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DYNAMICS OF ACIDITY (pH) AND TEMPERATURE DURING THE PRODUCTION OF TRADITIONAL MACEDONIAN GALICHKI KASHKAVAL

SUMMARY

The original technology and specificity of the raw milk are the most important characteristics for traditional cheeses. The present study aimed to investigate the acidity and temperature in the production processes in the first two days of the production of the traditional Galichki kashkaval during the summer period in a cheese plant in Galichnik village. The average chemical composition of sheep milk was examined. Acid development during renneting, syneresis, pressing, chedarization, stretching and molding was investigated. The average active acidity of raw sheep milk after renneting was pH 6.54 ± 0.084 and coagulation temperature of 37.96 ± 0.104°C and after curd pressure average pH was 6.23 ± 0.014, while the temperature was 25.18 ± 0.177°C. After chedarization the pH of the ripened curd was in range of 5.45 ± 0.013 and the temperature of 19.08 ± 0.149°C, after curd cutting pH was 5.32 ± 0.006 and a temperature of 19.08 ± 0.058°C and before stretching in hot brine was 5.28 ± 0.005 with a temperature of 19.77 ± 0.117°C. These acid and temperature development enable proper plasticization of the cheese curd. The obtained values for the microclimate parameters in the traditional kashkaval ripening storage, the relative humidity of 77.21 ± 0.159 % and the ambient temperature of 15.95 ± 0.033°C showed a statistically significant influence on the active acidity of the product. Only lactose showed a statistically significant influence on the active acidity and temperature of the intermediate products in the different stages of the production of the traditional kashkaval.

Keywords: active acidity, temperature, sheep milk, traditional kashkaval

INTRODUCTION

Development of acidity through the production process is an important parameter in cheese production. Acidity regulates the level and degree of

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syneresis, the degree of solubility of minerals during the production process, as well as the composition and pH of the final product. The concentration of hydrogen ions (pH) is a critical factor in several stages of cheese production and ripening.

Renneting parameters in cheese made of sheep milk are affected by physico-chemical properties, including pH, larger casein micelle, more calcium per casein weight, and other mineral contents in milk, which cause differences in coagulation time, coagulation rate, curd firmness, and amount of rennet needed (Park, 2007).

Each type of cheese has a characteristic pH which is an indication of the conversion of lactose to lactic acid in the process of cheese production (Lawrence, 1993). Acidity also prevents the growth of pathogenic bacteria, affects the activity of the coagulant during production and rippening, stimulates syneresis and affects the activity of enzymes during maturation. This affects the texture and taste of the cheese. Coagulation temperature and concentration of rennet are one of the factors which greatly influence the rennet-induced coagulation of milk during cheese formation.

One of the traditional cheeses with long history which is produced on mountain Bistra in the Republic of North Macedonia is kashkaval from the region in Galichnik. The specific climatic conditions, hilly mountain as well as the sheep breeding tradition, are excellent preconditions for the production of the cheese in this region (Srbinovska and Santa, 2017). Galichki kashkaval is produced traditionally from raw sheep's milk without the addition of starter cultures (Santa and Srbinovska, 2014). It belongs to the „pasta filata" cheeses which means "stretched curd", that refers to a unique plasticization and stretching process in these types of cheeses.

There is a very small amount of available information on the pH and temperature dynamics during the production of Macedonian kashkaval. The purpose of this study was to examine the acidity (pH) and the temperature in the first two days of the production of traditional Galichki kashkaval during the summer period in a cheese plant near village Galichnik.

MATERIAL AND METHODS

Kashkaval in the cheese plant in Galichnik is produced during the summer, from the second half of June to the first half of August. The dairy plant has a daily capacity of 800 liters of milk for processing into kashkaval. For the production of Galichnik cheese, sheep's milk is used from its own farm, from morning and evening milking.

Dynamics of acidity and the temperature were controlled in different stages during production, as follows: raw milk reception; renneting; cutting and stirring the coagulum; before pressing the curd; after pressing the curd; during the curd ripening (chedaring); curd on pieces; before stretching the curd in hot brine; after kneading and molding, immediate after pulling the „navel" from the cheese and after removing the mold (next day).

The active acidity (pH-value) measurement was performed with a pH meter - Mettler Toledo. The temperature control of the product was performed with a calibrated alcoholic thermometer.

The following parameters were analyzed in raw milk: fat, protein, lactose and dry matter on Milk analyzer Lactoscan SA; active acidity pH - pH-meter Mettler Toledo; titration acidity - ° SH (titration Soxhlet-Henkel). The cheese composition was analyzed by standard methods: total solids by standard drying method at 102±2ºC (IDF Standard 4A: 1982), fat (Gerber method), protein (Kjeldahl, IDF 20B:1993), salt, the contents of moisture on a fat free basis (MFFB) and fat in the dry matter (FDM) were calculated (Codex, 1978).

RESULTS AND DISCUSSION

Chemical parameters of sheep's milk used for the production of kashkaval

The average chemical composition of raw sheep milk that was used for the production of Galichnik kashkaval are shown in Table 1. The results are in accordance with the Rulebook on raw milk quality requirements (Official Gazette no. 96/2011, of the Republic of N. Macedonia).

Table 1. Chemical composition of raw sheep milk (%)

Parameter (n=90)	$\overline{x}$	**STDV**	$S_{\overline{x}}$	**Min**	**Max**
Fats	8.10	0.981333	0.126	5.81	9.72
Proteins	5.56	0.681768	0.088	3.79	6.41
Lactose	3.96	0.482478	0.062	2.71	4.56
Solids non fat	11.053	1.341408	0.173	7.57	12.71

Similar results regarding the milk fat content were obtained by Mioč *et al.* (2009), Gonzalo *et al.* (1994) and Pavić *et al.* (2002). Dozet *et al.* (1979) and Prpić *et al.* (2003) showed lower fat content in sheep milk 7.3 ± 1.47 % and 7.81 ± 0.84 %. accordingly.

Mioč *et al.* (2009) found that the average protein content during lactation was 5.89± 0.02%. According to the studies of Prpić *et al.* (2003), proteins in sheep milk in the same period were 5.59 ± 0.54% which are similar with our results. Pavić *et al.* (2002) found higher results which ranged from 5.94 ± 0.05% to 6.46 ± 0.14%.

The average content of solids non fat in the milk was 11.05%, with variations from 7.6% to 12.71%. Antunac *et al.* (2007) found slightly lower values for the solids non fat of East Friesian sheep milk (10.54±0.03% to 11.00 ± 0.03%).

In our studies, the lactose content showed a slightly lower content compared to the studies of other authors. Thus, in the studies of Antunac *et al.* (2007) the average value of lactose in sheep milk in the mainland of Croatia ranged from 4.89 ± 0.01% to 4.6 ± 0.01% for the same lactation period. According to Mioč *et al.* (2009), the average lactose content during lactation in the sheep breed *creska* was 4.39 ± 0.01%.

Dynamic of pH acidity and temperature during the production process

The average active acidity of the examined raw sheep milk used for the production of Galichki kashkaval was 6.63 ± 0.083 in accordance with the Rulebook on requirements for the quality of raw milk ("Official Gazette" No. 96/2011, of the Republic of Macedonia), where the prescribed pH value for sheep milk is from 6.5 to 6.8. Similar results are reported by Pavić *et al.* (2002), Prpić *et al.*, (2003) and Park *et al.*, (2007) and Samelis *et al.*, (2019). The average temperature of the raw sheep milk in the examined period was 26.91 ± 0.261 ° C. These values for the active acidity indicate a certain quality of the raw material due to the relatively good hygiene in the milking process of the sheep.

Table 2. Dynamic of pH acidity and temperature during the production process

No	Production phases	n	pH	t (°C)
			($\overline{x} \pm S_{\overline{x}}$)	
1	Raw milk	204	6.63 ± 0.083	26.91 ± 0.261
2	Renneting	139	6.54 ± 0.084	37.96 ± 0.104
3	Cutting and stirring the coagulum	128	6.47 ± 0.016	36.64 ± 0.235
4	Curd before pressing	100	6.49 ± 0.084	34.85 ± 0.078
5	Curd after pressing	415	6.23 ± 0.014	25.18 ± 0.177
6	Chedaring (baskija)	450	5.45 ± 0.013	19.08 ± 0.149
7	Baskija, slice cuted	560	5.32 ± 0.006	19.08 ± 0.058
8	Baskija before stretching in hot brine	542	5.28 ± 0.005	19.77 ± 0.117
9	Formed cheese in wheel	110	5.05 ± 0.014	52.45 ± 0.417
10	Cheese	105	5.36 ± 0.012	19.51 ± 0.506

The average coagulation temperature was 37.96 ± 0.104 ° C. The amount of added rennet and the coagulation temperature influenced the development of acidity in sheep milk. Based on the analyses, it was found that in case of milk with low acidity (high pH value of 6.65), it is necessary to increase the amount of added rennet and the coagulation temperature needs to be higher (about 39.2 ° C) to complete the coagulation in about 45 minutes. By shortening the renneting time, a slightly firmer curd can be obtained, and the whey can be separated faster. In the examined samples of the stirred coagulum, the average pH value was 6.47±

0.016, while the average temperature was 36.64 ± 0.235 ° C. Experiments have shown that curd with higher acidity (pH about 6.35) requires rapid mechanical processing of the grains to make the syneresis more intensive, while the curd with law acidity (pH – 6.6) has weak consistency. Curd acidification to a certain extent is of importance since it results in the characteristic fibre-like structure of the final cheese (Alichanidis and Polychroniadou, 2008). Delayed cutting of the coagulum, when it has reached a higher firmness, causes the faster separation of whey from the surface of the coagulum and reduces or completely stops the syneresis from the coagulum (Walstra, 2006).

The active acidity of the curd before pressing was measured at the time of processing the curd on the cheese desk. Based on the exeminations, was concluded that in case when the processing of the curd takes a longer time, the curd can get cool, which slows down the acidification, the curd grains lose their stickiness, and thus later the process of pressing slows down. The mean active acidity was 6.49 ± 0.084, with an average cheese dough temperature of 34.85 ± 0.078 ° C.

Dynamic of syneresis depends on the development of acidity, which determines the quality of processed curd. The results showed that the minimal pH of 5.46 and the temperature of 28.3 ° C in the curd after pressing occurs as a result of the low pH value of the milk intended for clotting, and in some cases due to improper processing of curd grains, resulting in improperly drained curd, with increased moisture and acidity.

The ripening of the curd (called Baskia) was at room temperature. The baskia then was slice cutted to separate the remaining whey and to obtain a uniform mass. In our study, the average pH of the cuted baskia was 5.32 ± 0.006, with an average temperature of 19,08 ± 0,058, while the average active acidity of the baskia before stretching under hot brine was 5.28 ± 0.005, with an average temperature of 19.77 ± 0.117 ° C, which means that lactic acid processes and changes in moisture content take place more evenly and allow the transformation of unplasticized curd into plasticized when immersed in hot water. The temperature of the hot brine was 73-75 ° C.

We have noticed that in case of lower active acidity (pH about 5.08 and temperature of 18.5 ° C) the curd plastication occurred and the curd became very crumble. On the other hand, in case at the maximum obtained pH value (about 5.48 and a temperature of 18.5 ° C), we noticed that the curd is too strong, processing in the hot brine is longer and generally does not stretch well. This is with accordance with Anifantakis (1991) who stated that the acidified curd is ready for further processing when its pH value is close to 5.2–5.3 for sheep's milk.

The average pH value of the cheese in the mold was 5.05 ± 0.014, while the average temperature of the cheese was 52.45 ± 0.417 ° C. The obtained results are in accordance with the studies of Law and Tamime (2010) and according them if the stretching is performed too fast and the temperature of the brine is too low, the temperature of the stretched curd will be low. Therefore, it will be

difficult to perform the kneading and stretching of the curd, which will result to breaking and fat and moisture loss.

The average pH value of the wheel of cheese without rind on the first day of production was 5.36 ± 0.012, with an average temperature of 19.51 ± 0.506 ° C. The results in pH were lower in coparison with the results reported by Santa and Srbinovska (2014), where the pH on the first day of ripening the average pH of the Galichki kashkaval was 5.47 ± 0.07. The pH values are in accordance with the results of Temizkan *et al.* (2014) on Kashar cheese made of ovine milk. Lower pH values were found in Kashkaval of Pindos cheese reported by Pappa *et al.* (2018).

Ripening temperature has a major influence on the rate of ripening and quality of cheese, and it is fairly characteristic of the variety (McSweeney *et al.*, 2017). The values of the ambient conditions in the room (relative humidity and room temperature) where the cheese was rippened in our research are shown in Table 3.

Table 3. Average values for the relative humidity and Temperature in the rippening room of the traditional kashkaval

	RH (%)	**t (^{o}C)**
	($\overline{x} \pm S_{\overline{x}}$)	
Kashkaval ripening room	77,21 ± 0,159	15,95 ± 0,033

Table 4. Mean values for chemical composition of the final product – traditional Galichki kashkaval (%)

Parameter (n=3)	**mean**	**SDEV**	**CV(%)**
Total solids	60.813	0.833	1.370
Moisture	39.187	0.833	2.127
Fats	26.017	0.975	3.748
Protein	27.847	2.086	7.492
Fat in dry matter	42.772	1.022	2.389
Moisture on a fat free basis	52.963	0.437	0.825
Lactose	1.003	0.095	9.473
Salt	2.307	0.615	26.662

Chemical parameters of the Galichki kashkaval

After six months of production, the chemical composition of the final product was analysed. According to the data shown in Table 4, it can be seen that the dry matter content is 60.813 ± 0.833% and the moisture content is 39.187 ± 0.833%.

Moisture on a fat free basis wass 52.963 ± 0.437%. Higher results regarding the fat content of the Galichki kashkaval were reported by Santa and Srinovska (2014). Similar fat and salt values to the present study but lower protein content was reported for 180-day Kashkaval of Pindos cheese (Pappa *et al.*2020). According the cheese classification of Codex Alimentarius, we can conclude that Galichki kashkaval belongs to the group of hard cheeses.

Interaction of pH and T on the chemical composition of milk and final product

According the results from the multivariate regression statistical model, presented in Table 5. the production process of traditional Galichki kashkaval showed statistically significant influence at the level of p <0.001 on the active acidity (pH-value) and the temperature of the intermediate products at different stages of the production of kashkaval.

Table 5. Interaction of pH and T on the chemical composition

Sources of variation	**Degrees of freedom**	**pH[a]**	**T[b]**
Model[a,b]	18	145.062,738***	9.894,192***
Product	10	2.434,865***	1.944,972***
Fat (F)	1	0,186^{NS}	1,589^{NS}
Latose (L)	1	10,785**	9,063**
Protein (P)	1	0,604^{NS}	1,942^{NS}
Dry matter (DM)	1	1,801^{NS}	0,196^{NS}
Relative humidity in ripening room (F-RH)	1	38,604***	5,846*
Ambient room temperature (F_T)	1	42,420***	4,688*
F x P x L x DM	1	56,100***	0,069^{NS}
F-RH x M_T	1	38,808***	5,223*
Error	1.596	0,020	7.166
Total	1.614		
[a]R^2 = 0,999; [b]R^2 = 0,991			

*** statistically significant at the level p<0,001

** statistically significant at the level p<0,01

* statistically significant at the level p<0,05, ^{NS} statistically insignificant

From the chemical composition of raw milk, only lactose showed significant influence at the level of p <0.01 on the active acidity and temperature of the intermediates at different stages of the production of traditional kashkaval.

The interaction of the components of raw milk (fat, protein, lactose and dry matter) showed a high significant influence at the level of p <0.01 on the active

acidity of the intermediates at different stages of the production of traditional kashkaval. However, the chemical composition of raw milk did not show a statistically significant influence on the temperature of the intermediate products. The microclimatic conditions in the cheese ripening warehouse (relative humidity and air temperature) and their interaction showed a statistically significant influence at the level of $p < 0.001$ on the active acidity of the product, while they have a statistically significant influence at the level of $p < 0.05$ on the temperature of intermediates at different stages of the production of the kashkaval

CONCLUSIONS

Galichki kashkaval is the most famous traditional cheese in North Macedonia. In this study the acidity and temperature in all steps of the production process are presented. Based on the obtained results, there is a positive impact on the dynamics of active acidity and temperature on the product, as a result of the activity of microorganisms in lactic acid fermentation, which leads to a decrease in pH at certain stages in the production process. In the maturation phase, the pH gradually increases as a result of protein degradation.

According the cheese classification of Codex Alimentarius, Galichki kashkaval belongs to the group of hard cheeses.

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