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Рекомендовано до публікації д-ром техн. наук В.М. Михайловим.
Отримано 01.08.2014. ХДУХТ, Харків.

УДК 637.338.4:637.353:544.352.2

INNOVATIVE TECHNOLOGY OF MELTED CHEESE PRODUCTS WITH THE USE OF FREEZING AND MECHANICAL DESTRUCTION

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This scientific work is devoted to the development of innovative technology of melted cheese products that includes the use of complex impact of freezing and mechanical destruction on raw material, mutual influence of which during the preparation of hard rennet cheeses for melting results in destruction of paracaseinatecalciumphosphate complex, its mechanolysis to separate amino acids, conformational changes of protein molecules that allows excluding the use of salts-melters. The innovative technology, process flowsheet, receipts of cheese-vegetable fillings for "Pancake" confectionery products, cheese sauces-dressings, melted cheese spreads without salts-melters have been developed.

Keywords: *melted cheese products, freezing, mechanical destruction, rennet cheeses, salts-melters.*

ІННОВАЦІЙНА ТЕХНОЛОГІЯ ПЛАВЛЕНИХ СИРНИХ ПРОДУКТІВ З ВИКОРИСТАННЯМ ЗАМОРОЖУВАННЯ І МЕХАНОДЕСТРУКЦІЇ

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Розроблено інноваційну технологію плавлених сирних продуктів, що включає використання комплексного впливу на сировину заморожування і механодеструкції, спільний вплив яких під час підготовки твердих сичугових сирів до плавлення призводить до деструкції параказеїнаткальційфосфатного комплексу, його механолізу до окремих амінокислот, конформаційних змін молекул білка, що дозволяє виключити застосування солей-плавильників. Розроблено інноваційну технологію, технологічну схему, рецептуру сирно-овочевих начинок для кондитерських виробів «Панкейк», сирних соусів-дресингів і пастоподібних плавлених сирів без солей-плавильників.

Ключові слова: *плавлені сирні продукти, заморожування, механодеструкція, сичугові сири, солі-плавильники.*

ИННОВАЦИОННАЯ ТЕХНОЛОГИЯ ПЛАВЛЕНЫХ СЫРНЫХ ПРОДУКТОВ С ИСПОЛЬЗОВАНИЕМ ЗАМОРАЖИВАНИЯ И МЕХАНОДЕСТРУКЦИИ

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Разработана инновационная технология плавленых сырных продуктов, включающая использование комплексного воздействия на сырье замораживания и механодеструкции, совместное влияние которых при подготовке твердых сычужных сыров к плавлению приводит к деструкции параказеинаткальцийфосфатного комплекса, его механолизу до отдельных аминокислот, конформационным изменениям молекул белка, что позволяет исключить применение солей-плавителей. Разработана инновационная технология, технологическая схема, рецептуры сырно-овощных начинок для кондитерских изделий «ПанКейк», сырных соусов-дрессингов и пастообразных плавленых сыров без солей-плавителей.

Ключевые слова: *плавленые сырные продукты, замораживание, механодеструкция, сычужные сыры, соли-плавители.*

Introduction. It is known that melted cheese products are very popular with the population all over the world. It can be explained by its high gustatory characteristics, nutrition value and simplicity of processing. They are a valuable source of important functional nutrients for the human body such as complete proteins, essential amino acids, lipids, minerals, B-group's vitamins, etc. However, they have a low content of biologically active substances and reduced shelf life. The range of melted cheese products with high content of biologically active substances is limited in Ukraine. The difficulties of their production with the use of rennet cheeses as raw material are conditioned by the fact that they have slightly soluble paracaseinatecalciumphoshate complexes (PCCPC) in which the polypeptide chains are so intertwisted with each other with the help of calcium bridges and phosphoamide disulfide bonds, hydrogen as

intramolecular and intermolecular and also other links. It prevents its peptization and dissolving during the melting cheeses and receiving homogeneous fluid mass. Besides, protein peptization is slowed down by a high content of lipids which together with protein form compound lipidprotein calciumphoshate complexes. One of the main technological operations during melted cheese processing is softening cheeses, receiving homogeneous fluid mass while heating with the presence of salts-melters. The product's pasteurization takes place at the same time. Traditionally, different salts-melters such as salts of citric acid, pyrophosphates, phosphates and other substances that are harmful for the human body are used in melted cheeses production. They are used for increasing PCCPC's peptization, softening and imparting the fluidity to cheese mass during the melted cheeses production in an amount of 30-100 kg per 1 tone of the product. Therefore, it is the search of technological methods aimed at disaggregation, destruction and hydrolysis of polypeptide chains PCCPC of hard rennet chesses, increasing their solubility – peptization, receiving homogeneous fluid cheese mass in order to reduce the amount of salts-melters during melted cheeses production is of current interest. The freezing and the low-temperature grinding were used as such processing methods. The processes in question haven't been previously used in melted cheeses production. There are no published data on this issue.

The Scientific school of professor R. Pavlyuk investigated the use of cryogenic grinding, processes of mechanical activation (without cold) and freezing in food industry while obtaining of fine dispersed powders and homogeneous pastes from fruits, berries, vegetables, medical and spicy-aromatic herbal materials, bee products for 25 years. For the first time in the world practice new phenomena and effects were revealed, mechanisms were disclosed and it was shown that mechanical activation and freezing processes lead to significant destruction and disaggregation of biological systems – biopolymers BAS as well as biopolymers (proteins, polysaccharides, pectins) that result in «fortification» effect and more complete extraction of low molecular biologically active substances such as vitamins, free amino acids, phenolic compounds mono- and disaccharides, soluble pectin substances, etc. from the raw materials [2, 3].

Some scientists have found that cryogenic grinding of gelatin led to significant change of its original characteristics and to dissolving at a room temperature. It was also found that the use of mechanical activation processes during the polymers grinding led to reducing their molecular weight, formation of new functional groups and chains, change in their solubility. Based on above mentioned research, it can be assumed that the use of the processes of freezing and cryo- and mechanical destruction leads to destruction, disaggregation, mechanolysis and peptization of PCCPC of hard rennet cheeses, that allows melting them better with reduced amount of

salts-melters. The ongoing search for technological methods aimed at reducing the amount of salts-melters in melted cheese production takes place in the dairy industry. The leading scientists of Ukraine and Russia managed to reduce their number by 20% [2]. The practicability of developing technology of melted cheeses and melted cheese products with reduced amount of salts-melters and enriched with natural plant BAS was stipulated by the works of Ukrainian and foreign scientists such as L. Shatnyuk, B. Spirichev, R. Pavljuk, V. Pogarskaya, A. Bezusov, A. Rudavskaya, N. Zakharova, L. Ostroumov etc.

This scientific work studies the affect of freezing and mechanical destruction on the changing paracaseinatecalciumphoshate complex of rennet cheeses, transformation of related protein amino acids to the free form, conformational changes in the protein molecules during their preparation for the melting with the aim of reducing or eliminating the use of salts-melters in technology of melted cheeses.

Objects and research methods. Objects of research are technological processes in the melted cheese production and cheese product manufacture.

Research methods such as standard chemical, physico-chemical, ion-exchange chromatography and mathematical processing of the experimental data with the use of computer technologies have been used. This research was conducted at the Department of Technology of processing fruits, vegetables and milk of The Kharkiv State University of Food Technology and Trade (KSUFT) on the base of the laboratory of «Innovative cryo- and nanotechnologies of herbal additives and healthful products,» and with the use of an experimental base of laboratory of quality assessment of feed and animal products of the Institute of Stockbreeding of forest-steppe and marshy woodlands of UAAN as well as l plant conditions of LLC «Forest Fairy Tale», SPF «FIPAR», SPP «Cryas-1», SUIP «Polus LTD».

Results and their discussion. In this research the freezing was performed in a traditional way which includes a refrigeration chamber or a quick-freezing machine till a final core temperature -18° C. Grinding (mechanical destruction) was made with the use of the cryogenic chopper at a low temperature -10...-18° C to a particle size of 40...60 microns or less, that was controlled with the use of a binocular microscope Granum R 5003 with the scale in the micrometer and nanometer range. The microscope is equipped with a video camera and software.

It was shown that freezing and mechanical destruction lead to disaggregation and destruction of lipoprotein complexes, mechanical protein destruction, increasing the mass fraction of free amino acids (1,1...2,9 times) in relation to their basic amount in the HRC (Table 1, picture 1).

A part of α-amino acids is transformed from a bound condition into free amino acids. So, the amount of free amino acids such as alanine, valine, phenylalanine, increases most of all and amounts to 2,8...2,9 times, the

amount of proline and aspartic acid –in 2,5 times, the amount of threonine, glycine, isoleucine, leucine, histidine, and arginine is increased in 1,9...2,0 times. The smallest amount of free amino acids was found in glutamic acid, tryptophan, serine, and cysteine. Various degree of formation of different amino acids during the protein mehanolysis is apparently related to the specificity of the amino acid composition of proteins of rennet cheeses. The mechanism of this process is apparently related to the increased resistance of PCCPC to heating, acid hydrolysis, dissolving, peptization, that is caused by the presence of Ca and P in their structure.

Table 1

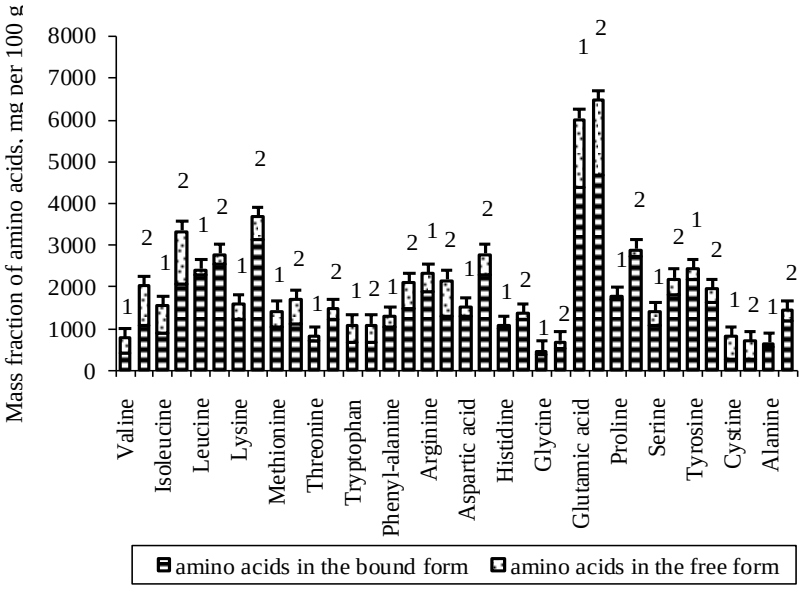
The content of bound and free amino acids of the protein of hard rennet cheese after freezing and mechanical destruction (n=3, P≥0,95)

Title of amino acid	Bound amino acids of hard rennet cheese				Free amino acids of hard rennet cheese			
	in source cheese, mg per 100 g	after freezing and mechanical destruction, mg per 100 g	% relatively to original	increasing to source, times	in source cheese, mg per 100 g	after freezing and mechanical destruction, mg per 100 g	% relatively to source	increasing to source, times
Valine	450	1080	240,0	2,4	340	960	282,3	2,8
Isoleucine	920	2100	228,0	2,3	650	1250	192,0	1,9
Leucine	2300	2550	111,0	1,1	130	250	192,0	2,0
Lysine	1240	3140	253,2	2,5	360	550	153,0	1,5
Methionine	1040	1120	108,0	1,1	400	600	150,0	1,5
Threonine	710	1240	175,0	1,7	120	240	200,0	2,0
Tryptophan	700	700	100,0	1,0	400	400	100,0	1,0
Phenyl-alanine	1070	1480	138,0	1,4	230	640	278,0	2,8
Arginine	1910	1300	67,9	-	430	870	202,0	2,0
Aspartic acid	1330	2310	174,0	1,7	200	490	245,0	2,5
Histidine	1010	1240	123,0	1,2	80	150	188,0	1,9
Glycine	410	560	137,0	1,4	70	140	200,0	2,0
Glutamic acid	4410	4700	107,0	1,1	1620	1790	110,0	1,1
Proline	1720	2760	160,0	1,6	60	150	250,0	2,5
Serine	1100	1840	167,0	1,7	310	370	119,0	1,2
Tyrosine	2210	1630	73,7	-	240	340	142,0	1,4
Cystine	300	300	100,0	1,0	540	420	-	-

Alanine	580	1200	207,0	2,1	90	260	289,0	2,9
TOTAL:	23410	31250	33,5	1,33	6270	9870	57,4	1,57

These elements in the complexes are linked with the help of calcium bridges, phosphoamide links, and also with the significant amount of lipids that compose protein-lipid complexes that inhibits the proteins hydrolysis to separate amino acids

There is also a more complete extraction of the protein from the lipid-protein's complexes – on 30-35% (Table 1). It was shown that both freezing and mechanical destruction of rennet cheeses intensify the process of protein-lipid complexes destruction significantly and contribute to mechanical destruction (mechanolysis) of proteins to separate free amino acids. So, 55-57% of amino acids transform into free form due to the removal of low molecular weight compounds – aminoacids (Fig. 1). The mechanism of this process is related to the fact that during the mechanical grinding as a result of mechanical cracking there are such critical energy potentials in the biopolymer chain of protein that lead to cleavage and destruction of peptide and hydrogen bonds, cleavage of calcium bridges and partial destruction of protein molecules to free amino acids. So, there are mechanical destruction, peptization and deterioration of protein molecules in rennet cheeses (Table 2, 3).



Picture 1. Changing of paracaseinatecalciumphoshate complex and trans-formation of protein's bound amino acids of hard rennet cheeses to a free

form under the influence of freezing and mechanical destruction: 1, 2 – hard rennet cheese source (1) and after freezing and mechanical destruction (2)

Table 2

The content of hydrophilic and hydrophobic amino acid residues in protein molecules of hard rennet cheese after freezing and mechanical destruction (n=3, P≥0,95)

Aminoacid	Mass fraction of protein's bound amino acids,%		The degree of hydrophobicity, ΔF kJ/mol	The degree of hydrophobicity of bound protein's amino acids (ΔF kJ/mol)	
	source hard rennet cheese	hard rennet cheese after freezing and mechanical destruction		source hard rennet cheese	hard rennet cheese after freezing and mechanical destruction
Hydrophilic amino acid's residues					
Alanine	2,48	3,84	3,05	7,56	11,71
Arginine	8,16	4,16	3,05	24,89	12,69
Cystine	1,28	0,96	2,71	3,47	2,60
Glutamic acid	18,84	15,04	2,50	47,10	37,60
Aspartic acid	5,68	7,39	2,26	12,84	16,70
Threonine	3,03	3,97	1,84	5,58	7,30
Serine	4,7	5,89	0,17	0,80	1,00
Glycine	1,75	1,78	0,0	0	0
Total:	45,92	43,03		102,24	89,60
Hydrophobic amino acid's residues					
Valine	1,92	3,46	7,06	13,55	24,43
Isoleucine	3,93	6,72	12,4	48,73	83,33
Leucine	9,82	8,16	10,10	99,18	82,42
Lysine	5,3	10,05	6,27	33,23	63,01
Methionine	4,44	3,58	5,45	24,20	19,51
Tryptophan	3,0	2,24	12,50	37,50	28,0
Phenylalanine	4,57	4,74	11,10	50,73	52,61
Histidine	4,31	3,97	5,85	25,21	23,22
Proline	7,35	8,83	10,85	79,75	95,80
Tyrosine	9,44	5,22	12,00	113,28	62,64
Total:	54,08	56,97		525,37	534,97
Hydrophilic and hydrophobic amino acid's residues					
Total:	100,0	100,0		627,61	624,57
The relation of sum of hydrophilic amino acid's residues to a sum of hydrophobic					

amino acid's residues	0,85	0,76			

Table 3

Comparative characteristics of the protein molecules of the basic and frozen and low-temperature ground rennet cheese (n=3, P≥0,95)

Parameter	Hard rennet cheese	
	source	after the processing
Content of polar amino acid's residues, Cn,%	45,92	43,03
Content of non-polar amino acid's residues, CH_n%	54,08	56,97
Relation $C_n/C_{нп}$	0,85	0,76
Molecular radius, r_o, mkm	$0{,}2265 \cdot 10^{-2}$	$0{,}2474 \cdot 10^{-2}$
Radius of molecule's kernel, r, mkm	$0{,}1765 \cdot 10^{-2}$	$0{,}1974 \cdot 10^{-2}$
Volume of molecule, V, mkm^3	$0{,}04 \cdot 10^{-6}$	$0{,}08 \cdot 10^{-6}$
Indicator of filling molecule's kernel with hydrophobic residues, b (on schedule)	0,90	0,45
Shape of protein's molecule	 oblong ellipsoid ($b > b_s$)	 permolecular structure ($b<b_s$)

The affect of freezing and mechanical destruction on the content of hydrophilic and hydrophobic amino acid residues in protein molecules of rennet cheese has been analyzed in this research. The results are presented in the table 2 below.

It was determined that during freezing and mechanical destruction alongside with destruction of the part of the protein to separate amino acids and simple peptides a reduction of mass fraction of hydrophilic amino acid residues (C_n), an increase of hydrophobic residues ($C_{нп}$) and the decreasing of relation between them ($C_n/C_{нп}$) take place in protein molecules (Table 2).

The obtained results allowed conducting comparison of the size and the shape of protein molecules of basic rennet cheese and after freezing and low temperature grinding according to the theory of Nobel laureate E.G. Fisher (Table 3).

It has been determined that freezing and mechanical destruction lead to increasing radius, volume of protein molecule, radius of its core, and also to reduction of filling of the core with hydrophobic residues. Moreover, the shape of protein molecules also changes. According to the theory of E. Fisher molecules of the original hard rennet cheese have the form of oblong ellipsoids, and after freezing and mechanical destruction they take a form of permolecular structures (Table 3). It increases availability, solubility, peptization of protein molecules during the preparation of rennet cheese for melting and obtaining homogeneous fluid cheese mass. Model experiments showed that the integrated use of freezing and mechanical destruction not only allows reducing the amount of salts-melters, but also eliminating them at all.

These technological methods of freezing and mechanical destruction were used in developing technology of melted cheese products (cheese and vegetable fillings for «Pancake» confectionery, cheese sauces-dressings, melted cheese spreads).

Conclusion and recommendations. As a result, it is shown that the use of freezing and intensive grinding (mechanical destruction) of rennet cheeses leads to significant destruction and disaggregation of gel protein structure, destruction of protein-lipid complexes, intensification of protein destruction and significant increase of mass fraction of separate free α-acids due to protein mechanolisys, conformational changes of protein molecules, that leads to exclusion of using salts-melters in production technology of melted cheeses and melted cheese products.

The technology of melted cheeses and melted cheese products was developed, which includes the use of the complex affect of freezing and mechanical destruction on raw materials, the mutual affect of which during the preparation of rennet cheeses for melting leads to destruction of paracaseinatecalciumphoshate complex, conformational changes of protein molecules was scientifically substantiated and developed n the basis of theoretical and experimental research. It gives the opportunity to eliminate the use of salts-melters and to obtain the homogeneous cheese mass during melting.

The regulatory documentation for the new types of melted cheeses and melted cheese products was created. This documentation has been integrated in a production environment. The new types of cheese-vegetable fillings for confectionery "Pancake" were introduced into series manufacturing.

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Рекомендовано до публікації д-ром техн. наук В.М. Михайловим.
Отримано 1.08.2014. ХДУХТ, Харків.