

The potential of milk fat for the synthesis of valuable derivatives

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Abstract The overall decline in milk fat consumption experienced in the last decades has promoted global research efforts seeking for alternate uses of this valuable natural fat. Milk fat possesses a pleasant flavor and a rich chemical composition, including a range of bioactive, health beneficial minor components. The main drawbacks of milk fat from the consumer point of view are its poor spreadability at refrigeration temperature and its high content in saturated fatty acids, which raises health concerns. However, the rich fatty acid composition of milk fat could be utilized for the production of a wide range of added-value derivatives in the food and cosmetic industries, including nutritionally enhanced modified fats, food emulsifiers, flavors, and tailor-made lipids. A promising strategy for the revalorization of milk fat encompasses the isolation and commercialization of the valuable minor components of milk fat, coupled with a broader utilization of physically or nutritionally improved milk fat fractions and derivative products.

Keywords Milk fat · Butter · Revalorization · Short-chain fatty acids · Milk fat engineering · Conjugated linoleic acid

Introduction

Milk from livestock has traditionally been an important element of the human diet. Milk is composed of a balanced amount of fat, protein, sugars, vitamins, and minerals [1, 2].

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The fat component of milk has been used for centuries to produce valued and nutritious food products such as butter, cream, and cheese [1, 3].

Milk fat has a complex and rich chemical composition. Its unique sensorial properties (flavor and mouthfeel) have been much appreciated historically, and its consumption was traditionally recommended [4] and associated with high living standards [3]. However, the consumption of milk fat in developed countries has been declining for the last decades, with a remarkable shift occurring since the 1980s due to the strong commercialization of margarines. The main reasons for this trend were evaluated in a US survey to be the following [3]:

- Price: milk fat is relatively expensive, unable to compete with vegetable oils as a food ingredient.
- Health image: its high content in saturated fatty acids and cholesterol is believed to increase the risk of coronary diseases and obesity.
- Limited functionality: due to its high solid fat content at refrigeration temperature, butter is poorly spreadable.
- Little product innovation and poor advertisement, in comparison with vegetable oil-based products.

The consumption decline of milk fat has led to the accumulation of milk fat stocks worldwide, which prompted global research efforts for the development of alternative uses of milk fat as a feedstock for added-value products [1, 5–7]. The current situation of the European milk fat market as well as the existing research trends and opportunities for milk fat revalorization is reviewed and discussed in this paper.

The dairy sector

Anhydrous milk fat (AMF) manufacture generally serves as a “safety valve” for the dairy industry [3], as it absorbs

excess milk supply above market requirements for other dairy products. Surplus milk is skimmed and the cream is converted consecutively to butter, butteroil, and AMF, as shown in Fig. 1. The skimmed milk is dried to produce skimmed milk powder (SMP). Upon a sudden shortage of milk supply for the manufacture of dairy products, stock AMF and SMP can be recombined and processed into the demanded products. However, even with a stationary milk supply, AMF tends to accumulate due to the imbalance between the market demands for low-fat and fat-rich products.

The European Union is a major world dairy producer [8]. About 135 million tons of dairy products are produced annually in the 27 member states of the European Union (EU-27), mostly for internal consumption (Table 1) [9, 10]. About 16% of the milk produced in EU is used for butter manufacture. Milk production is regulated by a quota system, implemented in 1984 in the frame of the Common Agricultural Policy (CAP). The quota is an effective limit on the amount of milk that dairy farmers produce every year [9], which prevents dairy overproduction and guarantees a minimum selling price of dairy products.

Fig. 1 Dairy production scheme. Adapted from [9]

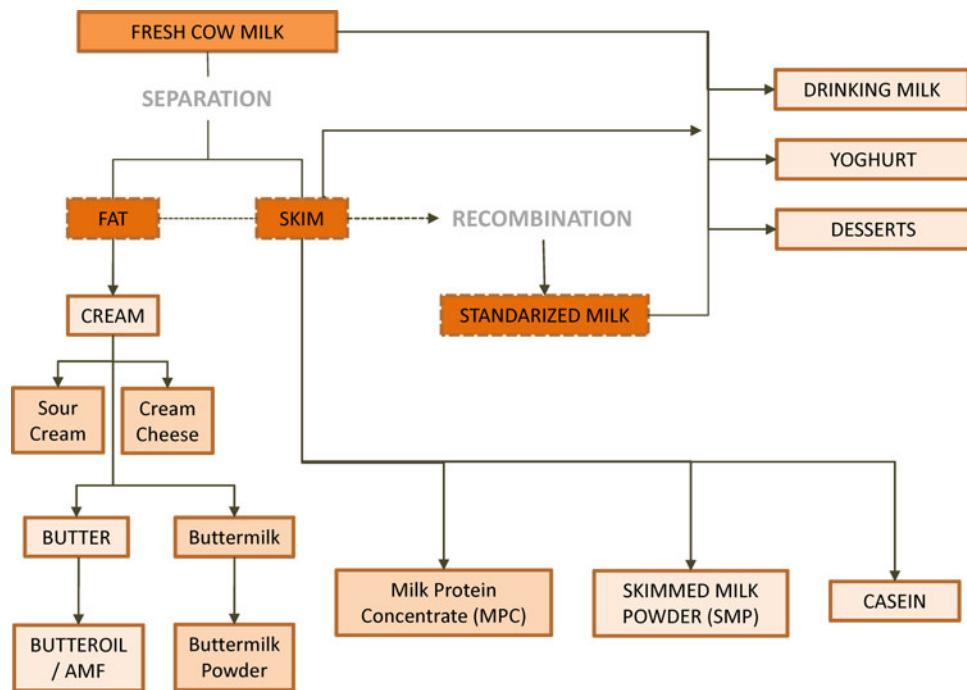


Table 1 Summary of the dairy market balances in the European Union, between 2004 and 2010 [10]

('000t)	EU Market balances						
	2004	2005	2006	2007 ^a	2008 ^a	2009 ^b	2010 ^b
	EU-25	EU-25	EU-25	EU-27	EU-27	EU-27	EU-27
Milk deliveries	130,383	131,421	130,654	133,600	134,200	134,200	134,600
Liquid milk production	33,436	33,070	33,200	33,500	33,500	33,500	33,500
Cheese	8,685	8,850	8,960	9,200	9,250	9,270	9,400
SMP	1,080	1,110	980	1,040	1,010	1,150	1,080
Butter							
Production	2,112	2,150	2,040	2,050	2,050	1,990	1,920
Imports	89	90	90	85	60	60	60 + 80 ^c
Exports	344	330	240	205	140	140	150
Consumption	1,937	1,950	1,930	1,930	1,910	1,890	1,910
Stock change	-80	-40	-40	0	60	20	0

EU-25 Data from the 25 member states of the European Union (2004–2007), EU-27 Data from the 27 member states of the European Union (from 2007), SMP skimmed milk powder, ^a Data including estimates, ^b Data including forecasts. ^c Amount proceeding from intervention

The EU is a major exporter of dairy commodities (butter, cheese, and milk powder), together with New Zealand and Australia [8]. The EU's world export share of butter was 39% in 2004. However, as the EU market price for dairy products is higher than the world price (because other major exporters produce at lower costs), exports generally take place with the support of subsidies [9].

Subsidized exports are one of the means to absorb excess butter and AMF. Other measures are aids for private storage, public intervention (purchase of surplus by the government at a set price), and internal disposal in the EU market [9]. Through the schemes for internal disposal, excess butter is given to non-profit organizations or sold at reduced prices for commercial pastry and ice-cream manufacture in competition with vegetable fats [3, 9]. The amount is significant: in 2004, 600,000 tonnes of butter was disposed in this way [9].

Table 1 shows the European market balances for milk and dairy production between 2004 and 2010, including more detailed information for butter products [10]. Although butter stocks completely disappeared in 2007 and again in 2010 (forecasted data) as a result of the above-mentioned measures, stocks are still estimated to be accumulated in 2008 and 2009. This could be a result of several factors, including a decrease in butter consumption and the elimination of export subsidies in mid-2007.

The 2003 Common Agricultural Policy reform aims to the deregulation of the dairy sector by gradually reducing export subsidies and intervention on dairy commodities. The quota system is planned to disappear by March 2015 [9, 10]. The final objective is to accomplish a self-regulated milk supply according to market demands and to align the EU milk prices with global prices. It can be foreseen that further accumulation of butter products can be an immediate consequence of the new policies. New solutions should be found for increasing milk fat consumption and for avoiding losses derived from butter disposal at prices below production costs.

In the following paragraphs, a review of the composition and potential of milk fat for the manufacture of added-value derivatives that can contribute to improve the current situation of the butter market is presented.

The potential of milk fat

Milk fat composition

Milk fat is present in bovine raw milk in concentrations of about 3.5–5 wt% [11, 12]. It is found in the form of small globules of a diameter 0.1–15 µm, coated with a membrane derived from the secreting cells [13]. About 98% of milk lipids are triacylglycerols, glycerol molecules esterified to

three fatty acids of variable chain length and saturation degree.

Many volatile and non-volatile compounds contribute to the unique flavor of milk fat, including lactones, ethyl esters, ketones, aldehydes, diacetyl, dimethyl sulfide, and free fatty acids. In addition, milk fat contains fat-soluble vitamins A, D, and E and cholesterol (0.2–0.4%). The overall composition of milk fat is significantly affected by the cow breed, the cow diet, stage of lactation, and the season [2, 3, 5]. Average values are summarized in Table 2.

The triacylglycerol composition of milk fat is the most complex from all edible fats [3, 11]. More than 100 different fatty acids have been identified, from which about 11 constitute the vast majority (Table 3) [11]. On average, milk fat contains 20 mol% short-chain fatty acids (C4–C10). Over 70% of the total fatty acids are saturated. Milk fat contains a very small amount of polyunsaturated fatty acids, yet it is the richest natural dietary source of conjugated linoleic acid (CLA). CLA, which is a group of positional isomers of linoleic acid (C18:2), has been shown to possess anticarcinogenic, antiatherogenic [11, 14, 15], and immunomodulating activities, among other health benefits [4, 16]. Recently, anti-tumoral activity has also been associated with butyric acid [4, 15–17].

The distribution of fatty acids in milk fat triacylglycerols is non-random, as indicated in Table 3. The majority of short-chain fatty acids C4–C10 are esterified in the primary positions (*sn*-1 and *sn*-3), while the middle position of the acylglycerol (*sn*-2) is mostly occupied by medium- and long-chain saturated fatty acids.

Most triacylglycerols contain 24–54 acyl carbon atoms. Due to this large variety of components, milk fat exhibits a large melting temperature range, between –30 °C and 37° [1]. Therefore, both a solid and a liquid phase are present in the temperatures normally encountered during processing and use. The solid phase forms a fine network of small crystals, which traps and holds the liquid phase by surface

Table 2 Composition of lipid fraction in bovine milk [3]

Component	Content (wt%)
Triacylglycerols	97–98
Diacylglycerols	0.3–0.6
Monoacylglycerols	0.02–0.04
Free fatty acids	0.1–0.5
Cholesterol	0.2–0.4
Phospholipids	0.2–1.0
Carotene	ppm
Flavor compounds (lactones, aldehydes, ketones)	ppm
Vitamins A, D, and E	ppm
Tocopherol	ppm

Table 3 Milk fat fatty acid composition, in mol% [11]

Fatty acid	Overall	Positional distribution		
		sn-1	sn-2	sn-3
Butyric (C4)	11.8	0	0	100
Caproic (C6)	4.6	0	7	93
Caprylic (C8)	1.9	25	12	63
Capric (C10)	3.7	17	27	56
Lauric (C12)	3.9	42	53	5
Myristic (C14)	11.2	29	52	19
Palmitic (C16)	23.9	47	45	8
Hexadecenoic (C16:1)	2.6	36	46	18
Stearic (C18)	7	49	45	6
Oleic (C18:1)	24	42	26	32
Linoleic (C18:2)	2.5	23	47	31

tension. The network structure of the solid and liquid phase is responsible for the plasticity and consistency of the fat [18].

The milk fat globule membrane (MFGM) is composed of lipids and proteins, in a ratio of approximately 1:1 by weight. Butyrophilin (40%) and xanthine oxidase (12–13%) are the main proteic components of the MFGM [13], while the lipid components include triacylglycerols (66%) and phospholipids (22%), in particular sphingomyelin, phosphatidylcholine, and phosphatidylethanolamine [11]. Both the protein and lipids of the MFGM have been associated with a variety of positive health effects, including anticarcinogenesis, antidepressant, and bactericidal activity [5, 13].

Milk fat revalorization

The success of any consumer product depends on a good balance between price, perception, and performance [3]. Milk fat is perceived by the consumers as a natural, high-quality product but its relatively high price compared to vegetable oils and fats hinders its consumption. On the other hand, the content of saturated fat and cholesterol still raises health concerns, although nowadays the weakness of the link established for many years between saturated fat consumption and hypercholesterolemia and cardiovascular disease is starting to be recognized [4, 16, 19].

Saturated fats play a key role in providing structure to food. In this respect, one of the main drawbacks of milk fat is its limited functionality, related to the consistency of the fat at range of temperatures. For example, milk fat is too firm to spread easily at refrigeration, but not firm enough for certain pastry applications [6].

In the authors' opinion, the revalorization of milk fat implies finding applications in which other fats or oils cannot compete. For this purpose, the special qualities (flavor,

texture, melting profile) or components (short-chain fatty acids, CLA, bioactive minor compounds) of milk fat have to be exploited.

Different approaches can be considered for the revalorization of milk fat:

- enhancing the nutritional or functional performance of milk fat, while maintaining its inherent qualities (milk fat engineering).
- producing added-value food or cosmetic ingredients by isolation or modification of major milk fat components
- isolating and commercializing the high-value minor components of milk fat

Hettinga [3] suggested that the success of milk fat revalorization relies on finding a large number of relatively small outlets for milk fat derivatives and/or innovative applications. This approach was applied with considerable success to the protein fraction of milk [3]. The health beneficial molecules of milk fat (MFGM components, CLA) could be isolated for commercialization or concentrated further in milk fat products. Although the potential commercial value of the minor components can be very high, only the usage of major components can lead to the reduction of butter stocks. Commercialization of minor components would however contribute to raising the value of milk fat, thus allowing using the major part of the fat in lower value applications.

Table 4 shows an overview of the different products and application fields of milk fat, milk fat fractions, and (potential) milk fat derivatives achieved either commercially or by different research groups around the world in recent years.

Milk fat engineering

Improving the performance of milk fat, both in nutritional and in physical terms (spreadability), is a promising area for research. Milk fat engineering concerns the modification of the fat structure or composition in order to achieve better properties of food products containing or composed of milk fat [1].

Currently, the major trends in milk fat engineering involve its physical or chemical modification, or altering the diet of the cow. Modification of the cow's diet, by introducing polyunsaturated oils or other dietary supplements, is a technique with relative success [5, 17]. Milk fat with a lower content of saturated fatty acids or enriched in CLA has been obtained from cows under special feeding regimes. For example, farmers in Ireland are producing milk for the manufacture of a naturally spreadable butter [5].

In the next paragraphs, only the "downstream" modification of milk fat (after separation from milk) will be discussed.

Table 4 Overview of common and (potential) alternative uses of milk fat

Product category	Product/application	Milk fat component/fraction	Modification technique	Additional component	Key factor exploited/improved	Reference
Specialty (food) ingredients	Buttery/cheese flavor concentrates	Flavor components, short-chain fatty acids	Hydrolysis Extraction		Sensory qualities	[1, 3, 5, 22, 24, 38, 40, 41]
	Milk fat for pastry, confectionery	HMF	Fractionation		Physical functionality	[1, 3, 6, 23]
	Milk fat for bakery	LMF	Fractionation			[1, 3, 6, 23]
	Food emulsifiers (MAG/DAG)	AMF	Hydrolysis, alcoholysis			[1, 39, 41]
	Edible films/coatings	HMF	Fractionation, encapsulation			[41, 42]
	Cosmetic emollients	AMF				
	Infant formula	AMF, HMF	Transesterification	PUFA concentrates	Nutritional properties	[41]
	Infant formula	Cholesterol	Extraction	Fish oils		[35]
	Nutraceuticals	MFGM, CLA, vitamins	Various		Bioactivity	[14, 32, 44, 45]
	Cold spreadable butter	HMF, LMF, AMF	Melt crystallization + blending Mechanical work		Physical functionality	[1, 3, 6, 23, 24, 26]
Enhanced table spreads	High-oleic butter	AMF	Temperature profiling of cream Interesterification	Oleic acid High-oleic vegetable oils	Improved nutritional properties	[27]
	PUFA-enriched butter	AMF	Acidolysis	PUFA concentrates		[26, 28–32]
	DAG-based butter	AMF		Vegetable oils		
	Fatty acid reservoir	Short-chain fatty acids CLA	Glycerolysis, alcoholysis Hydrolysis, alcoholysis		Nutritional properties/ bioactivity	[33, 34]
						[41, 43]

AMF Anhydrous milk fat, CLA conjugated linoleic acid, DAG diacylglycerol, HMF high-melting milk fat fraction, LMF low-melting milk fat fraction, MAG monoacylglycerol, MFGM milk fat globule membrane, PUFA polyunsaturated fatty acids

Physical modification Physical modification of milk fat involves mainly the improvement of spreadability [3]. This can be achieved by different techniques, including mechanical work (texturization), temperature profiling, blending with other oils, or fractionation [3, 6].

Fractionation consists of creating milk fat fractions with different melting point and crystallization patterns [1, 20]. Melt crystallization is the most developed fractionation technique, and it is widely applied commercially [3]. The low-melting and high-melting milk fat fractions produced by melt crystallization differ in the fatty acid composition of their triacylglycerols. Short-chain and unsaturated fatty acids predominate in the low-melting fractions and vice versa [21]. Short-path distillation and supercritical carbon dioxide fractionation have also been investigated. With these techniques, the separation is based on the difference in the molecular weight of triacylglycerols, rather than on their melting point differences [7, 22].

Nowadays, about 800 tonnes per day of milk fat is fractionated worldwide [23]. In general, all fractionation techniques yield milk fat fractions of similar functionality, but high-melting fractions that retain the flavor of milk fat can only be produced by melt crystallization [22]. Since short-, long-, saturated and unsaturated fatty acids are mixed in milk fat triacylglycerols, complete separation of fatty acid species is not possible by physical fractionation only.

Reduction of cholesterol was also an active area of research in the 1980s. However, it is nowadays recognized that the contribution of dietary cholesterol to coronary diseases is minor [1, 3], which has decreased consumer demands for low-cholesterol products.

Chemical or enzymatic modification Interesterification using chemical catalysts results in a random rearrangement of the fatty acids in the triacylglycerols. This has an impact on the melting profile of milk fat, resulting in more spreadable products. However, the nutritional properties of the fat might be also affected by the rearrangement of fatty acids in the glycerol *sn* positions [12]. In addition, the loss of the natural milk fat flavor in the process hinders the application of this technique [3, 24].

Lipase-catalyzed modification reactions are milder than chemically catalyzed reactions and have a lower tendency to affect the natural milk fat flavors. These have been mainly oriented to (a) releasing or concentrating flavor components by hydrolytic or transesterification reactions [1, 25] and (b) improving the nutritional properties of milk fat [24, 26–34]. From a nutritional point of view, the goal is generally reducing the content of the generally believed hypercholesterolemic saturated fatty acids (C12–C16) and/or increasing the content of (poly)unsaturated fatty acids without altering the sensory properties of milk fat. To this end, several lipase-catalyzed (trans-) esterification reactions

have been investigated. Some researchers found that lipase-catalyzed interesterification resulted in better spreadability of milk fat, but had the adverse effect of producing a wax-like mouthfeel [24]. Transesterification of milk fat with vegetable oils (soybean, rapeseed, corn) or with polyunsaturated fatty acid concentrates has been studied for producing physically or nutritionally enhanced spreads [26–32]. The obtained products were richer than milk fat in unsaturated fatty acids and also softer, spreadable at cold temperatures [26].

The natural structure of milk fat triacylglycerols, mostly containing a long-chain saturated fatty acid in the *sn*-2 position, makes it appropriate for the synthesis of human milk substitutes (HMS), by incorporation of polyunsaturated fatty acids in the *sn*-1,3 positions. This has been achieved by acidolysis using selective lipases [35].

Nevertheless, commercial production of interesterified or transesterified milk fat has not been realized so far. Milk and milk products enriched in oleic acid or PUFA exist in the market, but those are produced merely by blending with vegetable or fish oil concentrates. Lipase-catalyzed production of nutritionally improved oils and fats at industrial scale is limited to the production of structured lipids of vegetable origin, namely the human milk substitute Betapol®, cocoa butter replacers, and diacylglycerol-based oils [36–38]. The relatively high cost of specific lipases is still one of the major impediments for the development of such processes.

Use of major components

Butter and cheese flavor Production or isolation of buttery and cheese flavors is an existing field of milk fat utilization. Lipolyzed milk fat or milk fat fractions develop a stronger flavor. This is often an undesired effect, consequence of humidity in the fat. However, it can be applied to create a range of cheese flavors which can be incorporated to a variety of products. Established commercial applications can be found, in particular in the ice-cream and cheese industries [1, 24, 38]. Milk fat flavor has been isolated by extraction with supercritical carbon dioxide [40].

Mono- and diglycerides Mixtures of mono- and diacylglycerols are extensively used as emulsifiers in the food industry. MAG and DAG mixtures produced from milk fat are more hydrophilic than emulsifiers derived from other oils, because short-chain fatty acids are more polar than long-chain fatty acids. The hydrophilic/lipophilic balance of milk fat mono- and diacylglycerols can be useful for certain product applications [1, 38, 39]. The synthesis of a diacylglycerol-based milk fat analog with potentially enhanced nutritional properties has also been recently investigated [34].

Fatty acids Kaylegian [41] proposed the utilization of milk as fatty acid reservoir for the production of structured lipids (SL). Structured acylglycerols contain certain fatty acids in specific positions of the glycerol molecule, which gives them special nutritional properties. The short-chain fatty acid fraction of milk fat can be used for the synthesis of medium-chain triacylglycerols (indicated for parenteral and sports nutrition), low-caloric fats (triacylglycerols containing at least one short- and one long-chain fatty acid) [37], and short-chain sucrose polyesters to be used as fat substitutes [41]. Short-chain fatty acids for the synthesis of SL are currently obtained from coconut oil fractions containing C8-C10 fatty acids or synthetically. Milk fat, with its relatively high content of C4-C10 fatty acids, appears therefore as an interesting fatty acid source for the production of SL. Recent work by the authors reports the development of a process making integrated use of lipase-catalyzed ethanolysis and supercritical carbon dioxide extraction for the isolation of a short-chain fatty acid concentrate from milk fat [42].

Use of minor components

Components of the milk fat globule membrane (MFGM)

Ongoing research exists for isolating the bioactive proteins and lipids of the MFGM [5, 44]. Micro- and ultrafiltration, coagulation, and solvent- or supercritical extraction are being investigated. The raw material used is often butter-milk, where the MFGM molecules are most concentrated [44]. Isolated components of MFGM could be used in the pharmaceutical industry or incorporated as nutraceutical ingredients in food products.

Conjugated linolenic acid (CLA) Some research has been oriented to the development of techniques for concentrating conjugated linolenic acid (CLA) in milk fat, including transesterification with CLA concentrates [32] or supercritical fluid fractionation [45]. However, the resulting enrichment in CLA was relatively low and does not seem to be economically justified. A more promising approach for increasing CLA content in milk fat has been altering the diet of the cow, by incorporation of dietary supplements based on fish oils [5].

Cholesterol Cholesterol, despite not recommended in adult diets, is an important molecule for the infant brain development, and as such, it is suitable for being incorporated in infant food formulations. Cholesterol removed from milk fat can be utilized in this way. At the same time, the cholesterol-free milk fat obtained on the other hand has an increased value as well. Several methods exist for removing cholesterol from milk fat: steam stripping, short-path distillation, absorption, extraction, and enzymatic

techniques [3]. Absorption using cyclodextrines has been commercially applied for producing low-cholesterol cheese and butter, although resulting in relatively expensive products.

Conclusions

Despite the promising results on many research areas, the production and utilization of milk fat derivatives is nowadays limited to the production of flavors and milk fat fractions. A great potential exists therefore for the development and commercialization of a variety of innovative, added-value products, which would contribute to the reduction of the butter stocks and the overall revalorization of milk fat.

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