The Journal of Supercritical Fluids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Recovery of valuable components and inactivating microorganisms in the agro-food industry with ultrasound-assisted supercritical fluid technology

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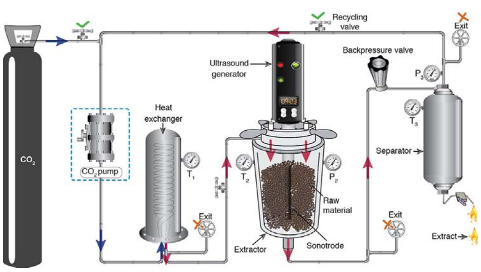
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Ultrasound
Supercritical fluids
Carbon dioxide
Assisted extraction
Valuable components
Microorganism inactivation

ABSTRACT

Food industry is increasingly interested in replacing conventional processes of plant extraction, as well as microbial inactivation, by alternative, greener and cheaper techniques. In many cases, chemical extraction processes are hindered by several drawbacks such as the use of chemical solvents, which is associated with many health and environmental issues. Furthermore, the use of high temperatures to improve and/or accelerate the processes, which may affect and degrade the thermolabile compounds, is usually required. Among the most promising techniques that could be competitive to the current extraction methods of molecules from plant matrices and microbial inactivation of food products, ultrasound assisted supercritical fluid extraction has taken great interest. This non-exhaustive review, covering the last 20 years, gives a critical commentary on the main published results using this emerging technology. Promising prospects opened up by new applications are described, without omitting the main limitations still to be overcome for a harmonious industrial development of these technologies.

1. Introduction

Traditionally, the recovery of valuable components (e.g., polyphenols, sterols, colorants, seed oils, etc.) from plant matrices is mainly based on pressing and/or liquid solid extraction (e.g., maceration, percolation, decoction, infusion, etc.), which consists of using hot water and/or organic solvents such as hexane, ethanol, etc. However, although reaching high extraction yields in some cases, undesirable consequences such as quality deterioration and degradation of valuable compounds may occur [1,2]. For instance, oil extraction from canola seeds is industrially based on several pre-processing steps followed by pressing, expelling most of the oil but also giving meal with ≈ 20% wt oil, which is then extracted meaning percolation with hexane. The recovered oil is then refined via a sequential process including i) degumming, ii) acidification and neutralisation, iii) washing, iv) bleaching, v) winterization, and vi) deodorisation. Besides the use of

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https://doi.org/10.1016/j.supflu.2017.12.012
Received 1 September 2017; Received in revised form 8 December 2017; Accepted 8 December 2017
0896-8446/

Please cite this article as: Koubaa, M., The Journal of Supercritical Fluids (2017), https://doi.org/10.1016/j.supflu.2017.12.012

toxic solvent (hexane) that is associated with health, environment, and economic issues, 1) the whole process requires high energy consumption (approximately 40 and 10 kWh/ton of canola seed processed, for oil extraction and oil refining, respectively) [3], and 2) oil recovered by hexane is of poor quality due to the degradation of thermolabile compounds, and the low solubility of high-added value compounds (i.e. polyphenols) in hexane. This example and others have incited both researchers and food industries to investigate and evaluate novel extraction or valorization processes that meet the requirements of a green process concept. This concept aims to avoid/minimize the use of organic solvents, along with other benefits such as shortening the treatment time, decreasing the processing temperature, intensifying the mass transfer process, increasing the extraction yields, preserving high extract quality, and reducing the energy consumption [4,5]. These novel extraction processes have been classified as emerging, alternatives, innovative, or non-conventional technologies and are including a wide range of techniques (e.g., ultrasound-assisted extraction, supercritical fluid extraction, microwave-assisted extraction, high-pressure processing, pulsed electric fields, high voltage electrical discharges, gas assisted mechanical expression, etc.) [6–8]. Besides the features cited above dealing with the green extraction concept, some of the non-conventional technologies allow pasteurising or sterilising the extraction medium and provide safer products by inactivating the microbial burden. For instance, it was widely known that high pressure processing [8–10], pulsed electric fields [11–13], ultrasounds [14], supercritical fluids [15], and other technologies are able to inactivate contaminating microorganisms including in some cases viruses [16,17]. This ability allows further reducing the heating steps (e.g., for sterilization, pasteurization), which minimizes the energy consumption and preserves the most thermolabile substances from degradation. Combining simultaneously a conventional process with a non-conventional one for further efficiency has been investigated through different research works. For instance, gas assisted mechanical expression (GAME) involving the combination of mechanical expression and supercritical fluid extraction has been investigated, and demonstrated interesting results compared to individually applied processes [18–20]. Other works have been focused on combining simultaneously two non-conventional extraction processes, such as the use of ultrasound technology assisted by supercritical carbon dioxide (sc-CO_2) as solvent. This technique called ultrasound- or ultrasonic- assisted supercritical fluid extraction (US-SFE) was successfully applied to extract seed oils, antioxidants and high-added value compounds, as well as to inactivate microorganisms. In fact, the use of sc-CO_2 as solvent instead of other organic solvents (e.g., hexane) contributes to limit and minimize the pollution hazards, although in the case of polar molecules extraction, adding co-solvents to CO_2 (i.e., ethanol) could be required. Ultrasounds, on the other hand, allow the extraction of both polar and non-polar molecules. Therefore, combining these two technologies is a key point to further enhance the mass transfer of targeted compounds from solid matrix to sc-CO_2 [21]. This review is thus devoted to discuss for the first time 1) the current insights into the use of US-SFE as emerging technology for the recovery of intracellular components from plant matrices, and its potential to efficiently inactivate microorganisms, in this latter case the process will be noted US-SFI and 2) the limits to be overcome towards the industrialization of this technology.

2. Current state of ultrasound assisted supercritical fluid extraction (US-SFE)

Ultrasound assisted extraction (UAE) is an advantageous alternative to conventional extraction techniques (liquid/liquid extraction (LLE), solid phase extraction (SPE), and Soxhlet). When a large negative pressure is applied to a liquid, sonochemical phenomenon associated with acoustic cavitation and the formation of micro-bubbles occurs (Fig. 1), constituting thus the base of UAE [22]. When growing to unstable size, the created bubbles collapse violently, which is associated with the release of an intense local energy with important chemical (i.e., free radicals) and mechanical effects (i.e., micro-jets) [23]. When bubble collapse phenomenon occurs, increased temperatures and pressures to several thousand degrees and more than 1000 atmospheres, respectively, are generated. Many parameters are affecting the extraction efficiency, including the effects of solution, power, frequency, sonication time, and the type of treated material. These parameters were recently reviewed [24].

UAE is a promising technique, with various benefits, that was widely applied to extract valuable compounds from plant matrices [25]. UAE is harmless for operators, safe to use, and with low maintenance costs. Therefore, it has been acquired by several industries to replace the conventional extraction techniques (i.e., LLE⋯), as it could be operated rapidly in a broad range of solvents for large-scale preparations suited for industrial purposes [26,27]. For instance, industrial scale-up extraction of polyphenols from apple pomace was reported in the literature, demonstrating relevance and more sustainable technology to current conventional methods [28,29].

UAE is usually using liquid solvents (e.g., water, ethanol, methanol, DMSO, etc.) [30–33]. However, during the last decade, the use of supercritical fluids as solvent for UAE experiments has drawn more attention [21,34–36]. The use of supercritical fluids instead of liquid solvents allows obtaining pure extract without subsequent removal of the extracting solvent, and often enhances the extraction yield due to the supplementary effect of pressure on the solute solubility. The most widely supercritical fluid used is carbon dioxide (sc-CO_2). This fluid takes its advantages from the relatively low critical point of CO_2 (critical temperature 304.2 K; critical pressure 7.38 MPa), making it suitable to extract thermo-sensitive compounds [37]. Furthermore, the non-flammability, non-toxicity, low cost, and availability at good purity, make it preferred supercritical fluid for industrial applications. Generally, sc-CO_2 is used to extract hydrophobic or slightly hydrophilic compounds. However, co-solvents or modifiers (e.g., ethanol, methanol, ethyl acetate, etc.) could be added when the extraction of more hydrophilic compounds is targeted. Many industrial applications for the extraction of valuable compounds using sc-CO_2 currently exist [38]. Among them the extraction of nicotine from tobacco as well as caffeine from coffee grains and tea leaves are the most commonly known [39].

The use of pressurized water (either sub- or supercritical) has also been reported for the extraction of several molecules from plants (e.g., phenolic and antioxidant compounds [38,40]). It can also be used to produce biofuels from agri-food residues or non-food plants [41,42].

2.1. Extraction of oils and fats using US-SFE

Mechanical expression and/or hexane extraction is nowadays the most commonly used process to extract oil from oilseeds (soybean, canola, sunflower, cotton, linseed, etc.). At industrial or semi-industrial scales, these processes could be combined (i.e., continuous mechanical pressing (expelling) with continuous solvent extraction, and batch hydraulic pressing followed by solvent extraction) [43,44]. After total defatting, the resulting meal is generally used for animal feed or aquaculture production [45]. The need to minimize the use of toxic hexane for oil extraction has led both food scientists and food industry to develop and evaluate novel "clean" extraction processes using alternative solvents with the numerous advantages cited above. As alternative to conventional processes based on mechanical expression and/or hexane extraction of vegetable oils, US-SFE was evaluated. Fig. 2 shows a schematic illustration of US-SFE equipment used at laboratory scale for the extraction of intracellular compounds.

Many works have been cited in the literature to discuss the feasibility of using US-SFE for vegetable oil extraction, and some of them are summarized in Table 1.

As shown in Table 1, different vegetable materials were used for investigation such as particle almonds [35], passion fruit (*Passiflora edulis* sp.) seeds [47], etc. The effects of operating conditions