

Optimization of the jellification process in semi-hard cheese production

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Abstract

Appearance and structure of semi hard cheese is an important factor in the consumer acceptance and directly related to product quality. The appearance or color is influenced by how it reflects, absorbs, or transmits light, which in turn is related to the physical structure and chemical nature of the food. Hardness of cheese samples was affected with the change of coagulation processes. Cow's milk was supplied from a EDE farm of AUT, and analyzed for protein, fat, moisture content and PH. The milk was immediately pasteurized at 72C for 15s. It is known that textural characteristics of cheese are affected by their structural characteristics, composition, cheese-making process, proteolysis during ripening and fat distribution. The influence of acidification, pH and the necessary time of clotting processes are very important in transformations (physical, biochemical, and microbial) during the manufacture and ripening of cheese. Two different starter cultures with 0.3% lactic acid bacteria, 0.03%, or 0.06% chymosin an aspartate-proteinase, 0.3 g/l CaCl₂ and several time intervals: 30, 45, 60 minutes were used to achieve the possible optimum in gel structure creation, which is very important in the maturing phase of semi-hard cheese. Acid is added while gently stirring the milk, leading to the formation of a coagulum. The coagulum was allowed to settle before the curd was gathered and pressed to remove whey. Milk was clotted by lowering the pH, mostly affected by lactic acid bacteria and proteolytic enzymes of the bacteria which are able to split κ -casein. Optimization of the cheese-making process, proteolysis and syneresis was significantly affected by temperature and compaction time of the cheese.

Keywords: coagulation processes; proteolysis; clotting processes; ripening of cheese; κ -casein.

1. Introduction

Appearance and structure of semi hard cheese is an important factor in the consumer acceptance and directly related to product quality. Color is influenced by the way it reflects, absorbs, or transmits light, which in turn is related to the physical structure and chemical nature of the food. The variety of milks and technologies used to manufacture semi hard cheeses, a combined acid and rennet coagulation is applied. Several factors affect the consistency of cheese, but it is not easy to establish quantitative relationships the same variable can affect a young cheese and an aged one in different ways. Acid is added while gently stirring the milk, and lactic acid coming from lactose fermentation by lactic acid bacteria which leads to the formation of a coagulum. The coagulum is allowed to settle; the curd is gathered and pressed to remove whey. Various acids can be added: acetic, citric, phosphoric, etc, or simply lime juice. After pasteurization, raw milk was cooled to 35°C and two different starter cultures 0.3% lactic acid bacteria, and *Streptococcus thermophilus* and 0.03%, or 0.06% chymosin an aspartate-proteinase, 0.3 g/l CaCl₂ and several time intervals 30, 45, 60 minute were used to achieve the possible optimum in gel structure creation, which is very important in the maturing phase of semi-hard cheese. The use of starters during the cheese making process affects the proteolysis during ripening and the textural properties. The curd of which after draining and acidification (pH~5.2) is subjected to a jellification process (kneading and forming) and dry salting. Salting promotes syneresis of whey from the curd, reducing the moisture content of the cheese. A small amount of salt (<0.8%) can cause a physical change in the proteins in cheese by increasing their water solubility and hydration. Calcium concentrations of 0.3% in milk are needed to prevent leaching of calcium from the cheese surface and its increased hydration resulting in "soft rind" defects. The objective of our research was first to investigate cheese weight and volume during storage of semi hard cheese in dry salt at 10-15°C temperatures and to relate these changes in the cheese microstructure. A small amount of salt 4-5% in cheese (Sample from the cheese stored in dry NaCl) were analyzed for hardness and

cutting. Texture analyses were conducted on a Texture Analyzer (TA-XT2i Texture Analyzer; Stable Micro Systems, NY).

2. Material and Methods

The starter culture used was a various strains of *Lactococcus lactis*, 0.3% *Lactobacillus* species, and *Streptococcus thermophilus* and 0.03%, 0.06% chymosin an aspartate-proteinase, 0.3 g/l CaCl_2 and several time intervals 30, 45, 60 minute were used to achieve the possible optimum in gel structure creation. Cow's milk was obtained from the FDE farm of AUT. Cheese making milk was pasteurized at 75°C for 15 s and was poured into an open cheese vat in the Dairy Products Laboratory at the Biotechnology and Food Faculty. Milk was warmed to 35°C, and 4 g of starter culture and 1 g of adjunct culture were added and allowed to for 30, 45, 60 min. 18 gr CaCl_2 , 10 gr KNO_3 , 20 ml of liquid rennet (0.03%, 0.06% in volume, 57 international milk clotting units/kg of milk) were added. The curd was cut after 30 min, 45 min or 60 min, using wire knives. About one-third of the whey was removed after 30, 45, and 60 min, before the curd and whey were transferred into 4 perforated rectangular stainless-steel molds. Afterwards, the curd allowed matting together and pressing under its own weight. The molds were turned 4 times at 20 min intervals and then 2 forms were transferred to a warm room (31°C) with the other 2 remaining at room temperature (~20°C) for overnight fermentation and continued whey drainage. The coagulum was allowed to settle before the curd was gathered and pressed to remove whey. Milk was clotted by lowering the pH, mostly affected by lactic acid bacteria and proteolytic enzymes of the bacteria which are able to split κ -casein. Optimization of the cheese-making process, proteolysis and syneresis was significantly affected by temperature and compaction time of the cheese. The next day, the cheese blocks were removed from the forms and were prepared for brining with dry NaCl.

The effect of the temperature is relatively small and corresponds to the dependence of the diffusion coefficient (through the viscosity) on the temperature. Serum proteins somewhat diminish chymosin activity. The calcium ion activity has insignificant effects. However, the pH level has a considerable effect. When decreasing the pH, the affinity of the enzyme for the micelles increases and leads to an increased reaction velocity. At a lower pH the velocity is smaller, because the enzyme is now adsorbed so strongly onto the (partly denuded) casein micelle that it takes considerable time before an adsorbed molecule is released again and can diffuse further. This implies that the reaction is no longer diffusion-limited. An additional effect of the increased adsorption at low pH is that the hairs are not removed at random, but the enzyme tends to form 'bare patches' on a micelle, before desorbing and diffusing away.

Aggregation starts when about 70% of the κ -casein has been split. The aggregation, the sticking together of paracasein micelles, is partly due to van der Waals attraction, but this attraction is in itself insufficient. The effect of the Ca ions is twofold; they diminish the electrostatic repulsion by neutralizing negative charges on the micelles in pH 5.6-5.2, Ca ions act more effectively than H^+ ions and the second the Ca ions can make bridges (salt linkages) between negative sites on the paracasein micelles. In that lowering pH of milk considerably increases its Ca ion activity. Also, the pH level has a twofold effect on the aggregation rate. First, a decrease of pH increases the Ca ion activity, as mentioned and the second, even at constant Ca^{2+} activity, the aggregation can be faster. This is because at low pH the enzyme does not remove the hairs randomly, but tends to split off nearby hairs and consequently bare patches on the micelle surface are formed at a lower degree of splitting κ -casein. Approximate aggregation rate of micelles during clotting at 30°C as a function of the percentage of the κ -casein that has been split and patches on the micelle surface are formed at a lower degree of splitting κ -casein 'Relative' implies as compared to true paracasein micelles at the given conditions (pH, temperature, Ca^{2+} activity, etc.). If the gel is weak at the moment of cutting, the knives tend to shatter the curd, leading to a lot of 'curd fines,' which are partly lost with the whey, while if the gel is quite firm, it means that more energy is needed to cut the curd. Due to clotting a continuous network of protein particles forms, usually consisting of paracasein micelles. The pores of the network are in the order of a few micrometers in width. Initially, the network encloses all of the milk, but it soon starts to contract, i.e., to show syneresis. The appearance or color is influenced by how it reflects, absorbs, or transmits light, which in turn is related to the physical structure and chemical nature of the food. Hardness of cheese samples was affected with changing of coagulation processes. Sample from the cheese stored

in dry salt NaCl were analyzed for hardness and cutting. Texture analyses were conducted on a Texture Analyzer (TA-XT2i Texture Analyzer; Stable Micro Systems).

An elastic modulus can be detected; therefore a gel is formed when the viscosity approaches infinity. At that time, the aggregation has advanced so far that the aggregates occupy the whole volume. The modulus of the gel increases, at first because more micelles (or small aggregates) are incorporated in the gel network, and somewhat later because the junctions between any two micelles become stronger due to fusion of the par casein micelles. At a lower temperature the junctions between the particles of the gel are stronger.

- Technological scheme:
- Filtration of cheese milk;
- Pasteurization
- Addition of CaCl₂ and starters at 30– 35°C
- Renneting with commercial or artisanal rennet
- Cutting after 30, 45,60 min into 1–3-cm cubes
- Rest for 10–15 min
- Molding into rectangular/square or cylindrical molds
- Draining (usually under pressure, some without pressure)
- Cutting the curd into the final cheese dimensions
- Salting with dry salt NaCl.
- Packaging in open containers and additional salting with dry salt;
- Pre-ripening at 16–18 °C for 5–15 d (until pH reaches a value of 4.6 or lower)

3. Results and Discussion

Testing conditions were as shown in Tab 1, where indications of the ingredients of raw milk used for cheese production in the Dairy Products Laboratory at the Biotechnology and Food Faculty are shown. Content values of protein, fat and lactose are very important for the structure of the gel and in the maturing of semi hard cheeses quality.

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Table 1. Indications of the ingredients of raw milk used for cheese production in the Dairy Products Laboratory at the Biotechnology and Food Faculty.

Campion	Fat %	Density	Lactose %	Protein %	Water %	Frozen point
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nr						°C
17.01.2018	5.07	1.026	3.45	2.33	0	-0.573
24.01.2018	5.67	1.022	4.57	2.68	0	-0.56

Table 2. Firmness (expressed as the elastic shear modulus) of renneted milk as a function of time.

Time (min)	20	25	30	35	40	50
Shear Modulus	0	15	25	50	100	100

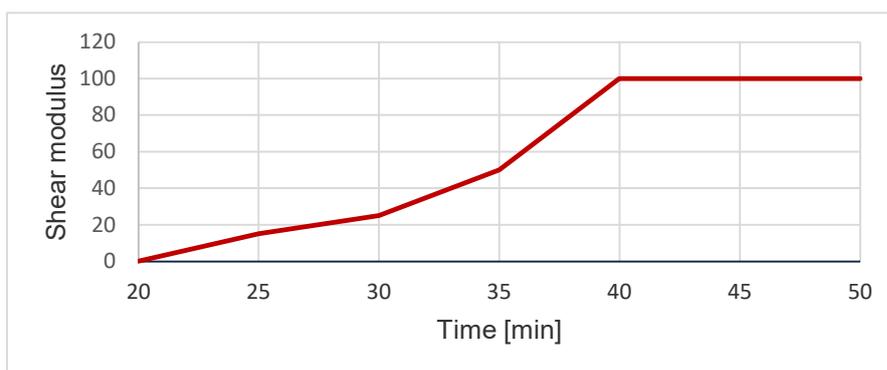


Figure 2. Firmness (expressed as the elastic shear modulus) of renneted milk as a function of time.

Milk shows considerable variation in renneting time, especially milk of individual cows. The variation is partly caused by variation in casein content: if it is high, clotting is faster. The main parameter, however, is the Ca^{2+} activity. If it is low, the aggregation is slow. The reaction can be accelerated by adding CaCl_2 . Increasing the amount of CaCl_2 to more than a given level does not result in much change because the enzyme reaction will now determine the reaction velocity. The influence of the pH is rather complicated. It appreciably affects the enzyme reaction, but little affects the aggregation rate of the paracasein micelles, provided that the Ca^{2+} activity is not too low. The hairs of are not removed at random at low pH, which causes the aggregation of the micelles to start at an earlier stage of the enzyme reaction. This effect explains much of the dependence of the clotting time on the pH. Factors that cause an increase in renneting time, generally also decrease the rate of firming of the gel, i.e., the rate of increase of the gel modulus. However, the changes are not proportional to each other; it also depends on what is taken as the characteristic time. This is illustrated in Figure 3 the aggregation time as defined in the figure is very close to the renneting time according to Storch and Segelcke. The cheese maker is more interested in the ‘clotting time,’ i.e., the time when the curd is (presumed to be) firm enough to start cutting the gel.

The renneting time is inversely proportional to the enzyme concentration. This relationship, known as the rule of Storch and Segelcke, does not fit precisely, nor can it be explained in a simple manner. The complicated combined action of the enzyme reaction and the aggregation (which increases in rate with time) can only be described by intricate formulas which, by chance, result in an almost linear relationship and the slower one of the two reactions mainly determines the renneting time, and it depends on conditions which reaction is the slower one.

Table 3. Time needed for visible aggregation, to start jellation, and to obtain sufficient firmness of the gel (clotting time), as a function of the rennet concentration CaCl_2 is added.

% enzyme	0.03	0.06	0.08
Aggregation (time in min)	13	18	63
Gelation (time in min)	23	36	61
Clotting (time in min)	33	48	62

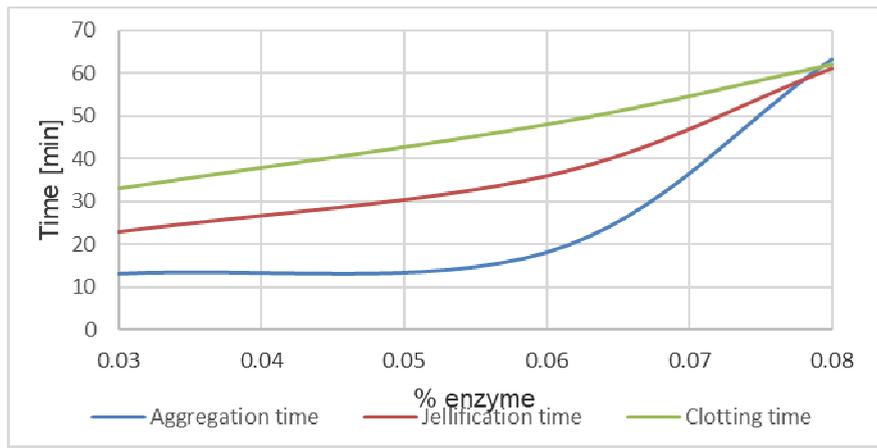


Figure 3 Time needed for visible aggregation, to start gelation, and to obtain sufficient firmness of the gel (clotting time), as a function of the rennet concentration CaCl_2 is added.

Table 4. Rheological properties modulus E, of cheese (excluding fresh and very soft cheeses). Effect of the temperature, the pH of cheese; the salt content; and the age of the cheese.

Temperature [°C]	0	15	20	25	30
Log E		5.7	5.5	5.3	5.1
pH	5.0	5.2	5.4	5.5	5.6
Log E	5.8	5.2	5	5	
% NaCl	0	3	6	10	
Log E		2.4	5.4	5.8	
Months old	0	5	10	15	
Log E	0	2.9	5.6	6.8	

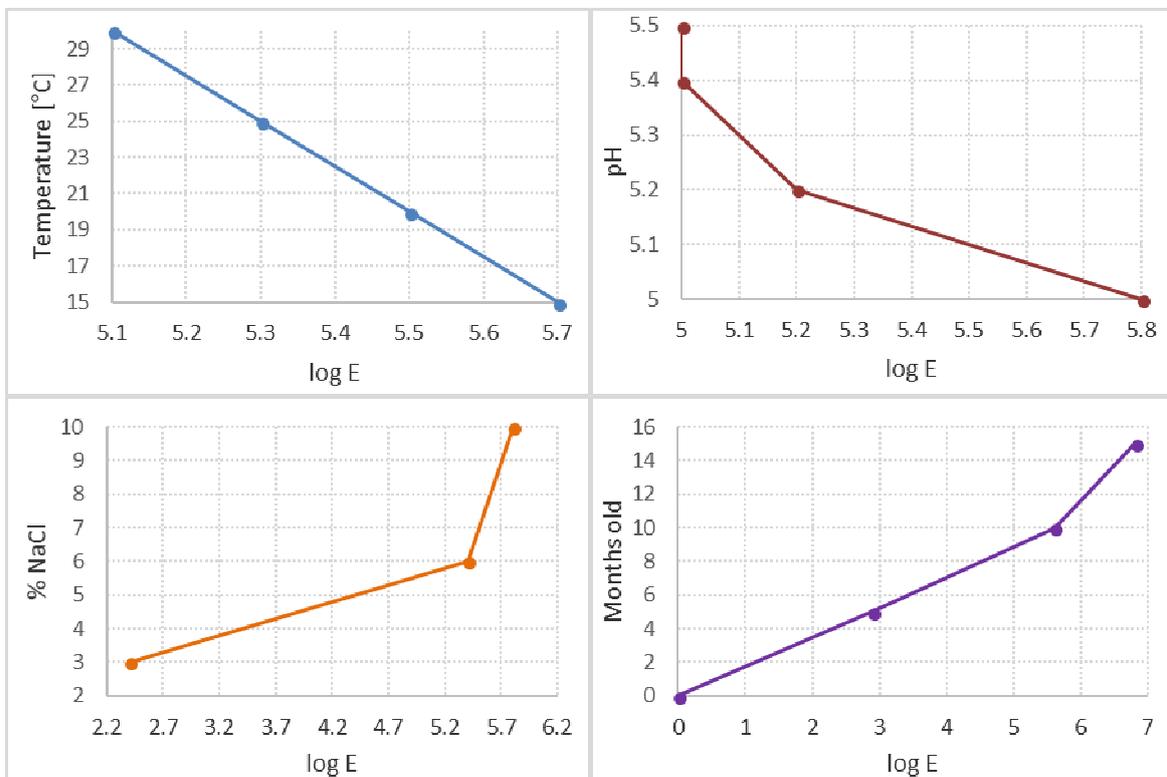


Figure 4. Rheological properties modulus E, of cheese (excluding fresh and very soft cheeses). Effect of the temperature, the pH of cheese; the salt content; and the age of the cheese.

Table 5. The relative deformation of a piece of cheese after bringing it under a constant stress at time $t = 0$. The deformation after removal of the stress at $t=10$ and 20 min, 30 min respectively.

Time [min]	0	5	10	15	20	30
Deformation	0.15	0.2	0.23	0.26	0.28	0.3

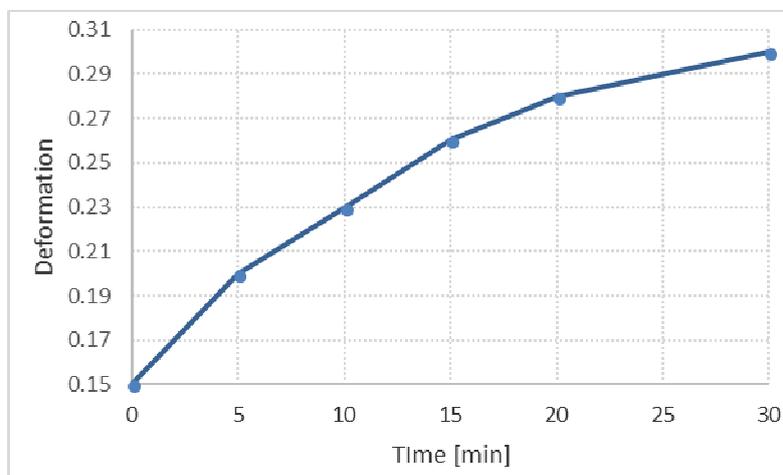


Figure 5. The relative deformation of a piece of cheese after bringing it under a constant stress at time $t = 0$. The deformation after removal of the stress at $t=10$ and 20 min, 30 min respectively.

4. Conclusions

- Appearance and structure of semi hard cheese is an important factor in the consumer acceptance and directly related to product quality. The appearance or color is influenced by how it reflects, absorbs, or transmits light, which in turn is related to the physical structure and chemical nature of the food.
- The effect of the fat content a cheese of the same type but with a higher fat content in the dry matter has a higher water content in the fat-free cheese, and thus a lower E.
- The pH has a considerable effect on each of the consistency parameters and also on the fracture mode. The shortness is definitely affected. The cheese is 'longest' at a pH of about 5.3 and the relationships between pH and consistency may, however, depend on other factors.
- The study shows that, for the type of milk considered, the optimal value for achieving a stable gel in semi hard cheeses is within the time interval of 40-50 minutes. Naturally, the gel's cutting time is chosen as an optimum between the firmness and processing time, which, for reasons of production efficiency and profit, needs to be minimized as much as possible.
- Calcium phosphate content in raw milk increases E, but its influence is not great unless the differences in concentration are large. Thus we deducted 0.3 g/l CaCl_2 to be an optimal dosage before the addition of rennet.
- Often, a higher salt content is associated with a far higher modulus, but in practice, a higher salt content mostly involves a lower water content and increases E but the food standards is 2.5%- 5% as NaCl.
- Proteolysis has a considerable effect but is poorly known because so many other factors also change when a cheese matures. This is affected by the protein content of raw milk as well as enzyme concentration, which in the study was determined to be 0.03-0.06%, considering that the renneting time is inversely proportional to the enzyme concentration.

5. References

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