Supercritical Fluids (SCF)
&
Supercritical Fluid Extraction (SFE)

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Introduction

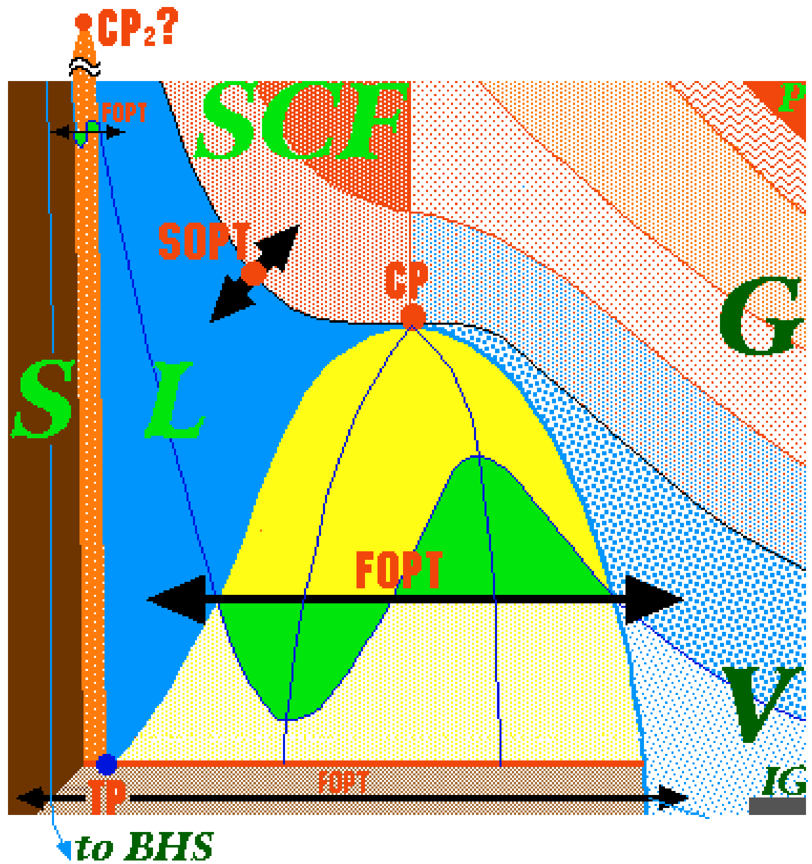
Supercritical fluids (SCFs) are increasingly replacing the organic solvents that are used in industrial purification and recrystallization operations because of regulatory and environmental pressures on hydrocarbon and ozone-depleting emissions. SCF-based processes has helped to eliminate the use of hexane and methylene chloride as solvents. With increasing scrutiny of solvent residues in pharmaceuticals, medical products, and neutraceuticals, and with stricter regulations on VOC and ODC emissions, the use of SCFs is rapidly proliferating in all industrial sectors.

Supercritical fluid extraction (SFE) plants are operating at throughputs of 100,000,000 lbs/yr or more in the foods industry. Coffee and tea are decaffeinated via supercritical fluid extraction and most major brewers in the US and Europe use flavors that are extracted from hops with supercritical fluids.

SCF processes are being commercialized in the polymers, pharmaceuticals, specialty lubricants and fine chemicals industries. SCFs are advantageously applied to increasing product performance to levels that cannot be achieved by traditional processing technologies, and such applications for SCFs offer the potential for both technical and economic success.

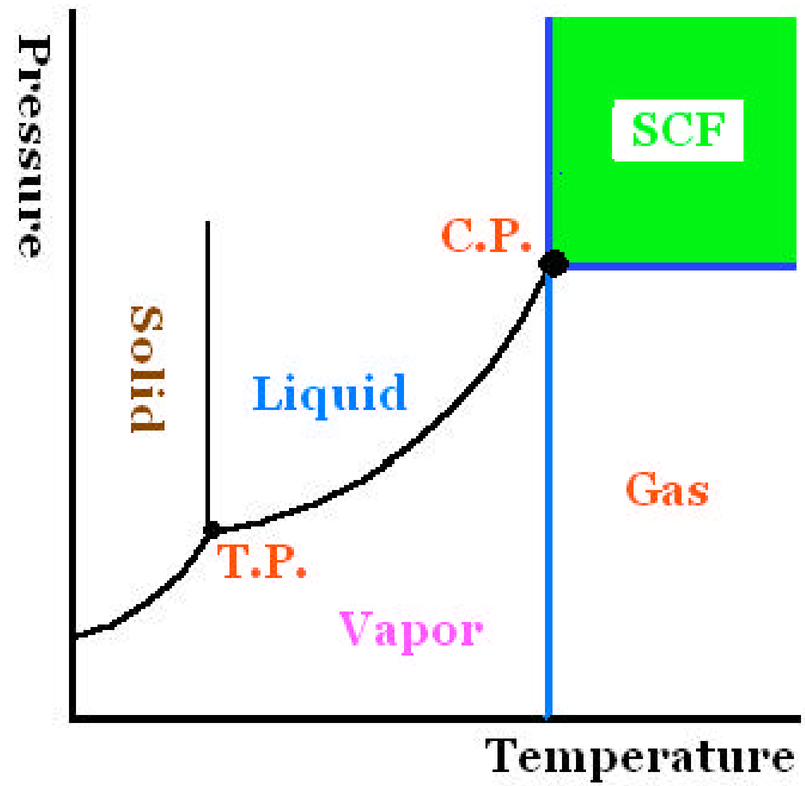
Supercritical Fluids

- The critical point (CP) marks the end of the vapor-liquid coexistence curve. A fluid is termed supercritical when the temperature and pressure are higher than the corresponding critical values. Above the critical temperature, there is no phase transition in that the fluid cannot undergo a transition to a liquid phase, regardless of the applied pressure.



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.**

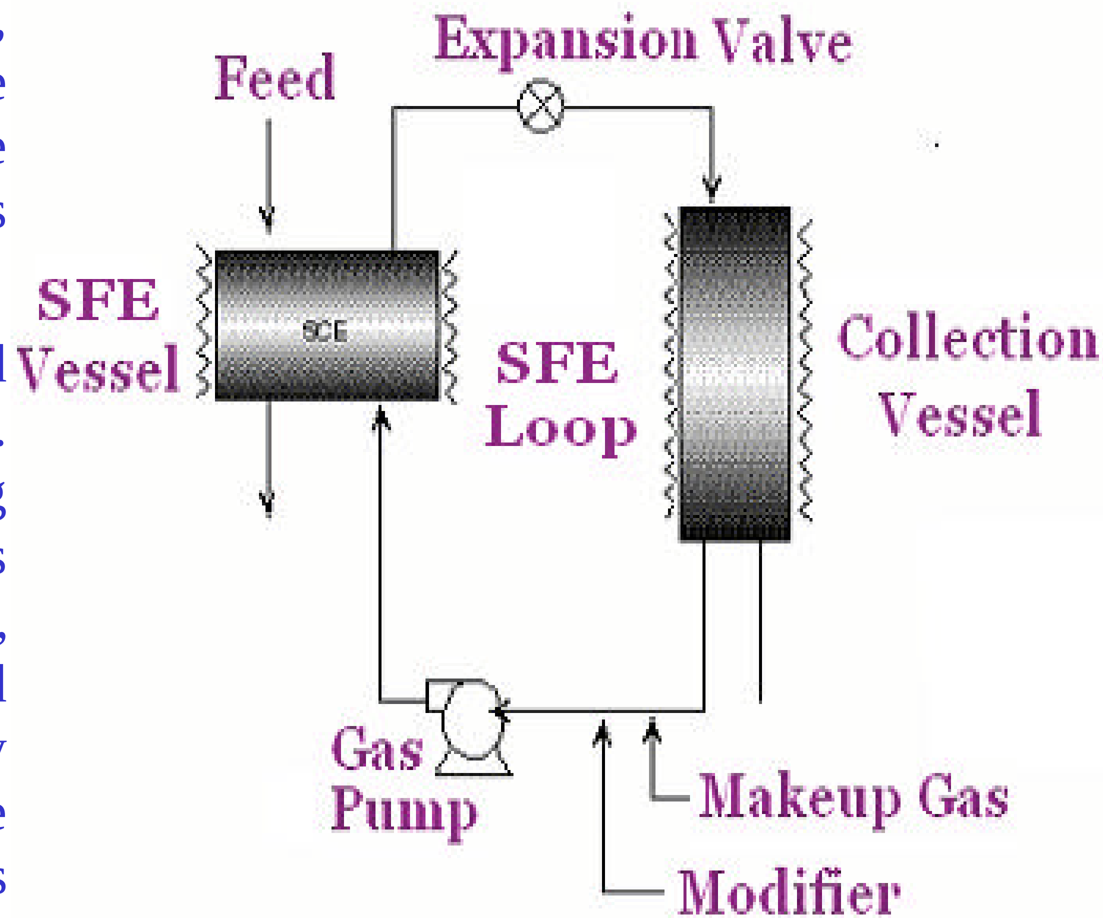


Properties of Supercritical Fluids

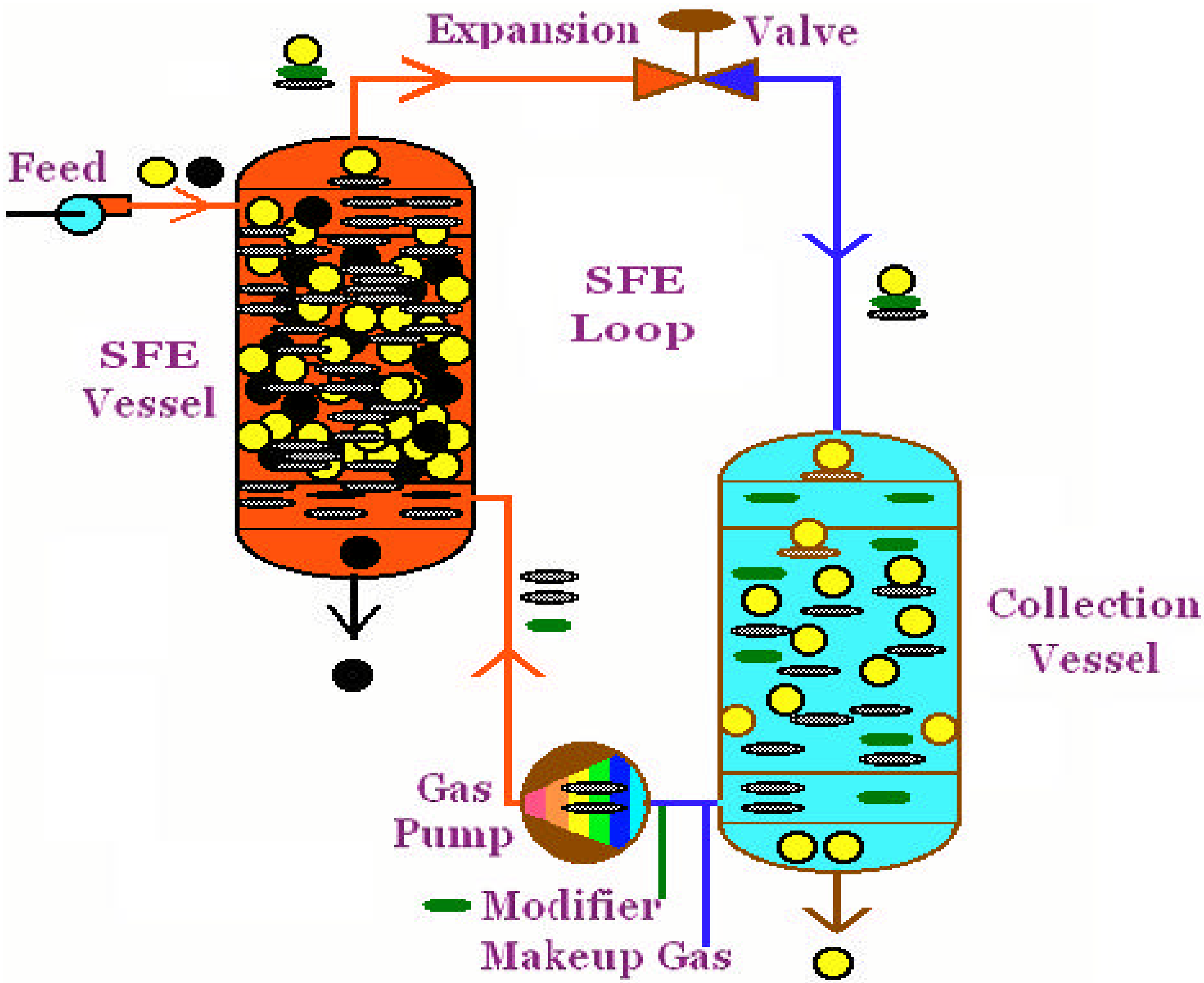
- There are drastic changes in some important properties of a pure liquid as its temperature and pressure are increased approaching the thermodynamic critical point. For example, under thermodynamic equilibrium conditions, the visual distinction between liquid and gas phases, as well as the difference between the liquid and gas densities, disappear at and above the critical point. Similar drastic changes exist in properties of a liquid mixture as it approaches the thermodynamic critical loci of the mixture.
- Other properties of a liquid fuel that change widely near the critical region are thermal conductivity, surface tension, constant-pressure heat capacity and viscosity. In comparing a liquid sample with a supercritical fluid (SCF) sample of the same fuel both possessing the same density, thermal conductivity and diffusivity of a SF are higher than the liquid, its viscosity is much lower, while its surface tension and heat of vaporization have completely disappeared. These drastic changes make a supercritical fuel appreciably preferred over that of a liquid fuel with the same density. Further, it is expected that the combustion phenomena resulting from that of a supercritical fuel will be quite different from that of a liquid fuel.
- Applications of SCF include recovery of organics from oil shale, separations of biological fluids, bioseparation, petroleum recovery, crude de-asphalting and dewaxing, coal processing (reactive extraction and liquefaction), selective extraction of fragrances, oils and impurities from agricultural and food products, pollution control, combustion and many other applications.

Supercritical Fluid Extraction (SFE)

- Supercritical Fluid Extraction (SFE) is based on the fact that, near the critical point of the solvent, its properties change rapidly with only slight variations of pressure.
- Supercritical fluids can be used to extract analytes from samples. The main advantages of using supercritical fluids for extractions is that they are inexpensive, extract the analytes faster and more environmentally friendly than organic solvents. For these reasons supercritical fluid CO_2 is the reagent widely used as the supercritical solvent.



Molecular Basis of SFE



Advantages of SFE

- **1.** SCFs have solvating powers similar to liquid organic solvents, but with higher diffusivities, lower viscosity, and lower surface tension.
- **2.** Since the solvating power can be adjusted by changing the pressure or temperature separation of analytes from solvent is fast and easy.
- **3.** By adding modifiers to a SCF (like methanol to CO2) its polarity can be changed for having more selective separation power.
- **4.** In industrial processes involving food or pharmaceuticals, one does not have to worry about solvent residuals as you would if a "typical" organic solvent were used.
- **5.** Candidate SCFs are gemerally cheap, simple and many are safe. Disposal costs are much less and in industrial processes, the fluids can be simple to recycle.
- **6.** SCF technology requires sensitive process control, which is a challenge. In addition, the phase transitions of the mixture of solutes and solvents has to be measured or predicted quite accurately. Generally the phase transitions in the critical region is rather complex and difficult to measure and predict. Our research has provided much insight into this phenomena.

- The Thermodynamics Research Laboratory at UIC is well equiped to produce data and predictive schemes for supercritical fluids and supercritical fluid extraction. For further information please contact <trl@uic.edu>.

Related Publications

- Ekhtera, M.R., Mansoori, G.A., Mensinger, M.C., Rehmat, A. and Deville, B. "Supercritical Fluid Extraction for Remediation of Contaminated Soil" in "Supercritical Fluids: Extraction and Pollution Prevention" M. Abraham and A. Sunol (Editors), ACSSS Vol. # 670, pp. 280-298, American Chemical Society, Washington, D.C., 1997.
- Kwak, T.Y. and Mansoori, G.A. "Van der Waals Mixing Rules for Cubic Equations of State - Applications for Supercritical Fluid Extraction Modelling", Chemical Eng. Science, 41, 5, pp.1303-1309, 1986.
- Kwak, T.Y., Benmekki, E.H. and Mansoori, G.A. "Van der Waals Mixing Rules for Cubic Equations of State (Applications for Supercritical Fluid Extraction Modeling and Phase Equilibria Calculations)", ACS Symposium Series 329, pp.101-114, American Chemical Society, Washington, D.C., 1987.
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- Mansoori, G.A. and Ely, J.F. "Density Expansion (DEX) Mixing Rules (Thermodynamic Modeling of Supercritical Extraction)", J. Chem. Phys., 82, 406, 1985.

Related Publications *Continued*

- Mansoori, G.A. "Phase Equilibrium of Mixtures Consisting of Molecules with Large Size and Shape Differences (Thermodynamic Modeling of Supercritical Fluid Extraction and Retrograde Condensation, SFE/RC)", GRI Document Number: GRI-88/0360 , 88p, Gas Research Institute, Chicago, IL USA, August 1988.
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- Mansoori, G.A., "Phase Equilibrium of Mixtures Consisting of Molecules with Large Size and Shape Differences (Thermodynamic Modeling of Supercritical Fluid Extraction and Retrograde Condensation, SFE/RC)", GRI Document Number: GRI-89/0159 , 121p, Gas Research Institute, Chicago, IL USA, June 1989.
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- Mansoori, G.A., Suwono, A., Sitompul, J.P. and Samudro, H.M. "Fractionation of wax by supercritical extraction: Solubility correlation" Ratnawati, Proceedings of the International Conference on Fluid and Thermal Energy Conversion '97, ISSN 0854-9346, pp. 573-580, 1997.

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- Martinelli, E., Schulz, K. and Mansoori, G.A. "Supercritical Fluid Extraction / Retrograde Condensation (SFE/RC) with Applications in Biotechnology", pp. 451-478, in "SUPERCRITICAL FLUID TECHNOLOGY", Edited by T.J. Bruno and J.F. Ely, CRC Press, Boca R aton, FL, 1991.
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