University of Maribor Press

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 •

CORRESPONDENCE ADDRESS: Gregor Kravanja, PhD, Full Professor, University of Maribor, Faculty of Chemistry and Chemical, Engineering, Laboratory of Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia, e-mail: gregor.kravanja@um.si. Maša Knez Hrnčič, PhD, Assistant Professor, University of Maribor, Faculty of Chemistry and Chemical, Engineering, Laboratory of Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia, e-mail: masa.knez@um.si. Darija Cör, PhD, Assistant, University of Maribor, Faculty of Chemistry and Chemical, Engineering, Laboratory of Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia, e-mail: darja.cor@um.si. Željko Knez, PhD, Full Professor, University of Maribor, Faculty of Chemistry and Chemical, Engineering, Laboratory of Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia, e-mail: zeljko.knez@um.si.

DOI https://doi.org/10.18690/978-961-286-211-4.10 ISBN 978-961-286-211-4
Available at: http://press.um.si.

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].

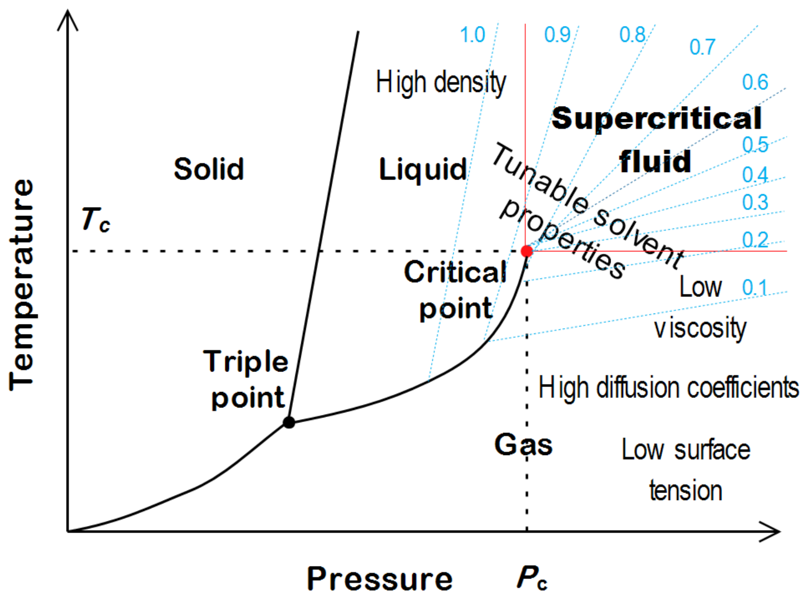

Figure 1: ***P-T*** **diagram for supercritical fluid with the lines of constant density.**

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 (CO_2) 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 CO_2 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, 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 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 pressured vessels. The size of vessels used in industry today varies from 1m^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. Hoverer, 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 CO_2 as a solvent. The lower line represents continuous operation where an increase in productivity is proportional to throughput feed.

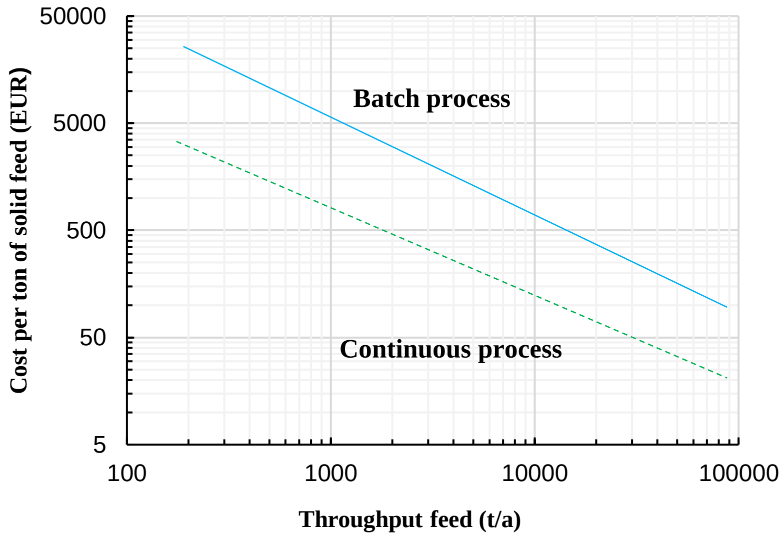

Figure 4: Economy of scale for SCE of solid using CO_2.

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 CO_2 is used as blowing agent. To obtain polymer or composite foams, the substrate is saturated with SC CO_2, 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 CO_2 [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 CO_2 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, CO_2 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 CO_2 recovery capability.

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

	RESS	GAS/PCA/SAS/ASES/ SEDS/SA	PGSS™
SCF used as	Solvent	Antisolvent	Dissolved
Gas quantity	High	Medium	Low
Organic solvent	Absent	Present	Absent
Pressure	High	Medium	Medium
Separation of gas	Easy	Easy	Easy

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 CO_2 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 CO_2 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 usege 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 CO_2 to maximize production from declining oil fields with a process known as enhanced oil recovery (EOR) [43]. Globally, CO_2-EOR has the potential to produce 470 billion barrels of additional oil and to store 140 billion metric tons of $CO_{2,}$ 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 form algae biomass. At higher temperatures, above 380 °C, hydrothermal gasification is performed.

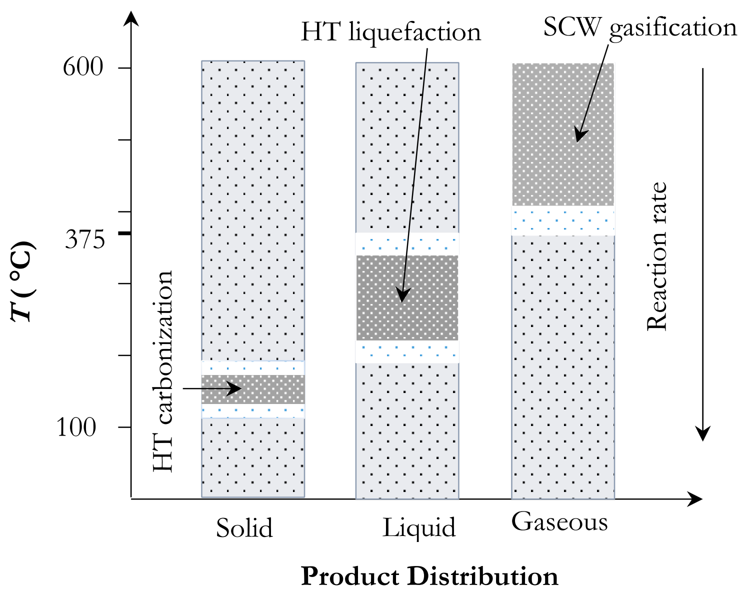

Figure 3: Hydrothermal treatment processes depending on temerature; (*T*c - critical temperature, *P*c - critical pressure).

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 CO_2 utilization processes (CCU), global warming potential (GWP), with units defined as the mass of CO_2 produced divided with 1 ton of CO_2 removed, is presented. Utilization of CO_2 at high pressure through enhanced oil recovery (EOR) is the best option (average value around 500 kg CO_2 eq./t CO_2). Direct utilization of CO_2 for supercritical extraction of coffee beans is the second best option and has an GWP close to 1.20 kg CO_2 eq./t CO_2. [16]. Carbon utilization for production diethanolamine (DME) is the worst option, with a GWP near 600 t CO_2/t CO_2, which is 100 times higher than supercritical extraction process [44].

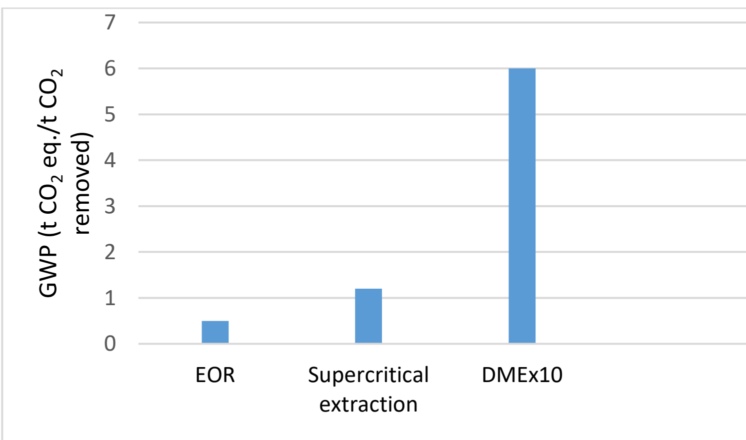

Figure 5: Average GWP (global warming potential) for enhanced oil recovery (EOR), supercritical extraction of coffee and direct production of diethanolamine (DME).

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.

Acknowledgments

The authors would like to acknowledge Slovenian Research Agency (ARRS) for financing research in frame of Programme P2-0046 (Separation processes and production design).

References

[1] Bolmatov D, Brazhkin V, Trachenko K. Thermodynamic behavior of supercritical matter. arXiv preprint arXiv:13033153. 2013.
[2] Knez Ž, Knez Hrnčič M, Škerget M. Particle formation and product formulation using supercritical fluids. Annual review of chemical and biomolecular engineering. 2015;6:379-407.
[3] Budisa N, Schulze-Makuch D. Supercritical Carbon Dioxide and Its Potential as a Life-Sustaining Solvent in a Planetary Environment. Life : Open Access Journal. 2014;4(3):331-40.
[4] Haldorai Y, Shim J-J, Lim KT. Synthesis of polymer–inorganic filler nanocomposites in supercritical CO_2. The Journal of Supercritical Fluids. 2012;71(Supplement C):45-63.
[5] Hrnčič MK, Kravanja G, Knez Ž. Hydrothermal treatment of biomass for energy and chemicals. Energy. 2016;116(Part 2):1312-22.
[6] Centi G, Perathoner S. Catalysis and sustainable (green) chemistry. Catalysis Today. 2003;77(4):287-97.
[7] Nakamura K. Biochemical reactions in supercritical fluids. Trends in Biotechnology. 1990;8:288-92.
[8] Smith RD. Method of making supercritical fluid molecular spray films, powder and fibers. Google Patents; 1988.
[9] Rao JP, Geckeler KE. Polymer nanoparticles: preparation techniques and size-control parameters. Progress in Polymer Science. 2011;36(7):887-913.
[10] Engelmeier L, Pollak S, Weidner E. Investigation of superheated liquid carbon dioxide jets for cutting applications. The Journal of Supercritical Fluids. 2017.
[11] Lebedev AE, Katalevich AM, Menshutina NV. Modeling and scale-up of supercritical fluid processes. Part I: Supercritical drying. The Journal of Supercritical Fluids. 2015;106(Supplement C):122-32.
[12] Perrut M. Sterilization and virus inactivation by supercritical fluids (a review). The Journal of Supercritical Fluids. 2012;66:359-71.

[13] Scognamiglio F, Blanchy M, Borgogna M, Travan A, Donati I, Bosmans JWAM, et al. Effects of supercritical carbon dioxide sterilization on polysaccharidic membranes for surgical applications. Carbohydrate Polymers. 2017;173(Supplement C):482-8.
[14] Yang J, Zhu L, Zhao Y, Xu Y, Sun Q, Liu S, et al. Separation of furostanol saponins by supercritical fluid chromatography. Journal of Pharmaceutical and Biomedical Analysis. 2017;145(Supplement C):71-8.
[15] Li M-J, Zhu H-H, Guo J-Q, Wang K, Tao W-Q. The development technology and applications of supercritical CO_2 power cycle in nuclear energy, solar energy and other energy industries. Applied Thermal Engineering. 2017;126(Supplement C):255-75.
[16] López-Padilla A, Ruiz-Rodriguez A, Reglero G, Fornari T. Supercritical extraction of solid materials: A practical correlation related with process scaling. Journal of Food Engineering. 2017.
[17] Marrone PA. Supercritical water oxidation—current status of full-scale commercial activity for waste destruction. The Journal of Supercritical Fluids. 2013;79:283-8.
[18] Ramsey E, Qiubai S, Zhang Z, Zhang C, Wei G. Mini-Review: Green sustainable processes using supercritical fluid carbon dioxide. Journal of Environmental Sciences. 2009;21(6):720-6.
[19] Herrero M, Cifuentes A, Ibañez E. Sub-and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae: A review. Food chemistry. 2006;98(1):136-48.
[20] Erkey C. Supercritical carbon dioxide extraction of metals from aqueous solutions: a review. The Journal of Supercritical Fluids. 2000;17(3):259-87.
[21] Herrero M, Mendiola JA, Cifuentes A, Ibáñez E. Supercritical fluid extraction: Recent advances and applications. Journal of Chromatography A. 2010;1217(16):2495-511.
[22] Brunner G. Supercritical fluids: technology and application to food processing. Journal of Food Engineering. 2005;67(1):21-33.
[23] Sharif K, Rahman M, Azmir J, Mohamed A, Jahurul M, Sahena F, et al. Experimental design of supercritical fluid extraction–A review. Journal of Food Engineering. 2014;124:105-16.
[24] Perrut M. Supercritical fluid applications: industrial developments and economic issues. Industrial & engineering chemistry research. 2000;39(12):4531-5.
[25] Nalawade SP, Picchioni F, Janssen LPBM. Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications. Progress in Polymer Science. 2006;31(1):19-43.
[26] Tsivintzelis I, Sanxaridou G, Pavlidou E, Panayiotou C. Foaming of polymers with supercritical fluids: A thermodynamic investigation. The Journal of Supercritical Fluids. 2016;110:240-50.
[27] Costeux S. CO_2-blown nanocellular foams. Journal of Applied Polymer Science. 2014;131(23).
[28] Tomasko DL, Burley A, Feng L, Yeh S-K, Miyazono K, Nirmal-Kumar S, et al. Development of CO 2 for polymer foam applications. The Journal of Supercritical Fluids. 2009;47(3):493-9.
[29] Knez Ž, Markočič E, Novak Z, Hrnčič MK. Processing polymeric biomaterials using supercritical CO_2. Chemie Ingenieur Technik. 2011;83(9):1371-80.
[30] Marizza P, Pontoni L, Rindzevicius T, Alopaeus JF, Su K, Zeitler JA, et al. Supercritical impregnation of polymer matrices spatially confined in microcontainers for oral drug delivery: Effect of temperature, pressure and time. The Journal of Supercritical Fluids. 2016;107(Supplement C):145-52.

[31] Paisana MC, Müllers KC, Wahl MA, Pinto JF. Production and stabilization of olanzapine nanoparticles by rapid expansion of supercritical solutions (RESS). The Journal of Supercritical Fluids. 2016;109(Supplement C):124-33.
[32] Lőrincz L, Bánsághi G, Zsemberi M, de Simón Brezmes S, Szilágyi IM, Madarász J, et al. Diastereomeric salt precipitation based resolution of ibuprofen by gas antisolvent method. The Journal of Supercritical Fluids. 2016;118(Supplement C):48-53.
[33] Prosapio V, Reverchon E, De Marco I. Formation of PVP/nimesulide microspheres by supercritical antisolvent coprecipitation. The Journal of Supercritical Fluids. 2016;118(Supplement C):19-26.
[34] Dal Magro C, Aguiar GPS, Veneral JG, dos Santos AE, de Chaves LMPC, Oliveira JV, et al. Co-precipitation of trans-resveratrol in PHBV using Solution Enhanced Dispersion by Supercritical Fluids technique. The Journal of Supercritical Fluids. 2017;127(Supplement C):182-90.
[35] Bleich J, Müller BW, Waßmus W. Aerosol solvent extraction system — a new microparticle production technique. International Journal of Pharmaceutics. 1993;97(1):111-7.
[36] Lévai G, Albarelli JQ, Santos DT, Meireles MAA, Martín Á, Rodríguez-Rojo S, et al. Quercetin loaded particles production by means of supercritical fluid extraction of emulsions: Process scale-upstudy and thermo-economic evaluation. Food and Bioproducts Processing. 2017;103(Supplement C):27-38.
[37] Martín Á, Weidner E. PGSS-drying: Mechanisms and modeling. The Journal of Supercritical Fluids. 2010;55(1):271-81.
[38] Weidner E. High pressure micronization for food applications. The Journal of Supercritical Fluids. 2009;47(3):556-65.
[39] Knez Ž, Markočič E, Leitgeb M, Primožič M, Knez Hrnčič M, Škerget M. Industrial applications of supercritical fluids: A review. Energy. 2014;77(Supplement C):235-43.
[40] Brunner G. Supercritical process technology related to energy and future directions–An introduction. The Journal of Supercritical Fluids. 2015;96:11-20.
[41] Chen H, Goswami DY, Rahman MM, Stefanakos EK. A supercritical Rankine cycle using zeotropic mixture working fluids for the conversion of low-grade heat into power. Energy. 2011;36(1):549-55.
[42] Iverson BD, Conboy TM, Pasch JJ, Kruizenga AM. Supercritical CO 2 Brayton cycles for solar-thermal energy. Applied Energy. 2013;111:957-70.
[43] Agarwal A, Parsons J. Commercial Structures for Integrated CCS-EOR Projects. Energy Procedia. 2011;4:5786-93.
[44] Olah GA, Goeppert A, Prakash GS. Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. The Journal of organic chemistry. 2008;74(2):487-98.