# Syneresis Rate of Cow's, Ewe's, and Goat's Curd. Effect of Thermal Treatment and Ultrafiltration

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The influences of ultrafiltration (UF), the intensity of heat treatment (70 °C for 5 or 30 min) applied to milk prior to UF processing, and species on the syneresis rate of curd from cow's, ewe's, and goat's milk were analyzed. The influence of the species was significant ($P < 0.05$) in the syneresis rate. The syneresis rate depended significantly on the intensity of the heat treatment applied before UF and the degree of concentration; these two parameters showed significant ($P < 0.05$) differences in the syneresis rate depending on the species studied. These results could indicate a possible difference in the structure of the curd formed. The differences in the curd structure could be due to the different relative composition of the retentates of the different species as well as the possible effect of the UF process on the physicochemical composition of milk.

**Keywords:** *Ultrafiltration; syneresis rate; cow's, ewe's, and goat's milk*

## INTRODUCTION

Ultrafiltration (UF) to separate and concentrate milk constituents is widely employed and can be applied to manufacture various cultured dairy products including some cheese varieties. Changes in the chemical composition of milk should be examined (St-Gelais et al., 1992), because changes in the relative composition, as well as physical changes such as casein aggregation, can occur during the UF process.

Fox (1984), working with milk concentrated by UF, concluded that complete control of cheese composition and ripening will be possible only when rennet coagulation, gel formation, and syneresis are fully understood and when scientifically based modifications can be made to the cheese-making process to compensate for uncontrollable variations in the composition of cheese milk.

Some factors (such as the degree of concentration, the intensity of heat treatment, the denaturation of protein, and the concentrate composition) that could affect the syneresis of curd from UF milk have been studied in curd manufacture from cow's milk (Marshall, 1982; Peri et al., 1985; Casiraghi et al., 1987; Guinee et al., 1995).

The influence of milk concentration on syneresis has been described. Peri et al. (1985) found that the syneresis of milk or milk concentrated up to 5-fold by UF followed a first-order reaction and was independent of protein concentration. van Dikj and Walstra (1986) found that the permeability of the gel decreases with the concentration of milk; however, Casiraghi et al. (1987) found that syneresis was greater in retentate than in unconcentrated milk.

Heat treatment applied before UF may also affect the syneresis process. Casiraghi et al. (1989a,b) also found that when the milk was heated before UF, the drainage was much slower from curd made pasteurized milk than that from raw milk. Casiraghi et al. (1989b) and Smith and McMahon (1996) found that increasing the extent of whey protein denaturation by heating reduced syneresis of the gel during storage.

Physicochemical changes in the composition of milk during UF could affect the structure of curd (Dalgleish, 1981; Korolczuk and Mahaut, 1991). van Dijk and Walstra (1986) found that the permeability of curd decreased with increasing fat content of milk. Other cheese manufacturing properties, such as a slight reduction of curd hardness and a decrease in whey separation rate, were described by Casiraghi et al. (1989a); these changes could be due to the mechanical and thermal stresses associated with the UF process.

The influence of the characteristics of the UF process has been also analyzed. Green et al. (1983) found that high flow rates, temperature (50 °C), and shear stresses associated with the recirculation of milk retentates through UF equipment may affect fat globule dispersion and casein micelle aggregation; these are critical factors in milk coagulation and curd formation.

The previously mentioned studies were performed with cow's milk. However, no information is available about the influence of heat treatment and UF in syneresis of ewe's or goat's milk. As has been described, these factors may have a different influence in the rennet clotting properties of milk from different species. The syneresis or curd drainage could be also affected by these factors. In this paper, the possible differences of curd drainage of curd from UF milk from different species, as well as the heat treatment before the UF process, have been investigated.

## MATERIALS AND METHODS

**Samples.** Raw bulk cow's, ewe's, and goat's milk from different herds in the central region of Spain were used.

Milk samples were skimmed by centrifugation before analysis. Whole milk was incubated in a water bath at 30 °C for 20 min before centrifugation at 3000*g* for 30 min at 5 °C; the milks were then placed in a water−ice bath, and after 30 min, the solidified fat was removed using a spatula. The skimmed milk was filtered through glass fiber pads to remove any residual fat.

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The pH value after heat treatment following UF was always lower than the pH of the raw milk. The pH was adjusted to the pH of the raw milk with 1 M NaOH. However, samples submitted only to the UF process showed a final pH value higher than those of raw milk; after the UF process, the pH value was adjusted to that of the raw milk with 1 M HCl.

Rennet solution was obtained by diluting 300 mg of rennet powder containing 85% of chymosin and 15% of bovine pepsine (Hansen, Copenhagen, Denmark; rennet strength = 1:100000) to 100 mL with 0.2 M sodium citrate buffer at pH 5.2.

**Ultrafiltration.** Milk, concentrated 2-fold (×2), and the corresponding ultrafiltrate were obtained by passing milk samples, at 50 °C in a water bath, through a Pellicon (Millipore, Madrid, Spain) stirred ultrafiltration cell fitted with a 10000 $M_r$ exclusion membrane. The ultrafiltrate and ×2 retentate were stored at 7 °C for 24 h. The ×1 and ×1.5 retentates were preparing by mixing the corresponding amount of the ultrafiltrate with the ×2 retentate.

**Heat Treatments.** Portions (10 mL) of milk were heated at 70 °C in a water bath for 5 or 30 min in tightly sealed Pyrex glass tubes (16 × 162 mm). Heated samples were immediately cooled in an ice–water bath and kept under refrigeration until analysis or until ultrafiltration.

All experiments were replicated four times using milk samples collected on different days.

**Evaluation of Syneresis.** Curd syneresis was evaluated according to the method of Marshall (1982). Curd was formed in 100 mL beakers by addition of 1 mL of rennet solution, prepared as indicated above, to 50 mL of milk and maintained at 30 °C.

The coagulation time was determined following the method of McMahon and Brown (1982). After 15 min of coagulation, the curd was cut crosswise and around the sides of the beaker with a spatula. After cutting, a plastic grid was placed on the curd surface. This retained the curd while allowing the whey to be poured off. Syneresis was measured by weighing the whey quantity removed at various intervals after cutting.

**Statistical Analysis.** First-order reactions were calculated for the syneresis curd drainage as a function of the incubation time in minutes. To study the influence of the intensity of the heat treatment applied before UF (unheated and heated at 70 °C for 5 or 30 min) as well as the concentration factor (×0, ×1, ×1.5, and ×2), four different experiments were performed for each of the studied factors.

The equations were calculated for the four different experiments at each assay condition; the slope values (*k* values) and their standard deviations were used to compare the four *k* values. When no significant differences ($P < 0.05$) between the *k* values were found, the *k* values and their standard deviations of the first-order equation were calculated by taking into account the results of the four experiments. These *k* values and their standard deviations for the experiments performed with the different factors mentioned above were used to establish the possible influence of these factors in the syneresis rate.

## RESULTS AND DISCUSSION

**Drainage of Curd from Cow's Milk. Influence of the Intensity of Heat Treatment and of the Factor of Concentration.** As was indicated under Materials and Methods, four different experiments were performed for each of the studied factors (concentration and heat treatment). A first-order reaction was calculated for each of the experiments. As can be observed in Figure 1, in four identical experiments carried out with four different raw milk samples, the results obtained were very similar. This behavior is observed in the ×0 concentrated milk (Figure 1), as well in each of the other concentrates studied (×1, ×1.5, or ×2). The same behavior was obtained in the experiments performed with the milk samples heated before ultrafiltration.

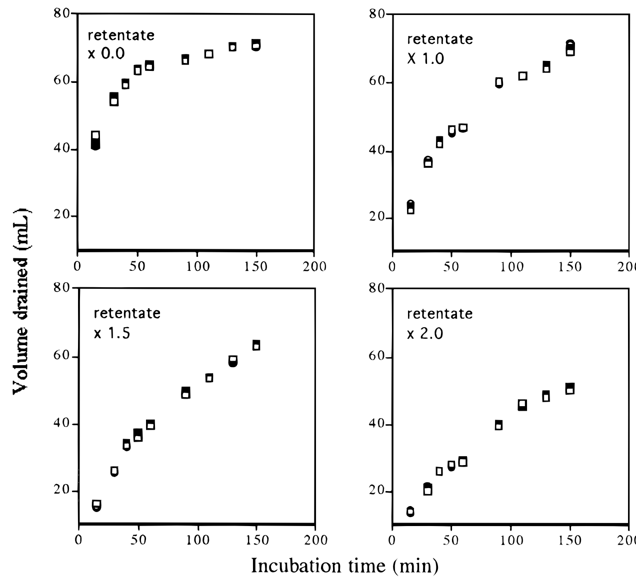


**Figure 1.** Syneresis rate of curd from ×0, ×1, ×1.5, and ×2 retentates from raw cow's milk as a function of curd incubation time (in minutes). Curd was cut 15 min after coagulation. Each panel shows the results of four different experiments.

No significant ($P < 0.05$) differences in the *k* values were found among the four experiments carried out on each studied factor; for this reason the results of the four experiments together were used to calculate the slope of the reaction (*k* value), and the results obtained are shown in Table 1. The calculated equations for the raw and heated milk samples and for the different factors of concentration studied showed an $R^2$ value ≥0.920, whereas the $R^2$ of the equations calculated for UF samples showed values >0.973. The results obtained indicate that the volume of whey drained as a function of incubation time can be adjusted to a first-order equation. A similar order of reaction was described by Peri et al. (1985) for the syneresis of milk concentrated up to 5-fold.

At all of the assayed values of concentration, a significant ($P < 0.05$) decrease of the *k* value was found when milk was heated, as well as an increased intensity of heat treatment. For unconcentrated samples the *k* value decreased when milk was heated; however, no significant ($P < 0.05$) differences were found between the two heat treatments assayed. The obtained results are in agreement with those described by Casiraghi et al. (1989a,b), who found that when the milk was heated before UF, the drainage was much slower in curd from pasteurized milk than in those from raw milk.

As was indicated in the Introduction, the degree of concentration could influence the syneresis. A significant ($P < 0.05$) decrease in the rate of syneresis was found with increasing concentration. The results obtained are in agreement with those found by van Dikj and Walstra (1986).

When the influence of the concentration was compared in the samples submitted to each heat treatment before UF, the influence of concentration was different from that found in raw milk samples. As can be observed in Table 1, when milk was heated at 70 °C for 5 min before UF, the *k* values decreased significantly ($P < 0.05$) with increasing concentration; however, no significant differences were found between the ×1 and ×1.5 concentrates. In milk samples heated at 70 °C for

**Table 1. Calculated Slope Value (*k* Value) Fitted to a First-Order Reaction with the Syneresis Rate as a Function of the Incubation Time (in Minutes) of Curd from Cow's Milk[a]**

| concn factor | heat treatment | | |
|---|---|---|---|
| | raw | 70 °C, 5 min | 70 °C, 30 min |
| ×0.0 | 0.0549 (0.00226)$^{a,A}$ | 0.0549 (0.00226)$^{b,A}$ | 0.0589 (0.00198)$^{b,A}$ |
| ×1.0 | 0.0225 (0.00094)$^{a,B}$ | 0.0150 (0.00146)$^{b,B}$ | 0.0071 (0.00084)$^{c,B}$ |
| ×1.5 | 0.0154 (0.00053)$^{a,C}$ | 0.0142 (0.00050)$^{b,B}$ | 0.0039 (0.00084)$^{c,C}$ |
| ×2.0 | 0.0138 (0.00077)$^{a,D}$ | 0.0103 (0.00060)$^{b,C}$ | 0.0079 (0.000474)$^{c,B}$ |

[a] The *k* value was calculated from four experiments performed in the same conditions. Standard deviation of *k* value is also included. Means in the same row without a common lower case superscript differ ($P < 0.05$). Means in the same column without a common upper case superscript differ ($P < 0.05$).

**Table 2. Calculated Slope Value (*k* Value) Fitted to a First-Order Reaction with the Syneresis Rate as a Function of the Incubation Time (in Minutes) of Curd from Ewe's Milk[a]**

| concn factor | heat treatment | | |
|---|---|---|---|
| | raw | 70 °C, 5 min | 70 °C, 30 min |
| ×0.0 | 0.0559 (0.00222)$^{a,A}$ | 0.0318 (0.00142)$^{b,A}$ | 0.0266 (0.00089)$^{c,A}$ |
| ×1.0 | 0.0187 (0.00145)$^{a,B}$ | 0.0142 (0.00092)$^{b,B}$ | 0.0051 (0.00068)$^{c,B}$ |
| ×1.5 | 0.0159 (0.00078)$^{a,C}$ | 0.0174 (0.00080)$^{a,C}$ | 0.0092 (0.00079)$^{b,C}$ |
| ×2.0 | 0.0220 (0.00049)$^{a,D}$ | 0.0201 (0.00047)$^{b,D}$ | 0.0012 (0.00054)$^{c,D}$ |

[a] The *k* value was calculated from four experiments performed in the same conditions. Standard deviation of *k* value is also included. Means in the same row without a common lower case superscript differ ($P < 0.05$). Means in the same column without a common upper case superscript differ ($P < 0.05$).

30 min, no significant differences were found between the ×1 and ×2 concentrates.

The differences found for the different heat treatments assayed could be due to the influence of the denaturation of whey protein during heat treatments; however, Montilla et al. (1995) did not find a significant difference in whey protein denaturation in cow's milk heated at 70 °C for 5 or 30 min. Heat treatment also changes the saline balance, and the changes in salt composition during the heat treatment and UF could affect the structure of curd and consequently the rate of syneresis (Casiraghi et al., 1989a). On the other hand, the mechanical and thermal stresses associated with UF treatment could have a different effect on raw or heated milk components, influencing curd formation.

**Drainage of Curd from Ewe's Milk. Influence of the Intensity of Heat Treatment and of the Factor of Concentration.** The results of the volume drained by curd from ewe's milk as a function of the incubation time were adjusted to a first-order reaction.

There were no significant ($P < 0.05$) differences among the four experiments carried out to study each factor; all of the values obtained in the four experiments were used to calculate the *k* value. The obtained *k* values for each studied factor are shown in Table 2.

The calculated equations for the raw and heated milks and for the different concentrations studied showed, in general, an $R^2$ value similar to those obtained for cow's milk samples; however, the best fit was obtained in the curds from milk concentrated to a factor ×2, with obtained values of 0.993, 0.993, and 0.988 for raw milk and for milk heated at 70 °C for 5 or 30 min, respectively.

The influence of the concentration in the *k* value was different from that found for cow's samples. In raw and heated samples, the *k* value was significantly influenced by the concentration. All samples showed a significantly ($P < 0.05$) lower *k* value for the ×2 concentrate than for milk; however, the *k* value was significantly higher in the ×2 concentrate than in the ×1 and ×1.5 concentrates.

Because the ×1 and ×1.5 concentrates were obtained by diluting the ×2 concentrate, it could be possible that the changes in the ionic composition influenced the curd consistency and the syneresis. Previous studies carried out in our laboratory (Espinoza and Calvo, 1998) showed that the concentration influences the curd firmness, and these authors' results showed that the curd from ×1 and ×1.5 ewe's retentates showed a lower firmness than those from ×2 retentates.

In general, at all of the assayed concentrations, the *k* values decrease when milk is heated; a significant ($P < 0.05$) difference was found between the two heat treatments, decreasing the *k* value with increasing intensity of heating. The results obtained were similar to those described previously for cow's milk. However, the unconcentrated ewe's milk showed a behavior different from that of cow's milk, and the syneresis of curd from ewe's milk showed a significant ($P < 0.05$) influence of the intensity of the heat treatment applied.

Balcones et al. (1996) found no significant differences in the curd firmness obtained from ewe's milk heated at 70 °C for 5 or 30 min. However, the consistency of curd from cow's milk decreases with increasing intensity of heating (Ustunol and Brown, 1985; Singh et al., 1988). These results did not explain the influence of heat treatment in the rate of syneresis of the two species.

Although different influences of heat treatment in curd firmness of cow's and ewe's curd have been found, the syneresis rate is also influenced by other factors such as milk composition and differences in the behavior of whey proteins during heating; these factors could influence the curd structure and consequently the syneresis rate.

**Table 3. Calculated Slope Value (*k* Value) Fitted to a First-Order Reaction with the Syneresis Rate as a Function of the Incubation Time (in Minutes) of Curd from Goat's Milk[a]**

| concn factor | heat treatment | | |
|---|---|---|---|
| | raw | 70 °C, 5 min | 70 °C, 30 min |
| ×0.0 | 0.0224 (0.00067)$^{a,A}$ | 0.0117 (0.00059)$^{b,A}$ | 0.0106 (0.00107)$^{b,A}$ |
| ×1.0 | 0.0262 (0.00175)$^{a,B}$ | 0.0173 (0.00075)$^{b,B}$ | 0.0183 (0.00051)$^{b,B}$ |
| ×1.5 | 0.0261 (0.00144)$^{a,B}$ | 0.0155 (0.00061)$^{b,C}$ | 0.0178 (0.00085)$^{c,B}$ |
| ×2.0 | 0.0220 (0.00083)$^{a,A}$ | 0.0147 (0.00101)$^{b,C}$ | 0.0170 (0.00115)$^{b,B}$ |

[a] The *k* value was calculated from four experiments performed in the same conditions. Standard deviation of *k* value is also included. Means in the same row without a common lower case superscript differ ($P < 0.05$). Means in the same column without a common upper case superscript differ ($P < 0.05$).

**Drainage of Curd from Goat's Milk. Influence of the Intensity of Heat Treatment and of the Factor of Concentration.** The results of the volume drained as a function of the incubation time were adjusted to a first-order reaction. The obtained *k* values for each of the studied factors are shown in Table 3.

The $R^2$ of the calculated equations for the raw and heated milks and for the different concentrations studied showed, in general, values higher than those obtained for the cow's and ewe's samples analyzed. The obtained values were >0.980.

The rate of drainage of curd from raw milk samples and concentrates was different from those of cow's and ewe's samples. No significant ($P < 0.05$) differences were found between the *k* value of no concentrate and the retentate to a factor ×2; the drainage was significantly faster in the ×1 and ×1.5 retentates than in the other mentioned samples. Because all curds were manufactured from raw milk, an influence of denatured whey protein is not possible.

The differences found could be due to the influence of the composition on curd formation. Previous studies carried out in our laboratory showed that the composition of total solids and ash are approximately double in goat's ×2 retentate than in cow's milk, whereas the concentration of caseins and ash was only 141% in the ×2 retentate considering that 100% was the concentration of goat's milk (Espinoza and Calvo, 1998). The differences in the relative composition could influence the curd structure and the syneresis.

On the other hand, the physicochemical changes in the composition of milk during UF could also affect the structure of curd, as was indicated by Dalgleish (1981) and Korolczuk and Mahaut (1991) working with cow's milk.

In general, at all of the assayed concentrations the $k$ values decrease when milk is heated; however, no significant ($P < 0.05$) difference was found between the two heat treatments assayed.

When the influence of concentration is compared in the samples submitted to each heat treatment before UF, the influence of concentration is different from those found in the other two analyzed species. As can be observed in Table 3, all of the retentates showed a significantly ($P < 0.05$%) higher $k$ value than milk samples. However, the retentates heated at 70 °C for 30 min prior to UF did not show a significant ($P < 0.05$) influence of the rate of concentration on the $k$ value, and no significant differences were found between the ×1.5 and ×2 retentates heated at 70 °C for 5 min. This could indicate that the curd structure from goat's retentates is not influenced by the rate of concentration or, if the curd structure is not influenced by the rate of concentration, the changes in the curd during syneresis could be very similar.

The obtained results indicate that the concentration of milk by UF and the heat treatment previous to the UF have different influences in the syneresis rate of curd manufacture from milk of different speciea when the conditions of cheese manufacture are similar. These data must be taken into account to manufacture cheese from ewe's or goat's milk.

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