International Dairy Journal 129 (2022) 105311

Contents lists available at ScienceDirect

International Dairy Journal

journal homepage: www.elsevier.com/locate/idairyj

Review

Thermal processing of buffalo milk – A review

Carolyn T. Mejares [a, b], Thom Huppertz [c, d, *], Jayani Chandrapala [a]

[a] School of Science, STEM College, RMIT University, Melbourne, VIC, 3083, Australia
[b] School of Technology, University of the Philippines Visayas, Miagao, Iloilo, 5023, Philippines
[c] FrieslandCampina, Amersfoort, the Netherlands
[d] Food Quality and Design Group, Wageningen University & Research, Wageningen, the Netherlands

A R T I C L E I N F O

Article history:
Received 24 September 2021
Received in revised form
16 December 2021
Accepted 17 December 2021
Available online 4 January 2022

A B S T R A C T

The nutritional, physicochemical, and functional properties of milk are affected by thermal processing. Buffalo milk make a substantial contribution to global milk production but there have been comparatively few studies on how thermal processing affects the properties of buffalo milk. This paper critically reviews the current knowledge regarding changes during thermal processing and storage of buffalo milk, buffalo milk-based products, and buffalo-bovine milk blends. Heating results in modifications of proteins and alteration in the salt balance, which subsequently affect stability against age gelation, sedimentation and creaming during storage. The extent of these changes is a function of milk composition. The mechanisms behind these observed changes are largely explainable based on studies from bovine milk. Hence, further studies on the heat-induced changes in the major constituents of buffalo milk are required to give a clearer picture on how these changes affect the final buffalo milk products.

Contents

* Corresponding author.
E-mail address: thom.huppertz@frieslandcampina.com (T. Huppertz).

https://doi.org/10.1016/j.idairyj.2021.105311
0958-6946/

1. Introduction

Throughout the development of human civilisation, milk and milk products have played a key role conferring several nutritional benefits due to its essential nutrients like protein, fat, lactose, vitamins, and minerals (Khedkar, Kalyankar, & Deosarkar, 2016). The Organisation for Economic Co-operation (OECD) and the Food and Agriculture Organisation (FAO) reported that global milk production is dominated by bovine milk (81%). In addition to cattle, many other kinds of livestock such as buffalo, goat, and camel provide milk that can be transformed into a variety of dairy products. Among these, only buffalo milk has a substantial global contribution, accounting for 15% of the world milk production (OECD/FAO, 2020).

The variations in compositional, physicochemical, and functional properties of bovine and buffalo milk make processing technology and settings for bovine milk sometimes not directly suitable for processing of buffalo milk (Becskei et al., 2020). Blending buffalo milk with bovine and non-bovine milk can be explored to further improve product properties. For instance, cream cheese made from a mixture of buffalo and bovine milk (50:50) had higher ash and lipid contents compared with cream cheese made from bovine milk (Fangmeier, Kemerich, Machado, Maciel, & De Souza, 2019). Additionally, buffalo milk can be mixed with bovine milk at a 25:75 ratio to produce chhana (Indian cottage cheese) with acceptable physico-chemical and organoleptic properties (Chakraborty, Singh, Shivhare, & Basu, 2020). When blended, the interactive effects of buffalo-bovine milk mixture increased the brightness and reduced the yellow colour intensity of chhana, and increased firmness and reduced stickiness compared with chhana made from bovine milk (Chakraborty et al., 2020).

Buffalo milk is often mixed with bovine milk when producing UHT treated milk in countries such as India, Pakistan, and Egypt (Deeth & Lewis, 2017). Trading milk mixtures, especially in India, could be traced to different milk handling practices, wherein most private and cooperative dairies do not have separate collection channels for bovine and buffalo milk (Aradhey, 2020). This could also be the reason why most vendors in Pakistan mix buffalo milk with bovine milk and sell it in open market. The vast majority (97%) of the milk supply in Pakistan is contributed by the informal sector in which milk is sold in raw form in urban and rural markets (Jawaid, Talpur, Nizamani, & Afridi, 2015). Utilisation of bovine and buffalo milk blends has also been explored in some dairy products such as cheeses (Arora & Khetra, 2017). Many countries, however, do not legally allow this practice (de la Fuente & Juárez, 2005). Nevertheless, from a farmer's perspective, an economic impact of milk mixtures makes this strategy feasible and interesting. In addition, production of dairy products from blends of milk species can promote and expand the dairy industry to many regions thereby strengthening the non-bovine production chain (Sant'Ana et al., 2013).

Irrespective of the origin, raw milk from any species has a relatively short shelf-life given its very nutritious nature, making it an excellent medium for growth of spoilage and pathogenic microorganisms. In addition, different enzymes in milk can also cause undesirable changes during storage; hence intervention is often necessary to extend the shelf-life of dairy products (Kelly, Datta, & Deeth, 2012). The majority of milk being consumed today is subjected to a variety of processing techniques to ensure safety and delay spoilage, and thermal treatment is the most common treatment utilised for raw milk (Mishra & Ramchandran, 2015).

However, numerous biochemical and physico-chemical changes occur in milk during thermal processing, which affect its keeping quality as well as nutritional and technological properties. This review will discuss the most significant of these changes that occur in buffalo milk, as well as in mixtures of buffalo and bovine milk, during thermal processing. Because heat treatment of milk during results in a number of physicochemical and structural changes in the milk constituents, this review will focus on the principal constituents of buffalo milk, as well as interactions between these constituents, in buffalo and bovine milk, as well as milk mixtures thereof. Approaches to minimise the undesirable heat-induced changes in buffalo milk and milk products are also covered.

2. Compositional differences between buffalo milk and bovine milk

2.1. Gross composition

Compositional aspects of buffalo and bovine milk have been studied and reviewed by many researchers (Ahmad et al., 2008; Becskei et al., 2020; Chakraborty et al., 2020; Choudhary, Arora, Kumari, Narwal, & Sharma, 2018; Fangmeier et al., 2019; Hamad & Baiomy, 2010; Kapadiya et al., 2016; Medhammar et al., 2012; Ménard et al., 2010). An overview of compositional properties of buffalo and bovine milk is shown in Table 1. Milk constituents for each species vary considerably because of various factors, e.g., genetic, physiological, nutritional, feed intake, seasonal, or related to the stage of lactation and animal husbandry practices (Ahmad, 2013; Kelly, 2010; Li, Yi, & Singh, 2019; van den Oever et al., 2021).

Buffalo milk is more densely white and has superior whitening properties compared with bovine milk owing to greater opacity of casein micelles (Ahmad, Anjum, Hima, Sameen, & Zahoor, 2013).

Table 1
Gross composition of buffalo milk in comparison with bovine milk.[a]

Milk constituent	Buffalo	Bovine
Protein	2.70# – 4.74‡	3.10# – 3.62‡
Fat	5.30# – 9.00#	3.30# – 5.50‡
Lactose	3.20# – 5.67§	3.82† – 5.60#
Ash	0.69‡ – 0.96†	0.68*– 0.80#
Total solids	11.90† – 19.18‡	11.93† – 14.20‡

[a] Values are percentages based on minimal and maximal values found in selected literature: *Hamad & Baiomy, 2010; †Fangmeier et al., 2019; ‡Kapadiya et al., 2016; #Medhammar et al., 2012; §Ménard et al., 2010.

Phospholipids are lower and saturated fatty acids are higher in buffalo milk (Ménard et al., 2010). Additionally, buffalo milk contains higher levels of conjugated linoleic acid than bovine milk (Guo & Hendricks, 2010). The pH of bovine milk ranges from 6.72 to 6.80 while that of buffalo milk ranges from 6.75 to 6.87 (Ahmad et al., 2008). Buffalo milk pH correlates with solid-non-fat and lactose content, but is not influenced by the lactation number or season and month of calving (Ahmad et al., 2013). The higher protein and fat contents of buffalo milk contribute to a higher viscosity compared with bovine milk (Sindhu & Arora, 2011).

2.2. Milk fat and milk fat globules

The fat content of buffalo milk can be up to two times higher than that of bovine milk (Table 1), which is chiefly responsible for its high energy density (Ahmad, 2013; Murtaza, Pandya, & Khan, 2017). Buffalo milk fat has a higher melting point, density, and saponification value, but a lower refractive index and iodine value compared with bovine milk fat (Ahmad et al., 2013). Buffalo milk fat also contains a higher proportion of high-melting triglycerides (9–12%) compared with bovine milk fat (5–6%) (Khedkar et al., 2016). In terms of fat globules, bovine milk typically contains >10 billion milk fat globules per mL, present in spherical droplets ranging from about 0.2 to 15.0 μm in diameter (Huppertz & Kelly, 2009). The amount of fat globules in buffalo milk is generally lower than bovine milk (~2.7 million fat globules per mL of buffalo milk) but they are mostly bigger (60% are in the size range 3.5–7.5 μm) (Arora & Khetra, 2017; El-Zeini, 2006; Ménard et al., 2010). At pH 4.5 to 4.6, buffalo milk fat globules are rendered chargeless (Sindhu & Arora, 2011). The milk fat globules are emulsified by a surface layer, the milk fat globule membrane (MFGM), which consists largely of proteins and lipids (MacGibbon & Taylor, 2006). Buffalo MFGM has an average lipid content of 38.5% while bovine MFGM has 35.7% (Sindhu & Arora, 2011).

2.3. Milk proteins

Buffalo milk, just like bovine milk, contains two major protein classes distinguished by their solubility in unheated milk at 20 °C and at pH 4.6: the insoluble caseins represent ~80% of total milk protein, and the remaining ~20% are the pH 4.6-soluble whey proteins (Fox, Uniacke-Lowe, McSweeney, & O'Mahony, 2015; Singh & Bennett, 2002). Since buffalo milk has a higher protein content than bovine milk (Table 1), it also contains higher concentrations of caseins and whey proteins (Arora & Khetra, 2017). The whey proteins of buffalo milk are similar to those in bovine milk. They are a heterogeneous polymorphic group of proteins composed of β-lactoglobulin (50%), α-lactalbumin (20%), serum albumin (10%), immunoglobulins (10%), and other minor proteins (<10%) such as lactoferrin, proteose peptone, and several enzymes (Ahmad, 2013; Fox et al., 2015). The whey proteins of buffalo milk have been reported to be more resistant to heat-induced denaturation than bovine whey proteins (Jainudeen, 2002; Mane & Chatli, 2015), which is discussed in further detail in Section 4.

Similar to in bovine milk, the caseins in buffalo milk are classified into four distinct gene products (α_{S1}-, α_{S2}-, β-, and κ-casein), which form supramolecular colloidal structures called casein micelles (Ahmad, 2013). The concentrations of the casein subfractions α_{S1}-, β-, and κ-are higher in buffalo milk than in bovine milk (Arora & Khetra, 2017). About 99% of the caseins in buffalo milk are present in micellar form (Ahmad et al., 2013), whereas in bovine milk, 90–95% of the casein is in micellar form and the rest is present in the soluble phase (Khedkar et al., 2016). Transmission electron microscopy (TEM) analysis of casein micelles in buffalo and bovine skim milk revealed smooth and circular close-packed structures of casein micelles (Adhikari & Mathur, 1993; Hooda, Mann, Sharma, & Bajaj, 2020), but the micelles were larger in buffalo milk (70–200 nm in diameter) than in bovine milk (50–180 nm in diameter) (Adhikari & Mathur, 1993; Ahmad et al., 2013; Hussain, Bell, & Grandison, 2013). Additionally, buffalo milk casein micelles are less hydrated and contain more colloidal calcium and colloidal inorganic phosphate than bovine milk casein micelles (Ahmad, 2013).

2.4. Milk salts

Buffalo milk has been found to contain higher concentrations of salts than bovine milk. The total calcium, magnesium, and inorganic phosphate concentrations were found to be higher in buffalo milk than in bovine milk (Kapadiya et al., 2016; Murtaza et al., 2017), but the concentrations of soluble calcium, magnesium, and inorganic phosphate were similar in both milks (Ahmad et al., 2008). At normal milk pH, the minerals are distributed between aqueous and micellar phase of milk. Similar to bovine milk, potassium, sodium, and citrate in buffalo milk are mainly in the aqueous phase, whereas magnesium, calcium, and inorganic phosphate are partly in the micellar and partly in the aqueous phase (Ahmad et al., 2008). The diffusible citrate content was measured to be lower in buffalo milk than in bovine milk, but the total citrate concentrations were similar in both milks (Table 2). Furthermore, buffalo milk has higher total and diffusible concentrations of magnesium and sodium than bovine milk (Table 2). This means that the quantities of calcium and inorganic phosphate associated with casein micelles are higher in buffalo milk than in bovine milk. Ahmad et al. (2008) found that 82% and 72% of calcium were in the micellar phase of buffalo and bovine milk, respectively. For inorganic phosphate, ~48% was in the micellar phase in bovine milk whereas approximately 66% was in the micellar phase in buffalo milk (Ahmad et al., 2008).

3. Thermal processing of milk

The objective for heat treatment of milk varies, but always involves enabling the production of stable and safe products through the reduction or elimination of spoilage and pathogenic microorganisms. The resulting product quality greatly depends on the intensity of the heat treatment, i.e., the combination of temperature and the duration of heat treatment. Since compositional, physicochemical, and functional properties of milk from different species vary, it is important that the time–temperature combinations for processing bovine milk or buffalo milk or their mixtures be standardised and suitably modified. The lower heat capacity and higher thermal conductivity of buffalo milk compared with bovine milk indicate that a lower amount of heat energy is required to achieve certain desired effects in buffalo milk (Sindhu & Arora, 2011). Regardless of the type of heat treatment, the process must be able to reduce the microbial population in raw milk, inactivate

Table 2
Mean concentration (in mM) of major salts in buffalo milk and in bovine milk.[a]

Minerals	Buffalo		Bovine	
	Total	Diffusible	Total	Diffusible
Calcium	47.1	8.2	30.5	8.6
Inorganic phosphate	27.7	9.2	19.2	9.9
Magnesium	7.3	3.5	4.6	3.0
Sodium	20.3	18.4	17.5	15.9
Potassium	28.7	26.0	42.0	37.3
Citrate	8.3	7.1	8.8	8.2

[a] Source: Ahmad et al. (2008).

enzymes, and minimise chemical reactions as well as physical changes.

3.1. Thermisation

In most countries, the mildest heat treatment in the form of thermisation, which is used to extend storage life of raw milk before it is subjected to the further processing. Thermisation involves heating milk at temperatures between 57 and 68 °C for 5–20 s and aims to destroy psychrotrophic bacteria that may release heat-resistant proteases and lipases into milk (Deeth & Lewis, 2017) and extends the shelf-life by up to 3 d provided prompt cooling is applied to the thermised milk (Panthi, Jordan, Kelly, & Sheehan, 2017). Humbert, Campbell, Blankenagel, and Gebre-Egziabher (1985) recommended a thermisation treatment of 65 °C for 20 s, as this was the minimum condition for extending the shelf-life of bovine milk by 4 d at 4 °C. Haq et al. (2014) reported that thermisation at 60 °C for a few seconds improved the taste/flavour of buffalo skim milk with shelf-life extended to 3 days upon storage at 4–8 °C. As thermisation is a mild heat treatment, thermisation is always followed later by pasteurisation or a more severe heat treatment.

3.2. Pasteurisation

Pasteurisation conditions are designed to inactivate the most heat-resistant, non-spore-forming pathogens (*Mycobacterium tuberculosis* and *Coxiella burnetii*) and spoilage bacteria in milk, as well as lipoprotein lipase, but are insufficient for inactivation of plasmin or bacterial proteases and lipases (Deeth & Lewis, 2017). Pasteurisation processes can be categorised as either low-temperature, long-time (LTLT; 62–65 °C for at least 30 min) or high-temperature, short-time (HTST; 72–82 °C for 15–30 s) pasteurisation followed by rapid cooling to less than 10 °C (Kelly et al., 2012). If stored at temperatures <5 °C, pasteurised products can have a shelf-life up to 30 d (Sepulveda, Góngora-Nieto, Guerrero, & Barbosa-Cánovas, 2005; Ziyaina, Govindan, Rasco, Coffey, & Sablani, 2018). Pasteurised (72 °C for 15 s) buffalo milk was reported to have a shelf-life up to 10 d when stored at 10 ± 1 °C (Nasr & Elshaghabee, 2019), slightly lower that of bovine milk subjected to the same pasteurisation and storage conditions (12 d; Ziyaina et al., 2018). Buffalo skim milk pasteurised at 65 °C for 30 min had a shelf-life up to 12 d at 4–8 °C (Haq et al., 2014).

3.3. Sterilisation

Sterilisation is a heat treatment designed to produce a commercially sterile product with an extended shelf-life. This can be achieved by either in-container sterilisation (110–116 °C for 20–30 min) or ultra-high temperature (UHT) treatment (135–145 °C for 1–10 s) (Deeth & Lewis, 2016). In-container sterilisation inactivates virtually all milk enzymes, but the treatment results in browning due to extensive Maillard reactions, a sterilised milk flavour, and denaturation of whey proteins (Deeth & Lewis, 2017). UHT treatment results in less chemical changes and a weak cooked flavour, but some bacterial proteases or lipases may survive the process. UHT treatment in combination with aseptic packaging can extend the ambient shelf-life of milk up to 12 months, with less chemical changes compared with in-container sterilisation. Selection of time–temperature combinations of UHT processing must be based on the inactivation of heat-resistant spores of *Geobacillus stearothermophilus* with least possible undesirable changes of physicochemical and sensory properties as well as retention of nutritional values (Datta, Elliott, Perkins, & Deeth, 2002; Deeth, 2010). UHT processing can be done with either direct or indirect heating systems. Direct heating results in instantaneous rise in temperature due to mixing with superheated steam, followed by rapid cooling through vacuum flash cooling process. Indirect heating results in slower heating and cooling as the heat transfer occurs across wall of stainless-steel plate or tube exchanger (Deeth, 2020; Eisner, 2021; Kelly et al., 2012).

Sterilisation (110 °C for 10 min) was reported to greatly improve the appearance/colour as well as the flavour of buffalo skim milk and extended its shelf-life up to 28 d when stored at 4–8 °C (Haq et al., 2014). Limited studies were made on determining actual shelf-life of UHT-treated buffalo milk or mixtures of buffalo and bovine milk, but commercially available products have an indicated shelf-life of 90 d (Hussain, 2011). Rehman and Salariya (2005) observed that commercial UHT whole buffalo milk has acceptable organoleptic qualities even after a 90-d storage at 10 °C and at 20 °C. Similarly, Hussain (2011) reported acceptable sensory qualities of commercially processed UHT buffalo skimmed milk after 90-d storage at 10 °C and at 25 °C.

4. Heat-induced changes in the constituents of buffalo milk

4.1. Heat-induced changes in milk proteins

The most significant heat-induced changes in milk are those that involve proteins, particularly whey protein denaturation, interactions of denatured whey proteins caseins and MFGM proteins, and casein micelle dissociation (Deeth & Lewis, 2017; Fox et al., 2015; Singh & Bennett, 2002). These processes can alter the physicochemical properties of milk and affect its functional and sensory properties, as well as the stability. Whey proteins are heat labile due to their high levels of secondary, tertiary, and quaternary structures. Denaturation of bovine whey proteins commences at temperatures as low as 40 °C but is largely reversible up to ~70 °C (Deeth, 2010). The extent of denaturation depends on the intensity of heat treatment and protein type, with bovine β-lactoglobulin being more heat sensitive than α-lactalbumin (Kinsella & Whitehead, 1989).

To determine the effect of heating on buffalo whey protein denaturation, Agrawal, Bund, and Pandit (2008) heated pH-adjusted (pH 5.3) buffalo whey at 70–95 °C for 10–120 min and reported that whey protein denaturation was directly proportional to the heating temperature. Serum albumin was the first whey protein to be denatured when buffalo whey is heated at 92 °C (Fig. 1). Using HPLC analysis of pasteurised buffalo whey, Gillani (2015) found that pasteurisation at 65 °C for 30 min resulted in higher α-lactalbumin and β-lactoglobulin denaturation compared with pasteurisation at 72 °C for 15–20 s (54% versus 45% and 48% versus 33%, respectively), which may be related to the higher total heat load in former process. Elagamy (2000) reported that heating buffalo skim milk at 65 °C for 10, 20 or 30 min did not lead to considerable whey proteins denaturation based on SDS-PAGE analysis. At higher temperature, however, denaturation of whey proteins was observed. Denaturation of whey proteins, particularly β-lactoglobulin in buffalo skim milk occurred at 75 °C and increased with heating time and was more pronounced in buffalo milk compared with bovine milk (Elagamy, 2000). Some of the observed variation in denaturation could be related to the genetic variants of milk proteins. Ahmad (2013) stated that buffalo milk β-lactoglobulin is homologous to bovine β-lactoglobulin B which has been reported to be more rapidly denatured than bovine β-lactoglobulin A, which is the dominant variant in bovine milk (Gough &

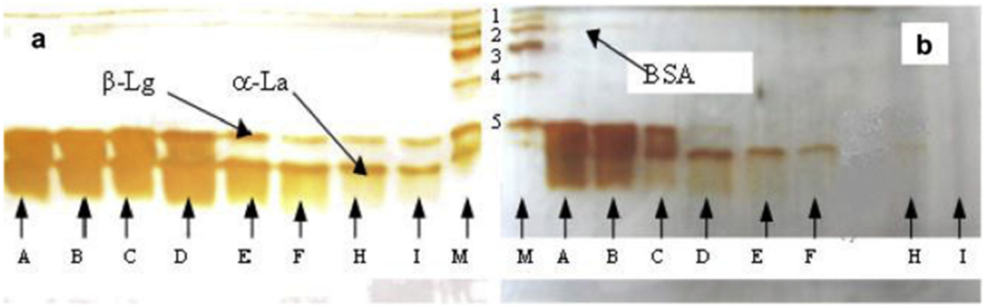

Fig. 1. SDS-PAGE of buffalo whey subjected to agitation rates of (a) 1.66 s^{-1} and (b) 10 s^{-1} during heating at 92 ± 2 °C as reported by Agrawal et al. (2008). A, native whey; B, heated for 5 min; C, heated for 10 min; D, heated for 15 min; E, heated for 20 min; H, heated for 45 min; I, heated for 60 min; and M, protein ladder corresponding to (1) 97 kDa, (2) 66 kDa, (3) 43 kDa, (4) 29 kDa, and (5) 18.4 kDa. Reproduced with permission from Agrawal et al. (2008).

Jenness, 1962; Robitaille, Britten, Morisset, & Petitclerc, 2002). Ismail, Mashaley, and Sirry (1969) reported a 43% reduction in native β-lactoglobulin when buffalo skim milk was heated at 75 °C as opposed to 34% in bovine skim milk heated at the same temperature. Increasing temperature >75 °C resulted in further denaturation of β-lactoglobulin in buffalo milk (Elagamy, 2000).

Indirect UHT treatment, or heating at temperatures <70 °C, foster hydrophobic interactions between β-lactoglobulin and κ-casein on the micelle surface; in contrast, rapid heating, such as direct UHT treatment, or heating at high temperatures allows β-lactoglobulin to form aggregates via disulphide bonds with serum κ-casein, with other whey proteins, or with proteins on milk fat globule membrane proteins (Mottar, Bassier, Joniau, & Baert, 1989; Najib et al., 2020; Sakkas, Moutafi, Moschopoulou, & Moatsou, 2014). Although many studies investigating the interaction between β-lactoglobulin and κ-casein were based on purified or partially purified proteins and bovine milk, it was shown that similar patterns for complexation were identified in boiled skim buffalo milk (Adhikari & Mathur, 1993), skim buffalo milk heated at 85 °C for 5 min (Patil et al., 2019), boiled buffalo milk during khoa preparation (Choudhary et al., 2018), and heated buffalo milk and mixtures of buffalo milk and bovine milk during chhana preparation (Chakraborty et al., 2020).

The mechanism involved in bovine whey protein denaturation and aggregation had been widely discussed in various studies and reviews (Brodkorb, Croguennec, Bouhallab, & Kehoe, 2016; Dissanayake, Ramchandran, Donkor, & Vasiljevic, 2013; Mulvihill & Donovan, 1987; Oldfield, Singh, Taylor, & Pearce, 1998; Owusu-Apenten, Khokhar, & Galani, 2002; Plana-Fattori, Doursat, Coutouly, Riaublanc, & Flick, 2020; Roefs & De Kruif, 1994; Verheul, Roefs, & De Kruif, 1998; Wolz & Kulozik, 2015). As described by Mulvihill and Donovan (1987), denaturation and aggregation of whey proteins is dominated by β-lactoglobulin as the major protein in whey and involves two distinct stages: (i) unfolding of the initially folded structure of globular β-lactoglobulin at temperatures >65 °C and (ii) interaction (due to fluid motion and collision) of the unfolded molecules to irreversibly form protein aggregates. A number of heat-sensitive MFGM proteins can be affected when liquid milk is subjected to thermal treatment as low as 60 °C. Some changes include certain denaturation and interactions with bovine whey proteins via sulphydryl-disulphide interchange reactions (Corredig & Dalgleish, 1996; Mehta, 1980; Mulder & Walstra, 1974; Singh & Bennett, 2002).

In chhana preparation, where milk is heated to 90 °C, Chakraborty et al. (2020) described that the adsorption of denatured whey proteins on fat globules affected the product yield. Comparing buffalo milk, bovine milk, and a mixture of buffalo and bovine milk, the researchers obtained highest chhana yield from mixed milk samples (75:25 buffalo to bovine milk ratio as shown in Table 3). Bovine milk whey proteins denature at a faster rate compared with their counterparts in buffalo milk (Mane & Chatli, 2015); hence the chance of adsorption of denatured whey proteins and subsequent entrapping with the fat globule occurs faster in partially substituted milk compared with pure buffalo milk. The exact mechanism by which these proteins interact with the fat globules was not elucidated by Chakraborty et al. (2020) but could involve the displacement of the original MFGM proteins by whey proteins, either by directly competing or because heating might cause the breakdown or reorganisation of the MFGM, leaving gaps to allow whey proteins to adsorb to the newly exposed fat surface (Fox et al., 2015; Singh & Gallier, 2017).

In contrast to whey proteins, the caseins in milk are remarkably heat stable due to their lack of well-defined secondary and tertiary structure. Additionally, the heat stability of caseins in casein micelles is due to inner stabilisation by calcium bridges and calcium phosphate as well as the presence of κ-casein on the surface of the micelle, where it forms a boundary layer between the micelle core and the serum phase surrounding the micelle (Dumpler, 2018; Maćej, Jovanović, Denin, & Djurdjević, 2002). Although caseins are heat-stable, heating temperatures more severe than pasteurisation can cause changes in the casein micelle, including in the zeta potential, size, hydration of micelles, and association–dissociation reactions (Dumpler, 2018; Hovjecki, Miloradovic, Rac, Pudia, & Miocinovic, 2020; Ono, Yoshuda, Tanaami, & Ohkosi, 1999). An increase in casein micelle size and a decrease in zeta potential (less negative) was observed by Perveen, Butt, Huma, and Nawaz (2015) when rehydrated sodium phosphocaseinate powder from buffalo milk was subjected to heating from 60 to 90 °C. Perveen et al. (2015) attributed these heat-induced changes in buffalo casein micelles to the denatured whey proteins that associated with the casein micelle surface and the partial aggregation of the (whey-protein-coated) casein micelles. Adhikari and Mathur (1993) observed through TEM analysis of boiled buffalo skim milk that smaller micelles attached to the larger micelles either through protein

Table 3
Effects of type of milk and seasonal variation on the mean yield of chhana.[a]

Type of milk	Yield (%)	
	Summer	Winter
Buffalo milk	15.45	15.82
Mixture of buffalo and bovine milk (75:25)	15.66	16.61
Mixture of buffalo and bovine milk (50:50)	15.52	15.90
Mixture of buffalo and bovine milk (25:75)	14.87	15.03
Bovine milk	14.02	14.28

[a] Source: Chakraborty et al. (2020).

bridging or fused closely to a single mass (Fig. 2). Ono, Yoshida, Tanaami, and Ohkosi (1999) implied that the interactions of small bovine casein micelles with hydrophobic sites on larger micelles with whey protein as a stimulator of micellar association could lead to heat-induced increase in casein micelle size. Heating milk up to 90 °C caused only minor changes in the size of casein micelles in bovine milk, but more severe heat treatments increased micelle size accompanied, by a large increase in the number of small particles which could be formed by disaggregation of casein micelles (Singh & Bennett, 2002).

The dissociation of individual bovine caseins from the micelle has been reported to be temperature dependent for specific caseins (Anema, 2021). In buffalo milk or mixtures of buffalo milk and bovine milk, however, the heat-induced dissociation of caseins is yet to be investigated. In bovine skim milk at natural pH, increasing proportions of α_S- and β-caseins were liberated into the serum when heated up to 60 °C, but these decreased as the temperature is increased to 90 °C; in contrast, the level of κ-casein dissociating from the micelles increased with increasing temperature (Anema & Li, 2000). This was confirmed by Liu et al. (2019) on whole bovine milk samples. Comparing the effect of pasteurisation (85 °C for 15 s) and that of UHT treatment (141 °C for 2 s, indirect system), Liu et al. (2019) reported a decreasing dissociation of α_S- and β-caseins from the micelle as heat treatment went from pasteurisation to UHT processing. Correspondingly, the dissociation behaviour of κ-casein is described by a continuous increase over the entire temperature range. This is probably related to the temperature-dependence of denaturation of whey proteins. At temperatures above 65 °C, whey proteins denature and interact with each other and with κ-casein (Singh & Bennett, 2002). This interaction at the micelle surface inhibits the dissociation of α_S- and β-caseins but promotes the dissociation of κ-casein (Anema & Li, 2000).

4.2. Heat-induced changes in milk fat and milk fat globules

Thermal degradation of lipids in milk is generally not observed although release of fatty acids and some inter-esterification may occur, but these changes are unlikely during the normal processing of milk (Claeys et al., 2014). Khan, Hassan, and Rauf (2018) reported increased amounts of trans fatty acids in buffalo milk fat sample (in the form of ghee) when temperature increased from 120 °C to 170 °C.

Changes in lipid domains, e.g., size, shape, number, lipid phase, and nanomechanical properties, in the outer bilayer of the MFGM as a function of temperature alter the mechanical properties of the fat globule. Elevated temperatures cause the removal of some of the original MFGM components such as triglycerides, phospholipids, and proteins, causing fat globules to be partially denuded and may therefore coalesce and form large clumps (Fox et al., 2015; Mulder & Walstra, 1974). There are, however, conflicting results on the effect of thermal treatments on polar lipids from whole milk fat globules. In situ structural investigations of buffalo MFGM showed that at temperatures up to 60 °C, phase separation of polar lipids takes place leading to different domains in the outer bilayer of the MFGM (Nguyen et al., 2016). Houlihan, Goddard, Kitchen, and Masters (1992) reported that heating at 80 °C for 20 min resulted in significant losses of triglycerides but had little or no effect on the phospholipids in the bovine MFGM. In contrast, loss of phospholipids from the MFGM was reported for bovine milk heated at 80 °C (Lee & Sherbon, 2002; Zanabria, Tellez, Griffiths, & Corredig, 2014). Variations could be ascribed to the differences in the treatment as well as the methodology used particularly in the isolation procedure, subsequently modifying the structure of the membrane.

The consequences of these heat-induced changes in the MFGM have not been widely studied, possibly because heated milk products are usually homogenised and an artificial membrane is formed with a different composition, mainly of casein and some whey proteins (Anema, 2019; Lee & Sherbon, 2002; Obeid et al., 2019; Wiking, Gregersen, Hansen, & Hammershøj, 2021). The behaviour of globules during and after heating is therefore different from that of natural milk fat globule. Homogenised fat globules act as large casein micelles because of the casein in their new membranes and thus participate in any reaction of the caseins (Singh & Bennett, 2002).

The size of bovine milk fat globule was not affected by heating alone but when accompanied with homogenisation either before or after heat treatment, the size of the globules decreased (Lee & Sherbon, 2002; Michalski & Januel, 2006). Abesinghe et al. (2020) reported an increase in the size of fat globule when homogenised buffalo milk was heated at 85 °C for 30 min. These conflicting results may be due to differences in intensity of homogenisation and heat treatment employed. Homogenisation could significantly modify the surface composition of MFGM which may retard agglomeration upon heating. Conversely, the attachment of disrupted milk fat globule to proteins and the formation of protein–protein interactions during heating may cause clumping of globules.

4.3. Heat-induced changes in milk salts

Depending on the severity of the process, thermal treatment modifies the salt balance between the aqueous and colloidal phases of milk (de la Fuente, Olano, Casal, & Juárez, 1999; Huppertz & Kelly, 2009; Nieuwenhuijse & Huppertz, 2021). Heating of milk results in a transfer of calcium phosphate from the soluble to colloidal phase leading to reduced ionic calcium and a concomitant decrease in

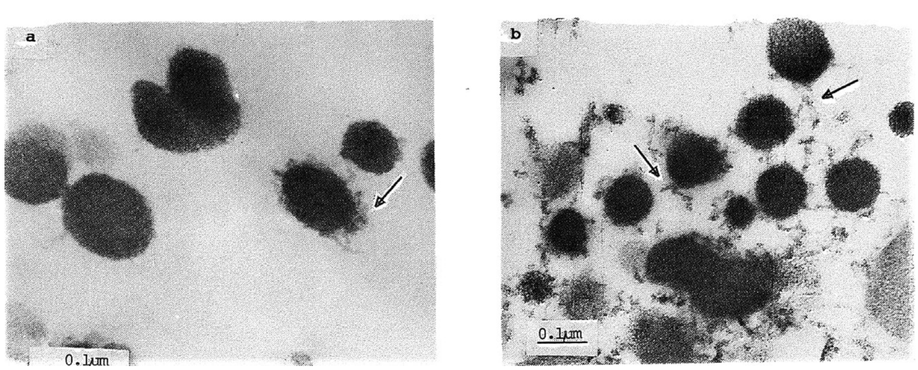

Fig. 2. Transmission electron micrographs of boiled (5 min) bovine milk (2a) and buffalo milk (2b). Arrows point to denatured whey proteins that precipitated onto the casein micelle surface. Reproduced from Adhikari and Mathur (1993).

bovine milk pH (Anema, 2009; Kelly et al., 2012). On heating at <95 °C, these changes are largely reversible when the temperature of the milk is restored to its initial value but could be irreversible under more severe heat treatments (Gaucheron, 2005; Nieuwenhuijse & Huppertz, 2021).

Adhikari and Mathur (1993) reported a considerable alteration in the salt balance of buffalo milk after heating at 101 °C for up to 25 min, which are shown in Fig. 3A; soluble calcium and phosphorus levels decreased as a result of precipitation of calcium-phosphate during heating. Similar trends were also observed for bovine milk (Fig. 3A; Adhikari & Mathur, 1993). After analysing the dialysates from bovine milk subjected to heat treatments of 85 °C–140 °C for 2 s, On-Nom, Grandison, and Lewis (2010) reported small but significant changes in total divalent cations (calcium and magnesium) suggesting that there might be heat-induced modifications in salt partitioning between colloidal and soluble forms, but these did not significantly influence milk pH and ionic calcium levels.

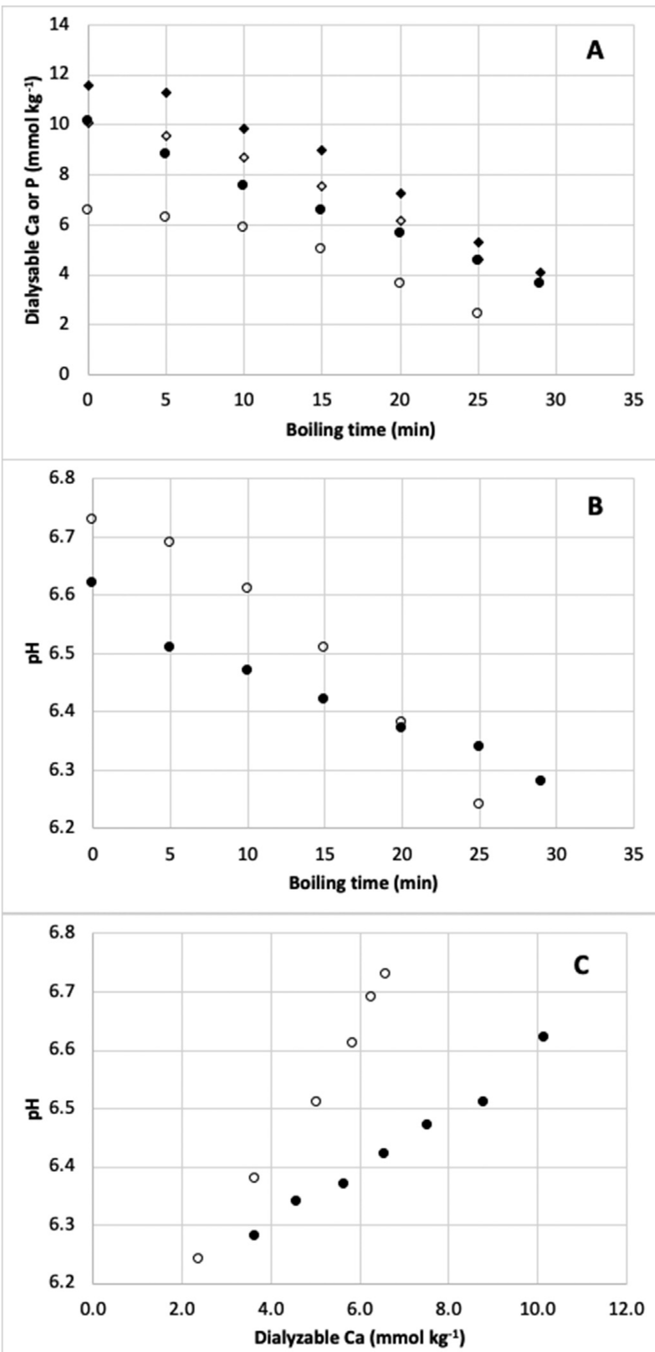

Fig. 3. (A) influence of boiling time on the concentration of dialysable Ca (●,○) and P (◆,◇) in bovine milk (●,◆) and buffalo milk (○,◇). (B) influence of boiling time on the pH of bovine milk (●) and buffalo milk (○). (C) relationship between dialysable Ca and pH of bovine milk (●) and buffalo milk (○) boiled for several times. Data from Adhikari and Mathur (1993).

5. Effect of heat treatment on properties of buffalo milk

5.1. pH

In fresh bovine milk, pH usually ranges from 6.7 to 6.8 and in buffalo milk from 6.7 to 6.9 (Ahmad et al., 2008). Milk pH is affected by temperature, generally decreasing with increasing temperature (Huppertz & Kelly, 2009). The heat-induced reduction of pH is primarily due to the shift in salt balance of milk, and is largely reversible on subsequent cooling (Dixon, 1963). According to Fox (1981), when milk is heated at elevated temperatures for prolonged periods of time, a further drop in pH can happen as a result of: (i) production of organic acids from lactose; (ii) precipitation of primary and secondary calcium phosphate as tertiary phosphate with concurrent release of H^+; and (iii) hydrolysis of organic phosphate and its subsequent precipitation as $Ca_3(PO_4)_2$ with release of H^+. pH reductions as a result of lactose degradation and dephosphorylation are irreversible on subsequent cooling, whereas pH reductions are a result of calcium phosphate precipitation are partially or completely reversible on cooling and subsequent storage (Fox, 1981). Heat-induced degradation of lactose and heat-induced dephosphorylation are commonly not observed during pasteurisation or UHT treatment, but can occur during in-container sterilisation (Huppertz, 2016).

In line with this, Ranvir, Sharma, Gandhi, Nikam, and Mann (2021) reported that pasteurisation and UHT treatment (4 s at 140 °C) did not significantly affect the pH of milk, which was a toned blend of buffalo and bovine milk (Ranvir, personal communication) compared with the raw milk from which they were prepared. Subsequent storage of the UHT-treated milk at 5 °C and 30 °C for up to 4 months resulted in a progressive reduction in pH, the extent was higher at 30 °C than at 5 °C. These reductions in pH during storage may be related to ongoing Maillard reactions, which were shown to occur in the sample during storage (Ranvir et al., 2021). In contrast to Ranvir et al. (2021), Haq et al. (2013) reported a higher pH for pasteurised (65 °C for 30 min; pH 6.46) or sterilised (110 °C for 10 min; pH 6.55) compared with raw skimmed buffalo milk (pH 6.38). Such effects are unexpected and have not been reported previously for bovine milk. It should be noted, however, that the pH of raw buffalo milk reported by Haq et al. (2013) is ~0.4 units lower than that commonly reported, indicating that notable acidification had occurred in this sample, which could be the result of microbial growth. It was also not specified when pH measurements were conducted in relation to milk receipt. As a result, the lower pH of raw milk than sterilised milk reported by Haq et al. (2013) may be related to acidification as a result of microbial activity. This is in line with the fact that titratable acidity in sterilised milk was lower than in raw milk (Haq et al., 2013) whereas reductions in acidity during heating are unlikely to occur. Adhikari and Mathur (1993) studied the influence of boiling time on the pH of buffalo and bovine milk. As shown in Fig. 3B, pH decreased with increasing boiling (101 °C) time for both milks, but decreases were more extensive for buffalo milk than for bovine milk. The strong relation between dialysable Ca and pH of the

Table 4
Effect of heat treatment on the viscosity of milk (3% fat).[a]

Milk source	Viscosity (mPa s)		
	Unheated	Heated	
		72 °C, 15 s	90 °C, 10 min
Buffalo milk	2.202	2.313	2.770
Bovine milk	2.036	2.155	2.460

[a] Source: Khalifa and Ghanimah (2013).

boiled milk samples (Fig. 3C) indicates that the heat-induced reductions in pH during boiling were primarily due to precipitation of calcium phosphate.

5.2. Viscosity

Viscosity of milk is dependent on the protein and fat content (Khedkar et al., 2016); the viscosity of buffalo milk (2.25 mPa s) is generally higher than that of bovine milk (1.45 mPa s; Sindhu & Arora, 2011). Walstra, Wouters, and Geurts (2006) stated that heating milk would increase viscosity due mainly to increased voluminosity of the casein micelles. This was confirmed in a study conducted by Ismail and El Deeb (1973) who reported that the viscosity of sterilised (116 °C for 15 min) buffalo milk and bovine milk was higher that of their pasteurised (65 °C for 20 min) counterparts. Khalifa and Ghanimah (2013) compared the viscosity of buffalo milk with that of bovine milk at the same fat content (3%) and observed that both milk samples showed increased viscosity as heating temperature was increased from 72 °C to 90 °C, with buffalo milk having a higher viscosity than bovine milk (Table 4). Despite having the same fat content, the higher viscosity value measured in buffalo milk could be due to its larger casein micelles and a higher protein content compared with bovine milk (Khalifa & Ghanimah, 2013). Anema, Lowe, and Li (2004) reported that an increase in the micelle volume as well as the interaction of denatured whey proteins with the micelles contributed to viscosity change during heating. The denaturation of whey proteins was also presumed by Ranvir et al. (2021) to be a contributory factor in viscosity increase when toned milk mixture of buffalo and bovine milk was subjected to pasteurisation and UHT treatment.

6. Heat stability of buffalo milk

6.1. Heat-induced coagulation of buffalo milk

Coagulation of milk or dairy products during heating is a consequence of loss of casein micelle stability due to numerous physical and chemical changes in its components. Particularly, heat-induced acidification and the heat-induced dissociation of κ-casein from the micelle surface render the system susceptible to coagulation (Huppertz, 2016). Owing to the high protein and calcium contents of buffalo milk, its heat stability is lower than that of bovine milk, i.e., buffalo milk coagulates faster than bovine milk (Khedkar et al., 2016).

Early studies by Sommer and Hart (1919, 1922) showed that proper salt balance, i.e., the ratio of the divalent cations (calcium and magnesium) to that of multivalent anions (phosphates and citrates) will prevent the coagulation of bovine milk during heating and that any deviation from this ratio reduces heat stability. The pronounced effect of salt composition on heat-induced coagulation of buffalo milk was verified in the study of Tayal and Sindhu (1983), who determined the heat coagulation time (HCT) of unconcentrated and concentrated buffalo milk at 130 °C; concentrated milk had a significantly lower HCT (3 min) compared with unconcentrated milk (33 min). Addition of 1.0% acid casein (from buffalo skim milk) to the concentrated buffalo milk led to greater stability of casein micelles and a significant increase in heat stability (Tayal & Sindhu, 1983). Numerous heat-induced changes in milk such as pH reduction, whey protein denaturation and subsequent association with casein micelles, precipitation of calcium phosphate onto the casein micelles, and dissociation of κ-casein from the micelle play an important role in the heat-induced coagulation of milk (Dumpler, Huppertz, & Kulozik, 2020; Huppertz, 2016). It remains unclear, however, which particular changes are directly responsible for coagulation and which are only incidental factors, or, are caused by the coagulation process. For instance, in boiling buffalo milk during the manufacture of khoa, Choudhary et al. (2018) suggested that the coagulation was due to protein–protein interactions. Electrophoretic image analysis of casein sample from boiled buffalo milk showed a β-lactoglobulin band, the evolution of which was assumed to be due to heat-induced interaction between β-lactoglobulin and κ-casein (Choudhary et al., 2018). Furthermore, Adhikari and Mathur (1993) reported that the decrease in soluble calcium (63% reduction) along with the denaturation of whey proteins and their concurrent interaction with the casein micelles during boiling of buffalo skim milk (Fig. 2) increased the micellar destabilisation, followed by heat coagulation. Their results ascertain that the association of casein micelles on prolonged heating is not only dependent on the deposition of whey proteins but also on the calcium ion concentration of the environment.

The high calcium content in buffalo milk along with its sharp transition from soluble to colloidal phase during boiling was assumed to be the major contributory factor for the faster precipitation during heating of buffalo milk (Adhikari & Mathur, 1993). Adhikari and Mathur (1993) hypothesised that phosphate and citrate might play a role in heat-induced coagulation of buffalo milk. As calcium-phosphate is converted from soluble to the colloidal state, it precipitates onto the casein micelles rendering these less stable. As a result, the precipitated calcium phosphate may shield the charge on the protein molecules thereby reducing the repulsive forces between the micelles leading complete destabilisation of the micellar system.

6.2. Influence of added salts on the heat-induced coagulation of buffalo milk

Manipulating the properties of serum salt composition casein micelles through the use of calcium chelators such as citrate, phosphate, or hexametaphosphate (HMP) has been known to improve the heat stability in bovine milk products (Augustin & Clarke, 1990; Fox et al., 2015). Chelator-induced increase in heat stability of milk is believed to be due to a shift in protein-mineral equilibrium leading to a decrease in the concentration of free calcium ions, depletion of CCP from the micelles, and release of specific caseins from the micelle (De Kort, Minor, Snoeren, Van Hooijdonk, & Van Der Linden, 2012; Holt, 1992). Furthermore, effects on the heat-induced dissociation of κ-casein and changes in the association of denatured whey proteins with casein micelles will contribute to the effects observed (Dumpler et al., 2020). Adding up to 0.20% monosodium phosphate has been reported to increase the heat stability of concentrated buffalo milk (Sindhu, 1985) and buffalo skim milk ultrafiltration retentate (Solanki & Gupta, 2009). Likewise, Khatkar, Gupta, and Khatkar (2014) reported that the heat stability of a dairy whitener from buffalo skim milk ultrafiltered retentate was enhanced by adding 0.4% of a 2:1 (w/w) mixture of monosodium and disodium phosphate.

6.3. Influence of lactose and urea concentration on the heat-induced coagulation of buffalo milk

Lactose is a primary contributor to the heat-induced acidification of milk at temperatures >100 °C, and can thereby reduce heat stability (Huppertz, 2016). It was assumed that a reaction that parallels the Maillard reaction during heat treatment of milk was the most relevant in relation to heat stability of milk (Fox et al., 2015). In addition to the formation of advanced Maillard products, the isomerisation and subsequent thermal degradation of lactose also leads to the formation of organic acids, principally formic acid, hence a decrease in pH in milk (van Boekel, 1998). This decrease in pH was assumed to negatively affect heat stability due to the reduction of the net negative charge of casein micelles in milk after prolonged heating (Sinaga, Bansal, & Bhandari, 2017). Modifying lactose content of concentrated milks (approximately 8.5% protein) had little effect on heat stability of bovine milk but a stabilising effect was observed when both lactose and urea were added; lactose optimum concentration was approximately 1%, when combined with 5–20 mM urea (Shalabi & Fox, 1982). Huppertz (2016) described that the stabilisation effect could be related to the reaction of lactose with homocitrulline formed as a result of the reaction of lysine with isothiocyanate, a degradation product of urea.

Urea is the only indigenous milk constituent that has been shown to correlate strongly with natural variations in heat stability of milk (Huppertz, 2016; Singh, 2004). Ahmad (2013) reported that the urea concentration in bovine milk (5.1 mM) is higher than in buffalo milk (4.0 mM). Earlier studies indicate that a level of >7 mM of urea is needed to improve the stability of bovine milk (Muir & Sweetsur, 1977). At natural milk pH, it has been suggested that elevated levels of urea prevent crosslinking and aggregation of proteins, and also keep the pH stable (Deeth & Lewis, 2016). At higher pH levels (≥6.9), the stabilising effect of urea is believed to be through the buffering capacity of one of its degradation products, ammonia (Crowley et al., 2014). Ghatak, Bandyopadhyay, and Gupta (1990) reported that adding 5 mM urea to raw buffalo milk greatly increased the heat stability at pH values in the range 6.4–7.4. Ghatak et al. (1990) further observed a significant improvement on the heat stability of raw buffalo milk and concentrated buffalo milk when urea addition was combined with 2-deoxyribose (7.5 mM). In skimmed buffalo milk, Rajput, Bhavadasan, Singh, and Ganguli (1982) reported that adding 4.2 mM urea improved the heat stability at pH 6.5–6.7; outside that pH range, the heat stability of skimmed buffalo milk was low and did not improve regardless of the amount of urea added (Rajput et al., 1982). Increasing the amount of added urea >16.65 mM greatly reduced the heat stability of skimmed buffalo milk (Rajput et al., 1982). Muir and Sweetsur (1977) reported that at pH 6.6–7.2, urea does not change the mechanism of the coagulation reactions thus addition of urea in this pH region does not lead to a longer HCT.

6.4. Influence of pre-heating on the heat stability of buffalo milk

Pre-heating or forewarming of bovine milk has been found to increase the heat stability of concentrated milk prepared therefrom, and is an integral part of concentrated milk processing before sterilisation (Dumpler et al., 2020). Nayak et al. (2004) found that preheating buffalo skim milk at 90 °C for 10 min resulted to a considerably lower HCT (30.8–32.0 min) compared with raw buffalo milk (61.6 min), as reported by Singh and Roy (1978). The presence of fat in milk up to the normal concentration caused higher stability which Ismail and El Deeb (1973) observed after preheating buffalo skim milk and standardised buffalo milk (3% fat) at 92 °C for 10 min. Ismail and El Deeb (1973) deduced that fat globules may provide nuclei which encourage the precipitation and crystallisation of basic calcium and magnesium phosphates, consequently contributing to a higher colloidal stability during heating.

7. Storage stability of heated buffalo milk and bovine-buffalo milk mixtures

Heat treatment of milk results in a product with extended shelf-life, but storage for long periods can result in many chemical, physical, and enzymatic changes to milk that can reduce the acceptability of the product, or in severe cases, end its shelf-life. A comprehensive review on the changes occurring in UHT milk during storage that affect instability (age gelation, sedimentation, and creaming) was made by Anema (2019). As most studies and reviews have dealt with bovine milk, this section will incorporate literature on heat-treated buffalo milk and mixtures as well as buffalo milk-based products.

7.1. Age gelation

Gelation during storage is a major defect that limits the shelf-life of UHT milk. It is characterised by a gradual increase in viscosity followed by a quite rapid increase in viscosity and formation of a custard-like gel, a three-dimensional protein network whose formation is irreversible (Anema, 2019). The progression of age gelation in bovine UHT milk is a well-studied phenomenon, yet understanding of the exact mechanism/s of age gelation are obscured by the interplay of factors such as milk production aspects, raw milk quality, milk composition, heat treatment, and storage temperature (Anema, 2019; Datta & Deeth, 2001; McMahon, 1996; Vaghela, Chaudhary, & Mehta, 2017). As such, two mechanisms had been proposed: (i) age gelation through proteolysis by native and/or heat-resistant bacterial proteases; and (ii) age gelation due to physicochemical changes in the milk (Anema, 2019; Nieuwenhuijse & Van Boekel, 2003). Other studies (Datta et al., 2002; Deeth, 2010; Manji & Kakuda, 1988; McMahon, 1996) proposed that age gelation is a two-stage process; i.e., a combination of the above-mentioned mechanisms.

In toned UHT milk, which was a mixture of buffalo and bovine milk (Ranvir, personal communication), Ranvir, Sharma, Gandhi, and Mann (2020) reported that age gelation due to proteolysis was higher in samples stored at 30 °C than in samples stored at 5 °C. Increased proteolysis at higher storage temperature correlated with a decrease in pH, increase in soluble calcium and magnesium contents, and a slight increase in zeta potential (Ranvir et al., 2020). Similar observations of increased gelation at higher storage temperature for UHT-treated whole buffalo milk were reported by Rehman and Salariya (2005). Several authors (Malmgren et al., 2017; Manji, Kakuda, & Arnott, 1986; Newstead, Paterson, Anema, Coker, & Wewala, 2006; Venkatachalam, McMahon, & Savello, 1993) have shown that age gelation of bovine UHT milk is higher at temperature range of 4 °C–30 °C compared with temperatures outside this range. Malmgren et al. (2017) suggested that the decreased gelation at temperatures higher than 30 °C is probably due to the speed of proteolysis not allowing physical interaction of casein micelles hence formation of a strong gel matrix is prevented. The difference in observation in the effect of temperature on the stability to age gelation between buffalo and bovine milk may be related to the higher casein content of the former, thereby affecting gelation kinetics (Ahmad, 2013).

The more severe the heat treatment, the longer age gelation is delayed. Hence, indirectly heated UHT milks are less susceptible to age gelation than UHT milk heated by direct steam injection and infusion methods. Malmgren (2015) showed that gelation may be an issue in UHT-treated buffalo milk, particularly if it is produced by direct heating. Indirect heating at 137 °C for 4 s was shown to be effective in preventing gelation during 6 mo of storage while milk treated by direct heating at 142 °C for 12 s gelled in 5 months (Malmgren, 2015). This could be due to higher level of enzyme inactivation leading to lower degree of proteolysis during storage. Another explanation for the reduced tendency of severely heated milk to gelation is the increased level of whey protein denaturation. McMahon (1996) concluded that the more severe heat treatment delays gelation due to enhancement of the extent of chemical cross-linking within the micelles. As a consequence, the dissociation of the denatured β-lactoglobulin-κ-casein complex from the micelle becomes slower as it is more strongly held to the micelle. It is apparent that there are numerous and complex reactions happening thus it would be difficult to establish a simple interpretation of milk behaviour during storage. As such, it might be necessary to study these different factors individually in model systems.

Information on various approaches to minimise age gelation in UHT-treated buffalo milk is still scarce. Findings from studies in bovine milk can be applied, but it is important to note that due to compositional variations, some approaches might not be directly translatable to buffalo milk. In bovine milk, age gelation due to proteolysis by plasmin can be minimised by increasing heat intensity during UHT treatment; i.e., the application of indirect UHT system that is capable of inactivating the plasmin system. In cases where direct UHT system is used, additional preheat treatments or extending UHT holding times will be needed (Anema, 2019). However, increased heat loads tend to initiate more non-enzymatic browning reactions, which can limit the product shelf-life (McMahon, 1996). The addition of low levels of polyphosphates such as NaHMP (0.05%–0.1%) before UHT treatment had been shown to be beneficial in delaying the onset of gelation in UHT-treated bovine milk samples (Kocak & Zadow, 1985), possibly through delaying the release of β-lactoglobulin-κ-casein complex from the micelle surface (McMahon, 1996). A method for preventing age gelation of a calcium-fortified UHT milk by adding 0.05–0.3% NaHMP was patented by Sher, Mallangi, Jacobson, Vadehra, and Wedral (2002).

7.2. Sediment formation

Another change that occurs during storage of heat-treated milk, particularly UHT milk, is sedimentation, where protein aggregates settle to the bottom of the pack as a thick layer (Anema, 2019; Gaur, 2017; Gaur, Schalk, & Anema, 2018; Zhang, Bijl, Muis, & Hettinga, 2020). This could potentially be a problem during storage of concentrated milk (Dalgleish, 1992). It is suggested that sediment consists of destabilised κ-casein-depleted micelles (Gaur et al., 2018) that gradually settle to the bottom through gravity influence, but this settling does not usually form a densely packed sediment and can usually be reversed by gentle inversion or shaking (Dalgleish, 1992) and hence this is not considered a defect and does not cause major issues. Aggregation of micelles, however, will further increase the rate of sedimentation (Dalgleish, 1992) and excessive sedimentation is a quality issue that should be avoided. In a study on commercially processed UHT whole buffalo milk, Rehman and Salariya (2005) reported that formation of sediments during storage of milk correlates with lower pH (6.10), which may have induced destabilisation of casein micelles. This remarkably low pH was attributed to formation of free fatty acids, lactic acid, and other organic acids, which casts doubt on the sterility of the product. The mechanisms for the formation of sediment in UHT milk are not particularly well understood, but Gaur et al. (2018) proposed that decreased pH (<~6.55) results to a shift in calcium equilibria leading to increased ionic calcium levels in serum and less colloidal calcium phosphate in the micelles, hence the casein micelles are destabilised, promoting aggregation of micelles and sediment formation.

Sediment formation is initiated during sterilisation of milk and is influenced by the extent and nature of heat treatment as well as milk compositional factors. Sedimentation in bovine milk was reported to increase as the severity of heat treatment is increased (Ramsey & Swartzel, 1984). However, Sharma and Prasad (1990) reported that processing temperature range of 120–150 °C for 2 s had very little effect on sediment formation in buffalo milk. These researchers showed that UHT treatment increased the viscosity of buffalo milk, which could have led to slower sedimentation rate. The conflicting effect of heat treatment on sedimentation as reported by Ramsey and Swartzel (1984) and Sharma and Prasad (1990) could be also due to the difference in the fat content between buffalo milk and bovine milk. It was postulated that sedimentable particles may become entrained with the fat globules as they rise toward the surface hence less material would be available for sedimentation (Ramsey & Swartzel, 1984). In toned UHT-treated mixtures of buffalo and bovine milk, Ranvir et al. (2021) attributed the increase in sediments with storage temperature to the aggregation of proteins or protein particles. Sharma and Prasad (1990) reported that sediment formation in UHT-treated buffalo milk increased with increased storage time, but found slightly higher amounts of sediment from samples stored at 15 °C compared with 30 °C.

As with age gelation, information on various approaches to minimise sedimentation in UHT-treated buffalo milk or mixtures is still scarce. Findings from bovine milk may be applied but it is important to note that due to compositional variations, some approaches might not be directly translatable to buffalo milk. Minimising the risk of sedimentation in bovine UHT milk can be achieved by utilising indirect UHT system although fouling (Ramsey & Swartzel, 1984) or increasing the pH of the milk and/or adding calcium chelators (Gaur et al., 2018). Downstream homogenisation of UHT milk can be used to reduce sedimentation, particularly for direct UHT milk samples (Deeth & Lewis, 2017).

7.3. Creaming

During storage of UHT milk, fat globules can aggregate and rise to the top, resulting in fat separation and fat adhesion to the packaging material. This creaming and this problem are closely correlated and will increase with the fat content, storage temperature, and fat globule size (Anema, 2019; Karlsson et al., 2019). Substantial fat separation can occur if the average fat globule size is too high. In commercial UHT-treated whole buffalo milk, Rehman and Salariya (2005) observed more visible fat separation after 3 months of storage at 40 °C than at 10 or 20 °C. The influence of storage temperature on fat separation can be explained by Stokes' law, because an increase in storage temperature results in a decrease in viscosity and an increase in density difference between fat and liquid phase, allowing faster movement of the fat globules (Karlsson et al., 2019). To avoid creaming, the average fat globule size should be around 0.7 μm with a maximum of 1–2 μm Deeth, 2010 with <5% fat globules having >2 μm (Deeth & Lewis, 2017).

8. Conclusion and future perspectives

Considerable progress had been achieved in understanding the composition and properties of buffalo milk and how these properties affect the perceived quality changes when buffalo milk undergoes processing. There had been scarce studies on heat-induced changes, particularly on the molecular level of major components although there are many studies that deal with changes on the proximate composition and how these translate to organoleptic changes in processed buffalo milk products. To elucidate these organoleptic changes, assumptions were made based on confirmed reports in bovine milk. As there are compositional variations between buffalo milk and bovine milk, well-established processes for bovine milk and molecular-level changes cannot be directly extrapolated for buffalo milk. Hence, for buffalo milk, there is a need to investigate molecular changes in major components and how these changes affect each other and consequently the final product. In terms of thermal processing, there seems to be a need to optimise thermal process parameters, as well as an investigation on possible quality improvement of dairy products utilising a mixture of bovine and buffalo milk wherein composition, particularly protein and fat, is standardised.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Abesinghe, A. M. N. L., Vidanarachchi, J. K., Islam, N., Prakash, S., Silva, K. F. S. T., Bhandari, B., et al. (2020). Effects of ultrasonication on the physicochemical properties of milk fat globules of *Bubalus bubalis* (water buffalo) under processing conditions: A comparison with shear-homogenization. *Innovative Food Science & Emerging Technologies, 59*. Article 102237.

Adhikari, A. K., & Mathur, O. N. (1993). Heat induced changes in the microstructure of casein micelles and mineral balance of cows' and buffalos' milk during prolonged boiling. *Japanese Journal of Dairy and Food Science, 42*, A171–A179.

Agrawal, S. G., Bund, R. K., & Pandit, A. B. (2008). Effect of agitation on heat-induced deproteination process of buffalo milk whey. *Journal of Food Engineering, 87*, 398–404.

Ahmad, S. (2013). Buffalo milk. In Y. W. Park, & G. F. W. Haenlein (Eds.), *Milk and dairy products in human nutrition: Production, composition, and health* (pp. 519–553). Oxford, UK: John Wiley & Sons, Ltd.

Ahmad, S., Anjum, F. M., Hima, N., Sameen, A., & Zahoor, T. (2013). Composition and physico-chemical characteristics of buffalo milk with particular emphasis on lipids, proteins, minerals, enzymes and vitamins. *Journal of Animal and Plant Sciences, 23*, 62–74.

Ahmad, S., Gaucher, I., Rousseau, F., Beaucher, E., Piot, M., Grongnet, J. F., et al. (2008). Effects of acidification on physico-chemical characteristics of buffalo milk: A comparison with cow's milk. *Food Chemistry, 106*, 11–17.

Anema, S. G. (2009). Effect of milk solids concentration on the pH, soluble calcium and soluble phosphate levels of milk during heating. *Dairy Science & Technology, 89*, 501–510.

Anema, S. G. (2019). Age gelation, sedimentation, and creaming in UHT milk: A review. *Comprehensive Reviews in Food Science and Food Safety, 18*, 140–166.

Anema, S. G. (2021). Heat-induced changes in caseins and casein micelles, including interactions with denatured whey proteins. *International Dairy Journal, 122*. Article 105136.

Anema, S. G., & Li, Y. (2000). Further studies on the heat-induced, pH-dependent dissociation of casein from the micelles in reconstituted skim milk. *Lebensmittel-Wissenschaft und-Technologie, 33*, 335–343.

Anema, S. G., Lowe, E. K., & Li, Y. (2004). Effect of pH on the viscosity of heated reconstituted skim milk. *International Dairy Journal, 14*, 541–548.

Aradhey, A. (2020). India: Dairy and products annual. *Foreign agricultural service*. United States Department of Agriculture. Report Number IN2019-0111. Retrieved 25 May 2021 from https://www.fas.usda.gov/data/india-dairy-and-products-annual-4.

Arora, S., & Khetra, Y. (2017). Buffalo milk cheese. In P. L. H. McSweeney, P. F. Fox, P. D. Cotter, & D. W. Everett (Eds.), *Cheese: Chemistry, physics and microbiology* (4th edn., Vol. 1, pp. 1093–1101). San Diego, CA, USA: Academic Press.

Augustin, M. A., & Clarke, P. T. (1990). Effect of added salts on the heat stability of recombined concentrated milk. *Journal of Dairy Research, 57*, 213–226.

Becskei, Z., Savić, M., Ćirković, D., Rašeta, M., Puvača, N., Pajić, M., et al. (2020). Assessment of water buffalo milk and traditional milk products in a sustainable production system. *Sustainability, 12*. Article 6616.

Brodkorb, A., Croguennec, T., Bouhallab, S., & Kehoe, J. J. (2016). Heat-induced denaturation, aggregation and gelation of whey proteins. In P. L. H. McSweeney, & J. A. O'Mahony (Eds.), *Advanced dairy chemistry* (4th edn.,, *1B* pp. 155–178). New York, NY, USA: Springer Science+Business Media.

Chakraborty, P., Singh, T., Shivhare, U. S., & Basu, S. (2020). Understanding the effect of milk composition and milking season on quality characteristics of chhana. *Journal of Texture Studies, 52*, 45–56.

Choudhary, S., Arora, S., Kumari, A., Narwal, V., & Sharma, V. (2018). Effect of type and quality of milk on heat induced protein-protein interactions in *khoa*. *Journal of Food Science & Technology, 55*, 4321–4329.

Claeys, W. L., Verraes, C., Cardoen, S., De Block, J., Huyghebaert, A., Raes, K., et al. (2014). Consumption of raw or heated milk from different species: An evaluation of the nutritional and potential health benefits. *Food Control, 42*, 188–201.

Corredig, M., & Dalgleish, D. G. (1996). Effect of different heat treatments on the strong binding interactions between whey proteins and milk fat globules in whole milk. *Journal of Dairy Research, 63*, 441–449.

Crowley, S. V., Megemont, M., Gazi, I., Kelly, A. L., Huppertz, T., & O'Mahony, J. (2014). Heat stability of reconstituted milk protein concentrate powders. *International Dairy Journal, 37*, 104–110.

Dalgleish, D. G. (1992). Sedimentation of casein micelles during the storage of ultra-high temperature milk products – a calculation. *Journal of Dairy Science, 75*, 371–379.

Datta, N., & Deeth, H. C. (2001). Age gelation of UHT milk – a review. *Food and Bioproducts Processing, 79*, 197–210.

Datta, N., Elliott, A. J., Perkins, M. L., & Deeth, H. C. (2002). Ultra-high-temperature (UHT) treatment of milk: Comparison of direct and indirect modes of heating. *Australian Journal of Dairy Technology, 57*, 211–227.

De Kort, E., Minor, M., Snoeren, T., Van Hooijdonk, T., & Van Der Linden, E. (2012). Effect of calcium chelators on heat coagulation and heat-induced changes of concentrated micellar casein solutions: The role of calcium-ion activity and micellar integrity. *International Dairy Journal, 26*, 112–119.

de la Fuente, M. A., & Juárez, M. (2005). Authenticity assessment of dairy products. *Critical Reviews in Food Science and Nutrition, 45*, 563–585.

de la Fuente, M. A., Olano, A., Casal, V., & Juárez, M. (1999). Effects of high pressure and heat treatment on the mineral balance of goats' milk. *Journal of Dairy Research, 66*, 65–72.

Deeth, H. C. (2010). Improving UHT processing and UHT milk products. In M. W. Griffiths (Ed.), *Improving the safety and quality of milk* (Vol. 1, pp. 302–329). Cambridge, UK: Woodhead Publishing.

Deeth, H. C. (2020). The effect of UHT processing and storage on milk proteins. In M. Boland, & H. Singh (Eds.), *Milk proteins: From expression to food* (3rd edn., pp. 385–421). San Diego, CA, USA: Academic Press.

Deeth, H. C., & Lewis, M. J. (2016). Protein stability in sterilised milk and milk products. In P. L. H. McSweeney, & J. A. O'Mahony (Eds.), *Advanced dairy chemistry* (4th edn.,, *1B* pp. 247–286). New York, NY, USA: Springer Science+-Business Media.

Deeth, H. C., & Lewis, M. J. (2017). *High temperature processing of milk and milk products*. Chichester, UK: John Wiley & Sons Ltd.

Dissanayake, M., Ramchandran, L., Donkor, O. N., & Vasiljevic, T. (2013). Denaturation of whey proteins as a function of heat, pH and protein concentration. *International Dairy Journal, 31*, 93–99.

Dixon, B. (1963). The effect of temperature on the pH of dairy products. *Australian Journal of Dairy Technology, 18*, 141–144.

Dumpler, J. (2018). *Heat stability of concentrated milk systems: Kinetics of the dissociation and aggregation in high heated concentrated milk systems*. Berlin, Germany: Springer Fachmedien Wiesbaden GmbH.

Dumpler, J., Huppertz, T., & Kulozik, U. (2020). Invited review: Heat stability of milk and concentrated milk: Past, present, and future research objectives. *Journal of Dairy Science, 103*, 10986–11007.

Eisner, M. D. (2021). Direct and indirect heating of milk – a technological perspective beyond time-temperature profiles. *International Dairy Journal, 122*. Article 105145.

El-Zeini, H. M. (2006). Microstructure, rheological and geometrical properties of fat globules of milk from different animal species. *Polish Journal of Food and Nutrition Sciences, 15/56*, 147–154.

Elagamy, I. I. (2000). Effect of heat treatment on camel milk proteins with respect to antimicrobial factors: A comparison with cows' and buffalo milk proteins. *Food Chemistry, 68*, 227–232.

Fangmeier, M., Kemerich, G. T., Machado, B. L., Maciel, M. J., & De Souza, C. F. V. (2019). Effects of cow, goat, and buffalo milk on the characteristics of cream cheese with whey retention. *Food Science and Technology, 39*, S122–S128.

Fox, P. F. (1981). Heat-induced changes in milk preceding coagulation. *Journal of Dairy Science, 64*, 2127–2137.

Fox, P. F., Uniacke-Lowe, T., McSweeney, P. L. H., & O'Mahony, J. A. (2015). *Dairy chemistry and biochemistry* (2nd edn.). Cham, Switzerland: Springer International Publishing.

Gaucheron, F. (2005). The minerals of milk. *Reproduction Nutrition Development, 45*, 473–483.

Gaur, V. (2017). *Sedimentation reduction in UHT milk*. Doctoral dissertation. Christchurch, New Zealand: University of Canterbury. Retrieved 24 November 2021 from https://ir.canterbury.ac.nz/handle/10092/14649.

Gaur, V., Schalk, J., & Anema, S. G. (2018). Sedimentation in UHT milk. *International Dairy Journal, 78*, 92–102.

Ghatak, P. K., Bandyopadhyay, A. K., & Gupta, M. P. (1990). Influence of 2-deoxyribose and urea on the heat stability of concentrated buffalo milk. *Indian Journal of Dairy Science, 43*, 402–405.

Gillani, Z. (2015). *Effect of different processing techniques on buffalo whey proteins*. Doctoral dissertation. Pakistan: University of Agriculture Faisalabad. Retrieved 16 May 2021 from https://core.ac.uk/download/pdf/132561479.pdf.
Gough, P., & Jenness, R. (1962). Heat denaturation of β-lactoglobulins A and B. *Journal of Dairy Science, 45*, 1033–1039.
Guo, M., & Hendricks, G. (2010). Improving buffalo milk. In M. W. Griffiths (Ed.), *Improving the safety and quality of milk* (Vol. 2, pp. 402–416). Cambridge, UK: Woodhead Publishing.
Hamad, M. N. E., & Baiomy, A. A. (2010). Physical properties and chemical composition of cow's and buffalo's milk in Qena governorate. *Journal of Food and Dairy Sciences, 1*, 397–403.
Haq, I., Khaskheli, M., Kiani, F. A., Talpur, A. R., Lochi, G. M., Soomro, A. A., et al. (2013). Effect of heat treatment on physico-chemical characteristics of skimmed milk. *Journal of Agriculture and Food Technology, 3*, 5–13.
Haq, I., Khaskheli, M., Salman, M., Marri, M. Y., Khan, I. A., Marri, M. A., et al. (2014). Effect of heat treatments on sensory characteristics and shelf-life of skimmed milk. *African Journal of Food Science, 8*, 75–79.
Holt, C. (1992). Structure and stability of bovine casein micelles. *Advances in Protein Chemistry, 43*, 63–151.
Hooda, A., Mann, B., Sharma, R., & Bajaj, R. (2020). Physicochemical characterization of native micellar casein concentrates from buffalo and cow skim milk harvested using microfiltration. *International Journal of Dairy Technology, 73*, 781–789.
Houlihan, A. V., Goddard, P. A., Kitchen, B. J., & Masters, C. J. (1992). Changes in structure of the bovine milk fat globule membrane on heating whole milk. *Journal of Dairy Research, 59*, 321–329.
Hovjecki, M., Miloradovic, Z., Rac, V., Pudia, P., & Miocinovic, J. (2020). Influence of heat treatment of goat milk on casein micelle size, rheological and textural properties of acid gels and set type yoghurts. *Journal of Texture Studies, 51*, 680–687.
Humbert, E. S., Campbell, J. N., Blankenagel, G., & Gebre-Egziabher, A. (1985). Extended storage of raw milk. II. The role of thermization. *Canadian Institute of Food Science and Technology Journal, 18*, 302–305.
Huppertz, T. (2016). Heat stability of milk. In P. L. H. McSweeney, & J. A. O'Mahony (Eds.), *Advanced dairy chemistry* (4th edn.,, *1B* pp. 179–196). New York, NY, USA: Springer Science+Business Media.
Huppertz, T., & Kelly, A. L. (2009). Properties and constituents of cow's milk. In A. Y. Tamime (Ed.), *Milk processing and quality management* (pp. 23–47). London, UK: Blackwell Publishing Ltd.
Hussain, I. (2011). Effect of UHT processing and storage conditions on physico-chemical characteristics of buffalo skim milk. *Journal of the Chemical Society of Pakistan, 33*, 783–786.
Hussain, I., Bell, A. E., & Grandison, A. S. (2013). Mozzarella-type curd made from buffalo, cows' and ultrafiltered cows' milk. 1. Rheology and microstructure. *Food and Bioprocess Technology, 6*, 1729–1740.
Ismail, A. A., & El Deeb, S. A. (1973). Effect of heat processing, storing and homogenization on the viscosity, opacity and stability of cow and buffalo milks. *Zeitschrift für Lebensmittel Untersuchung und Forschung, 152*, 202–207.
Ismail, A. A., Mashaley, R. I., & Sirry, I. (1969). Effects of heating at three temperatures on the nitrogen constituents of cow and buffalo skimmilks. *Journal of Dairy Science, 53*, 423–426.
Jainudeen, M. R. (2002). Buffalo husbandry | Asia. In H. Roginsky, J. W. Fuquay, & P. F. Fox (Eds.), *Encyclopedia of dairy sciences* (pp. 186–193). San Diego, CA, USA: Academic Press.
Jawaid, S., Talpur, F. N., Nizamani, S. M., & Afridi, H. I. (2015). Contamination profile of aflatoxin M1 residues in milk supply chain of Sindh, Pakistan. *Toxicology Reports, 2*, 1418–1422.
Kapadiya, D. B., Prajapati, D. B., Jain, A. K., Mehta, B. M., Darji, V. B., & Aparnathi, K. D. (2016). Comparison of Surti goat milk with cow and buffalo milk for gross composition, nitrogen distribution, and selected minerals content. *Veterinary World, 9*, 710–716.
Karlsson, M. A., Langton, M., Innings, F., Malmgren, B., Höjer, A., Wikström, M., et al. (2019). Changes in stability and shelf-life of ultra-high temperature treated milk during long term storage at different temperatures. *Heliyon, 5*, Article e02431.
Kelly, A. L. (2010). Milk biochemistry. In M. W. Griffiths (Ed.), *Improving the safety and quality of milk* (Vol. 1, pp. 3–26). Cambridge, UK: Woodhead Publishing.
Kelly, A. L., Datta, N., & Deeth, H. C. (2012). Thermal processing of dairy products. In D. W. Sun (Ed.), *Thermal food processing: New technologies and quality issues* (2nd edn., pp. 273–306). Baco Raton, FL, USA: CRC Press.
Khalifa, M. Y., & Ghanimah, M. A. (2013). Studies on fluid milk viscosity as affected by some factors. *Journal of Biological Chemistry and Environmental Sciences, 8*, 57–66.
Khan, M. U., Hassan, M. F., & Rauf, A. (2018). Effect of temperature on milk fats of cow, buffalo, and goat used for frying local food products. *Food Quality and Safety, 2*, 51–57.
Khatkar, S. K., Gupta, V. K., & Khatkar, A. B. (2014). Studies on preparation of medium fat liquid dairy whitener from buffalo milk employing ultrafiltration process. *Journal of Food Science & Technology, 51*, 1956–1964.
Khedkar, C. D., Kalyankar, S. D., & Deosarkar, S. S. (2016). Buffalo milk. In B. Caballero, P. M. Finglas, & F. Toldrá (Eds.), *Encyclopedia of food and health* (pp. 522–528). San Diego, CA, USA: Academic Press.
Kinsella, J. E., & Whitehead, D. M. (1989). Proteins in whey: Chemical, physical, and functional properties. In J. E. Kinsella (Ed.), *Advances in food and nutrition research* (Vol. 33, pp. 344–438). San Diego, CA, USA: Academic Press, Inc.
Kocak, H. R., & Zadow, J. G. (1985). Controlling age gelation of UHT milk with additives. *Australian Journal of Dairy Technology, 40*, 58–64.
Lee, S. J., & Sherbon, J. W. (2002). Chemical changes in bovine milk fat globule membrane caused by heat treatment and homogenization of whole milk. *Journal of Dairy Research, 69*, 555–567.
Liu, H., Grosvenor, A. J., Li, X., Wang, X., Ma, Y., Clerens, S., et al. (2019). Changes in milk protein interactions and associated molecular modification resulting from thermal treatments and storage. *Journal of Food Science, 84*, 1737–1745.
Li, S., Ye, A., & Singh, H. (2019). Seasonal variations in composition, properties, and heat-induced changes in bovine milk in a seasonal calving system. *Journal of Dairy Science, 102*, 7747–7759.
Maćej, O. D., Jovanović, S. T., Denin, J. D., & Djurdjević. (2002). The influence of high temperatures on milk proteins. *Hemijska Industrija, 56*, 123–132.
MacGibbon, A. K. H., & Taylor, M. W. (2006). Composition and structure of bovine milk lipids. In P. F. Fox, & P. L. H. McSweeney (Eds.), *Advanced dairy chemistry* (3rd edn., Vol. 2, pp. 1–42). New York, NY, USA: Springer Science+Business Media, Inc.
Malmgren, B. (2015). Challenges in processing of goat, buffalo and camel milk for longer shelf life. In M. de Renobales (Ed.), *(Session Chair), Novel products and emerging processing technologies [Keynote speech] 7th IDF International symposium on sheep, goat and other non-cow milk*. Cyprus: Limassol.
Malmgren, B., Ardö, Y., Langton, M., Altskär, A., Bremer, M. G. E. G., Dejmek, P., et al. (2017). Changes in proteins, physical stability and structure in directly heated UHT milk during storage at different temperatures. *International Dairy Journal, 71*, 60–75.
Mane, B. G., & Chatli, M. K. (2015). Buffalo milk: Saviour of farmers and consumers for livelihood and providing nutrition. *Agricultural Rural Development, 2*, 5–11.
Manji, B., & Kakuda, Y. (1988). The role of protein denaturation, extent of proteolysis, and storage temperature on the mechanism of age gelation in a model system. *Journal of Dairy Science, 71*, 1455–1463.
Manji, B., Kakuda, Y., & Arnott, D. R. (1986). Effect of storage temperature on age gelation of ultra-high temperature milk processed by direct and indirect heating systems. *Journal of Dairy Science, 69*, 2994–3001.
McMahon, D. J. (1996). Age-gelation of UHT milk: Changes that occur during storage, their effect on shelf life and the mechanism by which age-gelation occurs. In *IDF Special Issue 9602, Heat treatments & alternative methods* (pp. 315–325). Brussels, Belgium: International Dairy Federation.
Medhammar, E., Wijesinha-Bettoni, R., Stadlmayr, B., Nilsson, E., Charrondiere, U. R., & Burlingame, B. (2012). Composition of milk from minor dairy animals and buffalo breeds: A biodiversity perspective. *Journal of the Science of Food and Agriculture, 92*, 445–474.
Mehta, R. S. (1980). Milk processed at ultra-high-temperatures – a review. *Journal of Food Protection, 43*, 212–225.
Ménard, O., Ahmad, S., Rousseau, F., Briard-Bion, V., Gaucheron, F., & Lopez, C. (2010). Buffalo vs. cow milk fat globules: Size distribution, zeta-potential, compositions in total fatty acids and in polar lipids from the milk fat globule membrane. *Food Chemistry, 120*, 544–551.
Michalski, M. C., & Januel, C. (2006). Does homogenization affect the human health properties of cow's milk? *Trends in Food Science & Technology, 17*, 423–437.
Mishra, V. K., & Ramchandran, L. (2015). Novel thermal methods in dairy processing. In N. Datta, & P. M. Tomasula (Eds.), *Emerging dairy processing technologies: Opportunities for the dairy industry* (pp. 33–69). Chichester, UK: John Wiley & Sons, Ltd.
Mottar, J., Bassier, A., Joniau, M., & Baert, J. (1989). Effect of heat-induced association of whey proteins and casein micelles on yogurt texture. *Journal of Dairy Science, 72*, 2247–2256.
Muir, D. D., & Sweetsur, A. W. M. (1977). Effect of urea on the heat coagulation of the caseinate complex in skim-milk. *Journal of Dairy Research, 44*, 249–257.
Mulder, H., & Walstra, P. (1974). *The milk fat globule: Emulsion science as applied to milk products and comparable foods*. Commonwealth Agricultural Bureaux and Center for Agricultural Publishing and Documentation.
Mulvihill, D. M., & Donovan, M. (1987). Whey proteins and their thermal denaturation – a review. *Irish Journal of Food Science & Technology, 11*, 43–75.
Murtaza, M. A., Pandya, A. J., & Khan, M. M. H. (2017). Buffalo milk utilization for dairy products. In Y. W. Park, G. F. Haenlein, & W. L. Wendorff (Eds.), *Handbook of milk of non-bovine mammals* (2nd edn., pp. 284–342). Chichester, UK: John Wiley & Sons, Inc.
Najib, M., Hallab, M. W., Hallab, K., Hallab, Z., Hamze, M., & Chihib, N. (2020). Thermal processing of milk as a main tool in the production of Qishta, Khoa and Kajmak. *Journal of Materials and Environmental Sciences, 11*, 294–309.
Nasr, N. F., & Elshaghabee, F. M. F. (2019). Enhancement of shelf life of pasteurized milk using Nisplin® essential oils emulsion. *International Journal of Current Microbiology and Applied Sciences, 8*, 257–266.
Nayak, S. K., Makrariya, A., Singh, R. R. B., Patel, A. A., Sindhu, J. S., Patil, G. R., et al. (2004). Heat stability and flow behavior of buffalo milk added with corn starch. *Food Hydrocolloids, 18*, 379–386.
Newstead, D. F., Paterson, G., Anema, S. G., Coker, C. J., & Wewala, A. R. (2006). Plasmin activity in direct-steam-injection UHT-processed reconstituted milk: Effects of preheat treatment. *International Dairy Journal, 16*, 573–579.
Nguyen, H. T. H., Madec, M. N., Ong, L., Kentish, S. E., Gras, S. L., & Lopez, C. (2016). The dynamics of the biological membrane surrounding the buffalo milk fat globule investigated as a function of temperature. *Food Chemistry, 204*, 343–351.
Nieuwenhuijse, H., & Huppertz, T. (2021). Heat-induced changes in milk salts: A review. *International Dairy Journal, 126*. Article 105220.

Nieuwenhuijse, J. A., & Van Boekel, M. A. J. S. (2003). Protein stability in sterilized milk and milk products. In P. F. Fox, & P. L. H. McSweeney (Eds.), *Advanced dairy chemistry* (3rd edn., Vol. 1, pp. 947–974). New York, NY, USA: Kluwer Academic/Plenum Publishers.
Obeid, S., Guyomarc'h, F., Francius, G., Guillemin, H., Wu, X., Pezennec, S., et al. (2019). The surface properties of milk fat globules govern their interactions with the caseins: Role of homogenization and pH probed by AFM force spectroscopy. *Colloids and Surfaces B: Biointerfaces, 182*. Article 110363.
OECD/FAO. (2020). *OECD-FAO agricultural outlook 2020-2029*. FAO/OECD Publishing. https://doi.org/10.1787/1112c23b-en
Oldfield, D. J., Singh, H., Taylor, M. W., & Pearce, K. N. (1998). Kinetics of denaturation and aggregation of whey proteins in skim milk heated in an ultra-high-temperature (UHT) pilot plant. *International Dairy Journal, 8*, 311–318.
On-Nom, N., Grandison, A. S., & Lewis, M. J. (2010). Measurement of ionic calcium, pH, and soluble divalent cations in milk at high temperature. *Journal of Dairy Science, 93*, 515–523.
Ono, T., Yoshida, M., Tanaami, H., & Ohkosi, H. (1999). Changes in casein micelle size induced by heating. *International Dairy Journal, 9*, 405–406.
Owusu-Apenten, R. K. O., Khokhar, S., & Galani, D. (2002). Stability parameters for β-lactoglobulin thermal dissociation and unfolding in phosphate buffer at pH 7.0. *Food Hydrocolloids, 16*, 95–103.
Panthi, R. P., Jordan, K. N., Kelly, A. L., & Sheehan, J. J. (2017). Selection and treatment of milk for cheesemaking. In P. L. H. McSweeney, P. F. Fox, P. D. Cotter, & D. W. Everett (Eds.), *Cheese: Chemistry, physics and microbiology* (4th edn., Vol. 1, pp. 23–50). New York, NY, USA: Academic Press.
Patil, A. T., Meena, G. S., Upadhyay, N., Khetra, Y., Borad, S. G., & Singh, A. K. (2019). Effect of change in pH, heat treatment and diafiltration on properties of medium protein buffalo milk protein concentrate. *Journal of Food Science & Technology, 56*, 1462–1472.
Perveen, R., Butt, M. S., Huma, N., & Nawaz, H. (2015). Effect of pH and heat treatment on physicochemical characteristics of sodium phosphocaseinate powder. *Journal of Animal & Plant Sciences, 25*, 1146–1152.
Plana-Fattori, A., Doursat, C., Coutouly, A., Riaublanc, A., & Flick, D. (2020). A numerical model for studying the thermal denaturation-aggregation of whey proteins under continuous thermal processing. *International Journal of Food Studies, 9*, SI17–SI37.
Rajput, Y. S., Bhavadasan, M. K., Singh, A., & Ganguli, N. C. (1982). Heat stability of buffalo milk as affected by the addition of urea and glyceraldehyde. *New Zealand Journal of Dairy Science & Technology, 17*, 185–190.
Ramsey, J. A., & Swartzel, K. R. (1984). Effect of ultra high temperature processing and storage conditions on rates of sedimentation and fat separation of aseptically packaged milk. *Journal of Food Science, 49*, 257–262.
Ranvir, S., Sharma, R., Gandhi, K., & Mann, B. (2020). Assessment of physico-chemical changes in UHT milk during storage at different temperatures. *Journal of Dairy Research, 87*, 243–247.
Ranvir, S., Sharma, R., Gandhi, K., Nikam, P., & Mann, B. (2021). Physico-chemical changes during processing and storage of UHT milk. *Indian Journal of Dairy Science, 74*, 39–47.
Rehman, Z. U., & Salariya, A. M. (2005). Effect of storage conditions on nutritional quality of UHT processed buffalo milk. *Journal of the Chemical Society of Pakistan, 27*, 73–76.
Robitaille, G., Britten, M., Morisset, J., & Petitclerc, D. (2002). Quantitative analysis of β-lactoglobulin A and B genetic variants in milk of cows β-lactoglobulin AB throughout lactation. *Journal of Dairy Research, 69*, 651–654.
Roefs, S. P. F. M., & De Kruif, F. G. (1994). A model for the denaturation and aggregation of β-lactoglobulin. *European Journal of Biochemistry, 226*, 883–889.
Sakkas, L., Moutafi, A., Moschopoulou, E., & Moatsou, G. (2014). Assessment of heat treatment of various types of milk. *Food Chemistry, 159*, 293–301.
Sant'Ana, A. M. S., Bezerril, F. F., Madruga, M. S., Batista, A. S. M., Magnani, M., Souza, E. L., et al. (2013). Nutritional and sensory characteristics of Minas fresh cheese made with goat milk, cow milk, or a mixture of both. *Journal of Dairy Science, 96*, 7442–7453.
Sepulveda, D. R., Góngora-Nieto, M. M., Guerrero, J. A., & Barbosa-Cánovas, G. V. (2005). Production of extended-shelf life milk by processing pasteurized milk with pulsed electric fields. *Journal of Food Engineering, 67*, 81–86.
Shalabi, S. I., & Fox, P. F. (1982). Heat stability of milk: Synergistic action of urea and carbonyl compounds. *Journal of Dairy Research, 49*, 197–207.
Sharma, D. K., & Prasad, D. N. (1990). Changes in the physical properties of ultra high temperature processed buffalo milk during storage. *Journal of Dairy Research, 57*, 187–196.
Sher, A. A., Mallangi, C. R., Jacobson, R., Vadehra, D. R., & Wedral, R. E. (2002). *Shelf-stable calcium fortified milk and dairy products*. Switzerland: Patent US6455082B1 Nestec S.A.
Sinaga, H., Bansal, N., & Bhandari, B. (2017). Effects of milk pH alteration on casein micelle size and gelation properties of milk. *International Journal of Food Properties, 20*, 179–197.
Sindhu, J. S. (1985). Influence of sodium phosphate on the heat stability of buffalo milk and its concentrate. *Journal of Food Processing and Preservation, 9*, 57–64.
Sindhu, J. S., & Arora, S. (2011). Milk | buffalo milk. In J. W. Fuquay (Ed.), *Encyclopedia of dairy sciences* (2nd edn., pp. 503–511). New York, NY, USA: Academic Press.
Singh, H. (2004). Heat stability of milk. *International Journal of Dairy Technology, 57*, 111–119.
Singh, H., & Bennett, R. J. (2002). Milk and milk processing. In R. K. Robinson (Ed.), *Dairy microbiology handbook: The microbiology of milk and milk products* (3rd edn., pp. 1–38). Chichester, UK: John Wiley and Sons, Inc.
Singh, H., & Gallier, S. (2017). Nature's complex emulsion: The fat globules of milk. *Food Hydrocolloids, 68*, 81–89.
Singh, C. P., & Roy, N. K. (1978). Heat stability of buffalo milk. In *20th international dairy congress* (p. 696). Paris, France.
Solanki, P., & Gupta, V. K. (2009). Effect of stabilizing salts on heat stability of buffalo skim milk ultrafiltered-diafiltered retentate. *Journal of Food Science & Technology, 46*, 466–469.
Sommer, H. H., & Hart, E. B. (1919). The heat coagulation of milk. *Journal of Biological Chemistry, 40*, 137–151.
Sommer, H. H., & Hart, E. B. (1922). The heat coagulation of milk. *Journal of Dairy Science, 5*, 525–543.
Tayal, M., & Sindhu, J. S. (1983). Heat stability and salt balance of buffalo milk as affected by concentration and addition of casein. *Journal of Food Processing and Preservation, 7*, 151–160.
Vaghela, K. D., Chaudhary, B. N., & Mehta, B. M. (2017). A review on proteolysis rate in UHT milk: Its mechanism, pattern, assessment and enzymatic changes during storage. *Research and Reviews: Journal of Dairy Science and Technology, 6*, 1–16.
van Boekel, M. A. J. S. (1998). Effect of heating on Maillard reactions in milk. *Food Chemistry, 62*, 403–414.
van den Oever, S. P., Haselmann, A., Schreiner, M., Fuerst-Waltl, B., Zebeli, Q., Mayer, H. K., et al. (2021). Hay versus silage: Does hay feeding positively affect milk composition? *International Dairy Journal, 118*. Article 105024.
Venkatachalam, N., McMahon, D. J., & Savello, P. A. (1993). Role of protein and lactose interactions in the age gelation of ultra-high temperature processed concentrated skim milk. *Journal of Dairy Science, 76*, 1882–1894.
Verheul, M., Roefs, S. P. F. M., & De Kruif, K. G. (1998). Kinetics of heat-induced aggregation of β-lactoglobulin. *Journal of Agricultural and Food Chemistry, 46*, 896–903.
Walstra, P., Wouters, J. T. M., & Geurts, T. J. (2006). *Dairy science and technology* (2nd edn.). Boca Raton, FL, USA: CRC Press.
Wiking, L., Gregersen, S. B., Hansen, S. F., & Hammershøj, M. (2022). Heat-induced changes in milk fat and milk fat globules and its derived effects on acid dairy gelation – a review. *International Dairy Journal, 127*, 105213.
Wolz, M., & Kulozik, U. (2015). Thermal denaturation kinetics of whey proteins at high protein concentrations. *International Dairy Journal, 49*, 95–101.
Zanabria, R., Tellez, A. M., Griffiths, M. W., & Corredig, M. (2014). The antiproliferative properties of the milk fat globule membrane are affected by extensive heating. *Dairy Science & Technology, 94*, 439–453.
Zhang, C., Bijl, E., Muis, K. E., & Hettinga, K. (2020). Stability of fat globules in UHT milk during proteolysis by the AprX protease from *Pseudomonas fluorescens* and by plasmin. *Journal of Dairy Science, 103*, 179–190.
Ziyaina, M., Govindan, B. N., Rasco, B., Coffey, T., & Sablani, S. S. (2018). Monitoring shelf life of pasteurized whole milk under refrigerated storage conditions: Predictive models for quality loss. *Journal of Food Science, 83*, 409–418.