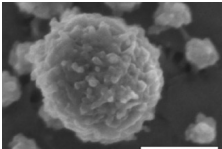


Milk and Cheese (& Ice Cream)

Milk is a basic nutritional component for all animals providing nutrients and immune proteins.



Electron micrograph of milk globule (above) and whipped cream (below)

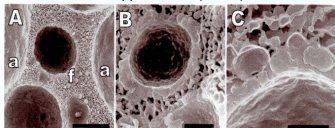


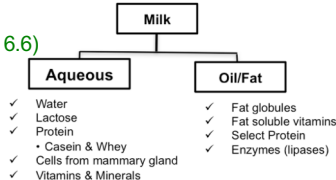
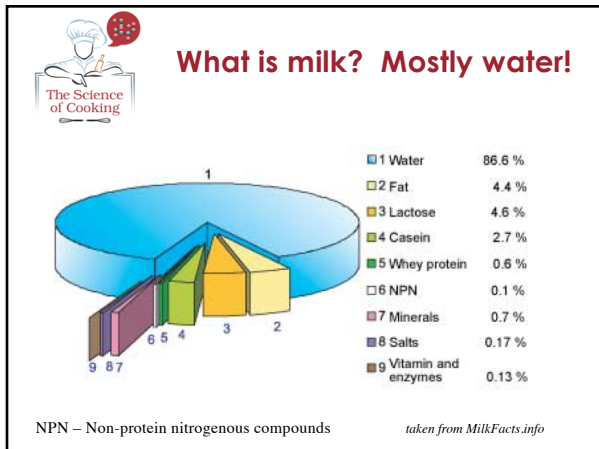
Figure 3-18 Electron Microscopy of Whipped Cream. A. Overview of (a) air and (b) fat globules. B. Internal structure of air bubble highlights the partially condensed fat. C. Interaction of fat globules within the fat layer. Courtesy of Prof. Douglas Goff, University of Guelph, Canada

What is milk – No, Really?

An emulsion of fat globules coated in protein suspended in protein-rich water – no really!

Composition of milk:

- **Liquid phase:**
 - Lactose
 - Slightly acidic water (pH 6.6)
 - Bundles of proteins
- **Fat phase:**
 - Droplets of oil cased in protein

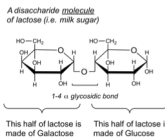
What is milk? Mostly water!

Species	Water	Fat	Casein	Whey	Lactose
Human	87.1	4.6	0.4	0.7	6.8
Cow	87.3	4.4	2.8	0.6	4.6
Buffalo	82.2	7.8	3.2	0.6	4.9
Goat	86.7	4.5	2.6	0.6	4.4
Sheep	82.0	7.6	3.9	0.7	4.8
Horse	88.8	1.6	1.3	1.2	6.2
Rat	79.0	10.3	6.4	2.0	2.6
Ass	88.3	1.5	1.0	1.0	7.4
Reindeer	66.7	18.0	8.6	1.5	2.8
Camel	86.5	4.0	2.7	0.9	5.4

What is milk – No, Really?

Composition of milk: **Liquid phase:**

- **Lactose** – nearly half of the calories
 - Disaccharide - glucose and galactose prepared as separate molecules and condensed into “milk sugar” through the secretory cells
 - Ability to digest (metabolize or “break down”) lactose requires a special enzyme – lactase
 - Lactase is produced in gut by children but levels decrease in adults.
 - Northern Europeans maintain levels but only 30% of others can produce significant quantities

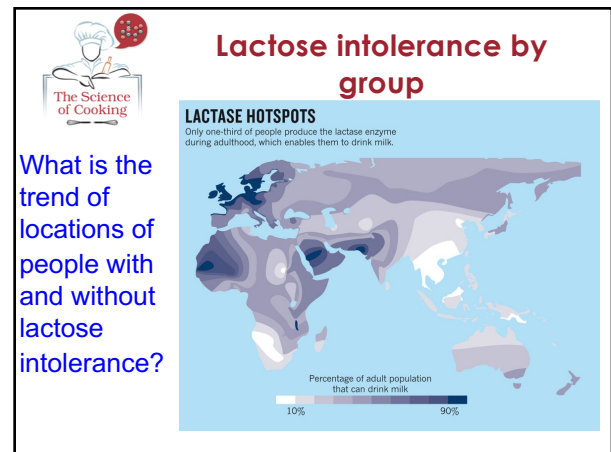


A disaccharide molecule of lactose (i.e., milk sugar)

1-4 α glycosidic bond

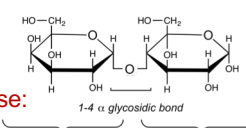
This half of lactose is made of Galactose

This half of lactose is made of Glucose



What is milk – No, Really?

A disaccharide molecule of lactose (i.e. milk sugar)



Composition of milk: **Liquid phase:**

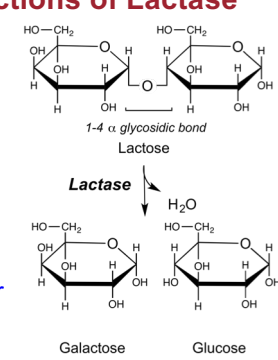
- **Lactose**
 - If the sugar isn't hydrolyzed sugar is transported to the gut where two things happen
 - Water rushes into the intestine from the belly – osmosis
 - Bacteria will start to metabolize the sugar to $\text{CO}_2(\text{g})$ and $\text{CH}_4(\text{g})$
 - Result – cramps, gas and diarrhea...diarrhea..

Called **Lactose intolerance**

- Enzymes mass produced in pill form can help

Actions of Lactase

The enzyme lactase hydrolyzes the glycosidic bond of lactose producing galactose and glucose – making available the monosaccharides for further metabolism



What is milk – No, Really?


Milk Proteins

Acid Insoluble	Acid Soluble
- Caseins	- Whey Proteins
o alpha casein	o lactoglobulin
o beta casein	o albumin
o kappa casein	o enzymes

Composition of milk: **Liquid phase:**

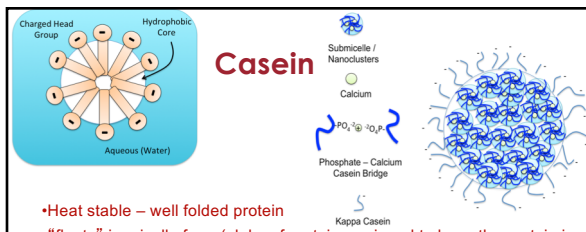
- **Proteins – Curds and Whey!**
 - 1000s of proteins divided by their stability in acid
 - Where does the acid come from? Hmmm?
 - Unstable – proteins which denature in acidic solutions bind to each other – aggregation or coagulate
 - These are Curds. When milk curdles, what is happening?

Curds and Whey



Cottage Cheese!

Casein



- Heat stable – well folded protein
- “floats” in micelle form (globs of protein arranged to keep the protein in solution)
 - Hydrophobic portion of protein in mi
- Calcium binds tightly to this protein – helps to carry calcium into the blood system!
- Four main forms of Casein – one “caps” micelles limiting the size
- At acid levels above 4.5, proteins are neg charged and repel.
- When acid increases to pH lower than 4, proteins denature and are not charged – thus they bind to each other and “curdle”
- Body builders sometimes use this as a “slow-digesting protein” (why)

Whey

The other protein found in liquid phase of milk

- Stay in solution in acidic conditions
- Many of these proteins are immunoglobins (antibodies for the young animal)
- Lactoglobulin has several sulfur atoms – provides flavor and odor to cooked milk
- Proteins in whey are used for animals as source of nutrition
- Under more extreme conditions than casein, whey proteins can form small clots – ricotta cheese
- These proteins help make ice cream... creamy



Milk Fat

The other phase of milk –

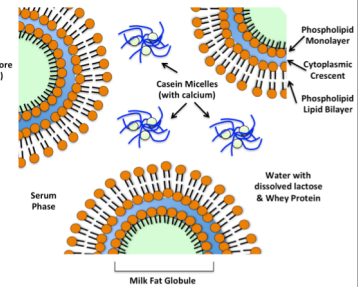
• The non-liquid part of milk is a globules of fat which are mixed with lots of different kinds of molecules

- Fats – the kinds of fats and amount of fat globules in milk vary as the types of food the cow eats, the season and temp of year and when the hormonal state of the cow
 - More fat in winter, and at end of lactation period
 - Mostly saturated fats and few polyunsaturated fats
- Fat soluble vitamins – A,D,E and K



Structure of Milk

Fat globules with three layers of lipid membranes encase the triacylglycerol (TAG) fat core. The serum phase with dissolved lactose and whey proteins contains the casein micelles coordinated with calcium ions.



Fat Globules

The richness of milk, creams or cheeses refers to the fat content –

Fat globule – coated with protein and charged phospholipids (emulsifiers)

- Creates charged spheres that repel each other
- If globules were to contact, they would pool resulting in a big batch of oil.
- This formation protects by “hiding” the fat from bacteria which would quickly digest/eat the oil



Pasteurization and Homogenization

Heat + Time = Sterilization.

- Subject food to enough heat to kill contaminating pathogenic bacteria but not cook food (too much)
- This is the basis for pasteurization or any kind of food preparation.
- High Temp Short time vs low temp long time

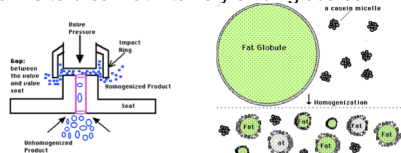
Irradiation – exposure to small amounts of gamma rays – kills parasites but like cooking can alter food nutrient value



Pasteurization and Homogenization

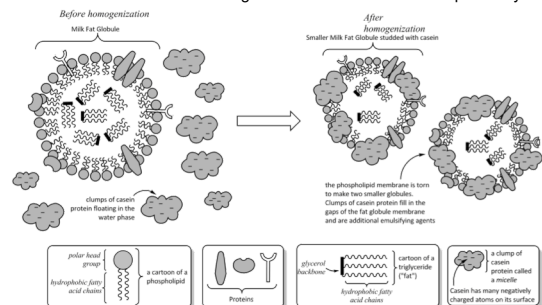
Homogenization

- Left alone, milk will separate – less dense large fat globules float and pool at top of more dense water layer
- Homogenization forces milk (while hot) through small nozzle to break fat into very small globules



Homogenization

- More, smaller fat globules result in higher surface area
- Not enough membrane to cover fat – so casein will coat the fat
- Smaller globes are less dense and repelled by casein



Common milks found in the market:

- **Vitamin D or Whole Milk:** Homogenized and pasteurized milk packaged with additional Vitamin D added. None of the fat has been removed prior to packaging (3.5% fat)
- **Low fat or skim milk:** Milk which some or nearly all of the milk fat has been removed. These milks range from 2% fat to less than 0.5% fat (non fat or skim milk). Because the body of the milk is more watery without the fat. These milks often are supplemented with whey protein.
- **Condensed milk:** sweetened or non-sweetened, whole milk with much of the water boiled away. This milk was created to serve as a concentrated form of milk and fight food poisoning during the U.S. Civil war in 1865. Now this is commonly used for a range of cooking and baking. Originally, sweetened condensed milk has added table sugar to limit bacterial growth.
- **Whipping and heavy creams:** Cream is the fat globule layer from milk which has creamed. Differences between heavy (30%) and whipping cream (36-40% fat) are primarily in the concentration of fat. Both creams can be used to make whipped cream, although the more fat the better the resulting foam. Half and half is a mixture of milk with cream for a lower percent fat (10-18%).

Milk Foam

Foam – a network of protein and or fat and sugar creating a cage around pockets of air.



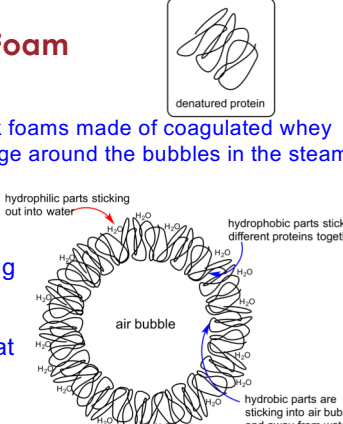
Foam

Espresso foams - milk foams made of coagulated whey proteins forming the cage around the bubbles in the steam

- Less protein than other foams and are thus unstable

Meringue foam – egg white protein and sugar foam

Whipped Cream – fat globule cages



Creams and Butter

Cream - Separated fat from raw milk

- what's left behind? **Skimmed milk!**

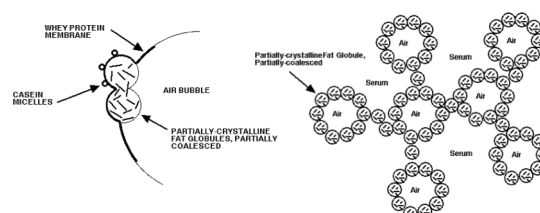
- Light and heavy whipping cream is about the fat content
- Creams used in cooking serve to keeping denatured proteins (like caseins) from binding to each other and clotting (aka curdling)
 - This happens because the globule membranes remain intact during cooking and bind to the proteins as they denature while cooking
- Try cooking high fat vs low fat yogurt or cream with or without an emulsifier

Whip it good...

Whipping cream – keep it cool and don't over do your whipping!

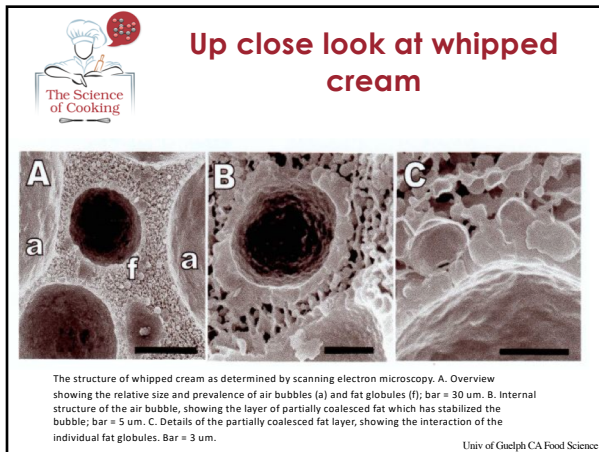
- These foams are a thick stable cage of fat globules
- Formed when mechanically shearing the heavy cream – why heavy and not light?
- Whipping breaks the fat into smaller pieces which the membranes can't fully cover
- This results in partial connected (crystalline) globes of fat with proteins wrapped around air bubbles

Up close look at whipped cream



(Not to scale)

Univ of Guelph CA Food Science



Whip it good...

Whipping cream – keep it cool and don't over do your whipping!

- Warm fat – oozes together and pools into one big blob – no air, no foam
- Over whipped fat (while cold) forms too many contacting fat globs and the cream turns into ... butter

I scream

Ice Cream is a result of chemical technology

- Ice Cream is a mixture of ice (water and partially solid milk fat), liquid (cream and sugared water) and air pockets (1/2 of the volume).
- Differences are in the fat and protein which create a creaminess, the amount of crystals of fat and water and the protein emulsifiers which stabilize the membranes of the fat and decrease crystallization

Left - Microscope images of ice cream
Fat droplets (orange)
Proteins (black)
-notice the level of fat crystals shown in the lines in the lower image

Right - Electron M-scope images
Air Bubbles (A)
Ice Crystals (C)
Fat Globules (F)
Un-frozen water, fat and sugar (S)

I scream

Ice Cream is a result of chemical technology

- More crystals (fat or water) lead to less smooth and more "crunchy" ice
- Whipping, emulsifiers and sugar all influence the crystals as they freeze
- To "ice the cream" all one has to do is create an environment colder than the freezing point of the water in milk
 - So the challenge is to create a lower temp than sugar water (less than 0°C)
 - BUT the temp of ice warmer (0°C) than the temp needed to freeze the cream
 - 13th Century Arabs knew how to create a colder than ice temp using salt

Freezing point depression

- A solution of water and solute (some other compound) will have a lower freezing point than pure water
- This is a result of ions interfering with the ability of water to form a lattice (cage) of bonded molecules – ICE ICE BABY!

Formally looking at melting point

Colligative Property – the freezing point is influenced and due to the small amount of dissolved solids (salt ions) rather than the solute (water molecules)

$$\Delta T_f = K_f C_m$$

ΔT_f = is the change of temp
 K_f = is a constant for the solvent (water)
 C_m = is the concentration

So what? The more salt particles - the bigger the freezing point depression
 - this is how frogs and other mammals can survive freezing

Taste of Ice Cream

Federal standards (21 CFR § 135.110) require ice cream to contain a minimum of 10% milk fat and 20% milk solids. Some premium ice creams contain 16% milk fat. -Ice cream contains not less than 1.6 pounds of total solids to the gallon, and weighs not less than 4.5 pounds to the gallon.

Overrun is a measure of the volume of air whipped into the ice cream mix. Overrun does not have to be declared on the label.

- Quality ice creams have lower overruns than those of reduced quality.
- Generally the more overrun, the lower the cost of the ice cream

Ice crystals form when some of ice cream's water separates from fat and eventually develops into larger ice crystals. The result is a grainy-textured ice cream. As long as water remains trapped in an emulsion with fat in ice cream, the original ice crystals do not get larger.

- To protect ice cream from developing large ice crystals, do not melt and refreeze ice cream, and do not store ice cream well below 0°F for a prolonged period.

Cheese

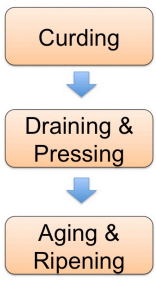
A durable form of milk! - 5-10 times milk concentrate

- Likely first prepared from soured milk and as milk was stored in stomach pouches
- Lactose (sugar) allows this to happen as it serves as a source of food for microbes



The Process of Cheese Making

- Curdling** – separation of milkfat and protein from whey
 - Acid, heat, enzyme (rennet) or combinations all cause curdling
- Curd setting – finishing**
 - pH, salt content, bacteria culture, cooking times
- Ripening - aging** – (react with oxygen) and allow molds and or other bacteria to alter fresh curd to hard aged cheese



Denaturation and aggregation of proteins and coagulation of fat globules – requires physical changes to proteins whose job is to keep micelles and globules separate

Removal of water and water soluble components like lactose and setting protein – fat structure

Chemical changes brought about by reactions with oxygen and fats/ proteins/organic molecules and reactions catalyzed by enzymes from bacteria or other microbes


Types of Cheese

Acid Coagulated Fresh Cheese (lactic acid from bacteria)

- no enzyme is used to finish the curd
- Cottage and Cream Cheese

Heat-Acid Precipitated Cheese (acid and heat precipitate/coagulate the protein and cause milk fat to curdle)

- Add low amounts of acid to 75-100°C temp milk
- High moisture and protein
- Ricotta (Italy) Channa and Paneer (India)




Types of Cheese

Semi-hard Washed Cheese (washing cheese removes acid and lactose)

- Acid and enzyme induced curdling
- But removal of milk sugar and acid results in no fermentation results in a moist and less finished cheese
- Gouda, colby, muenster, mozzarella ...

Hard Cheese (Low and High Temp)

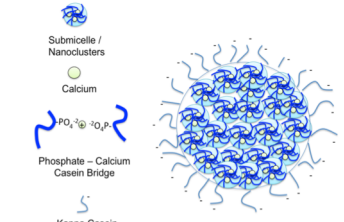
- Low moisture makes a more dense hard cheese
- Elevated temps and pressing drive off water
- Cheddar, Romano, Parmesan, Swiss




Casein – key for cheese

Sub micelles are held together by phosphorylated casein – calcium ion interactions

- k-casein caps the growing micelle, binds water and repels interactions with other casein micelles



Kappa Casein

$\text{H}_2\text{N}-\text{CH}(\text{CH}_2\text{OH})-\text{COO}^-$ (Serine) + ATP $\xrightarrow{\text{Casein Kinase}}$ $\text{H}_2\text{N}-\text{CH}(\text{CH}_2\text{OPO}_3^{2-})-\text{COO}^-$ (Phosphoserine) + ADP

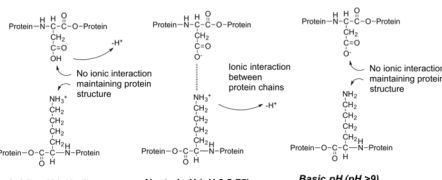
The amino acid is shown at pH7

Note the negative charge of the phosphate group

Curd Formation

Acidifying milk, increasing temperature and action of rennet lead to curd formation. i.e. disruption of casein micelles...

- acid formation (adding acid – acetic or citric) or production of lactic acid from metabolizing bacteria limit protein interaction



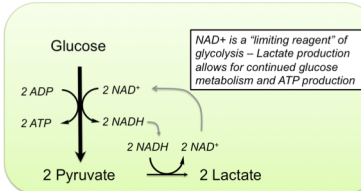
Acidic pH (pH <5) **Neutral pH (pH 6.5-7.5)** **Basic pH (pH >9)**

Loss of charged glutamates and aspartic acids diminishes ability of casein to bind to calcium and neutral charged k-casein stop repulsion and form weak aggregated precipitates (curd)

Metabolism – lactic acid production

Fermentation is a way for bacteria to replace limited amounts of NAD^+

- Lactate is side product
- Typically used for aged cheeses

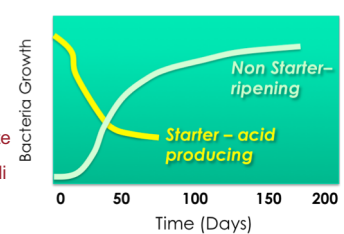


The diagram shows the conversion of Glucose to 2 Pyruvate, which then produces 2 Lactate. This process involves the conversion of 2 ADP to 2 ATP and 2 NAD^+ to 2 NADH. A text box notes: "NAD⁺ is a 'limiting reagent' of glycolysis – Lactate production allows for continued glucose metabolism and ATP production".

Different types of bacteria

Lactobacteria use lactose for fermentation. Used as "starter" culture to begin fermentation

- Both mesophilic (moderate temp) and thermophilic (heat tolerating) lactobacilli strains
- Neither can tolerate more than moderate acidic conditions
- If cooking curds thermophilic cultures are needed
- This first step is called "ripening"



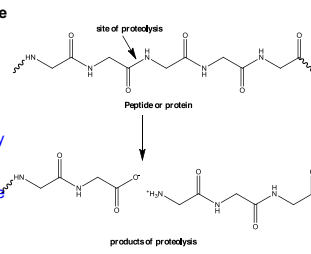
The graph shows two curves: "Non Starter-ripening" (yellow) and "Starter – acid producing" (green). The y-axis is "Bacteria Growth" and the x-axis is "Time (Days)" from 0 to 200. The green curve rises sharply and then plateaus, while the yellow curve rises more gradually.

A second "finishing/non-starter/ripening" bacteria is used to produce more acid and produce new flavor producing compounds

Enzyme catalyzed curd formation

Rennet – protease that hydrolyses the protein backbone

- Along with acid further degrades proteins in casein micelles and globules
- Found in 4th stomach of milk-fed calf
- Also found in some fruits – pineapple, kiwi or papaya (why don't you make jello using these fresh fruits?)
- Vegetable rennet is from thistle
- Most commercial cheeses use a cloned / engineered rennet called chymosin

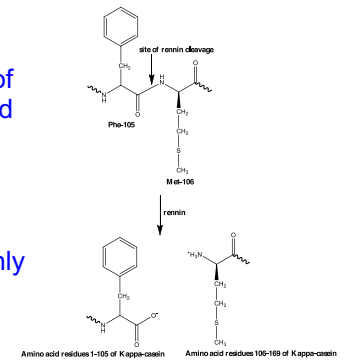


The diagram shows a peptide chain with a "site of proteolysis" indicated. An arrow points to the "products of proteolysis", which are shorter peptide fragments.

Rennet attacks kappa-casein

The negative tail of k-casein is cleaved by specific recognition by rennet

- Forms stronger curds than acid only precipitation




The diagram shows the chemical structure of kappa-casein, highlighting the "site of rennet cleavage" between Phe-105 and Met-106. The resulting fragments are labeled "Amino acid residues 1-105 of Kappa-casein" and "Amino acid residues 106-169 of Kappa-casein".

Temperature curd formation

If using culture, higher temps increase fermentation rates making more acid.

- Proteins denature at higher temps
- Combination of acid, rennet and heat make for tight curds.



A photograph showing a person's hands using a long-handled tool to stir or cut curds in a vat of milk.

Next step – Removing Moisture

Fresh cheeses retain moisture and sugars

Aged pressed cheeses are pressed to dry and have less lactose



The flowchart shows three steps: "Curding" (with note: "Denaturation and aggregation of proteins and coagulation of fat globules – requires physical changes to proteins whose job is to keep micelles and globules separate"), "Draining & Pressing" (with note: "Removal of water and water soluble components like lactose and setting protein – fat structure"), and "Aging & Ripening" (with note: "Chemical changes brought about by reactions with oxygen and fats/ proteins/organic molecules and reactions catalyzed by enzymes from bacteria or other microbes"). Below the flowchart is a photograph of a pressed cheese curd.

Drying the cheese curd

Gravity – through mold and drained – used for soft cheeses (camembert...)


Cutting curd – smaller the dryer, creates a more firm cheese due to increased surface area/mass ratio

Heating and stirring curds continues denaturation of proteins to release water from curd

- exposed hydrophobic protein amino acid side groups will not interact with water reducing "holding" capacity
- Activates bacteria and enzymes for more acid and creation of new flavor compounds

Temps impact final dryness of cheese

- Cheddar 100°F
- Gruyere 120°F
- Parmesan 130°F



Final Steps

Curds from the whey

Cheddaring – stacked and restacked at warm temps to encourage increased acid production

Pressing – squeeze curds together and remove water for hard, aged cheeses




Aging – (Ripening or Affinage)

Aging is the process of allowing starter and finishing bacteria and their enzymes to alter composition of fresh cheese

- The French term for ripening is *affinage*, which means 'end' or 'ultimate point'. As such, at times this stage of cheese making is carried out by an *affineur*, a cheese tenderer or finisher.
- The *affineur* takes care of the cheeses in the cheese-ripening cellars until the cheese has ripened adequately for packing and sale

Chemistry of ripening

Enzymes breakdown fat, protein and carbohydrates to new flavor compounds

```

graph TD
    Protein[Protein Casein] -->|proteolysis| AA[Amino Acids]
    AA --> Amines[Amines]
    AA --> KA[α Ketoacids]
    Amines --> Aldehydes[Aldehydes]
    KA --> Aldehydes
    Aldehydes --> Alcohols[Alcohols]
    Aldehydes --> CA[Carboxylic Acids]
    Alcohols --> Woody[Woody or Grass]
    CA --> Tart[Tart or Sharp Tastes]
    
    TG[Triacylglycerol Fat] -->|Lipases| FFA[Free Fatty Acids]
    FFA --> Alcohols2[Alcohols]
    FFA --> Lactones[Lactones]
    FFA --> Esters[Esters]
    Alcohols2 --> Long[Long Chain]
    Alcohols2 --> Alk[Alcohols & Ketones]
    Lactones --> Lactose[Lactose]
    Lactose --> Glucose[Glucose]
    Glucose --> Pyruvate[Pyruvate]
    Pyruvate --> Lactate[Lactate]
    Pyruvate --> Acetaldehyde[Acetaldehyde]
    Pyruvate --> Diacetyl[Diacetyl]
    Lactate --> CA2[Carboxylic Acids]
    Acetaldehyde --> Yoghurt[Yoghurt Aroma]
    Diacetyl --> Buttery[Buttery Flavor]
    CA2 --> Sharp[Sharp Tastes, some fruity flavors]
  
```

Cheese Flavoring

Protein, fat and metabolites (know this word!)

- Proteins – mostly degradation products of casein
- Amines – the amino portion of amino acids
 - Fish smell – trimethylamine
 - Putrescine – polymer of amines
 - Sulfur – from cysteine- amino acid side group
 - Ammonia – nitrogen from amino acids
 - Amino acids themselves have tastes
- Fats – different sized and modified fatty acids add different flavors and textures – molds typically alter fats
 - Short chain fatty acids – buttery or peppery taste
 - Smaller break down products – ketones – highly fragrant

The more finished the more flavors – why?

Macromolecules and flavor

Proteins (casein & whey) degrade to amino acids

- Glycine and alanine are sweet, Tryptophan is bitter
- Cysteine is eggy, Glutamate is MSG – savory flavor enhancing
- Some amino acids are further metabolized to ammonia, putrescine and trimethylamine

Fats are highly modified

- lipases release fatty acids altering acid and sharpness
- Fatty acids are further oxidized to ketones, alcohols or lactones
- Produces buttery (diacetyl) taste, grassy and other flavors



Cooking with cheese

Melting cheese – process of changing state of matter from solid to liquid

- Melting requires adding energy to defeat chemical bonds holding molecules in place (solid)
 - The more and stronger the bonds the higher the heat/energy it takes to break the bonds
- Cheese is a complex of many types of solids with different interactions
- Water, fat and protein content and type all alter ability of cheese to melt or cook well



Cheese Flavoring

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The more finished the more flavors – why?



Cheese melting

Moisture content impacts meltability

- High protein, low water cheeses (parmesan) melt poorly as the protein sticks together well
- Acid only curdled cheeses have too inter-bonded proteins and calcium to melt well

Fat will melt first – oil drops forming in heated cheese

Fat will break down and burn if not carefully handled and heat is added too quickly

Stringy cheese is due to cross-linked proteins lubricated by melting fat – moderate acid, high fat and water

- Mozzarella and cheddar work best for gooiness



Cooking with Cheese

Sauces and Soups

- These foods need to avoid stringy texture
- Use hard cheese grated finely to avoid clumping
- Add cheese last and avoid excessive stirring
 - This causes the proteins to further denature and bind to each other – strings!
- Use molecules (starch) to coat and emulsify proteins and fats.
 - This stops the interactions and separation of fat
- Acid (lemon juice and wine) can decrease interactions of proteins – hydrates protein, removes calcium.
 - Wine supplies tartaric acid – it isn't about the alcohol



Cooking with Cheese

Toppings and Gratins

Au Gratin – French style of cooking with bread crumbs and butter to top of dish – add cheese and even better!

- Excessive heat browns protein (casein), evaporates water (dehydration) and melted fats create a tough oily cheese topping
- Grating cheeses are good for this
- Try using leftovers with Cheese Au Gratin



Cheesy Tips

- Always bring a table cheese to room temperature before serving it--the flavor is much better.
- It's usually best to keep cheese in its original packaging. If the cheese has been cut, wrap it tightly in plastic wrap to hold in the moisture. If it hasn't been cut, wrap it first with waxed paper and then with plastic wrap--this allows the cheese to breathe.
- Store cheese near the bottom of the refrigerator, where temperature fluctuations are minimal.
- Don't serve cheese with citrus or tropical fruits. Cheese is usually made with pasteurized milk, which has been heated to remove harmful bacteria.