Food Chemistry 166 (2015) 316–323

Contents lists available at ScienceDirect

Food Chemistry

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

Simultaneous extraction of oil- and water-soluble phase from sunflower seeds with subcritical water

Matej Ravber, Željko Knez, Mojca Škerget *

University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form 2 June 2014
Accepted 5 June 2014
Available online 14 June 2014

Keywords:
Sunflower oil
Subcritical water extraction
Kinetics
Hydrothermal degradation
Hydrolysis

ABSTRACT

In this study, the subcritical water extraction is proposed as an alternative and greener processing method for simultaneous removal of oil- and water-soluble phase from sunflower seeds. Extraction kinetics were studied at different temperatures and material/solvent ratios in a batch extractor. Degree of hydrothermal degradation of oils was observed by analysing amount of formed free fatty acids and their antioxidant capacities. Results were compared to oils obtained by conventional methods. Water soluble extracts were analysed for total proteins, carbohydrates and phenolics and some single products of hydrothermal degradation.

Highest amount of oil was obtained at 130 °C at a material/solvent ratio of 1/20 g/mL after 30 min of extraction. For all obtained oils minimal degree of hydrothermal degradation could be identified. High antioxidant capacities of oil samples could be observed. Water soluble extracts were degraded at temperatures ⩾100 °C, producing various products of hydrothermal degradation.

1. Introduction

The aqueous oil extraction (AOE) is an alternative and greener processing method for removal of oil from oilseeds. It offers many advantages compared to conventional organic solvent extractions (Rosenthal, Pyle, & Niranjan, 1996), one of them being the unique ability of simultaneous extraction of oil- and water-soluble (usually protein and carbohydrate) phase. In the past, AOE has successfully been implemented on different types of oil sources e.g. peanuts (Cater, Rhee, Hagenmaier, & Mattil, 1974), coconuts (Cater et al., 1974), soybeans (Rosenthal, Pyle, & Niranjan, 1998), rapeseeds (Embong & Jelen, 1977), sunflower seeds (Hagenmaier, 1974) etc. with reported oil and protein yields ranging up to 93% and 92% of total obtainable yields, respectively. Mostly, these studies have been performed at temperatures lower than 100 °C, at different oilseed/water ratios (up to 1/20 g/mL) and with applied changes in pH of medium (acidic and basic).

Although the obtained yields for the above mentioned sources seem potentially attractive, for commercial use and large industrial-scale production, there are still many things to be considered. Long required agitation times, formation of stable emulsions with rigorous mixing of media during extraction and difficult separation of phases, as well as required changes of pH of the media (addition of acids or bases) have discouraged the further process design and development in the past (Rosenthal et al., 1996).

One solution that could potentially improve the above mentioned difficulties is an increase of applied extraction temperature. It is a well known fact that generally by increasing the temperature extraction rates can be increased to some extent. Until today AOE has only been implemented at extraction temperatures lower than the boiling point of water. Only a few studies have been performed at temperatures higher than the boiling point of water, i.e. in the subcritical region (Ndlela, Moura, Olson, & Johnson, 2012; Pourali, Salak Asghari, & Yoshida, 2009).

Subcritical water (SubCW) is a term commonly used for water heated under pressure from its atmospheric boiling temperature (100 °C) to its supercritical point (374 °C). At these conditions the thermal motion of water molecules increases, markedly changing its properties. Unlike ambient water, the highly hydrogen-bonded structure at subcritical conditions slowly starts to dissipate, resulting in a decrease of permittivity (polarity), increase of diffusion rate and a decrease in viscosity and surface tension (Smith, 2002).

Another interesting property of SubCW is its increasing self-ionization at increasing temperature, meaning that water at these conditions becomes more acidic, giving it a more hydrolythic nature.

Extractions applying SubCW differ quite significantly from conventional extraction methods. Firstly, they are known to be very fast (Aliakbarian, Fathi, Perego, & Dehghani, 2012; Carr, Mammucari, & Foster, 2011; Singh & Saldaña, 2011), due to the

* Corresponding author. Tel.: +386 2 22 94 463; fax: +386 2 2527 774.
E-mail address: mojca.skerget@um.si (M. Škerget).

http://dx.doi.org/10.1016/j.foodchem.2014.06.025
0308-8146/

mentioned changes in the physical properties. Also the decrease in polarity gives SubCW a tendency for dissolving less polar compounds (Carr et al., 2011). Secondly, the mentioned hydrolythic nature of SubCW means that applying this extraction medium for natural materials will result not only in water soluble extracts but also in hydrolysed products of the extract (Fernández-Ponce, Casas, Mantell, Rodríguez, & Martínez de la Ossa, 2012; Ruen-ngam, Quitain, Tanaka, Sasaki, & Goto, 2012). Also the insoluble cell material, normally comprised of numerous complex polymeric structures (proteins, polysaccharides etc.), can be simultaneously hydrolysed during extraction, producing various water soluble products (amino acids, sugars) thus increasing the overall extraction yield. The destruction of the complex structures would result in formation of less stable emulsions mentioned earlier, since normally these structures are the main cause for their stability (Sanguansri & Ann Augustin, 2010).

Furthermore, the increased acidity of the medium does not result only in hydrolythic reactions but also in other hydrothermal reactions characteristic for SubCW, such as dehydration and decarboxylation (Pavlovič, Knez, & Škerget, 2013). This means that the obtained hydrolysed products can react even further with the water molecules resulting in a variety of other products of hydrothermal degradation e.g. furfurals from carbohydrates. Some of these formed products can have a health diminishing effect, when present in large concentration. Their effect on human health should therefore be studied prior to consumption of food product.

When applying the AOE at subcritical conditions (subcritical water extraction) the possibility of triglyceride hydrolysis to free fatty acids and glycerol also arises. Such a result would cause a decrease in oil quality, since more intensive down-stream processing (refining) would be required for removal of these compounds. Also, another factor which diminishes oil quality is the hydrothermal degradation of naturally present vitamins and antioxidants e.g. phytosterols and tocopherols.

In this work, we propose the subcritical water extraction as a feasible processing method for removal of oil- and water-soluble phase from sunflower seeds. Extraction kinetics of both phases were investigated at different extraction temperatures and material to water ratios and the obtained oil yields of the subcritical water extraction (SubWE) were compared to those obtained with the standard Soxhlet extraction procedure. Degree of hydrothermal degradation of oil extracts (OE) was checked, by determining (1) the free fatty acid composition and (2) the total antioxidant capacity of lipid soluble compounds and results were compared to the oil obtained with the Soxhlet extraction procedure. Degree of hydrothermal degradation of water soluble extracts (WSE) was checked by analyzing the content of (1) proteins, (2) carbohydrates and (3) phenolic compounds. WSE were also analysed for products of hydrothermal degradation and the total antioxidant capacities of water soluble compounds.

2. Materials and methods

2.1. Chemicals and reagents

All reagents, standards and solvents were of analytical grade. Coomassie brilliant blue, albumin bovine serum (⩾96%), phenol, glucose (⩾98%) and sodium carbonate were purchased from Sigma–Aldrich (Slovenia). Oleic acid (⩾98%), linoleic acid (⩾98%), stearic acid (⩾98.5%), palmitic acid (⩾97%) and gallic acid (⩾98%) were purchased from Fluka (Germany). Sulfuric acid, Folin–Ciocalteu phenol reagent, acetic acid and ethanol were purchased from Merck (Germany). 5-Hydroxymethyl furfural (⩾98%), caffeic acid (⩾99%) and chlorogenic acid (⩾98%) were purchased from Acros Organics (Belgium). Phosphoric acid was purchased from Kemika (Croatia), hexane was purchased from Carlo Erba (Italy) and methanol was purchased from J.T. Baker (Netherlands). Photochem® reagents and standards were purchased from Chemass (Slovenia).

Helium 6.0 and nitrogen 5.0 were supplied from Messer (Slovenia).

2.2. Preparation of material

Dehulled sunflower seeds (Natura, Slovenia) were used for this research work. The seeds were ground in a grinder (Bosch, Germany) prior to every experiment. Material humidity was measured by a thermo-balance (Mettler-Toledo, Switzerland) and it was (3.68 ± 0.08)%. Total lipid content in seeds was determined by the AOAC official method 948.22 (Venkatachalam & Sathe, 2006) and it was (51.02 ± 1.95)%.

2.3. Extraction procedures

2.3.1. Subcritical water extraction

For extraction of grinded sunflower seeds with subcritical water a 60 mL cylindrical stainless steel high-pressure batch extractor (Autoclave Engineers, USA) was used. Temperature regulation was performed with a heating cable and stirring of the extraction media was performed by using a magnetic stirrer. The filled extractor was purged three times with inert nitrogen gas to remove present atmospheric oxygen, which could cause oxidation of oil during extraction. The applied extraction pressure for all extractions was equal to 30 bar and was held constant throughout the extraction.

Kinetics of extractions were studied at four different temperatures (T_e), namely 60 °C, 100 °C, 130 °C and 160 °C for extraction times (t_e) ranging from 5 min to 120 min at a material to solvent ratio (M/S) of 1/20 g/mL. The extraction kinetics at 130 °C were also observed at the M/S ratio of 1/10 g/mL and 1/30 g/mL. The extraction suspension was filtered and the obtained liquid extract along with 50 mL of hexane was introduced into a separation funnel which was then shaken rigorously for 3 min. The formed emulsion was centrifuged (Eppendorf, Germany) at 11,000 rpm for 2 min in order to separate the two phases, both of which were then collected and evaporated until dryness. Both oil (OE) and water soluble extract (WSE) samples were stored at −20 °C until further use.

2.3.2. Conventional extraction with the Soxhlet apparatus

Approximately 10 g of ground sunflower seeds were placed in a thimble, which was inserted into a Soxhlet apparatus and extracted with 200 mL of hexane (M/S = 1/20 g/mL). The extraction was performed at normal boiling point for 4 h and afterwards the solvent was evaporated until dryness. Obtained oil was stored at −20 °C until further use.

Kinetics of Soxhlet extraction were studied by collecting 1 mL of sample solution after every solvent cycle (approximately every 30 min) for 4 h. The solvent was evaporated from the collected sample and the mass of the remaining oil was determined.

2.4. Analysis of extracts

2.4.1. Analysis of free fatty acids

The extracted crude oil was analysed for the content of free fatty acids (FFAs) by gas chromatography (Kotnik, Škerget, & Knez, 2006). The analyses were performed for linoleic, oleic, stearic and palmitic acids. The 6890 HP model (USA) consisted of flame ionization detector (FID) with temperature set at 300 °C and capillary column (HP-FFAP 30 m × 0.25 mm × 0.25 μm). The oven time–temperature profile was as follows: 120 °C (1 min), 25 °C per min to 180 °C (1 min), 5 °C per min to 220 °C (10 min), 5 °C per min to 230 °C (30 min). The carrier gas was helium with total flow through the column 64.0 mL/min. The samples were analysed