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Supercritical Carbon dioxide: Adequately Sole Solvent

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Abstract

There is an enormous need to replace hazardous industrial solvents whose recycling is not economically viable. Supercritical carbon dioxide (sCO_2) could be a potential alternative for replacing some of these environmentally perilous solutions. sCO_2 can be considered as one possible way to essentially drive more green chemistry approaches to industrial solvent usage. This review article provides fundamentals of supercritical fluid (SCF) science particularly supercritical carbon dioxide (sCO_2). A concise review of the applications of supercritical carbon dioxide (sCO_2) is provided and factors affecting the extraction using supercritical carbon dioxide (sCO_2), special configurations and ultimately advantages and disadvantages for industrial applications are discussed.

1. Introduction

Sustainability and Renewability are mottos to this day and era. This includes focus within the scientific community inspiring the development of products to eliminate the use of hazardous substances [1]. The incessant need for effective and efficient drying and extraction technology which would be able to maintain the specific requirements of the products is imminent. The specific requirements include for example retaining high quality, physical structure and thermo sensitivity and leads to diverse R & D, especially in drying. These challenging needs have developed the supercritical fluid-assisted technology as an alternative to conventional drying or extraction technology which can sustain the above mentioned specific product requirements. Supercritical fluid-assisted drying uses the supercritical fluid as the drying medium instead of hot air or hot combustion gases at high temperatures. This technique has been developed in recent years [2–5].

Any component is considered to be in supercritical fluid state are at or above its critical conditions of temperature and pressure (T_c and P_c, respectively) [2,6] as shown in Figure . Supercritical fluids exhibit the unique properties which are densities and solubility are similar to liquids whereas compressibility and diffusivity are similar to that of the gases [2–4,6,7] as shown in Table 1. One of the key features for super critical fluids is that there is no requirement of liquid-gas phase change and no collapse of the solid structure during drying due to none existing surface tension effects [6,8].

Supercritical fluids are even termed as a compressed liquid, near-critical fluid, an expanded liquid, or a highly compressed gas [6]. Two supercritical fluids have gained particular importance which is water (H_2O) and carbon dioxide (CO_2). Water has a critical temperature of 373.85˚C and a critical pressure of 22.1 MPa due to its much high polarity. As a comparison, CO_2 has a critical temperature of 31.1˚C and a critical pressure of 7.4 MPa [6].

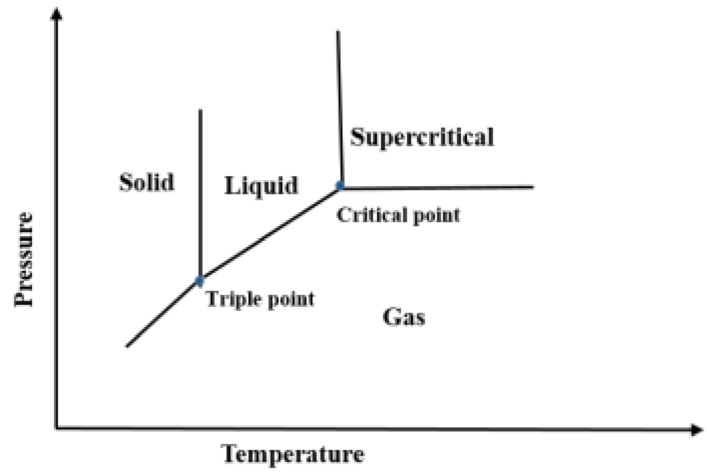

Figure 1 Supercritical state for a pure component.

Table 1 Characteristic values of gas, liquid, and supercritical state [2–4,6,7]

State of the fluid	Density (g/cm^3)	Diffusivity (cm^2/s)	Viscosity (g/cm/s)
Gas	(0.6–2.0) x 10^{-3}	0.1–0.4	(0.1–3.0) x 10^{-4}
Liquid	0.6–1.6	(0.2–2.0) x 10^{-5}	(0.2–0.3) x 10^{-2}
Supercritical fluid $P \geq P_c$; $T \geq T_c$	0.2-0.5	0.7 x 10^{-3}	(1–3) x 10^{-4}

CO_2 is more preferable to use as supercritical fluid because of its low critical values and it is inflammable, non-toxic, and low environmental impact [1,4,8]. It is miscible with different organic solvents and can be easily recovered. It is also a good drying medium as it diffuses faster than other liquids because of its smaller and linear molecule [6].

2. Physical and Chemical Properties of CO_2

CO_2 appears as colorless and odorless gas at atmospheric temperature and pressures. It is heavier than air and nontoxic and noncombustible. It is slightly acidic [9]. Physical Properties of CO_2 [6] can be referred from Table 2.

Table 2 Physical Properties of CO_2 [6,10–12]

Molecular Weight	44.01 g/mol
The density of gas at 21.1˚C and 1atm	1.833 kg/m^3
Critical temperature	31.1˚C
Critical pressure	7381.8 kPa
Critical density	468 kg/m^3
Latent heat of vaporization	276.8 kJ/kg
Latent heat of fusion	199 kJ/kg
Latent heat of sublimation	571 kJ/kg
Specific heat of the gas at 25˚C and 1 atm	
Cp at constant pressure	0.850 kJ/(kg) (˚C)
Cv at constant volume	0.657 kJ/(kg) (˚C)
Solubility in water, vol/vol at 20˚C	0.90
Viscosity at saturated liquid	0.000119 Pa.s

CO_2 can exist as solid, liquid, gas, or supercritical fluid depending upon temperature and pressure (Figure 2). CO_2 exists simultaneously as solid, liquid and gas at triple point (216.55 K; 5.18 bars) but at its critical point (304.25 K; 73.82 bars) CO_2 exists as liquid, gas and supercritical fluid, with density, enthalpy, and entropy equal to 467.9kg/m^3, 634.3 kJ/kg, and 3.552 kJ/(kg) respectively. CO_2 exists only as a supercritical fluid at temperatures and pressures greater than the values at the critical point [6]. sCO_2 has a very low viscosity which makes the mass transfer to face no resistance. The diffusion coefficient ranges from 0.1 to 3.3 x 10^{-4} cm^2/s. Thus, diffusion of solutes is better in supercritical fluids than in other liquids. In drying mechanisms, the diffusion rate is critical to simultaneous heat and mass transfer [6].

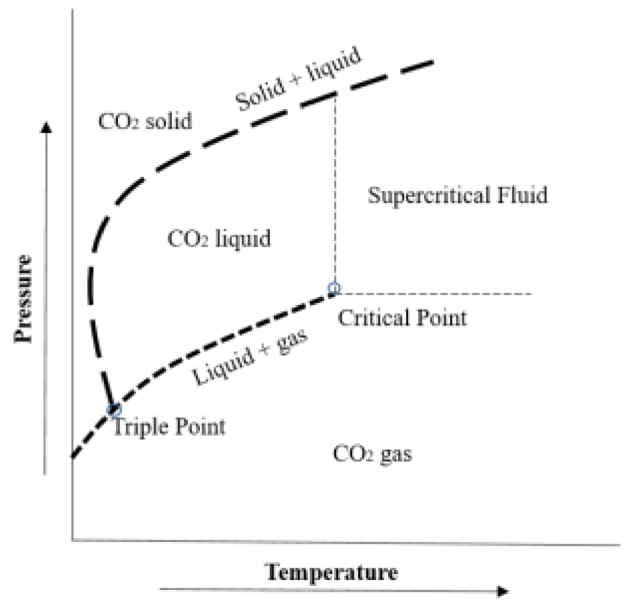

Figure 2 Phase diagram of carbon dioxide

3. Applications of Supercritical CO_2

There are a variety of supercritical processes which have been commercialized. Supercritical carbon dioxide has been used for drying or manufacturing of different types of aero gels such as carbon aero gels, silica gels, titania aero gels & agar gels at the industrial level [1,5,13–24]. At the laboratory scale, it has been found that sCO_2 can also be used for the dewatering of wood and coal which has the likelihood to scale up at commercial level [25,26]. Supercritical carbon dioxide can also be used for dewatering of municipal sewage sludge and it results in remarkable amount of water loss in a short span of time [27]. It has been reported that sCO_2 can also be used to remove micro pollutants or volatile organic compounds simultaneously along with the water removal [27]. Supercritical fluid extraction can be used for the extraction of desired or unwanted or harmful ingredients from various natural sources [28].

At the commercial level supercritical carbon dioxide has been used for decaffeination that is the extraction of caffeine from coffee and tea[29–31]. In pharmaceutical industries, supercritical carbon dioxide is being used for many applications such as separation and purification, drying and extraction of bioactive ingredients such as proteins for vaccines preparation and enzymatic reactions [8,31–36,3,36,37]. Some researchers has described the supercritical carbon dioxide as the twenty first century solvent for chemical industries [4] and considered it as not any other solvent for its unique capabilities in many industrial applications [1–3,15,37].

Supercritical CO_2 is being used in food industries for almost the decades for the extraction of flavors [2,3,8,38], extraction of particular ingredients or aroma compounds from seeds or other natural sources [2,15,28,32,38–40], extraction of carotenoids and other ingredients from the vegetable matrices [41,42]. Supercritical carbon dioxide is also being used at various biotechnological and bioprocesses including up streaming and down streaming such as fermentation, destruction of waste and microbes [3,15,28]. Supercritical fluid extraction has been used to remove toxic or contaminated components from soil [43,44], water [45,46], environmental solids [47–49]. Supercritical carbon dioxide has been used to remove Polyaromatic hydrocarbons (PAHs), Polychlorinated Biphenyls (PCB), petroleum hydrocarbons, Dichlorodiphenyltrichloroethane (DDT) and other types of hazardous and toxic organics [43–55].

Cannabis industry is the fast growing industry globally for its number of applications either in pharmaceutical, wellness and recreation, textile and food industries [56,57]. At commercial level, supercritical carbon dioxide is being used to extract aroma or volatile compounds from the different parts of the hemp plant such as the extraction of aroma or volatile compounds from the inflorescence of Cannabis Sativa which are suitable for cosmetic and food industry, where compounds can be fractionated along with supercritical fluid extraction technique [58]. Supercritical carbon dioxide is being used to extract different products of seed oil such as fatty acids, tocopherol and pigments from the seeds of the hemp using different extraction conditions [59]. There are numerous products such as essential oil, seed oil & cannabinoids present in the hemp which are of industrial interest which can be extracted using supercritical carbon dioxide [56,57]. Cannabinoids such as cannabidiol (CBD), tetrahydrocannabiol (THC) are of immense industrial applications especially pharmaceutical applications [56,57].

The unique properties of sCO_2 such as cheap, non-flammable, sustainable, non-toxic, readily available, green solvent and unrestricted by US Environmental Protection Agency (EPA) makes it suitable for the production of many commercial products [1]. Supercritical CO_2 is also being investigated to use for analysis of drugs in forensic studies as the extraction and chromatography technology [60,61]. sCO_2 has been used in supercritical fluid chromatography (SFC) for almost decades [2,37,60]. The novel method was developed to dye the cotton fabric and other types of fabrics using supercritical carbon dioxide [62–64]. Supercritical carbon dioxide has also been examined to be used for catalyst preparation [65]. Supercritical carbon dioxide has been used for the polymerization and particle design formulation [66–71]. Supercritical CO_2 has also been used to investigate it's performance for the fractionation of anhydrous milk fat [34]. Other than drying and extraction, lots of research is being done on the application of sCO_2 for power generation and has been practically tested also [67–70]. With supercritical CO_2, the size of the turbine can be reduced to several factors compared to steam driven power generation. The high pressure usage in the sCO_2 extraction process can also be used to kill the microorganisms apart from the extraction which could be beneficial for sterilization purpose [43–48]. At the laboratory and pilot plant scale, many other processes have been investigated which have the potential to be scaled up shortly. Major diverse applications of supercritical carbon dioxide which are mainly commercialized are summarized in Table 3.

Table 3 Diverse Applications of sCO_2

Field	Applications
Drying	Bioactive ingredients [31,32,34,35], Aerogels [5,13,14,17–24], nanomaterials [65], Dry cleaning [75], Softwood [76], Coal [26]
Agri-food	Decaffeination of coffee and tea [29,30]
	Extraction of fragrances and flavoring components [2,3,8,38]
	Microorganisms Inactivation and sterilization [77–79]
Pharmaceuticals	Replacement for toxic liquid solvents [4]
	Extraction of steroids[3,36,37]
Materials	Production of aerogels [5,13,14,16–24,80]
	Dyeing [62–64]
Fuels	Desulfurization of coal [28]
Chemistry & Biochemistry	Photochemical reactions [81], polymerization reactions [66], and enzymatic reactions [33,69,82]
Working Fluid	Domestic water heat pumps and refrigeration [83,84]
Power Generation	Generate electricity using desk size turbine and could power the whole town [85–88]
Sterilization	Kills the pathogens [72–74]
Hemp Industry	Extraction of essential oil, cannabinoids, fatty acids, terpenes [56–59]

4. Factors affecting extraction using sCO_2

The solubility of different compounds is different in sCO_2. Solubility is determined by the equation mentioned below [89]

$$C = dk \exp(a/T + b) \qquad 1.1$$

Where c is the concentration of a solute in gas in g/L, d is the density of a gas in g/L, k is an association number, a = ΔH/R, and b = In (M_A + kM_B) + q - k In M_B. M_A and M_B are the molecular weights of the solute and the gas, correspondingly. ΔH = ΔH_S + AHvap and q = qs + qv, ΔH_S is the heat of solvation, and qs is a constant. ΔHvap is the heat of vaporization of the solute, and qv is a constant. K is the number of molecules of gas. The solubility of various components changes with the temperature and pressure [89].

Similarly, diffusivity and internal mass transfer are connected as shown in the equation below [39].

$$ki = \frac{2\Omega}{3}\frac{Deff}{dp} \;\; (\text{asymptotic value}, t \rightarrow \infty) \qquad 0.2$$

$$ki = \sqrt{\frac{Deff}{\Pi t}(\text{initial value}, t \rightarrow 0)} \qquad 0.3$$

$k_i$is the internal mass transfer coefficient, D_{eff} is effective diffusivity, d_p is the particle diameter, Ω is shape constant and t is the time. Different researchers have studied the Supercritical Fluid Extraction (SFE) of different materials at different operating conditions. Fiori [39] studied the SFE of sunflower at different conditions of pressure, temperature, and solvent flow rate, the mass of substrate, and particle size. Kiriamiti[40] also observed the change in the yield of oil extracted from sunflower seeds using sCO_2 with the change in different parameters. It was observed, the yield was not dependent on the flow rate at the beginning and this was due to the process controlled by solubility in the beginning and at the end, extraction becomes mass transfer controlled. The smaller the particle size more is the yield [39,40]. An increase in temperature also increases the yield. The flow direction of the solvent also influences the yield. Some researchers [90,91] pointed that downward laminar flow promotes better mass transfer coefficients than upward but Kiriamiti[40], however, did not observe any change with downward and upward flow.

5. The polar attribute of sCO_2

CO_2 is considered as non-polar because of its zero-dipole moment and low dielectric constant. CO_2 has a considerable charge separation in its molecular structure with significant nonzero bond dipole moments which results in significant quadrupole moment [92,93]. Hence CO_2 is described as a quadrupole solvent. CO_2 can act as both weak Lewis acids (LA) as well as a Lewis Base (LB). This has been suggested that CO_2 can solubilize several dipolar and nondipolar molecular systems. The solubility of CO_2 in water can illustrate the polar nature of CO_2 [94].

6. Special Configurations of sCO_2

Supercritical carbon dioxide has been used for producing polymer and composite micro particles. Conventional methods used for producing micro particles and polymers require high temperature and use of organic solvents which are toxic, flammable, environmentally hazardous, and expensive [15]. Production of micro- and nanoparticles using supercritical fluids could be of high interest especially by pharmaceutical companies because of many challenges such as bioavailability of low soluble molecules, development of controlled release powdery formulations, effecting a less-intrusive release [70,71]. SCF-assisted micronization can be categorized based on the role played by the supercritical fluid that could be as a solvent, and solvent, solute, or a co-solute [6,15,68,70].

sCO_2 as a Solvent

The process commonly uses the sCO_2 as a solvent known as Rapid expansion supercritical solutions (RESS) where the material to be processed is dissolved into SCF, followed by rapid depressurizing of the solution through a nozzle or capillary which causes the rapid nucleation of the solid into highly dispersed product [15,71]. A special type of RESS is CSS (Crystallisation from supercritical solutions) where substances are formulated into fine particles that were soluble in supercritical solvents [36].

sCO_2 as an Anti-Solvent

The ant solvent mode is similar to the traditional recrystallization using the classic solvents such as ethanol and acetone depending on the nature of applications. The substance to be processed is first dissolved in a classic solvent and then treated with sCO_2 which triggers the precipitation. The organic solvent used to dissolve the solute must have a good affinity for sCO_2 and perfectly miscible. The principle is based on bidirectional mass transfer of solvent to sCO_2 and vice versa. After the evaporation of the solvent, the solute will be concentrated and reach the super saturation level. With the dissolution of sCO_2 in the organic phase it decreases its density and solvent power. The precipitation of solute will begin and micro particles are formed. The solutes should have low solubility in sCO_2 and another solvent should have high solubility in sCO_2 [6,15].

sCO_2 as a Solute

sCO_2 is dissolved in the liquefied compound in this process. The gas-saturated mixture is decompressed through the nozzle causing the precipitation and the formation of particles in the atomization region. Substances to be treated are not soluble in SCF but absorb a large amount of gas which would either swell the substrate or decrease the melting point. This process is known as a particle from gas-saturated solution (PGSS) [15,67,95].

sCO_2 as a Co-Solute

In this process, sCO_2 acts as a co-solute but the substrate of interest is not soluble in SCF. The goal is to saturate the solution containing the solute on interest with sCO_2 at high pressure using a static mixer. This facilitates the atomization of the solution into a spray of fine droplets [6].

7. Advantages and Disadvantages of sCO_2 [2,6,15,68]

It can be stated that supercritical carbon dioxide is an attractive alternative to some of the traditional organic solvents. Some of the benefits include the fact that it is environmental emissions related as it is not a volatile organic compound. Although it is a greenhouse gas it is not considered to contribute as an additional greenhouse gas as it is taken from the environment, used in the specific process and recycled appropriately. There are several current and potential applications and the scientific field is continuing to develop novel innovative approaches for its use. Some of the advantages and disadvantages include for example:

- Process parameters such as temperature, pressure, nozzle diameter, depressurization rate can be controlled
- During micronization, better control of particle size, morphology, and particle size
- Less-energy intensive process distribution.
- No use of an organic solvent which avoids the toxicity and environmental harm
- Operating temperature is very low offers the possibility of processing thermo labile compounds.
- Supercritical-assisted CO_2 drying could be suitable for thermo sensitive materials to avoid thermal degradation because of low critical temperature
- The water solubility of dried products could be enhanced which would foster the powder formulation process.
- CO_2 can be recycled, thus leads to greener technology
- During drying, no emissions of Volatile Organic Compounds (VOC)

Besides listed advantages, there are two main disadvantages of Supercritical Fluid extraction are high investment costs and high pressure requirement [2,6,15,68].

Conclusion

There have been significant developments concerning the use of supercritical carbon dioxide over the last 20 years. This could be as an alternative green solvent to other hazardous volatile organic compounds as well as efficient in enhancing carbon capturing and sequestration technique. sCO_2 would be a best option to replace hazardous solvents because of its low critical temperature, low critical pressure, non-toxicity, inflammability, cheap, and recyclable. Supercritical carbon dioxide can be used to enhance the performance of traditional drying processes dealing with thermo sensitive and sticky materials through extensive research and a series of innovations. sCO_2 are already being used for extracting compounds from natural materials, polymer processing, or bio catalysis. Extraction of hop constituents and spices and decaffeination of tea and coffee by sCO_2 are already performed on an industrial scale. sCO_2 is replacing traditional compounds, hazardous to health, and the environment. The sCO_2 extraction methods allow lower energy consumption compared to traditional technologies. sCO_2 drying is used in the production of aerogels.sCO_2 also found application in the field of energy production because of the excellent heat transfer properties such as supercritical Rankine and Brayton cycles, to reduce the cost of electricity. Supercritical drying is one of the most efficient drying alternatives for any industrial application. Further, more research is needed to understand the techno-economic aspects of this technology for industrial applications. This technology could be considered as on step forward towards the green chemistry.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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