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Wood hemicelluloses as effective wall materials for spray-dried microcapsulation of polyunsaturated fatty acid-rich oils

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ABSTRACT

The most commonly-used and effective wall materials (WMs) for spray-dried microencapsulation of bioactive compounds are either costly, or derived from unsustainable sources, which lead to an increasing demand for alternatives derived from sustainable and natural sources, with low calories and low cost. Wood hemicelluloses obtained from by-products of forest industries appear to be attractive alternatives as they have been reported to have good emulsifying properties, low viscosity at high concentrations, high heat stability and low heat transfer. Here, we investigated the applicability of spruce galactoglucomannans (GGM) and birch glucuronoxylyls (GX), to encapsulate flaxseed oil (FO, polyunsaturated fatty acid-rich plant based oil) by spray drying; and the results were compared to those of the highly effective WM, gum Arabic (GA). It was found that depending on solid ratios of WM:FO (1:1, 3:1 and 5:1), encapsulation efficiency of GGM was 88–96%, and GX was 63–98%. At the same encapsulation ratio, both GGM and GX had higher encapsulation efficiency than GA (49–92%) due to their ability to produce feed emulsions with a smaller oil droplet size and higher physical stability. In addition, the presence of phenolic residues in GGM and GX powders enabled them to have a greater ability to protect oil from oxidation during spray drying than GA. Physicochemical properties of encapsulated powders including thermal properties, morphology, molecular structure, particle size and water adsorption intake are also investigated. The study has explored a new value-added proposition for wood hemicelluloses which can be used as effective WMs in the production of microcapsules of polyunsaturated fatty acid-rich oils for healthy and functional products in food, pharmaceutical and cosmetic industries.

1. Introduction

The development of wood-based biorefineries offer the capability to manufacture new advanced products to meet the demands of consumers for sustainable plant-based products. At the same time, it can promote economic growth and secure jobs in rural areas. Wood mainly consists of 40–45 % cellulose, 20–30 % hemicelluloses and 20–30 % lignin (Sjostrom, 1993). For the last two centuries, cellulose has been the main refining target, resulting in products like fibers, nanocrystals, and derivatives for paper, pharmaceutical and food industries (Klemm et al., 2005). During cellulose refinement, hemicelluloses are treated as low-value by-products remaining outside of the biorefinery process during which hemicelluloses, along with lignin, typically end up in waste

streams and are primarily utilized for heat and energy (Mikkonen, 2020). However, hemicelluloses have been efficiently recovered from the process water of thermomechanical pulping (Thuvander et al., 2019; Bhattacharya et al., 2022), and from sawdust and wood chips using pressurized hot water extraction (PHWE) (Kilpeläinen et al. 2014), heat fractionation (Chadni et al. 2019a), steam explosion (Chadni et al. 2019b), and high voltage electrical discharge (Chadni et al. 2019c). The recovered hemicelluloses have been investigated as gels (Alakalhunmaa et al., 2016), films (Mikkonen et al., 2015), and hydrocolloids to stabilize emulsions (Mikkonen, 2020).

PHWE is a safe and environmentally-friendly extraction method, and free from hazardous chemicals (Kilpeläinen et al., 2014), thus the extracted hemicelluloses including galactoglucomannans (GGM) from

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softwoods and glucuronoxylans (GX) from hardwoods are considered safe to be used as food ingredients or additives, although their use as or within has not been approved by authorities (Granato et al., 2022; Kirjoranta et al., 2020; Kynkäänniemi et al., 2022; Pitkänen et al., 2018; Rosa-Sibakov et al., 2016; Valoppi et al., 2019). In addition, previous studies demonstrated that GGM and GX were effective emulsion stabilizers (Mikkonen, 2020); and had low viscosity at high concentrations (Mikkonen et al., 2016), high heat stability and low heat transfer (Edrich, 1980). These properties of GGM and GX potentially make them superior wall materials (WM) for the production of spray-dried microcapsule powders of many bioactive compounds. However, such applications of wood hemicelluloses have not been thoroughly investigated.

Non-communicable diseases such as cardiovascular and neurodegenerative disease, diabetes and cancers, which are responsible for almost 70 % of all deaths worldwide annually (WHO, 2022), are strongly associated with dietary factors. Consuming foods containing an adequate amount of polyunsaturated fatty acids (PUFAs), which are very rich in marine and vegetable oils, is one of the most effective ways to maintain a healthy diet and minimize the risk of non-communicable diseases i.e. 0.3–0.5 g of omega-3 and omega-6 per day as suggested by the WHO (Saremi and Arora, 2009). The human body is unable to synthesize PUFAs, and consequently they must be supplied via diets and/or dietary supplements, leading to a very high demand for food products/supplements containing PUFAs. However, their high susceptibility to oxidation, isomerisation and polymerization under processing conditions and environmental stressors, and unpleasant flavors limit their applications in many food products (Ganesan et al., 2014). Microencapsulation of PUFAs to produce microcapsule powders by spray drying is a widely-used strategy to improve oxidative stability, mask off-flavors, enhance water dispersibility, control release rate and location, and enhance handling properties. Many microencapsulation methods have been trialed, and have been summarized in several comprehensive reviews (Bakry et al., 2016; Encina et al., 2016; Mohammed et al., 2020; Yakhane et al., 2021).

In most reported studies about spray-dried microencapsulation of PUFAs, the commonly used WMs are either costly (e.g., cyclodextrins and guar gums), or derived from unsustainable sources such as bovine milk-based WMs which are associated with methane emissions during cattle raising (Bakry et al., 2016; Encina et al., 2016; Mohammed et al., 2020). Additionally, milk-based WMs make microcapsule powders unsuitable for lactose intolerant consumers when they are used for spray-dried microencapsulation of plant-based PUFAs, and milk leaves a significantly larger carbon footprint during production in contrast to plant-based materials. The use of wood celluloses and their derivatives either as stabilizers in the preparation of emulsions for spray drying of PUFAs, or in the combination with other WMs to protect PUFA during spray drying have been well investigated (Kolanowski et al., 2004; Singh et al., 2018). However, their high cost and the high viscosity of their solutions prevent them from being effective WMs for microcapsule production. Wood hemicelluloses could be a viable alternative to currently-used WMs as they are plant-based, non-allergenic, cost-effective and bring additional functionality to the products. The use of wood hemicelluloses has the added benefit of adding dietary fibres to the final powder products, which has the simultaneous benefit of reducing the risk of chronic diseases and cancers. Furthermore, the phenolic residues composed mainly of lignin, are partially covalently bound with wood hemicelluloses in the form of lignin carbohydrate complexes (LCCs) (Carvalho et al., 2021) introduce an antioxidant capacity to hemicelluloses (Lahtinen et al., 2019), which increases their capacity to protect PUFAs from oxidation (Lehtonen et al. 2016, Lehtonen et al. 2018).

In this study, applicability of PHWE GGM and GX in the spray-dried microencapsulation of PUFA-rich oils was investigated by using flaxseed oil (FO), which is a typical PUFA-rich plant-based oil. Feed emulsion properties and encapsulation efficiency of GGM and GX at various solid ratios with FO (GGM/GX:FO = 1:1, 3:1 and 5:1) as well as

physicochemical properties of their microcapsule powders were investigated, and the results were compared to those of the most widely-used WM, gum Arabic (GA). Additionally, the oxidative stability of FO during spray drying was evaluated by measuring peroxide values and volatile and non-volatile lipid oxidation products. The study illustrates that wood hemicelluloses have excellent WM properties for encapsulating PUFA-rich oils and for the protecting them against oxidation during manufacture.

2. Materials and methods

2.1. Materials

Flaxseed oil (FO) was obtained from Elix Oil company (Somero, Finland). According to the manufacturer, FO contains 59.0 % (w/w) ω -3 (α -linolenic acids), 14.9 % (w/w) ω -6 (linolenic acids), and 13.8 % (w/w) ω -9 (oleic acids). GX powders produced by spray drying (FSD Minor™ spray dryer, GEA, Helsinki, Finland) of birch extracts (recovered by PHWE) at inlet and outlet drying air temperatures of 170 and 70 °C, respectively (Kilpeläinen et al., 2014) were obtained from Natural Resources Institute Finland (Luke). Spray-dried spruce GGM (recovered by PHWE) was provided by Montinutra Ltd. (Turku, Finland). The lignin content and carbohydrate composition of GGM and GX were shown in Table S1 (Supplementary material). GA powder was purchased from Special Ingredients Ltd. (Chesterfield, United Kingdom).

Iron(III)chloride (FeCl₃, Titrisol®; Merck), iron(II)chloride-4-hydrate (FeCl₂·4H₂O; Fluka Chemie) and ammonium thiocyanate (NH₄SCN; Sigma-Aldrich) were used for the determination of peroxide values. Butylated hydroxytoluene (BHT; Sigma-Aldrich) was used as an antioxidant in the sEC-RI eluent and in diethyl ether used in the solid-phase extraction. All the solvents used in the chemical analyses were HPLC grade: acetone (Honeywell), 1-decanol (\geq 95 %; Merck), diethyl ether (including BHT, Honeywell), ethanol (EtOH; 99.5 %; ALTIA, Rajamäki, Finland), heptane (Honeywell), methanol (MeOH; Honeywell), 2-propanol (Honeywell), and tetrahydrofuran (THF; \geq 99.9 %; Honeywell).

2.2. Preparation of feed emulsions for spray-dried microencapsulation

The feed emulsions consisting of WM and FO at various ratios (WM:FO = 1:1, 3:1 and 5:1) were prepared. Total WM + FO content of all feed emulsions was fixed at 10 % (w/w). We chose this total concentration to keep viscosity of feed emulsions at level low enough for spray drying. To prepare feed emulsions, aqueous solutions of WM at various concentrations as indicated in Table 1 were first prepared by dissolving them into distilled water at room temperature for GGM and GX, or heated distilled water (~60 °C) for GA under constant magnetic stirring overnight (~24 h). Then, FO was added (at concentration as shown in

Table 1
Formulations of feed emulsions prepared from GGM, GX and GA with FO at various ratios.

Feed emulsions	WM:FO	WM (% w/w)			FO (% w/w)
		GA	GGM	GX	
GGM:FO = 1:1	1:1	–	5	–	5.0
GGM:FO = 3:1	3:1	–	7.5	–	2.5
GGM:FO = 5:1	5:1	–	8.3	–	1.7
GX:FO = 1:1	1:1	–	–	5	5.0
GX:FO = 3:1	3:1	–	–	7.5	2.5
GX:FO = 5:1	5:1	–	–	8.3	1.7
GA:FO = 1:1	1:1	5	–	–	5.0
GA:FO = 3:1	3:1	7.5	–	–	2.5
GA:FO = 5:1	5:1	8.3	–	–	1.7

GGM: Spruce galactoglucomannans; GX: Birch glucuronoxylans; GA: Gum Arabic; WM: Wall material; FO: Flaxseed oil; “–”: not involved in the formulation of feed emulsions.

Table 1), and the mixtures were subjected to an Ultra-Turrax homogenizer (T-18 basic, IKA, Staufen, Germany) at 12,000 rpm for 2 min, immediately followed by a high-pressure homogenizer configured with 75 mm Y-type F20Y and 200 mm Z-type H30Z chambers in a series (Microfluidizer 110Y, Microfluidics, Westwood, MA, USA) at 800 bar for three consecutive cycles. The homogenized feed emulsions were collected for analyzing physical stability, droplet size and viscosity; and for spray drying. During preparation, feed emulsion containers were always wrapped with aluminum foil to avoid possible oil oxidation induced by light.

2.3. Determination of feed emulsion properties

2.3.1. Droplet size distribution

Oil droplet size and its distribution of feed emulsions were determined by using a laser light scattering analyzer (Mastersizer Hydro 3000 SM, Malvern Instruments Ltd, Worcestershire, UK) connected with a dispersion accessory (Hydro EV, Malvern Instruments Ltd, Worcestershire, UK), and water as dispersant. During measurement, the rotor speed was set at 2000 rpm, and refractive indices of water and FO were 1.330 and 1.479, respectively (Karaca et al., 2013). Oil droplet size distribution, surface area-weighted diameter $D[3,2]$, volume-weighted diameter $D[4,3]$, and size distribution percentages $Dv(10)$, $Dv(50)$ and $Dv(90)$ were calculated using the Mastersizer v3.62 (Malvern Instruments Ltd, Worcestershire, UK). Three readings for each measurement were performed.

2.3.2. Viscosity

Flow behavior curves of feed emulsions were determined by using Haake Mars 60 rheometer (Thermo Electron GmbH, Dreieich, Germany) at a shear rate range of 0.3–500, and 500–0.3 1/s (at 22 °C). A plate and plate geometry with a diameter of 35 mm, and a gap between plates of 0.5 μm were employed. The apparent viscosities recorded at shear rate of 50 1/s from the flow curves with shear rate of 0.3–500 (1/s) were determined and reported.

2.3.3. Physical stability

Physical stability of feed emulsions stored at 22 °C over 96 h was determined using Turbiscan Lab Expert analyzer (Formulations, France). About 20 mL of each feed emulsion was decanted to transparent glass vials which were then analyzed as fresh ($t = 0$) and after 6, 24, 48, 72 and 96 h. The vials containing feed emulsions were kept undisturbed during storage. The physical stability of feed emulsions is evaluated via global Turbiscan stability index (TSI) using Turbiscan software (version 1.2). The higher TSI values indicate a lower physical stability of feed emulsions.

2.4. Spray-dried microencapsulation

Spray drying was carried out using a laboratory scale spray drier (B-290, Buchi Labortechnik GmbH, Essen, Germany) equipped with two-fluid spray nozzle (nozzle diameter of 0.7 mm). The freshly-prepared feed emulsions were fed into the drying chamber via a peristaltic pump at a flow rate of 10–15 mL/min. Compressed air pressure for the nozzle was 6 bar, and its flow rate was 473 L/h. Inlet and outlet air drying temperatures were controlled at 150 and 70 °C, respectively, and the air aspirator was fixed at 80 %, corresponding to the flow rate of drying air at 32 m³/h. During spray drying, the feed emulsion containers were wrapped with aluminium foil to prevent the samples from direct exposure to light which can induce oil oxidation, and were gently mixed to ensure homogeneity of feed solutions. The powders the in cyclone and sample container were collected and kept in 50 mL falcon tubes for further analyses.

2.5. Determination of encapsulation efficiency

Encapsulation efficiency (EE, %) was calculated as per equation (1).

$$EE(\%) = 100 \times \frac{\text{Total oil} - \text{Surface oil}}{\text{Total oil}} \quad (1)$$

Surface and total oils of microcapsule powders were extracted according to Damerou et al. (2014) after some modifications. The surface oil was extracted from 0.3 g of microcapsule powder with 5 mL of heptane. The extraction was performed by vortexing at 500 rpm for 1 min. The formed dispersion was centrifuged at 3000 g for 5 min after which the organic layer was collected for further analysis by sEC-RI (section 2.7.2.).

Extraction of total oil was performed by dispersing 0.3 g of microcapsule powder in 1.5 mL of MilliQ water first at 1500 rpm for 30 s followed by 1000 rpm for 5 min with pulse function. After dispersing the powder in water, lipids were extracted into 7 mL of heptane:2-propanol mixture (3:1, v/v) by vortexing at 1000 rpm for 2 min after which the organic layer was separated by centrifugation at 3000 g for 5 min and collected for further analysis by sEC-RI (section 2.7.2.). The extraction efficiency for triacylglycerols was 97 % (± 0.7 %).

2.6. Determination of physicochemical properties of microcapsule powders

2.6.1. Water content and water activity

Water content of microcapsule samples was quantified by following AOAC 925.45 method (AOAC, 1996). About 1.0–1.5 g of the samples was weighed into pre-weighed aluminum dishes and dried in an oven (Mettler UNE 600, Mettler GmbH Co. KG, Schwabach, Germany) at 105 °C until a mass change of the samples between measurements was <2 mg (approximately 24 h). The samples were cooled in a desiccator containing silica gel as desiccant before being weighed.

Water activity (a_w) of microcapsule samples at 25 °C was measured by using a water activity meter (LabMaster-AW, Novasina AG, Lachen, Switzerland).

2.6.2. Particle size distribution

The particle size distribution of the microcapsule powders was measured by using a laser light scattering analyzer (Mastersizer Hydro 3000 SM, Malvern Instruments Ltd, Worcestershire, UK) connected to an Aero S dry powder disperser (Malvern Scientific, Worcestershire, UK). The air pressure and vibration feeding rate were fixed at 1 bar and 50 %, respectively to allow dry dispersion of about 0.2–0.5 g of microcapsule powders. A refractive index of microcapsule powders used to calculate their particle size was 1.479.

2.6.3. Scanning electron microscope

Morphology of microcapsule powders was determined using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Tokyo, Japan). The powders were fixed on the double carbon tape which was pre-attached on the metallic specimens (stubs). Any unfixed powder particles were flushed with dry N₂ gas. The fixed samples were then coated with gold/palladium at a thickness of 4 nm using a high resolution sputter coater (208HR, Cressington Scientific Instruments, Watford, UK). The coating was performed with two cycles. The samples were rotated during coating to achieve the required thickness homogeneity. The coated samples were observed under FESEM at an accelerating voltage of 10 kV, an emission current of 10 μA, a working distance of 10 mm, and magnification of 2000.

2.6.4. X-ray diffraction

Internal structure of microcapsule powders was evaluated by X-ray powder diffraction (XRPD) using an Empyrean Alpha 1 X-ray diffractometer (Malvern Panalytical, Malvern, Worcestershire, UK). The measurements were performed using copper radiation ($\lambda K\alpha_1 = 1.541 \text{ \AA}$) at

current of 40 mA, voltage of 45 kV, and an angular range of $2\theta = 3\text{--}70^\circ$ with step size of 0.01° per second. The samples were packed into plastic sample holders and wrapped with kapton tape (Elgood Ltd., Vantaa, Finland). For each XRPD analysis, β -alanine crystal and the empty sample holder with kapton tape were run as controls for comparison with the microcapsule powders.

2.6.5. Differential scanning calorimetry

Glass transition temperature (T_g) of microcapsule powders were characterized using a differential scanning calorimetry (DSC823^e, Mettler Toledo AG, Greifensee, Switzerland). About 5–10 mg of microcapsule powders was weighed in 40 μ L aluminium crucibles (ME-51119870, Mettler Toledo AG, Greifensee, Switzerland) and sealed hermetically with lids (ME-51119871, Mettler Toledo AG, Greifensee, Switzerland). During measurement, a sealed empty crucible was used as reference, and dry nitrogen at flow rate of 50 mL/min was used to purge the measuring cell and prevent moisture condensation. The samples were scanned at a heating rate of $5^\circ\text{C}/\text{min}$ from -20 to 130°C , cooled from 130 to -20°C , and heated from -20 to 200°C . T_g values were calculated from onset points of endothermic transition peaks using STARE software version 16.0 (Mettler Toledo AG, Greifensee, Switzerland).

2.6.6. Fourier-transform infrared spectroscopy

Infrared absorbance spectra of microcapsule powders were recorded using a Fourier transform infrared spectrometer (PerkinElmer, Waltham, MA, USA) mounted with a universal Attenuated Total Reflectance (ATR) sampling accessory. The background of clean zinc selenide crystal was obtained before scanning for the samples. The samples were placed on the crystal and compressed by ART arm. Degree of compression was fixed for all samples (90 %). The scanning frequencies ranged from 4000 to 650 cm^{-1} . Spectra resolution was 4 cm^{-1} , and the number of scans were 32.

2.6.7. Dynamic vapour adsorption

Water uptake ability of microcapsule powders at various relative humidity (RH) levels was measured by using a dynamic vapor sorption apparatus (DVS Intrinsic, Surface Measurement Systems Ltd., Alperton, Middlesex, UK). About 5–10 mg of sample was weighed in a sample pan which was suspended in a microbalance within a thermostatically controlled chamber. In the chamber, dry compressed N_2 gas was passed over the sample at a flow rate of $200\text{ cm}^3/\text{min}$. The measurements were performed at 25°C and RH levels ranging between 10 and 90 %, increasing stepwise by 10 % RH. A step was completed as the sample was equilibrated at the respective RH and change in the sample weight was $<0.002\text{ %}/\text{min}$ for at least 30 min. Percentage of water uptake (%) was calculate using equation (2)

$$\text{Water uptake}(\%) = 100 \times \frac{m_m - m_d}{m_d} \quad (2)$$

Where m_m is the mass of the equilibrated sample at a chosen RH (mg), whereas m_d is the weight of the sample at 10 % RH (mg).

2.7. Determination of the oxidative status of microcapsule powders

In order to monitor the oxidative degradation of oil during spray drying, freshly prepared microencapsulated powders were dispersed in aqueous solution and lipids were recovered into a non-polar solvent. The extraction was performed similarly as for the encapsulation efficiency (section 2.5.) using 0.2 g of microcapsule powders, replacing 2-propanol with ethanol for the dispersion, and reducing the amount of heptane to 2 mL. Each microcapsule powder was extracted as triplicates ($n = 3$). The collected extracts were subjected to immediate further analyses.

2.7.1. Peroxide value

The initial stage of oxidation was evaluated by the total content of hydroperoxides determined by peroxide values (PV). 0.5 mL aliquots of

the freshly prepared oil extract were used for determining PV by ferric thiocyanate method as described previously (Lehtonen et al., 2018; Lehtonen et al., 2016). The obtained results were normalized against the determined oil content and reported as milliequivalents of O_2 per kilogram of extracted oil ($\text{mEqO}_2/\text{kg oil}$). Each sample extract was measured as duplicates ($n = 3 \times 2$).

2.7.2. Determination of oil composition and non-volatile oxidation products by sEC-RI

Encapsulation efficiency (section 2.5.) was determined based on triacylglycerols (TAGs) as they are the main constituents in FO ($>98\%$) (Indelicato et al., 2017). To monitor the propagation and termination stages of oxidation, non-volatile oxidation products were determined by fractionating them according to their polarity and by separating them based on their size. This was achieved by a combination of solid-phase extraction (SPE) and size-exclusion chromatography (SEC) utilizing refractive index (RI) detection.

For the fractionation of compounds based on their polarity (i.e., degree of oxidation), a 100-mg SiOH SPE cartridge (Strata® SI-1 Silica, 55 μm , 70 \AA ; Phenomenex, USA) was conditioned twice with 1 mL of heptane. Aliquot of freshly prepared FO extract corresponding to 1–2 mg of oil, was loaded on the cartridge after which the cartridge was washed two times with 1 mL of heptane. Fractions were collected with 1) 2 mL of 90:10 heptane:diethyl ether (v/v), 2) 2 mL of 50:50 heptane:diethyl ether (v/v), 3) 2 mL of acetone and 4) 2 mL of methanol. Collected fractions were dried by evaporation under a nitrogen stream at 35°C and redissolved into 0.5 mL of tetrahydrofuran (THF) including 1.1 mM BHT as an antioxidant. The recovery of described SPE method was $124 \pm 17\%$ for GGM, $109 \pm 5.1\%$ for GX and $81 \pm 13\%$ for GA.

Freshly prepared extracts and fractions were analyzed by sEC-RI according to Lampi and Kamal-Eldin (1998) and Lehtonen et al. (2016). In brief, compounds were separated using one 100- \AA and two 50- \AA PLGel columns (5 μm , 300 mm \times 7.5 mm i.d.; Polymer Laboratories Inc., Amherst, MA, USA) connected in series and a 0.6 mL/min flow of THF (1.1 mM BHT). The eluting peaks were monitored with a RI detector. Quantification was based on external standard method using rapeseed oil as standard sample in the range of 2.0–1000 $\mu\text{g}/\text{injection}$. The obtained results for the oxidation products were normalized against the determined oil content and reported as mg/g oil. The averages and standard deviations were calculated across three replicate extracts and the results were corrected with the SPE recoveries.

2.7.3. Determination of volatile oxidation products by HS-SPME-GC-MS

Volatile oxidation products were determined by extracting them from the sample headspace by solid-phase microextraction and analyzing them by gas chromatography coupled with mass spectrometry (HS-SPME-GC-MS) according to the previously described method (Lehtonen et al., 2016). In brief, microcapsule powders were weighed into 20-mL (75.5 \times 22.5 mm) amber glass vials and closed with gas tight caps. The weighed sample amount was standardized to correspond to 50 mg of oil per sample vial. Freshly prepared vials were placed in an autosampler maintained at 8°C . Volatile compounds were released for 20 min at 50°C and extracted with a DVB/CAR/PDMS fiber (10 mm length, 50/30 μm film thickness; Supelco, Bellefonte, PA, USA) for 30 min at 250 rpm. The extracted compounds were released at the GC injection port at 250°C for 10 min, separated on a SPB-624 capillary column (30 m \times 0.25 mm, 1.4 μm film thickness; Supelco) and detected with a single quadrupole mass spectrometer in full-scan mode (m/z 40–300). The volatile compounds were identified based on their mass spectra using Wiley 7n database (Wiley Registry™ of Mass Spectral Data, 7th ed., Hoboken, NJ, USA) and by comparing the retention times and mass spectra with those of the standards. Their contents were reported as the peak areas. Each microencapsule powder was analyzed as triplicates ($n = 3$).

2.8. Statistical analyses

All experiments were performed at least three replications if not stated otherwise, and results are expressed as mean values (\pm standard deviations). For determination of oil oxidation, three analytical replicates were done for each technical replicate. A one-way analysis of variance (ANOVA) and Tukey test were used to evaluate the significant differences in the mean values of feed emulsion properties, encapsulation efficiency and oxidation stability of microcapsule powders using OriginPro 2020 (OriginLab Corporation, Northampton, MA, USA). The Tukey's test was used as a post-hoc test for a pairwise comparison of the means with a statistically significant difference at $p \leq 0.05$.

3. Results and discussion

3.1. Properties of feed emulsions

Properties of feed emulsions such as emulsifying, stability, oil droplet size and viscosity greatly affect the spray-dried microencapsulation process. The stable feed emulsions are required for high encapsulation efficiency, and good protection ability to core materials and physical properties of microcapsule powders (Danviriyakul et al., 2002). Droplet size in feed emulsions determines morphology and particle size of

microcapsule powders. High viscosity of feed emulsions hinders atomization process, thus resulting in low spray drying rate and large powder particle size (Anandharamkrishnan and Padma Ishwarya, 2015). Therefore, determining these properties of feed emulsions is an important step to evaluate the applicability of new WMs like GGM and GX, and their suitability as new feed emulsion formulations in spray-dried microencapsulation. Feed emulsions must be stable and not exhibit any visual phase separation before being subjected to and during spray drying. Here, we investigated the physical stability at room temperature over 96 h, droplet size and its distribution, and viscosity of feed emulsions prepared from GGM, GX and GA at various solid ratios with FO (Fig. 1 and Table 2). Droplet size distribution percentages regarding Dv(10), Dv(50) and Dv(90) of all feed emulsions are shown in Table S2 (Supplementary materials).

3.1.1. Physical stability

As indicated in Fig. 1(a), physical stability of feed emulsions was greatly affected by types and concentration of hemicelluloses. For GGM, the highest feed emulsion stability was at WM:FO = 1:1, and increasing GGM concentration (WM:FO = 3:1 and 5:1) markedly reduced feed emulsion stability. In feed emulsions with high content of GGM, some GGM remained in the continuous phase, and their sedimentation during storage contributed to higher global TSI values and lower physical

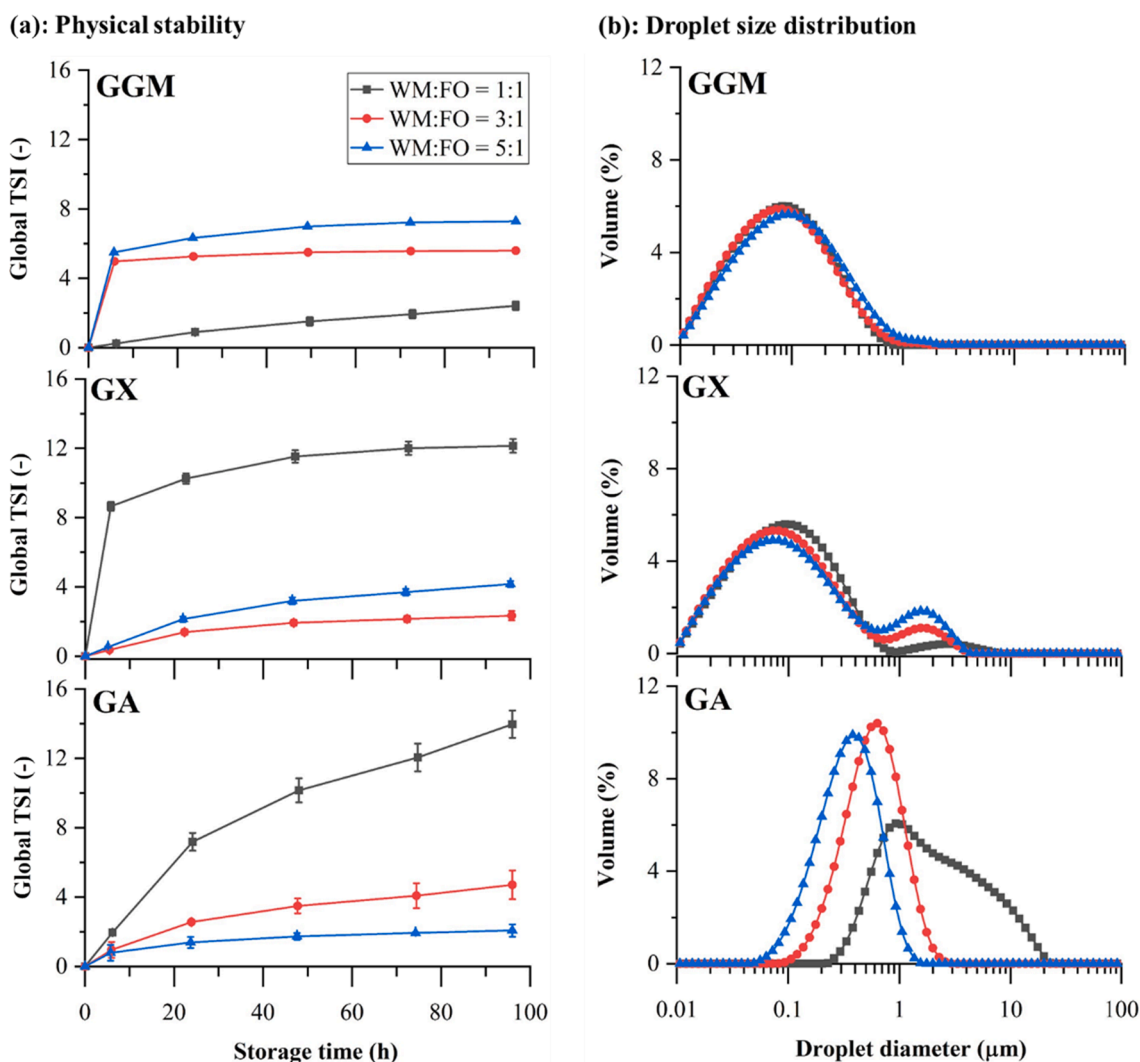


Fig. 1. (a): Physical stability expressed by global Turbiscan stability index (TSI) over 96 h of storage at 22 °C; and (b): oil droplet size distribution of freshly-prepared feed emulsions from spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) with flaxseed oil (FO) at various ratios (WM:FO = 1:1, 3:1 and 5:1). Refer to Table 1 for the formulations of feed emulsions.

Table 2

Properties of freshly-prepared feed emulsions (droplet size and viscosity) and microcapsule powders (moisture content, water activity, glass transition temperatures, T_g and particle size) prepared from spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) with flaxseed oil (FO) at 1:1, 3:1 and 5:1 ratios.

Samples	Feed emulsions			Microcapsule powders				
	Droplet size (μm)		Viscosity (mPa.s)	Moisture content (%)	Water activity (-)	T_g ($^{\circ}\text{C}$)	Particle size (μm)	
	D[4,3]	D[3,2]					D[4,3]	D[3,2]
GGM:FO = 1:1	0.11 \pm 0.00 ^a	0.05 \pm 0.00 ^a	2.8 \pm 0.32 ^a	4.50 \pm 0.49 ^a	0.11 \pm 0.01 ^a	112.5 \pm 1.65 ^a	12.10 \pm 1.31 ^a	8.92 \pm 0.47 ^a
GGM:FO = 3:1	0.14 \pm 0.03 ^a	0.06 \pm 0.01 ^a	3.6 \pm 0.38 ^b	4.38 \pm 0.55 ^a	0.10 \pm 0.01 ^a	119.3 \pm 5.70 ^a	9.73 \pm 1.63 ^a	7.30 \pm 0.54 ^b
GGM:FO = 5:1	0.16 \pm 0.01 ^b	0.06 \pm 0.00 ^a	3.7 \pm 0.23 ^b	5.09 \pm 0.90 ^a	0.10 \pm 0.00 ^a	120.0 \pm 0.87 ^a	9.73 \pm 1.08 ^a	6.56 \pm 0.17 ^b
GX:FO = 1:1	0.21 \pm 0.01 ^A	0.06 \pm 0.00 ^A	2.5 \pm 0.49 ^A	3.00 \pm 0.28 ^A	0.16 \pm 0.02 ^A	74.5 \pm 2.65 ^A	10.97 \pm 0.86 ^A	8.34 \pm 0.19 ^A
GX:FO = 3:1	0.28 \pm 0.02 ^B	0.06 \pm 0.00 ^A	3.7 \pm 0.83 ^A	5.19 \pm 0.91 ^B	0.13 \pm 0.05 ^A	74.3 \pm 2.98 ^A	8.94 \pm 0.46 ^B	6.43 \pm 0.23 ^B
GX:FO = 5:1	0.34 \pm 0.00 ^C	0.06 \pm 0.00 ^A	2.8 \pm 0.48 ^A	5.96 \pm 0.05 ^B	0.17 \pm 0.03 ^A	72.7 \pm 1.03 ^A	8.85 \pm 0.39 ^B	6.19 \pm 0.23 ^B
GA:FO = 1:1	3.28 \pm 0.08 ^A	1.28 \pm 0.02 ^A	3.2 \pm 0.21 ^A	2.86 \pm 0.42 ^A	0.10 \pm 0.00 ^A	127.7 \pm 0.56 ^A	46.17 \pm 7.01 ^A	19.07 \pm 1.53 ^A
GA:FO = 3:1	0.65 \pm 0.01 ^B	0.46 \pm 0.01 ^B	4.2 \pm 0.07 ^B	3.19 \pm 0.94 ^A	0.11 \pm 0.01 ^A	126.8 \pm 1.64 ^A	14.27 \pm 3.25 ^B	8.66 \pm 0.72 ^B
GA:FO = 5:1	0.41 \pm 0.01 ^C	0.29 \pm 0.02 ^C	4.8 \pm 0.21 ^C	4.36 \pm 0.42 ^A	0.10 \pm 0.01 ^A	125.4 \pm 1.15 ^A	14.07 \pm 1.17 ^B	7.96 \pm 0.52 ^B

Refer to Table 1 for the formulations of samples. There are insignificant differences in viscosities at 50 1/s between shear rate range of 0.3–500 and 500–0.3 1/s, and the values of the first shear rate range were reported. Within the same group of wall material in the same column (either GGM, GX or GA), means with different letters indicated statistically significant differences among samples ($p < 0.05$).

stability of feed emulsions. The sedimentation of the GGM continuous phase was visually observed. Opposite results were seen for GX feed emulsions by which the highest stability was at WM:FO = 5:1, closely followed by WM:FO = 3:1. After 48 h of storage, creaming was visually observed for GX feed emulsions at WM:FO = 1:1. The results indicate differences in an optimal formulation for stabilizing feed emulsions between GGM and GX due to their different molecular structures (Mikkonen, 2020). Our previous study (Ho et al., 2022) found that GGM and GX recovered from PHWE also differed in lignin content, degree of acetylation, molar mass and carbohydrate composition; and these differences led to alterations in physical stability of their emulsions (5 % hexadecane and 1 % hemicelluloses). Differences in emulsifying properties between GGM and GX were also reported for emulsions of 5 % rapeseed oil and 1 % hemicelluloses (Lahtinen et al., 2019), 40 % alkyd resins and 8 % hemicelluloses (Mikkonen et al., 2019), 25 % rapeseed oil and 5 % hemicelluloses (Mikkonen et al., 2016).

Similar to GX, ability to stabilize feed emulsions of GA increased with increasing solid concentration. Good emulsifying properties of GA are supported by the presence of proteins (Gharsallaoui et al., 2007), which is 1.14 % (w/w) according to GA's manufacturer. PHWE hemicelluloses contain a negligible amount of residual proteins that were not expected to correlate with their emulsion stability (Mikkonen et al., 2009). Lignin residues, which are 24.63 % (w/w) for GX and 22.0 % (w/w) for GGM (Table S1), were found to enhance emulsifying properties of hemicelluloses (Lahtinen et al., 2019; Lehtonen et al. 2018; Carvalho et al., 2021). In addition, Lehtonen et al. (2016) found that at 1 % (w/w) GGM subjected to ethanol precipitation to remove lignin was still more effective in stabilizing rapeseed oil emulsion (5 % oil) than GA at 5 % (w/w). Overall, all investigated feed emulsions are stable enough for spray drying as the visual phase separation of the least stable GX feed emulsions happened 48 h after preparation.

3.1.2. Droplet size distribution

The types and solid concentration of WMs also affected droplet size distribution of feed emulsions (Fig. 1b and Table 2). The smallest droplet diameter was observed for GGM ($D[4,3] = 0.11\text{--}0.16 \mu\text{m}$), followed by GX ($D[4,3] = 0.21\text{--}0.34 \mu\text{m}$), and then GA ($D[4,3] = 0.41\text{--}3.28 \mu\text{m}$) ($p < 0.05$). For both GGM and GX, increasing their solid concentration led to a slight increase of $D[4,3]$ values, and a shift of size distribution curves to larger droplet diameter. However, regardless of solid concentration, GGM feed emulsions had mono-modal droplet size distribution while GX counterparts had bi-modal distribution. Contrary to the general theory that an emulsion with mono-modal droplet size distribution is more stable than the one with bi-modal droplet size distribution (McClements, 2005), it could not be concluded that GGM feed emulsions were more stable than GX counterparts basing on their droplet size modality. Also, GGM and GX feed emulsions did not show

any correlation between their droplet size and physical stability. For GA feed emulsions, droplet diameter markedly reduced with increased solid concentration, and highly correlated with their physical stability where feed emulsions with a smaller droplet size had a higher physical stability. Droplet size of an emulsion greatly depends on its preparation method; nature and ratio of oil and continuous phases, and properties of emulsifiers (McClements, 2005). Considering only emulsifier, depending on its amount and rate of diffusion to and adsorption on the interface (determined by its nature), newly generated oil droplets can be stabilized immediately after they are produced thereby generating small emulsion oil droplets; or coalesce together into larger droplets before they are stabilized by emulsifier (McClements, 2007). Droplet size of feed emulsions is a decisive factor to encapsulation efficiency and ability to protect oil from oxidation during spray-dried microencapsulation. Large droplets can undergo shearing and breakdown during atomization, leaving excessive oil on disrupted droplet surface (Sootitawat et al., 2003). The smaller droplets with the higher total surface area exhibit the greater susceptibility to oxidation once oxygen has penetrated into them (Reineccius, 2004).

3.1.3. Viscosity

Viscosity of all investigated GGM and GX feed emulsions was low (2.8–3.7 mPa.s) and not significantly different ($p > 0.05$). Likewise, low viscosity of GGM and GX emulsions with 25 % rapeseed oil and 5 % hemicelluloses (4.5–6.5 mPa.s) was reported (Mikkonen et al., 2016). As compared to GGM and GX, a higher viscosity was observed for GA feed emulsions (3.7–4.8 mPa.s), which exhibits a highly ramified structure with long chains of GA, and its higher molar mass (250,000–1,000,000 g/mol) (Masuelli, 2013), as compared to PHWE GGM and GX (below 10 000 g/mol) (Mikkonen et al., 2019). Low viscosity of feed emulsions will facilitate the ease of atomization and protect active compounds by early crust formation. Also, feed emulsion viscosity is inversely proportional to particle size of microcapsule powders (Anandharamkrishnan and Padma Ishwarya, 2015). Shear rate dependent viscosity curves of all feed emulsions are shown in Figure S1 (Supplementary materials), indicating that all feed emulsions had shear-thinning behaviors.

Overall, due to high physical stability, small droplet size and low viscosity of GGM and GX feed emulsions, compared to GA counterparts, it could be expected that the use of GGM and GX as WMs enables high encapsulation efficiency and oxidation stability of spray-dried microcapsule powders of FO.

3.2. Encapsulation efficiency

Encapsulation efficiency (EE) is one of the most important parameters to evaluate successful microencapsulation of oils. Due to the involvement of surface oil in the calculation of EE (equation (1)), we

show the analyzed results of surface oil in Figure S2 (Supplementary materials). According to Fig. 2, the EE was significantly affected by types and concentration of WM. At WM:FO = 1:1, GGM had the highest EE (87.6 %), being much higher than that of GX (63.1 %) and almost double the value of GA (49.8 %). These results are well correlated with physical stability and droplet size of their feed emulsions as shown by GGM feed emulsions at WM:FO = 1:1 were the most stable and had the smallest droplet diameter, therefore showing the highest EE. For all WMs, increasing their solid concentration led to a significant increase in their EE, especially for GX and GA, and the increase narrowed the variation in among WMs. At low solid concentration of WMs, the amounts of WMs might not be sufficient to fully and effectively cover oil droplets, leading to high surface oil (Figure S2), and therefore low EE (Anandharamakrishnan and Padma Ishwarya, 2015). Similar effects of the increase of WM solid concentration on EE were also reported for spray-dried microencapsulate powders of FO with GA, whey protein concentrate, and modified starch Hi-Cap 100 (Tonon et al., 2012); and chickpea and lentil protein isolates, and maltodextrin (Karaca et al., 2013).

At WM:FO = 3:1 and 5:1, there was no difference in EE between GGM and GX ($p > 0.05$), and both of them were still higher in EE than GA ($p < 0.05$), indicating a very good oil encapsulation capacity of GGM and GX. One possible explanation for the higher EE of GGM and GX than GA is their ability to produce feed emulsions with a smaller oil droplet diameter (Table 2). Studies demonstrated that decreasing droplet diameter of feed emulsions increased EE (Jafari et al., 2008; Sootittantawat et al., 2003). According to GA's manufacturer, GA material contains 0.2 % fat which possibly leads to its high surface oil and low EE; however we were unable to detect any fat in the extracts obtained from GA powders with the method reported in section 2.5. A similar EE of GA for FO was reported elsewhere (Akram et al., 2021; Naz et al., 2020). The EE of GGM and GX for FO in this study was also higher than that of maltodextrin, GA, whey protein concentrate, or their mixtures (Akram et al., 2021; Carneiro et al., 2013).

3.3. Physicochemical properties of spray-dried microcapsule powders

3.3.1. Moisture content and water activity

Moisture content and water activity (a_w) of food powders are crucial factors in evaluating their shelf-life and stability against microbial attack and oil oxidation. For most dried food powders, the maximum level of moisture content and a_w are 3–4 % (w/w) and 0.2–0.3, respectively (Karaca et al., 2013). According to Table 2, moisture content and a_w of

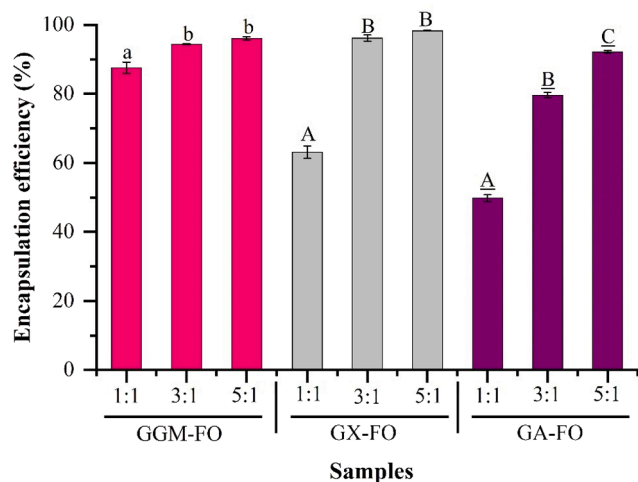


Fig. 2. Encapsulation efficiency (%) of spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) at 1:1, 3:1, and 5:1 ratios with flaxseed oil (FO). Refer to Table 1 for the formulations of samples. Within the same group of wall material (GGM, GX or GA), means with different letters indicate significant differences among wall material contents ($p < 0.05$).

most microcapsule powders were within these specifications. For all WMs, solid concentration did not affect moisture content and a_w of microcapsule powders ($p > 0.05$). However, GX microcapsule powders had a higher a_w than GGM and GA ones ($p < 0.05$). Meanwhile, at the same solid concentration, moisture content of GGM and GX microcapsule powders was quite similar ($p > 0.05$), but both had slightly higher values than that of GA counterparts ($p < 0.05$). This could be because of higher hydrophilic properties of hemicelluloses, which increases their ability to interact with water and therefore high moisture content. It was also reported that WM with high hydrophilic regions induced high moisture content of microcapsule powders (Naz et al., 2020).

3.3.2. Particle size and its distribution

Particle size is the primary characteristic that confers certain functional properties of microcapsule powders (e.g., bulk density, water solubility and digestibility) and food products in which microcapsule powders are added (e.g., textural and sensory) (Anandharamakrishnan and Padma Ishwarya, 2015). Particle size and its distribution of all investigated microcapsule powders are shown in Table 2 and Fig. 3a. Particle size distribution percentages for Dv(10), Dv(50) and Dv(90) of all microcapsule powders are shown in Table S1 (Supplementary materials). All GGM and GX microcapsule powders had similar monomodal distributions with a narrow peak representing a predominant size, demonstrating good powder homogeneity in these samples. Contrary to the effects of GGM and GX solid concentration on droplet size of their feed emulsions (Table 2 and Fig. 2b), increasing solid concentration of GGM and GX led to a reduction of particle size of microcapsule powders prepared from them ($p < 0.05$). For GGM and GX, there was no clear correlation between physical stability of their feed emulsions and particle size of their microcapsule powders.

Similar to GGM and GX, an increase of particle size with increased solid concentration was also observed for GA microcapsule powders, but changes in their particle size were positively correlated with changes in the droplet size, physical stability and viscosity of their feed emulsions. Note, all feed emulsions were spray-dried within 30 min after they were prepared during which their destabilization was negligible. Therefore, alterations of particle size of microcapsule powders are not attributed by physical stability of their feed emulsions. As illustrated in Table 2, for all types of WMs, the largest particle size was witnessed for WM:FO = 1:1, and it significantly reduced with increased WM solid ratio, but not different between WM:FO = 3:1 and 5:1. These could be because of the higher surface oil at WM:FO = 1:1 (Figure S2) which induces the stronger and more aggregation/stickiness of powder particles leading to increased particle size (Bhandari and Ho, 2020). Statistical results exhibit that at the same level of solid concentration, particle size (D[4,3] and D[3,2]) of GGM and GX microcapsule powders was not significantly different ($p > 0.05$), which is probably due to their similarity in feed emulsion viscosity (Table 2), but markedly smaller than that of GA ones ($p < 0.05$). The large particle size of GA microcapsule powders possibly results from large droplet size and high viscosity of GA feed emulsions (Anandharamakrishnan and Padma Ishwarya, 2015).

3.3.3. Morphology

The morphology of dried powders affects many of their key quality characteristics such as particle size distribution, flowability, friability and density (Anandharamakrishnan and Padma Ishwarya, 2015). As indicated in Fig. 3(b), regardless of type and solid concentration of WM, all microcapsule powders were mostly spherical-shaped particles with a wrinkled and uneven surface and varying in size, which are typical characteristics of spray-dried powders containing polymers (Vehring et al., 2007). Particle agglomeration was also witnessed for all microcapsule powders. The surface oil (Figure S2) and amorphous nature of spray-dried microcapsule powders (details in XRD result section) are the main reasons for the adhesion of powder particles when they collide during spray drying (Bhandari and Ho, 2020). Due to powder agglomeration, the particle size determined by static light scattering might be

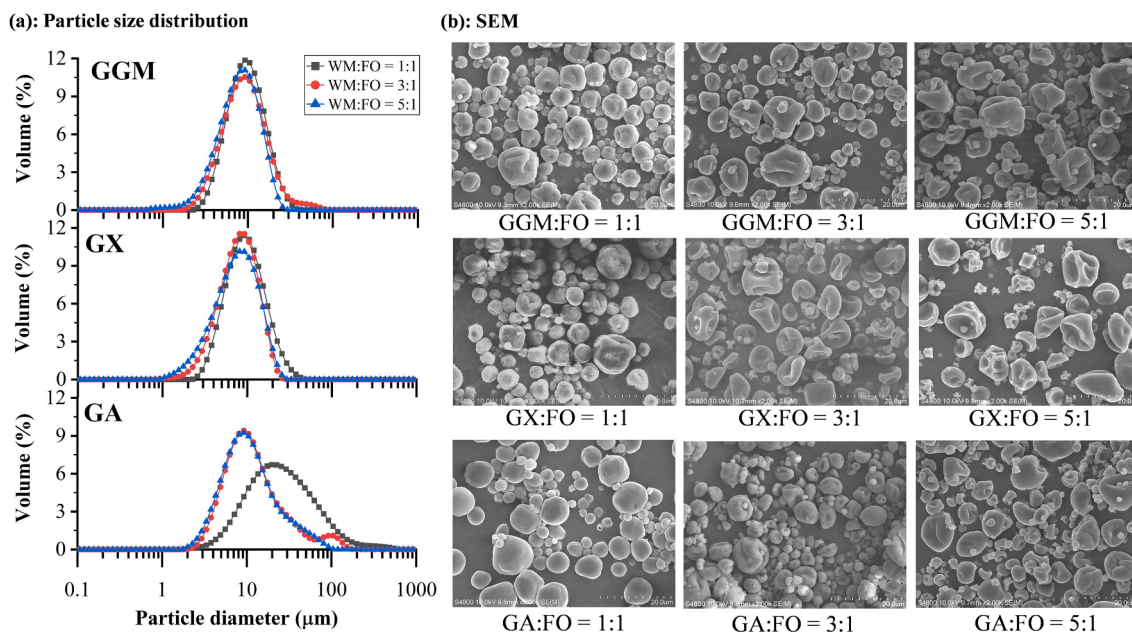


Fig. 3. (a): Particle size distribution; and (b): SEM of microcapsule powders prepared from spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) with flaxseed oil (FO) at various wall material (WM) ratios (WM:FO = 1:1, 3:1, and 5:1). Refer to Table 1 for the formulations of samples.

larger than the actual size. However, estimated particle size from SEM images was strongly in agreement with the particle size distribution curves in Fig. 3a. For all microcapsule powders, there were no apparent cracks or fissures on particle surface, indicating that hemicelluloses can offer protection and retention of FO as good as GA. A similar morphology of spray-dried microcapsule powders of GA with FO was also reported (Naz et al., 2020; Tonon et al., 2012).

3.3.4. X-ray diffraction

The internal structure of microcapsule powders (crystalline or amorphous) greatly affects their storage stability and functional properties such as solubility, flowability and compressibility. As shown in Figure S3 (Supplementary materials), all microcapsule powders have an almost completely amorphous structure shown by a very broad peak on their XRD patterns. The results indicated that the microcapsule powder structure is not affected by WMs and their solid concentration. Amorphous structure is a typical characteristic of spray-dried powders as the drying process in spray drying happens within a few seconds during which powder molecules do not have enough time to arrange into an ordered structure (Ho et al., 2020). An amorphous structure of spray-dried microcapsule powders of FO coated by GA and other WMs was also reported elsewhere (Akram et al., 2021; Naz et al., 2020).

3.3.5. Differential scanning calorimetry

Due to the amorphous structure of microcapsule powders (XRD results), determining their T_g is very important to partially explain the agglomeration of powders during spray drying and to select a suitable storage condition. Microcapsule powders prefer storage temperatures which are lower than their T_g to hinder their phase transformation to crystalline structure which induces the disrupting and collapsing of the powders (Roos, 2010). T_g of all microcapsule powders, determined as onset points of endothermic transitions on the DSC curves during the second heating cycle (illustrated in Figure S3, Supplementary materials), is shown in Table 2. T_g of GGM microcapsule powders was 112.5–120.0 °C, which was markedly higher than that of GX powders (72.7–74.3 °C), inferring that the former is less agglomerated during spray drying and more stable during storage than the latter. However, the SEM results (Fig. 3b) did not exhibit any differences in the powder agglomeration between GGM and GX microcapsule powders, which

infers that the surface oil plays a predominant role in the powder's agglomeration. Lower T_g values of GX microcapsule powders than GGM counterparts could be because of higher a_w of the former (Table 2).

Along with a_w , T_g of microcapsule powders also depends on T_g of WMs which is greatly affected by their molar mass and chemical structure. This is supported by the fact that for both GGM and GX, increasing their solid concentration did not affect the T_g of their microcapsule powders ($p > 0.05$). Polymers with higher molar mass, amounts of bulky and inflexible side groups, degree of cross-linking, and amounts of polar groups have a higher T_g (Roos, 2010). PHWE GGM had a molar mass of 8,200 g/mol, being double that of GX (4,000 g/mol) (Mikkonen et al., 2019), possibly leading to a higher T_g of GGM. It is noticed that the reported T_g values of wood hemicelluloses in the literature are somewhat inconclusive, for example 180 °C for either GGM or GX (Nypelö et al., 2016), 120–130 °C for GX (Carvalho et al., 2019), 55–65 °C for GGM (Hartman et al., 2006), and 43 °C for GGM (Xu et al., 2007). This could be because of both variations in the characteristics of wood hemicelluloses affected by extraction methods and starting wood materials, and in the experimental procedures. A previous study also reported that it was unable to detect T_g of α -tocopherol-GGM microcapsule powders produced by freeze drying due to the partial crystalline structure of produced powders (Laine et al., 2010).

T_g of microcapsule powders coated by wood hemicelluloses, especially GGM in this study were found to be higher than the values reported for polyunsaturated fatty acid microcapsules coated by other WMs such as pea protein isolate and its mixture pectin, 77–83 °C (Aberkane et al., 2014); skim milk powder, 55 °C (Aberkane et al., 2014), mixture of milk proteins, β -glucan and maltodextrin, 64–79 °C (Li and Shi, 2018). With high T_g values of wood hemicellulose-based microcapsule powders, it is expected that they will be resistant to the oil oxidation and temperature during storage. However, in this study T_g of GGM and GX microcapsule powders was much lower than that of GA ($p < 0.05$). High T_g of GA microcapsule powders, which was not affected by GA solid concentration, is due to high T_g of GA material attributed by its high molar mass and complex structure (Masuelli, 2013).

3.3.6. Fourier-transform infrared spectroscopy

Chemical structure of microcapsule powders was investigated by FTIR analyses, and the results are illustrated in Fig. 4(a). The FTIR

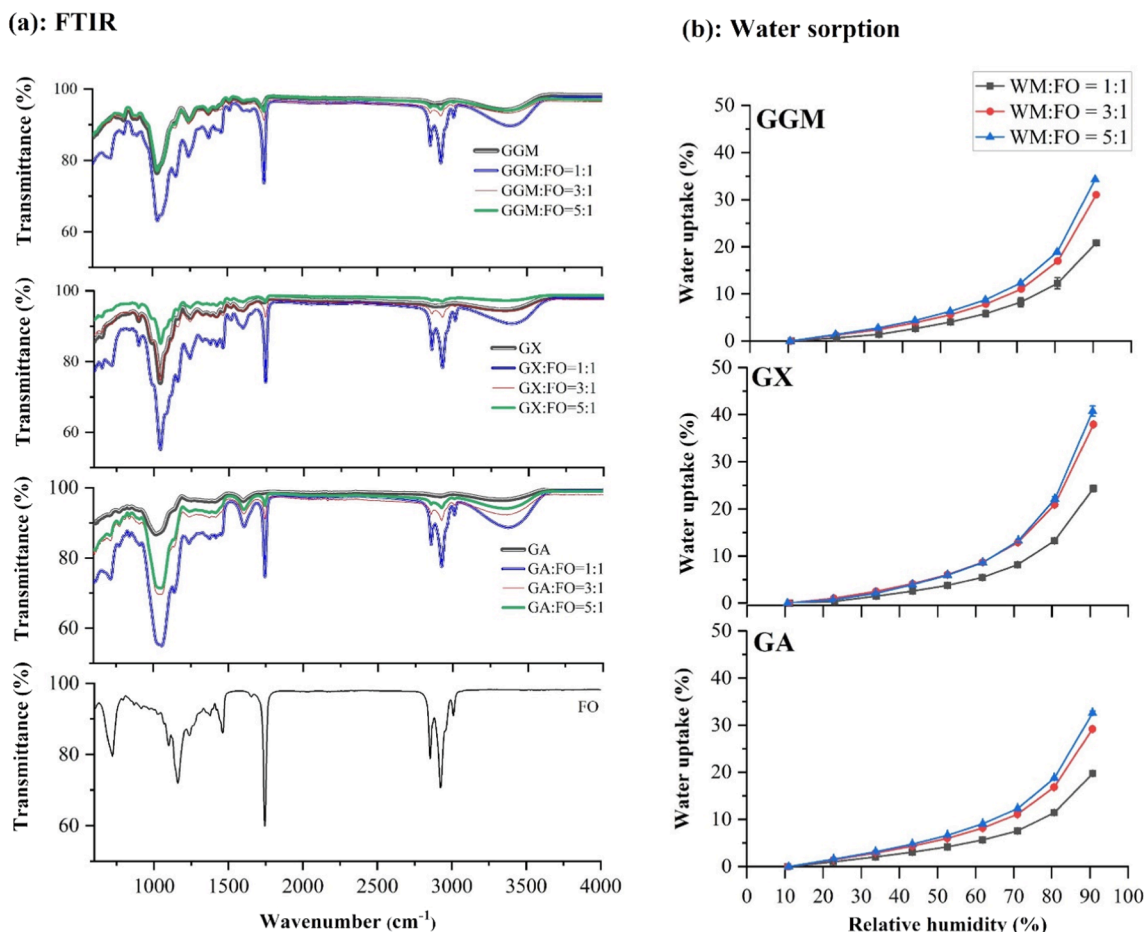


Fig. 4. (a): Fourier-transform infrared spectroscopy (FTIR) spectra; and (b): water sorption capacity of microcapsule powders prepared from spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) with flaxseed oil (FO) at various wall material (WM) contents (WM:FO = 1:1, 3:1, and 5:1). In Fig. 4(a), FTIR spectra of GGM, GX, GA and FO were also reported. Refer to Table 1 for the formulations of samples.

spectra of pure FO exhibit the characteristics of C–H stretch ($\sim 2900\text{ cm}^{-1}$), C–O stretch ($\sim 1700\text{ cm}^{-1}$) and C–O stretch ($\sim 1100\text{ cm}^{-1}$) of triacylglycerols (Elzey et al., 2016). For GA, its FTIR spectra are characterized by O–H stretch ($\sim 3278\text{ cm}^{-1}$), C–H stretch from carboxylic group ($\sim 2900\text{ cm}^{-1}$), C=O stretch or N–H bend ($\sim 1600\text{ cm}^{-1}$), CH₃ and C–H bend ($\sim 1410\text{ cm}^{-1}$), and C–O stretch ($\sim 1020\text{ cm}^{-1}$) (Karrar et al., 2021). The FTIR spectra of GGM and GX were quite similar as both of them display O–H stretch ($\sim 3278\text{ cm}^{-1}$), CH₂– and CH₃– stretch ($\sim 2930\text{--}2868\text{ cm}^{-1}$), a peak at $\sim 1725\text{ cm}^{-1}$ representing for acetyl groups, a peak at $\sim 1510\text{ cm}^{-1}$ due to lignin bonded to hemicelluloses, peaks at $\sim 1300\text{--}1000\text{ cm}^{-1}$ caused by C–O stretching from the carbohydrates (C–O–C) and the hydroxyl groups (C–O–H) (Carvalho et al., 2019; Hårdelin et al., 2020).

As FO was added to the microcapsule powders, their FTIR spectra changed as compared with those of GGM, GX and GA. Two new peaks specified for FO (~ 2900 and 1700 cm^{-1}) were clearly identified on the FTIR spectra of all microcapsule powders, and their intensity increased with increasing amounts of FO. It was reported that for spray-dried microcapsule powders of FO with mixtures of rice protein concentrate and modified starch Capsul®, increasing peak intensity at $2974\text{--}2852\text{ cm}^{-1}$ corresponds to the axial deformation of –CH bond attributed to the long carbon-hydrogen chains of fatty acids of FO (Perrechil et al., 2021). In addition, two peaks at ~ 1465 and 1100 cm^{-1} of FO disappeared on the FTIR spectra of microcapsule powders. The results indicate possible interactions between functional groups of FO and WMs, which requires further investigation to identify specific interactions. Differences on the FTIR spectra of GGM, GX and GA microcapsule powders were seen in peaks in the region of $1500\text{--}1000\text{ cm}^{-1}$, which are caused by the

different chemical structure of GGM, GX and GA.

3.3.7. Water sorption

For amorphous dried powders, water sorption during storage is the major factor responsible for T_g depression and then crystallization which induces changes in the structure, property and functionality of the powders. Water uptake capacity of all microcapsule powders at different relative humidities is illustrated in Fig. 4(b), which are typical water sorption isotherms of high sugar containing materials (Caballero-Cerón et al., 2015). The water uptake capacity increased very slowly with increasing relative humidities up to 60 %, beyond which there was a sharp rise in the water uptake capacity of all samples, and water had a predominant impact on powder stability. At the same WM:FO ratio, the highest water sorption ability was observed for GX microcapsule powders, followed by GGM ones which were just slightly higher than GA counterparts. The results indicate that GGM is better than GX in the protection of microcapsule powder against water adsorption during storage. For all WMs, increasing solid concentration, especially from WM:FO = 1:1 to 3:1 markedly increased the water sorption capacity of their microcapsule powders, indicating that the water uptake was clearly dominated by the WM. Low water uptake at WO:FO = 1:1 also results from high surface oil preventing interactions of microcapsule powders with water molecules. Differences in the water uptake among WMs could be due to differences in the amounts of hydrophilic groups (which easily bind to water molecules) in their structure.

3.4. Oxidative status of microcapsule powders

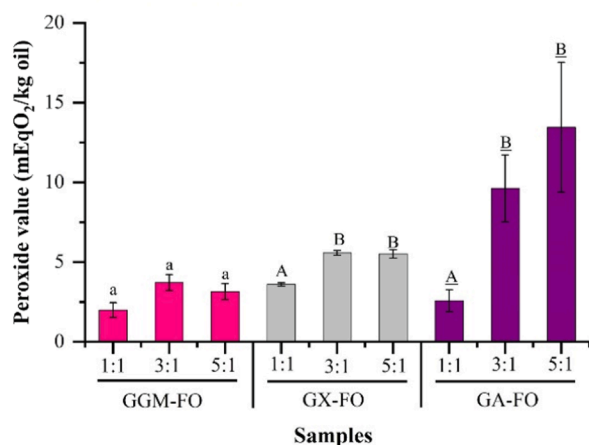
Oxidation of oils leads to the formation of various off-flavors and also reduces nutritional value and food safety. Once the oxidation is initiated in oils for example by heat or light, the reactions proceed spontaneously. At the initial stages of heat induced autoxidation, radicals form and they either react with oxygen, which is primarily seen as the formation of hydroperoxides, or undergo addition or recombination reactions, both of which are observed as the formation of diverse group of nonvolatile products. Oxidation products may decompose further forming also volatile products.

Peroxide value is an indicator of hydroperoxides (i.e., primary products of oxidation). In general, peroxide value of good quality oil should remain below 5 mEqO₂/kg and after reaching a value above 10 mEqO₂/kg, the oil is considered rancid (Codex Alimentarius, 2001). In the current study, peroxide values of FO in GGM and GX microcapsules remained below 10 mEqO₂/kg (Fig. 5a) while in two of the GA microcapsules (WM:FO ratio of 3:1 and 5:1, w/w) PV exceeded this limit. Similar results for FO microcapsules having PV below 10 mEqO₂/kg have been widely reported with several types of WM: GA and/or maltodextrin: 0.11–0.66 mEqO₂/kg oil (Akram et al., 2021); whey proteins isolate, maltodextrin and/or GA: ~0.79 mEqO₂/kg oil (Karrar et al., 2021); and mixture of maltodextrin with either GA, whey

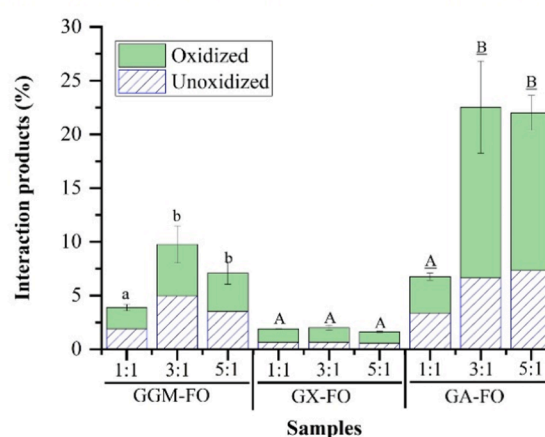
protein concentrate, Hi-Cap 100TM, or Capsul TA®: 6.12–8.77 mEqO₂/kg oil (Carneiro et al., 2013).

When oxidation proceeds, hydroperoxides react further forming more stable nonvolatile oxidation products, namely hydroxides, epoxides and ketones, a range of volatile products, and larger size interaction products. Our results show that in addition to hydroperoxides, FO in GGM and GA microcapsules contained other nonvolatile oxidation products (Fig. 5b) and larger size interaction products (Fig. 5c). Based on their contents, FO in GA microcapsules indeed oxidized at great extent during spray drying. Also, unlike peroxide values indicated, FO in GGM microcapsules oxidized at a high rate. This is due to hydroperoxides not being detected as they decomposed at a high rate forming further products. Up to 19–22 % of the triacylglycerols (TAGs) in GA and GGM microcapsules oxidized during spray drying. In GX microcapsules, the content of these products remained below 5 %. A significant difference was obtained in the formation of interaction products between the studied powders. While the number of these products remained below 2 % for GX and below 10 % for GGM, interaction products formed to high extent in GA microcapsules: Up to 23 % lipids had formed these high molecular weight products (Fig. 5c). Majority of the interaction products were oxidized. Interactions occurred most likely after oxidation as a relatively high number of oxidized monomers (i.e., oxidized TAGs) were detected.

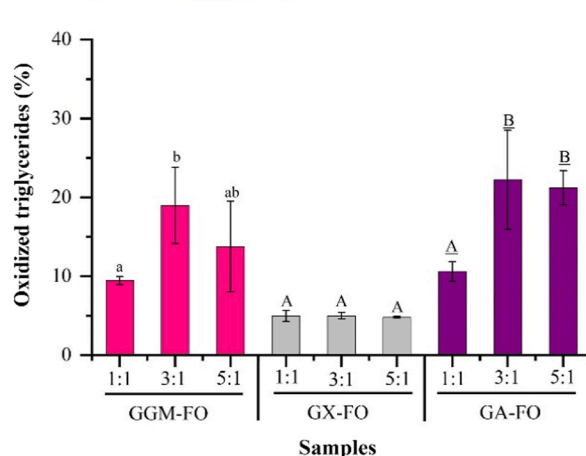
(a): Peroxide values



(c): High molecular weight interaction products



(b): Oxidized triglycerides



(d): Volatile products

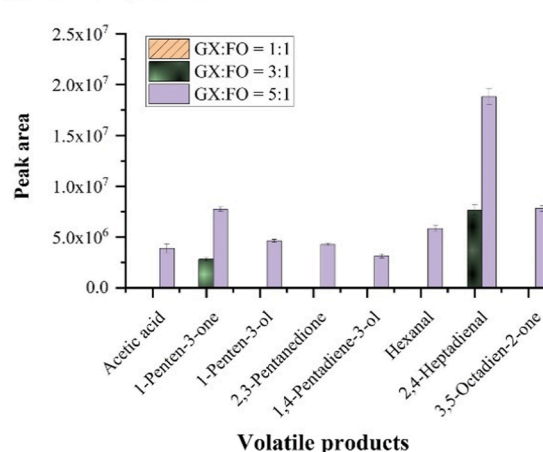


Fig. 5. Oil oxidation due to spray drying of microcapsule powders prepared from spruce galactoglucomannans (GGM), birch glucuronoxylans (GX) and gum Arabic (GA) with flaxseed oil (FO) at 1:1, 3:1 and 5:1 ratios, including (a): peroxide value, (b): proportion of oxidized triglycerides, (c): proportion of higher molecular weight interaction products, and (d): volatile oil oxidation products in GX microcapsule powders. Missing values in (d) were not observed from the graph or were not detected (=0), and due to missing values, statistical analyses were not performed. Within the same group of wall materials (GGM, GX or GA), means with different letters indicate significant differences among wall material contents ($p < 0.05$). Refer to Table 1 for the formulations of samples.

Obtained results indeed show that FO in the presence of GA was least stable and was oxidizing to a great extent: Up to 45 % of the TAGs were degraded via oxidation reactions during spray drying. This in turn causes a significant reduction in the nutritional value. At the same time, 21–29 % of oils in the presence of GGM and only 6–7 % in the presence of GX were degraded. GGM and GX have been shown to provide protection against oxidation in emulsions due to the co-extracted phenolic residues while GA lacks this property (Lehtonen et al., 2016; Lehtonen et al., 2018; Lahtinen et al., 2019). Phenolic content of GX was 70 mg GAE/g, being much higher than that of GGM (48 mg GAE/g) (Mikkonen et al., 2019).

It was evident that the oxidation of FO occurred via other pathways in GX microencapsules: Hydroperoxides decomposed into volatile products (Fig. 5d) while formation of other products remained at low levels. Detected volatile products give clear indication of oxidation of omega-3 fatty acids, namely alfa-linolenic acid: 1-penten-3-one, 1-penten-3-ol and 3,5-octadien-2-one and further as the formation of 2,3-pentadienone and 1,4-pentadiene-3-ol. Additionally, 2,4-heptadienal indicated the oxidation of linolenic acid and hexanal indicated the oxidation of omega-6 fatty acids, namely linoleic acid. However, no indication of 18:1 oxidation was observed. The content of volatile products was dependent on the surface area: The greater the area, the greater the number of volatile compounds. Interestingly, no volatile oxidation products were detected in GGM and GA microencapsules.

Glucuronic acid branches in GX provide negatively charged sites to the molecule. Positively charged transition metals, such as iron and copper, which are often present at trace levels, are likely attracted by these sites and this way transferred to the droplet surface where they may catalyze oxidation reactions in the formulation but also during spray drying and storage. In emulsions, transition metals are generally considered the most probable cause for induced oxidation (Waraho et al., 2011; Schaich, 2021). Additionally, they alter the pathways of oxidation. This is often seen as increased formation of volatile oxidation products rather than other products as observed in this study. Additionally, the greater the surface area and thus higher the number of negatively charged sites are the greater the number of volatile products (Fig. 5d).

For all microcapsule powders, increasing solid ratios of WM led to increased FO oxidation, which may be consequence of reduced particle size and thus increased surface area (Table 2). This provides more contact area firstly between oil and WM and secondly between oil and the continuous phase (i.e., water or air in the spray drying) and thus increases the probability of oxidation reactions.

Oxidation of oils in microencapsulated powders occur not only during spray drying but it may also take place during feed solution preparation. At this stage, not only the quality of the oil, but also the droplet surface materials, namely emulsifiers and stabilizers, and composition of the continuous phase (pH, salts, antioxidants and transition metal residues, just to mention a few) affect the possible initiation and progress of oxidation (Waraho et al., 2011). Additionally, air may be incorporated in the feed solutions during the homogenization step. We observed visually in the current study that the foam volume increased along with the increased solid ratio. Excess air present in the formulation provides asupply of oxygen for the oxidation reactions. For example, Drusch et al. (2007) did not detect hydroperoxides in fish oil itself, but in its feed emulsions with GA (6.1 mmol/kg oil), *n*-OSA starch and GA (2.2 mmol/kg oil), sugar beet pectin (<0.5 mmol/kg oil), and sodium caseinate (<0.5 mmol/kg oil). For GGM, corn fiber gum and GA stabilized rapeseed oil emulsions (having less PUFAs than fish oil) emulsion preparation did not induce oxidation (Lehtonen et al., 2016).

Overall, the aforementioned results demonstrate that spray-dried microencapsulation of polyunsaturated fatty acid-rich oils using GGM and GX as WMs is an effective approach to produce oil powders with high oil load, thermal stability, and oxidative stability. GGM-/GX-based microencapsulated oil powders enable a new way for the production of functional foods, by which the oil powders can be used as a fortification

to enhance the nutritional value, fatty acids intakes, mouth feel, and textural properties. Additionally, GGM and GX provide dietary fibers and prebiotics (Kynkäänniemi et al., 2022) to the oil powders, and consequently the food products fortified with the oil powders. Although a_w and moisture content of GGM-/GX-based microencapsulated oil powders are low enough to act against the microbial attacks, they need to be kept in airtight and moisture-barrier packages for long term storage due to their high water vapor uptake and amorphous structure.

4. Conclusion

This study has demonstrated that wood hemicelluloses recovered by PHWE method from spruce (GGM) and birch (GX) are excellent WMs for spray-dried microencapsulation of polyunsaturated fatty acids. Both GGM and GX exhibited higher encapsulation efficiency and better ability to protect oil against oxidation during spray drying than the well-known and highly effective WM – GA. However, it is noticed that the ability to encapsulate and protect oil during spray drying of WMs is highly dependent on the size of the droplet oils in feed emulsions and particles of encapsulated powders, which was 0.1–1.3 μm and 6.2–19.1 μm , respectively (D[3,2] values) in our study. High encapsulation efficiency and effective protection against oxidation of GGM and GX are achieved by high physical stability, low viscosity and small droplet size of their feed emulsions; and the presence of lignin in their composition. Due to an amorphous structure, low T_g and high water uptake capacity of microcapsule powders, their stability during storage at various conditions of relative humidities and *in vitro* digestibility needs further investigation. Moreover, optimization of the spray-dried microencapsulation process regarding the solid concentrations of feed emulsions and inlet/outlet drying air temperatures is also required to improve the encapsulation efficiency of wood hemicelluloses and their encapsulated powder stability. This study explores an innovative way to utilize wood hemicelluloses, which are abundant in forest industry but remain largely unexploited, therefore boosting hemicellulose biorefining activities of many pulp and paper industries. The underutilized wood hemicelluloses have been potentially upgraded to superior alternatives for WMs in the production of microcapsules of many other bioactive compounds for natural, healthy and functional ingredients which are in high demand in food, pharmaceutical, cosmetics and personal care products.

CRediT authorship contribution statement

Thao Minh Ho: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Data curation, Writing – original draft, Writing – review & editing. **Mari Lehtonen:** Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Heikki Rääkkönen:** Methodology, Investigation, Writing – review & editing. **Petri O. Kilpeläinen:** Methodology, Investigation, Writing – review & editing. **Kirsi S. Mikkonen:** Conceptualization, Methodology, Supervision, Investigation, Data curation, Visualization, Project administration, Funding acquisition, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodres.2022.112333>.

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