Industrial applications of supercritical fluid extraction: A review

Kamal Gandhi, Sumit Arora and Anil Kumar

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 CO2, 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. Sub stance 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 (CO2) is perhaps the most frequently sought after mass transfer of solutes from sample matrices. Carbon dioxide extraction unit consists of a pump for CO2, 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. CO2 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:

Supercritical CO2 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 CO2, 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. CO2 is then made to cool, recompressed and recycled, or discharged to the atmosphere.

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Table 1: Yield and quality of fatty oil extracted by SC-CO2 and by petroleum ether.

<table>
<thead>
<tr>
<th>Plant</th>
<th>SC-CO2 Extract</th>
<th>Petroleum ether extract</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (hours)</td>
<td>Yield (% w/w)</td>
</tr>
<tr>
<td>Flax</td>
<td>3</td>
<td>35.3±0.4</td>
</tr>
<tr>
<td>Wheat-DDGS</td>
<td>3</td>
<td>8.8±0.7</td>
</tr>
</tbody>
</table>

Chief compounds such as Omega-3 and Omega-6 fatty acids were enriched in the SC-CO2 extract obtained from the edible fatty oils such as flax seed (Linumusitatissimum L.) and Wheat Dry Distiller Grains with Soluble (DDGS) as reported by (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.

Fig 1: Pressure-Temperature phase diagram for CO2

Fig 2: Schematic diagram of SC-CO2 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.

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(Santos et al., 2011) [22] separated the Red pepper oleoresin from Egyptian food factories waste by using supercritical fluid CO2 followed by its microencapsulation and set forth that the microencapsulation played an important role in oxidation prevention process.

(Nguyen et al., 2011) [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.

(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−1 extract, 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-CO₂ 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 CO₂ can be a good, low fiber animal feed. He further more reported that SC-CO₂ extraction method for specialty oils was retaining the unique flavour and aroma while volatile aroma compounds are generally lost during traditional solvent extraction processing. Speciality oils comprise of high levels of bioactive components, such as polyunsaturated fatty acids, tocopherols, toctrienols, 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 curcuminoinds 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 curcuma xanthorrhiza. extraction rate with decreasing intraparticle diffusivity the effect of particle size, length of extractor, effective extracted from turmeric (Curcuma longa) soluble in the hydrocarbon solvents. Turmeric oil was obtained from SFE process making use of CO₂ can be a good, extraction method for specialty oils was retaining the unique components, such as polyunsaturated fatty acids, tocopherols, specialty oils comprise of high levels of bioactive activity for food and flavouring purposes.

(Yvere 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 CO₂ 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 CO₂ 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) [22] 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 (wt basis) for cheddar extracted at conditions of 200 bar, 40 °C, 1000 g CO₂ and 55.56 % fat reduction for Parmesan extracted at 350 bars, 35 °C, 1000 g CO₂.

(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-Macias 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 Gouda.
type 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) 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 using near-critical dimethyl ether.

Compared with the

8. Gopalan B, Goto M, Kodama A, Hirose T. Supercritical Carbon Dioxide Extraction of Turmeric (Curcuma longa)
capsaicinoids from malagueta pepper (Capsicum frutescens L.) assisted by ultrasound. Ultrasonics Sonochemistry. 2015; 22:78-88.


