SUPERCRITICAL FLUIDS AS SOLVENTS FOR THE FUTURE

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Abstract: High-pressure technologies involving sub and supercritical fluids offer the possibility of obtaining new products with unique characteristics or designing new environmentally friendly and sustainable processes. Supercritical fluids represent versatile tools in material processing. Their application spans mass-transfer processes, phase transitions, reactions, materials-related procedures, and the fabrication of nanostructured materials. Beyond extraction, supercritical fluids are helpful in applications such as impregnation, cleaning, multistage countercurrent separation, particle formation, and coating, and reactive systems like hydrogenation, biomass gasification, and supercritical water oxidation. Furthermore, supercritical fluids modify polymers, while their interaction with colloids, emulsions, and nanostructured materials yields intriguing phenomena with potential industrial applications.

Keywords: Carbon dioxide; Supercritical fluids; Supercritical water

1. Introduction

There is a growing interest in developing alternative technological processes with minimized environmental impact, such as reduced energy consumption, less toxic residues, better use of byproducts, and better quality and safety of final products. High-pressure technology is a relatively new tool, which led to the development of several processes, which resulted in entirely new products with unique characteristics. A privileged position in this field is occupied by supercritical fluids (SCFs). SCFs are substances for which pressure and temperature are above the critical values (Figure 1) [1].

Baron Charles Cagniard de la Tour discovered them in 1822 while conducting experiments involving various heated fluids and a cannonball in a sealed cannon barrel. SCFs can also occur in nature. For example, supercritical water (SCW) is formed in some underwater volcanoes due to high water pressure and volcanic eruption temperature [1–3].

A SCF's unique blend of gas-like viscosity, diffusivity, liquid-like density, and solvating capabilities renders it an exceptional solvent for diverse applications. Processes involving SCFs are characterized by their sustainability, environmental friendliness, and cost-effectiveness, offering avenues for developing novel products. Their main advantage lies in

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separating and drying the product by simple expansion, while the gas can be recovered, recycled, and reused without the need for purification steps [1,4–6].

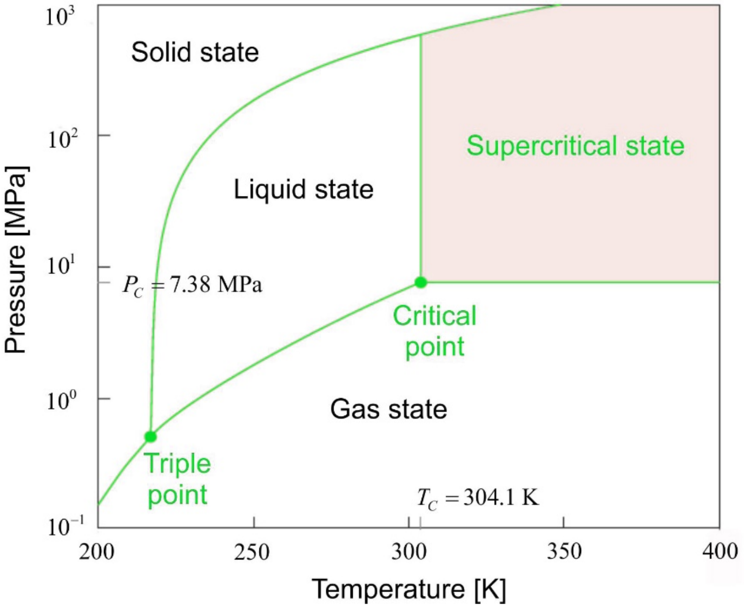

Figure 1. P-T diagram for CO_2 [1]

The environmental advantages of employing SCFs in industrial processes, notably their low energy consumption compared to conventional organic solvents, underscore their potential to serve as more sustainable alternatives, mitigating the environmental impact associated with traditional solvents. Therefore, SCFs are sometimes called green solvents for the future. Health and safety benefits are especially evident in using the most important SCFs: supercritical CO_2 (SC CO_2) and SCW. They exhibit characteristics such as being non-carcinogenic, non-toxic, non-mutagenic, and non-flammable, rendering them thermodynamically stable. Additionally, a significant advantage lies in the ability to adjust the thermophysical properties of SCFs, including diffusivity, viscosity, density, or dielectric constant, by simply manipulating the operating pressure and/or temperature. Furthermore, SCFs boast excellent heat transfer properties and have been investigated as environmentally benign heat transfer fluids. They have even been proposed as sustainable alternatives to the current fluids used in air conditioning and refrigeration systems, such as chlorofluorocarbons, ammonia, sulfur dioxide, and propane, many of which are either toxic or potent greenhouse gases [1–4,7].

SCFs are already applied in several processes developed to commercial scale in the pharmaceutical, food, and textile industries. Recent research into the application of SCFs has demonstrated their versatility as novel reaction media for both chemical and biochemical reactions, facilitating the synthesis of new materials and catalyst supports like aerogels. They

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are also instrumental in specialized separation techniques such as chromatography and extraction processes, as well as in particle formation and product formulation. SCFs hold immense potential for various industrial processing applications involving fats, oils, and their derivatives, showcasing a wide range of possibilities for enhancing efficiency and product quality. There is also an increasing interest in chemical reactions involving SCFs, especially SCW, for treating wastes and byproducts, which may generate value-added products such as energy carrier compounds (bio-oils and permanent gases such as hydrogen and methane) [1–5].

2. Applications of high-pressure technologies

Supercritical fluid extraction (SFE) from solids involves the continuous contact of the solid substrate with the supercritical solvent. The solid substrate is a fixed bed in most cases. The supercritical gas flows through the fixed bed, extracting the components of the product until the substrate is exhausted. The loaded solvent is then removed from the extractor and fed to a precipitator or separator. Extraction and precipitation of the extract can be carried out in various devices. Still, in most cases, one or more autoclaves are used as batch extractors, and precipitation is achieved in a single step by reducing pressure and temperature. Globally, several companies supply standard designs and customized plants. SFE technology is available for any plant size and feedstock quantity [4–8].

Most of the recently built industrial-size extraction plants are in Asia. For example, sesame oil is usually produced by roasting sesame seeds at more than 200°C and then extracting the oil by pressing at 180°C. The expressed sesame oil is prone to oxidation and loss of flavor. Extraction with CO_2, however, results in products without flavor loss. The active substances, sesamolin and sesame, are soluble in CO_2 and are nearly entirely present in the extracted oil. In 2004, a Korean venture company, UMAX Co., started to produce sesame oil in a large industrial SFE plant (~8000 liters of oil day−1) in Korea. NATEX (Natex Prozesstechnologie GesmbH, Ternitz, Austria) designed and constructed the UMAX plant, which consists of two extractors with a capacity of 2500 liters and a design pressure of 55 MPa [9–11].

Another new commercial application of SFE is cleaning rice. The Five King Cereal Industry Company Ltd. in Taiwan operates a rice-cleaning plant built by NATEX that includes three extractors of 5800 liters each. Five King Cereal Industry Company Ltd. claims that rice cleaned by supercritical CO_2 has advantages over the conventional product: Pesticides and heavy metals are removed, and germs and insect eggs are destroyed. The waxy layer and fatty acids are removed, preventing rice degradation. Cooking time is shortened by 30%, and the shelf life of the bagged rice is extended [3].

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Numerous recently published reviews and book chapters study procedures for extracting compounds from solid materials using supercritical fluids, notably CO_2. Industrial companies disclose crucial insights into the technical processes employing supercritical fluids within these resources.

Supercritical fluid micronization may significantly increase the dissolution rate of poorly water-soluble active pharmaceutical compounds. Dissolution rates are influenced by the surface area and particle size of the processed powder and are significantly affected by its morphology and wetting properties.

Supercritical fluid processes can lead to optimized formulations that increase the specific surface area. Composite particle generation by supercritical fluid processes incorporating hydrophilic polymers, cyclodextrins, and their derivatives leads to size-controlled particles that enhance the dissolution rate.

The use of SCFs in chemical and biochemical reactions arises mainly from a need to replace volatile organic solvents. Some chemical reactions performed in SCF media (Figure 2) have already been implemented at an industrial scale to obtain products with high-added value [1].

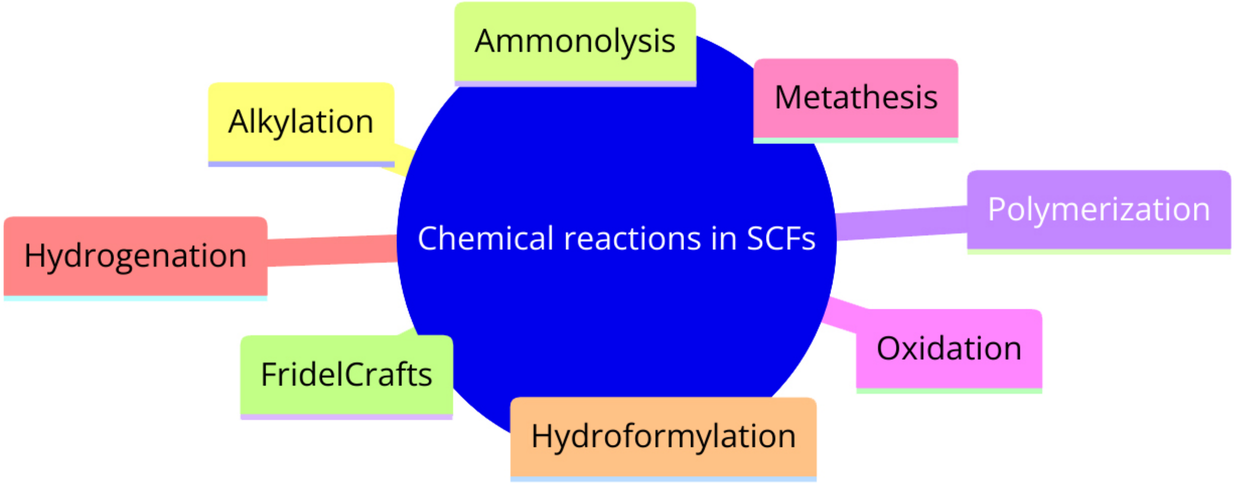

Figure 2. Chemical reactions performed in supercritical fluids at industrial scale [1]

In many reactions, supercritical fluids can be used as a reaction medium or reactive component. In many cases, phase equilibrium determines which reactions occur. Catalysis in supercritical fluids opens new opportunities because supercritical fluids can dissolve catalysts differently than typical reaction media. On one hand, enzymes can catalyze reactions in supercritical fluids. On the other hand, sub- and supercritical CO_2 can inhibit biological responses and be used for sterilization. Supercritical fluids also have been considered for recycling polymers. Hydrolytic and hydrothermal reactions and oxidative

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reactions in supercritical water (SCWO) are under consideration for waste treatment and biomass processing [1,3–12].

Initially regarded as the premier method for eliminating toxic and hazardous compounds and purifying liquids and solids, SCWO has encountered several challenges. These include salt precipitation, plugging, and severe corrosion, as revealed during process development and various applications.

The properties of supercritical CO_2 render it ideally suited for replacing organic solvents in polymer processing. The review covers the miscibility, phase separation, and morphological alterations observed in polymer solutions when exposed to supercritical fluids under high pressures. Carbon dioxide is an effective dilution agent for polymer melts, enhancing free volume and facilitating material processing by reducing viscosity and interfacial tension. Many examples in the literature demonstrate the unique capabilities of CO_2, ranging from producing fine particles to diffusive impregnation to continuous blending and extrusion processes. Polymer foams created using supercritical carbon dioxide as a processing solvent have been of interest for industrial applications in recent years and have been reviewed recently [12–15].

Supercritical fluids offer routes to functional nanostructured films and materials for next-generation microelectronic, energy conversion, and sensing devices. However, no industrial-scale processes appear to have been carried out so far.

One drawback of SCF technology is the perceived high energy demand needed to achieve the solvent's supercritical conditions. The elevated temperature and pressure required for the process, varying according to the type of solvents utilized, result in significant energy consumption, posing sustainability concerns over the long term.

In the SCF process, the extreme conditions of high temperature and pressure have led to debate over the operation's safety issue. For instance, in a supercritical methanol reaction, the reaction pressure is higher than 8.1 MPa, which is adequate to cause a catastrophe effect if there are any leakages on the reactor vessel. This possible hazardous scenario has led to concern regarding the safety of supercritical reaction plants, which has prevented most investors from investing in this technology. Hence, supercritical-based reactions have been labeled high-risk processes and insecure about being employed in biodiesel production [4–11].

In pharmaceuticals, particle formation is currently one of the most popular applications of supercritical fluids. The reasons can be found in the wide variety of particles obtained by the supercritical techniques. "Void-free" particles or very "soft" particles, composed of polar or non-polar compounds with sizes ranging from 50 nanometers to 50 microns, can be produced quickly.

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Applying supercritical fluids in CSS (Crystallization from Supercritical Solutions) allows us to obtain supersaturation and control nucleation- and growth rates by temperature-induced variation of the concentration of the solute in systems where no volatile organic solvents are present. The formation of small particles is favored when solids formation is maintained via primary nucleation throughout the batch crystallization.

The first report on CSS was in 1989, when benzoic acid was recrystallized from supercritical CO_2. The solvent power of CO_2 was reduced by simultaneous pressure and temperature reduction. Till today, no large-scale process has been implemented. The reason is that the process has to be performed in large vessels where a long cooling process is required, while pressure reduction should not be problematic [4–8].

The use of ultrahigh pressures for the pasteurization of foods is a topic, and space limitations do not permit a thorough discussion of its merits and industrial implementation. Using gas-fluid sterilization, such as can be accomplished with SC-CO_2, is an alternative to this technique. However, with the advent of ultrahigh-pressure SFE utilizing SC-CO_2, there appears, perhaps, to be a synergistic benefit from the application of high hydrostatic pressures for microbial reduction, extended shelf-life protection of the treated foodstuff, as well as the merits associated with using SFE. SCFs microbial and enzymatic deactivation has been demonstrated on liquid food substrates, such as fruit juices, milk, and alcoholic beverages [12–15].

Much research has been focused on obtaining antioxidant-laden extracts from natural products and industrial food waste streams using SWE and SC-CO_2, both with and without cosolvents.

Over the past twenty years, questions have been asked about the possibility of constructing an SFE plant near an alcohol fermentation facility that produces high-purity CO_2 as a by-product. Ethanol production at such a site facilitates its use as a preferred cosolvent for coupling with SC-CO_2, forming fatty acid ethyl esters for biodiesel use, or improving the SFF of lipid compounds.

SCW has been used as a processing medium for various biomass and model compounds such as cellulose, lignin, and glucose. Glycerol is a promising biomass feedstock for SCW reforming. Crude glycerol, containing water, can undergo hydrothermal conversion without drying. In addition to water, impurities such as methanol, fatty acid methyl esters, and salts are commonly found in crude glycerol. In SCW, the solubility of most ionic species is low; as a result, salts in the feedstock will tend to precipitate from the solution. They may precipitate on the reactor wall, in or on the pipes, or on the catalyst surface, reducing its effective surface area and activity. Therefore, salt removal is essential to SCW [2–11].

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Glycerol was decomposed in SCW to obtain chemical inter-mediates, mainly acrolein, which could be further used in chemical syntheses. Glycerol conversion and acrolein selectivity were the main parameters studied by all.

Supercritical drying is used to remove liquids from solids without altering the structure of the solid. It is based on the liquid-like properties of SCFs and their capacity for dissolving organic solvents. By passing SCFs through a wet solid, the solvent is removed without the occurrence of surface tension at the liquid-gas-solid interface, which may change the internal structure of a solid during conventional drying. Furthermore, drying with SCFs enables the final product to be efficiently dried without high temperatures. Supercritical drying produces aerogels and microelectromechanical systems and prepares biological specimens for scanning electron microscopy [3–9].

3. Conclusions

This paper presents a short overview of the processes involving SCFs and of their advantages. Processing natural products with SCF technologies has been an extensive area of research during- the past two decades. CO_2 and water have been the most used SCFs. SCFs are already applied in extracting compounds from natural materials, polymer processing, or biocatalysis. Many natural compounds, such as vitamins, aromas, natural pigments, or essential oils, are extracted with SCFs, thus avoiding using organic solvents and high temperatures.

The main advantages of using subcritical or supercritical fluids for micronization processes are their unique thermodynamic and fluid-dynamic properties, allowing for the tunability of accessible solvent properties. Furthermore, micronization processes can be easily integrated with subcritical or supercritical extraction processes or downstream processing for chemical or biochemical synthesis of products in subcritical or supercritical fluids.

Supercritical fluids are a unique class of solvents. Combined with components occurring in nature, chemical processes, and material design, including all matter structures from gas to solid, homogeneous to nonhomogeneous, the variety of possible applications for supercritical fluids is endless. The practical application of supercritical fluids requires designing technical components and plants for production.

Compared with other technical systems, supercritical fluid production plants are relatively simple from the mechanical and control points of view. However, the background is complex and must be transferred to process designers, engineers, and all who want to use supercritical fluids to produce a desired project.

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Supercritical drying and cleaning remove liquids or impurities from solids without altering their structure. Supercritical drying produces aerogels and microelectromechanical systems and prepares biological specimens for scanning electron microscopy. In contrast, supercritical cleaning is applied in microelectronics. In recent years, SCFs have been proposed for different applications in the energy field.

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