

# OLEOCHEMICALS

## FATTY ACIDS

This section will concentrate on Fatty Acids produced from natural fats and oils (i.e. not those derived from petroleum products). Firstly though, we will recap briefly on *Nomenclature*. We spent some time clarifying the structure of oleochemicals and we saw how carbon atoms link together to form carbon chains of varying length (usually even numbered in nature, although animal fats from ruminant animals can have odd-numbered chains). A fatty acid has at least one carboxyl group (a carbon attached to two oxygens (-O) and a hydrogen (-H), usually represented as -COOH in shorthand) appended to the carbon chain (the last carbon in the chain being the one that the oxygen and hydrogen inhabit). We will only be talking about chains with one carboxyl group attached (generally called "monocarboxylic acids").

The acids can be named in many ways, which can be confusing, so we will try and keep it as simple as possible. The table opposite shows the acid designations as either the "length of the carbon chain" or the "common name". While it is interesting to know the common name for a particular acid, we will try to use the chainlength in any discussion so you do not have to translate. Finally, it is usual to speak about unsaturated acids using their chainlength suffixed with an indication of the number of double bonds present. Thus, C16=1 is the C16 acid with one double bond; C18=2 is the C18 acid with two double bonds and so on.

### SELECTING RAW MATERIALS FOR FATTY ACID PRODUCTION

In principle, fatty acids can be produced from any oil or fat by hydrolytic or lipolytic splitting (reaction with water using high pressure and temperature or enzymes). In practice, only around eight or so fats/oils contribute to the bulk of fatty acid production, with some variation depending on geography.

	EUROPEAN UTILISATION	NORTH AMERICAN UTILISATION
Tallow Type	69%	55%
Coconut/Palm Kernel	9%	15%
Soya	7%	4%
Tall Oil Fatty Acid	11%	24%
Other	4%	2%

The utilisation of different oils produces acids with differing carbon chainlength distributions which allows the market to characterise a fatty acid into groups according to the major chainlength featuring in the acid.

The following table shows the approximate chainlength distributions of the main oils used -

COMMON NAME OF ACID	CHAINLENGTH	CNO	PKO	SOYA	RAPE	TALLOW	PALM
Caproic	C6						
Caprylic	C8	7	3				
Capric	C10	6	3				
Lauric	C12	47	47	1			
Myristic	C14	19	16	1		3	1
Pentadienoic	C15					<1	
Palmitic	C16	10	9	10	5	24	45
Palmioloic	C16=1					4	
Margaric	C17					<2	
Stearic	C18	3	2	4	2	20	4
Oleic	C18=1	6	17	22	60	43	40
Linoleic	C18=2	2	3	54	21	4	10
Linolenic	C18=3			8	9	1	<1
Arachidic	C20				1		
Eicosenoic	C20=1				2		

The main groups are *Laurics*, which contain mainly C12/C14 acids (C12 is known as Lauric Acid) and manufactured from Coconut/Palm Kernel oils; *Whole Cut*, with a chainlength that reflects the parent oil, e.g. Tallow and Rapeseed; *Saturates*, which contain mainly C16/C18 acids (sometimes known as Stearics, although technically only C18 is Stearic Acid); *Mono-unsaturates*, which are mainly Oleic (C18=1), but Erucic (C22=1) also features; and *Polyunsaturates*, which contain more than one double bond, e.g. Linoleic (C18=2) and Linolenic (C18=3).

A particular raw material is chosen by the producer to yield the appropriate chainlength profile for the desired product with a minimum of undesirable by-products and interferences with the chosen splitting process. The producer will also wish to make his acids at the most economical price and will ensure that his raw material is always accessible and available; hence the preponderance of indigenous oils used within the various geographical regions. It is rare though that all market needs can be serviced from one source. For example, while tall oil contains significant quantities of C18=1, C18=2 and higher unsaturates, it also contains sulphur compounds that poison hydrogenation catalysts and, therefore, limit the processability of tall oil fatty acids. This is an influence on the global trade in oils and fats.

## **THE PRODUCTION PROCESS**

It would be impossible to cover the detail of the processes used to produce fatty acids from their parent oils in any great depth in this booklet so, once again, we will concentrate on the “big picture” and leave the detail to the chemical engineering textbooks.

All fats and oils are composed of compounds known as “triglycerides”, i.e. three fatty acids linked to a glycerine backbone. By the addition of water and the application of high temperatures (~250°C) and pressures (~50 atmospheres), or by the addition of water and the addition of an enzyme catalyst called a “lipase” and controlled agitation at atmospheric pressure and temperatures about 37°C, it is possible to break apart these triglycerides to release the fatty acids and glycerine as separate materials. These processes are known as “fat splitting” and, in both of these processes (but especially in the high temperature one), it is vital that, having mixed oil and water intimately in the reactor, we can get the two phases apart again to recover the products.

Several naturally occurring components in the oils and other detritus introduced as the oil is extracted from the seed, nut or animal, militate against this happening by either creating or stabilising emulsions that affect the efficiency of the separation. There may, therefore, be a need for pre-treatment stages ahead of the hydrolysis process to remove or denature these materials. Examples of such stages include settlement or centrifugation (to remove finely divided solids) and washing with steam, acid or phosphates, followed by settlement (to remove various forms of proteinaceous and/or water soluble impurities). Assuming we have reached the dizzy heights of having recovered the product streams from the splitter, we will find that we have an aqueous solution containing about 10-14% glycerine, which goes off to be evaporated to about 80% glycerine content for sale as crude glycerine and a fatty material that is mainly raw fatty acid with some fatty impurities.

## **POST HYDROLYSIS PROCESSES**

Purification of fatty acids is mainly achieved by distillation, which makes use of the differences in boiling points between the desired fatty acids and the impurities, to effect a separation of the two species. The distillation is usually conducted at reduced pressure to save energy and is done in such a way that the fatty acids are vapourised and the vapours taken off and condensed back to liquid, leaving the impurities in the still-pot. The resultant acids will be known as “whole-cut” materials because all the chainlengths present in the parent oil will be present in the fatty acids in approximately the same proportions.

Sometimes a more sophisticated form of distillation is employed, called “fractionation”. The principles of separation of the fatty acids from the impurities is the same, but the vapours are condensed in a column designed so that removing condensed liquid at different levels of the column yields products of the required composition. Mixtures of fatty acids achieved by this process are generally referred to as “light-cut”, “mid-cut” or “heavy-cut” fatty acids, depending on whether they are taken from the top, middle or bottom of the fractionation column. Light-cuts consist mainly of C6, C8 and C10 chainlengths. Mid-cuts are largely C12 and C14 mixtures and heavy-cut acids will have all the remaining chainlengths (i.e. from C16 upwards). Through judicious use of fractionation column technology, it is even possible to produce “pure cuts”, i.e. single chainlength acids of >99% purity. A special separation process called “fractional crystallisation” is sometimes applied to fatty acid mixtures containing significant amounts of C18=2 (oleic acid), e.g. tallow fatty acids. In this process, use is made of the differing freezing points of saturated and unsaturated acids. As a molten mixture of the whole-cut acid is cooled, the saturates crystallise out and are removed, thus progressively increasing the level of unsaturated acids in the mixture. Upon completion of the crystallisation and subsequent distillation, the saturated fraction is sold as commercial separated stearic acid and the unsaturates as commercial oleic acid.

Finally, but very importantly, the level of unsaturation can be modified or eliminated from a mixture by hydrogenation (reaction with hydrogen) to add the missing hydrogen back into the double bonds in the material. This is also known as “hardening” and may precede or follow distillation or fractionation.

## USES OF FATTY ACIDS

Fatty acids tend to be used as intermediates in the production of other chemicals or products. The key product areas using fatty acids and their approximate consumption of what is available are -

Soap/Detergents/Surfactants	>50%
Rubber/Plastics	>20%
Paper	~10%
Lubricants	<10%
Food/Feed	<10%

Soap is probably the oldest washing aid known to man and still predominates in the market for personal cleansing (although synthetic shower gels, lotions and bars are on the increase). The earliest processes for soap production, although apparently simply reacting oils and fats with a caustic lye to split the triglycerides as described above were, in fact, quite complex reactions and quite resource intensive to control. From the late 1950s onwards, the traditional "kettle boiling" process began to be replaced by direct neutralisation of fatty acids as the soapmaking method of preference - the cycle time was much lower, energy was saved and the soapmaker no longer had to deal with the glycerine by-product. Synthetic detergent intermediates can be produced by reacting fatty acids with sulphur trioxide or ethylene oxide. Fatty acids have long been important in the compounding of natural rubber and in both the manufacture and compounding of synthetic rubber to attain optimum processing and vulcanisation characteristics. In food, fatty acids are used to produce monoglycerides to act as food emulsifiers and light-cut fatty acids are used to produce medium chainlength triglycerides for feeding premature babies.

The above are just a few examples of how fatty acids produced from fats and oils contribute to our current quality of life and serve to further illustrate the importance of oleochemicals in today's world..