

Buttermilk: the valuable, yet overlooked food ingredient

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Factors that affect milk composition

- Age of cow
- Breed of cow
- Stage of lactation
- Bacteriological state of milk
- Seasonality
- Diet of cow
- Milking frequency
- Processing effects: homogenization, storage temperature





What is buttermilk?

- High in lactose
- About ~1% fat, of which ¹/₅ are phospholipids
- Secondary product with low value (due to microbial counts)
- Good emulsifier (primarily due to casein contamination)
- May improve the flavour of low fat cheese
- Key ingredient: the milk fat globule membrane (MFGM)

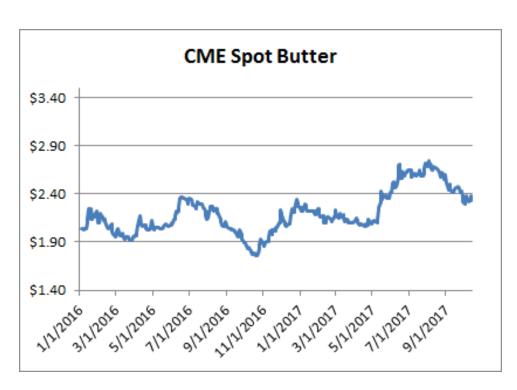
TABLE 17.1 Approximate Composition (% w/w) of Some Types of Powder

	Powder from				
Constituent	Whole milk	Skim milk	Whey	Sweet cream buttermilk	
Fat	26	1	1	5	
Lactose	38	51	72	48	
Casein	19.5	27	0.6	26	
Serum protein	4.8	6.6	8.5	6.2	
"Ash"	6.3	8.5	8	8	
Lactic acid	_		0.2 - 2	_	
Water	2.5	3	3	3	





Market price of butter





US market price per lb

Global Dairy Auction



Buttermilk powder market price

Results from the latest Trading Event

Event 197 / 3 October 2017



Butter Milk Powder Prices



Global Dairy Auction prices

Product usage:

Bakery products

Frozen desserts

Prepared dry mixes

Beverages

Frozen foods

Dairy products

Salad dressings

Snack foods

Cheese products



U.S. regulations

- Dry buttermilk (DBM) is light cream in colour with a clean, pleasing, sweet dairy taste.
- Typically, dry buttermilk is obtained by drying liquid buttermilk that was derived from the churning of butter and pasteurized prior to condensing.
- DBM has a protein content not less than 30% (dry buttermilk product can be <30%)
- It may not contain, or be derived from, non-fat dry milk, dry whey or products other than buttermilk and contains no added preservative, neutralising agent or other chemical.
- By removing moisture to the greatest extent possible, microbial growth is prevented.
- Product should be stored and shipped in a cool, dry environment with temperatures below 27°C and relative humidity below 65%.
- Stocks should be rotated and utilized within 8-9 months.
- Applications include bakery products, frozen desserts, dry mixes, beverages, dairy products, frozen foods, salad dressings and snack foods.



U.S. extra grade dry buttermilk (DBM)

American Dairy Products Institute

Classifications	Fat	Moisture	Protein	Titratable Acidity	Solubility Index	Scorched Particles
Spray Dried Extra Grade DBM	Min 4.5%	Max 4.0%	Min 30.0%	Min 0.10% Max 0.18%	Max 1.25 mL	Max 15.0 mg Disc B
Atmospheric Roller Dried Extra Grade DBM	Min 4.5%	Max 4.0%	Min 30.0%	Min 0.1% Max 0.18%	Max 15.0 mL	Max 22.5 mg Disc C

Standard Plate Count 75,000 cfu/g; Coliforms ≤ 10 cfu/g



Salmonella Listeria Coagulase positive Staphylococci Yeast & Mold negative negative <10 cfu/g ≤ 100 cfu/g

U.S. standard grade dry buttermilk (DBM)

American Dairy Products Institute

Classifications	Fat	Moisture	Protein	Titratable Acidity	Solubility Index	Scorched Particles
Spray Dried Standard Grade DBM	Min 4.5%	Max 5.0%	Min 30.0%	Min 0.10% Max 0.20%	Max 2.0 mL	Max 22.5 mg Disc C
Atmospheric Roller Dried Standard Grade DBM	Min 4.5%	Max 5.0%	Min 30.0%	Min 0.1% Max 0.20%	Max 15.0 mL	Max 32.5 mg Disc D

Standard Plate Count 75,000 cfu/g; Coliforms ≤ 10 cfu/g



Salmonella Listeria Coagulase positive Staphylococci Yeast & Mold negative negative <10 cfu/g ≤ 100 cfu/g

Butter and buttermilk manufacture

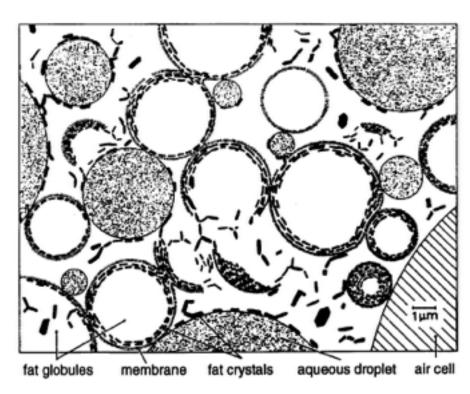


FIGURE 19.11 Butter microstructure at room temperature. Liquid fat is white. Membrane thickness is much (about 10 times) exaggerated. After H. Mulder and P. Walstra, *The Milk Fat Globule* (Wageningen: Pudoc, 1974).

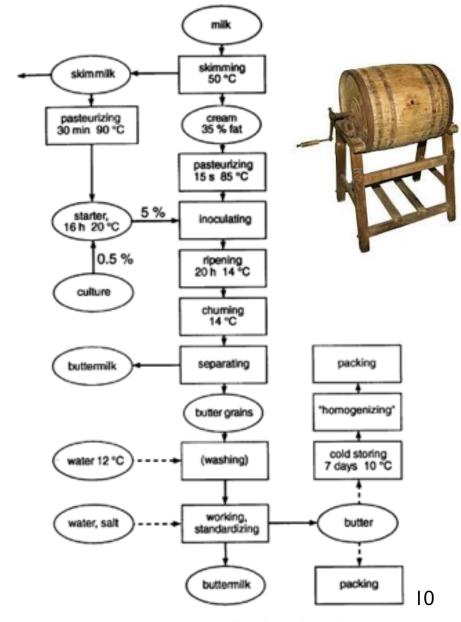




FIGURE 19.1 Example of butter making from ripened cream.

Butter and buttermilk manufacture





Commercial cream separation



Buttermilk powder available on a large scale, is inexpensive, but has functional problems



Cream churning

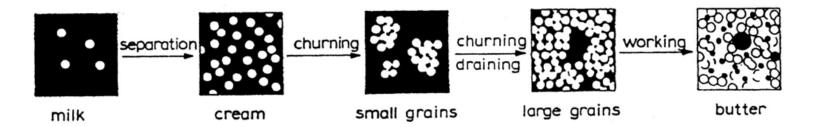
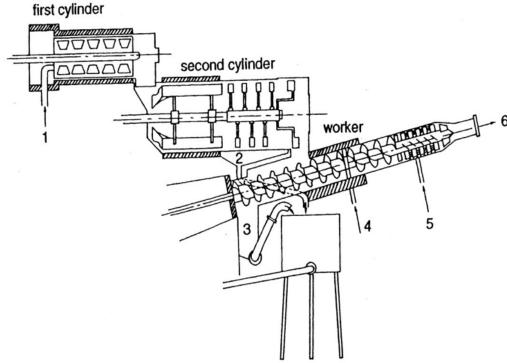


FIGURE 19.2 Stages in the formation of butter. Greatly simplified, not to scale. Black is the aqueous phase; white is fat. From H. Mulder and P. Walstra, *The Milk Fat Globule* (Wageningen: Pudoc, 1974).

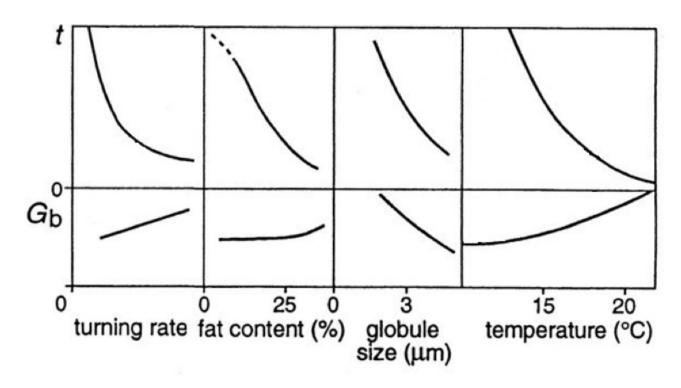




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Cream churning



t = turning time to produce butter from creamGb = efficiency of churning (% fat in buttermilk)

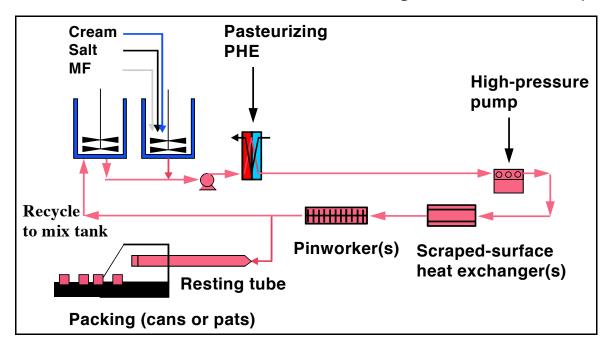
Walstra, P., T. J. Geurts, A. Noomen, A. Jelema, and M. A. J. S. van Boekel. 1999. Dairy Technology: Principles of Milk Properties and Processes. Marcel Dekker, Inc., New York.





Fritz butter churning process

Developed from the traditional batch churning process of crystallised cream About half of New Zealand butter manufacturing uses the Fritz process



Concentration of the milk to cream (40% fat)

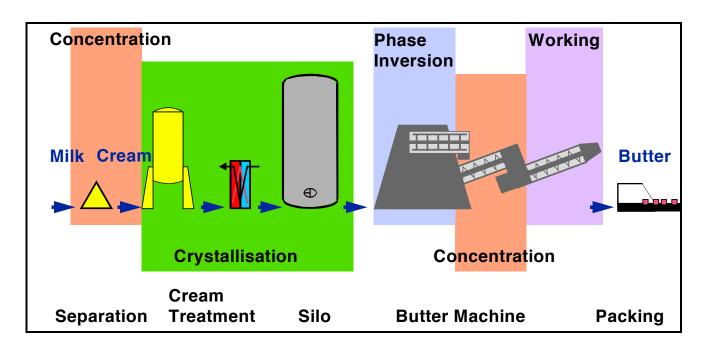
Crystallisation of the fat in the cream

Phase inversion of the cream (and further concentration by buttermilk draining) **Working** of butter to achieve fine moisture dispersion



Ammix butter churning process

Fresh milk fat is mixed with cream and salt and shock cooled to give rapid crystallisation



Concentration of the milk to cream (75% fat)

Phase inversion of the cream (and further concentration to fresh milkfat)

Crystallisation of fat in milkfat/serum mixture

Working of butter to achieve fine moisture dispersion



Types of liquid buttermilk

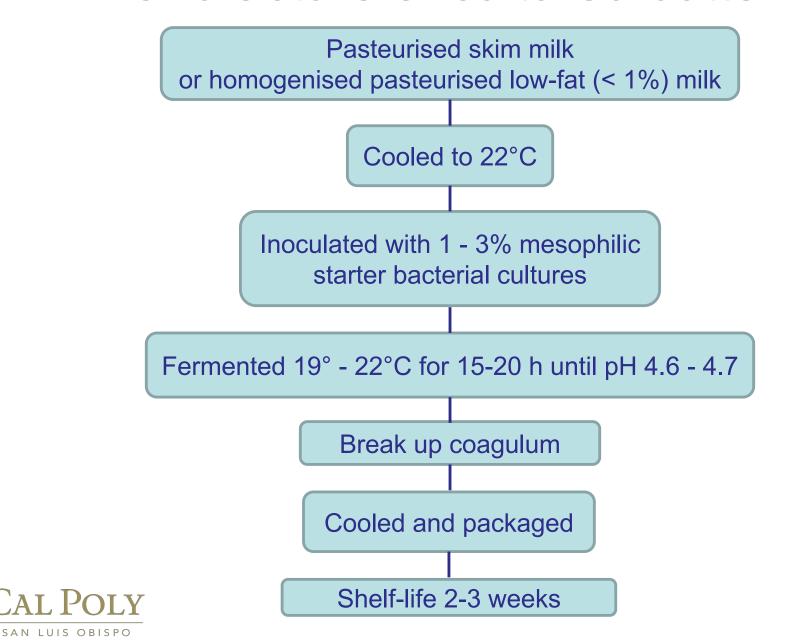
- Produced from the churning and separation of butter or cultured butter
- Mostly a consumer drinking product in Europe, and an ingredient in the United States
- Cultured buttermilk containing *L. lactis* ssp. *lactis* and spp. *cremoris* (ingredient and digestive aid); also can *use Lb. delbrueckii* ssp. *bulgaricus*
- *L. lactis* ssp. *lactis* biovar *diacetylactic* or *Lc. mesenteroides* ssp. *cremoris* sometimes used to impart a more buttery flavour from the chemical compound, diacetyl
- Buttermilk (cultured or otherwise) now more commonly made from skim milk with < 1% fat; traditional buttermilk is made from churning cream
- Acidity in cultured buttermilk due to lactic acid (transformed from lactose in the milk)
- Slight curdling of casein proteins makes this thicker than skim milk
- Sensitive to oxidation metallic off-flavour







Manufacture of cultured buttermilk



Composition of buttermilk (g /100g)

Component	Conventional	Cultured
Total solids	9.5 – 10.6	9.0 – 10.6
Fat	0.3 - 0.7	0.1 – 1.0
Phospholipids	0.07 – 0.18	~0.02
Protein	3.3 - 3.9	3.1 – 3.5
Lactose	3.6 - 4.3	3.6 - 4.3
Lactic acid	0.55 - 0.9	0.55 - 0.9

Conventional: made from buttermilk

Cultured: made from skim milk

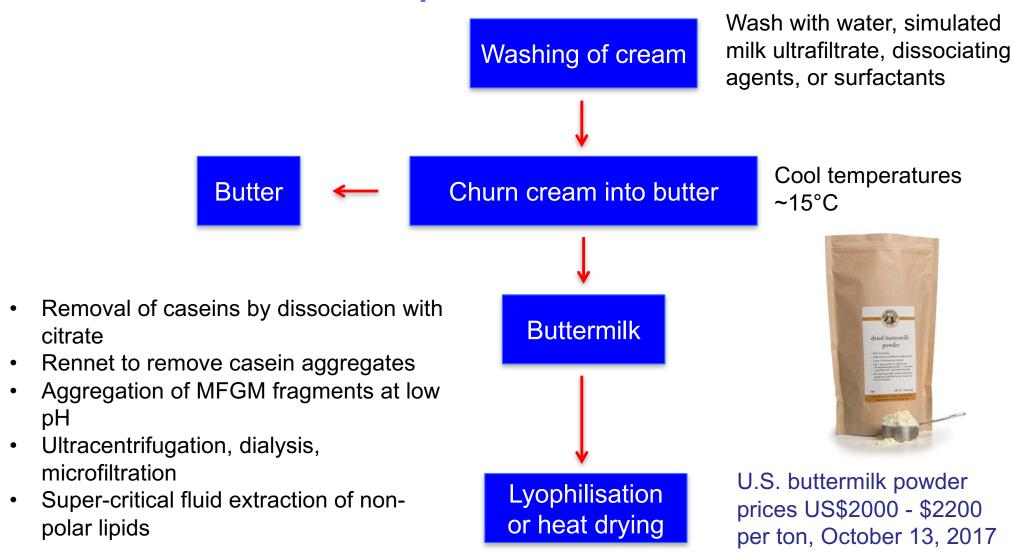


Other types of liquid buttermilk

- Dhallë, a type of buttermilk from Albania
- Chaas, a buttermilk drink native to the Rajasthan region
- Clabber, a Southern United States soured milk drink
- Doogh, a yogurt drink from Iran
- Filmjölk (Swedish)/Kulturmelk (Norwegian), a type of buttermilk from scandisalviaer the problotic effect of
- Gholdringtteringther ted dairy products
 Kefir, a fermented milk drink from the Caucasus
- Lassi, a yogurt drink native to the Punjab region
- Mala or Maziwa lala, a type of buttermilk in Kenya
- Mattha, an Indian buttermilk drink
- Mor Kuzhambu, a buttermilk and curry dish native to the Tamil Nadu region
- Pomazánkové máslo, from the Czech Republic
- Žinčica, sheep milk whey from Slovakia

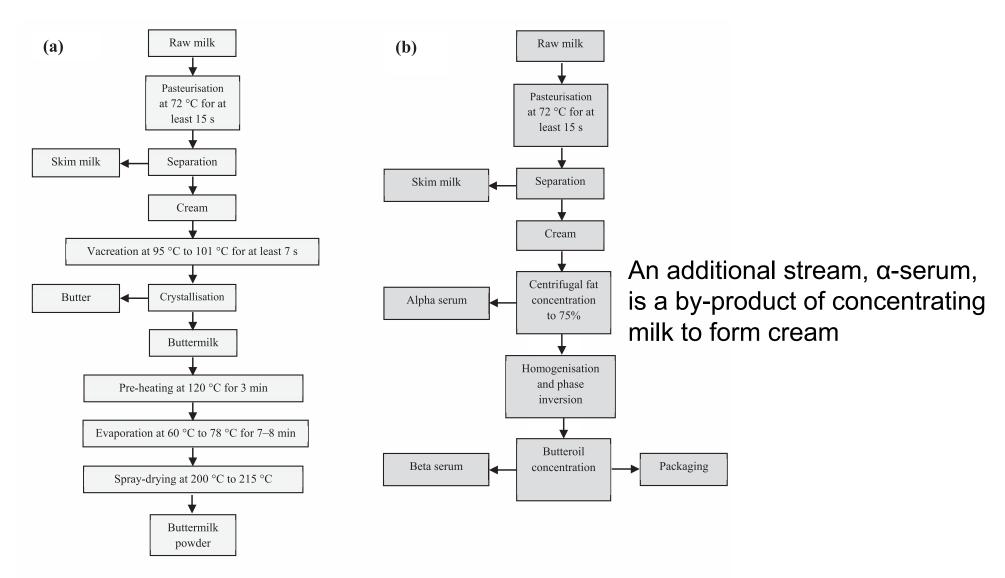


Buttermilk powder isolation





Buttermilk and serum





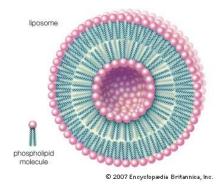
Haddadian, Z., Eyres, G. T., Carne, A., Everett, D. W., & Bremer, P. (2017). Impact of different milk fat globule membrane preparations on composition, xanthine oxidase activity, and redox potential. *International Dairy Journal*, 64, 14-21.

Buttermilk functionality

- Comprises most of the milk fat globule membrane (MFGM) layer that protects fat globules in milk
- Biologically relevant membrane with multitude of components
- Functional flavour and texture properties
 - Emulsification
 - Liposomes as carriers and flavour masking agents
 - Impact of isolation procedure
 - Improves heat-stability of recombined evaporated milk¹
 - Improves whipping properties of recombined cream²
 - Increases water-holding capacity and firmness of yoghurt³



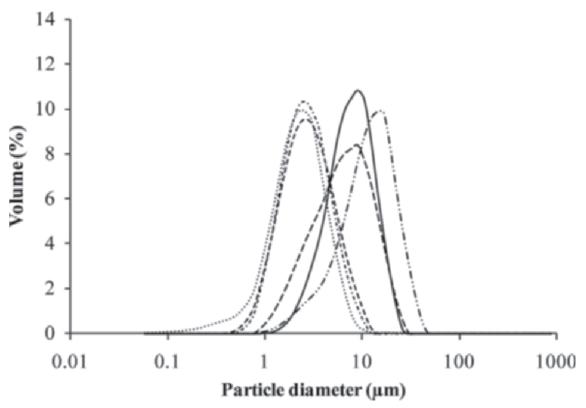
¹ Kasinos, M., Tran Le, T., & Van der Meeren, P. (2014). Food Hydrocolloids, 34, 112-118.



² Phan, T. T. Q., Moens, K., Le, T. T., Van der Meeren, P., & Dewettinck, K. (2014). *International Dairy Journal*, 39, 16-23.

³ Le, T. T., van Camp, J., Pascual, P. A. L., Meesen, G., Thienpont, N., Messens, K. et al. (2011). *International Dairy Journal*, 21, 798-805.

Emulsifying efficacy



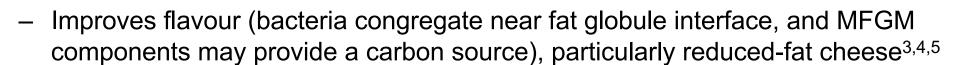
Buttermilk (BM) milk fat globule membrane (BM- MFGM100); \cdots], microfiltered BM whey (whey-MFGM100; -), Lacprodan PL-20 (Lac100; Arla Foods Ingredients Group P/S, Viby, Denmark; ----), mixture of microfiltered BM and BM powder (4:6, wt/wt; BM-MFGM40; - -), mixture of microfiltered BM whey and BM powder (4:6, wt/wt; whey-MFGM40; \cdot), and mixture of Lacprodan PL-20 and BM powder (4:6, wt/wt; Lac40; - -).



Phan, T. T. Q., Le, T. T., Van der Meeren, P., & Dewettinck, K. (2014). Comparison of emulsifying properties of milk fat globule membrane materials isolated from different dairy by-products. Journal of Dairy Science, 97, 4799-4810.

Buttermilk functionality

- Impact on cheese (added as buttermilk)
 - Increases moisture content and yield¹
 - Impairs casein aggregation during curd cooking
 - Decreases free oil in pizza cheese²



Increases pizza cheese moisture and decreases melt and stretch⁶

⁶ Govindasamy-Lucey, S., Lin, T., Jaeggi, J., Johnson, M., & Lucey, J. (2006). *Journal of Dairy Science*, 89, 454-467.





¹ Gauvin, M.-P., Pouliot, Y., & Britten, M. (2018). *International Dairy Journal*, 76, 10-17.

² Poduval, V., & Mistry, V. (1999). *Journal of Dairy Science*, 82, 1-9.

³ Foda, E., Hammond, E., Reinbold, G., & Hotchkiss, D. (1974). Role of fat in flavor of cheddar cheese. J. Dairy Sci., 57, 1137-1142.

⁴ Law, B., Sharpe, M., Chapman, H., & Reiter, B. (1973). *Journal of Dairy Science*, 56, 716-723.

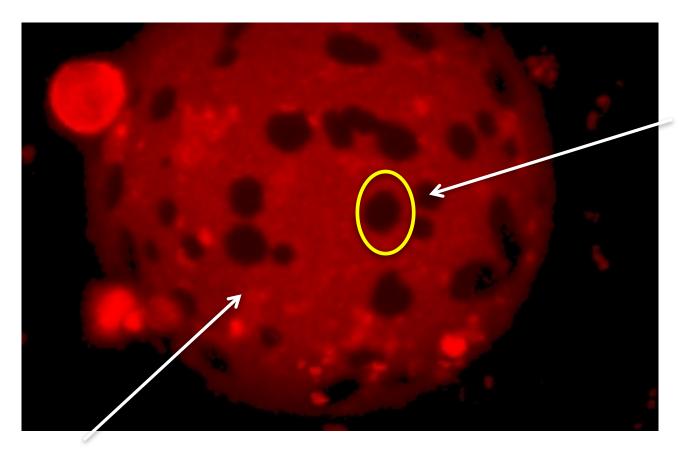
⁵ Mayes, J., Urbach, G., & Sutherland, B. (1994). Australian Journal of Dairy Technology, 49, 39-41.

MFGM topological model

Asymmetrical The phospholipid tri-layer, 4-10 nm thick Glycosylated proteins (mucins, CD36, PAS6/7 ...) location of Butyrophilin membrane proteins far from Glycolipids Liquid-ordered (cerebrosides, certain domain gangliosides) Symmetric bilayer Liquid-disordered Liquid-ordered phase: matrix of Sphingomyelin domain glycerophospholipids Xanthine Asymmetric bilayer Cholesterol (PC, PE, PI, PS) oxydase Adipophilin Bilayer of polar lipids Cytoplasm Monolayer of phospholipids Triacylglycerols



Surface chemistry and structure – the milk fat globule



Liquid ordered L₀ regions rich in sphingomyelin (highly saturated, longer chain) and cholesterol

Two-dimensional reactions on emulsion and other colloidal surfaces to generate texture and flavour reactions

Liquid disordered region

Gallier, S., Gragson, D., Jiménez-Flores, R., Everett, D.W., J. Agric. Food Chem. 58: 4250–4257 (2010)



Purported health benefits of the dairy matrix

- Cholesterol and sphingomyelin in close association in the MFGM
- Raw cream buttermilk treated with pepsin and microfiltered lowered cholesterol micelle solubility by 57%, but only 17% with pasteurised cream¹
- Superior antioxidant activity from MFGM peptides²
- Slight in vivo lowering of cholesterol absorption through intestinal epithelial cell layer by consumption of 45 g/day of buttermilk³
- Implicated inhibition of infectivity by rotavirus activity, attributed to the glycoprotein and carbohydrate components⁴

⁴ Fuller, K. L., Kuhlenschmidt, T. B., Kuhlenschmidt, M. S., Jiménez-Flores, R., & Donovan, S. M. (2013). *Journal of Dairy Science*, *96*, 3488-3497.

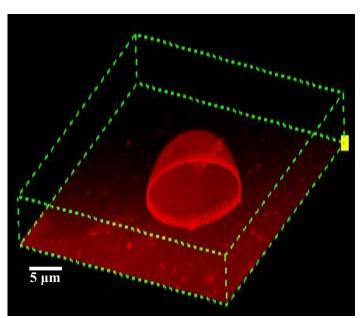


¹ Conway, V., Gauthier, S. F., & Pouliot, Y. (2010). Dairy Science & Technology, 90, 449-460)

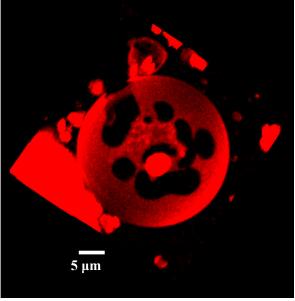
² Conway, V., Gauthier, S. F., & Pouliot, Y. (2013). Journal of Agricultural and Food Chemistry, 61, 364-372

³ Conway, V., Couture, P., Richard, C., Gauthier, S. F., Pouliot, Y., & Lamarche, B. (2013). *Nutrition, Metabolism and Cardiovascular Diseases*, 23, 1255-1262.

Giant unilamellar vesicle model systems



GUV generated from electroformation.



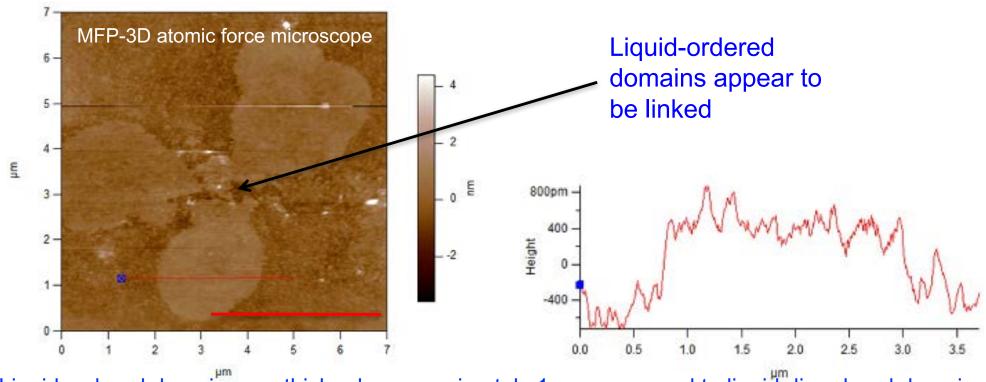
Non-fluorescent lipid domains formed with DPPC/DOPE 3/7 mol/mol in a GUV system.

Model milk fat globule vesicles to examine surface structures

Zheng, H., Jiménez-Flores, R., Gragson, D. & Everett, D.W. J. Agric. Food Chem., 62, 3236-3243 (2014)



Fat globule surface structure



Liquid-ordered domains are thicker by approximately 1 nm compared to liquid disordered domains

Gallier, S., Gragson, D., Jimenez-Flores, R., & Everett, D. W. (2010). Surface characterization of bovine milk phospholipid monolayers by Langmuir isotherms and microscopic techniques. *Journal of Agricultural and Food Chemistry*, 58, 12275-12285.

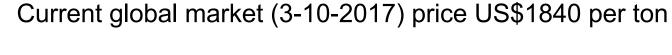


Buttermilk powders

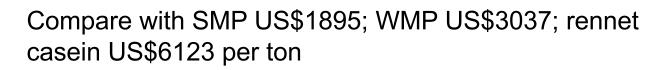


Valio sweet butter milk powder

Historically considered a low-value product...but huge potential!









Fonterra butter milk powder

Products usually promoted for their good solubility, clean flavor, and emulsifying efficacy.



High heat butter milk powder



MFGM health claims

Functional health properties* of MFGM phospholipids

- Sphingolipids, including sphingomyelin and metabolites (ceramide, sphingosine, sphingosine-1-phosphate, cermaide-1-phosphate)
 - colon anti-carcinogenic properties
 - cholesterol and LDL adsorption lowering effects by lowering liposome membrane fluidity, raises HDL levels (milk more potent than egg sphingomyelin)
 - trans-membrane signal transduction and regulation of immune cell development
 - cell growth and apoptosis
 - lipoprotein formation
 - mucosal growth in the gut
 - associated with age-related diseases, such as Alzheimer's
 - ameliorate inflammatory processes in atherosclerosis
 - treatment for insulin resistance, dyslipidemia, cardiovascular diseases
 - protection against bacterial and virus infections
- Fatty acid binding protein
 - anti-carcinogenic properties (colon, breast)



MFGM health claims

Functional health properties* of MFGM phospholipids

- Phosphatidylserine
 - positive effects on Alzheimer's patients
 - restoration of memory
 - alleviate muscular soreness
- Phosphatidylcholine
 - support liver recovery
 - protect human gastrointestinal mucosa against toxic attack
 - reduced life-threatening necrotizing enterocolitis
- Lactadherin
 - protection against gut viral infection
- Butyrophilin
 - suppression of multiple sclerosis
- Lyso-phosphatidylcholine and xanthine oxidase
 - bacteriocidal and bacteriostatic properties (S. aureus, E. coli, Sal. enteritidis)



Snow Brand



Your choice of Growing Up Milk is important because your child requires well-balanced nutrition to support their rapid growth and development.

snowbrand.com.my

Neo Kid-Plus

Sphingolipids
Gangliosides
Arachidonic acid
Nucleotides
Galactosyllactose

Sialic acid Docosahexaenoic acid Choline Phospholipids



Fonterra





www.fonterra.com

Phospholipid concentrates: sphingomyelin Cell growth and regulation

Gangliosides: mono-sialo ganglioside 3 (GM3), di-sialo ganglioside (GD3) and phosphatidylserine Infant learning and development, maintain gut health and balancing the immune system



FrieslandCampina





frieslandcampina.com

Nutritional milk powders for children 5x Docosahexaenoic acic Sialic acid

Dutch Lady Growing Up Milk 123 for ages 1+ Dutch Lady Growing Up Milk 456 for ages 3+ Dutch Lady Growing Up Milk 6+ for ages 6+



Arla Foods



Lacprodan® PL-20

Phosphatidylserine and sphingomyelin

Performance boost, contributes to healthy ageing, promotes

cognitive development in infancy

Lacprodan® MFGM-10 for infant nutrition.

Lactoferrin, IgG, sialic acid, phospholipids and gangliosides Neonatal gut maturation and myelination of the central nervous system Gangliosides for beneficial gut microflora, and intestinal maturation and cognitive development

MFGM components for anti-pathogenic effects Lactoferrin protects against microbial infections



Meiji – Global Brands Marketing

Meiji FM-T Meiji mamilac Meiji Fu



Fortified with docosahexaenoic acid Cerebral and retinal development









Novel ingredients from milk

Case study: the milk fat globule membrane (MFGM)

Originates from lipid droplet extrusion from the mammary epithelial cells

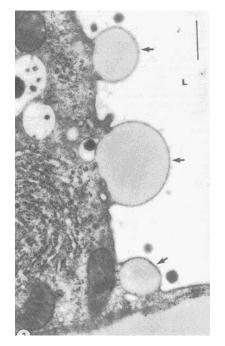
Protects milk fat globule from lipolysis and coalescence

Contains components with bioactive functionality

Major component of buttermilk

Emulsification, carriers of flavour compounds

Implicated inhibition of infectivity by rotavirus activity, attributed to the glycoprotein and carbohydrate components



Keenan, Mather & Dylewski, Physical Equilibria Lipid Phase, In N.P. Wong, *Fundamentals* of Dairy Chemistry, 3rd ed. (1988)



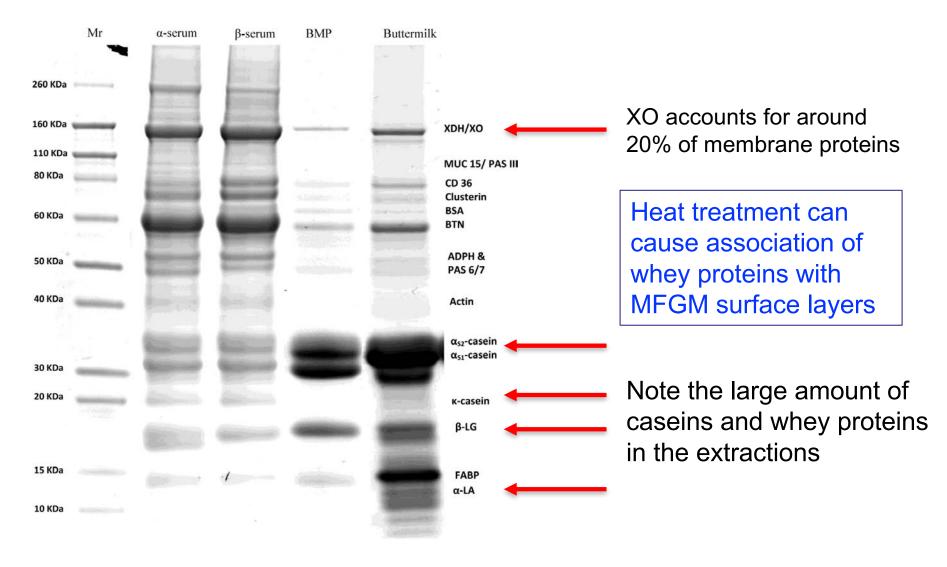
Composition of the MFGM

Component	mg/100g fat	mg/100mg MFGM
Proteins	1800	70
Phospholipids	650	25
Cerebrosides	80	3
Cholesterol	40	2
Monoacylglycerides	Present	Unknown
Water	Present	0
Carotenoids	0.04	0
Total	>2570	100

Composition depends upon the method of extraction



Proteins in MFGM extractions





Haddadian, Z., Eyres, G. T., Carne, A., Everett, D. W., & Bremer, P. (2017). Impact of different milk fat globule membrane preparations on composition, xanthine oxidase activity, and redox potential. *International Dairy Journal*, 64, 14-21.

Compartmentalisation of enzymes

Milk fat globule membrane

Redox enzymes

Xanthine oxidase
Cytochrome C reductase

Hydrolases

Acetylcholine esterase
Alkaline phosphatase
Acid phosphatase
5'-Nucleotidase
Glucose-6-phosphatase
Phosphodiesterase
Adenosine triphosphatase

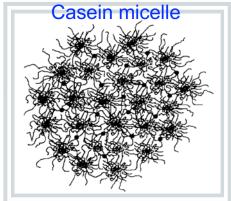
Lyases

Aldolase

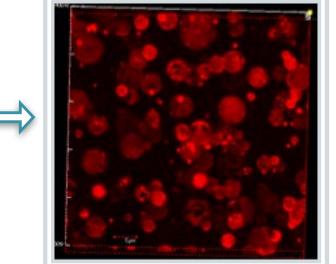
Transferases

γ-Glutamyl transferase Galactosyl transferase Sulfhydryl oxidase
Lactoperoxidase
Superoxide dismutase
Ribonuclease





Holt, C., Advances in Protein Chemistry, vol. 43: 63-151 (1992)



Gallier, S., Gragson, D., Jiménez-Flores, R., Everett, D.W., *J. Agric. Food Chem.* 58: 4250–4257 (2010)

Serum phase Lipoprotein lipase Plasmin (lower pH)



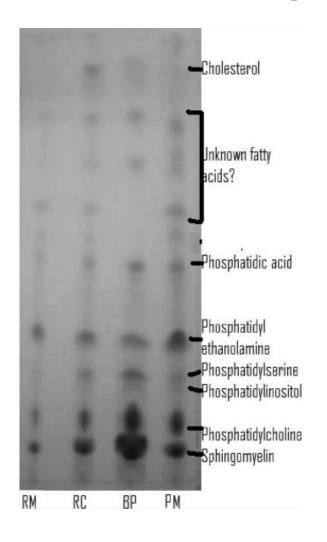
Polar lipids in MFGM

Polar lipid class	% of total polar lipids	
Phosphatidylcholine (PC)	36	
Phosphatidylethanolamine (PE)	27	
Sphingomeylin (SM)	22	
Phosphatidylinositol (PI)	11	
Phosphatidylserine (PS)	4	
Lysophosphatidylcholine (LysoPC)	2	

Composition depends upon the method of extraction



Polar lipids in the MFMG



Seemingly minor processing steps can affect lipid composition—

Cooling
Heating
Churning

Homogenization

RM: Raw milk

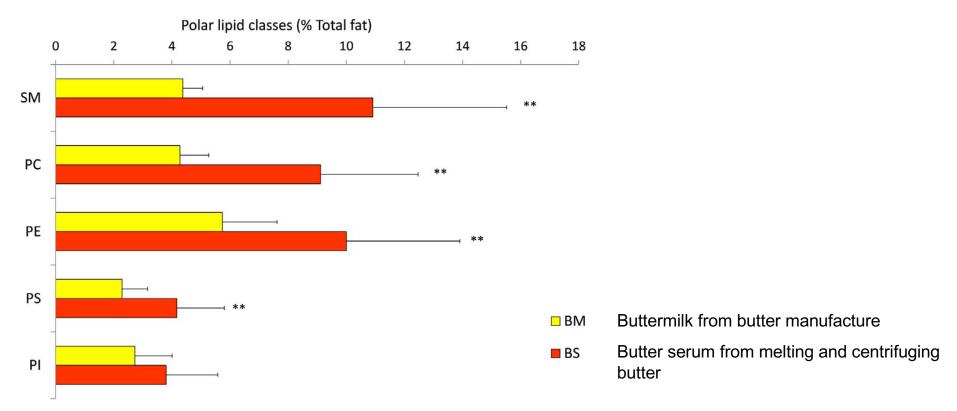
RC: Recombined cream BP: Buttermilk powder

PM: Processed milk (homogenized and pasteurised)



Gallier, S., Gragson, D., Cabral, C., Jimenez-Flores, R., & Everett, D. W. (2010). Composition and fatty acid distribution of bovine milk phospholipids from processed milk products. *Journal of Agricultural and Food Chemistry*, 58, 10503-10511.

Selective enrichment of polar complex lipids



Bourlieu, C., Cheillan, D., Blot, M., Daira, P., Trauchessec, M., Ruet, S. et al. (2018). Polar lipid composition of bioactive dairy co-products buttermilk and butterserum: Emphasis on sphingolipid and ceramide isoforms. *Food Chemistry*, 240, 67-74.



Case study: xanthine oxidase (XO)

In bovine milk, xanthine oxido-reductase is in the XO form

Capable of oxidising a wide range of aldehydes

Oxidises retinol to retinal, then to retinoic acid which is responsible for

most of the activity of vitamin A¹



XO has both bacteriocidal and bacteriostatic properties brought about by-

- 1. Production of reactive superoxide and hydrogen peroxide in the gut
- 2. Reduction of nitrite to nitric oxide, and to peroxynitrite
- 3. Stimulating lactoperoxidase system in milk (reductant + H₂O₂ → oxidant + H₂O)

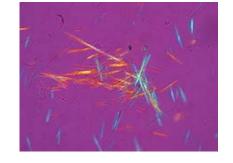


Oxidation reactions of XO



Uric acid elevated in blood; crystals implicated in gout*.

XO is the target of the widely used anti-gout drug, Allopurinol, an isomer of hypoxanthine and a xanthine oxidase inhibitor.



Xanthine oxidase	$XH + H_2O + O_2$ \longrightarrow	X=O + H ₂ O ₂
Xanthine dehydrogenase	$XH + H_2O + NAD^+ \longrightarrow$	X=O + NADH
Aldehyde oxidase*	RCHO + $H_2O + O_2$ \longrightarrow	RCOOH + H ₂ O ₂

^{*} Found mainly in liver

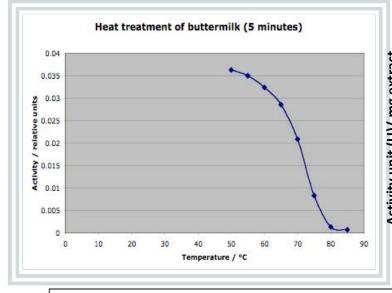


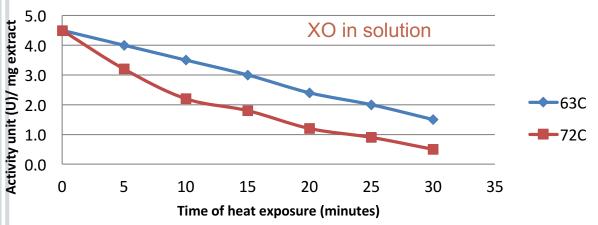
*Genetic, diet, and lifestyle causes
Consumption of alcohol, fructose-sweetened drinks, meat, seafood
Known as "rich man's disease, or "the disease of kings"

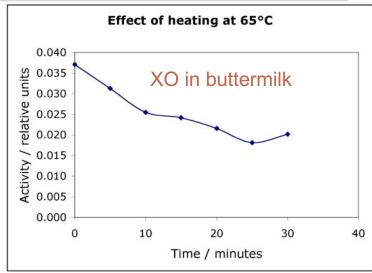
46

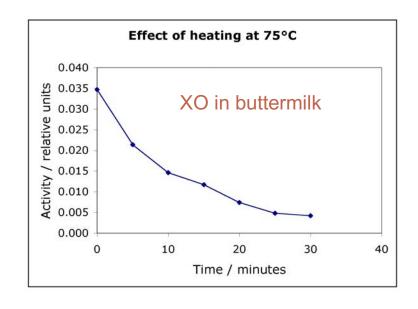
Dairy matrix effect on XO activity

XO in solution and in buttermilk









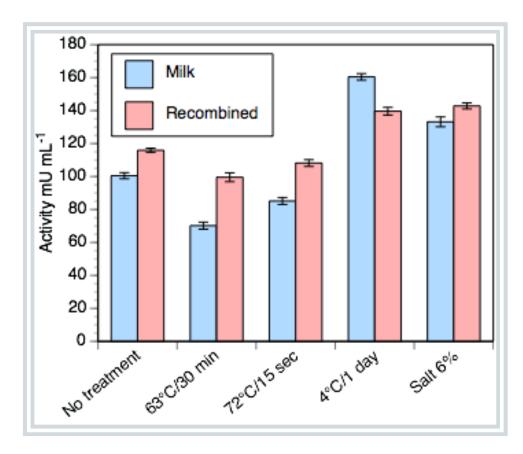


Xanthine oxidase activity in processed milk

$$XH + H_2O + O_2 \longrightarrow X=O + H_2O_2$$

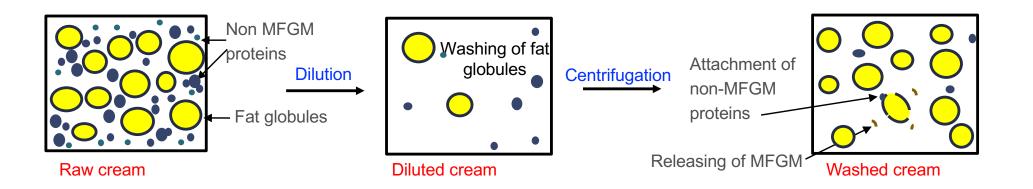
Located in the cytoplasmic region of the MFGM

Oxidation of aldehydes to acids Increase in n-fatty acids leading to methyl ketones, γ - and δ -lactones.





Washing cream with either simulated milk ultrafiltrate (SMUF) or water

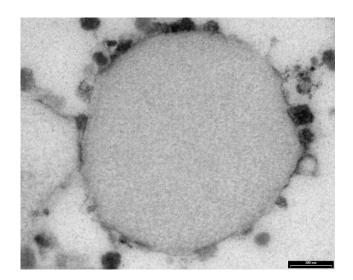




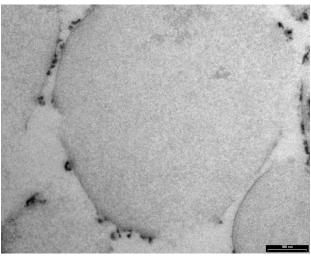


Washing fat globules

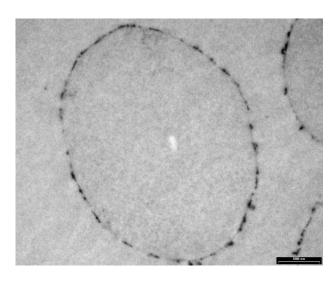
Scale bars: 5 µm



Native fat globule



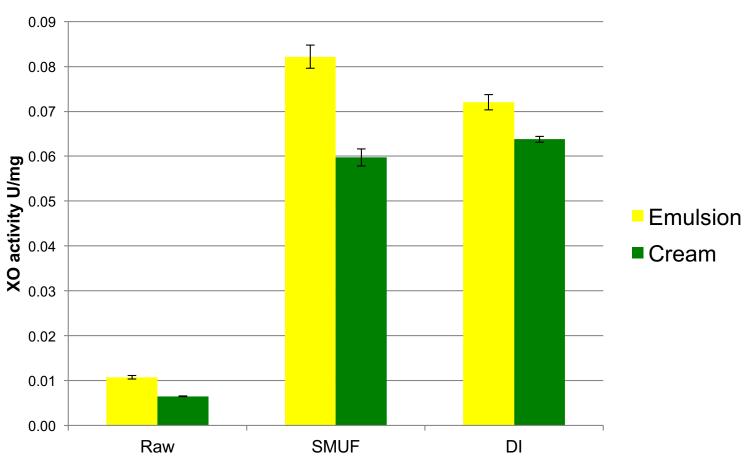
Fat globule washed with simulated milk ultrafiltrate (SMUF)



Fat globule washed with water



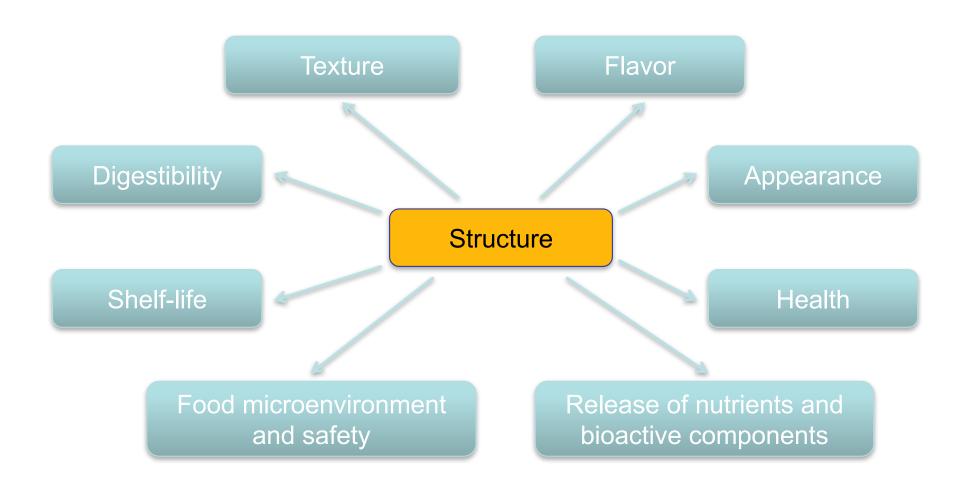
Xanthine oxidase activity on emulsion surfaces



* Specific activity of XO (mU mg⁻¹ of protein)



The importance of dairy food structure





Conclusions

- Milk has a complex native structure that impacts upon release of nutrients and, therefore, human health
- Extraction of MFGM components must take into account the impact of heat treatments
- Processing of milk can have a profound effect on dairy product flavor, release of nutrients, and health:
 - Location of complex lipids and enzymes on the milk fat globule surface
- Appropriate extraction methods can add value to buttermilk and buttermilk powders
- Understanding the structure-induced functionality of dairy products is a relatively new field that requires interdisciplinary research by food physicists, manufacturing technologists, and gastrointestinal physiologists



Time for questions

