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Baltic herring (*Clupea harengus membras*) oil encapsulation by spray drying using a rice and whey protein blend as a coating material

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ABSTRACT

As popular coating material for encapsulation like milk proteins and maltodextrin do not fully mask unpleasant fish flavors, rice and whey protein blend was tested to aid the use of Baltic herring (BH) oil in functional foods. Particle size and morphology of emulsions (7.5% whey protein, 7.5% rice protein, 15% BH oil and water) produced at pH 3, 6 or 8 with one or two step homogenization and resulting powders were characterized together with fatty acid composition, volatile compounds and oxidative stability. The use of rice and whey proteins lead to stable emulsions with bimodal size distribution and large dispersion (0.05–100 μm). Emulsion's pH affected powder particle sizes, with pH 3 resulting in powders with biggest particle sizes. Morphology of powders showed spherical shape with porous structure. Emulsions with pH 6.5 produced powders with the highest induction periods (1.59–1.73 h) and low content of volatile compounds.

1. Introduction

Baltic herring (BH; *Clupea harengus membras*) is a subspecies of Atlantic herring (*Clupea harengus*) which lives in the Baltic Sea area. It is the most important commercially fished species in Finland. For example, in the year 2019, the 113 million kilograms of BH caught accounted for 84% of the total fish catch in Finland (Natural Resources Institute Finland, 2020). BH is a fatty fish (5–10% of lipids depending on season) rich in long chain omega-3 polyunsaturated fatty acids mainly docosahexaenoic acid (22:6*n*-3, DHA) and eicosapentaenoic acid (20:5*n*-3, EPA) (Aro et al., 2000). DHA and EPA are crucial for growth and development, and important for cardiovascular health and inflammatory balance (Saini and Keum, 2018). Further, DHA has been shown to be essential for brain development of infants as well as maintenance of normal brain and eye functions (Hashimoto et al., 2017). The content of DHA and EPA in BH lipids is 8–10% and 4–6% of total fatty acids, respectively (Aro et al., 2000; Damerau et al., 2020b), which is comparable to the content of DHA and EPA found in several omega-3 supplements (Damerau et al., 2020a). Even with its high nutritional value, BH is underutilized for human consumption, as consumers prefer larger farmed fish. Currently, the majority of BH is used for feed for fur animals (Natural Resources Institute Finland, 2020). BH could be better utilized for human consumption as BH oil incorporated as a domestic ingredient in omega-3 enriched foods.

The high content of DHA and EPA in BH oil make it highly susceptible to lipid oxidation. Lipid oxidation yields a multitude of primary and secondary oxidation products, which decrease the sensory quality and can affect the safety of foods. Biologically active and toxic compounds formed such as oxo-fatty acids and their glycerophospholipid esters are a risk to human health when ingested (Serini et al., 2011; Vieira et al., 2017). Therefore, protection of BH oil against lipid oxidation is important especially, when the oil is used in the food chain.

Microencapsulation protects oil against oxygen and pro-oxidants, and thus to improves shelf life, and masks unwanted flavors. It also turns oil into an easy-to-handle powder (Kaushik et al., 2015). The most common method for encapsulation of fish oil in the food industry is spray drying (Encina et al., 2016). In the spray drying process, the core material (oil) is dispersed into a polymer solution containing the wall material, forming an emulsion. The feed emulsion is atomized, fine droplets created, and these are further dehydrated in a hot drying

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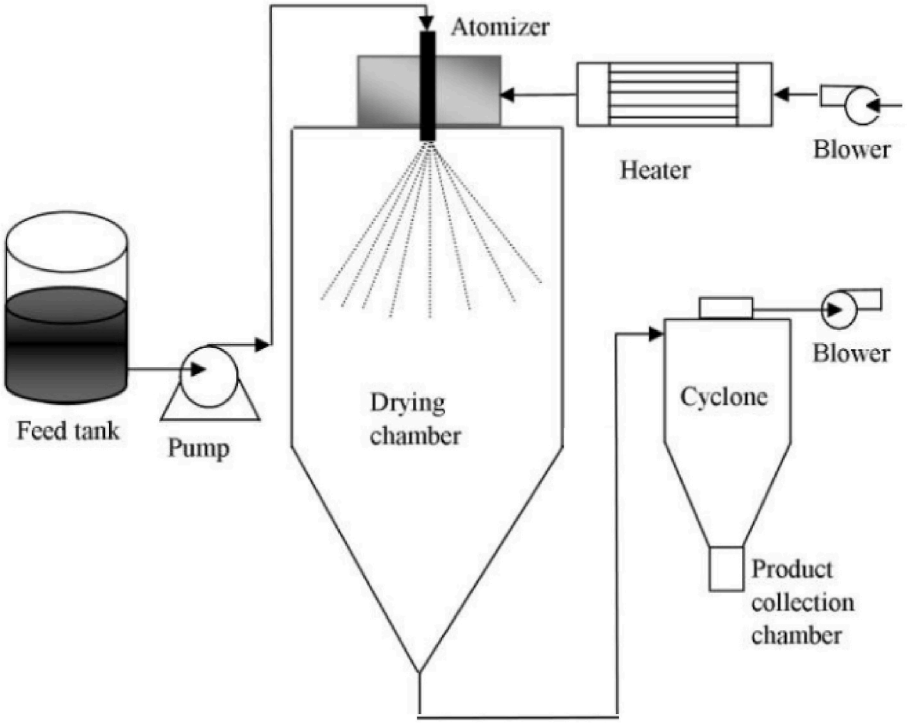

Fig. 1. Schematic illustration of spray drying system used in the study.

medium forming microcapsules (de Vos et al., 2010). The functionality and stability of encapsulated fish oil is affected by type of encapsulating agent, emulsion composition (fish oil/encapsulating agent ratio), emulsion parameters (like pH, droplet size) and spray drying parameters (Encina et al., 2016). Previous work suggest that mixtures of milk proteins and carbohydrates are well suitable wall materials to protect fish oil, because of the formation Maillard reaction products that are known for their antioxidant properties (Ifeduba and Akoh, 2016). However, Łozińska et al. (2020) reported that using of mixtures of protein and carbohydrates provides inferior results compared with using these compounds separately. Our previous research (Ogrodowska et al., 2020) has shown beneficial effects in using plant proteins as a coating material. For example, rice proteins mixed with whey proteins reduced odor and flavor intensity, and positively affected mouthfeel of capsules by decreasing their oiliness. Rice proteins are interesting for food industry also due to their hypoallergenic nature and increasing interest in plant proteins (Agboola et al., 2005; Amagliani et al., 2017a). Rice is thus considered one of the vegetable protein sources that could be used to replace milk and soy proteins in diets (Amagliani et al., 2017b). Previously, rice proteins were effectively incorporated in wall material mixed with maltodextrin for encapsulation of hemp oil (Kurek and Pratap-Singh, 2020), and as enzymatic hydrolyzed protein for encapsulation of flaxseed oil (Gomes and Kurazowa, 2020) by spray drying.

The aim of the present study was to create stable aqueous emulsions containing rice and whey proteins and BH oil, and to compare the effect of the production parameters (pH emulsion and homogenization type) on powder properties, including encapsulation efficiency (EE), oxidative stability, and volatile profile as an indicator for flavor masking.

2. Materials and methods

2.1. Emulsion properties

2.1.1. Preparation of the emulsion

Aqueous emulsions (5 L) containing 15% (w/v) crude BH oil (Ab Salmonfarm Oy, Kasnäs, Finland), 7.5% (w/v) rice protein concentrate (RPC; Unirice W80/300, Barentz Food & Nutrition, Hoofdorp, Netherlands) and 7.5% (w/v) whey protein concentrate (WPC, 80; Ostrowia company, Ostrów Mazowiecka, Poland) were formed using Thermomix (Vorwerk, Germany). The emulsion composition was chosen to be comparable to our previous study (Ogrodowska et al., 2020).

Emulsion had a pH value 6.5. Emulsions were adjusted to pH values 3 and 8 using 10% hydrochloric acid or 50% sodium hydroxide (StanLab, Lublin, Poland), and homogenized either in one (25 MPa) or two-steps (25 MPa and 5 MPa) using a high-pressure laboratory valve homogenizer (Panda 2 K, GEA Niro Soavi, Parma, Italy). Emulsions were named E3I, E3II, E8I, E8II, E6.5I and E6.5II, indicating emulsion, pH and one or two step homogenization.

2.1.2. Emulsion droplet size and distribution

Droplet size distribution of the dispersed phase was determined by laser diffraction analysis using Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, United Kingdom). The structure of the emulsion was described by Sauter mean diameter $D_{3,2}$ (the surface weighted mean diameter), De Brouckere mean diameter $D_{4,3}$ (the volume weighted mean diameter), median size of the distribution $d_{0,5}$, also $d_{0,1}$, $d_{0,9}$ (diameters of the droplets at which 10, 50 or 90% of the sample is smaller than the size measured, respectively), and specific surface area. Width of the distribution (span) were calculated using Eq. (1) (Malvern, 2007):

$$span = \frac{d_{0.9} - d_{0.1}}{d_{0.5}} \quad (1)$$

2.1.3. Emulsion stability index

Degassed emulsion sample (100 mL) was placed in a measuring vessel (Ø = 0.04 m, h = 0.08 m) of ELMETRON CPC 411 (Zabrze, Poland) conductometer equipped with CX 400/CX 500 v.5.0 data transmission software. The stability of the samples was determined at 23.2 ± 1.3 °C by relating the final conductance value, after 240 min, to its initial value (stability index K_{240}) using Eq. (2) (Al-Malah, 2000):

$$K_{240} = \frac{k_{240}}{k_0} \quad (2)$$

where:

k_{240} – conductance value in the upper layer of the emulsion sample after 240 min (mS/m),

k_0 – value of the conductance in the upper layer of the emulsion sample at the start of the measurement (mS/m).

2.2. Preparation of powders and determination of their properties

2.2.1. Spray drying of emulsions

The emulsions were spray dried in a pilot plant spray dryer (Zahn.u. Co, Berlin, Germany) (Fig. 1) with disk (0.2 mm diameter) as a spraying mechanism, with at inlet air temperature in the range of 123–129 °C, and outlet temperature in the range of 72–78 °C. An open-loop system without cooling was utilized. For the feed atomization a rotary atomizer (13,400 rpm) was used, and the mass flow of the feed was 17.00 ± 0.25 kg/h. The recovery rates for the obtained powders were 95.41%–96.31% and the moisture content ranged from 1.58% d.w. to 1.64% d.w. Resulting powders were named P3I, P3II, P8I, P8II, P6.5I and P6.5II indicating powder, pH and one or two step homogenization.

2.2.2. Powder morphology

Powder particle size and distribution was analyzed as for emulsions (described in 2.1.2). The following formula was applied for Uniformity Index (UI) (Visht and Kulkarni, 2015):

$$UI = \frac{D_{4,3}}{D_{3,2}} \quad (3)$$

Scanning electron microscopy (SEM, SEM Quanta 200; FEI Company, Hillsboro, OR) was used to visualize the surface of powder. Powder mounted on SEM stubs with the aid of two-sided adhesive tape and coated with palladium in a sputter coater. The samples were analyzed at accelerating voltage of 30 kV and × 200 magnification.

2.2.3. Determination of surface and total oil contents, and calculation of EE

Surface oil was extracted by mixing 2 g of BH oil powder with 15 mL of *n*-hexane (Sigma-Aldrich, Poznań, Poland) and shaking for 2 min at 30 rpm/min using Multi-Rotator Multi RS-60 (Biosan, Riga, Latvia) at room temperature (Takeungwongtrakul et al., 2015). The solvent was then filtered and collected solid residue was rinsed three times with 20 mL of hexane. The filtrate solution was evaporated using a rotary evaporator (Büchi Labortechnik AG, Switzerland). The residue was weighted, and the surface oil content (SOC) was expressed as percentage of the powder.

The total oil was extracted by dissolving 0.5 g of powder in 20 mL of chloroform/methanol mixture (2:1, v/v) (both solvents originated from Sigma-Aldrich) (Takeungwongtrakul et al., 2015). The powder was weighed into a tube, then 20 mL of a chloroform/methanol mixture was added and the whole sample was ultrasonicated for 10 min and shaken for 20 min at 30 rpm/min using Multi-Rotator Multi RS-60 (Biosan). The mixture was then centrifuged, and the solid phase was re-extracted two times more with the same volume of the extractant. The liquid phases were combined in a separatory funnel. 15 mL of 0.58% sodium chloride (POCH, Gliwice, Poland) was added, and the mixture was gently shaken. After phase separation, the chloroform phase was dried with anhydrous sodium sulphate (POCH, Gliwice, Poland). The extract was evaporated to dryness in the rotary evaporator (Büchi Labortechnik) under an N_2 stream. The residue was weighted, and the total oil content (TOC) was expressed as percentage of powder. The EE was calculated based on the following equation:

$$EE\ (\%) = \frac{(TOC\ -\ SOC)}{TOC} \cdot 100 \quad (3a)$$

2.3. Quality and composition of BH oil and BH oil powders

2.3.1. Oxidative stability analysis

A 743 Rancimat (Metrohm, Switzerland) eight-channel instrument was used to evaluate the oxidative stability index (OSI; expressed as hours). A capped reaction vessel with sample (2.5 g) was placed in a thermostatic electric heating block. The temperature was set at 110 °C and an air flow rate of 20 L/h was applied.

2.3.2. Fatty acid analysis

The BH oil was methylated as such after addition of internal standard (triheptadecanoin from Larodan, Solna, Sweden) in *n*-hexane (Honeywell International Inc., Riedel de Haën, Germany). Lipids were extracted in triplicate from encapsulated BH oil prior to methylation based on Baik et al. (2004) and Damerau et al. (2014b). The sample (0.3 g) with addition of the internal standard was re-suspended in 3 mL of 0.8% potassium chloride (Merck, Darmstadt, Germany) in MQ-water (40 °C) and lipids were extracted by vortexing for 2 min after addition of 10 mL of a *n*-hexane/2-propanal (Honeywell International Inc., Riedel de Haën, Germany) mixture (3:1, v/v). After the extraction, the mixture was centrifuged (1700×*g* for 2 min) and the organic phase was collected. The extraction was repeated with 5 mL of the *n*-hexane/2-propanal mixture (3:1, v/v). Organic phases of both extractions were combined.

Fatty acid profiles were analyzed with gas chromatography (GC) with flame ionization detector (FID) as methyl esters. The oil sample with internal standard was flushed to dryness with nitrogen and methylated using the methanolic hydrogen chloride method according to Christie and Han (2010). Acetyl chloride and methanol originated from Sigma-Aldrich (Steinheim, Germany). A Shimadzu GC-2030 equipped with an AOC-20i auto injector, an FID (Shimadzu Corporation, Kyoto, Japan) and DB-23 column (60 m × 0.25 mm x 0.25 μm; Agilent Technologies, J.W. Scientific, Santa Clara, USA) was used. GC conditions: helium flow 1.4 mL/min; 130 °C held 1 min, 6.5 °C/min to 170 °C, 2.75 °C/min to 205 °C, held for 18 min, 30 °C/min to 230 °C and held for 2 min. The peaks were identified by using external standards 37 Component FAME mix (Supelco, St. Louis, MO, USA), 68D, and GLC-490 (both from Nu-Check-Prep, Elysian, MN, USA) in addition to previous literature (Aro et al., 2000) and quantified using internal standard.

2.3.3. Volatile compounds analysis

Volatile compounds of encapsulated BH oil were analyzed according to the method of Damerau et al. (2014a). For the analysis, 0.3 g ± 0.001 g of each spray dried emulsion was weighed in triplicate in 20-mL headspace vials and flushed with nitrogen to stop further lipid oxidation during analysis. Volatiles were extracted using headspace solid phase microextraction (HS-SPME) using TriPlus RSH autosampler (Thermo Scientific, Switzerland) equipped with a DVB/CAR/PDMS-fiber (50/30 μm film thickness; Supelco, USA). Extraction parameters: incubation at 40 °C for 20 min, extraction at 40 °C for 30 min and desorption 6 min at 240 °C. Extracted volatiles were analyzed with TRACE 1310 GC (Thermo Scientific, Switzerland) equipped with a SPB®-624 capillary column (60 m × 0.25 mm × 1.4 μm; Supelco, USA) and coupled with a ISQ 7000 mass spectrometer detector (Thermo Scientific, Switzerland). GC-MS operation conditions: helium flow 1.4 mL/min; GC oven 40 °C held 5 min, 5 °C/min to 200 °C, held for 10 min, MS 70 eV, scan range 50–300 amu. Compounds were identified by using database NIST MS Search library (version 2.3. National Institute of Standards and Technology, Gaithersburg, Maryland, USA) and previous data of standards (Damerau et al., 2020a). Data was processed with Xcalibur software (Thermo Fischer Scientific, Switzerland).

2.4. Statistical analysis

Principal Component Analysis (PCA) was applied to peak area data to establish differences in volatile profiles using the Unscrambler® X version 10.4.1 (Camo Process AS, Oslo, Norway). Data were mean-centered and weighed (1/sdev) for PCA. Total volatile content and selected volatile oxidation indicators of spray dried BH oil emulsions were compared using one-way ANOVA in SPSS (IBM SPSS Statistics, version 25.0.0.1, IBM, New York, USA). Other data were analyzed

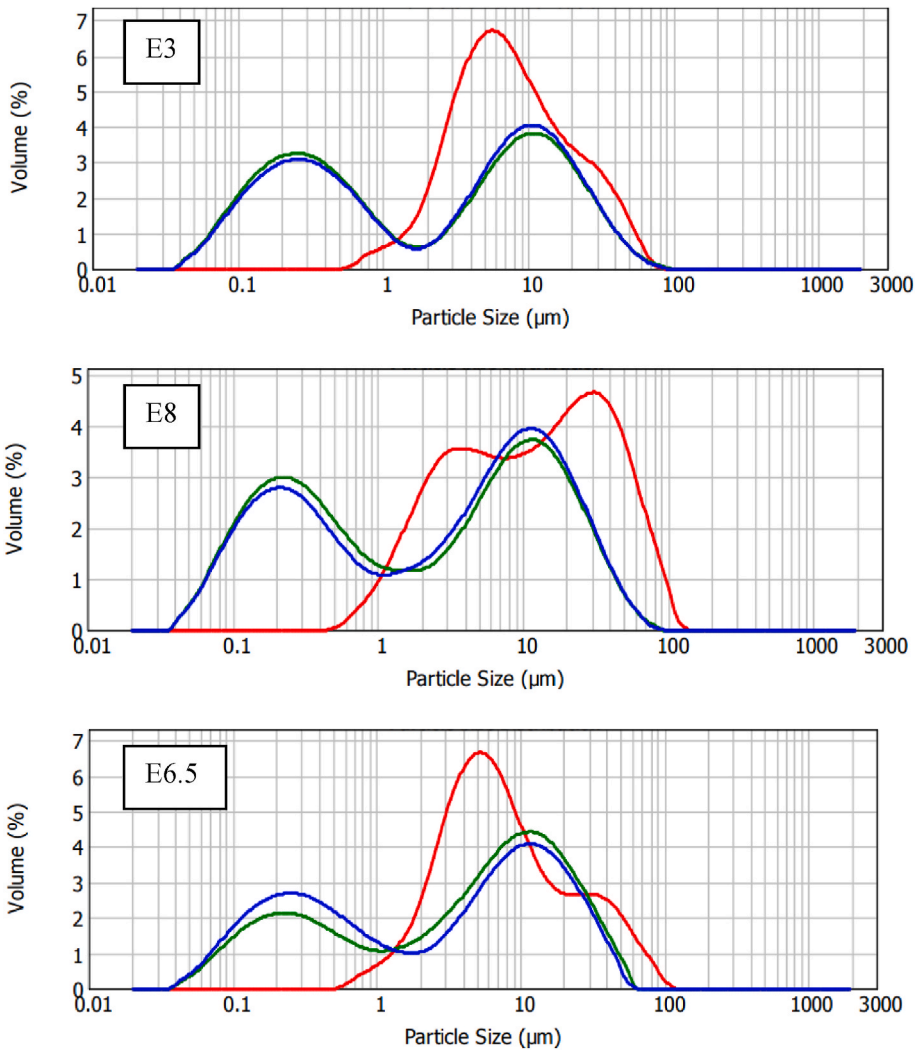

Fig. 2. Droplet size distribution in aqueous emulsions formulated with rice protein concentrate, whey protein concentrate and Baltic herring oil adjusted to pH 3 (E3), pH 8 (E8) and pH 6.5 (E6.5), before (red) and after on-step (green) and two-step (blue) homogenization process. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

statistically using one-way ANOVA with Duncan test in Statistica 13.1 software (StatSoft, Kraków, Poland). All analyzed differences were considered statistically significant if *p*-value was below 0.05.

3. Results and discussion

3.1. Droplet size characteristics and stability of BH oil emulsions

The range of oil droplet diameters in emulsion before homogenization process was between 0.9 and 100 µm (Fig. 2). Optical microscope images of the non-homogenized emulsions visualized that RPC either agglomerates or does not dissolve at pH 3 and pH 6.5 (Fig. 3).

The homogenization process, independent of type (one- or two-steps), significantly affected on droplet size distribution creating droplets in the range of 0.05–1 µm (Fig. 2). Bimodal size distribution of all emulsions was observed as droplets in the size range between 0.9 and 80 µm were also prevailed. Likely reason for the bimodal size distribution relates to the challenges in aqueous solubility of rice proteins. Rice proteins are rich in glutelins, which are not good emulsifiers (Agboola et al., 2005). Most likely, the first peak of the droplet size distribution includes oil droplets while the second peak contains protein particles as suspension. Further homogenization of the emulsion did not significantly affect the degree of protein dispersion, and the bimodal shapes are similar in all pH values studied (Fig. 2). This corroborates that part of the rice protein was present in the aqueous emulsion as a suspension, and the results further indicate that alteration of pH to 3 or 8 from the natural 6.5 does not have a large influence on this phenomenon.

As emulsion pH increased, the average droplet size decreased slightly (Table 1). The lowest droplet size (average $D_{3,2}$ = 0.75 µm and $D_{4,3}$ = 25.72 µm) was found for the one-step homogenized emulsion adjusted to pH 8 (E8I). More unified droplets were observed, as lower span, in emulsion adjusted to pH 3, independent of homogenization type (E3I, E3II). Emulsions with pH 3 were also characterized by low specific surface area of droplets. Agboola et al. (2005) reported average droplet sizes $D_{3,2}$ of emulsions with rice protein in the range of 0.76–1.94 µm for pH 7, which falls between our samples with pH 6.5 and 8. This is in accordance with solubility of glutelin increasing with the increase of pH as previously reported (Agboola et al., 2005). Also Wu et al. (2020) confirmed that rice protein isolate exhibits better solubility in alkaline environments than in acid environments. Thus, larger droplet sizes at lower pH can be linked with low solubility, as also Agboola et al. (2005) suggested. A similar effect of pH on emulsion droplet size was also seen by Puppo et al. (2005), who studied emulsifying properties of soybean protein isolates. They showed that sunflower oil emulsions with pH 8 had lower $D_{3,2}$ than those prepared with pH 3.

The values of the K_{240} (emulsion stability index) for all prepared

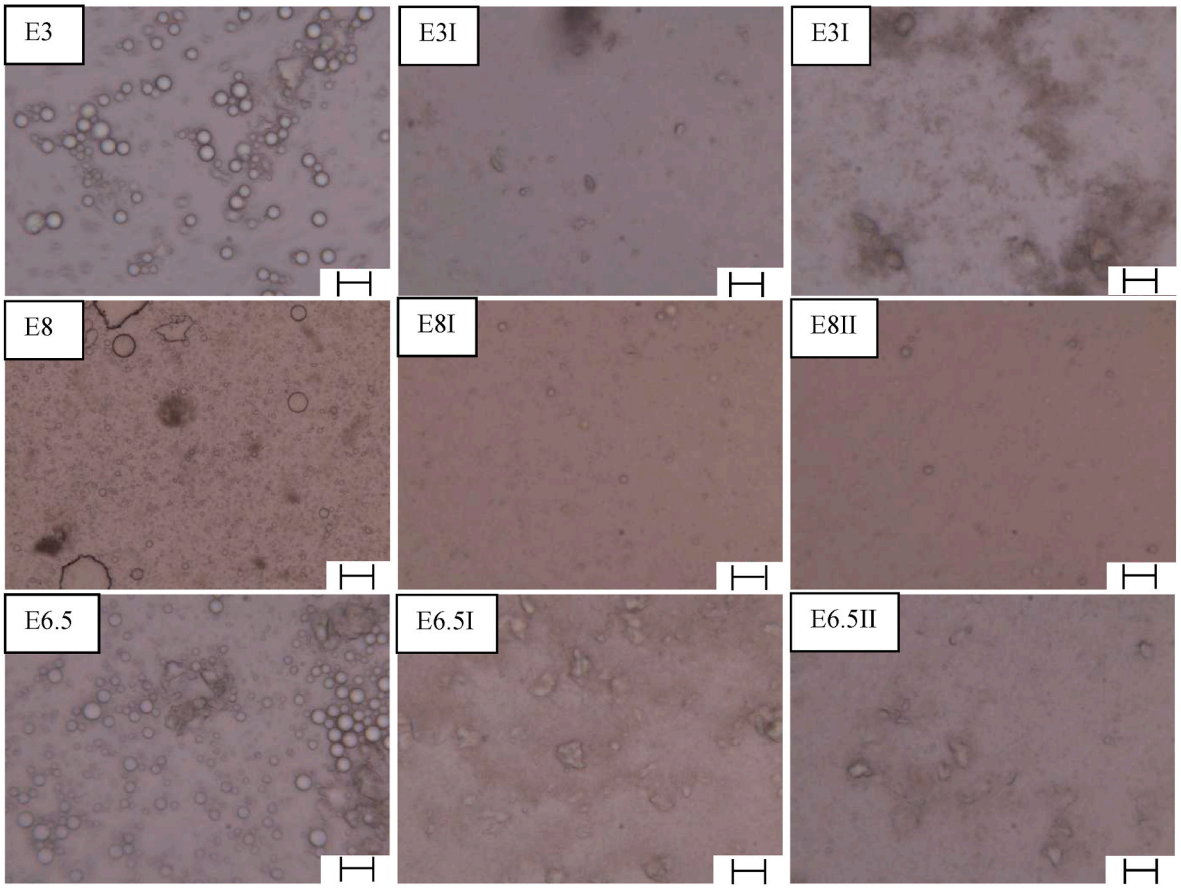

Fig. 3. Optical microscope images for aqueous emulsions formulated with rice protein concentrate, whey protein concentrate, and Baltic herring oil adjusted to pH 3 (E3), 8 (E8) and 6.5 (E6.5), before (E3, E8, E6.5) and after one-step (E3I, E8I, E6.5I) and two-step (E3II, E8II, E6.5II) homogenization process (scale bar = 100 μm).

Table 1
Physical properties of Baltic herring oil emulsions (E3I, E3II, E8I, EII8, E6.5I and E6.5II).

Sample	D50 (μm)			$D_{3,2}$ (μm)			$D_{4,3}$ (μm)			span (−)			SSA (m^2/g)			K_{240} (−)		
E3I	11.51	±	0.20^{e}	2.31	±	0.01^{e}	32.16	±	0.01^{e}	7.88	±	0.14^{a}	2.60	±	0.00^{a}	0.990	±	0.00^{d}
E3II	11.83	±	0.56^{f}	2.68	±	0.03^{f}	31.82	±	0.03^{d}	7.54	±	0.29^{a}	2.24	±	0.00^{a}	0.997	±	0.00^{e}
E8I	4.09	±	0.09^{a}	0.75	±	0.00^{a}	25.72	±	0.00^{a}	19.80	±	0.33^{e}	7.95	±	0.00^{e}	0.966	±	0.01^{b}
E8II	4.80	±	0.15^{b}	0.87	±	0.01^{c}	27.07	±	0.01^{b}	17.53	±	0.44^{d}	6.89	±	0.76^{c}	0.968	±	0.00^{b}
E6.5I	5.22	±	0.00^{c}	0.95	±	0.00^{d}	27.21	±	0.01^{b}	16.04	±	0.55^{b}	6.34	±	0.11^{b}	0.976	±	0.01^{c}
E6.5II	5.67	±	0.28^{d}	0.79	±	0.01^{b}	30.95	±	0.01^{c}	16.47	±	0.63^{c}	7.62	±	0.00^{d}	0.945	±	0.00^{a}

D50 – medium diameter (the value of the droplet diameter at 50% in the cumulative distribution), $D_{3,2}$ – Sauter mean diameter, $D_{4,3}$ – De Brouckere mean diameter, SSA – specific surface area, K240 – emulsion stability index after 240 min. All values are mean ± standard deviation (n = 6). Means within a column with different letters are significantly different ($p < 0.05$).

emulsions were close to 1 confirming high stability (Table 1). Despite the fact that RPC either agglomerated or did not dissolve at pH 3 (Fig. 3), emulsions with pH 3 ($K_{240} \geq 0.990$) were slightly more stable than emulsions with pH 6.5 or 8, and the average droplet size at pH 3 was bigger than that of the other emulsions. Stability of larger droplets was also observed by Kurek and Pratap-Singh (2021) for emulsions with hemp seed oil, maltodextrin and vegetable proteins. These authors suggested that in an emulsion, the stability and viscosity are more interdependent than stability and droplet size. The type of homogenization process had no significant impact on the droplet size as seen in

Table 2
Surface and total oil contents, and encapsulation efficiency (EE) of spray dried Baltic herring oil powders (P3I, P3II, P8I, PII8, P6.5I and P6.5II).

Sample	Surface oil (%, w/w)			Total oil (%, w/w)			EE (%, w/w)		
P3I	25.18	±	0.26^{a}	48.72	±	0.59^{c}	48.31	±	1.17^{c}
P3II	23.02	±	1.27^{b}	45.78	±	0.9^{ab}	49.67	±	3.77^{c}
P8I	25.08	±	0.47^{b}	48.96	±	0.62^{c}	48.75	±	1.61^{c}
P8II	24.41	±	0.79^{b}	46.02	±	0.16^{b}	46.96	±	1.91^{bc}
P6.5I	25.29	±	1.54^{b}	45.12	±	0.99^{a}	43.90	±	4.65^{b}
P6.5II	27.59	±	0.44^{c}	46.05	±	0.12^{b}	40.09	±	0.81^{a}

All values are mean ± standard deviation (n = 3). Means within a column with different letters are significantly different ($p < 0.05$).

Table 3
Physical properties of Baltic herring oil powders (P3I, P3II, P8I, PII8, P6.5I and P6.5II).

Sample	D50 (μm)			$D_{3,2}$ (μm)			$D_{4,3}$ (μm)			span (−)			SSA (m^2/g)			UI (−)
P3I	53.97	±	1.35^{c}	47.55	±	2.03^{b}	98.13	±	4.49^{b}	1.57	±	0.17^{a}	0.13	±	0.01^{b}	2.06
P3II	55.60	±	0.74^{d}	49.30	±	0.85^{b}	125.25	±	2.14^{c}	1.71	±	0.08^{a}	0.12	±	0.00^{a}	2.54
P8I	49.11	±	0.83^{b}	42.97	±	1.03^{a}	64.15	±	3.88^{a}	1.41	±	0.12^{a}	0.14	±	0.032^{c}	1.49
P8II	49.19	±	0.00^{b}	41.86	±	0.00^{a}	83.48	±	0.00^{ab}	1.60	±	0.00^{a}	0.14	±	0.01^{c}	1.99
P6.5I	48.49	±	0.16^{ab}	42.02	±	0.14^{a}	53.93	±	0.26^{a}	1.39	±	0.01^{a}	0.14	±	0.00^{c}	1.28
P6.5II	47.51	±	1.36^{a}	39.59	±	2.02^{a}	82.36	±	2.94^{ab}	1.63	±	0.14^{a}	0.15	±	0.01^{d}	2.08

D50 – medium diameter (the value of the particle diameter at 50% in the cumulative distribution), $D_{3,2}$ – Sauter mean diameter, $D_{4,3}$ – De Brouckere mean diameter, SSA – specific surface area, UI – uniformity index All values are mean ± standard deviation (n = 6). Means within a column with different letters are significantly different ($p < 0.05$).

Fig. 2. However, there was slight trend that two-step homogenization increased the droplet size compared to one-step (Table 1).

3.2. EE of BH oil powders

The retention of BH oil within the capsules was result of the ratio of surface and total BH oil (Table 2). The EE values were in the range from

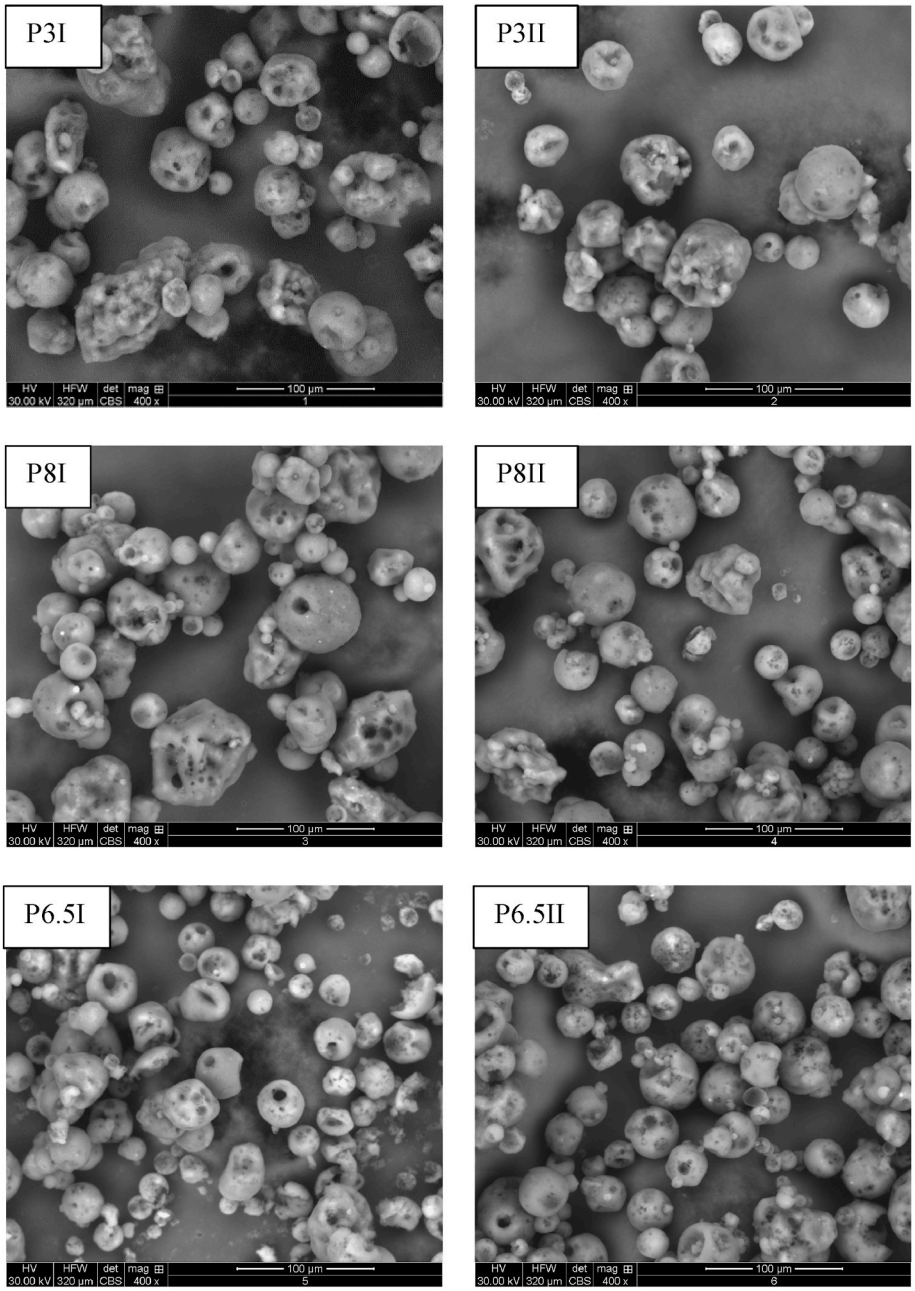

Fig. 4. SEM images showing Baltic herring oil powders (P3I, P3II, P8I, PII8, P6.5I and P6.5II).

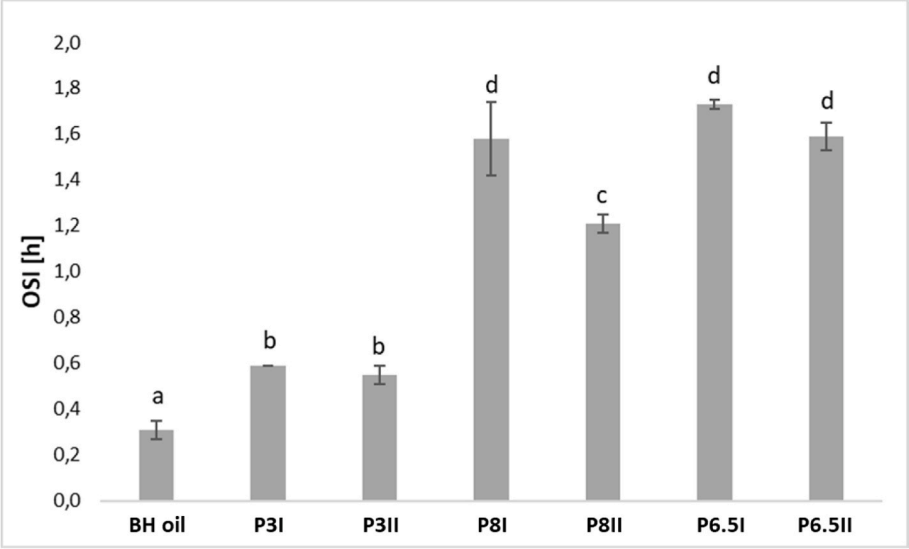

Fig. 5. Oxidative stability index (OSI) of Baltic herring oil and powders (P3I, P3II, P8I, PII8, P6.5I and P6.5II). All values are mean ± standard deviation (n = 3). Means with different letters are significantly different ($p < 0.05$).

40.9% (P6.5II) to 49.67% (P3II). Typically, the EE is related to the ratio of coating material to oil with higher EE's achieved with larger coating material to oil ratios. However, the use of minimum technically required often costly coating material is typically preferred by food industry. In the experiment of Wang et al. (2016) with whey protein isolates (WPI) and fish oil, the EE varied from 13.1 to 93.2%. Their emulsion containing 10% of WPI and 10% of fish oil was spray dried with very low efficiency (below 20%), which is significantly lower than ours with similar coating material to oil ratio. Wang et al. concluded that higher WPI content of the emulsion increased the oil retention by reducing the time to form a semi-permeable crust at the droplet-air interface. Also, Tonon et al. (2012) evaluated the effect of oil loading on EE of flaxseed oil microcapsules indicating that increasing oil concentration (10–40%) had a negative influence on EE. Chen et al. (2013) reported EE of 29.1–48.9% for samples using a ratio of wall to core 1:1 for fish oil encapsulated in milk proteins. High oil load led to larger droplet size and broader size distribution in reconstituted emulsions, which authors explained by the presence of surface oil after drying. Contrary, Wang et al. (2011) reported a high EE (95.5%) for microencapsulation of fish oil with barley protein at 1:1 core-to-oil ratio.

The SOC in our study was relatively high and ranged from 23.02% (P3II) to 27.59 (P6.5II) (Table 2). This can affect the quality of powders negatively as surface oil is less protected against lipid oxidation (Kaushik et al., 2015). Further, non-encapsulated BH oil may cause undesirable fish flavor in the final food product. Also previously (Shamaei et al., 2017) using protein as coating material has resulted in powders with an increased SOC. It is generally accepted that a smaller droplet size results in higher EE (Linke et al., 2020). However, in our study, the sample E3II contained droplets with the highest average size (Table 1), but the lowest surface oil and highest EE. Similar trend was confirmed by Chang et al. (2020). In turn, Shamaei et al. (2017) reported no regular correlation between droplet size and EE.

3.3. Morphology of BH oil powders

The powders obtained by spray drying emulsions with pH 3 (P3I and P3II) were characterized by greater particle sizes, $D_{3,2}$ (47.55–49.30 μm) and $D_{4,3}$ (98.13–125.25 μm), and lower specific surface area (0.12–0.13 m^2/g) compared to other powders (Table 3). Previously, Gomes and Kurozawa (2020) reported lower volume diameters ($D_{4,3}$) for spray dried flaxseed oil powders prepared with rice protein isolate (17.5 μm) and rice protein hydrolysates obtained with Alcalase (13.2–34.2 μm), and Flavourzyme (15.4–20.3 μm). This difference is maybe related to rice protein fraction used and differences in processing.

Powders obtained from two-step homogenization emulsion (P3II, P8II, P6.5II) were characterized by significant greater volume weighted mean diameter ($D_{4,3}$) compared to powders homogenized once. In our previously study (Ogrodowska et al., 2017), homogenization of emulsion before drying reduced the particle size. Ixtaina et al. (2015), who studied properties of encapsulated chia oil, reported inverse correlation between homogenization pressure and, volumetric and surface diameters. Also Kuhn and Cunha (2012) also reported that higher homogenization pressures resulted in higher span values. Samples homogenized twice were also characterized by higher droplet size distribution (span) compared to powders obtained by one-step homogenization.

Although all powder samples have similar $D_{3,2}$ values, there are some differences in $D_{4,3}$. Additionally, the uniformity index (UI) was calculated to show particle sphericity in the powder samples (Table 3). The UI values indicated that the samples obtained by spray drying the emulsions with pH 3 had the least spherical shape compared to others. This suggests that during the spraying process coalescence and agglomeration of sprayed droplets or sprayed droplets and powder particles occurred. Krishnan and Loth (2015) described five mechanisms of possible interactions of sprayed droplets in the drying chamber. The probability of occurrence of individual impacts is related, among others, to the physicochemical properties of the sprayed feed, including viscosity.

In the presented study, the continuous phase of the emulsion was composed of whey and rice protein. The solubility index of whey protein in the tested pH range is above 80% (Pelegrine and Gasparetto, 2005). On the other hand, rice protein is a sparingly soluble protein. The highest value of the solubility index does not exceed 30% (Mun et al., 2016). The different degree of dissolution of the dispersing phase ingredients could affect the drying process of the emulsion. The presence of agglomerates can be observed for powders P3I and P3II (Fig. 4). They have a non-spherical shape which may have been the result of the coalescence of emulsion droplets and/or droplets and circulating powder particles in the drying chamber.

SEM images of the BH oil powders revealed some differences in particles shapes and surface regularities (Fig. 4). The particles exhibited rather spherical shape with porous structure and varied sizes, typical for the spray dried powders. This kind of morphology was observed in all powders that presented similar globular morphology, resulting from the

Table 4
Fatty acid composition (% of total fatty acids, n = 3) of Baltic herring oil and powders (P3I, P3II, P8I, PII8, P6.5I and P6.5II), including sums of saturated fatty acids (Σ SFA), monounsaturated fatty acids (Σ MUFA), polyunsaturated fatty acids (Σ PUFA) and, *n*-3 and *n*-6 fatty acids.

Fatty acid	Oil	P3I	P3II	P8I	P8II	P6.5I	P6.5II
14:0	5.24 ± 0.01	5.39 ± 0.01	5.23 ± 0.05	5.27 ± 0.05	5.26 ± 0.05	5.19 ± 0.05	5.20 ± 0.10
16:0	19.38 ± 0.05	19.16 ± 0.06	19.12 ± 0.07	19.09 ± 0.02	19.20 ± 0.08	19.06 ± 0.05	18.91 ± 0.06
16:1(*n*-7)	4.99 ± 0.01	5.03 ± 0.02	5.03 ± 0.05	5.00 ± 0.06	5.06 ± 0.05	5.01 ± 0.04	5.00 ± 0.03
18:0	2.04 ± 0.01	1.99 ± 0.01	2.00 ± 0.01	2.00 ± 0.00	2.01 ± 0.01	2.00 ± 0.01	1.99 ± 0.01
18:1(*n*-9)	23.38 ± 0.06	23.50 ± 0.07	23.94 ± 0.05	23.37 ± 0.03	23.60 ± 0.09	23.46 ± 0.07	23.75 ± 0.07
18:1(*n*-7)	2.92 ± 0.01	2.97 ± 0.01	3.11 ± 0.04	3.06 ± 0.02	3.04 ± 0.06	3.04 ± 0.04	3.02 ± 0.05
18:2(*n*-6)	5.62 ± 0.01	5.44 ± 0.01	5.55 ± 0.01	5.37 ± 0.01	5.43 ± 0.02	5.48 ± 0.01	5.58. ±0.01
18:3(*n*-3)	3.53 ± 0.01	3.48 ± 0.01	3.50 ± 0.07	3.52 ± 0.06	3.47 ± 0.02	3.49 ± 0.07	3.48 ± 0.03
18:4(*n*-3)	3.17 ± 0.01	3.18 ± 0.01	3.15 ± 0.02	3.16 ± 0.01	3.15 ± 0.00	3.17 ± 0.01	3.14 ± 0.01
20:1(*n*-9)	1.23 ± 0.00	1.25 ± 0.01	1.26 ± 0.00	1.25 ± 0.01	1.26 ± 0.01	1.26 ± 0.01	1.25 ± 0.00
20:2(*n*-6)	1.15 ± 0.00	1.10 ± 0.00	1.09 ± 0.00	1.10 ± 0.00	1.10 ± 0.01	1.10 ± 0.00	1.08 ± 0.00
20:4(*n*-3)	1.11 ± 0.00	1.11 ± 0.00	1.10 ± 0.00	1.11 ± 0.00	1.10 ± 0.00	1.11 ± 0.00	1.10 ± 0.00
20:5(*n*-3)	7.81 ± 0.01	7.76 ± 0.01	7.66 ± 0.04	7.74 ± 0.03	7.69 ± 0.01	7.76 ± 0.02	7.70 ± 0.01
22:6(*n*-3)	11.13 ± 0.01	11.27 ± 0.01	11.13 ± 0.06	11.31 ± 0.03	11.22 ± 0.02	11.37 ± 0.02	11.26 ± 0.01
24:1(*n*-9)	1.20 ± 0.24	1.27 ± 0.25	1.17 ± 0.23	1.43 ± 0.02	1.23 ± 0.21	1.28 ± 0.02	1.27 ± 0.26
Others[a]	6.10 ± 0.12	6.09 ± 0.15	5.97 ± 0.25	6.23 ± 0.18	6.19 ± 0.16	6.23 ± 0.12	6.26 ± 0.17
Σ SFA	28.06 ± 0.07	27.82 ± 0.07	27.68 ± 0.08	27.75 ± 0.07	27.83 ± 0.05	27.64 ± 0.09	27.49 ± 0.16
Σ MUFA	34.41 ± 0.16	34.78 ± 0.16	35.21 ± 0.11	34.81 ± 0.04	34.89 ± 0.13	34.75 ± 0.05	35.00 ± 0.18
Σ PUFA	37.53 ± 0.08	37.41 ± 0.09	37.11 ± 0.14	37.44 ± 0.06	37.28 ± 0.13	37.61 ± 0.10	37.52 ± 0.17
Σ *n*-3	29.77 ± 0.08	29.87 ± 0.09	29.50 ± 0.12	29.98 ± 0.06	29.76 ± 0.11	30.05 ± 0.09	29.88 ± 0.16
Σ *n*-6	7.94 ± 0.01	7.68 ± 0.01	7.78 ± 0.03	7.62 ± 0.01	7.67 ± 0.02	7.73 ± 0.01	7.81 ± 0.02

[a] Others is the sum of all minor fatty acids (≤1%) including 12:0, 14:1(*n*-5), 18:3(*n*-6), 20:0, 20:3(*n*-6), 20:4(*n*-6), 20:3(*n*-3), 22:0, 21:1(*n*-9), 22:2(*n*-6), 22:3(*n*-3), 22:4(*n*-3), 22:5(*n*-3), 24:0, 24:4(*n*-3) and 24:5(*n*-3).

fast water evaporation during the spray drying process (Silva et al., 2014). Wang et al. (2016) encapsulated fish oil in protein-based emulsion through spray drying. In their experiment samples with relative high oil-protein ratio showed very porous structure. Our emulsion contained 15% of BH oil, which could also affected on porous structure of obtained powders.

3.4. Oxidative stability of BH oil and BH oil powders

The BH oil studied was characterized by low OSI of 0.31 h (Fig. 5). Encapsulation process increased the stability of BH oil, and pH of the emulsions had significant effect on the oxidative stability of the BH oil powder. The highest induction periods (1.59–1.73 h) were determined for P6.5I and P6.5II obtained from an emulsion with a pH 6.5, while the lowest values (0.55–0.59 h) were found for the powders obtained of emulsions adjusted to pH 3. Results of Horn et al. (2011) showed a tendency toward a faster progression in lipid oxidation at low pH (4.5) compared to high pH (7.0) for emulsions prepared with cod liver and WPI. Increased lipid oxidation due to low pH condition in emulsion stage is likely to lower the OSI for powders P3I and P3II.

The powders obtained with one-stage homogenization were characterized by higher induction period compared to the powders obtained with two-stage homogenization, the differences ranged from 6.78% to 23.42%. Mechanical stress and agitation due to shear and turbulence during emulsion preparation is likely to increase oxygen inclusion as seen previously (Serfert et al., 2009). Droplet disruption by cavitation and subsequent rearrangement of oil droplets during homogenization promote distribution of oxygen and lipid oxidation products among the newly arranged oil droplets, which accelerates lipid oxidation.

3.5. Fatty acid composition of BH oil and BH oil powders

The fatty acid composition of the BH oil and the spray dried emulsions composition (Table 4) were comparable to the fatty acid composition of lipid extracts of BH fillets or mince (Aro et al., 2000; Damerau et al., 2020b). The content of DHA was 11.1%, and the EPA content was 7.8% in BH oil, which was higher than previously found by Aro et al. (2000) with 7.7% and 5.4%, respectively, for lipids extracted from BH filets and by Damerau et al. (2020b) with 9.4% and 6.0%, respectively, for lipids extracted from BH mince. No significant differences were

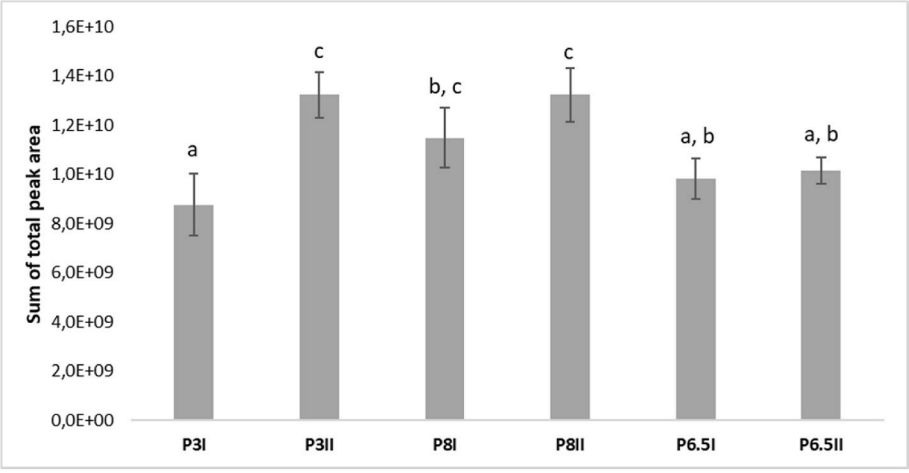

Fig. 6. Sum of total peak area (n = 3) of identified volatile compounds in Baltic herring oil powders (P3I, P3II, P8I, P8II, P6.5I, P6.5II). Different letters above bars indicate a statistically significant difference ($p < 0.05$) between sums of total peak area of dried Baltic herring oil emulsions.

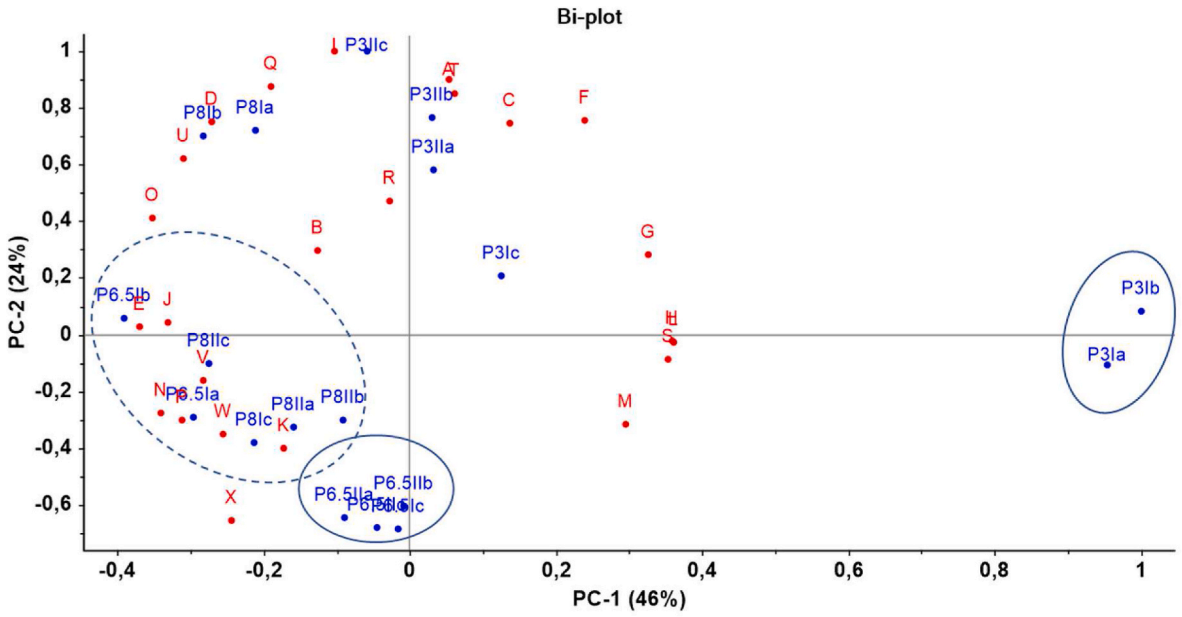

Fig. 7. Bi-plot of PCA of volatile compounds of Baltic herring oil powders (objectives = P3I, P3II, P8I, P8II, P6.5I, P6.5II with three replicates a to c; loadings = volatile compounds [A = propanal, B = 2,3-butanedione, C = acetic acid, D = 3-methylbutanal, E = 2-methylbutanal, F = 2-ethylfuran, G = 1-penten-3-ol, H = pentanal, I = 2-methylheptane, J = 4-methylheptane, K = 2,4-dimethylheptane, L = hexanal, M = 4-methyoctane, N = 2-hexenal (*E*), O = heptanal, P = 2-methylnonane, Q = hexanoic acid, R = 2,4-heptadienal (sum of *E,Z* and *E,E* isomers), S = 3,5-octadien-2-one (sum of E,Z and E,E isomers), T = nonanal, U = 2,6-nondienal (*E,Z*), V = α-pinene, W = 3-carene, X = γ-terpinene]). Mean-centered and weighed (1/sdev) peak area data (n = 3) was analyzed.

found between the fatty acid composition of BH oil and the extracted oil from the powders although the low EE. Therefore, the processing of dried emulsion had no considerable effect on the fatty acid composition, which is important to preservation of the nutritional value of the powders.

3.6. Volatile compounds of BH oil powders

Thirty-seven volatiles (Supplementary Table 1) were identified in the powders with the HS-SPME-GC-MS method applied. The most abundant volatile compound detected was hexanal, followed by 2,4-methylheptane, 2,3-butanedione, pentanal and propanal. In general, there was a trend that two-step homogenization increased the formation or release of volatiles regardless of the pH used. The total peak area of identified volatile compounds showed the lowest volatile release or formation for P3I, P6.5I and P6.5II compared to P3II, P8I and P8II, of which P3II and P8II had the highest release or formation (Fig. 6). This may be due to the observed greater volume ($D_{4,3}$) weighted mean diameter of two-step homogenization emulsions.

Most of the identified volatiles originated from BH oil, which was confirmed by comparing the volatile profile of powders with that of BH oil (Supplementary Table 1). The volatiles included typical ones found from fresh BH including 2- and 3-methylbutanal, Strecker aldehydes formed by naturally occurring degradation reactions, as well as hexanal and heptanal, which are aldehydes formed from lipid oxidation (Aro et al., 2003; Damerau et al., 2020b). We have previously detected 2, 4-heptandienal (*E,Z/E,E*), 1-penten-3-ol and 2-hexenal (*E*) in non-oxidized omega-3 supplements (Damerau et al., 2020a). Other volatiles identified in BH oil, acetaldehyde, propanal, 2-ethylfuran and acetic acid are more associated with oxidized omega-3 rich oils

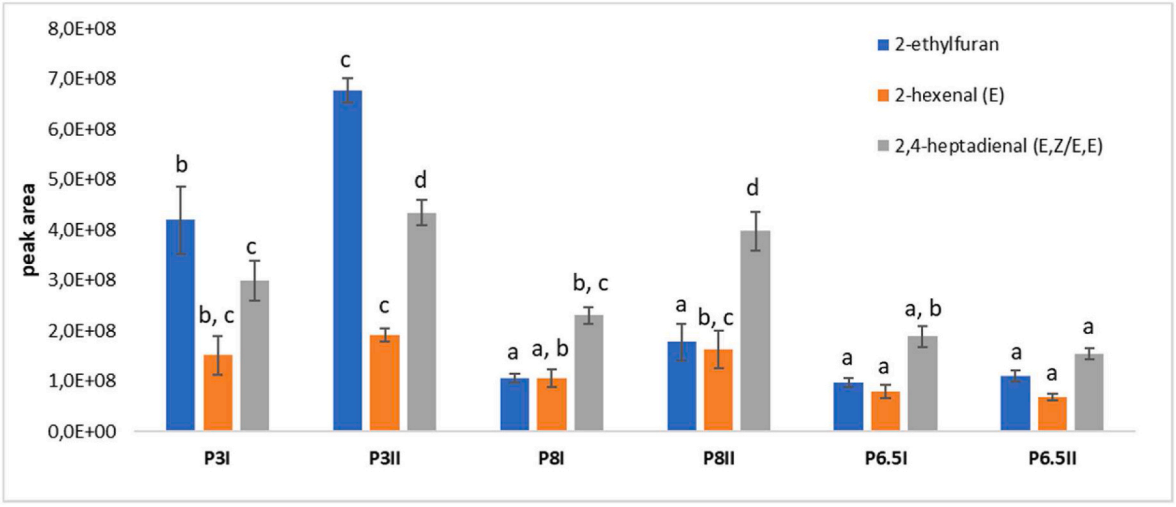

Fig. 8. Peak area data (n = 3) of 2-ethylfuran, 2-hexenal (*E*), 2,4-heptadienal (*E,Z/E,E*) in Baltic herring oil powders (P3I, P3II, P8I, P8II, P6.5I, P6.5II). Different letters above bars indicate a statistically significant difference ($p < 0.05$) between peak areas of different powders for each volatile compound.

(Gómez-Cortés et al., 2015). Volatile compounds detected in BH oil powders but not in the BH oil included α-pinene, 3-carene and γ-terpinene, which are terpenes most likely originating from the encapsulation matrix, and 3,5-octadien-2-one (*E,Z/E,E*) and, 2,6-nondienal (*E,Z*), which are lipid oxidation compounds found in oxidized BH (Damerau et al., 2020b).

Twenty-four volatile compounds identified from powders were selected to be analyzed by PCA based on their abundancy and/or their previously shown importance for BH (Aro et al., 2003; Damerau et al., 2020b). The PCA model is presented as a bi-plot in Fig. 7 explaining 70% of total variance. PC-1 accounted for 46% of the variation between samples and the main variables influencing PC-1 were hexanal and pentanal on positive side, and 2-methylbutanal, 4-methylheptane, heptanal and 2-hexenal (*E*) on negative side. PC-2 explained 24% of the variations and was mainly influenced by propanal, 2-methylheptane, 2, 4-dimethylheptane and γ-terpinene. Replicates of each dried emulsions grouped together, except for the third replicate of P3I, P8I and P6.5I. P3I was mainly associated with pentanal, hexanal and 3,5-octadien-2-one (*E,Z/E,E*). P3II and P8I both were found in upper half of bi-plot and correlated to propanal, 2-methylheptane, hexanoic acid and nonanal. P6.5II on other hand showed a negative correlation to propanal, 2-methylheptane, hexanoic acid and nonanal, and a positive correlation to γ-terpinene and 2,4-dimethylheptane (Fig. 7). P8II and P6.5I were located in the lower left corner of the bi-plot and related γ-terpinene, 2, 4-dimethylheptane, 3-carene, 2-methylnonane, 2-hexenal (*E*), α-pinene, 2-methylbutanal and 4-methylheptane.

The PCA model showed clear differences in volatile profile of dried emulsion produced by different process parameters. However, the difference could not be linked to a specific process parameter or to potential lipid oxidation as different volatiles, all formed from lipid oxidation, were mainly responsible for the differences in the volatile profiles. Previously, Yang et al. (2017) investigated the correlation between volatile formation and OSI for omega-3 oils. They concluded that not all formed volatiles increased linearly during lipid oxidation. Therefore, only selected volatiles, such as 2,4-heptadienal, are good indicator compounds for oxidation. Based on our previous research on omega-3 supplements (Damerau et al., 2020a) also 2-ethylfuran and 2-hexenal (*E*) have potential as oxidation indicators. The three selected indicator compounds suggest that the least lipid oxidation occurred in P6.5I and P6.5II followed by P8I, P8II and P3I (Fig. 8). Sample P3II contained the highest amount of lipid oxidation indicator volatiles suggesting low oxidative stability. The results were in line with OSI results (Fig. 5).

4. Conclusions

Rice proteins offer promising possibilities as matrices for microencapsulation of fish oil as our previous studies indicate that they could mask fishy flavor. Yet their use as coating material is associated with solubility challenges, which could be modified with alteration of the pH of the emulsion and addition of homogenization steps. According to the obtained results, production of emulsions with BH oil and WPC and RPC mixture as wall material components, resulted in stable emulsions with relatively small droplet size and large dispersion. However, while RPC was shown to either agglomerate or stay non-dissolved at pH 3, but surprisingly, at pH 3, the most stable emulsion was obtained. This effect must be inferred to WPC. Further, the powders obtained from emulsions at pH 3 showed the highest EE but the lowest oxidative stability. It could be concluded that changing the pH parameters of an emulsion containing rice proteins improved emulsion stabilization by the cost of lipid quality. Therefore, other methods of emulsion stabilization, such as gum or pectin addition seems to be unavoidable. Despite the relatively low EE, the spray drying process did not cause any significant change in fatty acid profiles. Two homogenization steps were shown to increase the release/formation of total volatiles. OSI results correlated well with data of selected volatile lipid oxidation indicator compounds. Both methods indicated that emulsions produced at the pH of 6.5 resulted in the highest oxidative stability for the produced BH oil powder.

Credit author statement

Annelie Damerau: Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. Dorota Ogrodowska: Conceptualization, Resources, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Funding acquisition. Paweł Banaszczyk: Methodology, Formal analysis, Investigation. Fabian Dajnowiec: Formal analysis, Investigation, Writing – review & editing. Małgorzata Tańska: Formal analysis, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. Kaisa M. Linderborg: Conceptualization, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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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.2021.110769.

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