The Study of Mineral Elements Participation in Brewing Products Foam Structure Formation

Irina Gribkova[1,*], *Mikhail* Eliseev[2], *Elena* Khorosheva[1], *Galina* Remneva[1] and *Olga* Borisenko[1]

[1]All-Russian Scientific Research Institute of Brewing, Beverage and Wine Industry – Branch of V.M. Gorbatov Federal Research Center for Food Systems, Alcoholic Beverages Department, Moscow, Russia
[2]Russian Economic University named after G.V. Plekhanov, Moscow, Russia

Abstract. The article is devoted to the study of the metal ion's role in the formation of the foam colloidal structure. The nitrogenous compounds prominent role as structuring compounds of the colloidal film on the carbon dioxide bubbles surface is noted. Based on the calculation of the correlation strength between beer samples organic compounds obtained based on light and dark malts, as well as barley and corn as unmalted raw materials, the effect of Ca, Mg, Mn, Co and Na mineral ions on the foam structure was evaluated. It was shown that Ca, Mg, Mn, Na, Co ions take part in the foam structure formation in conjunction with the grain raw materials thiol nitrogen, and Ca, Mg, Mn ions in conjunction with catechins of both grain and hop raw materials. High correlation coefficients between foam resistance and all ions (r-0.991÷0.998), foam resistance, catechins and Co ions (r 0.991), as well as foam resistance and Ca and Mg ions (r -0.987) ensure the elasticity of the foam structure colloidal film.

1 Introduction

Foam is a beer's classic quality attribute, and its structure and properties are closely related to the nitrogenous fractions of organic compounds, bitter hop resins, pentosans, gums, phenolic compounds, and other plant materials fractions that form a film on the carbon dioxide bubbles surface [1 ,2]. It is nitrogenous biomolecules that play the main role in the foam formation in brewing products, and there is differentiation: some of the proteins exhibit foaming properties, and the other part - stabilizing [3].

Lipid transfer proteins (LTP1) with a molecular weight of 9.7 kDa and 91 amino acids in the composition, as well as protein Z with a 40 kDa molecular weight and various hordein derivatives, ranging in size from 10 to 30 kDa, mainly of barley origin, have a sulfhydryl a group assigned to the active binding sites of ligand compounds and the protein base [4–7]. However, molecules of nitrogenous compounds, polyphenols, β-glucan, and others can be connected via Ca^{2+} and Mg^{2+} bridges with other biomolecules [8].

Therefore, the actual task of the study was to determine the ions of microelements related to the foam structure formation, and their organic partner compounds.

* Corresponding author: institut-beer@mail.ru

2 Materials and methods

The beer's samples fermented at the pilot brewing plant Brugge (Germany) from brewing barley malt, caramel brewing malt, roasted brewing malt, brewing barley, and corn were used as prototypes. The composition and content of the actual extract and alcohol are presented in Table 1.

Table 1. The beer's samples raw material composition, actual extract and alcohol content.

Indicators	**Content in samples depending on the composition of raw materials**				
	malt +				
	-	caramel malt	roasted malt	barley	corn
№ samples	1	2	3	4	5
Brix, °P	12.67±0.40	13.52±0.4	12.80±0.4	10.94±0.3	12.69±0.4
The content of actual extract, %	5.24±0.15	4.60±0.1	4.46±0.1	3.94±0.1	4.28±0.1
The content of alcohol, %(m/m)	3.81±0.20	4.63±0.3	4.32±0.3	3.57±0.2	4.36±0.3

The beer's samples were kept sealed for 5 days at a temperature of (10±2)°C. Melanoidins were isolated from beer samples according to [2].

As research methods, generally accepted methods were used: determination of the actual extract, alcohol and dry substances of the initial wort content - according to [9], soluble nitrogen - according to the EBC 4.9.3 method [10], nitrogen with thiol groups - according to [11], catechins - according to [12], determination of mineral elements - according to [13], foam height and foam resistance - according to [14]. Statistical data were processed by the Statistics program (Microsoft Corporation, Redmond, WA, USA, 2006). The experiments were carried out in 5÷6 repetitions with a confidence level p≥95%.

3 Results and discussion

The beer's laboratory samples with the characteristics indicated in Table 1 were examined for the organic compounds content and indicators characterizing the foam quality and structure, the results are shown in table 2.

Table 2. The organic compounds content and indicators characterizing the foam quality and structure.

Indicators	**The beer's samples content**				
	1	2	3	4	5
1	2	3	4	5	6
Brix, °P (X_1)	12.67±0.4	13.52±0.4	12.80±0.4	10.94±0.3	12.69±0.4
β-glucan content, mg/L (X_2)	100.9±7.0	77.6±5.0	95.4±8.5	108.6±10	93.10±8.0
soluble nitrogen content, mg/L (X_3)	693.2±55	665.0±70	647.2±65	726.4±70	610.3±60
nitrogen with thiol groups, μM/L (X_4):	79.0±3.5	65.6±3.0	42.3±8.0	37.2±2.5	32.9±1.8
the catechins content, mg/L (X_5)	25.98±1.3	56.93±4.0	35.5±2.0	22.89±1.0	24.75±1.5

The table 2 continuation

1	2	3	4	5	6
Ca^{2+}, mg/L (X_6)	17.6±0.02	25.4±0.02	22.7±0.02	15.7±0.02	15.5±0.02
Mg^{2+}, mg/L (X_7)	78.3±0.05	92.7±0.05	83.6±0.05	76.9±0.05	71.8±0.05
Mn^{2+}, mg/L (X_8)	0.09±0.01	0.15±0.05	0.11±0.05	0.04±0.01	0.04±0.01
Na^{+}, mg/L (X_9)	39.4±0.02	51.1±0.02	46.6±0.02	40.5±0.02	54.5±0.02
Co^{2+}, mg/L (X_{10})	0.02±0.001	0.005±0.001	0.06±0.01	0.04±0.01	0.06±0.01
Foam height, mm (Y_1)	65.0±1.0	55.0±1.0	45.0±1.0	40.0±1.0	40.0±1.0
Foam resistance, min (Y_2)	6.0±0.5	5.0±0.5	4.0±0.5	3.8±0.5	3.5±0.5

According to Table 2 data, a multiple correlation-regression analysis was carried out, the correlation coefficients describing the relationships between the values are shown in tables 3 and 4.

Table 3. Correlation coefficients between foam height (Y_1) and organic compounds content.

-	Y_1	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}
Y_1	1	0.46	-0.14	0.29	0.99	0.19	0.23	0.31	0.53	-0.46	-0.75
	X_1	1	-0.85	-0.61	0.45	0.68	0.68	0.55	0.75	0.52	-0.32
		X_2	1	0.55	-0.17	-0.89	-0.77	-0.71	-0.73	-0.73	0.36
			X_3	1	0.35	-0.19	-0.18	0.07	-0.07	-0.87	-0.48
				X_4	1	0.26	0.27	0.38	0.57	-0.46	-0.82
					X_5	1	0.93	0.94	0.88	0.44	-0.53
						X_6	1	0.95	0.95	0.30	-0.38
							X_7	1	0.93	0.14	-0.59
								X_8	1	0.12	-0.59
									X_9	1	0.28
										X_{10}	1

According to Table 1 data, the nitrogen content with thiol groups is most closely related to the foam height (r 0.99), and Co^{2+} ions (r -0.75) are less strongly related to the foam height, and most organic compounds have a high correlation between themselves (correlation coefficients are highlighted in green in the Table 3). The relationship between nitrogen with thiol groups and the foam height is natural, since it is due to SH-groups that the foam structure is formed [15].

Partial correlation coefficients show a close relationship between the foam height and: brix and - soluble nitrogen (r 0.853), nitrogen with thiol groups (r 0.992); β-glucan and nitrogen with thiol groups (r 0.994); nitrogen with thiol groups and – catechins (r 0.995), Ca (r 0.994), Mg (r 0.995), Mn (r 0.992), Co (r 0.999), Na (r 0.991) ions; catechins and Ca (r 0.93), Mg (r 0.947), Mn (r 0.939) ions.

In other words, all the studied ions (Ca, Mg, Mn, Na, Co) take part in the foam structure formation - from the side of the grains raw material thiol nitrogen and some of them (Ca, Mg, Mn) - from the side of catechins, that is, they have both grain and hop origin.

Table 4. Correlation coefficients between variables head retention (Y_2) and beer's samples organic compounds content.

-	Y_2	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}
Y_2	1	0.38	-0.07	0.39	0.99	0.16	0.19	0.30	0.49	-0.53	-0.78
	X_1	1	-0.85	-0.61	0.45	0.68	0.68	0.55	0.76	0.52	-0.32
		X_2	1	0.55	-0.17	-0.89	-0.77	-0.70	-0.73	-0.73	0.36
			X_3	1	0.35	-0.19	-0.18	0.07	-0.07	-0.87	-0.48
				X_4	1	0.26	0.27	0.38	0.57	-0.46	-0.82
					X_5	1	0.93	0.94	0.88	0.44	-0.53
						X_6	1	0.95	0.95	0.30	-0.38
							X_7	1	0.93	0.14	-0.59
								X_8	1	0.12	-0.59
									X_9	1	0.28
										X_{10}	1

With the foam height, according to Table 4 data, nitrogen with thiol groups has a strong direct correlation, which is similar to the data in Table 3, the rest of the organic compounds and ions are connected by indirect bonds. Thus, the foam height is associated with: brix and - soluble nitrogen (r 0.848), nitrogen with thiol groups (r 0.996), Na ions (r 0.906); β-glucan and - soluble nitrogen (r 0.994), nitrogen with thyol groups (r 0.999), Co ions (r -0.811); nitrogen with thiol groups and - catechins (r 1), all ions (r 0.991÷0.998); catechins and Co ions (r 0.991); Ca and Mg ions (r -0.987).

Note that the Table 3 and 4 data are similar, however, apparently, the competitive ratios of Ca and Mg ions in connection with the thiol molecules of nitrogenous compounds, as well as catechins, together with Co ions, act as structuring elements responsible for the foam colloidal structure strength on the bubble carbon dioxide surface that forms beer's foam.

Previous studies confirm the role of Mn ions, which enter beer from plant raw materials and affect the foam structure [16], as they bind to the N-terminus of protein components, and this is typical not only for Mn, but also for Ca [17]. It is confirmed that calcium Ca, cobalt (Co), copper (Cu), magnesium (Mg) and manganese (Mn) ions are co-factors of enzymes, therefore they are interchangeable, which also confirms the important role of Mn, Ca and Mg in the foam structure formation from the beer's protein structures [18]. The competitive nature of Ca, Mg and Mn ions with respect to the protein molecules of grain catalysts thus explains their important role in the formation of the beer foam structure.

4 Conclusions

The conducted studies allowed us to conclude that, in addition to protein compounds, non-starch polysaccharides and catechins, the structure of beer foam is affected by ions of mineral elements (Ca, Mg, Mn, Co, Na), which, depending on their position (presumably) in the thiol nitrogen structure are responsible for the colloidal film structure strength on the carbon dioxide bubble surface, or for its elasticity.

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