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Original article

UHT processed milk concentrates

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Abstract — Ultrafiltration and reverse osmosis concentrates made from milk with differing fat and protein contents were sheared in defined flow conditions to establish the critical concentration of the constituents beyond which flow properties and heat stability change. The viscosity of the concentrates at 20 °C was calculated for volume concentrations below 0.5. Non-Newtonian flow occurred above this concentration, and heat coagulation tests at 140 °C revealed a dramatic drop in heat stability. The dense packing of the constituents above a volume concentration of 0.5 led to altered flow properties and decreased heat stability. The heat stability at 140 °C and storage stability correlated with the ash content and these increase as the ash contents decrease. Milk may be treated by applying ultrafiltration and nanofiltration to reduce ash content and enable high quality milk concentrates with a long-life stability to be produced by means of ultra-high temperature heating.

milk / ultrafiltration / nanofiltration / rheology / ultra-high temperature

1. INTRODUCTION

The demand for processes which allow an ecologically friendly and high quality production of products with a long shelf life led to the question of introducing ultra-high temperature treatment (UHT) for milk concentrates. Intensive investigations were carried out to establish the effect of the UHT-heating process on the physico-chemical changes of milk. But there was insufficient information, except for Muir's investigations [5], especially on the influence that the concentration of milk concentrates has on the rheology and the heat stability at UHT-temperatures. Additionally, it was necessary to determine the storage stability of UHT-heated milk concentrates taking into account that the ratio of salts or lactose to protein or fat changed as a result of different membrane concentration processes.

The higher the volume concentration ratio, the denser the packing of fat globules and proteins, but depending on the concentration process (reverse osmosis RO, nanofiltration NF, ultrafiltration UF) the lactose and salt content was more or less concentrated. It is a well-known fact that the

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viscosity of milk increases as it is concentrated and that the heat stability decreases as the tendency towards age-gelation increases. For practical applications using evaporation, a limit for the concentration of whole milk seems to lie in the range of 31% total solids [6] because at higher concentrations, the heat stability is dramatically reduced and gelling is accelerated. In ultrafiltered skim milk, de Carvalho [2] also mentioned that gelling takes place above 28% total solids at 5 °C. Nevertheless, heat stability was enhanced when using ultrafiltration for concentration compared with evaporation [9]. Many attempts have been made to improve and optimize process conditions to achieve higher concentrations of the components but only additives (e.g. disodiumphosphate and polyphosphate) seem to be of assistance in such cases.

Our objective was to determine the critical concentration for concentrated milk beyond which the functional properties change, the influences of fat content and the effect of changed constituents on the heat and storage stability of milk concentrates when applying different concentration processes.

2. MATERIALS AND METHODS

2.1. Processing of concentrated milk

Raw cow's milk and cream purchased from the local dairy adjusted to the required fat content was heated to 100 °C for 300 s in a pilot heating plant (100 $L \cdot h^{-1}$, inner diameter 10 mm) [4] in order to achieve more than 95% whey protein denaturation [1]. The various products were homogenized (Type SH10A, Fa. Tetra Laval, Lund, Sweden) after heating at 65 to 70 °C with homogenization conditions related to the fat content for high emulsion stability [3] (in principle: decreasing pressure of the first stage with an increase in the fat content by using two stages with a Thoma number of 0.2). Directly after heating the milk was concentrated up to 5 times by ultrafiltration (process temperature ϑ = 50 °C, transmembrane pressure p = 0.3 MPa, mean flow velocity w_m = 0.2 $m \cdot s^{-1}$, type Minisette, 10000 $g \cdot mol^{-1}$, Fa. Pall, Dreieich, Germany) and reverse osmosis (ϑ = 50 °C, p = 4 MPa, type MB-RO 2540 CXZ, Fa. MemBrain, Düsseldorf, Germany), cooled to 18 °C, filled into 250 mL glass jars and stored 16 to 24 h until measurement. The various volume fractions were adjusted by the re-mixing of retentate with permeate to the desired volume concentration ratio (VCR = volume retentate divided by the volume milk prior to concentration). The composition of the various products is described in detail in [4]. The addition of 0.05% sodium azide guaranteed microbiological stability.

For the experiments concerning storage stability, the various milk concentrates were indirectly heated in a pilot heating plant at 140 °C for 10 s and aseptically filled into glass jars and stored at 30 °C [4].

2.2. Analytical methods

Analyses of the total solids, fat and protein content were performed on the milk and the milk concentrates using standard methods (described in detail in [4]).

The rheological properties were determined in a rotational viscometer at 20 °C (Rheomat 115, Fa. Mettler Toledo, Gieβen, Germany) with Couette flow conditions. The procedure is described in [3]. The viscosity coefficient K_{ow} and fluid index n were calculated for the power law model using non-linear regression (SigmaStat 1.0, Jandel Corporation), in which the amount of the shear stress τ is related to the shear rate γ with the fluid index n as the exponent:

$$|\tau| = K_{ow} \cdot |\dot{\gamma}|^n \quad (1)$$

The storage stability was monitored by the apparent viscosity. It was measured at a constant shear rate of 500 s^{-1}, at 20 °C after 3 min of shearing [4].

Concentrate ρ_{milk} and milk $\rho_{milk,0}$ density were determined by means of an oscillation U-tube (DMA 54, Fa. Paar KG, Graz, Austria). Milk fat $\rho_F = 916\ kg \cdot m^{-3}$ (20 °C) was taken from [13].

The heat coagulation time HCT was determined at 140 °C and calculated as the mean of three replicates [4].

3. RESULTS AND DISCUSSION

3.1. Rheology

The viscosity coefficients K_{ow} and fluid indices n were calculated from the rheological data of the milk concentrates and plotted against total solids (Figs. 1 and 2). In the comments of the figures, the fat and protein concentrations of the samples prior to concentration are shown. When the logarithm of the viscosity coefficient was plotted against the total solids the measured values were described by lines with a bend at a certain concentration. This bend is more marked for lower fat contents prior to ultrafiltration. In addition, in the Figure 2, the fluid indices decrease at lower total solids for lower fat contents of the milk prior to ultrafiltration.

These observations gave the rise to the question whether the dramatic increase in the viscosity coefficient K_{ow} at a certain content of total solids may be due to contact between the constituents during shear flow. Therefore the volume fraction of the various samples was calculated. For preheated milk concentrates the whole volume fraction Φ_{milk} of the dispersed phase can be estimated from the protein and fat content and the product density ρ_{milk} by

$$\Phi_{milk} = \rho_{milk}\,[C_p \cdot (0.8 \cdot \upsilon_C + 0.2 \cdot \upsilon_{dWp}) + C_F/\rho_F] \quad (2)$$

with the voluminosity of caseins of about $\upsilon_C = 3.57 \times 10^3\ m^3 \cdot kg^{-1}$ of denatured whey proteins of about $\upsilon_{dWp} = 3.09 \times 10^3\ m^3 \cdot kg^{-1}$ and the density of milk fat at 20 °C of $\rho_F = 0.916 \times 10^3\ m^3 \cdot kg^{-1}$ [3].

Figure 3 shows the relationship between the logarithm of viscosity coefficient and the volume fraction Φ_{milk}. All experimental

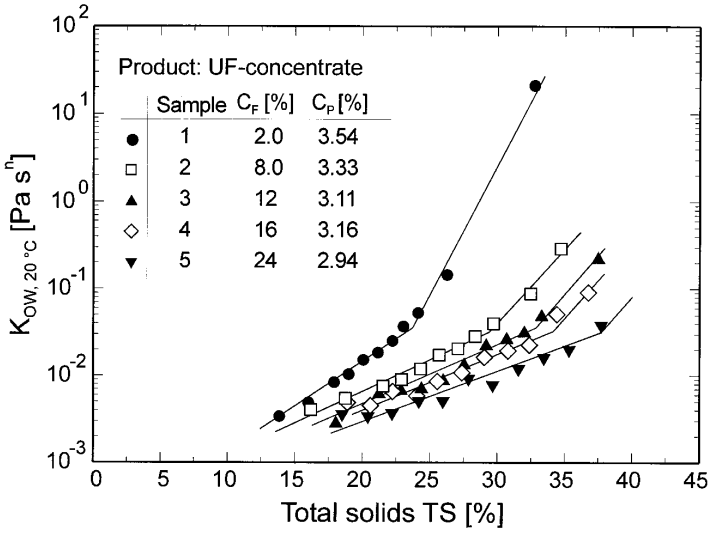

Figure 1. Viscosity coefficient of milk concentrate dependent on the total solids (table inside: fat and protein content prior to concentration [12].

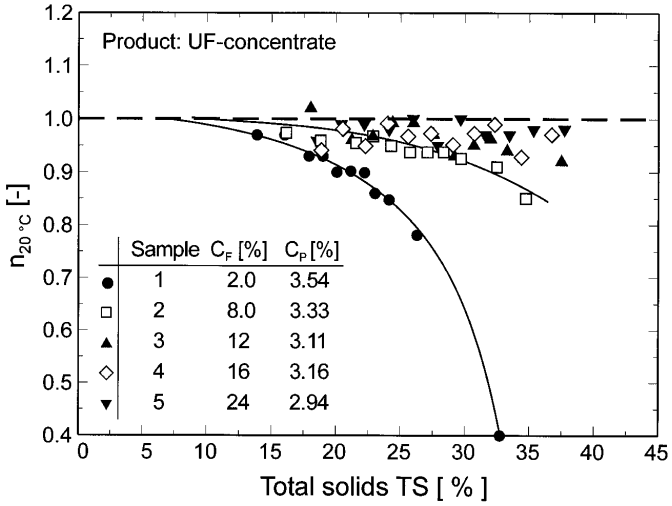

Figure 2. Fluid index of milk concentrates dependent on the total solids for milk [12].

points for the various milk concentrates resulted in a straight line with a bend at a volume fraction of about $\Phi_{milk} = 0.5$ which indicates that the volume fraction is the main physical characteristic describing the typical flow properties of milk concentrates. We were able to deduce from this that a critical dense formation of constituents exists for the sheared system. Denser formation or higher volume fractions led to contact between dispersed constituents so that free rotation was obstructed.

3.2. Heat stability

Heat coagulation time is reduced due to the fact that above $\Phi_{milk} = 0.5$ the dispersed constituents are in contact. So we determined heat coagulation time at 140 °C for ultrafiltration and reverse osmosis concentrates. The logarithm of the heat coagulation time HCT at 140 °C was plotted against the calculated volume fractions for ultrafiltration (Fig. 4) and for reverse osmosis concentrates (Fig. 5). In both cases the experimental points for the various fat concentration prior to concentration resulted in a decreasing straight line with a bend at a volume fraction of about 0.5, above which HCT was further reduced. No marked bends were detected for sample 1 (Fig. 4) and sample 7 (Fig. 5). The lower the fat content prior to concentration the longer the time until coagulation was visible.

The fat and protein concentrations at the bends were collected in Figure 6 and a calculated line was added for $\Phi_{milk} = 0.5$. The experimental bend points for ultrafiltration (UF) and reverse osmosis concentrate (RO) did not differ significantly from the fat/protein relationship given by the straight line. There is an area of critical concentration of $\Phi_{milk} = 0.5$ above the line, in which the dispersed particles come into contact and undesirable changes or spontaneous gelation may occur. But gelation may also take place close to the line because of the interaction of the particles. The figure includes open symbols for condensed milk (data taken from [8]) and a calculated line for $\Phi_{milk} = 0.4$ which would consider interactions due to particle forces [7]. It is interesting that this line separates the stable product, evaporated milk with 7.5% fat, from the product with 10% fat, which is only stable against gelation during storage if additives are used.

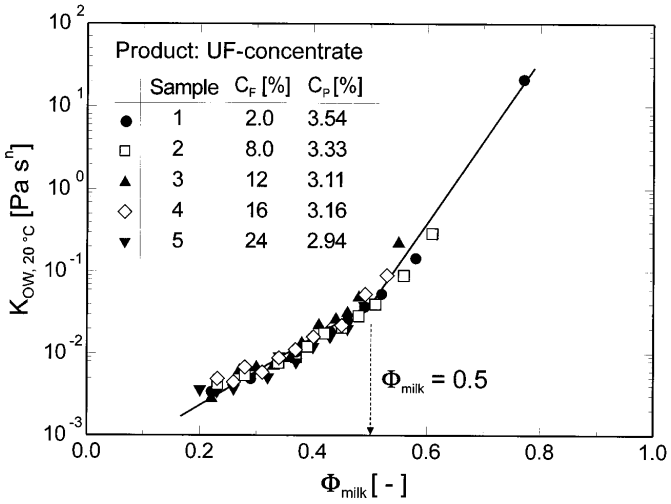

Figure 3. Viscosity coefficient of milk concentrates dependent on the volume fraction for milk [12].

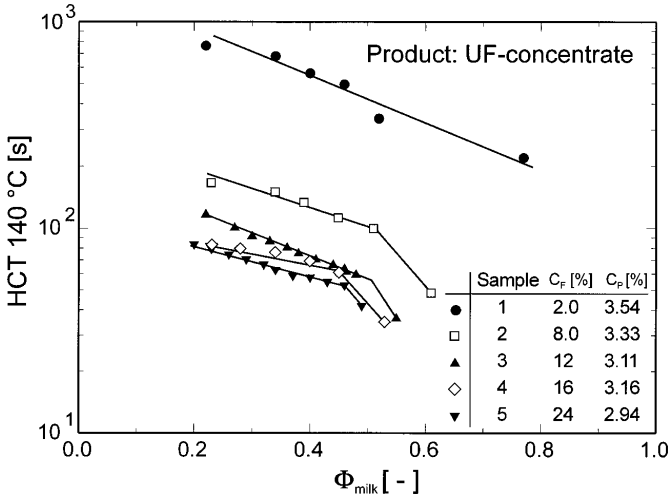

Figure 4. Heat coagulation time at 140 °C of milk concentrates dependent on the volume fraction with differing fat contents prior to ultrafiltration [12].

Furthermore, the initial aggregation reaction in milk is controlled by the salt concentration. In the case of reverse osmosis concentrate HCT is reduced (Fig. 5) when compared to the ultrafiltration retentate (Fig. 4). It is well-known that the ash and lactose permeate through the membrane in the case of ultrafiltration and are retained in the case of reverse osmosis with the result that they are as equally concentrated as the other constituents. The nanofiltration process is between both processes. Lactose is almost retained in the concentrate and ash is reduced, but there is only a very slight change to the calcium. The influence of the ash on the heat coagulation time of UF, NF and RO concentrates is shown in Figure 7. The experiment, mixing whole milk retentates after ultrafiltration, nanofiltration and reverse osmosis (VCR = 2.4), demonstrated that HCT decreases linearly as salt increases and was not influenced by lactose. A comparable influence was described for the heat stability of milk [10–12].

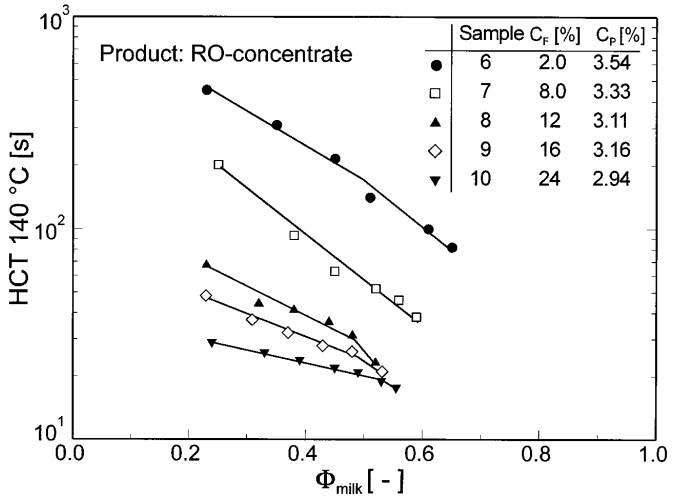

Figure 5. Heat coagulation time at 140 °C of milk concentrates dependent on the volume fraction with differing fat contents prior to reverse osmosis [12].

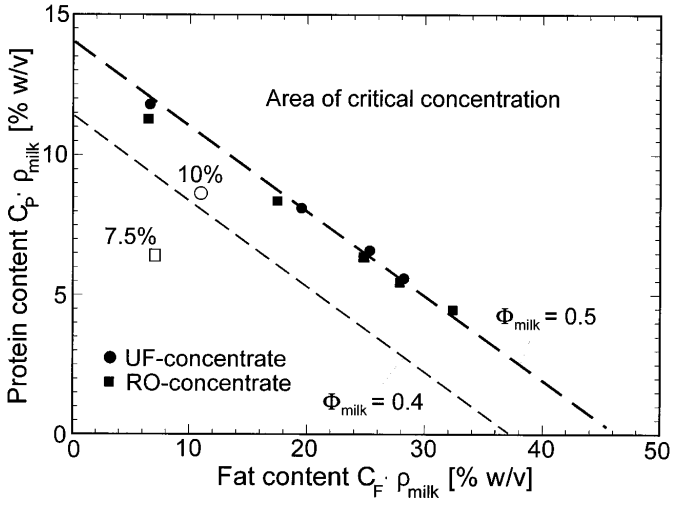

Figure 6. Protein/fat relationship for milk concentrates [12].

3.3. Storage stability

Whole milk was pre-heated and homogenized. Then the ash content of the whole milk was reduced by electrodialysis and reverse osmosis was used for concentration. Mixing the ash reduced concentrate with ”full” concentrate leads to products with differing ash contents. The concentrates were stored after indirect UHT heating. Figure 8 shows the apparent viscosity as a function of storage time for the various concentrates. The ash content is added in brackets on the curves. After 10–12 weeks of storage increases in viscosity are influenced by higher ash containing concentrates. A gel structure appears at a viscosity of about 0.2 Pas.

In order to examine the influence of lactose, nanofiltration and ultrafiltration concentrate was mixed in different proportions in order to vary the lactose content, which is given in brackets. In Figure 9, we used the

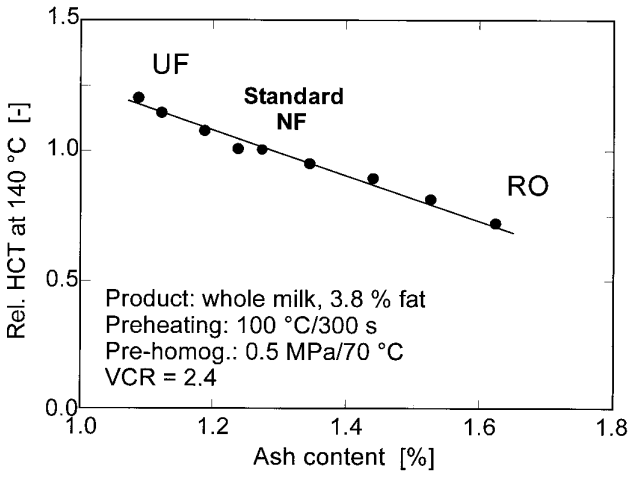

Figure 7. Relative heat coagulation time at 140 °C for mixed milk concentrates (UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis).

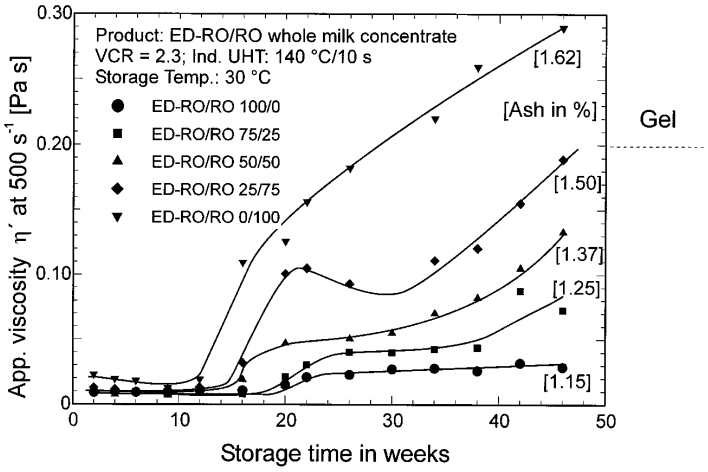

Figure 8. Viscosity increase during storage dependent of the ash content of the milk concentrates (table inside: e.g. ED-RO/RO 25/75: 25% demineralized reverse osmosis concentrate and 75% reverse osmosis concentrate).

same scale as before and this demonstrates that the lactose content does not have any influence on the storage stability. Only a slight increase of the product, in which the nanofiltration concentrate dominates, relationship 100/0 and 75/25, is visible. But the increase is due to the ash content of the product. The ash content of the nanofiltration concentrate is about 1.25%. And if compared with the curve for an ash content of 1.25 in Figure 7, a comparable increase in viscosity can be seen.

4. CONCLUSION

Milk can be treated by applying modern membrane technology in such a way that high quality milk concentrates without additives can be produced with a long-life stability by means of UHT heating. Considering the objectives it can now be said:

(1) The whole volume fraction of the milk constituents, protein and fat globules are the main physical characteristic

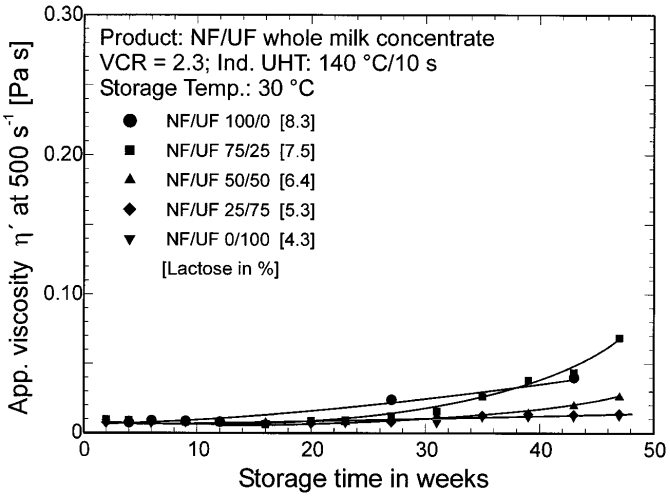

Figure 9. Viscosity increase during storage dependent of the lactose concent of the milk concentrates (table inside: e.g. NF/UF 25/75: 25% nanofiltration concentrate and 75% ultrafiltration concentrate).

describing the flow properties of milk concentrates. The viscosity of the concentrates at 20 °C was calculated for volume concentrations below 0.5 and non-Newtonian flow occurred above this concentration.

(2) The HCT at 140 °C of milk concentrates will be dramatically influenced by steric interactions if the whole volume fraction of fat and protein exceeds 0.5. The higher the fat content with the same whole volume fraction, the lower the heat stability was because visible flocs were formed earlier. Increased heat stability was detected for UF > NF > RO concentrate because of the reduced ash content (UF < NF < RO). There was no significant influence of the lactose content.

(3) In order to avoid gelation during storage the protein/fat relation should be adjusted in the area below the line of $\Phi_{milk} = 0.4$. For $0.4 \leq \Phi_{milk} < 0.5$ only additives or the reduction of salts using ultrafiltration or nanofiltration would increase stability during storage. The storage stability is improved if the ash content is reduced, which can be achieved by using electrodialysis, nano- or ultrafiltration. Lactose did not influence the storage stability. The low lactose content of ultrafiltration retentates reduced the tendency of browning due to Maillard reaction during storage but affected the taste.

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