

## **SUPERCRITICAL FLUIDS**

Ruhan Askin, Semih Ötles

Ege University of Bornova, Izmir, Turkey

**Abstract.** This study includes information concerning supercritical fluids. Beginning from the general description of the supercritical fluids, their historical background with physico-chemical properties is given. Special properties with the aid of which supercritical characteristics are obtained are attempted to be explained. Also, supercritical CO<sub>2</sub> (SCCO<sub>2</sub>), as a solvent for extraction related to the advantages of using such a solvent carrying supercritical properties, is discussed. In order to understand the mechanism of supercritical fluid extraction (SFE), the modelling concept of supercritical fluids (SCFs) and the criteria for various separation techniques are redefined.

**Key words:** supercritical fluids (SCFs), supercritical fluid extraction (SFE), modelling of SCFs, supercritical characteristics, SFE mechanism

## **INTRODUCTION**

The technology of supercritical fluids (SCFs) and supercritical fluid extraction offers an opportunity to efficiently and economically improve recovery, increase reproductibility, decrease the use of halogenated solvents, and provide cleaner extracts to the measurement instrument. To be truly useful in the analytical laboratory, the SFE technology must be thoroughly understood. A hasty approach to method development can lead to problems and even disillusionment with the technology. Lack of understanding regarding system parameters (e.g. type of fluid, density, pressure, temperature, flow rate, extraction time, extraction mode, analyte collection) can result in misinformation and erroneous conclusions. So, in order to do further SFE analysis, the system should be well understood. Ideally, SFE should be highly reproducible, fast, efficient, quantitative and free of contamination, should yield a concentrated sample solution which can be easily manipulated, and should preserve the chemical integrity of the analyte to be extracted. So, it should also be indicated that, in a growing number of instances, this ideal is becoming the norm.

## HISTORY OF SUPERCRITICAL FLUIDS

The first reported observation of the occurrence of a supercritical phase was made by Baron Cagniard de la Tour in 1822. He noted visually that the gas-liquid boundary disappeared when the temperature of certain materials was increased by heating each of them in a closed glass container. From these early experiments the critical point of a substance was first discovered. The first workers to demonstrate the solvating power of supercritical fluids for solids were Hanay and Hogarth in 1879. They studied the solubilities of cobalt (II) chloride, iron (III) chloride, potassium bromide, and potassium iodide in supercritical ethanol ( $T_c = 243^\circ\text{C}$ ,  $P_c = 63 \text{ atm}$ ). They found that the concentrations of the metal chlorides in supercritical ethanol were much higher than their vapour pressures alone would predict. They also found that increasing the pressure caused the solutes to dissolve and that decreasing the pressure caused the dissolved materials to precipitate as 'snow'.

Later, extraction and separation of mixtures with supercritical fluids (SCFs) aroused little interest during the first half of the twentieth century. In 1936 Wilson, Keith and Haylett devised a propane deasphalting process for refining lubricating oils. A few years later, the Solexol process was developed for the purification and separation of vegetable and fish oils. The process concentrated on the polyunsaturated triglycerides in vegetable oils and the 'so-called vitamin A values' from fish oils using propane as a selective solvent.

A significant development in supercritical fluid extraction (SFE) was the Zosel's patent, which provided incentive for extensive future work. In 1970, he reported the decaffeination of green coffee with  $\text{CO}_2$ . This process was accomplished by soaking the beans in water and then immersing them in supercritical  $\text{CO}_2$ . The presence of water was essential for the efficient extraction of the caffeine from within the bean.

Since 1980, there has been rapid development of supercritical fluid extraction of

- hops [Hubert and Vitzthum 1980],
- cholesterol from butter [Krukoniš 1988],
- perfumes and flavors from the natural products [Adasoglu et al. 1983],
- residual solvents and monomers from polymers [Krukoniš 1985],
- unsaturated fatty acids from fish oils [Krukoniš 1988].

In reality, SCF technology has become an interdisciplinary field shared by chemical engineers, chemists, food scientists, agronomists, researchers in biotechnology and environmental control. Since then, applications of SCF technology have been performed in many areas.

## PHYSICO-CHEMICAL PROPERTIES OF SUPERCRITICAL FLUIDS

Supercritical fluids can be used to extract analytes from samples. A pure supercritical fluid (SCF) is any compound at a temperature and pressure above the critical values (above critical point). Above the critical temperature of a compound the pure, gaseous compound can not be liquified regardless of the pressure applied. The critical pressure is the vapour pressure of the gas at the critical temperature. In the supercritical environment only one phase exists. The fluid, as it is termed, is neither gas nor liquid and is

best described as intermediate to the two extremes. This phase retains solvent power approximating liquids, as well as the transport properties common to gases.

By controlling temperature and pressure every substance can be set into supercritical state. Supercritical fluids, as they are called, are as heavy as fluid but there exists penetration power of gas. These qualities make supercritical fluids effective and selective solvents. This supercritical state can be illustrated as shown in Figure 1 below.

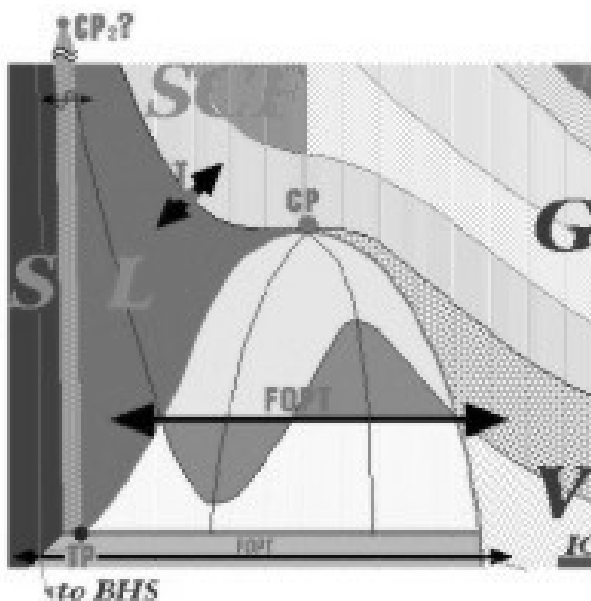


Fig. 1. Definition of supercritical state diagram for supercritical fluids (SCFs)

Rys. 1. Wykres stanów nadkrytycznych dla cieczy nadkrytycznych (SCFs)

The critical point (CP) is marked at the end of the gas-liquid equilibrium curve, and the shaded area indicates the supercritical fluid region. It can be shown that by using a combination of isobaric changes in temperature with the isothermal changes in pressure, it is possible to convert a pure component from liquid to gas (and vice versa) via the supercritical region without incurring a phase transition.

The behaviour of a fluid in the supercritical state can be described as that of a very mobile liquid. Considering the fact that the properties of the SCFs take place between gas and liquid state in Table 1, it can be said that the solubility behaviour approaches that of the liquid phase while penetration into a solid matrix is facilitated by the gas-like transport properties.

As a consequence, the rates of extraction and phase separation can be significantly faster than for conventional extraction processes. Furthermore, the extraction conditions can be controlled to effect a selected separation. Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature. The dissolving power of a SCF increases

Table 1. Comparison of physical and transport properties of gases, liquids, and SCFs  
 Tabela 1. Porównanie właściwości fizycznych i transportowych gazów, cieczy i cieczy nadkrytycznych

	Liquid Ciecz	Supercritical Ciecz nadkrytyczna T~T <sub>c</sub> P~1 to 4 P <sub>c</sub>	Gas Gaz (at room T et P)
Specific gravity Masa właściwa ρ, kg·m <sup>-3</sup>	600-1 600	100-900	0.6-2
Viscosity Lepkość η, Pa·s	10 <sup>-3</sup>	10 <sup>-5</sup> -10 <sup>-4</sup>	10 <sup>-5</sup>
Diffusivity Dyfuzyjność D, m <sup>2</sup> ·s <sup>-1</sup>	10 <sup>-9</sup>	10 <sup>-8</sup>	10 <sup>-5</sup>

with isothermal increase in density or an isopycnic (i.e. constant density) increase in temperature. In practical terms, this means a SCF can be used to extract a solute from a feed matrix as in conventional liquid extraction. However, unlike conventional extraction, once the conditions are returned to ambient the quality of residual solvent in the extracted material is negligible.

The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies in both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapour pressure of the solute and is generally negligible. In a SCF, however, solute solubilities of up to 10 orders of magnitude greater than those predicted by ideal gas law behaviour have been reported.

The dissolution of solutes in supercritical fluids results from a combination of vapour pressure and solute-solvent extraction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure.

Although the solubility of volatile liquids in SCFs is higher than in an ideal gas, it is often desirable to increase the solubility further in order to reduce the solvent requirement for processing. The solubility of components in SCFs can be enhanced by the addition of a substance referred to as an entrainer, or cosolvent. The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a cosolvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid.

Cosolvents also provide a mechanism by which the extraction and selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of cosolvents. A factor that must be taken into consideration when using cosolvents, however, is that even the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

### THERMODYNAMIC PROPERTIES OF SUPERCRITICAL FLUIDS (SCFS)

All pure compounds can be found in three states: solid, liquid or vapour (or gas). On the (pressure, temperature) diagram in Fig. 1, the three regions corresponding to these three states are separated by curves that meet at the triple point. Surprisingly, the vaporization/liquefaction curve presents an end point called critical point ( $P_c - T_c$ ) [Reid et al. 1988]. Beyond this point, ( $P > P_c$  and  $T > T_c$ ), only one phase exists, called Supercritical Fluid (SCF). At the critical point itself, the fluid compressibility becomes infinite:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \text{ et } \left(\frac{\partial^2 P}{\partial^2 V}\right)_T = 0$$

meaning that the fluid specific gravity rapidly varies with a slight change in pressure at constant temperature. Moreover, even out of the critical region itself, SCF exhibit large changes in specific gravity – and consequently its solvent power – as shown on Figure 2, and other physico-chemical properties with pressure or temperature.

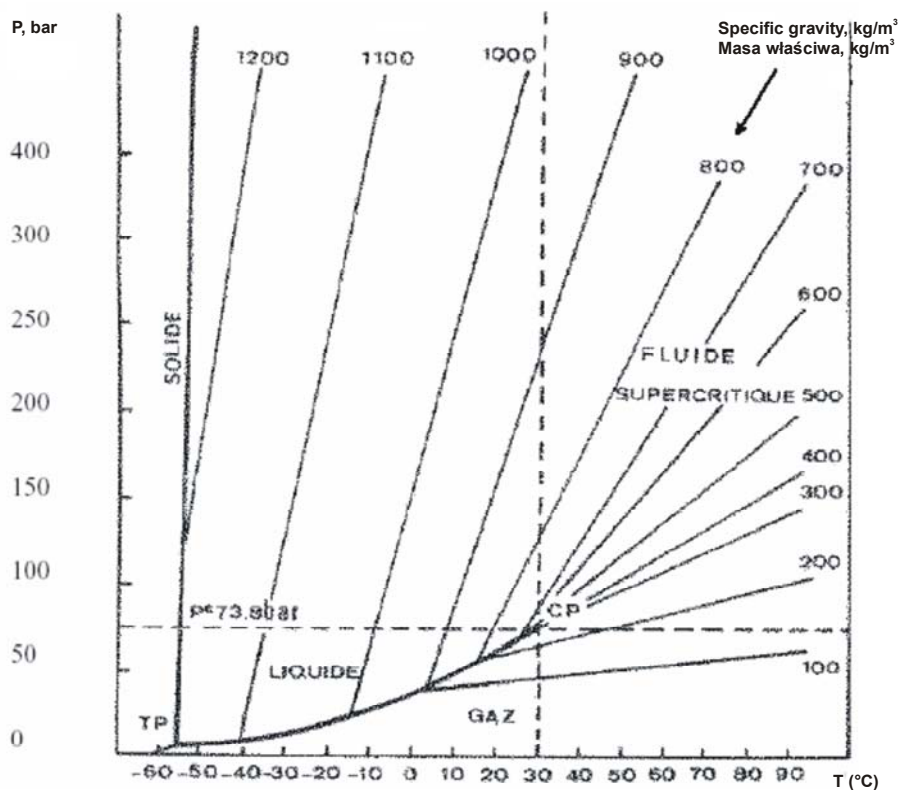


Fig. 2. Diagram (P,T,r) of carbon dioxide  
Rys. 2. Wykres (P,T,r) dwutlenku węgla

Most compounds exhibit a critical pressure in the range of 35 to 60 bar, except water (221 bar) and ammonia (113.5 bar). Critical temperature increases with the complexity of the molecule and very few compounds exhibit a critical temperature between 0 and 50°C (ethane, ethylene, CO<sub>2</sub>, N<sub>2</sub>O). Mixtures behave in a more complex way depending on their composition, but “critical” phenomena are also observed. The most interesting characteristics of SCF, on which all the SCF processes are based, is related to their “tunability” with pressure and temperature, especially of the tunability of their solvent power.

### **POLARITY OF SUPERCRITICAL FLUIDS (SCFS)**

Solvents are classified according to a scale of polarity depending on their ability to dissolve “polar” or “non-polar” molecules. Water is the most polar solvent, dissolving all kinds of compounds that can be ionized or that contains hydrophilic moieties like sugars, proteins or amino-acids. On the contrary, organic solvents like light alkanes (hexane, heptane,...) or chlorinated hydrocarbons do not dissolve these compounds, but only hydrophobic molecules that are not at all soluble in water like fats, oils, hydrocarbons or essential oils: they are called non-polar solvents. Other solvents like alcohols, amines or ketones exhibit intermediate behaviour. Most supercritical fluids behave like non-polar solvents exhibiting a strong affinity with lipids and hydrocarbons, but a weak affinity with oxygenated or hydroxylated molecules ; it is possible to tune their polarity by adding a polar co-solvent (ethanol or light alcohols, esters or ketones).

### **SUPERCRITICAL FLUIDS (SCFS) AND THEIR SOLVENT POWER**

Supercritical fluids are involved in numerous aspects of natural or industrial situations related to energy production or transfer. According to classical thermodynamic theory [Prausnitz et al. 1986], a fluid is in a supercritical state when it is at a pressure or temperature exceeding its critical value; the value of the pressure,  $p$ , temperature,  $T$ , or molar volume,  $v$ , divided by its corresponding critical value (subscript c) is called the ‘reduced’ (subscript r) value. What truly characterizes the supercritical state is the impossibility of a two-phase region. Indeed, when  $pr. 1$  or  $Tr. 1$ , in the  $(p,T)$  plane there is no longer the possibility of a two-phase (i.e. gas/liquid) region and instead there is only a single-phase region [Hirshfelder et al. 1964].

A pure component is considered to be in a supercritical state if its temperature and its pressure are higher than the critical values ( $T_c$  and  $p_c$ , respectively). At critical conditions for pressure and temperature, there is no sudden change of component properties. The variation of properties with conditions of state is monotonous, when crossing critical conditions, as indicated in Figure 3 by the hatched lines [Iso et al. 1995].

Yet the magnitude of the variation can be tremendous, thereby causing different effects on solutes and reactants within neighbouring conditions of state. Similar effects to that of the supercritical state can in some cases be achieved at near critical temperatures in the liquid state of a substance for  $p > p_c$  and  $T < T_c$ . Characteristic values for the gaseous, liquid, and supercritical state are listed in Table 1. In the supercritical state,

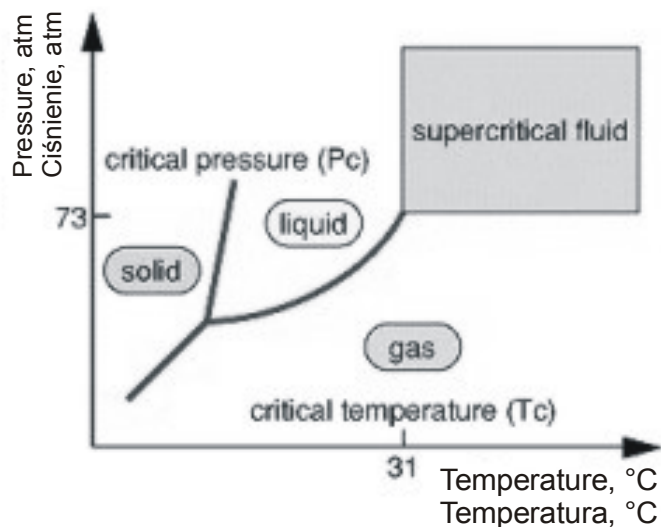


Fig. 3. Critical conditions for a pure component [Iso et al. 1995]  
 Rys. 3. Warunki krytyczne dla czystego składnika [Iso et al. 1995]

liquid-like densities are approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical liquids. In processes with supercritical fluids (SCFs), the driving potential for mass and heat transfer is determined by the difference from the equilibrium state. The equilibrium state provides information about:

- (i) the capacity of a supercritical (gaseous) solvent, which is the amount of a substance dissolved by the gaseous solvent at thermodynamic equilibrium;
- (ii) the amount of solvent, which dissolves in the liquid or solid phase, and the equilibrium composition of these phases;
- (iii) the selectivity of a solvent, which is the ability of a solvent to selectively dissolve one or more compounds, expressed by the separation factor  $\alpha$ ;
- (iv) the dependence of these solvent properties on conditions of state ( $p, T$ ) and,
- (v) the extent of the two-phase area, as limiting condition for a two-phase process like gas extraction.

The separation factor  $\alpha$  is defined by

$$\alpha = \frac{y_i / y_j}{x_i / x_j}$$

where  $x_i$  and  $x_j$  are the equilibrium concentrations of component  $i$  and  $j$ , respectively, in the condensed phase, in mole or mass fractions; and  $y_i$  and  $y_j$ , the corresponding equilibrium concentrations of the same components using equivalent units. If capacity and selectivity are known, a good guess can be made about whether a separation problem can be solved with SCFs. Figure 4 shows the solubility of a substance of low volatility, like a triacylglyceride, caffeine, or naphthalene in a sub- and supercritical fluid, for instance carbon dioxide ( $\text{CO}_2$ ) [Brunner 1994].

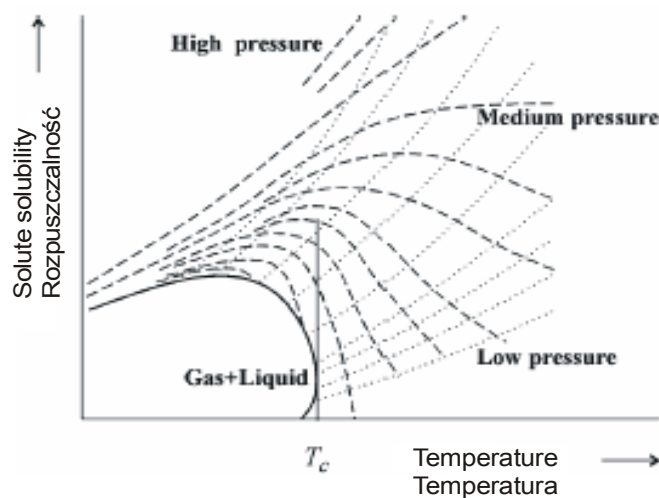


Fig. 4. Variations in the solubility of a low-volatility substance (liquid or solid) in a subcritical (temperature  $< T_c$ ) or supercritical fluid (temperature  $> T_c$ ) as a function of process temperature, process pressure (segmented lines correspond to equal pressure or isobaric conditions), and solvent density (dotted lines correspond to equal density conditions) [Brunner 1994]

Rys. 4. Różnice w rozpuszczalności substancji słabo lotnych (ciecz lub ciała stałe) w podkrytycznych (temperatura  $< T_c$ ) lub nadkrytycznych rozpuszczalnikach (temperatura  $> T_c$ ) jako funkcja temperatury procesu, ciśnienia procesu (linia kreskowana obrazuje ciśnienie lub warunki izobaryczne) oraz gęstości rozpuszczalnika (linia kropkowana ilustruje warunki gęstości) [Brunner 1994]

The solubility in the subcritical (liquid) fluid (solvent) increases at constant pressure up to temperatures slightly below the  $T_c$  of the solvent. A further increase in temperature leads at “low” pressures to a decrease of the dissolved amount of the low-volatility substance in the subcritical liquid solvent and at “high” pressures still to an increase. “High” and “low” pressures refer to a “medium” pressure level which for most systems (including the above mentioned) is about 10MPa. The same dependence of solubility of the low volatile component in the solvent remains at temperatures higher than  $T_c$ . At “low” pressures, solubility of the low-volatility substance in the supercritical and near critical solvent decreases with temperature since density of the supercritical solvent decreases rapidly with increasing temperature at nearcritical pressures. At “high” pressures, density changes with temperature are far more moderate, so that the increase of vapour pressure is the dominating factor, while at “low” pressures loss in solvent power induced by lower density prevails. Analogous solubility behaviour can be found in systems of a SCF with a solid substance or a low-volatility liquid. Carbon dioxide ( $\text{CO}_2$ ) is the most commonly SCF used as a solvent in food applications. It is not only cheap and readily available at high purity, but also safe to handle and physiologically sound to the very low levels at which it is present in foods (because it is easily removed by simple expansion to common environmental pressure values).



Consequently, it is approved for food processing without declaration [Brunner 1987]. Furthermore, when being recycled, it does not contribute to the environmental CO<sub>2</sub>-problem. The solvent power of supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) can be summarized by a few rules [del Valle and Aguilera 1999]:

- (i) it dissolves non-polar or slightly polar compounds;
- (ii) the solvent power for low molecular weight compounds is high and decreases with increasing molecular weight;
- (iii) SC-CO<sub>2</sub> has high affinity with oxygenated organic compounds of medium molecular weight;
- (iv) free fatty acids and their glycerides exhibit low solubilities;
- (v) pigments are even less soluble;
- (vi) water has a low solubility (< 0.5% w/w) at temperatures below 100°C;
- (vii) proteins, polysaccharides, sugars and mineral salts are insoluble; and,
- (viii) SC-CO<sub>2</sub> is capable of separating compounds that are less volatile, have a higher molecular weight and/or are more polar, as pressure increases.

### TRANSPORT PROPERTIES OF SUPERCRITICAL FLUIDS (SCFS)

Moreover, the SCF transport properties are very attractive as they are dense as liquids but “mobile” as gas (very low viscosity, intermediate diffusivity), as shown on Table 1. So, mass transfer (and similarly heat transfer) is fast in SCF in comparison with liquid solvents or water Table 2. Moreover, SCF rapidly diffuse in porous media, easing either extraction from solid materials or impregnation of solutes into porous media [Taylor 1996].

Table 2. Critical Conditions for Various Supercritical Solvents  
Tabela 2. Warunki krytyczne dla różnych rozpuszczalników nadkrytycznych

Fluid Ciecz	Critical temperature Temperatura krytyczna K	Critical pressure Ciśnienie krytyczne bar
Carbon dioxide	304.1	73.8
Ethane	305.4	48.8
Ethylene	282.4	50.4
Propane	369.8	42.5
Propylene	364.9	46.0
Trifluoromethane (Fluoroform)	299.3	48.6
Chlorotrifluoromethane	302.0	38.7
Trichlorofluoromethane	471.2	44.1
Ammonia	405.5	113.5
Water	647.3	221.2
Cyclohexane	553.5	40.7
n-Pentane	469.7	33.7
Toluene	591.8	41.0

## BIOLOGICAL PROPERTIES OF SCFs

Carbon dioxide – that is by far the most common SCF – exhibits biocide properties and is very active on fungi, bacteria and viruses. It has only a very low toxicity on humans, although asphyxia happens when it accumulates in non-ventilated areas, especially in lower parts of buildings (cellars...). N<sub>2</sub>O has different biological properties and it is commonly used for anesthesia (Note: Its use exposes to other hazards as it must be considered as a comburant that may lead to explosion when contacted with flammable solutes). Light hydrocarbons are not toxic (but present a very important explosion hazard). HFC are neither toxic nor flammable, but can decompose in highly toxic gases when submitted to flame.

## GENERAL PROCESS CONCEPTS

The processes using SCF are founded on the specific properties of these fluids, particularly on the possibility to vary their solvent power over a wide range. They are used as “good” solvents (extraction solvents, chromatography eluents, reaction media) when operating conditions lead to a high specific gravity (high pressure, temperature near the critical temperature), and they are later turned into compressed gases with very low solvent power (pressure below the critical pressure, temperature over the liquefaction temperature at this pressure) in order to perform fluid-solute separation. It has to be emphasized that one of the main interests of SCF is related to the ability to set very precisely their solvent power vis-à-vis different compounds by tuning pressure, temperature and co-solvent content, this permits to perform very selective fractionation of complex mixtures that cannot be resolved with classical organic solvents or by any other process. This is used either for sorting compounds belonging to the same chemical family but differing by their carbon numbers (i.e. fatty acids or oligomers/polymers), or of similar molecular mass but with slightly different polarities.

Moreover, it is possible to combine this “tunable” solvent power with selective means known in chemical engineering for completing difficult separations :

- For fractionation of liquid mixtures, high-performance multi-stage counter-current packed or stirred columns are preferred ; to increase selectivity, a reflux of extract is performed either by operating a temperature gradient along the contactor on pilot-scale equipment (causing solvent power decrease and consequently precipitation of the less-soluble compounds that reflux in liquid phase) or by an external reflux on large-scale equipment;
- Multi-stage separation of the fluid-solute mixture through separators in series operated at decreasing pressures in order to fractionate the solute according to its affinity with the fluid;
- Combination of extraction or fractionation with selective adsorption of the solute mixture dissolved in the depressurized fluid onto a selective adsorbent;
- Adsorption of the most volatile compounds of the solute in order to avoid recycling with the fluid and important losses of such compounds or selectivity decrease.

## EXTRACTION WITH SUPERCRITICAL FLUIDS

Supercritical extraction has been applied to a large number of solid matrices. The desired product can be either the extract or the extracted solid itself. The advantage of using supercritical fluids in extraction is the ease of separation of the extracted solute from the supercritical fluid solvent by simple expansion. In addition, supercritical fluids have liquid like densities but superior mass transfer characteristics compared to liquid solvents due to their high diffusion and very low surface tension that enables easy penetration into the porous structure of the solid matrix to release the solute [Dixon and Johnston 1997].

Extraction of soluble species (solutes) from solid matrices takes place through four different mechanisms. If there are no interactions between the solute and the solid phase, the process is simple dissolution of the solute in a suitable solvent that does not dissolve the solid matrix. If there are interactions between the solid and the solute, then the extraction process is termed as desorption and the adsorption isotherm of the solute on the solid in presence of the solvent determines the equilibrium. Most solids extraction processes, such as activated carbon regeneration, fall in this category. A third mechanism is swelling of the solid phase by the solvent accompanied by extraction of the entrapped solute through the first two mechanisms, such as extraction of pigments or residual solvents from polymeric matrices. The fourth mechanism is reactive extraction where the insoluble solute reacts with the solvent and the reaction products are soluble hence extractable, such as extraction of lignin from cellulose. Extraction is always followed by another separation process where the extracted solute is separated from the solvent.

Another important aspect in supercritical extraction relates to solvent/solute interactions. Normally the interactions between the solid and the solute determine the ease of extraction, i.e., the strength of the adsorption isotherm is determined by interactions between the adsorbent and the adsorbate. However, when supercritical fluids are used, interactions between the solvent and the solute affect the adsorption characteristics due to large negative partial molar volumes and partial molar enthalpies in supercritical fluids.

The thermodynamic parameters that govern the extraction are found to be temperature, pressure, the adsorption equilibrium constant and the solubility of the organic in supercritical fluid. Similar to the retrograde behaviour of solubility in supercritical fluids, the adsorption equilibrium constants can either decrease or increase for an increase in temperature at isobaric conditions. This is primarily due to the large negative partial molar properties of the supercritical fluids. In addition to the above factors, the rate parameters like the external mass transfer resistances, the axial dispersion in the fluid phase, and the effective diffusion of the organics in the pores also play a crucial role in the desorption process. A thorough understanding of these governing parameters is important in modelling of supercritical fluid extraction process and in designing, development and future scale-up of the process [Akgerman and Giridhar 1994].

## APPLICATION AREAS OF SUPERCRITICAL FLUID EXTRACTION (SFE)

The special properties of supercritical fluids bring certain advantages to chemical separation process techniques such as food and flavouring, petrolchemistry, pharmaceutical industry, other plant extractions, production of denicotinated tobacco, environmental protection, elimination of residual solvents from wastes, purification of contaminated soil, etc.

Some of various application areas of SFE can be defined as given below:

- For volatile and lipid soluble compounds.

The solvating power of supercritical carbon dioxide (SCCO<sub>2</sub>) can be compared with traditional organic solvents. It can be used for:

### **Extraction of high-value oils**

Some of oils are just too valuable to be spoiled by destructive techniques or to be lost due to low yields. With the aid of SFE high-value oils can be fully recovered in their natural composition. Examples of established products include sea buckthorn oil, black currant seed oil, saw palmetto oil.

### **Isolation of lipid soluble compounds**

A wide class of compounds are soluble in lipids. Some classes of lipophilic compounds that SFE can be used for: sterols, tocopherols, tocotrienols, carotenoids, simple phenols, fatty acids and waxes.

### **High grade natural aromas**

Sometimes, traditional isolation techniques can change the original chemical composition of the isolate. Thermal degradation of aroma compounds is avoided in this method, so highly concentrated pure aromas can be isolated in their natural form [Son-suzer et al. 2004].

### **Purification of raw materials**

If one wants to remove something from raw material, supercritical fluid extraction (SFE) can also be applied in order to avoid unwanted compounds. The following can be done with SFE:

- stripping of unwanted smells,
- removal of fats/oils,
- removal of pesticide residues,
- desolvenization.

## OTHER USES OF SFE

In addition to extraction of flavours and essential oils, antineoplastic agents can be extracted by this technique [Dixon and Johnston 1997].

Extraction of oil which is low in saturated fats and contains high amounts of tocopherols and carotenoids from claudberry seed is also applied while extraction of lipids and phenolic compounds from grapeseeds took place.

Antioxidants which are of great importance can be extracted from rosemary by supercritical carbon dioxide (SCCO<sub>2</sub>) in order to use in natural supplements [Couvelier et al. 1996].

Extraction of vitamin A and E from powdered milk, fluid milk, meat, extraction of lipids from variety of meats, nuts and seeds and fractionation of lipids of dairy products are applied using supercritical fluid extraction (SFE) [Rozzi and Singh 2002].

Among SCFs, carbon dioxide is the most common supercritical fluid in the food industry. Due to the non-toxicity and low critical temperature, it can be used to extract thermally labile food components and the product is not contaminated with residual solvent. Further, the extract's colour, composition, odour, texture are controllable and extraction by supercritical fluid carbon dioxide retains the aroma of the product [Akgerman and Giridhar 1994].

Supercritical carbon dioxide extraction is used as a replacement for hexane in extracting soybean-oil and has been tested for extraction from corn, sunflower and peanuts. Supercritical fluid extraction provides a distinct advantage not only in the replacement but also extracts oils that are lower in iron and free fatty acid. To satisfy the consumer's need for 'lighter' foods, developmental work on supercritical extraction of oils from potato chips and other snack foods are carried out. In addition, supercritical carbon dioxide has also been used to extract lilac, essential oils, black pepper, nutmeg, vanilla, basil, ginger, chamomile, and cholesterol.

A large amount of research has been concentrated on the decaffeination of coffee by supercritical carbon dioxide. Thus, it is not surprising to note that this was the first process to be commercialized (in 1978), whose primary step is supercritical extraction. Dry carbon dioxide cannot extract caffeine from dry coffee effectively and the beans should be pre-wetted by water. Soaking for of about 2 hours is necessary for efficient extraction of caffeine from coffee beans by supercritical carbon dioxide.

## CONCLUSION

The technology of supercritical fluid extraction (SFE) using supercritical fluids (SCFs) is an alternative to conventional liquid extraction due to its use of environmentally compatible fluids, oxygen free environment, shorter extraction times, etc. Among SCFs, because of being mostly used due to its many advantages, Supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) is the reagent used to extract plenty of materials. The special properties of SCFs bring certain advantages to chemical separation techniques. Several applications have been fully developed and commercialized. Some of them are food and flavouring, pharmaceutical industry, environmental protection for volatile and lipid soluble compounds, extraction of high-value oils, isolation of lipid soluble compounds, extraction of high-value natural aromas, recovery of aromas from fruits, meat and fish, etc. Also, in order to understand the mechanism of SFE, modelling considerations of SCFs and main criteria for SCF techniques were focused on.

## REFERENCES

- Adasoglu N., Dincer S., Bolat E., 1994. Supercritical fluid extraction of essential oil from Turkish lavender flowers. *J. Supercritical Fluids* 7, 93-99.
- Akgerman A., Giridhar M., 1994. Fundamentals of Solids Extraction by Supercritical Fluids. In: *Supercritical Fluids – Fundamentals for Applications*. Eds J.M.H. Sengers, E. Kiran. Kluwer Acad. Pub., 669-696.
- Brunner G., 1987. Stofftrennung mit überkritischen Gasen (Gasextraktion). *Chem. Ing. Tech.* 59, 12-22.

- Brunner G., 1994. Gas extraction, An introduction to fundamentals of supercritical fluids and the application to separation processes. Springer New York.
- Couvelier M.E., Berset C., Richard H., 1996. Antioxidative activity and phenolic composition of pilot-plant and commercial extracts of sage and rosemary. *JAOCS* 73, 5, 645-652.
- Del Valle J.M., Aguilera J.M., 1999. Extracción con CO<sub>2</sub> a alta presión Fundamentos y aplicaciones en la industria de alimentos. *Food Sci. Technol. Int.* 5, 1-24.
- Dixon D.J., Johnston K.P., 1997. Supercritical Fluids. In: *Encyclopedia of Separation Technology*. Ed. D.M. Ruthven. Wiley New York, 1544-1569.
- Hirshfelder J.O., Curtis C.F., Bird R.B., 1964. *Molecular theory of gases and liquids*. Wiley New York.
- Hubert P., Vitzthum O.G., 1980. Fluid Extraction of Hops, Spices and Tobacco with Supercritical Gases. In: *Extraction with Supercritical Gases*. Eds G.M. Schneider, E. Stahl, G. Wilke. Verlag Chemie Weinheim, 25-43.
- Iso S., Meguro Y., Yoshida Z., 1995. Extraction of Uranium (IV) from Nitric Acid Solution into Supercritical Carbon Dioxide Containing Tri-n-butylphosphate. *Chem. Lett.* 5, 365.
- Krukoniš V.J., 1985. Processing of polymers with supercritical fluids. *J. Polym. News* 11, 7.
- Krukoniš V.J., 1988. Processing with Supercritical Fluids: Overview and Applications. In: *Supercritical Fluid Extraction and Chromatography, Techniques and Applications*. Eds B.A. Chantier, M.R. Sevenants. ACS Symp. Ser. ACS 366, Washington, 30.
- Prausnitz J., Lichtenthaler R., de Azevedo E., 1986. *Molecular thermodynamics for fluid-phase equilibrium*. Prentice-Hall Englewood Cliffs.
- Reid R.C., Prausnitz J.M., Poling B.E., 1988. *Properties of Gases and Liquids*. McGraw-Hill, 741.
- Rozzi N.L., Singh R.K., 2002. Supercritical Fluids and the Food Industry. *Compr. Rev. Food Sci. Food Safety* 1, 33-44.
- Sonsuzer S., Sahin S., Yilmaz L., 2004. Optimization of supercritical CO<sub>2</sub> extraction of *Thymbra spicata* oil. *J. Supercrit. Fluids* 30, 189-199.
- Taylor T., 1996. *Supercritical Fluid Extraction*. Wiley New York.

## CIECZE NADKRYTYCZNE

**Streszczenie.** Praca zawiera informacje dotyczące cieczy nadkrytycznych i ogólny opis tych cieczy. Omówiono też ich właściwości fizykochemiczne wraz z historią badań nad nimi oraz podjęto próbę wytłumaczenia specyficznych właściwości, które mają wpływ na cechy nadkrytyczne cieczy. Przeprowadzono szczegółową dyskusję nad nadkrytycznym CO<sub>2</sub> (SCCO<sub>2</sub>) i jego zastosowaniem jako rozpuszczalnika do ekstrakcji. W celu zrozumienia mechanizmu ekstrakcji z użyciem cieczy nadkrytycznej (SFE), przedefiniowano koncepcję modelową cieczy krytycznych oraz warunków różnych technik separacji.

**Słowa kluczowe:** ciecze nadkrytyczne (SCFs), ekstrakcja w cieczy nadkrytycznej (SFE), modelowanie cieczy nadkrytycznych, właściwości nadkrytyczne, mechanizm cieczy nadkrytycznych

*Accepted for print – Zaakceptowano do druku: 4.04.2005 r.*

**For citation – Do cytowania:** *Askin R., Ötles A., 2005. Supercritical fluids. Acta Sci. Pol., Technol. Aliment. 4(1), 3-16.*