PROCESS AND PRODUCTS INNOVATION IN DAIRY INDUSTRY BY USING DENSE CARBON DIOXIDE

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ABSTRACT

The most important products of the dairy industry are: pasteurized liquid milk, casein and products derived by casein, and whey protein concentrates. Among the different advanced processes developed for getting better quality products in comparison to those obtained with traditional technologies, the processes based on the use of dense carbon dioxide are preferable from many points of view. In particular: a) high quality extended shelf life liquid milk, pasteurized at the body temperature of the animal, can be obtained using a continuous process which is simpler and less expensive in comparison to competitive non-thermal pasteurization process based on membrane filtration; b) casein can be separated without adding any kind of contaminating biochemical substances to the milk and, consequently, preserving or improving the quality of the milk whey; c) whey proteins can be precipitated as native proteins which can be further processed to produce serum protein concentrate having significantly better nutritional, organoleptic and functional properties in comparison to the traditional whey protein concentrate. In this contribution, the above mentioned dense carbon dioxide processes will be described in some details along with the indication of the optimal operating conditions and the improved quality of the products.

Keywords: *Milk, Caseins, Whey Proteins, Serum proteins, Dense* CO_2 *, Microbial inactivation, Dairy Industry.*

INTRODUCTION

Supercritical fluid technology is widely used at industrial scale from more than 20 years, mainly in the food industry. In particular, dense supercritical carbon dioxide is used for industrial production of decaffeinated coffee, extraction of hop for the beer industry, extraction of a variety of essential and functional oils from a number of vegetable materials. In addition, supercritical water is used for many purposes including supercritical water oxidation for purifying waste water contaminated by very small amount of very polluting compounds. In the case of gaseous dense carbon dioxide (GDCD) the operating temperature is in the range between 35°C and 40 °C, while the pressure is in the range between 5 MPa and 35 MPa. For the supercritical water (SCW) the operating temperature is much higher, and the pressure is around 40 MPa. It is worth to underline that both GDCD and SCW behave as non polar solvent, have liquid like density, high values of diffusivity in comparison to the corresponding liquid, are very abundant and can be easily removed from the products. However, if carbon dioxide and water are not completely removed from products intended for human consumption is not a problem at all. There are many R&D people and departments of companies operating all around the world in different sectors that are currently working in order to take advantages of the supercritical fluid technologies for developing advanced and better processes while improving the overall quality of their traditional products/services. In general, when working with GDCD the most attractive future is the possibility of processing thermo-labile substances or molecules at ambient temperature while avoiding any kind of contamination and preserving nutritional, organoleptic, and functional properties. In other cases the interest is attracted by the possibility of producing micro or nanogranular material or very thin layers characterized by a high degree of homogeneity. These emerging technologies are known with several names like SAS (Supercritical Anti-Solvent), RESS (Rapid Expansion of Supercritical Solutions), PGSS (Particles from Gas Saturated Solutions), SSI (Supercritical Solvent Impregnation), SPD (Supercritical Pyrolysis Deposition), and others. An additional property of carbon dioxide and of GDCD in particular is its antimicrobial activity along with its capability of producing enzymatic deactivation. In other words the GDCD technology appears to have a great potential innovation in many fields including pharmaceutical, regenerative medicine, food and beverages, food ingredients with functional properties, cosmetic, materials, environmental, sustainable development, and others.

Milk is a rich source of organic and inorganic nutrients that can be consumed directly as beverage, transformed into a range of traditional dairy foods and by-products, or fractionated into a wide range of milk components that can be used as food ingredient or even non food raw materials or ingredients for a variety of industrial processes and products. The concept of fractionating milk directly into value-added ingredients is called milk refining.

The purpose of this contribution is to show how the dairy industry is going to take advantage of the GDCD technology for milk refining and for producing extended shelf life (ESL) liquid milk characterized by better quality in comparison to the corresponding available products, as a consequence of the pasteurization treatment which can be efficiently operated at the body temperature of the animal. To this purpose the most interesting advanced process along with the related advanced products will be described and discussed with some details.

ESL LIQUID MILK

The quality of raw milk is strongly influenced by several factor including feeding and housing strategies of cows, animal and equipment cleanliness, season, feed and animal health, transportation, rinsing of milking machine and washing of milking equipment with unclear water and/or wrong procedure. In general, milk is characterized by a very short shelf life, even under refrigerated condition, as consequence of the presence of numerous and different bacteria.

ESL liquid milk is obtained by pasteurization or sterilization of raw fresh milk. Thermal pasteurization and sterilization are quite efficient and consolidated processes used from very long time ago to inactivate or to destroy dangerous and/or undesirable microorganisms and enzymes in order to prepare uncooked food and beverages characterized by some significant shelf life, without adding any chemicals. However, most of the edible and drinkable uncooked materials, like milk, are rich of thermo-labile but useful or simply desirable molecules that must be preserved in order to make high quality products. For these reasons, several new physical technologies have been developed which enable one to make pasteurization or sterilization of food, beverages, and biomedical materials at mild temperature [1-3]. Among these, High Hydrostatic Pressure (HHP) [4,5] at pressure above 100 MPa, Pulsed Electrical Fields (PEF) [6,7], and membrane filtration (MF/UF) [8,9] are the most effective and have been already implemented at industrial scale in the sector of the food and beverages industry, including fresh milk. The capability of carbon dioxide to inhibit the growth of bacteria under ambient T and P conditions was evidenced about 45 years ago [10]. Antimicrobial potential of GDCD was recognized about 25 years ago [11,12] and further demonstrated by a number of experimental studies [13-15]. This capability of GDCD is related to the formation of carbonic acid and to the penetration of small amount of GDCD into the cell walls of microorganisms. In fact, in comparison to normal gas, GDCD has lower surface tension, higher diffusivity value than its liquid counterparts, and better solvent properties for fatty substances in order to likely disperse more quickly through the bacterial wall.

It is worth to emphasize that in comparison to other liquid food or beverages, gentle pasteurization of milk with GDCD is much harder due to the amount and to the variety of microorganisms, enzymes, proteins, and other labile molecules dissolved or emulsified in this material. In addition, as shown in the following, processing milk with GDCD can produce the precipitation of both casein and whey proteins. In a previous work [16] the optimal operating conditions for producing ESL milk (from 15 to 20 days under refrigerated conditions) using GDCD were presented and discussed as result of laboratory experiments. In particular, it was found that at the body temperature of the cow, a pressure of 7.5 MPa and 12.5 of CO_2/milk ratio by weight, the casein did not precipitate, while a very good looking and smelling milk was obtained. In the experimental laboratory tests described above the residence time inside the autoclave was about 15 minutes but this parameter can probably be reduced significantly at industrial scale where it is possible to achieve much better contacting conditions by using a traditional packed tower.

CASEIN PRECIPITATION

Milk contains hundreds of types of substances like fat, sugar, salts, vitamins and proteins, most of them in very small amounts. Casein is the principal protein in milk, including human’s and caw’s milk. It is responsible for the white, opaque appearance of milk in which it is combined with calcium and phosphorus as cluster of casein molecules, called “micelles” [17]. The major uses of casein until the 1960 were in technical, non-food applications, but during the past 30 years the casein has been mainly used as an ingredient in foods to enhance their nutritional (fortified food) and functional properties like whipping and foaming, water binding and thickening, emulsification and texture. Casein is traditionally recovered from milk at 35-38 °C by acid precipitation (Acid casein) using either inorganic or organic acid, or by enzymatic coagulation (Rennet casein) using calf rennet. A further traditional option is the use of starters in order to produce lactic acid from lactose. Figure 1 shows all the steps involved in traditional process used for recovering casein from milk, while figure 2 shows all the steps involved in the downstream of the solid-liquid mixture made of casein curd and whey, in order to produce dry casein powder. More recently, membrane filtration processes were introduced in the dairy industry in order to directly isolate milk casein from milk serum proteins (native whey proteins) making advantage of their difference in size [18]. These processes do not require any addition of substances for recovering the casein, but the downstream processing is complicated since the retentate stream is an aqueous solution of lactose, salts, and whey proteins in addition to minor components. The most advanced and promising technology in recovering casein from milk is based on the use of GDCD at the same temperature used in the traditional process [19, 20]. This process is quite similar, in principle, to the acid casein precipitation. However, in this case, the casein precipitates as granular solid when the pH of the system is about 4.8, while the isoelectric point for the acid casein precipitation is localized at a value of pH equal to 4.6. The operating pressure is between 5 and 6 MPa and the residence time in the reactor is about 1 minute depending on the goodness of the contact between the liquid milk and the gaseous carbon dioxide. In comparison to the traditional casein acid precipitation, in this case the carbon dioxide can be recovered and recycled back, after precipitation. In addition the resulting whey is not chemically or biologically contaminated. In comparison to the membrane filtration technology the main advantage is in the higher purity of the casein precipitate with consequent easer downstream processing. Work is in progress in the laboratory of the authors and in many other laboratories located all around the world in order to develop a pilot plant scale, economic analysis, and industrial applicable process.

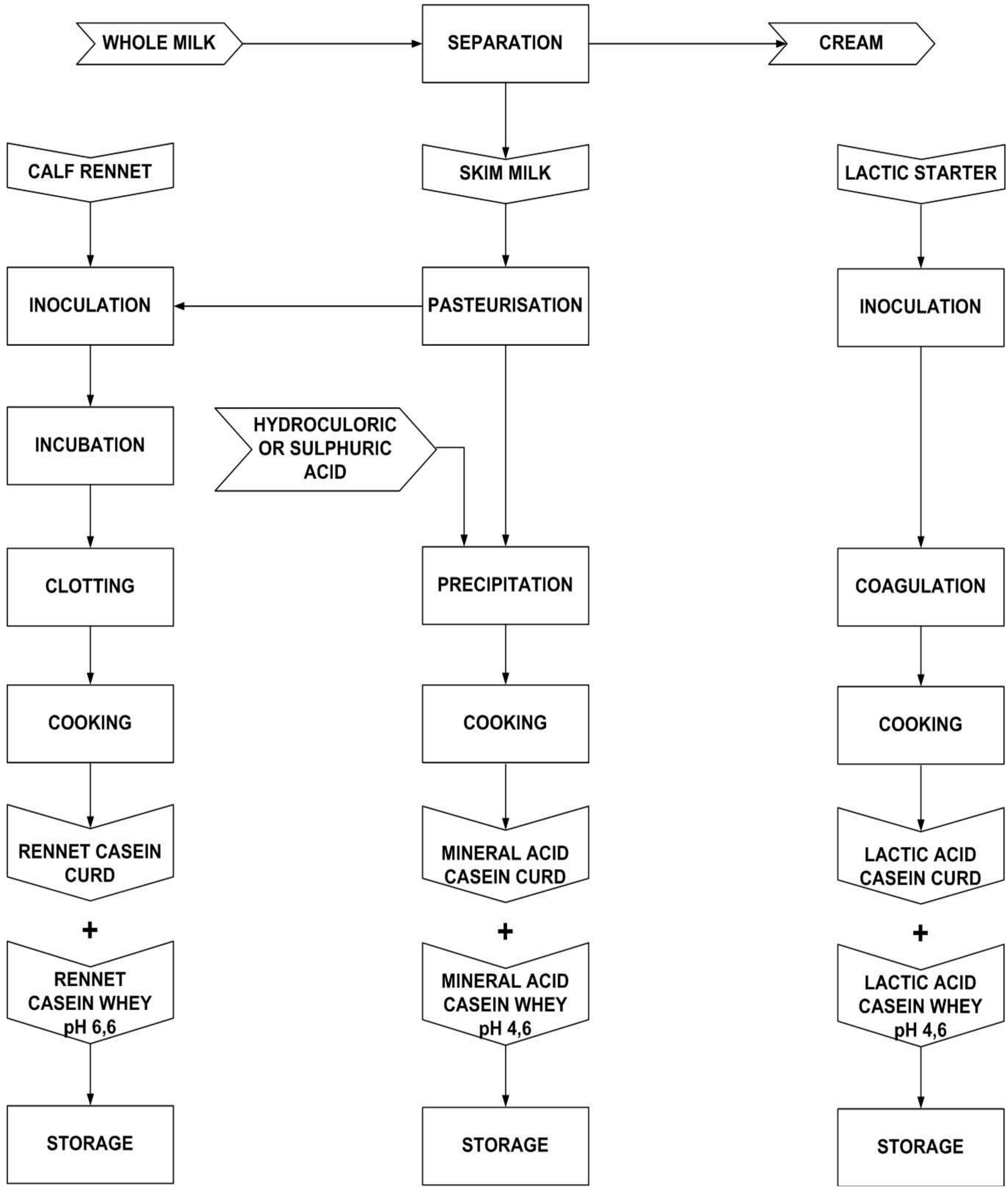

Figure 1: Processing steps involved in the precipitation of acid and rennet caseins from milk.

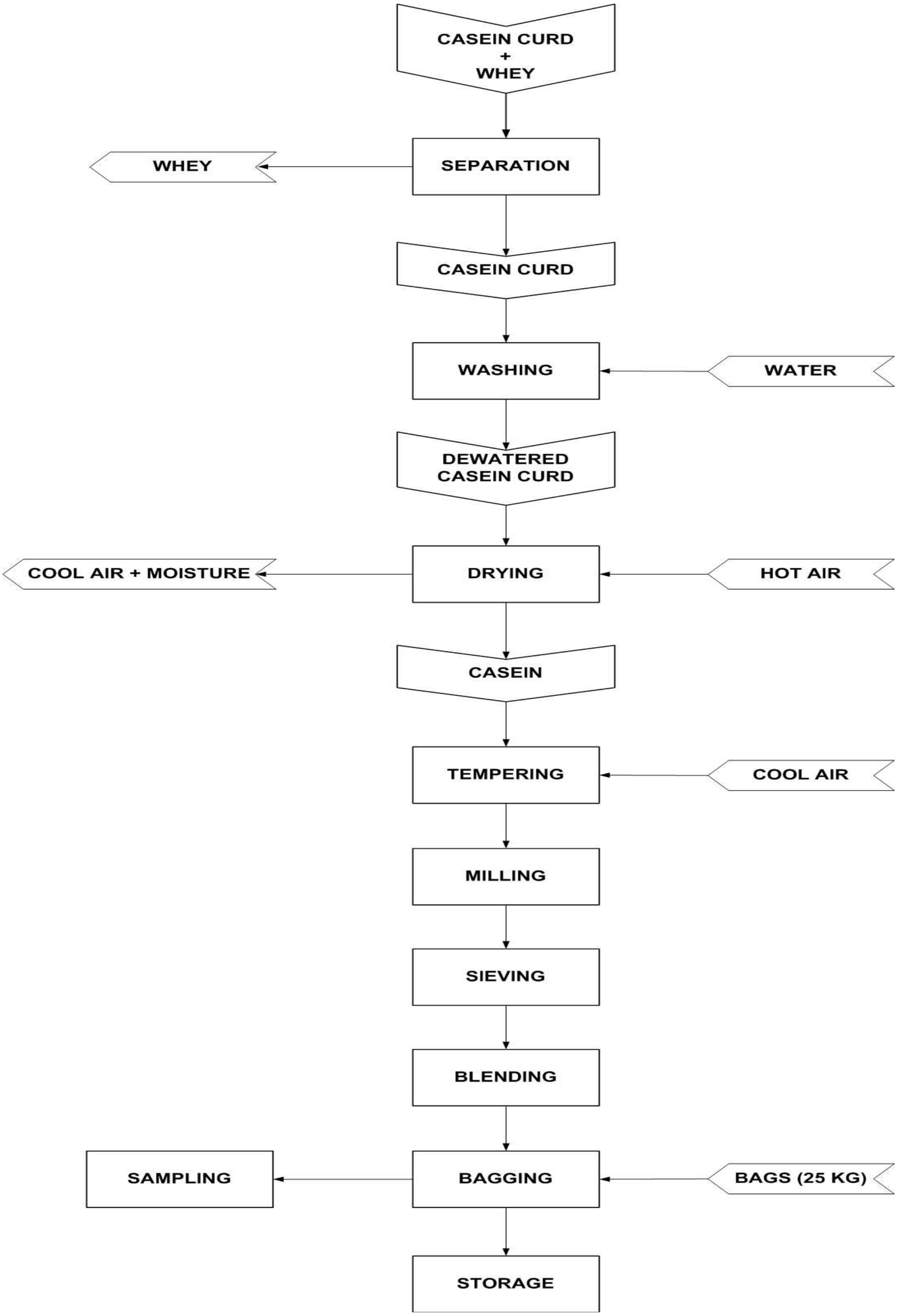

Figure 2: Processing operations in the washing and drying of caseins.

SERUM PROTEINS PRECIPITATION

Traditionally the whey proteins are precipitated by the milk whey which residue as by-product from the cheese production. After dehydration, the whey protein concentrate (WPC) appears as a white powder containing about 35% by weight of proteins, the remaining being essentially lactose. A better WPC with a title in proteins of 80% can be obtained by inserting a proper washing section, before the dehydration section. The functionality of WPC can be influenced by the cheese making process, powder composition and others downstream operations. Next-generation dairy ingredients gaining attention are whey proteins recovered directly from milk (native or serum proteins, SP), which can be further processed to obtain serum protein concentrates (SPC) as powder with a protein title of 80%, SPC80. Ongoing research has found that SPC80 have significant better whole quality in comparison to commercial WPC80 taken from a variety of sources [21]. In addition to the membrane filtration technology [18], GDCD can be used to precipitate the whey protein fraction directly from milk in order to make SCP80 powder [22, 23]. Figure 3 synthetically show the process to precipitate separately the casein and the SP directly from milk, along with the main operating conditions. It is worth to emphasize that in this case the downstream processing for getting SPC80 is quite simpler in comparison to the one required when using membrane filtration.

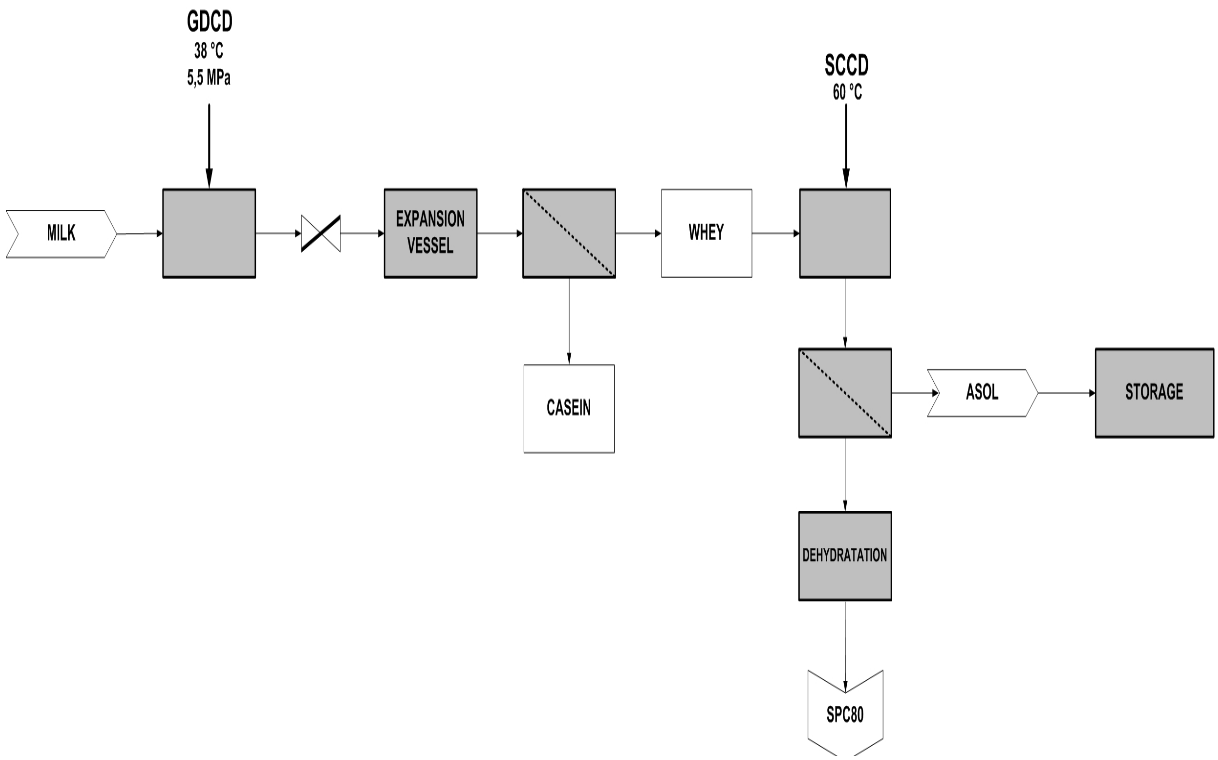

Figure 3: Integrated carbon dioxide milk refaining process (SCCD: Super Critical Carbon Dioxide; ASOL: Aqueous Solution of Lactose) .

CONCLUSIONS

Gaseous dense carbon dioxide based technology is the new frontier of the dairy industry in order to develop advanced processes and high quality products. In particular, the interest of researchers and investors is focused on milk refining for producing high quality casein and native whey proteins.

Great interest is also devoted to the pasteurization of liquid milk at the body temperature of the cow in order to obtain an extended shelf life product characterized by high quality in terms of both nutritional and organoleptic properties. To this purpose research is in progress to simulate quantitatively the interface mass transfer under different contacting modes in order to identify the operating conditions which enable one to prevent protein precipitation during the pasteurization process.

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