Milk Fat Fractionation by Solid-Layer Melt Crystallization

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ABSTRACT: The layer crystallization process has the potential to produce the same milk fat fractions as can be obtained by the suspension crystallization process. That is, milk fat fractions with solid fat content melting profiles similar to those obtained by suspension fractionation can be produced with this technique. The fatty acid profiles as well as the melting enthalpies of the different fractions confirm the separation of milk fat by the layer technique. Furthermore, there is potential to improve the results of separation presented in the first part of this paper. The two sources of improvement, temperature control of the process and controlled nucleation, lead to (i) a smooth crystalline layer with a low amount of entrapped mother liquor, contrary to the layers composed of agglomerated needles, and (ii) a good quality of attachment of the crystalline layer to the cooled surface. Moreover, the product quality can be increased using sweating as a postcrystallization step. "Sweating by warm gas" seems to have a better outlook concerning handling and controlling the process than "sweating by warm tube" because sloughing of the crystal layers can be avoided. Further investigations of the mass ratio of sweating fraction and amount of product as well as the aspect of energy consumption will determine the technical feasibility of solid-layer crystallization for fractionation of milk fat.

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KEY WORDS: Fractionation, milk fat, solid-layer techniques.

Milk fat mainly consists of triglycerides with a great variety of fatty acids. More than 400 fatty acids have been identified in milk fat, although it is generally accepted that 15 major and 12 minor fatty acids dominate the fatty acid spectrum (1). Nevertheless, each of the components has a distinct influence on the properties of milk fat, and even small compositional changes can bring about large effects on the overall melting point behavior (2). The wide variety of molecular species in milk fat results in a melting range of –40 to 40°C. As a natural substance, the composition of milk fat also varies with season, region, breed of cows, and type of feed. However, milk fat fractions with specific properties (e.g., melting profile) and guaranteed uniformity are required by many industries (confectionery and bakery). Thus, milk fractionation has achieved commercial status in many countries.

Crystallization from the melt. This process of phase transition occurs in the absence of a solvent. The driving force (subcooling) for melt crystallization is the difference between the melting point of a substance and the crystallization temperature. Crystallization from the melt, which can be performed by either layer or suspension techniques, is a well-known unit operation in chemical engineering (3). Temperatures at which this process occurs are lower than evaporation processes; therefore the treatment of temperature-sensitive goods, like milkfat, is especially feasible. Potential problems with incrustation and solid handling can be overcome through design of efficient equipment and process procedures (3).

Currently, commercially available milk fat fractions are produced by a suspension crystallization process, which consists of two steps: formation of a crystal suspension in a crystallizer and separation of the crystals from the remaining mother liquor. The triglycerides are separated according to their melting points. After the process of crystal formation and growth, a filtration step is used to separate the solid product from the remaining melt. Filtration efficiency is determined by the size, shape, and mechanical stability of the milk fat crystals and depends on the amount of the mother liquor adhering to the crystals.

Solid layer melt crystallization. This process has only recently been applied to fractionation of milk fat (4–6) although it is widely used in the chemical processing industry. In layer crystallization processes, crystals generally grow on the cooled surface of a specially designed multitube or plate heat exchanger. The crystalline product is removed by remelting crystals after draining the residual melt. A primary advantage is that there are no problems due to the handling of solids. Besides pumps, there are no moving parts in the process; and the filtration step, required in suspension crystallization, is not needed. A comparison between the two types of melt crystallization is presented in Table 1 (7).

Clearly, the weak points of one technique are the strong points of the other technique, and vice versa. For example, the achievable growth rates are typically about 100 times

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TABLE 1
Comparison Between Solid-Layer and Suspension Crystallization from the Melt

	Solid layer technique	Suspension technique
Melt temperature	Above, but close to solidification temperature	Below the solidification temperature
Heat removal	Through the crystal layer	Through the melt
Crystal growth rates	High, 10^{-5}–10^{-7} m/s	Low, 10^{-7}–10^{-8} m/s
Relative interface, crystal/melt	Small, about 10–10^2 m^2/m^3	Large, about 10^4 m^2/m^3
Apparatus	No moving parts except pumps and valves	Moving parts
Mass flow rate	Large	Small
Incrustation problems	No	Yes
Transportation of product	Easy, all liquid	Problems, due to solids handling
Solid–liquid separation	Easy, just draining	Difficult
Scale-up	Easy	Difficult

higher in the solid layer technique, whereas the surface area available for heat and mass transfer is about 100 times higher in the suspension technique. Other items like solid handling or scale-up seem to favor the solid-layer techniques.

Solid-layer melt crystallization from a stagnant melt is usually called static-layer crystallization, whereas layer growth from a flowing melt is referred to as dynamic-layer crystallization.

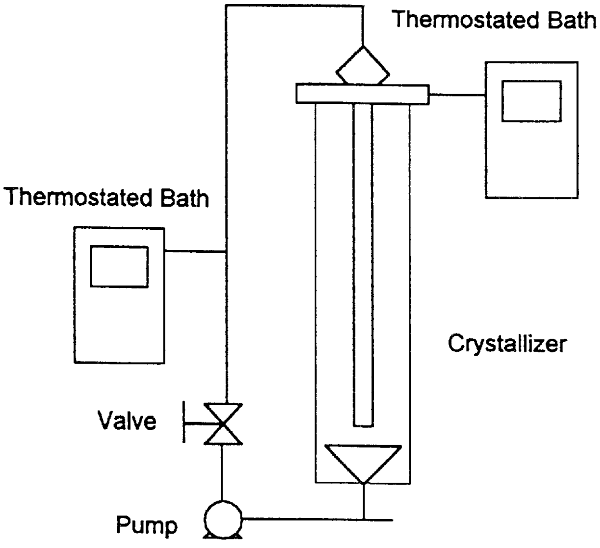
Sweating and washing are postcrystallization process steps to improve the overall performance of melt crystallization technology in solid-layer as well as suspension techniques (8–11). Sweating is a partial melting that occurs by increasing the temperature close to the melting point of the pure material. Impurities drain out of the interstices of the crystalline material and from the boundary layer adhering to the crystalline surface. Rinsing involves removing the adhering mother liquor by washing with a purified liquid. Diffusion washing is a concentration-driven process (liquid–liquid diffusion out of the interstices into the washing liquid) which needs, unlike rinsing, a significant contact time (about 15–30 min) between the washing liquid and the crystalline material in order for purification to occur (3). Postcrystallization processes improve purity in almost all cases and should therefore be applied as needed to enhance separation.

Fractionation of milk fats has been carried out by crystallization (12–14), distillation, and extraction with supercritical CO_2 (15,16). It is technically possible to separate milk fat into fractions with distinct chemical composition and melting points. However, crystallization of milk fat is even more difficult than for most other fats because of its complex composition. For 30 yr, milk fat has been fractionated with the Tirtiaux dry fractionation process (14). This technology, based on suspension crystallization, involves two main steps: crystallization and separation. On an industrial scale, milk fat is heated and then cooled in stainless-steel crystallizers equipped with a cooling coil and a variable-speed agitator (13).

The aim of this study was to show that solid-layer melt crystallization has the potential to fractionate milk fat. Data are needed for a comparison with the suspension crystallization techniques in order to determine which is the more economical process. The qualities of different milk fat fractions as described by technical data sheets (17) are also achievable with the solid layer technique. Moreover, the potential for improvement of the layer technique by postcrystallization processes was also studied.

EXPERIMENTAL PROCEDURES

Experimental setup in dynamic mode. For experiments carried out in dynamic mode, a falling film crystallizer was used, as shown in Scheme 1 (6). Before initiating crystallization, the melted milk fat was held at 60°C for 30 min in order to destroy any crystalline structure. After filling the milk fat into the feed tank, it was continuously circulated by a pump from the feed tank to the cooled surface at the top, where it was distributed in a thin film running down the cooled stainless steel tube. The crystal layer was produced on this cold surface. In the feed tank, the milk fat was kept slightly above its melting point. The temperatures of the cooled tube were 15°C for the production of the low-melting milk fat fraction, 20°C for the middle-melting fraction, and 30°C for the high-melting fraction. Compounds with melting points above the temperature of the cooled surface or the crystal layer surface, respectively,



SCHEME 1

will crystallize, whereas compounds with lower melting points remain liquid, return to the feed tank, and are heated up again in the riser pipe. All pipes were double-jacketed and made of glass, with temperature controlled by thermostats. Water was used as the heating or cooling medium. A control gear was used to operate a linear cooling program to maintain the driving force for crystallization and to compensate for the insulation effect due to the growth of a crystalline layer on the cooled tube. This allowed the surface temperature to be maintained at the desired crystallization temperature for the duration of each experiment. The duration of crystallization was 5 h. Different cooling protocols were needed for experiments performed at different melt flow rates.

Experimental setup in static mode. In static mode, simpler equipment can be used, as shown in Scheme 2 (6). Again, melted milk fat was held at 60°C for 30 min prior to crystallization in a glass, double-jacketed beaker, with temperature controlled by a thermostat. After setting the temperature of the beaker to 45°C, a cooled tube made of stainless steel was placed into the beaker. The cooled tube was set at temperatures of 15°C for the production of the low-melting fraction, 20°C for the middle-melting fraction, and 30°C for the high-melting fraction. A control gear was used to run a linear cooling program in order to compensate for the insulation effect of the growing layer. The duration of crystallization was 5 h. Growth rate of the layer was measured as the rate of increase in thickness of the layer with time.

Solid/liquid separation occurred by draining the residual melt from the crystalline layer. The temperature of the tube was raised to melt the crystals, which were collected as a liquid product. For all fractions produced, the clear points, solid fat content (SFC) profiles, melting enthalpies, and fatty acid profiles were measured.

Analyses. The clear point of each milk fat fraction was determined by the official AOCS method (18). After storing the milk fat at 4–10°C, two capillary tubes containing the samples and one capillary tube containing sunflower oil as a reference were fixed at the tip of a thermometer. It was placed in a water bath and heated at a rate of 2°C/min. The clear point was reached when the milk fat samples appeared as transparent as the sunflower oil.

The melting thermograms were recorded with a Mettler-Toledo (Hightstown, NJ) differential scanning calorimeter (DSC). The refrigerated milk fat samples were weighed into standard volatile-sample aluminum pans. Using an empty pan as reference in the DSC, the instrument heated the samples at 5°C/min from −10 to 60°C (19).

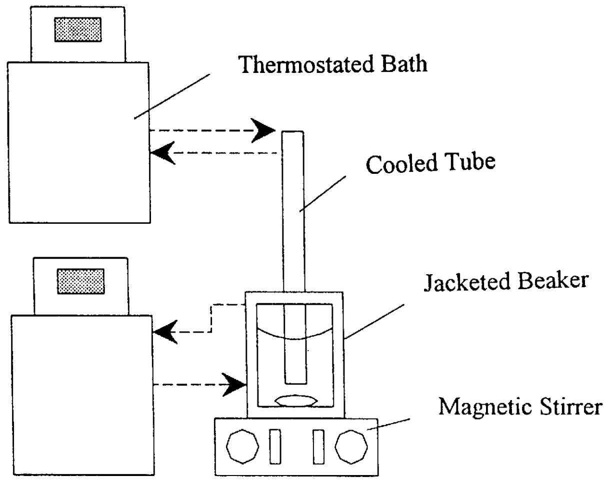
The fatty acid composition was determined by converting the triglycerides into methyl esters. To 200 mg milk fat was added 4 mL *n*-hexane and 0.1 mL sodium methoxide solution. The mixture was shaken for 1 min. The phases were separated, and the upper phase was used for analysis. A Siemens-Sichromat gas chromatograph was used with nitrogen as carrier gas. The temperature program was 140°C for 1 min, 8°C/min until 240°C and hold at this temperature for 5 min (20).

The analysis for SFC was performed according to the AOCS method (21) using a pulsed nuclear magnetic resonance (Bruker Minispec, Karlsruhe, Germany). Milk fat samples were tempered according to the AOCS temperature profile and SFC was read sequentially from 0°C to above the melting point.

RESULTS AND DISCUSSION

Separation of milk fat by the layer technique. Experiments in dynamic-layer crystallization processes were carried out to compare the qualities of different milk fat fractions with those produced by suspension crystallization. The different fractions were characterized by the change in SFC with temperature.

The SFC generally decreased with increasing temperature, as seen in Figure 1. The higher the melting point of a fraction, the higher the SFC at all temperatures. The different fractions



SCHEME 2

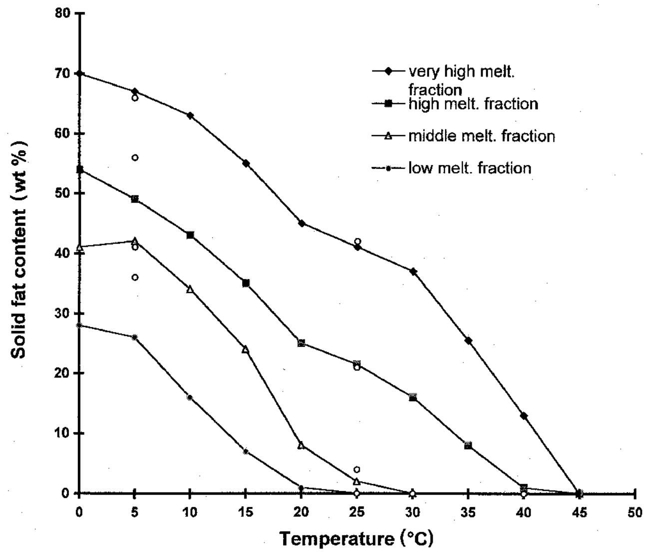


FIG. 1. Solid fat contents of milk fat fractions produced by solid-layer crystallization. The open circles represent data points for commercially available milk fat fractions, for comparison.

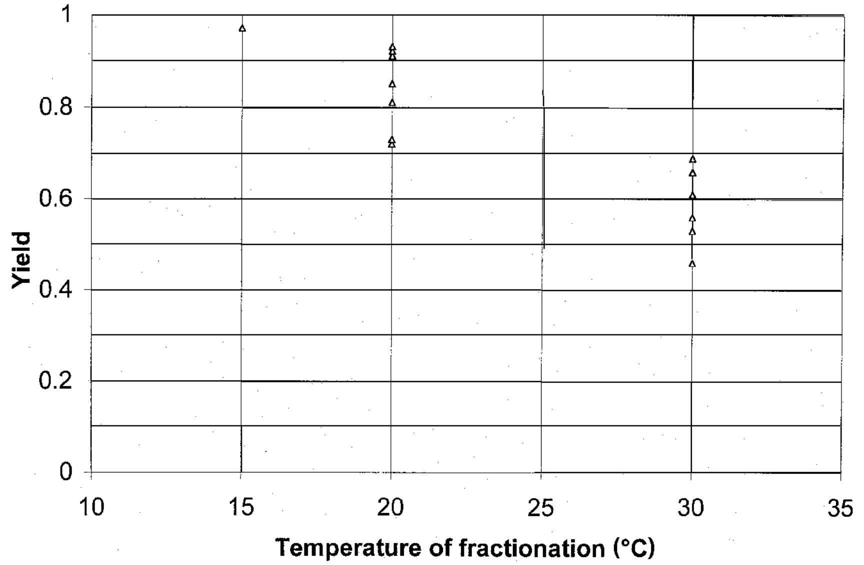


FIG. 2. Yields (as fractions of total starting material) of milk fat fractions separated by solid-layer crystallization at different crystallization temperatures.

obtained range from very high-melting (melting point > 45°C) to low-melting (melting point < 20°C) with multiple fractions between. Thus, the solid-layer crystallization process can produce milk fat fractions with melting profiles similar to those produced commercially by the suspension process. Moreover, the yields of the different milk fat fractions are shown in Figure 2.

To confirm the separation of milk fat by the layer technique, fatty acid profiles as well as melting enthalpies of each fraction were measured. As seen in Figure 3, the fatty acids characterized by short chain length (C4:0–C10:0) and unsaturated fatty acids were enriched in the low-melting fraction. In contrast, long-chain, saturated fatty acids (C16:0–C18:0) increased with increasing melting point of each fraction. Fatty acids of C12:0–C14:0 showed almost no change. The composition of the middle-melting fraction was similar to the composition of original, natural milk fat. These trends are similar to those found in milk fat fractions produced by suspension crystallization (22).

Another verification of the degree of separation between different fractions is the melting enthalpies as found by DSC. In Figure 4, the differences in melting enthalpies of the original, natural milk fat, the crystal phase, and residual melt after a layer crystallization process (at 15, 20, and 30°C, respectively, for low-, middle-, and high-melting fractions) are shown. The melting enthalpy of the high-melting fraction of the crystal phase (product) is strongly increased compared to the original, natural milk fat and the residual melt. The middle-melting fraction has a slightly higher melting enthalpy, whereas the low-melting fraction remains in the residual melt.

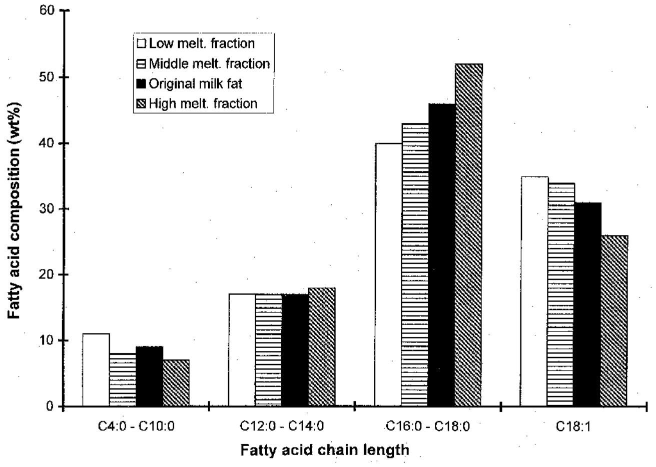


FIG. 3. Fatty acid composition of milk fat fractions separated by solid-layer technique.

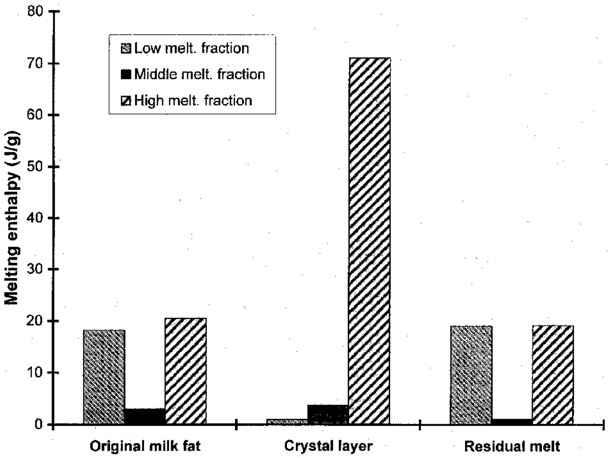


FIG. 4. Melting enthalpies, from differential scanning calorimetry, for different peaks of original, natural milk fat, crystal layer, and residual melt after a solid-layer crystallization process.

The differences between original, natural milk fat and residual melt are small.

Improvement potential of the layer technique. To investigate the potential for improvement of product quality, we carried out experiments in static mode. Layer crystallization from stagnant melt provides a simple and favorable method to obtain fundamental information about nucleation and growth phenomena. Here, the possibility to influence the quality of product by variation of temperature conditions during nucleation and growth was studied. In particular, the effect of various temperature protocols on the quality of a high-melting fraction was investigated. Measuring the clear point of each product represents a simple and rapid method to judge product quality. For a high-melting fraction, higher clear point indicates higher product quality.

As seen in Figure 5, the quality of the product can be influenced by varying the temperature of the bulk melt around the growing layer. Bulk temperature was controlled by adjusting the temperature in the double-jacketed beaker. Prior to the actual crystallization, the beaker was set at the desired temperature by the thermostat. After approximately 1 h, the desired temperature was also reached in the bulk melt. The temperature of the cooled crystallization surface was kept constant at 30°C. The clear point of the product was increased by increasing the temperature of the bulk melt (Fig. 5). Moreover, with increasing bulk temperature, the crystal layers became smoother. Low bulk temperatures lead to an agglomeration of needle-like crystals, which formed on the cooled surface. However, the growth rate was decreased by increasing the temperature of the bulk, and this resulted in a longer operation to get to the same yield.

To control the surface layer crystallization, the nucleation phenomena were also examined in more detail. In previous investigations (6), nucleation at the beginning of a crystallization process on the cooled tube was found to be problematic, because fast-growing crystals were needle-like in shape. These needles tended to trap a lot of mother liquor and reduce the clear point. Therefore, a thin primary layer (seed layer) was produced on the cooled surface by plunging the cooled tube into a molten product (clear point = 44°C). The temperature of the molten product was 60°C. After removing the tube from the molten product, this layer was cooled to the desired temperature (30°C for 15 min), and the actual crystallization started in the feed melt. In addition, variation of the growth rate was studied by varying the cooling rate of the tube.

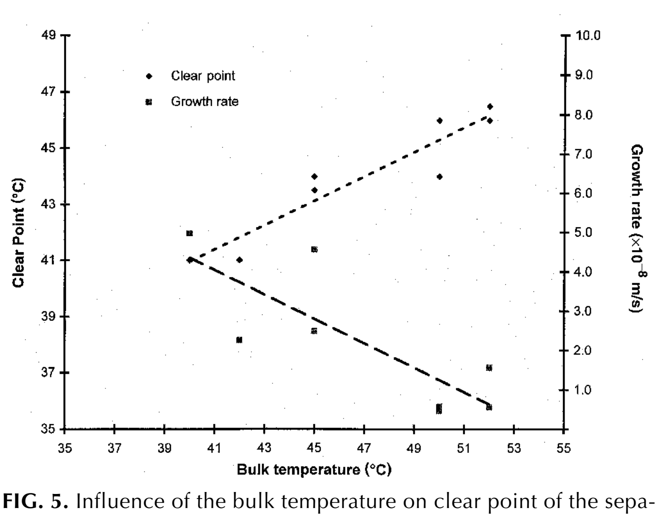


FIG. 5. Influence of the bulk temperature on clear point of the separated milk fat fractions and growth rate of the solid layer. Dashed lines represent linear regressions.

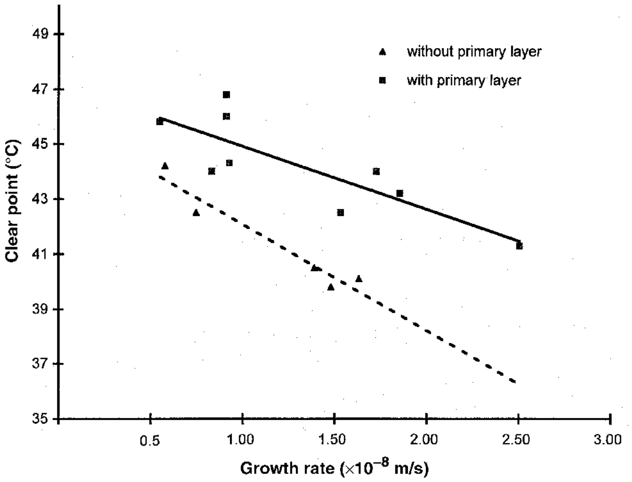


FIG. 6. Influence of a primary layer (nucleation layer) on clear point of the separated milk fat fractions. Straight lines represent linear regressions.

As shown in Figure 6, the clear points generally decreased while growth rate increased due to the presence of a primary layer. Comparison with Figure 5 shows that the use of a primary layer led to higher clear points of the high-melting fraction, although the growth rate was the same. It was also observed that the use of a primary layer led to a more homoge-

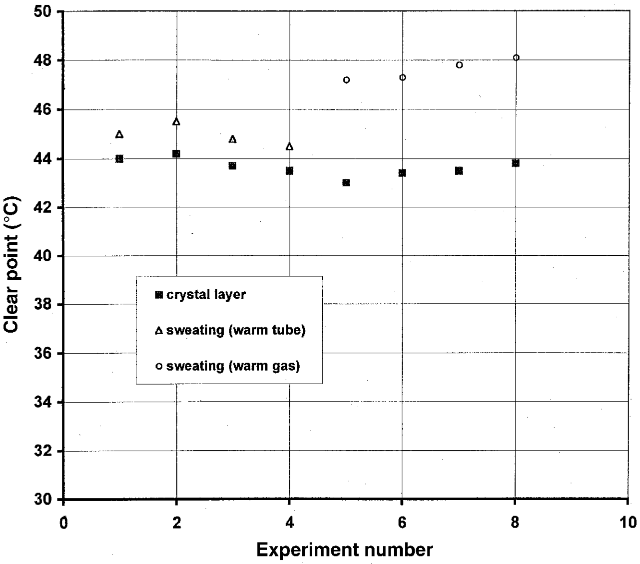


FIG. 7. Influence of different sweating methods (postcrystallization treatments) on clear point of the separated milk fat fractions.

neous crystal growth than when nucleation occurred at crystallization temperature.

Furthermore, it is possible to improve the quality of crystalline products by postcrystallization treatments like sweating and washing (8). Because of the porosity of milk fat layers, sweating presents a favorable opportunity. One possibility to accomplish sweating of the layer is to heat the tube (crystallization surface) after initial crystallization is complete. In this case, residual melt after crystallization was separated from the solid layer by draining for 10 min. The crystal layer was then heated to 35°C, near the melting point of the original, natural milk fat, by increasing the temperature inside the metal tube. The sweating time was 15–30 min. The adhering mother liquor and melt trapped in the interstices as enclosed impurities of the crystalline layer can be removed in this way.

Another possibility is to sweat by means of a controlled atmosphere around the crystalline layer. A warm gas was applied to the layer, while the cooled tube was set at a temperature lower than the melting point of the product. In this case, the tube was set to 30°C, whereas the gas was heated to 50°C. The sweating time was 5 h in this case.

Results for both kinds of posttreatments are presented in Figure 7. The differences between the original crystal phases and the remaining products after sweating are shown. Both sweating methods lead to improvements in product quality. When the sweating was conducted by means of heating the tube, the crystal layer slipped off the tube after a short time (about 15–30 min). Sweating by a warm gas was not limited by duration of sweating as the layer remained attached to the tube. Moreover, higher amounts of the sweated fraction (material with lower clear points) were obtained compared to sweating by a heated tube.

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