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Use of supercritical CO_2 in food industry

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Supercritical fluid extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids (SCF) as the extracting solvent. Carbon dioxide is the most commonly used supercritical fluid in food industry, especially being used for decaffeination. In this study, supercritical fluid extraction technique and its uses (especially carbon dioxide) in food industry (as essential oil production, fractional separation of oils, removing of cholesterol, debittering, inactivation of pectinmethylesterase, sterilization, extraction of aromas in juices and antioxidant compounds from vegetables, dealcoholisation of alcoholic beverages etc.) will be detailed.

Key words: *supercritical fluid, extraction, carbon dioxide, food*

INTRODUCTION

Extraction can be defined as the removal of soluble material from an insoluble residue, either liquid or solid, by treatment with a liquid solvent. It is therefore, a solution process and depends on the mass transfer phenomena [1].

A fluid is termed supercritical when the temperature and pressure are higher than the corresponding critical values (Figure 1). Thus, the physicochemical properties of a given fluid, such as density, diffusivity, dielectric constant and viscosity can be easily controlled by changing the pressure or the temperature without ever crossing phase boundaries [2]. Supercritical fluids (SCF) are suitable as a substitute for organic solvents in a range of industrial and laboratory processes because of regulatory and environmental pressures on hydrocarbon and ozone-depleting emissions. SCF-based processes has helped to eliminate the use of organic solvents such as hexane and methylene chloride [1,3]. The close relationship between the fluid density and its dissolving power and its favorable mass transfer properties makes supercritical fluids a useful processing medium for extraction and separation techniques [2,4].

Supercritical fluid extraction (SFE), supercritical gas extraction, and dense gas extraction are alternative terms to name the operation with a fluid at temperatures and pressures near the critical point [5]. It is defined as separation of chemicals, flavors from the products such as coffee, tea, hops, herbs, and spices which are mixed with supercritical fluid to form a mobile phase [2]. It can be used as sample preparation step for analytical purposes, or on a larger scale to either strip unwanted material from a product (e.g. decaffeination) or collect a desired product (e.g. essential oils) [1,6-9]. Supercritical fluids can offer a good catalytic activity and produce a product with no solvent residues [1,3].

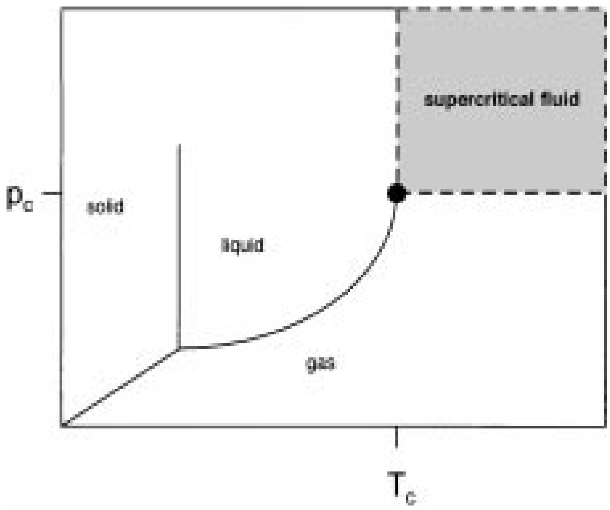

Fig. 1. Phase diagram for a single substance. P_c – critical pressure; T_c – critical temperature.

The first commercial supercritical fluid extraction was performed in Germany in 1978 by Hag AG for the decaffeination of green coffee beans. Two years later Carlton and United Breweries in Australia developed a process for the extraction of hop flavors using liquid carbon dioxide [10]. Both applications were commercially successful and have given rise to numerous variations and improvements which have also been developed on an industrial scale [11].

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A simplified process-scale SFE system is shown in Figure 2.

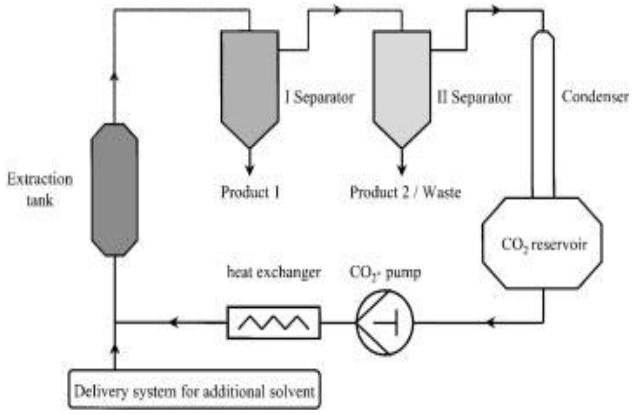

Fig. 2. A simplified drawing of a process-scale supercritical fluid extractor.

Raw material is charged in the extraction tank which is equipped with temperature controllers and pressure valves at both ends to keep desired extraction conditions. The extraction tank is pressurized with the fluid by means of pumps, which are also needed for the circulation of the fluid in the system. From the tank the fluid and the solubilized components are transferred to the separator(s), where the solvation power of the fluid is decreased by increasing the temperature, or more likely, decreasing the pressure of the system. The product is then collected via a valve located in the lower part of the separator(s) [2].

Advantages of SFE

In summary, the advantages of SFE are as follows [3]:

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 CO_2), its polarity can be changed for having more selective separation power.
4. Involving food or pharmaceuticals, one does not have to worry about solvent residuals if a "typical" organic solvent were used in industrial processes.
5. Candidate SCFs are generally 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.

Table 1. The critical properties for some components commonly used as supercritical fluids.

Critical properties of various solvents				
Solvent	Molecular weight, g/mol	Critical temperature, K	Critical pressure MPa, atm	Critical density, g/cm^3
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O) (acc. IAPWS)	18.015	647.096	22.064 (217.755)	0.322
Methane (CH_4)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C_2H_6)	30.07	305.3	4.87 (48.1)	0.203
Propane (C_3H_8)	44.09	369.8	4.25 (41.9)	0.217
Ethylene (C_2H_4)	28.05	282.4	5.04 (49.7)	0.215
Propylene (C_3H_6)	42.08	364.9	4.60 (45.4)	0.232
Methanol (CH_3OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C_2H_5OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C_3H_6O)	58.08	508.1	4.70 (46.4)	0.278

In Table 1, the critical properties for some components commonly used as supercritical fluids are shown [1]. All these fluids have a low critical temperature and pressure.

General applications of supercritical fluid include recovery of organics from oil shale, separations of biological fluids, bio separation, 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 [3,12]. The natural antioxidants produced by SFE are also of interest to the food industry because they do not alter the aroma, flavour or colour of foodstuffs. They are very easily dispersed since they are highly soluble, and they do not evaporate during frying or baking, unlike other synthetic antioxidants [4,5]. In dealcoholisation using SFE the separation efficiency is far greater than in distillation. Furthermore, extraction temperatures are moderate (between 15 and 40 °C) which means that the thermolabile components, which are largely responsible for the aroma and flavour, do not break down [13]. The supercritical extrusion fluid has the potential to produce a range of puffed food products, such as ready-to-eat cereals, pasta and confectionery with improved texture, colour and taste [4]. Additionally, SFE products from plants are complex mixtures of essential oils, esters, terpenes, fatty acids, waxes, resins, and pigments (cited in order of decreasing solubility) [14-16]. Figure 3 shows supercritical fluid technology applied to everyday’s food [16].

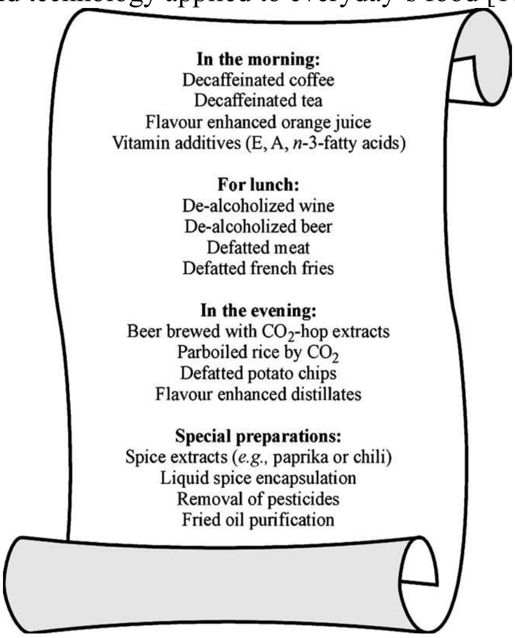

Fig. 3. Supercritical fluid technology applied to everyday’s food

Supercritical CO_2

Carbon dioxide is the most commonly used supercritical fluid in food industry, especially being used for decaffeination [4,17]. It is sometimes modified by co-solvents such as ethanol or methanol [1]. It usually behaves as a gas in air at standard temperature and pressure (STP), or as a solid called dry ice when frozen. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure [3]. The density of the supercritical CO_2 at around 200 bar pressure is close to that of hexane, and the solvation characteristics are also similar to hexane; thus, it acts as a non-polar solvent. Around the supercritical region, CO_2 can dissolve triglycerides at concentrations up to 1 % mass [1].

Carbon dioxide is non-toxic, nonflammable, odorless, tasteless, inert, and inexpensive. These properties make it suitable for extracting, for example, thermally labile and non-polar bioactive compounds but, because of its non-polar nature, it cannot be used for dissolving polar molecules. On one hand, it decreases the processing times, increases yields and makes it possible to use milder processing conditions, but on the other, it complicates [2,18]. Extraction conditions for supercritical CO_2 are above the critical temperature of 31 °C and critical pressure of 74 bar (Figure 4) [17,19]. As detailed, carbon dioxide (CO_2) has become the ideal supercritical fluid in the food industry due to its characteristics: the critical temperature is 31.06°C, the critical pressure is 73.83 bar and the critical density is 0.460 g/cm^3 [2,4]. Addition of modifiers may slightly alter this. Due to its low critical temperature, carbon dioxide is known to be perfectly adapted in food, aromas, essential oils and nutraceutical industries [1,20,21]. In addition, the solubility of many extracted compounds in CO_2 vary with pressure, permitting selective extractions. So, supercritical extraction mostly uses carbon dioxide at high pressure to extract the high value products from natural materials.

Supercritical CO_2 is particularly suitable for applications in which (i) processing costs are a limiting factor, (ii) conventional solvent extraction is restricted by environmental regulation, consumer demands, or health considerations, (iii) products have improved quality and/or marketability (for example, when the “natural” character of the product increases the market price), or (iv) traditional processing is not applicable because the product is thermally labile or morphologically unique [14].

Supercritical CO_2 tends to be selective towards lower molecular weight compounds (< 250 g/mol) or weakly polar groups such as lipids, cholesterol, aldehydes, ethers, esters and ketones, while high molecular weight (> 400 g/mol) or polar groups such as hydroxyl, carboxyl, and sugars, polysaccharides, amino acids, proteins, phosphatides, glycosides, inorganic salts, are relatively insoluble in dense carbon dioxide [4].

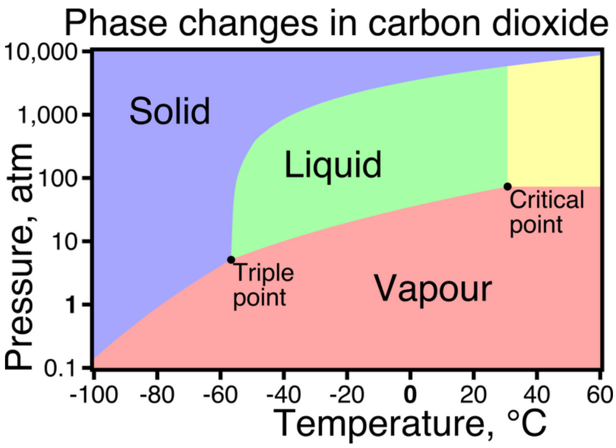

Fig. 4. Phase diagram of carbon dioxide as a function of temperature and pressure.

Carbon dioxide is forced through the green coffee beans which are then sprayed with water at high pressure to remove the caffeine. The caffeine can then be isolated for resale (e.g. to the pharmaceutical industry or to beverage manufacturers) by passing the water through activated charcoal filters or by distillation, crystallization or reverse osmosis. Supercritical carbon dioxide is also used to remove organichloride pesticides and metals from agricultural crops without adulterating the desired constituents from the plant matter in the herbal supplement industry[3]. Supercritical CO_2 extraction of various oil seeds, such as soybean, flaxseed, safflower, and cottonseed, has been reported [22-24]. Other researchers have studied the solubilities of various vegetable oils including canola, millet bran, and rice bran in supercritical CO_2 [25-27].

How does supercritical CO_2 extraction exist?

It involves heating the CO_2 to above 465 °C and pumping it above 75.84 bar. Usually, this is between 413.69 – 689.48 bar. Supercritical fluid CO_2 can best be described as a dense fog when CO_2 is used in a dense liquid state. Low-pressure CO_2 is often the best method for producing high quality botanical extracts. CO_2 loading rate in this state means that you have to pump many volumes of CO_2 through botanical. The loading rate is typically 10 – 40 volumes of product. For this reason, it is important to have pumped CO_2, which has a much faster loading rate 2 – 10 volumes and a wide range of uses [1]. The CO_2 storage tanks and extractors must be properly isolated and equipped with relief systems [18].

CONCLUSION

The successful commercial developments involves the processing of a high-value product, relatively simple extraction processes, that has finally brought about the level of growth that was initially forecast for SFE. The many advantages of the SFE can be summarized as follows: high quality and purity of the obtained product; quick extraction and separation phases; extract free of residues; selective extraction by a specific compound; reduction in separation cost. But the use of SFE in the food industry also has some disadvantages. The lack of continuous systems for extracting solid substrates imposes serious capacity restrictions on installed apparatus.

It is clear from this review that the application of supercritical fluid technology in the food industry is a field in which there is much research and development at present. In some cases, such as the extraction of caffeine from tea and coffee or aromas from spices and hops, SFE is already being used in industry. In other cases its practical applications could be seen, particularly in the area of food colourings and the refining of seed oils due to its economic potential.

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ПРИЛОЖЕНИЕ НА СУПЕР КРИТИЧЕН CO_2 В ХРАНИТЕЛНАТА ИНДУСТРИЯ

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(Резюме)

Екстракцията със суперкритичен флуид е процес на разделяне на една компонента (екстракта) от другата (матрицата), при което като екстрахиращ разтворител се използва суперкритичен флуид. Въглеродният диоксид е най-често използвания в хранителната индустрия суперкритичен флуид, особено при процеса декофеинизиране. В настоящото изследване ще бъде детайлизирана техниката на екстракция чрез суперкритичен флуид и нейните приложения (най-вече на при използването на въглероден диоксид) в хранителната индустрия (при производството на етерични масла, фракционното разделяне на масла, премахване на холестерол, отстраняване на горчивия вкус, деактивация на пектинметилестераза, стерилизация, екстракция на аромати в сокове и на антиоксидантни компоненти от зеленчуци, намаляване на алкохолното съдържание на алкохолни напитки и др.)