Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2020, Volume 11, Issue 2, Page 294-309

http://www.jmaterenvironsci.com

Thermal processing of milk as a main tool in the production of Qishta, Khoa and Kajmak

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Received 04 Dec 2019,
Revised 15 Jan 2020,
Accepted 17 Jan 2020

Keywords
- *Heat Treatment,*
- Milk,
- Qishta,
- Khoa,
- Kajmak.

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Abstract

Since their beginning, dairy industries have experienced different level of expansion. From adapting heating-milk process to applying spray drying process, a long journey of innovation has been gone through. Despite all the innovations made and all the new technologies implemented in this sector, heat treatment of milk, either for extending its shelf life or for creating new products, has been a key factor in that manner. Qishta, Khoa and Kajmak are typical examples of traditional dairy products respectively in Lebanon, India and Serbia and which only depend on the temperature as a main tool of their process. These three products share at the same time some similarities and some dissemblance. We believe that these products descend maybe from one ancestor, yet little changes have been implemented to the process of each, in order to suit the traditions and the practices applied in each country. While Kajmak is rich in fat (47-60%), Khoa and Qishta contains only 27 and 12% respectively. The effect of heat treatment of milk on the interactions between its components, in addition to the description of the process and the composition of these traditional products are discussed in this paper.

1. Introduction

Milk and dairy products are considered nowadays essential elements in each one's life and an important need for all humans in general. Before they are even capable of digestion, infant mammals use milk as a primary and unique source of nutrition [1]. The nutritional value of milk is determined according to the balance of nutrients that it contains. Regardless of their origin, fat, proteins and minerals are present in milk from any species, but within different values [2]. Table 1 shows the milk composition variations according to species [3,4].
Milk can be directly consumed, or valorised, through different treatments, into milk by-products. Historically, human civilization has always been searching for ways to store food for more scarce times. Henceforth, technologies to preserve food have been adapted for many years. These technologies did not only induce changes to the product's shelf life, but also left it with a new set of physiochemical and sensorial attributes. There are several principal categories of milk products such as liquid/beverage milk, cheese, milk powders, concentrated milks, fermented milk products, butter, ice-cream, infant formula, creams, protein-rich products…

Table 1: Chemical composition of milk in various species [3,4] .

Composition	Goat	Sheep	Cow	Human	Camel
Fat (%)	3.8	7.9	3.6	4.0	2.9
Solids-non-fat (%)	8.9	12.0	9.0	8.9	8.7
Lactose (%)	4.1	4.9	4.7	6.9	4.91
Protein (%)	3.4	6.2	3.2	1.2	2.5
Ash (%)	0.8	0.9	0.7	0.3	1.3
Moisture (%)	79	68.1	78.8	78.6	79.8

Milk by-products are defined according to the process they have been subjected to. Milk can be altered by acids, enzymes, temperature or microorganisms. When heated, the chemical constituents can undergo major changes depending on the intensity and the time of treatment applied. Several alterations in heat treatment in terms of time, temperature, pre- and post-treatments of milk, type of heat-exchanger used and others, will determine a unique final product. Through a specific treatment, a unique product is made with specific sensorial, chemical and physical properties [5].

Products obtained from heated milk remained widely accessible because heat treatment was mastered by all cultures around the world. Importing a food product to a new geographical area required sometimes adaptations depending on culture, climate and raw material availability. Lebanese Qishta ,Turkish Kaymar, Indian Khoa, Serbian Kajmak and Iraqi Geymer are examples of almost similar products present in different countries, probably descending form one ancestral [5,6] and obtained mainly by heating milk. Indian Khoa and Lebanese Qishta are subjected to almost the same heat treatment technique. Traditionally, these products are slightly different because of their making process techniques. During Khoa preparation, milk is stirred vigorously, while in Qishta production milk is not stirred leading to a much more soft and creamy texture; not forgetting the characteristic skin development (solids clotting on the liquid surface) rather than a complete transformation of the entire product [7-9]. Therefore, both humidity and solid dry matter of these two products are different. The concept of Kajmak preparation is different from those of Qishta and Khoa, however its texture can be similar to theirs. In certain areas, traditional products still have a major indigenous production, while in other places, industrial production is on the rise to take over the market [11]. In this paper, the characteristics of production and final composition of some of these traditional products will be investigated and compared.

This review aims to describe the process and the chemical composition of three partially dehydrated dairy products, all of which relying on heat treatment as the main and only tool during their processing. First of all, the making process of each of these popular traditional dairy products will be described. Then, an investigation on the effect of heat treatment on milk components will be done. Finally, those products will be compared in terms of parameters, composition and sensory aspects.

2. Industrial versus indigenous technology

During the last century, science invaded the dairy industry and succeeded, to a certain level, in clarifying and explaining the craft traditions of the past. The combination of old practices with technical innovations made the development of traditional products (such as cheeses and yogurts) possible. Innovative technology has created new products, such as spray dried milk products, milk protein concentrates and whey protein concentrates, that meet the needs of today's society and has increased the shelf life of certain dairy products to an unexpected level (such as spray dried milk products). Cow's milk has a primary role in the dairy industry today despite the growing trend towards buffalo, goat and sheep milk [11,12].

Since these traditional products have deep historical origins, they became part of culture; thus, they turned out to be an essential part of our everyday cuisine and a staple of most special occasions. As a result of welfare and increased population in many places worldwide, these products are now in greater demand than ever. Local manufacturers seek new and improved means of production and some have even taken the step to go from the indigenous and traditional artisanal production to an engineering project of complex science. While in some areas it started decades ago, this process still has barely begun in others.

2.1.Indian Khoa

Considering the manufacture of milk for all mammal species, India is at the top of rankings, consolidated by its buffalo milk producers. With respect to cows' milk alone, India is the second largest producer, after the USA, with 133.6 million tons between 2017 and 2018 [14]. Nine million tons of total milk produced in India are used in the production of Khoa; a traditional heat-dried Indian dairy product prepared by thermal concentration of milk in an open shallow pan with continuous stirring and scraping [9]. The majority of production is still artisanal in India, however substantial efforts were made to scientifically study the products and technologically enhance their production. Most of the Khoa produced in India belong to some small private merchants, whom have inherited this craft from ancestors and transmitted their traditional utensils of former times. Due to the small production scale (4-5 Liters of milk per batch) and the increasing demand on this type of product, different processes have been developed in order to improve the yield of Khoa's production [15]. In 1968, the first equipment to produce Khoa continuously with a capacity of 50 liters per hour has been created. The process included a steam jacketed cylinder fixed with rotational scrappers pursued by final concentration in an open flowing steam jacketed pan with mechanical scrapping agitators. Afterward, the process of Khoa making was optimized with many changes [16]. In 1968, Kumar et al.,[17] have created a machine in order to produce Khoa under rural conditions. In fact, the open shallow pan was semi jacketed and equipped with a mobile scraper in order to harvest the product during the heat treatment of milk [18]. National Dairy Development Board, Anand, India developed an Inclined Scraped Surface Heat Exchanger (ISSHE) for continuous khoa-making [17]. Currently, after 70 years of research and development, 70% of the volume is still produced by small, local producers and mostly with elementary technology.

2.2. Lebanese Qishta

In Lebanon, the situation is practically different. The lack of structured farms and the inconsistency in milk composition lead the producers of Qishta to use milk powder [19]. The historical origin of Qishta is not well known. In the Middle East different spellings are used for the Qishta such as Kishta, Kashta or Ghishta, in the present work the spelling Qishta will be used according to Kassaify et al., [8]. Today, Qishta is prepared from powdered or pasteurized liquid milk in either small dairy plants or in large-scale open shallow pan in order to be freshly consumed as a dessert. However, it will often be use in further reprocessing in order to produce typical oriental sweets. Milk is heated on one side in a large open shallow pan. Several minutes later and depending on the intensity of the flame, the phenomena of protein and fat denaturation will occur as the milk starts boiling, leading to the formation of a coagulum, called Qishta, at the surface. The boiling intensity pushes the Qishta formed to the opposite side of the pan. There has been no initiative to start the research and development of Qishta production up until the recent few years, except the work done by Kassaify et al., [8] on the chemical and microbiological characteristic. So far, the industry is practicing what can be classified as an artisanal approach of production (even though it is at factory scale), but a growing initiative to begin this process is now found. It is of huge interest to increase the volume and quality of Qishta production, mainly because of the increase demand of Qishta inside and outside Lebanon. The strategy they implemented so far was initially to contact the scientific community. From there on, they have to allow researchers to start bigger projects concerning shelf life, compositional determination of products and by-products, physicochemical mechanisms, as well as the industrial and standardized processing. This last part is an ultimate goal since recreating the same valued product, in all its features, but with an efficient industrial process instead of the kitchen-approach, is the crux of it all.

The success has been valuable so far, but there is a long way to go. Seeing how the Indians have worked for 70 years, it is observable that many years of strong effort and resources must be invested in order to reach even partial industrialization, but the situation might turn out completely different as a result of today's information availability.

2.3.Serbian Kajmak

In Serbia, the dairy sector depends on cow's milk processing. Milk production is stabilized at around 1.6 million tons liters per year. One half of the total quantity is purchased and processed in dairies while the other half is spent and/or processed in rural farms for cheese and cream and sold in markets [20]. According to the total cow's milk production and to the FAOSTAT data in 2008, Serbia took the 48th position worldwide [21]. Some of the cheeses which consist of 20% of the marketplace and regularly sold in green markets are: the special types of locally produced cheeses such as fresh or short shelf life cheese with geographic recognition and special cheeses like kajmak and sour cream [22]. The process of Kajmak formation is based on the top layer's surface activity of boiled milk. Hot milk is poured into the open shallow vessels where a sort of primary skin is formed on the top of the milk due to the evaporation and surface activity. The kajmak created is collected, salted and placed layer by layer in suitable vessels where maturation takes place [10]. What motivated various investigators to search out for a suitable solution to industrialize kajmak production and improve its market position was the regional superiority of kajmak and its delicious organoleptic qualities. In order to induce a product with standard characteristics, the industrial production of kajmak needs to be standardized. It is important to have better information of processes concerning production and maturation stages of kajmak. It is also important to gain information regarding Kajmak composition and characteristics [6]. Polimark company has lately developed a new process for the production of kajmak that shows a promising solution. This process covers all steps comprised in traditional kajmak production. However, they are accomplished by strategies considered acceptable for industrial implementation, in such way that they eliminate safety risks and enable standardization of production [6]. Their process incorporates manifestly two significant steps: cold agglutination and hot incubation, that yield to the creation of both upper and lower kajmak layers. The situation in Serbia is to some extent in between India and Lebanon. There was a detailed research over virtually 20 years, and a summary of most of the work has been done.

3. Constituents of milk

3.1.Water

Water is the principal component of most dairy products. It varies from 2.5 to 94% (w/w) according to the product. In addition to pH and temperature, water plays a key role in food technology since it can impact directly the texture of the products and therefore their utilization. It is considered an essential diluent in foodstuffs, since it can modify the chemical, physical and microbiological aspects of the final product [23].

3.2.Proteins

Milk and most of dairy product properties are influenced by their proteins content more than any other constituent. According to their properties, proteins are considered nowadays as one of the best characterized food systems. Research on milk proteins started since the early nineteenth century. Innovative work was accounted first by Schubler on the milk proteins and by Braconnot who was in charge of the appropriation of the word 'casein' in 1830. Bovine milk contains generally 2.5 to 3.5% of proteins. This amount depends on the breed, the individual variation of the animal, and to a lesser extent, on the stage of lactation, the nutritional status and the health of the animal [23,24]. Milk is considered as a good source of essential amino acids. In addition, it contains a wide array of proteins with biological activities, ranging from antimicrobial ones to those facilitating absorption of nutrients, as well as those acting as growth factors, hormones, enzymes, antibodies and immune stimulants [25,26].

Milk proteins are made out of whey proteins (20%) and caseins (80%). Caseins are recognized to convey phosphate and calcium, having numerous bioactive functions and contributing to proficient digestion [25]. Whey proteins have an assortment of dietetic and biological properties and consequently are extensively utilized in decreasing the possibility of diseases such as inflammation [27-28], cancer [29], human immune efficiency virus infection [30] and chronic stress-induced disease [31].

3.2.1. *Casein*

Caseins are defined as the milk fraction that precipitate by acidification to pH 4.6 at 20°C. Casein consists of four families: αS1-casein (α_{S1}-cn), αS2-casein (α_{S2}-cn), β-casein (β-cn) and κ-casein (κ-cn) representing 40%, 10%, 38%, 12%, of the total casein, respectively [32]. Caseins are characterized by different numbers of phosphorylated serine residues, which give them different properties [33]. α_{S1}-cn and β-cn do not contain any disulphide bonds however, α_{S2} and κ-casein own two. Due to their opened structure, caseins have a high surface hydrophobicity. This results in a fragile secondary structure and irregular coiling of the primary chain. Caseins are heat resistant due to their weak secondary and tertiary structures. This open structure similarly makes caseins sensitive against proteolysis within different enzymes, particularly pepsin [34].

The phosphate groups are situated in clusters bound to serine residues. Because of their negative charges, the phosphate groups have the capacity to bind ions, particularly Ca^{2+}. This ions binding is important in the transportation of phosphate and calcium to the neonate. Caseins are delicate to the variation in the calcium level of milk, and their precipitation can be induced when the calcium level is increased. The most sensitive type of calcium casein is the α_{S2}-cn, however κ-casein got the least amount of phosphate groups and is not influenced by the calcium concentration present in milk [35].

In order to stabilize their structure, caseins tend to connect to each other's, through hydrogen bonds, to form casein micelles with an average diameter of 200 nm. Almost 95% of the casein are consequently bounded in casein micelles. These micelles consist of 94% proteins, while the rest of the 6% are denoted as colloidal calcium phosphate that comprises phosphate, calcium, little amounts of magnesium, citrate and other components [36]. Different models have been established in order to clarify the structure of casein micelle, such as the nanocluster model displayed by Holt and Horne [37] and the sub-micelle displayed by Walstra [38]. Until this moment, none of the models are totally checked. It is then known that the core of the casein micelle is the location of the most hydrophobic and calcium sensitive caseins, α-cn and β-cn, while the surface with its polar C-terminal outside the micelle core is the location of the most hydrophilic and calcium insensitive κ-cn which makes the casein soluble.

3.2.2. *Whey Protein*

Whey proteins or serum proteins constitute around 20% of the overall proteins of bovine milk. Whey or milk serum, defined as the remaining soluble fraction after casein precipitation at pH 4.6, comprises four main protein categories, namely β-lactoglobulin (β-Lg), bovine serum albumin (BSA), α-lactalbumin (α-La), and immunoglobulins [39]. whey proteins in general and α-La in particular, have high nutritional value, which leads to the fact that whey proteins derivatives are widely used in food industries. In bovine milk, almost 50% and 12% of whey proteins are represented by β-Lg and α-La respectively. Whey proteins are highly structured proteins with stable secondary and tertiary structures. Hydrophobic interactions, disulphide bonds, ion-pair interactions hydrogen bonding, and van der Waal's interactions are the major forces responsible for sustaining their globular structure [40]. Whey proteins are highly soluble in milk over a wide range of pH due to their native composition and to the huge amount of hydrophilic buildups on the surface of the globular structure and the high quantity of disulphide bonds [41]. The proteins are then resistant to proteolysis due to their globular structure.

3.3.Fat

Milk is an emulsion where fat, which represents around 3 to 5%, is presented as small globules or droplets dispersed in the aqueous phase of the milk [42]. Their diameters vary from 0.1 to 20 µm. The stability of this emulsion is assured by a thin membrane called milk fat globule membrane (MFGM), which has an important role controlling the communication between the fat globule and the surrounding milk [43]. Triglycerides are the principal components of the milk fat. Moreover, we can find di- and monoglycerides, fatty acids, sterols, carotenoids, which give the yellow colour to the milk, in addition to the vitamins (A, D, E, and K), and all the other trace elements [44]. Milk fat globule membrane is composed of phospholipids, lipoproteins, cerebrosides, proteins, nucleic acids, enzymes, trace elements (metals) and bound water. The structure of this membrane is not fixed; however, it is dynamic due to the continuous exchange with the surrounding media; therefore, the thickness of this membrane varies from 5 till 10 nm. Due to their size and their low density, fat globule will migrate to the surface after a certain time if milk was left without any intervention [45]. Pasteurization has a slight effect on lipid composition and content. On the other hand, homogenization is a process that increases the number of lipid globules at least 100-fold and the surface area about 6 to 10 times, diminishes their diameter from around 3 to 0.8 µm and modifies the globule membrane composition and structure. The globule surface is mostly but not totally recoated with caseins.

3.4.Minerals

Table 2 shows the concentration range (expressed in mass and molar concentrations) of different minerals in cow milk. This composition is considered as generally steady yet slight deviations can be observed at different times. Thus, milk could be considered rich in proteins, containing high content of phosphate and calcium. Minerals concentration varies according to the lactation time period. The most significant variations in the composition occur at around parturition; in this manner the concentration of the calcium in colostrum is much higher than that of normal milk and close to the end of lactation [46].

Table 2: Mineral composition of cow milk [45].

Mineral	Concentration ($mg.kg^{-1}$)	Concentration ($mmol.kg^{-1}$)
Calcium	1043-1283	26-32
Magnesium	97-146	4-6
Inorganic phosphate	1805-2185	19-23
Total phosphorus	930-992	30-32
Citrate	1323-2079	7-11
Sodium	391-644	17-28
Potassium	1212-1681	31-43
Chloride	772-1207	22-43

3.4.1. *Calcium*

Milk is a major source of calcium for human consumption. The colloidal phase contains 66% of the total calcium present as calcium phosphate while, the remaining calcium is present in the soluble phase [46]. Ionic calcium represents around 10% of total calcium [47]. At pH 5.2, inorganic calcium phosphate is completely destroyed, therefore all inorganic phosphate will be solubilized. The complete solubilization of calcium occurs at pH 3.5. A significant role on the kinetics of protein denaturation was shown when the amount of calcium increased. In fact, the unfolding and aggregation stages of β-lactoglobulin and α-La were affected with the increase in Ca^{2+}concentration [48]. When there is an excess of calcium ions, the protein denaturation occurs at lower temperature than in standard case. Before heat treatment, the addition of $CaCl_2$ to skim milk provided a noticeable rise in the rates of whey proteins denaturation, apart from the immunoglobulins [49]. In order to understand the influence of increasing Ca^{2+} concentration on denaturation of whey proteins in milk, studies have been carried out. In 1984, Bernal and Jelen [50] demonstrated that when calcium ions are bounded to α-La, heat stability of this last is increased by promoting renaturation on cooling. Nevertheless, Li et al., [51] showed that Ca^{2+} stabilized the unfolded development of lactoglobulin and, consequently, advanced its denaturation.

3.5.Lactose

Lactose belongs to the group of organic chemical compounds called carbohydrates. Lactose is a disaccharide of glucose and galactose, and can be found only in milk [52]. Its hydrolysis occurs in the intestinal mucosal cells. In milk, lactose content varies from 4.5 to 5.5% [53]. Lactose is water soluble and has a low sweetness capacity evaluated as 16 comparing to that of sucrose estimated as 100 [52]. It plays a key role in fermentation process by impacting the amount of lactic acid produced during milk products fermentation. Human lactose intolerance arises from their incapacity to hydrolyse lactose due to the absence of lactase. This enzyme deficit is common in eastern

Asia and African countries [54]. Lactose is the principal component of milk powder. It creates an impact matrix for the dispersion of fat and proteins. Lactose has a primordial role, with the participation of proteins, in emulsion stability. Maillard reaction, discussed here after, which involves the ε-amino group of lysine and the carbonyl function of a reducing sugar (lactose) is the main reason along with fat oxidation behind the flavour, solubility and colour alteration during the storage of milk [55].

4. Heat treatment of milk

Milk stability is assured by the physiochemical properties of its components and by the equilibria resulted from the interactions between salts, proteins and fat. These equilibria are highly temperature-dependent. In the following chapter, the effect of heat treatment on pH, mineral balance, protein denaturation and the interactions between proteins and fat are studied.

4.1.Heat-induced changes in milk pH and mineral balance in milk

Ma and Barbano [56] demonstrated that upon heating milk at temperatures up to 80°C, the pH decreases from 6.8 to 6.2. In 1981, Fox [57] noted that milk may be heated for more than 3 hours at 140°C without any coagulation if the pH was adjusted continuously. According to Van Boekel [55], heat-induced acidification of milk is due to: 1) formation of organic acids and mostly formic acid, 2) insolubility of tertiary calcium phosphate and 3) casein's dephosphorylation. The continuous decrease in milk pH is due to the formation of organic acids, arising from the lactose degradation. Berg and Van-Boekel [58] noted that the formation of formic acids occurs through two ways. Lactose degradation is responsible of 80% and the rest is obtained as a result of Maillard reaction upon heating the milk at 110–150°C. The isomerization/degradation path is defined by the transformation of lactose to lactulose via the Lobry de Bruin-Alberda van Eckenstein transformation, then into galactose and other C5 and C6 compounds. The other 20% of formic acids are obtained upon the degradation of lactulosyllysine; an Amadori product obtained through the interactions of lactose with ε-amino group of lysine. Concerning the heat-induced dephosphorylation of casein, we distinguished two cases: the heat induced dephosphorylation of sodium caseinate and calcium caseinate. Belec and Jenness [59] have demonstrated that 50% of the sodium caseinate dephosphorylation occurs within the first hour of heating at 120°C, however less than 80% of dephosphorylation occurs after 5h at 120°C.

4.2.Heat-induced dissociation of caseins

κ-casein has a primary role in maintaining the integrity of casein micelle. In addition to other factors, its dissociation contributes to the heat induced coagulation of milk. Singh and Fox [59–63] have demonstrated its role during the heat stability phenomenon. In fact, the dissociation of κ-casein from micelle leaves this latter in a depleted way, more sensitive to calcium binding and therefore to coagulate. In addition to the temperature, different factors have a big impact on the dissociation of κ-casein such as the amount of whey proteins, the minerals and the solid contents of milk. Concerning whey proteins, we distinguish two scenarios according to the pH. Below 6.7, the addition of β-Lg decreases the extent of heat-induced dissociation of κ-casein, while inversely at pH> 6.7, the heat-induced dissociation increases [64].

4.3.Heat-induced denaturation of whey proteins and casein- whey protein interactions

Due to their globular structure, whey proteins are thermolabile. While heating milk above 60°C, serum proteins unfold then denature (Figure 1).

Denaturation of the major whey protein β-Lg involves two different phases. The first phase exposes the hydrophobic residues and disulphide bonds due to the unfolding of the native globular structure. At this moment, in case the heat treatment is interrupted or limited, the unfolded whey protein will refold. At high temperature, the unfolded whey protein can interact with other molecules such as caseins mostly via covalent and disulphide bonds and therefore it will lead to the formation of aggregates [39,65]. When heating milk at a temperature between 60 and 70°C, tertiary structure of the β-Lg will unfold, creating a sensitive monomer with free thiol group (Cysteine 121) and hydrophobic parts of the residues chain [66]. These monomers are able to interact with other monomers but also with caseins; therefore, forming protein aggregates [67].

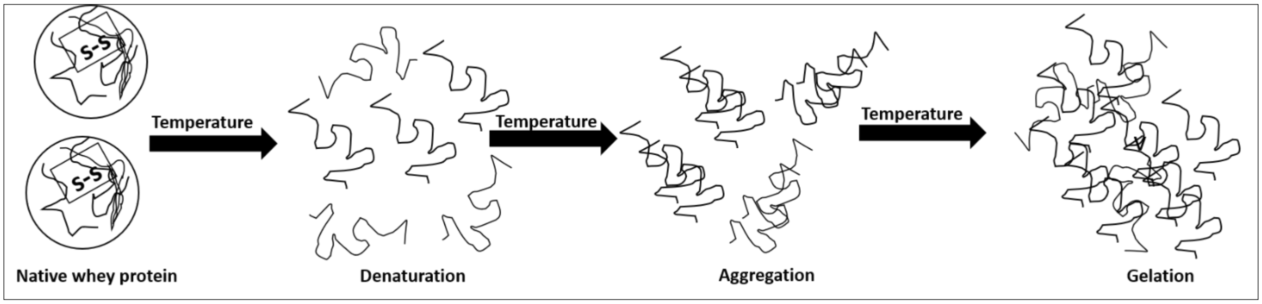

Figure 1: Stages of whey protein denaturation [66].

Temperature	Time	Structure/Reaction	Result
20°C	--	β-Lg (at pH<3.5 or pH>7.5 β-Lg (at 5.5<pH<7.5) or β-Lg (at 3.5<pH<5.5)	Native molecule
~ 40°C	--	↓ β-Lg	Dissociation/ Formation of monomers
~ 40-55°C	5-10 min	↓ β-Lg	Partial unfolding
~ 60-85°C	≥15 min	↓ -SH β-Lg; β-Lg $_{S-S}$ β-Lg; α-La/β-Lg; β-Lg/κ-cn; α-La/β-Lg	Formation of complexes with other proteins and/or
~ 125°C	5-10 min	↓ β-Lg; β-Lg$_{S-S}$/ β-Lg$_{SH}$	Complete unfolding

Figure 2 : Effect of temperature on the interactions between β-lactoglobulin and other proteins. Mechanism of thermal denaturation of β-lactoglobulin in a neutral or slightly alkaline pH including the possible complexes with other milk proteins [66,67].

According to their structure and the strength of their intramolecular bonds, whey proteins do not have the same resistance to temperature. α-La is the least thermo-resistant, followed by β-Lg, BSA and immunoglobulin [68,69]. Depending on the temperature intensity, different aggregates can be formed during heat treatment of milk (Figure 2). These aggregates can be the results of complexes formed between denatured whey proteins or between caseins and whey proteins. Interactions occur between β-Lg and κ-casein if the temperature is above 70°C through the disulphide bonds. Below this temperature, interactions occur through hydrophobic links [68-70]. The position of κ-cn has a primordial role in the complex formation with the whey proteins. In fact, placed on the surface of casein micelles, it is easier for κ-casein to interact with the β-Lg then when it is dissolved in serum where the compact structure can reduce the association ability between casein and whey protein [71,72]. Heat treatment process has also an important role on promoting the interactions between proteins and hence the formation of complexes. In reality, a process which requires a slow heating rates or low temperature kinetics, fosters the interactions between β-Lg and the casein micelles. However, heating at high temperatures drives the β-Lg to refold in a non-native structure and therefore it forms aggregates with other whey proteins instead of being associated with κ-casein. In this case, the formation of complexes between β-Lg and α-La is promoting. Actually, α-La requires a continuous heating at high temperatures and it does not interact directly with the casein micelles [72-74].

4.4.Heat-induced protein- fat interactions and emulsion instability

Dickinson and Parkinson [75] defined emulsion stability as its resistance to change over time. In milk emulsions, the composition and the concentration of proteins present in the continuous phase has a primordial role on protein's absorption at the fat membrane. In fact, during heat treatment of whole milk, caseins and whey proteins are opponents, in terms of which is going to be absorbed first at fat droplet surface [75,76]. Whey proteins are highly sensitive to heat treatment and are responsible of the emulsion instability during the technological process. As discussed before, heating milk between 60 and 70°C changes the properties of whey proteins therefore they aggregate. The preference between whey protein and casein adsorption on fat membrane will be decided according to protein concentration. At low protein concentration, whey proteins adsorb in preference to caseins at the oil droplet surface due to their limited spreading at interface. However, at high protein concentration i.e. above 3 wt%, the caseins adsorb in preference to the whey proteins [75-78]. As individual molecules or as small aggregates, caseins have been used as emulsion stabilizing owing that to their flexibility and their high surface activity.

Once aggregated, caseins form loops and tails extending during the continuous phase. According to Hunt and Dalgleish [76], the formation of these tails leads to the formation of a secondary protein layer. However, Ye [79] indicated that increasing the ratio whey/casein resulted in the formation of a secondary layer at the fat droplet interface. Till today, the effect of heat treatment on the interaction between proteins and fat droplet and on the competition between whey proteins and caseins has not been well studied due to the complexity of the milk matrix. At low protein concentration (below 3 wt%), a heat-induced flocculation of the oil droplets took place [75,80]. An intense heat treatment lead to the formation of a new interfacial layer thicker than a monolayer, [81,82] indicating that the non-adsorbed proteins fraction are primordial and play a key role in the fat droplet's flocculation mechanism. In fact, removing this fraction from the emulsion decreases extremely the aggregation of the fat droplets. On the other hand, increasing the whey proteins concentration enhances the coalescence of the fat droplets and the emulsion viscosity until the critical concentration of gelation was reached. This later was estimated at around 3 wt% of non-adsorbed whey proteins [81]. Above 3% the heat-denatured whey proteins non-adsorbed will connect the different fat droplets in a continuous network. Euston et al., [82] compared the whey proteins to a glue that connects the fat droplets in the continuous phase. However, below the critical concentration, whey proteins are not able to play the glue role and therefore the gelation will not occur.

5. Qishta, Khoa and Kajmak: overview, process and final product composition

5.1. Qishta

Qishta is a traditional Lebanese dairy product, made through subjecting a small area of a large shallow stainless-steel pan, filled with whole milk, to high heat via flame (figure 3) according to "Hallab 1881" company process. It is a mixture of a thin skin layer formed on the surface of milk and of a coagulum formed in the heated zone of the pan. Milk fat aggregates contribute to give Qishta some characteristics of butter.

Qishta is related to cheese family (figure 4 a-b), especially to cream cheese varieties due to the presence of milk proteins as well as their particular coagulation process during Qishta development. This product is identified somehow between cheese and cream. However, according to its composition, Qishta can be looked at as similar to Ricotta cheese with almost an equal amount of fat and protein of around 12% (Table 3). The final product has a sharp and white colour.

It is creamy, bulky with a smooth texture, and a sweet taste. Qishta can be consumed as it is or after further processing. It can be used as filler in different Lebanese desserts such as Knefe, Halewe, Mafrouke and many more. It has a shelf life of 4 hours at ambient temperature, and up to 4 days at 2-5°C. The pH of Qishta (6.5) is high comparing to other dairy products such as whipped creams, clotted creams and yoghurts. Such findings explain the short shelf-life of the product. Furthermore, combination of high moisture content with pH is a major factor in making the product susceptible to high microbial contamination and growth.

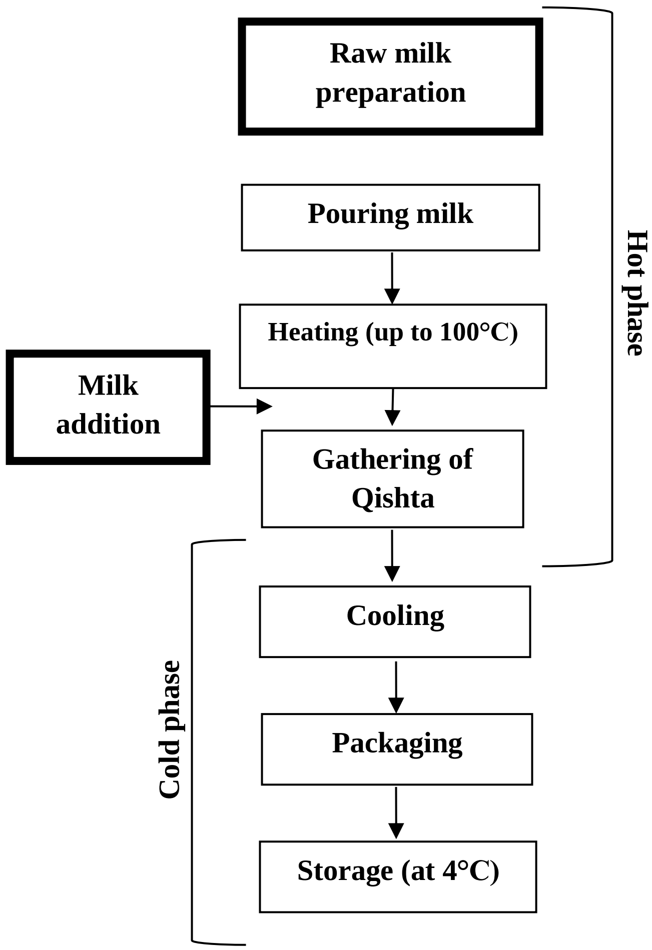

Figure 3: Major steps of Qishta's process according to the process used by "Hallab 1881" company Lebanon.

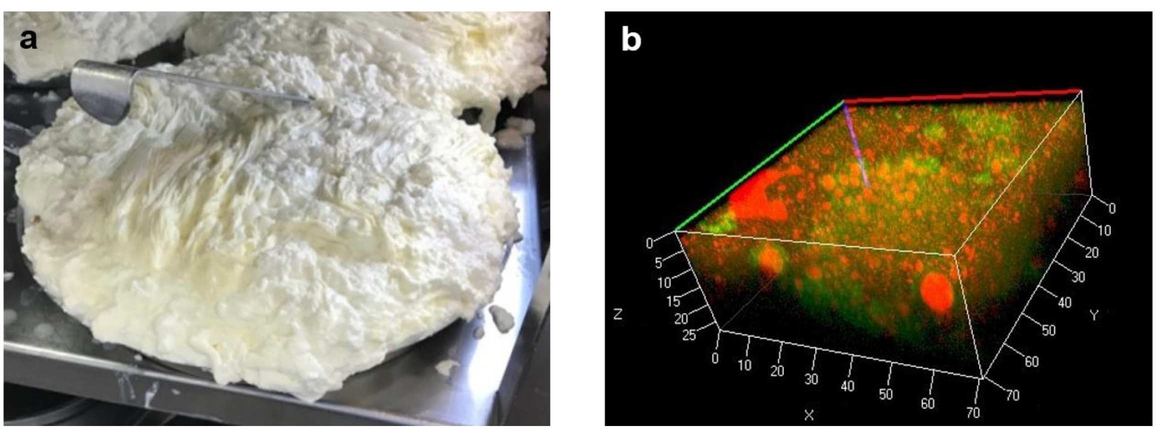

Figure 4: Qishta during draining step (a). Visualization of proteins (green) and fat (red) in Qishta (b) using confocal scanning laser microscopy. Nile red and fast green were used In order to stain fat globules and proteins.

5.2.Kajmak

Kajmak is a heat concentrated dairy product produced in regions of the Balkans, Turkey, Iran, Afghanistan and India [6]. In Serbia, the traditional process of Kajmak dominates almost all the production [10]. Regarding of its physio-chemical characteristics, Kajmak can be placed between cheese and butter [11]. The process of kajmak consists of pouring milk into an open shallow vessel where, due to both surface activity and evaporation, a skin is formed on the top of the milk (figure 5).

Table 3: The average composition (%) of butter, Qishta, cream cheese, kajmak and Ricotta cheese [5].

PARAMETER	BUTTER	QISHTA	CREAM CHEESE	KAJMAK		RICOTTA CHEESE
				Fresh	Ripenned	
MOISTURE	16	68	53-60	30-40	53-60	74.5
FAT	85	12	30-34	40-55	30-34	9
FAT IN DM	>98	37.5	70	65-80	70	35.29
PROTEIN	0.5	12	7-10	5-10	7-17	10.9
PROTEIN IN DM	0.6	37.5	20	7-17	20	42.7
ASH	0-1	1.6	0.5-0.8	0.5-2	0.5-0.8	0.6-4.5

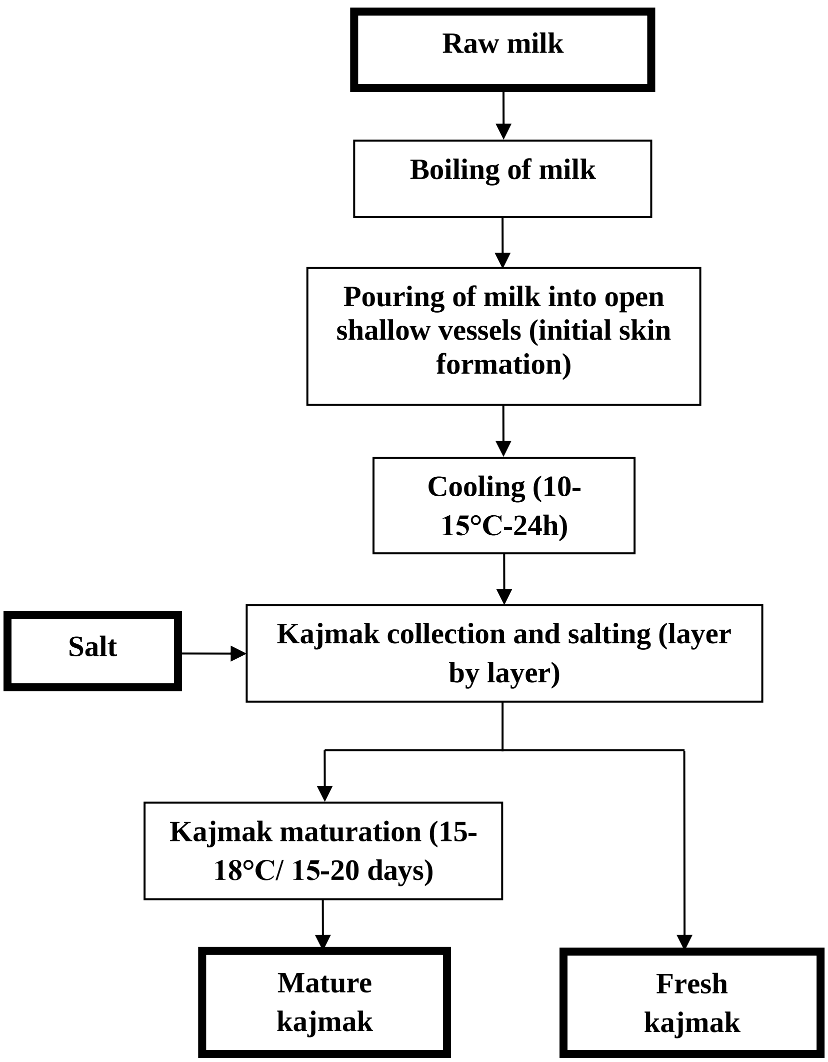

Figure 5: The procedure of traditional Kajmak production [5].

This process can be affected by different factors such as: initial milk temperature, milk composition, temperature difference between milk and air, temperature and humidity of the surrounding air and the type of raw milk used.

In fact, even though cow milk is mostly used in the Kajmak's production, some regions in Serbia like Bosnia and Montenegro are now replacing cow milk by ewe milk, or mixing the two types together. A gradual procedure of milk cooling occurs directly after initial skin formation and lasts for around 24 hours. Throughout the milk cooling procedure, fat globules arise from the most profound milk layers and join the recently formed initial skin. This action results in the development of a thin, yet smaller layer known as Kajmak. Kajmak formed on the top of milk is collected and salted then placed layer by layer in suitable vessels where maturation takes place. Kajmak's maturation occurs at 15 – 18°C, over 15 – 20 days. Matured kajmak, stored in cold conditions, below 8°C may last from 3 to 6 months, and sometimes even up to one year [11]. The yield of traditional kajmak production ranges from 4 to 5%. The residual milk that remains after Kajmak's collection is incompletely skimmed and has an average fat level of around 1.4 – 1.7%. This last is used in the production of some Serbian cheese [11]. The main components of Kajmak is milk's fat which constitutes around 45% of the fresh product and 60% of the ripened one. Protein part is less present with an average of 5 to 10% in the fresh product and 2 to 7% in the ripened one. According to Radovanovic et al., [10], the amounts of fat and protein are larger in the top layer than in the others. The difference between dry matter and protein contents matches with their textural appearances. Practically, lower layer is very viscous liquid similar to cream, with higher water content and much less proteins than the top layer which is similar to a crust. This considerable difference in protein content, as well as in overall appearance, results in the identification of different formation mechanisms of these two layers.

The colour of kajmak is mostly affected by the maturation period, amount of milk fat and milk type. During ripening period, the colour of Kajmak changes from white to yellow. The whiter colour of Kajmak in some regions is due to the usage of the ewe's milk in Kajmak preparation [11].

5.3.Khoa

Khoa or Mawa is a traditional Indian dairy product, generally utilized as a precursor for more complex desserts, yet it can be consumed alone. It is obtained by indirectly heating milk present in a stainless-steel pan. Milk is continuously stirred either mechanically or by hand, in order not to be burn. Water will then easily evaporate, leaving a semi-solid product having low moisture content of almost 30% in comparison to raw milk 90% [17]. Khoa is a traditional dehydrated dairy product prepared by thermal concentration of milk in an open shallow pan with continuous stirring and scraping [9]. The whole milk is heated and boiled in a stainless steel or an open pan and stirred continuously in order to avoid scorching. Due to the intense evaporation that occurs during the process of Khoa making, the thickness of milk increases as well as the concentration of the total solid's particles. Coagulation occurs when the concentration of milk reaches 2.5 and 2.8 times the initial milk's concentration in cow and buffalo milk respectively [15]. The Chemical composition varies considerably, with a moisture percentage ranging from 19.26 to 28.41. Khoa contained on average 27% fat, 19% protein, 25% lactose and no sucrose [83-84]. The type of milk used during the manufacturing of Khoa has a big impact on the final composition. It was reported that Khoa produced with cow milk appears more yellow that when produced with buffalo milk [15]. One kg of Khoa is produced within almost two hours by the traditional production, using 4 or 5 liters of buffalo milk. Recently, new developed techniques have expanded the yield to almost 1 kg/15 min/machine. The yield of Khoa is affected by several factors such as, quality of milk used, intensity and time of heating, processing, handling and lastly the moisture of the final product, which is considered as the main factor impacting the yield. Gupta and Gupta [85] showed that buffalo milk Khoa has more yield and better texture than cow milk Khoa. Depending on the texture, composition and quality, three categories of Khoa exist, named Pindi, Dhap and Danedar. Khoa can be further processed into large variety of indigenous sweets such as Burfi, Pera, Gulab jamun etc. It can also be used as filling in many food items. Among cheese and butter products, Khoa is the most dairy expended product in India [86]. Khoa is a perishable food having a short shelf life of 3 days at room temperature and 2 weeks under refrigerated conditions [15]. Shelf life of Khoa has been accounted for exceptional changes due to the huge change in milk quality, climate, hygiene practice and accessible cooling technology between the producers; however, it is still prone for microbial contamination. In fact, *Staphylococcus aureus* and *Bacillus cereus* are the most contributable contaminating microorganisms in Khoa, contributing to a lot of food-borne diseases. Narang et al., [87] showed that 48 hours after its production, Khoa started to have a rancid flavour which deteriorates the sensory quality of this product. It has been subjected to an intensive work in order to increase its shelf life. Jha and Verma [88] showed that the addition of potassium sorbate increases the shelf life for more than 40 days. Rao and Singh [89] showed that the combination of potassium sorbate addition and the nitrogen injection can increase the shelf life up to 18 days at 5°C.

Conclusion

Qishta, Khoa, and Kajmak represent a family of dairy products which relies on heat treatment of milk during their processes. Despite the deep investigations held on milk, these products still need a lot of research in order to understand the mechanism of their formation. These three products share almost the same process steps, with a slight difference applied in each country. However, their composition is widely different due to raw material used that differs from a region to another. In India, in spite of the efforts done on understanding and industrializing the products, almost all of the quantity is produced following the traditional method. In Serbia and Lebanon, more research has to be accomplished in order to understand the mechanisms involved in the Qishta and Kajmak formation before trying to industrialize products. However, the essential question which should be asked is the following: does the use of machines allows to conserve the traditional aspects of these kind of products?

Acknowledgment-This research was supported by specific grant from "Hallab 1881" Company, Tripoli Lebanon.

References

1. A. Haug, A. T. Høstmark, and O. M. Harstad, Bovine milk in human nutrition – a review, *Lipids in Health and Disease*, 6(1) (2007) 25.
2. D. Kelton, *Lactation and the Mammary Gland*, vol. 44. ISBN 0-8138-2992-5 (2003).
3. Y. W. Park, M. Juárez, M. Ramos, and G. F. W. Haenlein, Physico-chemical characteristics of goat and sheep milk, *Small Ruminant Research*, 68(1) (2007) 88–113.
4. G. Mint, I. Bouraya, A. Samb, and A. Houmeida, Composition of Mauritanian Camel Milk: Results of First Study, *International Journal of Agriculture and Biology*, 13(2011) 145–147.
5. M. Ritota, M. Gabriella Di Costanzo, M. Mattera, and P. Manzi, New trends for the evaluation of heat treatments of milk, *Journal of analytical methods in chemistry*, 2017(2017).
6. Predrag Pudja, J. Djerovski and M. Radovanović, An autochthonous Serbian product - Kajmak Characteristics and production procedures, J*ournal of Dairy Science and Technology*, 88 (2008) 163–172.
7. A. K. Seçkin, O. Gursoy, O. Kinik, and N. Akbulut, Conjugated linoleic acid (CLA) concentration, fatty acid composition and cholesterol content of some Turkish dairy products, *LWT - Food Science and Technology*, 38(8) (2005) 909–915.
8. Z. G. Kassaify, M. Najjar, I. Toufeili, and A. Malek, Microbiological and chemical profile of Lebanese qishta (heat-coagulated milk), *East. Mediterr. Health J.*, 16(9) (2010).
9. P. Rasane, B. Tanwar, and A. Dey, Khoa: A Heat Desiccated Indigenous Indian Dairy Product, *research journal of pharmaceutical biological and chemical sciences*, 6(5) (2015) 39-48.
10. M. Radovanovic, A. Nedeljkovic, M. Bogdanovic, J. Miocinovic, and P. Pudja, Composition and protein distribution of top and lower layers of kajmak., presented at the Proceedings of the 24th International Scientific-Expert-Conference of Agriculture and Food Industry, Sarajevo, Bosnia and Herzegovina, 25(28) (2013) 171–175.
11. P. Pudja, R. Mira & D. Jelena, Production and characteristics of kajmak, *Mljekarstvo: časopis za unaprjeđenje proizvodnje i prerade mlijeka*, 56(4) (2006) 221-232.
12. P.F. Fox, Milk Proteins: General and Historical Aspects, in *Advanced Dairy Chemistry—1 Proteins: Part A / Part B*, P.F. Fox & P.L.H. McSweeney, Eds. Boston, MA: Springer US, ISBN:978-1-4419-8602-3 (2003).
13. P. L. H. McSweeney and J. A. O'Mahony, Eds., *Advanced dairy chemistry*, Fourth edition. New York: Springer, ISBN 978-1-4939-2799-9 (2016).
14. mospi, Ministry of Statistics and Program Implementation Government Of India. Online. Available: http://www.mospi.gov.in/. Accessed: 02-Aug-2019..
15. S. Choudhary, A. Kumari, and S. Arora, Factors affecting heat induced changes in Khoa: A Review, *Indian Journal of Dairy Science*, 68 (5) (2015).
16. S. De and B. P. Singh, Continuous production of khoa., *Indian Dairyman*, 22(12) (1970) 294–298.
17. M. Kumar, O Prakash, S. Kasana, R. Dabur, *Technological advancement in khoa Making* 62 (2010) 64-70

18. I. K. Sawhney, G. R. Patil, and B. Kumar, Effect of temperature on the moisture sorption isotherms of a heat-treated whole milk product, khoa, *Journal of Dairy Research*, 58(3) (1991) 329–335.
19. Arja R., Haddad E., Mouawad H., and Serhan H, La filière lait au Liban, in *Les filières et marchés du lait et dérivés en Méditerranée : état des lieux, problématique et méthodologie pour la recherche*, Ben Saïd T., Hassainya J., Le Grusse P., and Padilla M., Eds. Montpellier: CIHEAM, 32 (2001)148–158.
20. B. Draskovic, Z. Rajkovic, and D. Kostic, MILK PRODUCTION IN SERBIA AND POSITION SMALL FARMERS, *Economics of Agriculture*, 57 (2010) 529–541.
21. "FAOSTAT." Online. Available: http://www.fao.org/faostat/en/#home . Accessed: 02-Aug-2019..
22. Kokovic, Nevena. Perspectives of the Serbian dairy sector in the process of integration into global markets. Diss. Master Thesis Humboldt University Berlin, 2011.
23. P. F. Fox, T. Uniacke- Lowe, P. L. H. McSweeney, and J. A. O'Mahony, *Dairy Chemistry and Biochemistry*, ISBN 9783319148922 (2015).
24. A. Haug, A. T. Høstmark, and O. M. Harstad, Bovine milk in human nutrition-a review, *Lipids in health and disease*, 6(1) (2007) 25.
25. G. Bobe, D. C. Beitz, A. E. Freeman, and G. L. Lindberg, Effect of Milk Protein Genotypes on Milk Protein Composition and Its Genetic Parameter Estimates1, *Journal of Dairy Science*, 82(12) (1999) 2797–2804.
26. D. A. Clare and H. E. Swaisgood, Bioactive Milk Peptides: A Prospectus1, *Journal of Dairy Science*, 83(6) (2000) 1187–1195.
27. A. Pihlanto-Leppälä, T. Rokka, and H. Korhonen, Angiotensin I Converting Enzyme Inhibitory Peptides Derived from Bovine Milk Proteins, *International Dairy Journal*, 8(4) (1998) 325–331.
28. D. A. Clare and G. L. Catignani and H. E. Swaisgood, Biodefense Properties of Milk: The Role of Antimicrobial Proteins and Peptides, *Current Pharmaceutical Design*, 9(16) (2003)1239–1255.
29. H. S. Gill and M. L Cross, Anticancer properties of bovine milk, *British Journal of Nutrition*, 84(S1) (2000) 161-166.
30. P. Micke, K. M. Beeh, and R. Buhl, Effects of long-term supplementation with whey proteins on plasma glutathione levels of HIV-infected patients, *European Journal of Nutrition*, 41(1) (2002) 12–18.
31. L. S. Ganjam, W. H. Thornton, R. T. Marshall, and R. S. MacDonald, Antiproliferative Effects of Yogurt Fractions Obtained by Membrane Dialysis on Cultured Mammalian Intestinal Cells, *Journal of Dairy Science*, 80(10) (1997) 2325–2329.
32. P. F. Fox and A. Brodkorb, The casein micelle: Historical aspects, current concepts and significance, *International Dairy Journal*, 18(7) (2008) 677–684.
33. D. G. Dalgleish, Bovine milk protein properties and the manufacturing quality of milk, *Livestock Production Science*, 35(1) (1993) 75–93.
34. P. F. Fox and A. L. Kelly, 3 - The caseins, in *Proteins in Food Processing*, R. Y. Yada, Ed. Woodhead Publishing, ISBN 978-1-84569-758-7 (2017).
35. M. R. Ginger and M. R. Grigor, Comparative aspects of milk caseins, *Comparative Biochemistry and Physiology Part B: Biochemistry and Molecular Biology*, 124(2) (1999) 133–145.
36. P. Walstra, On the Stability of Casein Micelles1, *Journal of Dairy Science*, 73(8) (1990) 1965–1979.
37. H. M. Farrell, E. L. Malin, E. M. Brown, and P. X. Qi, Casein micelle structure: What can be learned from milk synthesis and structural biology, *Current Opinion in Colloid & Interface Science*, 11(2) (2006) 135–147.
38. P. Walstra, Casein sub-micelles: do they exist, *International Dairy Journal*, 9(3) (1999) 189–192.
39. S. Visser, C. J. Slangen, and H. S. Rollema, Phenotyping of bovine milk proteins by reversed-phase high-performance liquid chromatography, *Journal of Chromatography A*, (548) (1991) 361–370.
40. H. Singh and P. Havea, Thermal Denaturation, Aggregation and Gelation of Whey Proteins, in *Advanced Dairy Chemistry—1 Proteins: Part A / Part B*, P. F. Fox and P. L. H. McSweeney, Eds. Boston, MA: Springer US, 2003, pp. 1261–1287.
41. M. Dissanayake and T. Vasiljevic, Functional properties of whey proteins affected by heat treatment and hydrodynamic high-pressure shearing, *Journal of Dairy Science*, 92(4) (2009) 1387-1397.
42. R. G. Jensen, A. M. Ferris, and C. J. Lammi-Keefe, The composition of milk fat, *J. Dairy Sci.*, 74 (9) (1991) 3228–3243.

43. H. Singh, The milk fat globule membrane—A biophysical system for food applications, *Current Opinion in Colloid & Interface Science*, 11(2) (2006)154–163.
44. S. Patton and T. W. Keenan, The Milk fat globule membrane, *Biochimica et Biophysica Acta (BBA) - Reviews on Biomembranes*, 415(3) (1975) 273–309.
45. Tetra Pak Dairy Processing Handbook. Online. Available: https://www.tetrapak.com/about/tetra-pak-dairy-processing-handbook. Accessed: 14-Oct-2019.
46. Gaucheron, Frédéric. The minerals of milk. *Reproduction Nutrition Development* vol.45(4) (2005) 473-483.
47. M.-J. Lin, M. J. Lewis, and A. S. Grandison, Measurement of ionic calcium in milk, *International Journal of Dairy Technology*, 59(3) (2006) 192–199.
48. A. D. Nielsen, C. C. Fuglsang, and P. Westh, Effect of calcium ions on the irreversible denaturation of a recombinant Bacillus halmapalus alpha-amylase: a calorimetric investigation, *Biochem. J*, 373(2) (2003) 337–343.
49. A. J. R. Law and J. Leaver, Effect of pH on the Thermal Denaturation of Whey Proteins in Milk, *J. Agric. Food Chem*, 48(3) (2000) 672–679.
50. V. Bernal and P. Jelen, Effect of Calcium Binding on Thermal Denaturation of Bovine α-Lactalbumin, *Journal of Dairy Science*, 67(10) (1984) 2452–2454.
51. H. Li, C. C. Hardin, and E. A. Foegeding, NMR Studies of Thermal Denaturation and Cation-Mediated Aggregation of beta-Lactoglobulin, *J. Agric. Food Chem.*, 42(11) (1994) 2411–2420.
52. G. Génin, Le lactose et ses applications dans l'industrie alimentaire, *Le Lait*, vol. 39(387) (1959) 394–401.
53. Kittivachra, Rubporn, et al. Factors affecting lactose quantity in raw milk *J. Sci. Technol* 29(4) (2007) 937-943.
54. T. H. Vesa, P. Marteau, and R. Korpela, Lactose Intolerance, *Journal of the American College of Nutrition*, 19(2) (2000)165S-175S.
55. M.A.J.S. Van Boekel, Effect of heating on Maillard reactions in milk, *Food Chemistry*, 62 (1998) 403–414.
56. Y. Ma and D.M. Barbano, Milk pH as a Function of CO2 Concentration, Temperature, and Pressure in a Heat Exchanger1, *Journal of Dairy Science*, 86(12) (2003) 3822–3830.
57. P.F. Fox, Heat-Induced Changes in Milk Preceding Coagulation, *Journal of Dairy Science*, 64(11) (1981) 2127–2137.
58. H.E. Berg and M.A.J.S. Van-Boekel, Degradation of lactose during heating of milk: 1. Reaction pathways, *Netherlands Milk and Dairy Journal*, 48(3) (1994) 157–175.
59. J. Belec and R. Jenness, Dephosphorization of Casein by Heat Treatment. I. In Caseinate Solutions1, *Journal of Dairy Science*, 45(1) (1962).
60. Singh, Harjinder, and Patrick F. Fox. Heat stability of milk: further studies on the pH-dependent dissociation of micellar κ-casein J*ournal of Dairy Research,* 53(2) (1986) 237-248.
61. H. Singh and P. F. Fox, Heat stability of milk: pH-dependent dissociation of micellar κ-casein on heating milk at ultra-high temperatures, *Journal of Dairy Research*, 52(4) (1985) 529–538.
62. H. Singh and P. F. Fox, Heat stability of milk: influence of colloidal and soluble salts and protein modification on the pH-dependent dissociation of micellar κ-casein, *Journal of Dairy Research*, 54, (4) (1987) 523–534.
63. H. Singh and P. F. Fox, Heat stability of milk: influence of modifying sulphydryl-disulphide interactions on the heat coagulation time–pH profile, *Journal of Dairy Research*, 54(3) (1987) 347–359.
64. H. Singh and P. F. Fox, Heat stability of milk: role of β-lactoglobulin in the pH-dependent dissociation of micellar κ-casein, *Journal of Dairy Research*, 54(4) (1987) 509–521.
65. H. Singh and J. M. Latham, Heat stability of milk: Aggregation and dissociation of protein at ultra-high temperatures, *International Dairy Journal*, 3(3) (1993) 225–237.
66. S. Iametti, B. De Gregori, G. Vecchio, and F. Bonomi, Modifications occur at different structural levels during the heat denaturation of β-lactoglobulin. *European Journal of Biochemistry* 237(1) (1996) 106-112.
67. A. Tolkach and U. Kulozik, Reaction kinetic pathway of reversible and irreversible thermal denaturation of beta -lactoglobulin, *Lait*, 87(4–5) (2007) 301–315.
68. D. J. Oldfield, H. Singh, M. W. Taylor, and K. N. Pearce, "Kinetics of Denaturation and Aggregation of Whey Proteins in Skim Milk Heated in an Ultra-high Temperature (UHT) Pilot Plant," *International Dairy Journal*, 8(4) (1998) 311–318.

69. M. Corredig and D. G. Dalgleish, Effect of temperature and pH on the interactions of whey proteins with casein micelles in skim milk, *Food Research International*, 29(1) (1996) 49–55.
70. S. G. Anema, Chapter 8 - The whey proteins in milk: thermal denaturation, physical interactions and effects on the functional properties of milk, in *Milk Proteins*, A. Thompson, M. Boland, and H. Singh, Eds. San Diego: Academic Press, ISBN978-0-12-405171-3 (2008).
71. J. E. O'Connell and P. F. Fox, Heat-Induced Coagulation of Milk," in *Advanced Dairy Chemistry—1 Proteins: Part A / Part B*, P. F. Fox and P. L. H. McSweeney, Eds. Boston, MA: Springer US, ISBN 978-1-4419-8602-3 (2003).
72. L. Donato and F. Guyomarc'h, Formation and properties of the whey protein/κ-casein complexes in heated skim milk — A review, *Dairy Science & Technology*, 89(1) (2009) 3–29.
73. D. J. Oldfield, H. Singh, and M. W. Taylor, Association of β-Lactoglobulin and β-Lactalbumin with the Casein Micelles in Skim Milk Heated in an Ultra-high Temperature Plant, *International Dairy Journal*, 8(9) (1998) 765–770.
74. D. J. Oldfield, H. Singh, M. W. Taylor, and K. N. Pearce, Heat-induced interactions of β-lactoglobulin and α-lactalbumin with the casein micelle in pH-adjusted skim milk, *International Dairy Journal*, 10(8) (2000) 509–518.
75. E. Dickinson and E. L. Parkinson, Heat-induced aggregation of milk protein-stabilized emulsions: sensitivity to processing and composition, *International Dairy Journal*, 14 (7) (2004) 635–645.
76. J. A. Hunt and D. G. Dalgleish, Adsorption behaviour of whey protein isolate and caseinate in soya oil-in-water emulsions, *Food Hydrocolloids*, 8 (2) (1994)175–187.
77. D. G. Dalgleish, Adsorption of protein and the stability of emulsions, *Trends in Food Science & Technology*, 8(1) (1997) 1–6.
78. A. R. Mackie, J. Mingins, and R. Dann, Preliminary Studies of β-Lactoglobulin Adsorbed on Polystyrene Latex, in *Food Polymers, Gels and Colloids*, E. Dickinson, Ed. Woodhead Publishing, 1991, pp. 96–112.
79. A. Ye, Interfacial composition and stability of emulsions made with mixtures of commercial sodium caseinate and whey protein concentrate, *Food Chemistry*, 110(4) (2008) 946–952.
80. A. HadjSadok, A. Pitkowski, T. Nicolai, L. Benyahia, and N. Moulai-Mostefa, Characterisation of sodium caseinate as a function of ionic strength, pH and temperature using static and dynamic light scattering, *Food Hydrocolloids*, 22(8) (2008)1460–1466.
81. E. Fuller, Enhanced heat stability of high protein emulsion systems provided by microparticulated whey proteins, *Food hydrocolloids*, 47 (2015) 41-50.
82. S. R. Euston, S. R. Finnigan, and R. L. Hirst, Aggregation kinetics of heated whey protein-stabilized emulsions, *Food Hydrocolloids*, 14(2) (2000) 155–161.
83. E. Dickinson, S. E. Rolfe, and D. G. Dalgleish, Competitive adsorption in oil-in-water emulsions containing α-lactalbumin and β-lactoglobulin, *Food Hydrocolloids*, 3(3) (1989) 193–203.
84. D. R. Ghodeker, A. T. Dudani, and B. Ranganathan, Microbiological quality of Indian milk products, *Journal of Milk and Food Technology*, 37(3) (1974)119–122.
85. H. C. L. Gupta and D. Gupta, Effect of type of milk on yield and qualities of khoa, *Research Journal of Animal Husbandry and Dairy Science* 4(2) (2013) 83-84.
86. R. V. Kulkarni and A. S. Hembade, An economic analysis of khoa production and its marketing in beed district of Maharashtra, Journal of Dairying Foods & Home Sciences 29(2) (2010).
87. B. D. Narang, K. S. Dhindsa, and S. P. Kohli, Physico-chemical studies of fat content in khoa on storage, (1969) 211-214.
88. Y. K. Jha and N. S. Verma, Effect of potassium sorbate on shelf life of khoa, *Asian Journal of Dairy Research*, 7(4) (1988)195–198.
89. O. V. Rao and S. Singh, Effect of packaging materials on the keeping quality of khoa, *Journal of Food Science and Technology* (1977).

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