

Direct Measurement of Thermal Fat Crystal Properties for Milk-Fat Fractionation

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ABSTRACT: The temperature dependency of the solid-fat content of a fat is important for predicting the consistency of the final product and for process control. Two direct analytical methods for determining the solid-fat content and the melting characteristics of milk-fat fractions have been developed. The fractions are analyzed during crystallization, and the results give reproducible information about the thermal behavior of the fractions and the actual crystal amount in the suspensions. The results are obtained within minutes, and no separation of the fractions before the measurement is necessary. New ways of reducing process time are proposed. It is possible to adapt crystallization time to seasonal variations of the initial milk fat and to the required properties of the final product. Partially crystallized milk fat was directly measured in a calorimeter and a pulsed nuclear magnetic resonance spectrometer. The data showed good correlations and even more accurate results than the conventional methods. The calorimetric method makes it possible to detect polymorphic changes and co-crystallization in the crystals so that the influence of processing parameters, such as energy input, on crystallization behavior can be investigated.

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KEY WORDS: Butterfat, crystallization, crystal amount, differential scanning calorimetry, fractionation, milk fat, nuclear magnetic resonance, process control.

Dry fractionation of milk fat is generally monitored by differential scanning calorimetry (DSC) or nuclear magnetic resonance (NMR) (1–5). These methods have replaced dilatometry due to the time needed for the measurement and other practical difficulties associated with dilatometry. Comparison of the results of these methods was made by several researchers (2,6,7). NMR measures more accurately the solid-fat index than dilatometry (8) and is also applicable over the entire range of solid-fat content (9), whereas dilatometry has an upper limit of 50% solids.

In industrial crystallizers for fractionating milk fat, crystallization can take as long as eight hours. There is no direct control of the actual fraction properties during production; the fractions are analyzed after separation. With analytical methods to control the fractionation process on-line, the process

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time could be minimized, and energy, e.g. for stirring and cooling, could be saved.

Conventional analytical methods for solid-fat content and melt enthalpy of milk fat and milk-fat fractions destroy “crystal memory” to standardize the measurements. For example, the texture of fats depends on the thermal history of the crystals (10). By melting the crystals for analytical characterization, no information is obtained about the dependency of modification, crystal habitus, and crystal network on the processing conditions.

The aim of this work was to evaluate new analytical methods for determining the crystal amount and melting behavior of fractions directly from the suspension to control crystallization during processing and the properties of the fractions.

MATERIALS AND METHODS

Sample. Anhydrous milk fat was obtained from Aargauer Zentralmolkerei Suhr (Suhr, Switzerland). The analytical characterization of the milk fat showed typical summer-milk fat properties with a melting point of 35°C (which corresponds to less than 1.5% solid-fat content measured by the conventional NMR method). The fatty acid composition of the milk fat is given in Table 1.

Standardized sample preparation for crystal suspensions. To obtain a suspension of crystals in a melt reproducibly and as fast as possible, milk fat was crystallized in a rheometer (Bohlin Visco 88; Bohlin Instruments Inc.; Searle principle; Cranbury, NJ) at defined temperatures. For evaluation of the

TABLE 1
Fatty Acid Composition of the Milk Fat^a

Fatty acid	Milk fat (%)	Fatty acid	Milk fat (%)	Fatty acid	Milk fat (%)
C _{4:0}	3.6	C _{12:0}	3.2	C _{18:0}	11.5
C _{6:0}	2.2	C _{14:0}	7.9	C _{18:1}	24.9
C _{8:0}	1.2	C _{16:0}	29.6	C _{18:2}	1.1
C _{10:0}	2.8	C _{16:1}	1.5	C _{18:3} + C _{20:1}	1.0
C _{10:1}	0.3	C _{17:0}	0.7	C _{20:0}	0.3

^aThe fatty acid composition was determined as methyl esters by gas chromatography and is expressed as mean average weight percentage on a fatty acid basis.

direct methods, milk fat was crystallized at a constant shear rate of 1041s^{-1} and constant temperatures.

Separation into fractions. For conventional analysis, the fractions must be measured separately. Therefore, the equilibrated crystal suspensions were filtered under low pressure in a pressure filter (BHS, Sonthofen, Germany).

Calorimetric measurements. The instrument used for the calorimetric measurements was a DSC Gold+ (Rheometric Scientific GmbH, Bensheim, Germany), with an accuracy of $1\ \mu\text{W}$. Mercury ($h = 2.725\ \text{cal/g}$, $T_{\text{melting}} = -38.85^\circ\text{C}$), and gallium ($h = 18.95\ \text{cal/g}$, $T_{\text{melting}} = 29.765^\circ\text{C}$) were used for temperature and enthalpy calibration, and the instrument was calibrated with the actual heating rate of the measurements. Aluminum pans were used, and the sample weight was about 1–5 mg. As a reference, an empty pan was measured at the same time. For analysis of the melt enthalpy, the area between the heat flow curve and the extrapolated baseline was determined. The cooling was done with liquid nitrogen as refrigerant.

Conventional method (DSC). Milk fat and separated low- and high-melting fractions were melted at 60°C , dehydrated by filtering through a filter paper (597 HY 1/2; Schleicher & Schuell, Dassel, Germany), and inserted into aluminum pans. The conventional program started under isothermal conditions at 60°C to eliminate any crystal germs. The sample was cooled down to -50°C at a cooling rate of $5^\circ\text{C}/\text{min}$ and held at a constant temperature of -50°C for 10 min to crystallize all triglycerides. The melting curves were determined at a heating rate of $5^\circ\text{C}/\text{min}$. From these curves, the melt enthalpy necessary for melting the existing crystals was calculated by integrating the area between curve and baseline. A variety of temperature ranges and rates for cooling and heating have been reported in the literature (11–14).

New calorimetric method (DSC direct). The time needed for one calorimetric measurement is a disadvantage of the conventional method for process control. Furthermore, detailed information about the crystallization process can only be determined if the history of the crystals is not destroyed but directly monitored during melting of the “original” crystals. Different crystal modifications due to processing can only be identified this way. One drop of a crystal suspension was inserted into an empty pan and immediately (within seconds) measured at a constant heating rate of $10^\circ\text{C}/\text{min}$ to register the heating curve.

Nuclear magnetic resonance. The instrument used in these investigations was a Minispec NMS 120 (Spectrospin; Bruker Analytical and Medical Instruments, Fällanden, Switzerland), which is a pulsed magnetic resonance spectrometer. Van Putte and Van den Enden (15) described the automatized measurement for determination of the solids fraction in a partly crystallized fat. The procedure is fully automated, and the percentage of solids is displayed. The measuring time is proportional to the number of scans carried out to reach the standard deviation required (15) but varies mostly between 3 and 20 s. The average standard deviation was less than 1% solid for pulsed NMR (8,16).

Conventional method (NMR). Low-resolution NMR is a standard method for determining the solid-fat content in fats and oils. To measure the solid-fat content by the IUPAC method (International Union of Pure and Applied Chemistry) (17), milk fat is tempered at 80°C to destroy any persistent crystal nuclei. A small amount (3.7 mL) of molten sample is inserted into a sample tube and contacted for about one minute with liquid nitrogen until completely solidified. Then, the tubes are tempered at the starting temperature of 0°C and kept for 30 min in a water bath until an equilibrium temperature is reached. For each temperature point, at least 30 min of tempering is required. The heating protocol is well defined for reproducible measurements because the solid-fat content is strongly dependent on crystallization and tempering (18,19). The method suggested by the AOCS (20) includes a tempering step during cooling, which was omitted here. Furthermore, the solid content depends on the composition of the triglycerides (8).

NMR “direct.” Because the signal of NMR spectroscopy provides information about the aggregate state of atomic nuclei, the solid-fat content of crystal suspensions was measured directly in the pulsed NMR spectrometer. Taylor *et al.* (9) already noted the possibility of detecting the solid content in a sample as received from a process. Suspensions of partly crystallized milk fat were filled directly into sample tubes and placed in the gap of the NMR magnet. The measurement took place on-line, giving results within seconds.

RESULTS AND DISCUSSION

Crystal suspensions. Windhab and Rohenkohl (21) showed for fat systems in general, and Grall and Hartel (11) showed for milk fat in particular that crystallization kinetics can be significantly enhanced by increasing agitator velocity. This was explained by the associated increase in impeller shear, which promotes secondary crystallization. Preliminary investigations were performed to evaluate a method for a fast and reproducible preparation of crystal suspensions in milk fat. It was shown, on laboratory scale, that mechanical energy input in a tempered melt of milk fat decreases crystallization time.

Figure 1 shows the viscosity as a function of time during crystallization at a constant temperature of 26°C . Before crystallization starts, the melt shows Newtonian behavior. With the formation and growth of crystals, the viscosity increases almost linearly with the crystal amount in the suspension until the suspension reaches a thermodynamic equilibrium. At this point, the suspension is shear thinning, which is distinctive at higher temperatures.

For the first fractionation step, milk fat was crystallized as previously described at different temperatures between 21 and 35°C and at constant shear rate of 1041s^{-1} . When the temperature equilibrium was reached (Fig. 1), the “direct measurements” were performed.

This method allows one to get reproducible crystal suspensions. By crystallizing the same milk fat under similar conditions until the thermodynamic equilibrium is reached, the

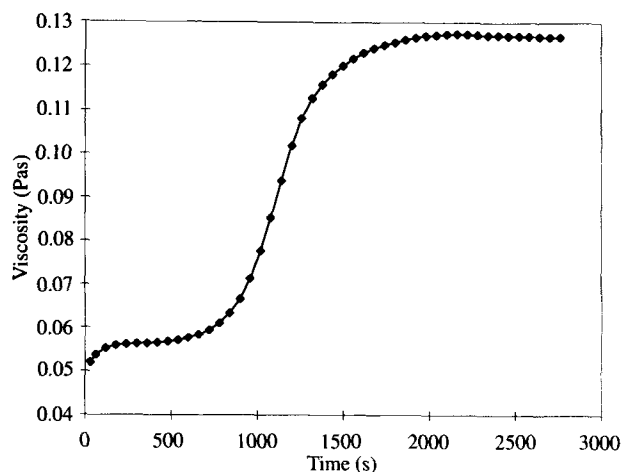


FIG. 1. Viscosity as a function of time at a constant shear rate of 1041s^{-1} and a constant temperature of 26°C (Couette 1.25 mm gap).

same triglyceride distributions are found in separated fractions, and the same enthalpies and solid-fat content result.

DSC. Melting of fat crystals requires the intake of the melt enthalpy. By melting the crystals at a specific heating rate, the melting curves of the fractions are registered (Fig. 2). Before melting starts and after all crystals are melted, the enthalpy changes are only due to the change in temperature. Depending on the calibration of the calorimeter, the baseline is straight. The temperature that indicates melting of the first crystals is called on-set temperature, while the end of melting defines the off-set temperature. The specific melt enthalpy, which is necessary for melting the existing crystals (at specified temperatures), is calculated by integrating the area between the enthalpy curve and the baseline (refer to Fig. 2).

Because milk fat contains triglycerides with fatty acids of different chainlengths and degree of saturation, the thermal history of the crystals is important. Due to cocrystallization and polymorphism, the melt enthalpy in a specified temperature range of the same sample may differ. Rossell (14) considered two possible explanations for the dependency of the

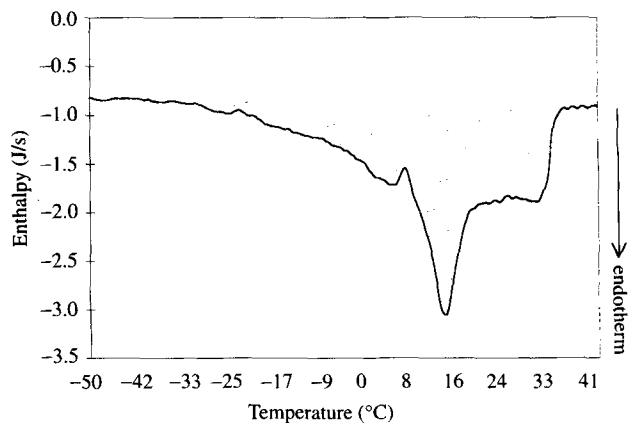


FIG. 2. Melting curve of milk fat as a function of temperature measured with the conventional calorimetric method.

shape variation of the cooling curves for palm kernel oil on the rate of cooling: polymorphic transformations and crystallization of separate triglyceride groups.

At high cooling rates, cocrystallization is preferred due to stronger undercooling. Krautwurst (22) showed that cocrystallization occurs in a mixture of triglycerides if the lengths of the fatty acids differ by less than 10%. Furthermore, different fractions may separate during melting or cooling.

Low heating rates ensure a higher resolution so that melting points close to each other are registered separately. Therefore, more accurate measurements are performed at low heating and cooling rates, but the time for one measurement is long. In addition, at low heating rates, polymorphic transformations may take place during melting, resulting in exothermic peaks (partial recrystallization of melted fractions).

The cooling and heating rate for calorimetric measurements should be defined as well as the range of the temperature program.

Conventional calorimetric method (DSC). Even under defined conditions, cocrystallization of different triglycerides at a specific cooling rate depends on the fatty acid composition (10). Therefore, the results of the conventional calorimetric method depend on the composition of each sample, which varies even more in different fractions. The calculation of the solid-fat content from melting curves registered by this method is based on the assumption that the fat mass at -50°C is totally crystallized (corresponding to a solid-fat content of 100%) and that the heat of fusion of all triglycerides is constant (6,23). In fact, the heat of fusion of milk fat is not constant over the whole temperature range. The heat of fusion of almost every triglyceride is different. Sherbon and Dolby (24) prepared several fractions from anhydrous milk fat by progressive crystallization from acetone. The reported heat of fusion of these fractions differs between 62J/g and 171J/g . Krautwurst (22) divided butterfat into 46 fractions by the same method; the heat of fusion of these fractions differed between 7J/g and 178J/g . The heat of fusion increases almost linearly with the melting temperature of the fractions. Calculating the crystal amount from the melt enthalpy is therefore difficult, and the real amount of crystals may differ greatly, depending on the temperature range of the part of the sample used for the calculation. The integration of the melting curves for determining solid-fat content depends on the fat composition and should be weighted proportional to the melting temperature.

Direct calorimetric method (DSC direct). Figure 3 shows the calorimetric measurements of a pure milk-fat melt (dotted line) and a milk-fat suspension that contained crystals (solid line). If a crystal suspension (resulting from fractional crystallization of milk fat at a specified temperature) is melted, only the melt enthalpy for the present crystals is needed. On the other hand, a crystal-free sample does not show any change in enthalpy by heating it in a calorimetric cell (dotted line). At a constant heating rate, the melting enthalpy for a defined suspension in a specified temperature range was reproducible and significant for the crystals of the solid frac-

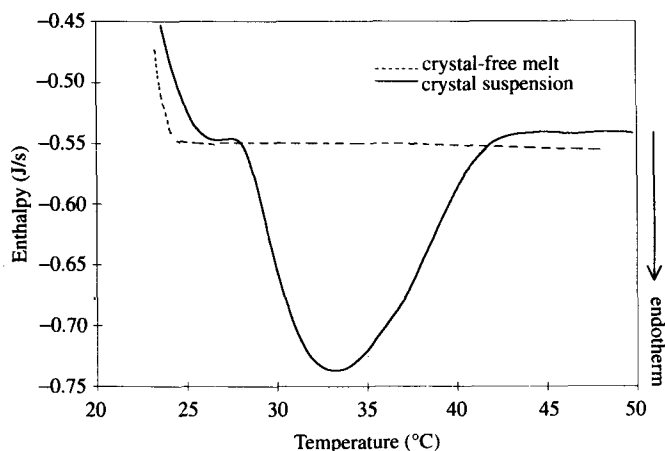


FIG. 3. Enthalpy of a crystal-free melt and a crystal suspension as a function of temperature detected with the direct calorimetric method (differential scanning calorimetry direct).

tion. The standard deviation was usually higher at lower crystal fractions.

The crystal suspensions are temperature-sensitive. If a suspension has reached an equilibrium temperature, temperature changes cause melting or further crystallization. If samples have not yet reached the crystallization equilibrium (at constant temperature), crystallization proceeds until a steady state is reached. Consequently, the melt enthalpy measurement for characterizing a present crystalline state should be carried out as fast as possible.

A second aspect to be considered is the fact that the sample pans that are inserted into the calorimeter cell need time to adapt to the actual oven temperature. Furthermore, the holding/load temperature of the cell is influenced by the room temperature while the sample pans are inserted. It was found

that heating should be started 2–3°C below the crystallization temperature to get a horizontal baseline before melting starts (Fig. 3). Otherwise, temperature equilibration of the sample pan to the state in the cell cannot be distinguished from melting. On the other hand, the load temperature should not be too low due to the possibility of further crystallization.

The melting curves depend as well on the heating rate ("inertia-effects" in temperature equilibration). The temperature shift and the enthalpy difference due to the heating rate can be corrected by calibration at different heating rates. However, at increased heating rates, the shape of the melting enthalpy curve is smoothed, and as a result, detailed information may get lost. The lower the heating rate, the more specific information can be derived from the melting curve. Because, in most fraction steps, the existing crystals melt above the melting point of water, dehydration of the sample is not necessary. The samples measured here contained almost no water.

Comparison of the calorimetric measurements. Table 2 shows the average values and standard deviations of the direct calorimetric measurements of samples at equilibrium at different constant temperatures between 21 and 35°C. Significant for the existing crystals is the temperature range of melting (difference between off-set temperature and on-set temperature) and the specific melting enthalpy. Figures 4 and 5 show melt enthalpy and on-set temperature, respectively, as a function of the crystallization temperature, which is correlated with the amount of crystals. The lower the crystallization temperature, the more triglycerides crystallize; consequently, melting starts at a lower temperature (during reheating). The higher the crystal amount, the greater is the specific enthalpy required to melt all existing crystals.

The dependency of the melting enthalpy for the same fat crystals on different crystal sizes (generated at different shear

TABLE 2
Melt Enthalpy, On-set and Off-set Temperatures and Standard Deviations of Milk-Fat Suspensions Crystallized at the Listed Temperatures Until an Equilibrium Was Reached at a Constant Shear Rate of 1041 s⁻¹

Crystallization temperature	Melt enthalpy	Standard deviation	On-set temperature	Standard deviation	Off-set temperature	Standard deviation
°C	J/g	J/g	°C	°C	°C	°C
21	15.86	0.53	23.15	0.17	40.96	0.77
22	14.96	0.25	24.12	0.10	42.34	1.01
23	14.31	0.67	24.84	0.19	42.13	0.89
24	13.47	0.21	25.98	0.08	43.39	0.81
25	12.60	0.41	26.62	0.18	42.17	0.95
26	11.86	0.24	27.76	0.28	43.88	0.78
27	10.73	0.06	28.47	0.09	43.73	0.61
28	9.59	0.11	29.57	0.14	43.44	0.57
29	8.11	0.21	30.76	0.08	43.28	0.34
30	7.54	0.31	31.59	0.33	43.30	0.94
31	6.80	0.05	32.26	0.10	42.72	0.46
32	5.48	0.08	33.66	0.08	44.74	0.49
33	4.28	0.42	34.62	0.15	44.87	0.31
34	2.73	0.27	35.36	0.21	44.95	0.48
35	0.96	0.08	36.49	0.45	46.39	0.83

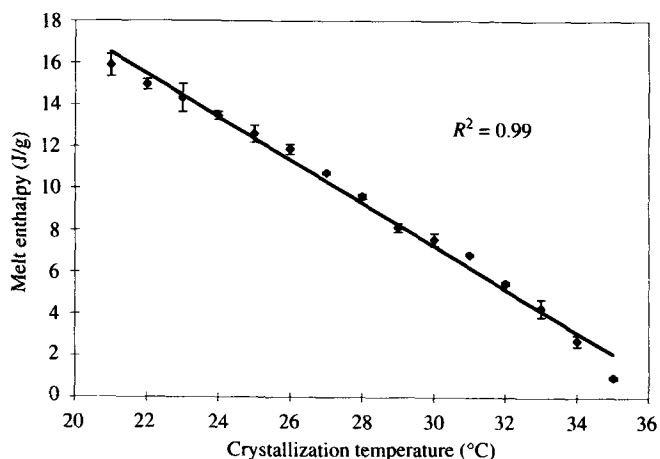


FIG. 4. Specific melt enthalpy (differential scanning calorimetry direct) as a function of the crystallization temperature.

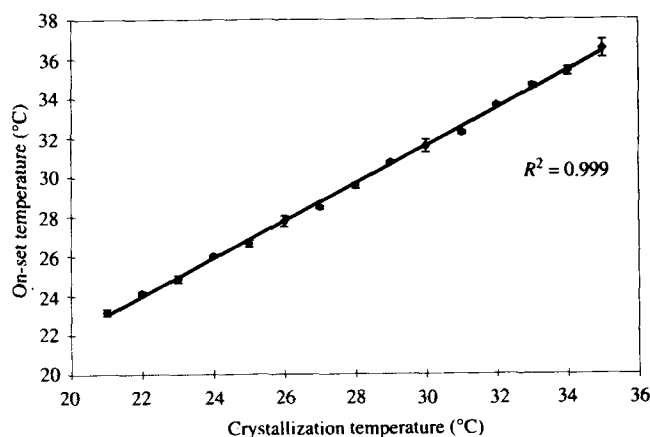


FIG. 5. Start temperature of melting (on-set temperature) (differential scanning calorimetry direct) as a function of the crystallization temperature.

rates) was not significant. Table 3 shows the results of different melting curves. The crystallization temperature of these suspensions was constant (26°C), and the particle size distribution differed. The sample crystallized at the highest shear rate (1041 s⁻¹) had the smallest crystals and a narrow particle size distribution. Differences in total enthalpy and on-set temperature, caused by the particle size distribution, were within the standard deviation. However, the off-set temperature was strongly influenced by the crystallization shear rate or crystal size. Figure 6 compares the enthalpy curves of three samples given in Table 3. At a higher shear rate, crystallization time in the crystallizer was faster. As one can see from Figure 6 and also from the off-set temperatures (Table 3), the temperature range of melting was reduced at higher shear rates (lowered off-set temperature). It was shown that fast crystallization favors cocrystallization, which leads to narrower melting ranges and thereby to lower melting maxima. The sample crystallized at 251 s⁻¹ took the longest time to reach the equilibrium at 26°C (which was double the time required at the highest shear rate) and showed the most stable crystals (widest temperature range of melting).

Separating the crystals and detecting their melting curves by the common conventional DSC method, Figure 7 shows no difference in the crystallization temperature range. That

means that there is a loss of the "cocrystallization effect" during sample preparation according to the conventional DSC method. In addition, the separation steps make the results less reproducible because in filtration different amounts of oil are included in the crystal fractions.

NMR. Figure 8 shows the solid-fat content as a function of temperature registered by the conventional NMR method. The melting point of the sample (as defined here) is 35°C, which is typical for a summer butter. Figure 9 compares the results of the conventional and the direct methods for determination of the solid-fat content by pulsed NMR spectroscopy. The solid-fat content measured directly from the suspension is lower than the conventionally measured solid-fat content. The difference decreases at higher temperatures and at lower solids content.

For the conventional method, it could also be shown that the solid-fat content depends on the temperature steps used during the measurement. If the initial temperature was 0°C and then the temperature was increased in steps, the solid-fat content was higher than if the sample was directly tempered at the higher temperature. This corresponds to the results reported (10,18,19) for margarine. If crystallization takes place at low temperatures (stronger undercooling), cocrystallization is supported (25). For reduced undercooling and lower

TABLE 3
Melt Enthalpy, On-set and Off-set Temperatures and Standard Deviations of Milk-Fat Suspensions Crystallized at a Constant Temperature of 26°C Until an Equilibrium Was Reached at Different Constant Shear Rates

Shear rate	Melt enthalpy	Standard deviation	On-set temperature	Standard deviation	Off-set temperature	Standard deviation
s ⁻¹	J/g	J/g	°C	°C	°C	°C
251	11.41	0.57	27.55	0.11	46.12	0.37
492	11.39	0.73	27.48	0.33	45.01	0.69
783	11.22	0.24	27.46	0.08	43.34	0.47
1041	11.86	0.24	27.76	0.28	43.88	0.78

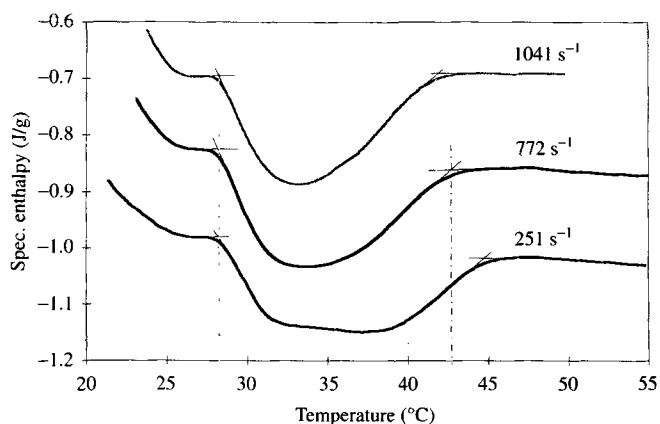


FIG. 6. Specific melt enthalpy (differential scanning calorimetry direct) of milk-fat suspensions crystallized at a temperature of 26°C until an equilibrium was reached at different constant shear rates.

crystallization rates, less mixed crystals are formed, and consequently, the crystal fraction is reduced. Jönsson and Anderson (16) showed the differences in the solid-fat content of the same butter fat crystallized at different times and temperature steps. The results showed that, due to stronger undercooling, samples had a higher solids content than stepwise and slowly cooled samples for which an equilibrium state in crystallization is reached. The difference in the solids content underlines that temperature equilibrium is important for NMR measurements. The directly detected solid-fat content of the suspensions shows the real content and real fraction distribution of crystals after the crystallization process. Changes were due to cocrystallization caused during crystallization and not

caused by the preparation of the sample. Consequently, only the direct method can provide information about the real crystal state.

Because the magnet of the NMR has a constant temperature of 40°C, the sample is heated up during the measurement. Heating up the crystal suspension causes partial melting of crystals. Therefore, the number of scans should not be too high, and the measurement has to be carried out quickly (within seconds). Because one measurement is done within seconds and needs almost no sample preparation, few scans and multiple sampling is suggested.

van Boekel (26) showed a dependency of the solid-fat content on the crystal size, while Chawla and De Man (27) found no significant influence. The differences in solid-fat content, due to larger or smaller particle size "prepared" by different shear rates in the crystallization process, varied within the standard deviation. It was not necessary to consider the influence of residual water in the sample because the milk fat contained less than 0.1% of water.

Comparison of the direct methods. Comparing the results of the direct methods (Fig. 10), a linear relationship between solid-fat content and melt enthalpy occurred within the temperature range investigated. Changes in the heat of fusion could not be detected.

The new method for determining the solid-fat content of partly crystallized milk fat by NMR spectroscopy gives the actual solid content within seconds, while the enthalpy measured with the DSC calorimeter is calculated after the measurement is finished and the real sample weight is known. The temperature range in which the crystals melt can be controlled during the calorimetric measurement (on a time scale of about

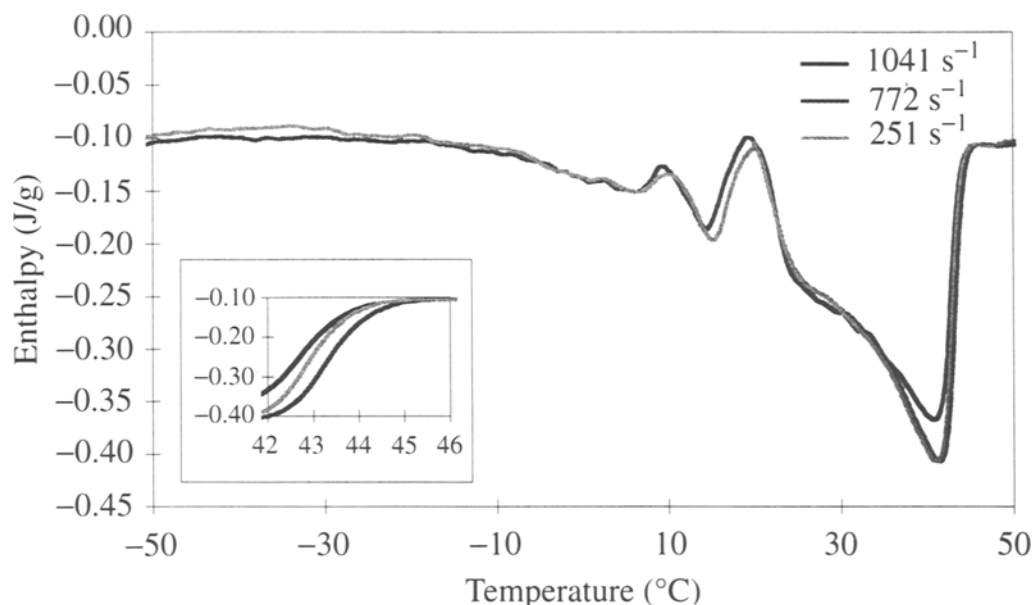


FIG. 7. Specific melt enthalpy of high-melting fractions, crystallized at a constant temperature of 26°C until an equilibrium was reached at different shear rates and separated into low- and high-melting fractions before measurement.

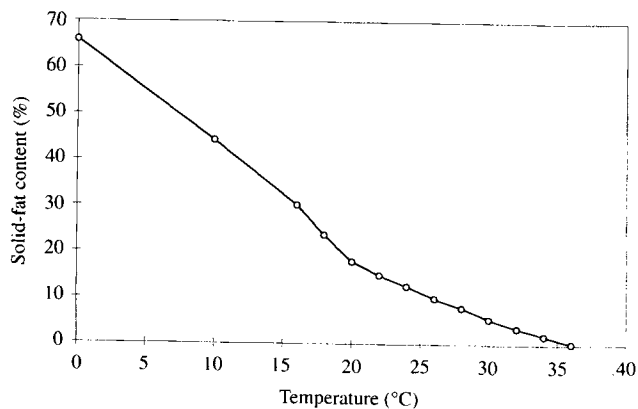


FIG. 8. Solid-fat content of milk fat registered by pulsed nuclear magnetic resonance, referring to the IUPAC method.

ten minutes). The on-set temperature is shown to be an indicator for the crystals generated at crystallization temperature, while the off-set temperature is significantly affected by polymorphic alterations. NMR spectroscopy is thought to give the most accurate results of the crystal amount but does not distinguish between crystals of different melting characteristics. Both methods together give maximal information about the crystal properties. The direct methods give fast and accurate information about the “degree of crystallization” during processing and may therefore be used for the control of crystallizing processes without losing much time for analytical measurements. The small sample amounts and the need for fast handling (and consequently the need to place the instruments close to the process line) are presumptions for using the direct methods.

Further investigations, which are in progress, will compare the thermal properties of the final fractions with other fraction properties (e.g., consistency) to gain additional information from the directly detected data.

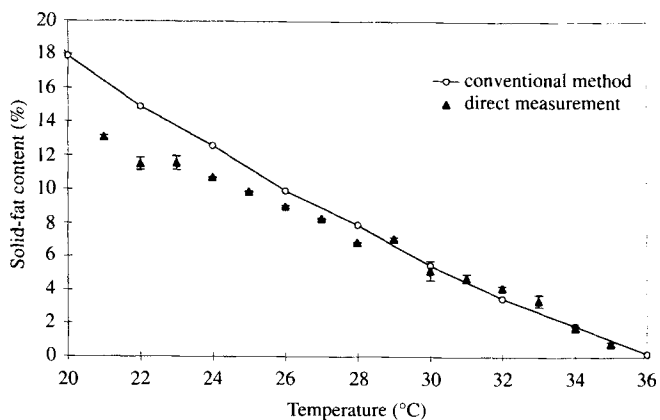


FIG. 9. Solid-fat content of milk fat analyzed by the conventional (IUPAC) method compared with directly measured solid content of crystal suspensions crystallized at a constant shear rate of 1041 s^{-1} and different temperatures between 21 and 35°C .

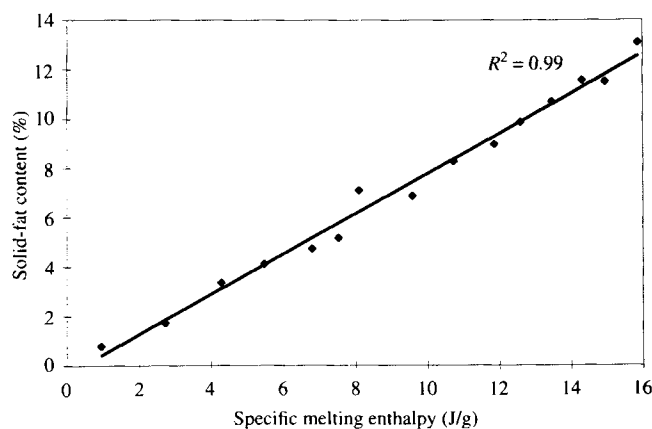


FIG. 10. Relationship between the direct measured solid-fat content (nuclear magnetic resonance direct) and specific melt enthalpy (differential scanning calorimetry direct) of milk-fat suspensions (refer to Table 2).

REFERENCES

1. Deffense, E., Milk Fat Fractionation Today: A Review, *J. Am. Oil Chem. Soc.* 70:1193–1201 (1993).
2. Bystrom, C.E., and R.W. Hartel, Evaluation of Milk Fat Fractionation and Modification Techniques for Creating Cocoa Butter Replacers, *Lebensm.-Wiss. u. -Technol.* 27:142–150 (1994).
3. deMan, J.M., and M. Finoro, Characteristics of Milk Fat Fractionated by Crystallization from the Melt, *Can. Inst. Food Sci. Technol. J.* 13:167–173 (1980).
4. Bornaz, S., J. Fanni, and M. Parmentier, Limit of the Solid Fat Content Modification of Butter, *J. Am. Oil Chem. Soc.* 71:1373–1380 (1994).
5. Chapman, D., R.E. Richards, and R.W. Yorke, A Nuclear Magnetic Resonance Study of the Liquid/Solid Content of Margarine Fat, *Ibid.* 37:243–246 (1960).
6. Walker, R.C., and W.A. Bosin, Comparison of SFI, DSC and NMR Methods for Determining Solid-Liquid Ratios of Fats, *Ibid.* 48:50–53 (1971).
7. van Beresteyn, C.H., Polymorphism in Milk Fat in Relation to the Solid/Liquid Ratio, *Neth. Milk Dairy J.* 26:117–130 (1972).
8. Templeman, G.J., J.J. Sholl, and T.P. Labuza, Evaluation of Several Pulsed NMR Techniques for Solid-In-Fat Determination of Commercial Fats, *J. of Food Sci.* 42:432–435 (1977).
9. Taylor, J.R., W.D. Pohle, and R.L. Gregory, Measurement of Solids in Triglycerides Using Nuclear Magnetic Resonance Spectroscopy, *J. Am. Oil Chem. Soc.* 41:177–180 (1964).
10. deMan, L., J.M. deMan, and B. Blackman, Effect of Tempering on the Texture and Polymorphic Behaviour of Margarine Fats, *Fat. Sci. Technol.* 97:55–60 (1995).
11. Grall, D.S., and R.W. Hartel, Kinetics of Butterfat Crystallization, *J. Am. Oil Chem. Soc.* 69:741–747 (1992).
12. Coni, E., M. Di Pasquale, P. Coppolelli, and A. Bocca, Detection of Animal Fats in Butter by Differential Scanning Calorimetry: A Pilot Study, *Ibid.* 71:807–810 (1994).
13. Merken, G.V., S.V. Vaeck, and D. Dewulf, Determination of the Technological Properties of Cocoa Butter by Means of Differential Scanning Calorimetry, *Lebensm.-Wiss. u. -Technol.* 14:195–198 (1982).
14. Rossell, J.B., Differential Scanning Calorimetry of Palm Kernel Oil Products, *J. Am. Oil Chem. Soc.* 52:505–511 (1975).
15. Van Putte, K., and J. Van den Eenden, Fully Automated Determination of Solid Fat Content by Pulsed NMR, *Ibid.* 51:316–321 (1974).
16. Jönsson, H., and K. Andersson, Study of the Crystallization Be-

- haviour of Butterfat with Pulsed NMR, *Milchwissenschaft* 31:593-598 (1976).
17. IUPAC Norm, Solid Content Determination in Fats by NMR (low-resolution nuclear magnetic resonance), 1991, pp. 59-61.
 18. deMan, L., J.M. deMan, and B. Blackman, Physical and Textural Evaluation of Some Shortenings and Margarines, *J. Am. Oil. Chem. Soc.* 66:128-132 (1989).
 19. deMan, L., J.M. deMan, and B. Blackman, Physical and Textural Characteristics of Some North American Shortenings, *Ibid.* 68:63-69 (1991).
 20. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, Solid Fat Index, American Oil Chemists' Society, Champaign, 1993, Method Cd 16b-93.
 21. Windhab, E., and H. Rohenkohl, *The Influence of Hydrodynamic Forces on the Crystal Structure of Fat Systems*, edited by A. Mersmann, Proceedings of the 11th Symposium on Industrial Crystallization, Garmisch Partenkirchen, Elsevier Verlag, Amsterdam, 1990.
 22. Krautwurst, J., Die Mischkristallisation der Triglyceride, *Kieler Milchwirtschaftliche Forschungsberichte* 22:255-284 (1970).
 23. Bentz, A.P., and B.C. Breidenbach, Evaluation of the Differential Scanning Calorimetric Method for Fat Solids, *J. Am. Oil Chem. Soc.* 46:60-63 (1969).
 24. Sherbon, J.W., and R.M. Dolby, Preparation and Fractionation of the High Melting Glyceride Fraction of Milk Fat, *J. of Dairy Sci.* 56:52-60 (1973).
 25. Walstra, P., *Fat Crystallization, Food Structure and Behaviour*, Academic Press, London, 1987, pp. 67-85.
 26. van Boekel, M.A.J.S., Estimation of Solid-Liquid Ratios in Bulk Fats and Emulsions by Pulsed Nuclear Magnetic Resonance, *J. Am. Oil. Chem. Soc.* 58:768-772 (1981).
 27. Chawla, P., and J.M. deMan, Effect of Temperature Cycling on the Crystalline Form, Size and Textural Properties of Shortening Fats, *J. of Texture Studies* 25:151-162 (1994).

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