



Is dehulling of peas and faba beans necessary prior to dry fractionation for the production of protein- and starch-rich fractions? Impact on physical properties, chemical composition and techno-functional properties

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ABSTRACT

Dehulling of peas and faba beans prior to milling and air classification was evaluated, namely its impact on physical properties, chemical composition and techno-functional properties of the fractions. Dry fractionation protocols for protein enrichment from whole and dehulled peas and faba beans were optimized and large-scale batches were produced. Fine fractions with protein contents of 44.0 and 46.2% dm from whole and dehulled peas and between 60.0 and 60.9% dm from whole and dehulled faba beans were obtained, respectively. A maximum protein recovery of 71.3% and 49.2% was obtained for peas and faba beans, respectively. Dehulling enabled a lighter colour of faba bean fractions and improved the starch enrichment in the coarse fractions from peas and faba beans. The total non-starch polysaccharides were significantly reduced in the coarse fractions when dehulling was conducted. Dehulling did not significantly improve the techno-functional properties of fine and coarse fractions.

1. Introduction

The continuous growing of the world population creates an increase in the protein requirement. Moreover, novel ingredients from plant origins that can replace animal-based food products are in growing demand. The use of plant protein ingredients to improve texture and the nutritional quality of foods is growing (Schutyser and van der Goot, 2011). A sustainable diet is normally described by a higher protein uptake from a wide variety of crops in order to decrease the dependency on single crops, such as soy (Van Der Goot et al., 2016). Pulses, such as field peas and faba beans, are potential raw materials (RM) for production of plant protein ingredients from a functional, technological and nutritional points of view. Peas and beans are starchy crops with a relatively high protein content (Sozer et al., 2017).

The conventional way to obtain protein ingredients is wet fractionation, which requires the utilization of great amounts of chemicals and water (Schutyser et al., 2015). An alternative route that avoids the

addition of water and chemicals and preserves the functionality of the constituents is dry fractionation, mainly including milling and air classification steps (Schutyser and van der Goot, 2011). During pin-milling, the starch granules are detached from the protein bodies, allowing their separation during subsequent fractionation step. The protein bodies, which are smaller than the starch granules are then separated by air-classification based on density, size and shape (Boye et al., 2010a). Protein and starch enriched fractions produced by dry-fractionation retain part of the native structure and functionality (Schutyser and van der Goot, 2011; Pelgrom et al., 2014a). One fact that should be considered though, is that protein fractions from pulses produced through dry-fractionation still contain bioactive constituents that are barely present in protein isolates produced by wet fractionation (Van Der Goot et al., 2016). These bioactive constituents comprise phytochemicals, dietary fibres and resistant starches, making pulses attractive for application in a wide variety of foods. Additionally, other bioactive constituents consist of phytates, enzyme inhibitors and lectins that are frequently considered as antinutritional factors (ANFs). These ANFs are

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List of abbreviations

a*	Redness	FF-WB	Fine fraction from whole faba beans
ANFs	Antinutritional factors	FF-WP	Fine fraction from whole peas
b*	Yellowness	FI	Foam instability
CF-DB	Coarse fraction from dehulled faba beans	GC-FID	Gas chromatography with flame ionization detection
CF-DP	Coarse fraction from dehulled peas	HB	Faba bean hulls
CF-WB	Coarse fraction from whole faba beans	HP	Pea hulls
CF-WP	Coarse fraction from whole peas	L*	Lightness
dm	Dry matter	LMW-CHO	Low-molecular weight carbohydrates
DB	Dehulled faba beans	LSF	Large-scale fractionation
DP	Dehulled peas	NSP	Non-starch polysaccharides
DSC	Differential scanning calorimetry	PSE	Protein separation efficiency
EAI	Emulsifying activity index	RM	Raw material
EC	Emulsifying capacity	SEM	Scanning electron microscopy
ESI	Emulsifying stability index	Tden	Denaturation temperature
FBC	Fat binding capacity	Tgel	Gelatinization temperature
FC	Foaming capacity	WB	Whole faba beans
FF-DB	Fine fraction from dehulled faba beans	WHC	Water holding capacity
FF-DP	Fine fraction from dehulled peas	WP	Whole peas
		ΔE	Colour difference

enriched in the pulse protein concentrate and can prevent many diseases (Singh et al., 2017) or influence the uptake of nutrients during digestion or the digestion process itself (Elkowicz and Sosulski, 1982).

Splitting and dehulling are processes, which can detach the hulls and the cotyledons from whole pulses (Neacsu et al., 2016). Dehulling can be used to enable the use of seed coats (hulls) in the manufacture of phytochemicals to be further incorporated in nutraceuticals, whereas the cotyledons can be exploited as a plant protein source (Singh et al., 2017).

One of the main legumes subjected to dry fractionation is field pea (*Pisum sativum* L.) owed to its nutritional and functional properties (Schutyser et al., 2015). Field peas are an exceptional source of protein, complex carbohydrates, folate, minerals and vitamins. In a dry basis, field peas normally contain around 48% of starch, 23% of protein, 8% of sugar, 4% total lipids and 3% of ash (Rempel et al., 2019). Dry fractionation of faba beans are not so explored as field peas. Faba bean (*Vicia faba* L.) are constituted by a high amount of protein, carbohydrates, vitamins (especially from the B-group) and minerals. It normally contains in a dry basis, 20–41% protein and 51–68% of total carbohydrates from which the major percentage (41–53% dm) is composed by starch (41–53% dm) (Frias et al., 1998).

Dry fractionation of pulses have been reported, namely concerning peas (Rempel et al., 2019; Wu and Nichols, 2005; Pelgrom et al., 2013a, 2013b, 2015a; Sosulski and Youngs, 1979; Vose et al., 1976), beans (Sosulski and Youngs, 1979; Van Der Poel and Aarts, 1990; Sosulski et al., 1982), lupine (Elkowicz and Sosulski, 1982; Sosulski and Youngs, 1979; Pelgrom et al., 2014b), chickpeas (Elkowicz and Sosulski, 1982; Pelgrom et al., 2015a; Sosulski and Youngs, 1979), lentil by-product (Schutyser et al., 2015) either by milling and air classification or milling and electrostatic separation (Pelgrom et al., 2015b). Protein concentrates from yellow field peas with protein contents around 51%–55% dm and a protein recovery of 77% were obtained by Pelgrom et al. (2013a). A fine fraction (protein concentrate) with a protein content of 55.6% dm was obtained by Pelgrom et al. (2015) after dry fractionation of peas (Pelgrom et al., 2015a). Cloutt et al. (1987) obtained a faba bean fine protein fraction containing 56.5–62.7% dm protein and a protein recovery between 44.2 and 86.5% (Cloutt et al., 1987). The literature is, however, very scarce regarding the impact of dehulling on the chemical composition of the fractions. Moreover, the existing studies did not focus on the impact of dehulling on the techno-functional properties of the produced fractions. For efficient utilization of legume seed flours, a study of the impact of dehulling on the nutritional and techno-functional

properties of produced ingredients is needed.

The aim of this study was to find out if dehulling of peas and faba beans prior to dry fractionation is necessary. The impact of dehulling on the physical properties, chemical composition and techno-functional properties of obtained protein (fine fractions) and starch concentrates (coarse fractions) was investigated.

2. Materials and methods

2.1. Materials

Yellow peas (*Pisum sativum* L. var. Ingrid) and faba beans (*Vicia faba* L. var. Kontu) were grown and harvested in 2017 at Vollebakk, Aas, Norway. Chemicals and materials used were of analytical grade and were purchased from common suppliers.

2.2. Dehulling

Dehulling of whole peas and faba beans was conducted in two stages through splitting the seeds using a Meadows 8" Stone Burr Grain Mill from Meadows Mills, Inc. (North Wilkesboro, USA), and by air separation of the hulls from the kernels. The hull fractions from peas (HP) and faba beans (HB) were milled using a Retsch ZM 100 mill (Retsch GmbH, Haan, Germany) comprising a 0.5 mm sieve for further characterization.

2.3. Milling and air classification

Crushing of whole and dehulled peas (WP and DP, respectively) and whole and dehulled faba beans (WB and DB, respectively) was performed prior to milling and air classification using a Retsch SM 300 cutting mill with a 1 cm × 1 cm sieve operated at 700 rpm. After crushing, the samples were milled once or twice using a Hosokawa Alpine 100 UPZ pin disc mill operated at a rotor speed of 17800 rpm (Hosokawa-Alpine, Augsburg, Germany). After milling, the milled whole/dehulled peas and faba beans were air classified using a Minisplit air classifier (British Rema Manufacturing Company Ltd., Chesterfield, UK). These trials identified dry fractionation parameters to obtain a good balance between mass yield, protein content and protein separation efficiency (PSE) in the fine fractions. The classifier wheel speed was varied between 4250 and 15000 rpm for the whole and dehulled peas and between 5000 and 15000 rpm for the whole and dehulled faba beans. The air flow used for both peas and faba beans was varied

between 100 and 220 m³ h⁻¹. In the optimization trials, 100 g sample size was utilized in each fractionation and the sample was fed in the classifier manually. Before the large-scale air classification, pea samples were milled once and faba bean samples were milled twice with pin disc mill. The selected air classification parameters in the large-scale were 12500 rpm and 220 m³ h⁻¹ for the whole peas and 15000 rpm and 220 m³ h⁻¹ for the dehulled peas, whole faba beans and dehulled faba beans. Batches of 1400–2500 g were fractionated using automated feeder. Fractionations in large-scale resulted in fine and coarse fractions from whole peas (FF-WP and CF-WP), dehulled peas (FF-DP and CF-DP), whole faba beans (FF-WB and CF-WB) and dehulled faba beans (FF-DB and CF-DB). Mass yield and protein separation efficiency (PSE) was calculated according to Tyler et al. (1981) and Silventoinen et al. (2019) (Tyler et al., 1981; Silventoinen et al., 2019). In the optimization trials the air classification procedures were only performed once whereas the optimized conditions were replicated four times for each raw material. The theoretical deviations of the protein content and PSE for the optimization trials were calculated based on the standard deviations of the fine fractions from the large-scale fractionations. Only the optimized large-scale fractions produced were further characterized.

2.4. Characterization of the enriched fractions

2.4.1. Morphology - SEM

Morphology of the fine and coarse fractions obtained from whole and dehulled peas and faba beans was studied by Scanning Electron Microscopy using a Zeiss EVO50 EP Scanning electron microscope from Carl Zeiss SMT Ltd (Cambridge, UK) at 5 kV. Samples were coated with a mix of gold and palladium using a sputter coater – Polaron SC 7640 from Quorum Technologies Ltd (Ringmer, UK).

2.4.2. Particle size distribution

The particle size distributions of the fractions were measured in triplicates by laser diffraction using a HELOS/BR laser diffraction sensor, combined with a RODOS dry dispersion unit from Sympatec GmbH (Clausthal-Zellerfeld, Germany).

2.4.3. Differential scanning calorimetry (DSC)

DSC analysis was performed using a Mettler Toledo DSC 823e (Parkway, Columbus, USA). The instrument was calibrated using indium as a reference material and an empty sealed pan was used as a blank. A 30 mg dry weight of sample was inserted into a 120 µL stainless steel pan and 60 µL of water was added. Sample pans hermetically sealed were heated at 5 °C.min⁻¹ from 10 to 120 °C. The temperatures of gelatinization and denaturation were determined using STAR SW 9.01 software.

2.4.4. Colour properties

The colour of milled WP and DP, milled WB and DB, as well as, milled HP and HB were evaluated in triplicates. Moreover, the respective fine and coarse fractions obtained after dry fractionation were also assessed using a Colorimeter (CR-400, Minolta, Japan) as lightness (L*), redness (a*) and yellowness (b*). Calibration of the colorimeter (illuminant D65) was conducted against a standard white tile. Three measurements were conducted for each sample. The colour difference (ΔE) was calculated according to equation (1):

$$\Delta E = \sqrt{(L - L_0)^2 + (b - b_0)^2 + (a - a_0)^2} \quad (1)$$

where the subscript "0" designates the initial colour values of the WP, DP, WB and DB prior to dry fractionation.

2.4.5. Proximate composition

The moisture content of the raw-materials (RM) and fractions was analysed using the moisture air oven method 44–15.01 from the AACC (AACC. American Association of Cereal Chemists, 1995). Protein content (N x 6.25) was determined according to the AOAC method 2001.11

using a Kjeldahl autoanalyzer (Foss Tecator Ab, Höganäs, Sweden) (Thiex et al., 2002). Starch content was analysed by the AOAC 996.11 (2014) method using a Megazyme kit (Megazyme, Wicklow, Ireland) (AOAC, 2014). Non-starch polysaccharides (NSP) were determined by the method described by Englyst et al. (1994) via analysis of alditol acetates by GC-FID (Englyst et al., 1994). Details of NSP composition and analysis of low-molecular weight carbohydrates (LMW-CHO) composition will be published as Part II of this study.

2.4.6. Techno-functional properties

2.4.6.1. Protein solubility, water holding capacity (WHC) and fat binding capacity (FBC).

Protein solubility were assessed at various pH (2–10) following to the methods of Betschart (1974) and the AOCS method Ac4-91 (AOCS, 1974) with some modifications. For more detailed information, the reader can refer to the Supplementary material (SM). The amount of protein in the supernatant was determined according to the method of Bradford (1976) using a RC DC Protein Assay Kit from Bio-rad (California, USA). Solubility was determined as the ratio between the protein in the supernatant and the total protein of the sample, expressed in percentage. Water holding capacity (WHC) of pea and faba bean flours and fractions was analysed following AACC Method 56–20 (AACC, 2000). Fat binding capacity (FBC) was determined following a previously reported method by Lin et al. (1974) using rapeseed oil (Lin et al., 1974). The analyses were performed in duplicate or triplicate and the results were expressed in g water.g⁻¹ dm and g oil.g⁻¹ dm, respectively.

2.4.6.2. Emulsifying properties (emulsifying capacity, emulsifying activity and stability indexes).

The emulsifying capacity (EC), emulsifying activity index (EAI) and the emulsifying stability index (ESI) were accessed according to the methods described by Karaca et al. (2011) with a modification on the amount of sample used (Karaca et al., 2011). For more detailed information, the reader can refer to the Supplementary material (SM). The EC results were reported as g of oil (homogenized).g⁻¹ of protein.

2.4.6.3. Gelling properties.

The gelling properties of the fine and coarse fractions were also assessed. Briefly, 1.5 g of dry sample was suspended/solubilized in 10 mL of MQ water with stirring overnight at room temperature and pressure to ensure maximal dissolution/hydration. Samples were degassed under vacuum and stirred gently to redistribute the non-solubilized material evenly throughout the sample before rheological testing. Heat induced gelation was investigated using a Malvern Kinexus Ultra + fitted with a deep base plate and 40 mm diameter serrated upper plate with a 1.5 mm gap. The sample was completely covered in low viscosity silicon oil during measurement to prevent any dehydration. The rheological behaviour of the sample was continuously monitored (1 Hz and 0.1% strain) under heat induced gelation (20–90 °C, 2 °C/min, 30-min hold at 90 °C, 90–20 °C, 2 °C/min). Results are presented as elastic modulus G' (solid like behaviour), viscous modulus G'' (liquid like behaviour), phase angle and temperature against test time.

2.4.6.4. Foam capacity and stability.

Foam capacity (FC) and stability of the fine fractions were determined as described by Ivanova et al., (2018) with some modifications (see SM) (Ivanova et al., 2018). Evolution of the foam stability represented the reduction of the foam volume (%) and was calculated as a ratio of the foam volume retained at each time point (mL) and the foam volume (mL) immediately after whipping (expressed in percentage). The obtained data were subjected to regression analysis and were fit with a power law model. The slope of the straight line in log-log coordinates (foam volume retention over time) corresponded to the power law exponent so the highest the slope (exponent) the lowest the foam stability. Digital image processing based on mathematical

morphology was done according to Rouillé et al. (2005), which allowed to assess the dispersion characteristics of air bubbles in the foams (Rouillé et al., 2005). A digital camera (MDCE-5Mp, Alltion Co., Ltd., Wuzhou, China) attached to a binocular microscope (BM-180 SP, Boeco, Hamburg, Germany) was used to obtain the images. All images were processed and analysed with ImageJ (U. S. National Institutes of Health, Bethesda, Maryland, USA), according to Vasileva et al. (2018) (Vasileva et al., 2018).

2.5. Statistical analysis

All data acquired in triplicates (at least) were subjected to ANOVA and Fischer's least significant difference multi-comparison test. Significance of differences was represented at $p \leq 0.05$ and high significance of differences were represented at $p \leq 0.001$. The statistical analyses were conducted by Minitab 18.1 Inc. (Pennsylvania, USA).

3. Results and discussion

3.1. Optimization of the dry fractionation protocols for protein enrichment

3.1.1. Effect of milling

Optimization of the dry fractionation protocol for protein enrichment included milling of the whole and dehulled peas and faba beans once and twice to observe the effect of the milling intensity on protein separation. In dry milling of pulses, the protein bodies and starch granules are separated from each other and from other larger cellular structures, allowing size and density-based protein-enrichment during the subsequent air classification (Schutyser et al., 2015; Elkowicz and Sosulski, 1982; Pelgrom et al., 2013a, 2015b; Tyler et al., 1981). Protein enrichment is usually favoured by large starch granule size since proteins are located in small protein bodies. For peas, the common size of a protein body is 2 μm and the common size of a starch granule is 15 μm (Pelgrom et al., 2013b). For faba beans, the greatest proportion of a

starch granule is in the range of 7–18 μm but some literature reported values in the ranges from 25 to 40 μm (Pauline et al., 2018). The protein bodies of faba beans varies between 1 and 10 μm (Adler and Mfintz, 1983). The impact of milling can influence the protein separation efficiency due to differences in the particle size distribution after milling. In the present study, it was observed that milling of pea samples twice prior to air classification tended to increase the protein contents of the obtained fine fractions slightly, as illustrated in Fig. 1a. The effect of milling on protein separation efficiency of the pea samples was even more pronounced (Fig. 1b) since, especially with higher mass yields of the fine fractions, the protein separation efficiencies exhibited higher values for the twice milled pea samples. Regarding faba beans, the effect of milling intensity on protein separation was less pronounced and no clear conclusions can be made regarding the effect of milling intensity on protein separation efficiency of faba bean fine fraction (Fig. 1c and d). It may be hypothesized that more intensive milling of the pea samples further decreased the particle size and thus reduced the adhesion between the protein bodies and starch granules and allowed better separation of the smallest sized protein bodies from the larger starch granules. On the other hand, further milling might not have decreased the particle size of the faba bean samples or it may have caused too intensive pulverization of the non-proteinaceous components, which would inhibit further protein enrichment, like has also been discussed by Pelgrom et al. (2015a). The differences in the obtained maximum protein contents from the two different pulse varieties most probably derive from the differing protein contents of the starting material, differences in the sizes of the protein bodies in faba beans and peas, and differences in the break behaviour of the seeds, which all affect separation of proteins from the starch granules during dry fractionation (Pelgrom et al., 2015a).

3.1.2. Effect of dehulling

The differences between dehulled and whole peas and faba beans in terms of protein enrichment during air classification were investigated by comparing the protein contents and protein separation efficiencies.

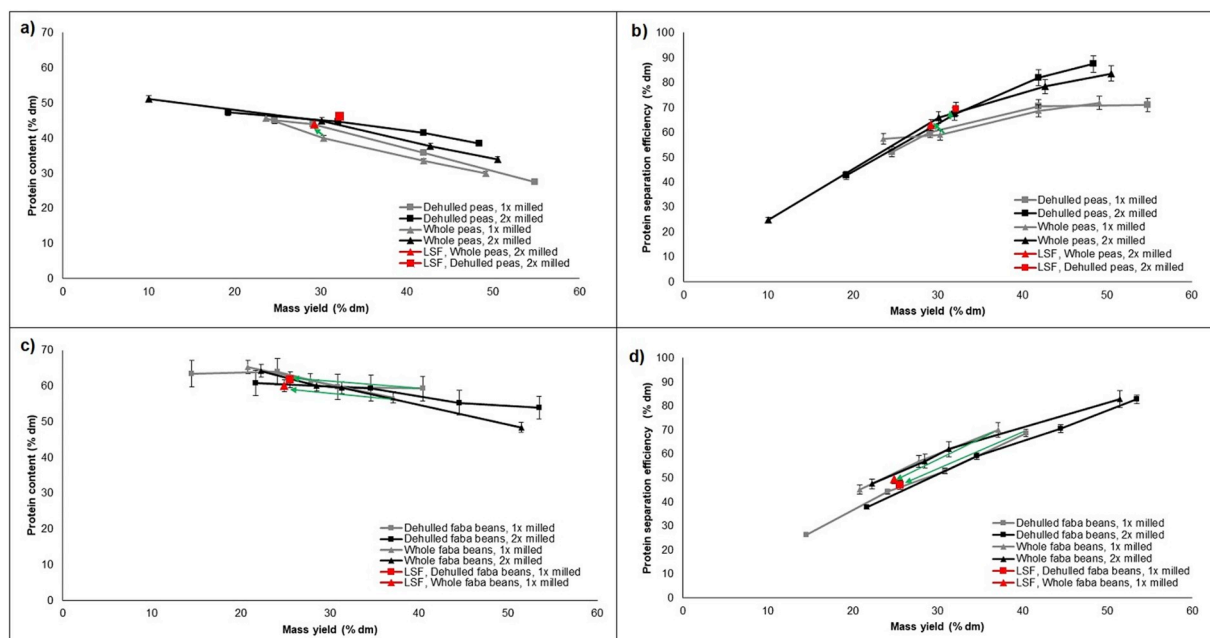


Fig. 1. a) Protein contents of the fine fractions as a function of mass yields for pea samples during optimization of the dry fractionation. b) Protein separation efficiencies of the fine fractions as a function of mass yields for pea samples during optimization of the dry fractionation. c) Protein contents of the fine fractions as a function of mass yields for faba bean samples during optimization of the dry fractionation. d) Protein separation efficiencies of the fine fractions as a function of mass yields for faba bean samples during optimization of the dry fractionation. LSF: large-scale fractionation. The green arrows in the images are pointing out the differences between mass yields, protein contents and protein separation efficiencies of the optimized fractions obtained in smaller scale (black/grey) and larger scale (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

For peas, the dehulling seemed to have a somewhat positive impact on protein enrichment, as observed from Fig. 1a and b. Both protein content and protein separation efficiency of the produced fine fractions were higher for the dehulled than for the whole pea samples. The result indicates that in the case of peas the hulls may reduce the protein separation efficiency most probably due to adherence of protein particles to the coarse hull fragments or due to impact of the hull particles on the flow or other physical properties of the raw material during air classification. Furthermore, a slightly smaller particle size was observed for the dehulled than for the whole pea material after milling (data not shown), which may suggest positive effect on the protein separation and fractionation. Additionally, it may be hypothesized that the presence of hulls impairs the milling efficiency and therefore does not allow as enough detachment of protein matrix and starch granules as observed in the case of the dehulled peas. However, it must be noted that the higher protein contents obtained from the dehulled samples also partly derive from the fact that the original protein content of the dehulled flour was higher than that of the whole flours (Table 1). For faba beans the impact of dehulling was not visible in the protein content curves. However, slightly higher protein separation efficiencies were obtained from the whole faba bean sample, indicating that in the faba bean fractionation the hull particles can have a slight positive impact on the efficiency of the protein enrichment, potentially due to their positive impact on the flow of the material during air classification.

3.1.3. Effect of production scale

The optimized conditions for fractionation of each of the four raw materials were selected based on the mass yields, protein contents and protein separation efficiencies of the fine fractions (Fig. 1). Fig. 1a–d shows the effect of production scale on the fractionation (LSF = large scale fractionation). For pea samples the LSF showed similar results as observed in the optimization trials, indicating that the flow of the material inside the classifier during the classification was similar in large and small scales. On the other hand, fractionation of faba bean samples performed clearly differently in large than in small scale fractionation. The protein contents remained similar in the large- and small-scale trials whereas the fine fraction mass yields and thus also the protein separation efficiencies remained clearly lower. This may be due to adherence of faba bean particles to the air classifier wheel which may have reduced the flow of the fine particles to the fine fraction.

3.2. Impact of dehulling on the physical properties of the fractions

3.2.1. Particle size

The volume-based average particle diameter ($D_{0.5}$) varied from 6.84 to 8.09 μm for FF-DP and FF-WP, respectively and from 6.46 to 8.77 μm

for FF-WB and FF-DB, respectively (Table 1).

These results are in agreement with the ones found by Pelgrom et al. (2015) and Rempel et al. (2019) for dry fractionation of peas (Rempel et al., 2019; Pelgrom et al., 2015c). Regarding the CF-WP and CF-DP, the particle size varied from 25.55 to 28.45 μm , respectively and from 32.02 to 33.74 μm for CF-DB and CF-WB, respectively. This indicates that the other cellular structures than proteins, such as starch granules and fibrous cell wall particles, were somewhat larger after milling in faba beans than in peas. From the results, slightly larger starch granules were identified for faba beans in comparison to peas, whereas the protein bodies seemed to be in the same size range for both peas and faba beans, as also visualized by scanning electron microscopy (SEM) (Fig. 2). Similar particle size results were also observed by Cloutt et al. (1987).

3.2.2. Colour

Colour of food ingredients, such as pea and faba bean concentrates, should have negligible effect on the food product. The colour of pea and faba bean flours and fractions obtained was evaluated and results are shown in Table 2.

The lightness (L^*) varied from 60.9 to 95.1 among all samples tested, where a higher value represents a lighter colour of the sample. As expected, the fibre fraction (hull portion) of peas (HP) and faba beans (HB) were the darkest (lower L^*) samples together with faba bean flour from milled whole beans (WB) and the coarse fraction from WB (CF-WB). Fine fractions obtained from both WP and DP as well as WB and DB did not present significant differences in darkness indicating that the fibrous components deriving from the hull fragments usually separate to the coarse fraction during air classification. As expected, coarse fractions obtained from WB showed darker colour compared to coarse fractions obtained from DB, due to the presence of dark coloured hull particles. On the other hand, regarding peas, CF-WP was only slightly darker than CF-DP, probably since the HP did not differ much in colour compared to the kernels. The colour difference (ΔE) was higher for the FF-WB and lower for CF-WB. This is explained by the fact that the hull portion of WB is separated into the CF and not to the FF. The observed differences in colour characteristics can be attributed to colour constituents in pulses. With regard to faba beans, dehulling seems to be an important step to produce protein and starch concentrates with minimal effect on the colour of final products, as also suggested by Toews et al., (Toews and Wang, 2013). According to Toews et al., (Toews and Wang, 2013), commercial pea protein concentrates presents values of 87.9, 1.5 and 15.91 for L^* , a^* and b^* , respectively (Toews and Wang, 2013). These results are in line with the ones obtained in the present study for pea protein concentrates (FF-WP and FF-DP). Different results were obtained for dry fractionation of peas in the work reported by Toews et al. (2013), in which 59.4, -6.6 and 32.1 was obtained for L^* , a^* and b^* ,

Table 1

Chemical composition of protein- and starch-enriched-fractions produced from whole and dehulled peas and faba beans by dry fractionation and their raw materials.

Flours/Fractions	Mean particle size (μm)	Mass yield (% dm)	Protein content (% dm)	PSE (% dm)	Moisture content (%)	Starch content (% dm)	Total NSP (% dm)
Whole Peas (WP) flour	–	–	20.4 ± 0.20	–	11.22 ± 0.03	49.27 ± 0.56 ^e	14.56 ± 0.17
Dehulled Peas (DP) flour	–	–	21.3 ± 0.20	–	8.73 ± 0.05	53.10 ± 0.09 ^d	7.49 ± 0.05
Peas hulls (HP)	–	–	13.8 ± 0.14	–	8.72 ± 0.02	26.78 ± 1.31 ^h	41.90 ± 1.04
FF-WP	8.09 ± 0.16	29.2 ± 0.53	44.0 ± 0.82	63.0 ± 2.27	5.40 ± 0.03	12.35 ± 0.75 ^j	17.84 ± 0.13
CF-WP	28.45 ± 0.02	67.7 ± 1.82	8.9 ± 0.37	29.6 ± 1.75	6.66 ± 0.20	63.69 ± 1.31 ^b	16.14 ± 0.48
FF-DP	6.84 ± 0.13	32.1 ± 1.04	46.2 ± 0.95	69.5 ± 2.64	5.22 ± 0.03	10.54 ± 0.18 ^l	16.99 ± 0.91
CF-DP	25.55 ± 0.19	64.8 ± 0.86	8.7 ± 0.39	26.3 ± 1.53	5.50 ± 0.06	72.51 ± 1.23 ^a	4.61 ± 0.02
Whole f. bean (WB) flour	–	–	30.1 ± 0.42	–	14.91 ± 0.11	38.23 ± 0.89 ^g	15.67 ± 0.07
Dehulled f. bean (DB) flour	–	–	34.8 ± 0.70	–	9.29 ± 0.07	43.41 ± 0.54 ^f	7.18 ± 0.004
Beans hulls (HB)	–	–	10.8 ± 0.03	–	7.60 ± 0.09	3.77 ± 2.73 ⁱ	58.27 ± 0.56
FF-WB	6.46 ± 0.09	24.9 ± 0.50	60.0 ± 1.70	49.7 ± 2.13	7.69 ± 0.03	7.92 ± 0.47 ^k	9.97 ± 0.13
CF-WB	33.74 ± 0.26	73.2 ± 0.72	21.5 ± 0.75	52.4 ± 1.89	8.55 ± 0.13	50.85 ± 1.99 ^{d,e}	14.92 ± 0.44
FF-DB	8.77 ± 0.15	26.5 ± 1.52	60.9 ± 3.56	46.3 ± 1.00	7.81 ± 0.01	14.91 ± 0.10 ^j	10.30 ± 0.23
CF-DB	32.02 ± 0.07	71.4 ± 1.67	25.5 ± 0.95	52.3 ± 3.05	9.01 ± 0.04	55.98 ± 0.16 ^c	6.41 ± 0.02

FF- Fine fraction; CF – Coarse fraction; WP – Whole peas; DP – Dehulled peas; WB – Whole faba beans; DB – Dehulled faba beans; PSE – Protein separation efficiency; NSP – Non-starch polysaccharides; dm – dry matter. Means that do not share a letter are significantly different $p < 0.05$

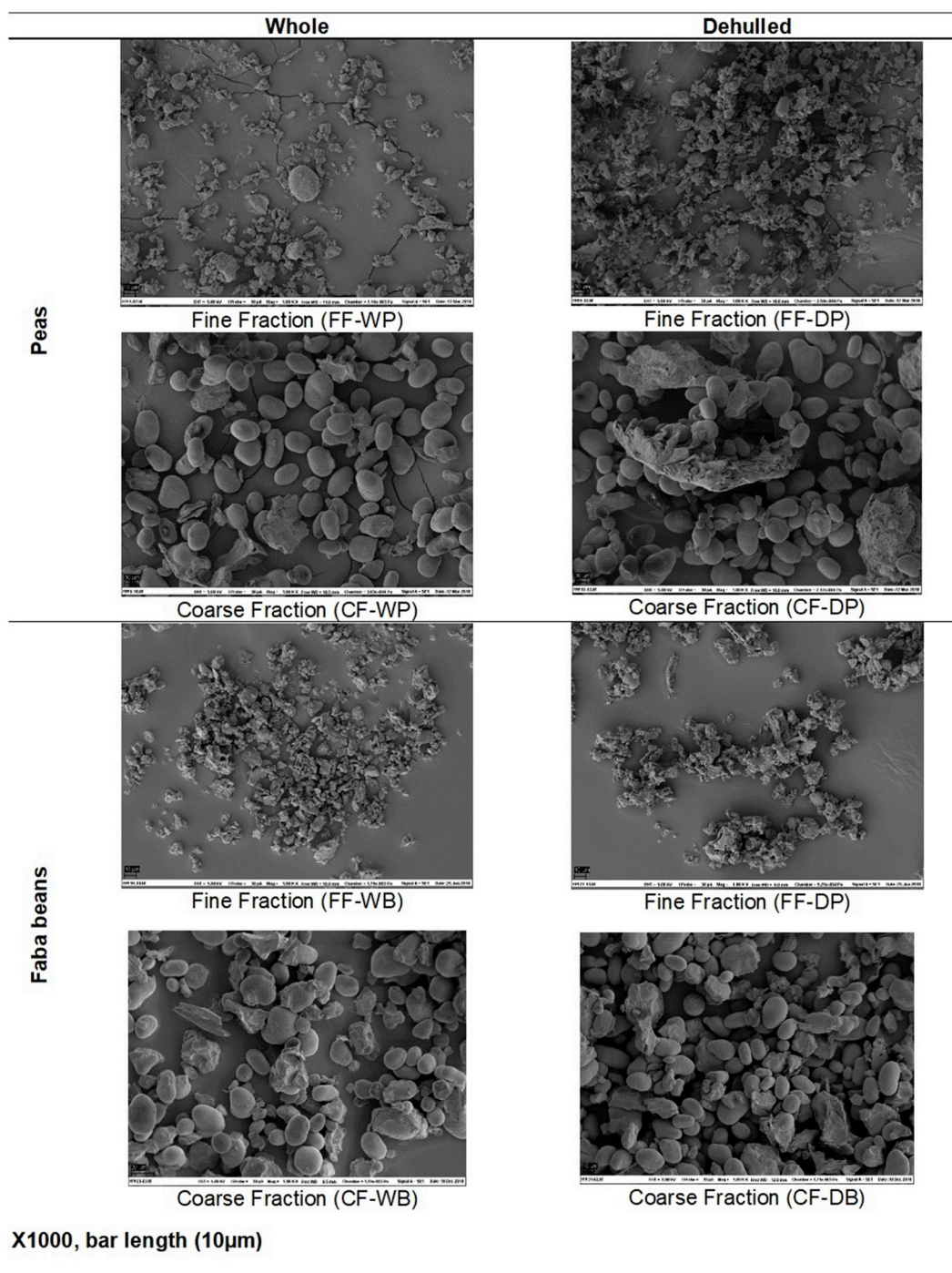


Fig. 2. Microstructure of whole (left) and dehulled (right) peas (top) and faba beans (bottom) fine- and coarse fractions. SEM images obtained at 1000x

respectively (Toews and Wang, 2013). These differences might be explained by the variety of peas used, which may have different cotyledon colours.

3.2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to assess the gelatinization and denaturation temperatures of the fine and coarse fractions. Denaturation temperature (T_{den}) of 89.9 and 89.6 °C were found for FF-WP and FF-DP, respectively and 93.16 and 93.69 °C for FF-WB and FF-DB, respectively. For the coarse fractions of whole and dehulled faba beans, also denaturation peaks were found due to the fact there is still 21.5–25.5% dm of protein in the coarse fractions. For the coarse fractions of peas, no denaturation peaks were detected due to the

lower amounts of protein present (8.7–8.9% dm). Both the fine fractions (protein concentrates) and the coarse fractions (starch concentrates) are not pure constituents, but a mixture of them, which needs to be considered. Concerning the gelatinization temperature (T_{gel}), endothermic peaks were detected at 66.28 and 66.17 °C for the CF-WP and CF-DP, respectively and at 66.77 and 64.88 °C for CF-WB and CF-DB, respectively. In the last case, dehulling could have had an impact due to possibly lower amount of total NSP (Table 1) in the CF-DB, decreasing the T_{gel} of the coarse fraction (Pelgrom et al., 2015b). However, the same was not verified among the coarse fractions of peas. Further studies on the detailed NSP composition of produced fractions are needed. A gelatinization peak was also detected for the FF-DB, once this fraction still contains 14.91% dm of starch. For the FF-DP, no gelatinization peak

Table 2

Thermal and colour properties of protein- and starch-enriched-fractions produced from whole and dehulled peas and faba beans by dry fractionation and their raw materials.

Flours/ Fractions	Thermal properties		Colour properties			
	Tgel (°C)	Tden (°C)	L*	a*	b*	ΔE
Whole Peas (WP) flour	-	-	92.04 ± 0.06 ^{fg}	-0.28 ± 0.05 ^f	18.63 ± 0.19 ^a	-
Dehulled Peas (DP) flour	-	-	93.01 ± 0.07 ^d	-0.18 ± 0.03 ^{ef}	17.66 ± 0.11 ^b	-
Peas hulls (HP)	-	-	89.52 ± 0.14 ^h	0.35 ± 0.06 ^c	16.40 ± 0.34 ^c	-
FF-WP	No peak	89.87 ± 0.54	94.15 ± 0.16 ^c	-0.54 ± 0.10 ^{hi}	14.15 ± 0.32 ^e	2.69
CF-WP	66.28 ± 0.19	No peak	92.79 ± 0.14 ^{de}	-0.41 ± 0.05 ^g	15.07 ± 0.28 ^d	3.64
FF-DP	No peak	89.56 ± 0.27	94.56 ± 0.22 ^b	-0.56 ± 0.04 ⁱ	13.89 ± 0.21 ^e	4.09
CF-DP	66.17 ± 0.34	No peak	94.22 ± 0.06 ^{bc}	-0.61 ± 0.04 ⁱ	15.29 ± 0.10 ^d	2.69
Whole f. bean (WB) flour	-	-	88.17 ± 0.13 ⁱ	0.53 ± 0.12 ^b	11.20 ± 0.41 ^g	-
Dehulled f. bean (DB) flour	-	-	92.37 ± 0.05 ^{ef}	-0.13 ± 0.04 ^e	11.45 ± 0.11 ^g	-
Beans hulls (HB)	-	-	60.87 ± 1.18 ^j	7.91 ± 0.25 ^a	11.32 ± 0.25 ^g	-
FF-WB	No peak	94.35 ± 0.05	94.56 ± 0.19 ^b	-0.46 ± 0.03 ^{gh}	8.34 ± 0.10 ⁱ	7.07
CF-WB	66.77 ± 1.15	93.16 ± 0.12	88.28 ± 0.12 ⁱ	0.10 ± 0.04 ^d	10.35 ± 0.34 ^h	0.96
FF-DB	65.05 ± 0.01	94.55 ± 0.52	95.12 ± 0.17 ^a	-0.62 ± 0.02 ⁱ	8.81 ± 0.04 ⁱ	3.84
CF-DB	64.88 ± 0.23	93.69 ± 0.29	91.75 ± 0.26 ^g	-0.45 ± 0.08 ^{gh}	12.73 ± 0.35 ^f	1.46

FF- Fine fraction; CF – Coarse fraction; WP – Whole peas; DP – Dehulled peas; WB – Whole faba beans; DB – Dehulled faba beans; Tgel – Gelatinization temperature; Tden – Denaturation temperature; L* - Lightness; a* - redness; b* - yellowness; ΔE – Colour differences between enriched fractions and respective initial flours.

Means that do not share a letter are significantly different $p < 0.05$.

was identified due to the lower amount of starch in this fraction (10.54% dm). Slightly different results were obtained by Pelgrom et al. (2014) for pea fractions, namely a Tgel of 70.3 and 71.0 °C for fine and coarse fractions of peas, respectively. However, similar results were obtained for the fine fraction of peas, namely a Tden of 89.2 °C (Pelgrom et al., 2014a). Also, in this study, both gelatinization and denaturation peaks were detected for fine and coarse fractions of peas, once starch and protein are still present in these fractions in considerable amounts, respectively. Regarding faba bean, the gelatinization temperature of a starch concentrate has been reported to be at 63 °C by Biliaderis et al. (1980), being slightly lower than the one obtained in this study (Biliaderis et al., 1980). Denaturation temperatures of 89 and 105 °C for faba bean vicilin and legumin were reported by Yang et al. (2018), being the first value in line with what was obtained in the present work (Yang et al., 2018).

Overall, with respect to the impact of dehulling on the physical properties, a positive impact was observed towards a neutral colour of the fine and coarse fractions only produced from faba beans.

3.3. Impact of dehulling on the chemical composition of the fractions

3.3.1. Protein content

Whole and dehulled pea and faba bean flours and respective fine and coarse fractions were analysed regarding composition and the results are shown in Table 1. The protein content of initial flours (before fractionation) from whole and dehulled peas and faba beans varied between 20.4 and 21.3% dm and 30.1 and 34.8% dm, respectively, indicating

that faba beans contained larger hulls than peas. These values are in line with the literature where protein contents ranging between 19.4 and 25.5% dm for pea flour (Pelgrom et al., 2014a, 2015c) and between 29.3 and 29.8% dm for faba beans (Schutyser and van der Goot, 2011; Sosulski and Youngs, 1979) have been reported.

The protein content of the FF-WP and FF-DP varied between 44.0 and 46.2% dm, respectively and 60.0 and 60.9% dm for FF-WB and FF-DB, respectively. The pea coarse fractions CF-WP, CF-DP contained 8.9 and 8.7% dm of protein and the faba bean coarse fractions still contained 21.5 and 25.5% dm of protein. The hull fraction from peas and faba beans still contained a certain amount of nitrogen (calculated as 13.8 and 10.8% dm protein, respectively) because some of the broken kernels were separated together with the hull. Similar results were obtained by Pelgrom et al. (2014) during dry fractionation of peas, in which the protein content of the fine fraction was 42.9% and the protein content of the coarse fractions was 8.2% dm (Pelgrom et al., 2014a). Coda et al. (2015) have studied the effect of air classification on faba beans flour and nutritional properties. They found that faba bean flour had 35.66% dm of protein, the fine fraction contained 52.49% dm and the coarse fraction 16.73% dm (Coda et al., 2015).

3.3.2. Starch content

In general, dehulling improved the starch transfer into the coarse fractions both for peas and faba beans. Moreover, the FF-DB also contained higher amount of starch than the FF-WB. As verified previously, also slightly higher protein enrichment for faba beans was obtained when dehulling was performed. The same was not verified for the peas. These values are in agreement with the work published by Pelgrom et al. (2014) for pea flour (Pelgrom et al., 2014a) and Sosulski et al. (1979) and Coda et al. (2015) for faba beans (Sosulski and Youngs, 1979; Coda et al., 2015). Comparing dry fractionation of peas and faba beans, starch enrichment was more efficient for peas, namely the coarse fraction from dehulled peas (CF-DP). This can be explained by probable higher agglomeration of starch granules and protein bodies from faba beans (Fig. 2) also explained by the high values of protein in the coarse fraction (Schutyser and van der Goot, 2011).

3.3.3. Non-starch polysaccharides (NSP) content

The non-starch polysaccharides (NSP) consist of various polysaccharides including cellulose, hemicelluloses and pectins. Soluble polysaccharides such as pectins and some hemicelluloses are physiologically important and constitute a considerable fraction of the total dietary fibre. Both soluble and insoluble fibre fractions contain a variety of sugars including arabinose, xylose, glucose, uronic acid and other sugars such as rhamnose, mannose and galactose (Tiwari et al., 2012). The total NSP content in this study varied between 7.5 and 14.6% dm for DP and WP, respectively and between 7.2 and 15.7% dm for DB and WB, respectively. These values are in the same range of other reported studies. Wang et al. (2008) reported a total dietary fibre for dehulled field peas of 14.8% dm (Sosulski and Youngs, 1979). Concerning faba beans, Gdala&Buraczewska, (1997) reported NSP values in the range between 17.3% and 18.1% dm among different faba bean varieties tested (Gdala and Buraczewska, 1997). These values agree with the NSP values obtained in the present study for whole faba beans. As expected, the hull fractions were the highest in total NSP once these components are mainly found in the hull of pulses (41.9% and 58.3% dm for HP and HB, respectively) (Ralet et al., 1993). Concerning the coarse fractions from peas, CF-WP contained the highest amount of NSP (16.1% dm) while CF-DP contained the lowest amount of NSP (4.6% dm). The same trend was observed for faba beans. This can highlight the impact of dehulling prior to dry fractionation. When dehulling is performed, less NSP goes into the coarse fractions. Moreover, for the whole peas, the distribution of NSP was similar between the fine and the coarse fractions. In contrast, when dehulling was performed the NSP content in the coarse fraction of peas (4.6% dm) decreased significantly compared with the coarse fraction obtained from whole peas (16.1% dm). Concerning

faba beans, similar results could be observed when dehulling was performed. Higher values of total NSP were found in the fine fractions except for the fine fraction obtained from whole and faba beans (FF-WB). Wang et al. (2019) also reported less total dietary fibre content in the coarse fraction (6.5% dm) than in the fine fraction (18.4% dm) of dehulled field peas (Wang and Maximiuk, 2019). Pelgrom et al. (2015) have determined the fibre content by difference and also reported less amount of fibre in the coarse fraction (21% dm) compared to the fine fraction (42% dm) (Schutyser et al., 2015). Overall, it could be concluded that the NSP follows the protein when dry fractionation is performed using dehulled peas and faba beans. When starting from whole peas the NSP is equally split to the coarse and fine fractions.

In summary, concerning the composition of the fine and coarse fractions, dehulling enabled higher starch-enrichment in the coarse fractions of peas and faba beans. However, no impact was verified in the protein enrichment of the fine fractions of peas and faba beans. Moreover, the total NSP content in the coarse fractions of peas and faba beans were reduced by dehulling the raw materials prior to dry fractionation.

3.4. Impact of dehulling on the techno-functional properties of the fractions

3.4.1. Protein solubility, water holding capacity (WHC) and fat binding capacity (FBC)

Protein solubility of peas and faba bean fine fractions was evaluated and results are presented in Fig. 3. Moreover, WHC and FBC of peas and faba bean fine and coarse fractions were also assessed, and results are presented in Table 3.

For all the protein-enriched pea and faba bean fractions (fine fractions) a U-shaped pH-dependent protein solubility curve was observed. A higher solubility of pea fine fractions was found at pH 2 (57 and 58% for FF-WP and FF-DP, respectively) and a lower solubility at pH 4 (6–10% for FF-DP and FF-WP, respectively). The reduced solubility at pH 4 is explained by the fact that this pH are close to the isoelectric point for pulses, thus protein-protein interactions are not promoting solubility as in the case of other pH levels assessed (Ma et al., 2011). Regarding the faba bean fine fractions a higher solubility was found at pH 9 (51 and 67% for FF-WB and FF-DB, respectively), pH 10 (72 and 80% for FF-DB and FF-WB, respectively) and pH 2 (55% and 56% for FF-WB and FF-DB, respectively). At pH 9 and 10, pea fine fractions also presented higher solubility (23–40%) but not as higher as faba beans that presented a 2-fold higher solubility compared to pea fine fractions. These results are in line with the ones obtained by Fernández-Quintela et al. (1997) that evaluated the solubility of pea and faba bean protein isolates containing 84.1% and 81.2% dm protein content and found out that the solubility

was low from pH 4 to pH 6 and high from pH 8 to pH 9 (Fernández-Quintela et al., 1997). These authors also found that pea protein isolates presented lower solubility than faba bean isolates as also observed in this studied. Boye et al. (2010) studied the functional properties of pea, lentil and chickpea protein fractions obtained by wet fractionation (Boye et al., 2010b). In general, for all pulses studied, the highest solubility was detected at pH from 1 to 3 and between 7 and 10 and was found to be very low at pH 4, 5 and 6 (2–30%), apart from red lentil that had a solubility of 58% at pH 4. In the present study, dehulling did not influence the solubility of the fine fractions among pH tested. However, a bigger difference between fractions obtained from whole and dehulled faba bean fine fractions (FF-WP and FF-WB) could be observed at pH 10 (basic), but not statistically significant. This fact can be possibly explained by the fact that fine fractions from pea contains more NSP and LMW sugars which can influence protein solubility at basic pH. No statistically significant differences were found at pH 2, 4 and 8 between pea and faba bean fine fractions. It is possible to conclude from Fig. 3, that a profile of an “U shape” was obtained for the samples studied, more pronounced for faba bean fine fractions. The same observations were found in other solubility studies for peas and faba beans (Fernández-Quintela et al., 1997; Boye et al., 2010b; Lam et al., 2018). It is important to mention that very little information on solubility of pea and faba bean concentrates were found in the literature (Boye et al., 2010b). Most of the studies concerns pea and faba bean isolates.

Concerning water holding capacity (WHC), the highest values were obtained for the coarse fractions obtained from whole faba beans (CF-WB) and whole peas (CF-WP), which can be explained by the higher fibre content in these fractions, leading to higher absorption of water (Singh et al., 2017). The lowest values of WHC were verified for the fine fractions of both peas and faba beans. Sosulki and Youngs, 1979 reported WHC of 0.72 and 0.33 g water/g dm for fine fractions WHC of 1.03 and 1.24 g water/g dm for coarse fractions of field peas and faba beans, respectively (Sosulski and Youngs, 1979). These results were in line with the ones obtained in the present study. Toews and Wang obtained a WHC between 3.2 and 3.7 g water/g dm for fine fractions from two varieties of peas (Toews and Wang, 2013). The same authors have reported a WHC of 2.1 g water.g⁻¹ dm for a commercial pea protein concentrate.

Fat or oil binding capacity also called fat or oil absorption capacity was determined as the weight of oil absorbed per weight of fine protein fraction used (Boye et al., 2010a). Results of the FBC of pea and faba bean fractions (fine and coarse fractions) are presented in Table 3. A higher FBC was obtained for all fine fractions from both the whole and dehulled peas and faba beans (1.11–1.15 g oil.g⁻¹ dm). This result can be possibly explained by the fact that the key proteins of concentrates and isolates from pulses (legume globulins) are naturally hydrophobic (Kiosseoglou and Paraskevopoulou, 2011). There were no significant differences between fractions obtained from whole or dehulled raw materials. The same could be verified for the coarse fractions that have shown less FBC (0.77–0.86 g oil.g⁻¹ dm). The FBC of faba bean coarse fractions were slightly higher than the pea coarse fractions. Fernández-Quintela et al. (1997) also obtained higher FBC for faba bean protein isolate (1.6 g oil/g protein) than for pea protein isolate (1.2 g/g protein) (Fernández-Quintela et al., 1997). Reinkensmeier et al. (2015) have reported similar WHC and FBC for pea fin-fraction (around 1.75 g water/g dm and 1.80 g oil/g dm, respectively) (Reinkensmeier et al., 2015).

3.4.2. Emulsifying properties

Proteins perform as emulsifiers by creating a layer around the oil droplets dispersed in the water phase. This prevents creaming, coalescence, sedimentation or flocculation that represent structural modification that can occur (Boye et al., 2010a). The emulsifying properties of pea and faba bean protein fractions (fine fractions) are presented in Table 3. Emulsifying capacity (EC) expresses the amount of oil emulsified by a fixed amount of protein in defined conditions (Pearce and

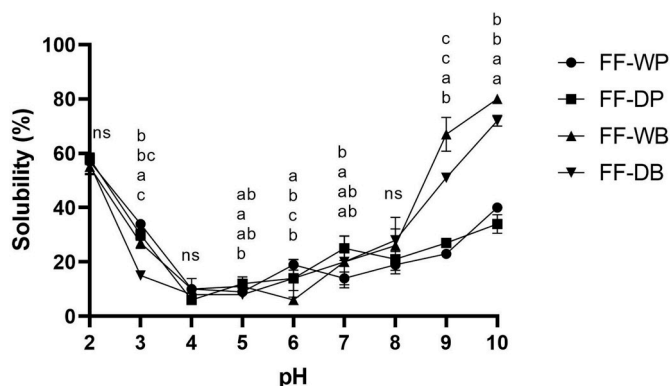


Fig. 3. Solubility of fine fractions obtained from whole peas (FF-WP), dehulled peas (FF-DP), whole faba beans (FF-WB) and dehulled faba beans (FF-DB) as a function of pH. Means that do not share a letter are significantly different $p < 0.05$. The letter order corresponds to the four samples represented in the graph, respectively.

Table 3

Summary of experimental results on the influence of dry-fractionation on the Techno-functional properties of protein- and starch-enriched-fractions produced from whole and dehulled peas and faba beans by dry fractionation and their raw materials.

Samples	WHC (g water.g ⁻¹ dm)	FBC (g oil.g ⁻¹ dm)	Emulsifying properties			Foaming properties		
			EC (g of FF.g ⁻¹ oil)	EAI (m ² .g ⁻¹)	ESI (min)	FC (%)	FI (slope) (-)	d ₅₀ (µm)
Pea fractions								
FF-WP	0.93 ± 0.03 ^c	1.12 ± 0.08 ^a	6/8	18.80 ± 1.61 ^a	14.24 ± 1.56 ^a	54.84 ± 9.12 ^a	0.06	92.62 ± 8.88
CF-WP	1.29 ± 0.01 ^b	0.77 ± 0.05 ^c	nd	nd	nd	nd	nd	nd
FF-DP	0.97 ± 0.09 ^c	1.14 ± 0.06 ^a	6/10	17.16 ± 0.42 ^a	13.24 ± 0.26 ^{ab}	55.56 ± 13.47 ^a	0.07	133.47 ± 26.33
CF-DP	0.98 ± 0.01 ^c	0.77 ± 0.01 ^c	nd	nd	nd	nd	nd	nd
Faba bean fractions								
FF-WB	0.58 ± 0.03 ^d	1.15 ± 0.07 ^a	6/8	12.32 ± 2.40 ^b	12.64 ± 0.44 ^{ab}	41.94 ± 8.53 ^{ab}	0.04	125.38 ± 14.94
CF-WB	1.51 ± 0.03 ^a	0.82 ± 0.01 ^{bc}	nd	nd	nd	nd	nd	nd
FF-DB	0.63 ± 0.03 ^d	1.11 ± 0.03 ^a	6/10	13.57 ± 0.62 ^b	12.22 ± 0.63 ^b	26.56 ± 2.21 ^b	0.03	156.55 ± 19.26
CF-DB	0.96 ± 0.02 ^c	0.86 ± 0.09 ^b	nd	nd	nd	nd	nd	nd

FF- Fine fraction; CF – Coarse fraction; WP – Whole peas; DP – Dehulled peas; WB – Whole faba beans; DB – Dehulled faba beans; WHC – Water holding capacity; FBC – Fat binding capacity; EC – Emulsifying capacity; EAI – Emulsifying activity index; ESI – Emulsifying stability index; FC – Foaming capacity; FI – Foam instability; d₅₀ – Median bubble size.

Means that do not share a letter are significantly different $p < 0.05$.

Kinsella, 1978). Results showed that dehulling had a slightly impact on the EC of pea and faba bean protein fractions. Fractions obtained from dehulled peas and faba beans presented higher EC. Both FF-DP and FF-DB were able to emulsify 10 g oil using 6 g of protein solution. Emulsifying activity index (EAI) and emulsifying stability index (ESI) are indices used to assess the emulsifying properties of protein ingredients. EAI describes the capacity of a protein to form an emulsion based on the turbidity of a diluted emulsion (Boye et al., 2010a). Regarding EAI, the highest values were obtained for the fine fraction obtained from whole peas (FF-WP) and the fine fraction obtained from dehulled peas (FF-DP) being statistically different from the fractions obtained from faba beans. The emulsifying stability index (ESI) evaluates the stability of the diluted emulsion for a specific period of time (Pearce and Kinsella, 1978). Concerning ESI, no significant differences were found between the fine fractions evaluated (Karaca et al., 2011). The highest ESI were found for FF-WP and FF-DP. Overall, faba bean fine fractions presented less emulsifying activity and stability indexes than the pea fine fractions. Little information can be found in literature concerning emulsifying properties of pea and faba bean fine fractions obtained through dry fractionation. Karaca et al. (2011) studied the emulsifying properties of pea, faba bean, chickpea and lentil proteins produced by wet fractionation (Karaca et al., 2011). The results obtained in the present study are opposite to the ones obtained by Karaca et al. (2011) in which pea protein isolate (PPI) presented less emulsifying capacity than faba bean protein isolate (FBPI) (Karaca et al., 2011). This can be possibly explained by the different methodologies used. Moreover, the EAI was similar for both PPI and FBPI, while FBPI presented higher ESI than PPI both prepared by isoelectric precipitation. In the present study, pea fine fractions had higher EAI and ESI than faba bean fine fractions.

3.4.3. Gelling properties

Gelation is considered as the process whereby a system undergoes a transition from a liquid state, which may be a solution, a suspension or a slurry, to a solid like state characterized by a liquid phase retained within a three-dimensional space filling matrix of connected macromolecules or particles. The matrix structure is responsible for the solid like elastic response of the material that is measured rheologically. Gel matrix formation may require multiple steps at the molecular level including hydration, solubilization or conformational changes before the initiation of the intermolecular interactions that provide long-range order, and in complex systems the gel matrix may consist of multiple molecular components (Banerjee and Bhattacharya, 2012).

Gelling behaviour for the pea and faba bean fractions is presented as elastic modulus G' (solid like behaviour; energy conservation), viscous modulus G'' (liquid like behaviour; energy loss), phase angle and

temperature against test time (Fig. 4).

All samples were observed to go through a heat induced gelation exemplified by rapidly increasing G' and G'' and drop in phase angle during the heating phase of the temperature cycle. All samples showed at least 80% of gel development (in terms of increase in the elastic modulus G') during the cooling phase of the temperature sweep. There was some increase in elastic modulus during the 90 °C hold phase, equivalent to around 10% of the total elastic modulus development for both pea and faba bean fine fractions, whereas for the coarse fractions there was a more limited development of elastic modulus during the hold phase (less than 5% of the total). It should be noted that before heating the samples are of low viscosity and extremely low torque is needed to access the low strain regime. This results in somewhat noisy data and, in some cases, particulate material and surface tension may contribute to a pseudo-elastic response, nevertheless the gelation behaviour is clearly captured in all samples. The dehulling process resulted in minimal changes in the gelation rheology of the resultant fractions.

The gelation behaviour of the coarse fractions from both pea and faba bean showed typical starch gelation profiles (Doublier, 1987) (Fig. 4). Upon reaching a critical temperature starch granules hydrate and swell rapidly with a transition from a crystalline to amorphous structure within the granules and leaching of amylose from the granules, this process is termed gelatinization and is seen here as a rapid rise in both the elastic and viscous moduli (G' and G'') as a result of the formation of a 3D network of amylose reinforced by strong interactions with swollen granules. The critical temperature for the coarse fractions reported here are all 64 ± 1 °C this suggests they have rather similar starch compositions and is similar to reported pasting temperatures for pea and faba bean starches obtained from air classified flours (Li et al., 2019). After reaching a peak in moduli values there is a reduction associated with breakdown of starch granules (and therefore a reduction in their contribution to the network) and during the cooling phase reordering and reassociation of the starch molecules leads to a strong gel matrix.

The gels formed from the fine fractions from pea and faba bean are typical of a coarse particulate network. Gelation is initiated as heat denatured protein swell and partially unfold, exposing amino acids that were previously hidden within the structured protein. These newly exposed amino acids drive aggregation of the swollen, denatured proteins, with increasing aggregation and swelling eventually leading to a continuous space filling 3D protein network (Foegeding, 2015; Munialo et al., 2018). As such the development of the gel network during heating is a response to multiple individual swelling and denaturation events with different typical temperatures resulting in a more gradual increase in moduli values and a greater dominance in the development of the

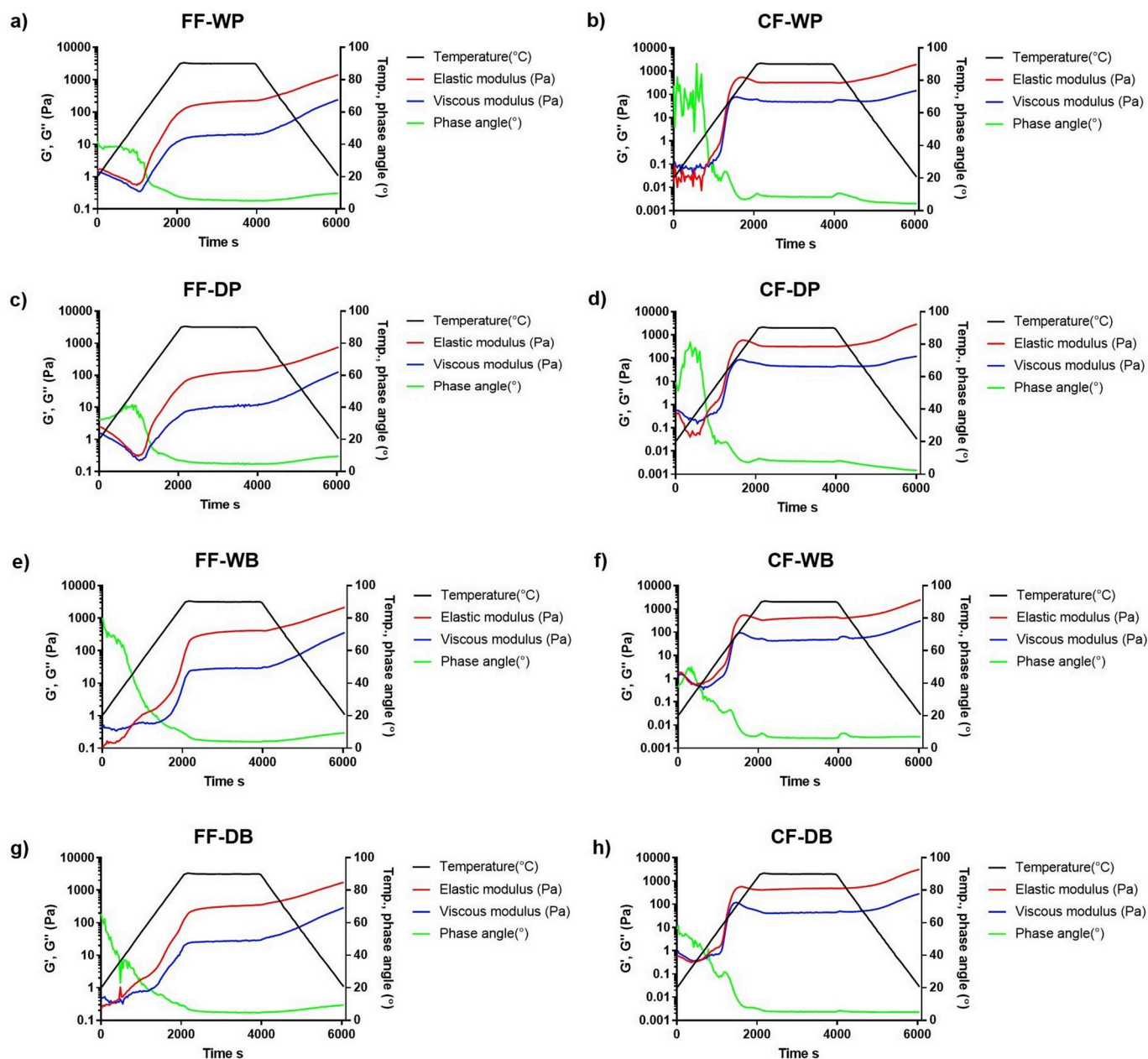


Fig. 4. Gelling properties of: a), c), e), and g) fine fractions (FF) and b), d), f), and h) coarse fractions (CF) obtained from whole peas (WP), dehulled peas (DP), whole faba beans (WB) and dehulled faba beans (DB).

elastic modulus over the viscous modulus when compared to the coarse fractions. Upon cooling the molecules of the matrix typically become less flexible leading to an increase in gel strength. Interestingly, there is a distinct difference in behaviour between fine fractions from pea and faba bean as the temperature increases before the initiation of gelation (protein denaturation). For pea samples the moduli initially decrease with increasing temperature whereas the opposite is the case for faba bean samples. This suggests there may be differences in the balance of intermolecular interactions present within samples initially, as the strength of hydrogen bonds decreases with increasing temperature whereas the strength of hydrophobic interactions increases with temperature. This suggests the pea fine fraction may initially support comparatively more hydrogen bonding or less hydrophobic interactions than the faba bean fine fraction.

The fractions here contain multiple components and although their gelation behaviour is in general typical of the major component, be that starch or protein, the gel matrices must be considered as complex mixed

systems with contributions from multiple components, both soluble and insoluble, which may both contribute to and inhibit the development of the gel matrix (Banerjee and Bhattacharya, 2012). It has recently been reported that highly processed pea protein fraction with a corresponding higher purity have poorer gelling ability than less highly purified fractions which contain more non-protein material (Kornet et al., 2019). Against this background it is perhaps not surprising that the small compositional changes resulting from the dehulling process did not result in any identifiable meaningful alterations in the gelation behaviour of the fractions.

3.4.4. Foaming properties

Table 3 represents the foaming capacity (overrun) of the tested pea and faba bean fine fractions. The highest foaming capacity (FC) was demonstrated by FF-WP and FF-DP while the lowest belongs to FF-DB. The demonstrated foaming capacities of the samples are relevant to other data available in the literature for different plant proteins sources

such as, 56.44% for canola, 44.56% for soy and 17.82% for flaxseed meal (Aider and Barbana, 2011). In overall these data can classify the tested samples as ones having moderate foaming capacity.

Table 3 also presents the results of foam instability (FI) based on the derived power law exponents. The analysis of the data indicates the highest foam stability is demonstrated by FF-DB and FF-WB while the lowest foam stability is demonstrated by FF-DP and FF-WP.

Foaming capacity (FC) might not essentially be related to their capability to stabilize the foam. FC is associated to the skill of molecules of protein to be disposed at the air-water interface. The capacity of proteins to stabilize foams depends on the protein-protein interactions (Kinsella, 1981). Therefore, FC of proteins may not essentially be linked to their capability to stabilize foams. Additionally, foam microstructure can be indicative of foam stability as demonstrated by Indrawati & Narsimhan, (2008) (Indrawati and Narsimhan, 2008). The bubble size distribution of all samples follows normal left skewed to centred unimodal distribution (Fig. 5).

The results clearly demonstrate the predominating bubble size classes in the different samples. In all samples more than 50% of the incorporated bubbles have diameter <160 μm with dominating samples FF-WP and FF-DP having respectively 69.1% and 66.1%. More differentiating results are demonstrated in Table 3 that represents the median bubble diameter (d50) of the analysed samples. Samples FF-WP and FF-WB demonstrated the lowest values of d50. Another important bubble size distribution parameter is the span of the distribution that can be calculated as follows: $\text{span} = (d_{90}-d_{10})/d_{50}$, in which d_{10} , d_{50} , d_{90} corresponds to the 10th, 50th and 90th quantiles of the normal size distribution. In this way span can be considered as a measure of the uniformity of the bubble size distribution which normally favours foam. The calculated span for samples FF-WP and FF-DP were the highest (2.1 and 1.5 respectively), which suggests that the resulting foams exhibit the lowest level of uniformity and therefore the deterioration of their foam stability due to the disproportionation effect (similarly to Ostwald ripening) can be expected. Overall, dehulling didn't have an impact (no significant differences) on the foaming properties of pea and faba bean fine fractions. Moreover, pea protein concentrates have shown to have higher foam capacity but lower foam stability than faba bean protein concentrates.

4. Conclusions

Results showed that milling of peas twice slightly increased the protein enrichment in the fine fractions. Regarding faba beans, the effect of milling on the protein separation was less pronounced. Large-scale fractionation showed similar results for peas as in the optimization trials but not similar for faba beans in terms of the mass yield, although the protein content obtained was the same. Dehulling of faba beans prior to dry fractionation seems to be an important step if a more neutral colour of the final products in which the protein and starch concentrates will be included is desired. Concerning the impact of dehulling on the chemical composition of the fractions, it was shown that dehulling had no impact on protein-enrichment in the fine fractions. However, increased starch-enrichment was observed when dehulling was performed prior to dry fractionation of peas and faba beans. Furthermore, the total NSP in the coarse fractions of peas and faba beans was significantly reduced when dehulling was conducted. Dehulling had no impact on the techno-functional properties of the produced fractions apart from a slight improvement on the emulsifying capacity of pea and faba bean fine fractions. Moreover, the WHC of coarse fractions from peas and faba beans was slightly improved when dehulling was not performed, due to the higher fibre content. The fine fractions from peas and faba beans possessed higher FBC. Regarding emulsifying properties, the EAI and the ESI was higher for peas compared to faba beans. Even though there are small compositional changes resulting from the dehulling process, no major alterations were identified in the gelation behaviour of the fractions. Peas showed higher foam capacity but lower foam stability than

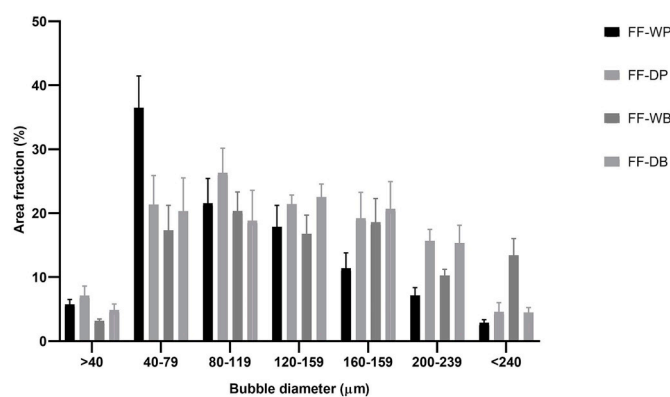


Fig. 5. Bubble size distribution of foams generated from whole peas (FF-WP), dehulled peas (FF-DP), whole faba beans (FF-WB) and dehulled faba beans (FF-DB).

faba bean fine fractions. Further research will be a deeper study and a comparison of the functionality of pea and faba bean fine fractions. A possible outcome is to tailor-make substitution of soya, egg and dairy proteins in different food applications.

Declaration of competing interest

The authors declare that they have no conflict of interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jfoodeng.2020.109937>.

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