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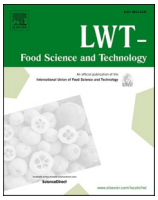

Dry fractionation of sunflower press cake as tool to improve its technofunctional properties

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ABSTRACT

Depending on the oil production technology, at least 60% of the oilseeds input such as sunflower, pumpkin or canola remain as by-product, which is usually denoted as press cake (PC) and contains a significant amount of fiber and protein. Its further valorization in food requires knowledge on the technofunctional properties of the press cake and on possibilities for improving its value. Aim of the current study was to evaluate the effect of two separation techniques, namely targeted sieving and air classification, on composition, and physical as well as technofunctional properties of fractions of sunflower press cake previously milled to <1.0 mm or <2.0 mm. It is evident for both separation techniques that fines fractions obtained by using smaller sieves or lower air volume flow showed an increased protein content, with a protein enrichment factor of up to 1.47. Using PC < 2.0 mm as raw material, protein separation efficiency, a combined measure for protein content and yield, was higher after separation by air classification. Whereas protein solubility was not affected by the particle size distribution of the separated fractions, emulsion activity and emulsion stability were improved especially for the small particle fractions separated from PC < 2.0 mm.

1. Introduction

The production of edible oil from oilseeds such as sunflower, pumpkin or canola results in a significant amount of by-product, usually denoted as press cake (PC). Its composition depends on seed type but also on the technology used in oil production. When using combined mechanical treatment and solvent extraction, sunflower PC contains up to 48 g protein and approximately 40 g dietary fiber per 100 g dry matter (Arrutia, Binner, Williams, & Waldron, 2020). When, mainly in the production of so-called native or cold pressed oil, only mechanical pressing is used, the residue contains still 16–24 g/100 g oil (Baümler, Carrin, & Carelli, 2016) and, therefore, a lower amount of protein and fiber. When intending to use PC as food ingredient instead of animal feed, its technofunctionality is of utmost importance (Ancuța & Sonia, 2020).

In case of PC from small scale mechanical oil production, it is favorable to initially remove residual oil (Capellini et al., 2020) but also to reduce dietary fiber content, as it reduces digestibility and impairs appearance of the target products due to the dark color of the hulls present in the raw material (Murru & Calvo, 2020). One prominent way to concentrate or isolate protein from protein-rich plant materials such as PC is wet extraction, involving deoiling with solvents, alkaline extraction with subsequent isoelectric precipitation, and final drying (Boye, Zare, & Pletch, 2010; Chéreau et al., 2016). However, the fact that sunflower seeds contain polyphenols, especially chlorogenic acid, makes wet extraction of proteins more challenging. At alkaline pH, mostly applied in wet extraction, chlorogenic acid reacts with amino acids and proteins leading to the formation of green-colored complexes and making extraction of pure proteins impossible. For this reason, protein isolation from sunflower seeds or press cake is more difficult in comparison to other plant proteins, in particular at high pH (Wildermuth, Young, & Were, 2016). To avoid the use of high amounts of energy, chemicals and the generation of waste water, dry fractionation is taken into account as alternative method (Arrutia et al., 2020; Cloutt, Walker, & Pike, 1987).

Dry fractionation processes include sieving, air classification, gravity separation and electrostatic separation that allow the separation of particles into fractions with different composition according to size, density, aerodynamic or electrostatic properties (Chéreau et al., 2016; Murru & Calvo, 2020). Compared to wet extraction, where an average protein concentration of 80 g/100 g may be reached, the concentration effect in dry fractionated samples is less pronounced but the native

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structure and properties of the raw material's components is maintained (Arrutia et al., 2020; Cloutt et al., 1987). Frequently, legumes are subjected to dry fractionation to separate protein from starch particles (Funke et al., 2022). However, in oilseed material, particles are separated into a protein-rich fines fraction and a fiber-rich coarses fraction according to their shape, size and density (Banjac et al., 2013; Laudadio, Bastoni, Introna, & Tufarelli, 2013). The result of the separation process is determined by the cut point of the raw material as well as by its dispersibility (Dijkink, Speranza, Paltsidis, & Vereijken, 2007). To achieve an effective separation, particles must be disaggregated to a large extent. Therefore, raw materials subjected to dry fractionation are almost always deoiled, and a step of milling or deagglomeration is also frequently performed (Arrutia et al., 2020; Assatory, Vitelli, Rajabzadeh, & Legge, 2019).

Sieving allows to separate particle collectives primarily according to the individual particle size, for instance by using a stack of sieves with decreasing mesh size (Schutyser and van der Goot, 2011). Sieving efficiency is influenced by the intensity of preliminary milling, sample moisture, size and shape of the particles, and the duration and method of sieving (Liu, 2009).

Air classification is used to enrich or reduce components from the raw material using gravitational, cascade (zigzag), fluidized bed, inertial or centrifugal air classifiers. The particles are dispersed in an air flow and separated with respect to mass and density, with small particles showing a size below the cut point being collected as fines fraction (e.g. proteins) and larger particles with a particle size above the cut point building up the coarses fraction (fibers, starch). Due to unavoidable particle collisions in the air stream and turbulences a precise separation is not entirely possible, and some particles end up in the opposite fraction (Dijkink et al., 2007; Laudadio et al., 2013; Shapiro & Galperin, 2005).

Preliminary work performed on technical scale by Murru and Calvo (2020) showed that coarser particles with lower density and more elongated shape are characterized by a high fiber content, while smaller particles separated from sunflower press cake have a higher protein content. Sunflower proteins have been reported to build and stabilize foams and emulsions in food systems (González-Pérez & Vereijken, 2007). This study focuses on evaluating two separation techniques for deoiled and milled sunflower press cake, and to analyze the composition, with particular emphasis on the protein content in the resulting fractions. Additionally, the research examined the technofunctional properties of the protein-rich fractions to assess their potential utility as food ingredients.

2. Materials and methods

2.1. Materials

Ölmühle Moog GmbH (Lommatzsch, Deutschland) provided press cake from sunflower oil production through single-stage mechanical pressing. The press cake was delivered as pellets with a diameter of 8 mm, and from 30 to 60 mm in length (mass of the individual pellets, 2.0–4.0 g). Raw material for oil production were hulled sunflower seeds.

2.2. Preliminary milling and deoiling

Press cake pellets were initially comminuted using a ZM 200 ultra-centrifugal mill (Retsch GmbH, Haan, Germany) equipped with a 12 teeth rotor. Rotation speed was 12,000 rpm, and ring sieves with reinforced rim and trapezoid holes of either 1.0 mm or 2.0 mm size were used for separating milled fractions.

Deoiling of milled press cakes was done using ethanol as environmental-friendly solvent (Morejón Caraballo, Rohm, & Struck, 2023). After mixing a suspension of 400 g PC in 4 L ethanol (96% v/v) at room temperature for 1 h at 250 rpm using a propeller stirrer mounted on a Eurostar power control-visc device (IKA-Werke GmbH & Co. KG, Staufen, Germany), the liquid phase was decanted and the remaining solids were again suspended in 4 L ethanol. After repeating this procedure for a third time, the deoiled PC was dried in a VT 6060 M vacuum oven (Thermo Fisher Scientific, Waltham, MA, USA) connected to an MD 4C membrane vacuum pump (Vacuubrand GmbH + Co. KG, Wertheim, Germany) for 24 h at 35 °C and 20 kPa to remove residual solvent. Finally, to destroy or remove agglomerates, the dried and deoiled press cake was sieved using an AS 200 digit CA vibratory sieve shaker (Retsch GmbH) at a sieving amplitude of 1.8 mm, either at a sieve size of 1.0 mm or 2.0 mm.

Fig. 1. View of the ziczac air classifier. 1, adjustment of air volume flow; 2, cyclone; 3, fines fraction collection unit; 4, air inlet; 5, coarses fraction collection unit; 6, ziczac channel; 7, vibratory tubular feeder.

2.3. Dry fractionation of sunflower press cake

2.3.1. Fractionation by sieving

Separation intensity curves were determined in threefold using the AS 200 vibratory shaker, equipped with woven wire mesh sieves with square openings of 80, 100, 125, 200, 250, 300, 400, 600 and 800 µm. After determining mass m_E of each empty sieve, 50 ± 0.1 g sample (m_S) were placed on the top sieve. Sieving duration was 10 min, and shaker amplitude was 1.8 mm. After that, masses m_F of the individual sieves and the bottom collection tray were determined. Yield Y (%) of individual fractions, and fractionation loss L (%) were calculated by considering the total mass of all individual fractions $m_{F,T}$:

$$Y = \frac{m_F - m_E}{m_S} \bullet 100\% \quad \text{Eq. (1)}$$

$$L = \frac{m_S - m_{F,T}}{m_S} \bullet 100\% \quad \text{Eq. (2)}$$

In subsequent experiments, deoiled PC was separated into two fractions

using sieves that were chosen based on sieving yield and protein content of the fractions.

2.3.2. Air classification

Separation intensity curves were also established by using a 1–40 MZM zigzag air classifier (Hosokawa Alpine, AG, Augsburg, Germany; Fig. 1). After determining the respective mass m_E of the collection vessels for the fines and the coarses fraction, 100 ± 0.1 g deoiled PC was delivered to the vertical zigzag channel by an SU-B50-1 vibratory tubular feeder (Aviteq Vibrationstechnik GmbH, Hattersheim, Germany) operated at level 8. Air volume flow was initially set to 0.5 m^3/h using a V31 variable area flow meter (Heinrichs Messtechnik GmbH, Köln, Germany). After classification, the air flow was increased to transfer fines particles adhering to the inner side of the zigzag tube into the fines fraction. Subsequently, masses m_F of the fines and the coarses fraction were determined.

The coarses fraction was then again delivered to the classifier at an air volume flow of 1.0 m^3/h, and the procedure was repeated. In this way, for the entire procedure, air volume flow was stepwise increased from 0.5 to 1.0, then to 1.25, 1.5, 1.75, 2.0, 3.0 and to finally 4.0 m^3/h, resulting in 8 different fines fractions and the remaining coarses fraction. Yield and fractionation loss, determined by Eqs. (1) and (2), and protein content were then used for adjusting air flow to the values that allowed obtaining most efficient separation.

2.4. Analysis of press cake and its fractions

2.4.1. Gross composition

Solids content was determined using the oven method. Approximately 3 g sample with its mass determined to an accuracy of ±1 mg was dried to mass constancy at 103 ± 1 °C using an IPP55 drying cabinet (Memmert GmbH + Co. KG, Schwabach, Germany). To determine ash content, approximately 3 g sample was incinerated using a bunsen burner and then placed in a B-170 muffle furnace set to 550 °C (Nabertherm GmbH, Lilienthal, Germany) until mass constancy was achieved. Crude protein content P_C was calculated from nitrogen content, determined using the Kjeldahl method (K-436 digestion unit, B-324 distillation unit, both Büchi Labortechnik AG, Flawil, Switzerland), by applying a conversion factor of 5.6 (Pickardt, Eisner, Kammerer, & Carle, 2015). After fat extraction following the Twisselman principle with a Soxtherm apparatus (C. Gerhardt GmbH & Co. KG, Königswinter, Germany) and petroleum ether, the solvent was evaporated and the mass of the extracted fat was determined. All determinations were executed in triplicate.

2.4.2. Physical properties

Microscopy images of the fractions were taken with a Basler Pulse 5.0 MP camera (Basler AG, Ahrensburg, Germany) mounted on an SZ61 stereo microscope (Olympus Europe SE & Co. KG, Hamburg, Germany). Color properties were determined in triplicate using sph900 spectral reflectance photometer with a D65 light source and the 10° standard observer (ColorLite GmbH, Katlenburg-Lindau, Germany). Using the CIE-L*a*b* coordinates, the color difference ΔE* between a respective fraction and the initial sample was calculated by:

$$\Delta E^{*} = \sqrt{\left(\Delta L^{*2}\right) + \left(\Delta a^{*2}\right) + \left(\Delta b^{*2}\right)} \quad \text{Eq. (3)}$$

After dispersing the samples using an EMS 750 electromagnetic sieve vibrator (Topas GmbH, Dresden, Germany), the particle size distribution of the individual particle collectives was measured in duplicate using a QicPic particle size and form analyzer (Sympatec GmbH, Clausthal-Zellerfeld, Germany).

2.4.3. Technofunctional properties

For analyzing protein solubility, a dispersion of 3 ± 0.01 g press cake fraction in 97 ± 0.01 g distilled water, prepared in duplicate, was stirred at room temperature for 30 min at 200 rpm and subsequently separated at 5000×*g* using a 3–30 K centrifuge (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany). Protein content P_S of the decanted supernatant was determined using the Kjeldahl method, and protein solubility S (%) was calculated using the dilution factor and the respective crude protein content P_C:

$$S = \frac{P_S}{0.03 \bullet P_C} \bullet 100\% \quad \text{Eq. (4)}$$

Foaming properties of the proteins were determined in duplicate according to Fenn, Wang, and Maximiuk (2022). A volume V_L = 45 mL of decanted soluble protein solution was transferred into a 100 mL graduated cylinder and foamed for 30 s at 22,000 rpm using a T22 ultra turrax (Ika-Labortechnik, Janke & Kunkel GmbH, Staufen, Germany). Total volume V_T was read from the cylinder after 1, 5, 10, 30, 60, 90 and 120 min. Foaming capacity FC (%) was defined as foam volume, i.e., total volume V_T minus V_L after 1 min of foaming, as related to V_L (Eq. (5)). Foam stability FS refers to foam volume at time t (=$V_{T,t}$ – V_L), as related to initial foam volume ($V_{T,1}$ – V_L) (Eq. (6)):

$$FC = \frac{V_{T,1} - V_L}{V_L} \bullet 100\% \quad \text{Eq. (5)}$$

$$FS = \frac{V_{T,t} - V_L}{V_{T,1} - V_L} \bullet 100\% \quad \text{Eq. (6)}$$

Emulsions with an oil volume fraction of 0.5 were prepared in triplicate by homogenizing 40 mL refined sunflower oil in 40 mL soluble protein solution (see above) at 22,000 rpm for 60 s using a T22 ultra turrax. Emulsifying activity EA (%) and emulsion stability ES (%) were determined as described by Yasumatsu et al. (1972) with modifications. For the determination of EA, a volume V_T of 10 mL emulsion were transferred into 15 mL graduated centrifuge tubes and then centrifuged at 2600×*g* for 15 min (EBA12, Andreas Hettich GmbH & Co. KG, Tuttlingen, Germany). Ten minutes after centrifugation stopped, the volume of the remaining emulsified layer V_E was read and related to V_T:

$$EA = \frac{V_E}{V_T} \bullet 100\% \quad \text{Eq. (7)}$$

Emulsion stability ES (%) was calculated in the same way, but after heating the emulsion in the tubes for 30 min at 80 °C in a water bath and subsequent centrifugation.

In addition, a Turbiscan Lab stability analyzer (Formulaction S/A, Toulouse, France) was used to analyze time-based phase separation. In single experiments, 20 mL emulsion were placed in the instrument, and backscattering BS (%) of an 880 nm NIR light was read at a scattering angle of 45° at 1 min intervals for 2 h. According to Salgado, Molina Ortiz, Petruccelli, and Mauri (2012) we determined emulsion capacity EC, destabilization kinetics and creaming. Here, EC (%) refers to the initial backscatter intensity BS_0 (%) averaged between 5 and 35 mm sample height. At a height of 5–10 mm, backscatter was also averaged, and $t_{1/2}$ (s) refers to the time span until BS_0 was halved. Backscatter of the creaming layer was measured at a height of 30–35 mm, also as a function of time. The coefficient of destabilization CD (%) refers to the relative decrease in backscatter during 2 h measurement, related to the initial backscatter intensity:

$$CD_{2h} = \frac{BS_0 - BS_{2h}}{BS_0} \bullet 100\% \quad \text{Eq. (8)}$$

2.5. Statistics

Results are expressed as arithmetic mean ± half deviation range for duplicate measurements, and as arithmetic mean ± standard deviation for n ≥ 3 measurements. Analysis of variance and subsequent multiple mean comparisons were executed using OriginPro 2021 (Originlab Corporation, Northampton, USA).

Table 1
Gross composition of the base press cake and deoiled press cake milled to 1.0 or 2.0 mm maximum particle size.

Component (g/100 g)	Base press cake	PC < 1.0 mm, deoiled	PC < 2.0 mm, deoiled
Dry matter	93.66 ± 0.24 a	91.26 ± 0.01 b	89.95 ± 0.04 c
Crude protein	22.15 ± 0.08 b	27.23 ± 0.12 a	26.16 ± 0.43 a
Fat	15.97 ± 0.23 a	1.35 ± 0.22 b	1.42 ± 0.45 b
Ash	4.61 ± 0.04 b	5.31 ± 0.04 a	5.15 ± 0.06 a
Carbohydrates	50.93	57.37	57.22

Mean values ± standard deviations from n = 3 replicate measurements. Mean values in a row having different letters differ significantly (P < 0.05). Carbohydrate content was calculated by difference.

3. Results and discussion

3.1. Preliminary classification experiments

The press cake used in this study contained 6.34 g/100 g moisture and 22.15 g/100 g crude protein, and residual fat content was approximately 16 g/100 g (Table 1). After milling to a maximum particle size of 1.0 or 2.0 mm and subsequent deoiling, residual fat content was 1.35 or 1.42 g/100 g, respectively, and crude protein in the deoiled PC increased accordingly. According to Arrutia et al. (2020), deoiling reduces the susceptibility of press cakes towards agglomeration but may increase a tendency towards electrostatic charging.

Fig. 2 depicts separation intensity curves of deoiled and milled press cake as obtained though sieving or by air classification. After sieving sunflower PC milled to <2.0 mm (left part of Fig. 2), the highest protein content was observed in the smallest fraction (<80 μm), showing a yield of approximately 9%. When separating PC < 1.0 mm, the <80 μm fraction had a comparable protein content but showed a yield almost twice as high. Irrespective of the initial particle size of the deoiled PC, protein content decreased with increasing particle size and showed a minimum for the fractions 250–800 μm. Protein content in the >800 μm fraction was then higher, presumably because of small protein particles adhering to large fiber particles. The fact that the protein content in the respective fractions was, on average, 1.8 g/100 g lower when PC < 1.0 mm was sieved can be explained by the higher milling intensity, presumably resulting in a more pronounced transfer of fractured fiber particles (Laguna et al., 2018; Schutyser et al., 2015). The separation intensity functions differed because of the different particle sizes in the raw materials, so that cumulative yield in all fractions was higher when PC milled to <1.0 mm was sieved. For instance, when taking the upper border of the 250–300 μm class as measure, approximately 60% of the particles were smaller whereas, when PC < 2.0 mm was sieved, the respective yield was significantly lower, namely ~40%. Independent of the press cake's initial particle size, a cumulative yield of almost 100% was obtained in the largest sieve fraction ≥800 μm.

As regards air classification, the protein content of the individual fractions decreased with increasing air volume flow and reached, in case of separating PC < 1.0 mm, a minimum of approximately 18–20 g per 100 g dry matter (dm) at the highest air flow rates where only the largest particles, mainly consisting of fiber with adhering protein (Banjac et al., 2017; Laudadio et al., 2013) were separated. In case of separating PC < 2.0 mm, protein content in the largest fraction was 24.6 g/100 g dm. However, as can be seen from the separation intensity functions, total yield only reached 61% and 48% for PC < 1.0 mm and PC < 2.0 mm, respectively. These significant fractionation losses can be attributed to electrostatic phenomena causing adhesion to the inner surfaces of the feeder and the zigzag classifier and are not considered further as, when increasing throughput and processing time, separation efficiency will definitely increase and L will become lower.

Using the yield of the individual fractions, we also calculated protein separation efficiency PSE (%) by (Silventoinen, Kortekangas, Ercili-Cura, & Nordlund, 2021; Tyler, Youngs, & Sosulski, 1981)

$$PSE = \frac{Y \bullet P_F}{P_C} \quad \text{Eq. (9)}$$

where P_F is the protein content of the respective fraction after

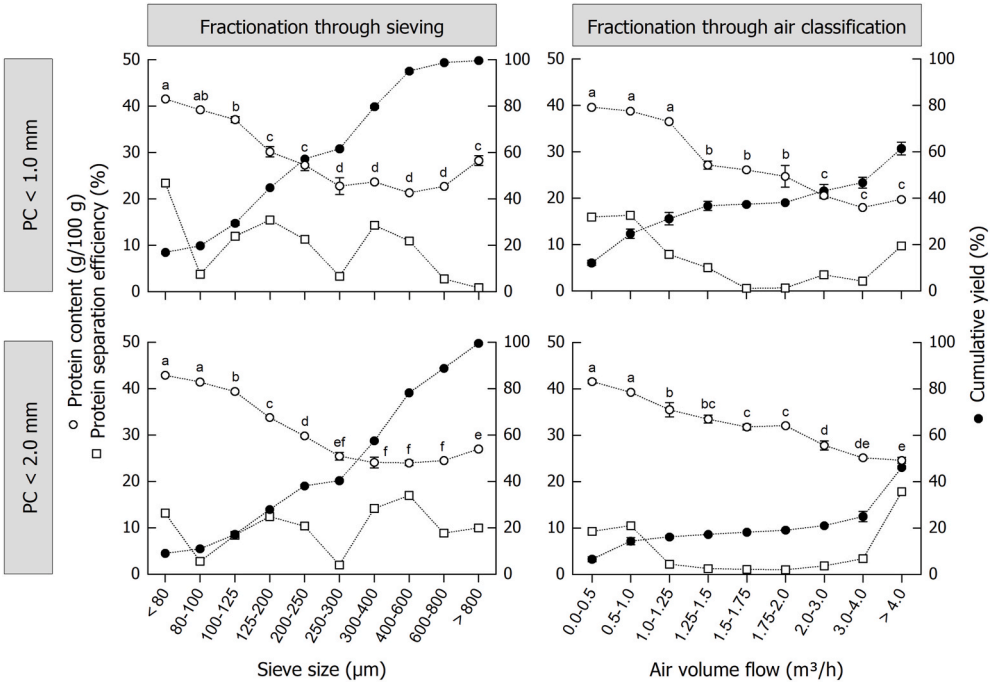

Fig. 2. Protein content (dry matter based), separation intensity functions expressed as cumulative yield, and protein separation efficiency of individual fractions of deoiled sunflower press cake (PC) milled to < 1.0 mm or < 2.0 mm obtained by sieving or by air classification. Mean values in a chart having different letters differ significantly (P < 0.05).

Fig. 3. Microscopic images of individual fractions of deoiled sunflower press cake (PC) milled to < 1.0 mm or < 2.0 mm obtained by sieving or air classification. Scale bar (1 mm, top row) is identical for all images.

Table 2
Yield, protein content, relative protein enrichment and protein separation efficiency of selected fractions separated by sieving or air classification of sunflower press cake (PC) milled to < 1.0 mm or < 2.0 mm.

	Milling size (mm)	Mesh size (µm)	Yield (%)	Protein content (g/100 g dm)	Protein enrichment (−)	PSE (%)
Sieving	1.0	80	19.6 ± 0.2 b	42.49 ± 0.28 a	1.42	27.8
		125	31.3 ± 0.7 a	41.16 ± 0.13 b	1.37	43.0
	2.0	80	9.2 ± 0.8 d	42.99 ± 0.03 a	1.47	13.6
		125	14.9 ± 0.6 c	41.52 ± 0.06 b	1.42	21.2
		200	29.1 ± 1.1 a	38.10 ± 0.11 c	1.30	37.9
	Milling size (mm)	Air flow (m^3/h)	Yield (%)	Protein content (g/100 g dm)	Protein enrichment (−)	PSE (%)
Air classification	1.0	0.50	29.4 ± 0.3 ab	39.11 ± 0.11 b	1.30	38.4
		1.25	36.9 ± 0.6 a	38.20 ± 0.02 c	1.28	27.4
	2.0	0.50	16.7 ± 1.5 c	40.10 ± 0.22 a	1.37	37.2
		1.25	26.5 ± 5.4 bc	37.48 ± 0.04 d	1.28	28.3
		2.00	31.4 ± 0.8 ab	36.77 ± 0.09 e	1.26	25.9

Mean values ± half deviation range from n = 2 replicate measurements. For each separation method, mean values in a column having different letters differ significantly (P < 0.05).

separation. (For definition of Y and P_C, see Eq. (1) and Eq. (4), respectively.) PSE therefore indicates how much of the protein ends up in a distinct fraction and is affected by, for instance, agglomerate formation (Funke et al., 2022; Wright et al., 1984). It is evident from Fig. 2 that smaller fractions obtained by sieving showed a tendency towards higher PSE than fractions obtained by low air flow rates. PSE as a combined measure of yield and protein content of individual fractions was therefore used for selecting the separation conditions for the second part of the study.

Fig. 3 shows the appearance of the individual fractions, obtained by sieving or air classification from deoiled sunflower PC milled to a maximum particle size of 1.0 mm or 2.0 mm. As compared to the fractions obtained by sieving, the ones separated by intermediate air flow appeared very similar. Starting with a sieve size of 125 µm and an air flow of 1 m^3/h, distinctly more elongated fiber particles are visible in the separated fractions.

3.2. Selection of separation conditions

For selecting separation conditions to obtain press cake fractions for technofunctionality investigations, we referred to protein content and cumulative yield obtained in the initial separation experiments. For PC milled to <1.0 mm, we selected conditions where the fractions with the highest protein content were separated, i.e., the <80 µm sieve or an air flow <0.5 m^3/h. The use of the 125 µm sieve or an air flow of 1.25 m^3/h resulted in an additional fraction with a protein content about 10% lower but a yield approximately twice as high (see Fig. 2). For PC < 2.0 mm, protein content and yield of the individual fractions was generally higher and lower, respectively. For this reason and, additional to identical separation conditions, we included a separation class of 200 µm or 2 m^3/h in the investigations.

3.3. Physical properties of fractionated sunflower press cake

Table 2 summarizes yield, protein content, relative protein enrichment (i.e., protein content of a fraction as related to initial protein content of the PC subjected to separation) and PSE of the fractions used for subsequent analyses. Yield of the 80 µm and 125 µm fractions was almost twice as high when PC < 1.0 mm was subjected to sieving, and approximately 30% for the largest sieve fractions. Independent of initial PC milling, protein content was similar for both the 80 µm and the 125 µm fraction, but decreased significantly with increasing mesh size. This is also reflected by the protein enrichment factor, which ranged between 1.30 and 1.47. PSE was highest for the fractions where the yield was highest, with about 43% for the 125 µm fraction separated from PC < 1.0 mm, and 38% for the 200 µm fraction from PC < 2.0 mm. When using air classification, PSE was ~38% for the fractions separated by

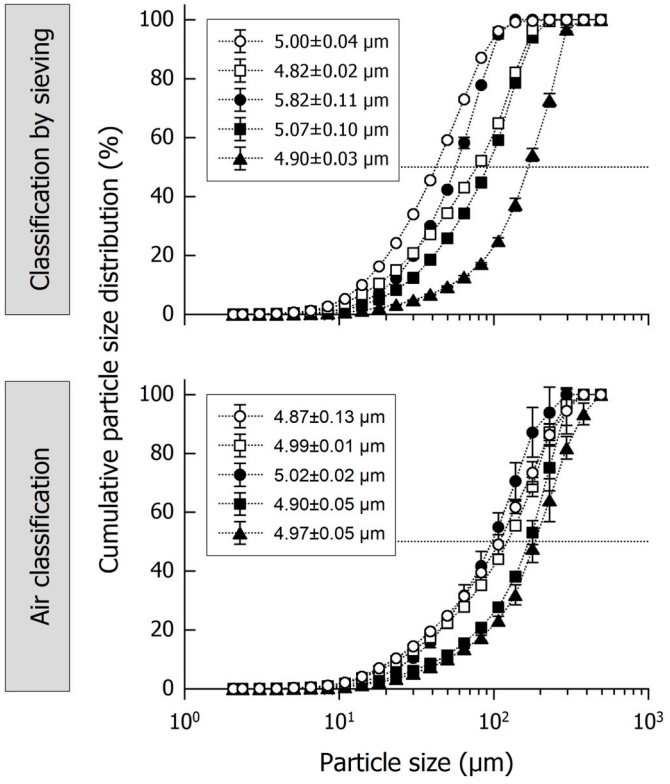

Fig. 4. Volume-based cumulative particle size distributions of press cake (PC) fractions obtained by sieving or air classification. Open symbols, base PC milled to <1.0 mm; closed symbols, base PC milled to <2.0 mm. Sieve size and air flow: Circles, 80 µm or 0.5 m^3/h; squares, 125 µm or 1.25 m^3/h; triangles, 200 µm or 2 m^3/h. Inserts show number-based x_{50} diameter. Data are arithmetic mean ± half deviation range from duplicate experiments.

means of the lowest air volume flow.

Fig. 4 depicts volume-based particle size distributions of the individual fractions obtained by both separation methods. The x_{50} median, calculated by the EQPC model, was approximately 42 and 78 µm when separating PC < 1.0 mm by 80 µm and 125 µm sieves, respectively, and significantly higher when PC < 2.0 mm was used as base material. Nevertheless, the impact of sieve size on size distribution is more pronounced than the raw material's particle size. The number-based x_{50} diameters were approximately one magnitude lower, indicating that the sieved fractions contain a large amount of small and a low number of large particles. All x_{90} diameters were higher than nominal sieve sizes

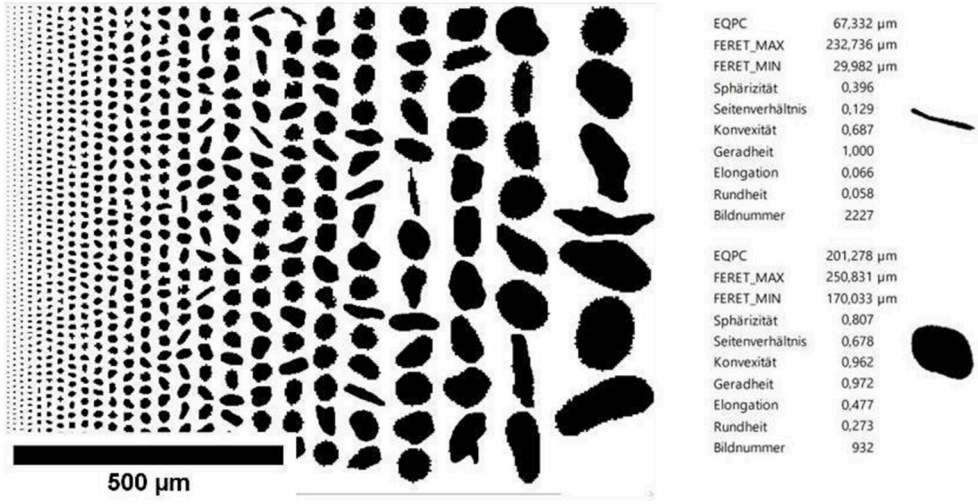

Fig. 5. QicPic images from particles separated from sunflower press cake by air classification at 0.5 m^3/h air volume flow. Translation of output parameters: Sphärizität, sphericity; Seitenverhältnis, aspect ratio; Konvexität, convexity; Geradheit, straighness; Elongation, elongation; Rundheit, roundness.

(data not shown), meaning that a certain amount of elongated fibers passed perpendicular to the sieve.

As regards air classification, the number-based x_{50} diameters were almost similar to those of the fractions obtained by sieving, whereas the volume-based median diameters were much higher. This indicates a higher relative amount of larger particles, presumable fiber, in the respective fraction which, in turn, may explain their lower protein content (see Table 2). Although working with a different fractionation system, Xing et al. (2020) observed a similar relationship when separating starch from legume meals. We observed two statistical groups of volume-based x_{50} diameters, with higher values of approximately 180 µm for higher air flow. The relatively large standard deviations at larger particle size can be considered as indicator for the presence of a certain amount of oversized particles.

Particle size analysis with the QicPic system allowed to illustrate individual particles, for example after separating PC < 1.0 mm using an air flow of 0.5 m^3/h. The right panel in Fig. 5 shows two of the larger individual particles, along with calculated measures. While the maximum Feret diameter is almost similar, the aspect ratio differs by a factor of more than five. When analyzing the mean aspect ratio as a function of particle size we observed that a ratio <0.6 was only evident for particles <5 µm or >200 µm. As, in case of small particles which are more relevant for protein enrichment, the aspect ratio cannot be estimated with the required accuracy, we did not consider this evaluation further.

Comparison of the color of the separated fines fractions with the base material revealed that neither the redness coordinate (a* = 0.6–0.9) nor the yellowness coordinate (b* = 6.4–7.1) were significantly affected by separation. In contrast, lightness differences were responsible for a color difference which increased with increasing fineness of the fractions. For instance, ΔE* was 1.31, 2.17 and 3.24 for the fines fractions separated from PC < 2.0 mm using either the 200, 125 or 80 µm sieves. This is partly above the sensory color threshold value of 1.75 and therefore also visible for the untrained eye (Fernández-Vázquez, Stinco, Hernanz, Heredioa, & Vicario, 2013).

3.4. Impact of press cake separation on technofunctional properties

The proteins soluble in water at pH 6.5 represent, according to the Osborne (1924) classification, the albumin fraction (Geneau-Sbartaï, Leyris, Silvestre, & Rigal, 2008) which, in case of sunflower protein, accounts for approximately 30% of the entire protein (González-Pérez & Vereijken, 2007). Although showing some significant differences, protein solubility was affected neither by the fractionation method nor by particle size of the respective fractions (Table 3), and ranged between 7.4% and 10.8%.

As regards foaming capacity, we observed significant effects of both raw material type and fractionation intensity. FC for base PC < 1.0 mm

Table 3
Technofunctional properties of selected fractions obtained by sieving or air classification from sunflower press cake (PC) milled to < 1.0 mm or < 2.0 mm.

	Milling size (mm)		Protein solubility (%)	Foaming capacity (%)	Emulsion activity (%)	Emulsion stability (%)
Base	1.0		9.2 ± 0.8 abc	34.0 ± 0.1 c	40.8 ± 2.9 ab	26.0 ± 1.7 ab
	2.0		8.7 ± 0.9 bc	28.3 ± 0.5 c	27.1 ± 3.5 g	8.4 ± 2.1 f
	Milling size (mm)	Mesh size (µm)	Protein solubility (%)	Foaming capacity (%)	Emulsion activity (%)	Emulsion stability (%)
Sieving	1.0	80	9.6 ± 0.4 ab	75.6 ± 2.1 a	40.4 ± 0.7 ab	24.1 ± 3.4 abc
		125	9.0 ± 0.1 abc	84.4 ± 0.1 a	39.6 ± 0.8 abc	28.7 ± 3.1 a
	2.0	80	8.2 ± 0.1 bc	52.2 ± 1.1 b	42.3 ± 0.8 a	24.1 ± 9.8 abc
		125	9.0 ± 0.38 abc	56.7 ± 2.2 b	38.3 ± 0.8 bcd	12.5 ± 4.2 ef
		200	9.2 ± 0.1 abc	35.6 ± 2.2 c	37.7 ± 0.9 cde	13.1 ± 1.5 def
	Milling size (mm)	Air flow (m^3/h)	Protein solubility (%)	Foaming capacity (%)	Emulsion activity (%)	Emulsion stability (%)
Air classification	1.0	0.50	8.0 ± 0.2 bc	84.4 ± 0.2 a	39.2 ± 1.8 abc	23.8 ± 2.1 abc
		1.25	7.4 ± 0.1 c	77.8 ± 0.1 a	31.7 ± 1.9 f	20.9 ± 2.4 bcd
	2.0	0.50	9.0 ± 0.2 abc	51.1 ± 3.9 b	34.6 ± 1.8 ef	15.4 ± 4.7 def
		1.25	10.8 ± 0.6 a	34.4 ± 0.2 c	36.4 ± 1.2 cde	12.7 ± 2.1 ef
		2.00	9.2 ± 0.6 ab	36.7 ± 3.3 c	34.9 ± 0.9 def	16.6 ± 1.6 cde

Mean values ± half deviation range from n = 2 replicate measurements. Mean values in a column having different letters differ significantly (P < 0.05).

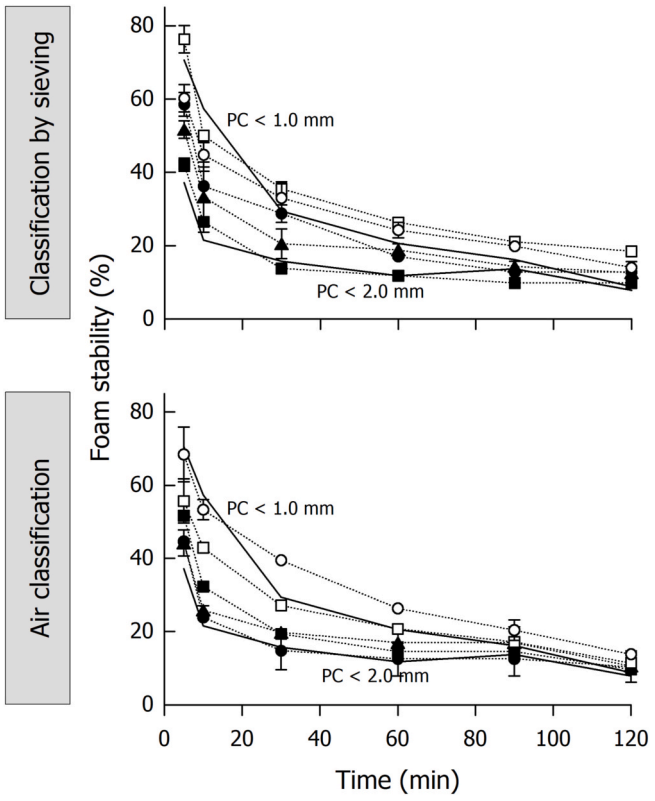

Fig. 6. Foam stability in solutions of press cake (PC) fractions obtained by sieving or air classification. Open symbols, base PC milled to <1.0 mm; closed symbols, base PC milled to <2.0 mm. Sieve size and air flow: Circles, 80 μm or 0.5 m^3/h; squares, 125 μm or 1.25 m^3/h; triangles, 200 μm or 2 m^3/h. Thick full lines, reference data from base PC. Data are arithmetic mean ± half deviation range from duplicate experiments.

and PC < 2.0 mm was 34.0% and 28.3%, respectively. Subjecting PC < 1.0 mm to either sieving or air classification caused an increase of FC up to approximately 85%. Separating fines from the larger base material (PC < 2.0 mm) resulted in an intermediate FC when using the 80 or 125 μm sieves or an air flow of 0.5 m^3/h. The lowest foaming capacity, almost similar to that of both base materials, was obtained with the largest sieve and a higher air flow. In this case, x_{50} of the fractions was 168 μm (sieving) or 171 μm and 187 μm for 1.25 m^3/h and 2.0 m^3/h, respectively. By considering the observations of Fenn et al. (2022) concerning differences between pea flour and protein concentrates thereof, and the data of Lin, Humbert, and Sosulski (1974) and Sosulski and Fleming (1977) concerning foaming capacities of sunflower meal and a protein isolate thereof, this indicates that mainly the enrichment of protein (see Table 2) is responsible for this behavior.

Time-based foam stability, referring to the relative amount of foam persistent after a distinct period of time was, after 5 min, 70% and 38% for the base PC < 1.0 mm and PC < 2.0 mm, respectively, and the residual foam after 2 h was approximately 10% of its initial volume (Fig. 6). A comparable time decay is evident for all fractions produced by either separation method. It is also evident that, especially at lower time scale, fines fractions obtained from PC < 1.0 mm exhibited a significantly higher FS. The fast loss of foam volume within the initial 40 min has been attributed to the stiffer structure of the 2S albumins in sunflower (Anisimova, Fido, Tatham, & Shewry, 1995; Guéguen et al., 1996) as compared to, for instance, canola protein which provides higher foaming capacity and foam stability (Nitecka, Raab, & Schwenke, 1986; Schwenke, Kim, Kroll, Lange, & Mieth, 1991).

A higher emulsion activity and improved thermal emulsion stability can be considered as indicator for smaller emulsion droplets more stable against centrifugal forces (McClements, 2015). As indicated in Table 3 and despite a comparable protein content, the base material milled to <1.0 mm exhibits a significantly higher EA and ES than PC milled to <2.0 mm. In case of sieved fines fractions separated from PC < 1.0 mm, neither EA nor ES of PC < 1.0 mm significantly improved. The situation is different when considering fines fractions separated from PC < 2.0 mm. Both EA and ES of these fractions were significantly higher than that of the respective base, and almost inversely related to target particle size. For the fines fractions obtained from the base press cakes by air classification, the effect of final particle size on EA and ES is evident in a similar manner. Finally, the fact that emulsion stability was lower than emulsion activity indicates that thermal impact leads to emulsion destabilization, presumably through coalescence, which is contradictory to the findings of Schwenke et al. (1991) obtained for sunflower meal.

For the samples subjected to time-based phase separation experiments, the mean initial backscatter intensities, taken from the respective backscatter profiles (Fig. S1), are displayed in Fig. 7. Compared to the base materials, BS_0 of the fines fractions is significantly higher, indicating that protein enrichment obtained through particle size fractionation results in smaller emulsion droplets that are densely packed. The fact that there is no significant difference within the tested fines fractions is in line with the EA results obtained by the centrifugation method. A comparison with results of other authors is however difficult,

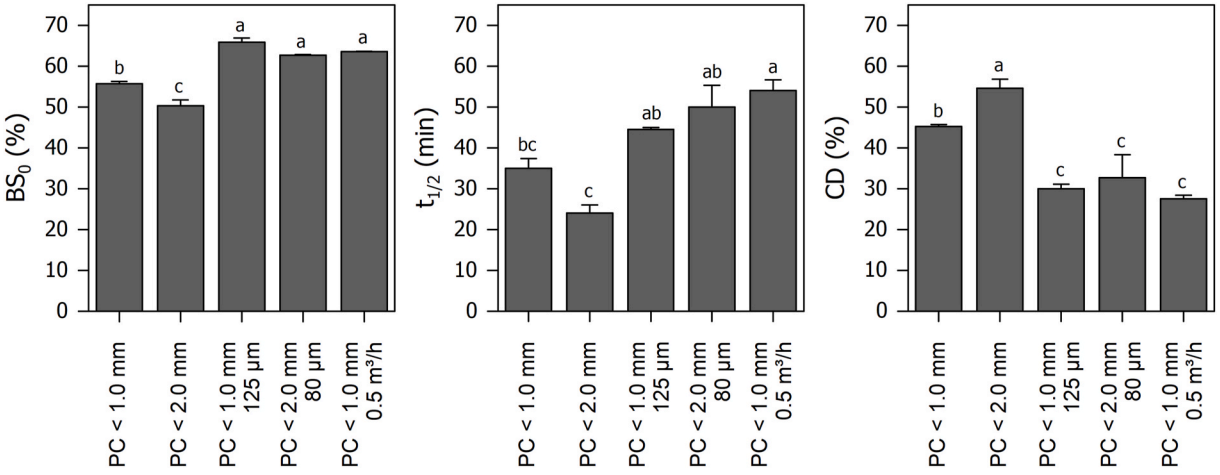

Fig. 7. Initial backscatter intensity BS_0, backscatter half-time value $t_{1/2}$ and coefficient of destabilization (CD) of base press cake (PC) milled to < 1.0 mm or < 2.0 mm and fractions thereof obtained by sieving or air classification. Data are mean values ± half deviation range from duplicate e measurements. Mean values in a chart having different letters differ significantly (P < 0.05).

as backscatter is influenced by oil volume fraction, and emulsification method and hence oil droplet size. Exemplary, for protein extracted from sunflower press cake, Salgado et al. (2012) observed an initial backscatter of 54–60% for emulsions with 25% oil volume fraction and an aqueous phase containing 1 g/L protein.

In the 2 h evaluation interval, creaming results in a reduction of backscatter intensity in the lower part of the sample vials, and becomes higher in the middle section of the vials (15–20 mm height) where drop density increases locally. Further coalescence and flocculation especially in the upper section may, however, also affect backscatter intensity (Palazolo, Sorgentini, & Wagner, 2005). Fig. 7 also depicts the characteristic time that was necessary for halving backscatter intensity at the bottom of the test vials. It is evident that the base materials and, especially, the emulsions made with PC < 2.0 mm, were less stable than the emulsions made with protein enriched fractions separated either by sieving or air classification. Finally, the coefficient of destabilization calculated from the relative decrease of the averaged backscatter intensity after 2 h also shows the positive effects of fractionation on emulsion stability.

4. Conclusions

The dry fractionation of milled and deoiled sunflower press cake by sieving and air classification enabled protein enrichment in the fines fractions. The highest protein enrichment of 1.47 was reached when sieving PC milled to <2.0 mm with 80 μm mesh size. However, the yield of this fraction was very low. The highest protein separation efficiency, the combined measure comprising of protein content and yield, was reached after separating PC milled to <1.0 mm with a 125 μm mesh sieve. Compared to sieving, air classification produced a larger amount of oversized particles, because particles were not only separated by their size but also depending on form and density.

While protein solubility of the separated fractions did not differ significantly from the base materials, foaming and emulsifying properties of several solutions of press cake were improved. Although the effort is higher, the use of the stability analyzer brought many benefits for the analysis of the emulsions compared to the centrifugation method. For example, emulsion activity and stability after centrifugation showed less significant differences among the samples compared to the results of time-based phase separation analysis. Additionally, initial backscattering intensity allowed to detect differences between emulsions from base materials and fines fractions even before separation occurred. In addition, backscatter analysis allows to observe separation phenomena such as creaming, clearing and coalescence were observed in real-time.

The main outcome of the study is that sieving and air classification are suitable methods to obtain fractions from sunflower press cake with enhanced protein content and technofunctional properties for the application in food.

CRediT authorship contribution statement

Sophie Morejón Caraballo: Writing – original draft, Methodology, Investigation, Data curation. **Stephanie Trültzsch:** Methodology, Investigation, Data curation. **Susanne Struck:** Writing – review & editing, Validation, Project administration, Conceptualization. **Harald Rohm:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Ethics

Ethics approval was not required for this research.

Declaration of competing interest

No conflict of interest exists in the submission of this manuscript. The manuscript has been approved by all authors for submission.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2024.117148.

Data availability

Data will be made available on request.

References

Ancuța, P., & Sonia, A. (2020). Oil press-cakes and meals valorization through circular economy approaches: A review. *Applied Sciences, 10*, 7432.
Anisimova, I. N., Fido, R. J., Tatham, A. S., & Shewry, P. R. (1995). Genotypic variation and polymorphism of 2S albumins of sunflower. *Euphytica, 83*, 15–23.
Arrutia, F., Binner, E., Williams, P., & Waldron, K. W. (2020). Oilseeds beyond oil: Press cakes and meals supplying global protein requirements. *Trends in Food Science & Technology, 100*, 88–102.
Assatory, A., Vitelli, M., Rajabzadeh, A. R., & Legge, R. L. (2019). Dry fractionation methods for plant protein, starch and fiber enrichment: A review. *Trends in Food Science & Technology, 86*, 340–351.
Banjac, V. V., Čolović, R. R., Vukmirović, Đ. M., Sredanović, S. A., Lević, J. D., & Teodosin, S. J. (2013). Protein enrichment of sunflower meal by air classification. *Food and Feed Research, 40*, 77–83.
Baümler, E. R., Carrin, M. E., & Carelli, A. A. (2016). Extraction of sunflower oil using ethanol as solvent. *Journal of Food Engineering, 178*, 190–197.
Boye, J., Zare, F., & Pletch, A. (2010). Pulse proteins: Processing, characterization, functional properties and applications in food and feed. *Food Research International, 43*, 414–431.
Capellini, M. C., Novais, J. S., Monteiro, R. F., Veiga, B. Q., Osiro, D., & Rodrigues, C. E. C. (2020). Thermal, structural and functional properties of rice bran defatted with alcoholic solvents. *Journal of Cereal Science, 95*, Article 103067.
Chéreau, D., Videcoq, P., Ruffieux, C., Pichon, L., Motte, J.-C., Belaid, S., et al. (2016). Combination of existing and alternative technologies to promote oilseeds and pulses proteins in food applications. *Oilseeds and Fats, Crops and Lipids, 23*, Article D406.
Cloutt, P., Walker, A. F., & Pike, D. J. (1987). Air classification of flours of three legume species: Fractionation of protein. *Journal of the Science of Food and Agriculture, 38*, 177–186.
Dijkink, B. H., Speranza, L., Paltsidis, D., & Vereijken, J. M. (2007). Air dispersion of starch–protein mixtures: A predictive tool for air classification performance. *Powder Technology, 172*, 113–119.
Fenn, D., Wang, N., & Maximiuk, L. (2022). Physicochemical, anti-nutritional, and functional properties of air-classified protein concentrates from commercially grown Canadian yellow pea (Pisum sativum) varieties with variable protein levels. *Cereal Chemistry, 99*, 157–168.
Fernández-Vázquez, R., Stinco, C. M., Hernanz, D., Heredioa, F. J., & Vicario, I. M. (2013). Colour training and colour differences thresholds in orange juice. *Food Quality and Preference, 30*, 320–327.
Funke, M., Loeffler, M., Winkelmeyer, C., Krayer, M., Boom, R., & Weiss, J. (2022). Emulsifying properties of lentil protein preparations obtained by dry fractionation. *European Food Research and Technology, 248*, 381–391.
Geneau-Sbartaï, C., Leyris, J., Silvestre, F., & Rigal, L. (2008). Sunflower cake as a natural composite: Composition and plastic properties. *Journal of Agricultural and Food Chemistry, 56*, 11198–11208.
González-Pérez, S., & Vereijken, J. M. (2007). Sunflower proteins: Overview of their physicochemical, structural and functional properties. *Journal of the Science of Food and Agriculture, 87*, 2173–2191.
Guéguen, J., Popineau, Y., Anisimova, I. N., Fido, R. J., Shewry, P. R., & Tatham, A. S. (1996). Functionality of the 2S albumin seed storage proteins from sunflower (*Helianthus annuus* L.). *Journal of Agricultural and Food Chemistry, 44*, 1184–1189.
Laguna, O., Barakat, A., Alhamada, H., Durand, E., Baréa, B., Fine, F., et al. (2018). Production of proteins and phenolic compounds enriched fractions from rapeseed and sunflower meals by dry fractionation processes. *Industrial Crops and Products, 118*, 160–172.

Laudadio, V., Bastoni, E., Introna, M., & Tufarelli, V. (2013). Production of low-fiber sunflower (Helianthus annuus L.) meal by micronization and air classification processes. *CyTA - Journal of Food, 11*, 398–403.
Lin, M. J. Y., Humbert, E. S., & Sosulski, F. W. (1974). Certain functional properties of sunflower meal products. *Journal of Food Science, 39*, 368–370.
Liu, K. (2009). Some factors affecting sieving performance and efficiency. *Powder Technology, 193*, 208–213.
McClements, D. J. (2015). Food emulsions. In *Principles, practices, and techniques* (3rd ed.). Boca Raton, FL, USA: CRC Press.
Morejón Caraballo, S., Rohm, H., & Struck, S. (2023). Green solvents for deoiling pumpkin and sunflower press cakes: Impact on composition and technofunctional properties. *International Journal of Food Science and Technology, 58*, 1931–1939.
Murru, M., & Calvo, C. L. (2020). Sunflower protein enrichment. Methods and potential applications. Oilseeds and Fats. *Crops and Lipids, 27*, 17.
Nitecka, E., Raab, B., & Schwenke, K. D. (1986). Chemical modification of proteins. Part 12. Effect of succinylation on some physico-chemical and functional properties of the albumin fraction from rapeseed (Brassica napus L.). *Nahrung-Food, 30*, 975–985.
Osborne, T. B. (1924). The vegetable proteins. *Nature, 114*, 822, 822.
Palazolo, G. G., Sorgentini, D. A., & Wagner, J. R. (2005). Coalescence and flocculation in o/w emulsions of native and denatured whey soy proteins in comparison with soy protein isolates. *Food Hydrocolloids, 19*, 595–604.
Pickardt, C., Eisner, P., Kammerer, D. R., & Carle, R. (2015). Pilot plant preparation of light-coloured protein isolates from de-oiled sunflower (Helianthus annuus L.) press cake by mild-acidic protein extraction and polyphenol adsorption. *Food Hydrocolloids, 44*, 208–219.
Salgado, P. R., Molina Ortiz, S. E., Petruccelli, S., & Mauri, A. N. (2012). Functional food ingredients based on sunflower protein concentrates naturally enriched with antioxidant phenolic compounds. *Journal of the American Oil Chemists' Society, 89*, 825–836.
Schutyser, M. A. I., Pelgrom, P. J. M., Van Der Goot, A. J., & Boom, R. M. (2015). Dry fractionation for sustainable production of functional legume protein concentrates. *Trends in Food Science & Technology, 45*, 327–335.
Schutyser, M. A. I., & van der Goot, A. J. (2011). The potential of dry fractionation processes for sustainable plant protein production. *Trends in Food Science & Technology, 22*, 154–164.
Schwenke, K. D., Kim, Y. H., Kroll, J., Lange, E., & Mieth, G. (1991). Modification of the low-molecular weight basic albumin fraction from rapeseed (Brassica napus L.) by acetylation. Part 2. Selected functional properties. *Food, 35*, 293–301.
Shapiro, M., & Galperin, V. (2005). Air classification of solid particles: A review. *Chemical Engineering and Processing: Process Intensification, 44*, 279–285.
Silventoinen, P., Kortekangas, A., Ercili-Cura, D., & Nordlund, E. (2021). Impact of ultra-fine milling and air classification on biochemical and techno-functional characteristics of wheat and rye bran. *Food Research International, 139*, Article 109971.
Sosulski, F., & Fleming, S. E. (1977). Chemical, functional, and nutritional properties of sunflower protein products. *Journal of the American Oil Chemists' Society, 54*, 100A–104A.
Tyler, R. T., Youngs, C. G., & Sosulski, F. W. (1981). Air classification of legumes. 1. Separation efficiency, yield, and composition of the starch and protein fractions. *Cereal Chemistry, 58*, 144–148.
Wildermuth, S. R., Young, E. E., & Were, L. M. (2016). Chlorogenic acid oxidation and its reaction with sunflower proteins to form green-colored complexes. *Comprehensive Reviews in Food Science and Food Safety, 15*, 829–843.
Wright, D. J., Bumstead, M. R., Coxon, D. T., Ellis, H. S., DuPont, M. S., & Chan, H. W.-S. (1984). Air classification of pea flour–analytical studies. *Journal of the Science of Food and Agriculture, 35*, 531–542.
Xing, Q., Utami, D. P., Demattey, M. B., Kyriakopoulou, K., de Wit, M., Boom, R. M., et al. (2020). A two-step air classification and electrostatic separation process for protein enrichment of starch-containing legumes. *Innovative Food Science & Emerging Technologies, 66*, Article 102480.
Yasumatsu, K., Sawada, K., Moritaka, S., Misaki, M., Toda, J., Wada, T., et al. (1972). Whipping and emulsifying properties of soybean products. *Agricultural and Biological Chemistry, 36*, 719–727.