High-Pressure Processing: A Smart Way to Increase Energy Efficiency with Less Toxic Residues

GREGOR KRAVANJA, MAŠA KNEZ HRNČIČ, DARIJA CÖR & ŽELJKO KNEZ

Abstract High-pressure processes involving sub and supercritical fluids enable the design of products with special physical characteristics, less toxic residues, low energy consumption, and are eco-friendly and sustainable. Supercritical fluids show potential as solvents in boosting green chemistry by replacing environmentally harmful conventional organic solvents. Tunable physical properties of the supercritical fluids enable selective extraction, purification and fractionation of value-added products and by-products. Absorption of compressed gas in polymer matrices results in a wide spectrum of possible applications in the field of sustainable polymer processing, for example, production of fibers, microparticles and foams. As a heat transfer fluid, supercritical CO2 has been reintroduced as an environmentally friendly refrigerant in heat pumps working cycles. There is also great potential in the treatment of sewage wastes with supercritical fluids and production of value compounds from waste streams. Several supercritical fluid applications are presented from the perspective of their environmental and economic benefits.

Keywords: • Supercritical fluids • Energy efficiency • High-pressure • Extraction • Biofuels •

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1 Introduction

Supercritical fluids (SCFs) were discovered in 1822 by Baron Charles Cagniard de la Tour, who proved the existence of a critical point by conducting an acoustics experiments in a sealed cannon. He noticed that a splashing sound generated by a solid ball in a liquid phase inside the cannon ceased above a certain temperature and pressure. That indicates no liquid-gas phase boundary and surface tension in a supercritical fluid phase \[1\]. Compared to these pioneering experiments, today’s industrial process involving supercritical fluids operate at pressures of several magnitudes higher, ranging from 10 MPa in extraction and formation processes up to 20 000 MPa in the production of artificial diamonds \[2\]. In nature, SCFs can occur below the Earth’s ocean floor, on the planet Venus, and probably on exoplanets such as Super-Earths. They can also considered to be life-sustaining solvents, since some bacteria species have been shown to be tolerant of SFCs \[3\].

![P-T diagram for supercritical fluid with the lines of constant density.](image)

SCFs are defined as any substances whose temperature and pressure are above their critical values. The phase behaviour of pure compounds is presented in a \(P-T\) diagram (Figure 1). SCFs can be easily removed from a product by depressurization since they are gaseous under atmospheric pressure. That means
there are no solvent residues in the final product and consequently lower processing costs. The choice of which supercritical fluid is used for chemical and industrial processes must be determined by a compromise of practical factors. Carbon dioxide (CO₂) is the most commonly used supercritical fluid because of its moderate critical constants ($T_c = 31.0°C, P_c = 7.38$ MPa), non-flammability, and non-toxic, non-corrosive nature [4]. It's available on the market for low prices and is considered to be the second cheapest solvent after water. Hot compressed water has attracted attention as an excellent green reaction and processing media for the conversion of biomass into biobased chemicals and biofuels. However, water has a relatively high critical point ($T_c =374.14°C, P_c =22.12$ MPa) and energy requirements are high. A possible solution to reduce the operating temperature and consequently energy requirements of processing biomass with water is to process at higher pressures or by adding supercritical CO₂ to the reaction mixture [5].

2 Applications of Supercritical fluids

High-pressure technology involving SCFs is German in origin, with the first large-scale application in the food industry (decaffeination of coffee or tea and hop extraction) mainly oriented toward the production of natural products. Today, many new SCF applications have been developed worldwide with an extensive potential for increase in capacity as new high-quality products are required.

SCF technology can be used as a new reaction media for chemical reactions, in large-scale operations in petrochemical plants [6], for biochemical reactions in the pharmaceutical industry for production of intermediate and final products [7], for powder coatings [8], for polymer processing including particle formation and encapsulation [9], for jet cutting [10], dry cleaning [11], for sterilization processes, virus inactivation in plasma fractions [12] and bone implants [13], for separation process in supercritical chromatography [14], as an alternative refrigerants in power cycles [15] and for extraction of value added products and by-products [16]. There is also great potential in the treatment of sewage wastes with SCFs and generated value products from waste streams [17]. Several SCF applications will be briefly presented from the perspective of their environmental and economic benefits.
2.1 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) has been successfully introduced in many fields, from decaffeination of coffee beans and black tea leaves, isolation of some flavouring from hops, fatty acid refining, to the production of herbal production [18]. Tuneable physical properties of the most frequently used SCF, \( \text{CO}_2 \), enables selective extraction purification and fractionation [18]. Lipids and carotenoids can be easily isolated from the natural source (algae, microalgae, dairy production) [19]. Since \( \text{CO}_2 \) is a non-polar solvent, a small amount of ethanol can be added to extend the range of its solvating strength to extract polar components like phenolic and metal-ligand complexes [20]. Recently, new processes have been developed to recover components from wastes ranging from manure to packing residuals. In the food industry, SFE can be used to extract value products from by-products that are generated during food manufacturing. Another interesting field is the removal of heavy metals from solid matrices and liquids, where using SFEs presents an excellent option [21].

SFE can be carried out in different modes of operation; the most frequently used is extraction from solids, which is carried out in batch and single stage mode since solids are difficult to handle continuously in pressurized vessels. The size of vessels used in industry today varies from 1 m\(^3\) up to 40 m\(^3\) volume. The maximum throughput of a single industrial plant for extraction from solids is above 10 000 t/a. [22]. Like many other processes, SFE has to be properly adjusted before every single run. Extraction yield depends on temperature, pressure, amount and type of modifier, amount and particle size of a sample and use of a dispersing agent. One option is experimental design and proper statistical analyses with a small number of trials [23].

Most companies believe that supercritical extraction is too expensive and because of high investment costs in comparison with classical methods, should be restricted only to high-quality products. However, that is far from true when a very large amount of material is treated, as in the case of coffee and hops processing and waste treatment [24]. Reported costs for production of solid feed with a capacity around 1000 t/a are around 3 EUR/kg. The economy of scale may bring the cost down to less than 0.5 EUR/kg for batch operation. In the case of continuous operation, the cost can be reduced even more [22]. Figure 2 presents an economy of a scale for SCE of solids using \( \text{CO}_2 \) as a solvent. The
lower line represents continuous operation where an increase in productivity is proportional to throughput feed.

![Graph showing economy of scale for SCE of solid using CO₂](image)

Figure 4: Economy of scale for SCE of solid using CO₂.

### 2.2 Polymer processing

Supercritical fluids (SCFs) are well established for use as a green processing solvent in polymer applications such as polymer modification, the formation of polymer composites, polymer blending, microcellular foaming, polymerization and particle production [25].

In the field of polymeric foams, supercritical CO₂ is used as blowing agent. To obtain polymer or composite foams, the substrate is saturated with SC CO₂, followed by rapid depressurization at a constant temperature (pressure quench) [26]. This method takes advantage of the large depression of the glass transition temperature ($T_g$) observed for many polymers in the presence of dense CO₂ [27]. In the polymer industry, polyurethane (PU) foams comprise the largest segment of the foams market in many products, followed by polystyrene (PS) foams. The replacement of ozone-depleting foaming agents like R12 and R22 by CO₂ has the potential to create a great impact in the foam industry [28]. Nucleation growth can be optimized by changing the saturation pressure, temperature and the rate of release gas. At higher temperature, less gas is dissolved in the polymer matrix;
therefore, low growth of pores is expected. When pressure is increased, CO₂ solubility in polymer matrices increases, creating more small size nuclei available for the formation and growth of pores. Rate of gas release also significantly influences the size of porous structures. At higher rates, more nuclei are generated with a smaller size compared to lower rates [29].

Special attention is dedicated to using biodegradable polymers in particle size reduction processes that are related to pharmaceutical applications for controlled drug release [30]. Particles have been obtained with rapid expansion of supercritical solutions (RESS) [31], the gas antisolvent process (GAS) [32], supercritical antisolvents (SAS) [33], solution enhanced supercritical dispersion processes (SEDS) [34], aerosol solvent extraction systems (ASES) [35], supercritical fluid extraction of emulsions (SFEE) [36] and particles from gas-saturated solutions (PGSS™) [37]. Weidner [38] has considered an economic evaluation of a PGSS™ plant with a capacity of 1.5 t/h. The process with low energy consumption features low operating costs, as low as 0.20 €, including investment, consumables maintenance, interest and personal. Additionally, the feasibility of a plant of that size can be increased by installing a CO₂ recovery capability.

Table 1: High-pressure technologies for producing powder particles [39].

<table>
<thead>
<tr>
<th></th>
<th>SCF used as</th>
<th>Gas quantity</th>
<th>Organic solvent</th>
<th>Pressure</th>
<th>Separation of gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESS</td>
<td>Solvent</td>
<td>High</td>
<td>Absent</td>
<td>High</td>
<td>Easy</td>
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<tr>
<td>GAS/PCA/SAS/ASES/</td>
<td>Antisolvent</td>
<td>Medium</td>
<td>Present</td>
<td>Medium</td>
<td>Easy</td>
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<tr>
<td>SEDS/SA</td>
<td>Dissolved</td>
<td>Low</td>
<td>Absent</td>
<td>Medium</td>
<td>Easy</td>
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<td>PGSS™</td>
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2.3 Supercritical fluids in the energy domain

SCF was first introduced in the energy domain in steam cycles in order to increase the thermal efficiency of fossil-fired power plants. Steam at supercritical conditions was used for recovering heat from flue gases and transforming the energy into kinetic and electrical energy [40]. Recently, SCFs have been studied as heat transfer fluids (HTF) in refrigeration systems, advanced power cycles,
solar collectors, as a processing media in fuel cell applications, in carbon capture and storage (CCS) processes and as reactants in biofuel production.

The Supercritical Rankine Cycle (SRC) has been widely studied in terms of efficiency and conversion of energy at lower temperatures. Compared to the organic Rankine cycle, there is a better thermal match between the working fluid and the heat source at the pinch point. In SRC, fluid is heated directly from the liquid phase into the supercritical region, bypassing the two-phase region, which results in less energy loss [41]. As an HTF, supercritical CO₂ can also be integrated with solar energy in power cycles. Over the past several years, there has been a significant amount of research done on supercritical Brayton cycles. Thermal efficiency above 50% can easily be achieved. The main advantages lie in significantly reduced compressor work. Supercritical CO₂ Brayton is present in many applications, ranging from nuclear, geothermal to solar-thermal [42]. There are many opportunities in the development of turbomachines for supercritical power cycles, in research for heat transfer near the critical condensation and evaporation points, and also in recovery processes for hydrocarbons, and in enhanced oil recovery processes at great depths [40].

Global warming and air pollution resulting from the use of enormous quantities of fossil fuels can be significantly reduced with the use of carbon sequestration processes. One way of making CCS more economically attractive, while at the same time contributing to energy security, is to use captured CO₂ to maximize production from declining oil fields with a process known as enhanced oil recovery (EOR) [43]. Globally, CO₂-EOR has the potential to produce 470 billion barrels of additional oil and to store 140 billion metric tons of CO₂, which are equivalent to the greenhouse gas emissions from 750 large one GW size coal power plants over 30 years.
2.3.1 Hydrothermal reactions

Hydrothermal (HT) processes are technologies for the conversion of biomass into biobased chemicals and biofuels, using pressurized water (343 °C, 22.1 MPa) as processing media. Hydrothermal processes are divided into four main processes:

- hydrothermal carbonization (HTC),
- aqueous phase reforming (APR),
- hydrothermal liquefaction (HTL),
- hydrothermal gasification (HTG).

HT carbonization is carried out at mild temperatures, typically below 250 °C. Solid products have a high content of carbon and are suitable for different applications. Hydrothermal liquefaction is demonstrated as a process that is typically carried out at temperatures between 250 °C K and 375 °C and is ideal process for production of biofuel from algae biomass. At higher temperatures, above 380 °C, hydrothermal gasification is performed.

![Diagram showing product distribution for different hydrothermal processes]

Figure 3: Hydrothermal treatment processes depending on temperature; ($T_c$ - critical temperature, $P_c$ - critical pressure).
A topic that has been enjoying increasing attention in recent years is the hydrothermal carbonization. The first step in this process is hydrolysis of cellulose chains to different oligomers and glucose, which can isomerize to fructose. Next products are organic acids, which decrease the pH value close to 3. The oligomers also hydrolyze into their monomers, which further pass through dehydration and fragmentation reactions leading to formation of different soluble products. Acid/aldehydes and phenols are obtained by decomposition of the furfural-like compounds. Polymerization or condensation reactions of the monomers and/or their decomposition products lead to the formation of soluble polymers.

3 Environmental impacts

In order to make a good comparison between the environmental impacts of different CO₂ utilization processes (CCU), global warming potential (GWP), with units defined as the mass of CO₂ produced divided with 1 ton of CO₂ removed, is presented. Utilization of CO₂ at high pressure through enhanced oil recovery (EOR) is the best option (average value around 500 kg CO₂ eq./t CO₂). Direct utilization of CO₂ for supercritical extraction of coffee beans is the second best option and has a GWP close to 1.20 kg CO₂ eq./t CO₂ [16]. Carbon utilization for production diethanolamine (DME) is the worst option, with a GWP near 600 t CO₂/t CO₂, which is 100 times higher than supercritical extraction process [44].

![Figure 5: Average GWP (global warming potential) for enhanced oil recovery (EOR), supercritical extraction of coffee and direct production of diethanolamine (DME).](image-url)
4 Conclusion

SCFs have a great potential in many areas and new applications are developing daily. Several high-pressure applications involving SCFs have already found a way to industrial scale production. They offer ways to develop new products with special physical characteristics, less toxic residues, low energy consumption, and which are eco-friendly and sustainable. SCFs can be easily removed from a product by depressurization since they are gaseous under atmospheric pressure. Additionally, the economy of scale may bring the cost down to be economical competitive with conventional processes.

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