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Supercritical CO_2 Extraction: Fundamentals, Industrial Relevance, and Future Perspectives

Running title: Supercritical CO_2 extraction

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ABSTRACT

Supercritical carbon dioxide extraction is an advanced separation technique that is increasingly applied in various industries due to its environmental friendliness, selectivity and efficiency. This method enables the extraction of bioactive compounds without the use of toxic chemicals and at lower temperatures compared to classical extraction techniques. This review paper outlines the fundamental principles of supercritical extraction, including the physicochemical properties of supercritical CO2, its advantages over conventional methods, and key process parameters such as pressure, temperature, flow rate, extraction time, and modifiers. Special attention is paid to the industrial applications of this technique, particularly in the pharmaceutical, food, and cosmetic industries, where it is utilised to extract essential oils, antioxidants, polyphenols, lipids, and other valuable components. Moreover, environmental aspects of supercritical extraction were discussed, with an emphasis on sustainability and the potential for minimizing the environmental impact. Through the analysis of current research and technological innovations, this paper provides insight into the perspectives of further development and optimization of supercritical extraction using CO_2, as well as its possible application in new industrial areas.

Keywords: *supercritical extraction, carbon dioxide, sustainable technology, separation, bioactive compounds, industrial application*

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Introduction

The application of supercritical extraction for obtaining natural products has advanced significantly in recent years. Many studies focus on developing such processes (Reverchon et al., 2006). Supercritical fluids (SCF) are of great interest owing to their unique properties that blend characteristics of gases and liquids, making them ideal for extraction. Supercritical fluid extraction (SFE) involves a mass transfer process conducted under pressure and temperature conditions above the solvent's critical point. The concept of a biorefinery emerged from the need to replace non-renewable energy sources in the production of fuels and chemicals. In a biorefinery, various chemical products are derived from renewable resources using separation, isolation, and chemical or biochemical transformation methods (Attard et al., 2016). The ability to implement supercritical extraction at different stages of a biorefinery is particularly valuable due to the advantageous properties of this method (Temelli et al., 2009). From a green chemistry perspective, extraction processes should ideally use natural solvents such as water, ethanol, and carbon dioxide. Supercritical carbon dioxide is a popular extraction solvent, generally recognized as safe (GRAS), which means it is a non-polluting chemical capable of producing highly pure products, aligning with green chemistry principles (Yıldırım et al., 2024). However, one of the key challenges in process optimization is removing the solvent from the solute to achieve the highest purity of the final product, and in many cases, supercritical extraction is the best option.

Biorefineries contribute to sustainability by reducing harmful gas emissions and preserving natural resources through the use of renewable feedstocks and waste recycling. Economically, they can create new industries, jobs, and markets, reducing dependence on fossil fuel imports and promoting local production. By integrating supercritical extraction, biorefineries can enhance efficiency and environmental benefits, reinforcing their role as a sustainable alternative in fuel and chemical production (Mantell et al., 2013).

The primary raw materials used in biorefineries and the potential applications of SFE technology are outlined below:

- **Sugar/Starch-rich Crops**: These are the most common raw materials in current biorefineries. They contain large amounts of sucrose, which can be easily extracted and fermented to produce ethanol or bio-based chemicals. Sugarcane is the most preferred feedstock due to its economic and environmental benefits, as it's easier to produce. In this case, water is typically used as the solvent to extract the solutes, and supercritical fluid extraction is not necessary at this stage. However, there are several studies that explore the use of supercritical fluid extraction with a counter current column to separate ethanol from aqueous solutions (Di Giacomo et al., 1991; Pereyra et al., 1995; Ruiz-Rodriguez et al., 2010)
- **Vegetable Oil**: This raw material is mainly used to produce biodiesel through the transesterification process. The oil can come from natural sources such as palm, soybean, rapeseed, and sunflower seeds, or as a waste product like used cooking oil or animal fat.

Producing biodiesel from vegetable oils faces challenges related to land use, sustainability, and the high cost of refining impure waste oils (Anagha et al.,2025; Chabni et al., 2025; Mantell et al., 2013; Mouahid et al., 2024; Sahena et al., 2009).

- **Lignocellulosic Biomass**: This type of biomass comes from non-edible plant material, mainly composed of cellulose, hemicellulose, and lignin. It is considered a promising second-generation feedstock for the future production of biofuels and bio-based chemicals using various conversion technologies. Many studies focus on using supercritical fluid extraction to separate secondary metabolites from agricultural waste and lignocellulosic materials (Barbini et al., 2021; Da Costa Lopes, 2016; Mantell et al., 2013).
- **Microalgae**: This group consists of a wide variety of single-celled organisms that can be photoautotrophic or heterotrophic. Microalgae can produce a range of valuable compounds. These include carotenoids, polyunsaturated fatty acids, and antioxidants, which are useful in the food industry, as well as various lipids that can be used to produce biodiesel through transesterification. Additionally, the remaining carbohydrates in microalgae can be fermented to produce bioethanol. To maximize the efficiency of bioactive compound recovery, supercritical fluid extraction is being explored as an advanced method for their separation (Grierson et al., 2012; López-Limón et al., 2025; Mantell et al., 2013; Singh et al., 2021).

One of the most important applications of supercritical extraction is the extraction of bioactive substances from plant materials (Ivakhnov et al., 2024; Mohammadi et al., 2024). Supercritical CO_2, as a solvent, enables the efficient extraction of lipophilic compounds, which makes it particularly suitable for the following substances:

1. **Essential oils**: Supercritical CO_2 is commonly employed for extracting essential oils from plants such as lavender, rosemary, eucalyptus, lemon, and many others. These oils are often sought after for their aromatic, fragrant, and therapeutic properties (Kessler et al., 2024).
2. **Flavonoids and phenolic compounds**: These bioactive compounds are present in many plants and are known for their antioxidant, anti-inflammatory, and other health benefits (Díaz-Reinoso et al., 2006). Flavonoids from plants such as onions, citrus fruits, and tea can be effectively extracted with supercritical CO_2 (Christaki et al., 2024; Talmaciu et al., 2015).
3. **Alkaloids**: Alkaloids, such as caffeine from coffee, theobromine from cocoa, and nicotine from tobacco, can also be extracted using supercritical CO_2. These compounds are of interest due to their stimulating effects and pharmacological properties (Saldaña et al., 1999).
4. **Carboxylic acids**: Supercritical CO_2 is used for the extraction of fatty acids, such as omega-3 fatty acids from plant sources (e.g., flaxseed and hemp) and essential fatty acids from plant oils (e.g., olive oil) (Kumar et al., 2024; Min et al., 2010).

5. **Carotenoids**: These plant pigments, such as beta-carotene, lutein, and zeaxanthin, play a key role in defending against oxidative stress and being vital for human health (Sabio et al., 2003). Supercritical CO_2 is an efficient solvent for carotenoids from plant materials such as carrots, papayas, and spinach.
6. **Terpenes**: Terpenes, which are often responsible for the scent and aroma of many plants, such as limonene from lemon peel or pinene from pine, can also be extracted with supercritical CO_2. Terpenes are widely used in the perfume, food, and beverage industries (Bañares et al., 2024).
7. **Steroidal saponins**: Plants containing saponins (such as ginseng or licorice root) can be used for the extraction of these bioactive compounds, which have potential health benefits.
8. **Vitamin E (tocopherol)**: Vitamin E, which is found in plant oils like wheat germ oil, can also be extracted using supercritical CO_2 (Shi et al., 2024; Shi et al., 2025).

Market and Industrial Applications

Supercritical fluid extraction can be applied on large industrial scales (tons of raw materials). It has several important industrial applications, particularly in the extraction, purification, and fractionation of edible oils, fats, and waxes. The goal of this process is to separate specific compounds from natural solid materials, such as seeds, fruits, and citrus peels. "Refining" refers to the removal of certain substances, such as carotenoids, phospholipids, and free fatty acids, that can promote oxidation and cause rancidity in oils. Fractionation, on the other hand, allows the selective separation of short-chain triglycerides, unsaturated vegetable and animal oils, and valuable compounds from natural sources, such as vitamins, flavors, and polyunsaturated fatty acids.

One of the earliest applications of supercritical fluid extraction was the extraction of alkaloids from plant materials, including processes like decaffeinating coffee and tea. To preserve aroma and flavor, caffeine extraction is typically performed on green coffee beans before roasting and grinding. Today, supercritical CO_2 decaffeination accounts for 20% of the global coffee production.

The growing trend in SFE process is propelled by the growing consumer demand for natural and health-promoting food additives. Consumers are increasingly seeking products derived from natural sources, as the market shifts toward eco-friendly extraction methods. Supercritical fluid extraction has made significant industrial progress in this area, particularly for obtaining food additives such as colorants, flavors, and antioxidants from natural products (Fersi et al., 2024). The use of agricultural by-products for these extractions adds value and reduces waste. Additionally, numerous studies have investigated the health benefits of natural compounds, including anticancer, antimutagenic, and anticonvulsant properties, which further enhance the appeal of these products.

The growing preference for natural products with clean labels in the market has significantly increased the adoption of SFE in the food and cosmetics industries. As consumers become increasingly aware of the health and environmental risks associated with synthetic chemicals, natural alternatives derived from SFE are becoming the preferred choice. For example, in the cosmetics industry, the demand for organic skin care products has created opportunities for SFE to extract pure active ingredients, such as essential oils, antioxidants, and vitamins, that meet the growing consumer preference for non-toxic and environmentally friendly formulas. Additionally, SFE is expected to play a crucial role in the biofuel production sector as industries seek more sustainable alternatives to fossil fuels (Sato et al., 2022). As the focus intensifies on lowering greenhouse gas emissions, supercritical CO_2 offers a promising solution for extracting valuable biofuels and bio-based chemicals with minimal environmental impact.

CO_2 as a Supercritical Fluid

Supercritical fluid is any substance that exists in a state above its critical temperature (T_c) and critical pressure (P_c). A typical temperature-pressure diagram for a pure substance can be used to visualize this, which divides the diagram into three distinct regions corresponding to the solid, liquid, and gas phases. Two other key points are visible in the diagram shown in Figure 1: the triple point, where all three phases (solid, liquid, and gas) coexist, and the critical point, which marks the end of the liquid-gas transition. The critical point is defined by critical temperature and critical pressure, beyond which distinct liquid and gas phases no longer exist, and a supercritical fluid phase emerges.

When either pressure or temperature (or both) changes, it also alters the density of the supercritical fluid. This is significant because the solvent power of a substance depends largely on its density. Solvation occurs when intermolecular forces in the solvent cause molecules to surround and interact with the solute molecules. These forces are influenced by the solvent's density, meaning the solvating ability of supercritical fluids can vary widely, ranging from gas-like to liquid-like densities, depending on the conditions.

The density of an SCF can be controlled to modify its solubility power, allowing for selective extraction or fractionation of multiple solutes. The most efficient conditions for these processes are found near the critical point, where even slight changes in pressure or temperature can result in significant variations in density and, therefore, solvent power.

In addition to these density and solvent power characteristics, SCF exhibit other beneficial properties, particularly in terms of mass transfer. While the solvent power of an SCF is similar to that of a liquid, its viscosity and diffusivity resemble that of gases. This means SCF combine the dissolving ability of liquids with the rapid movement and transfer properties of gases, enhancing transfer characteristics compared to traditional liquid solvents.

Given these unique properties, SCF provide significant advantages over conventional solvents. Separations using SCF tend to be much more efficient, and the process is simple by adjusting the pressure, the supercritical fluid can be easily transformed into a gas, allowing for easy separation of the products.

Carbon dioxide is the most widely used supercritical solvent due to its low critical temperature (31.1 °C) and pressure (73.8 bar), which are easy to achieve (Mantell et al., 2013). Carbon dioxide is also fully miscible with low-molecular-weight hydrocarbons and oxygenated organic compounds, making it an effective solvent for many organic materials. Additionally, it has low mutual solubility with water, which makes it a good choice for selective extractions where water needs to be excluded.

Carbon dioxide offers several benefits as a supercritical solvent. It is non-toxic, non-flammable, non-corrosive, and environmentally friendly. Additionally, it is inexpensive, abundant, and can be obtained in various purity levels. Carbon dioxide also has advantageous transport properties, such as low viscosity, high diffusion coefficients, and suitable heat conductivity and heat of vaporization, particularly near the critical point. These properties make it energy-efficient for many processes. Moreover, after the extraction process is complete and the pressure is reduced, carbon dioxide transitions to a gas under normal environmental conditions. It can then be compressed and recycled for repeated use, ensuring no residue remains in the extracted product and minimizing environmental impact.

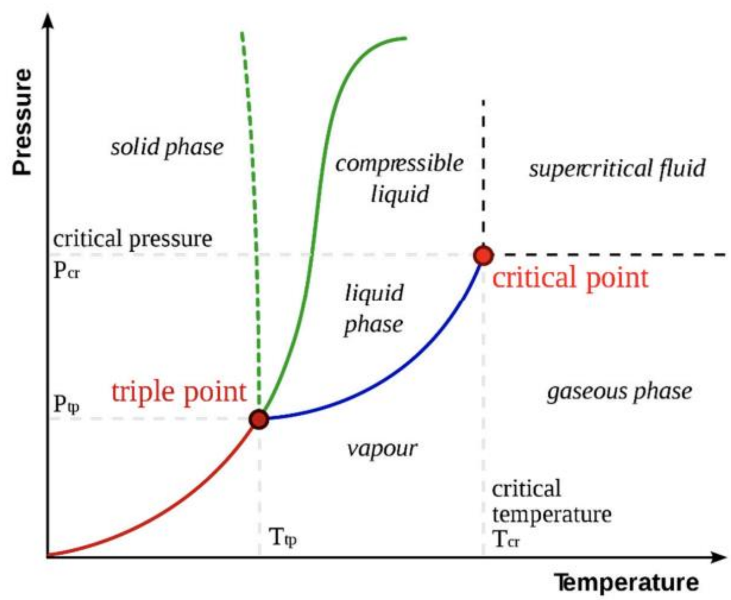

Figure 1. Phase diagram (Image taken from the Yıldırım et al., 2024, according to CC BY licence).

The technological scheme of the plant for extraction using supercritical CO_2 (SC-CO_2) is shown in Figure 2., illustrating all parts of the facility and the complete extraction process.

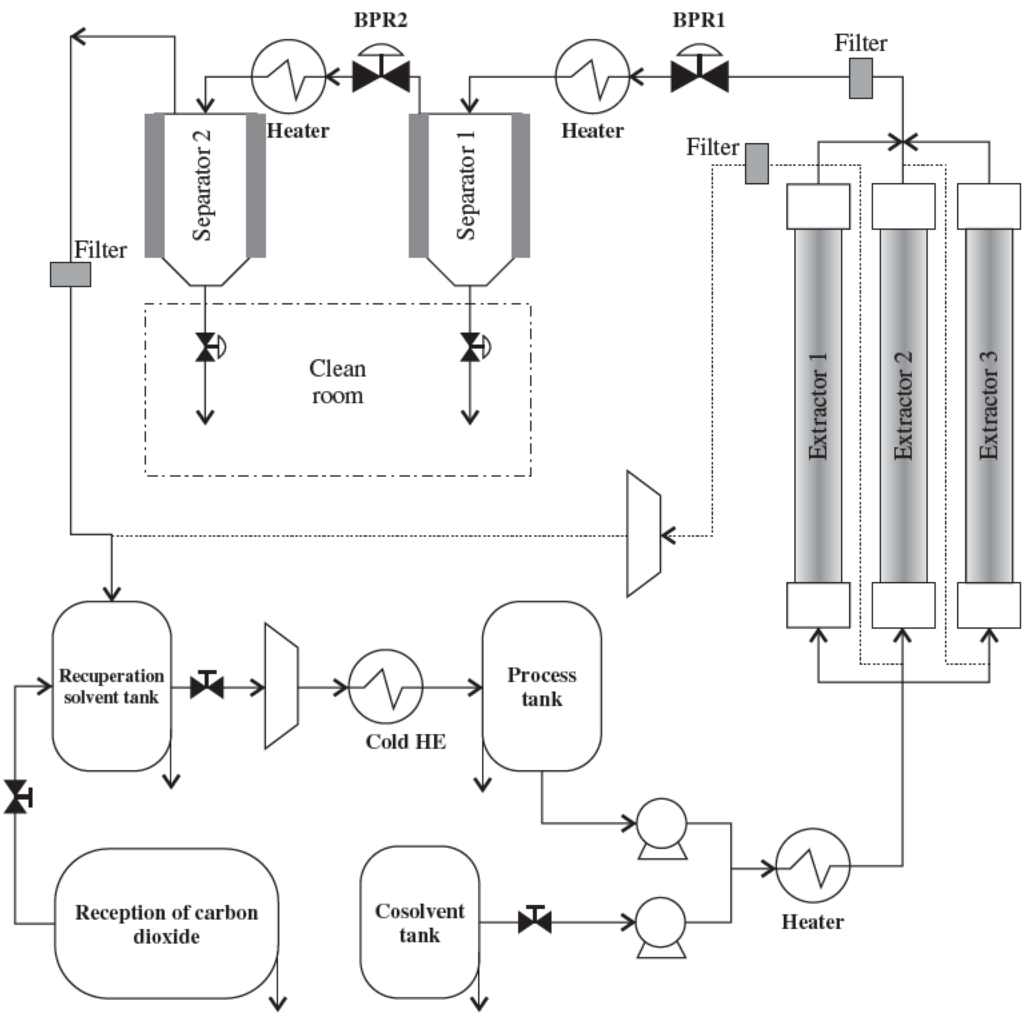

Figure 2. Schematic diagram of SC-CO_2 system (Image taken from the Mantell et al., 2013 with the permission of Copyright Clearance Center).

Supercritical CO_2 extraction systems typically operate in a discontinuous mode for the solid phase and a continuous mode for the supercritical fluid. To enhance process efficiency, three extractors are often used in parallel: one undergoes extraction, the second is in the loading and pressurization stage, while the third is in depressurization and unloading. Fractionation of extracts is achieved through progressive depressurization across a series of cascade separators. By adjusting pressure and temperature conditions, the solvent density and solubility are gradually reduced, leading to the sequential precipitation of compounds according to their solubility: less soluble substances precipitate first, while more soluble components remain in solution until reaching subsequent separators. A critical economic aspect of the process is solvent recovery and recycling, typically performed using two tanks. One operates at low pressure to collect the separated solvent, while the other maintains higher pressure conditions to replenish and prepare the CO_2 for reintegration into the extraction cycle.

Comparing the Advantages and Disadvantages of Supercritical Fluid Extraction with Other Methods

Supercritical fluid extraction and hydrodistillation are two different techniques for extracting bioactive compounds from plants, but they differ in their application, equipment, and the types of substances that can be effectively extracted. During the hydrodistillation, plants are exposed to steam, which helps release essential oils or other volatile substances. The steam passing through the plant material carries with it the volatile components, which are then condensed and collected. Hydrodistillation is simple and inexpensive technology, which does not require high temperatures or complex equipment. It is good choice for easily evaporating components, such as essential oils and can be classified as natural process, as it only uses steam and minimal handling of plant material. It is most applied in the production of essential oils, perfumes, and for obtaining floral waters (hydrosols). It is also used for extracting flavors and fragrances in the food industry.

SFE is especially effective for extracting lipophilic (fat and oil) and thermolabile components, such as essential oils, flavonoids, terpenes, and sterols. It can also be used to extract other bioactive molecules such as alkaloids. Supercritical extraction is used in industries that require high efficiency and selectivity, such as the production of essential oils, dietary supplements, cosmetics, pharmaceuticals, and bioenergy materials (Cassel et al., 2000).

Microwave-assisted extraction (MAE) and SFE while share the common goal of efficient extraction of compounds, they rely on different principles and technologies. Microwave-assisted extraction uses microwave radiation to plant material causing them to vibrate and rapidly generate heat, which increases the rate of extraction. Microwaves are sometimes used in combination with solvents (such as water, ethanol, or acetone) to enhance the extraction efficiency. Microwave-assisted extraction can be used for a wide range of bioactive substances, including phenols, flavonoids, alkaloids, terpenoids, proteins, enzymes, and other water-soluble and organic-soluble compounds. Microwave-assisted extraction is fast and energy-efficient method, as microwaves enable rapid heating and temperature rise of plant material as well as lower solvent consumption compared to traditional extraction methods, reducing environmental impact. Additional benefits are: quicker heating for bioactive compounds extraction, reduced use of solvents, low risks and short extraction time (3-30 min). Microwave-assisted extraction is commonly used in laboratory research, as well as in industries for extracting bioactive substances from plants, such as polyphenols, alkaloids, and flavonoids. It is also used in the production of food, beverages, and pharmaceuticals.

Advantages of SFE

SFE enables high efficiency in extraction, especially for thermolabile substances, as it does not use high temperatures. It is more environmentally friendly compared to traditional solvents, as it uses CO_2, which is non-toxic and easily removed after extraction. Moreover, it provides greater selectivity for certain components, as parameters (temperature and pressure) can be adjusted to optimize extraction.

Supercritical extraction is known for its high selectivity for certain components because parameters (temperature and pressure) can be fine-tuned to enhance extraction efficiency. Moreover, it provides high efficiency in extracting thermolabile substances without the need for high temperatures. It is more environmentally friendly method, as it uses CO_2, which is non-toxic and easily removed from the extract. Additional benefits are: moderate extraction time (10-60 min), possibility to on-line coupling with chromatographic process, reduced use of organic solvents, small amount of sample (1-5 g) and better separation of solute from solvent.

Disadvantages of SFE

SFE usually requires high initial capital and equipment complexity, as it requires specialized systems to achieve supercritical conditions (high pressure and temperature). For this reason, it can be more expensive than other methods, such as hydrodistillation.

Supercritical extraction demands high initial capital and equipment complexity, as it requires specialized systems to achieve supercritical conditions. This process may be economically challenging for small- and medium-scale applications and has limited ability to dissolve polar compounds.

Disadvantages of hydrodistillation and MAE

Hydrodistillation has limited efficiency in extracting components that are not easily volatile and may lead to loss of some thermolabile or non-volatile components due to high temperatures. Additionally, large water consumption can be impractical in large-scale industrial processes.

Microwave-assisted extraction has limited application for certain substances that do not respond well to microwaves. Due to rapid and uneven heating, potential degradation of some thermolabile components can be occurred. Additionally, careful monitoring of parameters (microwave power, heating time, solvent type) is necessary because the system is more sensitive to process conditions. It requires additional steps such as filtration and has poor efficiency when either the target compounds or solvents are non-polar or volatile. It should be kept in mind that the solvent must absorb microwave energy.

Table 1. summarizes and compares the investment costs for MAE and SFE procedures.

Table 1. Comparative investment costs of MAE and SFE procedures (Data adapted from Talmaciu et al., 2015).

Extraction technique	MAE[1]	SFE[2]
Capital cost	medium	high
Operating cost	medium	low
Total value ($/kg extract)	120-150	150-200

[1]microwave-assisted extraction; [2] supercritical fluid extraction

Supercritical Fluid Extraction Efficiency Using Cosolvent

A cosolvent, or entrainer, is an organic compound that has a volatility between that of the SCF solvent and the solute being extracted. It is typically added in very small amounts (1 to 5 mol%) to the SCF solvent to alter its properties, such as polarity and specific interactions, without substantially altering the density and compressibility of the original SCF solvent.

The SCF solvent mixed with a cosolvent becomes supercritical when its pressure exceeds the mixture's critical pressure and its temperature is higher than the mixture's critical temperature, which are usually close to the critical values of the pure SCF solvent. In Figure 3.a, the mixture's critical pressure is shown as the highest pressure on an isothermal P–x diagram of the binary mixture, beyond which there is no two-phase region for a given temperature. The mixed SCF solvent remains supercritical at all pressures above its mixture's critical pressure, indicated by the shaded area. If the pressure is below the critical pressure, such as at point A, the system is in a gaseous state, since it lies outside the two-phase region. However, as seen in Figure 3.b, the two-phase vapor-liquid region can extend past the mixture's critical temperature for a specific pressure. This means that a mixture is not necessarily supercritical at temperatures above its mixture's critical temperature. The critical point (CP) marks the distinction between the gas phase and the liquid phase.

When a binary mixture of an SCF solvent and a cosolvent is used above the critical pressure of the binary mixture to dissolve a liquid solute, the system is represented by a ternary diagram (Figure 3.c). In these situations, all three components are typically distributed between both the liquid and SCF phases. The extent to which each component is dissolved in the two phases is described by the distribution coefficient, as shown by the two endpoints of a tie line.

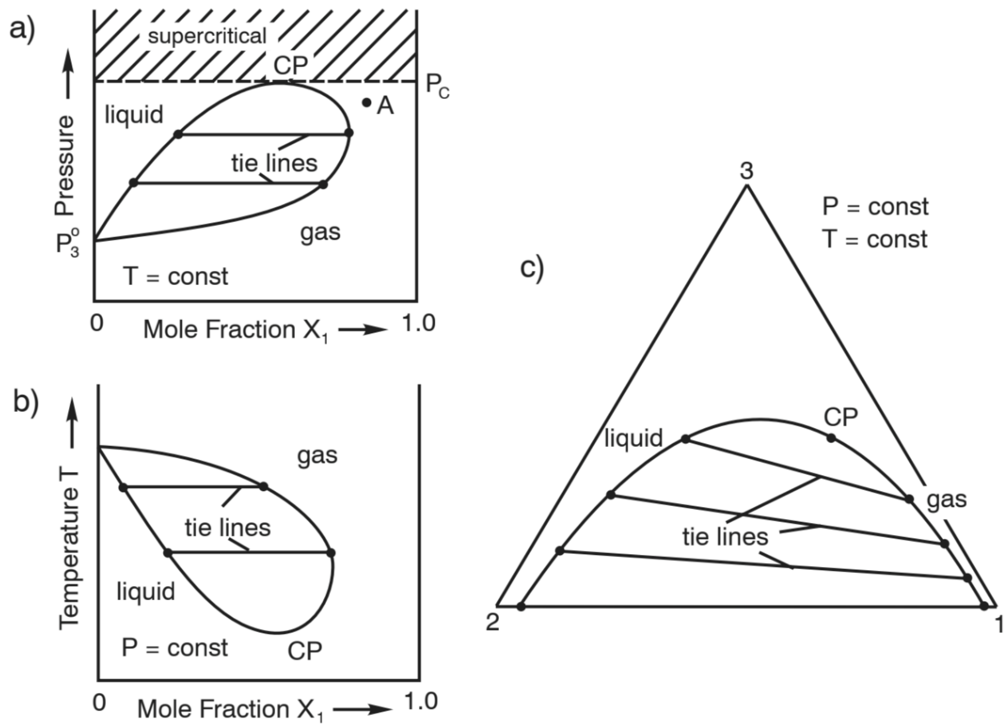

Figure 3. Critical points in a), b) binary and c) ternary mixtures (Image taken from the Mukhopadhyay, 2000).

A comparison of the physical properties of gases, liquids, and supercritical fluids is shown in Table 2. Supercritical fluids (SF) have densities similar to those of liquids, while their viscosity and diffusivity resemble those of gases. As the density increases, their ability to dissolve substances also improves, allowing them to dissolve more compounds than gases. Thanks to higher diffusivity and lower viscosity, SFs can easily penetrate the pores of solid structures, further enhancing their dissolving power. Their physical properties can vary significantly depending on temperature and pressure, as shown in Table 2., which presents the physical constants of the gas, liquid, and supercritical fluid phases under different conditions (P and T).

Table 2. A list of physical constants for gases, liquids, and supercritical fluids (Data adapted from Yildirim et al., 2024).

Solvent	Density g/cm^3	Viscosity $g/(cm \cdot s)$	Diffusion cm^2/s	Surface tension N/m
Gas[1]	$6 \cdot 10^{-4}$-$2x10^{-3}$	$1 \cdot 10^{-5}$-$3 \cdot 10^{-5}$	0.1-0.4	0
Liquid[1]	0.6-1.6	$2 \cdot 10^{-4}$-$3 \cdot 10^{-3}$	$2 \cdot 10^{-6}$-$2 \cdot 10^{-5}$	3-$6 \cdot 10^{-2}$
SF[2]	0.2-0.5	$1 \cdot 10^{-4}$-$3 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	0
SF[3]	0.4-0.9	$3 \cdot 10^{-5}$-$9 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	0

[1]*P=1 bar, T=298 K;* [2]*P=Pc, T=Tc;* [3]*P=4Pc, T=Tc*

The addition of cosolvents, typically polar solvents like ethanol, methanol, acetone, or water, can:

1. **Increase the solubility of polar substances**: CO_2 is a nonpolar gas, so it struggles to dissolve polar substances. Adding cosolvents enhances the solubility of polar molecules, allowing their extraction under supercritical conditions.
2. **Improve extraction selectivity**: Cosolvents can modify the solubility of specific components, enabling selective extraction of certain substances. For example, a combination of CO_2 and ethanol can effectively extract bioactive compounds from plant sources, such as flavonoids, alkaloids, and essential oils.
3. **Lower extraction temperature**: The addition of cosolvents can reduce the temperature and pressure required for extraction, which is beneficial for protecting heat-sensitive substances like certain vitamins and antioxidants.
4. **Expand application range**: Using cosolvents broadens the scope of supercritical CO_2 extraction, allowing the extraction of bioactive compounds from food, medicinal plants, polymers, and other materials that are otherwise difficult to dissolve in pure CO_2.

In conclusion, cosolvents can enhance the capabilities of supercritical CO_2 extraction by enabling more efficient and selective removal of a wide range of substances, including those that are traditionally hard to dissolve in pure CO_2.

Parameters of CO_2 Supercritical Fluid Extraction

Several factors influence the efficiency of SFE, including temperature, pressure, flow rate, and the use of modifiers. Additionally, aspects such as sample grinding, size, and drying agents also play a role. While other factors may be important, they are less commonly discussed in research. Here's a breakdown of these key parameters:

Temperature

Temperature impacts the extraction efficiency by altering the solubility of the solute. As the temperature increases, the vapor pressure of the solute rises, enhancing solubility, but the solvent concentration decreases, which can reduce the overall extraction efficiency. The effect of temperature on yield can vary depending on the plant's characteristics. For example, a study on rice bran oil found the highest yield at 40 °C, while a different study on lycopene extraction from tomatoes showed increased yields with higher temperatures (Yıldırım, et al., 2024).

Pressure

Pressure is one of the most crucial factors in SFE. When pressure increases, so does the solvent density and its solvation power, improving extraction efficiency. High pressure enhances the density of supercritical CO_2, reducing resistance to mass transfer, which helps isolate both polar and non-polar compounds. However, high pressure can affect the stability of some compounds and raise operational costs, so it must be carefully controlled.

Flow Rate

Flow rate, which refers to the amount of CO_2 passing through the plant material over a set period, greatly influences extraction efficiency. A higher flow rate speeds up the process but may lead to incomplete dissolution or transport of components. Lower flow rates allow for longer interaction times between the supercritical fluid and plant material, enhancing extraction, but also extending the process and increasing costs. The ideal flow rate strikes a balance between efficiency, energy consumption, and equipment performance.

Modifiers

Carbon dioxide is not very effective at extracting polar compounds, so modifiers like water, ethanol, or methanol are often added to enhance the extraction of these compounds. These modifiers change the behavior of supercritical CO_2, but they also come with challenges. They can affect critical temperature and pressure of carbon dioxide, which may compromise its beneficial properties, like low viscosity and high dispersibility. Additionally, separating modifiers from CO_2 after extraction can be difficult and costly, often requiring more energy and additional processes, which can reduce the environmental sustainability of the extraction.

Grinding Time and Particle Size

The size and texture of the plant material can significantly influence extraction results. Smaller particles provide more surface area for the supercritical fluid to interact with, reducing mass transfer resistance and increasing extraction efficiency. However, excessive grinding can raise the temperature of the plant material, potentially causing the loss of volatile compounds, which negatively affects extraction efficiency.

Preparation of Plant Material for SC-CO_2

The timing of plant collection plays a crucial role in determining the composition of the extract that will be obtained. Factors such as the season, time of day, specific location, and whether it’s a rainy or dry day can all influence the chemical makeup of the plant. Plants for extraction can either be harvested from the wild or bought from suppliers and herbalists. Once collected, the specific part of the plant to be extracted (such as flowers, fruits, stems, roots, bark, seeds, etc.) is carefully separated from the rest of the plant material. The plant is then dried, either naturally or by using heat in drying systems resembling ovens. Procedures like grinding and drying can greatly impact the phytochemical content of the plant. To prevent enzymes from misfunctioning and to stop the plant’s metabolism, it’s essential to remove the water from the plant material. The drying temperature must be carefully regulated to prevent promoting microorganism growth while maintaining the plant's chemical integrity. Drying can be done under either natural or controlled (artificial) conditions. Natural drying typically involves leaving the plant material in an open or semi-open environment, avoiding direct sunlight. In artificial conditions, drying can be managed by adjusting temperature and pressure. It's crucial to carefully choose the drying temperature to maintain volatile components and avoid degradation of important compounds. Methods such as freeze-drying, vacuum chambers, ovens, tunnel dryers, and shaft dryers are commonly used in laboratories for drying purposes.

Before performing supercritical fluid extraction, the moisture content of the plant should be under 10%, and the material should be ground into very fine particles. Using techniques that preserve the plant's volatile components and phytochemical content while reducing moisture and particle size is key. As moisture increases, the extraction yield tends to decrease. Furthermore, smaller particle sizes allow the supercritical fluid to interact more effectively with the plant material, leading to a higher yield of extraction. Once the grinding process is completed, the plant material is passed through sieves with specific pore sizes, and if necessary, the particle size of the remaining material can be calculated. After completing all these steps, the plant material should be stored in dark bottles to prevent exposure to light and placed in a deep freezer (between −4 and −20 °C) until the extraction process begins.

Extraction examples utilizing SC-CO_2

Supercritical fluid extraction is an extremely efficient technique for isolating essential oils and other bioactive compounds from plants. Yields and parameters for supercritical extraction can vary depending on the plant, but the main parameters to consider include temperature, pressure, solvent type (most commonly CO_2), as well as extraction time.

Here is an overview of possible yields and parameters for supercritical extraction of essential oils from plants such as lemon, lavender, orange, chamomile, and rosemary:

Citrus peels (*Citrus limon, Citrus reticulata* and *Citrus sinensis*)

Rich in bioactive compounds, citrus peels represent a valuable economic resource with potential applications in the food, cosmetic, and pharmaceutical industries. In the study by Romano et al., the peels of orange (*Citrus sinensis*), tangerine (*Citrus reticulata*), and lemon (*Citrus limon*) were subjected to CO_2 extraction to obtain bioactive compounds (Romano et al., 2022). Carbon dioxide was applied under both liquid and supercritical (SC) conditions at various temperatures and pressures, and the results were compared with ethanol extraction, which served as a control. The study also investigated the use of ethanol as a co-solvent at low concentrations (up to 20%) during the CO_2 extraction process.

Supercritical extraction at 20 MPa with 20% ethanol as a co-solvent (SC-20-20) produced lower yields (14.56%, 13.01%, and 24.32% for orange, tangerine, and lemon peels, respectively) compared to liquid CO_2 extraction (L-20), despite both being conducted at the same pressure (20

MPa) and with the same ethanol concentration (20%). However, SC-20-20 was performed at a higher temperature (60 °C) than L-20. At 20 MPa, the higher temperature reduces the density of the solvent, which decreases the solubility of the solutes and consequently lowers the extraction yield.

Temperature has two opposing effects on solute solubility: on one hand, it increases the vapor pressure of the solutes, enhancing their solubility in the fluid phase and improving the extraction yield. On the other hand, it decreases the solvent density, reducing its solvating power. At pressures near the critical point, the effect of temperature on solvent density tends to dominate over its effect on solute vapor pressure, often leading to lower yields.

The yields obtained from SC-20-20 were also lower than those from SC-30-20, as the higher pressure of 30 MPa at 60 °C increased the density and solvent power of CO_2, enhancing ethanol penetration into the matrix and improving the extraction yield. However, it is important to note that excessive pressure can reduce extraction efficiency. A similar trend was observed with SC-20-10, which resulted in a lower yield (7.51%) than both L-10 and SC-30-10 in the case of lemon peels.

Lavender (*Lavandula angustifolia*)

Lavender essential oil is extensively utilized in the cosmetic, pharmaceutical, and food industries for its well-established aromatic, antimicrobial, and anti-inflammatory properties. In the study by Cruz-Sánchez, the authors optimized the extraction process based on yield by evaluating the effects of pressure, temperature, and the addition of a co-solvent (Cruz-Sanchez et al., 2024). The performance of lavender essential oil extraction was performed at pressures ranging from 180 to 300 bar and temperatures of 40 °C and 60 °C, with and without co-solvent. The results show that the extraction yield increases with higher temperatures at constant pressure. Specifically, the process is more efficient at 60 °C compared to 40 °C. As discussed in previous sections, this improvement is attributed to the higher vapor pressure of solutes at elevated temperatures. The maximum oil solubility and extraction yield were achieved at 250 bar and 60 °C. Moreover, the addition of ethanol as a co-solvent (0.2% v/v) resulted in a significant increase in extraction yield.

Chamomile (*Matricaria chamomilla*)

Supercritical CO_2 extracts of chamomile are extensively applied in the cosmetic, pharmaceutical, and food industries because of their high content of bioactive compounds like matricine, bisabolol, and flavonoids. Kotnik et al. conducted SFE experiments using CO_2 in a semi-continuous flow system (Kotnik et al., 2007). The system was specifically designed to operate at pressures reaching up to 500 bar and temperatures up to 100 °C. Approximately 15 grams of finely ground material were placed into the extractor (volume: 60 cm^3). The water bath temperature was carefully controlled and maintained within ±0.5 °C. The system was first purged with nitrogen, followed by the introduction of the extraction gas. CO_2 was then continuously pumped at high pressure (450 bar) through a preheating coil and across the sample bed in the extractor. The extracted product was collected in a glass trap, where separation took place at 1 bar and 0° C. The collected extract was weighed (±0.1 mg), and the extraction yield was calculated. In a two-step separation process, the first separator was a high-pressure vessel capable of operating at 120 bar and 100 °C, while the second separator was a glass trap at atmospheric pressure and 0 °C. The extracts were immediately analyzed after collection.

The chamomile flower heads were extracted with CO_2 at pressures 100, 150 and 250 bar and temperatures 30 and 40 °C followed by one step separation. According to extraction yield the best extraction conditions were 250 bar and 40 °C where the yield was 3.81%. Extraction yield increased with increasing solvent density and at constant solvent density the extraction yield was increased with higher temperature. According to the content of active compounds in extracts, the best extraction conditions using one step separation were determined to be 250 bar, 30 ºC, where the content of matricine reached 9.81 mg/g.

Rosemary (*Rosmarinus officinalis*)

Supercritical carbon dioxide extraction is an efficient method for isolating natural antioxidants from rosemary, offering several advantages over traditional extraction techniques. By adjusting process parameters such as pressure and temperature, the selectivity of SC-CO_2 for specific components can be enhanced, enabling phase separation to obtain solvent-free extracts.
Some studies have incorporated modifiers like ethanol to increase antioxidant yields from rosemary, although higher concentrations of modifiers may reduce CO_2 selectivity. It is generally not recommended to use modifiers at high pressures (e.g., 50 MPa and above) as they can decrease antioxidant activity in the extracts.
Research of Ivanović et al. has demonstrated that antioxidant fractions can be effectively extracted from Lamiaceae herbs, including rosemary, sage, thyme, and oregano, using SC-CO_2 without modifiers at pressures ranging from 50–100 MPa and temperatures between 90–110 °C (Ivanović et al., 2009). Other studies have employed lower pressures (15–35 MPa) and temperatures (40–60 °C), either with or without small amounts of ethanol, to isolate antioxidants. Additionally, some researchers have combined traditional methods, such as distillation, with SC-CO_2 extraction to concentrate antioxidant fractions from rosemary. SC-CO_2 extraction of rosemary yields antioxidants with equal or stronger activity compared to synthetic alternatives. The resulting extracts are semi-solid at room temperature and can be further processed by grinding at low temperatures and dissolved in oils.
Table 3. collects yields of rosemary antioxidant fractions at different P and T from the study of Ivanović et al. (2009).

Table 3. Yields of rosemary and sage antioxidant fractions in the performed experiments (Data adapted from the Ivanović et al., 2009).

Herbaceous material	P MPa	t °C	W wt.%
Rosemary	30	40	1.10
		100	1.57

Conclusion

Supercritical extraction is an effective technique for extracting essential oils and other bioactive compounds from plants. Yields depend on the plant species, as well as specific extraction parameters, such as temperature, pressure, flow rate, and extraction time. Using CO_2 as a solvent enables the production of high-quality products without toxins or solvent residues, which is an advantage in the essential oil and bioactive compound industries.

SC-CO_2 is a selective and environmentally friendly separation technique that is increasingly applied in various industrial sectors. Its advantages, such as low toxicity, preservation of thermolabile compounds and the possibility of fine control of extraction conditions, make it superior to conventional extraction methods. It is particularly important in the food, pharmaceutical, and cosmetic industries, where it enables the obtaining of high-quality bioactive compounds without organic solvent residues.

Although supercritical extraction has already been well-examined and applied in many fields, further research is necessary to improve the process's efficiency, reduce costs, and expand its use in new industries. The development of new modifiers, optimization of operating parameters, and integration with other technologies could further expand its application.

Given the increasing demand for sustainable and environmentally friendly technological solutions, supercritical CO_2 extraction has the potential to become the dominant extraction method in the future. Further research and innovation in this area can enhance its economic profitability and contribute to the development of new green technologies in industry.

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Declarations of interest:

The authors declare that they have no conflict of interest.

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