Lait 80 (2000) 417–432

Original article

Characterisation of whey drainage kinetics during soft cheese manufacture in relation with the physicochemical and technological factors, pH at renneting, casein concentration and ionic strength of milk

Célina DAVIAU, Alice PIERRE, Marie-Hélène FAMELART*, Henri GOUDÉDRANCHE, Daniel JACOB, Maurice GARNIER, Jean-Louis MAUBOIS

Laboratoire de Recherches de Technologie Laitière, INRA, 65 rue de Saint-Brieuc, 35042 Rennes Cedex, France

(Received 18 October 1999; accepted 29 February 2000)

Abstract — The kinetics of whey drainage of Camembert soft cheese was studied using an instrumented drainage device to record the pH and the weight of the whey with a variation coefficient amounting to 1.8% during the first 100 min and 0.34% at the end of drainage. Drainage data were fit with a two step equation to obtain a descriptive model of the drainage kinetics. The effect of the pH at renneting, the casein concentration and the ionic strength on the drainage kinetics was investigated with a 2 level experimental design. Milk was modified by a combination of ultrafiltration and dilution with a lactose solution. The pH at renneting had a negative effect on the amount of whey expelled in the early drainage (up to 100 min) and a positive one after 400 min. The effect of the casein concentration was negative on the amount of whey expelled and on the rate of drainage. The ionic strength had a slight positive effect on drainage. An equation was obtained allowing the prevision of whey drainage kinetics according to the milk composition. Calculated values fit experimental data with a correlation coefficient of r = 0.994.

whey drainage / kinetics / milk composition / pH / renneting / soft cheese manufacture

Résumé — Caractérisation des cinétiques d'égouttage au cours de la fabrication d'un fromage type pâte molle en relation avec les facteurs physico-chimiques et technologiques : effet du pH d'emprésurage, de la teneur en caséine et de la force ionique des laits. L'égouttage du fromage

---

* Correspondence and reprints
Tel.: (33) 2 23 48 53 22; fax: (33) 2 23 48 53 50; e-mail: famelart@labtechno.roazhon.inra.fr

à pâte molle de type Camembert a été étudié à l'aide d'un prototype d'égouttage instrumenté qui permettait d'enregistrer le poids de sérum et son pH. Le coefficient de variation était de 1,8 % pendant les 100 premières minutes et de 0,34 % à la fin de l'égouttage. Les cinétiques d'égouttage obtenues ont été ajustées à l'aide d'un modèle mathématique descriptif à deux phases. L'effet sur l'égouttage du pH à l'emprésurage et de modifications de la composition du lait, telle la concentration en caséine et la force ionique, ont été testés à l'aide d'un plan d'expérience à deux niveaux. La composition des laits était modifiée en combinant une concentration par ultrafiltration et une dilution par une solution de lactose. L'effet du pH sur le poids de sérum expulsé était négatif au début de l'égouttage puis devenait positif. L'effet de la concentration en caséine était négatif sur la quantité de sérum obtenue et sur la vitesse d'égouttage. La force ionique avait un léger effet positif sur l'égouttage. Une équation a été obtenue permettant de prévoir la cinétique d'égouttage en fonction de la valeur des trois facteurs étudiés. Les valeurs calculées s'ajustaient aux valeurs expérimentales avec un coefficient de corrélation r = 0,994.

lactosérum / égouttage / cinétique / composition du lait / pH / emprésurage / fromage pâte molle

1. INTRODUCTION

Cheesemaking involves the formation of a solid coagulum from liquid milk, followed by a spontaneous expulsion of whey from the gel, the syneresis. In cheese manufacture, the coagulum formation is achieved by the addition in milk of starters and rennet. That leads to the destabilisation of the colloidal system, due to changes in structural and physicochemical properties of the casein micelles.

The stability of the native casein micelles is controlled both by a balance of electrostatic attractions and steric repulsions between individual caseins and between micelles themselves [14]. The caseinomacropeptide (CMP) part of κ casein and also the mineral equilibria between casein micelles and the diffusible phase play a prominent part in micelle stability [8, 12, 13]. The release of CMP from κ casein by rennet, and the solubilisation of the colloidal calcium phosphate by starter acidification of milk [5, 6, 15, 18] allow a decrease of the stabilizing energetic barrier between casein micelles [21], allowing thereby a closer contact between micelles leading to the formation of a solid network entrapping the aqueous phase.

The subsequent whey expulsion from coagulum by syneresis is not yet fully understood. Several mechanisms have been proposed in the literature, and have been reviewed [40], for explaining the shrinkage or endogenous syneresis of rennet or acid curd in the absence of any mechanical effects such as cutting, stirring or pressing. The main cause of syneresis is likely a rearrangement of the network which implies a deformation of the paracasein particles, Brownian motion and breaking of the strands [34, 42]. In fact, syneresis depends both on the pressure gradient exerted on the whey, and also on permeability of the matrix, which varies with time and with the shrinkage of the gel [35].

The rate and extent of whey drainage and syneresis depend on many other factors. Among them, the most important are the composition and pretreatment of milk, such as the concentration or heat treatment [2], the renneting conditions and the characteristics of coagulum [38]. On the other hand, some factors are related to drainage conditions, such as geometrical constraints, temperature, extent and time of cutting and of pressing [27, 40]. Control of whey expelling during cheesemaking, including the control of syneresis and of the complementary drainage obtained through mechanical and physical actions, is a crucial step in cheese technology, as it determines the dry matter (level and composition) of drained curd and consequently that of the cheese.

To characterise more precisely the coagulation and drainage steps during the manufacture of Camembert soft cheese in relation with physicochemical and technological factors was the purpose of this work.

In a previous paper the effect of three factors was studied: pH at renneting (ren.pH), casein concentration in milk (CN) and ionic strength (IS), on milk rennet coagulum formation and properties, and on the drainage ability of the coagulum. The methodology used involved centrifugation tests and collection of whey versus time by a manual method [7].

We report here the characterisation of the drainage ability of a rennet coagulum, using an instrumented drainage device conceived in the laboratory to collect drainage data [32]. From the registered whey drainage kinetics obtained, the effects of the factors ren.pH, CN and IS on drainage and on whey composition were quantified using an experimental design. From the obtained data, a descriptive mathematical model was built, able to predict as well as whey drainage kinetics, the weight of the factor levels.

2. MATERIALS AND METHODS

2.1. Milk preparation

Raw bulk milk from a local factory was ultrafiltered at 50 °C on a 2 × 3P19 multichannel ceramic membrane (Membralox, 1.8 m^2 area; 0.05 µm pore diameter, SCT, Tarbes, France) up to a 2.5 volumic concentration factor, to obtain retentate and permeate fractions. These fractions were combined together along with a 50 $g{\cdot}L^{-1}$ lactose solution in order to obtain milks with different casein concentrations (about 27 and 37 $g{\cdot}kg^{-1}$) and/or different aqueous phase dilution ratios (1.0 and 0.6). It is noteworthy that ultrafiltration increased the soluble protein concentration in milk by the same ratio as the casein one. Thermised cream containing about 450 g $fat{\cdot}kg^{-1}$ was added to the milk to obtain a fat/casein ratio equal to 1. The milk was then heat treated at 72 °C for 20 s, using an Actijoule apparatus (Actini, Evian les Bains, France).

2.2. Pilot drainage device

The device was previously described [32]. It measured the drainage of a weight of curd corresponding to one Camembert cheese. It was composed of the following parts: a thermostated drainage room, containing the moulding unit where the curd was poured, a whey flow out system where the pH was measured, a whey fraction collector equipped with data capture equipment. The whey was collected into 100 mL fractions. During the whole process, the temperature, the pH and the weight of whey were measured at a frequency varying from 0.1 to 10 points per min, according to the flux of whey, and recorded.

2.3. Curd preparation and drainage

Curd preparation was made with 2 kg of cheese milk. An addition of 1.54 $g{\cdot}100\ L^{-1}$ of a mesophilic starter was done (MM100 from Texel, Dangé-St-Romain, France), which corresponded to 7×10^6 CFU in the milk, and a preincubation was performed during 17 h at 12 °C. The milk was then warmed up to 33 °C and poured into a polypropylene vat (15 × 15 × 20 cm) for incubation. When the pH of milk reached 6.4 or 6.0, renneting was performed by addition of a liquid rennet solution (520 $mg{\cdot}L^{-1}$ chymosin, from SBI, Gand Gassiot, France), in order to obtain 7.4 mg $chymosin{\cdot}100\ L^{-1}$. Forty minutes later, the coagulum was cut into 2 cm cubes with rectangular frames having metallic threads and then left to settle for 40 min. Moulding was then performed by pouring the coagulum with a ladle into a perforated soft cheese mould placed in the drainage room of the device. At this time, automatic data capture began and the weight of the whey was registered over 18 h. The temperature in the chamber was set at the following values: 28 °C for 1 h; 25 °C for 4 h; 20 °C for 11 h; 18 °C for 2 h. Two turning overs of the draining curd were done, after 1 h and 4 h of drainage respectively.

2.4. Characterisation of whey drainage kinetics

Characterisation of whey drainage kinetics was made according to 2 different approaches. On the one side, were compared the crude whey amounts experimentally obtained after different draining times (2.4.1). On the other side, the variation of the weight of whey as a function of time was considered as a whole and each experimental kinetics curve was fit to a mathematical model (2.4.2). Then, the factor levels used in the experiments were checked either to the crude amounts of whey (2.4.1) or to the mathematical parameters obtained by fitting (2.4.2), to quantify the effects of the factors.

2.4.1. Checking of crude whey amounts

The crude whey amounts obtained after some different times of drainage were directly collected from the experimental whey drainage data. These values were analysed by multiple regression analysis, keeping as variables the levels of the factors used in the experimental design. This allowed determination of the significant factors, to quantify their effects on the weights of whey at each considered time, and to obtain the average values of the weights of whey at these times.

2.4.2. Fitting of experimental kinetics curves to a model

Each whey drainage kinetics curve was fit to a descriptive mathematical model, chosen of the exponential type, owing to the general shape of the curve. The equation used was:

$$W(g \cdot kg^{-1}) = W1\,(1 - \exp(-t/\tau 1)) + W2\,(1 - \exp(-t/\tau 2)). \quad (1)$$

It involved 2 steps and 4 parameters, W1, W2, $\tau 1$ and $\tau 2$. W was the total weight of whey expelled at time (t), W1 and W2 the whey amounts obtained at the end of steps 1 and 2, and $\tau 1$ and $\tau 2$ the kinetics times of the steps 1 and 2 of whey drainage. This equation was already used in a previous work [7]. A two step exponential equation was chosen to describe W, as it gave a better adjustment to experimental data than a single step equation. Values for the parameters W1, W2, $\tau 1$ and $\tau 2$ were calculated for each experiment, by fitting the W values of equation (1) to the experimental values of the whey drainage kinetics, using the least square method. Each experiment thus led to one value for each of the 4 parameters of the equation. All the values obtained for the parameters were then analysed by a multiple regression analysis, keeping as variables the levels of the factors in the experimental design. This led to a quantification of the effects of factors on the parameters involved in equation (1) and to the determination of their average value in the design.

2.5. Biochemical analyses

Biochemical analyses were performed on milk, whey and drained curd. Fractionation of total nitrogen matter in milk was according to the Rowland procedure [29] to separate non casein nitrogen (NCN) and non protein nitrogen fractions (NPN). Total nitrogen matter (TN) in milk and nitrogen matter in the NCN and NPN fractions were obtained from N analysis using the Kjeldahl method and the converting factors 6.38, 6.25 and 6.19 respectively for TN, NCN and NPN; values which take into account the corrections for precipitate volume during fractionation, if any. Casein (CN) in milk was calculated as TN-NCN and soluble proteins as NCN-NPN. Dry matter (DM) of milk, whey and drained curd was obtained by weighing before and after drying in an oven during 7 h at 102 (±2) °C. Calcium and potassium contents were determined using atomic absorption spectrophotometry [1] .

The ionic strength level (IS) in the non-modified milk was kept as a reference (IS = 1.0). In modified milks, the IS decrease was referred to by the dilution performed in milk through the addition of the lactose solution. The dilution performed was quantified from the difference in total potassium concentrations in the milks. The dilution factor was calculated as the ratio of total potassium in treated milks compared to that in the non-modified ones.

2.6. Experimental design

The effects of the factors, ren.pH, CN and IS, were studied in a similar experimental design consisting of 8 combinations of factors on 2 levels. Fat content in milk was varied in the same extent as casein content to maintain a fat/CN ratio equal to 1. However, fat was not studied separately as a factor so that its effect was included in the variation observed for the CN factor. A 4 time repetition of one experimentation was performed to test the repeatability, which was calculated as the variation coefficient (VC), calculated from the standard deviation (SD) and the average value (AV) as: VC = 100 × SD/AV.

The range of variation of the factor levels was 27 to 37 $g \cdot kg^{-1}$ for CN, 6.0 to 6.4 for ren.pH and 0.6 to 1.0 for IS. These factor levels were coded as –1 and +1 for the lower and higher levels respectively. A correction was made, if necessary, to consider the real level achieved during the experimentation. The quantification of the effects of the factors on drainage kinetics data was made using a linear regression model. Thus was obtained an average value for each of the dependant variables in the design and the value of the effects corresponding to each of the three factors studied. An effect quantified the variation of the average value induced by a variation of one coded unit of the factor level, meaning from 0 to +1. First order interactions between factors were tested. They measured the difference in a factor effect existing according as the factor was tested at the high or low level of a second factor. Significant effects were retained at the level $P = 0.05$.

3. RESULTS AND DISCUSSION

3.1. Curd making mass balance

Whey drainage data were collected from 11 experiments. The mass balance during the drainage process was calculated from the weights of milk, whey and curd obtained, and from their DM and TNM composition. For example, mass recovery for the total weight was the weight of whey plus the weight of curd reported to the weight of milk and expressed as a percentage. The recoveries were thus: 98.92% (SD = 0.36) for total weight, 98.83% (SD = 0.38) for the weight of water, 99.60% (SD = 0.94) for the dry matter and 100.77% (SD = 1.38) for the total nitrogen matter.

3.2. Experimental whey drainage kinetics

3.2.1. Description

An example of the crude data obtained from drainage experiments is shown in Figure 1 for 4 different milks. The weight and pH of the whey were recorded as a function of time with a variation coefficient for the weight of whey varying, for the same milk from 1.8 to 0.34% between the beginning and the end of the drainage process. The higher variability observed in the early drainage corresponded to the turning over of curd pieces which caused profile

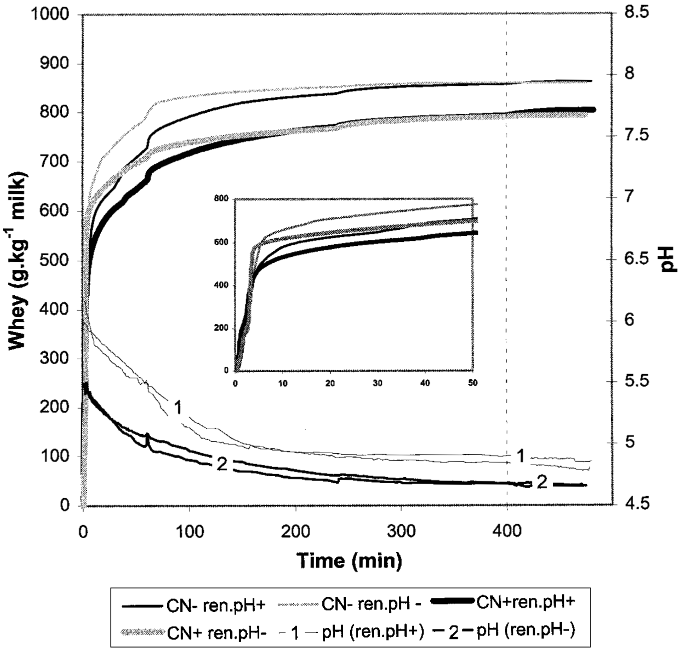

Figure 1. Experimental whey drainage kinetics and evolution of pH of the whey during experiments on four different milks: IS = 1, casein 27 $g \cdot kg^{-1}$ (CN–) or 37 $g \cdot kg^{-1}$ (CN+), ren.pH 6.4 (pH+) or 6.0 (pH–). Expanded scale in the insert.

Figure 1. Cinétique de l'écoulement du lactosérum et pH du lactosérum dans le cas de 4 expérimentations sur des laits à force ionique IS = 1.0 et ayant 27 $g \cdot kg^{-1}$ (CN–) ou 37 $g.kg^{-1}$ (CN+) de caséine et emprésurés à pH 6.4 (pH+) ou 6.0 (pH–). Expansion d'échelle dans le médaillon.

disturbances. The general shape of whey drainage kinetics was the same for all experiments. During the first 10 min of the early drainage, the weight of whey increased at a very high rate (Fig. 1, insert), which presumably corresponded to the flow of whey expelled by the coagulum in the vat before moulding. Then there was observed a second stage of quite rapid drainage for about 400 min, followed by a late drainage at a lower rate up to 1 000 min. These observations confirm the reports of Walstra et al. [42] and of Renault et al. [28].

An effect of the CN concentration and the renneting pH on the amount of whey expelled was observed (Fig. 1). The differences in the whey amounts obtained between 50 to 100 min of drainage were apparently related to ren.pH while those observed in the late drainage (400–1 000 min) were dependent on CN.

The pH values of whey are also reported in Figure 1. A difference in the pH of whey was related to ren.pH, the higher the ren.pH, the higher the pH of whey during the whole drainage. In addition, the rate of pH decrease in whey during the first 100 min was lower at the high level of ren.pH. This presumably resulted from the higher buffering capacity of the draining curd obtained in the ren.pH = 6.4 experiments, in which remained a higher part of the colloidal minerals of micelles. This point will be discussed later. No effect of the CN concentration on whey pH was observed.

The weights of whey obtained between 10 min and 800 min of drainage were

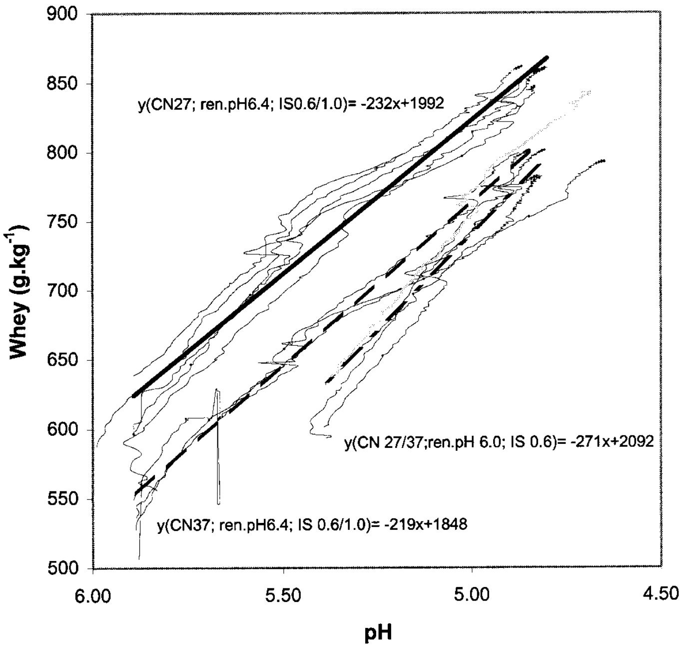

Figure 2. Relation between the amount of whey (g·kg^{-1}) and the pH of whey at each time of drainage (from 10 min to 800 min).

Figure 2. Relation entre la quantité de lactosérum écoulée (g·kg^{-1}) et le pH du lactosérum au cours de l'égouttage 10 min à 800 min.

plotted against the pH of whey at the same moment (Fig. 2). A linear course of the increase in the weight of whey was observed as the pH of whey decreased whatever the levels of CN, IS and ren.pH. An effect of CN was apparent mainly for ren.pH = 6.4; a lower weight of whey was obtained at higher CN values. However, the slopes of all the curves were similar. This would agree with the variation in the rate of whey expulsion from curd being mainly determined by the variation of pH during curd drainage.

3.2.2. Effect of factors on the crude amounts of whey expelled at different times

The amounts of whey obtained after 4 drainage times, 10, 40, 400 and 800 min, during the different whey drainage stages were compared to the factor levels in the experiments to quantify the effect of ren.pH, CN and IS factors (See Sect. 2.4.1). This allowed the experimental average values of whey amounts to be obtained at these times and to quantify the effect of factors on these values (Tab. I). The average amount of whey expelled was 585.0 g·kg^{-1} after 10 min of drainage which increased up to 824.8 g·kg^{-1} after 800 min. The 3 factors showed significant effects. The effect of ren.pH, initially negative at 10 min, turned positive at 800 min, while the CN effect was quite constant over the whole drainage leading to a mean value in the –30.8 (SD = 2.1) g·kg^{-1} range. A positive effect of IS, decreasing from 10 min to 800 min of drainage was observed. Effect values were then calculated at lower intervals of time all along the drainage process to define more precisely

Table I. Effect of renneting pH (ren.pH), of casein level in milk (CN) and of ionic strength (IS) factors on the crude amounts of whey (g·kg^{-1} milk) obtained at different times during the experimental whey drainage kinetics. (P = 0.05). ns: not significant.

Tableau I. Effet du pH à l'emprésurage (ren.pH), de la teneur en caséine du lait (CN) et de sa force ionique (IS) sur les quantités de sérum (g·kg^{-1} lait) obtenues lors des expérimentations après différentes durées d'égouttage. (p = 0,05). ns : non significatif.

Drainage time (min)	Effect of factors				
	ren.pH	CN	IS	Average value	r^2
10	–28.3	–29.3	ns	585.0	0.770
40	–27.3	–33.9	8.2	676.0	0.946
400	ns	–30.4	5.4	822.9	0.983
800	4.3	–29.8	3.8	824.8	0.990

their variations (Fig. 3). The results highlighted the inversion of the ren.pH effect. A negative effect of the ren.pH was observed during the early drainage within 100 min, no more effect occurred in the interval 100–400 min, a positive effect appeared in the late drainage.

The effect of factors on the final yields of whey and on whey composition were also calculated and are reported in Table II.

3.2.2.1. The casein effect

The increase in CN level, meaning in fact the simultaneous increase in casein,

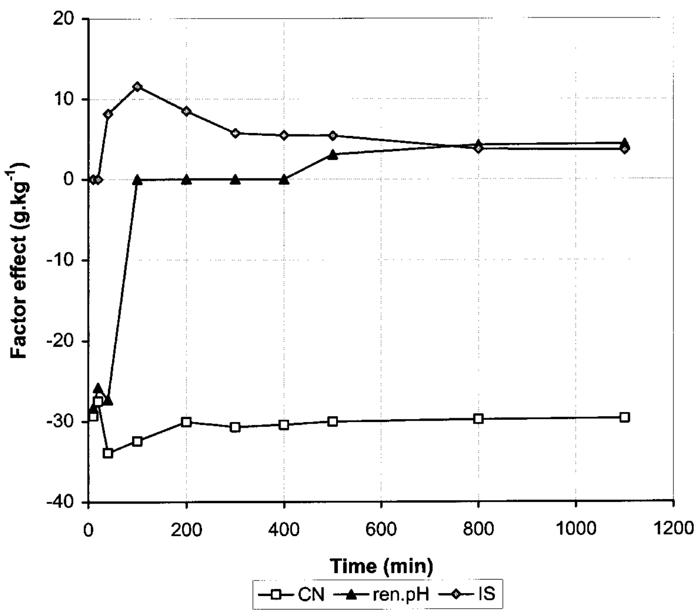

Figure 3. Values of the effects (g·kg^{-1}) calculated for CN, ren.pH, IS factors after different drainage times.

Figure 3. Valeurs des effets calculés (g·kg^{-1}) pour les facteurs CN, pH, IS à différents temps d'égouttage.

Table II. Effect of renneting pH (ren.pH), of casein level in milk (CN) and of ionic strength (IS) factors on the yield of whey obtained after 1 100 min of drainage (g·kg^{-1} milk) and on the average composition of the whey collected during the whole drainage (g·kg^{-1}). ($P = 0.05$). ns: not significant.

Tableau II. Effet du pH à l'emprésurage (ren.pH), de la teneur en caséine du lait (CN) et de sa force ionique (IS) sur les rendements en lactosérum (g·kg^{-1} lait) obtenus après 1 100 min d'égouttage et sur la composition moyenne du lactosérum collecté (g·kg^{-1}). (p = 0,05). ns : non significatif.

	Effect of factors				
	ren.pH	CN	IS	Average value	r^2
Yield of whey	4.0	–29.2	3.3	824.7	0.983
DM	ns	2.6	0.9	67.3	0.914
TNM	ns	1.71	0.69	10.24[(a)]	0.996
Total calcium	–0.095	0.118	0.040	0.952[(b)]	0.998
pH	0.20	ns	ns	5.45	0.743

DM, dry matter ; TNM, total nitrogen matter.
[(a)] significant interaction CN × IS = 0.15.
[(b)] significant interaction, CN × pH = –0.009.

soluble proteins and fat concentrations in milk, led to a reduction of the amount of whey expelled during the early drainage (–29.3 g·kg^{-1}, after 10 min drainage), as well as on the late drainage (–29.8 g·kg^{-1}, after 800 min drainage). These results agree well with the observations already made on ultrafiltrated skimmed milk [3, 22, 24, 26]. The effect was quite constant all along the drainage process leading to a similar effect on the final yield of whey (Tab. II). The decrease of final whey amounts in high CN milks could be attributed mainly to the reduction of the aqueous phase content of the milk due to ultrafiltration. As a matter of fact, both casein micelles and fat globules can be considered as particulate material in milk, although micelles are in fact "soaked" in the aqueous phase. Hence, an increase in the particulate material volume of milk decreased the extramicellar aqueous phase content of the same volume. Micelle voluminosity is reported to be in native milk in the 3.3 mL·g^{-1} range [31, 39]. Voluminosity of fat, taking into account a value of 0.92 for its density [41], is about 1.1 mL·g^{-1} fat. Thus, in the current experiments involving a constant CN/fat ratio, an increase of the CN level in milk of 1 g corresponded thereby to an increase in particulate volume of: 3.3 + 1.1 = 4.4 mL, meaning 4.4 mL less extramicellar aqueous phase in milk. For 5 g of casein, which corresponds to the coded unit for CN in the current design, this led to 4.4 × 5 = 22 mL less of extramicellar aqueous phase per kg of ultrafiltrated milk. After renneting, the voluminosity of micelle decreases to about 2.4 mL [4, 36] and the same calculation leads to a difference in the extramicellar volume of 17.5 mL. This explains only partly the CN effect observed. However, the increase in fat content in milk could also contribute by itself to hindering the curd drainage, since a negative correlation has been observed between fat content and syneresis rate [11]. Fat could act either in interrupting the protein network structure [16] and impeding the shrinkage of gels [30], or in decreasing the permeability [35].

The milk CN concentration also modified the composition of whey (Tab. II). An increase in dry matter and in total nitrogen matter contents was observed in whey as CN plus fat content increased in milk. The ultrafiltration treatment of milk resulted in an increase in the whey protein content of milk by quite the same concentration factor as the casein, consequently, they were recovered in higher amounts in whey. Colloidal minerals were also increased by ultrafiltration, then solubilised in higher amounts as the pH decreased, leading to a positive effect of CN on the mineral content of whey.

3.2.2.2. The ren.pH effect

The effect of ren.pH was negative in the early drainage (–28.3 $g \cdot kg^{-1}$ at 10 min). The lower ren.pH resulted in a lower pH at cutting, both favouring the syneresis of coagulum [42] and by the way increasing the early drainage. Hence, a higher ren.pH decreased the early drainage, but as the pH slowly decreased in the curd during the course of drainage, a delayed whey drainage occurred during the second stage of drainage (Fig. 2), to finally obtain at the end of the drainage process higher yields of whey for higher ren.pH (Tabs. I and II). A negative effect of ren.pH on drainage has been already reported [20, 22, 23, 25, 31, 40]. However these authors did not observe the late positive effect we describe, as they studied whey drainage for shorter draining times, up to 150 min only.

Differences in ren.pH induced different rates in the course of decrease of whey pH, as shown in Figure 1. A decrease in pH goes along with solubilisation of colloidal minerals. The lower level of ren.pH, 6.0, led to a pH at moulding of about 5.5 (Fig. 1) at which most of the colloidal minerals were solubilised [19] and then were expelled in whey during the early drainage. The higher ren.pH, 6.4, corresponded to a pH at moulding of about 6.2, meaning that about 70% of colloidal minerals remained associated with caseins [19] as the early drainage intervened. The subsequent decrease in pH occurring in the curd during drainage was then slowed down by the solubilisation of the colloidal calcium and phosphate remaining in the curd which increased its buffering capacity.

The ren.pH effect on drainage could also result from differences in the structure and properties of the rennet coagulum when formed at different renneting pH. When ren.pH was 6.4, nearly all of the colloidal minerals remained in the micelles, resulting in a network having a more rigid structure and a lower permeability. However, the subsequent solubilisation of the mineral part of the structure as pH decreased, led to a smooth proteinaceous network having a high porosity and permeability, which explained the positive effect of ren.pH at the end of drainage [42]. In contrast, when ren.pH was 6.0, coagulum formation intervened on a partially demineralised micelle, as about one half of colloidal phosphate was solubilised [1, 19]. The resulting structure had thus a higher initial permeability [33, 34], mainly due to the pH dependency on the voluminosity [36], which favoured the early drainage. In contrast, the structure showed a higher ability to retain water at the end of drainage.

The average pH of the whey collected during the whole drainage (Tab. II) was dependent on the ren.pH. The higher the ren.pH, the higher was the pH of the whey, as drainage proceeded mainly before the decrease in pH of the curd.

3.2.2.3. The ionic strength effect

The initial IS of milk at pH 6.7 was about 0.08 $mol \cdot L^{-1}$ [41]. The average dilution performed on milk was $\times$ 0.6, from the total K contents, thus giving IS = 0.048 $mol \cdot L^{-1}$. The amount of soluble calcium was also determined in these milks. The soluble Ca ratio after and before dilution was $\times$ 0.65, meaning slightly higher than the K ratio. This was due to an adjustment of the soluble-colloidal mineral equilibria after the dilution through the solubilisation of a part of the colloidal calcium, amounting to about 45 $mg \cdot kg^{-1}$, which corresponded to 5% of the total colloidal Ca. A positive effect of IS was observed on the amounts of whey expelled during the 40 to 800 min drainage (Tab. I), thus a reduction in the ionic strength of milk, led to a decrease in drainage. These results are in agreement with those reported by Marshall [22] and Peri et al. [26] which reported a decrease in the rate and extent of syneresis after a reduction of the ionic strength of the milk soluble phase performed by dilution or diafiltration. However, the results are different from those we obtained in a previous work [7], in which different technological conditions were used for coagulation. In this first work, the amount of rennet was 3 times higher, the time before moulding was 2 times higher and these conditions led to an opposite effect of IS, meaning a negative effect of ionic strength on drainage [7]. These discrepancies seem related to the modification of the ratio “time before cutting to coagulation time”, considered by Marshall [22] as important for drainage, so that curd development and coagulum strength at cutting time were not the same in the two experiments, presumably explaining the discrepancies in curd drainage [20, 27]. Indeed, it is reported that the ability of curd to syneresis becomes progressively lower as the gel was left for a longer time before cutting or drainage [34].

The changes in IS obtained by the ultrafiltration/diafiltration process allowed the colloidal mineral level in micelles to be maintained in a quite native state (95% of colloidal Ca remaining on the micelle at pH 6.7, calculated from the previously reported analytic determinations) and to obtain during acidification a course of demineralisation similar to that occurring in the non-modified milk (results not shown), which confirmed the results of Famelart et al. [10]. Thus, the effects obtained could be strictly attributed to the IS variation. In contrast, when IS is modified through a salt addition, such as $CaCl_2$ or NaCl [22, 37], salt equilibria in milk are also modified [9, 19], which, in addition to the variation of IS, interferes with the results finally obtained for coagulation and drainage.

As a result of the dilution of the soluble phase of milk, the average whey composition obtained was different (Tab. II). Total nitrogen matter and dry matter contents of whey decreased with the reduction of the ionic strength, due to the decrease in non-protein nitrogen and, most generally, soluble component levels. A positive effect of IS on the total yield of whey was also observed.

3.2.3. Characterisation of whey drainage kinetics by fitting

3.2.3.1. Fitting to the model and effect of factors

Fitting of the experimental draining curves to equation (1) allowed values for the parameters to be obtained. An example of such a fitting is given in Figure 4 for the following combination of factors: ren.pH = 6.4, CN = 27, IS = 1.0. The correlation coefficient obtained was 0.993. The mean value for the correlation coefficient for all the fittings was 0.992 (SD = 0.006). The higher discrepancy between adjusted data and the experimental ones was observed in the early draining time (in the 60–240 min time interval) and was presumably due to the disturbances caused by the turning over of curd pieces. Parameter values obtained from the fitting of each whey drainage kinetics allowed the calculation of their average values and the factor effects (Tab. III). The results showed that during step 1 the higher amount of whey was expelled, W1 = 637.3 $g \cdot kg^{-1}$, at a high rate, as $\tau 1$ had a low value. During step 2, the average amount of whey was smaller, W2 = 189.5 $g \cdot kg^{-1}$, and $\tau 2$ had a high value, meaning a very low drainage rate.

These kinetics parameters were modified by factors as shown by the factor effects reported in Table III. CN had a negative effect on W1 and no effect on W2. These results confirmed those obtained in Section 3.2.2 and outlined the importance of milk casein concentration in the early drainage. Similarly, the effect of ren.pH was negative on W1 and was positive on W2, which fit well with the experimental data in Figure 3. The time parameter $\tau 1$ was modified by the factor CN. This confirmed the

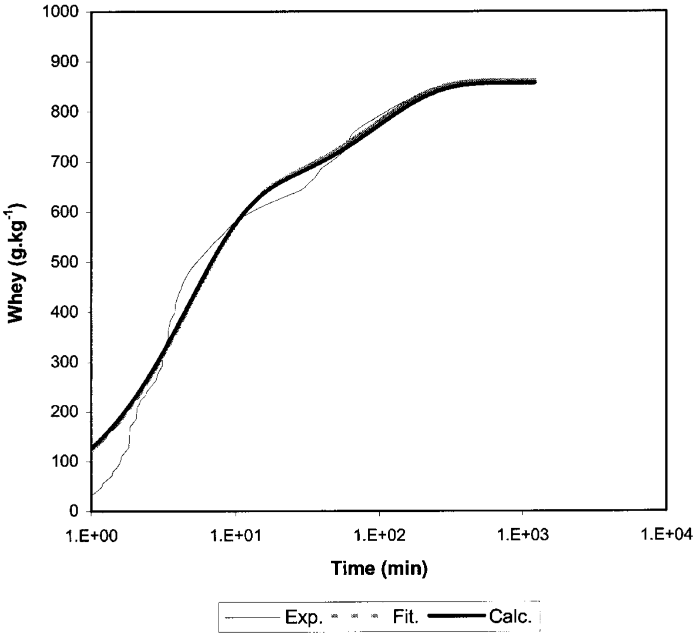

Figure 4. Whey drainage kinetics for the milk sample: ren.pH = 6.4, CN = 27, IS = 1.0; (Exp.), experimental data; (Fit.), adjustment of equation (1) to the experimental curve by the least squares method, which gave: W(Fit.) = 622.6 (1 – exp (–t/4.6)) + 239.2 (1 – exp (–t/93.2)); *r* = 0.993; (Calc.), calculated kinetics from equation (2): W(Calc.) = 620.5 (1 – exp (–t/4.5)) + 236.5 (1– exp (–t/97.5)); *r* = 0.994.

Figure 4. Comparaison des cinétiques d'égouttage obtenues pour les valeurs des paramètres : ren.pH = 6,4, CN = 27, IS = 1,0 ; (Exp.), cinétique expérimentale ; (Fit.), ajustement obtenu par la méthode des moindres carrés avec l'équation (1), W(Fit.) = 622,6 (1 – exp (–t/4,6)) + 239,2 (1 – exp (–t/93,2)), *r* = 0,993 ; (Calc.), courbe calculée à partir de l'équation générale, équation (2): W(Calc.) = 620,5 (1 – exp (–t/4,5)) + 236,5 (1 – exp (–t/97,5)) ; *r* = 0,994.

results of Peri et al. [26] concerning the effect of casein on the draining rates. A negative effect of IS was observed on $\tau1$ as well as a significant interaction with CN, CN $\times$ IS = –1.1. Thus, a decrease in IS decreased the rate of drainage during step 1. On the other hand, $\tau1$ is certainly related to the moulding conditions and to the geometrical characteristics of the mould, as the density of holes on mould walls or the size of the mould [27, 40]. In contrast, $\tau2$ was dependent on casein concentration and on ren.pH. The casein concentration had a positive effect meaning that an increase in milk casein content led to a lowered drainage rate during the second step. On the contrary, ren.pH had a negative effect on $\tau2$, meaning a higher rate of drainage at higher ren.pH, as already reported [17]. Some authors explained the increase in the drainage rate by differences in curd strength and in the ability of coagulum to shrink [3, 30]. On the whole, the results obtained with the fitting method confirmed those obtained experimentally on the crude whey amounts at different times (Tab. I); apart from the effect of IS on the total weight of whey which was observed from experimental data in Table I and was no more observed on W1 nor on W2 in Table III. However, the results of

Table III. Effect of renneting pH (ren.pH), of casein level in milk (CN) and of ionic strength (IS) factors on the parameters of the whey drainage kinetics calculated according to the relation:

$$W = W1 \times (1 - \exp(-t/\tau1)) + W2 \times (1 - \exp(-t/\tau2)).$$

W, W1, W2 in $g \cdot kg^{-1}$; τ1, τ2 in min. $P = 0.05$. ns: not significant.

Tableau III. Effet du pH à l'emprésurage (ren.pH), de la teneur en caséine du lait (CN) et de sa force ionique (IS) sur les paramètres de l'équation permettant de décrire la cinétique d'égouttage :

$$W = W1 \times (1 - \exp(-t/\tau1)) + W2 \times (1 - \exp(-t/\tau2)).$$

W, W1, W2 en $g \cdot kg^{-1}$; τ1, τ2 en min. ($p = 0,05$). ns : non significatif.

	Effect of factors				
	ren.pH	CN	IS	Average value	r^2
W1	–43.2	–26.4	ns	637.3	0.864
τ1	ns	0.6	–0.8	4.8 [(a)]	0.738
W2	47.0	ns	ns	189.5	0.880
τ2	–9.9	15.3	ns	114.6 [(b)]	0.808

[(a)] significant interaction, CN × IS = –1.1.
[(b)] significant interaction, CN × ren.pH = –8.1.

fitting thereby provided a quantification of the drainage rates, which was not obtained by the treatment of the crude whey amounts at different times.

Thus, the final equation describing the weight of whey expelled during the drainage and keeping into account the factor effects was:

$$\begin{aligned} W_{calc.}(g \cdot kg^{-1}) = {} & (637.3 - 26.4 \times CN - 43.2 \times ren.pH) \times (1 - \exp(-t/(4.8 \\ & + 0.6 \times CN - 0.8 \times IS - 1.1 \times CN \times IS))) \\ & + (189.5 + 47.0 \times ren.pH) \times (1 - \exp \\ & (-t/(114.6 + 15.3 \times CN - 9.9 \times ren.pH \\ & - 8.1 \times CN \times ren.pH))). \qquad (2) \end{aligned}$$

3.2.3.2. Forecasting of drainage data

The characterisation of the drainage kinetics and the quantification of the effect of factors in equation (2) allowed the calculation of previsional drainage curves. For example, the predictive drainage curve for a milk was calculated for the following experimental conditions: ren.pH = 6.4, CN = 27, IS = 1.0. In the linear regression model of equation (2) the factor levels were introduced at their right value in the experiment (coded values), which allowed the values of parameters W1,W2, τ1 and τ2 to be obtained. After that the values of W were calculated at different times, which gave the kinetics shown as curve "Calc." in Figure 4. This kinetics compared with the experimental curve (curve "Exp.") obtained for the same factor levels, with a correlation coefficient $r = 0.995$. Comparatively, a direct fitting of this "Exp." curve by adjustment to equation (1) was done, giving the curve "Fit." reported in Figure 4 ($r = 0.997$). These results showed the accuracy of the linear model of equation (2), since the correlation factor ($r = 0.995$) was close to that obtained by fitting of experimental values ($r = 0.997$). That supported the idea that the whey drainage kinetics can be described by equation (2) in the studied range of variation of the factors.

In another example, presented in Figure 5, the time of drainage to obtain a determined fraction of the total whey (0.95, 0.97, 0.99, 0.999) was calculated from equation (2) for different CN concentrations of the milk. Total whey at the end of drainage was calculated as the amount of whey expelled after

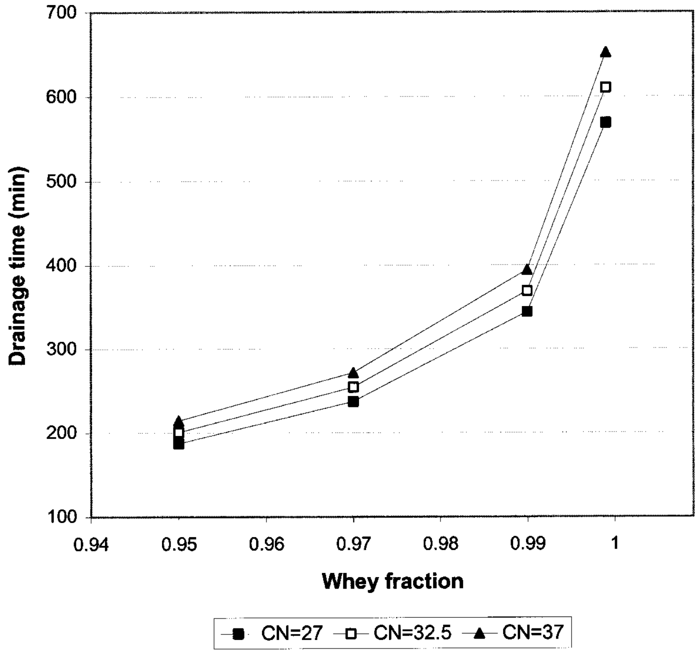

Figure 5. Time of drainage calculated from equation (2) to obtain a determined fraction (0.95 to 0.999) of the total whey (kept as the whey amount obtained at 1 100 min) for milks at different CN contents and renneted at pH 6.4.

Figure 5. Temps d'égouttage nécessaire pour obtenir une fraction déterminée (0,95 à 0,999) du lactosérum total (soit le lactosérum obtenu à 1 100 min), en fonction de la teneur en caséine du lait, calculé à partir de l'équation (2).

1 100 min. The results showed that the drainage times to obtain the same fraction of total whey increased drastically as casein concentration increased, meaning a lowering in the drainage rate.

4. CONCLUSION

Whey release from Camembert curd was precisely characterised thanks to the device developed which allows determination of not only kinetics of drainage but also changes in whey composition vs. time or vs. biochemical and biophysical modifications of the used cheese milk.

From the results obtained in this study, it becomes possible to estimate the behaviour in cheesemaking of a milk in terms of ability to expel whey under given technological parameters and evidently, on the opposite, to adjust milk characteristics for obtaining a given whey release. Such a potentiality finds its interest when new processes involving for example increase of casein content, partial demineralisation, lactose removal, are studied.

Drained curds obtained in the present study have been analysed and characterised. The obtained results and the complementary developments to which they lead will be presented in a future paper.

ACKNOWLEDGEMENTS

We are indebted to J.Y. Gassi and to J.M. Samson for their help during experimentation. We thank J. Léonil for advice and for a critical reading of the manuscript. The study has been carried out with financial support from the Commission of the European Communities, Agriculture and Fisheries (FAIR) specific RTD programme, CT 96-1056, Cheese Texture Improvement through Rationalisation and Optimisation of Structure. It does not necessarily reflect its views and in no way anticipates the Commission's future policy in this area.

REFERENCES

[1] Brulé G., Maubois J.-L., Fauquant J., Étude de la teneur en éléments minéraux des produits obtenus lors de l'ultrafiltration du lait sur membrane, Lait 54 (1974) 600–615.

[2] Calvo M.M., Espinoza N.F., Syneresis rate of cow's, ewe's, and goat's curd. Effect of thermal treatment and ultrafiltration, J. Agric. Food Chem. 47 (1999) 883–887.

[3] Casiraghi C.P., Piazza L., Effect of calcium equilibria on the rate of syneresis and on the firmness of curds obtained from milk UF retentates, Milchwissenschaft 42 (1987) 232–234.

[4] Creamer L.K., Water absorption by renneted casein micelles, Milchwissenschaft 40 (1985) 589–590.

[5] Dalgleish D.G., Brinkhuis J., Payens T.A.J., The coagulation of differently sized casein micelles by rennet, Eur. J. Biochem. 119 (1981) 257–261.

[6] Dalgleish D.G., Law A.J.R., pH induced dissociation of bovine casein micelles. 2. Mineral solubilization and its relation to casein release, J. Dairy Res. 56 (1989) 727–735.

[7] Daviau C., Famelart M.-H., Pierre A., Goudédranche H., Maubois J.-L., Rennet coagulation of skim milk and curd drainage: effect of pH, casein concentration, ionic strength and heat treatment, Lait (2000) 397–415.

[8] de la Fuente M.A., Changes in the mineral balance of milk submitted to technological treatments, Trends Food Sci. Technol. 9 (1998) 281–288.

[9] Famelart M.-H., Le Graet Y., Raulot K., Casein micelles dispersion into water, NaCl and $CaCl_2$: physico-chemical characteristics of micelles and rennet coagulation, Int. Dairy J. 9 (1999) 293–297.

[10] Famelart M.-H., Lepesant F., Gaucheron F., Le Graet Y., Schuck P., pH induced physicochemical modifications of native phosphocaseinate suspensions: influence of aqueous phase, Lait 76 (1996) 445–460.

[11] Grandison A.S., Ford G.D., Millard D., Owen A.J., Chemical composition and coagulating properties of renneted milks from cows during early lactation, J. Dairy Res. 51 (1984) 407–416.

[12] Holt C., Structure and stability of bovine casein micelles, in: Anfinsen C.B., Edsall J.D., Richards F.K., Eisenberg D.S. (Eds.), Advances in Protein Chemistry, Academic Press, New York, USA, 1992, pp. 63–151.

[13] Holt C., Horne D.S., The hairy casein micelle: Evolution of the concept and its application for dairy technology, Neth. Milk Dairy J. 50 (1996) 85–111.

[14] Horne D.S., Casein interactions: casting light on the black boxes, the structure in dairy products, Int. Dairy J. 8 (1998) 171–177.

[15] Horne D.S., Davidson C.M., The effect of environmental conditions on the steric stabilization of casein micelles, Colloid Polym. Sci. 264 (1986) 727–734.

[16] Johnston D.E., Murphy R.J., Effects of fat content on properties of rennet–induced milk gels, Milchwissenschaft 39 (1984) 585–587.

[17] Kaytanli M., Erdem Y.K., Tamer I.M., Factors affecting whey drainage rate of renneted skim milk gels: A kinetic approach, Milchwissenschaft 49 (1994) 197–200.

[18] Law A.J.R., Leaver J., Effects of acidification and storage of milk on dissociation of bovine casein micelles, J. Agric. Food Chem. 46 (1998) 5008–5016.

[19] Le Graët Y., Brulé G., Les équilibres minéraux du lait : influence du pH et de la force ionique, Lait 73 (1993) 51–60.

[20] Lelievre J., Rigidity modulus as a factor influencing the syneresis of renneted milk gels, J. Dairy Res. 44 (1977) 611–614.

[21] Lomholt S.B., Worning P., Ogendal L., Qvist K.B., Hyslop D.B., Bauer R., Kinetics of renneting reaction followed by measurement of turdibidity as a function of wavelength, J. Dairy Res. 65 (1998) 545–554.

[22] Marshall R.J., An improved method for measurement of the syneresis of curd formed by rennet action on milk, J. Dairy Res. 49 (1982) 329–336.

[23] Patel M.C., Lund D.B., Olson N.F., Factors affecting syneresis of renneted milk gels, J. Dairy Sci. 55 (1972) 913–918.

[24] Pearse M.J., Mackinlay A.G., Biochemical aspects of syneresis, a review. J Dairy Sci. 72 (1989) 1401–1407.

[25] Pearse M.J., Mackinlay A.G., Hall R.J., Linklater P.M., A microassay for the syneresis of cheese curd. J. Dairy Res. 51 (1984) 131–139.

[26] Peri C., Lucisano M., Donati E., Studies on coagulation of milk ultrafiltration retentates. II. Kinetics of whey syneresis, Milchwissenschaft 40 (1985) 650–652.

[27] Ramet J.P., L'égouttage du coagulum, in: Eck A. (Ed.), Le Fromage. De la science à l'assurance qualité. Lavoisier, Tec et Doc, Paris, 1997, pp. 42–61.

[28] Renault C., Gastaldi E., Lagaude A., Cuq J.L., Tarodo de la Fuente B., Mechanisms of syneresis in rennet curd without mechanical treatment, an hypothesis paper, J. Food Sci. 62 (1997) 907–910.

[29] Rowland S.J., The determination of the nitrogen distribution in milk, J. Dairy Res. 9 (1938) 42–46.

[30] Storry J.E., Grandison A.S., Millard D., Owen A.J., Ford G.D., Chemical composition and coagulating properties of renneted milks from different breeds and species of ruminant, J. Dairy Res. 50 (1983) 215–229.

[31] Tarodo de la Fuente B., Alais C., Solvation of casein in bovine milk, J. Dairy Sci. 58 (1975) 293–300.

[32] Tiros European Contract, FAIR, CT 96–1056, 1999.

[33] van den Bijgaart H.J.C.M., Syneresis of rennet induced milk gels as influenced by cheesemaking parameters, Thesis, Agricultural University Wageningen, The Netherlands, 1988.

[34] van Dijk H.J.M., Syneresis of curd, Thesis, Agricultural University Wageningen, The Netherlands, 1982.

[35] van Dijk H.J.M., Walstra P., Syneresis of curd. 2. One dimentional syneresis of rennet curd in constant conditions, Neth. Milk Dairy J. 40 (1986) 3–30.

[36] van Hooydonk A.C.M., Hagedoorn H.G., Boerrigter I.J., pH–induced physico–chemical changes of casein micelles in milk and their effect on renneting. 1. Effect of acidification on physico–chemical properties, Neth. Milk Dairy J. 40 (1986) 281–296.

[37] van Hooydonk A.C.M., Hagedoorn H.G., Boerrigter I.J., The effect of various cations on the renneting of milk, Neth. Milk Dairy J. 40 (1986) 369–390.

[38] van Vliet T., van Dijk H.J.M., Zoon P., Walstra P., Relation between syneresis and rheological properties of particle gels, Colloid Polym. Sci. 269 (1991) 620–627.

[39] Walstra P., The voluminosity of bovine casein micelles and some of its implications, J. Dairy Res. 46 (1979) 317–323.

[40] Walstra P., The syneresis of curd, in: Fox P.F. (Ed.), Cheese: Chemistry Physics and Microbiology. 1. General Aspects, 2nd Ed., Chapman and Hall, London, 1993, pp. 141–191.

[41] Walstra P., Jenness R., Dairy chemistry and physics. John Wiley and Sons, New York, USA, 1984.

[42] Walstra P., van Dijk H.J.M., Geurts T.J., The syneresis of curd. 1. General considerations and literature review, Neth. Milk Dairy J. 39 (1985) 209–246.