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.