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Supercritical Fluid Extraction: A Review

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ABSTRACT: Supercritical fluid Extraction (SFE) is a green technology as use of supercritical CO_2 (SC-CO_2) is the most widely used since it is nontoxic, non-flammable, non-corrosive, and easy to handle allowing supercritical operation at low pressures and near room temperature. Supercritical CO_2 (SC-CO_2) is cheap and readily available in bulk quantities with a high degree of purity, ensuring minimal alteration of the bioactive compounds and to preserve their curative or functional properties, possesses the ability to solubilize lipophilic substances, and can be easily removed from the final products. It is environmentally friendly and "generally recognized as safe "GRAS" technique. This paper presents an overview of the literature addressing the genesis of SFE to the application of supercritical fluids in various aspects of the food industry and is divided into eight different areas: SFE Principle, Extraction Parameters, Extraction/Separation Methods, Carbon Dioxide as Supercritical Fluid Extraction, Other Super Critical Fluids, Instrumentation and Working Apparatus, Extraction/Separation Methods. The review also discusses subsequent advantages of this method over other extraction process.

Keywords: Carbon dioxide; Extraction parameters; GRAS; Green Technology and Supercritical Fluid Extraction.

INTRODUCTION: Across globe research is been conducted to assess the efficacy of many emerging non-thermal technologies in food processes to minimize the deleterious effects of thermal conventional process like, pulsed electric field[1], Ohmic heating[2], ultraviolet light[3], pulsed-light technology[4,5], ultrasound[6], cold plasma[7], high hydrostatic pressure[8] and ultra-high pressure homogenization[9].

Consumers crave for food with better nutritional quality, coupled with food safety and use of green technology.[10] The number of potential applications for supercritical fluid extraction (SFE) continues to grow globally, which is verified through the increase in patents deposited in the last few years. It is observed that its application is already part of the present scenery, being mainly impelled by the growing demand of high quality products demand and economy's globalization. Besides that, it also stands out in its use in the commerce of pharmaceutical, food, chemical, and cosmetic materials. The increase in the application of this technology in the industrial area is mainly due to the selectivity, facility, and separation capacity that the technique allows in obtaining a great number of organic compounds, of which many are impossible or nonviable to extract through traditional processes, or those whose purification needs high resolution columns, not always available in the national market, thereby making the utilization very costly. The high utilization of organic solvents in the different industrial processes, such as fat and oil extraction, obtaining bioactive functional compounds, removal of heavy metals, polymer processing, fuel production, among others, represent a globally discussed issue, due to the harm caused to the environment. In light of this picture, in 1987, the Montreal Protocol was introduced, and in 1997 the Kyoto Protocol, which had as the main objective to restrict or eliminate the production and utilization of solvents that cause harm to the ozone layer.[11] The great interest of the scientific community and the industrial sector for SFE is directly related to the restrictions to the use of organic solvents, both in the preparative processes of samples used in the various industries, and in a higher ecological consciousness in the use of different analysis methods involving extraction.

The extraction technique most widely known as supercritical fluid Extraction (SFE) Since its inception has been touted for its exceptional performance.[12] Presently, the utilization of SFE is extensively applied not only to the food and drug areas, but also in the areas of toxicology, chemistry, environment, textile, petrochemical, polymers, among others.[13] Significant achievements in the area of supercritical fluid technology over the past three decades have pushed the extraction of natural plant materials using this method of extraction and has been described as an environmentally safe technology.[14] These natural sources could be plants, algae, and microalgae, among others. Moreover, the goal of this technique is the high selectivity, short times of extraction, increased pollution prevention, and the use of nontoxic organic solvents.[15] SFE is based on some properties of the fluids, such as density, diffusivity, dielectric constant, and viscosity and usually involves modification of some conditions such as pressure and temperature to attain a supercritical fluid.[16] Under these conditions, a fluid is between gas and liquid because the density of an SF is similar to that of liquid and its viscosity is similar to that of a gas.[17] Thus, the supercritical state of a fluid is the state in which liquid and gas are identical from each other.[15] In addition, SFs have better transport properties than liquids because it depends on its density which, unlike liquid solvents, is adjustable by changing pressure and temperature.[16,14]

The number of applications in food has increased drastically in the last few year as there has been an incredible amount of research and commercialization activity for the extraction of plant materials to generate 'natural' extracts for use as ingredients in functional foods.[18] From the various studies it is evident that oils are common extraction targets components especially Specialty oils, such as those from nuts and seeds, as they tend to be of high value, yet low volume. Since these oils have high concentration of bioactive components, conversely the low critical temperature supercritical CO_2 (SC-CO_2) helps in marinating their safety and bioactivity. Among carotenoids the β-carotene and lycopene are mostly extracted by using SC-CO_2.[19] Phytosterols are viewed as having a variety of health benefits, including cholesterol lowering and antioxidant functionality.[20] SC-CO_2 extraction has been utilized for the extraction of phytosterols from plant materials and/or for edible applications, both on their own and in conjunction with other major or minor lipid components[21] and Other lipid soluble components like phospholipids[22], squalene[23] and Co-Enzyme Q-10.[24] Despite the low solubility of phenolics in SC-CO_2, such extractions have been investigated quite extensively, especially in recent years.[25] Multistage extractions, or cycles of pressurization–depressurization, are more prevalent with SC-CO_2 extractions of phenolics and polar compounds compared to lipid-soluble compound extractions.[26] Essential oils[27], Caffeine[28], Polyols[29], stevia glycosides are also extracted by using SC-CO_2 extraction. In addition inactivation of micro organisms is achieved through a series of mechanisms based on SC-CO_2.[30]

TERMINOLOGY:

Supercritical: The term "supercritical" refers to a substance in a non-condensing and single-phase fluid when brought above its critical temperature (Tc) and critical pressure (Pc). Beyond this point, there is a supercritical region where the substance shows some typical physicochemical properties of gases or liquids, such as high density, intermediate diffusivity and low viscosity and surface tension.[31]

Supercritical Fluid: A fluid at temperature and pressure conditions above its critical point is referred to as a supercritical fluid, which is a dense fluid with interesting properties in between those of a gas and a liquid. Its density is similar to that of a liquid, while its viscosity and diffusivity are similar to those of a gas. Therefore, a supercritical fluid can act as a solvent similar to a liquid, but with enhanced mass transfer kinetics.

Extraction: Extraction is a contact equilibrium separation process where a solid material containing a solute of interest is brought into contact with a liquid solvent, time is allowed for the equilibrium to be reached and the target component to be transferred from the solid phase to the liquid phase and finally, the solid and liquid phases are separated by physical means. This also applies to liquid/liquid extractions.[32]

Supercritical fluid Extraction (SFE) principle: Supercritical carbon dioxide technology (SC-CO_2 technology) utilizes pressure in combination with carbon dioxide to destroy microorganisms without affecting the nutritional content, organoleptic attributes, being a promising alternative for pasteurization of bioactive compounds in food and medicine[33] in which compounds would be destroyed by conventional thermal processes.[34] The driving force for any extraction process is the solubility of the target compound in the selected solvent, which depends on the interactions between the solvent and solute**.** Supercritical fluid extraction (SFE) has emerged as a superior alternative technique for extraction of bioactive species from natural produces, because of its reduction of extraction time, less consumption of organic solvents, being suitable for thermo-sensitive substance; production of cleaner extracts a environmental benignity.[35] SFE is based on the solvating properties of supercritical fluid (SF), which can be obtained by employing pressure and temperature above the critical point of a compound, mixture or element. By proper controlling of SFE parameters, the extractability of supercritical fluid can also be modified which enable this process to find its field from food to pesticide researches. Even though CO_2 is the preferred extraction solvent (for extracting non-polar compounds), the polarity of supercritical SC-CO_2 can be increased by the addition of a miscible polar compound (such as ethanol) as modifier.[36] Due to the selectivity involved in the SFE process, the extracts obtained by this technique possess low concentration of undesired compounds.[37] Besides, SC- CO_2 becomes gaseous after depressurization and can be easily eliminated from a flow system.[38]

Extraction Parameters: The application of supercritical fluid is directly related to its physicochemical properties. The high-density values combined with the pressure dependent solvent power provides high solubility and selectivity to the supercritical fluid. In addition, low viscosity values and intermediate values of diffusivity combined with the absence of surface tension of these fluids allow its rapid penetration into the cells and particles of the sample matrix extracting their interior material.[39,40] These characteristics facilitate process of extraction and inactivation of vegetative cells. In some cases, similar effects to the supercritical state can be reached at temperatures near to its critical, the liquid state of a substance, with $P > Pc$ and $T < Tc$ characterizing the subcritical state.[41] Similar to conventional extraction techniques, supercritical fluid extraction of targeted components from a plant matrix is dictated by several parameters, including pretreatment of plant material, particle size, temperature, pressure, time, solvent flow rate, and solvent-to feed ratio.[42] These parameters impact the efficiency of extraction, which is determined in terms of yield and recovery of the targeted components. Yield is the amount of total extract obtained per unit mass of starting feed material, whereas the recovery is the percentage of targeted component originally present in the feed material recovered in the extract.[43]

Carbon Dioxide as supercritical fluid extraction: The extraction process using supercritical fluids is presently considered a feasible alternative for conventional extraction methods. The solvents in supercritical state show intermediate physical-chemical properties similar to that of liquid and gas, which increases the extracting power of the solvent. The high density of these fluids gives them a high solvation power, whereas its high diffusion and low viscosity values provide a desired penetration power in the solid matrix.[44] Selection of SFs is very important for the development of a SFE process, and a wide range of compounds can be used as solvents in this technique.[16] However, despite the fact that there are many compounds that can be used as SFs (ethylene, methane, nitrogen, xenon, or fluorocarbons), most separation systems use carbon dioxide due to its safety and low cost.[45]

Among various supercritical fluids used for extraction, supercritical CO_2(SC-CO_2) is the most widely used since it is nontoxic, non-flammable, non-corrosive and easy to handle allows supercritical operation at low pressures and near room temperature. Cheap and readily available in bulk quantities with a high degree of purity.[46] Carbon dioxide has been described to ensure minimal alteration of the bioactive compounds and to preserve their curative or functional properties.[47] Supercritical carbon dioxide (SC- CO_2) is an attractive alternative to organic solvents because it is non explosive, nontoxic, inexpensive, and possesses the ability to solubilize lipophilic substances, and can be easily removed from the final products.[15,17,48] Another advantage is that is gaseous CO_2 at room temperature and pressure, which makes compound recovery very simple and provides solvent-free extracts. In addition, this molecule is environmentally friendly and "generally recognized as safe" (GRAS) by FDA (U.S. Food and Drug Administration) and EFSA (European Food Safety Authority).

The good understanding of the solubility behavior of the components of interest for food processing in SC-CO_2 is essential. Solubility of a solute in SC-CO_2 is highly dependent on temperature and pressure, which influence CO_2 density and subsequently solvent power. Increasing the pressure leads to liquid-like density of SC-CO_2, thus increasing the probability of interactions between the solute and solvent, leading to a dramatic increase in solubility. On the other hand, increasing the temperature causes a decrease in SC-CO_2 density while at the same time increasing the vapor pressure of the solute. The net effect of these two opposing factors dictates the change in solubility. At low pressures close to the critical point, the decrease in SC-CO_2 density is more dramatic such that a temperature increase results in a decrease in solubility, whereas at higher pressures the vapor pressure effect takes over since the density drop is relatively smaller, leading to a solubility increase. The consequence of these transitions is the well-known crossover behavior of the solubility isotherms. Solute properties, especially molecular weight, polarity, and vapor pressure also influence solubility in SC-CO_2 .The solubility of substances in SC-CO_2 is affected by solute–solvent as well as solute–solute interactions, such as hydrogen bonding. Due to the non-polar nature of CO_2 the solubility of non polar components is usually higher than that of polar components with a similar molecular weight. An increase in molecular size of a solute decreases the solubility in the supercritical fluid. Therefore, non polar solutes of low molecular weight and high vapor pressure are preferentially solubilized in SC-CO_2 at relatively low-density conditions, while higher-density conditions are needed for larger, slightly polar, and less volatile solutes. Thus, high selectivity's can be achieved by simply adjusting the temperature and pressure, which is a major advantage of the SC-CO_2 extraction technology, thus minimizing additional refining requirements in most cases. If the target compound is polar, polarity of the supercritical solvent can be adjusted with the addition of a polar co-solvent, which is also referred to as a modifier or entrainer. The co-solvent can interact with the solute through hydrogen bonding, charge transfer complex formation, and dipole–dipole coupling as well as the solvent, leading to an increase in the density of the solvent mixture, thereby impacting solubility positively. The co-solvent of choice for food applications has been ethanol for obvious reasons of ethanol being considered a GRAS (generally recognized as safe) solvent for food processing.[49] Many research groups have used this type of gradient with a hold at the highest modifier composition for fast SFC separations of polar compounds.[50]

Other super critical fluids: Since Carbon Dioxide is least polar, it is less effective in extracting highly polar compounds from their matrices.[14] Polar molecules are poorly soluble in SC- CO_2 and hence are not extractable.[45] For this reason, the use of other solvent compounds is needed in order to enhance solubility and the selectivity of the process and they must be added only in small quantities.[16] This phenomenon is attributed to various components acting as solubility enhancers and is called "co-solvent effect." Co-solvents or modifiers include hexane, methanol, ethanol, isopropanol and dichloromethane, among others. However, ethanol is recommended as a co-solvent in SFE because of its lower toxicity and miscibility in CO_2[51], although its applications is limited due to its unfavorable properties with respect to safety and environmental considerations.[15] Other co-solvents used are Nitrous Oxide, Similar in solvating and separations properties to CO_2, alkanes better solvent characteristics for non-polar solutes.

INSTRUMENTATION AND WORKING OF SUPERCRITICAL EXTRACTION APPARATUS: The various components for Supercritical Fluid Extraction setup include a pump, an extraction vessel, a depressurization valve, and a separator. The fluid source, commonly a tank of carbon dioxide, Syringe pump having a pressure rating of at least 400 atm. There is valve to control the flow of the critical fluid into a heated extraction cell. There is an exit valve leading to a flow restrictor that depressurizes the fluid and transfers it into a collection device. During the process of SFE, raw material is placed in an extractor vessel, which has temperature and pressure controllers to maintain the desired conditions. The pretreated plant material with desired moisture content and particle size is usually placed into a basket equipped with filters at both ends to hold the solid material in place but allow the CO_2 pass through.[52]

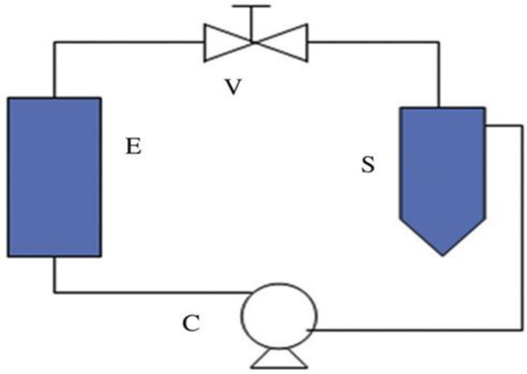

Figure 1: Supercritical Fluid Extraction Apparatus.

The basket is then placed into the extraction vessel. The laboratory-scale units available commercially may or may not come with such a basket. Once the basket is placed inside the extraction vessel and the vessel is sealed properly, the system is filled with CO_2 at tank pressure while the depressurization valve is closed, ensuring that there are no leaks in the system. The thermocouple should be located inside the extraction vessel for proper temperature control as thermocouples on the outside of the vessel fail to record the temperature increase due to pressurization of CO_2. Upon stabilization of the extractor temperature and pressure, the depressurization valve can be opened to start the flow of SC-CO_2 through the cell. Once the fluid and the dissolved compounds are transported to separators, the products are collected through a tap located in the lower part of the separators Thus, SC-CO_2 extracts the components that can be solubilized under the set of temperature and pressure conditions and carries them out to the separation vessel. Upon depressurization, SC-CO_2 becomes a gas, separates from the extract and the extract is collected in the separation vessel. In addition, this valve needs to be heated to prevent freezing due to the well-known Joule– Thomson effect upon Depressurization.[53] Then, the expanded CO_2 passes through a flow meter and a gas meter to determine the total volume of used CO_2 throughout an experiment. In general, laboratory-scale units are not equipped to recycle the CO_2, the exhaust CO_2 is vented. Obviously, this is not feasible at large-scale industrial plants and the exhaust CO_2 is collected in a tank and recycled back to the extraction vessel. Finally, the fluid is regenerated and cycled or released to the environment.[16]

Extraction/Separation Methods: There are multiple methods that can be utilized to separate the solute from the supercritical fluid, which is acting as the solvent. There are three basic concepts that can be used to accomplish this. The first is to change the temperature or pressure so that the solvent capability of the supercritical fluid changes. The other is to "wash" the solute out of the supercritical fluid using a solvent that can strip the solute from the supercritical fluid. In addition to the separation of the solute from the supercritical fluid, it is possible to separate multiple solutes within the supercritical fluid using a packed column.

The simplest method to remove the solute from a supercritical fluid is to change the pressure of the supercritical fluid so that either the fluid is no longer supercritical or that the solute is no longer soluble in the supercritical fluid. Various scientists utilized this method to remove their respective solutes from the supercritical fluid. In all three cases the individuals performing the study routed the solute/solvent combination through a restriction valve and into a collection vessel. Inside the collection vessel, the pressure was reduced to room pressure, causing the supercritical fluid to return to its gas state, and the solvent to be released into the collection vessel. Inside the collection vessel, there can be a solvent to receive the solute, so that further analysis can be performed. Other times the vessel may be left empty so that the solute can crystallize upon leaving the supercritical fluid. Another variation of the previous method to remove the solute from the supercritical fluid is to change the temperature of the supercritical fluid. This may cause the fluid to leave the supercritical region, but it allows for the pressure of the fluid to be maintained. This could save money by allowing for the pressurized fluid to be recirculated, without having to repressurize it. This means that less money would have to be spent on the energy to pressurize the fluid. Lancas et al.[54] utilized this method to remove their respective solutes from the supercritical fluid. This method simply involves the removal of the solute by dropping the temperature of the solvent until the solute is no longer soluble and precipitates from the supercritical fluid. This is also referred to as a cryogenic trap. Once the extraction has been completed, the system can be depressurized and the extract can be removed from the sample chamber. The solute can also be removed from the supercritical fluid by "washing" it from the solvent. This allows for the process to be maintained at a constant pressure much as the cryogen trap did, but it also allows for the removal of the solute from the process without having to shut the process down. An example of this type of removal is used in the decaffeination of green coffee beans to remove the caffeine from the supercritical CO_2.[55]

Applications of SFE: The application of SFE is based on the experimental observation that many gases increase their dissolution power when compressed above a critical point.[56] Some studies have described different supercritical applications, usually using CO_2 gas a S. F. Liza and others (2010) studied the feasibility of the SFE method to extract lipid compounds such as tocopherols, phytosterols and free fatty acids from sorghum and the preventive role of these compounds in many diseases. On the other hand, scientific studies indicated possible antioxidant effects of many spices such as rosemary, sage, thyme, and oregano, among others.[52] For this reason, Cavero and others (2006) assessed the possibility of using oregano leaves as a source of antioxidants under a wide range of extracting conditions (different pressures and temperatures and considering ethanol as a co-solvent). Their results show that the extracts obtained by SC-CO_2 possess high antioxidant capacity against the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical, especially when a co-solvent is used. In this context, SF-CO_2 is important for the natural compound extractions and the food industry, because it allows the extraction of thermally labile or easily oxidized compounds.[11]

Nowadays, SFE is much used in many industrial applications including coffee decaffeination, fatty acid refining and the extraction of essential oils and flavors from natural sources with potential use in nutraceuticals and functional foods.[45] This method is an important alternative to conventional extraction methods using organic solvents for extracting biologically active compounds.[15] However, to develop a successful SFE, several factors need to be taken in consideration including SFs, raw materials, co-solvents, and extraction conditions for the extraction of a particular compound of interest in order to maximize the extraction. Moreover, it has been proved with good success that SFE can be used to obtain active substances in micro particles as dry powders in which stability and activity are maintained.

This approach opens a new opportunity for the use of these compounds in the food and pharmaceutical industries. The application of various supercritical techniques to the preparation of active powders and particles and future challenges has been reviewed recently by Cape et al. (2008). Presently, the utilization of SFE is extensively applied not only to the food and drug areas, but also in the areas of toxicology, chemistry, environment, textile, petrochemical, polymers, among others.[57]

Supercritical fluids show low viscosity as a gas, high density as liquids, and intermediate diffusion between gases and liquids, varying with its density.[27] They are easily adaptable to the various separation processes, which involve wide levels of temperature and pressure. Such characteristic allows supercritical fluids to be used to separate technically unstable materials (oils and polyunsaturated fats acids, vitamins, carotenoids, antioxidant compounds) at low temperatures, and even realize separations with small variations of pressure, due to the high compressibility and exponential solubility.[56] These characteristics turn these fluids adequate as substitutes to organic solvents in extraction processes.

It is currently widely accepted that super critical extraction is a green alternative to normal-phase separation technology without most of its associated problems.[58] In addition, moderately polar compounds can be separated by adding organic modifiers, such as methanol, isopropanol, and acetonitrile.[59] On the other hand, even if it is still on a manageable level, the use of this technology has steadily increased over the last few years.[60] This trend is a clear indication of recent technical advances and the general benefits of this separation technique. Other natural compounds than lipids, such as polyphenols[61], biogenic amines[62] and polyacetylenes[63] investigated as well in food from vegetable origin. In addition, several lipid classes have been simultaneously analyzed in a complex vegetable extract[64] and bilberry[65] by using super critical technology.

CONCLUSION: SC-CO_2 Extraction technology is emerging as high valued ,green and efficient extraction technology finding wider application as food ingredient industry is catching up with its materials engineering and pharmaceutical counterparts and expanding beyond extraction. SC- CO_2 offers solutions for problems such as product purity, process efficiency, health, and environmental impact that traditional technologies fail or are unable to solve. Last few decades has therefore seen a substantial expansion in research and development. The newer areas like membrane processing, nano based improved nutraceutical delivery system and considerable reduction in use of organic solvents is pushing for cutting edge research in SC-CO_2 technology. Morover the SC-CO_2 extraction technology should not be viewed as a replacement to any existing technique or a technique with some unmatched application rather, it should be viewed as a complementary technique which can significantly widen the ambit of the products both sourced from plants and animals to be extracted by this technology.

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