MAIN ADDRESS

OIL FOR THE OLEOCHEMICAL INDUSTRY *

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World production of oils and fats; oleochemicals

A glance at a world map illustrating world-wide production of oils and fats, in millions of tons, shows that the largest single production area is in the Far East, for instance in Malaysia and the Philippines. Production has however increased enormously throughout the world over the last few decades, and this increase has been particularly noteworthy as regards oils and fats of vegetal origin, including sunflower, whereas other fats such as tallow have not undergone any marked change in volume of production.

The total volume of oils and fats produced world-wide in 1990/91 amounted to 81.5 million metric tons, of which 61 metric tons was of vegetal origin and 20.5 million tons of animal origin. By far the largest proportion of total volume was consumed in edible applications(65 million tons) while a small amount was used in animal feed (6 million tons); the oleochemical industry used only 10.5 million tons, equivalent to about 14% of the total. Further breakdown of applications by the oleochemical industry shows that the major portion, 6.3 million tons, is still used in the classical soap application, while 3.7 million tons are used in oleochemicals, 0.2 in lubricants and 0.3 in coatings.

Among the various base products produced by the oleochemical industry an important role is played by

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glycerine, as will be mentioned again later. Fatty acids and methyl esters can be produced directly from the triglycerides. Soap can likewise be produced directly from triglycerides or else it can be obtained from fatty acids, and similarly methyl esters can derive directly from tryglycerides or from fatty acids. Both methyl esters and fatty acids can in their turn be used as base products for production of fatty amines and fatty alcolhol. Together with these typical products of the oleochemical industry, a wide variety of other specialty products are also produced, such as many kinds of esters.

Many of the above base products have increased markedly over the last few decades; in particular, there has been a steady growth of fatty acids and methyl ester production. But in general growth of the various products needs to be analyzed in terms of the end markets. Oleochemicals are used in detergents, polymers, coatings, lubricants, cosmetics, in mining, and in an extensive range of other applications, including even in food, such as liqueurs. This article aims to focus on two of these interesting markets, namely detergents and lubricants, and then to give an overview of new vegetal sources for oleochemicals.

<u>Detergents and surfactants</u>

The world detergent market is extremely vast, and the overwhelming proportion of material produced is in the form of detergent powder for fabric washing (14.4 million tons in 1990), though production of soap bars is also strong (6.8 million tons in 1990). A small amount of production is taken up by less frequently used forms of detergent, such as liquid detergent (3 metric tons in 1990) or detergent bars (0.8 million tons in 1990), though these minority forms tend to fluctuate depending on trends of consumer interest.

From the point of view of the oleochemical industry, the important element is not represented by the detergents themselves but rather by the *actives* present in the detergents. Surprisingly, soap, the simple fatty acid soap, still constitutes roughly 50% of the active of a commercially available detergent, with the remaining 50% constituted by an extensive range of surfactants. These surfactants are essentially composed of an enormous variety of different fatty alcohol derivatives, such as ethoxylated fatty alcohols, benzene, linear alkylbenzenes, sulfanates.

Surfactants made by the oleochemical industry cannot be distinguished from surfactants made by the petrochemical industry in terms of their effectiveness: they are in fact identical. At the present time it can be said that the vast majority of surfactants originate from petrochemical-derived materials, but over the last few years clear evidence has come from the market that the consumer is asking for non-petrochemical actives. As an example one may cite APG's, the sugar fatty-acid derivatives, which have excellent detergent properties and are prepared from renewable green raw materials, precisely the characteristics the modern consumer wishes to see.

Lubricants

The market for lubricants is extensive: in Western Europe, the engine lubricant market alone consumed 2,9 million metric tons in 1990, while the industrial lubricant market used 1,9 million metric tons of material. Applications are extremely varied. Engine lubricant applications include machine oils (12% of total volume), two-stroke petrol (3%), brake fluids (1%), chain oils (1%), four-stroke diesel (35%), gear oils (7%), four-stroke petrol (32%) and other applications (8%). Industrial lubricants are used in hydraulics (31% of total volume), metal working (32%), gear oils (3%), process oils (23%), functional fluids (7%), compressor lubricants (3%), refrigerator lubricants (1%).

Only a minor part of this market, however, (scarcely more than 5%) is supplied by the oleochemical industry. The overwhelmingly predominant source is represented by petrochemical materials, and more specifically the main raw material is mineral oil, which is processed in refineries by petrochemical processes into Ultra High Viscosity Index Oil and Poly-Alpha Olefins. These products allow production of top quality engine oils. As far as the minority oleochemical source is concerned, vegetal oil is the major source of raw material, which may be used in the form of triglycerides or processed into esters. The latter present the advantage of having extremely good performance characteristics.

The kinds of processes used in the oleochemical industry for production of lubricants include splitting glycerides into the fatty acids and glycerine, followed by the rebuilding of esters in what is essentially an application more ingenious than nature itself: trimethylethyl propane esters are applied, or penta-aerosytol esters or short and mid-chain fatty acids. These applications are possible because the fatty acids undergo modification before esterification, and this allows creation of esters possessing high performance characteristics.

If lubricant esters produced by the oleochemical industry are compared with mineral oil-based materials, the latter are seen to have certain limitations in their use. The pour point of mineral oil-based lubricants is in many cases not low enough, they can be rather volatile, the oxydation stability is unreliable and their lubricity compares unfavorably to that of esters. Furthermore, the important issue of biodegradability must also be considered: mineral oil-based lubricants are non-biodegradable, and they have considerable toxicity and water-endangering properties. In some areas the risk to water quality is considered to be so serious that bans on use have been introduced: for instance, on the Lake of Geneva in Switzerland and the Bodensee in Germany/Austria, lubrication of outboard engines on boats is permitted only with biodegradable esters from the oleochemical industry. The degree of biodegradability of these esters can be controlled by the esterification process, without jeopardizing the performance. Indeed, where high performance is required, esters are the prime choice as compared with mineral oil-based lubricants: for example, in the aviation industry, no mineral oil-based lubricants are used.

As an alternative to use of esters, vegetable oil can be used without esterification, as mentioned earlier, and indeed in Germany nowadays there are many hydraulic applications in agriculture making use of rapeseed oil. Rapeseed, however, has the disadvantage of inadequate oxydation stability.

Sunflower presents greater oxydation stability but suffers from pour point troubles, especially in colder climates such as those of northern Europe. Esters are thus vastly preferable to these oils, but are considerably more expensive to produce on account of the high investment in all the equipment required to carry out the chemical processing.

From a cost point of view, therefore, esters appear to compare very unfavorably both to vegetable oils and to the much cheaper petrochemical lubricants. Over a period of 5-6 years, however, the situation could well be more favorable to esters in certain applications: for instance use of rapeseed or petrochemicals as lubricants in hydraulics applications in agriculture could be expensive over a 5-6 period because of the need for frequent oil changes, whereas esters are more durable because of their stability and do not require frequent oil change.

New vegetable oils

In recent years a number of new vegetable oils have been developed for industrial use, deriving from new crops. Several different motivations for this trend towards new productions can be perceived, accompanied by a number of problems. Most importantly, this trend provides a new outlet for agricultural overcapacities, but in this sense one may question whether industry and the market really need these products. Development of new productions also provides a means of replacing imports by indigenous, i.e. European or American, raw materials, though in this case economic problems arise because the imports to be replaced, deriving from the Philippines or from Malaysia, are extremely cheap, probably much cheaper than the products that would replace them. Another reason lies in modern attitudes, which are partly oriented towards the desire to substitute all synthetic materials by renewable green materials, and this may create a market demand.

But if one examines the properties new crops and new oleochemicals should ideally have in order to represent a profitable proposition for industrial production,it becomes clear that difficulties will be encountered in attempting to satisfy all the requirements. Thus as far as supply is concerned, the oleochemical industry needs good availability and low price levels, together with secure supplies. Certain specific properties would also be desirable: oils of different chain lengths, preferably tailored to the specific needs of the individual industries; similarly, tailored double distribution of double bonds, high monomer unsaturates, low polyunsaturates, new functionalities in the fatty acids.

All of these characteristics can be of great interest to industry, but they represent high-risk long-term development because they are in competition with the well-established technology that has become standard practice in production techniques and in the fractionation process. Well-established technology can be relied on to produce fatty acids of a specific purity, but new oils also require development of new technological processes, and this means investment without certainty of successful results. Furthermore, industrial applications of new oils are relatively minor so far, and therefore more applications research is required. There are also constraints based on volume: since the new crops are mainly in the experimental stage, volumes tend to be rather small, which is not cost-effective for industry and in many cases not even feasible to handle. For instance, at our UNICHEMA factories the smallest lot that can be handled is 100 tons.

Another serious problem is represented by the question of glycerine. If the question of overproduction on the edible side is tackled by boosting industrial production from oilseed crops, there will always be side production of 10-14% glycerine as a result of the splitting process utilized in oleochemical technology. Unless new glycerine outlets are found, large volume projects will adversely affect glycerine markets by creating a glut of glycerine, and consequently prices fetched by glycerine will fall. This means that costing of projected new crop applications will not be realistic if based on the current market price of glycerine. Unrealistic forecasts of costs have for example been made for the new bio-diesel fuels applications in Germany and France. In actual fact glycerine prices risk falling so low that industry would actually have to pay to eliminate the glycerine instead of obtaining a profit from it.

Despite these limitations, it is certainly worthwhile to give an overview of some of these new crops and innovations introduced by breeding and selection into existing crops. One interesting development is the ***high oleic sunflower***, in particular if it is over 90% oleic. With high oleic sunflower one can simply split and purify the oleine, and sell it or utilize it for other applications. It should be remembered, however, that this would mean competing against the very cheap tallow separation process, which is the most widely used purification process in the oleochemical industry and is highly cost-effective.

The high oleic sunflower can be used in dimer fatty acid production, and it also has potential lubricant and hydraulic fluid applications. In addition, fatty acid amides can be produced, from which a fine anti-block agent can be obtained.[1]

Another remarkable new crop in Western Europe is *crambe abyssinica*, on which a considerable amount of research has already been carried out in the United States by the USDA. Crambe has about 65% erucic acid; it also allows preparation of very interesting dimers, as well as dicarboxylic acids, and it has applications as lubricants and amides. In Western Europe cultivation of this crop is still in its infancy, but in the Netherlands successful *cultivation is carried out now* on a 300-acre basis by a well-known agricultural company that supplies our firm with the oil.

The high-erucic property of crambe is particularly important, because it makes this crop a potential substitute for the high-erucic rape. The high-erucic rape needs to be harvested in isolated areas to overcome cross-fertilization with the low-erucic rape. In the past these isolated areas were located in Poland and the former East Germany, but these areas no longer function as reliable suppliers, whereas industry needs security of supplies, as mentioned earlier. Crambe does not suffer from this kind of limitation in its

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[1] The acid derived from *helianthus annuus* is cis-9-octadecenoic acid.

cultivation, and therefore could well be a promising substitute for the high-erucic rape[2].

Vernonia, or ***Euphorbia***, is another example of a new crop, which has epoxe functionality in the fatty acids which can be applied in the coating industry, in plastics production, in cosmetics and in polymer chemicals[3].

Lesquerella has ~~been~~ developed fairly extensively in the United States, with potential applications in cosmetics and toiletries, lubricants and dimer fatty acids, polyesters and polyurethanes[4].

Finally, another interesting crop is Meadowfoam (***Limnanthes alba***), also produced in the United States, although on a limited scale. with potential applications in dimer fatty acids, ozonolysis (dicarboxylic acids), lubricants, and fatty amides (anti-block agent)[5].

Conclusions

A number of exciting innovations are being introduced into the field of oleochemicals, and industry is watching all these developments with great interest. Much more research is still required, in agronomy, breeding, selection, in order to improve quality, because high quality products will facilitate successful chemical experimentation and production of successful materials. The real problem at this stage, unfortunately, is that the present period is one of "technology push" rather than "market pull": in fact there is

[2] The acid derived from *crambe* is cis-13-docosenoic acid.
[3] The acid derived from *vernonia* is 12,13-epoxy-cis-9-octadecanoic acid.
[4] The acid derived from *lesquerella* is 14-hydroxy cis-11-eicosenoic acid.
[5] The acids derived from *limnanthes alba* are: cis-5-eicosenoic acid, erucineic acid, gadoleineic acid.

hardly any market demand for these new functionalities and new fatty acids, and considerable effort needs to be made to promote the new applications. But if this new trend succeeds and oleochemicals become predominant compared to petrochemicals, the world will certainly be a much more pleasant place.