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SUPERCRITICAL CO_2 EXTRACTION – A NEW PERSPECTIVE IN THE UTILISATION OF FOOD INDUSTRY BY-PRODUCTS

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Abstract

The food industry, same as any other industry, aims to utilise raw materials as efficiently as possible in the production process, but it also tries to create minimum amounts of waste, where waste is not necessarily "waste", but a by-product or a raw material for some subsequent process. Today there is great interest in utilising food industry by-products for various purposes because they contain many potentially useful substances, and they could become significant raw materials in the production/development of new products due to that fact. This paper places special emphasis on the influence of modern green extraction techniques, like supercritical CO_2 extraction, on the utilisation and extractability of certain biologically active components from selected by-products which have an application in food, cosmetics, and pharmaceutical industries.

1. INTRODUCTION

The human awareness regarding the protection of nature and the environment is growing daily. Sustainable development, one that meets today's requirements and does not jeopardise the needs of future generations, has become an important issue, and all of the research on reducing the use of toxic chemicals, conserving energy, and managing waste and by-products is welcome at the international level. All over the world, there is research dedicated to this area, demanding that each researcher follows the tradition of sustainable development directed at a certain area, which also includes long-term decision making in the agriculture and food production sectors. The high quality of food production and the commitment to environmental protection has contributed to the successful marketing of agriculture and food products (Perretti, 2006). Large quantities of solid (shells, peels, seeds, leaves) and liquid waste (wastewater) are created during the processing of raw materials from plants in the food industry every year, and their storage, processing, or management present a serious ecological and economic problem. The large quantities of by-products created every day are mostly managed through disposal sites or by making cattle fodder. Therefore every industry, including the food industry, has the goal of fully using their raw materials in the production process, while creating as little waste as possible, where waste is not necessarily "waste", but a by-product or a raw material in some future process. Today there is great interest in using by-products from the food industry for various purposes because they contain many potentially useful substances, and they could represent significant raw materials in the production/development of new products (Schieber et al., 2001; O'Shea et al., 2012).

The use of food industry by-products has become extremely interesting because they represent cheap and nutritionally valuable raw materials, and that is enough to affect the reduction in waste. From the economic standpoint, large amounts of by-products, especially grape pomace and olive pomace, are still not being used in the best possible way in the Republic of Croatia. Furthermore, there is no competition on the domestic market in the area of highly profitable final products that could be created from those initial raw materials, and they are used for some of the most highly sought after food, cosmetics, and pharmaceutical products in the world.

Modern extraction techniques, like supercritical CO_2 ($SC\text{-}CO_2$) extraction, that represent new, mild, and selective food processing technologies, with the purpose of environmental protection, are becoming more prominent in the world. In recent years, this technique has been applied in the extraction of potentially useful substances from food by-products (**Table 1**).

2. SELECTED FOOD INDUSTRY BY-PRODUCTS

2.1. Grape pomace

Grape pomace created in the process of wine production, as well as olive pomace created in olive oil production, are just some of the potentially valuable by-products that could be successfully used in the production of some functional food products, but also in creating various extracts rich in active substances (Palma and Taylor, 1999; Ibáñez et al., 2000; Marti et al., 2001; Louli et al., 2004). Grape pomace represents a major problem due to its quantity and properties, primarily the leftover acids that make processing, usually composting, more difficult. If the pomace is not treated properly, it can represent a serious risk for the environment, starting with surface and deep pollution, to unpleasant odours created if it is left unprocessed. Na-

Table 1. Selected examples of SC-CO_2 extraction of high-value food industry by-products of plant origin

Sample	Extraction parameters						Analyte	Reference
	Temperature (K)	Pressure (MPa)	Time (h)	Flow rate (g/min)	Co-solvent (%)	Particle size (mm)		
Grape seed	313	16 18 20	---	10.2	---	0.75	Grape seed oil	Passos et al. (2008)
Grape seed	310 353	25	7	---	---	1.125 0.638 0.363	α-tocopherol enriched oil	Bravi et al. (2007)
Grape seed	313 323 333	20 30 40	1.5	32.33	---	0.380	Grape seed oil	Jokić et al. (2016)
Grape pomace	308 328	10 40	3	0.8	Ethanol (5)	0.165 0.261 0.319	Resveratrol	Casas et al. (2010)
Grape pomace	318	10 15 25	---	18.3	Methanol (5)	---	Phenolic compounds	Louli, Ragoussis and Magoulas (2004)
Grape skin	313	15	0.25	2	Ethanol (7.5)	---	Resveratrol	Marti et al. (2001)
Elderberry pomace	313	21	1.6	---	CO_2 (0-90) Ethanol (0.5-100) H_2O (0–95)	---	Anthocyanins	Seabra et al. (2010)
Apricot by-products	316–350	13.3–47.3	1.5	1	Ethanol (2–28)	0.07-0.6	β-carotene	Sanal et al. (2005)
Apricot seed	313-343	30-60	---	1-5	Ethanol (0-3)	0.425-1.5	Apricot seed oil	Özkal, Yener and Bayındırlı (2005)
Peach seed	303 313 323	10 20 30	2.5	8.3	Ethanol (2.5)	0.25-0.35	Peach seed oil	Mezzomo et al. (2010)
Tomato skin	313-373	20-40	1.5	1-2	---	---	Lycopene	Chun et al. (2009)
Tomato skin	313 343	25 45	0.17-0.33	6.38	Ethanol (5.15)	0.5-1	Lycopene	Kassama, Shi and Mittal (2008)
Tomato skin and seed	313 333 353	30 38 46	---	---	---	0.3 0.4 0.6	Carotenoids, tocopherols sitosterols	Vagi et al. (2007)
Apple and peach pomace	313–333	20–60	0.17-0.67	2	Ethanol (14–20)	0.638	Phenolic compounds	Adil et al. (2007)
Cherry seed	313-333	18-22	---	---	---	1.25-2.25	Cherry seed oil	Bernardo-Gil et al. (2001)
Orange peel	293 – 323	8-28	---	8.3-58.3	---	0.1-10	Essential oil	Mira et al. (1999)
Orange peel	313	10	1	29.3	---	0.324	Essential oil	Jerković et al. (2015)
Citrus peel	333	9.5	0.75	---	Ethanol (15)	---	Naringin	Giannuzzo et al. (2003)
Olive pomace	323	35	3	33	Ethanol (10)	---	Tocopherol	Ibáñez et al. (2000)
Olive pomace	313-323	10-30	2.5	1.8-2.7	Ethanol (10)	0.30-0.55	Olive oil	De Lucas, Rincon and Gracia (2003)
Cocoa shell	323 358	15-45	---	---	---	2-4	Theobromine	Rossi (1996)
Hemp pressed cake	313 323 333	20 30 40	1.5-7.5	11.7 29.1 46.7	---	---	Hemp oil Defatted cake	Aladić (2015)
Rice by-products	353	68	---	1.082	---	---	Tocochromanols Oryzanols	Perretti et al. (2003)

mely, large quantities of pomace attract vermin and flies, and can lead to occurrences and spreading of various diseases. Tannin solutions and solutions of other wine pomace components, which are separated during resting, can cause the reduction of oxygen levels in the soil, but they can also penetrate into the soil and groundwater (Voća, 2010). If the pomace is used as fertilizer in vineyards, the soil in the vineyards becomes acidic over time, which is also a problem. Because of that, more and more attention is dedicated to processing waste or by-products from wineries that mostly consist of solid bio products (skins, stems, and seeds), which comprise on average 20-30% of the mass of the processed grapes, and 15% of the solid waste are grape seeds. Its use in the food industry may contribute to the reduction of production costs, as well as to the development of new products. The extraction process using SC-CO_2 can be used, for example, to completely extract oil from grape seeds, which is very significant in industrial processes, because it creates minimal losses in the production process and the full utilization of the initial raw material (Jokić et al., 2016). Oil obtained by using SC-CO_2 extraction is greenish-yellow in colour with a characteristic aroma; it is rich in vitamin E and can be used for cooking, medicine, and in pharmaceutical and cosmetic industry. The proportion of linoleic acid is higher when compared to any other oil, like sunflower or corn oil, which makes grape seed oil suitable for storage because it is highly stable. Defatted grape seed flour, which is created as a by-product of SC-CO_2 extraction, can also be used for other purposes (in making enriched extruded products, bakery industry, etc.). Grape seed pomace is also characterised by high phenolic compounds content due to low extraction during the wine production process. In the total amount of phenolic substances that can be extracted from grapes, 10% is in the pulp, 60-70% in the grape seeds, and 28-35% in the grape skin (Palma and Taylor, 1999; Murga et al., 2000; Louli et al., 2004) so the tablets and capsules based on extracts rich in polyphenolic compounds with antioxidant properties could be developed.

2.2. Olive pomace

Another by-product created in the process of olive oil extraction is olive pomace that includes skins and seeds. By-products of olive processing are rich in antioxidants, and various extraction techniques are used to isolate them from the plant material (Ibáñez et al., 2000; De Lucas et al., 2003). The use of the appropriate green technology, such as SC-CO_2 extraction, can result in the production of oil from olive pomace, where the quality and utilization of oil would be significantly higher than with using the standard pressing procedure. The goal is to get completely defatted olive pomace created as a by-product of SC-CO_2 extraction, which could then be used for the development of new functional products, i.e. in the process for the production of corn snack products enriched with defatted pomace.

2.3. Apricot kernels

Apricot kernels as by-products of processing are a valuable source of amygdalin (in literature often referred to as vitamin B17). Aside from that, apricot kernel seeds contain a high proportion of oil rich in mono- and polyunsaturated fatty acids, and a series of ingredients with lower proportions, like tocopherols and phenolic compounds (Turan et al., 2007). The oil extracted from apricot kernels using SC-CO_2 may have significant applications in cosmetics.

2.4. Cherry seeds

Cherry processing generates significant amounts of kernels for which there is no further use. However, since cherry seeds are a valuable source of oil (which can be obtained by SC-CO_2 extraction) rich in essential fatty acids, as well as in compounds like carotenoids, tocopherols, squalene, phytosterols, etc., they can be utilised as a potential natural source of nutraceutical ingredients in the pharmaceutical industry (Bak et al., 2009; Górnas et al., 2015).

2.5. Citrus peel

Three main by-products of citrus are dry pulp, molasses, and citrus oil (from the peel). Essential oils from citrus have many applications as aromas and for aromatising various products (Kesterson and Hendrickson, 1958). Essential oils can be produced from selected varieties of citrus peels by using various extraction techniques, where SC-CO_2 extraction is the preferred technique (Jerković et al., 2015).

2.6. Coffee processing by-products

By-products of coffee processing, such as mucilage and parchment, have been less studied, despite the fact that they contain important bioactive components (Esquivel and Jimenez, 2012). They can be an alternative source of natural antioxidants. Cocoa shells, which are removed during the processing of cocoa beans (*Theobroma cacao* L.), represent at least 10% of the weight of cocoa fruit (Owusu-Domfeh, 1972). In countries that produce cocoa beans, processing of such waste can provide an economic advantage and reduce the extent of environmental problems. The cocoa bean shell is also a potential source of theobromine (Hartati, 2010), which can be extracted using SC-CO_2, since it has a great pharmacological function, it is a powerful diuretic, it promotes diuresis and stimulates circulation to the kidneys, and consequently helps to remove harmful substances from the urinary tract.

2.7. Tomato waste

A significant amount of waste is accumulated during the tomato canning process; it consists of seeds, skins (peel), and a small quantity of pulp (Avelino et al., 1997). Some of the created by-products are mostly used as additives to cattle fodder, and the unused remains are not managed, and as such represent a problem for the environment (collection, disposal, and processing). The oil that can be created from tomato seeds by applying SC-CO_2 is attracting interest because of the abundance of unsaturated fatty acids, especially linolenic acid (Roy et al., 1996), as well as lycopene, a carotenoid responsible for the red colour of the tomato, the highest concentrations of which are in the skin (Favati et al., 1997; Baysal et. al., 2000; Ollanketo et al., 2001; Rozzi et al., 2002).

2.8. Oilseed cakes

During the production of oil from oilseeds, it is of great importance to obtain higher extraction yields and oil quality. After oilseed processing, the remaining cake is commonly used in animal nutrition (Sorin-Stefan et al., 2013). The by-product (cake) from the process of oil pressing has great potential applications in food production due to the high content of residual oil, protein, fibre, minerals, and other substances. By using SC-CO_2, it is possible to get a totally defatted cake (Aladić, 2015) with the potential application for other purposes (i.e. in the enrichment of extruded products, bakery industry, etc.).

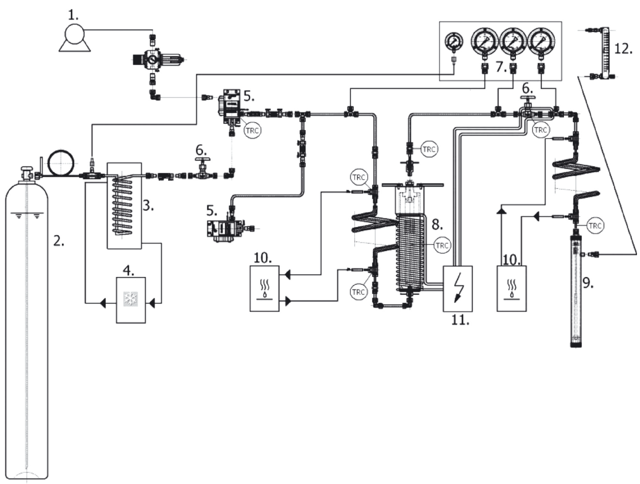
3. SUPERCRITICAL FLUID EXTRACTION

With the discovery of supercritical fluids, toxic and ecologically unacceptable organic solvents are being gradually replaced. Supercritical fluid extraction (SFE) is an innovative technology and it represents an excellent alternative to standard extraction procedures using organic solvents. Additional reasons for that are the numerous advantages of supercritical fluids, like better diffusion, lower viscosity, and lower surface tension, which enables them to better penetrate the material used for extracting the targeted substance. In addition, this procedure enables high selectivity and solvent capacity control of the desired component in the supercritical fluid, by changing the pressure and temperature, and simply removing the solvent from the extracts. Furthermore, SC-CO_2 is considered completely safe for industrial application and food processing. This energy efficient process is considered as "clean technology", because it does not create secondary products that are harmful for the environment and as such is very significant for the food industry (Brunner, 2005; Wang and Weller, 2006; Reverchon and De Marco, 2006; Abbas et al., 2008; Sahena et al., 2009; Temelli, 2009; Cvjetko Bubalo et al., 2015).

In the last few decades, this powerful separation process has drawn an increasing interest in commercial application, particularly due to its technical and environmental advantages compared to the current classical extraction methods using organic solvents. Extracts obtained using SC-CO_2 as the extraction solvent are solvent-free / without any trace of toxic extraction solvents, and are thereby highly valued (Jokić et al., 2014a). CO_2 is an adequate solvent for the extraction of lipophilic non-polar constituents. As such, it has a low affinity to polar compounds. This is one of the main drawbacks of extraction with SC-CO_2. The low polarity of SC-CO_2 can be overcome by employing polar modifiers (co-solvents, mainly ethanol and methanol) to change the polarity of the supercritical fluid and to increase its solvating power towards the analyte of interest. As such, according to Herrero et al. (2010), the addition of a low percentage of ethanol or methanol (1-10%) to CO_2 expands its extraction rates to include more polar analytes.

3.1. HM-SFE System

More than a few hundred commercial plants in the world today are using SFE in different fields (Jokić et al., 2015). The handmade supercritical fluid extraction (HM-SFE) system enables extraction in an inexpensive way. The obtained extraction yields and composition are very similar to those obtained by a commercial SFE system (Jokić et al., 2015; Jokić et al., 2014b). Just like a commercial SFE system, the HM-SFE system is composed of various components that need to be in tune in order to achieve the optimal extraction process. Parameters such as temperature, pressure, and fluid flow rate need to be monitored and controlled in order to enable an efficient and economical extraction process. Furthermore, the system must contain safety features with the possibility of an emergency system shutdown in the event of system failures. When designing the device, it is crucial to pay attention to several factors that make the device safe for work, because supercritical fluids and liquefied gases present a big hazard risk (explosion). Based on our experience in designing the HM-SFE system, we give special importance to the safety of the process. A certificate for working pressure was obtained for each used component, while calculations were carried out for the tube. All parts of the HM-SFE system should be made of stainless steel (AISI 304, AISI 316 Ti) to prevent any corrosion of the material. It is desirable to use certified filters with stainless steel



(1. Compressor; 2. CO_2 tank; 3. Stainless steel coil; 4. Cooling bath; 5. Air driven fluid pump; 6. High pressure needle valves (B-HV); 7. Manometers; 8. Extraction vessel; 9. Separator vessel; 10. Water bath; 11. Centralised system glass fibre heater; 12. Flow meter) (Jokić et al., 2015)

Figure 1. The HM-SFE system at the Faculty of Food Technology Osijek

mesh wire, coated with replaceable fine hard filter paper, in order to prevent plugging and possible hazard events.

When designing the extractor, aside from safety, it is very important to make an extractor which is very easy to maintain regarding loading and unloading, cleaning, connecting, and handling. From our experience in designing the HM extractor, we decided to make an extractor with a screw closure system (Jokić et al., 2015). Greater efficiency and continuous work are accomplished by using systems with the multiple parallel-connected extractors. The best closing system for a separator is also a screw type because of the fast extract collecting during the process at any time after depressurising. Due to the fact that it is necessary to heat and cool the fluid, heat exchangers are required in the HM-SFE system. Heat exchangers have the role of conditioning the fluid stream to required temperatures for pumping, extraction, separation, and holding (process storage) (Del Valle et al., 2014). From our experience, the heat exchanger should be placed just before the entrance of the extractor. This enables preheated CO2 at extraction temperature to enter the extractor. On the HM-SFE system, an air driven non lubricated liquid pump is used to obtain the desirable carbon dioxide pressure. To prevent cavitation and irregularity in the operation of the pump, the head of the pump is additionally cooled through a cooling bath with a stainless steel coil.

The schematic diagram of the designed HM-SFE system (Faculty of Food Technology Osijek, Croatia) is given in **Figure 1** and explained in detail in the previous chapter of our book (Jokić et al., 2015).

4. CONCLUSION

In recent years, SC-CO_2 extraction was demonstrated as a good alternative for processing food industry by-products. There is a great diversity of potential functional products which can be obtained from food by-products. Therefore, the use of food industry by-products has become extremely interesting because they represent cheap and nutritionally valuable raw material, and also have an impact on waste reduction. Modern companies are increasingly investing in research related to the reduction in the amount of waste and in research that would maximise the utilisation of raw materials. By applying SFE technology, it is possible to achieve the ”zero waste approach” by ensuring that large amounts of organic waste are not created, which represents a huge environmental and financial problem in almost all branches of the food industry today.

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