



EXTRACTION OF OLEORESIN & ESSENTIAL OILS FROM SOLVENT EXTRACTION & SUPERCRITICAL FLUID EXTRACTION TECHNIQUES



Spices

Definition

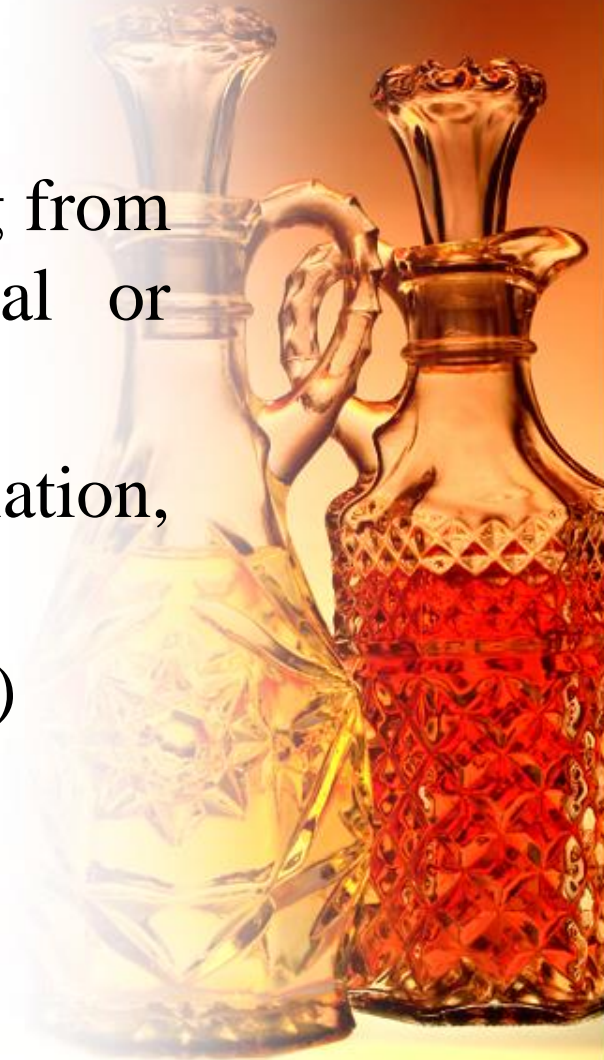
- ✓ “Aromatic, pungent vegetable substance used to flavor food”
- ✓ Originated from “species aromatacea” (*Latin*)
- ✓ FDA includes it as aromatic vegetables.
- ✓ It imparts flavor and seasoning to food rather than nutritional value.



Extraction

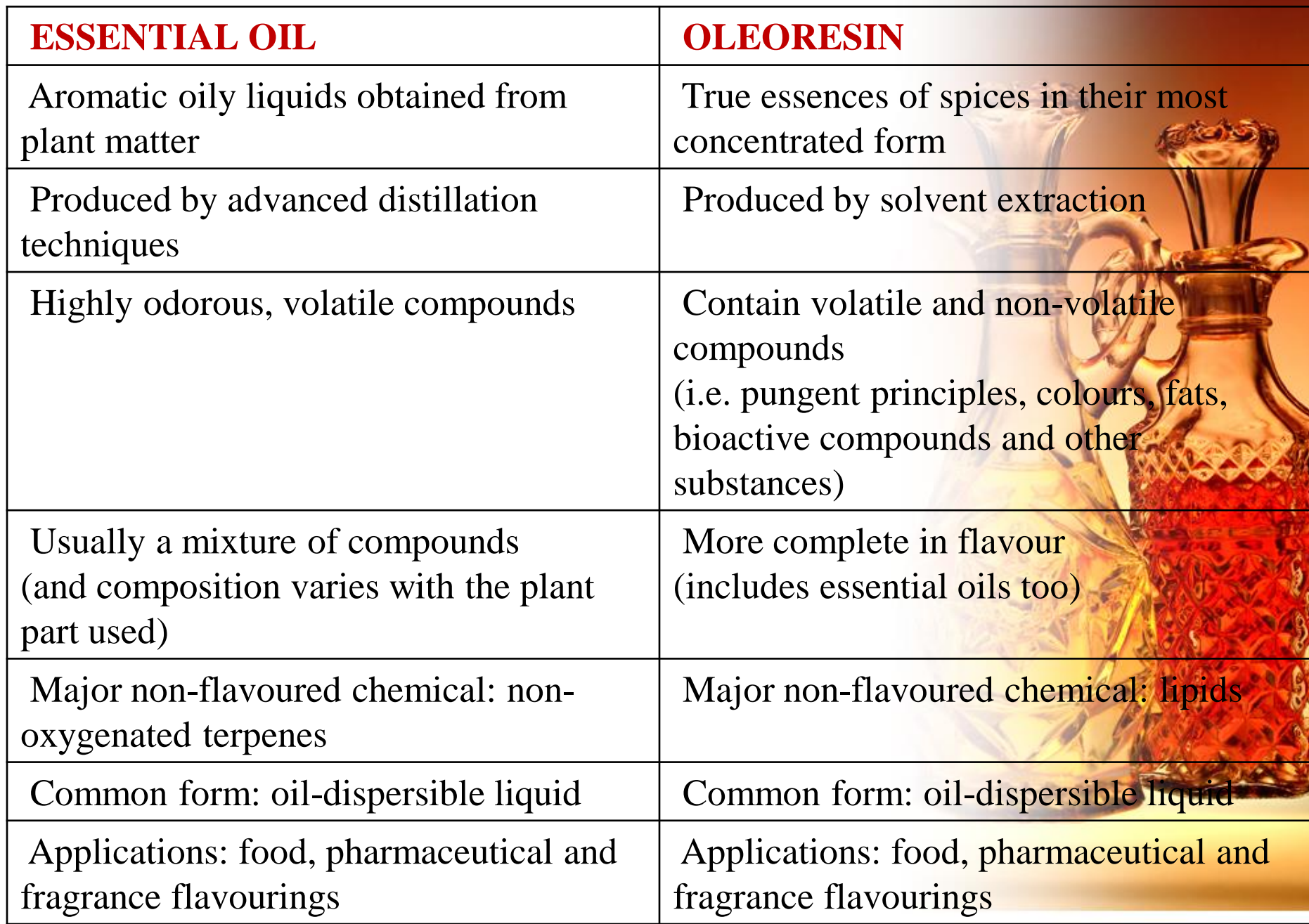
The process of obtaining something from a mixture or compound by chemical or physical or mechanical means

- **Physical extraction** (maceration, distillation, expeller, etc...)
- **Chemical extraction**(solvent, SCF etc...)



Difference Between Essential Oil & Oleoresin

ESSENTIAL OIL	OLEORESIN
Aromatic oily liquids obtained from plant matter	True essences of spices in their most concentrated form
Produced by advanced distillation techniques	Produced by solvent extraction
Highly odorous, volatile compounds	Contain volatile and non-volatile compounds (i.e. pungent principles, colours, fats, bioactive compounds and other substances)
Usually a mixture of compounds (and composition varies with the plant part used)	More complete in flavour (includes essential oils too)
Major non-flavoured chemical: non-oxygenated terpenes	Major non-flavoured chemical: lipids
Common form: oil-dispersible liquid	Common form: oil-dispersible liquid
Applications: food, pharmaceutical and fragrance flavourings	Applications: food, pharmaceutical and fragrance flavourings



SOLVENT EXTRACTION

Introduction

- ✓ Solvent extraction, also called *liquid-liquid extraction*, can be used to separate a substance from a solution by extraction into another solvent.
- ✓ It can be used either to recover a valuable substance from the original solution, or to purify the original solvent by removing an unwanted component.



Solvents used

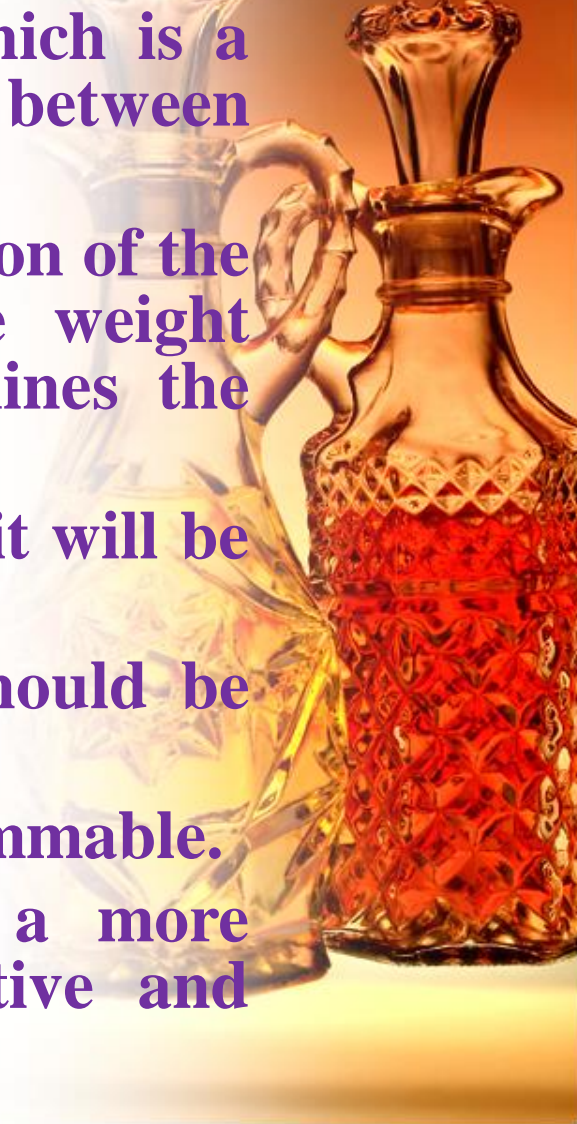
Chemical	Residue (mg/kg)	Boiling point(⁰C)
Acetone	Not more than 30	56
Methanol	Not more than 50	72
Ethanol	Not more than 50	78
Iso-propanol	Not more than 50	63
Di-chloro methane or 1,2- di-chloro ethane	Not more than 30	45
Light petroleum (hexane)	Not more than 25	69









SOLVENT SELECTION CONSIDERATIONS



- **Affinity for solute** : The selectivity, which is a measure of the distribution of the solute between the two solvents.
- **Partition ratio** : This is the weight fraction of the solute in the extract divided by the weight fraction in the raffinate. This determines the quantity of solvent needed.
- **Density**: The greater the density easier it will be to separate the solvents.
- **Miscibility**: Ideally the two solvents should be immiscible.
- **Safety**: Not toxic, nor dangerously inflammable.
- **Cost**: It may be worth considering a more expensive solvent if it is more effective and easier to recover.



Equipment used

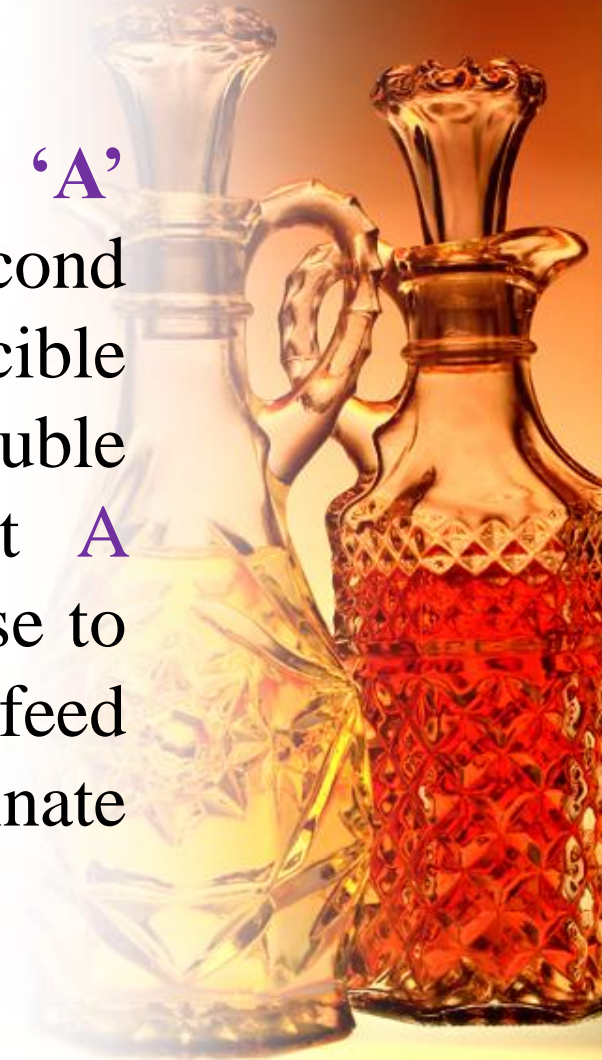
-  Mixer-settlers
-  Spray extraction towers
-  Packed extraction towers
-  Perforated-plate(sieve-tray) extraction tower
-  Pulsed packed and sieve-tray tower
-  Mechanically agitated extraction tower



Principle

Feed phase contains a component 'A' which is to be removed. Addition of a second phase (solvent phase) which is immiscible with feed phase but component A is soluble in both phases. Some of component A (solute) is transferred from the feed phase to the solvent phase. After extraction the feed and solvent phases are called the raffinate (R) and extract (E) phases respectively.

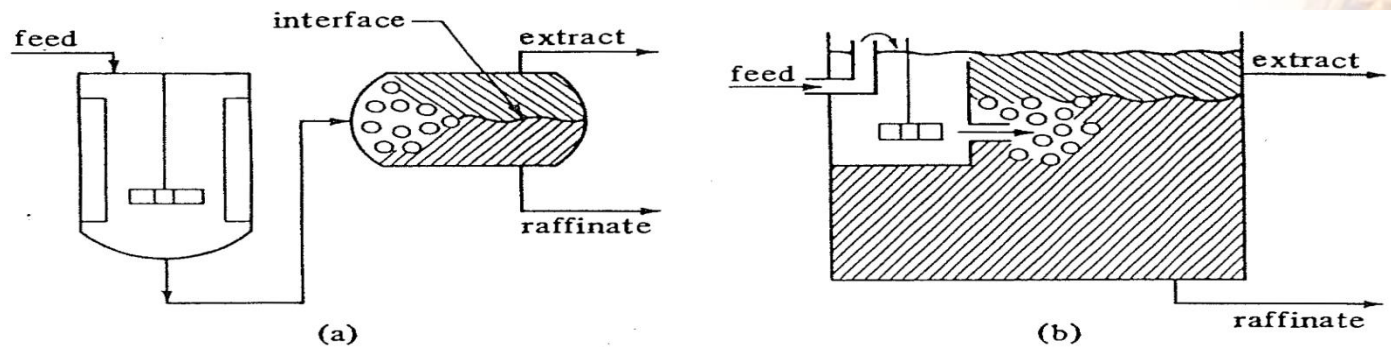
(Paul Ashall 2007)



Process

Mixer-settlers

- ✓ One phase is usually dispersed into the other in the form of small droplets.
- ✓ Sufficient contact time should give.
- ✓ Small droplets produce large interfacial area and faster extraction

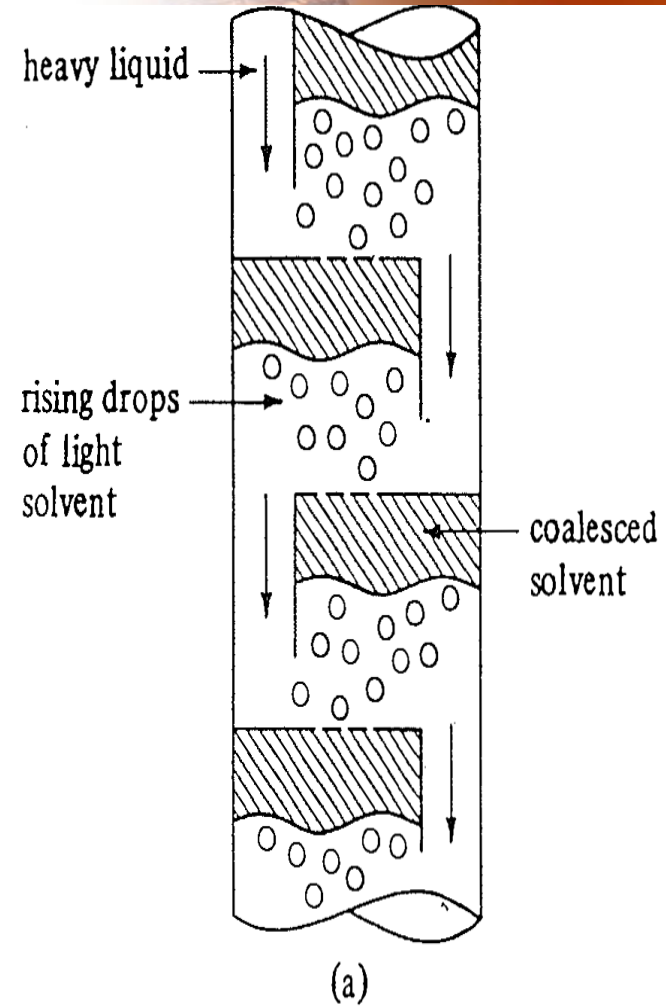


Typical-mixer-settlers for extraction: a) Separate mixer-settler, b) Combined mixer-settler



Spray Extraction Towers

- ✓ Mixing and settling proceed continuously and simultaneously.
- ✓ Heavy liquid enters at the top of the spray tower, fills the tower as a continuous phase, and flows out through the bottom.
- ✓ Light liquid enters through a nozzle distributor at the bottom, which sprays the droplets upward.



CONCLUSION

- ✓ Where the components in the feed have close boiling points. Extraction in a suitable solvent may be more economic if the relative volatility is below 1.2.
- ✓ It is more useful If the feed components form an azeotrope.
- ✓ If the solute is heat sensitive, and can be extracted in to a lower boiling solvent, to reduce the heat history during recovery.



Super Critical Fluid Extraction

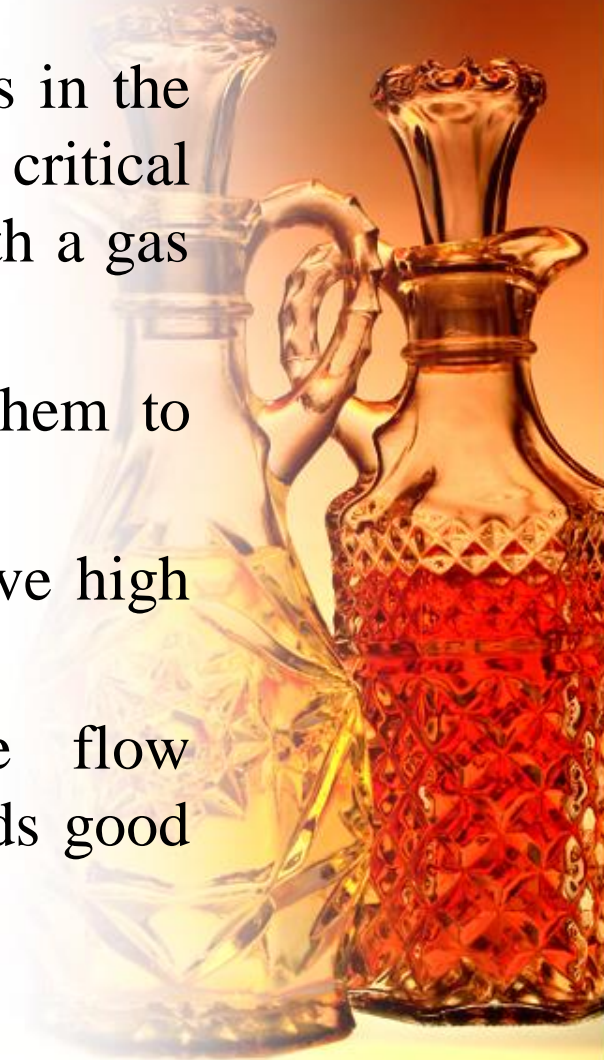
- ❖ Solvents are used largely.
- ❖ Attention is being paid to super critical fluids for wide variety of applications.








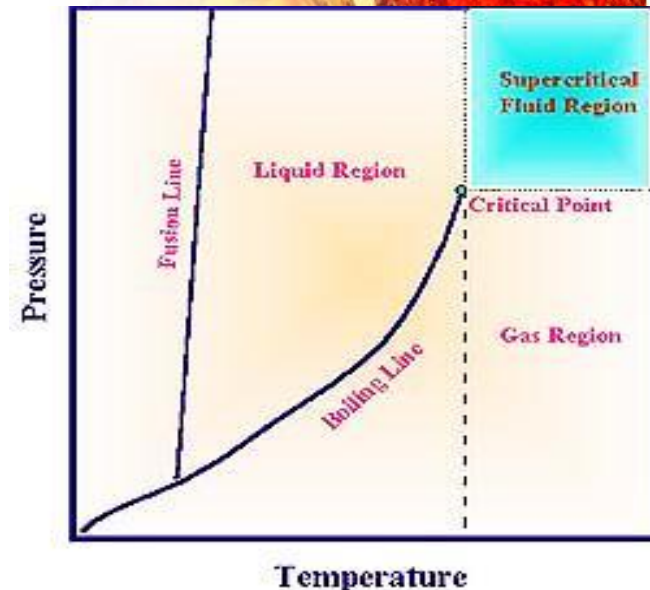
INTRODUCTION

- Supercritical fluids can be described as fluids in the temperature and pressure state over their critical point. They have properties that resemble both a gas and a liquid.
- Their gas-like diffusion coefficients allow them to penetrate solid materials;
- Their liquid-like densities enable them to have high solvating properties.
- Their low viscosity provides favourable flow characteristics, which make supercritical fluids good solvents with excellent efficiency and speed.



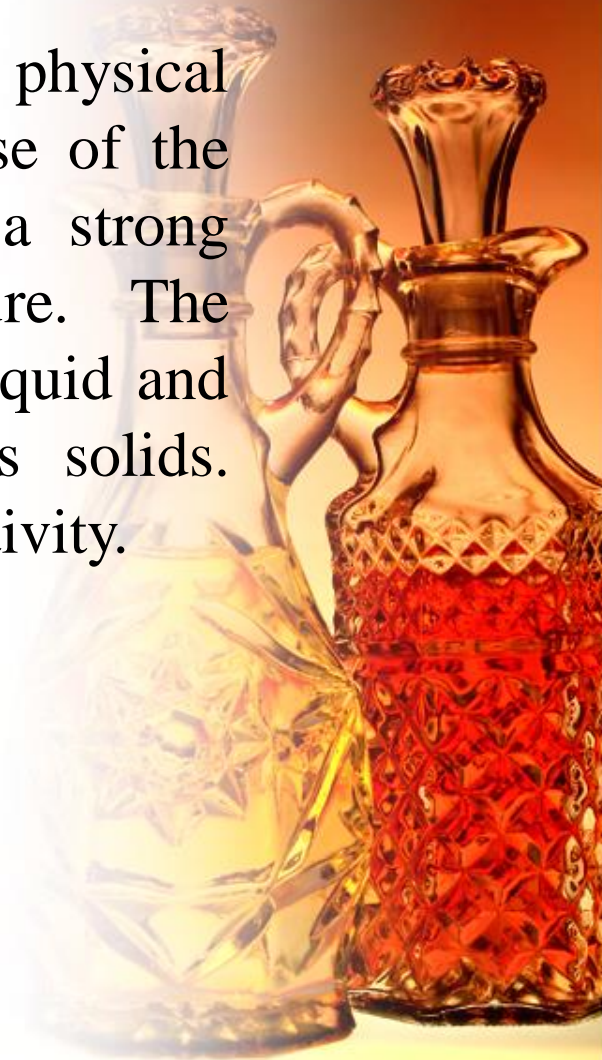
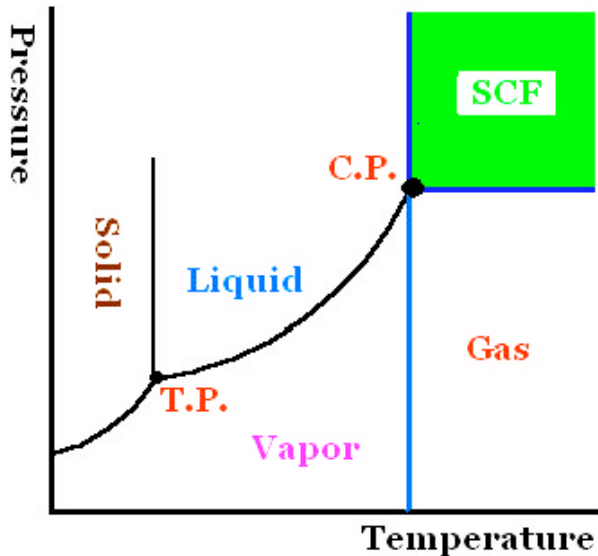
Definitions

-  **Critical temperature:-** The highest temperature at which a gas can be converted to a liquid by an increase in pressure.
-  **Critical pressure:-** The highest pressure at which a liquid can be converted to a traditional gas by an increase in liquid temperature.
-  **Critical point:-** It is the point where both the C_p and T_c are met.



Supercritical Fluids

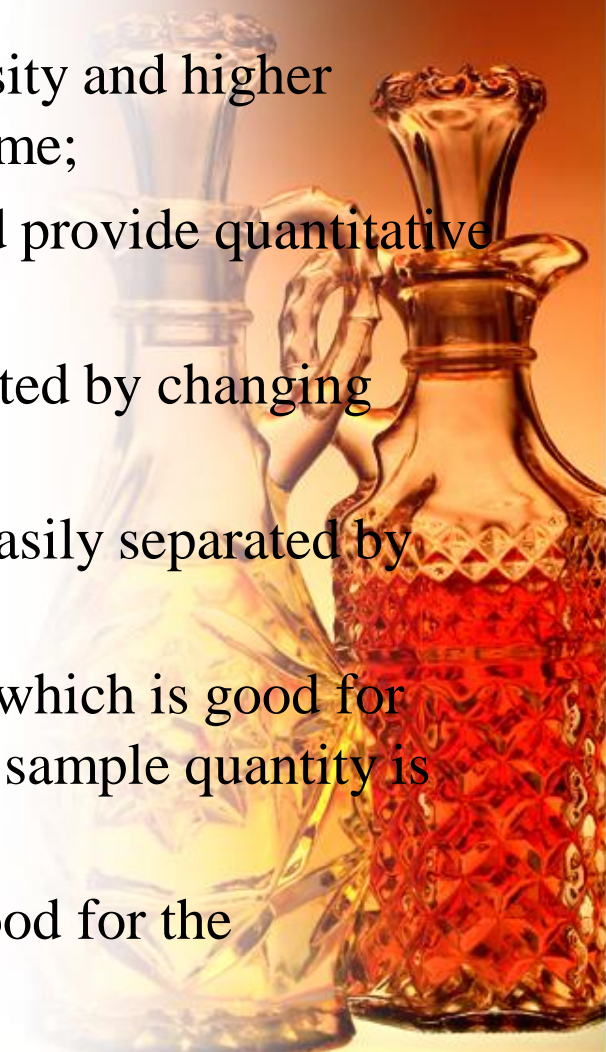
A supercritical fluid (*SCF*) is characterized by physical and thermal properties that are between those of the pure liquid and gas. The fluid density is a strong function of the temperature and pressure. The diffusivity of SF is much higher than for a liquid and *SCF readily penetrates* porous and fibrous solids. Consequently, SCF can offer good catalytic activity.



ADVANTAGES

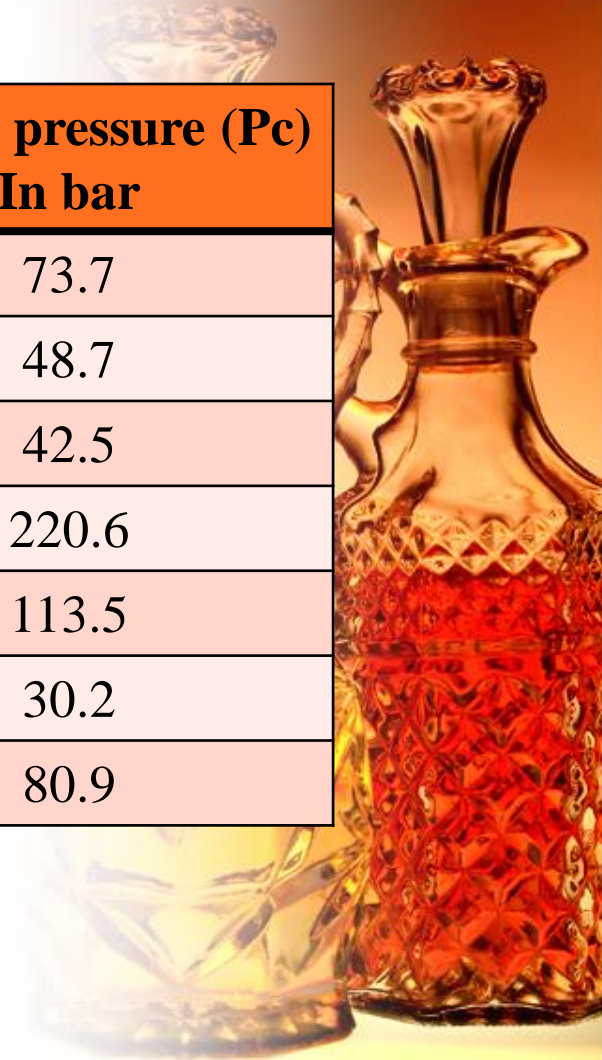
- (1) Supercritical fluids have relatively lower viscosity and higher diffusivity, which results in shorter extraction time;
- (2) Continuous fluid flowing through samples could provide quantitative or complete extraction;
- (3) The solvent power of the fluid can be manipulated by changing pressure and/or temperature;
- (4) Solutes dissolved in supercritical fluid can be easily separated by depressurization;
- (5) SFE is usually performed at low temperatures, which is good for studying thermally labile compounds;
- (6) Little sample quantity is needed;
- (7) Little or no organic solvent is needed, which is good for the environment.

Based on these advantages, SFE is regarded as an environmentally friendly alternative to conventional industrial solvent extraction (Haythel 2001)



Critical Properties Of Fluids

Fluid	Critical temperature (Tc) in K	Critical pressure (Pc) In bar
CO ₂	304.12	73.7
Ethane	305.3	48.7
Propane	369.8	42.5
Water	647.1	220.6
Ammonia	405.4	113.5
n-hexane	507.5	30.2
methanol	512.6	80.9



Properties Of Carbon Dioxide

- Non toxic.
- Non reactive.
- Low critical point.
- Cheaply available.
- SCC offers the ability to solute many non-polar materials.
- Non-flammable.
- Environmentally acceptable.

(Joseph et al. 1993)



Equipment's

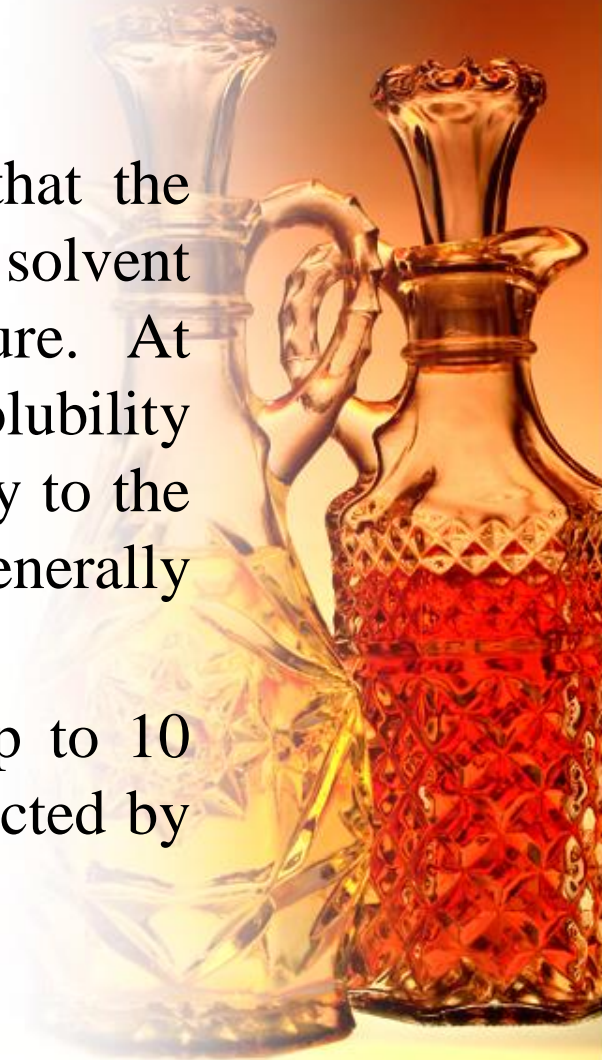
- Vessels
- Pumps and compressors
- Heat exchangers
- Piping and valves
- Control system



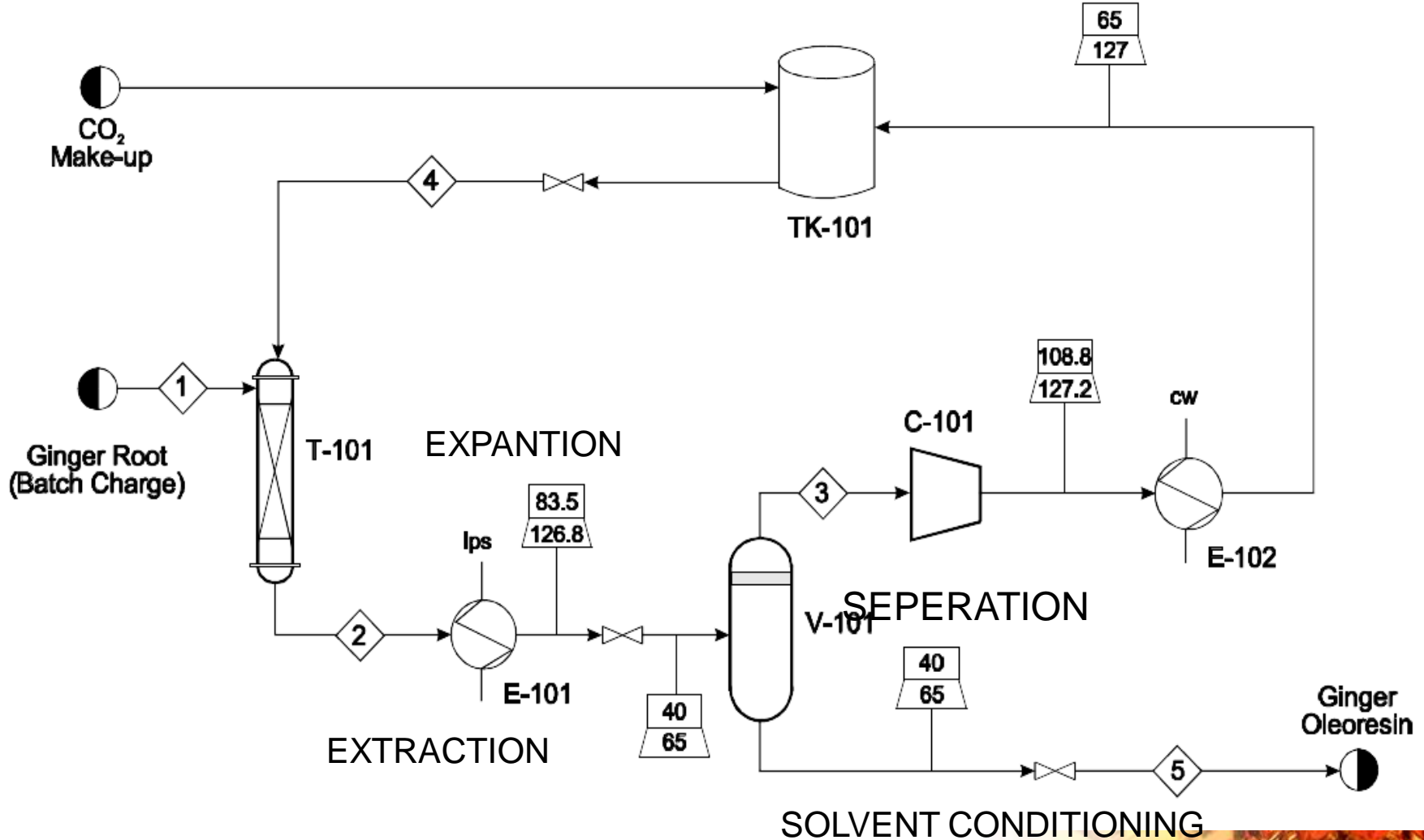
Laboratory Scale SFE.

Principle

- The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapour pressure of the solute and is generally negligible.
- In a SCF, however, solute solubility's of up to 10 orders of magnitude greater than those predicted by ideal gas law behaviour have been reported.



PROCESS



- 1) **T-101** Ginger Oleoresin Extraction Vessel
- 2) **E-101** Flash Vessel Pre-heater
- 3) **V-101** Flash Vessel
- 4) **C-101** CO₂ Recycle Compressor
- 5) **E-102** Recycle Cooler
- 6) **TK-101** CO₂ Storage Tank

Extraction From Flowers

(Example: Lavender)

- ❑ Temperature and pressure have been fixed
- ❑ Extractor—90 bar & 48⁰c
- ❑ First separator—80 bar & -10⁰c
- ❑ Second separator—25 bar & 0⁰c



Difference B/N Solvent And SCF Extraction

Solvent extraction	Super critical fluid extraction
Solvent presence is unavoidable. The residual ppm level of the solvent depends on the type of solvent used.	Is totally free of solvents and hence very pure.
Solvent removal requires extra unit operations and hence the cost and recovery of useful material is lower.	No extra unit operations needed and yield of useful material is very high.
Both polar as well as non polar colours are extracted.	Only non polar colours get extracted.
Inorganic salt content cannot be avoided, using the solvent extraction.	Totally free of inorganic salts using the SCF extraction.
Heavy metal content is also unavoidable and depends on the solvent, the recycle method for the solvent, the source of the raw material, and the material of construction of the contact parts of the machinery.	Totally free of heavy metals since they are not extractable even if they are present in the raw material. No heavy metals are present in CO₂ and the equipment.

Yield comparison of SE and SCFE

Spices	Yield (SE)	Yield(SCCE)
Clove	16.18	23.8
Cumin	12.2	21.0
Coriander	20	3.6
Ginger	4.9	4.6
Cinnamon	5.11	3.0
pepper	5.0	4.6
Ajwain	5.18	4.5

Source:- Mukhopadhyay, M., Natural Extracts Using Super Critical Carbon Dioxide, CRC press, Boca raton, FL., 2000





APPLICATIONS IN FOOD INDUSTRIES

- Decaffeination Of Coffee And Tea.
- Spice Extraction (Oil And Oleoresin).
- Deodorization Of Oils And Fats.
- Extraction Of Herbal Medicines.
- Extraction Of Color.
- Anti-oxidant From Plant Materials., etc.



Conclusion

- ✓ In particular, oleoresins extracted with supercritical fluids have a higher price, offer higher quality, and have less variations in the final product than those extracted with organic solvents.
- ✓ Replacement of organic solvents such as hexane, ethyl acetate, and chlorinated hydrocarbons with a kind solvent such as supercritical CO₂ is also considered desirable from an environmental standpoint.



References

- ② Tianchuan Du, 2006. Thesis On Super Critical Fluid Extraction And Analysis Of Plant Oil, *Louisiana State University*, USA
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- ② Jose.L.Martinez, 2007, *Supercritical Fluid Extraction of Nutraceuticals & Bioactive Compounds*, CRC Press, London
- ② Christie J. Geankoplis, *Transport Processes and Unit Operations*, 3rd edition, Prentice-Hall International, Inc

