

Effect of “Cooking” Method on the Hulled and Unhulled Barley Grain Composition

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Summary

Barley is one of the oldest cultivated crops in the world and in the past represented a significant grain in human nutrition. The main purpose of barley cultivation today is for the livestock needs and the brewing industry, where it is used in the form of malt, but also is increasingly used in human nutrition as barley porridge. During the barley grain processing for human consumption, to provide better digestibility, barley is hulled and such grain has a reduced nutritional value. To improve the nutritional properties of barley after hulling, the grains are subjected to a thermal cooking treatment due to the starch gelatinization. This investigation includes two varieties of hulled and unhulled barley Vedran and Titan. In all samples, the nutritional composition according to standard methods was investigated, namely the content of moisture, ash, fat, protein and starch were determined. After the cooking method (adapted "cooking" method), at a pressure of 0.5 bar and a time of 10 and 15 minutes and convection drying of samples with air temperatures of 50 °C, 60 °C and 70 °C, the nutritional composition of all samples was also determined. The research showed that the cooking method and drying affected the change in the nutritional composition of hulled and unhulled barley, and in all investigated nutritional composition parameters there were changes compared to the initial samples.

Key words

hulled barley, unhulled barley, drying, cooking method, nutritional composition

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Introduction

Barley has been known in the world for thousands of years and it is one of the oldest cereals used by human for his diet. Barley is the fourth largest grain in the world and is produced in about 150 million tons per year (Akar et al., 2004). Today, the use of barley is primarily in the brewing industry and in livestock feeding (Bergh et al., 1999; Štafa and Stjepanović, 2015). In the human diet it is used peeled for easier digestion. It is obtained by removing the outer hull and bran and thus obtaining the so-called. white barley. However, this reduces the percentage of protein, fat, minerals and vitamins (Mohapatra and Rao, 2005).

The chemical composition of barley grains is similar to the composition of other cereals. In principle, dry matter-based contains 9-17% protein, 59-68% non-nitrogenous extractives, 1.9 - 3.9% fat, 12.6 - 22.6% fibers and 2.3 - 3.0% ash (Pospisil, 2010).

After harvest, the barley grains are transported to the processing plant where they are sorted and cleaned on sieves. In order to be suitable for human consumption, barley processing takes place in four phases: peeling to obtain hulled barley, grinding to obtain flour and similar products, thermal and hydro thermal processing to obtain appropriate quality for better digestibility and barley ingredients fractionation for obtaining starch, protein and other foods in various industries (Krička et al. 2012).

Thermal processing is any process by which the grain is exposed for a certain time to the influence of elevated temperature. If the grain is treated with water or steam, then it is the hydrothermal process (Katić, 1997). Thermal and hydrothermal treatments include drying, roasting, microwave irradiation, extrusion (dry or wet), pelleting (dry or wet), expansion (dry or wet) and evaporation or "cooking methods".

Drying is one of the oldest methods used to preserve and store grain. The task of drying is to remove exactly as much water from the grain as necessary for it to be stored, without a negative impact on the grain quality, i.e. to the equilibrium moisture (Krička et al., 2000). Although there are several ways of drying grain (convection, conduction, radiation) the most common way is convection drying (Babić and Babić, 2000). It is a method of drying by which water is removed from the grain by a hot air stream which at the same time carries away the moisture released on the grain surface.

Due to the climatic conditions that prevail in Croatia during barley harvest, the grain can have a moisture content of more than 12 - 14% (equilibrium humidity), so drying is required in its processing. This leads to long-term (6-12 months) storage (Wilcke and Hellevang, 2002).

As the digestibility in dried barley grains is low, the method of evaporation increases the gelatinization of starch in the grain, i.e. its digestibility increases. It is a hydrothermal evaporation process, a method by which barley grains are treated with elevated pressure using steam until starch gelatinization occurs (Voća et al., 2007).

Based on all the above, the nutritional properties of unhulled and hulled grains of Titan and Vedran barley after convection drying in a laboratory dryer in a stationary layer with three air temperatures of 50, 60 and 70 °C, and convection drying at the same temperatures after the conditioning of samples using steam

(cooking) on 10 and 15 minutes at 0.5 bar will be investigated. Barley grains (unhulled and hulled) before and after heat treatment will determine the water content (before and after rehydration), so that the drying equation of water release and the content of ash, oil, starch and protein could be made.

Materials and Methods

The research was conducted on two varieties of hulled and unhulled barley. The investigated barley cultivars were early vegetation lengths of the Agricultural Institute Osijek - Titan and medium late vegetation lengths of the Bc Institute Zagreb - Vedran. The research was conducted in 2019.

The research started with dried unhulled and hulled barley grains with initial moisture content between 10.62% w.b. and 12.66% w.b.. In order to be able to construct drying curves of barley grains, both varieties were rehydrated by standard procedure by adding water to the required moisture content of 19.5% w.b.. The rehydration process was carried out by direct action on the mass of grain with a precisely determined amount of distilled water according to the instructions of the State Institute for Standardization and Metrology. The rehydrated sample was set as the initial sample used in further research. After the rehydration procedure, and before drying in the laboratory dryer, all samples moisture content was analysed. Rehydrated samples were defined as initial samples used in further research.

Determination of moisture content in the grains of two varieties was performed according to the protocol HRN ISO 6540: 2002 in the laboratory dryer INKO ST-40, Croatia.

The determination of the ash content in barley grains of both cultivars was carried out according to the CEN TS 14 775: 2004 protocol in the Naberthem B170 muffle oven, Germany. During the process, organic matter from the samples was burned, leaving ash.

Determination of oil (fat) content in the grains of both cultivars was performed according to the HRN ISO 6492: 2001 protocol using Soxhlet extractor R 304, Germany. The process of obtaining the oil was done by extraction, and the obtained amount of oil was weighed on an analytical balance.

Determination of starch content in barley grains of both cultivars was performed according to the protocol HRN ISO 6493: 2001 by Evers using the Kruss polarimeter, P 3001, Germany, after the soluble state was previously carried out by acid hydrolysis.

Determination of protein content in barley grains of both varieties was carried out according to the protocol HRN EN ISO 5983-2: 210 by Kjeldahl, where the organic matter is destroyed by heating with sulphuric acid in the presence of a catalyst or salt that increases the boiling point of the acid.

The adapted conditioning of samples using steam method was made as a high-pressure hermetically sealed vessel on which there is a thermometer and a manometer to control the desired temperature and pressure. Unlike the classic "cooking" column in which steam is supplied from the outside, in this adapted method the barley grain is conditioned with water located at the bottom of

pores with a porous bottom, and below it is an aluminum washer with a hole separating the grain from direct contact with water. After heating, the steam passes freely over the grains and water begins to evaporate through the grains to the desired time.

All samples were treated with steam at a temperature of 100 °C for 10 minutes at 0.5 bar overpressure and 15 minutes at 0.5 bar overpressure. The temperature and pressure inside the vessel were controlled and regulated by a safety valve.

The laboratory dryer is made of three parts, of which the lower part (stand) measures 300x350x120 mm. It has a fan that sucks in ambient air that is heated by a 1kW heater.

The heated air passes through a perforated sheet metal with a diameter of 15 mm and a dense mesh to homogenize the air flow. The air enters the second unit of a round shape with a diameter of 200 mm and a height of 270 mm. Here, the heated air is directed towards the dried part of the dryer with a round shape and its diameter is 78 mm. The third unit is inserted into this part, ie. a perforated vessel with a diameter of 76 mm and a height of 120 mm. Air speed or fan control, as well as air temperature are performed using two independent regulators.

The air velocity in the dryer was maintained at 1.0 m s⁻¹, and the barley grain (sample) was dried at three air temperatures, 50, 60 and 70 °C. Before drying, the mass and moisture content of both varieties of barley were determined and every 5 minutes the mass loss was measured using a technical scale, ie. the water and mass loss was calculated.

Results and Discussion

Moisture was determined by samples before and after rehydration, as well as after evaporation of both varieties of barley grain Vedran and Titan, unhulled and hulled. Table 1 shows the obtained results.

Grgić (2015) states that the average moisture content should be 9.60%, while Jordanovski et al. (1993) state a moisture content of 10.52%. Kolak (1994) emphasizes that the grain moisture content of barley for the needs of food industry must be less than 13%, Hrgović (2006) emphasizes that the harvest should not be done

until the grain moisture content falls below 14%, which are values according to this research. After rehydration and conditioning of samples using steam, the samples were dried in a laboratory oven at 50 °C, 60 °C and 70 °C.

Table 2 shows the exponential equations of water release from barley grains as well as the coefficient of determination.

In the case of samples of the Vedran variety (unhulled and unhulled) as well as the Titan variety (unhulled and unhulled), samples that were only rehydrated had the longest drying time. The shortest drying times were observed in samples evaporated for 15 minutes at 0.5 bar.

All samples that were evaporated showed a reduction in drying time. Samples evaporated for 15 minutes had the shortest drying time, as in non-peeled samples.

By analyzing the obtained results in table 2, ie. the exponential equations of the investigated parameters, it was noticed that there were no significant differences in the water release rate because the rehydrated samples always released the water more slowly. This is confirmed by the time required to release the water to equilibrium humidity and the average lower value of the exponent. The coefficient of determination was between 0.918 and 0.996 for all investigated exponential equations, which confirms that the research of water release from the grain was conducted precisely and that the obtained results were mutually comparable. This was confirmed by comparison with the literature data for the grain drying process (Krička and Pliješć, 1994; Krička and Pliješć, 1997; Voća, 2007).

After determining the moisture content and the drying equation of unhulled and hulled barley grains (varieties Vedran and Titan) in table 3, the ash, oil, starch and protein were determined on raw material.

According to the results in table 3, the ash content is higher in unhulled samples of both varieties and amounts to more than 3%, while it is significantly lower in hulled samples of about 1.75%, which is evidently related to the hull chemical structure. In unhulled barley samples Jordanovski et al. (1993) state that the percentage of ash was 2.62%, while Pospišil (2010) states that the share of ash was 2.3 - 3.0%.

Table 1. Moisture content in barley samples

Moisture %	Vedran		Titan	
	Unhulled	Hulled	Unhulled	Hulled
Raw material	12.55 ^a ± 0.12	10.62 ^a ± 0.06	12.66 ^a ± 0.12	11.49 ^a ± 0.08
Rehydrated samples	19.68 ^b ± 0.18	19.74 ^b ± 0.15	19.44 ^b ± 0.21	19.35 ^b ± 0.16
After cooking (0.5 bar, 10 min.)	27.38 ^c ± 0.08	25.5 ^c ± 0.28	25.09 ^c ± 0.29	24.17 ^c ± 0.21
After cooking (0.5 bar, 15 min.)	27.45 ^c ± 0.21	26.89 ^d ± 0.22	25.69 ^c ± 0.46	26.05 ^d ± 0.18

Note: The mean values ± SD, with the same letter are not significantly different ($P < 0.05$) according to Tukey's HSD test

Table 2. Exponential equations of water release and coefficients of determination R^2 to equilibrium humidity

Sample	Cooking time (min)	Air drying temperature (°C)	Exponential equation	R^2
Hulled Vedran	-	50	$w = 18.369e^{-0.04\tau}$	0.9583
		60	$w = 18.203e^{-0.053\tau}$	0.9183
		70	$w = 18.817e^{-0.066\tau}$	0.9488
	10	50	$w = 25.219e^{-0.056\tau}$	0.9854
		60	$w = 25.72e^{-0.067\tau}$	0.9921
		70	$w = 25.81e^{-0.074\tau}$	0.9903
	15	50	$w = 28.763e^{-0.065\tau}$	0.9963
		60	$w = 27.546e^{-0.067\tau}$	0.9946
		70	$w = 27.056e^{-0.073\tau}$	0.9906
Unhulled Vedran	-	50	$w = 18.545e^{-0.042\tau}$	0.9611
		60	$w = 20.955e^{-0.086\tau}$	0.9943
		70	$w = 20.043e^{-0.089\tau}$	0.9566
	10	50	$w = 26.32e^{-0.109\tau}$	0.9589
		60	$w = 29.886e^{-0.16\tau}$	0.9845
		70	$w = 30.212e^{-0.179\tau}$	0.9814
	15	50	$w = 29.58e^{-0.127\tau}$	0.9893
		60	$w = 30.304e^{-0.154\tau}$	0.9925
		70	$w = 34.716e^{-0.262\tau}$	0.9967
Hulled Titan	-	50	$w = 19.507e^{-0.058\tau}$	0.9877
		60	$w = 19.512e^{-0.0082\tau}$	0.9662
		70	$w = 19.977e^{-0.11\tau}$	0.9648
	10	50	$w = 22.946e^{-0.085\tau}$	0.9543
		60	$w = 25.462e^{-0.149\tau}$	0.9649
		70	$w = 26.465e^{-0.195\tau}$	0.9641
	15	50	$w = 26.435e^{-0.11\tau}$	0.9586
		60	$w = 27.312e^{-0.14\tau}$	0.9697
		70	$w = 28.306e^{-0.183\tau}$	0.9796
Unhulled Titan	-	50	$w = 19.216e^{-0.049\tau}$	0.9779
		60	$w = 18.832e^{-0.074\tau}$	0.9414
		70	$w = 19.936e^{-0.12\tau}$	0.9482
	10	50	$w = 24.389e^{-0.089\tau}$	0.9535
		60	$w = 24.925e^{-0.108\tau}$	0.9700
		70	$w = 31.424e^{-0.251\tau}$	0.9947
	15	50	$w = 25.666e^{-0.085\tau}$	0.9841
		60	$w = 28.558e^{-0.143\tau}$	0.9949
		70	$w = 29.423e^{-0.205\tau}$	0.9758

Table 3. Ash, oil, starch and protein content in raw barley samples

Variety	Ash (%)	Oil (%)	Starch (%)	Proteins (%)
Hulled Vedran	1.93 ^a ± 0.06	4.90 ^{ab} ± 0.21	59.11 ^b ± 0.42	11.70 ^b ± 0.13
Unhulled Vedran	3.33 ^b ± 0.12	4.91 ^{ab} ± 0.18	48.79 ^a ± 0.71	12.40 ^d ± 0.08
Hulled Titan	1.62 ^a ± 0.12	5.11 ^b ± 0.10	57.97 ^b ± 0.46	10.67 ^a ± 0.12
unhulled Titan	3.02 ^b ± 0.08	4.72 ^a ± 0.14	46.28 ^a ± 0.68	12.00 ^c ± 0.15

Note: The mean values ± SD, with the same letter are not significantly different ($P < 0.05$) according to Tukey's HSD test

In raw material, the fat content of barley, whether hulled or unhulled, was around 5%. The obtained fat content was higher than according to the literature. Thus Jordanovski et al. (1993) in their research obtain the result that the average fat content is 2.24%, while Šimić (2009) in his work states the fat content of 2 to 3%. Lower values are stated by Ljubisavljević (1985)- of 2.5% fat.

The starch content was higher in hulled samples than in the unhulled ones. The Vedran variety had more starch, in hulled samples it contained about 59% and in unhulled about 49%. Šimić (2009) in his research states that the share of starch in unhulled barley is 51 - 67%.

More protein, as expected, was obtained in unhulled samples. The higher protein content was contained in the Vedran variety, in unhulled it content was 12.40%, and in hulled 11.70%. Gagro (1997) states about 10-15% protein in barley grain. In their research, Jordanovski et al. (1993) notice that the protein content in barley grain is 11.81%, while Šimić (2009) states 8-15%. Ljubisavljević (1985) states that the protein content of barley must be about 10%, which is less than in the obtained results.

After conditioning of samples using steam and drying samples of unhulled and hulled barley grains of the Vedran and Titan varieties, ash, oil, starch and protein content were again determined. Table 4 shows the obtained results.

According to the results from Table 4, it can be seen that in the variety Vedran all samples, except samples steamed for 15 minutes at 0.5 bar, have a lower ash content compared to the raw material of hulled and unhulled barley (1.79% and 3.08%). The same is also seen in the variety Titan (1.50% and 2.79%). A higher ash content is observed in unhulled samples. The difference in ash content in dry matter due to drying at different temperatures is not noticeable.

The obtained results show a decrease in the fat content in all samples compared to the initial values. In the Titan variety, there was a decrease in the fat content of all samples compared to the initial value, except for the samples of unhulled barley steamed for 15 minutes at 0.5 bar.

Samples of the hulled and unhulled Vedran and Titan varieties showed a decrease in the starch content, except for samples that were only dried after rehydration.

For most samples, a decrease in the protein content compared to the initial sample is visible. An increase in the protein content is visible in the hulled Vedran variety, after drying at a temperature of 60 °C.

Table 4. Ash, oil, starch and protein content in dried and cooked samples for both barley varieties

Variety	Cooking (min)	Drying (°C)	Ash (%)	Oil (%)	Starch (%)	Proteins (%)
Hulled Vedran	-	50	1.36 ^a ± 0.06	4.87 ^a ± 0.21	57.92 ^a ± 0.38	9.84 ^a ± 0.12
		60	1.69 ^a ± 0.10	4.37 ^a ± 0.12	66.02 ^b ± 0.62	11.91 ^c ± 0.16
		70	1.69 ^a ± 0.08	4.12 ^a ± 0.23	59.08 ^a ± 0.46	10.98 ^b ± 0.08
	10	50	1.75 ^a ± 0.06	4.43 ^a ± 0.10	57.05 ^a ± 0.43	11.58 ^b ± 0.21
		60	1.66 ^a ± 0.06	4.78 ^a ± 0.18	50.33 ^a ± 0.38	11.41 ^b ± 0.16
		70	1.77 ^a ± 0.08	4.82 ^a ± 0.16	48.57 ^a ± 0.52	9.97 ^a ± 0.12
	15	50	1.80 ^a ± 0.04	4.32 ^a ± 0.12	47.55 ^a ± 0.62	10.28 ^b ± 0.26
		60	4.13 ^b ± 0.12	4.45 ^a ± 0.21	35.77 ^a ± 0.28	9.99 ^a ± 0.10
		70	5.94 ^c ± 0.08	4.12 ^a ± 0.08	46.52 ^a ± 0.54	9.22 ^a ± 0.16
Unhulled Vedran	-	50	2.49 ^a ± 0.12	4.91 ^b ± 0.16	49.33 ^a ± 0.32	9.01 ^a ± 0.10
		60	2.55 ^a ± 0.04	4.87 ^b ± 0.12	57.57 ^c ± 0.58	10.69 ^b ± 0.16
		70	2.24 ^a ± 0.10	4.67 ^a ± 0.08	53.79 ^b ± 0.39	10.57 ^b ± 0.18
	10	50	3.01 ^b ± 0.12	4.13 ^a ± 0.06	44.84 ^a ± 0.60	9.99 ^a ± 0.12
		60	2.59 ^a ± 0.06	4.48 ^a ± 0.18	36.87 ^a ± 0.32	12.25 ^b ± 0.08
		70	2.61 ^a ± 0.08	4.57 ^a ± 0.21	34.04 ^a ± 0.28	9.92 ^a ± 0.14
	15	50	2.78 ^a ± 0.06	4.35 ^a ± 0.16	34.74 ^a ± 0.85	10.10 ^a ± 0.06
		60	5.73 ^b ± 0.12	4.53 ^a ± 0.12	46.46 ^a ± 0.46	9.86 ^a ± 0.18
		70	6.51 ^c ± 0.09	4.34 ^a ± 0.16	37.25 ^a ± 0.68	8.92 ^a ± 0.16
Hulled Titan	-	50	1.29 ^a ± 0.06	4.61 ^a ± 0.10	56.89 ^a ± 0.35	10.67 ^a ± 0.12
		60	1.59 ^a ± 0.08	4.66 ^a ± 0.12	70.05 ^c ± 0.48	10.35 ^a ± 0.21
		70	1.52 ^a ± 0.10	4.57 ^a ± 0.16	61.86 ^b ± 0.36	10.62 ^a ± 0.08
	10	50	1.55 ^a ± 0.04	4.18 ^a ± 0.12	57.54 ^b ± 0.38	10.35 ^a ± 0.23
		60	1.58 ^a ± 0.04	4.89 ^b ± 0.14	42.39 ^a ± 0.42	10.17 ^a ± 0.12
		70	1.7 ^a ± 0.06	4.57 ^a ± 0.10	48.71 ^a ± 0.50	9.54 ^a ± 0.18
	15	50	6.82 ^b ± 0.06	4.80 ^b ± 0.16	46.92 ^a ± 0.36	9.24 ^a ± 0.16
		60	6.11 ^b ± 0.02	4.19 ^a ± 0.18	39.95 ^a ± 0.642	9.88 ^a ± 0.21
		70	4.38 ^a ± 0.08	4.11 ^a ± 0.13	48.09 ^a ± 0.44	8.76 ^a ± 0.22
Unhulled Titan	-	50	2.55 ^a ± 0.08	4.68 ^a ± 0.16	45.20 ^a ± 0.32	10.01 ^a ± 0.12
		60	2.72 ^a ± 0.04	4.66 ^a ± 0.12	60.13 ^b ± 0.54	10.86 ^b ± 0.16
		70	2.90 ^a ± 0.09	4.80 ^a ± 0.20	47.22 ^a ± 0.38	10.58 ^a ± 0.08
	10	50	2.80 ^a ± 0.04	4.01 ^a ± 0.18	49.46 ^a ± 0.38	10.93 ^b ± 0.14
		60	2.68 ^a ± 0.12	4.78 ^a ± 0.14	36.01 ^a ± 0.52	11.52 ^b ± 0.14
		70	2.72 ^a ± 0.09	4.51 ^a ± 0.10	32.53 ^a ± 0.64	10.23 ^a ± 0.12
	15	50	6.07 ^b ± 0.06	5.20 ^a ± 0.12	42.25 ^a ± 0.48	9.97 ^a ± 0.18
		60	6.02 ^b ± 0.06	5.35 ^a ± 0.16	39.04 ^a ± 0.32	8.66 ^a ± 0.14
		70	5.12 ^a ± 0.09	5.78 ^a ± 0.14	35.04 ^a ± 0.68	8.92 ^a ± 0.16

Conclusions

Based on the exponential equations, it can be concluded that the Titan variety releases water faster than the Vedran variety, and the unhulled grain releases water faster than the hulled one. After conditioning of samples using steam and convection drying at three different temperatures, the content of ash and fat decreases in both varieties, regardless of the processing conditions. The starch and protein contents also decrease during most processing operations. The obtained results show that the conditioning of samples using steam method affects the barley composition, ie. changes in the content of ash, fat, starch and protein have occurred.

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