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Assessment of heat treatment of various types of milk

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ABSTRACT

Raw milk (RM), reconstituted condensed milk (CM) and three types of reconstituted milk powders (SMPs) were heated indirectly at 80–140 °C for 4 s. Native β-lactoglobulin after 90 °C treatment of RM was 1132 ± 167 mg/L but no reliable quantities were estimated at temperatures >100 °C, whereas 218 ± 43 mg/L residual α-lactalbumin were found at 130 °C. Average lactulose contents from 51 to 1549 mg/L were detected at ⩾100 °C; average furosine was 1.9 and 126.5 mg/L in raw and 140 °C treated milks respectively. The behaviour of heated CM was similar to that of heated RM except for higher furosine concentration. Reconstituted SMPs contained high quantities of lactulose and furosine, the ratio of which was lower than in similarly treated RM. Among the market milks analysed, the group of high-pasteurised milks was highly variable; i.e. native β-lactoglobulin was 69–2831 mg/L, lactulose 0–824 mg/L and furosine 3.3–68.8 mg/L.

1. Introduction

The production of heat treated milk for human consumption covers the spectrum from pasteurisation to in-container sterilisation with respect to the shelf life and the heat-induced changes of milk. The efficacy and the effects of heat treatments are related to the temperature–time combinations, heating method utilised and milk pre-treatment conditions (Walstra, Wouters, & Geurts, 2006). Between the two well-known categories of drinking milk, i.e. (low) pasteurised and UHT milk, there is the peroxidase negative extended shelf life (ESL) milk, marketed in several countries as high-pasteurised milk. It can be stored up to 60 d under refrigerated conditions, while its flavour is expected to be similar to pasteurised milk. Various processing and packaging technologies are combined for the production of ESL milk, i.e. 130–145 °C for <1 s by means of direct infusion method or combination of bactofugation, microfiltration, pasteurisation and specific packaging technologies. The simplest approach is high-temperature pasteurised milk at ⩾85 °C for 20 s and usually at 115–120 °C for 2–5 s. (Moatsou, 2013; Rysstad & Kolstad, 2006; Walstra & Wouters, 2006).

There are two types of effects of heating on milk. The first comprises the effects on components of special interest for the keeping quality and technological and nutritional properties of milk. Degradation of lactose to organic acids and formation of lactulose, denaturation of whey proteins, destruction of some vitamins and enzymes, hydrolysis of proteins and lipids and disturbance of calcium/phosphorous equilibrium belong to this group. The second type of effects related to cooked flavour and loss of nutritional value is due to new substances formed by Maillard reaction, which continues during the storage of heated milks (Elliott, Dhakal, Datta, & Deeth, 2003; Pellegrino, De Noni, & Resmini, 1995a). Several approaches have been proposed for the assessment of heating history of milk using indices that come from the abovementioned mechanisms considered by Clayes, Van Loey, and Hendrickx (2002b) as "intrinsic time temperature integrators (TTIs) for thermally processed milk". The most well-known are the enzymatic assays of alkaline phosphatase and lactoperoxidase that are mandatory in the control of market milks, whereas the thermal behaviour of other indigenous enzymes has been studied (Claeys et al., 2002b; Moatsou, 2013; Wilbey, 1996).

Susceptibility of whey proteins to heat denaturation resulting from their high level of secondary and tertiary structure has been studied extensively; findings with respect to the present study are summarised below. Their heat sensitivity is in the order α-lactalbumin (α-la) < β-lactoglobulin (β-lg) < bovine serum albumin (BSA) < immunoglobulins (Igs). Considering their initial concentration in raw milk and their behaviour under heat treatments, the residual native β-lg and α-la in heated milks, estimated as acid-soluble concentrations, can be indices of thermal treatment; the opposite is true for BSA and Igs. At temperatures

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>65 °C, unfolding of β-lg, i.e. first stage of denaturation, occurs. According to Claeys, Ludikhuyze, Van Loey, and Hendrickx (2001a), denaturation follows first order kinetics with *z*-values of 7.9 °C ($D_{75°C}$ = 49.9 min) from 70–80 °C and *z*-values of 24.2 °C ($D_{85°C}$ = 3.53 min) from 83–90 °C. Cystine disulphide bonds disrupt and along with the free sulfhydryl group of the native molecule are available to participate in thiol/disulfide exchanges; they react intra- or inter-molecularly mainly with κ-casein on the micelle surface and with proteins on milk fat globule membrane (MFGM). The main result of this reaction is the formation of β-lg/κ-casein complexes, which are a characteristic feature of heat-treated milks. At higher temperatures, i.e. between 70 and 96 °C, denaturation of α-la takes place that forms complexes with aggregates of β-lg. Denatured α-la forms also complexes with α_{s2}-casein and with MFGM at high temperatures (Considine, Patel, Anema, Singh, & Creamer, 2007; Corredig & Dalgleish, 1996; Jeanson, Dupont, Grattard, & Rolet-Répécaud, 1999).

Several studies on residual native whey protein content of heat-treated milk have been carried out (e.g., Corzo, Delgado, Troyano, & Olano, 1994a; Corzo, López-Fandiño, Delgado, Ramos, & Olano, 1994b; Elliott, Datta, Amenu, & Deeth, 2005; Elliott et al., 2003; Feinberg, Dupont, Efstathiou, Louâpre, & Guyonnet, 2006; Jeanson et al., 1999; Lorenzen et al., 2011; Mayer, Raba, Meier, & Schmid, 2010; Morales, Romero, & Jiménez-Pérez, 2000; Villamiel, Arias, Corzo, & Olano, 1999; Villamiel, López-Fandiño, Corzo, & Olano, 1997). According to them, residual acid soluble β-lactoglobulin (β-lg) content of low pasteurised milks ranges from 1606 to 4140 mg/L, of ESL milk from 140 to 3680 mg/L, of UHT-direct heating method (UHT-DM) milk from 150 to 1120 mg/L, of UHT-indirect method (UHT-IM) milks is <170 mg/L and in sterilised milks is <10 mg/L. The respective values for native residual α-lactalbumin (α-la) are from 850 to 1570 mg/L, from 740 to 910 mg/L, from 850 to 1000 mg/L, from 230 to 1130, <500 and < 50 mg/L. Acid-soluble native β-lg content is considered steady during the storage of heated milks (Pellegrino, Resmini, & Luf, 1995b), which is advantageous with respect to its use as a heat-treatment index. However, Corzo et al. (1994b), Elliott et al. (2005) and Feinberg et al. (2006) consider that formation of lactose adducts through Maillard reaction or complexes with other proteins taking place during the storage of UHT milk results in changes in the shape of β-lg HPLC peaks.

Isomerisation products, due to heating of lactose, i.e. lactulose and epilactose, have been also proposed as heat treatment indices. The latter is 10% of the isomerisation products and it is detected only in sterilised milks (López-Fandiño & Olano, 1999); therefore it is not adequate for the majority of heat treatments applied to milk. On the other hand, lactulose (LCT) is considered as a very useful index. It is not a substance of raw milk, is not detected in pasteurised milk and results from the conversion of glucose to fructose during heating. Its formation follows pseudo-zero order kinetics with an E_α-value of 90.2 kJ/mol and $K_{110°C}$ = 51.5 mg/L, min (Claeys, Ludikhuyze, Van Loey, & Hendrickx, 2001b). It is proposed as an index for UHT milks, considering that LCT content >600 mg/L corresponds to sterilised milk, and as a tool for the discrimination between UHT-DM and UHT-IM milks, being rather stable during storage (Cattaneo, Masotti, & Pellegrino, 2008; Claeys et al., 2002b; Elliott et al., 2005; Morales et al., 2000; Pellegrino et al., 1995a, 1995b). However, Feinberg et al. (2006) report a significant increase of its concentration during 90 d of storage of UHT and sterilised milk at room temperature but according to Pellegrino et al. (1995a) further isomerisation occurs only at storage at 35 °C. According to the majority of the reports, it can be detected only in UHT milks at concentrations of 50–850 and 190–830 mg/L for direct and indirect heating respectively and in sterilized milks at 1080–1400 mg/L (e.g. Olano, Calvo, & Corzo, 1989; Birlouez-Aragon et al., 1998; Villamiel et al., 1999; Morales et al., 2000, Elliott et al., 2003, 2005, Cattaneo et al., 2008), but it has been found in some pasteurised and high temperature pasteurised milks at up to 15 and 80 mg/L, respectively (Feinberg et al., 2006; Marconi et al., 2004).

Furosine (FRS) detected at low quantities of 3–5 mg/100 g protein in raw milk is related to the first stages of Maillard reaction. It is the stable product produced by the acid hydrolysis of unstable lactuloselysine, which is accumulated in heat-treated milks. During heated milk storage, its concentration increases depending on storage temperature, due to the continuous formation of lactuloselysine through Maillard reaction (Corzo et al., 1994a, 1994b; Pellegrino et al., 1995a; Van Renterghem & De Block, 1996; Van Boekel, 1998, López-Fandiño & Olano, 1999, Claeys et al., 2001b; Elliott et al., 2005; Feinberg et al. 2006). Pellegrino et al. (1995a) observed that this mechanism is evident even at 4 °C and estimated that 7 mg furosine per 100 g protein are produced every 10 days at 23 °C. Moreover, they report that the kinetics of the reaction during storage is expected to be practically the same in the different types of heat-treated milk. In general, furosine is a more convenient index than lactulose, since it covers nearly all types of heat treatments. Its formation in milk follows pseudo-zero order kinetics and it is characterised by an E_α value of 88.7 kJ/mol, with $K_{110°C}$ = 16.2 mg/100 g protein, min (Claeys et al., 2001b). An upper limit of 8 mg/100 g proteins for (low) pasteurised milk and 20 and 250 mg/100 g proteins for high-temperature pasteurised and UHT milks respectively has been proposed, as cited by Claeys et al. (2002b) and Mayer et al. (2010). The furosine content of raw and low pasteurised milk has been reported in the range 4–14 mg/100 g protein, in ESL milks 10–260 mg/100 g protein, in UHT-direct method milks 16–485 mg/100 g protein, in UHT-indirect method milks 40–430 mg/100 g protein and in sterilised milks 250–440 mg/100 g protein (Corzo et al., 1994a; Corzo et al., 1994b; Pellegrino et al., 1995a, 1995b, Van Renterghem & De Block, 1996, Birlouez-Aragon et al., 1998; Jeanson et al., 1999; Villamiel et al., 1999, Elliott et al., 2003, 2005, Feinberg et al., 2006; Cattaneo et al., 2008; Mayer et al., 2010; Lorenzen et al., 2011).

Other compounds related to the Maillard reaction proposed for the distinction of UHT and sterilised milks are hydroxymethylfurfural (HMF) and carboxymethyllysine (CML), which were not studied in the present work (Morales & Jiménez-Pérez, 1999; Van Boekel, 1998).

A great part of the abovementioned high variability of various indices is due to the wide range of combinations of heating conditions and methods utilised for the production of each category of drinking milk. Other technological factors are also related to this variability. Cattaneo et al. (2008) concluded that plant equipment and management conditions like milk recirculation or run time before cleaning may contribute substantially to the final heat damage of milk. Prolonged preheating of milk at temperatures <100 °C in the UHT process can result in high furosine values and low levels of acid soluble β-lg that are not in accordance with lactulose content; the latter is not formed at temperatures <90 °C (Pellegrino et al., 1995a). Also, the storage of raw milk before processing decreases the furosine and HMF initially after processing and during storage of UHT milk (Elliott et al., 2003). Finally, milk gross composition could affect the behaviour of some indices. Heat-induced interactions of β-lg with MFGM although limited can reduce the amount of native β-lg in heated milks (Corredig & Dalgleish, 1996). In this regard, Claeys, Van Loey, and Hendrickx (2002a) found that $D_{75°C}$ and *z*-values decreased with increasing milk fat content indicating a faster β-lg denaturation clearly depicted at temperatures >72 °C. The same group (Claeys, Van Loey, & Hendrickx, 2003) report that fat content does not influence formation kinetics of lactulose and HMF and that the significant differences observed for furosine kinetics in milks with different fat contents were too small to be relevant. The conclusion of the