Post Harvest Operations and Processing of Fruits, Vegetables, Spices and Plantation Crop Products

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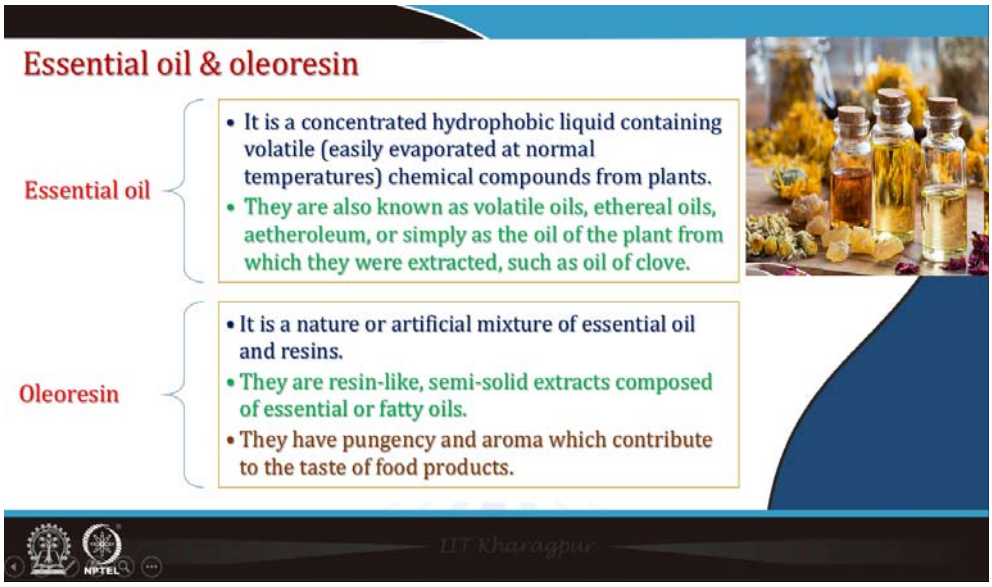
Lecture 44
Essential Oil and Oleoresin

This lecture is about Essential Oil and Oleoresin.

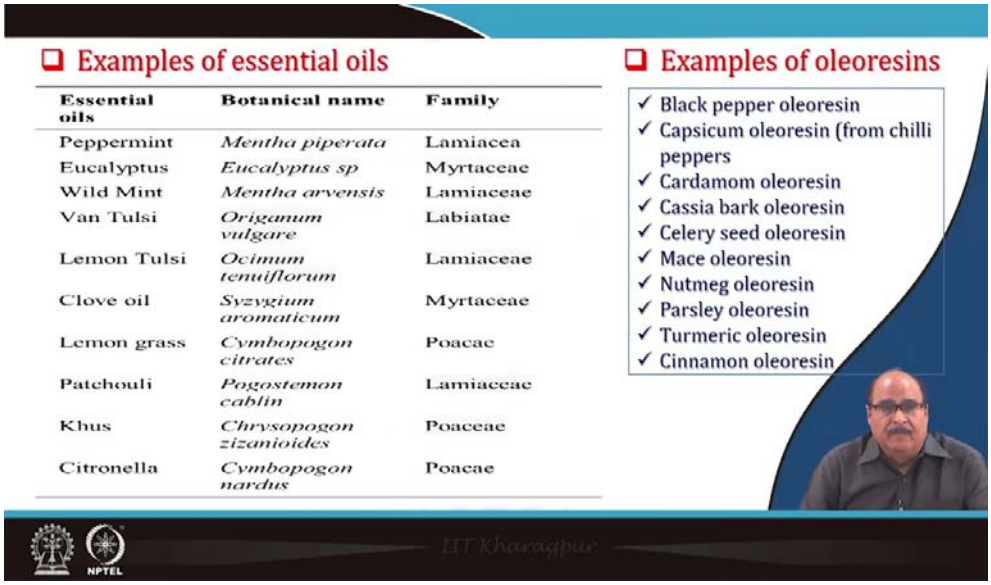
The concept covered in this lecture are the essential oil and oleoresin, their extraction techniques, maybe conventional and novel extraction techniques, and a few case studies like extraction of clove oil, turmeric essential oil and lemon grass oil.



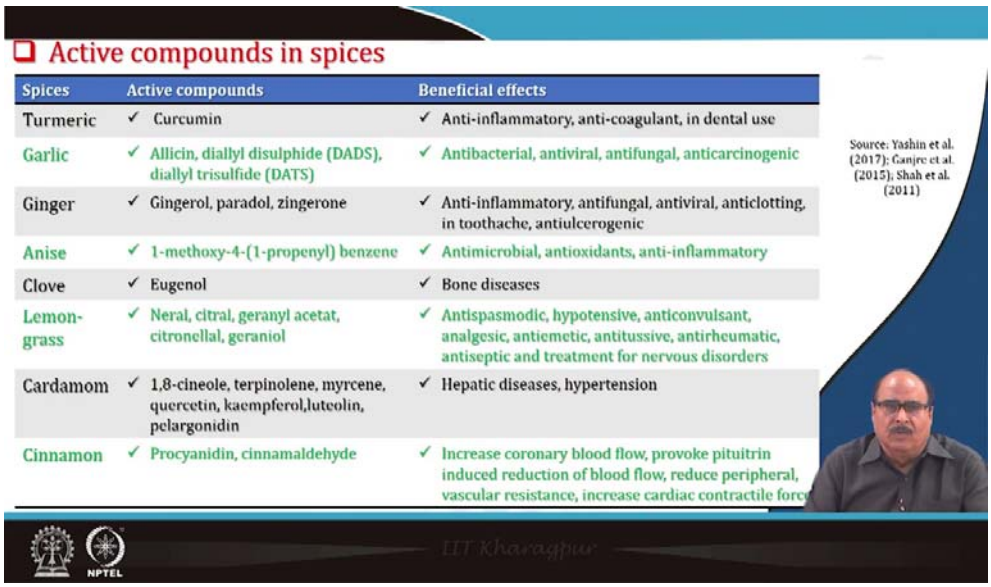
Essential oil and oleoresin

Essential oil is a concentrated hydrophobic liquid containing volatile chemical compounds from the plants, which is easily evaporated at normal temperature. They are also known as volatile oils, ethereal oils, aetheroleum, or simply as the oil of the plants from which they were extracted, such as oil of clove, turmeric oil and so on.

The oleoresin is nature or artificial mixture of essential oils and resins. They are resin-like, semi-solid extracts composed of essential oils or fatty acids or fatty oils. So, both essential oil and fatty oils are present in the resins, they are a little bit thick than the essential oils. They have the pungency and aroma which contribute to the taste of the food products. The essential oils normally do not have the taste and flavor, but the oleoresin definitely will have the characteristic taste and flavor of the particular commodity from which they are made.



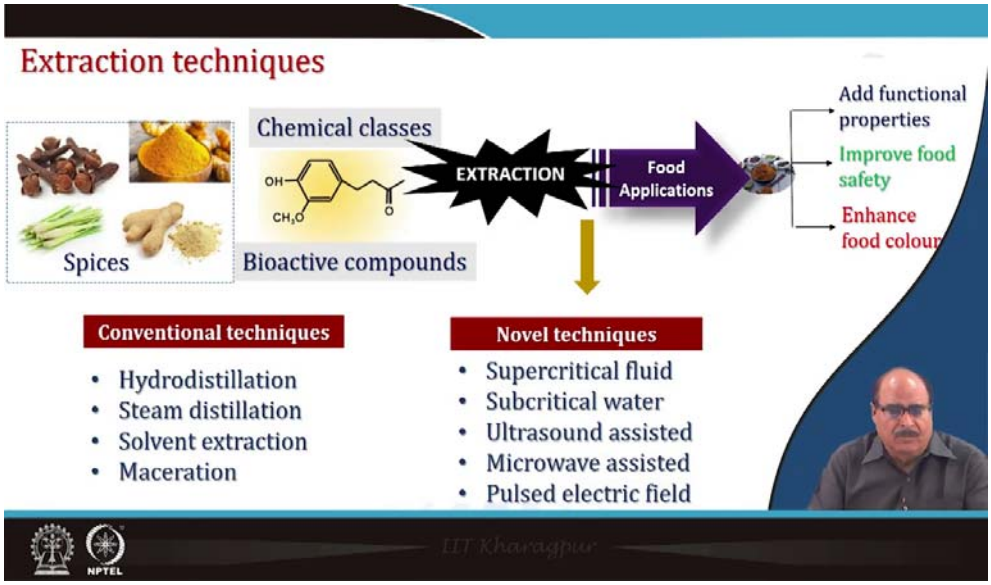
Here these are the some of the examples of essential oils and oleoresins in this table. Essential oils like peppermint oil, eucalyptus oil, wild mint, van tusli, lemon tulsi, clove oil, lemon grass, khus, and citronella. So, these are the some of the common categories of materials which are known for their essential oil content. Some oleoresins like black pepper oleoresin, capsicum oleoresin, cardamom, cassia bark, celery seed, mace, nutmeg, parsley, turmeric, cinnamon, all these are used for, there oils are made with the oleoresins.



Active compounds in spices

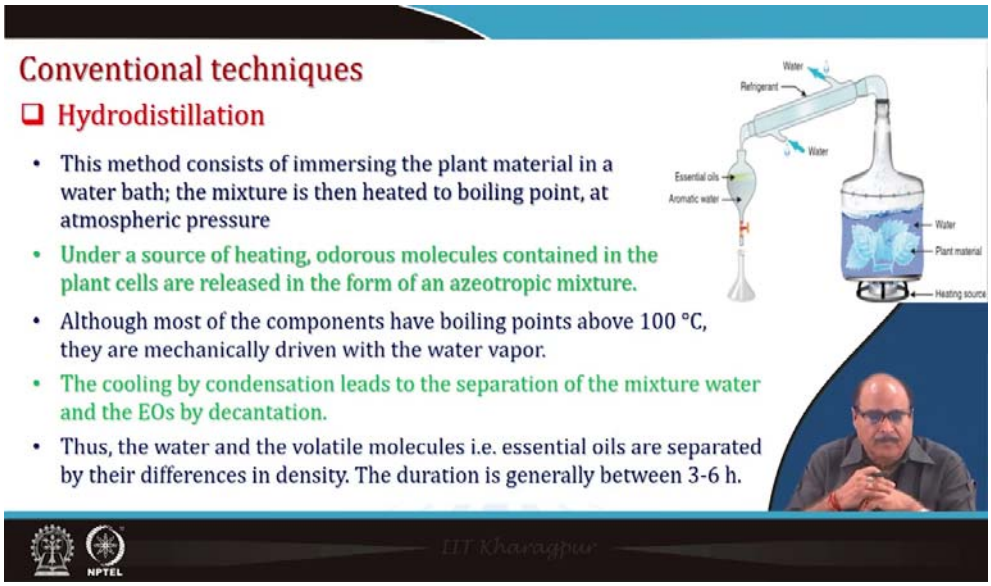
Spices, their active compounds and beneficial effects are shown in the table. For example in turmeric, curcumin is the major active compound, it has anti-inflammatory, anti-cogulant, and it is used for dental purposes. Garlic has allicin, diallyl disulphide, or diallyl trisulphide active compounds and are known for its antibacterial, antiviral, antifungal, or anticarcinogenic activities. In ginger, there is gingerol, paradol, or zingerone, these all compounds are known for their antibacterial, anti-fungal, antiviral activities, etc. Anise, the active compound is 1-methyl-4-1-propenyl benzene. In clove, it is the eugenol. In lemon

grass, it is the neral, citral, geranyl acetate, citronellal, and geraniol. In cardamom, it is 1,8-cineole, terpinolene, myrcene, quercetin, and luteolin. In cinnamon, it is procyanidin, cinnamaldehyde, etc. All these active compounds present in different spices are known for their anti-bacterial, antioxidant, anti-hyper protective, etc. that is they have the medicinal properties.



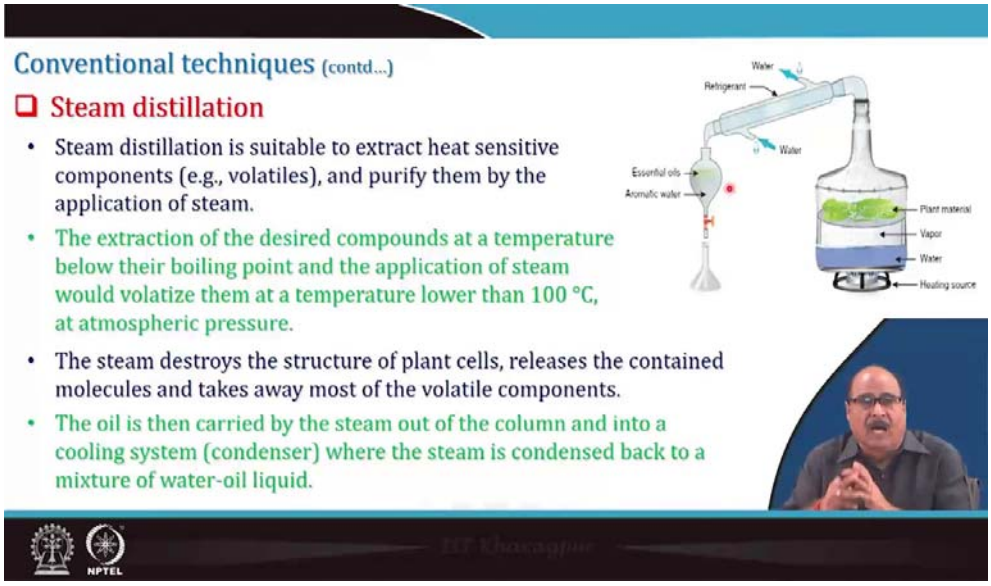
Extraction techniques

For the extraction of these essential oils and oleoresins, different techniques are used. Appropriate extraction technologies like in conventional method, hydrodistillation, steam distillation, solvent extraction, or maceration whereas the novel techniques like supercritical fluid extraction, subcritical water, ultrasound-assisted, microwave-assisted, or pulsed electric field assisted extraction technology is used to obtain the extract oils and oleoresins. They are then subjected to various food applications to add functional properties into the food, improve food safety, because many of them has antimicrobial activities, or also they are used to enhance food colors like curcumin, etc. as they are known as natural colorant.



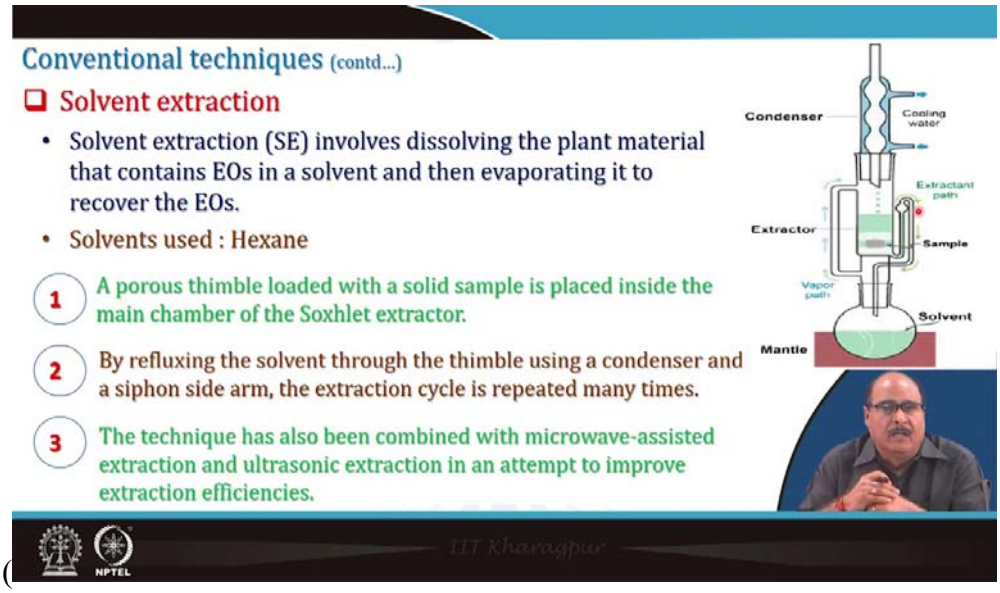
Conventional techniques

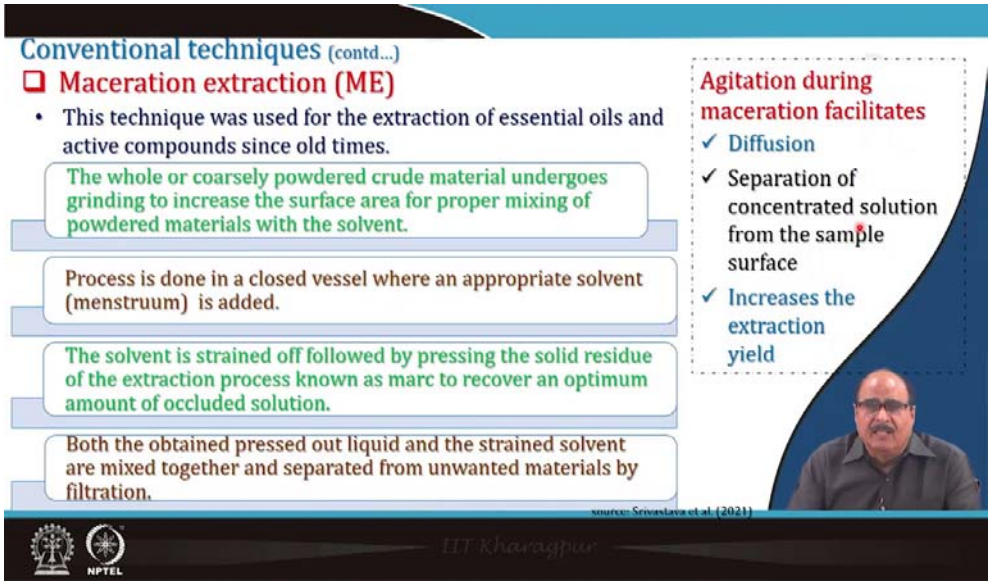
Hydrodistillation method consists of immersing the plant material in a water bath, the mixture is then heated to boiling point at atmospheric pressure. Under a source of heating, the odorous molecules which are contained in the plant cells are released in the form of an azeotropic mixture. Although most of these components have boiling point above 100 °C, they are mechanically driven with the water vapor. The cooling by condensation leads to separation of the mixture water and the essential oils by decantation. The water and the volatile molecules i.e. essential oils are separated by their differences in the density. The duration generally may take around 3 to 6 h.



Steam distillation is suitable to extract heat sensitive components or volatiles and purify them by the application of steam. The figure is almost similar to that of Hydrodistillation, but here the water is boiling water or steam is used. The extraction of the desirable components at a temperature below their boiling point and the application of steam would volatize them at a temperature lower than 100 °C, at atmospheric pressure. The steam destroys the structure of the plant cells, releases the contained molecules and takes away most of the volatile components. The oil is then carried by the steam out of the column into a cooling system i.e. condenser where the steam is condensed into a mixture of water-oil liquid.

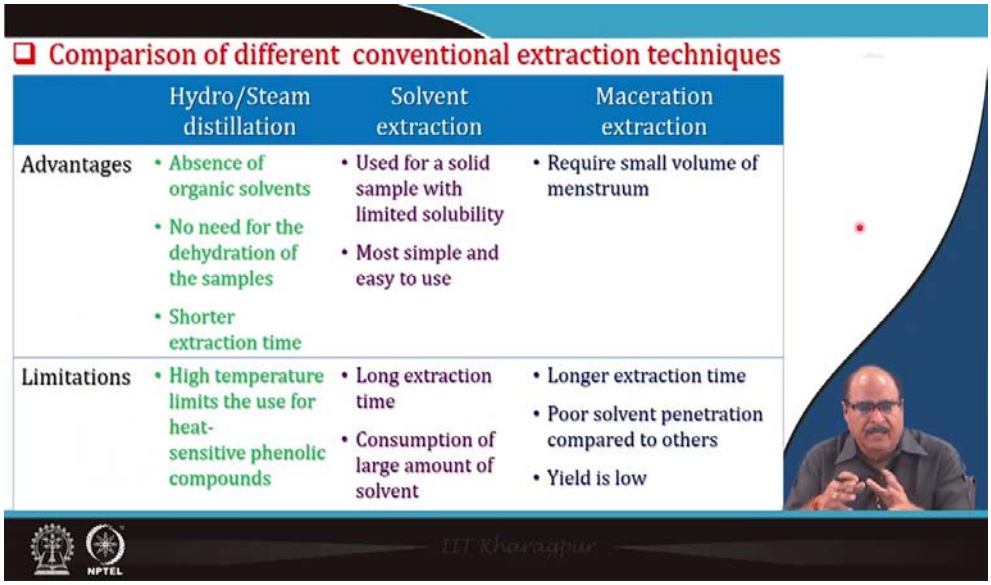
Solvent extraction involves dissolving the plant material that contains essential oils in a solvent and then evaporating it to recover the essential oils. Solvent normally used are hexane. There is a porous thimble that is loaded with the solid sample and is placed inside the main chamber of the soxhlet extractor. Then by refluxing the solvent through the thimble using a condenser and a siphon side arm, the extraction cycle is repeated many times. The extraction technique can also be combined with the microwave-assisted extraction and ultrasonic-assisted extraction in an attempt to improve the extraction efficiency.





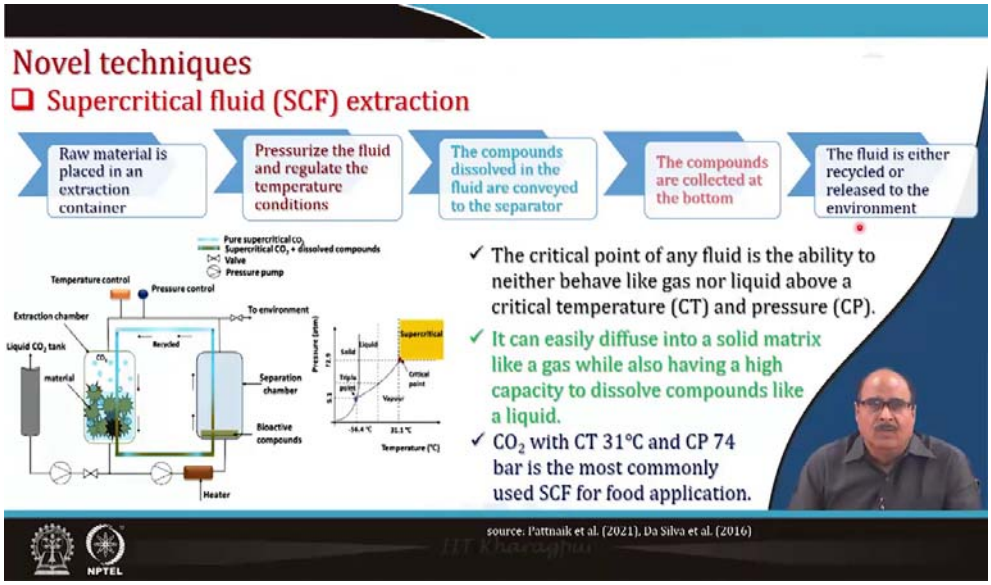
Maceration extraction technique is used for the extraction of essential oils and active compounds since old times. The process involves the whole or coarsely powdered crude material which undergoes grinding to increase the surface area for proper mixing of the powder material with the solvent and then this process is done in a closed vessel where an appropriate solvent is added, the solvent is strained off followed by pressing the solid residue of the extraction process known as marc to recover an optimum amount of occluded solution. Both the obtained pressed out liquid and the strained solvent are mixed together and separated from unwanted materials by filtration.

Agitation during maceration facilitates diffusion, separation of concentrated solution from the sample surface, and it increases the extraction yield.



Comparison of different conventional extraction techniques

In this table, there are advantages and limitations of different conventional extraction techniques. Hydro or steam distillation does not use any organic solvent, so it is advantageous. There is no need for the dehydration of the sample and it has a shorter extraction time. However, the high temperature limits the use of heat sensitive phenolic compounds. In the solvent extraction, it uses a solid sample with limited solubility and it is most simple and easy to use. However, it takes a long extraction time and the consumption of large amount of solvent is a limitation. Then, in the case of maceration extraction, it requires a small volume of menstruum that is the advantage, but the limitation is longer extraction time, poor solvent penetration compared to others and also here the yield is low.

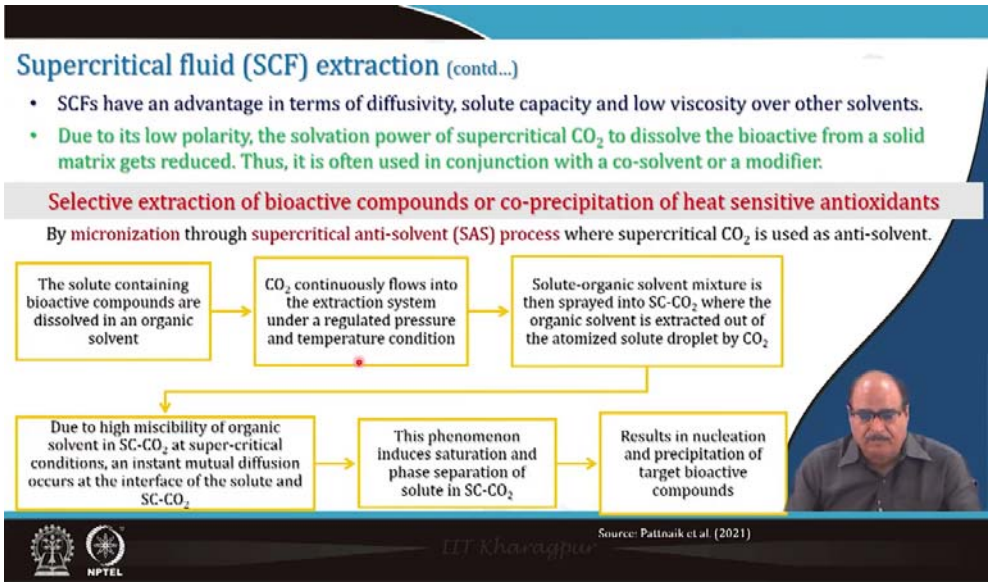


Novel techniques

One of the most important novel extraction technology which is used presently by many industries is the supercritical fluid extraction. In this process, raw material is placed in an

extraction container, where the fluid is pressurized and regulate the temperature conditions, and then the compounds are in the extraction column which is mixed with the basically the pressurized carbon dioxide and temperature and pressure are controlled regulated to the desired level. The compounds are dissolved in the fluid, they are conveyed to the separator, and collected at the bottom and the fluid is rather rejected or released to the environment. The critical point i.e. there is a critical temperature and critical pressure and above which these liquids (carbon dioxide, water), they behave as a supercritical fluid. So, it can easily diffuse under those conditions into a solid matrix like gas while also having a high capacity to dissolve compounds like liquid. So, supercritical fluids have both the properties of a liquid as well as gas.

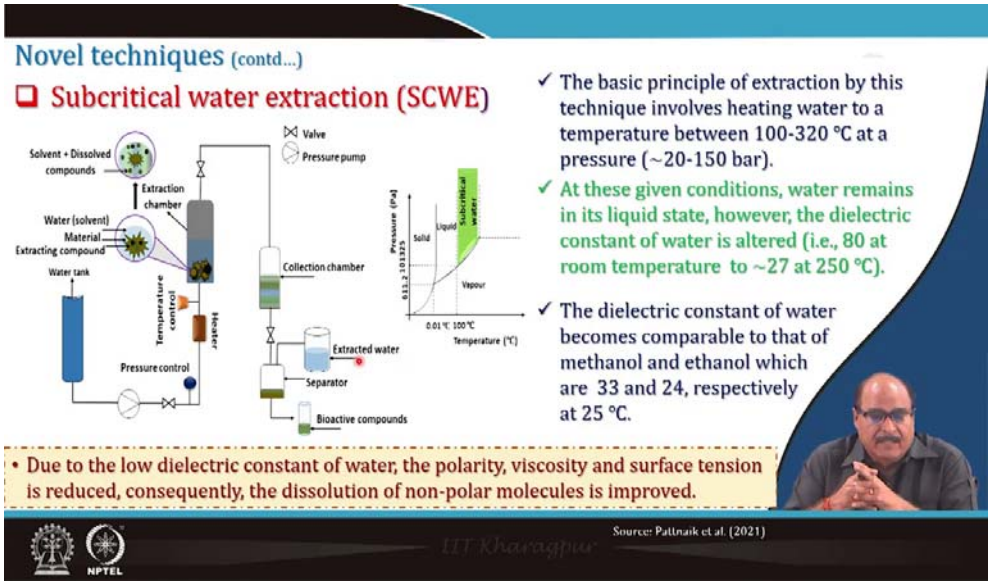
For carbon dioxide the critical point that is critical temperature is around 31 °C and the critical pressure is about 74 bar, above which the carbon dioxide will be in a supercritical fluid state.



So, these supercritical fluids have an advantage in terms of diffusivity, solid capacity, and low viscosity over other solvents. Due to its low polarity, the salvation power of the supercritical carbon dioxide to dissolve the bioactive from a solid matrix get reduced. Thus, it is often used in conjunction with co-solvent or a modifier. Many times, depending upon the nature of the compound which needs to be extracted, the co-solvent or intruder generally ethyl alcohol, ethanol, etc. are used. The selective extraction of bioactive compounds or co-precipitation of heat sensitive antioxidants can be done using SCF as well as a mixture of SCF or intruder or co-solvent. By micronization through supercritical anti-solvent (SAS) process, where supercritical carbon dioxide is used as an anti-solvent.

The solute containing bioactive compounds are dissolved in an organic solvent. Carbon dioxide continuously flows into the extraction system under a regulated pressure and temperature condition. The solute-organic solvent mixture is then sprayed into supercritical carbon dioxide, where the organic solvent is extracted out of the atomized solute droplet by carbon dioxide. Due to the high miscibility of organic solvent that is supercritical carbon

dioxide at its supercritical conditions, an instant mutual diffusion occurs at the interface of the solute and the SCF and this phenomenon induces saturation and phase separation of the solute in the supercritical carbon dioxide. Finally, this results in the nucleation and precipitation of the target bioactive compounds. So, by using this, selective extraction of bioactive compound can be possible.

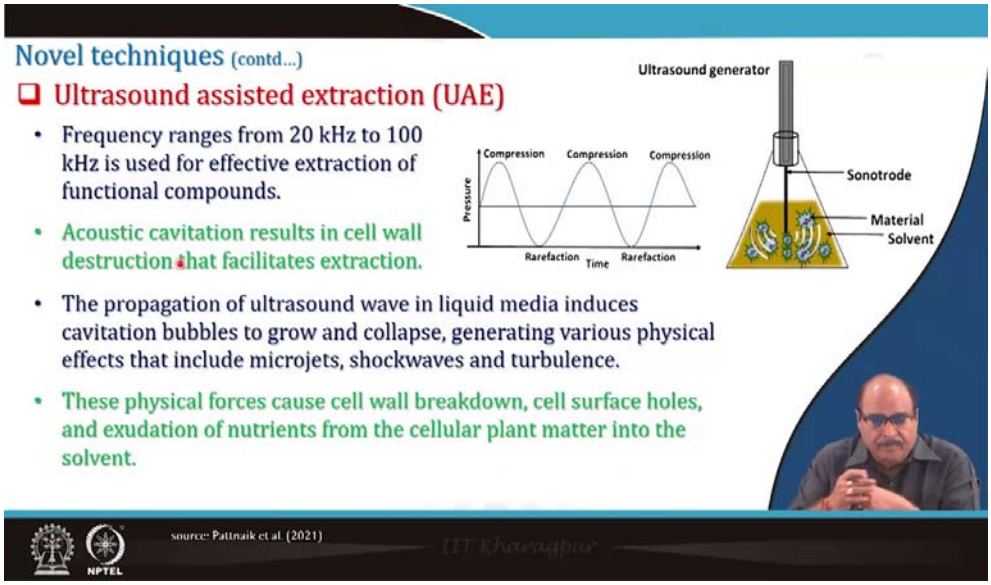


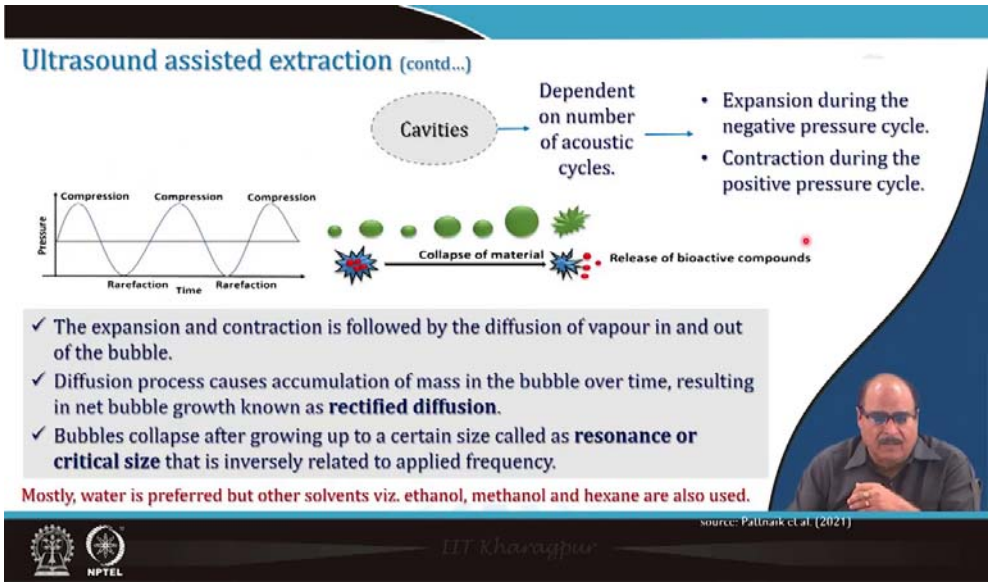
Subcritical water extraction

This method also on the similar principle as SCF, but here other than CO_2, water is used. The basic principle of extraction by this technique involves heating water to a temperature between 100 to 320 °C at a pressure of about 20 to 150 bar. At these given conditions, water remains in the liquid state. However, the dielectric constant of water is altered from 80 at room temperature to approximately 27 at 250 °C. The dielectric constant of water becomes comparable to that of the methanol and ethanol which are 33 and 24, respectively at 25 °C. Due to these low dielectric constant of water, the polarity, viscosity and surface tension is reduced, and consequently, the dissolution of the non-polar molecules is improved which helps in extracting the bioactive compounds.

Ultrasound-assisted extraction

The ultrasound having frequency ranges from 20 to 100 kHz is used for effective extraction of functional compounds. Ultrasound causes acoustic cavitation which results in a cell wall destruction and that facilitates extraction. The propagation of ultrasound wave in liquid media induces cavitation bubbles to grow and collapse, generating various physical effects that includes microjets, shockwaves and turbulence. These physical forces cause cell wall breakdown, cell surface holes, and exudation of nutrients from the cellular plant matter into the solvent.



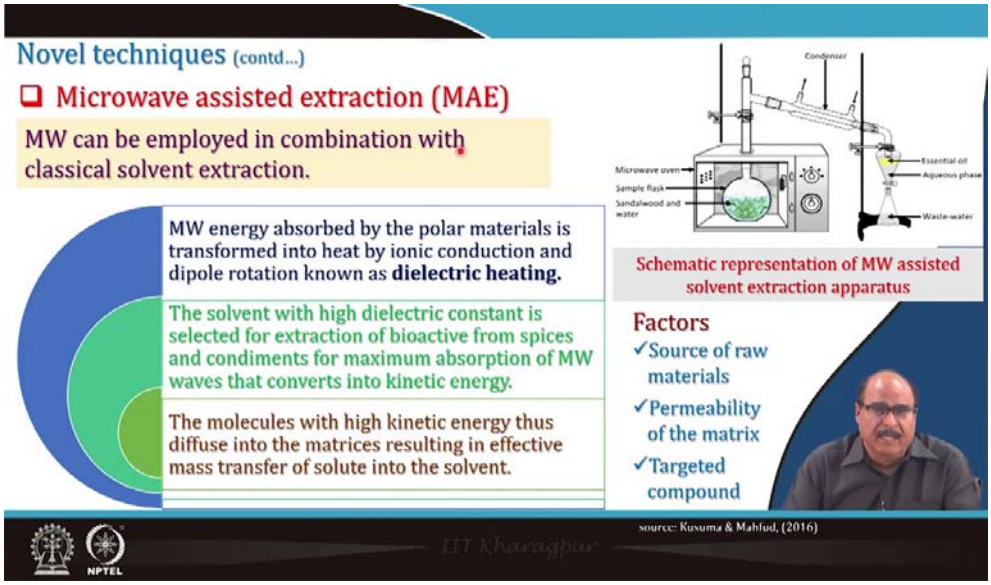


Cavities are dependent on the number of acoustic cycles, and then there is an expansion during the negative pressure cycle or contraction (compression) during the positive pressure cycle. The expansion and contraction is followed by the diffusion of vapour in and out of the bubble. A diffusion process causes accumulation of mass in the bubble over time resulting in the net bubble growth which is known as rectified diffusion. So, bubbles collapse after growing up at a certain size called as resonance or critical size that is inversely related to the applied frequency. Mostly water is preferred, but other solvents like ethanol, methanol, hexane, etc. can also be used in the ultrasound-assisted extraction.

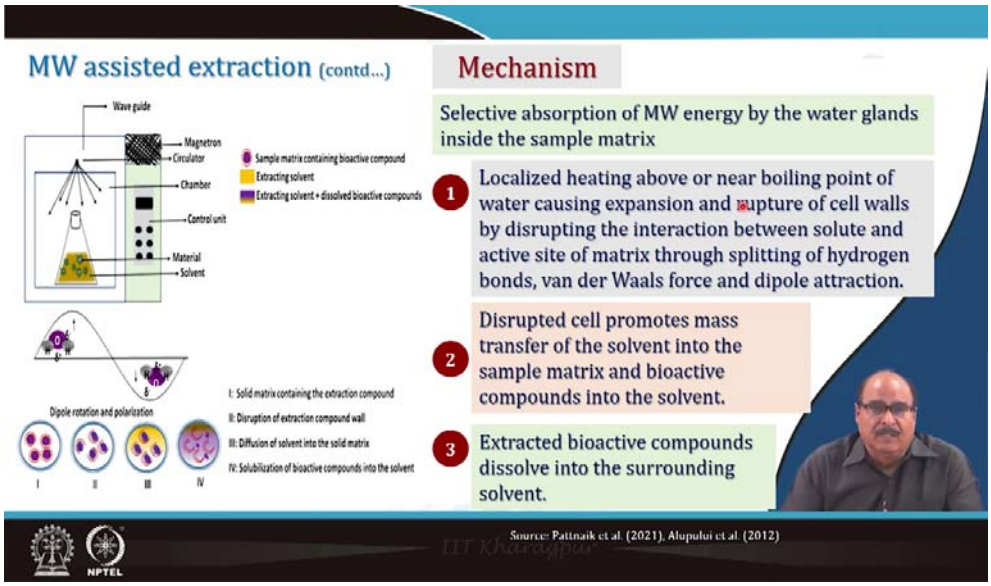
Microwave-assisted extraction

In a microwave oven, some container (flask) is kept and sample is placed in the flask and the heating system is through the microwave as seen in the figure. Microwave can be implied in combination with classical solvent extraction. Microwave energy absorbed by the polar materials is transformed into heat by ionic conduction and dipole rotation which is known as dielectric heating. The solvent with high dielectric constant is selected for the extraction of

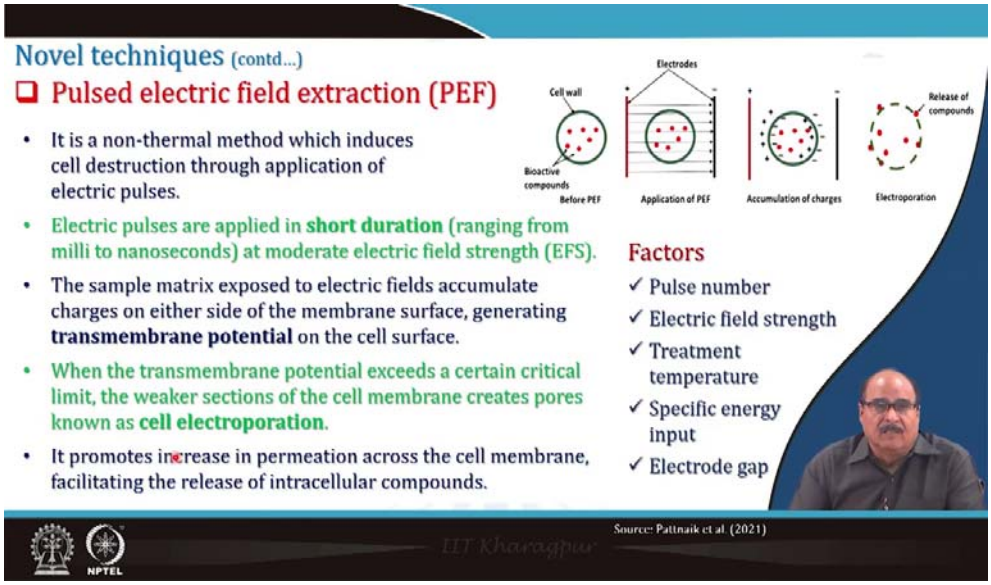
bioactive from spices and condiments and for maximum absorption of microwaves that converts into kinetic energy. The molecules with high kinetic energy thus diffuse into the matrices resulting in effective mass transfer of solute into the solvent.



The factors needs to be controlled during this microwave-assisted extraction process are the source of the raw materials, permeability of the matrix, and targeted compounds.



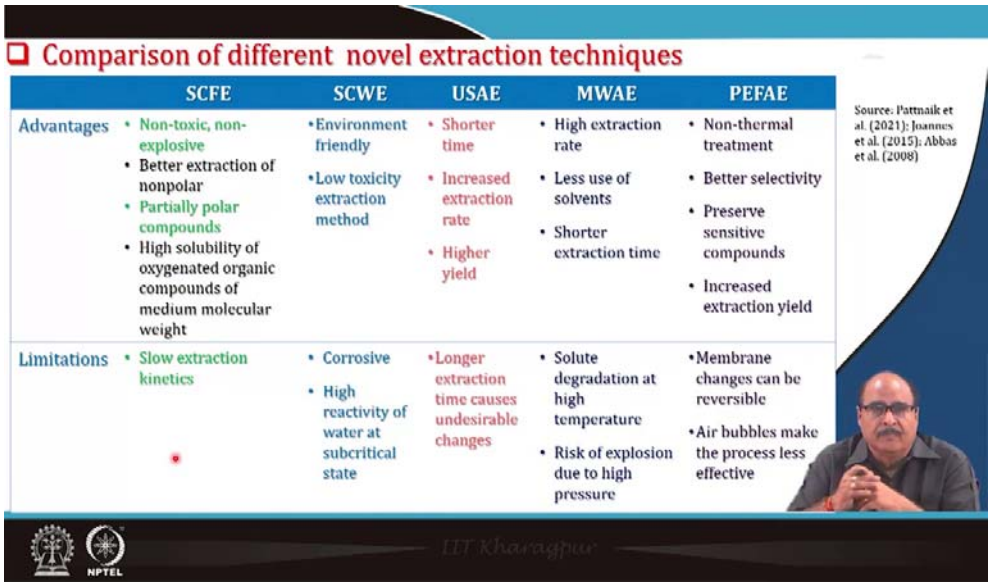
The mechanism of microwave-assisted extraction is the selective absorption of microwave energy by the water glands inside the sample matrix. Then, there is a localized heating above or near boiling point of water causing expansion and rupture of cell walls by disrupting the interaction between solute and active sites of the matrix through a splitting of hydrogen bonds, Van Der Waals forces, and dipole attraction. Then, the disrupted cell promotes mass transfer of the solvent into the sample matrix and bioactive compounds into the solvent. Finally, the extracted bioactive compounds dissolve into the surrounding solvent.



Pulsed electric field extraction (PEF)

PEF is a non-thermal method which includes cell destruction through application of electric pulses. Electric pulses are applied in short duration ranging from milli to nanoseconds at moderate electric field strength. The sample matrix exposed to electric field accumulate charges on either side of the membrane surface, generating transmembrane potential on the cell surface. When the transmembrane potential exceeds a certain critical limit, the weaker section of the cell membrane creates pores, which are known as cell electroporation. This cell electroporation promotes the increase in permeation across the cell membrane, facilitating the release of intercellular compounds.

The factor which are responsible or which have the significant effect on this process include pulse number, electrical field strength, treatment temperature, specific energy input, and electrode gap.

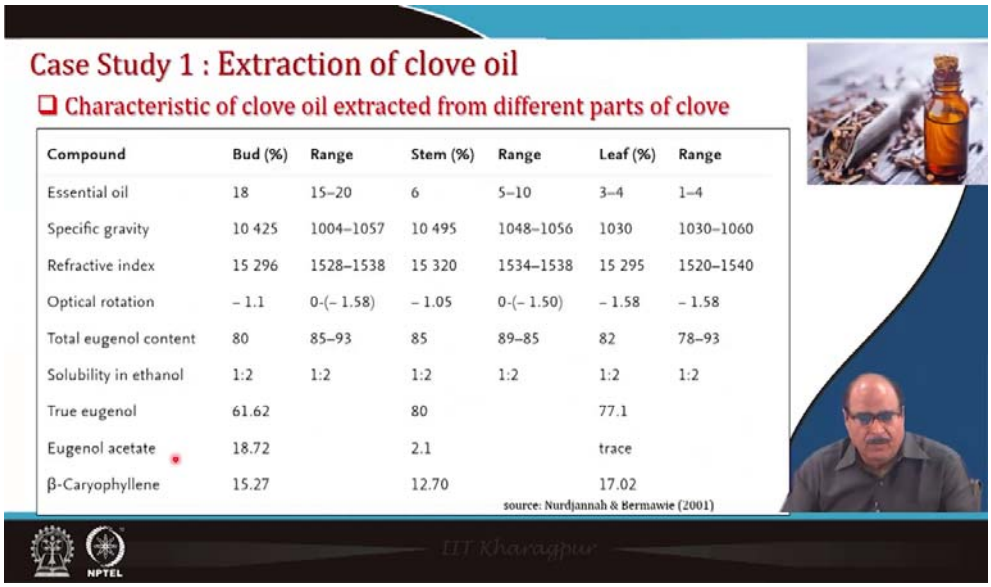


Comparison of different novel extraction techniques

Supercritical fluid extraction is nontoxic, non-explosive, there is a better extraction of nonpolar components, results in partial extraction of partially polar compounds also. It has high solubility of oxygenated organic compounds of medium molecular weight. However, the limitation is the slow extraction kinetics.

Subcritical water extraction is an environment friendly technology. It is low toxicity extraction method, so this is advantageous and the limitations are it is corrosive, and the high reactivity of the water at subcritical state. The ultrasound-assisted extraction, it is shorter time, increase extraction rate, higher yield, but limitations are longer extraction time causes undesirable changes.

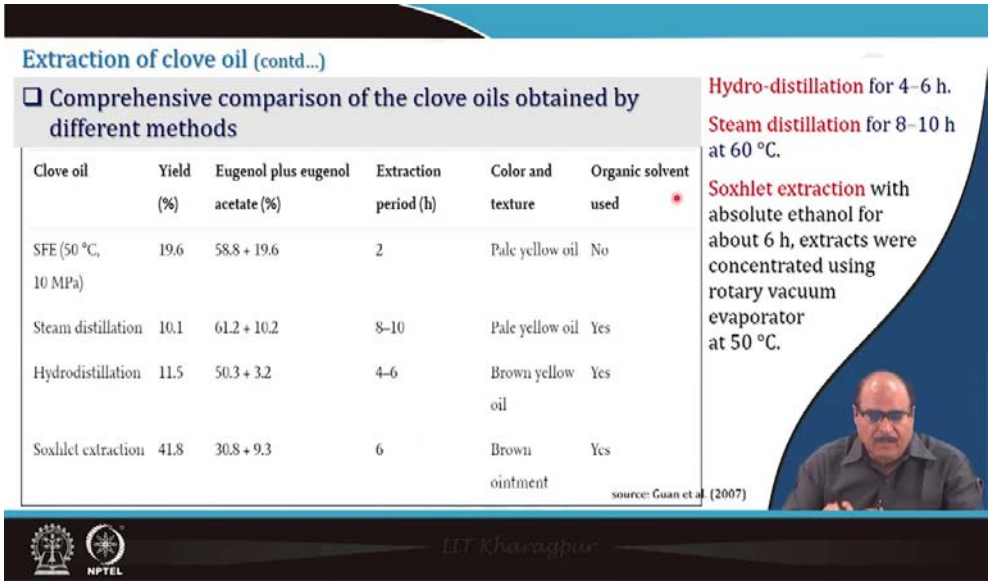
Microwave assisted extraction, its advantage is it has a high extraction rate, less usage of solvents and shorter extraction time but the limitations include solute degradation at high temperature and risk of explosion due to high pressure. The PEF assisted extraction is a non-thermal treatment, better selectivity, it preserves sensitive compounds, and there is increased extraction yield. However, the limitations of this system include membrane changes can be reversible, and air bubbles make the process less effective.



Compound	Bud (%)	Range	Stem (%)	Range	Leaf (%)	Range
Essential oil	18	15–20	6	5–10	3–4	1–4
Specific gravity	10 425	1004–1057	10 495	1048–1056	1030	1030–1060
Refractive index	15 296	1528–1538	15 320	1534–1538	15 295	1520–1540
Optical rotation	– 1.1	0-(– 1.58)	– 1.05	0-(– 1.50)	– 1.58	– 1.58
Total eugenol content	80	85–93	85	89–85	82	78–93
Solubility in ethanol	1:2	1:2	1:2	1:2	1:2	1:2
True eugenol	61.62		80		77.1	
Eugenol acetate	18.72		2.1		trace	
β-Caryophyllene	15.27		12.70		17.02	

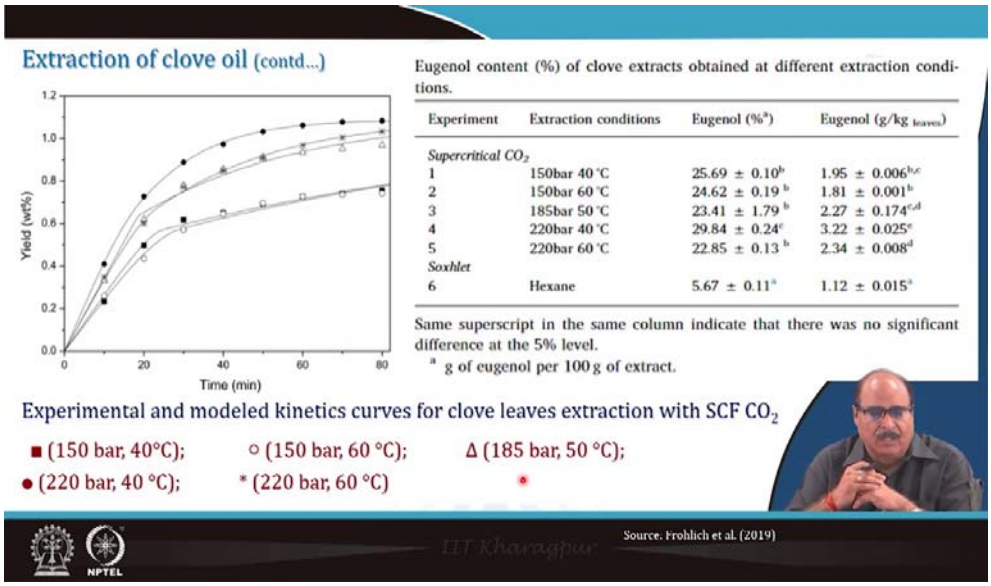
Case Study 1: Extraction of clove oil

The characteristics of clove oil extracted from different parts of the clove plant (bud, stem, and leaf) are shown in the table. The essential oil obtained from bud is 18 %, range is 15 to 20 %, from stem it contains 6 %, range is 5 to 10 %, and from the leaf it is 3 to 4 %, the range maybe 1 to 4 %. Similarly, specific gravity, refractive index, optical rotation, total eugenol content, solubility in ethanol, true eugenol, eugenol acetate, or beta caryophyllene all these compounds from the bud, stem and leaf is shown.



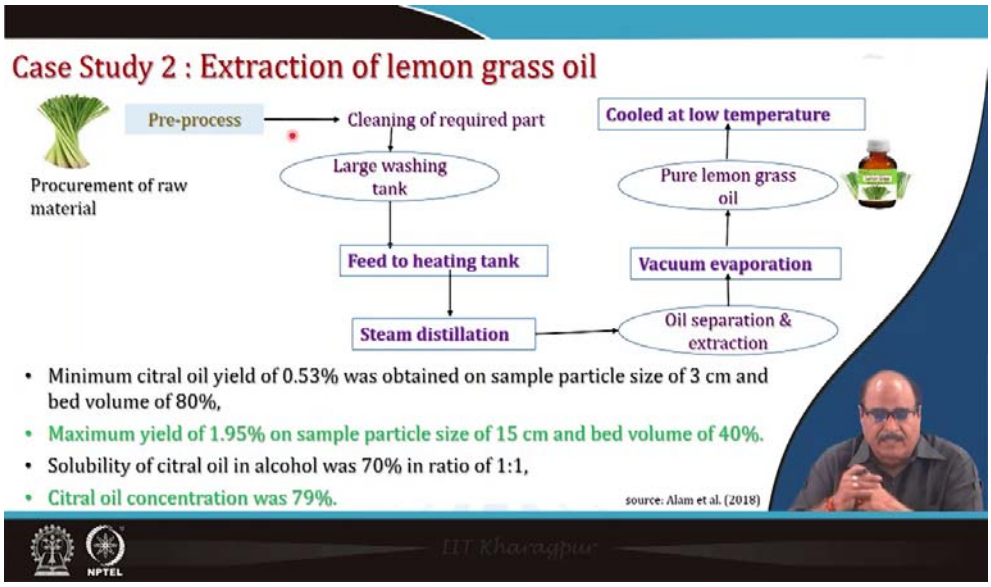
The comprehensive comparison of the clove oil obtained by different methods is shown. Methods used are supercritical fluid extraction at 50 °C and 10 MPa pressure. Hydrodistillation for 4 to 6 h, steam distillation for 8 to 10 h at 60 °C, and soxhlet extraction with absolute ethanol for about 6 h, and here in the soxhlet extraction, extracts were concentrated using rotary vacuum evaporator at 50 °C. The yield is reported maximum in the case of soxhlet extraction i.e. 41.8 % followed by 19.6 % in supercritical fluid extraction and then hydrodistillation or steam distillation are almost similar, but the eugenol plus eugenol acetate i.e. the active compound yield is maximum in the steam distillation and SCFE followed by hydrodistillation and is minimum in the soxhlet extraction process.

Similarly, the extraction time is minimum in SCFE and maximum in steam distillation or soxhlet extraction. The color and texture in the SCFE and steam distillation is pale yellow oil, but in the soxhlet extraction there is some discoloration maybe brown ointment. The organic solvent obviously in the SCFE, no organic solvent is used, in steam distillation, hydrodistillation and soxhlet extraction, organic solvent is used.



The extraction of clove oil i.e. the eugenol content (%) of clove extracts obtained at different extraction conditions is shown. Five SCFE conditions viz. 150 bar at 40 °C, 150 bar at 60 °C, 185 bar at 50 °C, 220 bar at 40 °C, and 220 bar at 60 °C are taken. One condition for Soxhlet extraction with hexane solvent is used.

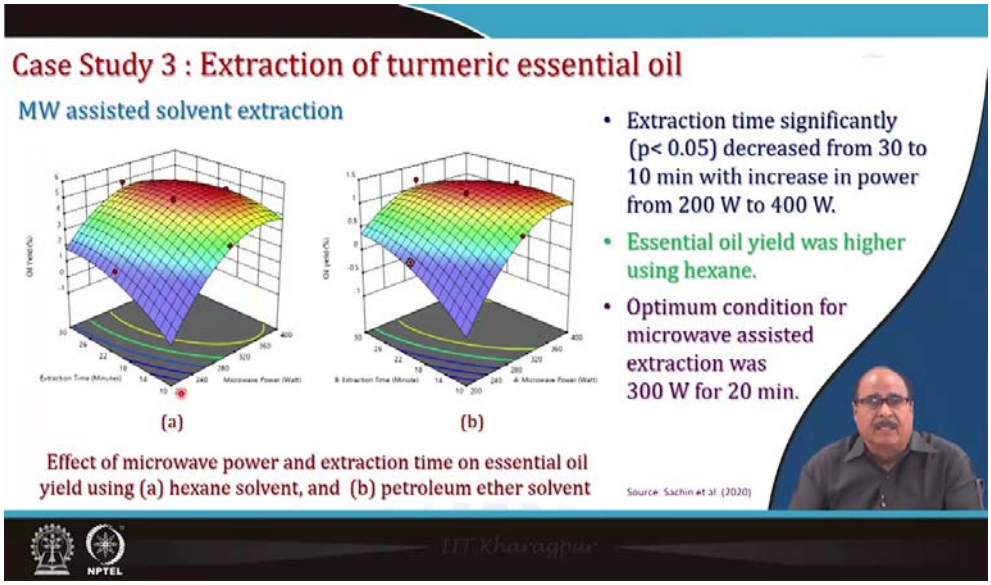
The eugenol content varies with the temperature and pressure both and the maximum eugenol content is found at 220 bar and 40 °C SCFE condition and SCFE has more eugenol content in comparison to the Soxhlet extraction. The same thing can be seen in the yield and time curve. In the case of SCFE conditions, 220 bar and 40 °C gave better extraction.



Case Study 2: Extraction of lemon grass oil

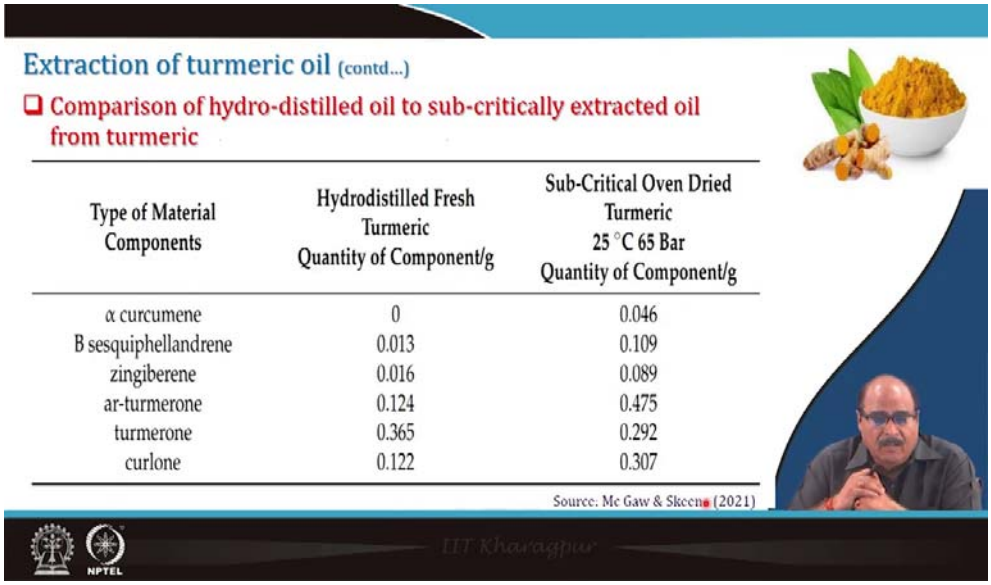
The second case study is the extraction of lemon grass oil. This lemon grass, raw material is preprocessed, cleaning of the required part, large washing tank, feed to heating tank, steam distillation, followed by oil separation and extraction, vacuum evaporation, to get a pure lemon grass oil which is cooled at low temperature.

The minimum citral oil yield of about 0.53 % was obtained on the sample particle size of 3 cm and bed volume of 80 %. The maximum yield of about 1.95 % on the sample particle size of 15 cm and bed volume of 40 % was reported by Alam et al. (2018). Solubility of citral oil in the alcohol was around 70 % is the ratio of 1:1 and the citral oil concentration was around 79 %.



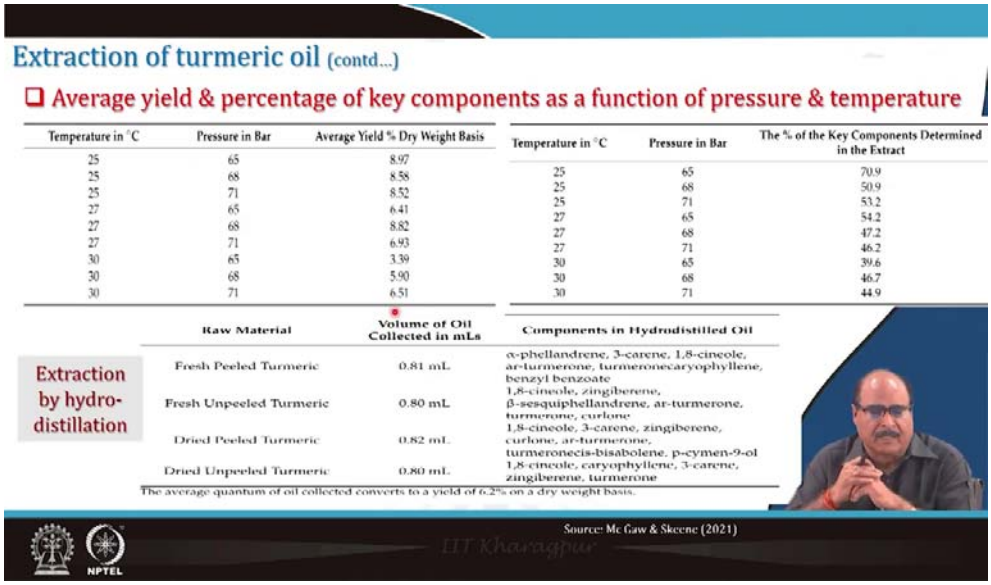
Case study 3: Extraction of turmeric essential oil

Here, the extraction is done by microwave-assisted solvent extraction. The effect of microwave power and extraction time on essential oil yield using hexane and petroleum ether solvent is shown in figure. In both the cases, RSM plot showed that the extraction time significantly decreases from 30 to 10 min with the increase in the microwave power from 200 to 400 W. Essential oil yield was higher when hexane was used as a solvent. Optimum condition for microwave-assisted extraction was found to be 300 W microwave power and 20 min extraction time.

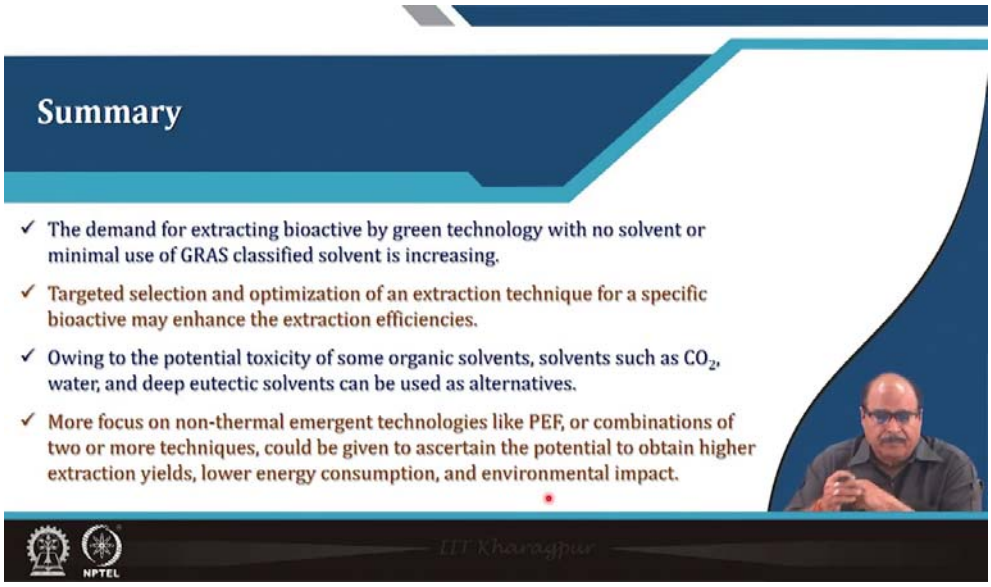


Type of Material Components	Hydrodistilled Fresh Turmeric Quantity of Component/g	Sub-Critical Oven Dried Turmeric 25 °C 65 Bar Quantity of Component/g
α curcumene	0	0.046
B sesquiphellandrene	0.013	0.109
zingiberene	0.016	0.089
ar-turmerone	0.124	0.475
turmerone	0.365	0.292
curlone	0.122	0.307

Comparison of hydro-distilled oil and sub-critically extracted turmeric oil is shown in the table. The compounds extracted are α-curcumene, β-sesquiphellandrene, zingiberene, turmerone, and curlone. The hydro distilled fresh turmeric gives no α-curcumene, whereas the subcritical oven dried gives α-curcumene about 0.046 per gram.



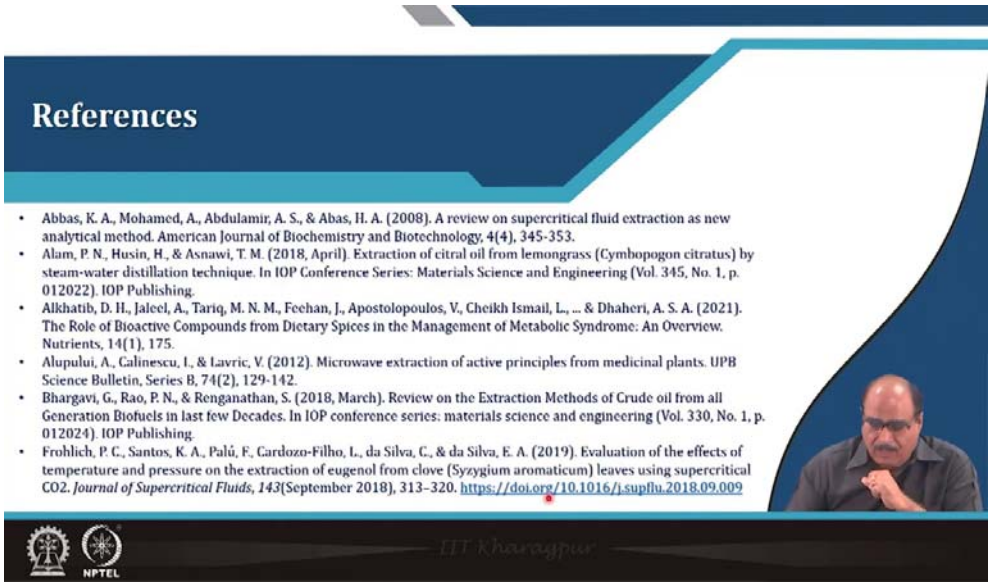
The average yield and percentage of key components as a function of pressure and temperature is provided in the table. In the extraction temperature, 3 extraction temperatures are used 25, 27 and 30 °C and for each extraction temperature three pressure 65, 68 and 71 bar was taken. The average yield in % dry weight basis is determined in the extract. With the bearing that both temperature and pressure, the yield percentage as well as extracted key components are changing. So, for fresh peeled turmeric, fresh unpeeled turmeric, dried peeled turmeric, and dried unpeeled turmeric, the volume of oil collected is approximately same. Obviously, in both the cases, the peeled turmeric gives you the more volume of oil in comparison to the unpeeled one.

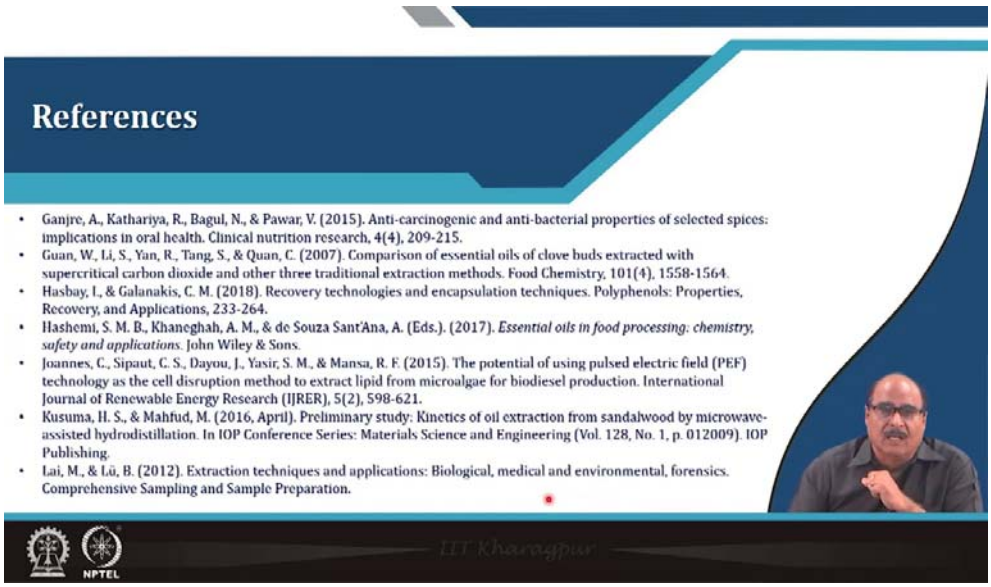


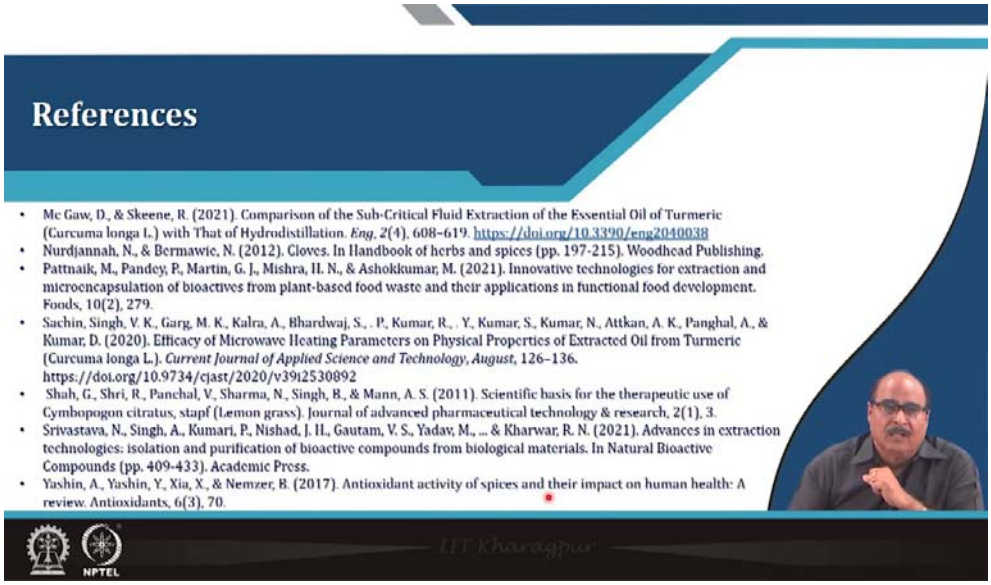
Summary

The demand for extracting bio actives by green technology with no solvent or minimal use of GRAS classified solvent is increasing. However, the selection of appropriate method, optimization of the extraction process techniques, etc. is required to retain the extraction efficiency, characteristic flavor and bioactive nature of the compound. Owing to the potential

toxicity of some organic solvents, solvents such as carbon dioxide, water, and deep eutectic solvents can be used as an alternatives. However, the more focus is on the non-thermal emergent technologies like PEF, or combination of two or more techniques like microwave assisted extraction or that PEF assisted extraction, ultrasound assisted extraction, they have better potential, they offer promise as per the extraction of essential oils and oleoresins with good characteristic flavoring potential, bioactive and antioxidant potential.







These are the references used in this lecture. Thank you.