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Physicochemical characterisation of barley malts available for the Argentine craft beer industry

Caracterización fisicoquímica de maltas de cebada disponibles para la industria de la cerveza artesanal Argentina

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Abstract

According to market statistics, the consumption and production of craft beer in the world and in Argentina have exponentially grown in recent years. However, there is no complete characterisation of the malts available for these small producers, even though they are one of the fundamental raw materials in beer production. The aim of this work was to characterise the base malts used in craft production, given that their physicochemical properties are a fundamental parameter for conditioning the final product. Moisture, ash, protein, lipids, total fibre and carbohydrates were determined according to EBC and AOAC methods, obtaining the following results, respectively: 5.15 g/100g ± 0.85; 1.91 g/100g ± 0.12; 10.44 g/100g ± 0.21; 1.76g/100g ± 0.17; 4.46 ± 0.62; 76.28g/100g ± 1.59. Protein profiles of the malt extracts were also characterised by vertical SDS-PAGE electrophoresis according to the Laemmli method, which have a direct impact on beer quality. Finally, a principal component statistical analysis was performed on the collected data. The values obtained are in agreement with those reported by other authors for malts of other varieties and geographical origin.

Keywords: Barley malt; Craft beer; Physicochemical analysis; Principal component analysis.

Resumen

Según estadísticas de mercado, el consumo y producción de cerveza artesanal en el mundo y Argentina han crecido exponencialmente durante los últimos años. Sin embargo, no existe una caracterización completa de las maltas, disponible para estos pequeños productores, aun siendo éstas una de las materias primas fundamentales en la elaboración de cervezas. Como objetivo de este trabajo se propuso realizar la caracterización de maltas base que se utilizan en la producción artesanal, dado que las propiedades fisicoquímicas de las mismas son un parámetro fundamental para condicionar el producto final. Se realizaron determinaciones de humedad, cenizas, proteínas, lípidos, fibra total e hidratos de carbono, según métodos EBC y AOAC, obteniéndose los siguientes resultados respectivamente: 5,15 g/100g ± 0,85; 1,91 g/100g ± 0,12; 10,44 g/100g ± 0,21; 1,76g/100g ± 0,17; 4,46 ± 0,62; 76,28g/100g ± 1,59. También se caracterizaron perfiles de proteínas de los extractos de malta, por electroforesis SDS-PAGE vertical según el método de Laemmli, que tienen un impacto directo en la calidad de la cerveza. Por último, se hizo un análisis estadístico de componentes principales con los datos recolectados. Los valores obtenidos están en concordancia con los informados por otros autores sobre maltas de otras variedades y origen geográfico.

Palabras clave: Malta de cebada; Cerveza artesanal; Análisis fisicoquímico; Análisis de componentes principales.

Introduction

According to the American Brewers Association, craft beer sales in the U.S. beer market increased to cover 21.5% (by volume) in 2019 (1). Craft production is basically carried out by microbreweries: small-scale, independent beer producers. This figure was quickly replicated in other countries in what is now known as The Craft Beer Revolution (2).

Over the past 20 years, the growth of the global craft beer market has been shocking (4). In 2018, the number of active microbreweries in the US alone was 4522 (5) and in Europe 8094 (6). In Argentina, beer sales in the last decades were progressively increasing, representing

an increase of almost twice the volume in 20 years (7). According to surveys published in 2018, it is estimated that there are more than 1600 craft beer producers distributed throughout the country (3).

This process of industry expansion continues to this day and has led to the development of other small emerging industries related to beer production, such as the production of barley malt or other cereals (wheat, oats, rye, millet or sorghum).

However, these small and medium-sized industries often do not have the necessary technology to ensure the quality of their products as is the case in the large-scale industry. In addition, some raw materials such as barley malts are not fully characterised and this characterisation, if it exists, is not available to the small brewer.

In order to obtain the desired product, it is essential to have a sound knowledge of the raw materials, understanding that the physicochemical properties of the raw materials have a direct impact on the quality of the beer produced (8).

During brewing, malt is milled and then mixed with water in a process called mashing. The former increases the specific surface area of the malt (9) (10). The latter, consists of bringing the ground grain into contact with water, which promotes the action of the enzymes contained in the malt. This is achieved with a certain proportion of grain and water, conditioning the temperature of the mixture and the contact time to optimize the activity of each enzyme. During this process, the malt components necessary for the following stages are transformed and extracted. In beer production, different malts are used together: base malts and specialty malts. Base malts, which make up almost 80% of the grains used in a recipe, provide carbohydrates, proteins and enzymes. These enzymes promote the modification of starches into fermentable and non-fermentable sugars, together with the transformation of proteins into free peptides and amino acids. The influence of this type of malt on beer production will be mainly linked to the alcoholic strength and body of the beer. On the other hand, specialty malts, which include caramel, crystal or roasted malts, contribute mainly to the colour, flavour, foam retention, mouthfeel and aromas of the beer, without contributing enzymes in significant quantities (12).

The functional groups analysed to characterise the malts were: water (moisture), ashes, lipids, proteins and total carbohydrates. Fibre content was also determined, although these do not directly impact the quality of the final product. Each functional group interacts at different stages of the production process and determines the characteristics of the final product, namely:

Moisture

Grain moisture has a direct influence on milling as it modifies the susceptibility to breakage. In addition, this variable influences storage or preconditioning costs, since higher percentages of moisture increase the degree of malt deterioration and facilities require investments in infrastructure to maintain moisture balance (13). Excess moisture in malt is the main determinant of batch failure (14).

Ashes

Inorganic substances in malt, which are inert to the thermal modification process, are quantified by the ashes test. Most of these substances have beneficial effects on beer production. Metal ions increase the efficiency of the extraction process during mashing by acting as catalysts in enzymatic reactions. In addition, they influence the formation of foam, forming complexes that help to stabilise the bubbles. Some countries, such as Canada, have established minimum ashes content in beers such as Ale, Lager, Porter or Stout (15).

Lipids

In beer production, the yeast used for fermentation requires the presence of lipids and fatty acids for the growth mainly of the cell membrane (16). However, high levels of lipids from malt contribute to beer turbidity, increasing the formation of gels, which prevent proper filtration and clarification of the final product (17). Thus, the lipid content of the grain is a binding variable if fermentation is to be controlled without compromising the flavour and turbidity of the product.

Proteins

Foam is a dispersion of gas bubbles within a liquid. In beer there are hydrophobic, hydrophilic and other compounds that have amphipathic behaviour. When the latter reach the surface of the liquid, together with the presence of carbon dioxide, they produce bubbles that constitute the foam in beer (18). Proteins have the aforementioned characteristics and the protein content of malt is closely related to foaming capacity and mainly to foam stability, a critical factor when assessing the quality of a beer (19).

On the one hand, a high protein content improves foam stability (20) (21). However, certain proteins can contribute to turbidity. On the other hand, low amounts of protein lead to sluggish fermentations, as well as to a deficiency of amino acids available to the yeast during the fermentation phase (22).

Regarding the molecular weight of proteins, some

studies show that the range in beer is relatively narrow: from 10 kDa to 46 kDa (23). Many authors agree that the range of proteins causing turbidity in beer is between 15 kDa and 30 kDa (24).

Carbohydrates

Most carbohydrates come from starch which, during mashing, absorbs water and is degraded by β-amylase which acts on the non-reducing ends of the starch chain to form fermentable sugars. Subsequently, α-amylase will degrade amylose to form reducing sugars and, from amylopectin, form maltotriose and dextrins.

The main function of carbohydrates is as a substrate for enzymes and yeasts to produce alcohol during wort fermentation. They also influence foam formation and foam stability, as a higher proportion of polysaccharides in beer favours outward migration of gas which is trapped in the foam rather than dissolving within the liquid (18).

Fibres

They are part of the cereal husk and are mainly the support for the wort production process, forming the specific filter cake for the desired product.

The objective of this work was the physicochemical characterisation of the base malts available on the Argentinean market, since, as mentioned in previous paragraphs, they constitute the fundamental raw material for the production of craft beer.

Materials and Methods

The trials were conducted on barley malts provided by local craft beer suppliers, working on a total of 12 samples. The malts correspond to genetically different barley varieties, from different geographical areas, including Argentinean and European malts from different producers. The main aim was to have diversity in order to better characterise this raw material, as well as to consider the different possibilities of the local market.

Triplicate tests were carried out for each sample, statistically evaluating the results according to the European Brewing Convention (25) and the Association of Official Analytical Chemists (26).

Milling

Standardisation of the samples was carried out in triplicate, using a series of three Macotest sieves, the IRAM (Argentine Institute for Standardisation and Certification) meshes N° 25, 50 and 100. The milling was carried out with an IKA brand blade mill, double blades, fixed speed of 20000 rpm, stainless steel chamber and the milling time was set at 9 seconds (9, 10).

Moisture

5 g of ground and standardised sample was weighed to the tenth of a milligram on a filter weigher. It was placed in an oven at 105 °C ± 0.5 for three hours. Cooled in a desiccator and weighed to constant weight (EBC 4.2).

Ashes

Weighed to the tenth of a milligram 3-5 g of ground sample in a porcelain dish and muffled at 550 °C for 5 hours (or until greyish white ash was obtained). It was then allowed to cool to room temperature in a desiccator and weighed to constant weight (AOAC 923.03).

Lipids

6 g of sample were weighed to the tenth of a milligram, worked with Soxhlet extraction equipment and hexane was used as extraction vehicle. The cycle was run for 6 hours at a rate of 10 cycles/hour, the micelle was distilled and the residue was dried in an oven at 103 ºC for 1.5 hours. Finally, the balloon plus the dried residue was weighed to constant weight (AOAC 991.43).

Total protein

Total protein content was determined using the Kjeldahl method using 1.4 g (±0.1 g) of samples in triplicate. Total nitrogen was obtained and to estimate total protein this value was multiplied by the factor 6.25 (AOAC 945.18B).

Polypeptide profiling

The polypeptide profile was carried out on the musts obtained by maceration of the ground samples according to EBC method 4.5.1. (9). The must samples were concentrated in a vacuum desiccator using a Boeco R-300 pump at room temperature. SDS-PAGE electrophoresis was performed according to the method of Laemmli (27) with molecular weights between 14 and 94 KDa.

Polyacrylamide was formed using a 15 % v/v run gel (pH 8.8) and a 12 % v/v stacking gel (pH 6.8). The resolution lengths were 50 and 15 mm for the run and stacking gels, respectively. A BioRad model 1653301 (Bio Rad Laboratories Inc Hercules, CA, USA) was used. The gels were developed after staining with Coomassie Brilliant solution in methanol. PB-L Bio-Logic products were used as molecular weight markers. INDIGO Pre-stained Protein Marker. Cat. No MC01. SDS-PAGE analysis was done using GelAnalyzer 1.0 software (28).

Total Fibre

It was carried out according to the enzymatic-gravimetric method 985.29 of the AOAC (Sigma TDF-100A) (26).

Total carbohydrate

The total carbohydrate content was obtained by the percentage difference between all the above-mentioned constituents (moisture, ashes, lipids, proteins and fibres) and the total (100%).

Data analysis

A Principal Component Analysis was also performed on the samples to obtain information on some hidden relationships between the studied variables. Multivariate statistics were used through InfoStat software (29).

Results

The obtained results are summarised in table 1, also incorporating the expected values for optimising the production process (8, 12).

Table 1: Physicochemical characterisation of barley malts.

Properties	$\bar{x} \pm 2\,\vartheta$	Expected values *
Moisture dry basis	5,15 ± 0,85	2,0 - 6,0
Ashes	1,91 ± 0,12	1,9 - 2,6
Lipids	1,76 ± 0,17	1,5 - 3,0
Proteins	10,44 ± 0,21	9,0 - 11,5
Carbohydrates	76,28 ± 1,59	76,0 - 81,0
Fibre	4,46 ± 0,62	3,0 - 5,9

(*Percentages on dry basis)

For the Principal Component Analysis, two principal components were taken to explain 62.4% of the variability of all the data, an acceptable value to perform a biplot representation (as can be seen in Figure 1 with eigenvalues $\lambda 1 = 1.90$ and $\lambda 2 = 1.84$) and replace all the original variables.

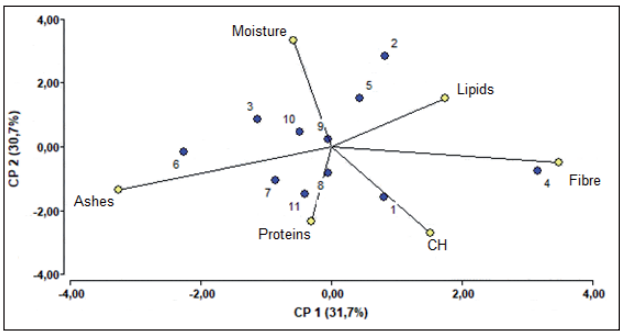

Figure 1: Principal component analysis of the samples.

In this figure, each point represents a sample and each vector a variable. The ashes and fibre variables have a strong influence in discriminating the data set given the higher modulus of the vectors. In this analysis, it can be seen that Principal Component 1 (PC1) is positively related to lipid, fibre and carbohydrate content and negatively related to ashes, protein and moisture content. Principal Component 2 (PC2), on the other hand, is positively related to moisture and lipid content and negatively related to protein, carbohydrate and ashes content. It could be mentioned that the fibre content is almost neutral with respect to this component.

The polypeptide profile analysis on the wort is shown in Figure 2 and shows the molecular weight distribution considering malts of different barley varieties, malting plants and geographical origin (see Table 2).

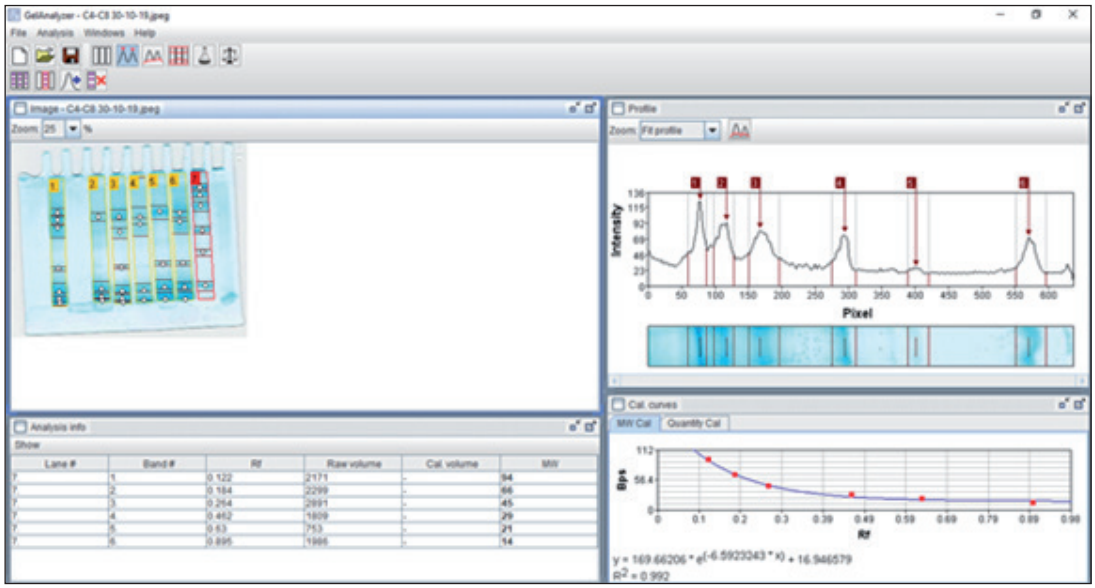

Figure 2: Molecular weight distribution using GelAnalyzer software (28).

As documented in Figure 2, all samples have proteins with molecular weight below 45 kDa, approximately 40 kDa, which is crucial as this fraction favours foam formation. In samples 1, 4 and to a lesser extent 3, there are 29 kDa fractions, this is not the case for samples 2 and 5. Sample 2, on the other hand, shows a lower fraction resolution, which would indicate a similar concentration of all molecular components. Each sample has a high concentration of low molecular weight polypeptides, fractions below 14 kDa. The results of the determination of the molecular weight fractions can be seen in more detail in Table 3.

Table 2: Identification of samples by origin of the malt variety, malting plant and geographical origin of the malting plant.

Sample #	Variety	Malting Plant (Origin)
1	Europe	Weyermann (Germany)
2	Argentina	Cargill (Argentina)
3	Europe	Other (Argentina)
4	Europe	Boortmalt (Belgium)
5	Argentina	Boortmalt (Argentina)

Table3: Details of molecular weights.

Band	Lane	Rf	Raw Volume	MW
1	1	0.268	2207	46
	2	0.323	2932	37
	3	0.388	4027	30
	4	0.705	777	19
	5	0.889	4477	17
	6	0.943	2844	17
	7	0.976	1825	17
2	1	0.32	2025	38
	2	0.893	3987	17
	3	0.893	3987	17
	4	0.987	1322	17
3	1	0.317	3958	38
	2	0.433	1895	27
	3	0.711	471	19
	4	0.9	3074	17
	5	0.959	2623	17
	6	0.987	939	17
4	1	0.324	2710	37
	2	0.379	2594	31
	3	0.907	2441	17
	4	0.979	0	17
5	1	0.294	4619	41
	2	0.708	624	19
	3	0.894	4349	17
	4	0.989	4400	17
6	1	0.314	2226	38
	2	0.381	3792	31
	3	0.712	646	18
	4	0.899	3931	17
	5	0.994	4479	17
	1	0.122	2171	94
	2	0.184	2299	66
	3	0.264	2891	45
	4	0.462	1809	29
	5	0.63	753	21
	6	0.895	1986	14

Conclusions

The aim of this work was to physicochemically characterise the barley malts available to craft beer producers in Argentina. Regarding the results obtained, most of the samples present characteristics similar to those found by other authors in the references consulted (30) (31) (4).

Some variables, such as moisture content, may be out of specification due to poor storage procedures of this raw material, which may be detrimental to its quality. This can happen on the part of the malting plant, the distributor or even the producer. Malt with these characteristics should be discarded and is not recommended for use in brewing, as the high moisture content has a negative impact on the potential extract of the malt and, consequently, on brewing yields. Furthermore, this moisture content favours the development of fungi that can degrade the raw material (32).

In addition to this isolated fact, the observation of Figure 1 in the Principal Component Analysis shows that most of the samples have a similar characteristic composition, and no significant differences can be seen in the studied population. Consequently, the authors will continue to study more samples from different sources to find relationships that could be helpful for the craft brewer who depends on this raw material. The aim is to find relationships between these malt characteristics and the different variables that play a role in the brewing process in order to provide guidance to local producers, which will be part of future research by the authors of this paper.

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