Fatty acids: a versatile and sustainable source of raw materials for the surfactants industry

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Summary : Fatty acids have been used as a major source for the hydrophobic part of surfactants since the discovery of soap, more than 4,500 years ago. Despite the wide variety of different hydrophobes that have become available during recent decades, fatty acids are still playing a significant role in the surfactants industry thanks to their versatility, natural origin and reliable supply. The aim of this presentation is to give an overview of the developments and trends in the use of fatty acids in the surfactants industry, the properties of fatty acids related to their application in surfactants and detergents and the underlying influencing trends in the oils and fats industry.

Keywords : fatty acids, surfactants, detergents, oleochemicals, surfactant hydrophobes, galenic softeners, personal cleansing.

ARTICLE

Fatty acids have been serving mankind in the form of soaps at least for 4,500 years [1]. There are many versions of the story of how soap was invented or rather discovered [2], but one thing is clear: the combination of fatty matter from natural, organic origin and caustic led to a product that delivered a superior cleaning performance compared to the standard of the day.

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For the overwhelming majority of the time since the discovery of soap, it has been the only surfactant that was available for use in the three traditional surfactant application areas: personal cleansing, textile washing and industrial applications.

For all this time - the largest part of our history - fatty acids have been the only hydrophobic surfactant building block.

It was only in the early part of the twentieth century that other hydrophobic surfactant building blocks based on natural oils and fats were developed: the fatty alcohols and fatty methyl esters. A few decades later, hydrophobes derived from petrochemical sources entered the playing field, with petrochemical fatty alcohols, alkylbenzene and alkylphenol as their major representatives. This broad range of available hydrophobes, combined with a consumer and industry need for better performance and a strongly developing chemical industry led to the real explosion in the number of different types of surfactants that are currently available [3].

This paper will focus on the oldest member of the family of surfactant hydrophobes, the fatty acids. It will become apparent that at an age exceeding 4,500 years, this great grandfather of the surfactants industry is still youthful.

**Oleochemical hydrophobes for surfactants**

Oleochemical raw materials for the surfactant industry offer the manufacturer three degrees of freedom that enable fine-tuning the properties of his hydrophobe for optimum performance, lowest cost or the best cost/performance ratio. These are:

- raw material choice: oils and fats;
- chemical functionality: oleochemical building blocks;
- tailoring: oleochemical processing of fatty acids.

Before further discussing developments in the area of fatty acid based surfactants; we will first look at these three degrees of freedom in more detail.

**Raw material choice: oils and fats**

Oleochemical hydrophobic building blocks for the surfactants industry are based on natural oils and fats. Therefore, we should first take a look outside, to the animals and plants around us to get a view on the most important factors with regards to raw material choice: availability, composition and cost effectiveness.

**Availability**

Natural oils and fats can be derived from a wide range of vegetable and animal sources. The global production of the 17 most important oils and fats is estimated at 107 million tons for the harvest year 1998/1999 [4]. Volume wise, the most important vegetable oils are soybean oil, palm oil, rapeseed oil and sunflower oils. The most important animal source is tallow.
The global production of oils and fats has grown strongly over the twentieth century. Around 1911, the global production was estimated at 13 million tons. By 1959, this had doubled to a total global volume of 28 million tons [5].

Since then, the global production of oils and fats has doubled every 20 years: 55 million tons in 1979 and 110 million tons in 1999 (Figure 1).

Around three quarters of global oils and fats production is used for human consumption. Therefore, the drivers for the growth in production should mainly be sought in this area: increasing fat consumption per capita in developing economies and the growth of the world population. The current growth rate of 3.8% per annum would imply another doubling of oil and fat production in the coming 20 years time (Figure 2). Whether we can really expect a global production of oils and fats of 220 million tons in 2019 will depend on the continuation of the current relatively stable global economic development that strongly underpins the growing demand in human consumption in e.g. China and India.

The majority of the growth in oils and fats production comes from vegetable sources, which have been growing at over 4% per annum for the past 20 years. The main vegetable growers are palm, palm kernel, rape and corn, each with annual growth rates in excess of 6%. Animal fat production is strongly linked to meat consumption, which has shown a steady annual growth rate of around 1% over the past 20 years. Currently, the ratio between animal and vegetable oils and fats production is 20/80 (Figure 3).

The main use of oils and fats is in human food applications. The global population consumes 76% or around 81 million tons. Of the rest, about 6.5 million tons is used for animal feed applications. The remaining 19.5 million tons is used in technical applications: 7.5 million tons is converted to soap, 10.5 million tons is used by the oleochemical industry as a raw material and 1.5 million tons is used in other applications (Figure 4).

**Composition**

All major oils and fats have the same chemical structure: they are triesters of fatty acids with glycerol. With regards to the type of fatty acids that are present in oils and fats, nature is beautifully selective. Except for a number of specialties, some of which will be discussed later in this paper, the vast majority of these fatty acids have the following characteristics:

- the backbone is a straight chain of carbon atoms;
- the backbone contains an even numbers of carbon atoms;
- there is only one carboxylic acid function, located at one end of the chain;
- the total number of carbon atoms is between 8 and 22;
- unsaturations in the chain have the *cis*-conformation;
- unsaturations are usually not present at the end of the chains;
- unsaturations occur mainly in C16 and longer carbon chains.
We tend to take it as a given, but it is actually amazing to think about this natural chemistry that is continuously going on at extremely high selectivity, high yields and low energy consumption in all animals and plants.

Reflecting on the characteristics of natural fatty acids with the eyes of a surfactant manufacturer in search for a good hydrophobe, it is clear that there is a good match between what nature supplies and what the surfactant manufacturer needs. Straight chains ensure a good biodegradability, the chain length is exactly in the area required for a good surfactant performance and the reactive group is at a place where most surfactant manufacturers want to have it: at the end of the chain. Knowing the rules that nature applies during fatty acid production, we can now take a look at the way the different types of fatty acids are distributed over the different oils and fats (Table 1).

Again, there is a good match between what nature supplies and what the surfactant manufacturer needs. The main three types of hydrophobes needed are: medium chain (C10-C14) saturated (laurics), long chain (C16-C18) saturated (stearines) and long chain unsaturated (oleines), all of which are available from natural oils and fats. We have now looked briefly at the availability and the composition of the different oils and fats. In order to make the picture complete, we now need to consider cost effectiveness.

**Cost effectiveness**

For long chain saturated- and long chain unsaturated fatty acids, the main source has traditionally been tallow, in most cases, tallow based products are still the most cost effective for the surfactant manufacturer. However, over the last decades, vegetable alternatives like rape and palm oil have become available for customers that require a vegetable feedstock.

With regards to the lauric type hydrophobes, the oils of choice are coconut oil and palm kernel oil. There is no animal source with sufficient lauric type fatty acids to make exploitation commercially attractive. Just a few decades ago, only coconut oil was available in sufficient quantities to serve as a raw material for lauric type surfactant hydrophobes. The strong growth in palm plantation areas in the eighties and nineties led to palm kernel oils becoming available as an alternative to coconut oils. It is clear from the table above, that even if they are both high in lauric type fatty acids, they still contain differences in the short end and the amount of unsaturates.

This gives the following, simplified picture with regards to the selection of the main types of hydrophobic building blocks for the surfactant industry (Table 2).

**Chemical functionality: oleochemical building blocks**

The oleochemical industry uses natural oils and fats as its raw material, and converts these to three major oleochemical building blocks, all of which are relevant for the surfactants industry as a source of hydrophobes. These are fatty acids, fatty methyl esters and fatty alcohols respectively (Figure 5).

Fatty acids are made in a one step process from oils and fats by hydrolysis. This hydrolysis is generally referred to as splitting, and is usually carried out in continuous splitting columns by contacting the oil or fat with excess water at temperatures of 250-270°C and pressures of over 50 bar. The products from this process are crude fatty acids and a glycerol/water mixture as a by-product stream.
They offer the surfactant manufacturer a carboxylic acid functionality that can be esterified, alkoxylated, amidated, chlorinated or saponified. Fatty acids will be discussed in more detail in the rest of this paper, but first, a few words about the other two oleochemical building blocks: fatty methyl esters and fatty alcohols and the petrochemical hydrophobes.

Fatty methyl esters are also made in a one step process from oils and fats. In this case, the oil or fat is trans-esterified with methanol (methanolysis). The products from this process are crude methyl esters and a glycerol/methanol mixture as a by-product stream. Fatty methyl esters offer the surfactant manufacturer a carboxylic methyl ester functionality that can be inter-esterified, inter-amidated, alkoxylated and saponified.

Natural fatty alcohols are produced by hydrogenation of fatty acids and fatty esters; fatty methyl esters being the main source of oleochemical fatty alcohols. Fatty alcohols offer the surfactant manufacturer a hydroxy functionality, that can be sulphated, alkoxylated, and etherified (Figure 6).

Next to the 3 oleochemical hydrophobes mentioned before, there are also 3 petrochemical hydrophobes of main importance to the surfactants industry. These are petrochemical fatty alcohols, alkyl benzene and alkyl phenol.

From a global point of view, the petrochemical alkylbenzene is the largest volume hydrophobe currently used [8]. Regionally, this dominance is most clear in Asia, Africa and South America. It is clear that the most important surfactant hydrophobe in Europe, Japan and North America these days is fatty alcohol, with a share of around 50%. Fatty acid has a share of around 15% in these regions (Figure 7).

It is interesting to note that on average, fatty acids are used in the higher valued surfactants: the European volume share is around 13%, whereas the value share is around 17% (Figure 8). The reason for this becomes clear when we look at the share of fatty acids in the main surfactant classes: fatty acids are used predominantly in amphoteric and cationic surfactants, which overall have a higher value than anionics and nonionics (Figure 9).

Tailoring: oleochemical processing of fatty acids

The third degree of freedom for the surfactant manufacturer comes from the ability to tailor properties in order to optimise the hydrophobe for his purposes. This discussion will focus on fatty acid processing, but some of the basic principles will also apply to fatty methyl esters and fatty alcohols.

The first process step normally carried out on fatty acids after splitting is a purification by distillation. During this distillation, a small top fraction of volatile, odorous components and a small bottom fraction of highly coloured by-products are removed. In several cases, the purified fatty acid mixtures from this distillation can be used as such for surfactant manufacture. Typical distilled fatty acids that are used frequently by the surfactants industry are distilled tallow fatty acids (mainly for cationic surfactants) and distilled coconut and/or palm kernel fatty acids (for personal cleansing surfactants such as fatty isethionates and fatty amidopropyl betaines).
In other cases, more tailoring is required. Usually this involves a further separation of the fatty acid mixtures into their different components, either by chain length or by degree of unsaturation.

Chain length is related to the boiling point of the different fatty acids, so a separation by chain length can be carried out via fractional distillation of the fatty acid mixture. Degree of unsaturation is related to the melting point of the fatty acids, so a classification by degree of unsaturation can be carried out via crystallisation, either with or without a solvent (Table 3).

When a higher oxidative or colour stability and/or a higher melting point are required, the fatty acids can be either partly or fully hydrogenated. One of the consequences of partial hydrogenation is the near-complete removal of polyunsaturated fatty acids that can have a strong influence on heat- and storage stability of the fatty acids and their derivatives. Esterquat manufacturers who need good odour stability and optimum softening performance use partly or fully hydrogenated fatty acids. Partly or fully hydrogenated coconut or palm kernel fatty acids are used in low colour/low odour personal cleansing surfactants.

A wide variety of fatty acids building blocks are available to the surfactant manufacturer based on the raw materials nature offers, separations based on boiling and melting point and part or full hydrogenation.

Some specialities deserve a separate mention:

- long chain fatty acids: some applications require longer chain fatty acids than is normally delivered with a standard stearine, e.g. for superior hydrophobing with certain speciality quats. Fatty acids and mixtures containing C20 and C22 are available for these purposes;

- branched fatty acids: applications that need the low viscosity or low temperature properties that come with an oleine derived surfactant and the colour and oxidation stability that comes with a stearine derived surfactant can use branched fatty acids such as isostearic acid as their hydrophobe;

- dimerised fatty acids: when a particularly bulky hydrophobe is required in applications such as corrosion inhibition, dimerised fatty acids may be the hydrophobe of choice.

**Surfactants based on fatty acids**

Now let us look at the main surfactant types that are based on fatty acids.

As mentioned above, fatty acids offer the surfactant manufacturer a carboxylic acid functionality to work with. This carboxylic acid functionality can be converted via 5 different chemical transformations to surfactants or surfactant intermediates. These processes are (Figure 10):

- amidation, either with ammonia to produce alkyl quats and fatty amines via the nitrile route or with an amine to produce the intermediates for betaines and imidazolines;

- esterification to produce fatty isethionates, polyol esters and intermediates for ester quats;

- alkoxylation to produce fatty acid alkoxylates. Strictly speaking, these can also be classified as esters;
- chlorination to produce intermediates for the personal care speciality surfactants sarcosinates and taurates;
- saponification to produce soap.

The scope of this paper does not allow for an in depth coverage of all the surfactants based on fatty acids so let me just say a few words about fatty acid building blocks for some of the most important end markets for fatty acid derived surfactants:

- fatty acids for fabric softener surfactants;
- fatty acids for personal care cleansing surfactants.

Fatty acids for fabric softener surfactants

The active surfactants in fabric softening are cationic types, all with similar chemical characteristics:

- the molecule contains a quaternary nitrogen atom that gives the molecule its positive charge and allows it to "stick" to negatively charged surfaces;
- the molecule contains two long hydrophilic tails (C16-C18) that provide the apolarity/hydrophobicity which imparts softening properties.

The need for a long chain, cost effective hydrophobe generally makes tallow an attractive source of raw material for fabric softener actives.

Given these rules of thumb, there are still several fatty acid parameters that can be optimised to obtain the required performance:

- chain length and chain length distribution;
- degree of unsaturation;
- degree of branching;
- \textit{cis/trans} ratio of the double bonds;
- "quality".

Chain length and chain length distribution influence softening performance. Longer chains increase the hydrophobicity of the quat molecule and thereby improve the softening performance. The optimum is achieved with C18; longer chain lengths appear not to bring appreciable benefits. The degree of unsaturation has a strong influence on formulation flexibility. A higher degree of unsaturation gives a more liquid quaternary surfactant that is easier to formulate, allows the production of transparent fabric softener formulations, and gives better rewetting properties than quats based upon saturated fatty acids [9].
The same effects that can be obtained by introducing unsaturation in the fatty acid chains can also be introduced by using branched fatty acids. An additional benefit of branched fatty acids over unsaturated fatty acids is the fact that they are much more stable against oxidation and discoloration.

"Quality" is put between quotation marks, as this is not something that can simply be measured on a scale from one to ten, but is something that is determined in close collaboration between the surfactant manufacturer and the fatty acid supplier. The required fatty acid quality can be different:

- for different end markets;
- whether targeting for the top or the bottom segment of a certain market;
- for different types of quaternaries;
- depending upon the process the surfactant manufacturer uses;
- etc.

"Quality" is also related to something less tangible; understanding the relationship between the fatty acid building block and its effects in the chemical and physical processes of the customer and his the end application. This end application is often several physical and chemical processing steps removed from the fatty acid origin. Often, effects two or more processing steps downstream from the fatty acid cannot be covered by a sensible specification on the fatty acid.

To give an example: fatty acid specifications on heat stability are at most only a very rough indication of discoloration during the esterification step in esterquat manufacture. Carrying out a lab scale esterification to get an idea of colour stability would take too much time, cost too much and is generally not representative for what happens in the factory anyway.

"Quality" in this sense is related to a deep understanding of fatty acids on the one hand AND a deep understanding the surfactant manufacturer’s physical and chemical process steps and end application on the other hand. Experience shows that there is still an untapped potential of special effects, cost savings, efficiencies, etc., that can be explored with close collaboration between the fatty acid supplier and the surfactant manufacturer. It is possible to determine the right "Quality" for every need.

**Fatty acids for personal cleansing surfactants**

The three main classes of fatty acid based surfactants for personal cleansing applications are:

- soap;
- acyl isethionates;
- amphoteric-like alkylamido betaines and imidazoline derivatives.
Soap cannot be covered with the depth it deserves in this paper, but it may be useful to realise that soap still is the most widely used surfactant for personal and fabric cleaning. As mentioned before, it is the oldest surfactant, and despite the enormous advances in science and technology and the invention and wide use of new classes of surfactants, it has still been able to maintain its number one position worldwide.

Having said that, it is clear that in the Western world, the overall soap market is declining by over 3% per annum, driven by a consumer need for milder products. This decline is partly offset by fast growth in mild soap and syndet bars. Some of the mildest alternatives to soap are based on fatty acid derived surfactants: acyl isethionates for mild cleansing soap and syndet bars and amphotericics like alkylamido betaines and imidazoline derivatives for liquid shower products and shampoos.

Generally, surfactants used in cleansing applications are based on mid chain saturated hydrophobes. As we have seen earlier in this paper, this offers the surfactant manufacturer the opportunity to use two different types of vegetable based raw material sources: coconut and palm kernel. This is in line with the consumer perception that a vegetable-based raw material is even more natural than an animal derived raw material.

Looking in detail at the fatty acid composition of coconut and palm kernel oil, it is clear that even if they are both high in lauric type fatty acids, they still contain differences in the short end and the amount of unsaturates. These differences can influence the properties of the surfactants derived from them, often preventing a simple switch from one type to the other. Expertise from the oleochemical industry can help in the decision making process accompanying a possible switch between these oil types.

We have now fixed two of the previously mentioned three degrees of freedom, namely the vegetable source of raw materials, and the fatty acid oleochemical building block. The next question is how much tailoring is needed to achieve optimum properties for the surfactant manufacturer in his or her application?

If we take coconut fatty acids as an example, the baseline is a distilled coconut fatty acid mixture, obtained from splitting coconut oil and minimum "topping" and "tailing" during distillation. Starting from this baseline, various degrees of tailoring are possible to achieve the required end result for the surfactant manufacturer in his or her application:

- increasing "topping" and/or "tailing" during distillation can change the odour profile of the fatty acids, which may lead to a reduction in the addition levels of fragrances, often one of the more expensive ingredients in a personal cleansing formulation;

- various degrees of hydrogenation can lead to better colour-, odour- and heat stability, often necessary when aiming for transparent and colourless end formulations;

- fractional distillation will lead to fatty acid fractions with a purity of over 98%. In this way, unwanted side products can completely be avoided, the chain length with well defined properties can be selected and a good stability is guaranteed;
- blending fatty acids from different raw material sources or blending fractions from fractional distillation can lead to fatty acid compositions that give unexpected application benefits or offer cost saving opportunities.

Again, the right solution for the surfactant manufacturer in his or her end application is depending on many different factors that need to be established in close cooperation between experts from the fatty acid supplier and the surfactants industry.

**L'ASPA, le CESIO, l'AISD et l'AISE**

Les producteurs d'agents de surface et de produits auxiliaires en France sont rassemblés au sein de l'ASPA qui est membre de l'Union des industries chimiques.

L'ASPA ainsi que les organisations similaires des autres pays européens constituent le CESIO (Comité européen des agents de surface et leurs intermédiaires organiques), lui-même rattaché au CEFIC (Conseil européen des fédérations de l'industrie chimique) à Bruxelles.

Le CESIO organise tous les quatre ans un congrès mondial alternativement dans chaque pays européen. Le congrès de l'année 2000 s'est tenu à Florence, le prochain aura lieu en 2004 à Berlin (les actes du congrès de Florence sont disponibles auprès de l'ASPA tant sous forme de fascicule que de CD-rom).

De leur côté, les producteurs de détergents, gros utilisateurs d'agents de surface, sont réunis au sein de l'AISD (Association des industries des savons et détergents). Là aussi, l'AISD et ses homologues européens forment une association européenne, l'AISE (Association internationale de la savonnerie, de la détergence et des produits d'entretien).

Le CESIO et l'AISE ont développé depuis plusieurs années déjà une coopération technique importante pour l'étude des propriétés environnementales des agents de surface utilisés dans la détergence.

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**Note :**

* Texte de la conférence prononcée dans le cadre du congrès CESIO 2000.

**CONCLUSION**

Fatty acid, the oldest surfactant hydrophobe is still playing a significant role as a surfactant raw material over 4,500 years after its first use. Especially in cationic and amphoteric surfactants, fatty acids are by far the most important hydrophobe. In addition to their versatility, the use of fatty acid hydrophobes may be a small step towards sustainability, i.e. "Meeting the needs of the present without compromising the ability of future generations to meet their needs" [10].
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Illustrations

Figure 1. *Global oils and fats production, 1998/1999.*
Figure 2. Development of global oils and fats production in the 20th century.

Figure 3. Cumulative annual growth rates for the oils and fats, 1980-1999.
Figure 4. Global uses of oils and fats, 1999.

Figure 5. Oleochemical building blocks.
Figure 6. Routes to oleochemical building blocks.

Figure 7. Volume shares of the major surfactant hydrophobes in Western Europe, North America and Japan in 1997 (from Modler et al. [7]).
Figure 8. Volume share versus value share for West European surfactant hydrophobes, 1997.

Figure 9. Volume share of fatty acids as hydrophobes for the different surfactant classes, West Europe, 1997.
Figure 10. Routes to fatty acid derived surfactants.
### Table 2. Major surfactant hydrophobes and their oleochemical sources.

| Type of hydrophobe       | Common name | Animal source | Vegetable source |
|--------------------------|-------------|---------------|------------------|
| Medium chain, saturated  | Laurics     | None          | Coconut, Palm kernel |
| Long chain, saturated    | Stearines   | Tallow        | Rape, Palm       |
| Long chain, unsaturated  | Oleines     | Tallow        | Rape, Palm       |

### Table 3. Separation processes in fatty acid production.

| Separation by              | Physical parameter | Process                      |
|----------------------------|--------------------|------------------------------|
| Chain length               | Boiling point      | Fractional distillation      |
| Degree of unsaturation     | Melting point      | (Solvent) crystallisation    |
