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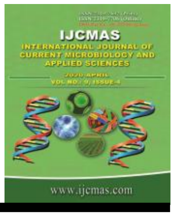

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Supercritical Fluid Extraction of Bioactive Compounds from Bioresource: A Review

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ABSTRACT

The Supercritical Fluid extraction is also considered as a novel technology for extracting soluble products into a fluid from a wide range of materials using supercritical conditions of solvents. Bioactive compounds are secondary metabolites produced from a broad diversity of structures and functionalities. In the present article the potential bioresources mainly from agriculture and allied sectors have been reviewed which constitutes excellent pools for bioactive and nutraceutical compounds. These natural compounds play an important role in enhancing health, improving immunity, maintaining well being and thereby preventing as well as treating specific diseases. The present generation which is more proactive in identifying the intake of healthy food is also cautious about its processing technologies involved in it. The use of conventional solvents, thermally decomposing and unsustainable technologies in the food, pharmaceutical, and nutraceutical industries have created marketing concern for their products. Hence there is a need for cutting edge technology which can overcome these legal limitations. Supercritical Fluid Extraction (SFE) is the process of separating one component (the matrix) from another (the extractant) using supercritical fluids. The properties of the fluid (liquid and gases), under supercritical conditions, are used to extract most complex compounds. CO_2 is nontoxic, inexpensive and non-flammable could be applied as a replacement for conventional solvents in an extractive process using supercritical fluid extraction process. The present paper reviews the basics of supercritical extraction technology and extraction of bioactive compounds from various agricultural and bio-resources.

Keywords

Essential oil, Triple point, Green technology, Waste industries, Agro-industries

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Introduction

Supercritical Fluid Extraction (SC-CO_2) has emerged as a new, additive-free, non-thermal extraction technology with a wide range of applications in the food and pharmaceutical industry. The next stage is to identify the opportunities SFE presents for the production of safe and healthy food products and ingredients. This article, in short, describes the recent findings in the applications of SFE to extract bioactive components from plant food materials, many studies indicated that SFE has significant potential for such applications and, thus, there is considerable opportunity for the food industry to exploit these opportunities to bring the next generation of SFE food products to the market.

Supercritical extracts proved to be of superior quality, with better functional and biological activities[6]. Furthermore, studies also showed better antibacterial and antifungal properties for the supercritical product. Apart from other conventional extraction processes of bio-active compounds, more recent studies have focused on the Supercritical fluid extraction with carbon dioxide (SFE-CO_2) is a promising and challenging method for the isolation of valuable essential oils and other phytochemicals with such advantages as safety and easy removal of solvent on health attributes and allergenic potential of foodstuff to develop the next generation of convenience foods. Unusual vegetable oils such as wheat germ oil, green coffee oil, rice bran oil or crude palm oil, essential oils, fatty acids, phospholipids and bioactive compounds have been extracted from fruits and vegetables using SC-CO_2.

Fractionation and purification are also viable applications of SFE technology in the food industry. Decaffeination of beverages such as tea and coffee, fractionation of fish oils with SC-CO_2 to obtain omega-3 enriched fractions is possible (Ciftci *et al.*, 2012; Patterson, 2005)

Formation of supercritical phase of CO_2

A supercritical fluid is the substance that diffuses through solids like a gas and dissolves materials like a liquid at a critical point, the point is known as supercritical point. Thus, the formation of critical phase at critical temperature and critical pressure makes the fluid as supercritical fluid. These fluids own combined properties of liquid and gases phases, as it can behave like both a liquid and a gas. The process formation of a supercritical fluid is the result of dynamic equilibrium. When a material is heated to its specific critical temperature at constant pressure in a closed system, a dynamic equilibrium is generated. This equilibrium includes the same number of molecules coming out of liquid phase togas phase by gaining energy and going into liquid phase from gas phase by losing energy. At this certain point, in the phase curve between liquid and gas, both the phases disappears and supercritical material appears.

For better understanding, the figure 1 shows the of phase diagram CO_2, the colloidal areas of three phases. The phase diagram defines the temperature and pressure limits in which CO_2 exits in solid liquid, gas and supercritical state. The black, blue and green line indicates the equilibrium between solid and gas, solid and liquid, liquid and gas respectively.

Whereas, the figure 2a shows the triple point at 5.11 bar and -56.7 ^{o}C where system containing CO_2 forms indistinguishable solid, liquid and gases phase simultaneously. Figure 2b shows the existence of subcritical point of CO_2, where the pressure is maintained while the temperature is taken below the supercritical threshold, causing it to become a (non-supercritical) liquid.

The liquid-gas phase boundary is called the subcritical line, as a liquid evaporating directly into a gas is called subcritical. Figure 2c shows the above critical point (73.8 bar and 31.1 °C), the liquid and gas phases cannot exist as separate phases, and CO_2 develops supercritical properties, where it has some characteristics of a gas and others of a liquid.

Typically, supercritical fluid extraction using CO_2 involves the uses of specialized extraction unit which lowers the temperature and compresses the CO_2 until it reaches liquefied stage, this liquefied CO_2 gas passes through food material to pullout the target component concentrates. After the successful extraction process, the CO_2 depressurized to allow it to turn from liquid into gas. The CO_2 obtained at the end is either reused or released it into environment safely making it green extraction technology with no harmful footprints to nature.

Supercritical fluid extraction process

The extraction process using SFE technology contains 3 main processes, as shown in the figure 3.

Pumping process

From CO_2 Cylinder, the CO_2 is usually pumped at about 50 bar and at temperature below 5°C to maintain liquid conditions. Usually, the pump used in the system is for compressing the fluid rather than pumping operation. Reciprocating CO_2 pumps or syringe pumps are often used for small scale extraction whereas, for large scale diaphragm pumps are mostly used.

The pressure in the system is maintained from the pump right through the pressure vessel by using simple regulator or back pressure regulator.

Preheating process

After Pressurization, the liquid (CO_2) is pumped to a heating zone, where it is heated to supercritical conditions, thus preheating prevents excessive cooling. Electrically heated restrictors are used for this purpose.

Extraction process

A pressure cell to contain the sample, a means of maintained pressure in the system and a sample collecting vessel. The CO_2 under supercritical condition is then passes into the extraction vessel, where it rapidly diffuses into the solid matrix and dissolves the material to be extracted.

The dissolved material is swept from the extraction cell into a separator at lower pressure, and the extracted material settles out. The supercritical fluid can then be cooled, re compressed and recycled (Ayre *et al.*, 2013; Sapkale, *et al.*, 2010) .

Optimization of SFE process

The main aim of optimization is to increase the yield, reduce the input cost and duration of extraction. Using Response Surface Methodology (RSM) optimization of extraction cycle is carried out, where maintenance of pressure, temperature, and solvent flow rate and time duration of operation is optimized. On other hand the main objective of optimization of SFE–CO_2 process is to maximizing diffusion and solubility.

Maximizing diffusivity

Diffusivity of CO_2 into sample matrix can be achieved by reducing the particle size, increasing the temperature or swelling the matrix (this can be increased by increasing the solvent pressure or by adding co-solvents).

Maximizing solubility

Solubility of extracted components into CO_2 can be achieved by increasing the pressure and decreasing the pressure within the critical temperature and pressure. Further, Solubility can be also increased by adding co-solvent such as methanol and ethanol which adds more polar compounds along with the solvent CO_2.

Table.1

Bioactive compounds	Material	Extraction condition				Target compound	Reference
		Temperature (°C)	Pressure (bars)	Time (min)	Flow rate (g/min)		
Fruits and Vegetable processing Industries	Apple pomace	80	300			Total triterpenic content (9.6 mg/g)	Ferrentino *et al.*, 2018
	Citrus fruits	40 - 60	85-200			Volatile compounds	Jerkovic *et al.*, 2016 Jokic et al., 2016
		30 – 60	100-300	360	3 (ml/min)	Volatile compounds (90-92.5%) and Limonene (74-78%)	Roy *et al.*, 2007
		28 - 60	80-150	120	16 (g/min)	Essential oil (3.4- 4 %)	Nautiyal and Tiwari 2014
	Tomato	80	275		8 (ml/min)	Lycopene (82.5%)	Malik et al., 2015
						Lycopene (86%)	Kehili et al., 2017
	Tomato peels	50-80	300-500	105	3-6 (g/min)	Lycopene (32-60%) and □- carotene (28-59%)	Nobre et al., 2012
		59 °C	300	30	15	□- carotene Lutein Lycopene (%)	Lima *et al.*, 2013
	Apricot					98.7 79.9 -	
	Pumpkin					92.4 - 87.4	
	Peach					99.8 - -	
	Green pepper					98.6 99.8 -	
	Yellow pepper					99.8 99.6 -	
	Red pepper					- 98.1	
Seed materials	Hemp,	40-60	300-400			Oil	Aladic *et al.*, 2011; Cardoso *et al.*, 2013, Uribe *et al.*, 2011; Pederssetti *et al.*, 2011
	Passion seed,	40-60	150-250				
	chia,	40-80	136-408				
	canola	40-60	200-250				
Oleoresin Industries	Capsicum spp	31-35	74			Capsithin	Guimar *et al.*, 2017
	Ginger,	25-35	200-250			Gingerin	Zancan *et al.*, 2002
	Horsetail	30,40	120-300			Methenolone, phytosteriod	Michielina *et al.*, 2005
	Turmeric	50	250	90	3 ml/min	Curcumin (1.69)	Radzali *et al.*, 2016
Herbal Industries	Aleo vera	45.91	320	140	0.84 ml/min	α- tocopherol (53.41%)	Bashipour and Ghoreishi, 2015
	Basil	40	400	-	1.6 g/min	essential oil (2.2%)	Coelho *et al.*, 2018
	Noni	37	210	104	20 L/min	Essential oil (20.13%)	Bai *et al* 2012
	Rosemerry	50	180	-	1 g/min	pentacyclic triterpenes (45.22%)	Bensebia *et al.*, 2016
Agro-Waste Industries	Spent coffee	40	250	40	100 g/min	Biodiesel	Paiva, 2015
	Corn biomass	118	200	25-30	4 g/min	Lignin (9.20%)	Neata *et al.*, 2015
	Silkworm Pupae	45	203	145	24 g/min	Oil (30%)	Srinivas *et al.*, 2019
	Tobacco	40	300	5	1 l/min	Solanesol (0.44 %)	Ruiz–Rodriguez *et al* 2008
Marine Industries	Whole Fish	40-80	250-400	300	2ml/min	Fish Oil (10-50 %)	Ivanovs & Blumberga 2017.
	Shrimps	56.88	215.68	120	1.89 ml/min	Astaxanthin (58.50 µg/g)	Radzali *et al.*, 2016
	Marine micro algae	40	500	300-810	33.33 g/min	Polyphenol (20 mg/g) and other macro and micro elements	Michalak *et al.*, 2016
Brewery Industries	*Cabernet Sauvignon*	35	180	-	0.5 ml/min	Phenolic (14%)	Silva *et al.*, 2017
	Green Tea	60	250	-	10 g/min	Caffine (1.8%) and Catechins (2.7%)	Sokmen *et al.*, 2018
	Coffea Arabica	70	200	180	5 g/min	Cafestol (85%) Kahweol (80%)	Oliveira *et al.*, 2014
	Hops	50	300	360	-	α-acids (41%), β-acids (19.5%).	Roj *et al.*, 2015

Fig.1 Three phase diagram of CO_2

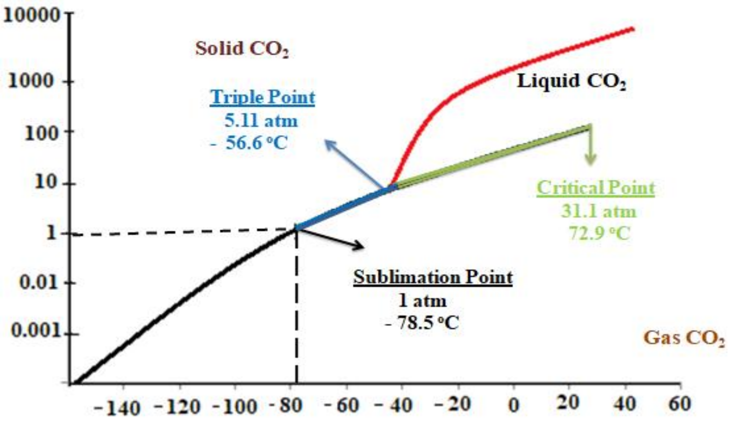
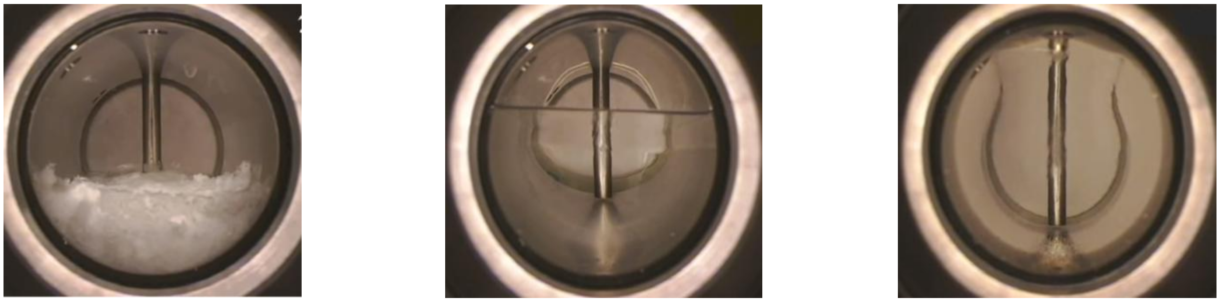
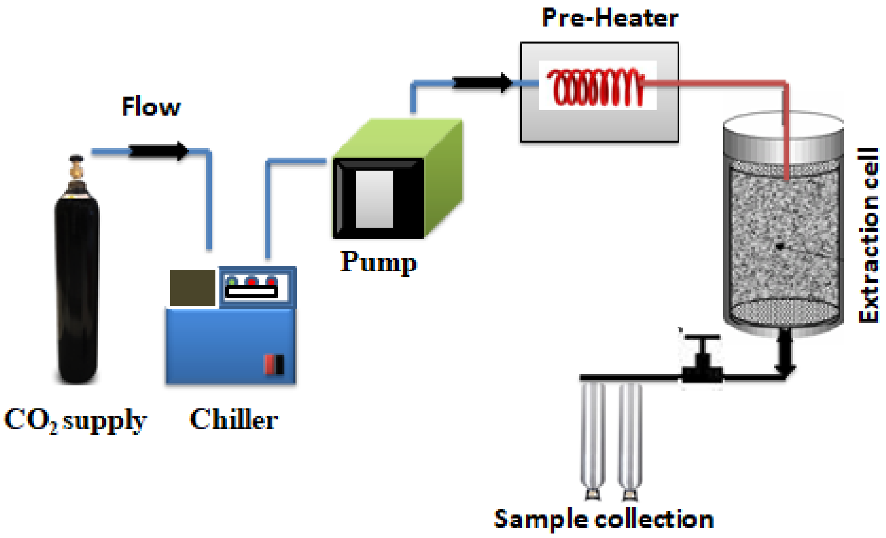


Fig.2



a Triple point of CO_2 2b. Subcritical point of CO_2 2c. Supercritical Point of CO_2

Fig.3 Overview setup of supercritical fluid extraction ($SC\text{-}CO_2$)



SFE technology in extracting bioactive compounds

Demand for secondary metabolites recovery from plant food materials and their by-products is increasing due to their nutraceutical properties and other health benefits. Biologically active compounds of medicinal herbs (antioxidants), essential oils (volatile compounds), nutraceuticals and pharmaceuticals (lycopene, astaxanthin, hyperforin etc.), seed oils (tocopherols etc.), oleoresins from spices, and natural colours (carotene, chlorophyll) etc. (Table 1) Shows some of the recent findings on the extraction of bioactive compounds using SFE-CO_2 from different bio resource.

In conclusion supercritical fluid extraction (SC-CO_2) has captured considerable attention in various food and pharmaceutical industries due to safe and quality product output. With a green and efficient technology, it is finding its wider application beyond the extraction process. It has become complimentary technology which can significantly widen the ambit of the products both sourced from animal and plants to be extracted. Owning expeditious advantages supercritical fluid extraction (SC-CO_2) can be next generation extraction technology with huge potential and thus merits further investigation.

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