OLEOCHEMICALS
A SUSTAINABLE ALTERNATIVE

In this section on Oleochemicals we will look at the important role that these chemicals play in all of our lives, cover some general aspects of the industry and the technology, and look at three of the most important categories of oleochemicals (Fatty Acids, Methyl Esters and Fatty Alcohols) in more detail.

WHAT IS AN OLEOCHEMICAL?

The simplest definition of an oleochemical, is *a chemical produced from natural oils and fats.* Of the 105 million tonnes or so of fats and oils produced worldwide, every year, about 80% is utilised for human food. About 5% is consumed as part of animal feeds and about 15% is used to produce chemicals. About 16 million tonnes finds its way into the chemical industry, usually in the form of coconut oil, palm kernel oil, palm oil and tallow (animal fat). These oils fall into two groups - lauric oils (coconut and palm kernel) that are rich in carbon chains consisting of 12 and 14 linked carbon atoms, and those with carbon chains of 16 and 18 carbon atoms (tallow and palm). Both of these categories are very important to the surfactant industry where, for domestic use, a balance between cleansing properties and mildness towards the skin is especially important. Other oils like rapeseed, soya and sunflower are also used, but those mentioned above have long been the main workhorses in the industry.

UNDERSTANDING THE TECHNOLOGY AND TERMINOLOGY OF OLEOCHEMICALS PRODUCTION

In the course of discussing the major oleochemicals groups, it is inevitable that a lot of fairly specialised terminology will be used. Now is the time to explain some of the more commonly used terms and jargon likely to be encountered. As already stated, oleochemicals are made from natural oils, but the crude oils generally need some form of pre-treatment before processing. The most common pre-treatments are *refining*, to remove free fatty acids and some impurities from the oil prior to *bleaching*, to remove colour and then *deodorising* to strip out odoriferous and further chemical impurities. The final product of these pre-treatment processes is referred to, not surprisingly, as refined, bleached and deodorised or, more commonly, RBD oil.

Some *whole oils* (i.e. oils that still have their complete range of carbon chainlengths) are fractionated or otherwise separated, to give rise to liquid portions (known as *oleines*) and more solid portions (known as *stearines*). Stearines are said to be highly *saturated* (i.e. each carbon is surrounded by the full number of hydrogen atoms allowed for the molecule), whereas oleines contain more *unsaturated* molecules (where there is not enough hydrogen to give saturation and some of the carbon atoms bind to each other with multiple (usually double) bonds). This oil is now ready to be subjected to one or more of the processing steps that will result in its conversion to one of the major groups of oleochemicals. It might be *hydrolysed* (reacted with water at high temperature and pressure) to form fatty acids and glycerine. It might be subjected to *methanolysis* (reaction with methanol using a catalyst) to generate methyl esters of the component fatty acids and, of course, glycerine. It might seem to some that the whole point of the processing steps used is to break the oil molecule up to give access to the bit with the long carbon chains for further processing, while removing the glycerine backbone of the triglyceride molecules (which is what all fats and oils are, chemically). This, while being a huge oversimplification is, however, not too far from the truth to prevent it serving as a usable model. The products of these reactions might now be *hydrogenated* (reacted with hydrogen at high temperature and pressure in the presence of a catalyst), either to remove unsaturation or to reduce one chemical species to another (as in the case of the hydrogenation of methyl esters to make fatty alcohols).

Finally, further purification and separation steps may be applied to tailor the chemical for its proposed market. It may be *distilled* simply to remove impurities from the main chemical by exploiting the difference in their boiling points, or a more sophisticated form of distillation, known as *fractionation*, may be applied to generate chemical mixtures containing the appropriate lengths of carbon chain. If we assume that the oils used are made up of carbon chains ranging from 6 to 22 carbons long, fractionation into materials containing 6 to 10 carbons *(light-cut* chemicals), 12 to 14 carbons *(mid-cut* chemicals) or 16 to 22 carbons *(heavy-cut* chemicals) widens the usage of the particular oleochemical in question. If necessary, fractionation can be tailored to give single molecular species of high purity (99%+). For example, lauric acid (C12 fatty acid) of 99.5% purity is not uncommon.

A BIT ABOUT ECONOMICS

The Palm Oil Utilisation Chart (overleaf) clearly reflects the predominant use of fats and oils in direct food usage. The categories at the periphery of most of the flowchart routes do much, however, to add value to the fat/oil molecule produced. Considering just palm oil selling at about US$ 390/MT, fatty alcohols sell at approximately US$ 1200/MT, methyl esters at US$ 980/MT and fatty acids at about US$ 760/MT. These prices, of course, fluctuate with the oil price and also depending on the price of ethylene, which is also a raw material from which

the above chemical species can be manufactured. The big advantage for oleochemicals is that they are produced from renewable resources and are thus sustainable and viewed by many as the "green" alternative to chemicals from hydrocarbon oils.
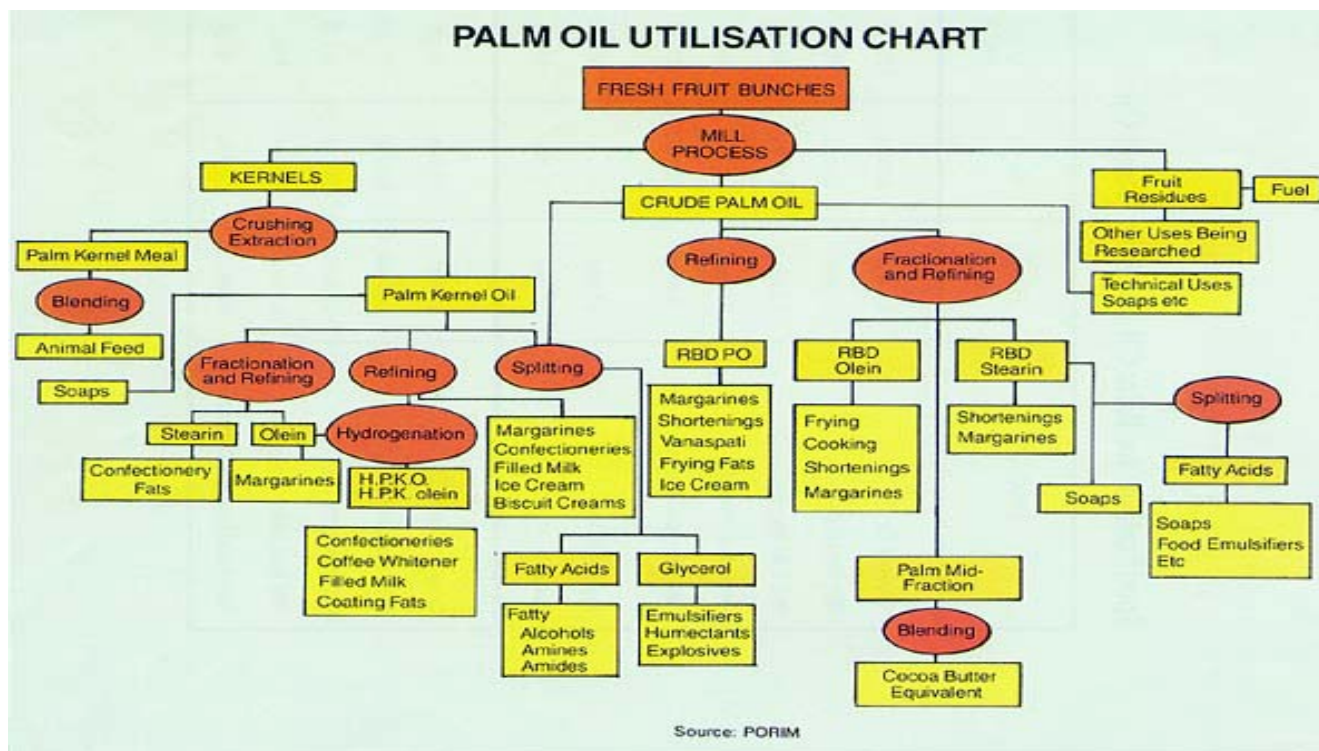
OLEOCHEMICALS - FATTY ACIDS

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
Palmiololeic	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; *Saturate*s, which contain mainly C16/C18 acids (sometimes known as Stearics, although technically only C18 is Stearic Acid); *Mono-unsaturate*s, which are mainly Oleic (C18=1), but Erucic (C22=1) also features; and *Polyunsaturate*s, 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.

OLEOCHEMICALS - METHYL ESTERS

INTRODUCTION

We have previously mentioned that these materials could be viewed as a "green" alternative to the use of materials derived from our ever-diminishing petroleum reserves. This fact is especially true of methyl esters, which, as well as enabling the formulation of biodegradable surfactants, are now being used to replace diesel oil and petroleum-based solvents. Historically, methyl esters were viewed as chemical intermediates, that is, a stepping stone to other useful materials like fatty alcohols. While this continues to be their major role, they are now slowly developing markets in their own right and their production from renewable resources such as vegetable oil or tallow makes them an attractive option in the 21st Century oleochemicals portfolio.

PRODUCTION

Methyl esters can be produced from either natural oils (coconut, palm kernel, tallow) or from fatty acids. Today, most esters are produced directly from the oils. The process involves reacting the oils with methanol (wood

alcohol) in the presence of an acid or base catalyst. As we saw earlier, oils like coconut oil are composed of chemicals called triglycerides which themselves are compounds of fatty acids and glycerol (another alcohol). In the ester making process, the fatty acids attached to the glycerol are released and become attached to the methanol. This results in a mixture of fatty acid methyl esters (sometimes abbreviated to FAME) with the glycerol (glycerine) freed. The crude, whole-cut methyl esters have the catalyst neutralised with acids or alkalis, depending on which catalyst was chosen for use, and excess methanol removed by distillation. The methanol is returned to the process to produce more methyl esters. The esters will now be distilled and/or fractionated to remove traces of oil and catalyst and provide either a clean, whole-cut ester (all of the chainlengths of the parent oil present) or broad-cut esters (grouped chainlengths - usually light-cut (C6-C10), mid-cut (C12-C14) or heavy-cut (C16-C18). Further separation into pure-cut (single chainlength) esters is also possible. The glycerine, having a much higher density than the fatty material, readily separates and residual amounts remaining can be further removed by washing with water at a later stage. The glycerine is a saleable product in its own right and the various separations and washings are taken off to be distilled and bleached to yield high purity glycerine (>99.5%).

Production facilities tend to spring up close to the source of their raw materials and the world's largest ester production facility produces around 260,000 tonnes per year of lauric oil based methyl esters. Methyl esters are non-corrosive to carbon steel and most other common storage vessels, but one unique feature of these materials is that they will attack concrete. They will also swell and degrade some gasketting materials. Otherwise, they are inert and safe materials to store and handle.

USES OF METHYL ESTERS

Methyl esters are generally viewed as chemical intermediates between the parent oils and some other chemical and this should be borne in mind as you read the following. Market interest in methyl esters really got going in the 1950s when they were seen as providing a fruitful route to fatty alcohols. Fatty alcohols themselves were of interest as a means of manufacturing synthetic detergents which, at that time, were growing in importance. As the man said, "The more things change, the more they stay the same" and, not surprisingly, this is very true in this instance.

Fatty alcohol production, with a world market of something like two million tonnes, is still the biggest user of methyl esters. More recently, another large volume use has come to the fore and, amazingly, this too has its roots in the past, this time as far back as 1912 and the advent of the Dieselengine. Rudolf Diesel himself remarked at this time on the fact that because his invention could use vegetable oils, these might one day become as important as mineral oils were then, and further pointed out (rather prophetically) that because of the use of vegetable oils, motor power would still be possible, even when stores of solid and liquid fuels were exhausted. What Diesel did not foresee was the increased abundance of rapeseed oil in the EU, initially brought about by overproduction of rape on EU farms, due to subsidy. Necessity being the mother of invention, as ever, led to a quest to find additional uses for this excess of oil and the bio-fuels industry went into growth mode.

The recent commercial production of "bio-diesel" fuels was estimated at in excess of 800,000 tonnes worldwide with new production facilities coming on-line every year. Later, because of the growth in demand, the utilisation of "set-aside" land in the EU (land taken out of food production usage) has been allowed for crops destined specifically for fuel use. Methyl esters of C18 and longer chainlengths are suitable for direct use in engines (although some proprietary additives are usually necessary to provide year-round suitability). Esters of Soyabean (largely in the US), Rapeseed and Sunflower oils have been successfully utilised and, with the exception of oxides of nitrogen, are generally held to give lower emissions than petroleum-based diesel products while matching them in other respects.

In surfactant production, as well as supporting the manufacture of alcohol-based materials, the esters themselves can be sulphonated (reacted with sulphur trioxide either directly or via oleum or chlorsulphonic acids). The resulting Methyl Ester Sulphonate (MES) is used in detergents. This usage apparently grew out of the search for a gentler way of accessing vitamins inherent in the parent fats and oils so that the vitamin products would not be destroyed in the processing. Unfortunately, the by-product of this extraction process is a large amount of methyl ester and, to make the whole process viable, a use had to be found which added value to this stage. The result was the production of MES. The overall economics of these linked processes just about works and leads to the production of a few tens of thousands of tonnes of MES surfactant. As a standalone route into surfactant production, this process has not been a major success to-date. If methyl esters are subjected to the same type of reaction as was discussed in their production (above) viz: substitution of one alcohol component with another (called interesterification), some useful products can result. Probably the most well-known of these is Isopropyl Myristate (IPM) which is produced by reacting C14 methyl ester with isopropyl alcohol. IPM is used in small volumes in the plasticizer industry but has widespread uses in cosmetics in aerosol antiperspirants, bath oils, shaving preparations and creams and lotions. IPM's main role is as either a lubricant or an emollient. Methyl esters are gaining recognition for their solvent properties which are rated highly.

There is an obvious attraction towards the esters and that is the potentially hazardous nature of the alternatives, which are normally aromatic or chlorinated hydrocarbons in derivation. Mid-cut methyl ester finds solvent-type uses in the printing industry, while heavy-cut esters are being increasingly used for heavy-duty solvent applications such as tool cleaning in road-making (removing tar and pitch residues). This use as a "green" solvent is growing.

AND FINALLY . . .

The production of methyl esters is just one more route in which value is added to natural oils through the expertise of the chemical industry. With rapeseed oil as an example, the parent oil might be bought for 450-550 Euros/tonne. Light-cut esters sell for about 900 Euros/tonne, Mid-cut for about 1000 and heavy-cut for about 500- 700 Euros/tonne. Perhaps the greatest value that these important intermediates add though is in the pathways that they provide to other, life-experience-enhancing products (such as cosmetics) and in their ability to replace and therefore provide an alternative to products whose raw material supply is finite and will eventually be exhausted. This is perhaps another area where we might ultimately owe the preservation of our lifestyle in the future, to the products of the humble oilseed.

OLEOCHEMICALS - FATTY ALCOHOLS

We will now look at Fatty Alcohols and how they fit into today's oleochemicals pipeline. As with most of the oleochemicals that have been covered in this booklet, we tend to be mildly surprised at where these chemicals turn up and how they affect our lives. Fatty alcohols are the workhorse raw materials that facilitate the existence of products such as shampoos, shaving creams, laundry detergents, etc, and are produced at a rate of about one-and-a-half million tonnes per year and growing.

WHAT IS A FATTY ALCOHOL?

We all know something about alcohol. The human race has waxed lyrical about various concoctions containing alcohol that have livened up many a party. Whisky (from the Gaelic Uisqe Beagh meaning water of life), contains about 40% alcohol as ethanol (ethyl alcohol). Alcohols occur as straight carbon chains with one or more hydroxyl (-OH) groups attached and, in exactly the same way as was outlined previously, there is a series of alcohol homologues distinguished by increasing carbon chain length.

Some examples which might be familiar are the aforementioned Ethanol, which has a 2-carbon chain; Octanol, where the carbon chain is eight carbons in length; Lauryl alcohol (dodecanol) with 12 carbons; Cetyl alcohol (hexadecanol) with 16 carbons and Stearyl alcohol (octadecanol) with 18. The lower chainlengths (C2-C10) are liquid at room temperature, whereas above C10 they vary from low melting colourless crystalline materials to white waxy solids (C16-C18), melting around 55°C. Those of you who take the time to read product labels in supermarkets cannot have failed to have encountered these materials in detergents, shampoos or cosmetics.

We will now focus a little more on the straight-chain alcohols generally produced from oils and fats. It is important to remember though that other types of alcohol exist. Production from petrochemicals gives rise to branched chain alcohols as well as straight chain species and it is also possible to have alcohols with more than one -OH, called polyhydric alcohols, much used in the manufacture of resins. A very important member of the last class is 1, 2, 3-propanetriol (or glycerine to most of us). This is such an important material in the oleochemicals industry that we will include a few words on its manufacture and uses later on. With the -OH at the end of the carbon chain, we get what is known as a primary alcohol and all of the materials we shall discuss fall into this category. With branched chain materials, the -OH can be surrounded by two or even three carbon chains, giving rise to secondary and tertiary alcohols respectively.

HOW DO WE GET ALCOHOLS FROM OILS AND FATS?

There are a number of ways that fatty alcohols can be obtained from fats and oils. Most involve reaction with hydrogen at high temperature and pressure and so require specialist plant to conduct the reactions safely. There are two main ways of working with fats and oils directly. Probably the oldest process is sodium reduction where metallic sodium is slurried in a solvent such as xylene and the triglyceride oil, a reducing alcohol (such as cyclohexanol) and more solvent are added to the reactor. The reaction occurs at about one atmosphere pressure and, in a second stage, the reaction mixture is dropped into water to hydrolyse the sodium alkoxides formed. The solvent and reducing alcohols are recovered by distillation for re-use and the by-product alcohol is generally fractionated to give the appropriate chainlength ranges commensurate with planned usage. This process has the advantage of retaining the unsaturation of the parent oil and gives very pure product. The disadvantages are high operating costs (due to the consumption of metallic sodium) and the elaborate equipment needed to recover both the solvent and the reducing alcohol.

Oils and fats can be converted directly to alcohols by hydrogenolysis in which process the triglycerides are hydrogenated at high temperature and pressure in the presence of specific catalysts. A mixture of fatty alcohols and glycerine results and, again, there is a significant amount of equipment and effort needed to separate these products before the alcohol is obtained and fractionated.

In a variation of the above process, called methanolysis, the triglycerides are reacted with methanol in the presence of a base catalyst. Fatty acid methyl esters and glycerine are formed and, after removing the glycerine, the esters are hydrogenated to make the alcohols which are fractionated as before. As methyl esters themselves have grown in importance, it is now possible to purchase these as the intended feedstock for hydrogenation and short-cut the process above with the advantage of not having to separate and deal with the glycerine. Similarly, triglyceride oils can be hydrolysed to fatty acids and the acids catalytically hydrogenated to alcohols and variation of catalysts and conditions can permit the retention of any unsaturation, if desired.

USES OF FATTY ALCOHOLS

Almost uniquely for oleochemicals, alcohols are sometimes less known by their common or chemical name, but more by their use. Thus, we often see the light-cut alcohols (C6-C10) called plasticizer range alcohols and C12-C18 known as detergent range alcohols. That gives us a clue to two of the major uses, but there are many more. Detergent uses in one form or other consume the largest proportion of alcohol produced. This usage depends on the ability of the alcohol to add fat-loving or lipophilic character to the detergent molecule. Alcohols are successful here and also provide, via the hydroxyl group, a reactive site which can add water-loving (hydrophilic) character of varying intensity depending on which chemical groupings get reacted into the molecule. This hydrophilic-lipophilic balance (or HLB) is key in identifying which detergents are good for removing fatty soiling and which remove non-fatty material. The HLB is generally modified through sulphation (reaction with sulphur trioxide in some form) to produce an alcohol sulphate, or through ethoxylation (reaction with ethylene oxide) to produce ethoxylates which can then be sulphated and used as is. These sulphates and ethoxylates are the active cleansing ingredients in laundry detergents, shampoos and shower gels.

In cosmetics and pharmaceuticals, we find alcohols being used as is because of their own specific properties, usually as emollients. For example, Cetyl (C16) alcohol is important in cleansing, shaving and vanishing creams, hair lotions, and lipsticks. Cetyl and Stearyl (C18) alcohol bring similar properties to antihistamine creams, bath preparations and dermatologic bases. Beyond this, fatty alcohols provide the starting point for chemicals used as defoamers, emulsion stabilisers, evaporation control agents, metal working lubricants, corrosion inhibitors, fire retardants, inks and perfumes - a wide-ranging (but still not exhaustive) list indeed.

GLYCERINE

No article on alcohols derived from fats and oils would be complete without a few words about glycerine. Glycerine occurs as a by-product of most of the reactions we have encountered as we have set out to make something else out of oils and fats. Hydrolysis, methanolysis and saponification all break the triglyceride molecule to yield glycerine. The glycerine accrues either as a 10-15% solution in water as a result of hydrolysis or as a consequence of washing esters or soap to remove the glycerine prior to further processing. This dilute solution is either quickly evaporated to 80%+ concentrations before being purified by distillation and carbon bleaching, or is pre-treated with lime to remove fatty impurities as insoluble soaps, before being ion-exchanged and distilled. The final product is water white and contains 99.5+% glycerine.

If we were surprised about the number and range of uses of the other fatty alcohols, those of glycerine will astound. It has been described as the widest used single high purity chemical in the chemical portfolio. Used primarily for its viscosity and humectancy, we find glycerine listed in mouthwashes, lotions, paints, plastics, baked goods, cosmetics, and pharmaceutical products, as both an excipient and an active ingredient. It might be easier to list where it is not used. With fatty alcohols selling for about 130 Euros/Kg and glycerine for about 0.7 Euros/Kg the value added to the parent fats and oils can be considerable.

Adding in the link to renewable resources, the minimisation of environmental impact due to the ready biodegradability of these materials and their potential for widespread use, it is easy to see that the alliance and partnership of the oil and fat producing industries with the technologies of the chemical industry is a very strong and potentially sustainable one whose products reach into every corner of our lives and, hopefully, will continue to do so.

GLOSSARY

The following is a glossary of terms used in the oleochemicals industry.
It is by no means all-inclusive, nor is it meant to be.

Alkryd Resin : The reaction product of polyols, diacids, acids and anhydrides used primarily in the surface coating industry in which fatty acids, oils and glycerine are used to impart properties, e.g. chemical resistance, hardness, drying speed and flexibility.

Amines : Amines are produced from fatty acids for use as surface-active compounds. The primary and secondary amines can be converted to tertiary amines, quats and amine oxides, all of which have valuable surface-active properties. Based on their cationic nature and ability to be strongly absorbed on many surfaces, they have many industrial and cosmetic applications.

Castor Oil : Oil from *Ricinus communis* produced mainly in India, Brazil and China. Castor oil differs from all other common oils in being rich (~90%) in the hydroxyl acid, ricinoleic. Castor oil is a source of several important oleochemicals including Turkey-red oil, 12-hydroxystearic acid, dehydrated castor oil, heptanal, 10-undeconoic acid, 2-octanol and sebacic acid.

Dibasic Acids : Refers to acids with two carboxyl groups, of which the most common have the general structure $HOOC(CH_2)nCOOH$. They include (value of n in parenthesis): oxalic* (0), malonic* (1), succinic* (2), glutaric* (3), adipic* (4), suberic* (6), azelaic (7), sebacic (8), dodecanedioic* (10) and brassylic* (11). Systematic names such as nonanedioic acid indicate the presence of two carboxyl groups and the total number of carbon atoms in each molecule (in this case nine). Some of these are used in the production of polyesters and poly-amides. (*Azelaic, brassylic and sebacic are the only commercial dibasic acids from natural sources).

Emulsifiers : Additives that allow oils to be mixed with water and water to be mixed with oils. They alter the surface properties of materials they contact because of their amphiphilic nature. That is to say, they have chemical affinity to both lipid and aqueous phases. Because of this property, the molecules become oriented along the surfaces or interfaces of these normally immiscible substances.

Epoxidation : The reaction by which unsaturated acids are converted to epoxy acids. This is a *cis* addition of oxygen to the double bond, usually affected by a peroxy acid such as peroxyformic or peroxyacetic. The reaction is carried out on an industrial scale to produce epoxidised soybean oil, epoxidised linseed oil, etc. These are used primarily as plasticisers-stabilisers for polyvinylchloride (PVC).

Erucic Acid : Erucic acid (13-22:1), whose systematic name is 13-docosenoic acid, is derived primarily from high-erucic rapeseed, mustard and Crambe seed oils. Erucic acid is used as an intermediate to make derivatives such as erucamides, amines and behenamide. End applications include lubricants, heat transfer fluids, surfactants, slip agents, emollients, cosmetics and coatings.

Esterification : The reaction by which esters are formed from alcohols and acids, usually in the presence of an acidic catalyst, or with the more reactive acid anhydrides or chlorides for which no catalyst is required. Esters can also be changed to other ester by alcoholysis, acidolysis and interesterification.

Ethylene : A petrochemical feedstock for production of detergent-range alcohols and for the production of ethylene oxide, which is used in the manufacture of many surfactants.

FFB : The acronym for Fresh Fruit Bunch, FFB, refers to the bunch harvested from the oil palm. Each bunch weighs 5-50 kg (about 11-110 lbs) and may contain 1,500 or more individual fruits.

FAME : Fatty Acid Methyl Esters (FAME), sometimes referred to as Vegetable Oil Methyl Esters (VOME), are used as transportation biofuels in varying proportions with diesel and as feed for the production of natural fatty alcohols. They are obtained by esterification of the oils with an alcohol (methanol).

Fat : A chemical unit resulting from the chemical combination or esterification of one unit of glycerine with three units of fatty acids. The special ester thus formed is a "triglyceride". A natural fat is a mixture of different triglycerides and may contain small quantities of mono- and diglycerides and fatty acids along with small amounts of other oil-soluble constituents. When referring to a fat, under normal ambient temperatures, the product would be in semi-solid form.

Fatty Acids : Alkanoic and alkenoic acids are saturated or unsaturated organic acids generally having an unbranched chain of an even number of carbon atoms. They are major components of most lipids and are primarily obtained directly from animal or vegetable sources. Primary markets for fatty acids include greases and lubricants, rubber, soaps and detergents, plastics, cosmetics and toiletries, foods and emulsifiers, paper chemicals, and paints and coatings.

Fatty Alcohols : Medium- and long-chain alcohols related to the fatty acids that occur naturally in lauric oils and wax esters are produced commercially by the catalytic reduction of the acids or their methyl esters. Fatty alcohols (C12 and up) are vital components of surfactants used in personal care products. When reacted with ethylene oxide, fatty alcohols give polyoxyethylene derivatives, and both may also be used as sulfates. Hydrogenoloysis of methyl ester, free acid or wax ester all yield fatty alcohols from lauric oils, tallow or palm stearin.

Glycerol or Glycerine : Glycerol is an important structural compound of fats and oils. A complete splitting by hydrolysis of fats or oils results in glycerol and free fatty acids. Glycerol is used as a humectant, a food ingredient, in pharmaceutical products and in explosives.

Hydrolysis : The initial process used to obtain fatty acids from fats and oils is hydrolysis, resulting in mixed fatty acids and dilute glycerine. Purification of the mixed fatty acids is accomplished by distillation or by separation into individual fatty acids of different chain lengths by fractional distillation.

Interesterification : A term given to the production of esters by interaction of two esters in the presence of an alkaline or enzymatic catalyst.

Lauric Fats and Oils : The largest volume lauric fats and oils are coconut and palm kernel, which are vital to the manufacture of surfactants among other applications. Lauric oils typically contain 40-50% lauric acid (C12) in combination with lesser amounts of other relatively low-molecular-weight fatty acids.

Lipid : The general term used to describe fats, oils and waxes, together with more complex molecules.

Markets : Markets for oleochemicals continue to evolve, with niche markets developing continually. Nonetheless, the main end-use markets include building auxiliaries, candles, cleaning agents, cosmetics, detergents, fire extinguishing agents, flotation agents, food emulsifiers, insecticides, pharmaceuticals, plastics, rubber, soaps and detergents, textiles and tyres.

Oleic Acid : This monounsaturated acid is the most widely distributed of all fatty acids, found in practically every vegetable oil and animal fat. Rich sources are olive and peanut oils and palm olein. Oleic acid contains 18 carbon atoms and one double bond in the *cis* configuration. The classic route for making oleic acid and pressed-type stearic acids is to separate mixed fatty acids by crystallisation from either an organic solvent or a surfactant/water solution.

Oleochemicals : Oleochemicals are chemicals derived from biological fats or oils and are analogous to petrochemicals, which are chemicals derived from biological fats or oils and are analogous to petrochemicals, which are chemicals derived from petroleum. The hydrolysis of the triglycerides composing oils and fats produces fatty acids and glycerol. If oils or fats are made to react with an alcohol instead of with water, the process is alcoholysis and the products are fatty acid esters and glycerol. Other important oleochemicals include fatty alcohols, methyl or other esters, amides and amines, dimer acids and dibasic acids.

Palm Olein : Palm oil is separated into palm stearin (30-35% of the original oil) and palm olein (65-70%). The latter finds a ready market as a high-quality, highly stable frying oil. With improved filtration procedures the yield of olein has been raised to 71-78%.

Palm Stearin : As mentioned above, palm oil is separated into palm stearin and palm olein. The olein is the more valuable product, but the stearin can be used as a hard fat in margarine stock or as an alternative to tallow in the oleochemical industry where it serves as a source of stearic, palmitic and oleic glycerides.

Processes : Basic oleochemicals are produced primarily through splitting, distillation, fractionation, separation, hydrogenation, methylation and hydrophilisation. Derivatives of basic oleochemicals are produced mainly through amidation, chlorination, dimerisation, epoxidation, ethoxylation, quarternisation, sulfation, sulfonation, transesterification and saponification.

Raw Materials : The primary raw materials of the oleochemicals industry are tall oil, tallow, coconut oil, palm oil, palm kernel oil, soybean oil, sunflower oil and canola oil.

Ricinoleic Acid : Ricinoleic acid, whose systematic name is 12-hydroxyleic acid, is found in high degree in castor oil. The oil, ricinoleic acid, or its derivatives, are important to the cosmetics and lubricants industries.

Soapstock : In the chemical refining of crude oils, free fatty acids are removed by neutralisation with alkali and settle to the bottom as alkali soaps, known as soapstock.

Surfactants : Surfactants, or surface active agents, are substances that, when dissolved in water, give a product the ability to remove dirt from surfaces such as the human skin, textiles, and other solids. Each surfactant molecule has a hydrophilic (water-loving) head that is attracted to water molecules and a hydrophobic (water-hating) tail that repels water and simultaneously attaches itself to oil and grease in dirt. These opposing forces loosen the dirt and suspend it in the water. Surfactants derived from fats and oils are by far the largest oleochemical market at present. Virtually all types of fats, oils and fatty acids are used in this area.

Tall Oil Fatty Acids (TOFA) : An important industrial feedstock that is a by-product of the wood pulp industry. The term "tall oil" is derived from the Swedish word for "pine oil", or *tallolja*. Production occurs mainly in North America and Scandinavia. TOFA are obtained from crude tall oil via fractional distillation and yield between 25-35% fatty acids (oleic and linoleic).

Tallow : Beef fat is the primary source of tallow, whereas hog and poultry fats are the sources for greases. The ample availability of beef tallow in the last 50 years has made it the feedstock of choice for the fatty acid industry, both in the United States and Europe. Animal fat is divided into classes depending on the solidification temperature, or titre point. If the titre is above 40°C, it is classified as tallow. If below 40°C, it is considered a grease. Tallow contains mainly saturated (60%, 16:0 and 18:0) and monounsaturated fatty acids (40%, mainly 18:1 with some 16:1).