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Variability of brewer's spent grain within a brewery

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Abstract

Brewer's spent grain (BSG) is the residue left after separation of the wort during the brewing process. Composition of BSG may vary with barley variety, time of harvest, characteristics of hops and other adjuncts added, and brewery technology. This paper, demostrates the variability in composition (moisture, protein, fat, ash and total phenolics) of eight lots of spent grain supplied by a brewery. Fresh samples were oven-dried (60 °C, 18 h) to ensure preservation. The eight lots of BSG were found to be homogeneous in protein and fat contents, with slight variations in ash and total phenolics. In order to evaluate the possible effects of oven-drying, results from oven-dried samples were compared with those from freeze-dried and frozen samples. Oven drying of BSG gave rise small decreases in protein and fat contents in comparison with the wet (frozen) sample. Oven drying was similar to freeze-drying, a less-harsh preservation method. However, oven drying is indeed the method of lowest economic cost, which make it more suitable for preserving the BSG for exploitation in different processes.

Keywords: Brewer's spent grain; Barley; Freeze-drying; Oven drying; Freezing

1. Introducion

During the elaboration of beer and spirits, such as whisky, large amounts of residual spent grain (normally called brewer's spent grain, BSG) are produced. BSG is composed of protein (31% dry weight), pentosans (19%), lignin (16%), starch and β-glucans (12%), cellulose (9%), lipids (9%) and ash (4%) (Prentice & Refsguard, 1978). Up to this point, BSG is mainly used as a feedstuff rich in protein and fibre (Hough, 1990; Huige, 1995). BSG contains glutamine-rich protein (Kanauchi & Agata, 1997) of high biological value (Hernández, Rodríguez, López, & Zerquera, 1999), and its nutritive value is 75.3 F.U. for meat production/100 kg of dry matter (Sabbioni, Superchi, & Bonomi, 1995). Due to its relatively low cost and potential nutritional value, BSG has been considered as an attractive adjunct for human food. Dietary fibre-rich and protein-rich flours, of potential use as ingredients in baking and formulated foods, are obtained by grinding and sifting of dry BSG (Chaudhary & Weber, 1990). Moreover, high fibre bread containing BSG has been shown to reduce plasma total lipids and cholesterol in rats (Hassona, 1993).

Apart from uses in animal and human nutrition, energy recovery from BSG, either by generation of biogas or direct combustion, is being investigated (Keller-Reinspach, 1992). BSG has been enzymatically treated for release of added-value compounds, such as pentoses (xylose and arabinose) and hydroxycinnamic acids (ferulic acid), with potential uses in the food industry (Bartolomé & Gómez-Cordovés, 1999; Santos, 1999). BSG has also proven to be a suitable cultivation medium for species such as *Pleurotus ostreatus* (García et al. 2000).

Due to its high humidity (> 70% w/w) and fermentable sugar content, brewer's spent grain deterioates very easily (Valverde, 1994). In this sense, the use and marketability of BSG as feedstuff is significantly improved if the material is dried. A certain kind of drying is also required for the other uses of BSG cited above. But drying is also interesting in terms of reducing the volume of the product and, therefore, decreasing transport and storage costs. Nowadays, there are plants for drying BSG. The process consists of two

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steps: pressing (to get a material with $<65\%$ humidity) and drying (to get a material with $<10\%$ humidity) (Valverde, 1994).

Standardisation of a product, which mainly depends on raw materials, is always desirable. With BSG, composition may vary with barley variety, time of harvest, characteristics of hops and other adjuncts added, and brewery technology. The aim of this paper was therefore to determine the variability in the main components of BSG supplied by a brewery. Determination of the main characterisation parameters of BSG (moisture, protein, fat, ash and phenolics) was carried out. Content of pentoses was calculated as the sum of xylose and arabinose, determined previously (Bartolomé, Santos, Jiménez, del Nozal, & Gómez-Cordovés, in press). The effect of oven drying, which is the most common preservation method used in the industry, was studied by comparison with other less-harsh preservation methods, such as freeze-drying and freezing. Statistical analyses were performed in order to find differences among the different spent grain lots and among those preserved by the three methods, and to establish relationships between determinations.

2. Materials and methods

2.1. Samples

Eight lots of brewer's spent grain from different grists of malt/corn (80:20,%/%) were provided by Mahou SA (Madrid, Spain). Grists were from blends of different barley and corn cultivars, but were processed in the same manner. An aliquot of each fresh sample was frozen, another aliquot was oven-dried at 60 °C for 18 h, and a third aliquot was freeze-dried. Both oven dried and freeze-dried samples were milled in a Pin Mill, 160Z (Hosokawa Alpine, Germany), to a fine powder of particle size less than 50 μm.

2.2. Moisture determination

Moisture of BSG (2 g for the freeze-dried and oven dried samples, and 5 g for the frozen samples) was determined by weight difference before and after heating at 130 °C for 1.5 h. Before weighing, samples were placed in a desiccator for 30 min. Determinations were carried out in quintuplicate.

2.3. Protein determination

Protein in BSG (0.05 g for the freeze-dried and oven dried samples, and 0.25 g for the frozen samples) was determined as total nitrogen content by the Kjeldahl method, following the Spanish Official Methods of Analysis for cereals. Determinations were carried out in quintuplicate.

2.4. Fat determination

Fat in BSG (3 g for the freeze-dried and oven dried samples, and 7 g for the frozen samples) was determined by weight difference before and after extraction with diethyl ether (250 mL) in a Soxhlet system for 14 h (around 120 cycles). Before weighing, samples were maintained at 110 °C for 30 min, and then placed in a desiccator for 30 min. Determinations were carried out in quintuplicate.

2.5. Ash determination

Ash in BSG (2 g for the freeze-dried and oven dried samples, and 5 g for the frozen samples) was determined by weight difference before and after incineration at 900 °C for 1.5 h. Before weighing, samples were placed in a desiccator for 50 min. Determinations were carried out in quintuplicate.

2.6. Total phenolic content

Total phenolic content in BSG was determined after alkali hydrolysis. Spent grain (10 mg for the freeze-dried and oven dried samples, and 50 mg for the frozen samples) was incubated with NaOH 1N (550 μL) for 16 h at 20 °C under N_2. The mixture was neutralised with acetic acid (200 μl) and centrifuged (20,000 × g, 15 min). The supernatant was assayed for total phenolic content following the Folin-Ciocalteu method (Singleton and Rossi, 1965). Results were expressed as gallic acid. Samples were prepared and analysed in triplicate.

2.7. Statistical analysis

Statistical analysis (two-way analysis of variance, principal component analysis and discriminant analysis) of the data were performed using the PC software package, Statgraphics Plus 2.1 (Graphics Software Systems, Rockwille, MD, USA).

3. Results and discussion

Moisture of the oven dried samples of brewer's spent grain (BSG) was between 8.7 and 10.8% (w/w) (Table 1). These values were similar to those obtained with a less-harsh preservation method, such as freezing-drying (Table 1). In both processes, moisture of BSG was almost 9-fold reduced in comparison with the wet sample (frozen sample) (Table 1). The variation coefficient of the assay varied between 0.3 and 0.8% for the frozen samples, and between 3 and 14% for the freeze-dried and oven dried samples. Freeze-dried and oven dried samples rapidly absorbed water from the atmosphere, which explained the lower repeatability found in the

assay. Contents of protein, fat, ash and total phenolics were expressed as% dry weight, considering the values of moisture.

Protein is the main parameter for the chemical characterisation of BSG used in animal and human nutrition. Protein content in the oven dried samples of BSG was 24.2% dry weight (as the average of the eight lots) (Fig. 1), which was higher than the freeze-dried samples (21.8% dry weight), but lower than the frozen samples (26.4% dry weight) (Fig. 1). The variation coefficient of the assay was around 2.4% for the frozen samples, and around 3.5% for the freeze-dried and oven dried samples. To check for significant differences ($P < 0.05$) in the protein content of different spent grain lots, and that shown by lots preserved by the three different methods, an analysis of variance of both factors was performed. The lots seemed not to be different according to their protein content (Table 2). However, significant differences were found among oven dried, freeze-dried and frozen samples (Table 2). The lower protein content in the freeze-dried and oven dried samples was attributed to losses in volatile nitrogen compounds during freezing and drying that affected protein quantification by the Kjeldahl method.

Fat content in the oven dried samples of BSG was 3.9% dry weight (as the average of the eight lots) (Fig. 1), which was similar to the freeze-dried samples (3.6% dry weight), but lower than the frozen samples (5.8% dry weight) (Fig. 1). Fat determination in the frozen samples was more accurate, with a variation coefficient of 3%. Freeze-dried and oven dried samples exhibited a variation coefficient of around 10%. As seen for protein, two-way analysis of variance (ANOVA) showed significant differences ($P < 0.05$) in fat content among preservation methods, but not among lots (Table 2). Around 30% of the fatty compounds present in BSG, susceptible to extraction by diethyl ether (more volatile compounds), were lost during the freeze-drying and oven drying processes in comparison to freezing (Fig. 2).

Ash is a parameter to be considered in the use of BSG for combustion. The ash content in the eight lots of BSG analysed were very similar ($\approx$ 3.4% dry weight), except for lot #8, with values of 15.1% dry weight for the frozen sample, 11.6% for the freeze-dried sample, and 7.4% for the oven dried sample (Fig. 1). Not only barley cultivate characteristics, but also addition of certain filtration soils (<2%) (Valverde, 1994), may explain these high values for lot #8. The variation coefficient of the assay varied between 2 and 4%, except for lot #8, that increased up to 8%. Two-way analysis of

Table 1
Moisture (%, w/w) of the eight lots of brewer's spent grain preserved by three methods: oven drying, freeze-drying and freezing

Sample	Oven drying	Freeze-drying	Freezing
# 1	9.8	9.8	78.9
# 2	10.3	10.2	77.3
# 3	10.2	10.2	77.4
# 4	10.5	10.5	77.9
# 5	10.8	9.1	78.6
# 6	8.7	8.8	78.3
# 7	8.7	8.5	77.3
# 8	9.7	7.7	76.8

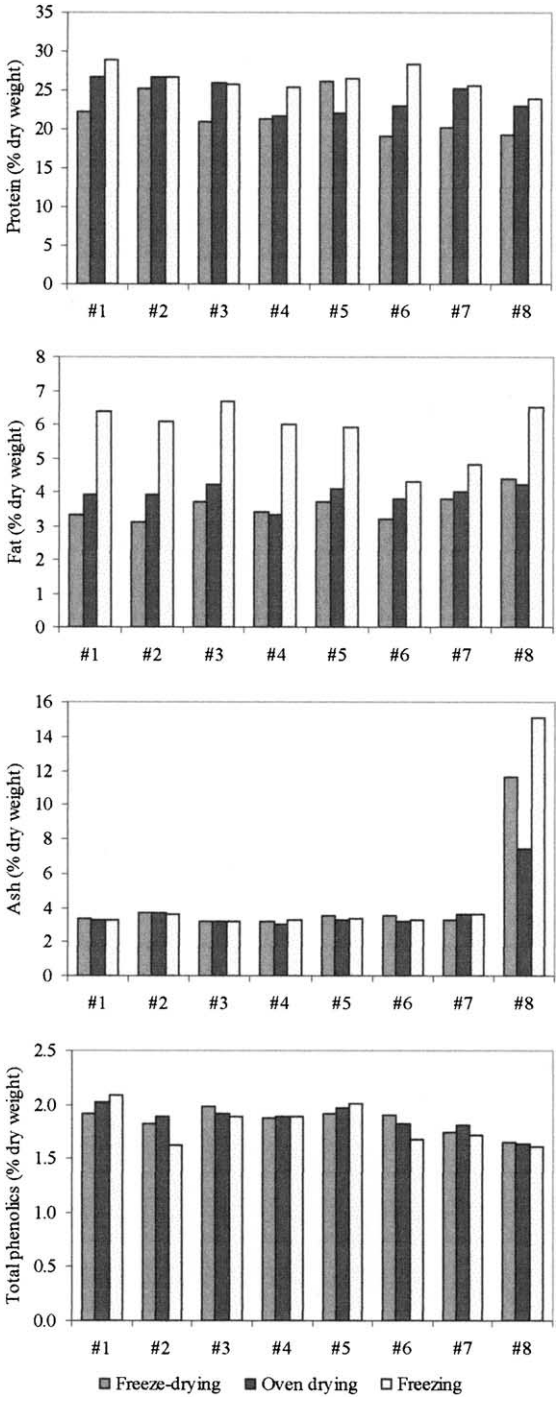

Fig. 1. Protein, fat, ash and phenolic content in the eight lots (1–8) of brewer's spent grain preserved by three methods: freeze-drying, oven drying and freezing.

variance (ANOVA) of the fat content showed that the lots were not homogeneous ($P<0.05$) (Table 2). However, no significant differences ($P>0.05$) were found among preservation methods (Table 2). Analysis of the data after discarding sample #8 still showed significant differences ($P<0.05$) among lots (results not shown), probably due to variations during the wort maceration and filtration processes, and to differences among the barley cultivates, as indicated above.

Cereals are rich in hydroxycinnamic acids, particularly ferulic acid (Clifford, 1999). Enzymatic treatment of cereal residues from agro-industrial processes, has been proposed as a way to naturally obtain ferulic acid for further purposes in the food industry (Williamson, Kroon, & Faulds, 1998). Total alkali-extractable phenolic content in the BSG oven dried samples was 18.7% dry weight (as the average of the eight lots), which was similar to the freeze-dried (18.5%) and frozen (18.1%) samples (Fig. 1). The variation coefficient of the assay was slightly higher for the frozen samples (7.3%) than for the freeze-dried (3.2%) and oven dried (5.0%) samples. Two-way analysis of variance (ANOVA) showed significant differences ($P<0.05$) in total phenolic content among lots, but not among preservation methods (Table 2). Phenolic content in cereals varies with variety, time of harvest and the characteristics of the growing region, which explains the differences found in phenolic content among the different BSG lots. Oven drying and freeze-drying did not alter phenolic content since the temperature used was below 60 °C.

Values for protein, fat and ash reported in this paper agreed with those reported by other authors (Hernández et al., 1999; Huige, 1995; Keller-Reinspach, 1992; Prentice & Refsguard, 1978; Valverde, 1994). We have found no reference, in the literature, to the total phenolic content in BSG. From a previous study (Bartolomé et al. in press), we calculated that the pentose content (sum of xylose and arabinose) in these same BSG lots varied between 23.0 and 27.3% dry weight for the freeze-dried samples, between 21.0 and 27.3 for the oven dried samples, and between 21.5 and 24.7% for the frozen samples. Pentoses are the main components of the dietary fibre fraction of cereals. Together with protein, dietary fibre is a characterisation parameter for BSG used as feed and foodstuff.

In order to determine the relationship among the different analyses carried out in the BSG samples (protein, fat, ash, phenolics and pentoses), a principal component analysis was performed. The first two principal components explained, respectively, 35.8 and 30.3% of the variance. Component 1 was strongly correlated with components of the cell wall (phenolics and pentoses) and mineral content (ash), whereas component 2 correlated strongly with protein and fat (Fig. 2).

The determinations of protein, fat, ash, phenolics and pentoses were also subjected to a discriminant analysis with respect to the qualitative variable "lot". Due to their diversity, samples from lot #8 were not included. Fig. 3 displays the distribution of the samples versus the two main functions with the greatest discriminating power (91.1%). Lots #1, 2, 3 and 7 were separated from the remaing lots (#4, 5 and 6) that showed close scores (between #4 and 5, and between #4 and 6). These differences among lots were attributed to differences in

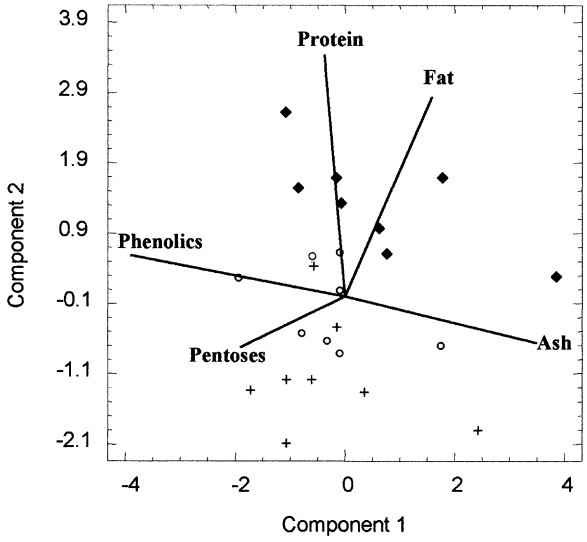

Fig. 2. Biplot of factor weights of fat, protein, ash, total phenolics and pentoses, and factor scores for the eight lots (1–8) of brewer's spent grain preserved by three methods: freeze-drying (+), oven drying (○) and freezing (◆).

Table 2
Two-way analysis of variance (ANOVA) of the protein, fat, ash and total phenolic content corresponding to eight lots of brewer's spent grain preserved by three methods: oven drying, freeze-drying and freezing

	Lot as grouping variable		*Preservation method* as grouping variable	
	$F_{experimental}$	$F_{critical}$	$F_{experimental}$	$F_{critical}$
Protein (% dry weight)	1.64	2.76	10.9*	3.74
Fat (% dry weight)	1.95	2.76	46.8*	3.74
Ash (% dry weight)	112.8*	2.76	1.06	3.74
Total phenolics (% dry weight)	10.9*	3.12	1.35	3.96

* $P<0.05$.

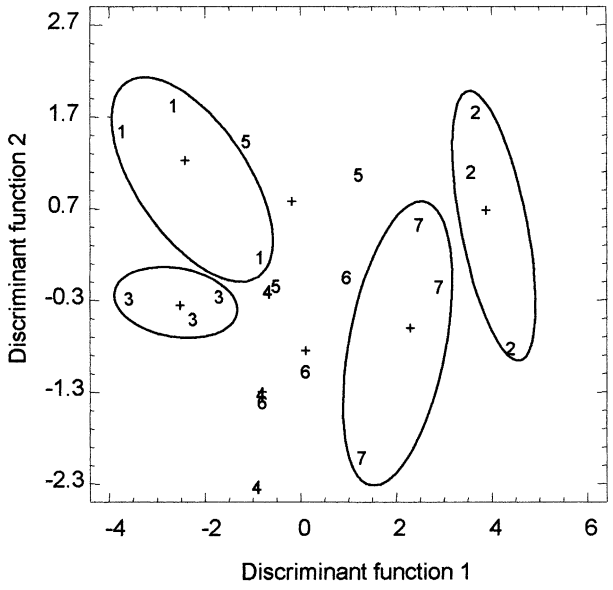

Fig. 3. Plot of discriminant function scores for the seven lots (1–7) of brewer's spent grain preserved by three methods: freeze-drying, oven drying and freezing.

barley origin, in malting process, and, more probably, to different processes for obtaining the wort.

In summary, different lots of spent grain from the same brewery showed small variations in composition, only in minor components (ash and phenolics). Oven-drying of BSG gave rise to a small decrease ($\approx 2\%$) in protein (total nitrogen) and fat content in comparison with the wet (frozen) sample. Oven drying was similar to freeze-drying, a less-harsh preservation method. However, oven drying is indeed the method of lowest economic cost, which make it more suitable for preserving the BSG for exploitation in the different processes mentioned in the Introduction.

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