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Production of proteins and phenolic compounds enriched fractions from rapeseed and sunflower meals by dry fractionation processes

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ABSTRACT

Rapeseed (RSM) and sunflower (SFM) meals are highly abundant and protein-rich by-products from the oilseed industry. Besides their basic use as animal feed, they are seen nowadays as interesting raw materials for the production of high value added products such as protein isolates, peptides, emulsifiers and biomaterials. In other respects, they contain significant amounts of phenolic compounds exhibiting antioxidant or antimicrobial properties but widely untapped so far. Therefore, any process allowing the single-step separation of both the protein and phenolic parts of meals would be beneficial to the whole oilseed sector. To achieve this double objective this study attempted to separate the RSM and the SFM into their major constituents by using dry fractionation technologies. In a first step, ultrafine milling was applied to the meals. As a function of raw material type, the grid size turned out to be decisive on the particle size distribution and its modality. Then two separation technologies based either on particle charge (electrostatic sorting – ES) or density (turbo-separation – TS) were applied to the previously obtained fractions. Regardless the separation technique, the best results were obtained from fractions of an average particle diameter by mass (D_{50}) of 23.7 ± 1.0 µm and 105.5 ± 8.3 µm, for RSM and SFM respectively. Electrostatic sorting allowed increasing simultaneously the protein and phenolic contents by 50–55% and 80–100% for RSM and SFM respectively, while a lower increase was observed for turbo-separation (23–29% and 58–64% for RSM and SFM respectively). Finally, depending on the process and meal types, the overall recovery yield of the most enriched fractions was in the range of 30–40%.

1. Introduction

Rapeseed and sunflower are the most important oil crops in Europe (Carré and Pouzet, 2014). Their oils are considered as one of the healthiest due to their high content in mono- and poly-unsaturated fatty acids and tocopherols (Luigicioni, 2005; Shahidi, 1990). Rapeseed meals (RSM) and sunflower meals (SFM) are co-products of the pressing and de-oiling process of their seeds. In 2016, the production of RSM and SFM in France were estimated to be 2.6 Mt and 0.6 Mt respectively (Terres Univia 2016). RSM and SFM are heterogeneous materials that contain proteins (36–38 g/100 g DM) (28–30 g/100 g DM), lignin (9–11 g/100 g DM) (11–13 g/100 g DM), cellulose (13–15 g/100 g DM) (25–27 g/100 g DM) and phenolic compounds (≈2 g/100 g DM) (≈ 4 g/100 g DM). For both RSM and SFM, proteins and phenolic compounds are mainly present in the kernel (Carré et al., 2016; González-Pérez and Vereijken, 2007; Weisz et al., 2009) while lignin, cellulose, and hemicellulose are more concentrated in the hull (Cancalon, 1971; Carré et al., 2016). If meals are currently mostly intended for cattle feed, oleaginous proteins, especially from soybean, canola or sunflower, may be transformed into high added-value products such as bio-packaging or emulsifiers (Zhang and Mittal, 2010; Shi and Dumont, 2014) but also adhesives and fiberboards (Wang et al., 2014; Evon et al., 2015). Moreover, several studies have demonstrated the antioxidant activity of peptides from rapeseed meals protein

Abbreviations: CAE, chlorogenic acid equivalent; CF, coarse fraction recovered after turbo-separation; DM, dry matter; DDM, delipidated dry matter; D_{50}, mass-median-diameter of particles (average particle diameter by mass); ES, electrostatic sorting; FF, fine fraction recovered after turbo-separation; NFc, negatively charged particles collected on the corresponding jar; NFe, negatively charged particles collected on the positive electrode; PFc, positively charged particles collected on the corresponding jar; PFe, positively charged particles collected on the negative electrode; RSM, rapeseed meal; SAE, Sinapic acid equivalent; SFM, sunflower meal; TPC, total phenolic compounds; TS, turbo-separation; UFM, ultrafine milling

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hydrolysates (Aider and Barbana, 2011; Zhang et al., 2008), while proteins associated with phenolics can act as emulsifier displaying antioxidant activities (Guimarães Drummond e Silva et al., 2017; Rawel et al., 2005).

Besides, naturally occurring phenolic compounds are known to be bioactive molecules exhibiting antioxidant (Dimitrios, 2006), anti-inflammatory (Hwang et al., 2014) and antimicrobial activities (Xu et al., 2016) to name a few. This is why they are already widely used as preservatives in the agri-food and cosmetic industries for the protection of unsaturated lipid-containing systems and enhancement of their shelf life (Durand et al., 2015; Shahidi and Ambigaipalan, 2015).

Even today, it remains a challenge to separate the proteins from the other constituents of RSM and SFM, i.e lignin, phenolics, carbohydrates. To do this, different methodologies have been developed such as solid-liquid extractions (Aider and Barbana, 2011; Das Purkayastha et al., 2013; Kachrimanidou et al., 2015). Unfortunately, these routes not only generated effluents but were also ineffective to individually segregate meal constituents.

As a promising alternative to solvent-assisted processes, dry fractionation technologies have been recently developed and successfully applied to various raw materials including oleaginous meals. These dry fractionation processes can be divided into two steps. First, the milling step in which the different constituents of the meals are detached from the cellular matrix. Then, the separation step which is based on the differences in the physicochemical properties of the different constituents. Recently, ultrafine milling (UFM) coupled to electrostatic sorting (ES) or turbo separation (TS) emerged as eco-friendly technologies suitable for the concentration of proteins, cellulose, lignin and polyphenols from many agro-resources (Chuetor et al., 2015; Hemery et al., 2011; Pelgrom et al., 2014). Moreover, these processes are significantly more energy efficient than solid-liquid fractionation processes and are able to produce enriched fractions with retained (native) functionality.

Although ES of fractionated RSM and SFM has already been implemented (Barakat et al., 2015; Basset et al., 2016), the influence of the particle size distribution on the separation steps was not studied. Plus, a fine characterization of the different phenolic compounds of the different fractions was not fully done. In addition, to the best of our knowledge, the TS of the RSM and SFM have never been studied. Knowing this, the aim of this study was to compare the dry fractionation processes of RSM and SFM by applying UFM coupled to ES and TS technologies.

In this work, the study of the UFM conditions and the influence of the particle size distribution on the separation steps were of paramount importance. Here, shear and impact milling were applied to the RSM and SFM. To obtain ultra-fine meals with different particle size distributions, three different grid size were used. Then, the three ultra-fine meals were separated by a single step ES or TS to investigate the impact of the milling conditions. To know whether the separation was effective, the chemical composition (protein, lignin, individual and total phenolic compounds (TPC) contents) and the particle size distribution of the different fractions were determined. After establishing the best milling conditions, a methodology to increase the recovery yield of the fractions of interest during ES was developed.

2. Materials and methods

2.1. Chemicals

Sinapine thiocyanate (99.0% HPLC) was isolated from a methanolic extract of rapeseed meal according to the method outlined by Mailer *et. al* (Mailer, 2008). 3,4-; 3,5- and 4,5-di-O-caffeoylquinic acids (> 99.0% HPLC) were isolated from yerba maté leaves by the method outlined by Tong *et. al* (Tong et al., 2015). Sinapic acid (98%) was from AlfaAesar (Karlsruhe, Germany). 5-caffeoyl quinic (Chlorogenic) acid (95%), caffeic acid (> 98%), methanol and water (for HPLC, > 99.9%) were purchased from Sigma–Aldrich (Saint-Quentin-Fallavier, France).

2.2. Raw materials

Experiments were carried out on rapeseed (RSM) and sunflower (SFM) meals prepared at the pilot oil plant of OLEAD (Pessac, France), according to the following methods.

2.2.1. Preparation of the rapeseed meal (RSM)

Whole rapeseeds (120 kg) were first cold pressed on a MBU20 screw press (OLEXA, France), fed at 75 kg/h of seeds, to remove 75% of the initial oil amount. The residual oil of the press cake was further extracted by steeping in hexane at 50 °C, in a Guedu Pilot Agitated Filter Dryer (De Dietrich Process Systems) of 480 L total capacity. Extraction was performed on 73 kg of press cake by immersion in hexane for 15 min followed by filtration. Five successive steps of immersion-filtration were required to remove oil from the cake. The defatted cake was then desolventized in the same device, under vacuum at 60 °C and without injection of steam. The water and lipid content of the resulting RSM were of 11 ± 0.0% and 1.7 ± 0.1% respectively.

2.2.2. Preparation of the sunflower meal (SFM)

Whole sunflower seeds (75 kg) were first cold flaked in a flaker (Damman-Croes N.V., Belgium) equipped of two contra-rotating smooth cylinders of 500 mm in diameter, spaced of 0.3 mm (capacity: 200 kg/h). The flakes (73 kg) were then deoiled by hexane-extraction at 50 °C in a Guedu Pilot Agitated Filter Dryer (De Dietrich Process Systems) for 15 min, followed by filtration. The immersion-filtration step was repeated six times. The defatted cake was finally desolventized in the same device, under vacuum at 60 °C and without injection of steam. Finally, sunflower meal were coarsely milled with a knife milling using a 2 mm gird The water and lipid content of the resulting SFM were of 7.5 ± 0.0 and 2.0 ± 0.1% respectively.

2.3. Ultrafine milling

Raw RSM and SFM were previously coarsely crushed with a Retsch SM 300 knife mill (Retsch Technology GmbH, Haan, Germany) operating at 2000 rpm with a two millimeters grid. Then, the samples were finely ground by impact and shear mill UPZ100 (Hosokawa-alpine, Augsburg, Germany) using different grids of 0.5, 0.3 and 0.1 mm (0.2 mm for the SFM). The device was operated at room temperature, at a speed of 18 000 rpm, and a feeder speed of 4 kg h^{-1}. The material was milled until it passed through the grid. The particle size distribution of the samples was determined by laser diffraction using a Mastersizer 2000 in combination with the Scirocco 2000 dry dispersion unit (Malvern Instruments, Worcestershire, UK). All measurements were performed in triplicate.

2.4. Electrostatic sorting

A pilot electrostatic separator (TEP System, Tribo Flow Separations, Lexington, USA) was used for the fractionation of the different ultrafine RSM and SFM. The feeding system of the separator was operated at 1.2 kg/h with an initial amount of meal of 250 g; the particles were then conveyed by compressed air (gas flow rate = 5.1 m^3 h^{-1}) in a teflon tube (250 cm, $Ø_{in}$ = 11 mm, $Ø_{ext}$ = 13 mm) where they were charged by triboelectricity, i.e. by impacting each other and against the walls of the charging line. Finally, charged particles passed through a separation chamber containing two high voltage electrodes (7.5 cm x 28.0 cm; 10 000 V), where the positively charged particles are attracted by the negative electrode and the negatively charged particles are attracted by the positive electrode. A particle recovery system equipped with two collecting jars allowed to separately recover two fractions: one containing the positively charged particles named the collected positive fraction “PFc” and the other, the negatively charged particles named