Advancement in Solvent Extraction Process

By

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Aim of oilseed processing is to extract maximum oil and byproduct meal.

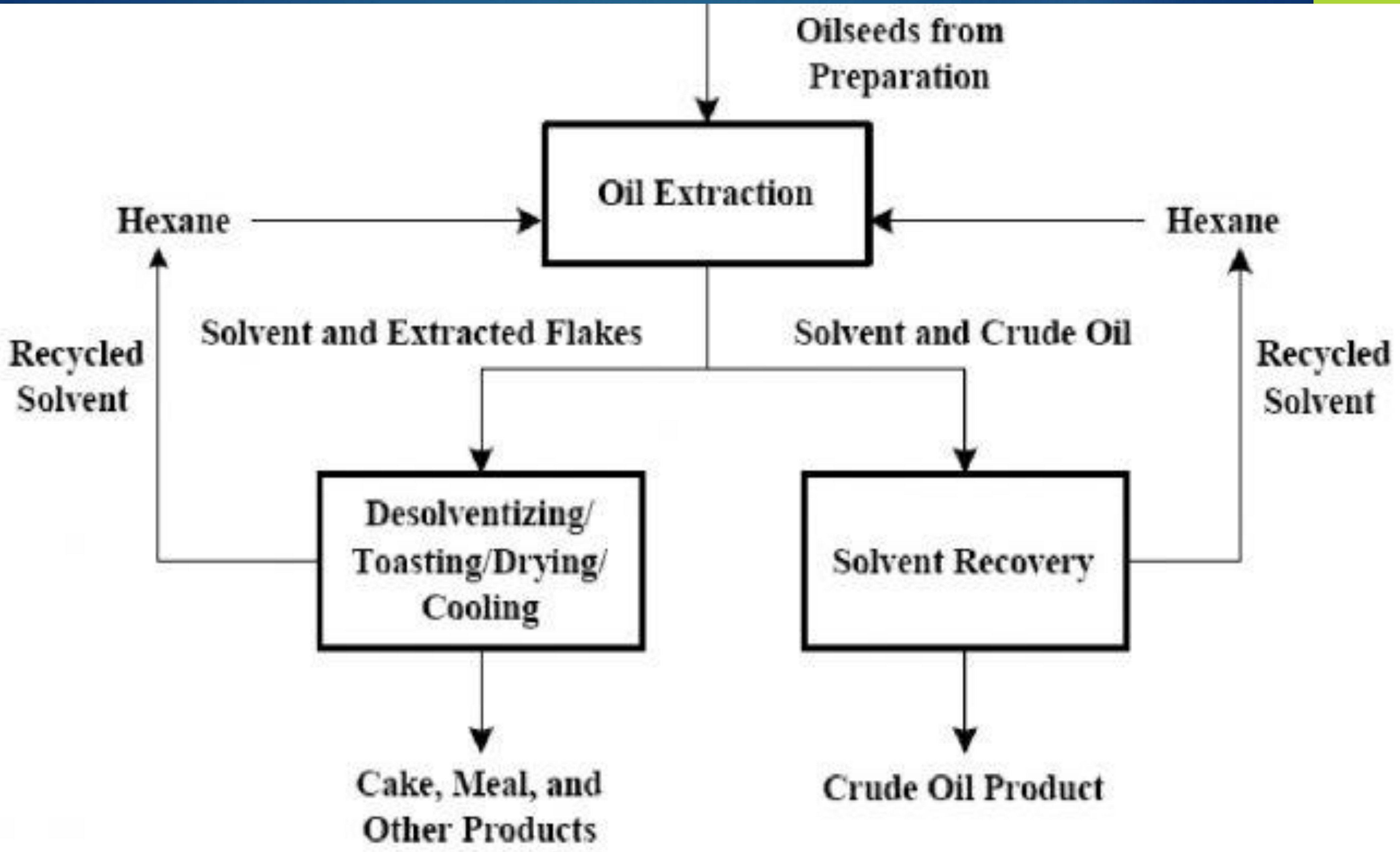
The conventional technology used for oil extraction from oilseeds is by solvent extraction. In solvent extraction, n-hexane is used as a solvent for its attributes such as simple recovery, non-polar nature.

Solvent extraction (solid-liquid extraction) refers to preferential dissolution of oil by contacting oilseeds with a liquid solvent. This is the most efficient technique to recover oil from oilseeds. The efficiency depends on the oilseed preparation prior to extraction, temperature, mode of operation (batch vs. continuous and co-current vs countercurrent)

The solvent is separated from the meal, and evaporated from the oil.

Flaking: to prepare materials for solvent extraction to increases the surface area of the material for better contact between solvent and seed during the solvent extraction process

Typical flake thickness is in the range of 0.01-0.015 inch or 0.25-0.37 mm.


Oilseeds from
Preparation
Oil Extraction
Hexane
Hexane
Solvent and Extracted Flakes
Solvent and Crude Oil
Recycled
Solvent
Recycled
Solvent
Desolventizing/
Toasting/Drying/
Cooling
Solvent Recovery
Cake, Meal, and
Other Products
Crude Oil Product

Initially, batch type oil extraction systems were used.

Use of large-scale continuous processes began in the early 1920s.
Immersion and percolation type continuous extractors are used for commercial solvent extraction of oilseeds.

In immersion-type extractors, flaked oilseeds are completely submerged in solvent. Particle size should be as small as possible to achieve maximum contact between seed and solvent. Immersion-type extractors are suitable for small-scale production facilities.

In percolation-type extractors, solvent is sprayed on flaked seeds. Solvent drains through the bed and extracts oil.

The newer extractor designs are horizontal and rotary type. The design principle for horizontal extractors is similar to the earlier extractors. But the baskets rotate in a single horizontal plane rather than vertically.

A popular rotary-type design extractor, holds the flaked seeds in cells, which rotate in a horizontal plane around a vertical axis. The extractor has four countercurrent extraction stages.

Due to the relative inertness of the non-oil constituents of the oilseed, equilibrium is reached when the concentration of oil in the micella within the pores of the solid is equal to the concentration of oil in the free micella, outside the solid.

The rate of extraction can be increased considerably by increasing the temperature in the extractor. Higher temperature means higher solubility of the oil, higher diffusion and lower micella viscosity. An open, porous structure of the solid material is preferable, and facilitates diffusion & percolation.

Most of the resistance to mass transfer lies within the solid, the rate of extraction can be increased by providing agitation and free flow in the liquid phase around the solid particles. Too much agitation is to be avoided, in order to prevent extensive disintegration of the flakes.

Counter-current multistage extraction: the flakes and the solvent move in opposite directions.

Flakes with the lowest oil content are contacted with the leanest solvent, resulting in high oil yield and high driving force throughout the extractor.

Desired properties of ideal solvents

* Good solubility of the oil.

* Poor solubility of non-oil components.

* High volatility (i.e. low boiling point), so that complete removal of the solvent from the micella and the meal by evaporation is feasible and easy.

* Also the boiling point should not be too low, so that extraction can be carried out at elevated temperature to facilitate mass transfer.

* The solvent should be chemically inert to oil and other components of seed.

* Non toxic, Non-inflammable, non-explosive, Non-corrosive

* Commercial availability in large quantities and economical

But the ideal solvent possessing all these properties is not in existence.

Most of the requirements, with the notable exception of flammability and explosiveness, are met by low-boiling hydrocarbon fractions obtained from petroleum.

A typical commercial solvent for oil extraction would have a boiling point range (distillation range) of 65 to 70^{o}C and would consist mainly of hexane. The main limitation of light hydrocarbon solvents is the flammability.

Shortcomings of hexane as a solvent lead to the development for alternative solvent

Trichloroethylene, was in commercial use for a short period in the early 1940's, but had to be abandoned when it was discovered that the meal prepared in this way was toxic to animals.

Aqueous Extraction

Aqueous extraction (AE) is traditionally used in many developing countries. The process called water-flotation has been used for extracting coconut and palm oil. It involves heating oily material, grinding with or without water, and boiling with water to liberate the oil.

The oil, which appears on the surface, is collected and heated to remove moisture.

Oil extraction yields < 50 %.

This process can be used to extract oil as well as high quality proteins.

To improve oil and protein extraction yields: Enzymes or surfactants have been added to the extraction medium.

Limitations: Lower efficiency of oil extraction,

Regulatory, safety, and environmental issues have prompted the development of aqueous enzymatic extraction (AEE) for extracting components from oil-bearing materials

In comparison with solvent extraction, the use of an aqueous medium is much safer, environmental-friendly. Aqueous medium allows simultaneous separation of phospholipids from the oil (degumming can be avoided)

Alternative Solvents

- ✓ Water
- ✓ Methanol, ethanol, isopropanol
- ✓ Benzene, toluene
- ✓ Chloroform, carbon tetra chloride
- ✓ Di methyl ketone, ethyl methyl ketone
- ✓ Di ethyl ether, di methyl ether
- ✓ CS2 and CO2

Despite considerable research efforts to develop alternative solvent systems, extraction with light hydrocarbons continues to be, practically, the only commercial solvent extraction process for oil.

Advance Methods of Extraction

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MICROWAVE ASSISTED EXTRACTION

INTRODUCTION

- Microwave-assisted extraction is an efficient method for deriving natural compounds from raw plants.
- Microwave extraction allows organic compounds to be extracted more rapidly, with better yield as compared to conventional extraction methods.

MICROWAVE THEORY

- Microwaves are non-ionizing electromagnetic waves of frequency between 300MHz to 300 GHz and positioned between the X-ray and infrared rays in the electromagnetic spectrum.

- Microwaves are made up of two oscillating perpendicular fields i.e.
  - Electric field
  - Magnetic field

EXTRACTION PRINCIPLE

- The MAE process is as follows:
  - Microwave radiation
  - Moisture get heated up
  - Moisture evaporates
  - Generation of tremendous pressure on cell wall
  - Swelling of plant cell
  - Rupture of the cell
  - Leaching out of phyto-constituents

- This phenomenon can be intensified if the plant matrix is impregnated with solvents with higher heating efficiency under microwave.

FACTORS AFFECTING MAE

Solvent and solvent to feed ratio –

- Appropriate solvent is very important for obtaining optimal extraction yields.
- Solvent should absorb microwave energy(ethanol, methanol, water).
- Solvent required is less in MAE as compared to conventional extraction process.

FACTORS AFFECTING MAE

Extraction time –

- By increasing extraction time, quantity of analytes is increased but there is the risk of degradation.

- Extraction times in MAE are very short compared to conventional techniques and usually vary from a few minutes to a half-hour, avoiding possible thermal degradation and oxidation.

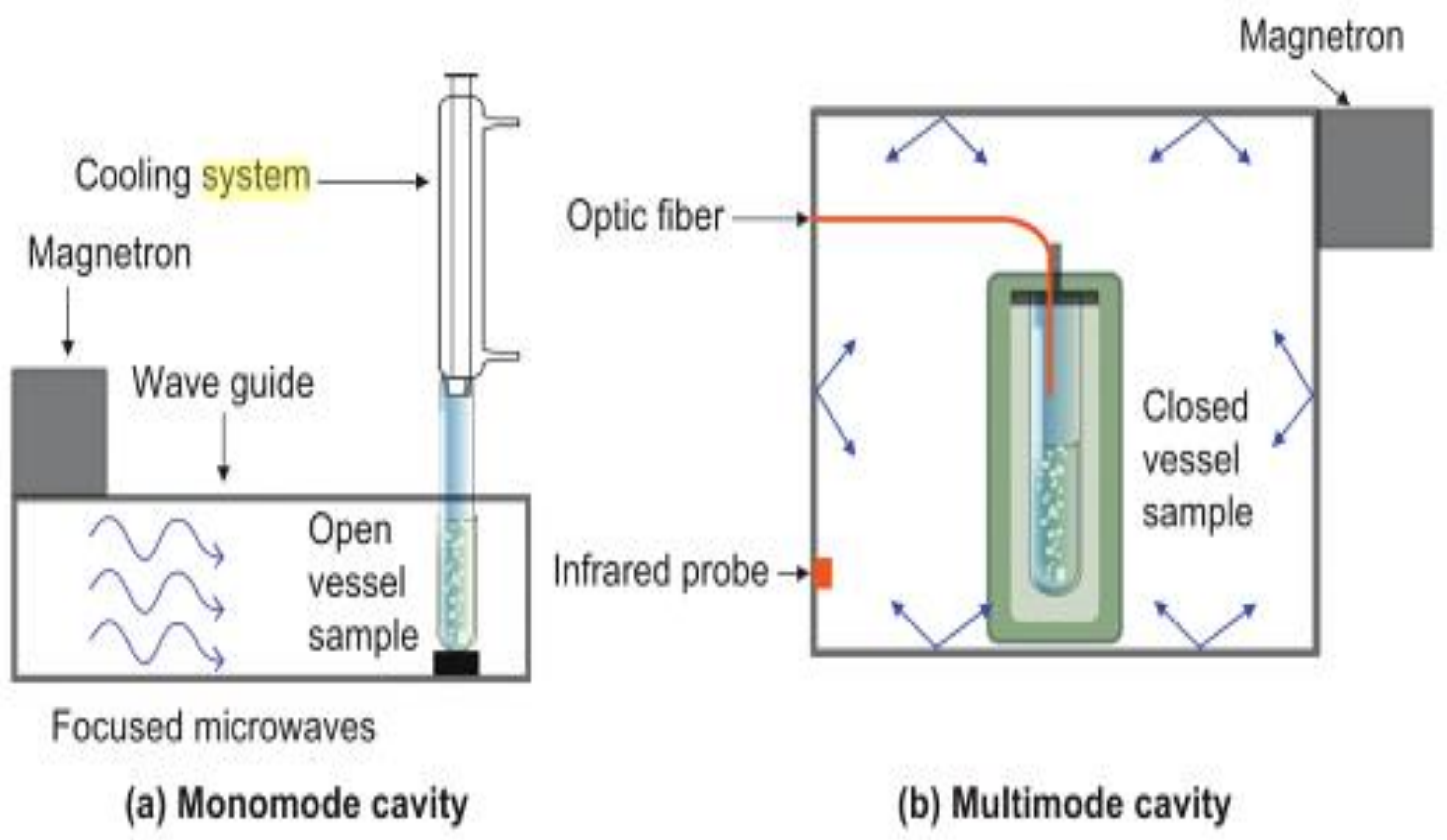
INSTRUMENTS

- There are two types of commercially available MAE systems:
  - Closed extraction vessels
  - Focused microwave ovens

- The former performs extraction under controlled pressure and temperature.

- In the latter, only a part of the extraction vessel containing the sample is irradiated with microwave.

Open and Closed-vessel system



Schematic view of (a) open vessel in monomode focused microwave oven and (b) closed vessel in multimode microwave oven, adapted from M. Letellier and H. Budzinski, *Analysis*, 1999, **27**, 259.

INSTRUMENTS

- Both closed vessel type and the focused type are available as multi-mode and single-mode or focused system.
- A multi-mode system allows evenly radiation of sample by random dispersion of microwaves.
- Single-mode (focused system) allows focused radiation on a restricted zone by a much stronger electric field.

INSTRUMENTS

- Both multi-mode and focused system comprises of the following four components:
  - Microwave generator: magnetron which generates microwave energy.
  - Wave guide: propagate microwave to microwave cavity.
  - The applicator: where the sample is placed
  - Circulator : allow microwave to move in forward direction.

Advantages

- The advantages that MAE has over Soxhlet are:
  - Reduction in extraction time
  - Improved yield
  - Better accuracy
  - Suitable for thermolabile substances

SUPERCRITICAL FLUID EXTRACTION

- The most common method for extraction: hydrocarbon or chlorinated organic solvents using a Soxhlet extractor.
- Unfortunately, liquid extraction frequently fails to meet several of

  the ideal criteria. It disadvantages include

  - the extraction time is long;

  - a large amount of solvent is used;

  - agitation can not be provided in the Soxhlet device to accelerate the process;

  - the large amount of solvent used requires a evaporation/concentration procedure;

  - also there is a possibility of thermal decomposition of the target compounds for a long time.
- Thus the use of Supercritical fluids for the separation of analytes was explored

What is supercritical fluid extraction?

- Supercritical fluid extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent.

Supercritical Fluid

- Supercritical state is achieved when the temperature and the pressure of a substance is raised over its critical value
- Supercritical Fluids :

- have characteristics of both gases and liquids.

It can diffuse through solids like a gas, and dissolve material like a liquid.

- the dissolving power of a solvent depends on its density, which is highly adjustable by

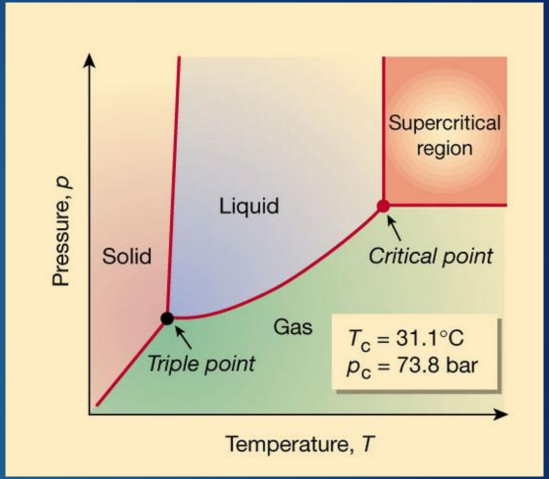
changing the pressure or/and temperature;

- has a higher diffusion coefficient and

- lower viscosity and lower surface tension than a liquid solvent, leading to more favorable mass transfer.

- also it leaves no toxic residue behind.

Thus Supercritical Fluids are suitable as a substitute for organic solvents



Critical Properties of Some Compounds

Compound	Boiling point at 1 atm °C	Critical temperature °C	Critical pressure bar	Critical density kg/L
CO_2	-78.9 *)	31.3	73.8	0.448
NH_3	-33.4	132.3	112.8	0.240
H_2O	100.0	374.4	227.8	0.344
N_2O	-89.0	36.2	72.4	0.457
Methanol	64.7	240.5	79.9	0.272
Ethanol	78.4	243.4	64.0	0.276
2-propanol	82.5	235.3	48.0	0.273
Ethane	-88.0	32.4	49.3	0.203
n-propane	-44.5	96.8	43.0	0.220
n-Butane	-0.5	152.0	38.5	0.228
n-Pentane	36.3	196.6	34.3	0.232
n-Hexane	69.0	234.2	30.6	0.234

- Supercritical CO_2 is the most widely explored fluid for extraction of analytes
- Supercritical fluids such as Freon-22, nitrous oxide and hexane have been considered. However, their applications are limited due to their unfavorable properties with respect to safety and environmental considerations

Supercritical CO_2

- Critical state of CO_2 is at a temperature of only 304 K and pressure of 7.3 MPa.
- CO_2 is

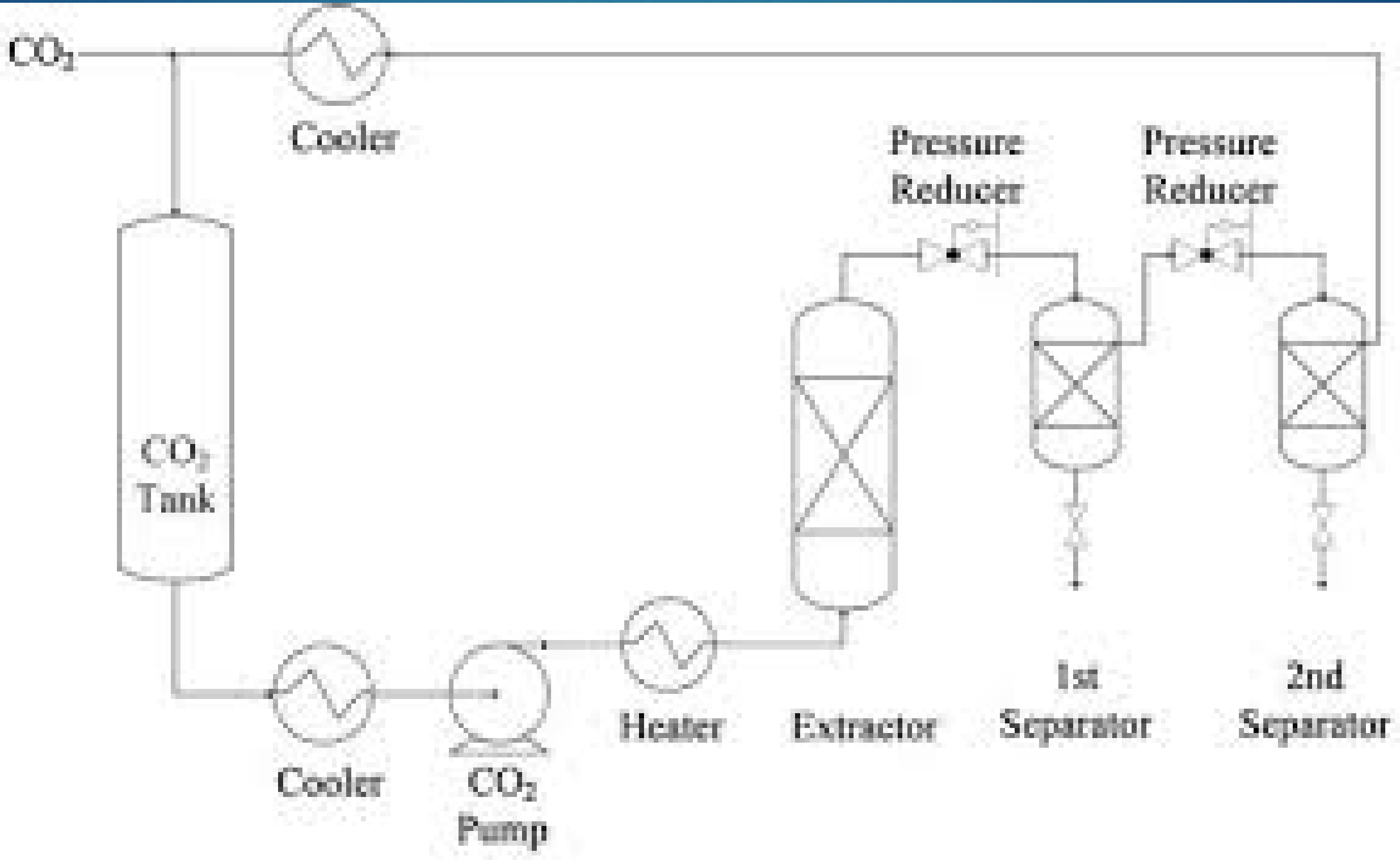
  - non-flammable, non-explosive and non-toxic

  - odorless and tasteless

  - cheap and widely available

  - easy recovery
- Supercritical CO2 is a good solvent for the extraction of non-polar compounds such as hydrocarbons.
- Addition of polar co-solvents (modifiers) to the supercritical CO2 significantly increase the solubility of polar compounds.
- Among methanol, ethanol, acetonitrile, acetone, water, ethyl ether and dichloromethane, methanol is the most commonly used because it is an effective polar modifier and is up to 20% miscible with CO2.
- However, ethanol may be a better choice in SFE of nutraceuticals because of its lower toxicity

The Extraction Process



Various Factors to keep in mind

- To develop a successful SFE, several factors must be taken into consideration.
- These factors include the selection of

  - supercritical fluids,

  - plant material preparation method,

  - modifiers and

  - extraction conditions like

    - Temperature

    - Pressure

Various components that be extracted using SFE

- Seed oil
- Essential oils
- Antioxidants like
  - Phenolic compounds
  - tocochromanols
  - vitamins
  - carotenoids
  - flavanoids
- Alkaloids
- Gylcosidic compounds
- Bioactive compounds

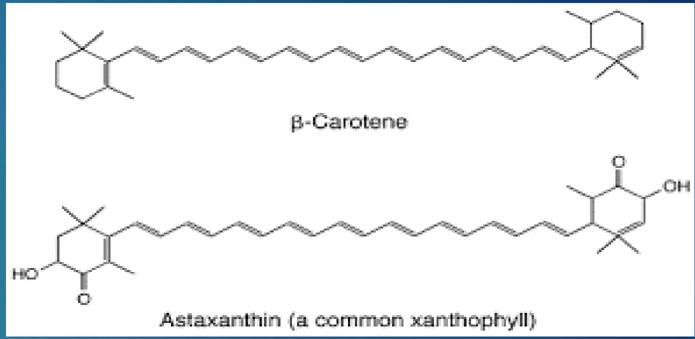
Since SFE is an expensive techniques it is usually used to extract high value products.

Carotenoids

- Carotenoids in food are recognized as antioxidants and pigments and are divided into two subgroups:

  - carotenes and

  - oxygenized hydrocarbons xanthophylls.



- Organic solvent do not have the desired selectivity for the extraction of carotenoids also they may decompose at elevated temprature.
- It was observed that a higher yield was obtained by using SFE to extract carotenoids, even at low temperature,
- A large number of studies have been conducted using a range of raw materials.

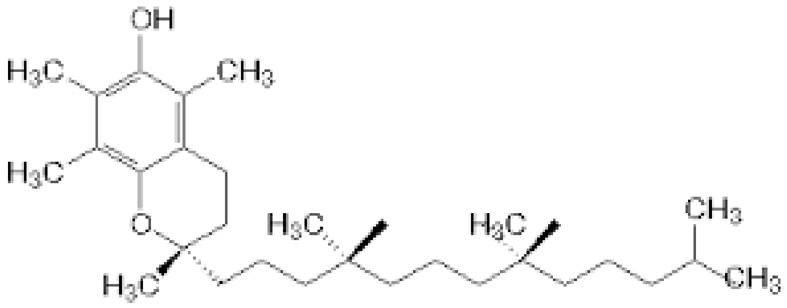
Compounds	Plant Material	Extraction Method/ Solvent
Astaxanthin	Microalgea (Chlorella vulgaris)	SFE/CO_2
Lutein	Pumpkin	SE, SFE/CO_2
Lycopene	Tomato	SFE/CO_2 + ethanol, water, canola oil
Zeaxanthin	Microalgea	SFE/CO_2 + ethanol
β-carotene	Palm oil	SFE/CO_2

Tocochromanols

- SCFE offers several advantages for the enrichment of tocochromanols over conventional techniques such as vacuum distillation, in particular a lower operating temperature
- Most promising as feed materials are crude palm oil (CPO) and soybean oil deodorizer distillate (SODD).
- Since these products show higher solubility in CO_2 than TG, they can be easily separated from the oil.

Vitamin E

- Vitamin E is an antioxidant, it also acts as an enzymatic regulator and has an effect on gene expression and is used to prevent and repair cell and tissue damage.
- Recent studies have demonstrated that synthetic vitamin E, is less effective than natural vitamin E. Thus extraction of vitamin E from natural sources has received increasing interest.
- Several natural sources have been used to isolate vitamin E using supercritical carbon dioxide extraction



Vitamin E (α-tocopherol)

- In a study conducted by Ge et. al. using wheat germ it was observed that the amount of total vitamin E extracted was higher than those obtained using traditional extraction methods.
- Also, the quantities of α, γ and δ-tocopherol much higher using SFE.
- However, the n-hexane extracts, and mainly, the chloroform/methanol extracts, showed higher selectivity towards β-tocopherol
- Vitamin E was also extracted from the by-products of the oil industry eg: olive pomace and soybean deodorizer distillate

Flavonoids

Component	Plant material	Method/solvent
Anthocyanins	Raspberry, Blueberry, Cranberry	SFE/CO2
Apigenin	Chamomile	SFE/CO2 + ethanol
Apigenin	Olive	SFE/CO2
Catechin	Tea	SFE/CO2 + ethanol
Cinnamic acid	Olive oil residues	SFE; SE/CO2; ethanol
Coumarins	Rice	SFE/CO2 + ethanol
γ-oryzanol	Rice	SFE/CO2

Essential Fatty Acids

Component	Plant material	Method/solvent
Linoleic acid	Borage	SFE/CO_2 + methanol
Linoleic acid	Olive	SFE/CO_2
α-linolenic acid	Flax	SFE/CO_2

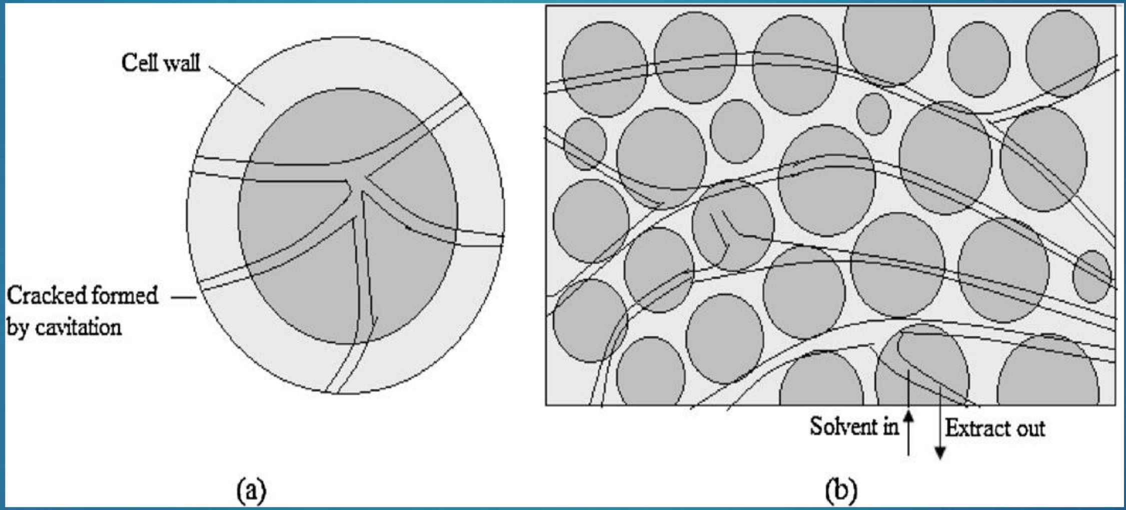
ULTRASOUND EXTRACTION

Introduction

- This technique was developed in 1950 at laboratory-scale size equipment
- The used ultrasonic waves have a frequency of 20 kHz–1 MH
- EO stored in internal and external structure
  - External- sonication
  - Internal- Milling
- Extraction mechanism
  - diffusion through the cell walls
  - washing out the cell content once the walls are broken

Principle

- Sound waves, which have frequencies higher than 20 kHz, are mechanical vibrations in a solid, liquid and gas.
- cavitation phenomena.

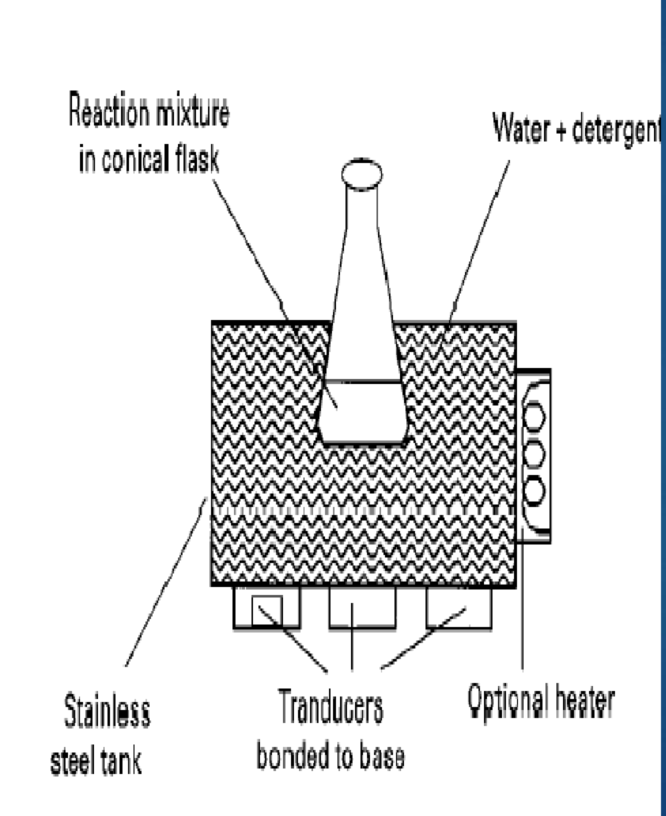


Improves mass transfer

Instruments

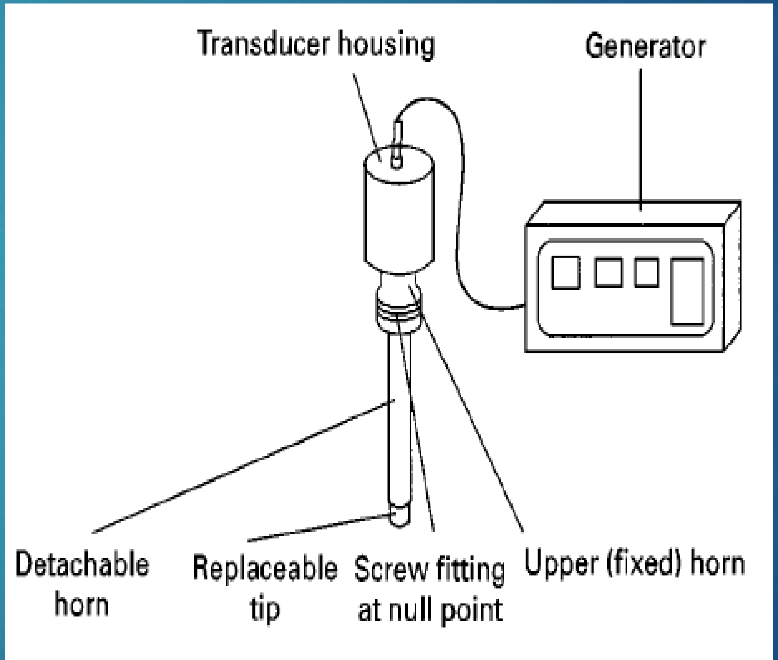
1. Bath System

- Tranducer located below the tank
- **Application**- Degassing, extraction of adsorbed metal and pollutats
- **Drawback-** Lack of power adjustment control

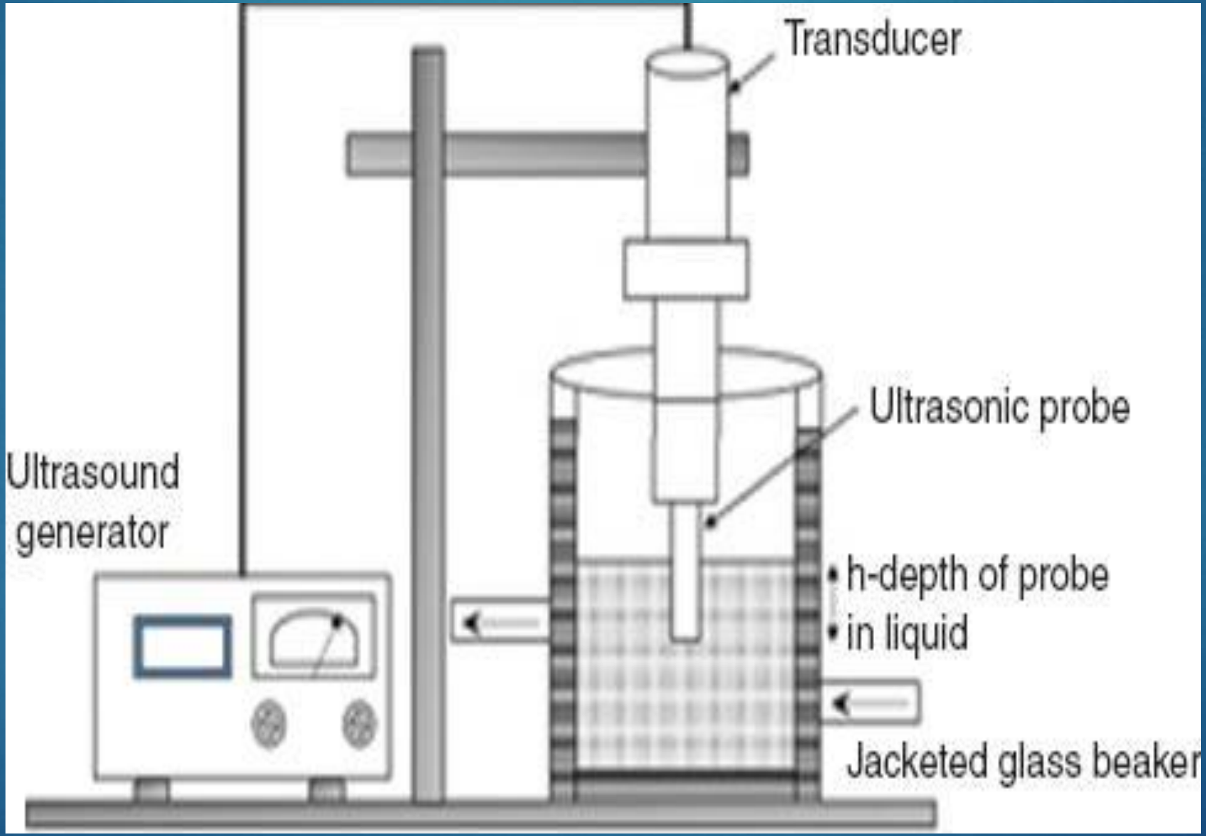


- 2. Probe system

  - 100 fold greater power
  - **Feature**- ultrasonic energy directly introduce into system
  - **Probe**- Generator
    - - Upper horn
    - - Detachable horn



Extraction using probe



Advantages

- Ultrasound-assisted extraction is an inexpensive, simple and efficient alternative to conventional extraction techniques.
- Increase of extraction yield and faster kinetics.
- Ultrasound can also reduce the operating temperature allowing the extraction of thermolabile compounds.
- Compared with other novel extraction techniques such as microwave-assisted extraction, the ultrasound apparatus is cheaper and its operation is easier.

Disadvantages

- Scale up can be problem
- Higher energy requirement
- Special training required for handling the instrument
- One disadvantages of the procedure is the occasional but known deterious effect of ultrasound energy(more than 20 khz) on the active constituents of medical plants through formation of free radicals and consequently undesirable changes in the drug molecules.

Application

- Ultrasound-assisted extraction has been used to extract nutraceuticals from plants such as essential oils and lipids.
- Extraction of protein
- Bioactive extraction from plant materials- polyphenol, anthocyanins, tartaric acid, aroma compound, etc.
- Sonication can be used for the production of nanoparticles, such as nanoemulsions, nanocrystals, liposomes and wax emulsions, as well as for wastewater purification
- Production of biofuels
- It is applied in pharmaceutical, cosmetic, water, food, ink, paint, coating, wood treatment, metalworking, nanocomposite, pesticide, fuel, wood product and many other industries.
- Sonication can also be used to initiate crystallisation processes and even control polymorphic crystallisations.