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Physicochemical properties of hull-less barley fibre-rich fractions varying in particle size and their potential as functional ingredients in two-layer flat bread

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Abstract

The performance of barley fibre-rich fractions (FRF), as high dietary fibre ingredients, in two-layer flat bread was investigated. In addition, the effects of particle size reduction by pin milling on functional properties of FRF were studied. FRF enriched in non-starch polysaccharides (b-glucans and arabinoxylans) were obtained by roller milling of hull-less barley. Pin milling (PM) of FRF significantly reduced their particle size, slightly increased the solubility of b-glucans and arabinoxylans, and increased the viscosity of water slurries containing FRF. The addition of 20% of barley FRF to wheat flour significantly increased dough water absorption and weakened the dough properties, as indicated by farinograph mixing curves, but the FRF-enriched doughs exhibited good handling characteristics at the dividing and sheeting stages. The appearance, diameter, layer separation, crumb, and aroma of the FRF-enriched flat breads were comparable to that of the control. The PM of FRF did not significantly affect the dough handling or the quality characteristics of flat breads. The addition of 20% of barley FRF to wheat flour flat bread provided substantial health benefits by significantly increasing the total and soluble dietary fibre contents and by decreasing starch digestibility.

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Keywords: Arabinoxylans; Barley; β -Glucans; Dietary fibre; Flat bread; Functional foods

1. Introduction

Barley grain is an excellent source of both soluble and insoluble dietary fibre (DF), with clinically proven health benefits ([Newman & Newman, 1991](#page-9-0)). β -Glucans (BG), the major fibre constituents in barley, have been shown to lower plasma cholesterol, reduce glycemic index and reduce the risk of colon cancer ([Brennan & Cleary, 2005\)](#page-8-0). Their efficacy in reducing the risk of coronary heart diseases (CHD) has recently been recognized by the Food and Drug Administration (FDA), and whole grain barley and barley-containing products are now allowed to carry a claim that they reduce the risk of CHD in the United States [\(FDA, 2005](#page-8-0)). The nutritional values of other fibre components in barley, most notably arabinoxylans (AX), have not been investigated to the same extent as BG. However, recent studies revealed positive effects of water-soluble maize, wheat and rye AX on cecal fermentation, production of short-chain fatty acids and consequently on reduction of serum cholesterol and improved adsorption of calcium and magnesium ([Hopkins et al., 2003;](#page-8-0) [Lopez et al., 1999\)](#page-8-0). Also, psyllium AX have long been known for their efficiency in inducing laxative effects ([Mar](#page-9-0)[lett & Fischer, 2003\)](#page-9-0).

The nutritional value of food products containing barley depends on the level of supplementation as well as on the type of tissue or milling fraction of barley grain used.

Abbreviations: AX, arabinoxylans; BG, β -glucans; CHD, coronary heart diseases; DF, dietary fibre; FRF, fibre-rich fraction; HA, high amylose starch; N, normal amylose starch; PM, pin milled; WRC, water retention capacity; WX, waxy starch; FDA, Food and Drug Administration.

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The distribution of nutrients and functional constituents in the barley kernel is not uniform. Therefore, various tissues and/or fractions obtained via physical grain fractionation are enriched in different components ([Izydorczyk, Symons,](#page-8-0) [& Dexter, 2002](#page-8-0)). For example, the pearling by-products are potentially concentrated sources of bioactive components such as phytate, vitamin E (including tocotrienols), phenolic compounds, and insoluble DF. Barley fractions rich in BG have been obtained by various combinations of pear-ling, grinding, sieving and air classification [\(Andersson,](#page-8-0) [Andersson,](#page-8-0) [&](#page-8-0) Å[man, 2000; Andersson et al., 2003; Bhatty,](#page-8-0) [1992; Izydorczyk et al., 2003; Knuckles, Chiu, & Betshart,](#page-8-0) [1992; Kiryluk, Kawka, Gasiorowski, Chalcarz, & Aniola,](#page-8-0) [2000; Klamczynski & Czuchajowska, 1999; Knuckles &](#page-8-0) [Chiu, 1995; Lee, Scog, & Cho, 1997; Marconi, Graziano,](#page-8-0) 0 [&](#page-8-0) [Cubadda,](#page-8-0) [2000;](#page-8-0) [Sundberg](#page-8-0) & Å[man, 1994; Sundberg,](#page-8-0) [Tilly,](#page-8-0) [&](#page-8-0) Å[man, 1995; Vasanthan & Bhatty, 1995; Yoon,](#page-8-0) [Berglund, & Faustnaught, 1995](#page-8-0)).

The addition of DF preparations to foods is usually aimed at improving their nutritional characteristics [\(Bren](#page-8-0)[nan & Cleary, 2005; Izydorczyk et al., 2002\)](#page-8-0). However, DF preparations have both physiologically and technologically functional properties, and their addition will also alter processing and handling of foods as well as their texture, colour, flavour, and taste. The extent to which specific DF preparations exert their physiological and technological effects is dependent on the interrelated structural, chemical and physical properties of DF preparations. Furthermore, the functional properties of DF preparations can be considerably modified during the DF preparation as well as during the food processing ([Kunzek, Mueller, Vet](#page-9-0)[ter, & Godeck, 2002\)](#page-9-0).

Apart from chemical composition of DF preparations, the properties that are nutritionally relevant include the particle size and bulk volume, the surface characteristics, the hydration and rheological properties, and the adsorption or entrapment of minerals and organic molecules. The viscosity and entrapment capacity contribute to the metabolic effects (such as glucose and lipid metabolism), whereas particle size, bulking effects, and hydration are strongly involved in effects on colonic function ([Guillon](#page-8-0) [& Champ, 2000\)](#page-8-0). It is also prudent to predict that these physical properties of DF preparations will also affect the handling and quality of fibre-enriched food products. A prime example is high volume bread, whose properties are determined by multiple factors. Both BG and AX are known to influence bread quality. For example, it has been shown that addition of a small amount of purified high molecular weight water-soluble AX to wheat flour increases the viscosity of the dough aqueous phase and has a positive effect on dough structure and stability, as well as on loaf volume [\(Biliaderis, Izydorczyk, & Rattan,](#page-8-0) [1995\)](#page-8-0). However, higher than optimum amounts of added AX causes viscosity build up and lower bread loaf volumes. Water-unextractable and insoluble AX, on the other hand, are well known to suppress bread quality [\(Courtin & Del](#page-8-0)[cour, 2002](#page-8-0)). It has been shown that soluble BG may have a

negative effect on bread volume, although their effect will depend on the level of supplementation and quality of wheat flour [\(Brennan & Cleary, 2005; Jacobs, Izydorczyk,](#page-8-0) [Preston, & Dexter, in press\)](#page-8-0) as well as on the intrinsic properties of BG, such as their molecular weight ([Cleary,](#page-8-0) [Andersson, & Brennan, 2007](#page-8-0)). Particle size of DF-rich constituents would also be expected to impact bread volume, although the impact of wheat bran particle size on bread quality is contentious. [Pomeranz, Shogren, Finney, and](#page-9-0) [Bechtel \(1977\), Moder, Finney, Bruinsma, Ponte, and](#page-9-0) [Bolte \(1984\), and Lai, Hoseney, and Davis \(1989\)](#page-9-0) reported that coarse bran particles had adverse effects on bread quality, whereas Özboy and Köskel (1997) and De Kock, [Taylor, and Taylor \(1999\)](#page-9-0) found that coarse bran particles produced better baking results than finely ground bran.

Flat breads are better able to accommodate high DF ingredients than pan or hearth bread without loss of quality because of more modest flour quality requirements [\(Qarooni, Ponte, & Posner, 1992](#page-9-0)). Barley has been successfully incorporated into single layer flat breads including chapatis [\(Sidhu, Harinder, Kaur, & Ram, 1990\)](#page-9-0) and Turk-ish bazlama bread [\(Ba](#page-8-0)şman & Köksel, 1999). Two-layer flat bread is widespread in Middle Eastern and North African countries ([Paulley, Williams, & Preston, 1998](#page-9-0)), and is becoming increasingly popular in western countries [\(Houraney & Daneshmayeh, 2000; Taylor, Brester, &](#page-8-0) [Boland, 2005\)](#page-8-0). Two-layer flat bread is commonly produced from high extraction flour, making it likely to find widespread acceptance as a high DF food.

[Izydorczyk et al. \(2003\)](#page-8-0) reported a simplified roller milling procedure that gives a high yield of a fibre-rich fraction (FRF) from hull-less barley. FRF has been successfully incorporated into pasta ([Dexter, Izydorczyk, Marchylo,](#page-8-0) [& Schlichting, 2005\)](#page-8-0) and Asian noodles [\(Izydorczyk, Lag](#page-8-0)assé, Hatcher, Dexter, & Rossnagel, 2005). Incorporation of FRF into pan bread to produce a satisfactory product is more challenging [\(Jacobs et al., in press\)](#page-9-0), particularly for straight-dough processes. In this study, we investigated incorporating FRF as a high DF ingredient in two-layer flat bread. Additionally, the effects of particle size reduction of FRF by pin milling on FRF functional properties were studied.

2. Experimental

2.1. Materials

Three hull-less barley genotypes (grown in 2003) with variable starch characteristics were used in this study. Dr. Brian Rossnagel, Crop Development Centre, University of Saskatchewan, supplied the high amylose starch (HA) line, SB94893. The waxy starch (W) genotype, CDC Alamo, was supplied by Agricore United, and the normal amylose starch (N) genotype, CDC McGwire, by Secan. The contents of β -glucans in N, W, and HA whole grain samples were $4.28 \pm 0.05\%, 7.86 \pm 0.30\%, \text{and } 8.54 \pm 0.50\%, \text{respectively},$ whereas the contents of arabinoxylans were $4.10 \pm 0.10\%$,

 $3.80 \pm 0.20\%$, and $4.30 \pm 0.30\%$, respectively. The N, W, and HA whole grain samples contained $61.2 \pm 0.5\%$, $56.8 \pm 0.5\%$, and $53.8 \pm 0.6\%$ of starch and 13.0, 13.7, and 14.5 proteins, respectively.

2.2. Milling

Milling of whole barley grain (tempered to 16% m.c.) took place in a climate-controlled room (21 $^{\circ}$ C and 60% RH) with a five-stand mill equipped with 25 cm diameter rolls according to the short milling flow described by [Izy](#page-8-0)[dorczyk et al. \(2003\)](#page-8-0). The milling procedure involved four break passages without intermediate sifting. Following the last break passage, the ground material was sieved, and the coarse and fine fractions were passed through a shorts duster. The coarse material ($>183 \mu m$) was given a sizing passage and again was passed through a shorts duster and sieved. This milling procedure allowed efficient separation of barley into flour and a fibre-rich fraction (FRF). A portion of the FRF was pin milled (Model 160Z, Alpine Corp., Augsburg, Germany) at a feed rate of 81 g/min. The pin mill was operated at 3090 RPM. A single pass was used for all three genotypes.

Commercially grown No. 1 Canada Western Red Spring wheat was milled on the GRL pilot mill described by [Black](#page-8-0) [\(1980\)](#page-8-0) by the mill flow of [Symons and Dexter \(1991\)](#page-9-0) to produce a straight grade flour of approximately 75% extraction, which served as the base wheat flour in the flatbreads. A reconstituted whole-wheat flour typically produced by Canadian mills (95% extraction equivalent) was prepared by adding 20% hammer-milled bran (throughs of $18W$ sieve [980 μ m] and overs of 183 nitex sieve [183 μ m]) to the 75% extraction rate flour ([Ambalamaatil](#page-8-0) [et al., 2002](#page-8-0)). The protein content (14% mb) of the whole wheat flour was 14.6% , and ash content $(14\% \text{ mb})$ was 1.40%.

For flat bread preparation, a blend of 80% straight grade wheat flour and 20% whole wheat flour was used as the control. When FRF was incorporated, straight grade wheat flour content was reduced to 60%, whole wheat flour content was kept at 20%, and FRF was incorporated at 20%.

2.3. Characterization of FRF and wheat flour

All FRF and wheat flour characterization tests were carried out in duplicate unless stated otherwise. Moisture content was determined after heating a 10 g sample at 130 $^{\circ}$ C for 1 h in a semi-automatic moisture oven (CW Brabender, South Hackensack, NJ). Total starch, starch damage and BG contents were determined enzymatically using Megazyme kits (Megazyme International, Bray, Ireland), according to [AACC \(2000\)](#page-8-0) Approved Methods 76–13, 76–31, and 32–23, respectively. Total (AX) content was determined colourimetrically by the phloroglucinol reaction method of [Douglas \(1981\)](#page-8-0). BG and AX were made soluble by shaking a suspension of 0.5 g FRF in 25 ml sodium phosphate buffer (20 mM, pH 6.5) for 2 h at 45 °C. Total free phenolics were determined colourimetrically using a method adapted from [Beta, Nam, Dexter,](#page-8-0) [and Sapirstein \(2005\)](#page-8-0).

The development of viscosity of barley FRF slurries $(4.0 \text{ g suspended in } 25 \text{ ml of } 0.1\% \text{ AgNO}_3)$ was determined with a Rapid-Visco Analyzer (RVA, Newport Scientific, Warriewood, Australia). The FRF slurries were heated from 25 °C to 45 °C over a 2 min period, and the viscosity development was monitored for 30 min at a stirring speed of 160 rpm (initial mixing, 0–30 s, 960 rpm). FRF colour was evaluated using a spectrocolourimeter (Labscan XE, HunterLab, Reston, VA, USA) equipped with a D65 illuminant using the CIE 1976 L^* , a^* , and b^* colour scale. The average of three measurements is reported. Water swelling of the FRF was determined with deionised water at 20 °C following the method of Robertson et al. (2000) with some modifications. Deionised water (10 ml) was added to FRF (150 mg) and the slurry was initially stirred and then equilibrated for 18 h at 20 \degree C. Afterwards, the bed volume was recorded and expressed as volume/g original substrate dry weight.

Flat breads were subjected to in vitro digestion by mixing a 2 g sample of ground bread with enzyme solution (166U porcine pancreatic a-amylase, Sigma Chemical, in 25 ml of 20 mM sodium phosphate buffer, pH 6.9). The mixtures were incubated at 37° C for 15 and 60 min. After centrifugation (4000g, 10 min), the amount of solubilized carbohydrates was determined by further digestion with thermostable a-amylase (Bacillus licheniformis, Ankom Tech. Corp., Fairport, NY, USA) and amyloglucosidase (Aspergillus niger, Boehringer Mannheim, Laval, Quebec, Canada). The resulting glucose contents in the supernatant were measured with a GOPOD reagent according to the method of [McCleary, Solah, and Gibson \(1994\).](#page-9-0) The results indicate the amount of solubilized carbohydrates expressed as gram of solubilized starch per gram of starch available in the sample.

A sonic sieve shaking method was used for dry particle size determination. The pre-weighed sample (10 g) was placed on the top sieve of the set of sieves (500, 425, 325, 300, 212, 150, 105, 75, 53, and 37 lm openings) and shaken with a sieve shaker (Allen-Bradley Sonic Sifter, Fisher Scientific Ltd., Ottawa, Ontario, Canada). After 58 min of shaking the material on each sieve was weighed and recorded.

2.4. Flat bread preparation and quality analysis

Flat breads were prepared in triplicate according to the procedure developed by [Williams, Jaby El-Haramein, Nel](#page-9-0)[son, and Srivastava \(1988\)](#page-9-0) using equipment described by [Paulley et al. \(1998\).](#page-9-0) Standard ingredient levels (expressed as a percentage of flour weight) included salt (1.0%), sugar (1.0%) , fresh compressed yeast (1.5%) and water (optimum as assessed by dough feel at sheeting). The ingredients were mechanically mixed, fermented $(45 \text{ min}, 30 \degree \text{C})$, divided,

rested (10 min), manually pinned into circular sheets (20 cm), proofed (25 min, 30 °C), and baked (540 °C for 70 s) in an electrically heated Pavalier (Bourg Les Valence, France) travelling flat bread oven.

Flat bread quality was assessed using a scoring system developed by [Williams et al. \(1988\)](#page-9-0). Flat bread colour (L^*, a^*, b^*) was determined with a Chroma Meter (CR-200/CR-231, Minolta Canada, Mississauga, ON) by examining at least three different areas of each bread sample.

Texture measurements were performed using the TA-XT2i texture analyzer (Texture Technologies Corp., Scarsdale, NY). Once the flat breads were cooled to room temperature, three disks (30 mm in diameter) were cut out of the middle of the flat bread using a cylindrical scoring device. The texture analyzer was equipped with a 25 mm lapped perspex cylinder probe, and the flatbreads were tested for hardness and chewiness (40% strain) ([Bourne,](#page-8-0) [1978\)](#page-8-0).

2.5. Statistical analysis

All statistical analyses were executed using SAS statistical software (release 9.1.3; SAS Institute Inc., Cary, NC). Analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine differences in mean values based on data collected from replications of each measurement. Significance was established at $P \le 0.05$.

3. Results and discussion

3.1. Characterization of FRF

The barley FRF from roller milling, made of material retained on a 183 μ m screen, contained fragments of aleurone and endosperm cell walls [\(Izydorczyk et al., 2005\)](#page-8-0). On average, a two to 2.5-fold increase in BG and AX contents was obtained in the FRF after milling, compared to the content of these polymers in the whole barley grain (Table 1). FRF from the W and HA barley contained substantially higher amounts of BG than those from N barley (Table 1); this was consistent with differences in total BG contents in whole grains. Compared to whole barley, the FRF were enriched in proteins, but contained a lower amount of starch (Table 1); the content of starch, and proteins in FRF differed only slightly among the genotypes. FRF from waxy barley contained a lower amount of AX compared to that in FRF from normal and high amylose samples.

A portion of FRF was pin milled (PM) and further analyses were carried out to determine the effect of PM on the physicochemical characteristics of the FRF. [Fig. 1](#page-4-0) shows a plot of the cumulative size distribution of the particles before and after PM. The non-PM preparations contained about 10% of particles retained on the 300 µm sieve, 40% retained on the $212 \mu m$ sieve and another 30% on the 150 µm sieve. The size of the remaining particles $(\leq 20\%)$ ranged mainly between 150 and 105 μ m. The PM preparations contained very little material $(\leq 3\%)$ retained on the 300 µm sieve and only about 20% retained on the 212 µm sieve. The majority of material was distributed equally on the 150 and 105 μ m sieves (about 30% on each sieve). About 10% of the PM material had particles ranging from 75 to 105 μ m and another 10% particles ranging from 53 to 75 lm. Perpendicular lines have been drawn to indicate the sieve size at which 50% of the particles were held or passed through $(d_{0.5})$. When the $d_{0.5}$ values were examined little difference was observed in the particle size among the genotypes for the non-PM material, but there appears to be more variability for the PM preparations among the genotypes. HA-FRF-PM had 50% of its particles retained above 158 µm, followed closely by WX-FRF-PM at 152 μ m. On the other hand N-FRF-PM had 50% of its particles above $139 \mu m$ suggesting that PM created slightly smaller particles for this sample. It is important to point out that although the N-FRF-PM had a lower $d_{0.5}$ value, the HA-FRF-PM and W-FRF-PM contained approximately 6% more material below the 75 μ m sieve.

Table 1

Composition and physicochemical properties of barley FRF before and after pin millinga

Barley type/ FRF	Total β - glucans $(\%)$	Water-soluble β -glucans ^b (%)	Total arabinoxylans $(\%)$	Water-soluble arabinoxylans ^c $(\%)$	Proteins (%)	Starch $(\%)$	Starch damage $(\%)$	Free phenolics ^d $(\mu g/mg)$	Swelling capacity m1/g	L^*
Normal (N)										
N-FRF	8.93 ± 0.05	4.55(50.9)c	10.11 ± 0.04	1.41(13.9)b	19.1 ± 0.1	36.2 ± 0.3	1.62d	3.68a	9.09c	79.02e
N-FRF-PM		4.79(53.6)c		1.47(14.5)a			2.02c	3.77a	8.16d	80.59d
Waxy(W)										
W-FRF	13.84 ± 0.30	6.88(49.7)a	8.87 ± 0.003	0.87(9.8)e	20.0 ± 0.1	38.1 ± 0.2	2.58b	3.51 _b	10.95 _b	84.00c
W-FRF-PM		7.21(52.1)a		0.91(10.3)e			3.05a	3.70a	9.28c	84.95bc
High amylose (HA)										
HA-FRF	14.06 ± 1.10	6.25(44.5)b	9.98 ± 0.28	0.99(9.9)d	19.5 ± 0.1	36.4 ± 0.2	1.10f	2.17d	12.04a	85.46b
HA-FRF-PM		6.90(49.1)a		1.06(10.6)c			1.29e	2.36c	11.89a	86.83a

^a Means in columns followed by a different letter are significantly different ($P \le 0.05$) as determined by Duncan's multiple range test.

 b The values in brackets indicate solubility expressed as % of total β -glucans.</sup>

 c The values in brackets indicate solubility expressed as % of total arabinoxylans. d Expressed as ferulic acid.

Fig. 1. Sieve analysis for FRF and FRF-PM (pin milled) for normal (N), waxy (W) and high amylose (HA) barley.

The colour parameters for the FRF are listed in [Table 1.](#page-3-0) The FRF from N barley had lower L^* values then those from waxy and high amylose. For all genotypes, PM slightly increased the L^* values. It is important to realize that these colour shifts due to PM are due to the particle size shift observed for dry powders ([Symons & Dexter,](#page-9-0) [1991](#page-9-0)), and are not indicative of a compositional difference.

In general, the starch damage in FRF was very low and it was only slightly increased by PM ([Table 1\)](#page-3-0). The W-FRF-PM and HA-FRF-PM samples showed a slight increase in the amount of phenolic compounds extractable with alcohol, compared to their non-PM counterparts. The lowest amount of free phenolics was observed in the FRF of HA whereas similar contents were observed for N and W. The FRF from HA and W barley contained significantly higher amount of water-soluble BG than those from N barley. The solubility of BG after PM increased by 2.7%, 2.4%, and 4.6% for N-, W-, and HA-FRF, respectively; only the HA-FRF-PM exhibited a statistically significant increase of water-soluble BG compared to their non-PM counterparts. In general the solubility of AX in FRF was much lower than that of BG. The highest amount of water-soluble AX was detected in FRF from N barley and the lowest in FRF from W barley. The PM slightly increased the solubility of AX in N- and HA-FRF. The increased solubility of DF constituents is normally quite desirable since it is postulated that solubility and viscous properties of non-starch polysaccharides in aqueous media are responsible for reduction of plasma cholesterol and postprandial serum glucose levels in humans and animals ([Jenkins et al., 1995; Newman & Newman, 1991; Yokoy](#page-9-0)[ama et al., 1997\)](#page-9-0). The insolubility of BG and AX in grain has been attributed to both covalent and non-covalent interactions among grain constituents, as well as to their physical entrapment in the cell wall matrix [\(Carpita](#page-8-0) [& Gibeaut, 1993\)](#page-8-0). The particle size reduction of DF preparations can, therefore, be expected to improve the solubility and extractability of DF components by exposing new surfaces and enabling better interactions of the fibre constituents with the solvent. It appears, however, that particle size reduction obtained in this study only slightly increased the solubility of BG and AX. [Izydorc](#page-8-0)[zyk, Storsley, Labossiere, MacGregor, and Rossnagel](#page-8-0) [\(2000\)](#page-8-0) explored the effects of various hydrothermal and physical treatments on solubility and viscosity of BG, and reported that only the presence of hydrolytic enzymes (proteases or esterases) significantly improved the extractability of BG from ground barley.

The swelling capacities of FRF in water at room temperature are listed in [Table 1](#page-3-0). The HA-FRF showed the highest swelling capacities among the three genotypes. The swelling capacity of N- and W-FRF decreased slightly after PM. Swelling is a function of the chemical composition and the physical structure of the fibre matrix ([Auffret, Ralet,](#page-8-0) [Guillon, Barry, & Thibault, 1994](#page-8-0)). When measuring the effect of size reduction on the swelling capacity of fibre from various sources, [Auffret et al. \(1994\)](#page-8-0) also found a decrease in swelling with a decrease in particle size. While the surface area per weight of smaller particles is usually higher than that of larger particles, the reduction of particle size of DF preparations often changes the physical structure of fibre and reduces the spaces available for free water by collapsing the matrix structure [\(Auffret et al., 1994](#page-8-0)). As a result, the porosity of the fibre matrix is reduced and the ground fibre preparations are unable to imbibe as much water as rough fibre.

The development of viscosity of barley FRF slurries during a 30 min period of mixing at a constant shear rate and 45° C is shown in Fig. 2. Large differences in the attainable viscosity were observed among FRF from different barley cultivars. The FRF preparations from W and HA barley exhibited a relatively fast evolution of viscosity during the initial 10 min period. Thereafter, the HA-FRF exhibited further development of viscosity but at a much slower rate, whereas the viscosity of the W-FRF remained unchanged. In contrast, the N-FRF exhibited much lower

Fig. 2. RVA viscosity profiles for FRF and FRF-PM (pin milled) for normal (N) , waxy (W) and high amylose (HA) barley in 0.1% silver nitrate.

viscosity values. The differences between viscosity profiles obtained for N-FRF versus those for W-FRF and of HA-FRF can be ascribed most likely to significant differences in the total and soluble BG contents ([Table 1](#page-3-0)). In addition to concentration, the molecular weight of BG is known to significantly affect the viscosity of solutions containing these polymers ([Lazaridou, Biladeris, & Izydorc](#page-9-0)[zyk, 2003](#page-9-0)). [Knuckles, Yokoyama, and Chiu \(1997\) and](#page-9-0) [Storsley, Izydorczyk, You, Biliaderis, and Rossnagel](#page-9-0) [\(2003\)](#page-9-0) showed that significant differences in the molecular weight may exist among BG extracted from different barley varieties; these differences could reflect genetic variability as well as environmental and storage effects. Although a very low activity of b-glucanase, an enzyme responsible for depolymerization of BG chains, is expected in barley before germination, [Izydorczyk et al. \(2000\)](#page-8-0) showed substantial differences in the activity of this enzyme in various barley cultivars. If whole barley or barley fractions are to be incorporated into food systems to take advantage of the biological activity of BG associated with their viscosity building properties, the β -glucanase activity has to be controlled (e.g., by heat treatment).

Some increases in the attainable viscosity were observed after PM ([Fig. 2\)](#page-4-0). These viscosity increases corresponded with the increases of water-soluble BG in FRF after PM, i.e., the greatest for HA and the smallest for N barley [\(Table 1\)](#page-3-0). The influence of size and distribution of particles on slurry rheology is also not negligible ([Tangsathitkulchai](#page-9-0) [& Austin, 1988\)](#page-9-0). However, the flow behaviour of colloidal suspensions can be complicated, because several parameters including particle size, size ratio, particle distribution, as well as the presence of any soluble dispersant have to be considered ([Tangsathitkulchai & Austin, 1988\)](#page-9-0). The slurries containing the barley FRF contain some soluble DF constituents in addition to insoluble particles.

3.2. Characterization of flour blends

The addition of 20% FRF to the control wheat flour had a dramatic effect on farinograph mixing curves ([Table 2\)](#page-6-0). Depending on the genotype, dough water absorption increased by 10–18% compared to the control flour. The porous structure and large surface area of the particles in the FRF ([Izydorczyk et al., 2005\)](#page-8-0), together with the hygroscopic nature of BG and AX increased the water requirements of the wheat flour-FRF blends. Blends containing W-FRF and HA-FRF had higher water absorption than N-FRF due to the higher contents BG in the former. In all cases the dough development time decreased slightly with enrichment by FRF. Tolerance to over mixing was also reduced by enrichment with FRF as indicated by shorter stabilities and higher tolerance indices. The largest decrease in dough strength, as indicated by the shortest stability and highest tolerance index, was observed for enrichment with N-FRF. For all genotypes, differences in farinograph properties between PM and non-PM material were slight.

3.3. Characterization of flat bread

The FRF-enriched doughs, despite the weakened properties as indicated by farinoraph mixing curves, exhibited good handling characteristics at the dividing and sheeting stages [\(Table 2](#page-6-0)). The actual baking water absorptions were lower than those indicated by the farinograph. During baking, layer separation of FRF-enriched breads was very good, and the breads did not show any tendency to burning. Characteristics of FRF-enriched flat breads such as appearance, diameter, layer separation, crumb, and aroma were comparable to that of the control [\(Table 2](#page-6-0)). Quality of FRF-enriched flat breads was not substantially influenced by PM.

The colour parameters for the flat breads are listed in [Table 3](#page-7-0). Some differences were observed in L^* (brightness) values between the PM and non-PM flat breads, but differences among genotype were not consistent. The W-FRF-PM-enriched flat bread was slightly brighter than its non-PM counterpart, whereas the opposite was observed for the N-FRF and HA-FRF enriched flat breads. All the FRF-enriched flat breads were significantly ($P \le 0.05$) darker than the control, except for HA-FRF, where no significant difference in the L^* value compared to the control was observed. The flat breads containing N-FRF had the lowest L^* values, consistent with the L^* values obtained for the FRF alone [\(Table](#page-3-0) [1\)](#page-3-0). Significant differences ($P \le 0.05$) were observed in a^* (redness) and b^* (yellowness) due to both barley genotype and PM. All of the FRF-enriched flat breads were less yellow than the control. The HA-FRF-enriched flat breads were less red than the control, and the least red of the genotypes. The effect of PM on a^* and b^* values was inconsistent.

Enrichment of the flat breads with FRF increased hardness and chewiness with HA-FRF exerting greater effects than N-FRF and W-FRF ([Table 3\)](#page-7-0). These differences may be due to the different starch amylose contents and associated differences in pasting properties and rate of starch retrogradation among FRF from various barley genotypes. No significant differences in the texture of the flat breads supplemented with non-PM FRF and PM FRF were observed.

The addition of 20% FRF significantly increased the amounts of total and soluble BG in the flat breads ([Table](#page-7-0) [4\)](#page-7-0). Compared to the control wheat flour flat bread, the content of total BG in barley FRF-enriched breads increased from eight to 13 times, whereas that of water-soluble BG increased from six to 16 times depending on the barley genotype. The flat breads supplemented with HA-FRF exhibited the highest contents of total and soluble BG among the barley FRF-enriched breads. The addition of FRF also significantly increased the content of total AX in the flat breads. The amount of water-soluble AX, on the other hand, changed little with the addition of barley FRF, indicating the insoluble nature of barley arabinoxylans.

^a Means in columns followed by a different letter are significantly different ($P \le 0.05$) as determined by Duncan's multiple range test.

^b Each quality parameter was given a score from 0 to 5. None of the means in each column were significantly different as determined by Duncan's multiple range test.
^c Division = step in flat bread processing where the

^d Sheeting $=$ step in flat bread processing where the dough is pinned into circular sheets followed by proofing and then baking.

^e Control wheat flour: 80% straight grade CWRS flour, 20% whole wheat flour.

 \overline{a} \overline{a} \overline{a}

Means in columns followed by a different letter are significantly different ($P \le 0.05$) as determined by Duncan's multiple range test.

Means in columns followed by a different letter are significantly different ($P \le 0.05$) as determined by Duncan's multiple range test.

 a β -Glucans and arabinoxylans were solubilized by stirring flat bread samples in water at 40 °C for 120 min.

 b Results expressed as gram of starch released upon digestion with α -amylase per gram of available starch in the flat bread samples.

According to the recent recommendation of the US [Food and Drug Administration \(2005\)](#page-8-0), barley-containing food must provide at least 0.75 g of soluble β -glucan fibre per serving of food to qualify for the health claim. Given the content of β -glucans in the FRF-enriched flat breads (Table 4), and making the assumption that a single flat bread equals one serving, it was calculated that the barley flat breads prepared in this study would easily qualify, providing between 1.84 and 2.97 g of soluble β glucan fibre, with the N-FRF enriched flatbread providing the least and HA-FRF enriched flat bread providing the most.

There is also compelling evidence that DF constituents can have an impact on food structure, carbohydrate availability, rate and extent of starch degradation, and hence the glycemic index (GI) of foods ([Brennan, 2005](#page-8-0)). Indeed, the results of the in vitro digestibility of starch showed that the inclusion of barley FRF into flat bread significantly decreased the solubilization and digestibility of starch at two different time intervals (Table 4). The PM-FRF exerted a slightly greater effect than the non-PM FRF in most cases. The reduction in starch digestibility of FRF-supplemented flat breads cannot be explained just on the basis of the barley FRF exerting a dilution factor on the starch content of pita breads. [Brennan and Samyue \(2004\)](#page-8-0) postulated that the digestion of starch and sugar release from foods might be delayed due to DF constituents adhering to starch granules and possibly increasing digesta viscosity. It appears that the *in vitro* starch digestibility experiments are in agreement with in vivo experiments on GI of foods. [Jenkins, Jenkins, Zdravkovic, Wursch, and Vuksam](#page-9-0) [\(2002\)](#page-9-0) showed that in a 50 g carbohydrate food portion (a prototype b-glucan-enriched breakfast cereal and bar), each gram of β -glucan could reduce the GI by 4 units, making it a useful functional food component for reducing postprandial glycemia. [Cavallero, Empilli, Brighenti, and](#page-8-0) [Stanca \(2002\)](#page-8-0) achieved similar GI reduction with β -glucan-enriched bread.

4. Conclusions

This study demonstrated the potential of using barley FRF to prepare flat breads. The addition of 20% of barley FRF to wheat flour flat bread not only provided substantial health benefits by significantly increasing the total and soluble dietary fibre content and by decreasing starch digestibility, but also produced an acceptable product. The presence of barley FRF in the blends with wheat flour significantly increased dough water absorption. The FRFenriched flat bread dough handled well, and the flat breads produced in a laboratory setting were equal to flat breads without FRF added.

This study also established that replacing 20% wheat flour with barley FRF produces a product that would meet the requirements of the newly released US Food and Drug Administration (2005) health claim for barley-containing products, while still possessing the necessary appeal and quality to a health-conscious consumer. FRF fractions are obtained via a chemical free, physical fractionation of barley grain, and are excellent functional food ingredients because, in addition to their high dietary fibre content, they also contain other phytochemicals (phenolics, tocols, vitamins and minerals) naturally present in the grain tissue. Pin milling of FRF obtained by roller milling of barley grain significantly reduced their particle size, slightly increased the solubility of β -glucans and arabinoxylans, and increased the viscosity of water slurries containing the FRF. These changes potentially improved the nutritional properties of FRF preparations. PM of FRF did not significantly affect the dough handling or the quality characteristics of the flat breads. It is possible, however, that at a higher level of supplementation and/or in a different food system, the size reduction and the consequent changes of the physicochemical properties of the barley FRF would exert more noticeable effects on the technological properties of food products. The supplementation of flat breads with barley FRF may also be beneficial to manufacturers from a cost perspective due to the higher yield of bread units per unit of flour on a fresh moisture basis, due to the higher water absorption of the FRF-wheat flour blends compared to wheat flour alone.

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References

- AACC (2000). Approved methods of the AACC (10th ed.). St. Paul, MN, USA: The Association.
- Ambalamaatil, S., Lukow, O. M., Hatcher, D. W., Dexter, J. E., Malcolmson, L. J., & Watts, B. M. (2002). Milling and quality evaluation of Canadian hard white spring wheats. Cereal Foods World, 47, 319–327. 0
- Andersson, A. A. M., Andersson, R., & Åman, P. (2000). Air classification of barley flours. Cereal Chemistry, 77, 463–467.
- Andersson, A. A. M_t, Armö, E., Grangeon, E., Fredriksson, H., Andersson, R., & Åman, P. (2003). Milling performance of North European hull-less barleys and characterization of resultant millstreams. Cereal Chemistry, 80, 667–673.
- Auffret, A., Ralet, M.-C., Guillon, F., Barry, J.-L., & Thibault, J.-F. (1994). Effect of grinding and experimental conditions on the measurement of hydration properties of dietary fibres. Lebensmittel-Wissenschaft und Technology, 27, 166–172.
- Başman, A., & Köksel, H. (1999). Properties and composition of Turkish flat bread (bazlama) supplemented with barley flour and wheat bran. Cereal Chemistry, 76, 506–511.
- Beta, T., Nam, S., Dexter, J. E., & Sapirstein, H. D. (2005). Phenolic content and antioxidant activity of pearled wheat and roller-milled fractions. Cereal Chemistry, 82, 390–393.
- Bhatty, R. S. (1992). β -Glucan content and viscosities of barleys and their roller milled flour and bran products. Cereal Chemistry, 69, 469–471.
- Biliaderis, C. G., Izydorczyk, M. S., & Rattan, O. (1995). Effect of arabinoxylans on bread-making quality of wheat flours. Food Chemistry, 33, 165–171.
- Black, H. C. (1980). The GRL pilot mill. Association of Operative Millers Bulletin, pp. 3834–3837.
- Bourne, M. C. (1978). Texture profile analysis. Food Technology, 32, 62–66.
- Brennan, C. S. (2005). Dietary fibre, glycemic response, and diabetes. Molecular Nutrition and Food Research, 49, 560–570.
- Brennan, C. S., & Cleary, L. J. (2005). The potential use of cereal ($1 \rightarrow 3$, $1 \rightarrow 4$)- β -D-glucans as functional food ingredients. *Journal of Cereal* Science, 42, 1–13.
- Brennan, C. S., & Samyue, E. (2004). Evaluation of starch degradation and textural characteristics of dietary fiber enriched biscuits. International Journal of Food Properties, 7, 647–657.
- Carpita, N. C., & Gibeaut, D. M. (1993). Structural models of primary cell walls in flowering plants: Consistency of molecular structure with physical properties of the walls during growth. The Plant Journal, 3, $1 - 30$
- Cavallero, A., Empilli, S., Brighenti, F., & Stanca, A. M. (2002). High (1- $3,1-4$) β -glucan barley fractions in bread making and their effects on human glycaemic response. Journal of Cereal Science, 36, 59-66.
- Cleary, L. J., Andersson, R., & Brennan, C. S. (2007). The behaviour and susceptibility to degradation of high and low molecular weight β glucan in wheat bread during baking and in vitro digestion. Food Chemistry, 102, 889–897.
- Courtin, C. M., & Delcour, J. A. (2002). Arabinoxylans and endoxylanases in wheat flour breadmaking. Journal of Cereal Science, 35, 225–243.
- De Kock, S., Taylor, J., & Taylor, J. R. N. (1999). Effect of heat treatment and particle size of different brans on loaf volume of brown bread. Lebensmittel-Wissenschaft und Technology, 32, 349–356.
- Dexter, J. E., Izydorczyk, M. S., Marchylo, B. A., & Schlichting, L. M. (2005). Texture and colour of pasta containing mill fractions from hullless barley genotypes with variable content of amylose and fibre. In S. P. Cauvain, S. E. Salmon, & L. S. Young (Eds.), Using cereal science and technology for the benefit of consumers. Proceedings of the 12th ICC cereal and bread congress (pp. 488–493). Cambridge: Woodhead Publishing Ltd.
- Douglas, S. G. (1981). A rapid method for the determination of pentosans in wheat flour. Food Chemistry, 7, 139–145.
- Food and Drug Adminstration (2005). FDA allows barley products to claim reduction in risk of coronary heart disease. FDA News, December 23, 2005. [<http://www.fda.gov/bbs/topics/news/2005/](http://www.fda.gov/bbs/topics/news/2005/NEW01287.html) [NEW01287.html>](http://www.fda.gov/bbs/topics/news/2005/NEW01287.html) Accessed November, 2006.
- Guillon, F., & Champ, M. (2000). Structural and physical properties of dietary fibres, and consequences of processing on human physiology. Food Research International, 33, 233–245.
- Hopkins, M. J., Englyst, H. N., Macfarlane, S., Furrie, E., Macfarlane, G. T., & McBain, A. J. (2003). Degradation of cross-linked arabinoxylans by the intestinal microbiota in children. Applied Environmental Microbiology, 69, 6354–6360.
- Houraney, F. W., & Daneshmayeh, S. M. (2000). Partially baked pocket pita bread and method of making same. US Patent 6,063,413.
- Izydorczyk, M. S., Dexter, J. E., Desjardins, R. G., Rossnagel, B. G., Lagassee, S. L., & Hatcher, D. W. (2003). Roller milling of Canadian hull-less barley: Optimization of roller milling conditions and composition of mill streams. Cereal Chemistry, 80, 637–644.
- Izydorczyk, M. S., Lagassé, S. L., Hatcher, D. W., Dexter, J. E., & Rossnagel, B. G. (2005). The enrichment of Asian noodles with a fibrerich fraction derived from roller milling of hull-less barley. Journal of the Science of Food and Agriculture, 85, 2094–2104.
- Izydorczyk, M. S., Storsley, J., Labossiere, D., MacGregor, A. W., & Rossnagel, B. G. (2000). Variation in total and soluble B-glucan content in hulless barley: Effects of thermal, physical and enzymic treatments. Journal of Agricultural and Food Chemistry, 48, 982–989.
- Izydorczyk, M., Symons, S. J., & Dexter, J. E. (2002). Fractionation of wheat and barley. In L. Marquart, J. L. Slavin, & R. G. Fulcher (Eds.),

Whole grain foods in health and disease (pp. 47–82). St. Paul, MN, USA: American Association of Cereal Chemists.

- Jacobs, M. S., Izydorczyk, M. S., Preston, K. R., & Dexter, J. E. (in press). Evaluation of baking procedures and wheat flours for incorporation of high dietary fibre barley fractions into bread. Journal of the Science of Food and Agriculture.
- Jenkins, A. L., Jenkins, D. J. A., Zdravkovic, U., Wursch, P., & Vuksam, V. (2002). Depression of the glycemic index by high levels of β -glucan fiber in two functional foods tested in type 2 diabetes. European Journal of Clinical Nutrition, 56, 622–628.
- Jenkins, D. J. A., Jenkins, A. L., Wolever, T. M. S., Vuksam, V., Venket Rao, A., Thompson, L. U., & Josse, R. G. (1995). Effect of reduced rate of carbohydrate absorption on carbohydrate and lipid metabolism. European Journal of Clinical Nutrition, 49, S68–S73.
- Kiryluk, J., Kawka, A., Gasiorowski, H., Chalcarz, A., & Aniola, J. (2000). Milling of barley to obtain b-glucan enriched products. Nahrung, 44, 238–241.
- Klamczynski, A. P., & Czuchajowska, Z. (1999). Quality of flours from waxy and nonwaxy barley for production of baked products. Cereal Chemistry, 76, 530–535.
- Knuckles, B. E., & Chiu, M. M. (1995). β -Glucan enrichment of barley fractions by air classification and sieving. Journal of Food Science, 60, 1070–1074.
- Knuckles, B. E., Chiu, M. M., & Betshart, A. A. (1992). β -Glucanenriched fractions from laboratory-scale dry milling and sieving of barley and oats. Cereal Chemistry, 69, 198–202.
- Knuckles, B. E., Yokoyama, W. H., & Chiu, M. M. (1997). Molecular characterization of barley β -glucans by size-exclusion chromatography with multiple-angle laser light scattering and other detectors. *Cereal* Chemistry, 74, 599–604.
- Kunzek, H., Mueller, S., Vetter, S., & Godeck, R. (2002). The significance of physicochemical properties of plant cell wall materials for the development of innovative food products. European Food Research and Technology, 204, 361–376.
- Lai, C. S., Hoseney, R. C., & Davis, A. B. (1989). Effects of wheat bran in breadmaking. Cereal Chemistry, 66, 217–219.
- Lazaridou, A., Biladeris, C. G., & Izydorczyk, M. S. (2003). Molecular size effects on rheological properties of oat β -glucans in solution and gels. Food Hydrocolloids, 17, 693–712.
- Lee, Y., Scog, H., & Cho, M. (1997). β -Glucan enrichment from pearled barley and milled barley fractions. Korean Journal of Food Science and Technology, 29, 888–894.
- Lopez, H. W., Levrat, M.-A., Guy, C., Messager, A., Demigne, C., & Remesy, C. (1999). Effects of soluble corn bran arabinoxylans on cecal digestion, lipid metabolism, and mineral balance (Ca, Mg) in rats. Journal of Nutritional Biochemistry, 10, 500–509.
- Marlett, J. A., & Fischer, M. H. (2003). The active fraction of psyllium seed husk. Proceedings of the Nutrition Society, 62, 207–209.
- Marconi, E., Graziano, M., & Cubadda, R. (2000). Composition and utilization of barley pearling by-products for making functional pastas rich in dietary fiber and β -glucans. Cereal Chemistry, 77, 133–139.
- McCleary, B. V., Solah, V., & Gibson, T. S. (1994). Quantitative measurement of total starch in cereal flours and products. Journal of Cereal Science, 20, 51–58.
- Moder, G. J., Finney, K. F., Bruinsma, B. L., Ponte, J. G., & Bolte, L. C. (1984). Bread making potential of straight-grade and whole-wheat

flours of Triumph and Eagle-Plainsman V hard red winter wheats. Cereal Chemistry, 61, 269–273.

- Newman, R. K., & Newman, C. W. (1991). Barley as a food grain. Cereal Foods World, 36, 800–805.
- Özboy, O., & Köskel, H. (1997). Unexpected strengthening effects of a coarse bran on dough rheological properties and baking quality. Journal of Cereal Science, 25, 77–82.
- Paulley, F. G., Williams, P. C., & Preston, K. R. (1998). Effects of ingredients and processing conditions on bread quality when baking Syrian two-layered flat bread from Canadian wheat in a travelling oven. Cereal Foods World, 43, 91–95.
- Pomeranz, Y., Shogren, M. D., Finney, K. F., & Bechtel, D. B. (1977). Fiber in bread making: Effects on functional properties. Cereal Chemistry, 54, 25–41.
- Qarooni, J., Ponte, J. G., & Posner, S. (1992). Flat breads of the world. Cereal Foods World, 37, 863–865.
- Robertson, J. A., de Monredon, F. D., Dysseler, P., Guillon, F., Amado`, R., & Thibault, J.-F. (2000). Hydration properties of dietary fibre and resistant starch: a European collaborative study. Lebensmittel-Wissenschaft und Technology, 33, 72–79.
- Sidhu, J. S., Harinder, K., Kaur, A., & Ram, M. B. (1990). Functional and chapati making properties of hull-less barley supplemented wheat flour. Journal of Food Science and Technology, 27, 311-313.
- Storsley, J. M., Izydorczyk, M. S., You, S., Biliaderis, C. G., & Rossnagel, B. (2003) . Structure and physicochemical properties of β -glucans and arabinoxylans isolated from hull-less barley. Food Hydrocolloids, 17, 831–844. 0
- Sundberg, B., & Åman, P. (1994). Fractionation of different types of barley by roller milling and sieving. Journal of Cereal Science, 19, 179–184. \overline{a}
- Sundberg, B., Tilly, A.-C., & Åman, P. (1995). Enrichment of mixedlinked $(1 \rightarrow 3, 1 \rightarrow 4)$ - β -D-glucans from a high-fibre barley-milling stream by air classification and stack sieving. Journal of Cereal Science, 21, 205–208.
- Symons, S. J., & Dexter, J. E. (1991). Computer analysis of fluorescence for the measurement of flour refinement as determined by flour ash content, flour grade colour and tristimulus color measurements. Cereal Chemistry, 68, 454–460.
- Tangsathitkulchai, C., & Austin, L. G. (1988). Rheology of concentrated slurries of particles of natural size distribution produced by grinding. Powder Technology, 56, 293–299.
- Taylor, M. R., Brester, G. W., & Boland, M. A. (2005). Hard white wheat and gold medal flour: General Mills' contracting program. Review of Agricultural Economics, 27, 117–129.
- Vasanthan, T., & Bhatty, R. S. (1995). Starch purification after pin milling and air classification of waxy, normal and high amylose barleys. Cereal Chemistry, 72, 379–384.
- Williams, P. C., Jaby El-Haramein, F., Nelson, W., & Srivastava, J. P. (1988). Evaluation of wheat quality for the baking of Syrian-type twolayered flat breads. Journal of Cereal Science, 7, 195–207.
- Yokoyama, W. H., Hudson, C. A., Knuckles, B. E., Chiu, M.-C. M., Sayre, R. N., Turnlund, J. R., & Schneeman, B. O. (1997). Effect of barley β -glucan in durum what pasta on human glycemic response. Cereal Chemistry, 74, 293–296.
- Yoon, S. H., Berglund, P. T., & Faustnaught, C. E. (1995). Evaluation of selected barley cultivars and their fractions for β -glucan enrichment and viscosity. Cereal Chemistry, 72, 187–190.