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Applications and opportunities of supercritical fluid extraction in food processing technologies: A review

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ABSTRACT

The food industry is always in search of best processing technologies to achieve a natural compound with maximum purity. An increase in interest of functional food has brought a sharp rise demand of naturally occurring compounds achieved via natural processes. The traditional solvent extraction processes have shown certain limitations; such as flammability, toxicity, carcinogenicity, mutagenicity and limited recovery. The studies on cost-effective and eco-friendly processes are still limited. This review focuses on an innovative, environmentally clean tool for food processing technologies and their role in improving food sustainability. Supercritical Fluid Extraction (SFE) technique, however, is already in use for more than 40 years by academia and industries. This can be a successful tool for food processing and can be used for the extraction of selective components. Development of a sustainable and environmentally clean process to achieve natural ingredients is an area undergoing intense studies in food science. Here, we discuss principle applications of SFE to extract natural ingredients from different food materials and by-products. A supercritical fluid is non-flammable, non-toxic, eco-friendly and easily recoverable. These can be easily eliminated from the extract by altering the pressure and temperature conditions. Supercritical fluids are preferred method of extraction from solid samples, different fractional liquids and for chromatographic separations. The cost of SFE is competitive, moreover, in some cases, SFE is the only way to achieve product satisfaction. The design and development of analytical and industrial plants are reviewed. An overview of commercial applications and illustrations of recent development describes new horizons for SFE in food processing industries.

1. Introduction

In recent years, various remarkable consumer trends have been appeared for example, increased concern for nutritional values, growing preference for organic (natural) products against synthetic materials, quality and safety of food products. Attentions of governments towards regulation on toxicity level in manufacturing processes. It is believed that everything natural is safe and valuable, hence this has given positive incentive for the development and growth of natural products producing industries, especially in food flavoring, medicinal and fragrance sectors (Da Silva et al., 2016). Increasing environmental concerns, strict regulations on hazardous and carcinogenic solvents, huge energy consumption, labour cost and solvent recovery have badly affected the growth of food processing industries (Amaral et al., 2017). Approaches that can compete with synthetic materials are now getting more attention of food scientists. Green processes have potential to replace conventional food processing technologies. SFE is a promising technology for sustainability,

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environment friendly and healthier society. The SFE can achieve the consumer preference, effective regulator control, cost effectiveness. All traditional processes for example; crystallization, filtration, distillation and precipitation are being replaced by SFE technology.

SFE used for extraction from solids and liquids at particular temperature (20-60 ˚C) and pressure (50-250 bar) above their critical points. At this region supercritical fluids diffuse like gas and dissolve the analytes like a liquid. Power of dissolving capacity can be modified by changing its conditions above critic point (Vega, 2018). Fig. 1 shows two key points; triple point and critical point. A point where three states coexist is called as triple point, while critical point lies at boiling point here two states (liquid and gas) coexist. Above this point the region is called supercritical point. Supercritical fluids possess both physico-chemical properties of liquid and gas, hence these have wide capacity to dissolve compound that are less soluble and/or completely insoluble in separate gas or liquid state (Varshosaz et al., 2018). Furthermore, in case of dense viscous liquids, decreased viscosity and increased diffusivity of supercritical fluids increases the high mass transfer rate of analytes into fluids, this enhances the efficiency and speed of extraction of compounds from food sample.

Critical points of certain fluids are shown in Table 1. Among these, carbon dioxide is widely used as extracting solvent. Carbon dioxide (critical conditions= 31.1 °C and 72.8 atm) is environmental friendly, inexpensive and documented as safe by regulating authorities such as, FDA and EFSA (Režek Jambrak et al., 2018). Carbon dioxide at room temperature is gaseous, hence after the extraction process, carbon dioxide is removed via decompression. Extract achieved with SFE remained free of residue. Furthermore, in industrial scale carbon dioxide can be recycled. SFE possesses several advantages over other extraction process, due to their low viscosity and high diffusivity. Supercritical fluids easily diffuse within solids and in high dense liquids with better transport efficiency providing increased yields. The tunable density modification by changing in temperature and pressure conditions can alter the density, which increase the solubility. A range of solvents can be used for SFE (Table 1).

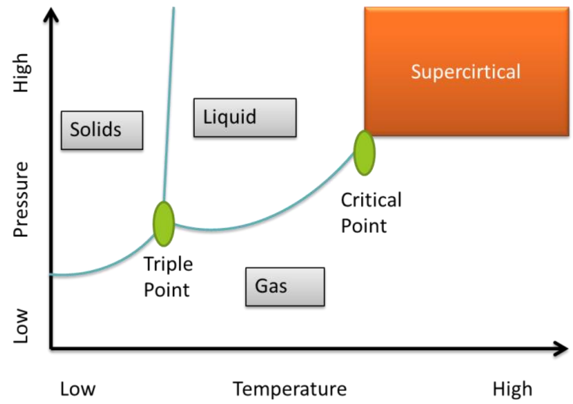

Fig. 1: Phase diagram of carbon dioxide with reference to temperature and pressure variations

Table 1: Supercritical points and other physical properties of different fluids

Solvents	Molecular Wight g/mol	Temperature (critical) ˚C	Pressure (Critical) atm	Density (Critical)/ cm³	Boiling Points ˚C
Water	18.01	374.096	217.55	0.322	100
Carbon Dioxide	44.01	31.1	72.8	0.469	-78.5
Methane	16.04	-82.6	45.4	0.162	66
Ethane	30.07	32.3	48.1	0.203	-88
Propane	44.09	96.8	41.9	0.217	-43
Ethylene	28.05	9.34	49.7	0.215	−103.7
Propylene	42.08	91.9	45.4	0.232	-47.7
Methanol	32.04	239.6	79.8	0.272	64.7
Ethanol	46.07	240.9	60.6	0.276	79
Acetone	58.08	232.8	46.4	0.278	50.5

Supercritical carbon dioxide is more attractive compared to other fluids due to its easily maintainable solvent strength; it is in gaseous state at room temperature and pressure that facilitate the simple and complete solvent free sample recovery. In SFE using carbon dioxide for food and natural product analysis is very important, due to its low temperature operation, which is highly required for extraction of thermally liable or easily oxidizable compounds. However other solvents are also under attention but majority of them appeared with some drawbacks, likewise, high critical temperature and critical pressure of water, high flammability of hydrocarbons and chemical reactivity and toxicity of ammonia (Marcus, 2018). Designing of SFE system is very simple to highly complex. It can be simple in analytical instrument to achieve milligrams of extract or very complex for variety of samples at same time and extraction yield of kilogram at industrial scale. Fig. 2 shows the pilot scale diagram of SFE consisting of a solvent pump delivers the fluid, extraction chamber, heat coils, separator, where extract is collected and buffer vessel for depressing of fluid. Extractor, separator and buffer vessels are fitted with heat exchangers and pressure valves. Quantity and number of separator can be increased to achieve different compounds at different solubility of supercritical fluids. In addition a refrigeration unit can be installed to trap the high volatile compounds and for recycling of system fluid.

The disadvantages of SFE are less compared to other extraction techniques, although greater investment cost required for equipment, some fluids such as, ammonia and water requires elevated pressure for their critical state and these solvents need higher energy cost for their recycling.

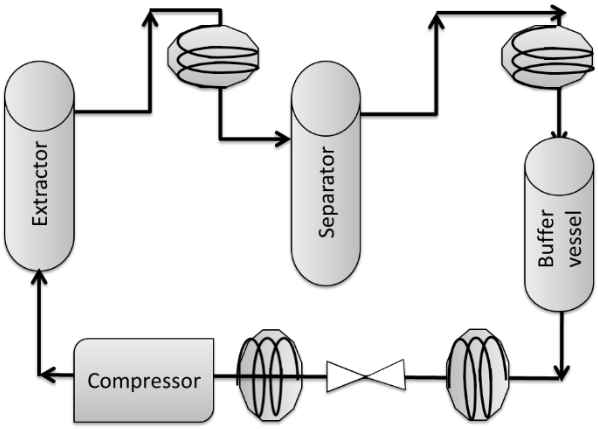

Fig. 2: Operating principle of a supercritical fluid extraction system

There are two key steps involve in SFE; extraction and separation. Materials needs to be extracted are kept in extractor along with supercritical fluids at temperature and pressure above critical points; if analytes are solid, process should be batch-wise as shown in Fig. 2. The sterilized extraction column is filled with solid sample and closed from the collecting vessel liquid. Carbon dioxide flows to heat exchanger then to compressor. Fluids are compressed to required pressure and flows to the heat exchanger, where required temperature is provided then it is transferred to extraction vessel. Sample dissolved in the supercritical fluid as they pass through the extraction vessel. The supercritical fluids, loaded with the dissolved analytes, are then transferred to the separator. Where pressure and/or temperature adjusted and dissolving capacity of supercritical fluids is reduced, this leads to precipitation of extracted analytes. The gaseous fluids is liquefied in condenser (refrigerated) and stored in collecting vessel. If analytes are liquid the process is carried out in continuous way. In SFE of liquid stock the counter column is used instead of extraction vessel (Patil et al., 2018).

2. Functional ingredients from food industry by-products

Different studies have been carried out to extract β-carotene and lycopene from tomato processing waste stream (Saini et al., 2018). These compounds are natural pigments possess natural antioxidant activity. This study has gathered data of applications in food technology related to meat and its products, vegetables and fruits, where SFE is applied. The data is summarized to list the processes and the types of food, extracted products, instrument specifications, process conditions and with information available from different sources. Table 2 shows the one example of development, where this technology has been applied. β-carotene and lycopene extracted from tomato paste waste was 54 % higher over the tradition extraction methods. Furthermore, in increase in temperature up to 65 °C increased 5 % recovery (Szabo et al., 2018).

Table 2: Extraction of cholesterol and other fat from egg yolk using supercritical carbon dioxide as solvent

Process	Process Conditions	Effects/results
Extraction of cholesterol and some other fats without removing polar fats that is liable for sensory characteristics (Ghosh et al., 2018)	Extractor: Capacity 300mL Pmax: 713 bar Separator: Capacity 103mL Sample: 115 g dried egg yolk Extraction (P-T-Density CO2) 186 bar-40⁰ C-0.81 g/cm3 271 bar-45⁰ C-0.86 g/cm3 349 bar-45⁰ C-0.90 g/cm3 426 bar-55⁰ C-0.90 g/cm3 CO2 flow-rate: 5–10 L/min Separation: 39±3 bar	Whole sample is reduced by enhancing the pressure and the temperature at the extractor. Under these extreme conditions (426 bar/55 _C) 36% of the total fat and about 66% of whole cholesterol is extracted. – At 349 bar/45⁰ C and at 426 bar/55⁰ C reliable quantities of phospholipids (largely accountable for the favorite emulsifying characteristics) are not extracted. – The emulsion stability of the mayonnaise only suffers an important (p<0.005) negative effect at 426 bar/55⁰ C. – The amount of bakery products is just only affected under conditions of 426 bar/55⁰ C. – After extraction of these fats color of the yolk become lighter and less red and yellow. – Excellent results obtained at conditions of 349 bar and 45⁰ C providing a good quality product.
Extraction of cholesterol and lipids (Pourmortazavi et al., 2018)	Extraction: 300 bar, 40 and 50⁰ C Co-solvent: ethanol	A 66–74% extraction of cholesterol and a total removal of the neutral lipids are obtained. –No extraction of phospholipids occurred – The product gotten is not distinguishable from non-extracted yolk when used in custard and mayonnaise. Omelettes have improved sensory characteristics. – An interesting by-product is achieved: egg oil. It contains cholesterol (4%) and triglycerides that contains high monounsaturated fatty acid content, which can be used in the cosmetic and pharmaceutical industries. – Co-solvent enhances yield but reduced the selectivity in comparison with pure CO2.
Extraction of cholesterol and fats at optimum particle size and moisture content (Pourmortazavi et al., 2018)	Extraction: 310±3.5 bar, 45±1⁰ C Particle size: 45 g CO2/g sample Moisture: 30 g CO2/g sample Separation: 34.4±3.5 bar Flow rate CO2: 5–10 L/min Density CO2: 0.90 g/cm3	The SFE of unmoisturized egg yolk samples with a larger particle size (32.2%,>25 mm) removed more fat and cholesterol than the smaller particle size –(0.6%,>25 mm) due to the easier and even diffusion of CO2 throughout the sample

Other important applications of SFE are such as decaffeination of tea (Ilgaz et al., 2018), extraction of flavors from herbs (Vieitez et al., 2018), extraction of fats and oils (Jahurul et al., 2018), dealcoholisation of alcoholic beverages (Silva et al., 2017), extraction of aromas of from different juices (Sharifi at al., 2019), extraction of sugars from bamboo (Zou et al., 2018), extraction of coloring compounds such as carminic acid (Prabhu and Bhute, 2012), extraction of antioxidants such as vitamin E and C (Gustinelli et al., 2018), de-acidification of oil for example olive oil (Garmus et al., 2019), rice brain oil (Sookwong and Mahatheeranont, 2017), extraction of tocopherols from vegetable oils (Majid et al., 2019) and inhibition of pectinase of orange juice (Mushtaq et al., 2015). The other food products specially, puffed food such as ready to eat cereals, pasta and confectionary with improved texture, color and taste can be produced by combination of extrusion technology with SFE and combination of this new technology is named as Supercritical Extrusion Fluids (SCFX). Traditional extrusion technology showed limitations which supercritical fluid can overcome. Combination of both technologies can produce a multipurpose food processes (Liu et al., 2018). SFE have been used for extraction and characterization of antimicrobial compounds from algae. Antimicrobial activity of *Chaetoceros muelleri* is connected with supercritical extracts with its content in docosapentaenoic acid (DPA) and triglycerides. Carotenoids are high value functional compounds for human health due to their antioxidants activity. However, they are unstable at higher temperature or in presence of oxygen. SFE is recommended to reduce risks of activity lost. The use of canola oil as co-solvent highly enhanced the production of carotenes. SFE carbon dioxide with canola oil α and ß-carotene were recovered along oxygenated carotenes (lutein) (Sun and Temelli, 2006). Derivatization of solute has also been applied in case of lower solubility and it also helps for the selectivity towards specific group (Lipka et al., 2019). SFE polarity modification can increase the solvent dissolving capacity towards solute of interest by adding the modifier in small amount (1-10%), these modifier can also decreases the solute-matrix interaction which increases the quantitative extraction.

The commercial applications in food processing technology are highly advisable and more research is required. Sometimes supplementary process is needed for the industrial use of CO_2 as solvent for manipulating of new products. Pre-treatment of some food stuff is essential for efficient extraction. These pre-treatment includes; decreasing of moisture content, crushing or grinding or to make these in tablets like in hop extracts. Food industry faces great pressure of consumers to use higher proportion of natural compounds. However natural ingredients are less stable and more costly compare to synthetic alternatives. Sensory characteristics are complex and could not replace with synthetic alternatives. More over higher cost of CO_2 should be managed by increased prices because these products have higher quality and are in natural condition. Flavor and fragrance industry get higher attention towards the SFE and it has been developed extensively and number of plant in various countries have been developed. Coloring also have same situation as fragrance and flavors, natural coloring compound get higher attention of consumers.

SFE using CO_2 as solvent applied in food processing industries is highly recognized particularly in fields like, in decaffeination of coffee, extraction from hop, extraction of flavonoids from herbs, separation of cholesterol from egg yolk, meat or milk fat. The many advantages of SFE are given as; greater quality and purity of extracted sample, rapid extraction and separation phases, complete solvent free residue, selective extraction of desired compounds by modification of solvent and co-solvent or derivatization of solutes, decreased cost of separation. However there are some disadvantages of using SFE in food technology has been documented. Specially, in solid extraction there is lack of continuous system. As it is already described that continuous process cannot be used for extraction of solids sample, it means in economic point of view, SFE is attractive only for traditional extracts as compare to solid sample. Another disadvantage of SFE is the cost of instrument. Currently, only increased cost and low amount food products are being processed. But it is hope that in future this method can be competitive for extraction of higher volume products as well.

3. Conclusion

In summary, SFE can be applied in developing of long lasting niche in food technology. It is used as extraction solvent in analytic technique such as extraction of fat content by gravitational method or in large scale extraction, for example, decaffeination of coffee; due to non-hazardous property of this technology it has been proven that it is replacement of use of organic solvent. Increasing concerns regarding the application of organic solvents and their disposal, supercritical fluids are getting more rapid popularity. The future looks hopeful for application of supercritical fluids, with new constantly developing methods of extractions, as with other innovative uses for the food processing industry.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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