Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Fractionation of Milk Fat by Falling Film Layer Crystallization

K. Belkacemi[a]; P. Angers[a]; O. Fischer[b]; J. Arul[a]
[a] Department of Food Science and Nutrition, Laval University, Sainte-Foy, PQ, Canada [b] Sulzer Chemtech Ltd., Buchs, Switzerland

Online publication date: 07 September 2003

To cite this Article Belkacemi, K. , Angers, P. , Fischer, O. and Arul, J.(2003) 'Fractionation of Milk Fat by Falling Film Layer Crystallization', Separation Science and Technology, 38: 12, 3115 — 3131
To link to this Article: DOI: 10.1081/SS-120022589
URL: http://dx.doi.org/10.1081/SS-120022589

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 3115–3131, 2003

Fractionation of Milk Fat by Falling Film Layer Crystallization

K. Belkacemi,[1] P. Angers,[1] O. Fischer,[2] and J. Arul[1,*]

[1]Department of Food Science and Nutrition, Laval University, Sainte-Foy, PQ, Canada
[2]Sulzer Chemtech Ltd., Buchs, Switzerland

ABSTRACT

Falling film layer crystallization (FFLC) is a promising approach to milk fat fractionation into oil and plastic fat fractions and can be an alternative to the conventional suspension melt crystallization (SC). The fractionation of milk fat by means of the FFLC process was investigated. Efforts were focused on the maximization of the stearin yield with satisfactory separation efficiency. The performance of the FFLC was also compared with that of the SC process. The experimental runs were conducted at varied Reynolds numbers ranging from 5 to 75, crystallization temperatures from 28 to 32°C, and sweating temperatures from 36 to 39°C, at a constant cooling rate (0.1°C/minute) and a crystallization time of 3 hours. The sweating step was necessary and acted as a refinement step to remove low-melting triglycerides that adhered to crystals. A difference in dropping (melting) points of stearin and olein fractions of 12°C and

*Correspondence: J. Arul, Department of Food Science and Nutrition, Laval University, Sainte-Foy, PQ, Canada G1K 7P4; E-mail: joseph.arul@aln.ulaval.ca.

DOI: 10.1081/SS-120022589 0149-6395 (Print); 1520-5754 (Online)

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

a stearin yield of 20% were obtained at a crystallization temperature of 30°C, Reynolds number of 12, and sweating temperature of 36°C. The dropping point of the stearin fraction reached 45°C compared with 31°C for the olein fraction, and 33°C for milk fat. Falling film layer crystallization and SC processes were comparable in terms of solid yield, as well as physicochemical properties of the fractions.

Key Words: Falling film; Layer crystallization; Fractionation; Melt; Triglycerides; Milk fat.

INTRODUCTION

Milk fat is a complex mixture of triglycerides. It possesses unique flavor and mouth-feel characteristics, desired in both dairy and nondairy food products. However, its broad melting plastic range makes it less suitable in many food-fat applications. In an effort to increase the utilization of milk fat in many food applications, its modification by physical, chemical, and enzymatic methods has been the objective of several investigations. There are several processes available for modifying milk fat functional properties. These include hydrogenation, interesterification, and fractionation. Hydrogenation is used to increase the hardness and oxidative stability of oils. The major drawback of this technique is the production of undesirable *trans* fatty acids.[1] Interesterification modifies the triglyceride structure of fats and oils. However, it is known to be accompanied by the loss of flavor.[2] Both of these approaches involve a chemical reaction at moderate to high temperatures.

Fractionation involves the separation of milk fat triglycerides without chemical modification of their structure and offers the possibility of retaining the natural advantages of milk fat in terms of its flavor and dairy image. Short-path distillation produces a high degree of molecular separation, but it is operated at high temperatures.[3,4] Supercritical CO_2 extraction fractionates milk fat by varying the solvent power of CO_2.[5–8] However, this fractionation method is considered cost intensive. The most convenient process for fractionating milk fat is by far the fractional crystallization method, which is performed at low temperatures.[9–11]

Fractional-melt crystallization is classified into two types depending on the solid–liquid interfaces, referred to as the continuous interface for suspension crystallization (SC) technique and discontinuous interface for layer crystallization (LC).[12] Suspension crystallization is generally operated batchwise, and crystal suspension is filtered to recover the crystalline mass.[9–11,13,14] Layer crystallization is operated batch wise either in static

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

(SLC) mode or in dynamic mode or falling film (FFLC), which produces crystal layers grown on a heat-transferring surface by progressive freezing of the melt.[15–18] In LC processes, the residual melt is separated by gravity (draining), and the crystal layer is melted and recovered. A sweating step, contributing to further purification of the crystal layer, is used as a postcrystallization treatment. This method is well developed for separation of a mixture of organic chemicals.[19–21] and can be an alternative to suspension melt crystallization, which involves a solid handling step.[17,22] Wynn[20] reported a comparative evaluation between SLC and FFLC. In the SLC technique, the crystallization is very slow, and the growth rate of crystal layer is limited to 0.2 cm/hour. In fact, faster growth rates destabilize the layer growth and lead to buildup of impurities at the solid–liquid interface. On the other hand, the FFLC technique induces shear by the fluid dynamics, allowing the transfer of the impurities into the bulk of melt. Interface instabilities are avoided, and faster crystal growth rates can be reached.[15,16]

The objective of this work was to investigate the fractionation of milk fat with the FFLC approach and determine the important parameters governing the separation efficiency of milk-fat triglycerides. Process variables, such as Reynolds number, crystallization, and sweating temperatures, were optimized. A comparative study between the FFLC and the SC is presented and discussed in terms of separation performance, physical and chemical properties (dropping point, triglyceride and fatty acid compositions), as well as the melting profiles of the fractions.

EXPERIMENTAL

Materials

Commercial-grade anhydrous milk fat without any fine protein particles (Ault Foods Ltd., Mitchell, Ontario) was used for the fractionation study.

Crystallizer

The crystallizer shown in Fig. 1 is composed of two concentric tubes: a jacketed glass column (C) (Jenaer Glaswerk from SCHOTT) and stainless steel crystallization tube (TB) (finger-type crystallizer, diameter 20 mm and length 1 m). The glass column consists of two sections: a collecting tank at the bottom of the column and a cylindrical jacketed glass column surrounding the crystallization tube. The melt is distributed as a falling film over the outer

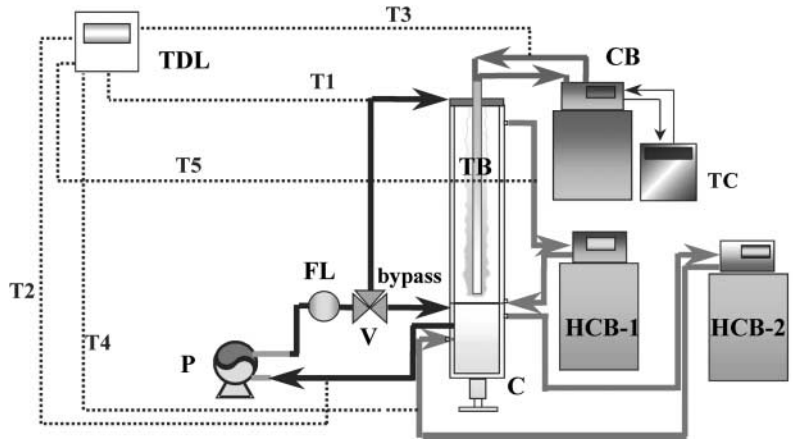

Figure 1. Experimental setup of FFLC process. TDL, temperature data logger; TB, crystallization tube; P, circulation pump; C, FFLC glass column; CB, cooling bath; HB, heating baths; FL, flowmeter; V, valve; and TC, temperature controller.

surface of the crystallization tube, while the cooling medium (cold water) is circulated through the inside tube, along the length of the crystallization tube. The uncrystallized melt flows down on the surface of the crystallization tube, is collected in the collecting tank, is pumped upward by means of a circulation pump (P). It is redistributed uniformly on the outer surface of the crystallization tube. The crystal layer grows on the outer walls of the tube. The jacketed glass column is kept at a constant temperature by means of two heating/cooling water baths (HCB-1 and -2), while the temperature of the crystallization tube, representing the crystallization temperature, is adjusted and controlled by means of temperature controller/programmer (TC). The inlet and outlet temperatures of the melt (T_1 and T_2, respectively), those of water baths (T_4 and T_5), and the temperature (T_3) of chilled water in the crystallization tube were continuously measured by thermocouples and recorded by a data acquisition system (TDL). The flow of the circulating melt is measured by a flowmeter (FL).

Milk Fat Fractionation

Anhydrous milk fat was melted and stabilized at 65°C for 1 hour to destroy residual-crystal memory and then poured in to the FFLC collecting

tank. This represents phase 1 in the temperature–time profile of the cooling tube, as shown in Fig. 2. The melt was pumped to the top of the crystallizer and cooled slowly while flowing out over the outer surface of the tube for selective crystallization. This corresponds to phase 2 in the same figure. During this phase, formation of small crystals (nuclei) was observed in the feed section, and a thin, uniform film of these nuclei was formed on the outer surface of the cooling tube. The desired crystallization temperature, T_C, was reached at controlled cooling rate, C_R, of 0.1°C/minute, and maintained constant during the crystallization period, t_C (phase 3). During this phase, crystals grew and adhered to the crystallization tube by forming a thicker film. At the end of this phase (after 3 hours of crystallization), the crystallization process was interrupted, and the melt remaining in the collecting tank was drained off. Collection of this melt represented the olein fraction. Thereafter, the crystal phase was heated above its melting point or sweating temperature, T_S, and held at this temperature for 30 minutes so that the crystal phase is slightly melted or sweated to partially remove the impurities from the crystal phase. This treatment allowed the impurities of lower melting point (adhered to the crystal phase or occluded into it) to trickle down. This melted material, consisting of low-melting point triglycerides (impurities), represented the sweat fraction. Finally, the crystal phase still adhering to the tube was heated and melted. The collected fraction represented the stearin fraction. In these experiments, T_C was varied between 28 and 32°C, T_S between 36 and 39°C, while the Reynolds number was varied from 5 to 75 (laminar flow).

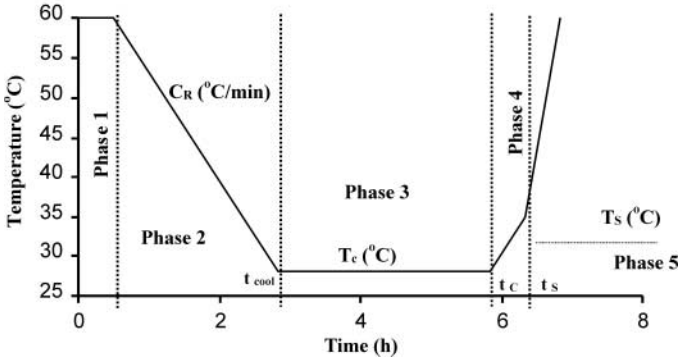

Figure 2. Temperature–time profile of the crystallization tube.

Physicochemical Properties

Triglyceride composition for the various fractions were determined on a GLC equipped with an FID (HP5890 Series II, Hewlett Packard, Avondale, PA) using the cold on-column injection technique.[23,24] The separation was carried out in a J&W Scientific fused silica capillary column (15 m × 0.25 mm i.d.) coated with SE-54 Durabond (0.1 μm) (Chromatographic Specialties, Brockville, ON). Triglycerides from C-18 to C-24 were identified from the retention times of a standard mixture of triglycerides (Nu-Chek Prep, Inc., Elysian, MN). Samples were diluted to 10 mg/mL in distilled decane (Caledon, Georgetown, Ontario), and ca. 0.3 μL was injected onto the column. The detector temperature was kept at 355°C. The initial oven temperature was held at 200°C for 2 minutes, subsequently increased at a rate of 10°C/minute to 250°C, at a rate of 5°C/minute to 350°C, and held at this temperature for 10 minutes. The carrier gas was hydrogen, and the column-head pressure was maintained at a constant pressure of 55 kPa. Fatty acids from various fractions were converted into their methyl esters by the classical method,[25] and fatty acid composition analyzed by GC, as described elsewhere.[14] Melting curves were performed on a Dupont Model 9900 thermal analyzer (DSC) (Dupont Instrument, Toronto, Ontario) by the method of Timms.[26] Solid-fat content was determined using melting curves.[14] Dropping point (the temperature at which a solid fat turns into liquid, measured by warming the solid fat until a first liquid drop is formed) of native milk fat and its fractions was performed using the Mettler Thermo-System FP 800 (Mettler Instrument Corp., Columbus, OH).

RESULTS AND DISCUSSION

Effect of Reynolds Number

A series of anhydrous milk fat (AMF) fractionation runs by means of the FFLC process was carried out under different sets of operating conditions. Figure 3 shows the effect of flow on the yield of fractions obtainable by the FFLC process. Reynolds number (Re), as a flow characteristic, was chosen to follow distribution profiles of olein, stearin, and sweat fractions. Reynolds number was calculated as:

$$\mathrm{Re} = \frac{dV\rho}{\mu} \tag{1}$$

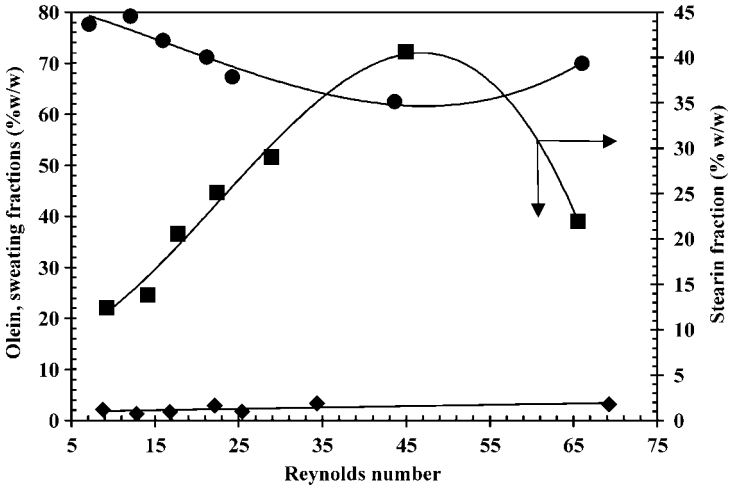

Figure 3. Effect of Reynolds number on the yields of fractions. Symbols: ■ stearin fraction; ● olein fraction; ◆ sweat fraction.

where d is the crystallization tube diameter; V, ρ, and μ are the flow velocity, density, and viscosity of the milk fat, respectively. The variable, V, is measured by the flowmeter (FL) (see Fig. 1). It was shown by Kaylegian and Lindsay[27] that strong fluid mechanical forces negatively affect the generation of nuclei and crystals, presumably by the shearing of particles from the seed crystal surface. Thus, the variation of Re was kept within the laminar-flow region of 10 to 70. Figure 3 shows that stearin fraction increases with the increase of Reynolds number up to a value of 45, where a maximum amount of 40 wt% is reached. Further increase of Re decreases the amount of stearin adhering on the outer surface of the crystallization tube. The yield of sweat fraction remained essentially constant and represented about 2 to 4 wt% of total AMF, regardless of the Reynolds number.

The difference of the dropping points (ΔDP) between the stearin and olein fractions can be regarded as an indicator of AMF fractionation efficacy. The higher this difference, the better is the fractionation, and the greater is the effectiveness of separation between the two fractions. In the AMF fractionation by the FFLC process, the Re number appears to have a significant effect on the separation efficiency. Strong differences in dropping points (DP) are obtained when Re does not exceed 15 (Fig. 4). An excellent separation between olein and stearin fractions is obtained at Re $\approx$ 12. Beyond Re $=$ 15, fractionation is less effective; the loss of fractionation

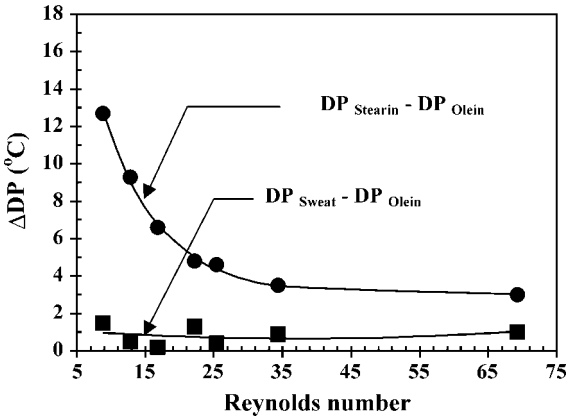

Figure 4. Effect of Reynolds number on separation efficiency.

efficacy is attributable to higher shearing forces on the crystals causing attrition and occlusion of mother liquor in the crystal matrix. In addition, the contact time between the melt and the crystallizer surface is reduced to allow solidification of the supercooled triglycerides in the desired crystal format for efficient separation of the stearin from the crystal suspension. The stearin fraction increased with the increase of Re up to 45 (see Fig. 3), whereas the efficiency of separation decreased. The *ΔDP* between the sweat fraction and the olein fraction was not affected by the increase of Re. The dropping point (DP) of sweat fraction varied between 32 and 33°C and was close to the *DP* of the whole milk fat.

Effect of Crystallization Temperature

The effect of crystallization temperature on the yield of stearin fraction and the separation effectiveness, measured by *ΔDP*, was studied by varying the crystallization temperature, T_C, in the range of 28 to 32°C. The choice of this range was based on the cooling curves of the AMF at different cooling rates (0.1 to 0.5°C/minute). The cooling curves showed that T_C could be located in a narrow interval of 29 to 31°C. The Re number was maintained constant at 12 during all these experiments. Figures 5 and 6 show that crystallization temperature had a significant effect on the stearin fraction yield, as well as separation efficiency. The increase of crystallization temperature enhanced separation efficiency and crystal purity, while it

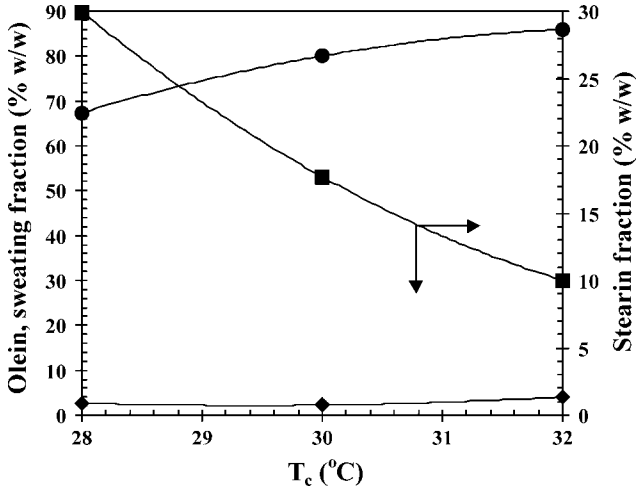

Figure 5. Effect of the crystallization temperature on the yields of fractions. Symbols: ■ stearin fraction; ● olein fraction; ◆ sweat fraction.

adversely affected the stearin yield. A high degree of separation between olein and stearin fractions was obtained at $T_C = 32$°C, with ΔDP value of about 17°C. However, the yield of stearin fraction adhered to the crystallization tube was low, with a yield of 10 wt%. It appears that T_C of 30°C is a good

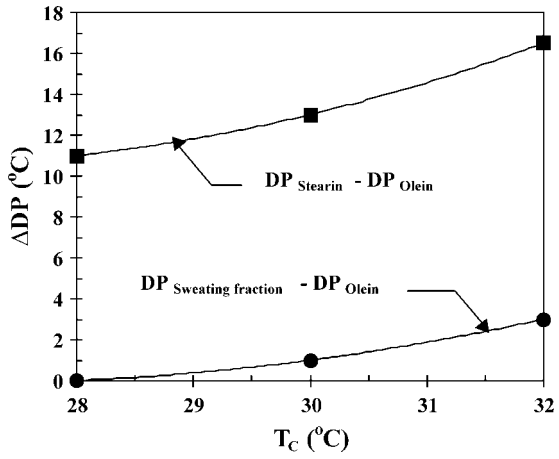

Figure 6. Effect of the crystallization temperature on separation efficiency.

compromise between an acceptable stearin yield and good separation efficiency. At this crystallization temperature, the yield of stearin fraction was 18 wt% and ΔDP of nearly 13°C. The yield of sweat fraction remained constant and was 2 to 3 wt% of the original milk fat. In all cases, the DP of the sweat fraction was close to the DP of the whole milk fat. Nevertheless, a more pronounced difference existed in the melting characteristics between olein and sweat fractions at higher crystallization temperatures. At $T_C = 32$°C, the DP of sweat fraction was 3°C higher than that of the olein fraction, while at $T_C = 28$°C, the sweat and olein fractions are more or less the same. This indicates that purer olein can be obtained at higher T_C.

Effect of the Sweating Temperature

The product purity is greatly affected by the amount of melt that remains on or in the crystals matrix. The sweating step is necessary to improve the purity of the achieved products. Runs were carried out at different sweating temperatures ranging from 36 to 39°C. When the sweating temperature increased, the separation efficiency increased, while the stearin yield decreased and tended to stabilize at T_S values between 37 to 38°C, before decreasing again at $T_S > 38$°C (Fig. 7). This is attributable to the impurities of low-melting triglycerides being stripped off from the crystal matrix, lowering the solid fraction yield.

Comparison Between FFLC and SC Fractionation Processes

Comparative studies of milk fat fractionation by FFLC and the well-established suspension crystallization[14] were made in terms of stearin yield and difference in the dropping points of the obtained fractions. The FFLC is comparable to the SC process in terms of stearin yield. A very slight difference was observed between the two processes in terms of separation efficiency, where a relatively narrow improvement in separation was obtained with the FFLC process. These observations were also verified with the solid fat content (SFC) profile of the fractions from the two processes. Figure 8 shows the SFC of stearin and olein fractions obtained from the FFLC and the SC processes relative to the SFC of native milk fat. Stearin fractions obtained from both processes were richer in solid fat, with high-melting triglycerides, than the original milk fat and olein fractions.

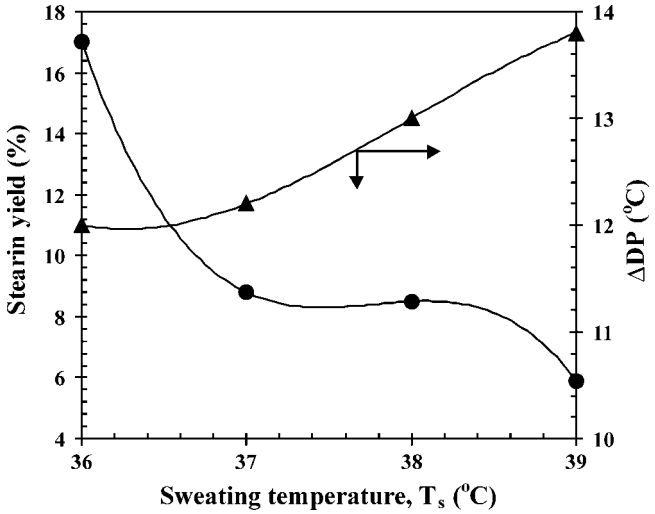

Figure 7. Effect of the sweating temperature on stearin purity.

Comparative analyses of triglyceride and fatty acid compositions of different fractions achieved by the two crystallization processes are presented in Tables 1 and 2. The short- (C18 to C32) and medium- (C34 to C40) chain triglycerides are more concentrated in olein fractions, while the long- (C42 to C54) chain triglycerides were more abundant in the stearin fractions for both the processes. Falling film crystallization exhibits a higher concentration of long-chain triglycerides in the stearin fraction and a lower concentration of short-chain triglycerides in the olein fraction in comparison to suspension crystallization. This confirms the observations made previously based on dropping points and solid fat contents. Similar trends were also evident in the fatty acid composition (see Table 2).

The melting behavior of milk fat, olein, and stearin fractions for both crystallization processes is depicted in Fig. 9. For both crystallization processes, the melting behavior of stearin fraction differs markedly from that of the whole milk fat and olein fraction. The melting curve of the stearin fraction from the FFLC process showed a large-peak melting temperature at 45°C, indicating the presence of very high-melting triglycerides. Identical behavior was noted for the SC process, except that the peak melting temperature of the stearin fraction was at 40°C. The olein fractions from both the processes also exhibited similar melting profiles, with a peak melting point of 20°C, corresponding to medium-melting

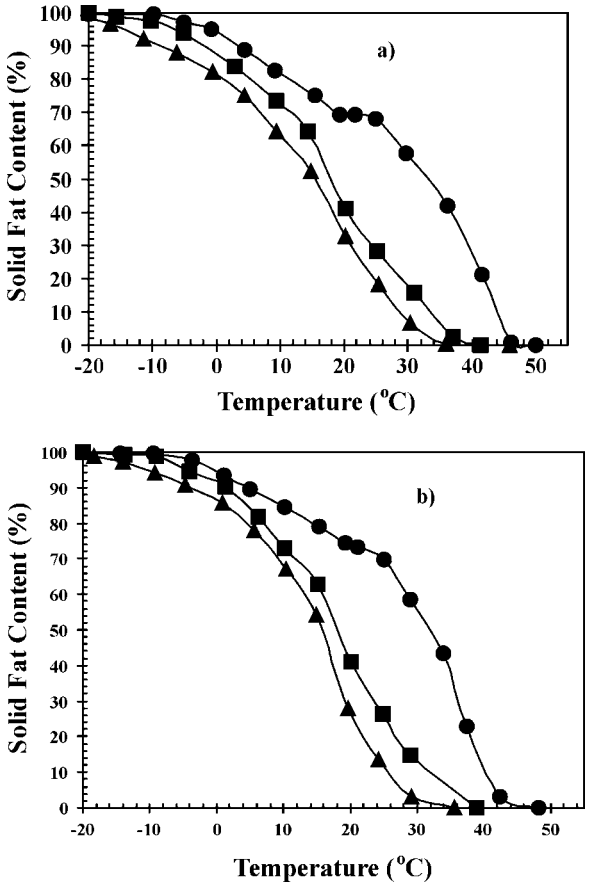

Figure 8. Solid-fat content of milk fat and fractions obtained by a) FFLC process; b) SC process. Symbols: ● stearin; ■ milk fat; ▲ olein.

triglycerides of milk fat. Melting curves of milk fat, olein, and stearin fractions show a broad, low-temperature melting triglycerides between −20°C and 10°C, with peak melting at 10°C. These melting curves show clearly that milk fat is fractionated into two distinct fractions, which differ markedly in their physical and melting characteristics. The fractionation capacity of both crystallization processes is comparable as shown by the melting behavior of the obtained fractions. This was also observed for other organic feedstock.[28]

Table 1. Triglyceride composition of milk fat and fractions obtained by FFLC and SC processes.

	FFLC		SSC		
Triglycerides (molar %)	Olein	Stearin	Olein	Stearin	Milk fat
<C18–C23	0.78	0.68	0.64	0.76	0.47
Cholesterol	0.6	0.04	0.78	0.32	0.04
C24–C32:0	6.57	4.72	12.28	7.31	5.03
C34–C42:0	35.05	26.46	37.13	31.37	29.74
C44–C54:0	9.09	24.84	4.53	19.45	22.13
C34–C42:1	18.91	14.45	15.61	11.94	12.84
C34–C42:2	2.31	1.8	2.76	2.31	1.49
C44–C54:1	16.73	16.86	11.85	14.54	19.59
C44–C54:2	7.03	6.48	6.48	7.56	5.67
C40–C54-Poly.	4.14	3.9	2.38	4.44	3.25
C34–C36–C38	26.11	18.61	30.12	23.41	20.44
C40–C42–C44	8.82	6.85	8.79	12.22	6.62

CONCLUSION

Falling film layer crystallization is a flexible and promising technique for milk fat fractionation. The flow characteristic (Re) affects product yield and quality. Higher product purity was achieved at low Re (5 to 15), while stearin yield increased at higher Re (35 to 55). The suitable crystallization

Table 2. Fatty acid composition of milk fat and fractions obtained by FFLC and SC processes.

	FFLC		SSC		
Fatty acid (molar %)	Olein	Stearin	Olein	Stearin	Milk fat
Long chain (C14–C20)	73.97	79.11	68.36	73.93	76.36
Medium chain (C10, C12, C13)	8.25	7.34	9.95	9.33	7.59
Short chain (C4 to C8)	17.78	13.55	21.69	16.74	16.04
Saturated	75.55	79.73	78.95	82.86	75.83
Unsaturated	24.45	20.27	21.05	17.14	24.17

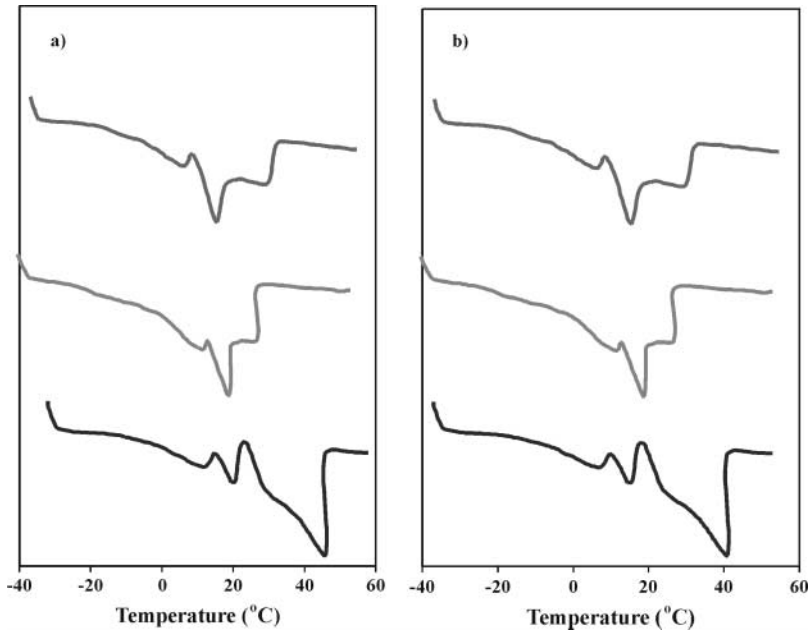

Figure 9. Melting behavior of milk fat and fractions obtained by a) FFLC process; b) from SC process.

temperature for AMF fractionation ranged between 29 and 31°C by FFLC. A crystallization temperature of 30°C was found optimum between stearin yield and separation efficiency. A sweating step at a temperature of 36°C was found useful post-crystallization treatment to enhance the purity of the stearin fraction. Falling film layer crystallization and SC processes were comparable in terms of solid (stearin) yield as well as physicochemical properties of the fractions.

ACKNOWLEDGMENTS

Agropur Cooperative agro-alimentaire (Quebec), Natural Sciences and Engineering Research Council of Canada, and Dairy Farmers of Canada provided funds for this research. The authors wish to thank J. P. Lyonnais and R. Meilleur for their experimental help and C. Ngo-Do and E. Toussignant for the triglyceride and fatty acid analyses.

REFERENCES

1. Feldman, E.B.; Kris-Etherton, P.M.; Kritchevsky, D.; Lichtenstein, A.H. ASCN/AIN task force on *trans* fatty acids, position paper on trans fatty acids. Reproduced from Am. J. Clin. Nutr. **1996**, 63, 663–669.
2. Rozendaal, A. Interesterification of oils and fats. In *Edible Fats and Oils Processing: Basic Principles and Modern Practices*; Erickson, D.R., Ed.; American Oil Chemists Society: Champaign, IL, 1990; 152–166.
3. Arul, J.; Boudreau, A.; Makhlouf, J.; Tardif, R.; Grenier, B. Distribution of cholesterol in milk fat fractions. J. Dairy Res. **1988a**, *55*, 361–371.
4. Arul, J.; Boudreau, A.; Makhlouf, J.; Tardif, R.; Belavia, T. Fractionation of anhydrous milk fat by short path distillation. J. Am. Oil Chem. Soc. **1988b**, *65*, 1642–1646.
5. Arul, J.; Boudreau, A.; Makhlouf, J.; Tardif, R.; Sahasrabudhe, M.R. Fractionation of anhydrous milk fat by supercritical carbon dioxide. J. Food Sci. **1987**, *52*, 1231–1235.
6. Rizvi, S.H.H.; Lim, S.; Nikoopour, H.; Singh, M.; Yu, Z. Supercritical fluid processing of milk fat. In *Engineering and Food, Vol. 3, Advanced Processes*; Spiess, W.E.L., Schubert, H., Eds.; Elsevier Applied Science: New-York, 1990; 145–150.
7. Bhaskar, A.R.; Rizvi, S.S.H.; Harriott, P. Performance of a packed column for continuous supercritical carbon dioxide processing of anhydrous milk fat. Biotechnol. Prog. **1993a**, *9*, 70–74.
8. Bhaskar, A.R.; Rizvi, S.S.H.; Sherbon, J.W. Anhydrous milk fat fractionation with continuous countercurrent supercritical carbon dioxide. J. Food Sci. **1993b**, *58*, 748–752.
9. Tirtiaux, F. Le fractionnement industriel des corps gras par cristallisation dirigée- procédé tirtiaux. Oléagineux **1976**, *31*, 279–285.
10. Tirtiaux, A. Dry fractionation. A proven technology. Lipid Technol. **1989**, *1* (1), 17–20.
11. Deffense, E. Milk fat fractionation today: a review. J. Am. Oil Chem. Soc. **1993**, *70*, 1193–1201.
12. Matsuoka, M.; Fukuda, T.; Takagi, H.; Takiyama, H. Purification of organic solid solutions by melt crystallization: comparison between layer and suspension crystallization. J. Crystal Growth **1996**, *166*, 1035–1039.
13. Grall, D.S.; Hartel, R. Kinetics of butterfat crystallization. J. Am. Oil Chem. Soc. **1992**, *69*, 741–747.
14. Yang, F.Z.; Bacca-Diaz, R.; Shen, D.; Boudreau, A.; Arul, J. Melt crystallization of long chain milk fat triglycerides. In *ACS Conference Proceedings Series, Crystal Growth of Organic Materials*;

Myerson, A.L., Green, D.A., Meenan, P., Eds.; American Chemical Society, 1996; 185–195.
15. Tiedtke, M.; Niehörter, S.; Ulrich, J.; Hartel, R.W. Separation of milk fats by solid layer crystallization. In *Proceedings of Bremen International Workshop for Industrial Crystallization (BIWIC 94)*; Ulrich, J., Ed.; 8–9 September; Verlag: Mainz-Aachen, 1994a; 32–39.
16. Tiedtke, M.; Ulrich, J.; Hartel, R.W. Multi-step fractionation of milk fat. An application for solid layer crystallization. In *Proceedings of Bremen International Workshop for Industrial Crystallization (BIWIC 94)*; Ulrich, J., Ed.; 8–9 September; Verlag: Mainz-Aachen, 1994b; 577–582.
17. Tiedtke, M.; Ulrich, J.; Hartel, R.W. Multi-step fractionation of milk fat—an application for solid layer crystallization. *13th Symposium on Industrial Crystallization Proceedings*; Toulouse France, September 16–19; 1996; Vol. 2, 577–582.
18. Erjawetz, S.P.; Ulrich, J.; Tiedtke, M.; Hartel, R.W. Milk fat fractionation by solid-layer melt crystallization. J. Am. Oil Chem. Soc. **1999**, *76* (5), 579–584.
19. Wynn, N.P. Separate organics by melt crystallization. Chem. Eng. Prog. **1992**, *88*, 52–60.
20. Wynn, N.P. Crystal clear without solvents. Processing **1990**, *August/September*, 19.
21. Jingkang, W.; Qiuxiang, Y.; Jianjun, J.; Xiang, Z. Melt crystallization in a falling liquid film. In *Proceedings of Bremen International Workshop for Industrial Crystallization (BIWIC 94)*; Ulrich, J., Ed.; 8–9 September; Verlag: Mainz-Aachen, 1994; 693–698.
22. Breeding, C.J.; Marshall, R.T. Crystallization of butter oil separation by filter-centrifugation. J. Am. Oil Chem. Soc. **1995**, *72*, 449–453.
23. Freeman, R.R. *High Resolution Gas Chromatography*; Hewlett Packard: Avondale, PA, 1981.
24. Taitler, H.; Prévot, A. Séparation des triglycérides en fonction de leur insaturation par chromatographie en phase gazeuse sur colonnes capillaires de verre. Rev. Fse. Corps Gras **1981**, *6*, 263–272.
25. Luddy, F.E.; Barford, R.A.; Herb, S.F.; Magidman, P. A Rapid and quantitative procedure for the preparation of methyl esters of butteroil and other fats. J. Am. Oil Chem. Soc. **1968**, *45*, 549–552.
26. Timms, R.E. The phase behaviour and polymorphism of milk fat, milk fat fractions and fully hardened milk fat. Aust. J. Dairy Technol. **1980**, *35*, 47–53.
27. Kaylegian, K.E.; Lindsay, R.C. Milk fat fractionation technologies. In *Handbook of Milkfat Fractionation Technology and Application*;

Kaylegian, K.E., Lindsay, R.C., Eds.; AOCS Press: Champaign, IL, 1994; Chap. 2, 39–79.

28. Guardini, R.; Neiro, S.M.S.; Bulan, H.; Ulrich, J. Experimental comparison and simulation of static and dynamic solid layer melt crystallization. Chem. Eng. Sci. **2001**, *56* (7), 2371–2379.