Chapter 2
Evolutive Profiles of Caseins and Degraded Proteins in Industrial Cow’s Milk Curds

Caterina Barone, Marcella Barbera, Michele Barone, Salvatore Parisi and Izabela Steinka

Abstract The importance of prepackaged curds in the current cheese market is increased in the last years because of the persistence of cyclic periods with remarkable diminution of stored raw materials. Consequently, the cyclic deficiency of cow’s milk may determine the subsequent lack of correlated derivatives and force manufacturers to use prepackaged curds. Because of the critical importance of the chemical and microbiological ‘quality’ of these curds, the study of evolutive profiles of casein contents in selected industrial curds should be recommended. The aim of this chapter has been to show the analytical results of an industrial study carried out on seven different cow’s milk curds during storage. Obtained data and calculated results seem to suggest that curd samples under refrigerated conditions can show increased proteolysis. In addition, moisture and pH values may show notable augments during refrigerated storage. On the other side, deep-frozen storage is recommended when speaking of curd use after extended storage times.

Keywords Casein · Cow’s milk curd · CYPEP:2006 · Frozen storage · Lipids · Moisture · Refrigerated storage
Abbreviations

CYPEP:2006 Cheesemaking Yield and Proteins Estimation according to Parisi:2006
CUR Curd sample
FC Fat matter
MC Moisture
PC Proteins

2.1 Introduction

The importance of prepackaged cow’s milk curds in the current market of cheeses is increased in the last years because of the persistence of cyclic periods with remarkable diminution of stored raw materials for cheesemaking purposes. Actually, these ‘pauses’ have determined the overproduction of cheeses and other dairy foods in certain periods of the year (Barbieri et al. 2014a). The current economic crisis on a global scale is also important and should be taken into account (Parisi 2016): as a result, the cyclic deficiency of cow’s milk may determine the subsequent lack of correlated derivatives (butters, caseins, yoghurts, etc.).

With exclusive reference to cow’s milk-made cheeses—other milks have certainly their own importance (Alais 1984), one of the most critical factors in the production of these foods is the good condition (also named ‘quality’ by cheesemakers) of the initial milk, in terms of microbiological counts and profiles on the one hand, and chemical–physical features on the other side (Pacheco and Galindo 2010; Zagare et al. 2014).

As a consequence, ‘good’ milk can be used to produce good cheeses, on condition that initial conditions are acceptable or excellent. However, the production of normal cheeses cannot be performed without a necessary (and crucial) step: the production of the intermediate ‘curd’. This step is not described in detail when speaking of cheeses and cheese-like products obtained with complex formulations such as ‘low moisture’ mozzarella cheeses (Banks 2007; Barbieri et al. 2014a). By the chemical viewpoint, curd is the coagulated and precipitated heterogeneous matter from the original milk (Alais 1984).

In general, the composition of similar intermediates concerns five main components (Barbieri et al. 2014a; McSweeney 2007a):

- Water (curds are substantially solid solutions)
- Lipids, chemically defined as esters, derived from glycerol and three fatty acids. These large molecules are trapped into the curd agglomeration by means of a protein matrix (Parisi and Caruso 2013)
- Proteins, casein molecules above all. These coagulated molecules can trap fats and other compounds into the precipitated curd
• Mineral salts, generally calcium salts. Added sodium chloride may be important depending on the peculiar cheese (McSweeney 2007b)
• Carbohydrates in small quantities.

Basically, each parameter has an important role when speaking of initial milk and the correlated cow’s milk curd, with the exclusion of carbohydrates and mineral salts, although calcium and phosphate compounds are important when speaking of caseins. In general, it can be affirmed that:

(a) Water is the liquid medium for curds and original milks. With relation to cheese production, the higher the amount of water in curds, the lower the incorporation of additional water molecules during the next steps. However, because of the remarkable variety and differentiation of cheese types, the increase of product weights may be not important. For example, semi-hard and hard cheeses have to naturally contain small aqueous amounts

(b) The amount of lipids is important when speaking of cheese palatability. In general, the more abundant the fraction of fat matter on the dry content, the higher the perceived sweet taste in soft and unripened cheeses. On the other hand, certain products with prevailing microbial fermentation can exhibit peculiar flavours and tastes depending on the action of selected microorganisms on lipids. In fact, lipolytic life forms such as yeasts and lactobacilli can produce volatile substances and other degradation products with interesting features by the consumers’ viewpoint (Barbieri et al. 1994; Centeno et al. 1996; Delgado et al. 2016; Fox and Wallace 1997; Medina et al. 1995; Reiter et al. 1969)

(c) Proteins are the real key factor in milk coagulation. Actually, the most part of these organic chains constituted of different caseins (Kelly 2007; Parisi 2006; Parisi et al. 2006a, 2009). After the formation of a protein agglomeration around a hypothetical centre (Barbieri et al. 2014a; Fox and McSweeney 1998; Guinee 2007) and the incorporation of lipids, carbohydrates, mineral salts and water, caseins may also be linked to additional water molecules by means of hydrogen bonds. On the other side, this absorption can be limited depending on the condition of lipids, the composition of partially demolished proteins, and the availability of binding calcium ions (these particles are present in the original protein as phosphate salts).

On these bases, it may be also remembered that chemical–physical parameters for the intermediate curd and the final product depend on the chemical characterisation of lipids, water and proteins. As a result, analytical determinations such as pH and acidity are notably influenced if lipids are partially decomposed, water is excessively incorporated, and/or caseins are fragmented, with or without calcium ions. It should be mentioned also that additional water amounts are continually generated by hydrolysis because of microbial activity and other chemical reactions. Consequently, several unripened and/or packaged soft cheeses products appear to increase aqueous amounts, pH and redox potential values after some storage months, depending also on storage conditions (Parisi 2002, 2003).
As a result, the composition of caseins has a remarkable and critical influence on properties of final cheeses (Barbieri et al. 2014a), including good textural properties. In general, high yield values and good texture in cheese production are linked with the amount and the average molecular weight of caseins above all. Consequently, an interesting field of research is the study of evolutive profiles of selected molecules and protein aggregations in cheeses. When speaking of nitrogen-based molecules, the analytical research is normally carried out by means of direct experimental protocols such as Kjeldahl and Dumas methods (Alais 1984). However, the study of proteolysis in certain cheeses has been already tried by means of an indirect method, the ‘Cheesemaking Yield and Proteins Estimation according to Parisi: 2006’ (CYEP:2006) approach (Parisi et al. 2006b; 2016a,b). This mathematical and simulative procedure has been used with the aim of evaluating potential differences between industrial curds.

The aim of this Chapter is the possibility of tracking evolutive profiles of casein contents in selected industrial curds for subsequent cheese production. An industrial study has been carried out on seven different cow’s milk curds near a cheesemaking company (none of examined curds has been produced by this industry). General differences between these curds (prepackaged products) concern the chemical composition, pH values, and the possibility of prolonged frozen storage instead of refrigerated conditions.

2.2 Evolutive Profiles of Selected Cow’s Milk Curds During Storage

2.2.1 Materials

Seven different productions of cow’s milk curds have been considered for this study. In detail, five lots by different curd Producers have been sampled at the arrival near a cheesemaking industry under refrigerated storage (delivery temperature: 2 ± 2 °C; two 200.0 g—samples per lot) and subsequently re-sampled after eight and 15 days of storage (temperature: ≤ 10 °C; two 200.0 g—samples per lot). As a result, six samples have been obtained for each curd production. The remaining curds have been received and sampled under refrigerated storage (delivery temperature: 2 ± 2 °C; two 200.0 g—samples per lot); however, subsequent samples have been obtained after eight and 15 days of deep-frozen storage (temperature: ≤ −18 °C; two 200.0 g—samples per lot).

All received curds have been found to be vacuum-packaged as 25–50 kg—blocks with thermosealable films, generally polypropylene or polyamide/polyethylene plastic matters.

As a result, 42 total samples have been considered and stored at 2° ± 2 °C before analyses. With relation to this study, one single curd sample (CUR) has been named ‘CUR xxx’ (‘xxx’ is an acronym used for the representation of the external
lot and producer) and immediately analysed after 24 h (two samples per lot, two analyses). The remaining two sample groups (four samples: two sampled after eight days; two sampled after 15 days) have been named ‘CUR xxx-a’ ('a' means the number of days after the arrival) and analysed after eight and 15 days. For instance, the second sample group for curd CUR 001 has been named ‘CUR 001-8’ and analysed after 8 days.

All sampled cheeses have been analysed according to the above mentioned schedule. Moisture, fat Matter, pH, and proteins have been evaluated for all sampled products.

### 2.2.2 Analytical Methods

Moisture (MC), fat matter (FC), and pH have been obtained for all sampled products with the following methods respectively: IR thermogravimetric method; AFNOR NF V04-287 (Barbieri et al. 2014b); pH Meter method. The most reliable amount of proteins (PC) has been calculated by means of the ‘Compact Cheese Spreadsheets’ software, version 1.1, CYPEP Lite.bas, and CheeSim$.bas (Parisi et al. 2016a, b). These software are all based on CYPEP:2006 indirect method. All results have been obtained as the average of two data per sample.

### 2.2.3 Results and Discussion

Average data for sampled cheeses (chemical results) are displayed in Table 2.1 in function of days after the arrival and analysis (one, eight, and 15 days). Displayed data correspond to the average value of the whole group of samples for MC, FC, pH and PC respectively. In addition, Table 2.2 shows pH and PC average data for two different subgroups:

<table>
<thead>
<tr>
<th>Table 2.1 Chemical data for stored curds, average data</th>
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<tbody>
<tr>
<td>Storage days</td>
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<td>---------------</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>8</td>
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<td>15</td>
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</tbody>
</table>

MC is for: moisture, FC is for: fat matter, PC represents proteins (the most reliable amount for proteins, according to CYPEP:2006). The most reliable amount of proteins (PC) has been calculated by means of the ‘Compact Cheese Spreadsheets’ software, version 1.1, CYPEP Lite.bas, and CheeSim$.bas. These software are all based on CYPEP:2006 indirect method.
Table 2.2 pH and protein values for stored curds under refrigerated conditions, average data

<table>
<thead>
<tr>
<th>Storage days</th>
<th>Stored curds, refrigerated conditions (average data)</th>
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<tbody>
<tr>
<td></td>
<td>CUR 001</td>
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<tr>
<td>1</td>
<td>pH</td>
</tr>
<tr>
<td>8</td>
<td>5.28</td>
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<tr>
<td>15</td>
<td>5.30</td>
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</tbody>
</table>

MC represents proteins (the most reliable amount for proteins, according to CYPEP:2006. PC has been calculated by means of the ‘Compact Cheese Spreadsheets’ software, version 1.1, CYPEP Lite.bas, and CheeSim$.bas. These software are all based on CYPEP:2006 indirect method.

- CUR 001-005. This group concerns five curds stored under refrigerated conditions until 15 days
- CUR 005-006. This group concerns two curds stored under deep-frozen conditions until 15 days.

In general, initial sampled curds show a variegated composition when speaking of moisture, fat matter, pH, and proteins. MC is between 42.0 and 45.9% (average value: 43.8%, Table 2.1); FC ranges from 26.0 to 28.0% (average value: 27.1%); pH values are between 5.19 and 5.38 (medium calculated result: 5.27). As a consequence, calculated amounts for PC give a general average value of 24.5% (minimum value: 23.9%; maximum value: 25.3%, Tables 2.2 and 2.3).

After refrigerated and deep-frozen storage, results show a notable increase of MC and pH values, while FC and PC amounts tend to lower values (Table 2.1). In detail, MC increases from 43.8 to 44.9% after eight days (augment: +1.1%) and 45.8% after 15 days (augment: +2.0%). The same trend is apparently shown by pH values (+0.10 after 15 days), while FC decreases (difference: −1.2% after 15 days). Consequently, PC profiles seem to show a clear diminution: −0.3 and −0.7% after eight and 15 days respectively (Table 2.1).

Table 2.3 pH and protein values for stored curds under deep-frozen conditions, average data

<table>
<thead>
<tr>
<th>Stored curds, deep-frozen conditions (average data)</th>
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<tbody>
<tr>
<td>CUR 006</td>
</tr>
<tr>
<td>Storage days</td>
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<td>1</td>
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<td>8</td>
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<td>15</td>
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</tbody>
</table>

PC represents proteins (the most reliable amount for proteins, according to CYPEP:2006. PC has been calculated by means of the ‘Compact Cheese Spreadsheets’ software, version 1.1, CYPEP Lite.bas, and CheeSim$.bas. These software are all based on CYPEP:2006 indirect method.
However, two sample curds have been stored under deep-frozen conditions (Table 2.3) differently from the first five samples (Table 2.2). Obtained and calculated results show that:

(a) pH increase and PC diminution are strictly correlated during the 15 days storage in both situations, when speaking of average data

(b) Deep-frozen storage (Table 2.3) seems to slow down the degradation of nitrogen-based molecules (proteins), because the observed diminution is only −0.2%. On the other side, pH values (average data) appear to be increased after 15 days. Probably, experimental analytical bias may have some influence

(c) Refrigerated curds (Table 2.2) show a very notable increase of pH values: +0.13 after 15 days. On the other side, PC values decrease from 24.6 (average data on five samples) to 24.0 and 23.6% after eight and 15 days respectively. This trend confirms the general situation of Table 2.1.

2.3 Conclusions

Obtained data and calculated results seem to suggest that curd samples under refrigerated conditions can show increased proteolysis (Parisi et al. 2004), while lipolysis may be observed with minor importance. In addition, moisture increases notably (as the result of enhanced proteolysis) and pH values grow up during storage. On the other side, deep-frozen storage is recommended when speaking of curd use after extended storage times. Actually, protein profiles seem to decrease slightly even in these conditions, but observed differences may be also ascribed to experimental and analytical bias.

References


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