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27th International Conference Ecological Truth and Environmental Research

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PREFACE

Today's growing environmental and ecological imbalances require a multidisciplinary approach in finding adequate sustainable solutions. That is why environmental and ecological issues are at the focus of the 27th International Conference Ecological Truth and Environmental Research 2019 (EcoTER'19), which will be held at Bor Lake, Serbia, 18-21 June 2019. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

The EcoTER'19 is organized by the University of Belgrade, Technical faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, University of Zagreb, Faculty of Metallurgy – Sisak, University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

The primary goal of EcoTER'19 is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

These proceedings include 105 papers from authors coming from universities, research institutes and industries in 15 countries: Russia, Belarus, Turkey, Kazakhstan, Czech Republic, Portugal, Sweden, Switzerland, Slovenia, Bulgaria, Croatia, Bosnia and Herzegovina, North Macedonia, Montenegro, and Serbia.

The support of the donor and their willingness and ability to cooperate has been of great importance for the success of EcoTER'19. The Organizing Committee would like to extend their appreciation and gratitude to the donor of the Conference for their donation and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'19. Sincere thanks to all the people who have contributed to the successful organization of EcoTER'19.

On behalf of the 27th EcoTER Organizing Committee,

Snežana Šerbula, PhD Full Professor

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SUPERCRITICAL FLUIDS AS GREEN SOLVENTS

Vladan Mićić[1], Jaroslava Budinski-Simendić[2*], Stefan Pavlović[3], Vesna Teofilović[2], Ayse Aroguz[4], Ivan Krakovsky[5], Jelena Pavličević[2]

[1]University of East Sarajevo, Faculty of Technology, Zvornik,
BOSNIA AND HERZEGOVINA
[2]University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad,
SERBIA
[3]University of Belgrade, Institute of Chemistry, Technology and Metallurgy,
Njegoševa 12, 11001 Belgrade, SERBIA
[4]Istanbul University, Engineering Faculty, 34320Avcilar, Istanbul, TURKEY
[5]Charles University, Faculty of Mathematics and Physics, 18000 Prague, CZECH REPUBLIC
[*]jarkamer@gmail.com

Abstract

Supercritical fluids (SCFs) offer the possibility for obtaining and designing of new environmentally friendly and sustainable products with special characteristics. Recently, SCFs have been applied for polymer processing, polymer extraction and purification, preparation of optical materials, supercritical blending of additives into polymers, as a foaming agent for microcellular materials, impregnation, fractionation, purification and formation of powdered polymers. This review is focused on some applications of supercritical fluids with special emphasis on their properties of supercritical fluids in water and carbon-dioxide green industrial chemical processes.

Keywords: supercritical fluids, carbon dioxide, water, technology, process

INTRODUCTION

The wide industrial application of different organic solvents represents a serious threat to the environment. However, modern industrial processes are focused on development of organic solvents free processes, such as supercritical fluids (SCFs), which are based on the high-pressure theory and green chemistry principles [1,2]. SCFs present an adequate substitute for processes, which use toxic chlorinated, aromatic, and chlorofluorocarbon solvents. In the supercritical state, there is no phase boundary between the gas phase and the liquid phase. The properties of SCFs are in between that of gas and liquid. SCFs are highly compressible, particularly near the critical point, and their density and thus the solvation power can be carefully controlled by small changes in temperature and/or pressure [3,4]. The special combination of gas–like viscosity and liquid–like density and solvating properties of a SCF makes it an excellent solvent for various application. The environmental benefits of using SCFs in industrial processes, such as low energy consumption during operation, show their potential of replacing the far more environmentally damaging convential organic solvents [5–7]. Therefore SCFs are sometimes called green solvents for the future. Water and carbon dioxide in their supercritical states are primary candidates as solvent for green chemical processes, since they are compatible with the environment and have enhanced transport properties for reaction and separations. Gases such as nitrous oxide or ethane have low critical values, but can generate explosive flammable mixtures. Although the properties of SCFs are well known, they are as yet not fully exploited for industrial application [8].

APPLICATION OF SUPERCRITICAL FLUIDS

Supercritical fluid extraction (SCFE) has been successfully introduced for a range of industrial processes, examples include: coffee decaffeination, isolation of some flavoring components from hops, fatty acid refining and production of herbal products. There is still much activity in the food, chemical and pharmaceutical fields in processing and product development with SCFs. SCFs fluids applied to food products have met with commercial acceptance as noted in the chemical engineering literature [9–11]. Recent research on the application of SCFs showed that they could be used as new reaction media for chemical and biochemical reactions, for synthesis of new materials and new catalyst supports such as aerogels, for special separation techniques such as chromatography using SCFs and extraction processes, and for particle formation and product formulation. There is a great variety of potential applications of SCFs in the industrial processing of fats, oils and their derivatives. Several industrial plants, which use different gases for isolation/ fractionation of components, are in operation for extraction of oils from seeds, fruits, leaves and flowers, which are further applied in food, pharmaceutical and cosmetic industry. The application of SFE in vegetable oil industry has been extensively investigated as an alternative to conventional refining, separation and fractionation processes. Several industrial plants are in operation also for extraction of spices for food industry and natural substances for use in cosmetics. In pharmaceuticals and biomedical areas, however, although there are commercial developments that use SCFs, industrial acceptance of SCFs produced products including particle technology has lagged, which is probably due to the necessity of clinical studies that are required. Extractions with SCFs will continue to play an important role in separation science and engineering. The promising new areas of SCFs application are functional foods from algae and microalgae, micronization and high-liquid free-flowing powders for foods, bioactive compounds and lipids. Much activity exists in the areas of energy conversion, biomass gasification, biofuels, biodiesel, wet algae conversion, and petroleum upgrading. The use of SCFs for heat transfer is a relatively new field, which has been recently intensively studied; however, the data about the efficiency and applicability of these features in practice is still scarce. The heat transfer and refrigeration properties of SCFs found also other applications, such as conductor cooling to obtain superconductivity effects, cooling of rockets and military aircrafts, of turbine blades, supercomputer elements, magnets and power transmission cables. SCFs have been also applied for sustainable biodiesel production. Biodiesel has become attractive recently due to its carbon-neutral effect and environmental benefits. Recently, SCFs have been applied for polymerization, swelling, impregnation, fractionation, purification and formation of powdered polymers and polymer processing with supercritical fluids. Frequently, it is necessary to extract small molecules (plasticizers, antioxidants, solvent and monomer residues, oligomers, stabilizers) from polymer matrices. SCFs can interact not only with polymers at temperatures higher than the softening point but also with polymers in the glassy state [12]. In the dyeing processes of the textile industry, the use of SCFs an alternative solvent instead of water based processes has been gaining much interest for environmental reasons. The environmentally friendly SCFs dyeing process does not require any water, dispersing agents or surfactants and also does not involve any drying stage after dyeing.

SUPERCRITICAL CARBON DIOXIDE AND WATER

The best known and widely employed SCF is carbon dioxide (CO_2) used industrially on a large scale for the decoffeination of coffee. CO_2 is environmentally friendly. Its contributions to the greenhouse gas inventory is negligible compared to that resulting from the burning of fossil fuels. It is nonflammable, nontoxic (at low concentration), and noncorrosive to common structural materials and is cheap. Supercritical CO_2 is becoming an important solvent due to its role in chemical extraction. The relatively low temperature of the process and the stability of CO_2 also allow most compounds to be extracted with little damage or denaturing. $SCCO_2$ has been used in polymer processing as solvent, anti-solvent or plasticizer for microcellular foaming, particle production, polymer blending, obtaining polymer composites, impregnation of polymers and solvent extraction. In the field of polymeric foams, $scCO_2$ was used as blowing agent (Figure 1).

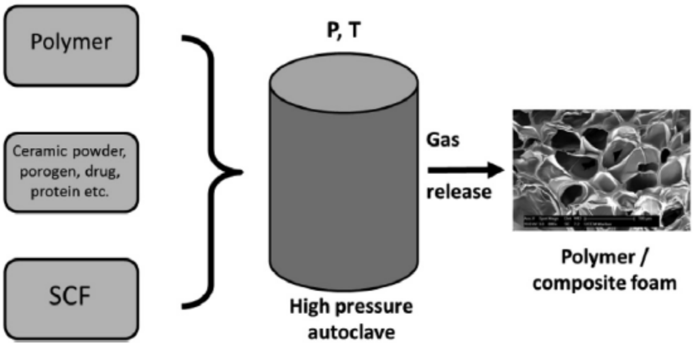

Figure 1 *The preparation of polymer and composite foams using supercritical fluid technologies*

In heating and ventilating systems, CO_2 is seen as a competitive fluid for heat pumps. The commercial EcoCute transcritical CO_2 water heater developed by Japanese manufacturers reached installation of more than 2 million units as of October, 2009 and has a remarkably high COP (coefficient of performance) of 3.5 or more than for heating hot water for domestic and commercial-scale. $SCCO_2$ is a superior mass-separation agent compared with liquid solvents because it can easily be recovered and recycled. The use of CO_2 as a mass separation agent not only makes the separation efficient, but more importantly, it protects worker health and thus is the beginning of a green chemical process. $SCCO_2$ can be used to reduce the viscosity of an ionic liquid mixture and this viscosity reduction can also allow reactions to occur. Some examples of classical organic synthetic procedures that have been successfully performed in $SCCO_2$ include: Friedel Crafts, Diels-Alder, Aldol, Claisen rearrangement, Michael addition and Kolbe-Schmitt reaction in $scCO_2$ media [13-15]. $SCCO_2$ has provided a successful reaction medium for the production of some polymers including: amorphous fluoropolymers, polysiloxanes, some hydrocarbon polymers, polybutylacrylate and polystyrene [16]. The use of $scCO_2$ to produce polymers provides polymers free of solvents, in many cases also water, that are required for many applications. CO_2 is a good solvent for many non-polar and some polar molecules with low molecular weights but it is a very poor solvent for most macromolecules at normal operating conditions. Although the solubility of most polymers in CO_2 is extremely low its, solubility in many polymers is substantial. This can lead to the enormous decrease of the polymer glass transition temperature at modest pressures. The plastification of polymer materials using CO_2 plays a key role for processing, purifying, extracting or foaming of thermally sensitive materials. Particle design using $scCO_2$ is demonstrating significant potential in applications involving the pharmaceutical, cosmetic and specialty chemical industries. The dyeing of fabrics using $scCO_2$ as a dye solvent has been the focus of increasing research. $scCO_2$ emulsion extraction of the organic phase has been successfully applied to the production of microparticles and microcapsules for controlled drug delivery. The general idea of electrospinning in $scCO_2$ is to produce the fiber in a high pressure vessel filled with $scCO_2$, enhancing solvent extraction and obtaining also porous fibers. Levit at al. [17] demonstrated the feasibility of this process using two electrodes immersed in $scCO_2$ located at a distance of 3 mm. In presence of $scCO_2$, a polymer can show a reduced viscosity (and surface tension) due to the capacity of CO_2 of penetrating inside the polymeric structure; at these conditions. Polydimethylsiloxane (PDMS) and PLA fibers were electrostatically produced without the use of a liquid solvent, processing the polymers at 40°C and 14 MPa. Supercritical water (SCW) is also used as solvent, especially in last year. It has properties differing considerely from those of $scCO_2$. Its critical temperature is twice and its critical pressure almost three times higher. Its ranges of application are about 400 – 600ºC and 30 – 100 MPa. Water at ambient conditions is a polar solvent of polar molecules. It is a good solvent for polar compounds and salts. At supercritical conditions at e.g. 550ºC and 20 MPa, water behaves as a nonpolar organic solvent like pentane with good solubility for organic components and gases and low solubility for salts. Generation of hydrogen and other compounds that may be used as fuel is one of the most studied applications of SCW. Recently, hydrogen production from wet biomass and organic compounds in sub and supercritical water has gained significant attention. The advantages of SCW gasification over conventional biomass gasification (such as steam reforming) refers to the possibility of processing feedstock with high water content and the generation of pressurized gases, which simplifies their transportation and further use. However, there are a number of limitations to the SCW gasification process, such as the formation and deposition of carbon, which may cause plugging of the reactor or deactivation of the catalyst, and the specific requirements for reactors and other high pressure equipment. Supercritical water oxidation (SCWO) initially was seen as the best method to destroy toxic and dangerous compounds and to clean liquids and solids. Process development and various applications soon showed that several problems are connected with SCWO including salt precipitation, plugging, and severe corrosion. Although the technology has matured, it still has challenges related to corrosion and solids handling although some of these issues are being addressed through reactor design [17]. SCW can be used to develop material formation processes that operate at low temperatures (ca. 400ºC) as opposed to present industrial processes that operate at high temperatures (ca.

1200ºC). Supercritical water gasification (SCWG) can convert organic waste streams from industrial activities into energy. SCW gasification technology can potentially gain energy in the form of combustible gases from organic waste streams. Along with energy gain via gas production, it also minimizes pollution from waste stream and as a result reduces its potential noxious and dangerous effects. Thus, SCWG of waste stream is a future perspective /potential solution to solve two problems at once. SCWG is a thermochemical conversion process, which includes also pyrolysis, liquefaction, dry gasification and combustion. Among them, gasification is one of the most favorable processes since the products can be used for different markets such as heat, electricity and transportation. During SCWG, the organic matter decomposes into char, tar, gas, or other intermediate compounds. These products are subsequently reformed into gases such as CO, CO_2, CH_4 and H_2. Gasification in SCW involves mainly thermal decomposition and reforming reactions. The main disadvantages of the process are high capital and operating costs. The required extreme temperatures and pressures cause higher costs in the system leading to the need for special materials and operating equipment. In addition to water and CO_2, compounds such as ethane, propane, methanol, ethanol are also used in their supercritical phase for certain applications (extraction, chemical reactions).

CONCLUSION

SCFs are already applied in several processes developed to commercial scale in industries. CO_2 and water have been the most used SCFs. Many natural compounds, such as vitamins, aromas, natural pigments or essential oils, are extracted with SCFs, thus avoiding the use of organic solvents and of high temperatures. SCFs were proposed for different applications in the energy field. The practical application of SCFs requires the design of technical components and plants for production. Compared with other technical systems, SCFs production plants are relatively simple from the mechanical and control points of view. SCFs processes are also energy efficient, particularly when they can replace organic solvent based processes that at some stages require removal of organic solvents by energy consuming procedures. The development of sustainable processes is one of the aims of the SCFs technologies.

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