



Elling-Olav Rukke, Sara Mohamed Gaber, Siv Skeie, Tove Gulbrandsen Devold, Anne-Grethe Johansen and Reidar Barfod Schüller

Faculty of Chemistry, Biotechnology and Food Science (KBM), Norwegian University of Life Sciences, P.O.Box 5003, N-1433 Aas, Norway.

BACKGROUND AND OBJECTIVES

Quark is a traditional fresh acid coagulated cheese produced from milk and/or cream by biological acidification to around pH 4.6. This pH causes the casein proteins to coagulate at their isoelectric point pH 4.6. The coagulum may or may not be cooked during manufacturing. The curd is not pressed. Acid coagulated cheeses are characterized by a high moisture content. They are usually consumed soon after manufacture as Quark belong to the so-called fresh dairy products.

As quark is an essential ingredient in many dishes, it is of great interest to maintain a steady supply of this product throughout the seasons. Freezing of quark is therefore interesting to extend the shelf life of this product. The dairy industry has made a tremendous success of the frozen dessert category. But freezing has been used to much smaller extent for other dairy products.

The main objective with this introductory study were as follows¹⁻⁹:

- investigate eventually structural effects of long time freezing of Quark, both as a product by itself and/or as an ingredient in other dishes.
- observe if some acidic additives during the diafiltration process applied in the production, would affect the rheological measurements of Quark samples before- and after freezing.

MATERIALS AND METHODS

Quark manufacture:

Skimmed milk was pasteurized (A3-HRB, Alfa Laval, Lund, Sweden) at 73 °C/15s, microfiltered (MF) and diafiltered with different water media (UF/MF pilot MCC RV 0118340, APV, Silkeborg, Denmark) using a 0.14 µm ceramic membrane (INSIDE C6RAM™, TAMI Industries, GE, Nyons, France) at 50 °C ± 0.1 and uniform trans-membrane pressure (UTMP) to produce 8% ± 0.1 casein concentrates (CC). Process described by Gaber et al.⁵

The casein concentrates were pasteurized at 73 °C for 15 s, cooled to 30 °C and transferred into cheese vats. Starter culture Probat 505 (Probat 505 FRO 500 DCU, CHOOZIT™ Cheese Cultures, Danisco) at 2% was inoculated. Incubation conditions: 18hr at 25-30 °C.

At pH 4.7, the curd was cut and drained by hanging cloths at 4-5 °C for 4 hrs. The drained curd was mixed by a colloid mill and packaged into 250 g containers. Some samples were stored as fresh at 4-5 °C. Other were stored at -20 °C until analysis after six months. The frozen samples were thawed slowly in a refrigerator at +4 °C before analysis.

The Quark samples are denoted following the used media for diafiltration: citric acid (CDR), lactic acid (LDR), carbonation (ODR) and just water as the reference (RDR). Two types of milk, denoted A (normal lactation period) or B (very early lactation milk), were used in this study. The RDR variant is only made from milk type A.

Table 1. Approximate composition pr. 100 g of fresh natural Quark produced in Norway. Values declared by the manufacturer.

Content	Amount	Unit
Energy	325	kJ
Protein	11	g
Sugar	4	g
Fat total	1.9	g
Saturated fat	1.3	g

Instrumental analysis and experimental set-up:

The Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) was used in oscillation to characterize fresh quark and quark after 6 months of freezing.

A PPS0 plate/plate system was used with a Peltier for temperature control. Amplitude sweep tests were performed at an increasing strain from 0.001 to 0.1 at a constant frequency of 1 Hz and temperature of 5 °C to determine the stiffness of the gel and the linear viscoelastic range.

Samples were stirred prior of placing them on the plate using a plastic spoon. Fresh samples stored at 4-5 °C were measured within 7 days after manufacturing. Frozen samples were thawed at +4 °C during 40 hours prior to measurement. For each experimental quark batch duplicates were tested, and an average value was calculated⁶.

Statistical analysis:

The data were analysed in RheoPlus and exported to Excel for plotting. The analysis determined the limit of the linear viscoelastic range by running a macro that determined the point where the value of the stiffness, G' , was reduced by 3%. The value of the strain and the stress at this point were denoted the strain limit and the strength. The value of stiffness, is the G' value at the start of the amplitude sweep⁷.

RESULTS

The results from the rheological analysis of Quark are shown in Fig. 1, 2 and 3. The samples are named according to the treatment during processing and according to the type of milk (A and B). Media used for diafiltrating; RDR - water as the reference; CDR - citric acid; ODR - CO₂; LDR - lactic acid. Samples made from normal milk are denoted A including the RDR sample. Milk from very early lactation is denoted B. The six months frozen Quark samples at -20 °C were thawed slowly at +4 °C before measurement.

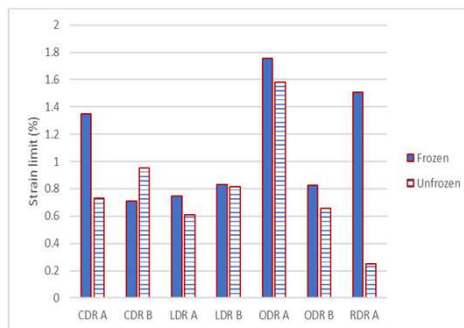


Figure 1. Strain limit results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration.

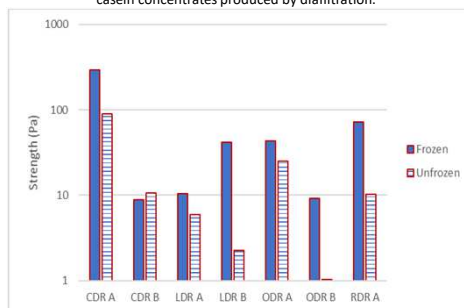


Figure 2. Strength results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration

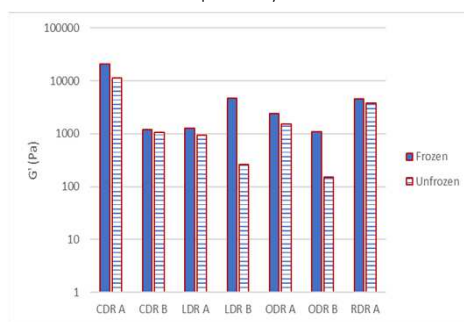


Figure 3. Stiffness results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration.

Quark is a typical acid-curd cheese. Table 2 summarizes the start- and end pH after fermentation of the curd.

Table 2. Start- and end pH after fermentation of the microfiltered casein concentrates diafiltered with different additives.

	pH	Start	End
Citric acid, CDR		6.58	4.6
Lactic acid, LDR		6.55	4.6
CO ₂ , ODR		6.61	4.6
Ref. water, RDR		6.66	4.8

DISCUSSION

In this study the fresh casein concentrate was used as raw material for Quark production. The motive for this investigation was to look at eventually rheological effects after freezing Quark for 6 months, both as a product by itself and/or as an ingredient in other dishes.

Looking at Fig. 3 it seems that these G' results (stiffness) confirm a previous study⁶, although the differences before- and after freezing are very small in this case for some of the samples (CDR B, LDR A and RDR). From a commercial point of view these findings are positive. It means that frozen Quark is OK both for the consumer market, and for further processing in the industry.

Fig. 2 summarizes the strength of the Quark products before- and after freezing. A general trend seems to be that the strength of the products has increased after freezing. One exception is Quark produced from milk very early in the lactation period (CDR B). The measurement for this variant shows about the same strength value before- and after freezing.

When it comes to the strain limit in Fig. 1, most of the samples observed had an increase after freezing. Also, here the Quark sample produced from milk very early in the lactation period added citric acid (CDR B) was an exception. The strain limit was higher before-, than after freezing.

In this study it was also of interest to observe if some acidic additives during the diafiltration process would affect the structure of Quark before- and after freezing. The rheological measurements did not provide clear answers to this, although both the values for strength and strain limit appeared to increase after freezing. Detection of correlations between texture properties and the microstructure of the acid gel produced with various additives, seems complicated. From the literature it is also known that such investigations are challenging and requires further research⁹.

According to Table 2, the pH after fermentation of the microfiltered casein concentrates diafiltered with different additives (CDR, LDR, ODR and RDR), are almost the same in all samples. They are at the isoelectric point for casein which is pH 4.6. It is just water as an additive during diafiltrating that contribute slightly higher pH; pH 4.8. Possibly the 0.2 pH unit difference after fermentation of the casein concentrate, may explain some of the differences in the rheological measurements results for the RDR-sample before and after freezing.

CONCLUSIONS

This screening test of six months frozen Quark samples at -20 °C thawed slowly at +4 °C indicates the following:

- Both the strength, the strain limit and the stiffness (G') of the Quark samples seemed to have increased a bit after freezing.
- From a commercial point of view these findings are positive regarding sensory properties which did not deteriorates during the freezing period, but rather achieved some improvements.
- The above-mentioned trends seemed to be the same for Quark made from both milk at normal lactation period and for milk at very early lactation. The reference sample showed "more or less" the same development before- and after freezing.

ACKNOWLEDGMENTS

This research used the Infra Food Pilot Plant facilities at KBM that received a grant from the Norwegian Research Council in 2011 (NFR-grant 208674/F50).

REFERENCES

- Narvhus, J., Rukke, E.O. and Schüller, R.B. (2019), "Rheological analysis of ropy fermented milk", *Annual transactions - The Nordic Rheology Society*, vol 27, p 159-163.
- Fox, P.F., Guinee, T.P., Cogan T.M. and McSweeney, P.L.H. (2000), "Fundamentals of cheese science", An Aspen Publication, Gaithersburg, Maryland, ISBN 0-8342-1260-9
- Fox, P.F., McSweeney, P.L.H., Cogan T.M. and Guinee, T.P. (2004) "Cheese Chemistry, Physics and Microbiology", third edition, Elsevier Academic Press, Vol 2, ISBN 0-1226-3653-8
- Daweke, H., Haase, J. and Irmischer, K. (2013), "Diätatlas - Ernährungstherapie, Indikation und klinische Grundlagen", Springer Verlag, p. 215-255, ISBN 978-3-6429-6537-1.
- Gaber, S.M., Johansen, A.G., Devold, T.G., Rukke, E.O., Schüller, R.B. and Skeie, S. (2020), "Minor acidification of diafiltration water using various acidification agents affects composition and coagulation properties of the resulting MF concentrate." *Journal of Dairy Science*, Accepted for publication
- Gaber, S. M., Johansen A.G., Schüller, R.B., Devold, T.G., Rukke, E.O. and Skeie, S. (2020), "Effect of freezing temperatures and time on mineral balance, particle size, rennet- and acid coagulation of casein concentrates produced by micro-filtration", *Int. Dairy Journal*, 101, p 1-11
- Steffe, J.F., (1996) "Rheological methods in food process engineering (Second edition)", East Lansing: Freeman Press ISBN: 0-9632036-1-4
- Goff, H. D., & Sahagian, M. E. (1996), Freezing of dairy products. In L. E. Jeremiah (Ed.), *Freezing effects on food quality* (pp. 299-335). New York, NY, USA: Marcel Dekker.
- Schroda, P., Hechler, A. and Kessler, H.G. (1999), "Effects of minerals and pH on rheological properties and synthesis of milk-based acid gels," *International Dairy Journal*, 9, p 269-273.