International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2017; 5(3): 336-340

Received: 25-03-2017
Accepted: 26-04-2017

Industrial applications of supercritical fluid extraction: A review

Kamal Gandhi, Sumit Arora and Anil Kumar

Kamal Gandhi
Dairy Chemistry Division, National Dairy Research Institute, Karnal, Haryana, India

Sumit Arora
Dairy Chemistry Division, National Dairy Research Institute, Karnal, Haryana, India

Anil Kumar
Center for Rural Development and Technology, Indian Institute of Technology, New Delhi, India

Correspondence
Kamal Gandhi
Dairy Chemistry Division, National Dairy Research Institute, Karnal, Haryana, India

Abstract
Super Critical Fluid Extraction (SCFE) is basically an approach that utilizes a fluid phase possessing characteristics midway between that of a gas and liquid, to induce the solubilization of solutes in a matrix. Extraction could be set up selective to some extent as the solvating power (which is driven by density) of SCFE can be altered over a wide range by changing the pressure, the temperature or both. Compared to traditional organic liquids, having higher diffusivity and lower viscosity, SCFE gives significantly better mass transfer of solutes from sample matrices. The review sums up the studies conducted using Super Critical Fluid Extraction of high-value compounds from the natural products earlier to have applications in food, pharmaceuticals, agriculture, dairy industry etc. It discusses the processing parameters optimized using pilot scale to be upgraded to industry set up.

Keywords: supercritical fluid extraction, applications, industry, dairy

1. Introduction

Petroleum based solvents, for instance, hexane, toluene, dichloromethane, chloroform etc. were utilized to isolate desired components from natural products traditionally. National and international food laws regulate merely a few solvents of established purity to be utilized for extraction in the processing of food materials. Further, from the processing angle, the choice is governed by the capability of extraction of characteristics components of the individual spices, optimization in respect of yield of oleoresin with excellent handling properties and economy of desolventizing to the permitted residual solvent level in the final product, and recovery of solvent. Processes involving green solvents such as liquid-CO2, supercritical-CO2, pressurized liquid, and microwave-assisted solvent extraction (MASE), being operationally safe and less damaging to health and environment, have given a great impetus for development for extraction of food flavours, cosmeceutical, nutraceutical and biopesticides from plant products. These 'green extraction technologies' when developed fully can conform to all the present as well as likely future regulations pertaining to safety, health, and environment (Beckman, 2004) [3], (Huie, 2002) [10]. These technologies have ushered in enhanced scrutiny recently owing to decreased energy costs over the organic solvents, and more effective separation.

Super Critical Fluid Extraction (SCFE) is a technique that employs a fluid phase having properties intermediate between that of a gas and liquid, to affect the solubilization of solutes in a matrix. The critical point is a point in pressure-temperature phase diagram above which liquid state of the gas is unchangeable at any applied pressure (Fig 1). At this point, substance behaves both like liquid as well as gas. Densities of gasses above its critical limit increase with increasing pressure and this desirable change increase the solvent power of liquids. The result of this enhanced solvating power of CO_2, make solute to solubilize in the supercritical solvent medium. As the density of fluid changes, diffusivity also changes and increase mass transfer between solute and solvent. Contrastingly, values of viscosity for supercritical fluid remains same as found in normal gas and liquid. Supercritical fluids have enhanced solvent power as a liquid but also behave as gasses devoid of surface tension.

Substance above its critical temperature and pressure becomes a pure supercritical fluid. Above the critical temperature, it doesn't condense to form a liquid, but is a fluid (dense gas), with properties changing continuously from gas-like to liquid-like as the pressure increases at fixed temperature (Kiran *et al.,* 2009) [11]. The extraction could be made selective to some extent as the solvating power (which is driven by density) of SCFs can be altered over a wide range by changing the pressure, the temperature or both.

Compared to conventional organic liquids, having higher diffusivity and lower viscosity, SCFs allows more efficient mass transfer of solutes from sample matrices. Carbon dioxide (CO_2) is perhaps the most frequently sought after supercritical fluid. Advantages include inertness, non-toxicity, non-flammability, non-explosiveness, and availability with high purity at a reasonable cost (del Valle *et al.,* 1999) [25], (Lang and Wai, 2001) [12], and (Luz *et al.,* 2013) [13]. Furthermore, relatively low critical properties make CO_2 (TC=304, 1 K, pc=73, 8 bars) an ideal solvent when it comes to the extraction of thermally labile components such as carotenoids. The superiority of SC-CO_2 extraction over the conventional method of petroleum ether extraction is shown in table 1.SCFE finds applications in areas as diverse as extraction of botanicals, spice extraction, flavour and fragrance extraction, decaffeination of coffee and tea, deasphalting petroleum fractions, recovery and purification of lube oils, coal liquefaction, chemical separations and purification, polymer processing, supercritical crystallization and supercritical drying (Mukhopadhyay, 2000) [17].

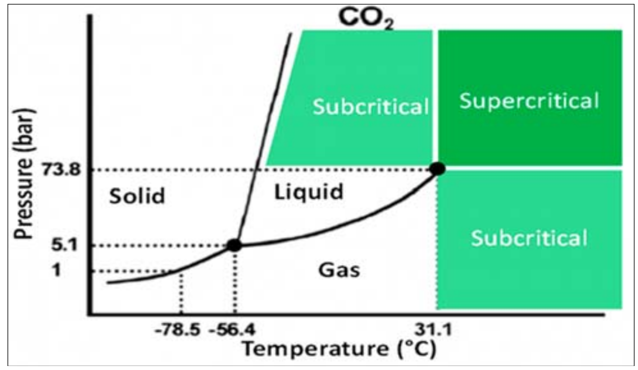

Fig 1: Pressure-Temperature phase diagram for CO_2

Table 1: Yield and quality of fatty oil extracted by SC-CO_2 and by petroleum ether.

Plant	SC-CO_2 Extract			Petroleum ether extract		
	Time (hours)	Yield (% w/w)	% of major component	Time (hours)	Yield (% w/w)	% of major component
Flax	3	35.3±0.4	Omega-3-fatty acid (55.0%)	10	38.8±0.6	Omega-3-fatty acid (50.0%)
Wheat-DDGS	3	8.8±0.7	Omega-6-fatty acid (38.6%)	10	10.6±0.8	Omega-6-fatty acid (33.2%)

Supercritical CO_2 extraction (Fig 2) is undoubtedly a good technology for extraction of high molecular weight compounds. The design of a typical supercritical carbon dioxide extraction unit consists of a pump for CO_2, a chamber to keep the sample, pressure regulator and a collecting vessel. There will be a heating zone, wherein the liquid would be heated to supercritical conditions. It is then made to diffuse into the sample to solubilize it. Dissolved material is then swept from the extraction cell into a separator at lower pressure, and the extracted material settles out. CO_2 is then made to cool, recompressed and recycled, or discharged to the atmosphere.

Some of the studies carried out employing supercritical fluid extraction of the components from the natural products are summarized below:-

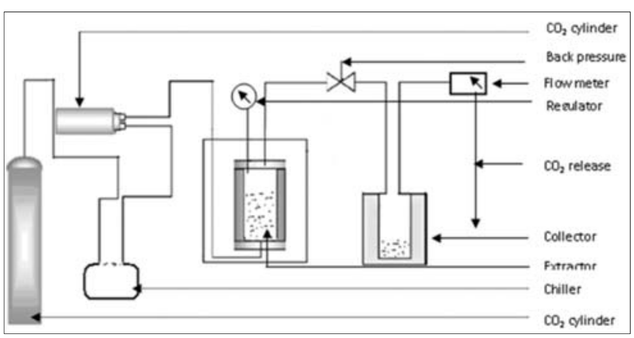

Fig 2: Schematic diagram of SC-CO_2 system

(Roy *et al.,* 1996) [21] revealed that the supercritical fluid extraction process is controlled by intraparticle diffusion within a particle of ginger root. The extraction rate increased as the particle size decreased owing to a decrease in the diffusion path. A crossover effect was observed where the higher temperature facilitated the extraction at 24.5 Mpa, while the lower temperature advocated the extraction at 10.8 Mpa.

Several applications for the supercritical fluid extraction have been reported in bioprocessing, including, extraction of fermentation products, bio-oil production, production of pharmaceutical ingredients, removal of biostatic agents and organic solvents from fermentation broth, SCF disruption of yeasts and bacteria, destruction of industrial waste, fractionation and purification of biopolymers, removal of chlorinated compounds from water and treatment of lingo-cellulosic materials (Priyanka and Shabina Khanam, 2014) [20].

Chief compounds such as Omega-3 and Omega-6 fatty acids were enriched in the SC-CO_2 extract obtained from the edible fatty oils such as flax seed (*Linumusitatissimum* L.) and Wheat Dry Distiller Grains with Soluble (DDGS) as reported by the (Pradhan *et al.,*. 2010) [19]. The lower yield of the extract with a higher concentration of Omega-3 and Omega-6 fatty acids were observed when compared to the traditional soxhlet extraction process.

(Seliem *et al.,* 2015) [26] separated the Red pepper oleoresin from Egyptian food factories waste by using supercritical fluid CO_2 followed by its microencapsulation and set forth that the microencapsulation played an important role in oxidation prevention process.

(Santos *et al.,* 2015) [23] extracted the oleoresin from Malagueta Pepper (capsicum frutescens) using supercritical fluid extraction (SFE) assisted by ultrasound and recorded higher yield from that obtained using supercritical fluid extraction individually.

(Nguyen *et al.*, 2011) [18] developed the process for extracting oleoresin from spice and fractionating it into fixed and essential oil components. The extraction of the oleoresin from spice is carried out on the ground spice using supercritical fluid carbon dioxide under a pressure ranging from about 400 bars to about 600 bars and at a temperature ranging from about 80 °C to about 120 °C. Oleoresin fractions are precipitated from the supercritical fluid at reduced pressure of 280-380 bar and 100-200 bar at 80°-100° C, while the last fraction is obtained from the non-critical fluid at a pressure of 30-50 bar and a temperature of 0°-30° C.

(Margono *et al.,* 2003) [14] used a mathematical model based upon shrinking-core model of the supercritical extraction process and calculation of the model were applied to measure the effect of particle size, length of extractor, effective intraparticle diffusivity and concluded that increasing extraction rate with decreasing intraparticle diffusivity significantly impacted the supercritical fluid extraction of curcuma xanthorrhiza.

(Fabrowska, 2016) [7] extracted carotenoids and phenolic compounds from Cladophora glomerata, Ulva flexuosa and Chara fragilis and established that C. fragilis extracts were the richest in total carotenoids and total phenols (24.90 mg fucoxanthin equivalents g−1 extract and 30.20 mg gallic acid equivalents g−1extract, respectively), whereas those produced from U. flexuosa possessed the highest antioxidant activity (0.944 mmol trolox equivalents g−1 extract). Extracts obtained from the studied algae using SFE can be considered to be of potential interest in cosmetic, food and pharmaceutical industry as a means to valorize these underexploited materials.

(Talmaciu *et al.,* 2015) [1] separated bioactive phenolics compounds from spruce bark (Picea abies), using sub- and supercritical fluids. He optimized the conditions which gave maximum yields and assured a higher recovery of the phenolic compounds.

(Akanda *et al.,* 2012) [16] declared that SFE is the ideal method for exploitation in the extraction of palm oil on an industrial scale. SFE method using SC-CO_2 as a solvent can reduce wastewater compared to traditional mechanical extraction. It is a cost effective technique at both the laboratory- and industrial-scale for the extraction of palm oil, palm kernel oil and minor components such as carotenes and tocopherols from palm oil and palm leaves. Generally, tocopherol levels in palm leaves were not high enough to allow an economic industrial-scale extraction. SFE can still act as a sterilizer for palm fiber oil, a by-product of palm oil extraction. Furthermore, the residual palm kernel meal obtained from SFE process making use of CO_2 can be a good, low fiber animal feed. He further more reported that SC-CO_2 extraction method for specialty oils was retaining the unique flavour and aroma while volatile aroma compounds are generally lost during traditional solvent extraction processing. Specialty oils comprise of high levels of bioactive components, such as polyunsaturated fatty acids, tocopherols, tocotrienols, phytosterols, carotenoids, and squalene. Due to the public awareness as well as demand, food industries are always looking for such kind of oils which are naturally extracted.

From solubility point of view, the curcuminoids are poorly soluble in the hydrocarbon solvents. Turmeric oil was extracted from turmeric (*Curcuma longa*) with supercritical carbon dioxide in a semicontinuous-flow extractor (Gopalan *et al.,* 2000) [8]. The extraction rate increased with an increase in CO_2 flow rate and with a reduction of particle size. The effect of pressure and temperature on turmeric extraction suggested the use of higher pressure and lower temperature at which solvent density is greater and thus the solubility of the oil in the solvent is greater. The major components (∼60%) of the extracted oil were identified as turmerone and *ar*-turmerone by GC-MS.

Ginger oleoresin and ginger oil are the two main products of ginger after processing (Govindarajan, 1982) [28]. Monoterpenes and sesquiterpenes are the components responsible for pungency effect in ginger. Ginger and shogaol are these major terpenes which give characteristic pungency effect due to which ginger have a special aroma and used as flavourings in many food preparations and beverages. Gingerol is a major pungent antioxidant compound naturally present in ginger while shogaol, zingerone are less pungent secondary products formed due to chemical changes in gingerol. Ginger oil is a rich source of some phytochemicals α-curcumene, Zingibeene, α-farnesene, β-sesquiphellandrene. Ginger and its bioactive compounds gingerol have some pharmacological properties like anti-inflammatory, antioxidant, anticancer, anti-ulcer, analgesic and cardiovascular effect. Use of solvent extraction and supercritical extraction techniques for extraction of bioactive compounds from ginger has recently been operated (Yeh *et al.,* 2014) [6], (Mesomo *et al.,* 2013) [14]. Extracts of these study exhibit good potency of antioxidant and antimicrobial activity for food and flavouring purposes.

(Yver *et al.,* 2011) [25] fractionated whey protein using supercritical carbon dioxide (sCO2) as an acid to produce enriched fractions of α-lactalbumin (α-LA) and β-lactoglobulin (β-LG) from a commercial whey protein isolate (WPI) comprising 20% α-LA and 55% β-LG, through selective precipitation of α-LA. The most profitable conditions resulted in 57% pure α-LA, with 71% α-LA recovery in the solid fraction and 89% β-LG recovery in the soluble fraction, and production cost of $5.43 per kilogram of WPI treated at T = 62 °C, C = 10% WPI and P = 5.5 Mpa. The two fractions obtained were ready-to-use and contained no residual acid or chemical contaminants.

(Barry *et al.,* 2017) [2] developed the process for the production of dairy ingredient enriched in phospholipids (PLs) from a buttermilk powder (BMP) substrate utilizing a combined process of targeted enzymatic hydrolysis of the native milk proteins accompanied by ultrafiltration with a 50 kDa membrane. The retentate was directed to supercritical CO_2 fluid extraction (SFE to generate a purified lipid fraction. SFE with ethanol as a co-solvent yielded a purified lipid extract with enriched PLs level of 56.24 ± 0.07 % on a dry matter basis.

(R. Bradely and L. Jir, 1989) [4] stripped 90% of the cholesterol (examined using an AOAC procedure and gas chromatography) from the milk fat contained in the extraction chamber using ascending pressure profile extraction and declared that the fatty acid composition plays a pivotal role in supercritical extraction; short-chained acids complicate extraction and the selectivity of supercritical CO_2 for cholesterol is a temperature-dependent and pressure-dependent phenomenon.

Supercritical carbon dioxide has been turned up to be a good solvent for the extraction of flavor components (lactones, ketones, aldehydes) from milk fat (Haan *et al.,* 1990) [9]. If the flavor extract is produced in two steps, these flavor components could be concentrated 500 to perhaps 1000 times.

(Yee *et al.,* 2007) [27] produced low-fat cheddar and parmesan cheese using supercritical fluid extraction (SCFE) retaining flavor compounds which generally do not develop using other methods of fat extraction. The process resulted in 51 % fat reduction (wet basis) for cheddar extracted at conditions of 200 bar, 40 ^{0} C, 1000 g CO_2 and 55.56 % fat reduction for Parmesan extracted at 350 bars, 35 ^{0}C, 1000 g CO_2.

(Spence *et al.,* 2009) [23] applied microfiltration integrated with supercritical fluid extraction (SFE) to derive non-polar lipids from buttermilk powder to incorporate them in novel ingredients. Better lipid extraction was came to the realization utilizing diatomaceous earth (biosilicates) as an aid.

(Sánchez-Macías *et al.,* 2013) [21] evaluated impact of supercritical fluid extraction on the chemical composition, particularly the amount of fat removed, microbial inactivation, lipid profile, and microstructure of goat Goudatype and Majorero cheese and stated that the cheese had reduced fat maintaining the phospholipid content with reduction in the microbial population suggesting longer shelf life, hence avoiding economic losses. The cheese obtained had lower triglycerides and cholesterol especially, with all the healthy benefits inherent to goat milk.

(Catchpole *et al.,* 2008) [5] extracted the neutral and complex lipids from beta-serum. Neutral lipids were extracted using supercritical CO_2 followed by the extraction of polar lipids using near-critical dimethyl ether. Compared with the antisolvent process, proteins were not denatured during either CO_2 or DME processing of the spray dried powders, and the de-fatted powders are thus suitable for a array of functional foods.

Conclusion

Green extraction technologies like Supercritical Fluid Extraction (SCFE) can conform to all the current as well as likely future regulations pertaining to safety, health, and environment. Supercritical fluid (SCF) extraction has gained growing consideration in a variety of industries because it can provide high solubility, improved mass transfer rates, and increased selectivity with small changes in process temperature and pressure. The technique is environmentally friendly, reasonable, selective, fast and permits recovery of the even those analytes which are thermally labile. It has set up a great influence not only in extracting high-value compounds from food and natural products but in areas such as heavy metals recovery, enantiomeric resolution or drug release systems. The technique has great potential for application in industries and further research should be taken up in the future to harness it fully.

References

1. Talmaciu AI, Ravber M, Knez Ž, Popa VI. Isolation of bioactive compounds from spruce bark waste using sub- and supercritical fluids. The Journal of Supercritical Fluids. 2016; 1(117):243-251.
2. Barry KM, Dinan TG, Kelly PM. Pilot scale production of a phospholipid-enriched dairy ingredient by means of an optimized integrated process employing enzymatic hydrolysis, ultrafiltration, and supercritical fluid extraction. Innovative Food Science & Emerging Technologies. 2017; 41:301-306.
3. Beckman EJ. Supercritical and near-critical CO2 in green chemical synthesis and processing. The Journal of Supercritical Fluids. 2004; 28(2-3):121-191.
4. Bradley R. Removal of Cholesterol from Milk Fat Using Supercritical Carbon Dioxide. Journal of Dairy Science. 1989; 72(10):2834-2840.
5. Catchpole O, Tallon S, Grey J, Fletcher K, Fletcher A. Extraction of lipids from a specialist dairy stream. The Journal of Supercritical Fluids. 2008; 45(3):314-321.
6. Yeh H, Chuang C, Chen H, Wan C, Chen T, Lin L. Bioactive components analysis of two various gingers (Zingiber officinale Roscoe) and antioxidant effect of ginger extracts. LWT - Food Science and Technology. 2014; 55(1):329-334.
7. Fabrowska J, Ibañez E, Łęska B, Herrero M. Supercritical fluid extraction as a tool to valorize underexploited freshwater green algae. Algal Research. 2016; 19:237-245.
8. Gopalan B, Goto M, Kodama A, Hirose T. Supercritical Carbon Dioxide Extraction of Turmeric (Curcuma longa). Journal of Agricultural and Food Chemistry. 2000; 48(6):2189-2192.
9. Haan AD, Graauw JD, Schaap J, Badings H. Extraction of flavors from milk fat with supercritical carbon dioxide. The Journal of Supercritical Fluids, 1990; 3(1):15-19.
10. Huie CW. A review of modern sample preparation techniques for the extraction and analysis of medicinal plants. Analytical and Bioanalytical Chemistry. 2002; 373(1-2):23-30.
11. Kiran E. Polymer miscibility, phase separation, morphological modifications and polymorphic transformations in dense fluids. The Journal of Supercritical Fluids. 2009; 47(3):466-483.
12. Lang Q. Supercritical fluid extraction in herbal and natural product studies a practical review. Talanta. 2001; 53(4):771-782.
13. Luz MA, Duban G, Julian Londoño-Londoño. Recovery of Carotenoids from agroindustrial byproducts using clean extraction techniques: Supercritical Fluid Extraction and Ultrasound-assisted extraction. III Iberoamerican Conference on Supercritical Fluids Cartagena de Indias (Colombia). 2013, 1-6.
14. Margono, Sumarno, Sugeng W, Farah B. Supercritical fluid extraction of oleoresin from curcuma xanthorrhiza: modeling and simulation. International symposium on supercritical fluids. Supercritical fluids von Institut national polytechnique de Lorraine, Vandoeuvre, France. 2003; 1:71-76.
15. Mesomo MC, Corazza ML, Ndiaye PM, Santa OR, Cardozo L, Scheer AD. Supercritical CO2 extracts and essential oil of ginger (Zingiber officinale R.): Chemical composition and antibacterial activity. The Journal of Supercritical Fluids. 2013; 80:44-49.
16. Akanda MJ, Sarker MZ, Ferdosh S, Manap MY, Rahman, NN, & Kadir MO. Applications of Supercritical Fluid Extraction (SFE) of Palm Oil and Oil from Natural Sources. Molecules. 2012; 17(12):1764-1794.
17. Mukhopadhyay M. Natural extracts using supercritical carbon dioxide. Boca Raton, FL: CRC Press. 2015.
18. Nguyen HN, Gaspillo PD, Maridable JB, Malaluan RM, Hinode H, Salim C *et al.* Extraction of oil from Moringa oleifera kernels using supercritical carbon dioxide with ethanol for pretreatment: Optimization of the extraction process. Chemical Engineering and Processing: Process Intensification. 2011; 50(11-12):1207-1213.
19. Pradhan RC, Meda V, Rout PK, Naik S, Dalai AK. Supercritical CO2 extraction of fatty oil from flaxseed and comparison with screw press expression and solvent extraction processes. Journal of Food Engineering. 2010; 98(4):393-397.
20. Priyanka, Khanam S. Supercritical Fluid Extraction of Natural Products: A Review, International Journal of Engineering Development and Research. 2014; 2(4):14-17.
21. Roy BC, Goto M. Hirose T. Extraction of Ginger Oil with Supercritical Carbon Dioxide: Experiments and Modeling. Industrial & Engineering Chemistry Research. 1996; 35(2):607-612.
22. Sánchez-Macías D, Laubscher A, Castro N, Argüello A, Jiménez-Flores R. Effects of supercritical fluid extraction pressure on chemical composition, microbial population, polar lipid profile, and microstructure of goat cheese. Journal of Dairy Science. 2013; 96(3):1325-1334.
23. Santos P, Aguiar AC, Barbero GF, Rezende CA, Martínez J. Supercritical carbon dioxide extraction of

capsaicinoids from malagueta pepper (Capsicum frutescens L.) assisted by ultrasound. Ultrasonics Sonochemistry. 2015; 22:78-88.

24. Spence A, Jimenez-Flores R, Qian M, Goddik L. Short communication: Evaluation of supercritical fluid extraction aids for optimum extraction of nonpolar lipids from buttermilk powder. Journal of Dairy Science. 2009; 92(12):5933-5936.
25. Valle JD, Aguilera J. Revision: Extraction con CO_2 an alta presion. Fundamentos y aplicaciones en la industria de alimentos / Review: High-pressure CO2 extraction. Fundamentals and applications in the food industry. Food Science and Technology International. 1999; 5(1):1-24.
26. Seliem EI, Mahmoud KF, Amin AA, Salama MF. Extraction of oleoresin by supercritical fluid extraction, capsulation, and its physiochemical properties. International Journal of Current Research and Academic Review. 2015; 3(5):1-11.
27. Yver AL, Bonnaillie LM, Yee W, Mcaloon A, Tomasula PM. Fractionation of Whey Protein Isolate with Supercritical Carbon Dioxide—Process Modeling and Cost Estimation. International Journal of Molecular Sciences. 2011; 13(12):240-259.
28. Yee JL, Khalil H, Jiménez-Flores R. Flavor partition and fat reduction in cheese by supercritical fluid extraction: processing variables. 2007.
29. Govindarajan VS. Ginger chemistry, technology, and quality evaluation: part 1. Critical Reviews in Food Science and Nutrition. 1982; 17:1-96.