Innovative low temperature methods of milk whey processing

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Abstract. Reasonable use and waste-free deep processing of milk raw materials represent serious issues for the most milk processing companies. Therefore, processing of milk whey and manufacturing products of full biological value is a promising trend. Its resources are enormous, exceeding 5 million tons per year, although only 40 % are recycled throughout the country. In addition, this problem is of high environmental importance. Milk whey is a product of cheese, cottage cheese and casein manufacturing. The chemical composition of milk whey is unique owing to biologically active peptides of whey proteins, which participate in physiological processes of human body. It contains 50 % dry milk substances and about 200 types of different compounds. Up to date engineering and technology processes aimed at the dehydration offer a solution to the problem of whey processing. The paper reports on low temperature technologies used in whey processing to produce protein concentrate. When freezing out water, a nutritionally valuable protein casein and albumin mass are concentrated. The cryoconcentration of milk whey on the inner surface of a crystallizer was carried out at a temperature of the heat exchanging surface minus 4 ± 2 °С. Chemical composition, physical, chemical, and organoleptic characteristics of the whey concentrate have been investigated. The chemical composition of the whey protein concentrate contains 20.19 % of dry substances, 12.80 % of protein, 2.87 % of whey proteins. The freezing out of water in the set conditions has brought about a 25-time increase of whey protein fraction. Therefore, a whey mass can be recommended as a source of animal protein in human diets.

1. Introduction

To date, dairy raw materials are thought to be relatively expensive for the state and their production – labour intensive, so advanced processing of milk and processed raw materials is economically efficient. For instance, milk whey is a product of cheese, cottage cheese and casein production. Further, it is divided into cheese, cottage cheese, casein whey and an ultra-filtrate with regard to an output product. Its composition and properties depend on a main product type and its production technologies [1, 2]. As estimated, it contains 50 % dry milk substances, up to 200 various compounds, i.a. finely divided milk fat, dissolvable nitrides, i.a. fractions of whey proteins, mineral salts, lactose, vitamins, ferment, and organic acids. Besides a high nutritive value, milk whey and its products are dietary and healthy.

A number of companies have been facing a problem of reasonable and waste-free whey use. Recently, a group of Russian scientists (A.G. Khramtsov, P.G. Nesterenko, A.A. Khramtsov, I.A. Evdokimov, S.V. Vasilisin, S.A. Ryabtseva, etc.) has been researching and developing innovative technologies in this field.
The research carried out at the Central Research Institute for Food and Health (Germany) is focused on biologically active whey peptides, which play a vital role in digestion, activate the secretion of enterohormones, and modulate the immune system [3-10]. The biological value of whey protein is similar to fish protein, being even higher than that of a main milk protein and wheat.

The concentration of essential sulfur-containing cysteine amino acid is quite high in fractions of whey proteins, being 7-19 times higher than in casein. Natural albumin and globulin of whey protein are similar to the chicken protein, which is thought to be ideal in terms of the nutritive value. Moreover, the number of free amino acids in cheese and cottage cheese whey is six to nine times higher than in milk.

A high nutritive value of lactose, its high concentration (70-90 % present in dry substances) is the reason for its extraction from whey and wide use in the food processing industry, in particular, in the production of a variety of milk sugar: raw milk sugar, edible milk sugar, refined milk sugar, and pharmacopeia milk sugar [1, 2, 11, 12].

Milk whey is eutherapeutic, having a health-promoting effect on human digestion, nerves, and cardiovascular system. In addition, it contains different minor nitrogen-containing compounds: lactoreffin, glycomacropeptides, lactoperoxidase, cytokines (growth factors), immunoglobulin, carnitin, and angiogenin. N.A. Tikhomirova extracted angiogenin ferment from the cheese whey in her research and emphasized its significant role for the human health due to the immune stimulation and catalytic effect on the blood vessel growth [7, 8, 9, 13, 14]. Milk whey and its components are almost completely digested.

It is reported on vast amounts of milk whey produced in the domestic and foreign food industry. On a global scale, around 20 million tons per annum of cheese is produced, the output of whey is estimated to be as much as 160 million tons. The dairy industry in economically developed countries (the USA, Canada, Germany, France, Sweden) processes 60 to 95 % whey recourses; whereas this factor in Russia represents approximately 40 % [15].

The basic spheres in the worldwide industrial processing and use of milk whey are as follows: dry and concentrated milk whey, demineralized milk why, concentrates of whey proteins, and lactose.

Here, the U.S. and EU countries supply 70 % whey and its products to the global market. In 2018 the U.S. increased their market share of whey products by 29 % (465 thousand tons) and got ahead of EU countries. A target market of whey products is Asia, where China imports 37 % of the global volume. Mexico represents the second important market of whey products, having increased its import share to 72 thousand tons in 2018. The volume of whey product export from EU countries was estimated to be 452 thousand tons in 2018, 30 % were exported form the Netherlands, France, Poland, and Germany [16, 17].

A mainstream in whey processing is production of highly nutritive and user friendly dry or concentrated whey, containing nearly all components of raw materials. These products are in high demand of manufacturers and consumers [1, 2, 18, 19, 20, 21].

Innovative concentration technologies allow efficient removing of excessive water, increasing a share of useful nutrients and make possible the output of a greater variety of products. An analysis of existing dehydration processes has revealed the most efficient ones to manufacture a high-quality product as well as reduce power consumption.

Whey is processed in various ways, such as concentration, drying, electromembrane (electrodialysis, electroactivation) and baromembrane processes (ultra-filtration, nano-filtration, reverse osmosis) [2, 22, 23]. For instance, low temperature regions are used to remove water from an object via freezing out. This method is called cryoconcentration. Freezing out is a method to produce protein for the manufacturing of casein and albumin mixture, protein concentrates containing polysaccharides (pectin, chitozan), and whey protein concentrates. It is a low temperature region that makes it possible to preserve properties of raw products, avoiding protein denaturation in milk whey and preserving components labile to temperatures [24 - 33].

Concentrates of whey proteins represent a highly demanded product on the global market. Similarly, the present day Russian market enjoys a high demand for these products, but whey
ingredients are hardly manufactured in Russia and are imported from abroad despite a significant potential of own raw materials [14, 15, 34].

Besides concentrates, products are popular, which are manufactured from protein concentrates as a principal component or as an ingredient in existing and being developed technologies of innovative dairy products.

To sum up, this research field represents a future subject for a comprehensive study and outlines aims and objectives of further work.

2. Purpose of research

Low temperature manufacturing of concentrates from milk whey is suggested to be a solution to a critical problem of dairy industry, i.e. recycling of processed milk raw materials. Cryoconcentration allows the extraction of proteins from milk whey – the most valuable component, avoiding unintended denaturation of protein fractions and preserving valuable components liable to temperatures [25, 26].

The study aims to analyze technological factors of milk whey cryoconcentration in manufacturing whey protein concentrates, and quality control.

3. Object of research

For the purpose of research we analyzed milk whey produced when manufacturing of cottage cheese in milk processing companies, such as ООО “МПО “Скоморошка””, SHPK “Подворье”, ООО “Натурное молоко”. These companies produce whey through the acid coagulation of milk proteins; a pasteurization temperature of a normalized mixture is set 78-80 °C, quick ripening intensifies coagulation and separating of whey from a curd. Whey is separated via self-pressing in a pool. The study was focused on a protein whey fraction, a concentrate of whey protein was extracted from a liquid phase of milk whey via freezing.

4. Materials and methods

In the study we explored chemical composition, organoleptical, physical and chemical properties of input milk whey produced by different manufacturers. Milk whey under study was assessed according to quality criteria stated in GOST (Russian State Standard) 34352-2017 “Milk whey – raw materials. Technical conditions” and in TR CU (Technical Regulation of Customs Union) 033/2013 [35, 36].

A content of dry substances in whey, in the unfrozen portion of water phase and in the frozen whey portion was estimated according to GOST 3626-73 – a sample was dried up in a drying chamber up to a constant weight at a temperature of 105°C. A fat content was measured following the recommendations of GOST 5867-90 by the Gerber method, a protein content was determined with the help of refractometry according to GOST ГОСТ 25179-90, a carbohydrate content (lactose) – according to GOST Р 54667-2011 “Milk and milk processing products. Assessing methods of sugar content”.

A chiller tank with a pre-heated cooling agent (minus (8...10) °C) was filled up with whey cooled to a temperature of 1 °C to produce a whey protein concentrate. The cryoconcentration of milk whey was carried out on the inner surface of a chiller, a temperature of heat exchanging surface was set minus 4±2 °C.

To register and control process temperatures we used chromel-copel thermocouples, an analogue input module MBA 8, a measuring regulator ТРМ 202, an interface converter AC 4, and a PC.

Experiments and research into the separate freezing out were carried out using facilities of research laboratories at the Department of Animal Origin Products, and Department of Heating and Refrigerating Equipment, Kemerovo State University.

A technological process took 4.5 hours on average. As a chiller was operated, ice crystals formed on the inner side of a heat exchanging surface. In the central part of a processing tank there was a non-frozen part of a concentrated whey solution. Generally, this concentrate is a protein substance (whey protein concentrate). Once the freezing out was completed, it was removed through an opening on the bottom of the chamber. Crystallized water phase was collected in the chamber and defrosted.
Then we analyzed properties of a whey concentrate obtained. Titrated acidity was measured by the titrimetric method via titrating of alkali solution with a phenol-phthalein indicator according to GOST 3624-92; active acidity was determined by the electrometrical method, using a potentiometer \( pH \) in a range from 3.0 to 8.0 \( pH \) as recommended in GOST P 53359-2008. Organoleptical characteristics were assessed with the help of specially developed 10 points scale according to GOST 28283-89: taste and flavour - 5 points, optical characteristics and thickness - 3 points, colour - 2 points, a total maximum - 10 points.

A fraction composition of a whey protein concentrate was studied. An amount of protein was assessed by the Dumas method with the help of a protein nitrogen analyzer “Rapid N Cube”. A sample was burnt in a reactor; combustion products and forming nitrogen were recorded by a thermal conductivity detector. A content of general nitrogen was calculated via multiplying the value obtained by a coefficient of 6.38.

The Laemmli method was applied to research the distribution of protein fractions with the help of Poly-acrylamide Gel Electrophoresis. The fractionating was carried out using buffer solutions (0.066 M Tris, 0.1 % sodium dodecyl, 0.19 M Glycine). Samples were separated at an electrical current of 50 and 75 mA with the subsequent flushing gel and its treatment with three treating agents. To image gels, we used a UF-transilluminator TCP-20M. Data obtained were processed using a gel imaging system Vitran-Photo.

5. Results and Discussion
A quality of the concentrated product depends on raw materials, making necessary their investigation. High organoleptical characteristics require a certain quality of raw materials. The moisture is coupled with dry substances by certain bonding energy; therefore, a content of dry substances was analyzed both in raw materials and in the protein concentrate after water removal.

A nutritive value of whey is attributed to its chemical composition, so a number of components was determined (protein, fat, minerals, lactose); critical physical and chemical properties (titrated and active acidity, density, viscosity) were assessed. Research data are presented in Table 1.

| Table 1. Chemical composition and characteristics of milk whey manufactured in different milk processing companies |
|---|---|---|
| Organoleptical characteristics | Data on characteristics | OOO “MPO “Skomoroshka”” | SHPK “Podvorie” | OOO “Naturalnoye moloko” |
| Thickness and optical properties | Homogenous liquid with a small amount of protein sediment | Light green | Typical for milk whey, sourish |
| Colour | Water | 94.11 | 94.88 | 96.02 |
| Taste and flavour | Dry substances: | 5.88 | 5.12 | 3.98 |
| | Proteins | 0.5 | 0.6 | 0.4 |
| | Fats | 0.1 | 0.1 | 0.1 |
| | Carbohydrates | 4.7 | 3.7 | 2.6 |
| | Minerals | 0.5 | 0.7 | 0.9 |
| Chemical composition | Acidity: | 4.61 | 4.39 | 4.53 |
| | - active, units, pH | 73 | 87 | 63 |
| | - titrated, °Т | 1026 | 1027 | 1026 |
| Physical and chemical characteristics | Relative viscosity, Pаx | 1.1711×10^{-3} | 1.2531×10^{-3} | 1.2352×10^{-3} |
| | Kinetic viscosity, mm²/s | 1.2179 | 1.2355 | 1.2190 |
An analysis of the data obtained has pointed out a biological full value of raw materials; whey samples met all requirements specified in GOST 34352-2017, so were usable as a raw material to manufacture a whey protein concentrate in the chiller [18, 19].

A product of the freezing out of water represents a cottage cheese whey concentrate; its optical characteristics are given in Figure 1.

![Figure 1. Whey protein concentrate obtained via experimental water freezing out](image)

For quality assessment of the whey protein concentrate produced in its chemical composition, organoleptical physical and chemical characteristics as well as microbiological safety factors were investigated (Table 2).

| Characteristic                          | Data on characteristics                                  |
|-----------------------------------------|----------------------------------------------------------|
| Thickness and optical properties        | soft, loose, with visible particles of milk protein       |
| Colour                                  | Creamy white, uniform in the whole sample                |
| Taste and flavour                       | clear, sour-milk, no strange taste and flavour           |

| Component                               | Concentration of a component, % |
|-----------------------------------------|-------------------------------|
| Mass content of general protein         | 12.80                         |
| Content of whey proteins                | 2.87                          |
| Content of casein proteins              | 7.98                          |
| Content of general nitrogen             | 2.04                          |
| Content of non-protein nitrogen         | 0.313                         |
| Mass content of dry substances          | 20.19                         |

| Characteristic                          | Value            |
|-----------------------------------------|-----------------|
| Acidity:                                |                 |
| - active, units, pH                     | 4.35            |
| - titrated, °Т                          | 95              |
6. Conclusion

Organoleptical, physical and chemical characteristics of milk whey supplied by different dairy manufacturing companies were analyzed as potential raw materials for cryoconcentration; nutritive and biological value of the produced protein concentrate was assessed. Technological processes of separate freezing out in the chiller (minus 4±2 °C) allow the production of a full protein substance (concentration of milk protein – 12.8 %, mass content of dry substances – 20.19 %, and acidity – 95 °T). Therefore, whey concentrate is a valuable food product containing all necessary nutritive elements and recommended for the human diet.

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