# Alchemy 201: Saponification

All your base are belong to fatty acids.

Lucia de Moranza, Trillium Wars AS 54

## What a weird word, where did it come from?

Early 1800s, from the French saponification, which comes from saponifier, from modern latin saponificare.. Sapon - soap + ficare - to make. ("saponification | Origin and meaning of saponification by Online Etymology Dictionary," n.d.)

## What is saponification anyhow?

In the most basic (ha! Chem pun!) of terms, saponification is the reaction that combines a fat with an alkali and poof, magic happens (aka chemistry) and you come out the other end with soap and some extra stuff. We're going to look at each of those bits in turn, including the poof, to determine what's going on in there.

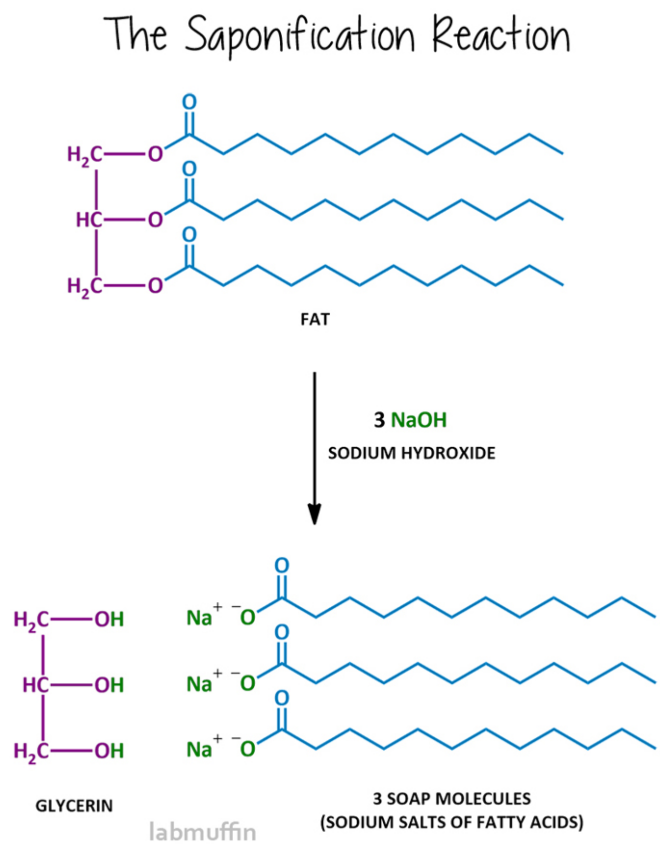



*Figure 1 Saponification (source: https://labmuffin.com/make-your-own-soap-part-1-the-chemistry-behind-soap-making/ )*

First off, some definitions.

## What do you mean by soap? Are there other soaps?

By rights, soaps could be called fatty acid salts because they are the result of an acid and a base neutralizing (plus water and extras), but generally they just get called soap. Soaps are a surfactant, which is a substance that reduces the surface tension of water, to help it spread and make water 'wetter'. What is in that base determines a lot about the soap. The two that work as what we would expect from the normal definition of soap are sodium and potassium. Sodium produces a hard soap, potassium a soft soap and both effectively grab the dirt and oils and wrap them up in little pockets with hydrophilic (water loving) groups on the outside and lipophilic (fat loving) groups on the inside. That whole little micelle (fancy word for the pocket) gets washed away and tadah! Things are clean.

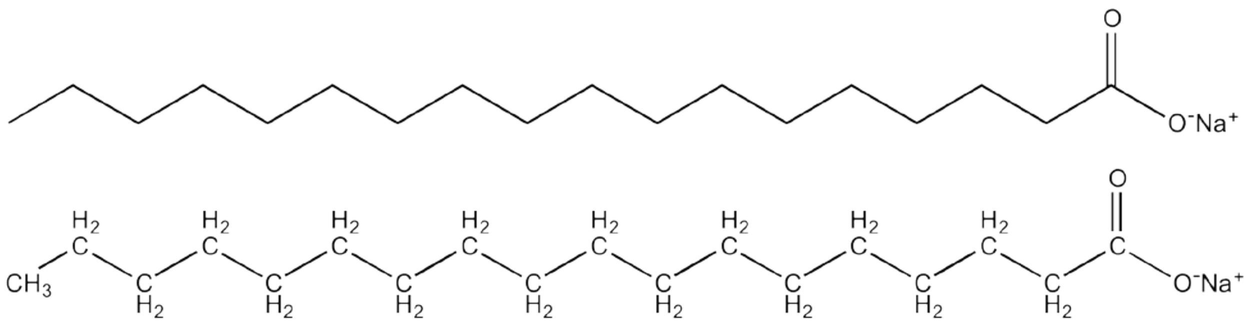



*Figure 2 Sodium Stearate*

*(image by: Smokefoot - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=20293318)*

Other metals also make soap, but not for washing. Lithium soaps are often lubricants, and potassium based soap is also used as the basis for wet chemical fire extinguishers. ("Fire extinguisher," 2019) Metal soaps can also turn up unexpectedly, such as when metal in pigments reacts with the fatty acids of the oil binder in oil paints and over time, saponification produces metal soaps under the paint layer of artwork. (Centeno & Mahon, 2009)

Soap is notorious for not playing nice with hard water, but the reality is that it plays too nice with hard water. Water is considered hard when it contains mineral salts, such as Calcium and Magnesium and sometimes others. Those mineral salts react with the soap and make soap scum. That insoluble precipitate doesn't rinse away well and tends to stick to everything and make fabric feel stiff and look yellowed. Detergent is the modern answer to that. They were developed in the first world war due to a shortage of animal fats to make soap and are produced often from petrochemicals to not react with hard water. ("Information about Soaps and Detergents | Healthy Cleaning 101," n.d.)

## Alkali.. What's an alkali?

In the simplest terms, most use alkali and base to mean just about the same thing, but they are not quite the same in chemistry terms. Alkalis are bases that dissolve in water (and provide those all important OH ions) Bases have a pH of higher than 7.1, and they will burn you. Respect the bases. Caustic burns suck, they sneak up on you. Don't be scared of them, but respect them. Basic solutions feel slippery to the touch, almost soapy (hey.. Waitaminute.. yep!).

For our purposes, there's only two that we care about:  Sodium Hydroxide (NaOH), and Potassium Hydroxide (KOH). Both of those, in distilled water, become either Na+ or K+ and lots of OH- floating around looking for trouble.

$$NaOH_{(s)} \rightarrow Na^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

*Figure 3 Sodium Hydroxide in solution*

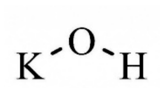


*Figure 4 Potassium Hydroxide*

Potassium Hydroxide is the one that is, for medieval purposes, easy to come by. Broadleaved hardwood trees (think ash, hickory, beech, oak, sugar maple) absorb potassium from the soil and store it. Softwoods (fir, pine etc) don't store much at all, they aren't any use for this purpose. When burned, the potassium compounds are left behind in the ash, and they are soluble in water to become that all important KOH. Hotter fires produce better ashes to work with and be sure to sieve out any charcoal! That's just pure carbon and totally in the way here. Rain water (or distilled water) is important, to minimize any extra minerals hanging around also getting in the way. This lye is of varying quality and strength. Lye for soap is generally considered strong enough if a chicken egg floats in it showing only about as much shell as the size of a quarter. For milder soap, there's recipes calling for the egg to float with as much lye above as below. ("To Make Black Sope (a manual for making soft soap from scratch) | susan verberg -

*Figure 5 Egg floating in homemade KOH*

Academia.edu," n.d.) If your egg sinks too much, your lye needs to be run through the ashes again, or boiled down to remove more water. If your egg is showing too much shell, dilute it down with more rain (or distilled) water. ("Making lye – THEORY," 2015)

Sodium hydroxide is a bit of a pain to achieve through most of our locations in period. The procedure is exactly the same as above, but the ashes need to come from marine plants as they absorb more sodium than potassium. Kelp, or Barilla (a shrubby salt tolerant collection of plants found primarily along the Mediterranean coasts), or an Egyptian mineral called 'trona' (sodium sesquicarbonate). (Kostick, 1994) None of these, save the kelp, are screamingly local to most of Western Europe. Possible, but not common. Nicolas Leblanc figured out how to decompose sea salt into sodium hydroxide in 1791, which eventually was adopted into a consistent and reliable source of pure sodium hydroxide by the early 19$^{th}$ century. (Kiefer, n.d.)

Modern soap makers generally buy their sodium and potassium hydroxide in pure crystal form and dissolve a very precise amount of it in water to produce their lye. (NB. That reaction produces a lot of heat (exothermic). ALWAYS add hydroxide crystals to water, never the other way around, and be prepared that the solution could go from room temp to a boil in a blink. Respect the lye.)

## Fat? What kinda fat? What is fat, anyhow? Fatty acids for everyone!

For our purposes here, fats are not just greasy stuff that's solid at room temperature, but any oils as well. We generally think of lard and tallow as being fat, and olive and canola oil being oils, but when playing in the chemistry world, we just call it a fat. In specific, the fats that we want to play with in soap making are triglycerides, which is derived from glycerol and three fatty acids. Those fatty acids are the other half of what makes up the qualities of the soap you are producing.

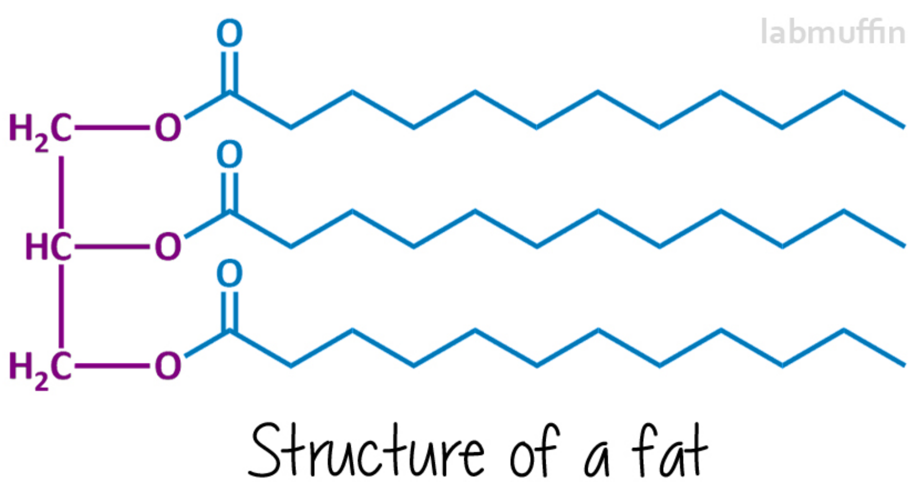
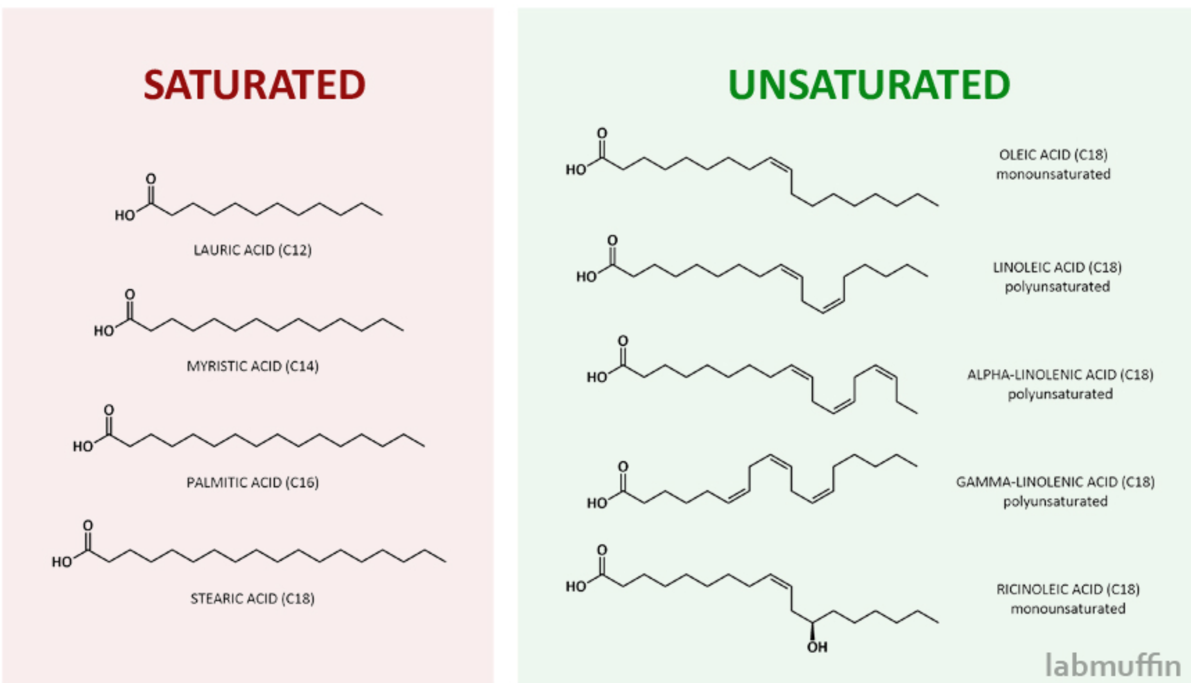



*Figure 6 Triglyceride (source: https://labmuffin.com/make-your-own-soap-part-1-the-chemistry-behind-soap-making/ )*

A fatty acid is a hydrocarbon group, with an acidic group on the end, and the ones we are interested in are the ones that are long hydrocarbon chains. Not all fatty acids will saponify, which is why not all fats are suitable for soap making. Fatty acids are distinguished not only by the length of their hydrocarbon chain, but also the degree of saturation. Saturated fats have straighter chains, thanks to a lack of double carbon bonds, and therefore are more effective at stacking together in those pockets we talked about, so strip oil better. Great for clothes, rough on skin. Unsaturated fats are a little gentler on skin, but not quite so effective for cleaning.
Fat from various sources have a variety of fatty acids in them and they all have slightly different properties over and above their fondness for stripping oils. The general composition of a few fats used for soapmaking has been included in Appendix A.




Saturated vs. Unsaturated Fatty Acids for Soapmaking

Modern soap makers have sorted out which fatty acid supplies which property to their soaps, and tailor the ratios to what they are looking for, and have a wide variety of fats and oils from around the world at their Prime fingertips. (Found in Appendix B) In our period, the best soaps came from Marseilles, Savona, Genoa, Venice, which used olive oil as the primary fat. Northern Europe tended to tallow and commercial soap in London was a mix of olive oil and tallow. Fish oil (primarily whale) didn't really arrive 'til the 17$^{th}$ century. (Brunello, 1973)

The main differences between tallow soap and castile soap (soap made from olive oil) comes in the oleic acid. Olive oil has lots, tallow has some. Olive oil also has more Linoleic acid than tallow, and quite a bit less stearic acid. Mixing and matching just exactly what fats make a soap that suits the purpose is often what brings it from pure science into an artform.

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# Appendix A

Percentage Fatty Acid Content of Various Fats used for Soapmaking

| | Lauric acid | Myristic acid | Palmitic acid | Stearic acid | Oleic acid | Linoleic acid | Linolenic acid |
|---|---|---|---|---|---|---|---|
| ***fats*** | **$C_{12}$ saturated** | **$C_{14}$ saturated** | **$C_{16}$ saturated** | **$C_{18}$ saturated** | **$C_{18}$ monounsaturated** | **$C_{18}$ diunsaturated** | **$C_{18}$ triunsaturated** |
| Tallow | 0 | 4 | 28 | 23 | 35 | 2 | 1 |
| Coconut oil | 48 | 18 | 9 | 3 | 7 | 2 | 0 |
| Palm kernel oil | 46 | 16 | 8 | 3 | 12 | 2 | 0 |
| Laurel oil | 54 | 0 | 0 | 0 | 15 | 17 | 0 |
| Olive oil | 0 | 0 | 11 | 2 | 78 | 10 | 0 |
| Canola oil | 0 | 1 | 3 | 2 | 58 | 9 | 23 |

https://en.wikipedia.org/wiki/Soap

# Appendix B

**Fatty acid properties in soap**

| | |
|---|---|
| Lauric Acid | Hard bar, excellent cleansing, lots of fluffy lather, can be drying to skin |
| Myristic Acid | Hard bar, cleansing, fluffy lather |
| Palmitic Acid | Hard bar, cleansing, stable lather |
| Stearic Acid | Hard, long lasting bar, stable lather |
| Oleic Acid | Conditioning, slippery feel, stingy lather, kind to skin |
| Linoleic Acid | Conditioning, silky feel |
| Ricinoleic Acid | Softer bar, conditioning, moisturizing, lots of fluffy, stable lather, kind to skin |

http://www.summerbeemeadow.com/content/properties-soapmaking-oils