Table VI shows the evaluation of 5 types of biomass in comparison to mineral oil. From these data it seems to be justified to assume that fats and oils are the best raw material for various chemicals. In other words, the prospects for oleochemicals are obviously very promising.

TABLE VI

Usefulness of Biomasses as Raw Materials for Chemicals

	Mineral oil	Lignin	Cellulose	Starch	Sugars	Fats and oils
Density of energy	+++	++	+	+	+	++
Reactivity	++	+	++	++	++	+++
Production of well defined compounds	++	–	++	++	+++	+++
Multiple application of structural elements	+++	–	–	–	–	++
Vicinity to end-producer	++	–	–	–	–	++
Possibility of homogeneous reactions	+++	–	–	+	++	+++

+++Very useful.
++Useful.
+Applicable.
–Useless.

Oleochemicals: Feedstock or Auxiliary

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ABSTRACT

Today's oleochemicals are substances which are used not mainly because of their sophisticated chemical structures or their chemical reactivity, but rather because of their adaptability as auxiliaries in a great variety of formulated products. This has determined their success in the marketplace. The conversion to long-chain building blocks for polymers is one possibility to move oleochemicals into a larger scale position as feedstocks. In the near future, this objective cannot be reached because two factors limit their economical chemical derivation; namely, the missing technologies to separate chemical individuals with one or two double bonds in the alkyl chain from the natural mixtures, and to cleave double bonds in a controlled way, without forming larger quantities of byproducts. In any case, before oleochemicals (e.g., fatty acid methyl esters) are used as substitutes for gasoil, as is already tried in certain countries, the chemical potential of oleochemicals should be exploited. That means: "Use it–don't burn it!" Today's chemical processes and uses for oleochemicals are discussed.

OLEOCHEMICALS–FEEDSTOCK FOR THE FUTURE

Key chemicals derived from natural oils and fats are basically different from products obtained by today's petrochemical industry or possibly by the future coal-based chemical industry (Table I).

Primaries or intermediates from crude oil and coal are short-chain building blocks from which chemical compounds of the most varied nature may be synthesized. If the appropriate path of conversion is chosen, e.g., the Mobil process, it will be possible in the future to create products of ethylene chemistry via methanol (1). The American Institute of Chemical Engineers (AICHE) says, "today's feedstock for the chemical industry will undoubtedly remain the feedstocks of the future, but they will have their origins in different raw materials" (2). This can hardly be contradicted.

TABLE I

Key Chemicals from Different Resources

Crude oil	Fats and oils	Coal/methanol
Ethylene	Fatty acids	Ethylene
Propylene	Fatty alcohols	Propylene
Styrene	Glycerol	Formaldehyde
Vinyl chloride	Fatty amines	Acetic acid
Methanol		Ethylene glycol
Formaldehyde		

Even if a report published by the organization for Economic Cooperation and Development (OECD) (3) possibly exaggerates the trend by stating that in 1990 chemicals from coal will total 20 million tons/year and by the year 2000 40 million tons/year, it will be coal which will first supplement crude oil as raw material. The inevitable use of the existing infrastructure for ethylene chemistry will make this necessary.

THE POSITION OF OLEOCHEMICALS

According to a calculation published by the US Department of Agriculture (USDA), only 24% of the heat of combustion of soybean oil is used to produce it (4). This percentage is significantly below the energy necessary to produce diesel oil from coal.

In spite of that, the long-chain differently saturated fatty acids of triglycerides will not be utilized in the future to crack them into chemical building blocks, since they can already compete very well in specialized areas with petrochemical products. This can be shown clearly for oleochemicals (Fig. 1).

For glycerin and fatty alcohol, the basis in natural raw materials can still be enlarged.

Fatty acids are priced below their potential petrochemical competitors like olefins and even most paraffins. Therefore, they will maintain their unique position in the area of long-chain aliphatic compounds when improvements in oxo-synthesis and other reactions of carboxylation take place. This will be especially the case if economic considerations play a decisive role. The application of oleochemicals is determined by the chemical reactivity of the terminal carboxyl group and hence by the distinctly ambivalent mode of reaction of subsequent products and their application as surface-active agents.

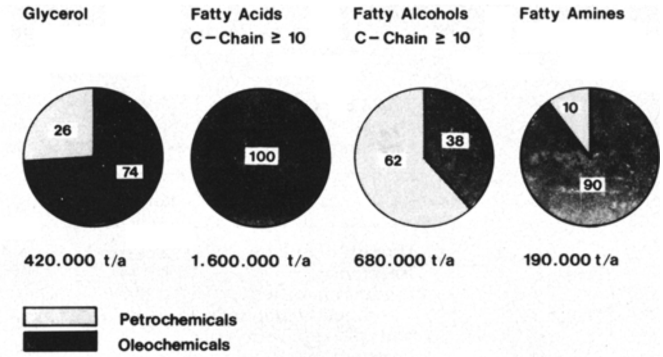

FIG. 1. Oleochemicals: share of world production, 1982 (paraffin oxidation fatty acids not included).

TODAY'S CHEMICAL PROCESSES OF OLEOCHEMICALS

Figure 2 illustrates that nowadays more than 95% of the consecutive reactions of native key chemicals are performed on the carboxyl function.

Reactions at the double bond or the chemically reactive α-C atom contribute less than 5% to the products. This also includes reactions with hydroxy substituted fatty acids or their derivatives, e.g., castor oil.

For the following reasons, reactions along the alkyl chain have been less utilized:

- Historically speaking, it was easy for oleochemicals to grow-in markets where the ambivalent character of the molecules was desirable.
- Basic research for fats and oils is influenced predominantly by the food industry and not by technical applications.
- Fats and oils are neither uniform with respect to their chain length, nor to their double bonds. Nature delivers no chemical individuals.

With more than 80% of the fats being used for food, it is not surprising that basic research in the area of triglycerides is concerned mainly with questions of nutrition. One example will illustrate that the aim of research for nutrition is not identical with goals for the technical use of double bonds.

Research into the oxidation of fatty materials is primarily to investigate the autoxidation of nutritional fats. The goal is to avoid flavor deterioration and potentially toxic and unsafe products by gaining an understanding of the reaction steps (5). Of the numerous studies in this field, only a few are concerned with the oxidation of double bonds to arrive at difunctional fatty acids.

The average composition of fats used in the world (6) shows that mainly C_{18} fatty acids with 1-3 double bonds dominate the structure of fats. The prerequisite for different conversions would be the availability of economic and efficient processes which are capable of producing pure oleic, linoleic and erucic acids.

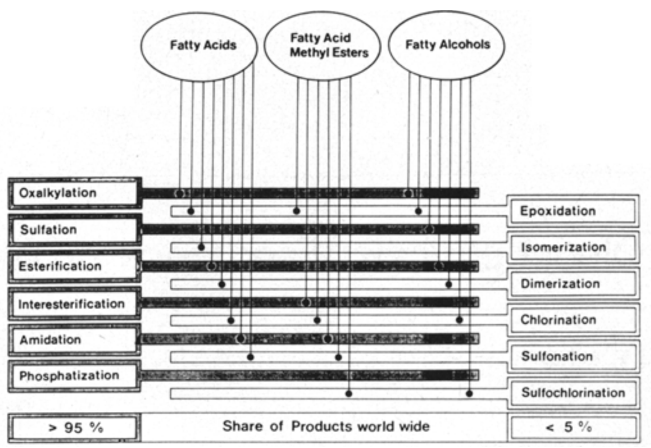

FIG. 2. Reactions of key oleochemicals.

FIELDS OF APPLICATION

More than 95% of the oleochemicals which are chemically transformed at the carboxyl group dominate the fields of application. A critical view of some examples in different areas of use follows, with consideration of whether or not a change in this percentage can be expected (Table II).

TABLE II

Estimated Consumption of Oleochemicals[a]

Use	%
Detergents and cosmetics	40
Plastics, rubber, textiles, plasticizers	22
Paints and coatings	13
Food	11
Metal-working lubricants	11
Other	3

[a]Soaps excluded.

Detergents, Cosmetics

Washing and cleaning agents, including cosmetics, constitute the largest coherent field of application for the majority of oleochemical derivatives, due to their surface-activity.

Only in this field does the chain length of oleochemicals deviate substantially from the average worldwide fat composition. Whereas the medium chain length (C_{12}-C_{14}) present in nature is ca. 10%, in detergents and cosmetics, the proportion is 30%.

The following trends in the technology of washing will influence the use of surfactants:

—Washing at lower temperature will become more important because of energy savings.
—The market share of synthetic fibers will increase further.
—The reduction of phosphate content in detergents will be enforced in highly industrialized regions for ecological reasons.

Consequently, both the application of nonionics and the demand for medium-chain initial alcohols will grow. The contradicting prognoses about the growth of nonionics during recent years can be countered by the following statement in the area of medium-chain alcohols: "The annual growth of fats containing lauric acids is estimated to be less than 3%."

This would be the probable rate of growth for the medium-chain nonionics if such variables as the proportion of synthetic to native products, or the proportion of nutritional fat to waste fat remained constant after processing, and no unforeseen applications for C_{12}-C_{14} derivatives suddenly arise.

Plastics, Plasticizers and Textiles

The use of fats and fatty acids as reactive components with textiles will be explained later. The points made here refer to emulsifying, lubricating and softening (Fig. 3).

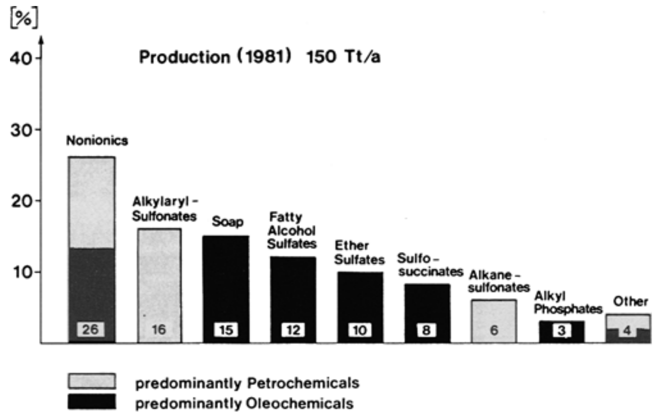

FIG. 3. Polymerization emulsifier (synthetic rubber excluded).

The worldwide consumption of emulsifiers for polymerization shows that nearly half of the emulsifiers could be based on natural raw materials. It must be pointed out that the use of soaps and disproportionated resin soaps for the production of synthetic rubber in quantities of 250,000 tons/year have not been included, because in the statistics they are listed under the heading of elastomers (7).

The bulk market for polymers produced by emulsion technology is growing slowly and only a few fundamental new developments for polymerizable monomers seem to be in progress (8). Therefore, no big increase in consumption is to be expected, but the types of emulsifiers will undergo changes with increasing need for more highly sophisticated polymerization technologies. For flexible PVC, 2-ethyl-hexyl-phthalate (DOP) is the most important plasticizer at present. The substitution of 2-ethyl-hexanol by short-chain linear alcohols is achieved by oxo-products rather than by native C_6-C_8 alcohols. Epoxidized soybean oil (ESO), however, is a completely natural-based plasticizer, which can displace DOP at least to some extent—and has already done so—in PVC recipes, due to the rising price of the petrochemical. It is not only the expanding amount of ESO, but the advancing knowhow of epoxidizing technology, which may promote oleochemicals from auxiliary products towards "feedstock" for polymers.

For the industrial textile industry, fatty acid esters, ether esters, amides and amines, as well as sulfonated products, are widely used as lubricants for converting fibers into fabrics. With the increased use of synthetic fibers, more lubricants are needed simultaneously. Similar to the finishing processes in the textile industry is the application of textile softeners in the household. Here dimethyl-distearyl-ammoniumchloride is the most acceptable fatty chemical worldwide. Newer trends toward more highly concentrated consumer products increase the need for better water-soluble substances. Besides quaternary imidazolinium sulfates (9,10), a substitution of the tallow alkyl chain by unsaturated or branched alkyl chains may be an answer. The guerbet reaction offers an interesting pathway for obtaining long-chain branched material from oleochemicals.

Paints and Varnishes

The use of air-drying oil in industry is regressing: tailor-made synthetics are moving into this area. This inroad could only be stopped if it were possible to work native oils into modern formulas of synthetic varnishes by using an appropriate emulsifier system to obtain dispersions free of solvents. This could mean an increased consumption of oils as well as oleochemical emulsifiers (11).

On the other hand, water-based, heat- and air-drying alkyd resins, could gain in the future due to their low processing costs and their positive environmental properties (12-14). This means that a change could occur in the polyol component and catalyst system rather than in fatty acids or neutral oil modifications.

The difficulties resulting from insufficient metal adhesion, and thus worsened anticorrosion performance as well as color stability, now seem to be overcome. Despite high costs for the evaporation of water, this technology will have a future in which oleochemicals will participate. If this type of alkyd resin is successful, it will most likely take over some areas now covered by polyacrylates.

Food Industry

In the food industry, developments for natural-based additives will bring no important changes in composition and volume because of very strict governmental restrictions.

Metal-Working and Lubricants

Ever since Friedrich published his summary on lubricants in 1979 (15), no new material has been presented which would allow an estimate of whether there has been a change in the use of fat-based synthetic lubricants (15,16). For the development of special formulations for lubricants with good low-temperature properties and excellent thermal stability, products based on fat (dibasic acid esters, polyol esters, complex esters) are particularly suitable. The broad use of such products in lubricating oils which would influence the demand for oleochemicals, especially of short-chain fatty acids, even if C_7 and C_9 fatty acids had to be made synthetically, remains questionable in the next few years. Because of the need for short chains C_8-C_{10}, which are less prevalent in nature, such a development would probably overburden the native basis.

General Observations about Conventional Applications

Products of oleochemistry (conversion at the reactive end of the molecule) show that, in general, no significant changes on raw materials are required except for the increased use of medium-length alkyl chains in the area of detergents and cosmetics.

The application of oleochemicals characterizes them as auxiliary products and it can be shown that the changing trends of worldwide raw material usage are predictable (Fig. 4).

Since it takes 5-8 years for polymers from the first day of commercial production until a volume of 10,000 tons/year is reached (8), an auxiliary product (e.g., an additive incorporated or an emulsifier used) at a concentration of 5% would take the same time to reach a worldwide demand of 500 tons/year.

OLEOCHEMICALS—REACTIVE COMPONENTS IN THE FUTURE

Prospective reactions involving oleochemicals as feedstocks include expoxidation (ring-opening), hydroformylation, hydrocarboxymethylation, metathesis and oxidation.

Dimer fatty acids and dibasic acids from different manufacturing processes have a certain importance today as special ingredients for polyesters, polyurethanes, polyamides and alkyds (17). Considering the volume of production, however, they are minor products compared to the monomers of the petrochemical raw materials. The use of fatty acids in alkyd resins are an exception.

One of the important reasons why the double bonds of oleochemicals are not used more widely is that pure oleic acid, its methyl ester or oleyl alcohol, are technically not available and cannot be produced economically in the near future. The breeding of sunflowers containing 90% oleic acid in their triglycerides will not solve the problem as long as the price of sunflower oil remains much above that of tallow or palm oil.

Highly selective separation processes, e.g., the Pacol-Olex-Process (18) of the petrochemistry for paraffins/olefins are not employed technically in fat chemistry. A separation process, by which products of high purity with a single double bond can be separated economically from inexpensive fats such as tallow, is the prerequisite for a number of reactions where oleochemicals could play a role in long-chain building blocks for plastics and elastomers.

Epoxides

The epoxidation of soybean oil and its derivatives (Fig. 5) is an industrial process which has proved its economic viability for many years. Transferring this process to other specially designed oleochemicals could perhaps open an interesting way to a number of multifunctional compounds.

An interesting starting material for this process could be unsaturated alcohols, for which there are no direct equivalents available in petrochemistry.

Hydroformylation

For a long time, the reaction of hydroformylation (Fig. 6) starting from olefins has been a competitive alternative way for the production of fatty alcohols. This reaction can also be applied to oleochemicals. The conversion of oleic acid methyl esters or unsaturated alcohols with the aid of this chemical reaction will lead to diols or hydroxy esters which are suitable as raw materials for polyurethane foams (19-21).

Hydrocarboxylation

Hydrocarboxymethylation (Fig. 7) has recently been suggested as a suitable method to produce fatty acid methyl esters economically from C_{12}-C_{14} olefins to obtain medium-chain fatty alcohols (22).

Only one report states that, by using oleic acid methyl ester in a combination of isomerization and hydrocarboxymethylation, the resulting product is predominantly α,ω C_{19} dicarboxylic acid dimethylester (23). If this reaction is developed further, it could result in a long-chain starting

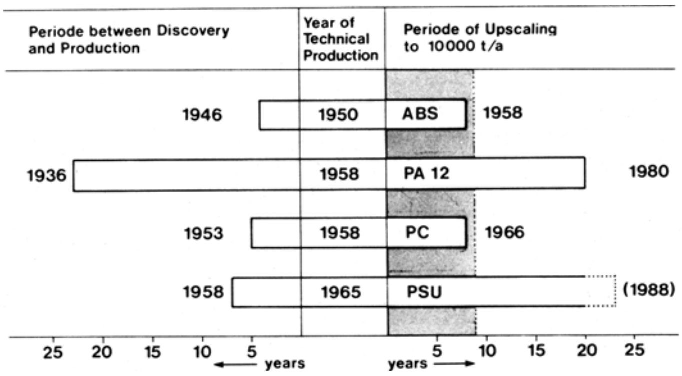

FIG. 4. History of technical polymers (according to Weirauch [8]). ABS: Styrene copolymer; PA 12, polyamide 12; PC, polycarbonate; PSU, polysulfone.

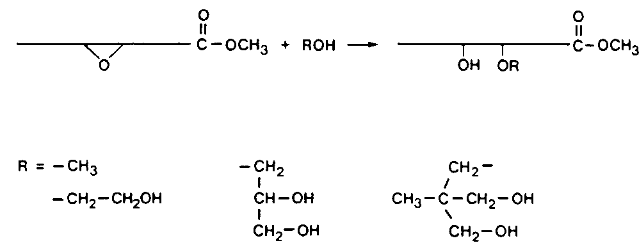

FIG. 5. Epoxides of oleochemicals as intermediates in polymers: generalized structures.

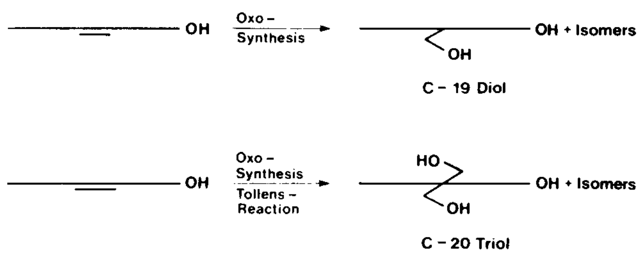

FIG. 6. Hydroformylation products as intermediates in polymers: generalized structures.

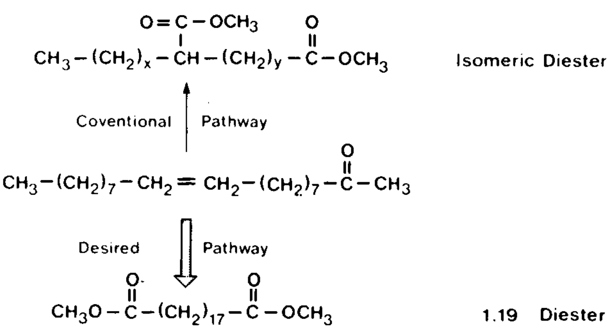

FIG. 7. Hydrocarboxymethylation of methyl oleate.

material for polymers which could impart better properties to polyesters, polyamides and ester plasticizers than 9/10 carboxystearic acid that has not yet found commercial use (17,24).

Metathesis

Under certain conditions, metathesis could play an important role in oleochemistry (25,26), but several obstacles have to be overcome.

The statement that "industrial application of the metathesis of fatty oils will largely depend on further improvement of the catalyst systems" is not the only restriction. Especially for metathesis it is essential that unsaturated components must be extremely pure to limit an excessive formation of byproducts. A separation of the complex mixture of functionalized isomeric conversion products of the metathesis reaction will be very expensive, or even technically impossible in many cases.

For the synthesis of very special products, however, such as triacontanol (Fig. 8), described as a plant growth regulator, metathesis offers an elegant method (27,28).

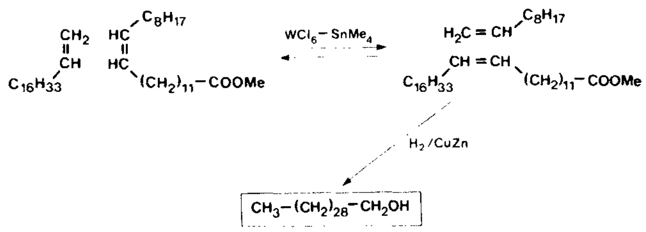

FIG. 8. 1-Triacontanol by cometathesis.

Oxidation

Ozonolysis is the most feasible process for producing azelaic acid or brassylic acid from unsaturated fatty acids. In the future, this process could perhaps gain even more importance due to continuous technology (29,30). Although high capital expenditure and rather high costs of electrical energy are limiting factors in ozonolysis, no other industrial oxidative processes are used for the production of dibasic acids from oleic acid at present.

The detour via epoxidation appears to be promising because of the well known and economically proved process and because of the advances achieved in epoxide ring-opening to diols (31). From catalytic processes working with cooxidants, e.g., acetaldehyde, one has to expect too much acetic acid as a byproduct.

On the other hand, no commercially feasible process for the necessary consecutive reaction, the diol cleavage, has been reported yet (32).

Although there is a connection between oxidation processes with hydroxy substituted and unsaturated fatty acids, the desired chemical pathway for oxidation reactions in fatty chemistry is predominantly the oxidation of the double bond. The reason is that oleic acid from different sources is a more available and cheaper raw material than castor oil.

Oxidation of oleic acid with potassium permanganate does not seem to be very selective (33). Recent advances in oxidation of oleic acid with excess ruthenium tetroxide or perruthenate show quantitative cleavage of the double bond, although the molar ratio of 4:1 between oxidant and double bond is not promising (34). An industrial application of this method of cleavage is not very likely.

How far chemistry in general is away from the solution of catalytic oxidation is described in a recent statement: "The catalyzed oxidative cleavage of alkenes by molecular oxygen is relatively unexplored and work is in progress to clarify the merits of the reaction" (35).

The cited publication (35) delineates the state-of-the-art for short-chain olefins. The results of these experiments show that oleochemistry should not expect a basic solution of this problem within the next decade.

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