Novel Technologies for Food Processing and Shelf Life Extension
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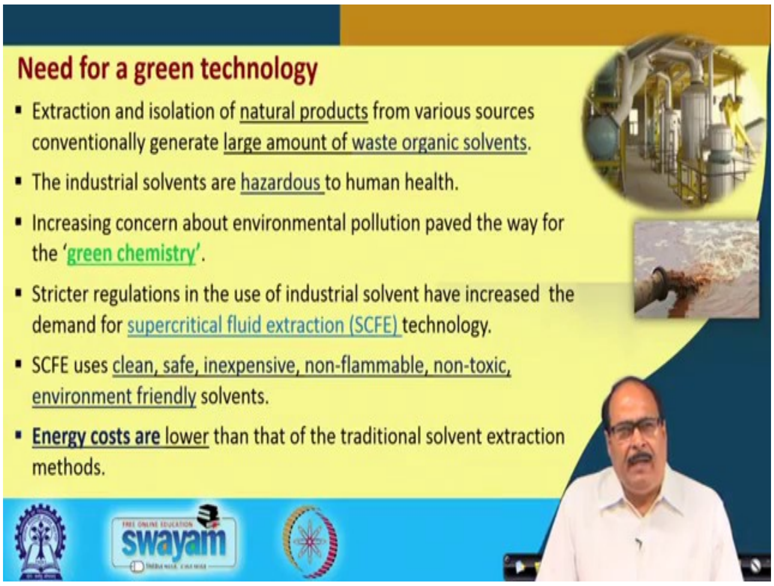
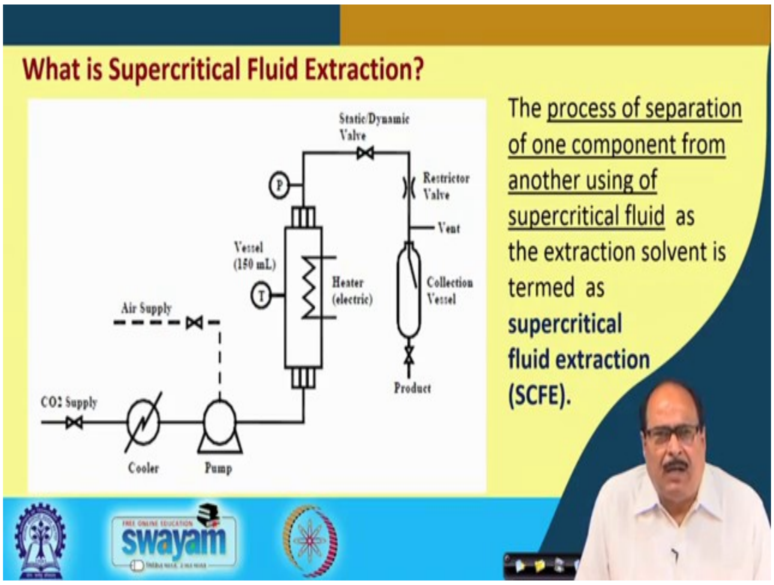
Lecture - 19
Supercritical Fluid Extraction (Part 1)

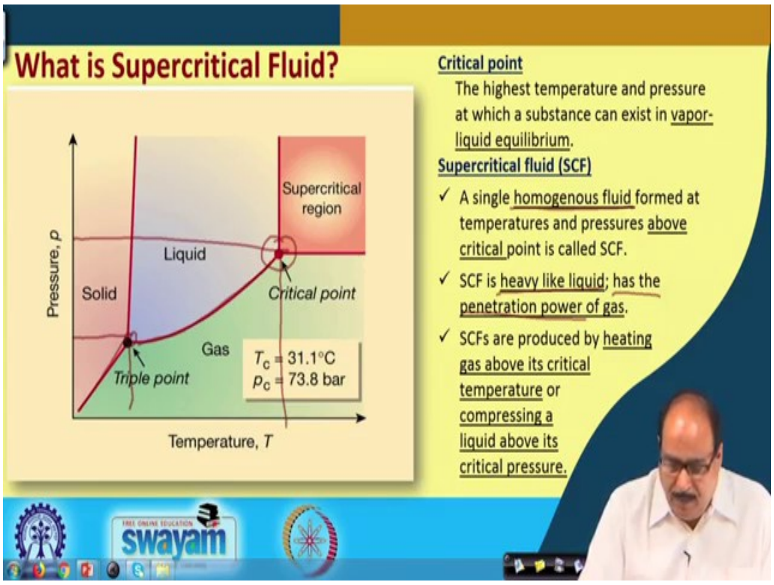
The topic of Supercritical Fluid Extraction will be taken in two parts. In Part 1, the principles of the process and technological aspects including the systems available for supercritical fluid extraction will be discussed. In part 2, the application of this technology in food processing shall be studied.



There is a need felt for the development of green technology. In the food processing, from time immemorial, these extraction and isolation of natural products from various sources have been done by using large amount of organic solvents. These industrial solvents which are generally used traditionally for the extraction processes, many of them are hazardous to human health and generate large amount of organic waste that further leads to environment pollution. Also, the stricter regulations in the use of industrial solvents have increased the demand of green technology like supercritical fluid extraction. Supercritical fluid extraction method uses clean, safe, inexpensive, non-flammable, non-toxic and environment friendly solvents. Also, the energy costs are lower in this process when compared to that of the traditional solvent extraction processes.

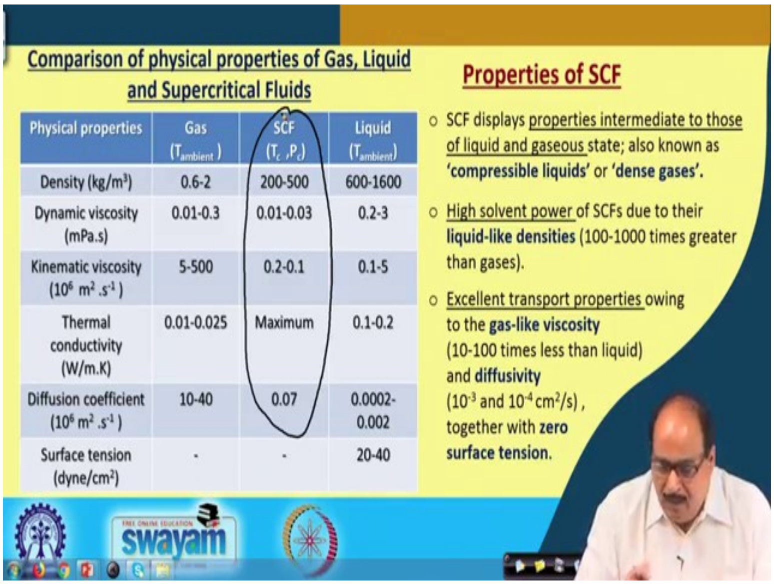


Supercritical fluid extraction is the process of separating one component from another using a supercritical fluid as the extraction solvent. As it can be seen here in this flow diagram that, the material from which the component to be extracted is placed in a vessel, where the supercritical fluid is introduced under certain conditions. At these conditions the supercritical fluid extracts the selected components from the particular materials. And then finally, the extracted materials are separated using appropriate methods and obtained in the collection vessel. This aspect, in further will be elaborated in little more detail when the technological aspects of the process is discussed.

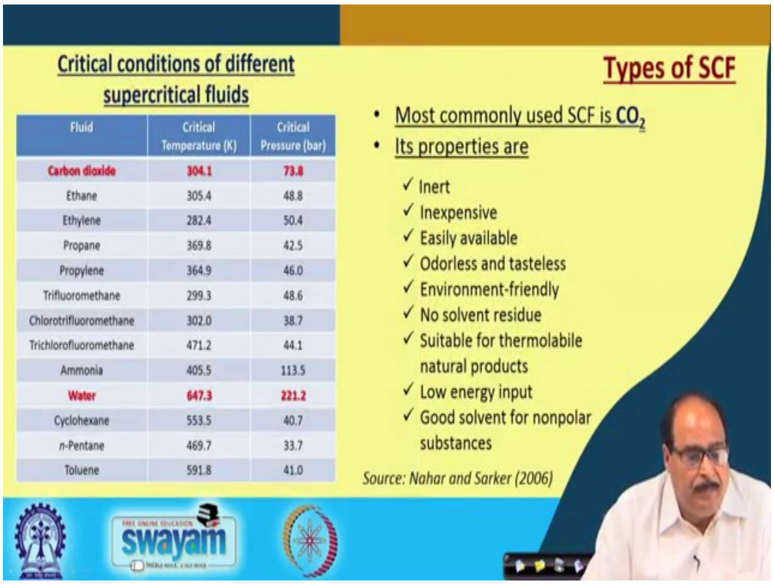


Supercritical fluid: In graph (pressure vs temperature) shown, a critical point can be observed which is the highest temperature and pressure above which a material can exist in vapour liquid equilibrium (supercritical region). Further increase in the pressure and temperature beyond the critical point, the liquid gets converted into a unique state of nature and this is the supercritical region. It becomes a supercritical fluid in this zone; material exists in equilibrium between vapour and liquid. So, supercritical fluid is single homogeneous fluid formed at the temperature and pressure above the critical point.

These have the properties intermediate to liquid and gas like they have the properties of liquid as far as their weight etc. is concerned i.e. they are heavy like liquid, but they have the penetration power of the gas. So, for the production of the supercritical fluid, either the material temperature can be increased or the material pressure can be brought to the desired level either by compressing or by some other methods.

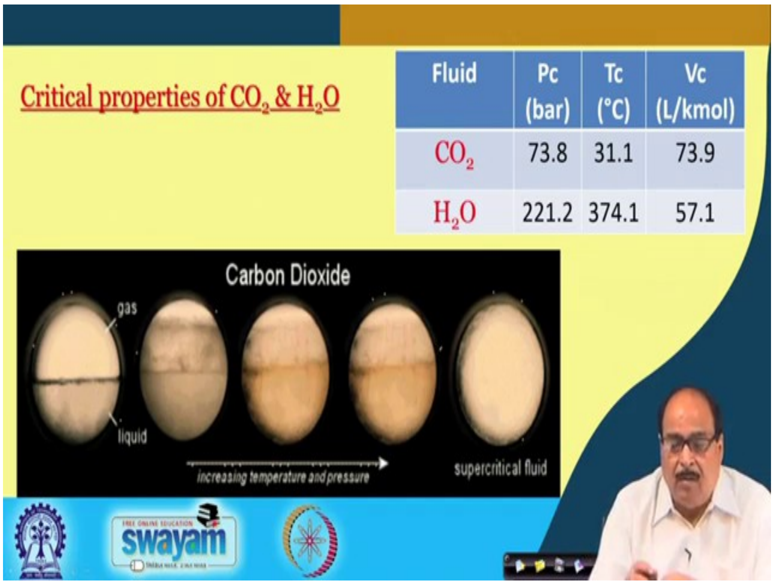


Comparison between the physical properties of gas, liquid and supercritical fluid: The important physical properties are density, dynamic viscosity, kinematic viscosity, thermal conductivity, diffusion coefficient and surface tension. The supercritical fluid (SCF) has the properties intermediate to those of the liquid and the gaseous state. And accordingly sometime these SCFs are also known as compressible liquids or dense gases. They have higher solvent power which is mainly due to their liquid like density; their density is much higher, i.e. 100-1000 times greater than gases. And they have excellent transport properties owing to the gas like viscosity which is 10-100 times less than the liquid. They possess gas like diffusivity together with the zero surface tension.

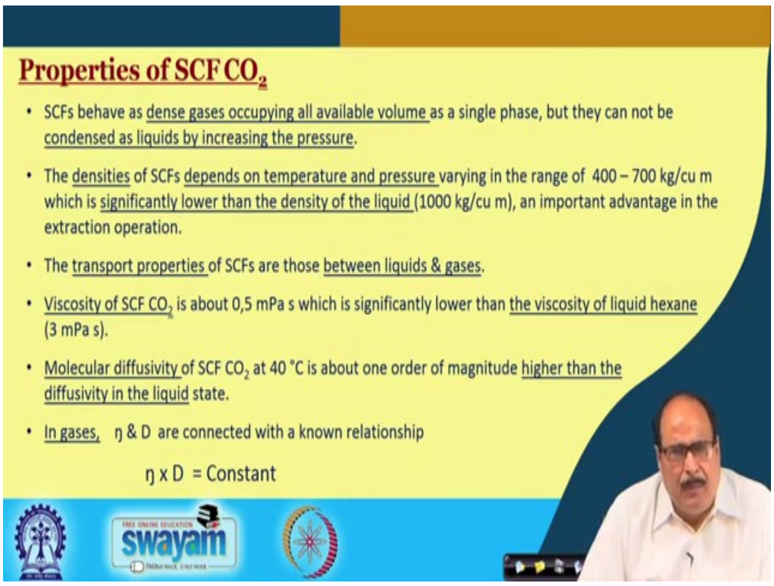


In this table, critical pressure and temperature of different supercritical fluids are shown. The two fluids indicated by red are worth seeing i.e. carbon dioxide, it has a critical temperature (T_c) 304.1 °K and critical pressure (P_c) 73.8 bar but for water, the critical temperature is 647.3 °K and pressure is 221.2 bar. The temperature requirement in case of water is more, that higher temperature cannot be attained or is risky.

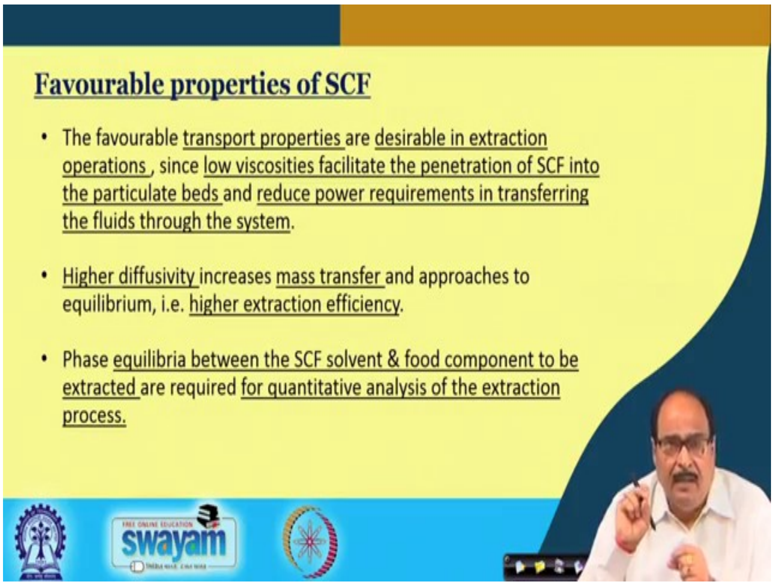
So, the most commonly used supercritical fluid in the food industry is the carbon dioxide. It is inert, inexpensive, easily available, odourless, tasteless, environment friendly and has low energy inputs. There is no solvent residue in the food after the extraction and it is suitable for non-polar substances and thermo labile natural products. So, these are the desirable characteristics of the supercritical carbon dioxide which make it a very good solvent for use in food processing industry.



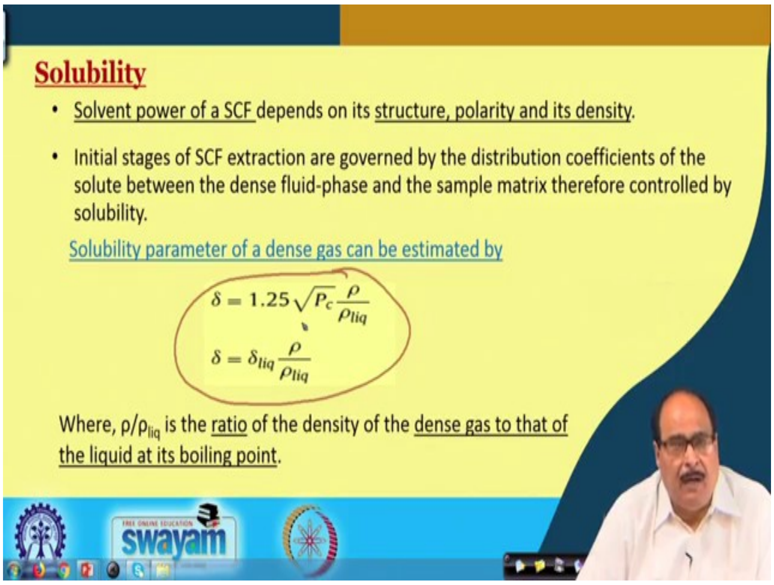
From the data in table, it can be noticed that carbon dioxide has a T_c of 31.1 °C and P_c of 73.8 bar, and its critical volume at this stage is 73.9 l/kmol. Water, as far as its properties are concerned, it may also be considered as a good solvent, but both the temperature and pressure required to bring water in supercritical stage are comparatively very high. The temperature in fact is 374 °C and the pressure accordingly is 221 bar and under these conditions, its critical volume is also comparatively lower i.e. is 57.1 l/kmol. So, from the practical application point of view, the use of water as a supercritical fluid rather becomes impractical or infeasible that is why mostly it is not used and carbon dioxide is used many a times because of its easy conversion into supercritical stage. In this pictorial diagram shown the state changes when the liquid CO_2 is converted into supercritical CO_2 by increasing temperature and pressure.



The supercritical fluids behave as a dense gas occupying all available volume as a single phase, but they cannot be condensed as liquid by increasing the pressure. The densities of SCFs depend on temperature and pressure varying in the range of 400-700 kg/m^3 and which is significantly lower than the density of the liquid which is normally 1000 kg/m^3. So, this significantly lower density of SC-CO_2 is an important advantage in the extraction processes. Also, the transport properties of the supercritical fluids are those between the liquids and gases. Viscosity of supercritical carbon dioxide is about 0.5 mPa/s which is significantly lower than the viscosity of the hexane. Even the molecular diffusivity of SC-CO_2 at 40 °C is about one order of magnitude higher than that of the diffusivity in the liquid state. These properties particularly transport properties, density, viscosity, etc. make it useful for extraction.



The favourable transport properties are desirable in extraction operations, since low viscosities facilitate the penetration of SCF into the particulate beds and reduce the power requirements in transferring the fluids through the system. Higher diffusivity increases the mass transfer, and approaches to the equilibrium. It means the higher diffusivity of the SCF gives higher extraction efficiency in the processes. The phase equilibria between the SCF solvent and food component to be extracted are required for quantitative analysis of the extraction processes.

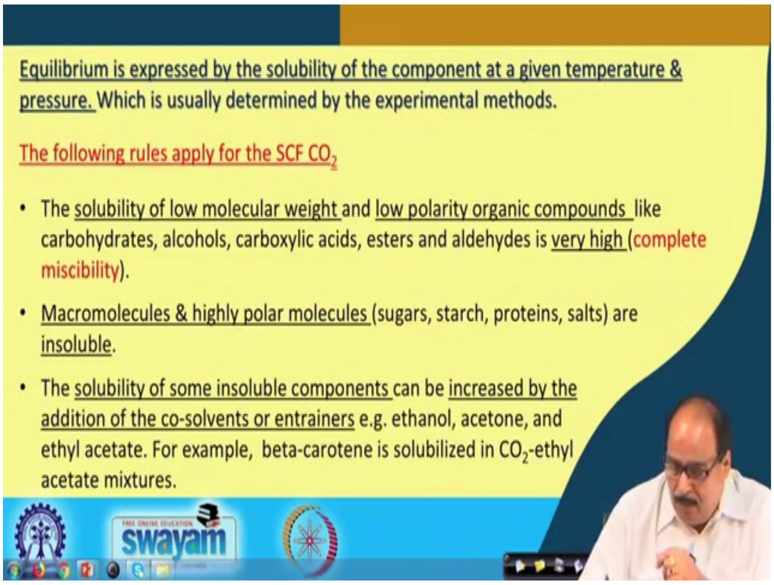


Solubility is the solvent power of the supercritical fluid that depends on its structure, polarity, and density. Initial stages of SCF extraction are governed by the distribution coefficients of the solute between the dense phase and the sample matrix. Therefore, it is controlled by the solubility. So, solubility parameters of a dense gas can be estimated by these equations,

$$\delta = 1.25\sqrt{P_c}\frac{\rho}{\rho_{liq}}$$

$$\delta = \delta_{liq}\frac{\rho}{\rho_{liq}}$$

where ρ/ρ_{liq} is the ratio of the density of the dense gas to that of the liquid at its boiling point and Pc is the critical pressure.



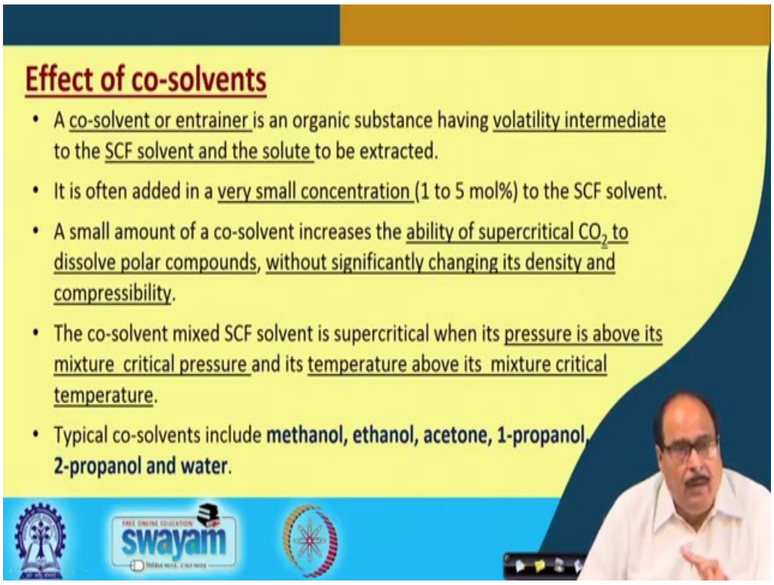
Equilibrium is expressed by the solubility of the component at a given temperature and pressure. And this is usually determined by the experimental methods for particular product, depending upon material characteristics, etc.

There are three main rules to be applied for SCF-CO_2:

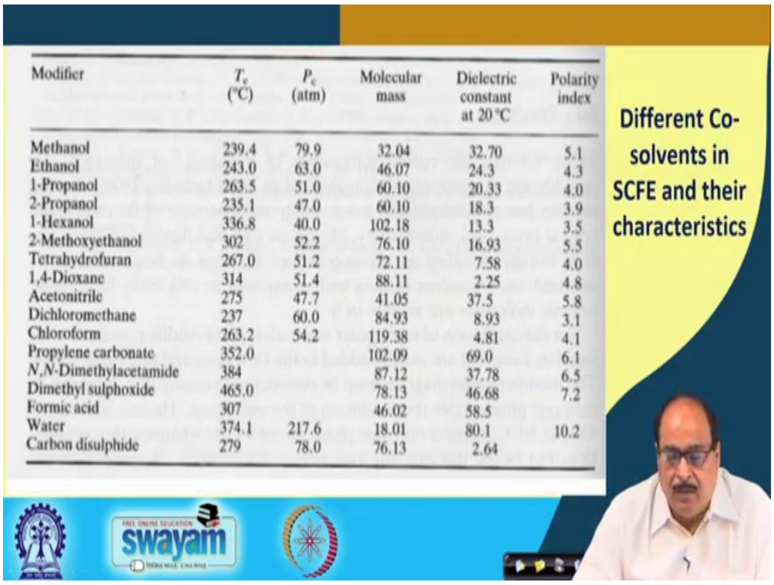
i. The solubility of low molecular weight and low polarity organic compounds like carbohydrates, alcohols, carboxylic acid, esters, aldehyde, etc. is very high in SCF CO_2. These are completely miscible and get easily extracted.

ii. Macromolecules and highly polar molecules, like sugars, starch, proteins, salts, etc. are not soluble and remain in food.

iii. The solubility of some insoluble components can be increased by the addition of some co-solvents or entrainers such as ethanol, acetone, etc. For example, the solubility of β-carotene is increased to a great extent by using a mixture of supercritical carbon dioxide and ethyl acetate; here ethyl acetate is used as a co-solvent.

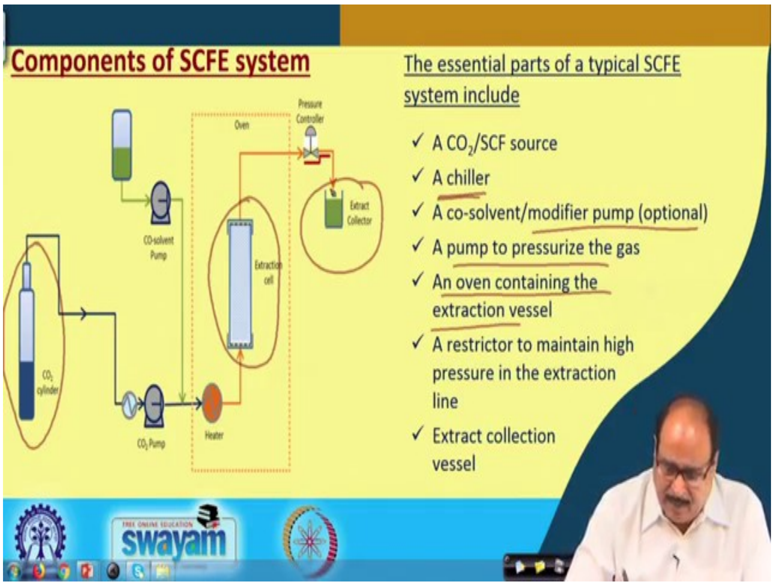


The co-solvents have important effect; they improve the efficiency of the process by increasing the extractability of a particular compound. So, the co-solvents or entrainers are actually the organic substances which have volatility intermediate to supercritical fluid solvent and the solute to be extracted. And generally it is added in small concentration may be 1-5 mol%. A small amount of co-solvent increases the ability of supercritical carbon dioxide to dissolve polar compounds, without significantly changing its density and compressibility. Its solubilisation power and extractability is improved but other characteristics are not disturbed. The co-solvent mixed with SCF solvent also behaves as supercritical fluids i.e. the mixture has also to come under the supercritical state. Individually solvent and co-solvent may be having different critical pressure and temperature to come into the supercritical state, but when the co-solvent is mixed with the SCF, there may be certain change in the temperature. So, the co-solvent mixed with SCF will be supercritical when its pressure is above the mixture critical pressure and its temperature is above the mixture critical temperature. The common type of co-solvents used are methanol, ethanol, acetone, and propanols, etc.



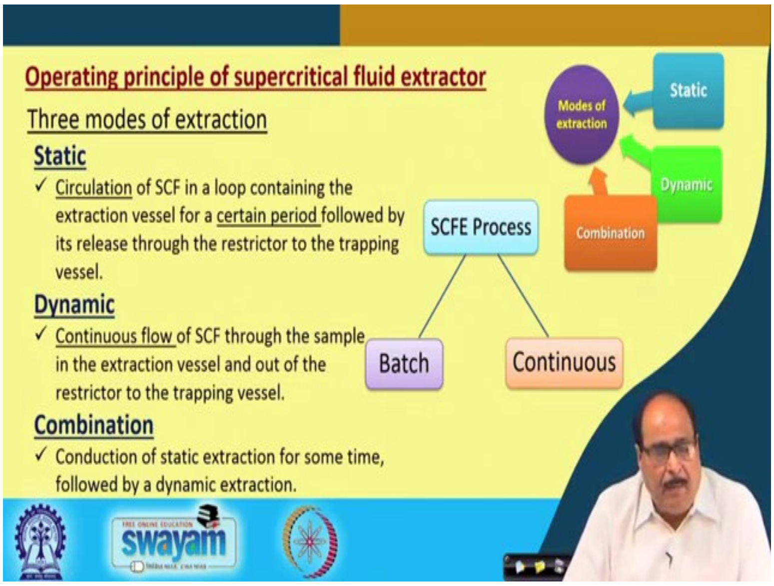
Modifier	T_c (°C)	P_c (atm)	Molecular mass	Dielectric constant at 20 °C	Polarity index
Methanol	239.4	79.9	32.04	32.70	5.1
Ethanol	243.0	63.0	46.07	24.3	4.3
1-Propanol	263.5	51.0	60.10	20.33	4.0
2-Propanol	235.1	47.0	60.10	18.3	3.9
1-Hexanol	336.8	40.0	102.18	13.3	3.5
2-Methoxyethanol	302	52.2	76.10	16.93	5.5
Tetrahydrofuran	267.0	51.2	72.11	7.58	4.0
1,4-Dioxane	314	51.4	88.11	2.25	4.8
Acetonitrile	275	47.7	41.05	37.5	5.8
Dichloromethane	237	60.0	84.93	8.93	3.1
Chloroform	263.2	54.2	119.38	4.81	4.1
Propylene carbonate	352.0		102.09	69.0	6.1
N,N-Dimethylacetamide	384		87.12	37.78	6.5
Dimethyl sulphoxide	465.0		78.13	46.68	7.2
Formic acid	307		46.02	58.5	
Water	374.1	217.6	18.01	80.1	10.2
Carbon disulphide	279	78.0	76.13	2.64	

In this table, the data shown are taken from the literature. The characteristics, like critical temperature, critical pressure, molecular mass, dielectric constant, polarity index, etc. of different co-solvents are given in this table. They become useful consideration; from this, it becomes easy to select a proper co-solvent which is suitable for extraction of a particular material.

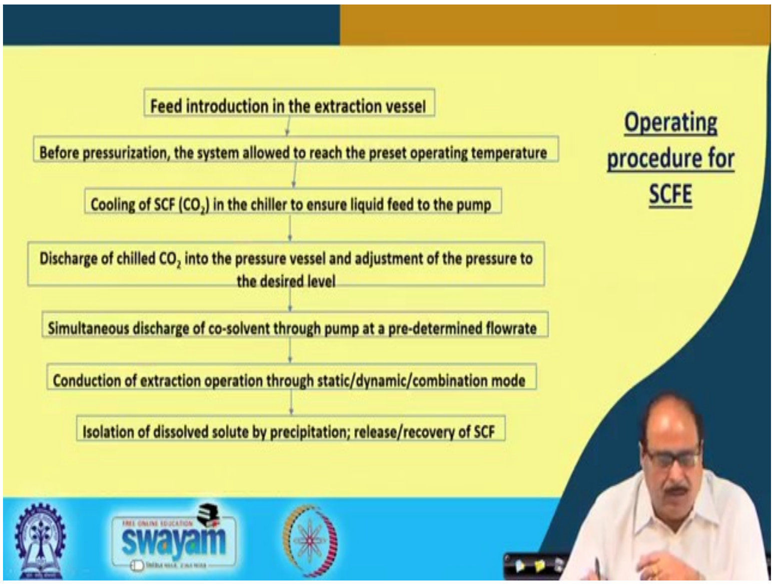


Components of Supercritical Fluid Extraction system:

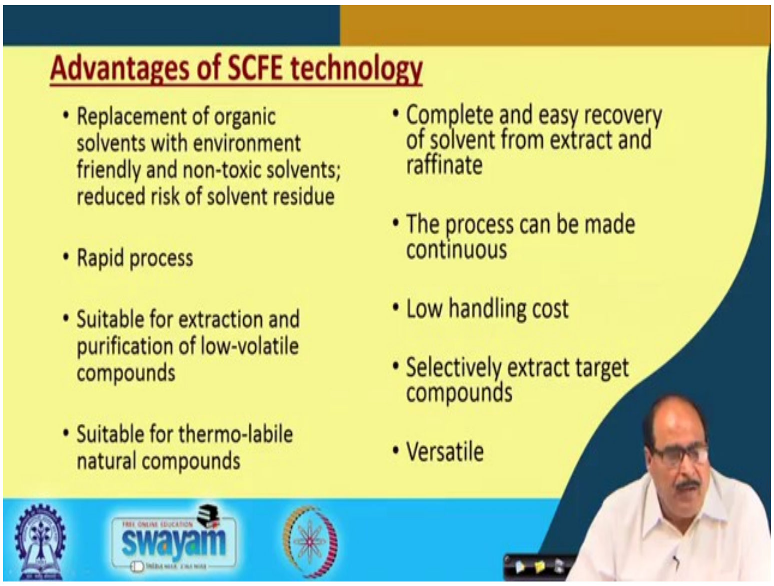
The system has a CO_2 or SCF source, a chiller unit, a co-solvent or modifier pump (optional), a pump needed to pressurize the gas, and an oven containing the extraction vessel. So, in the vessel, the material and carbon dioxide come in contact. It has a restrictor to maintain high pressure in the extraction line and finally an extract collecting vessel. And accordingly as in case of any other system, there are necessary instrumentation for controlling and maintaining the pressure, temperature, flow and other parameters.



So, regarding operating principle of the supercritical fluid extractor, it can operate in static mode, dynamic mode or in a combination mode. The process can be made batch or continuous. In the static mode, the supercritical fluid is circulated in the extraction vessel for a certain period of time after which it is released through the restrictor to the trapping vessel. In the dynamic mode of extraction, there is a continuous flow of SCF, i.e. the SCF is allowed to flow continuously through the sample in the extraction vessel and go out to the restrictor to the trapping vessel. Also there are combination systems where static extraction for some time is followed by a dynamic extraction.



Process flowchart of general supercritical fluid extraction process: The feed is introduced into the extraction vessel. Before the pressurization, the system is allowed to reach the pre-set operating parameters. The supercritical fluid is cooled in the chiller to ensure liquid feed to the pump. And then after that this chilled carbon dioxide is discharged into the pressure vessel and adjustment of the pressure is done to the desired level. Simultaneous discharge of co-solvent through the pump at the predetermined flow rate is done in the system, where the co-solvents are used and then the conduction of the extraction operation is allowed either in the dynamic mode, combination mode or static mode either in batch or continuous systems. The last step is the isolation of the dissolved solute by precipitation, adsorption or by any other appropriate method and then followed by release or recovery of the supercritical fluid.



The supercritical fluid technology has many advantages like it is a very good green process, it results in the replacement of organic solvent with environment friendly and non-toxic solvent, it reduces the risk of the solvent residue. It is a rapid process, it is suitable for the extraction and purification of low volatile component, and even suitable for thermo labile natural products. So, both low volatile as well as highly volatile thermo sensitive products etc. can be extracted easily and even the quality extracted product can be improved.

Complete and easy recovery of solvent from the extract or the raffinate both is possible. The process can be made continuous. It has low handling cost, selectively extracts target compounds, and is a versatile set of technology. This is in fact one of the very emerging technology and novel technology for food processing application, for obtaining the value added products from the food materials.