Fractionation of Anhydrous Milk Fat by Short-Path Distillation

Joseph Arul[a], Armand Boudreau[a,*], Joseph Makhlouf[a], Rene Tardif[a] and Tony Bellavia[b]
[a]Département de Sciences et Technologie des aliments and Centre de recherche en nutrition, Université Laval, Québec, Québec, Canada G1K 7P4, and [b]The Pfaudler Co., Rochester, NY 14692

Anhydrous milk fat was fractionated by short-path distillation into four fractions at temperatures of 245 and 265 C and pressures of 220 and 100 μm Hg. Two fractions (LF1 and LF2) were liquid, one fraction (IF) was semi-solid and one fraction (SF) was solid at room temperature. The fractions were characterized by melting temperature profile, solid fat index and triglyceride and fatty acid compositions. The peak melting temperature progressively increased (8.8 to 38.7 C) from liquid to solid fractions. The solid fat content ranged from 0 to 27.5% at 20 C, while native milk fat was 15.4%. The short chain (C24-C34) triglycerides were enriched in the LF1 fraction, long chain (C42-C54) triglycerides were concentrated in the SF fraction, and medium chain (C36-C40) triglycerides in the IF fraction; in the LF2 fraction, though, both short and medium chain triglycerides were enriched. Short chain (C4-C8) fatty acids gradually decreased from liquid to solid fractions and the trend was reverse for long chain (C14-C18) fatty acids, both saturated and unsaturated. The weight average molecular weights and geometric mean-carbon number of milk fat fractions were in the range of 590.7-782.8 and 31.9-46.3, respectively, compared to 729.3 and 41.0, respectively, for native milk fat, suggesting short-path distillation effects a very high degree of molecular weight separation.

Milk fat has been used traditionally for the most part as butter, being the most important fat product in the dairy industry. Milk fat with its great variety of fatty acids is a mixture of triglycerides of a range of molecular weights and degree of unsaturation, exhibiting a broad and variable melting range (1). The pleasing flavor of milk fat is among its most important advantages. However, its unique physical characteristics, especially its melting characteristics, do not suit it to a number of food-fat applications. Fractionation of milk fat into liquid and solid fat fractions which differ markedly from one another in chemical composition and physical characteristics shall facilitate an increased utilization of milk fat in specialty food products such

TABLE 1

Composition[a] of Milk Fat and Vapor Pressure—Temperature[b] Relationship of its Components

Lipid class	Concentration (%)	Vapor pressure (mmHg) and temperature (°C)
Glycerides		
Triglycerides (TG)	97–98	
Short-chain TG (C24-C34)	(12.6)	0.4200–0.0064 @ 210
Medium-chain TG (C36-C40)	(35.4)	0.0215–0.0080 @ 235
Long-chain TG (C42-C54)	(52.0)	0.0190–0.0033 @ 260
Diglycerides	0.26 –0.59	1 @ 213–283
Monoglycerides	0.016 –0.038	1 @ 175–211
Neutral glyceryl ethers	0.016 –0.020	—
Free fatty acids	0.10 –0.44	1.0 @ 25–176
Phospholipids	0.8 –1.0	—
Sterols	0.22 –0.41	0.5 @ 233
Squalene	0.007	1.70 @ 280
Carotenoids (incl. Vit. A)	0.0007–0.0009	—
Vitamins		
Vitamin E	0.0024–0.0050	0.1 @ 220
Vitamin K	0.0001–0.0005	0.001 @ 145
Vitamin D	0.8–2.1 × 10^{-6}	sublimes @ 135
Volatiles		
Methyl ketones	0.0276[c]	10.0 @ 17 to 167
Lactones	0.0176–0.212[c]	1.0 @ < 187
Aldehydes and others	0.0636[c]	—

[a]Composition, adapted from Kurtz (9).
[b]Vapor pressures of triglycerides from Perry et al. (8) and others from Weast and Astle (10) and Lange (11).
[c]Potential concentration.

*To whom correspondence should be addressed.

as convenient (e.g., frigo-spreadable) and dietetic (e.g., short and medium chain-triglyceride enriched or cholesterol-reduced) butter types. Differences in molecular weight, melting temperature (molecular weight and entropy of fusion), volatility and intermolecular interaction energy of constituent triglycerides provide the basis for separation of milk fat triglycerides.

Short-path distillation is a relatively known process and consists of evaporation of molecules into a substantially gas-free space, e.g., vacuum. The controlling factor is the rate at which the molecules escape from the heated surface of the distilling liquid and are received by the cooled condenser surface. Hickman (2,3) has reviewed in depth, the principles, technology and scope of high vacuum short-path distillation and equipment design. Stripping of vitamins A and E, sterols and volatiles from natural oils and separation of mono- and diglycerides and fatty acids are applications related to food (4), besides chemical and pharmaceutical areas. Forss and Holloway (5) and Stark et al. (6) have applied molecular distillation to recover volatile compounds from butteroil. Bracco (7) used molecular distillation to reduce cholesterol content in milk fat.

Milk fat, being a mixture of triglycerides differing in molecular weights (470-890), volatility (8) and intermolecular interaction energies, is an ideal candidate to effect separation of triglycerides by short-path distillation. There are other relatively volatile, minor constituents in milk fat, besides triglycerides (Table 1). Short-path distillation offers simultaneously an opportunity to strip sterols, mono- and diglycerides, and vitamins and flavor compounds (aldehydes and lactones) from milk fat. Short-path distillation of triglycerides which have high boiling points can sometimes be viewed with pessimism due to the requirement of high temperatures. Triglycerides can decompose or polymerize, particularly those with high unsaturation even when distilled under high vacuum. However, this thermal hazard can be minimized by reducing the time of thermal exposure, as achieved by wiped-film evaporator or centrifugal stills. Hickman and Embree (12) introduced the concept of decomposition hazard, D, defined as the product of time, t, in sec and pressure, P, in μm Hg, which is expressed as logD or Dh. For example, natural vitamin D will decompose above Dh = 1 and crude and refined oils above Dh = 3 and 4, respectively. Milk fat fractionation is a good application of this technique, provided thermal decomposition hazard requirements are met for safe distillation of the compounds.

The purpose of this study was to determine the feasibility of fractionation of anhydrous milk fat into fractions, differing from one another in molecular weights and physicochemical characteristics.

EXPERIMENTAL

Commercial grade butteroil (AgroPur Coopérative Agro-Alimentaire, Granby, Quebec, Canada) was used after removal of protein residues by centrifugation of melted milk fat at 55 C for 20 min at 1000 × g.

Distillation. Short-path distillation of milk fat triglycerides was carried out in a high vacuum wiped film pilot scale evaporator (The Pfaudler Co., Rochester, New York). The evaporator is an agitated thin film evaporator which uses rotating slotted wiper blades that spread the feed material into a uniform thin film. The slots in the wipers provide a pumping action to move the film down the heated wall with constant agitation. The rapid and positive action of the wiper blades in moving the residue down and off the heated wall controls the residence time to about one sec. Vaporized material passes through the entrainment separator and condenses on the internal U-bundle condenser, and noncondensables flow out through the vapor outlet. The pilot unit had 0.1115 m^2 evaporation surface and 0.15 m^2 of condensing surface and was fitted with

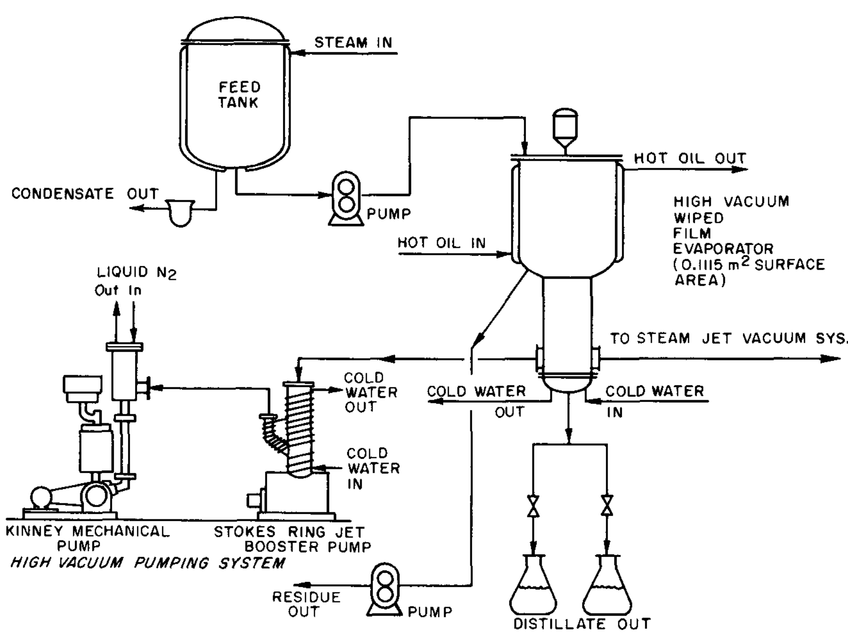

FIG. 1. Equipment flow chart.

TABLE 2

Experimental Conditions of Short-Path Distillation of Milk Fat

Process step	Feed Temp. (°C)	Feed rate (kg/hr)	Distillation conditions Temp. (°C)	Pressure (μm Hg)	Distillate Rate (kg/hr)	% Feed	% Total	Mass transfer rate (kg/m².hr)	Residue Rate (kg/hr)	% Feed	% Feed	Temp. (°C)
Degassing and dehydration	90	—	93	700	—	—	—	—	—	—	—	—
Distillation I	90	43.20	245	220	0.91	2.1	2.1	8.16	42.38	97.9	97.9	227
Distillation II	90	26.40	245	100	2.56	9.7	9.5	22.42	23.83	90.3	88.4	227
Distillation III	100	14.91	265	100	5.45	36.6	32.0	48.88	9.45	63.4	56.4	247

a Chevron type entrainment separator between the evaporator and condenser, which were 3.5 cm apart. The equipment flow chart is shown in Figure 1.

Milk fat was melted under nitrogen blanket and then vacuum distilled (93 C and 700 μm Hg) to dehydrate and degas the fat. Subsequently, the milk fat was distilled in three steps at temperatures of 245 and 265 C and pressures of 220 and 100 μm Hg. The desired pressures were reached by varying the feed rates. The experimental conditions of distillation are presented in Table 2. The pressures of the still were adequately low to effect thermal hazard free distillation of the triglycerides.

Analytical methods. The native anhydrous milk fat and its fractions were analyzed for their melting point profile, solid fat index and triglyceride and fatty acid compositions. Melting curves were performed on a Dupont model 990 thermal analyzer (DuPont Instruments, Toronto, Ontario) by the method of Timms (13). Solid fat index was determined by dilatometry as described by Jasperson and McKerrigan (14). A correction factor for thermal expansion of 4.25 μl/5 C/g fat was applied as proposed by Riel (15). The triglyceride and fatty acid compositions were determined by gas chromatography as described previously (16).

RESULTS AND DISCUSSION

Four fractions of milk fat were obtained by distillation; their yields are presented in Table 3. Fractions LF1 and LF2 were liquid at room temperature, and fractions IF and SF were semi-solid and solid, respectively.

The thermograms show differences between fractions and native milk fat in their melting point distribution (Fig. 2). Three major melting zones of milk fat, corresponding to liquid (low temperature melting), intermediate and solid (high melting point) portions, were gradually repartitioned in different proportions of liquid to solid in the fractions, going from LF1 to SF. Fraction LF1 was composed entirely of the liquid portion of the milk fat with two peak melting points at -1 C and 8.8 C. Fraction LF2 was composed of liquid and intermediate portions with peak melting point at 12.5 C. Fraction IF was greatly increased in the intermediate portion of the milk fat with a peak melting point at 18.8 C. Fraction SF was composed largely of the solid portion with peak melting point in the range of 30-39 C, with small proportions of liquid and intermediate melting portions.

The solid fat content of the milk fat fractions as a function of temperature is presented in Figure 3. Fraction SF was composed of higher solid fat than the native milk fat. The solid fat content of the fractions progressively decreased from fraction SF to LF1, while fraction LF1 had no solid fat at 15 C.

The triglyceride composition (acyl carbon number) and the distribution of triglyceride groups in various fractions are presented in Table 4. The short chain (C24-C34) triglycerides formed the major portion of the LF1 fraction, and they were almost absent in the SF fraction, which was rich in long chain triglycerides (C42-C54). The LF2 fraction was more concentrated in both short chain and medium chain (C36-C40) triglycerides, while the IF fraction was enriched in medium chain triglycerides.

Table 5 shows the fatty acid composition of milk fat and its fractions. The short chain (C4-C8) and medium chain (C10-C12) fatty acids gradually decreased going from fraction LF1 to SF, and this was reversed for long chain (C14-C18) fatty acids, both saturated and unsaturated. The gradual increase in the concentration of unsaturated long chain fatty acids from liquid fraction to solid is contrary to that observed in the

TABLE 3

Yield of Various Milk Fat Fractions by Short-Path Distillation

Fraction (F)	Appearance at room temperature	Yield (%)
Liquid (L)		
LF1 (Distillate I)	Liquid	2.1
LF2 (Distillate II)	Liquid	9.5
LF[a]	Liquid	11.6
Intermediate (I)		
IF - (Distillate III)	Semi-solid	32.0
Solid (S)		
SF Residue	Solid	56.4

[a]Total liquid fraction.

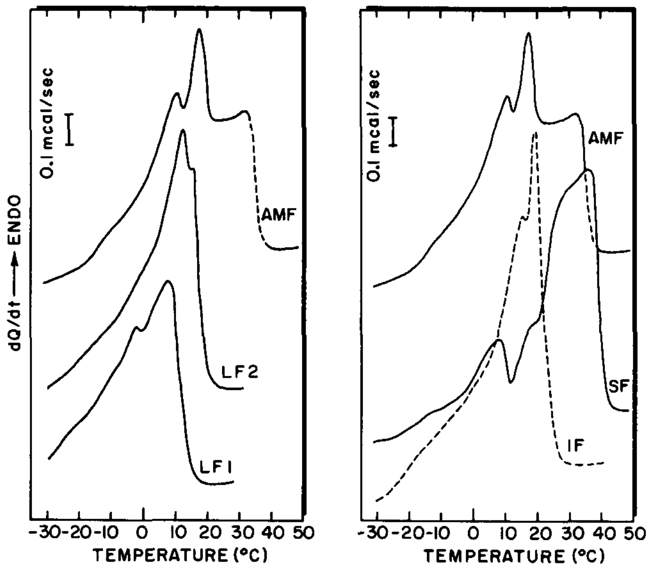

FIG. 2. Melting curves obtained by differential scanning calorimetry. AMF, anhydrous milk fat; LF1 and 2, liquid fractions; IF, intermediate fraction; SF, solid fraction.

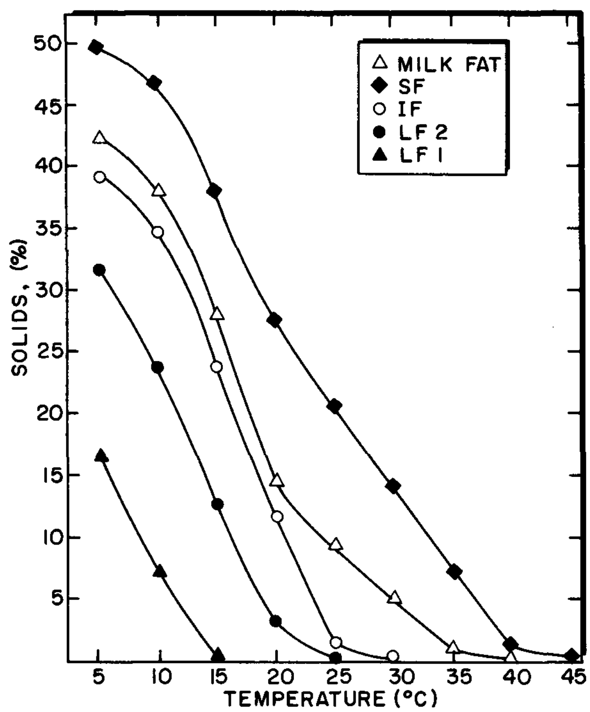

FIG. 3. Solid content of native milk fat and milk fat fractions as a function of temperature.

melt crystallization process for the fractionation of milk fat (17). This suggests a difference in the basis of separation between these two processes.

The weight average molecular weight (Mw) and the geometric mean-carbon number (GMCN) of the native milk fat and its fractions are presented in Table 6. GMCN was obtained from the square root-normal distribution plot on a probability scale. There was a gradual increase in Mw and GMCN of the fractions, going

TABLE 4

Triglyceride Composition of Native Milk Fat and Milk Fat Fractions Obtained by Short-Path Distillation (wt%)

Triglyceride carbon number	Milk fat	LF1	LF2	IF	SF
C24	0.4	8.2	1.8	0.3	0.1
C26	0.2	6.1	1.3	0.1	0
C28	0.8	10.8	3.9	0.5	0.1
C30	1.3	12.1	6.7	1.5	0.1
C32	2.6	13.5	10.3	3.6	0.3
C34	6.3	15.9	15.2	10.5	0.8
C36	12.0	14.9	22.4	22.8	3.3
C38	13.4	10.1	15.7	24.1	7.1
C40	10.2	3.7	7.2	14.4	8.9
C42	7.8	1.6	5.9	8.2	8.0
C44	6.6	0.9	1.9	4.8	8.9
C46	7.2	0.7	1.2	3.4	10.5
C48	8.5	0.6	1.7	2.7	13.1
C50	9.9	0.7	2.2	2.2	16.7
C52	8.7	0	2.9	1.0	14.8
C54	4.2	0	0.8	0	7.4
Short chain (C24-C34)	11.6	66.6	39.2	16.5	1.4
Medium chain (C36-C40)	35.6	28.7	45.3	61.3	19.3
Long chain (C42-C52)	52.9	4.5	16.6	22.3	79.4

from LF1 to SF. The average triglyceride size of the liquid, intermediate and solid fractions was not only different from that of the native milk fat, but also was close to that of short, medium and long chain triglycerides of the milk fat, respectively (Table 6). This suggested that short-path distillation effected a high degree of molecular weight separation. The difference in the volatility of triglycerides, which is the controlling principle in their separation by this process, arises from the differences in their molecular weights. The presence of double bonds in a triglyceride molecule has little influence on its vapor pressure (8). The presence of the liquid portion of milk fat in the SF fraction (Fig. 2), though it is limiting in short chain triglyceride (Table 4), may be due to the presence of unsaturated long chain triglycerides which possess high entropy of fusion. Short-path distillation is superior to melt crystallization as a process for separating of triglycerides; the latter suffers from significant overlapping of molecular weights of triglycerides (17).

Short-path distillation thus offers an excellent opportunity to obtain fractions from milk fat with distinctive chemical and physical properties. Because melting point and solid fat content are important criteria in the selection of fats and oils in the food-fat applications, fractionation of milk fat should facilitate its increased utilization. Development of frigo-spreadable butter with a high proportion of liquid fractions is another possibility. The high ratio of solid to liquid fat content of butter is probably the most important factor contributing to its hardness and poor spreadability (18). The high solid fat content is due in part to the formation of mixed crystal (1,19), which reduces the

TABLE 5

Fatty Acid Composition of Native Milk Fat and Milk Fat Fractions (mol %)

Fatty acid	Milk fat	Fractions LF1	LF2	IF	SF
C4:0	8.3	18.6	15.6	9.8	2.0
C6:0	4.0	7.3	6.3	4.9	1.5
C8:0	1.8	4.0	3.2	2.2	1.0
C10:0	3.1	6.8	5.6	4.2	2.4
C10:1	0.4	0.7	0.6	0.4	0.2
C12:0	3.8	7.3	6.1	4.2	2.8
C14:0	11.4	15.8	14.9	11.8	9.8
C14:1	1.1	1.0	0.9	0.9	1.1
NI[a]	2.8	2.8	2.5	3.0	3.3
C16:0	26.2	21.6	24.2	29.2	28.0
C16:1	1.2	0.9	1.0	1.2	1.5
NI	2.4	1.2	1.5	2.4	2.9
C18:0	10.6	3.9	5.8	8.6	13.2
C18:1	20.1	7.1	9.6	15.0	27.0
C18:2	2.0	0.7	0.9	1.5	2.4
C18:3	0.8	0.3	0.3	0.7	1.1
Short chain (C4-C8)	14.1	29.9	25.1	16.9	4.5
Medium chain (C10-C12)	7.3	14.8	12.3	8.8	5.4
Long chain (C14-C18)	78.6	55.3	62.6	74.3	90.1
Saturated	53.4	45.3	49.9	55.0	57.0
Unsaturated	25.2	10.0	12.7	19.3	33.0

[a]Not identified.

TABLE 6

Average Triglyceride Size of Native Milk Fat and Milk Fat Fractions

	Mw[a]	GMCN[b]
Native milk fat	729.8	41.0
Fraction LF1	590.7	31.9
Fraction LF2	653.1	34.8
Short chain triglycerides	584.0	32.5
Fraction IF	674.2	36.9
Medium chain triglycerides	666.8	37.2
Fraction SF	782.8	46.3
Long chain triglycerides	806.3	46.9

[a]Weight average molecular weight.
[b]Geometric mean carbon number.

liquid phase content in the fat mixture. Fabrication of butter with a high proportion of liquid fractions would improve the spreadability of butter by decreasing the solid to liquid fat content of butter, decreasing the viscosity of the dispersing phase and by lubricating the solid fat particles, which would offset the effect of mixed crystal formation (17). Development of dietetic butter enriched in short and medium chain triglycerides for dyspeptic patients (2) is possible with the high proportion of liquid and intermediate fractions obtained by this process. Stripping of cholesterol and recovery of flavoring compounds are other attractive features of this process. Semi-quantitative analysis indicated the LF1 fraction was highly concentrated in cholesterol (results not shown) compared to the native milk fat. Short-path distillation is an acceptable process, provided thermal decomposition hazard free conditions are adapted. In spite of all the positive features of the process, it may suffer from high thermal requirements; it has a low thermal efficiency because the hot evaporator faces the cooled condenser.

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