Innovative Food Science and Emerging Technologies 29 (2015) 209–214

Contents lists available at ScienceDirect

Innovative Food Science and Emerging Technologies

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

Effect of novel drying techniques on the extraction of anthocyanins from bilberry press cake using supercritical carbon dioxide

Sebastian Kerbstadt [a,b], Lovisa Eliasson [a], Arwa Mustafa [a,c], Lilia Ahrné [a,*]

[a] SP Technical Research Institute of Sweden, Food and Bioscience, Box 5401, Gothenburg SE-402 29, Sweden
[b] Faculty of Agricultural Science and Landscape Architecture, Hochschule Osnabrück, University of Applied Science, Am Kruempel 31, Osnabrueck D-49090, Germany
[c] NutraGreen–Research and Technical Solutions, Södra Murvägen 3, Hjärup SE-245 65, Sweden

ARTICLE INFO

Article history:
Received 23 November 2014
Received in revised form 10 February 2015
Accepted 11 February 2015
Available online 23 February 2015

Keywords:
Bilberry
Press cake
Anthocyanins
Drying
Pretreatment
Supercritical carbon dioxide extraction

ABSTRACT

The objective of this study was to assess the effect of novel drying techniques on the total anthocyanin content of extracts from bilberry press cake using supercritical carbon dioxide with ethanol as co-solvent. Prior to extraction, bilberry press cake was dried at 40 °C and 70 °C to moisture contents of 6% and 20% (w/w) by infrared drying, infrared impingement drying, and microwave-assisted hot-air drying and compared to freeze drying. The total anthocyanin content of extracts varied in the range of 13.67 ± 0.25 mg/g dry weight to 43.66 ± 0.79 mg/g dry weight, dependent on the choice of drying technique, temperature, and moisture content. Bilberry press cake treated with infrared impingement drying at 70 °C to 20% (w/w) moisture content resulted in the highest total anthocyanin content of extracts. The findings of this study show the importance in combining supercritical carbon dioxide extraction with an appropriate drying technique.

Industrial relevance: Supercritical carbon dioxide extraction is a green technology that offers mild extraction conditions for sensitive compounds. Drying prior to the extraction is usually necessary and may limit the extraction efficiency by degrading sensitive compounds or influencing the matrix and thereby the release of solute in the subsequent extraction step. More knowledge about the effect of different drying techniques on the extraction efficiency is of industrial interest to optimize both the yield and quality of extracts.

1. Introduction

Sweden is one of the biggest producers of wild berries, with about 20,000 tons of berries picked annually. The most common berry is bilberry (*Vaccinium myrtillus*), which contains anthocyanins at levels of 40–90 mg/g dry weight (DW) (Stolt, 2013). Studies on anthocyanins show protective properties against vision problems and diseases such as Alzheimer's, cancer, heart disease, and urinary disease (Kalea et al., 2006; Norton, Kalea, Harris, & Klimis-Zacas, 2005; Schmidt, Erdman, & Lila, 2005; Sweeney, Kalt, MacKinnon, Ashby, & Gottschall-Pass, 2002; Wu et al., 2004). Anthocyanins are polyphenols, which give the red, blue, and purple colors of many plants and fruits (Patras, Brunton, O'Donnell, & Tiwari, 2010). The anthocyanins are concentrated mainly in the epidermal cells that form the skin of bilberries (Prior et al., 1998). Bilberry press cake, a by-product of juice production, largely consists of skins and is a good source for anthocyanin extraction, which could further be processed into healthy foods.

Conventional solvent extraction, involving the use of organic solvents such as methanol in combination with acetone (Garcia-Viguera, Zafrilla, & Tomás-Barberán, 1998) or acidified water with hydrochloric acid (Kong, Chia, Goh, Chia, & Brouillard, 2003), is commonly used for the extraction of anthocyanins. This often implies long extraction times, high heat treatments, and purification steps, thus creating extracts of lower quality for further use or processing (Wang & Weller, 2006).

The use of green technologies such as supercritical carbon dioxide (SC-CO_2) extraction provides a promising alternative for conventional solvent extraction (Sahena et al., 2009). Carbon dioxide reaches the critical point at 31 °C and 73.8 bars and thereby provides favorable extraction conditions for thermo-labile compounds. Furthermore, SC-CO_2 extraction restricts oxidation reaction due to the absence of light and oxygen (Diaz-Reinoso, Moure, Dominguez, & Parajó, 2006). SC-CO_2 is chemically inert, non-toxic, and non-flammable and results in solvent-free extracts of high purity (Vatai, Škerget & Knez, 2009). Both the possibility of producing extracts free from hazardous solvents and the application of mild process conditions, thus preserving bioactive compounds, makes SC-CO_2 extraction to an advantageous technique for the production of extracts intended for human consumption.

Pure SC-CO_2 is, however, a relatively non-polar solvent, and therefore a polar co-solvent such as water, alcohol or a mixture of both is

---

Abbreviations: SC-CO_2, supercritical carbon dioxide; TAC, total anthocyanin content; DW, dry weight; IR, infrared drying; IRI, infrared impingement drying; MW, microwave-assisted hot-air drying; FD, freeze drying; MC, moisture content.

* Corresponding author. Tel.: +46 10 516 6623; fax: +46 31 83 37 82.
E-mail address: lilia.ahrne@sp.se (L. Ahrné).

http://dx.doi.org/10.1016/j.ifset.2015.02.002
1466-8564/

needed to extract polar molecules like anthocyanins (LCSG, 2013). SC-CO_2 extraction with the addition of co-solvent, usually ethanol or methanol, has been applied on grape by-products for extracting anthocyanins and other polar polyphenols (Da Porto, Natolino & Decorti, 2014; Mantell, Rodríguez, & Martínez de la Ossa, 2003). SC-CO_2 extraction requires a relatively dry carrier phase to extract the solute, and therefore a wet matrix, like bilberry press cake, needs to undergo drying prior to extraction. The presence of substantial amounts of water can decrease the extraction yield by disturbing the interaction between the solute and solvent. On the other hand, the presence of some water could improve the extraction yield by swelling the matrix and thereby facilitating the contact between the solute and solvent (Pourmortazavi & Hajimirsadeghi, 2007). In addition to the previous mentioned effects on the extraction process, the presence of water has several effects on biological materials since it accelerates, e.g., microbial growth, enzymatic activity, and oxidation reactions (Singh & Heldman, 2009). The degradation of anthocyanins is described to be accelerated with increased water activities (Garzón & Wrolstad, 2001; Gradinaru et al., 2003). A recent work of Jiménez et al. (2012) found a negative effect on the stability of anthocyanins with reduced water activity when combined with high temperatures. The moisture content of the material intended for extraction influence the stability of anthocyanins during handling and storage of the material, as well as the extraction efficiency during the extraction process.

Anthocyanins are further sensitive to high temperatures, light, and oxygen (Patras, Brunton, O'Donnell, & Tiwari, 2010), and therefore the choice of drying technique is important in minimizing anthocyanin degradation. Freeze drying is considered favorable in preserving anthocyanins for drying berries (Michalczyk, Macura, & Matuszak, 2009; Somsong, 2012), and the technology is applied prior to SC-CO_2 extraction (Chatterjee, Jadhav, & Bhattacharjee, 2013) due to the low temperature of the sublimation process. Freeze drying is, however, a time- and energy-consuming drying technique and is therefore more costly than conventional drying (Fellows, 2000). Conventional air drying, ranging from room temperature to 60 °C, is reported prior to SC-CO_2 extraction (Da Porto, Natolino & Decorti, 2014; Farías-Campomanes, Rostagno, & Meireles, 2013; Ghafoor, Park, & Choi, 2010). Conventional hot-air drying, however, is reported to result in a more severe degradation of anthocyanins compared to freeze drying (Michalczyk, Macura, & Matuszak, 2009; Somsong, 2012). Other alternative novel drying technologies are available. Infrared and microwave drying are based on electromagnetic heating, which heats the product directly without the need to preheat the surrounding air, thus reducing processing times compared to conventional heating (Fellows, 2000; Shi et al., 2008; Venkatachalapathy & Raghavan, 1998).

Infrared radiation represents the wavelengths 0.76 μm–1 mm of the electromagnetic spectrum. The mechanism of infrared heating is based on changes of molecular rotations and vibrations, resulting in an energy absorption that further is transformed into heat when the molecules return to its normal state (Skjöldebrand, 2001). Due to a direct and rapid heating of the product, drying by infrared heating has shown advantages in reduced processing times and improved sensorial quality compared to conventional hot-air drying of fruits (Nowak & Lewicki, 2004; Shi et al., 2008). However, infrared heating has a limited penetration depth into the product and therefore a careful design of the process and optimization of the product thickness is necessary to not overheat the surface of the product (Staack, Ahrné, Borch, & Knorr, 2008).

Impingement heating is based on high velocities of hot air that is directed to the surface of the product. This enhances the heat transfer since the thickness of the boundary layer, between the product surface and the bulk flow, is reduced. The combination of infrared heating and impingement has shown potential to reduce processing times compared to the application of each technology separately (Olsson, Trädgårdh, & Ahrné, 2005).

Microwave energy makes up the wavelengths 1 mm–1 m (frequencies 300 MHz–300 GHz) of the electromagnetic spectrum. The heating mechanism is based on electrical field's ability to rotate dipoles (e.g., water), creating rotational energy that further is transformed into heat. In similarity with infrared heating, microwaves create a fast heating rate due to a direct heating of the product. In contrast to infrared heating, microwaves result in a volumetric heating of the product, thus making it suitable for heating large bulk of materials. Structural changes of the surface of the product are avoided. The microwave process must be designed carefully to avoid an inhomogeneous heating, known as hot and cold spots, of the material (Fellows, 2000). Venkatachalapathy and Raghavan (1998) found that blueberries dried with microwave-assisted air drying showed a product quality (color, texture, and sensory value) almost equal to freeze drying but in a much shorter drying time.

To the best of our knowledge, the effects of rapid and mild drying technologies such as infrared and microwave have not been used previously for drying bilberry press cake prior to SC-CO_2 extraction. The aim of this study was therefore to investigate the effect of novel drying techniques on the total anthocyanin content (TAC) of bilberry press cake extracts, using SC-CO_2 with ethanol as co-solvent. Infrared drying (IR), infrared impingement drying (IRI), and microwave-assisted hot-air drying (MW) were studied and compared to freeze drying (FD).

2. Materials and methods

2.1. Raw material preparation

Bilberries (*V. myrtillus*), of moisture content 86.61% ± 0.27% (w/w), were purchased from Olle Svensson AB (Olofström, Sweden). The bilberries were harvested in Sweden in July–August 2012 and stored in the dark at −20 °C prior to the experiments. Frozen bilberries were thawed in the dark at 8 °C overnight. The thawed berries were mechanically pressed (Hafico, Germany), generating bilberry press cake of moisture content 75.31% ± 0.21% (w/w). The press cake was put into sealed plastic bags and stored in the dark at −20 °C until the drying trials were performed. The press cake was thawed in the dark at 8 °C overnight before drying.

2.2. Pretreatment of the bilberry press cake

Bilberry press cake was dried with infrared drying (IR), infrared impingement drying (IRI) and microwave-assisted hot-air drying (MW) and freeze drying (FD) to a final moisture content of 6% or 20% at 40 °C or 70 °C.

The drying times to reach the target moisture contents were determined by monitoring the weight loss along the drying and based on this estimate the theoretical moisture content of the material. When the desired weight loss was reached, the moisture content of the sample was confirmed by the method described in 2.3.

After drying, and cooling to room temperature, the bilberry press cake was milled for 30 sec in a knife mill (2393, OBH Nordica, Sweden). The powders were placed in 50 ml dark Falcon tubes and stored at −20 °C up to 2 days until the extractions were performed.

2.2.1. Infrared drying (IR) and infrared impingement drying (IRI)

The infrared dryer was a custom-made lab-scale oven (Ircon Drying Systems AB, Vänersborg, Sweden) with the dimensions 500 mm × 450 mm × 330 mm. The oven contained four near-infrared radiators attached above the sample tray. The radiators were quartz tubes with tungsten filaments and halogen gas, resulting in a peak emission of 1.2 μm (2100 °C) at full power. The distance between the infrared radiators and the sample tray was 200 mm. Two drying temperatures (40 °C and 70 °C) with and without the use of impingement were investigated to reach the intended moisture contents of 6% and 20% (w/w). For each trial, two Petri dishes (Ø 110 mm) with 20 g thawed press cake in each were placed in the middle of the infrared oven. When impingement was applied, the same infrared equipment as previously described was used, with the addition of a slot nozzle with a slit of 10 mm × 150 mm