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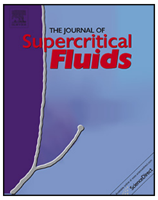

Sub- and supercritical fluid technology applied to food waste processing

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ABSTRACT

Food industries produce annually billions of tons of non-edible residues, which can cause pollution, management and economic problems worldwide. Environment damages such as water, soil and air contamination are global concerns, and are the main reason for the development of different strategies to use agricultural and industrial residues as source of new products. To apply the food wastes, environment-friendly processes are recommendable, in which renewable sources are used and the products do not offer environmental risks. Sub- and supercritical fluid technologies can meet such requirements when using green solvents. This review gives an overview of the potential of food residues as raw materials for the production of nutritionally interesting compounds, chemicals and biofuels. Aiming to recover components from food residues, processes in which sub- and supercritical technologies can be used, in single or combined ways, are discussed. Several applications are reported.

1. Introduction

In recent decades, food wastage has been considered a serious social, economic and environmental problem. The spoil of food products represents a missed opportunity to mitigate environmental impacts, but also to improve global food security and the use of resources from food chains [1]. Agriculture and cattle production, postharvest handling, storage, processing, distribution and consumption are activities that produce wastes along the food supply chain. According to the Food and Agriculture Organization (FAO) [1,2] data, approximately one-third of all food produced for human consumption in the world is lost or wasted, which equates to approximately 1.6 billion tons per year. Among this volume, 54% are lost in production steps, postharvest handling and storage, and other 46% are caused by steps downstream of entry in the industry, i.e., processing, distribution and consumption. In weight basis approximately 30% of cereals, 40–50% of root crops, fruits and vegetables, 20% of oilseeds, meat and dairy products, and 35% of fish are lost.

This wastes which include liquid, solid and gaseous residues are the most abundant, cheap and renewable resources on earth. Many of these residues can cause pollution problems, and be an environmental hazard when they are not managed properly [3]. Decomposition processes of food wastes produce gases such as methane, which contribute to the greenhouse effect, and liquids (sludge) that contaminate soil, groundwater and springs. Water used in unit operations and cleaning processes of dairy and meat industries have organic load enough to cause loss to aquatic life and compromise the quality of water streams. The gases released by food industries complement those from fossil fuels to raise problems such as greenhouse, ozone layer depletion, atmosphere acidification and acid rain, besides reducing air quality and causing human health problems especially respiratory diseases.

The benefits of reusing wastes are not environmental. The application of techniques aiming the efficient use of industrial food wastes can add value to these materials that have little or no economic value. The valorization of food wastes has been receiving special attention in recent years. Some studies have explored the conversion of wastes to food ingredients and drug components [3,4]. Other researches indicate that food wastes are sources of several important components, such as polyphenols, fatty acids and carotenoids [5–10], all of high nutritional value, which have many health benefits, as antioxidant, anticancer, anti-inflammatory, antiviral, neurosedative activities, among others [5,11]. In addition, several researches have reported the use of food wastes to produce fuels such as bioethanol, biodiesel and hydrogen [12–15]. Although in the last 20 years researchers have reported that several food wastes are potential sources of interesting compounds, the vast majority of them is still not exploited at industrial scale to produce the mentioned valuable compounds [11].

The reuse of food wastes as raw materials can be achieved by directly using the wastes, converting them by means of several

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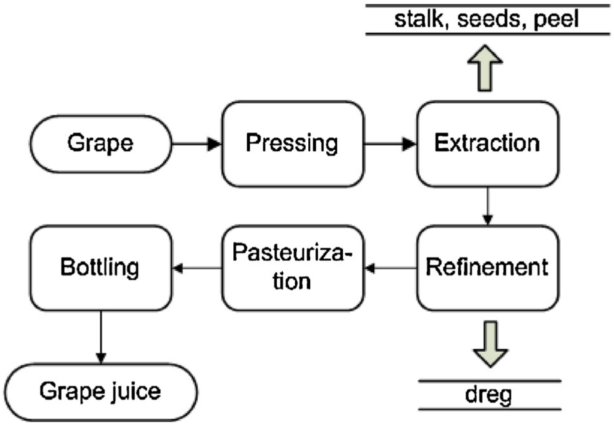

Fig. 1. Simple flowchart f grape juice and wastes production.

processes, or by fractionating them into their components. Whatever the treatment that these raw materials will undergo, there is always a need for environment-friendly techniques. In this context, technologies employing fluids at high pressures (supercritical or subcritical states) are presented as good alternatives, mainly when generally recognized as safe (GRAS) fluids are applied.

The aim of this review is to discuss on the actual applications of sub- and supercritical technologies, and future perspectives to obtain interesting compounds from food wastes by means of novel methods used in single or combined ways.

2. Food wastes

Food industries produce several wastes with potential to be reused. Some segments of food industries, whose processes offer opportunities for material reuse, are shown in this section. Attention is given to waste reuse techniques where sub- and supercritical are applied.

2.1. Fruit and vegetable processing

The industrial processing of fruits and vegetables includes manufacturing of many products such as juice (fresh and concentrated), purees, frozen pulp, fermented drinks, jellies, candies, ice cream, among others. According to Sousa et al. [16], it is estimated that 30 to 40% (w/w wet basis) of all fresh fruits processed are discarded as waste. The types of wastes depend on the applied process and the kind of fruit, but in general they consist of peel or shell, seeds and bagasse, as can be observed in Fig. 1, in which the extraction process of grape juice is exemplified. Despite the large availability of studies approaching the advantages of using fruit wastes for adding value, it is common to see wastes being used as animal feed or fertilizer to the soil in agriculture.

Indeed, the chemical composition of fruit and vegetable wastes enable their better exploitation. These wastes are sources of valuable compounds such as minerals, vitamins, sugars, aromatic compounds, carotenoids, phenolic compounds, fibers, etc. Several of these compounds are synthesized in the secondary metabolism of plants to act in their protection against environmental adversities [8]. In human nutrition, they are considered bioactive compounds responsible for antioxidant, anticancer, anti-inflammatory, antiviral, neurosedative activities, among others.

The recovery of bioactive compounds may provide a wide range of new commercial products, as well as raw materials for secondary processes, substitutes for traditionally used ingredients, or ingredients of new products [17]. According to Wijngaard et al. [11], the world market for polyphenols and carotenoids is significant. The current worldwide marketing of polyphenols was estimated by these authors at 200 million dollars, while the marketing of carotenoids in 2010 made about 1.07 billion dollars. However, in order to explore these resources from industrial food wastes, commercially viable strategies for the extraction and provision of these compounds need to be developed.

Several researches have concentrated their efforts in the recovery and processing of compounds from fruit and vegetable wastes. In this context, extraction, fractionation/purification and encapsulation techniques are reported. Regarding extraction, an important step in the recovery of bioactive compounds, besides conventional methods, various new techniques have been employed to obtain bioactive compounds from food wastes [4]. According to Wijngaard et al. [11], pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) are extraction techniques that are gaining popularity due to their ability to increase target molecule specificity and reduce waste solvent production.

However, SFE has some characteristics that limit its application. This technique is appropriated to extract nonpolar substances, thus it does not present good performance to recovery compounds from wastes rich in water, which is most of the cases. To overcome the problem of polarity PLE is a good alternative, since with the use of solvents such as water and ethanol, the range of polar compounds and intermediate polarity can be covered. About wet wastes, when the target compound has affinity with CO_2, previous treatments such as dehydration need to be applied. On the other hand, when the target compound is polar, PLE can be directly applied on wet samples.

Research papers published in the last five years in which supercritical (SCFs) and subcritical fluids were used to obtain compounds from fruit and vegetable wastes are shown in Table 1. It can be observed that most of the cited works were performed using plant wastes to recover phenolic compounds and fatty acids. The implicit objective of these works is the search for substances that have some biological activity for use in therapeutic medicaments, cosmetics or food ingredients. As can be observed in Table 1, fatty acids from fruit wastes are recovered mostly by SFE at temperatures between 40 °C and 60 °C and pressures from 10 to 30 MPa. The main reasons to use these parameter ranges are the thermal protection of thermally sensitive compounds and their solubility in CO_2. Low temperatures (just above the critical point of CO_2) and high pressure increase CO_2 density, and then solubility of nonpolar compounds also increase. Phenolic compounds are mainly obtained by PLE at temperatures around of 100 °C and pressures nearly 10 MPa. Solvents as water at temperatures above 100 °C and high pressures remain in the liquid state, and consequently higher yield values of thermally stable compounds are reached.

The tunability of the solvent power of carbon dioxide with pressure allows isolating target compounds during the extraction or fractionation of products obtained on the extraction procedure. An example of isolation during the extraction of food wastes is given by Seabra et al. [18]. In this work the authors performed fractionated high pressure extractions from elderberry pomace using supercritical CO_2, followed by enhanced solvent extraction (ESE) with diverse CO_2/ethanol/H_2O solvent mixtures and different pressures. The authors observed that the sequential process had a substantial effect on the extract's yield and composition. Regarding the fractionation of target compounds after the extraction, Zibetti et al. [19] obtained and purified by supercritical fluid chromatography (SFC) some antioxidant compounds from plant material and plant waste of rosemary, and achieved products with different compositions. First, the supercritical fractionated rosemary extract with different composition was obtained from the leaves (higher concentration of eucalyptol—compounds with proved antimicrobial activity), and next, a potent antioxidant, rosmarinic acid, was successfully extracted from waste produced from the supercritical