it, a pricing, etc.
Examples of food industry co-products: oil cakes (rape, sunflower, flax), spent cereal grain (wheat, barley), beet pulp, potato fibre and proteins, etc.

Principle 5.

By-product

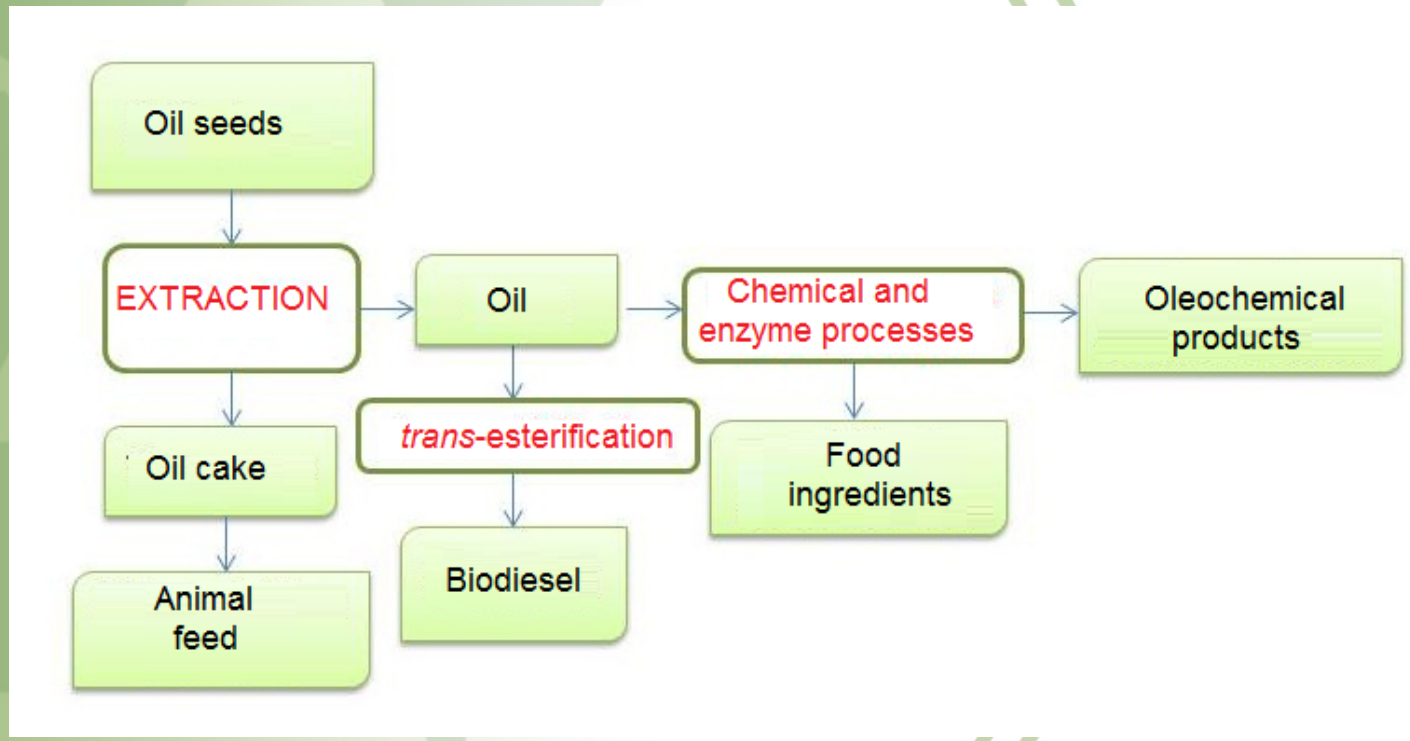
Bio-raffinery Concept



Principle 5.

By-product

Bio-raffinery Concept



Principle 6.

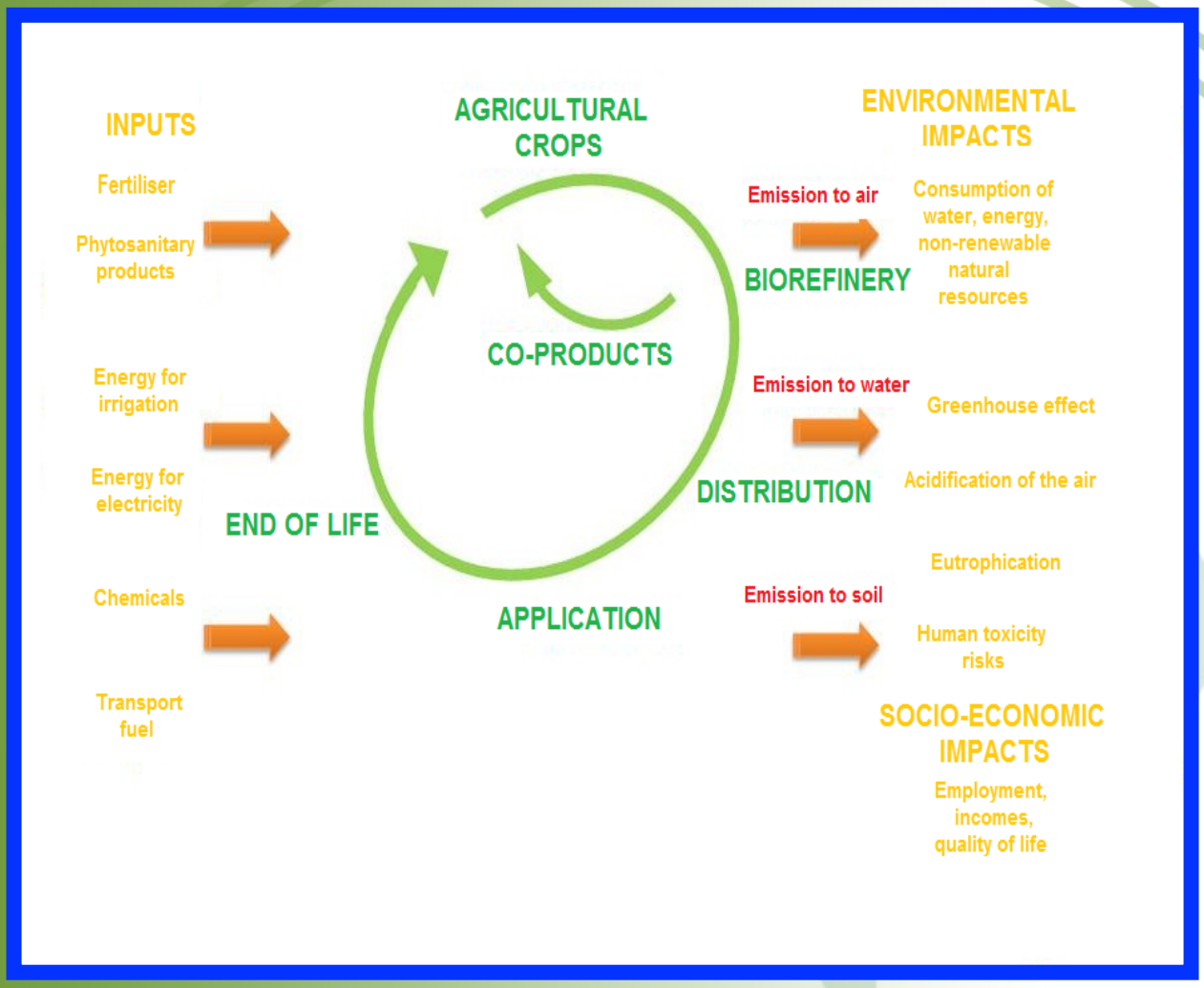
Principle 6 : Aim for a non-denatured and bio-degradable extract without contaminants with “green” values.

Product

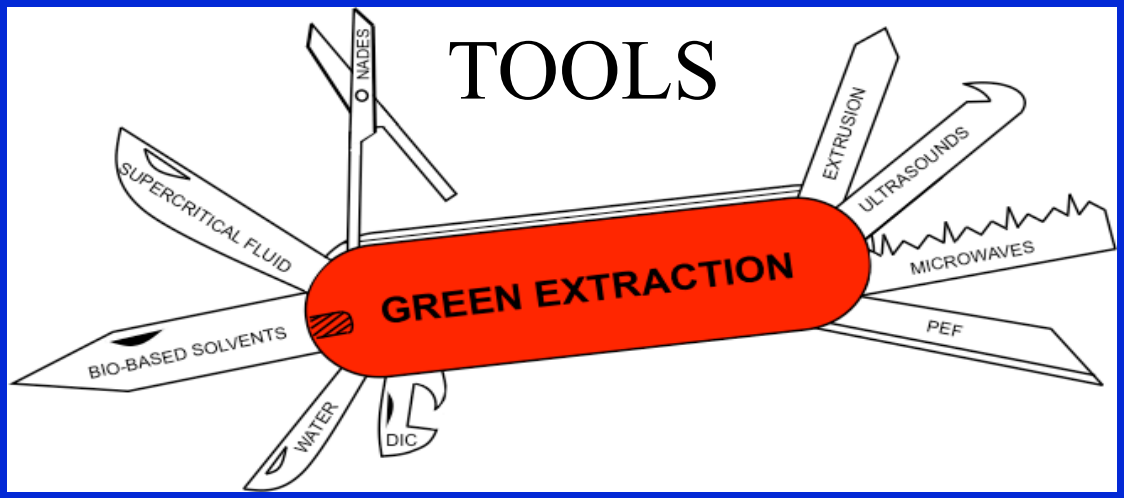
- **Allergenic substances** — Furocoumarins
- **Toxic pollutants** — Pesticides, Heavy metals, Radioactive elements
- **Microbiological contaminants** — Bacteria, Mycotoxins
- **Other** — GMO, Solvent residues

Recommandations

Life Cycle Analysis



EU Ecolabel
www.ecolabel.eu

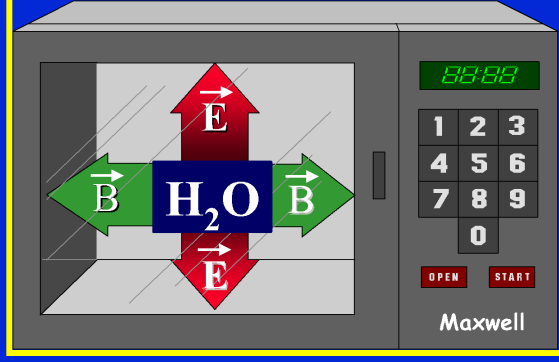


Alternative solvents

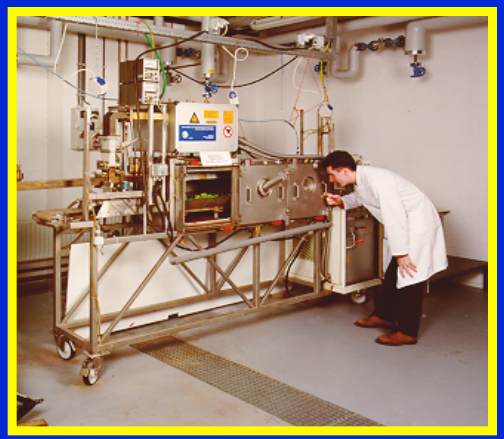
- Solvent Free
- Water (normal, subcritical, emulsions)
- CO_2, HFC, other gaz
- Vegetable oils
- Byproducts as terpenes (limonene..)
- Byproducts (glycérol…)
- Ionic liquids

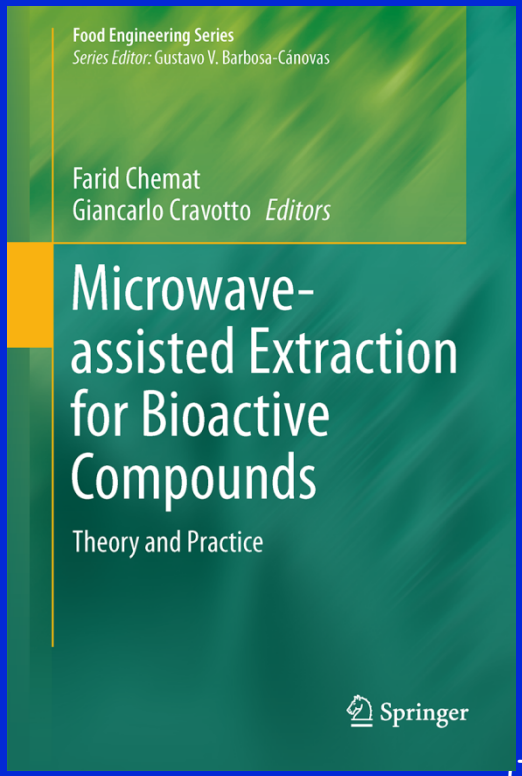
Innovative techniques

- Turbo-extraction
- Ultrasound assisted extraction (UAE)
- Accelerated solvent extraction (ASE)
- Microwave assisted extraction (MAE)
- Pulse electric field (PEF)
- Instantaneous decompression (DIC)
- Extrusion, induction…

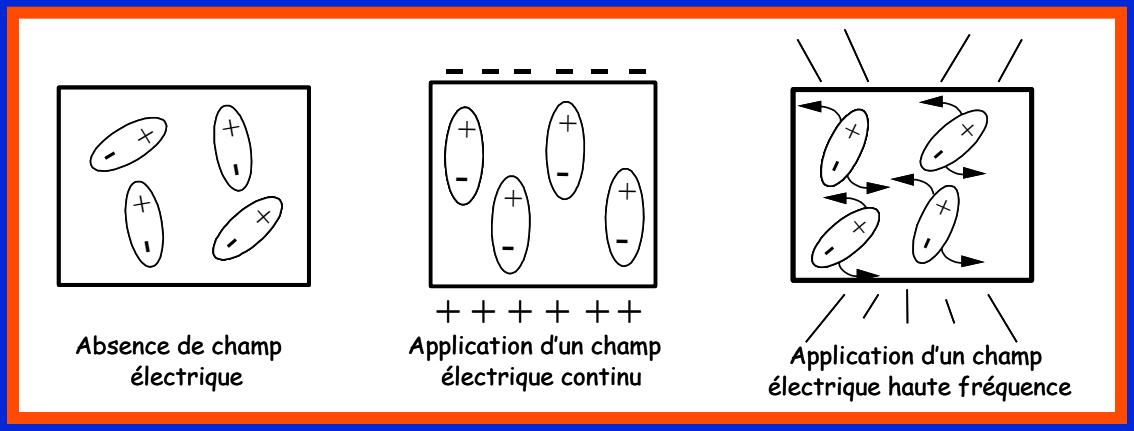


Microwave Assisted Extraction
Solvent free et energy less





Échelle microscopique

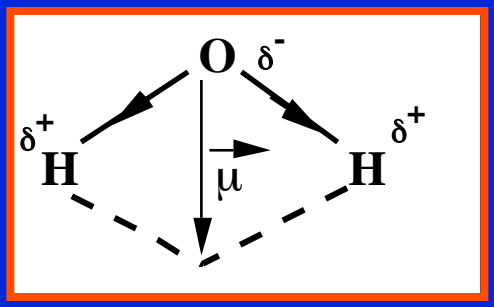


Énergie électrique → **Énergie cinétique** → **Chaleur**

Rotation dipolaire

Friction interne
Chocs moléculaires

Propriétés diélectriques



Constante diélectrique ou permittivité ε'

Elle caractérise la **facilité** avec laquelle une molécule se laisse polariser par un champ électrique, c'est à dire sa polarisabilité.

Perte diélectrique ε''

Elle mesure la **capacité de conversion** de la radiation électromagnétique en chaleur. En général, la valeur de ε'' passe par un maximum lorsque la permittivité ε' tend à diminuer

Facteur de dissipation (tangente de pertes électrique) tg δ

La capacité d'un matériau à **convertir** l'énergie électromagnétique en chaleur à une température et une fréquence données est souvent représentée par l'angle de perte:

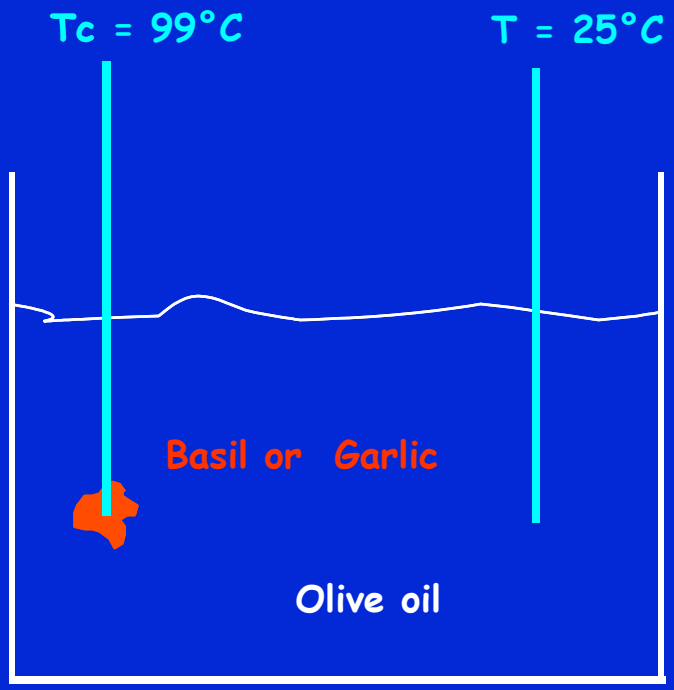
$$tg\ \delta = \varepsilon'' / \varepsilon'$$

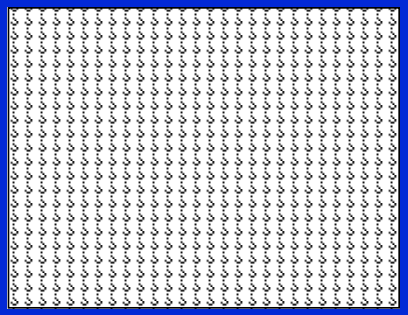
ε' : permittivité du milieu ($F.m^{-1}$)
ε'' : perte diélectrique ($F.m^{-1}$)

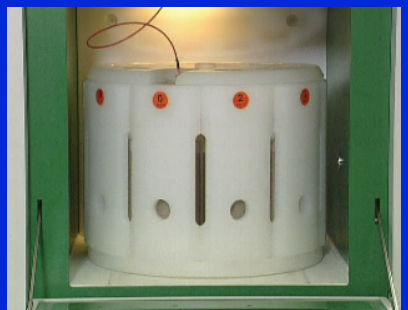
Four à micro-ondes industriels

Microwave : Selective heating

Solvent	Constante diélectique F/m	Dissipation factor tan δ ($x10^4$)
Olive oil or solvent (hexane)	2	1
Water	80	1600

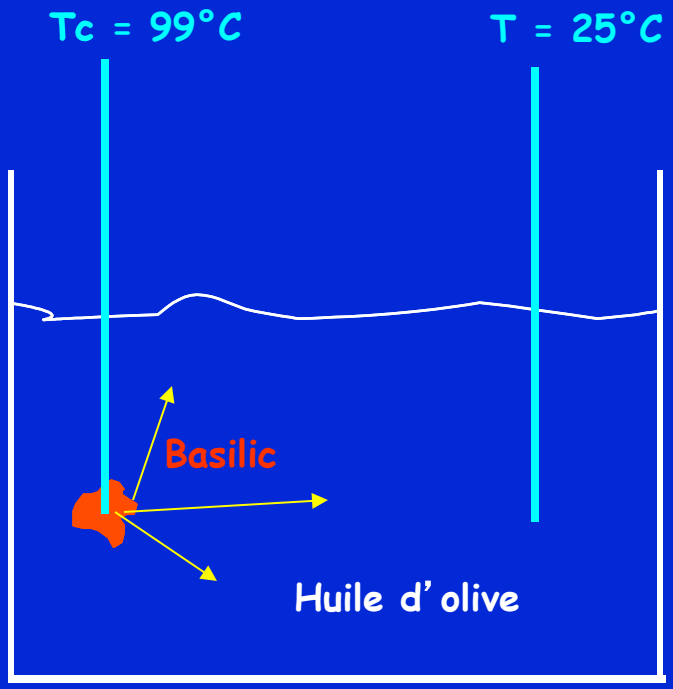






Aromatisation of olive oil

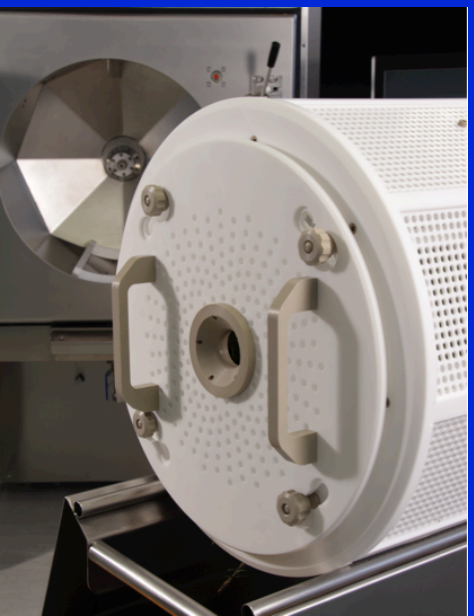
Huile d' olive + ail
25 euros /L

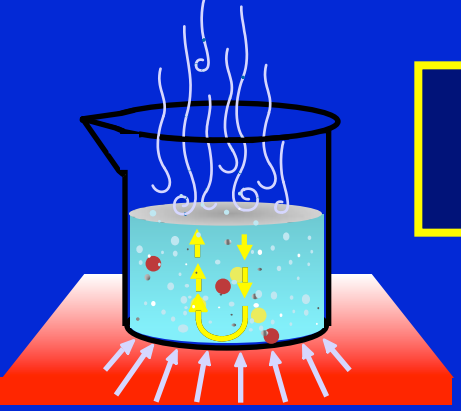


Huile d' olive + Basilic
25 euros/L

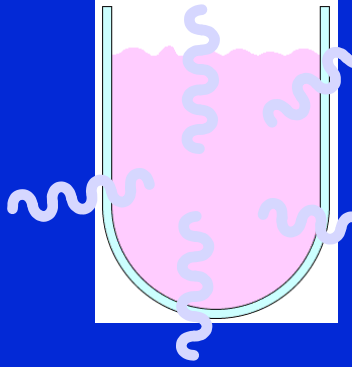
Olive oil: 2 – 3 euros / litre
Aromatised oilive oil: 20 – 30 euros /litre

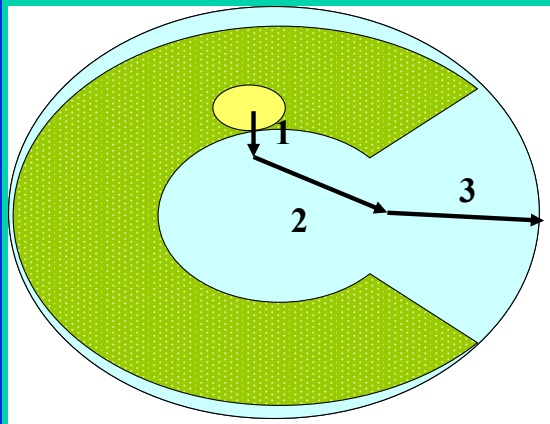

MICROWAVE ACCELERATED SYNTHESIS
DIRECT MERCURY DETERMINATION
MAC-75





Microwave : no need of transfer medium





1. Solubilisation-Desorption
2. Internal diffusion
3. External diffusion

Microwave heating

heat transfer →

mass transfer →

Conventional heating

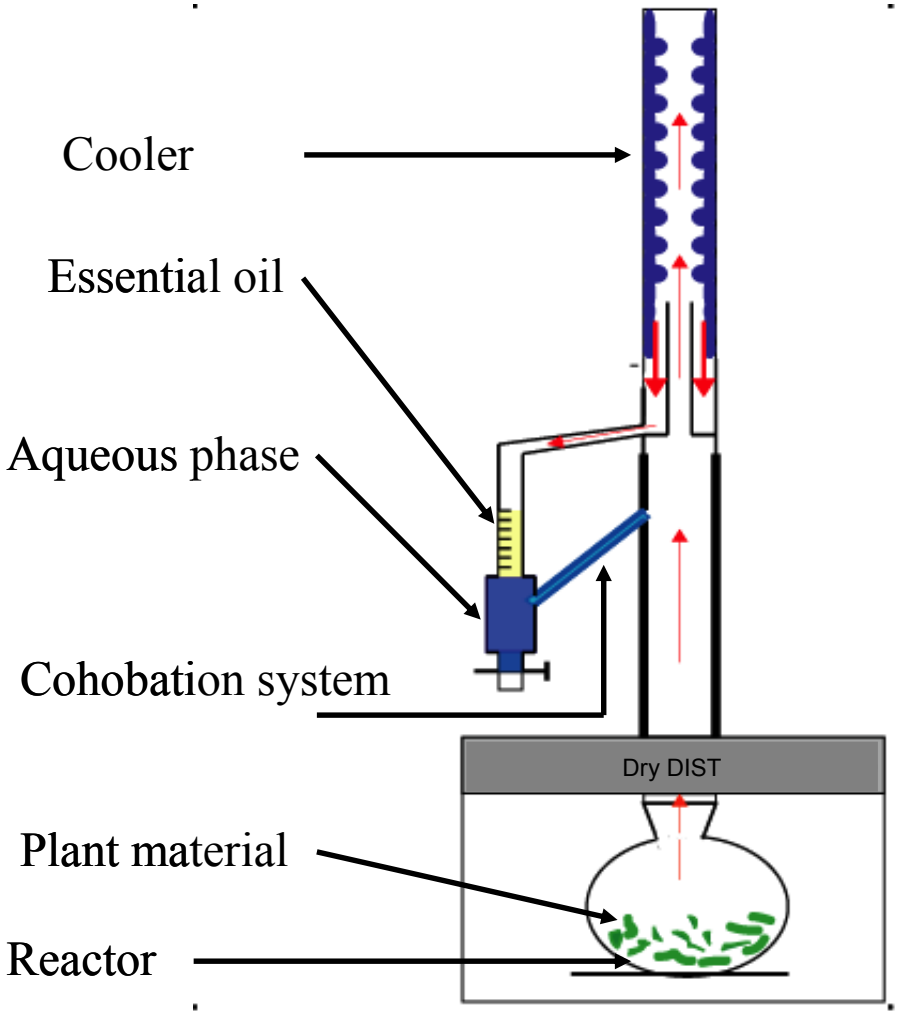
← heat transfer

mass transfer →

Hydro-distillation : 1 kg of roses + 10 litres of water

Microwave Dry Distillation : 1 kg of roses

Dry Dist : Microwave dry Distillation Patents EP et USP 2004 by Chemat et al.



1-5 litres

MW

Modèle industriel 10-100 litres
ARCHIMEX

Archimex

Gattefossé

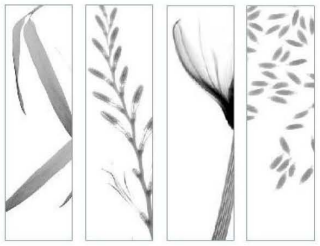
A LA SOURCE DU SOIN

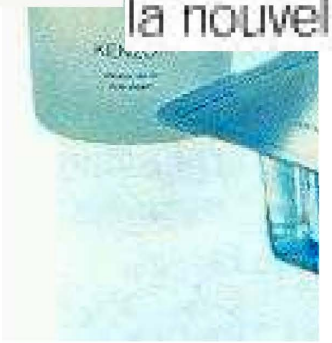
La force de la nature émotionnelle, esthétique ou biologique est l'essence des créations de Kenzo. Ainsi Kenzoki a puisé le soin à sa source : au cœur des plantes. Réserves naturelles d'énergie, elles renferment une eau aux richesses insoupçonnées, une eau vivante et pure : l'eau végétale. Liquide de constitution des végétaux, elle transporte sels minéraux, oligo-éléments et huiles essentielles. **Extraite sans chimie**, elle devient un actif cosmétique inédit qui distille ses bienfaits dans les formules Kenzoki. Mais ce n'est pas tout : sa biocompatibilité lui permet d'être parfaitement assimilable par la peau. L'eau végétale se fait co-actif pour véhiculer des actifs complémentaires.

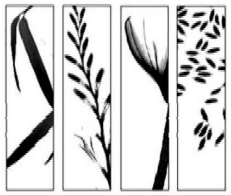
Hyper-Fréquences / ce procédé d'extraction breveté, exploité par les laboratoires de Gattefossé consiste à transformer le constitution naturel du végétal en vapeur d'eau. Il obtenir l'eau végétale. La plante température l'eau, et de de température eau végétale ainsi macération ni toute sa richesse.

KENZOKI

la nouvelle cosmétique du bien-être







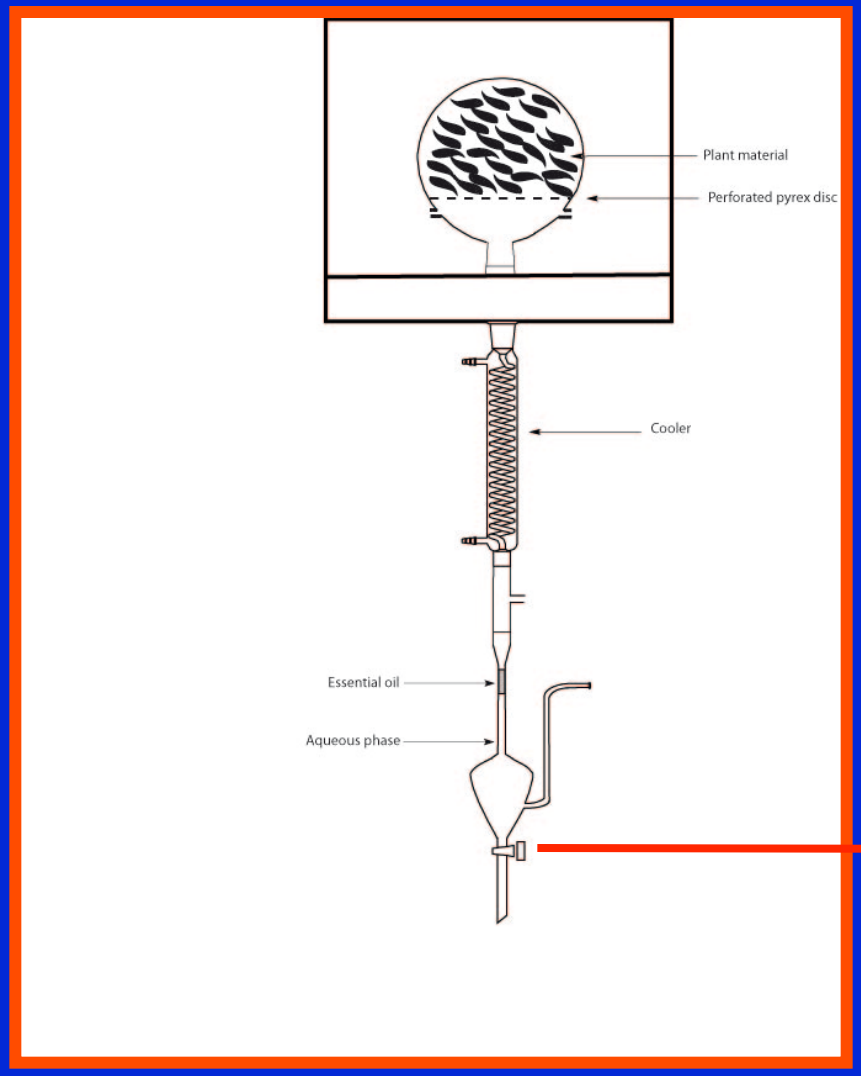
KENZOKI
la nouvelle cosmétique du bien-être

KENZOKI
la nouvelle cosmétique du bien-être

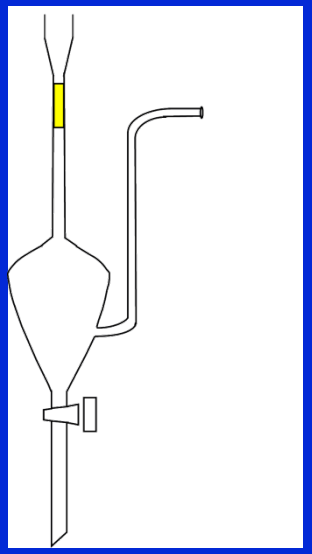

MAC-75


MAC-75

Microwave Hydrodiffusion and Gravity
Extraction des arômes, huiles essentielles, antioxydants, colorants…



UNIVERSITÉ D'AVIGNON



F. Chemat et coll., European Patent 07100935.1, 2008

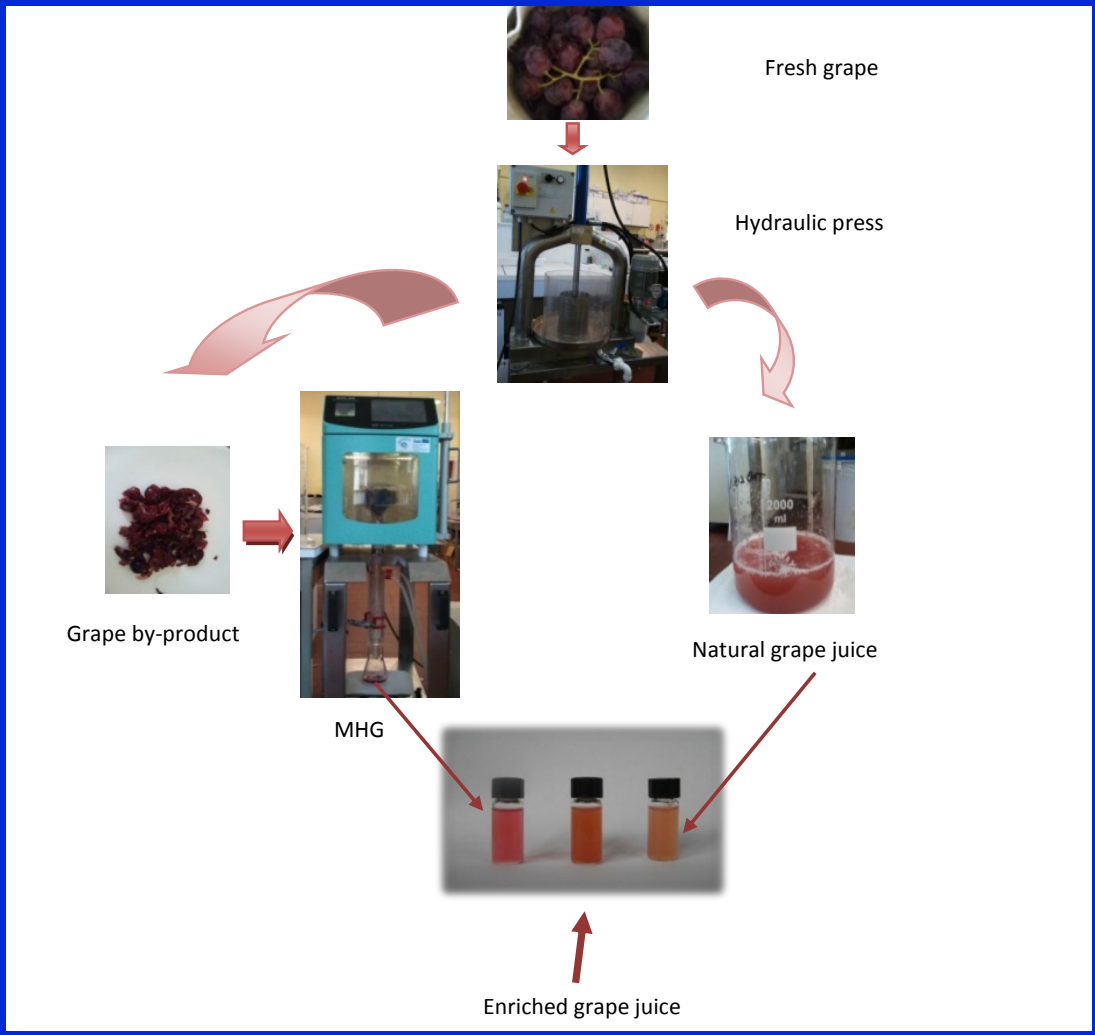
MHG : Industrial Version

MILESTONE TECHNOLOGIES

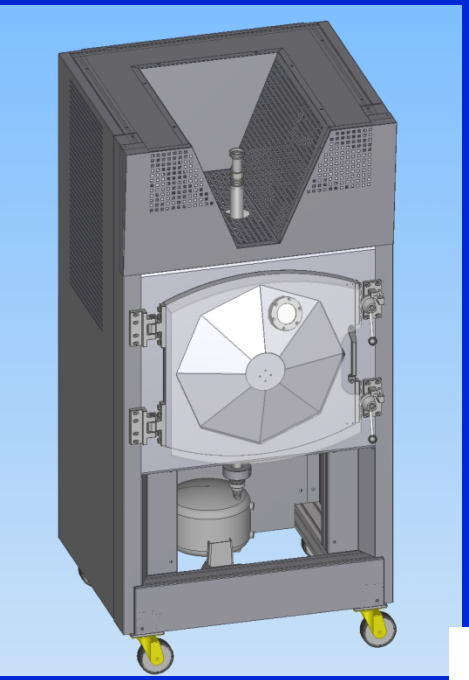
NEOS-GR

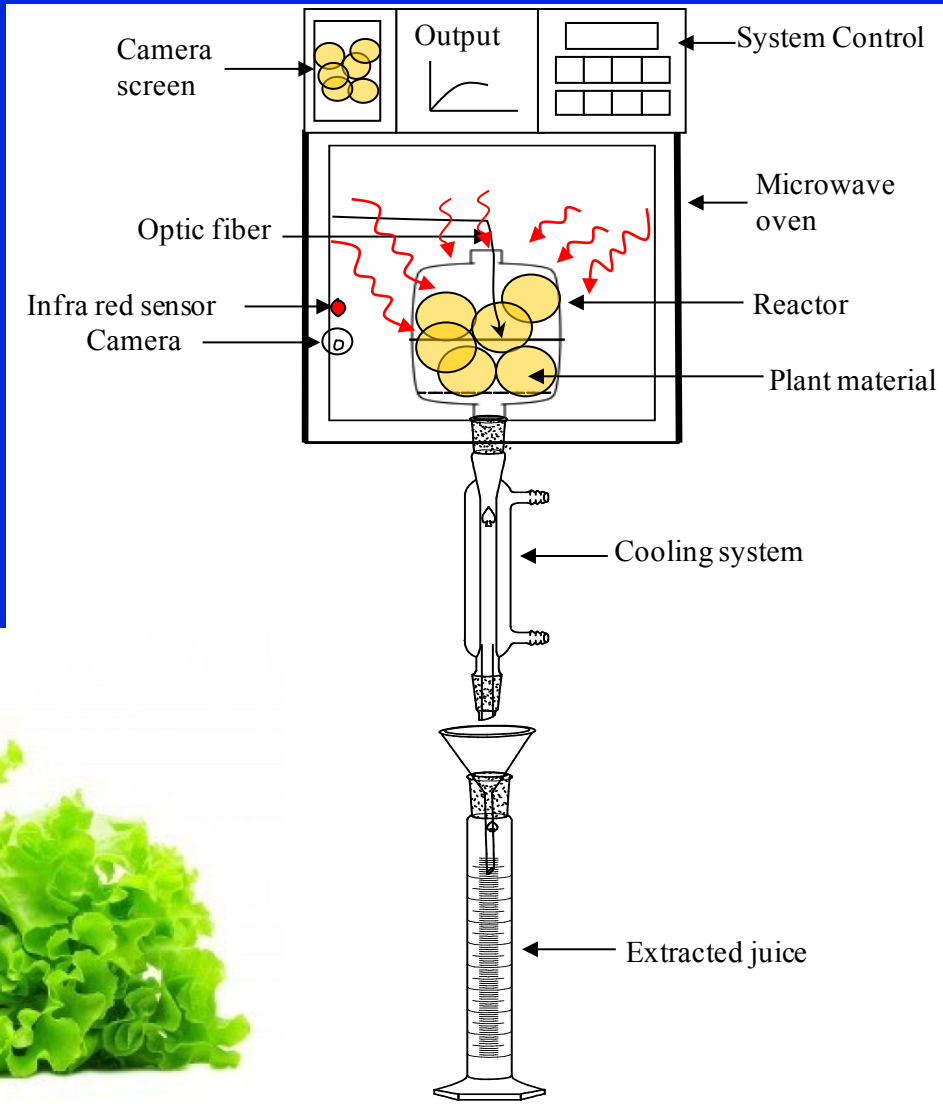
Rapid, Solvent-Free Extraction by Microwave Hydrodiffusion and Gravity (MHG)

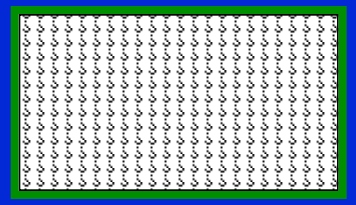
An innovative grape juice enriched in polyphenols by microwave-assisted extraction



Valorisation of of food by products (lettuce) using microwave energy







Ultrasound Assisted Extraction
Cold extraction and enhanced mass transfer

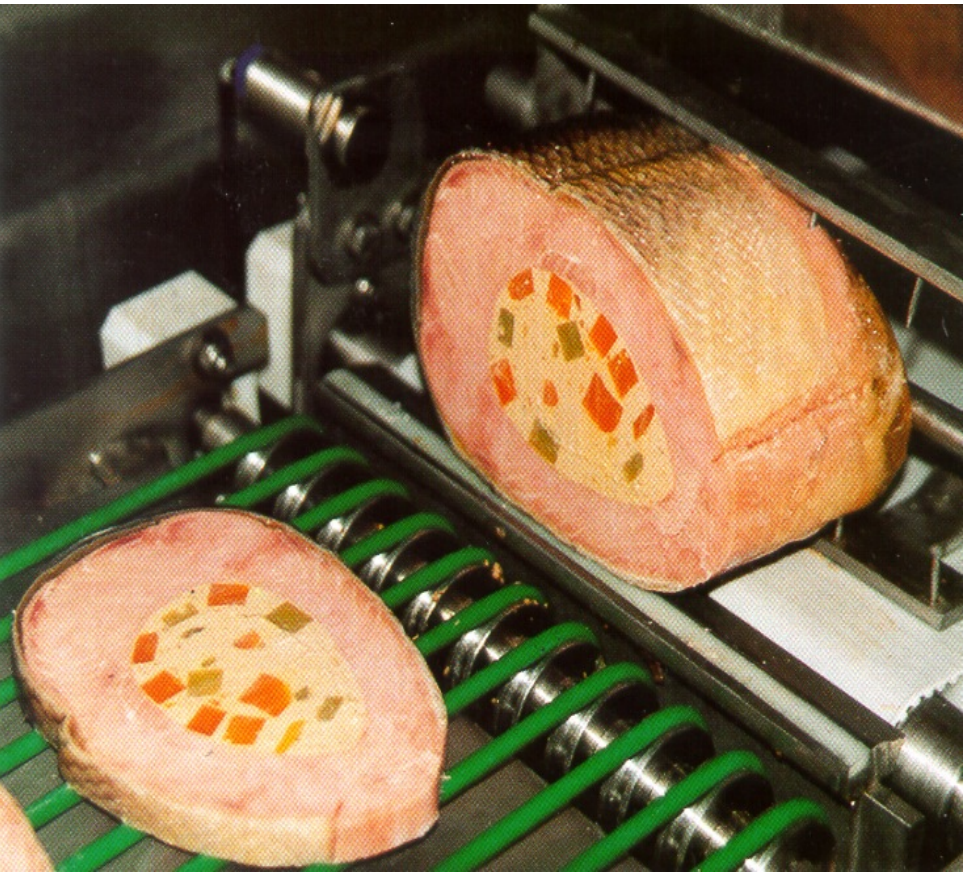
& Applications of US in Food Industry

Mechanical Effects	Chemical and Biochemical Effects
Crystallisation of fats and sugars	Accelerated oxidation and aging
Degassing	Alteration of enzyme activity
Destruction of foams	bactericidal action
Extraction of flavourings	Modification of growth of living cells
Ultrasonic cutting	Sterilisation of equipment

US in Food Processing

& Ultrasound Food Cutting

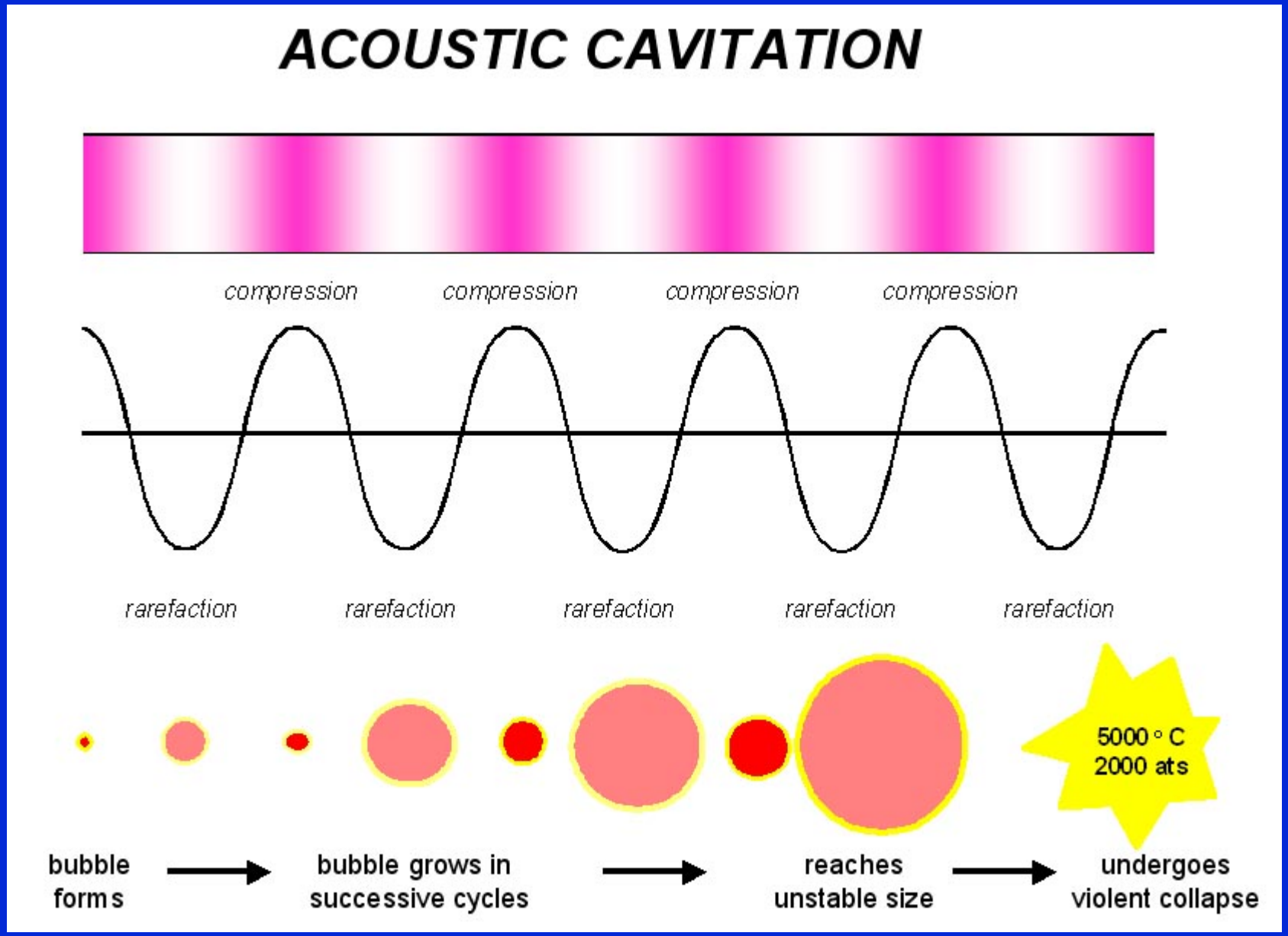
FISH



BENEFIT OF US CUTTING

- The quality of the cut face is visually excellent
- The product is virtually undisturbed
- Ultrasonic cutting can be easily automated
- US cutting speeds are similar to conventional cutting speeds
- Crumb and debris (product loss) are reduced
- Blade is self-cleaning
- Multi-layered products cut easily

& US cavitation : High Power Ultrasound

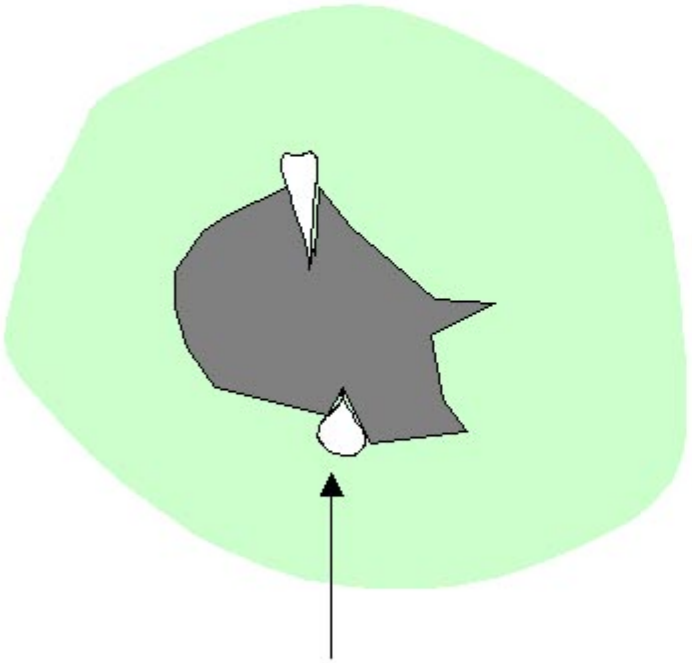


& Heterogeneous S-L : cavitation

ACOUSTIC CAVITATION

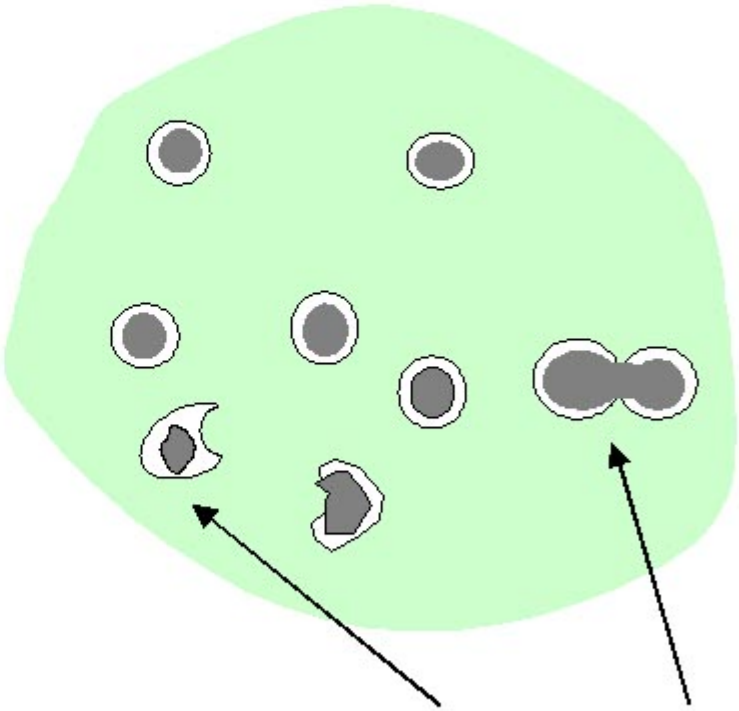
In the presence of a suspended powder

LARGE PARTICLES



surface cavitation due to defects leading to **fragmentation**

SMALL PARTICLES



collision can lead to

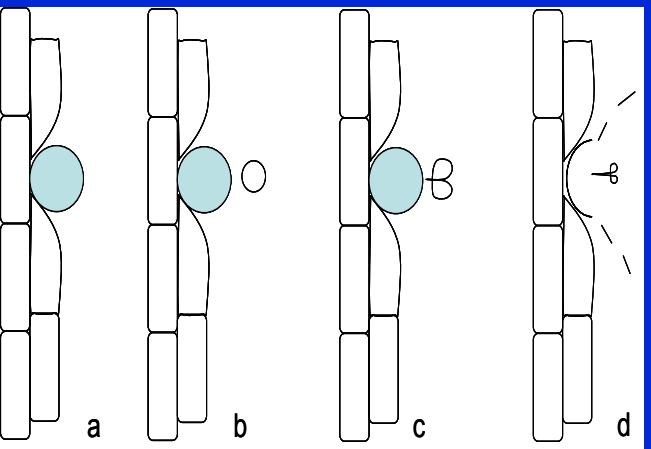
SURFACE EROSION or **FUSION**

US extraction of active compounds directly in edible oil

Solvent extraction of dried carrots using Hexane

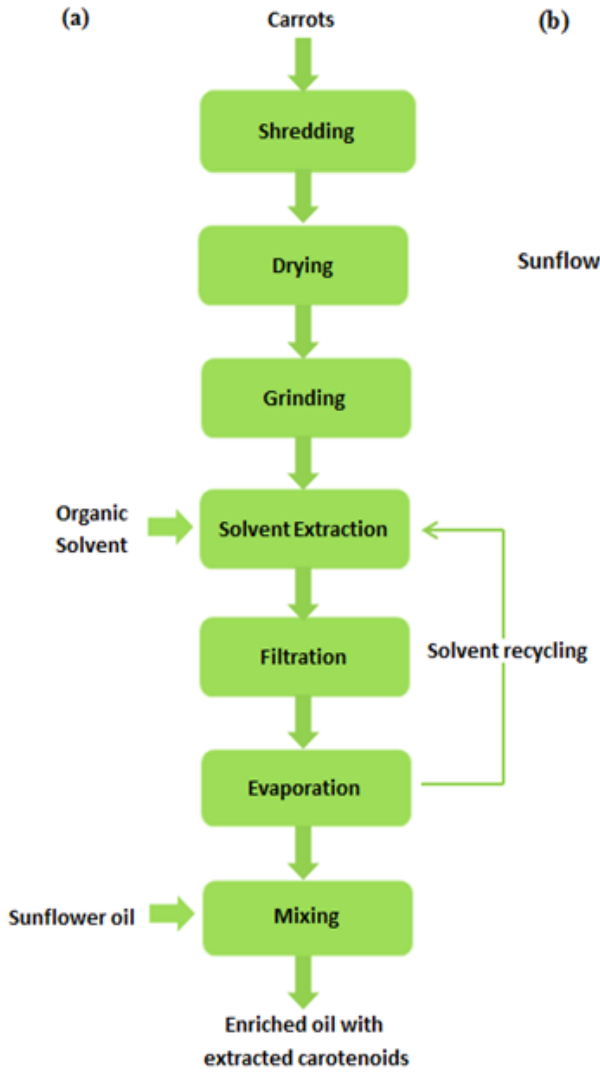
Evaporation of solvent

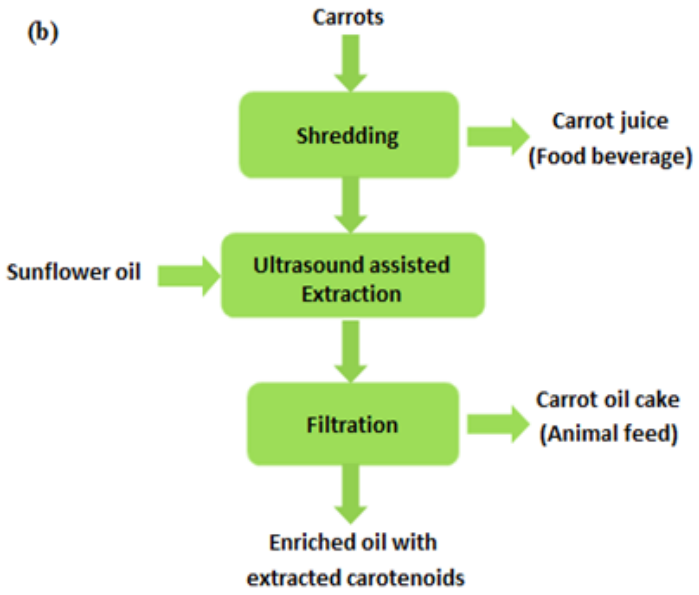
Mixing beta carotene powder with edible oil



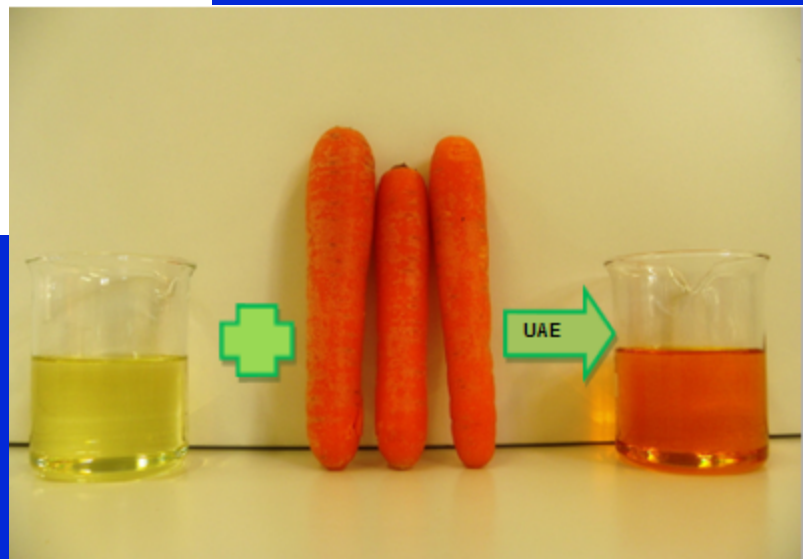
oil : 2 – 3 euros / litre

Organic Carrot oil
200 – 300 euros /litre





REUS
Ultrasound reactors
3 to 500 litres



& US accelerated maceration/extraction in industry

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Direct enrichment of olive oil in oleuropein by ultrasound-assisted maceration at laboratory and pilot plant scale

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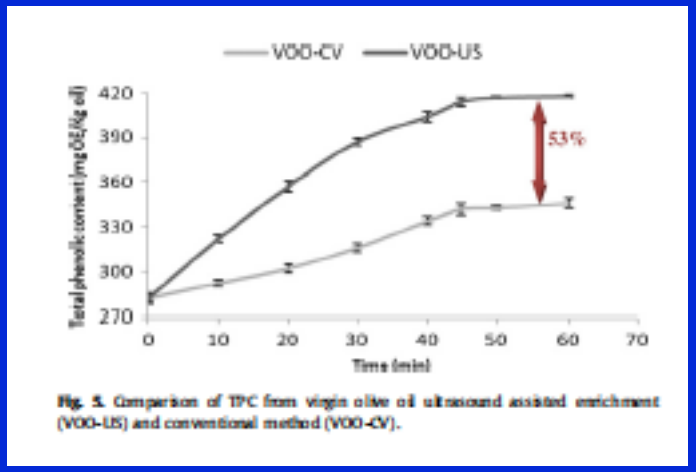

Fig. 5. Comparison of TPC from virgin olive oil ultrasound assisted enrichment (VOO-US) and conventional method (VOO-CV).

International Workshop on

"Alternative Solvents for Extraction, Purification and Formulation"

University of Avignon, Thursday 4 June 2015

http://blogs.univ-avignon.fr/international-workshop-on-alternative-solvent/

Contact: farid.chemat@univ-avignon.fr