Module : 10
Supercritical Fluid Extraction

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Supercritical Fluid Extraction

Critical Condition:

At a certain temperature and pressure condition (critical condition), liquid and vapor phases of a substance become indistinguishable. A substance whose temperature and pressure are higher than its critical point is known as supercritical fluid (SCF). Fig. 10.1 shows typical pressure – temperature history of a substance.

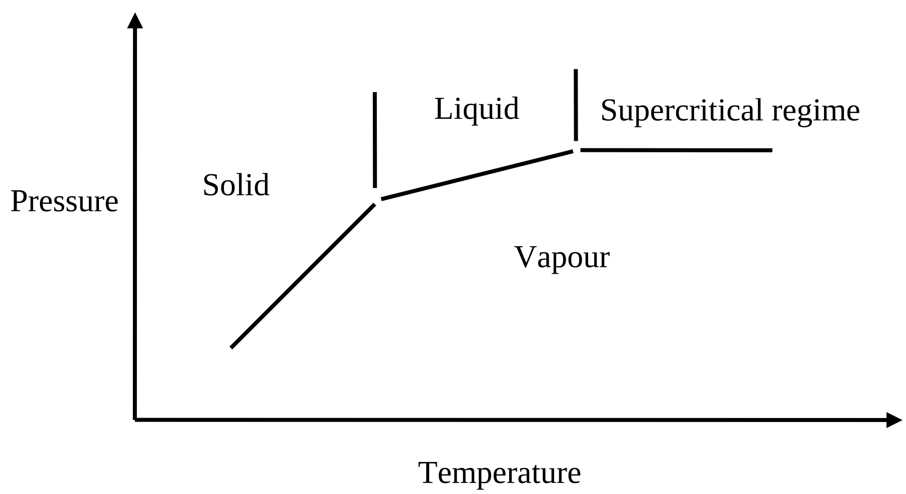


Fig. 10.1: Typical pressure – temperature history of a substance

Physical and thermal properties of SCFs are in between pure liquid and gas. Changes in properties are for a SCF are as follows:

(i) Liquid like densities

(ii) Reduction in surface tension

(iii) Gas like viscosity

(iv) Gas like compressibility properties

(v) Diffusivities higher than liquids

Commonly used supercritical (SC) solvents:

Some commonly used supercritical solvents are carbon di oxide, nitrous oxide, ethylene, propylene, propane, n-heptane, ethanol and ammonia. Among these, CO_2 is widely used as a supercritical solvent.

Substance	T_c (^0K)	P_c (atm)	Density (g/cc)
CO_2	304.2	73	0.47
Ethane	305.5	48.2	0.20
Ethanol	516.6	63.0	0.28
Propane	370.3	42.0	0.22

Why CO_2 is a supercritical fluid (SCF)?

Following properties of CO_2 make it qualified to be an SCF.

(i) Low critical pressure (74 atm) and low critical temperature (32^0C)

(ii) Relatively non-toxic

(iii) Non-flammable

(iv) Available as high purity

(v) Low cost

(vi) Easily removable from extract

(vii) It has polarity like liquid pentane at supercritical conditions and thus, best suited for liophilic compounds.

Drawback: It cannot extract polar solutes.

Nitrous Oxide:

It is good for removal or solubilize polar solutes, as it has a permanent dipole moment. N_2O is better than CO_2 for extraction of polychlorinated dibenzodioxines from fly ash.

Disadvantage: It is highly explosive

H_2O:

Disadvantage:

(i) High P_c and T_c (T_c > 374^0C, P_c > 221 bar)

(ii) At these conditions, H_2O is corrosive.

Important parameters for SCF extraction:

(i) ***Threshold pressure:*** Pressure at which miscibility of solute starts. Fig. 10.2 shows typical solubility curve of a material at a particular temperature.

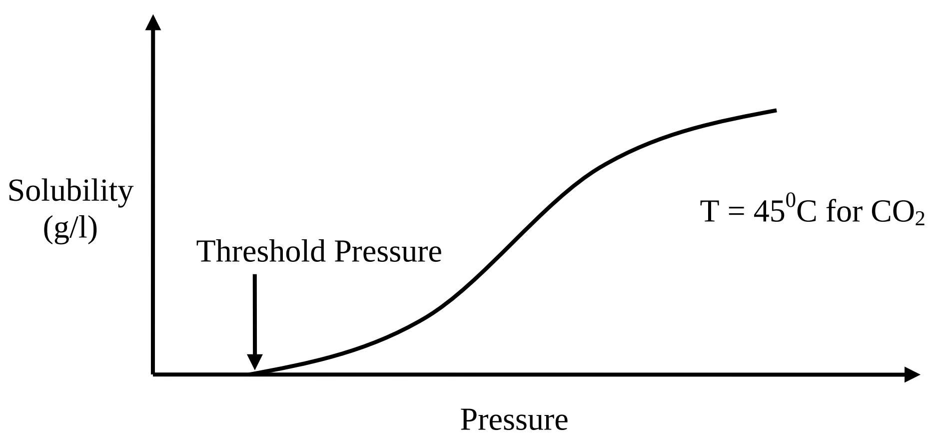


Fig. 10.2: Typical solubility curve of a material at a particular temperature.

(ii) Pressure at which solute reaches its maximum solubility.

(iii) Knowledge of physical properties of solutes (particularly, melting points). Solutes are dissolved better in liquid state.

Co-solvents or Modifiers:

Co-solvents are added to modify the polarity of the SCF, so that the power of SCF to solvate polar solutes increases.

Ex: CO_2 should be mixed with 1-10% of methanol to solubilize more polar solutes.

Advantages of SCF extraction:

(i) Simple expansion of SCF leads to lowering in solubility capacity of it. Thus, dissolved solutes are separated.

(ii) They have liquid like density but superior mass transfer behaviour compared to liquids due to high diffusivity and low surface tension so that they can penetrate into the porous structure of solid matrix to release the solute.

Mechanism of solubilization of solutes from solid materials:

There exists four mechanisms for solubilization of solutes in SCF:

(i) If there is no interaction between solute and solid phase, the process is dissolution of solute in suitable solvent.

(ii) If there is interaction between solute and solid, extraction is desorption. Adsorption isotherm of solute on the solid in presence of solvent determines the equilibrium.

(iii) Swelling of solid phase by the solvent accompanied by extraction of entrapped solutes through the first two mechanisms.

(iv) Reactive extraction.

Insoluble solutes react with solvent and products are soluble and hence extractable. For example, lignin extraction from cellulose.

Thermodynamic Parameters:

Temperature, pressure, adsorption equilibrium constant and solubility of solute in solvent are the major thermodynamic properties in this regard.

Basic Techniques in SCF technology:

1. RESS (Rapid expansion of supercritical solutions):

A typical flow chart of a supercritical fluid extraction process is outlined in Fig. 10.3. A supercritical solvent saturated with a solute is allowed to expand rapidly, leading to precipitation of solute. Rapid expansion is achieved by allowing it to pass through a nozzle at supersonic speed.

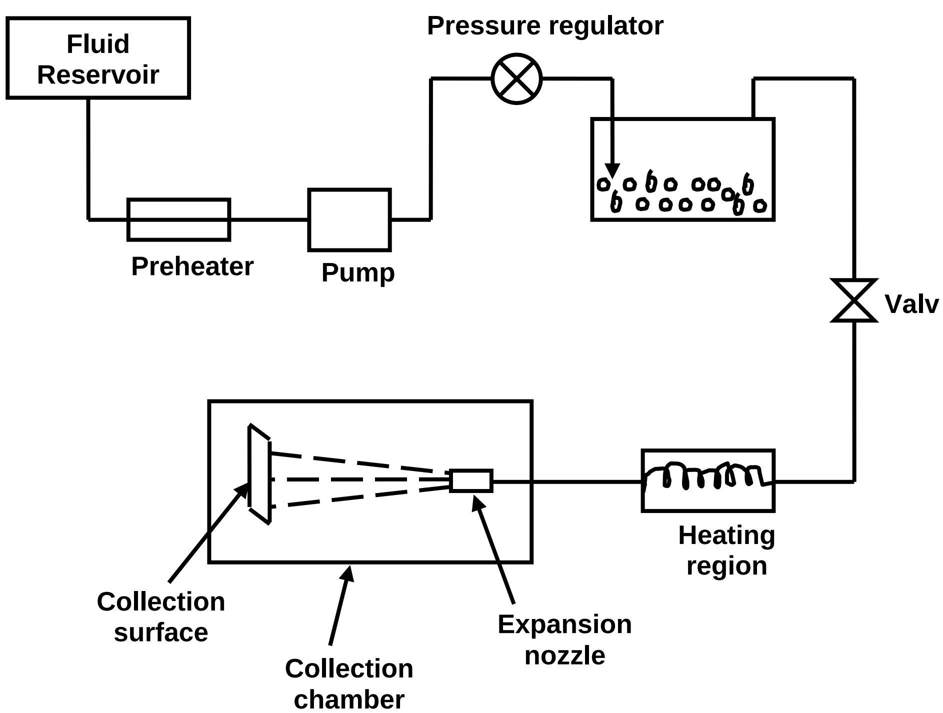


Fig. 10.3: A typical flow sheet of a SCF process

Supercritical fluid (SF) is pumped through a pre heater into the vessel containing solid solute and the resultant solution is sent into a precipitation chamber by expansion through capillary or laser drilled nozzle. At precipitation chamber, pressure is much lower and solute solubility in SF is quite low and solute precipitates out of it. Size distribution and morphology of precipitated material is a function of pre-expansion concentration and its conditions. Pre-expansion concentration in term depends on SF, nature of solute, addition of co-solvent, operating pressure and temperature. Particle size is smaller and distribution is narrower if pre-expansion concentration is higher.

Example: Naphthalene extraction process

A typical naphthalene extractor is shown in Fig. 10.4.

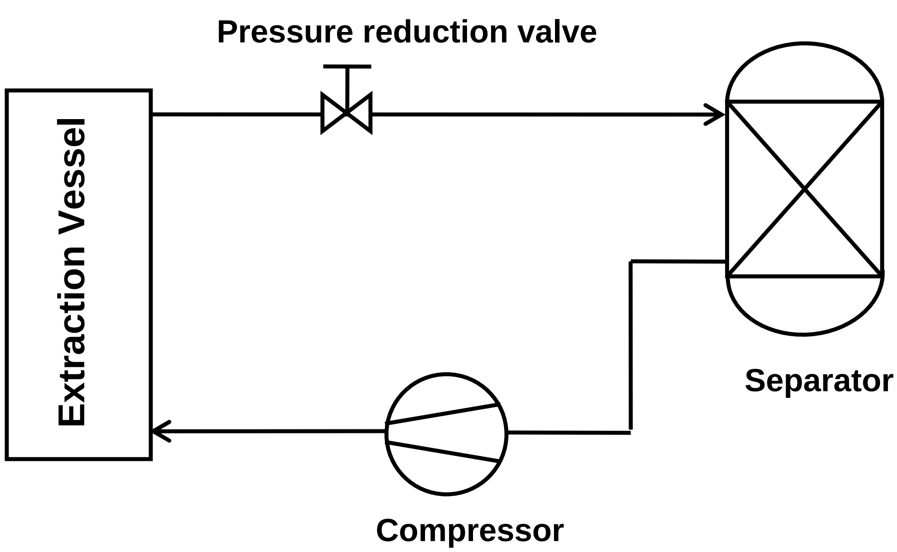


Fig. 10.4: A typical naphthalene extractor

The solubility diagram of naphthalene is shown in Fig. 10.5.

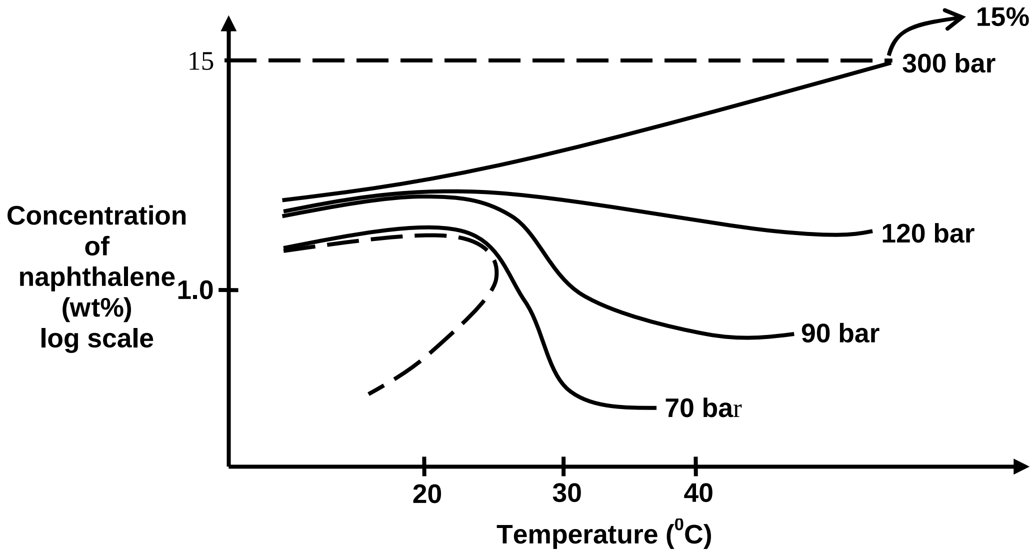
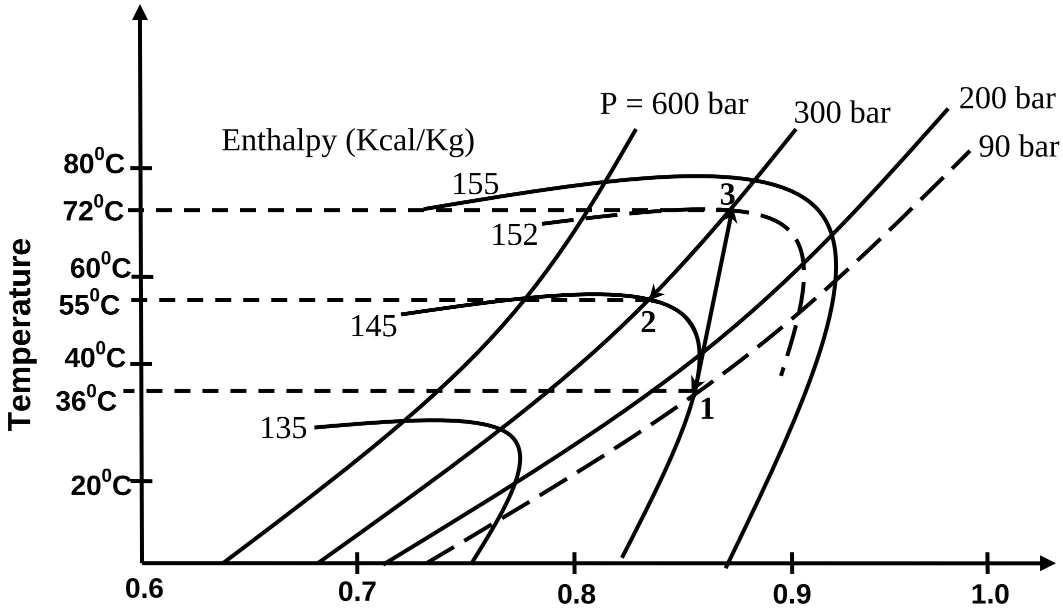


Fig. 10.5: Solubility diagram of naphthalene under supercritical condition

A naphthalene-chalk dust mixture is fed to the extraction vessel. Assume, extraction condition is 300 bar and 55^{0}C. At this condition CO_2 SCF contains naphthalene dissolved at 15 wt%. Then it is expanded to 90 bar through pressure reduction valve (assuming isenthalpic expansion). After expansion its temperature is 36^{0}C at 90 bar. Solubility of naphthalene is 2.5%. So, it falls out of solution. Precipitated naphthalene is collected and CO_2 is compressed to 55^{0}C and 300 bar and recycled to extractor.

Mollier Diagram:



(1) → 55^0C, 300 bar

(2) → 36^0C, 90 bar (after expansion)

(3) → 72^0C, 300 bar (after compression)

Energy required to compress from 90 to 300 bar is,

$$(152-145)=7 \text{ Kcal/kg} \qquad (12.6 \text{ BTU/lb})$$

Then it is cooled to 55^0C

(4) → 72^0C, 300 bar to 55^0C, 300 bar

Decrease in solubility is 15 to 2.5 wt%

1 lb CO_2 contains → *0.15 lb* Naphthalene

After extraction

1 lb CO_2 contains → *0.025 lb* Naphthalene

Extracted naphthalene $=0.15-0.025=0.125$ lb

0.125 lb naphthalene extracted for 1lb CO_2

So, *0.125 lb* naphthalene extracted for $= \frac{1000}{125} = 8 \text{ lb } CO_2$

So, we require *8 lb* CO_2 to recycle for extraction of 1 *lb* naphthalene.

Energy required for compression from 90 to 300 *bar* is $= 12.6 \times 8$ BTU

$= 100.8$ BTU for extraction of 1 lb naphthalene

Some Special Applications of supercritical fluid extraction:

1. Removal of fat from foods
2. Extraction of vitamin E from natural resources
3. Removal of alcohol from wine and beer
4. Extraction of pesticides
5. Extraction of polyaromatic hydrocarbon, polychloro benzene

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