New Developments in the Fatty Acid Industry in America

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ABSTRACT

Although acquisition, divestiture and other organizational changes within the American oleochemical industry are still the most startling and attention-attracting, the development of new technology continues to be of paramount scientific interest. Noteworthy among the new developments are (a) the continuing development of new vegetable oil raw materials like 90% erucic acid rapeseed oil and 80% oleic acid sunflower; (b) the intense process development under way in some areas for the minimization of thermal energy requirements of certain reactions like polymerization (dimer acids), glycerolysis (mono- and diglycerides) and fat splitting; (c) the ever-increasing substitution of methyl esters for fatty acids in the production of a whole series of oleochemicals; (d) development of new esterification catalysts; (e) lipase catalysis of interesterification; (f) development of new corrosion-resistant materials of construction; (g) the use of irradiation sulfoxylation as a preferred production route to randomly sulfonated methyl esters; and (h) superemulsification as an aid to hydrophobic/hydrophilic liquid chemical reactions. Continued attention to alternative feedstocks, biotechnology, microprocessor technology, pollution control and lower energy consumption are certain to receive considerable attention for the next several years.

INTRODUCTION

Dynamic changes in technology within the complex oleochemical industry are often so obscure and imperceptible that one is occasionally lulled into the misconception that there are little changes under way. One has only to examine the changes from a different perspective and over a longer period of time, perhaps 1, 2 or 3 years, to ascertain that extensive changes are really occurring in many of the traditional unit operations that fatty acid and derivatives manufacturers have been concerned with for over 50 years.

Inflation has influenced oleochemical technology just about as significantly as it has the rest of the chemical industry. High prices for raw materials have always encouraged the search for newer, cheaper ones; and consequently, technology may inevitably be altered. High energy costs touch off a sequence of developments. First, energy conservation in the present process is maximized. If this is not economically satisfactory, then the process conditions are altered to require less energy (e.g., by using a catalyst to drop the reaction temperature 5, 10 or 20 C in a reaction that had been uncatalyzed or catalyzed by a less efficient catalyst). If this is still not economically satisfactory, the search is undertaken for a new process requiring substantially less overall energy than the older one (e.g., a room-temperature free-radical polymerization process may be evaluated to replace a high-temperature clay-catalyzed polymerization process). Also, high labor-costs encourage a search for automation. Sometimes, high labor-costs may be the last straw in the deliberation of continuous, over batch processing. High freight costs may also enter in; and, although rare, plants may be relocated because of them. Whatever the type of cost increases, the overall change in technology during inflationary periods is more acute, frequent and generally more significant than anything which would normally occur during periods of stable economy. And, of course, plant shutdowns and company failures are inevitable when overall costs become too quickly prohibitive.

We can readily detect the insidious effect of continuing cost increases on many of the unit operations carried out in the USA. Although it is true that several organizations continue to be blessed with new products and new processes for them, the majority of the effort by most appears to be concerned with making the same old product, making it better, and making it more economically by an improved process from a new, cheaper raw material. After they have achieved that, most American oleochemical manufacturers then, and only then, find the time to anticipate and hope that their new products arriving on the scene from their research departments are at least half as good as their marketing departments had predicted.

NEW RAW MATERIALS

Although traditionally very cost-conscious with respect to their fat and oil raw materials, oleochemical manufacturers may on occasion pay "list" or even premium prices for certain desirable fats and oils. Two examples are "fleshing" grease, an animal fat used for the manufacture of premium quality low-linoleic oleic acids, and high-erucic acid rapeseed oil (HEAR), for erucic and behenic acid derivatives. Where everyday oleochemical products are concerned, cheap and readily available raw material fats and oils are paramount. Since stearic and palmitic acids can be obtained from a large variety of animal and vegetable (even marine) fats and oils; and since an edible grade is not required (except for food additive manufacture), the least costly material can usually be selected. Thus, upgraded and recovered fatty acids from vegetable-oil soapstocks left over from the refining of soybean, cottonseed, peanut and other oils find uses. New developments in the upgrading of all these products continues; especially in the utilization of methyl ester intermediates in the upgrading step, and where methyl esters may be used eventually in place of fatty acids. The limitation in this kind of development is, of course, that the cost of the upgrading processing plus that of the low grade fatty acid (soapstock) must still be somewhat less than the cost of the higher-quality fatty acid source, which in most cases is that of the refined edible grade of the vegetable oil less glycerol credits.

Two new developments in vegetable oils intended primarily for use in oleochemical manufacture are under way. The first comes as an aftermath of the development of canola oil in Canada, a re"engineered" edible oil in which, because of inferior edible properties, erucic acid has been eliminated by genetic development of the oilseed. Although canola oil is, of course, no longer an erucic acid oil, but is now rather like a soybean oil, canola oil has displaced most of the Canadian rapeseed oils from the food market. The result is that the Canadian farmer grows high-erucic acid oils for industrial applications only as a second choice to growing canola oil for the edible market. Furthermore, the high-erucic acid rapeseed oil suffers from the disadvantage of containing glycosinolate, a toxic component, in the meal.

Not only are Canadian developments of HEAR types of low glycosinolate content, but genetic changes toward 80% or 90% erucic acid content rapeseed oils are imminent (1). These oils appear to justify premium prices from oleochemical manufacturers who produce C_{20} saturated (arachidic), C_{20} unsaturated (erucic) or C_{22} saturated (behenic) fatty acids.

Another development is the prospect for early quantities of a high-oleic sunflower oil for use primarily as an industrial oil. It is probable that oleic acid contents of 80 or perhaps even 90% can be achieved from the oilseeds of recent grown nontemperature-sensitive plants (2). Growers of these high-oleic sunflower oils also have the possibility of

achieving deep frying edible uses for this new oil. It is only a question of time before industrial applications, such as a whole new line of superior quality oleic acids, are commercial realities. Furthermore, developments such as the production of high-quality azelaic acids from these oleic acids by ozonization technology are also likely.

SLOW AND CONTINUING REPLACEMENT OF FATTY ACIDS BY METHYL ESTERS

It has been appreciated for over 30 years that for the production of a number of fatty acid derivatives, methyl esters are superior to fatty acids. Examples include the superamides, certain fatty acid esters (by interchange technology) and fatty alcohols (by copper chromite catalyzed hydrogenolysis) (3). The broad-scale replacement of fatty acids by methyl esters has been slowed in the past 3 decades by a number of developments and factors among which the following are noteworthy:

(a) Generally speaking, fatty acids have been more readily available than methyl esters, except possibly in the case of coconut oil derivatives where the large volumes involved have made methyl esters cheaper.

(b) Large investments in fat splitters and glycerol recovery and drying equipment have not permitted the oleochemical industry to concentrate equally on methyl ester production, although much of this equipment has long since been capitalized.

During the past 10 or 20 years, there has been a recognition of new factors which have slowly and steadily tipped the scales in favor of methyl ester production.

(a) Methyl esters can be produced with less thermal energy expenditure than fatty acids, i.e., methyl ester interchange from vegetable oils and methanol operates at 100-200 C; while fat splitting is very thermally dependent, usually requiring 1-2 hr at 260 C.

(b) Glycerol obtained from oil methanolysis reactions is substantially dry. Glycerol from continuous fat splitting operations contains 80-90% water.

(c) If fractionation is required, fractional distillation is more efficient with methyl esters than with fatty acids because of their lower boiling points, and greater range of boiling points between methyl ester homologs than with those of fatty acids. Methyl esters have much better thermal stability than fatty acids and do not yield anhydrides as fatty acids do in still reboiler units.

All the advantages of methyl esters add up to cheaper production costs if substantial volumes are involved.

Recently, escalating fuel prices have increased thermal energy costs. A combination of all these aforementioned factors at about the beginning of the 1980s has culminated in a large growth of methyl ester production and usage. Coincidentally, many fatty acid producers are also methyl ester producers.

Relative volumes of fatty acids and methyl esters produced in the USA are difficult to estimate. Although the Fatty Acid Producers Council (Soap and Detergents Association) has long reported production volumes of fatty acids representing member production, it ceased compiling production data in 1981. Methyl ester production volumes have never been tabulated. Based upon a recent survey which includes estimated methyl ester production in the USA for cocamides, fatty alcohols, some esters and other derivatives. We estimate that 340 million lb of methyl esters will be produced in the USA in 1983, compared to an estimated production of 1,050 million lb of fatty acids

(excluding tall oil fatty acids). This estimate for methyl ester production is already 32% of the amount of fatty acid production in the USA (excluding tall oil fatty acids).

Among the product areas where we can expect to see a large increase in methyl ester production and use are sugar esters, fatty alcohols and, possibly, nitriles as intermediates for fatty amines.

DEVELOPMENTS IN HIGH HEAT-DEPENDENT OLEOCHEMICAL REACTIONS

Among the common oleochemical unit operations that are more or less heat-dependent are fat splitting, glycerolysis (for monoglyceride production), and clay-catalyzed heat polymerization of unsaturated fatty acids to dimers and trimers.

Except for occasional batch-splitting operations on special oils such as babassu oil, and occasionally coconut oil, fat splitting is primarily operated in the oleochemical industry by innovations made on the continuous Colgate-Emery fat splitting process. Although the operation efficiently yields large volumes of split fatty acids from fats and oils having iodine values of below ca. 120, the process has some drawbacks. One is the requirement of expensive high-pressure equipment built of corrosion-resistant materials. A second disadvantage is that during periods of high relative fuel costs, it is less economical.

Although liquid water homogeneously dissolved in the liquid fat phase is the primary requirement for Colgate-Emery splitting, the process actually operates in a heterogeneous, nonemulsified manner in which a stream of excess water is permitted to flow by gravity downward in a column containing upward moving fat and washes away dissolved glycerol, the hydrolysis byproduct, thus enabling the reaction to be completed (4). Simply put, the Colgate-Emery process requires the heating of ca. 5 lb of water to temperatures of ca. 260 C for each 10 lb of fat to be split.

About 1966, a US patent (5) suggested that fats and oils could be split rapidly with the use of superheated steam at near atmospheric pressure with use of a catalyst. However, to achieve this, it is apparently necessary to use superheated steam above a temperature of 300 C, so that byproduct glycerol could be volatilized off the reaction medium and thus permit the hydrolysis reaction to go readily to completion. The high costs for heat has not made this process economically attractive, and attention has now shifted towards the study and development of room-temperature enzymatic hydrolysis processes (6).

Traditionally, the oleochemical industry operates glycerolysis unit processing for monoglyceride manufacture almost entirely in a batch manner (7). Extensive heat to achieve a reaction temperature of 255-260 C is required primarily because the high miscibility of hydrophilic glycerol in hydrophobic fat triglycerides and diglycerides is only attainable at high temperatures. Process development to conserve heat for glycerolysis, accordingly, has involved increasing miscibility of glycerol/triglyceride-diglyceride mixtures by improved mechanical agitation, and by superemulsification, induced by a number of innovative methods.

Heat polymerization of unsaturated fatty acids like tall oil fatty acids is catalyzed by a number of catalysts, including clays. New developments currently receiving research and development attention in the USA include the use of promoted catalysts, preliminary conjugation methods for the feed unsaturated fatty acids, use of methyl esters, and the possibility of the employment of corona discharge energy for initiating free radicals for room temperature polymerization. With the decrease in the cost of generating corona discharge energy over the past 20 years, and the

increase in the cost of heat energy, there is a justification for a review of room-temperature polymerization by this technique. One factor which must be considered when shifting from an "ionic" mechanism of polymerization to a free radical mechanism is that the products are of somewhat different chemical structure, and are likely to be produced in different degrees of polymerization.

DEVELOPMENTS IN CONVENTIONAL PHYSICAL SEPARATION UNIT OPERATIONS

The vegetable oil grower and the food industries using fats and oils have shown great interest in the prospects of extracting oils with liquid carbon dioxide in supercritical fluid extraction. Current oleochemical interest in this separative technique is developing, and can be expected to accelerate at the point where work is reported, not on oilseed extraction, but on fatty acid fractionation. This has been the previous pattern of extractions carried out using propane, furfural, etc.

With the changeover of some batch processes to continuous technology, there has been a distinct need for reliable methods of continuous filtration of solids from liquids. Occasionally, where the solid is the desired (or valuable) product, methods for recovering small amounts of solids (such as catalysts) from large volumes of liquids continuously are desired. The need to avoid the use of filter aid material is obvious. Developments in new equipment have apparently provided us with new filters capable of achieving both these objectives.

Several methods of removing filter cakes from filter surfaces on equipment designed for continuous service have been devised, including inverting the plate for gravity discharge, scraping, brushing or blowing off the cake, and jarring, vibrating or dislodging the cake by other means. The Idrex continuous filter (8) employs a gentle, patented brushing operation, and the "Hydra Shoc" filter of Industrial Filter and Pump Mfg. Co., uses a reversed hammer-like blow from air pressure to remove the cake. The "Vibra-Shoc" type filter removes the cake by using mechanical vibrations of different frequencies and amplitudes (9).

In an industry as large and as diversified as the oleochemistry industry, there is a great deal of effort spent on discovering new fractional distillation methods, particularly those that are innovative. Unfortunately, much of this information is in the category of "trade secrets" and cannot be discussed and disseminated. However, the increased interest in fractional distillation of methyl esters is manifest especially in evaluations as to whether separating C_{18}, $C_{18}^=$ and C_{16} esters is any easier than separating fatty acids. It is doubtful that meaningful improvements are possible in this direction. As a consequence of recent information (10), there is considerable excitement as to the significance of the Higee concept, from ICI in England, which involves separating mixtures by equilibrating them within a rapidly spinning, doughnut-like drum rather than with a conventional fractionating column. (This is, of course, a British and not an American development.)

DEVELOPMENTS IN CONVENTIONAL OLEOCHEMICAL OPERATIONS

Aside from the conventional unit operations already mentioned, many other oleochemical operations have come in for somewhat more than their usual review attention. Among these are continuous esterification, homogeneous-catalyzed hydrogenations, "superemulsification," direct esterification, and random irradiation sulfoxylation of methyl esters.

About the only previous example of semicontinuous methyl esterification in the oleochemical industry consisted of the direct esterification of acidulated cottonseed soap-stocks with methanol catalyzed with Twitchell reagent (11,12). The process was operated by Vege-Fat, Inc., at Dupo, Illinois, about 1959 on cottonseed, corn and soybean acidulated soapstocks to a reported annual volume of 15 million lb in ordinary steel pipe at 150 psig, and, apparently, when corrosion destroyed the pipe, small sections were replaced periodically (13). Although such a process is almost pathetic by present standards, it is surprising how much interest has presently been redirected to continuous, catalyzed methods of pressure esterification; although, today, corrosion-resistant alloys are more likely to be employed. Although current American attempts at continuous esterification are largely proprietary in nature, they bear resemblance to reported esterification of low grade animal fat and fatty acid mixtures with methanol vapor and sulfuric acid in two separate steps with recovery of dry glycerol (14).

Batch methanolysis processing for converting fats and oils to methyl esters operates so efficiently that the unit operation has resisted attempts to alter it to continuous operation. Nevertheless, it is entirely likely that when large volumes of methyl esters are required in the future they will be produced directly from fats and oils in equipment similar to fat splitters in which byproduct glycerol is recovered at the bottom of the column and methyl esters at the top with liquid methanol introduced at about a lower center point and the molten fat near the top; the entire system operating at low pressures. A few methyl ester products will not require clean-up distillation before use.

Homogenous catalyzed hydrogenations have recently been developed to offer good possibilities for selective hydrogenation of linolenic and linoleic acids with minimum trans-isomer formation. One of the major problems for oleochemical organizations which manufacture oleic acids by separation technology is the removal of polyunsaturates. Attempts to achieve this by selective hydrogenation with conventional heterogeneous catalyst systems like nickel or copper chromite result in trans-isomer formation giving rise to separation difficulties and an oleic acid product with a high titer or double bond migration which causes trouble if the oleic acid is to be ozonized. Recent developments indicate that selective hydrogenations of soybean oil with homogeneous catalysts like 1% chromium hexacarbonyl in hexane at 500 psig produces less than 3% linolenate content and also less than 3% trans-isomer formation (15), a low level for both these contaminants not achievable from heterogeneous catalysts. If further work shows even lower levels to be possible, this method may find a use within the oleochemical industry. Removal of homogeneous catalysts and recovery of the metal remains a problem to be solved, however.

As mentioned earlier, emulsification methods are being evaluated for the possibilities of improving the reaction rate (as well as lowering the temperature requirements) of a number of oleochemical reactions. Among these are super-emulsification, direct esterification and interchange esterifications such as those for sugar esters (16,17) and for poly-glycerol ester production (18).

When the Persian Gulf oil crisis arrived and resulted in immediate price boosts for benzene hydrocarbons, more than one reaction settled in among detergent sulfonates. Alpha-sulfonated fatty acids, waiting for this opportunity, readied for the long-awaited breakthrough. Never quite the equal in detergency to the alkylarylsulfonates, they had not achieved the commercial position that had been predicted for them. Even though many a market researcher in the detergent industry have predicted that they would finally

be used in large volume, the predictions have not materialized. Frankly, it appears they still may not be highly successful. There always appears to be a plethora of competitive products that for one reason or another are capable of capturing the bulk of the market. This time, the new entry might be a random monosulfonated product prepared from methyl esters or hydrocarbons by irradiation sulfoxylation technology. That might be so if, indeed, the engineering problems of designing and operating satisfactory photoreactions with sulfur dioxide and oxygen can be solved. Certainly methyl esters are available and might be somewhat cheaper than the counterpart fatty acids. But, then, even the alpha-sulfonated methyl esters are getting new attention (19-21).

New process development, largely from Japan, France and West Germany, will probably set the stage as to whether randomly sulfonated paraffins will prove to be satisfactory and economical. On the other hand, in the long run, methyl esters derived from replenishable natural raw materials are apt to be cheaper than paraffinic hydrocarbons. With all the uncertainty, American sulfonation equipment manufacturers are reacting cautiously. No new irradiation sulfonators have yet made their appearance.

BIOTECHNOLOGY

No chemical industry is immune from the new developments occurring in biotechnology, and the oleochemical industry is no exception. The outstanding new developments include enzymatic fat splitting, lipase-catalyzed interesterification, and lactic acid manufacture.

Fat splitting beautifully demonstrates how within the span of perhaps 45 years we will have seen both extremes of a technological range. It is not often that an operation at 260 C may very likely become one carried out satisfactorily at room temperature. I remember as a student boiling up and fermenting castor beans in a laboratory exercise to hydrolyze coconut oil. The operation was a terrible mess. I also recall writing in Bailey's 4th Edition, Volume 2, published as late as 1982 (22), "enzymatic hydrolysis has not been commercially developed, chiefly because of its incompleteness, sluggishness, and the general difficulty in handling it as a unit operation." If I had the opportunity I would revise my sentence in Bailey to read, "enzymatic hydrolysis probably offers the greatest hope of successfully splitting fat without substantial investment in expensive capital equipment and the expenditure of large amounts of thermal energy."

Dr. Linfield's paper (6) illustrates how the enzyme *Candida rugosa* splits common fats; olive oil hydrolyzes fastest, coconut and tallow somewhat slower. But, more important still is the prospect of using this or other enzymes to produce mono- or diglycerides by esterification of glycerol and fatty acids.

Lipase-catalyzed interesterification is another relatively new development (23); however, up to this point only the food industry has taken notice of it. They are vitally interested in rearranging the fatty acids of fat triglycerides for chemical utility in products such as margarine, hard butters, shortenings and other fats. But, when these developments are inevitably extended to glycerolysis and methanolysis, the oleochemical industry may be the greatest benefactor.

Finally, let us prognosticate about fermentation-grade lactic acid compared to the relatively more expensive synthetic lactic acid. Frankly, it cannot be too much longer

that we will continue to see a quality-deficient natural lactic acid attempting to compete with the expensive synthetic acid. Developments in biotechnology are occurring much too rapidly to permit this to continue.

We can tabulate a number of typical developments:

—Energy costs are rising higher and higher. In some instances they have exceeded labor costs for some oleochemicals.

—Efficient oleochemical organizations are devoting more and more time and effort to process energy conservation.

—Coal has reemerged as a primary fuel source.

—Fatty acid derivative plants are no longer using aluminum for storage tanks, Monel for reactors and iron or plain steel for general piping.

—Asbestos has disappeared as a heat insulating material.

—New materials of construction now make it possible to use seawater as a cooling medium.

—Use of ethoxylated alcohols is increasing at the expense of fat alcohols as a consequence of the phasing out of zeolites in synthetic detergents (24).

—Plant air exposure minimums for hazardous gases like hydrogen cyanide and ethylene oxide continue to decrease.

—Purchase of used equipment is increasing.

—Chemical consultants are selling less and less multiclient surveys; individual, smaller and more specific surveys are flourishing (25).

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