New Developments in the Fatty Acid Industry

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ABSTRACT

Many changes are taking place in the fatty acid industry, both corporation wise and technology wise. Some are sudden and obvious; others are gradual on a day-to-day basis. Important newer developments are highlighted and discussed.

The changes in name, management and ownership of many of the traditional American fatty acid organizations may appear to the general public to be the only significant changes that have occurred within the fatty acid industry. Gone from the ranks of producers are such well known and respected names as Archer Daniels Midland, General Mills, Drew, Armour, Foremost, and Wilson-Martin. In fact, between the writing and the verbal delivery of this very presentation, two more well known names, those of Emery and Ashland, will have been added to the list of organizations which have undergone these substantial changes. Within the last fifteen years, only three fatty acid organizations, two of them traditionalists, have not been subject to these sometimes good, rarely bad, but always startling aspects of change: Procter & Gamble Company's Chemical Division, Darling and Company, and Glyco Chemicals, Inc.

Those of us within this rapidly changing industry almost without exception react with surprise when changes of this sort occur. We are much less surprised, frequently unaware, and apparently much less influenced by the steady, day-to-day somewhat insidious changes which occur in the technology, in the analytical chemistry and methodology, in the availability of new and completely altered raw materials, and in other such matters including the advent of synthetics, both raw material and competitive finished products within our industry. Few, indeed, are those of us who are instantly alert to the potential or broad significance of the very latest developments that occur in the realm of fundamental organic chemistry. This is always a little strange since we pride ourselves upon our alertness and sensitivity to developing matters in the area of business health and economics. We are aware of the impending effects of inflation, to increased costs for labor, packaging, power, and practically everything else, to pollution control, government regulations, preservation of the environment, and the responsibilities of large and small corporations to their communities. When we think upon *these* things it is usually with some small feeling of trepidation and apprehension. Particularly (and unfortunately) is this true when our thoughts turn to those ominous words which to some of us have been the cause of abbreviated trouble–EPA, OHSHA, and TSCA, for example. Most assuredly, not everything in the changing business or economic area can be considered entirely "good news," but many developments in the industry *are* good news.

FATTY ACID COMPOSITION CHANGES IN RAW MATERIAL VEGETABLE OILS

In the papers by Pryde and Smouse, some reference to soybean oil as a fatty acid raw material was made together with several inherent problems involved in its use. The causative factor undoubtedly in current soybean oil is the 7.5-8% linolenic acid component. Note that we have been making steady progress towards lowering linolenic acid content in edible soybean oils (1,2). In the case of soybean oil used for the manufacture of alkyd resins, the linolenic acid content of the desirable high IV oils in the 135-150 range is usually 8-12% and is intimately related to the oleic/linoleic acid ratio. While it is desirable to lower the linolenic content of fatty acids or oils for alkyd resins too, the problem of achieving this is somewhat more difficult than that for the normal edible soybean oils, and some sacrifice of iodine value would have to be made. In the case of normal edible soybean oil, reliable estimates are that eventually with proper attention to genetics and other growing factors, the linolenic acid content could be reduced to ca. 3.5%. Nothing in American agriculture is instantaneous; perhaps five years would be required to achieve this presuming an intensive effort were to be made. Certainly the edible uses and those fatty acid uses (or nonedible industrial uses other than alkyd resin manufacture) would be certain to benefit. All that has been said thus far is in reference to unsaturated fatty acids from soybean oil; the producer who hydrogenates soybean oil prior to splitting for the production of a 88-92% stearic acid is not particularly concerned with these developments.

The worldwide change in rapeseed oil is well underway (3-7). The presence of 13-docosenoic (erucic) acid is suspected to be physiologically harmful; Canada prohibits the presence of more than 5% of this acid (mostly from so-called "high erucic acid rapeseed oil") in margarine or other edible products (8). Genetic changes in rapeseed oils both in Canada and Europe are already so extensive that new types either have very little (less than 3.5%) in so-called "canbra" oil, or nil in other varieties. A developing effort on replacement vegetable oils like *Crambe abyssinica* (ca. 52-57% erucic acid content) (6,9,10) could materialize in time to afford the U.S. sufficient quantities of erucic acid, or (after hydrogenation) the C-20, 22 (behenic) and 24 saturated fatty acids; but polyunsaturated fish oils can be counted on only for the saturated C-20, 22 and 24 acids (with hydrogenation).

Although certain vegetable oils are used mostly for edible purposes and will probably continue to be so, their fatty acid composition is in a state of transition. It is possible that new inedible uses could be developed in the future, but, if edible uses grow rapidly, fatty acids could be available from soapstocks in the refining of these oils, just as in the case of soybean and cottonseed oils. Sunflower oil is one example. Sunflower oil grown in Minnesota contains ca. 70% linoleic acid, whereas that grown in Alabama is likely to contain 45% linoleic acid (11), and there are numerous intermediate compositions from various seed strains (12). Safflower is another example. There are "high-oleic" acid oils (75-80%) and so-called "high-linoleic" oils (72-78%), and some oils are characterized as "45% maximum-oleic," "45% minimum-linoleic," "80% maximum-linoleic," along with a "10% minimum-linoleic," and a "10% maximum-stearic acid" type (13-16). True, the kind that will ultimately be grown, if any, will be dictated largely by the market demand in the edible oil area, but even if no industrial fatty acid applications ever develop for the oil itself (and that is by no means certain), at least the availability of lots of soapstock is a prospect.

Palm oil is available in higher quality than heretofore especially with respect to free fatty acid content, stability, iron content and in other important respects (17) – and is a potentially fine raw material for industrial applications despite the fact that its fatty acid composition is quite different from that of tallow, the major source of industrial fatty acids. Palm oil comprises a somewhat variable fatty acid composition depending upon the source, that is, Malaysian, Zaire or otherwise, but it ranges from 32-47% palmitic acid, and 40-52% oleic acid in its triglycerides. Beef tallow, on the other hand, contains less palmitic acid than palm oil, usually 22-26% with 45-46% oleic acid; mutton tallow, while similar to beef tallow in palmitic acid content, has much higher stearic acid content (ca. 30%) and somewhat lower oleic acid content (30%).

This illustrates that beef tallow and palm oil aren't interchangeable. For example, a separated oleic acid from palm oil would have an approximate 15% linoleic acid content compared to 7-8% in most common tallow-derived oleic acids. However, when the price is right, palm oil could be another general raw material to consider. Lately, palm oil importation into the U.S. has been drastically curtailed as a consequence of decreases in the price of soybean oil. (This would constitute largely edible raw material.) There is tariff protection on most of the palm oil-derived industrial products amounting to ca. 30-35%.

SUPERHEATED STEAM FAT-SPLITTING

The conventional fat-splitting methods that are employed today for the industrial large scale production of fatty acids involve the use of medium or high pressure steam and require relatively expensive equipment as discussed in an earlier paper. It is possible to avoid the use of high pressure steam and to conduct the hydrolysis at atmospheric pressure with the use of superheated (gaseous) steam in the presence of a catalyst. The claim that tallow is 16% split at 200-280 C in only 10-30 seconds, and 70% split with a second pass infers that such hydrolyses could be quite rapid (18). Although many, if not all, of the industry's existing fat splitters have long ago been completely capitalized, possibly the large expense involved with future 725 PSIG fat splitters, roughly ca. 1.5-2M $, could be substantially reduced if low pressure splitting were employed.

IMPROVED CATALYSTS FOR DIRECT ESTERIFICATIONS

Concurrent with the development of new alloys better able to withstand the highly acidic corrosion induced by the conventional type direct esterification catalysts like sulfonic acids, phosphoric acid, or even hydrochloric acid, has been the development of less corrosive and effective direct esterification catalysts. Today, hypophosphorous acid can replace phosphoric acid with advantage, and a number of nonacidic, metal-containing compounds may also be used such as dibutyl tin oxide and certain titanium-, silicon- and boron-containing materials.

CONTINUOUS MONOGLYCERIDE PRODUCTION AND OTHER INNOVATIONS

Seven American patents issued during 1945 and 1967 (19-25) attest to the fact that continuous processing is feasible for monoglyceride production by fat glycerolysis. Despite these patents, a large proportion of the U.S. production of "40% and 60% monoglycerides" is still made by nonsolvent batch glycerolysis processing. Typical "60% monoglyceride" products from such batch processing conform to an optimum total monoglyceride content of 58-60%, and it is not practical for several reasons to force the atmospheric pressure glycerolysis reaction to higher conversions.

The use of solvents has long been known to give improved reaction medium homogeneity, and consequently, to afford somewhat higher yields of monoglycerides, but the number of solvents which offer simultaneous miscibility of glycerol with the fat components is not large. Examples include 83% total (and 75% α-mono-) with sunflower oil using pyridine (26), and also the use of phenol and cresols (27) or dioxane (28). The use of solvents for monoglyceride production necessitates the need for solvent storage, handling, solvent recovery, as well as the removal of solvent more or less completely from the product. The toxicity of several available solvents does not permit their use for the production of edible products. Furthermore, solvent use decreases the production capacity of the reactor, and for these various reasons, solvent-based methods have not been extensively developed.

The use of pressures higher than atmospheric for carrying out glycerolyses is also known to improve yields, but recent work indicates that the effect is greater than previously anticipated. A 1967 U.S. patent (25) demonstrates that the production of conventional 60% monoglycerides can readily be achieved corresponding to 58.2% α-mono content if the glycerolysis is conducted at medium pressures such as 40 PSIG. The use of CO_2 as both catalyst and blanketing agent is said to yield at 100 PSIG an 82% α-monoglyceride from castor oil; similarly, from peanut oil the yield is 73% α-mono- and from coconut oil, 74.5% (29). These high yields appear to economically justify processing based upon continuous pressure glycerolyses.

Another innovation is the possibility of using glycerolysis of methyl esters for the production of monoglycerides. A Japanese report (30) indicates that 50.6-54.9% α-monoglycerides result from the glycerolysis of methyl esters (1 mole methyl esters and 1.5-4.0 moles glycerol) with 0.1% KOH at 215-220 C in only 25-30 min with the removal of methanol by distillation. Israeli work (31) substantiates these claims.

TECHNOLOGY BREAKTHROUGH IN SUGAR ESTERS?

Extensive research and development in the early 1950s on sugar esters appeared certain to be translated to an early industrial scale reality. The products possessed excellent functionality for detergent applications, possibly also for cosmetics. They were based upon cheap, readily available raw material and were nontoxic and biodegradable. Early in the process development it was apparent that fatty acids could not be used to esterify the sensitive hydroxyl groups of the sucrose molecule; sucrose carmelized if held for long at temperatures of 105 C. Only methyl esters, possibly phenyl esters (32), offered any promise at all for success, and even with the cheaper methyl esters the establishment of the proper reaction medium and conditions for satisfactory conversion was difficult. Solvents like dimethylsulfoxide (33,34), dimethylformamide (33, 35-40), methylbenzylamine (41) and substituted morpholine or piperidines (42) were evaluated; none were successfully developed and applied for large production. Xylene was investigated as a heterogeneous extractive solvent (33,43).

About 1967 the "micro-emulsion" process (44) was proposed to eliminate the use of solvents; propylene glycol was employed as a reaction vehicle. In 1970 Feuge and coworkers (45) were able to interesterify sucrose with monopalmitin, distearin, or technical grades of 40% monoglycerides from hydrogenated cottonseed oil at temperatures of 170-187 C without exhorbitant decomposition using mixtures of lithium, sodium and potassium soaps as catalyst-emulsifiers. With lithium oleate the products were 90% of tetraesters or higher; lower esters could be produced by blending the emulsifiers to include sodium or potassium soaps. A German patent assigned to Tate and Lyle, Ltd. (46) describes the preparation of sucrose esters from a nonsolvent media at 125 C. The process involves sucrosolysis of methyl esters such as those obtained from tallow with K_2CO_3 highly emulsified through the use of an emulsifier system consisting of sucrose monoester and tallow fatty acids. But perhaps a major breakthrough in methyl ester processing is exemplified in a nonsolvent, two-step emulsion process developed by Procter & Gamble Company (47). It involves the preparation of sucrose polyesters (SPE) which permits the use of less soap emulsifiers than heretofore based upon the use of metallic sodium or potassium or their hydrides added to the mixture of sucrose, methyl esters and soap at temperatures as low as 130 C. In the first step, methyl esters and sucrose at a 3:1 molar ratio are reacted emulsified with potassium soap to form low sucrose esters. In the second step, more methyl esters are added and reacted to produce SPE in yields up to 90% based on sucrose.

METHYL ESTERS AS SUBSTITUTES FOR FATTY ACIDS

In the earlier papers by Sonntag and by Farris the preferred use of methyl esters as replacements for fatty acids was mentioned. Actually, for several uses methyl esters are not replacements for fatty acids, for in these instances the methyl esters *are* useful and the fatty acids do *not* perform. Examples include the preparation of sucrose esters and "superamides." In other applications methyl esters possess singular advantages over fatty acids but the acids *do* perform. Examples are fractional distillation, simple amide preparation and nitrile preparation.

It is difficult to estimate the volume of methyl esters produced both for use as such and for conversion into many derivatives. Much of the production is directly from fats and oils; only a small part is directly from fatty acids, and perhaps 20% is from acidulated vegetable oil or animal fat soapstocks. The volume used is certain to grow substantially, and sooner or later it will be desirable to report and tabulate this production, just like the monthly compilation of fatty acids by the FAPC.

TRENDS IN NEW MATERIALS OF CONSTRUCTION

The development of new metals has afforded us materials of significantly improved resistance to acid corrosion, of lighter weight, and, in some cases, superior strength. Examples of valuable new metals variously suited for uses in fatty acid equipment are Incoloy 825, "E-Brite," Carpenter $20C_b$ and AL-6X (Allegheny Ludlum). We are observing a decrease in the use of conventional metals like Monel, Inconel and aluminum in the fatty acid industry. Perhaps, in retrospect, nothing has occurred quite so quickly as the observed trend in the last three years to completely eliminate asbestos as an insulating material. Certainly this change appears to be justified.

THE ADVENT OF WATER EMULSION SEPARATION

Faced with a choice of separative processing within the last five years, two American companies (Darling & Company, Chicago, IL and A. Gross & Company, Millmaster Onyx Group, Newark, NJ) and one Canadian organization (Canada Packers, Ltd., Toronto, Ontario) selected the "Henkel process" (48-51), a technique employing water-containing emulsifiers like sodium lauryl sulfate and salts like magnesium sulfate to emulsify liquid (unsaturated) fatty acids away from solid (saturated) acids with the use of centrifuges. Apparently, we can conclude that the economics for water emulsification separation does compare satisfactorily with that for low temperature solvent crystallization.

PROSPECTS FOR ETHOXYLATION AS A UNIT OPERATION

While most of us have already accepted ethoxylation as an established fatty acid unit operation, the prospects for further utilization of this technology appear quite attractive. Ethoxylated sugar esters are one product group that will require close attention as the products are potentially very useful. "Tailormaking" can be applied to this family of ethoxylates with good success, according to early results.

Among the required analytical techniques for ethoxylation in general is one capable of separating all of the homologs in the Poisson distribution of components that are formed in the ethoxylation of raw materials such as fatty acids, alcohols, glycols, amines and amides, and ultimately, ethoxylated carbohydrates like sugar esters. Such analytical methods now appear to be at hand as judged by the development of separative methods based upon trifluoroacetyl or silylated derivatives in GLC methodology or more recently, by HPLC, and should be of inestimable value in the characterization of ethoxylated products.

The enthusiasm for ethoxylation, however, must be tempered by the realization that we are handling a potentially dangerous raw material. A recent report (52), which was widely distributed, bore the caption "Ethylene Oxide Linked to Leukemia" and related information indicating that the Swedes have found it necessary to lower the eight hour time weighted average exposure limit for Swedish factory workers from 20 to 10 ppm for ethylene oxide as a consequence of this disturbing data.

POLYUNSATURATED FATTY ACIDS FROM FISH OILS

Papers previously mentioned the possibility of utilizing polyunsaturated fatty acids derived from fish oils. The raw materials are cheap, available and abundant, but the development of appropriate technology remains to be achieved before any commercialization for these acids can be realized. Splitting techniques would require extraordinary gentle methods such as enzymatic hydrolysis to avoid structural changes in the sensitive polyunsaturated systems of double bonds of the fish fatty acids; furthermore, methods of recombining the fatty acids to the required derivatives are not as yet fully developed. The challenge is broad (both edible products and polymerized acids are just two of several attainable end products) and the potential is large.

FAT MODIFICATION BY ESTER INTERCHANGE

Triglyceride ester-ester interchange is an established unit operation in the food industry for the improvement in the physical properties of products like lard, margarine, shortening, and "hard butters." While it appears that the unit operation is applicable to inedible products such as synthetic lubricant esters, there has been, thus far, no large application of this technology to inedible products. The potential utility for modification of triglyceride esters with ethyl (or methyl?) esters by the process of interchange has been recently developed. Palm oil, interesterified with ethyl oleate, could be converted to a salad oil if saturated ethyl esters were eliminated by fractional distillation (53). A continuous industrial scale plant with a capacity for the interesterification of 100 tons/24 hr of palm oil is said to be contemplated for Israel. The prospects for the modification of triglycerides for industrial purposes represent an attractive possibility.

SYNTHETIC FATTY ACIDS

Despite the fact that Russian and eastern-European production of synthetic fatty acids by hydrocarbon oxidation is estimated at ca. 1.1 billion pounds (1978), compared to U.S. "natural" production of 956 million pounds, exclusive of tall oil fatty acids, there is still no significant American production (1979) of SFA. Best possibility continues to be Ethyl Corporation's U.S.-produced SFA, apparently by Ziegler alcohol technology followed by caustic fusion (54,55), which are straight chain, even-numbered acids designed to be competitive with hydrogenated coconut oil fatty acids. Potential production of shorter chain fatty acids include caproic (hexanoic) and heptanoic acids, presumably by oxidation of the corresponding aldehydes.

REFERENCES

1. Howell, R.W., C.A. Brim, and R.W. Rinne, JAOCS 49:30 (1972).
2. Hammond, E.G., W.R. Fehr, and H.E. Snyder, Ibid. 49:33 (1972).
3. Rakow, G., and D.I. McGregor, Ibid. 50:400 (1973).
4. Downey, R.K., B.M. Craig, and C.G. Youngs, Ibid. 46:121 (1969).
5. Appelqvist, L.A., Ibid. 48:851 (1971).
6. Downey, R.K., Ibid. 48:718 (1971).
7. Craig, B.M., T.M. Mallard, R.E. Wight, G.N. Irvine, and J.R. Reynolds, JAOCS 50:395 (1973).
8. Sahasrabudhe, M.R., JAOCS 54:323 (1977).
9. McGhee, J.E., L.D. Kirk, and G.C. Mustakas, JAOCS 42:889 (1965).
10. Grynberg, H., and H. Szczefranska, JAOCS 43:151 (1966).
11. Kinman, M.L., and F.R. Earle, Crop Sci. 4:417 (1964).
12. Kinman, M.L., JAOCS 49:36 (1972).
13. Corrao, A., G. Tazio, V. Celluffo, A.M. Gattuso, and B.L. Cascio, Riv. Ital. Sost. Grasse 53(10):273 (1976).
14. Knowles, P.F., JAOCS 49:27 (1972).
15. Craig, B.M., Can. J. Technol., 31:202 (1953).
16. Kuemmel, D.F., JAOCS 41:667 (1964).
17. Cornelius, J.A., JAOCS 54:943A (1977).
18. Lunde, K.E., (to Carad Corp.) U.S. Pat. 3,253,007, May 24, 1966.
19. Arrowsmith, C.J., and J. Ross, (to Colgate-Palmolive Co.) U.S. Pat. 2,383,581, August 28, 1945.
20. Birnbaum, H., (to Hochmeister, Inc.) U.S. Pat. 2,875,221, February 24, 1959.
21. Birnbaum, H., and J. Lederer (to Hochmeister, Inc.) U.S. Pat. 3,102,129, August 27, 1963.
22. Giddings, R.W., and A.C. Davis (to Lever Brothers Co.) U.S. Pat. 3,095,431, June 25, 1963.
23. Alsop, W.G., and I.J. Krems (to Colgate-Palmolive Co.) U.S. Pat. 3,083,216, March 26, 1963.
24. Chang, S.S., and L.H. Wiedermann (to Swift & Co.) U.S. Pat. 3,079,412, February 26, 1963.
25. Allen, R.R., and R.L. Campbell, Jr., (to Anderson, Clayton & Co.) U.S. Pat. 3,313,834, April 11, 1967.
26. Franzke, C., F. Kretzschman, D. Kubel, L. Zahn, and E. Hollstein, Nahrung, 11 (7-8):639 (1967).
27. Hilditch, T.P., J.G. Rigg, J. Chem. Soc. 1774-1778 (1935); (to Imperial Chemical Industries, Ltd.) U.S. Pat 2,073,997, March 16, 1937.
28. Richardson, A.S., (to Procter & Gamble Co.) U.S. Pat 2,251,692, August 5, 1941. Richardson, A.S., and E.W. Eckey (to Procter & Gamble Co.) U.S. Pat 2,251,693, August 5, 1941.
29. Kochar, I.R.K., and R.K. Bhatnagar (to Council of Scientific and Industrial Research) Indian Pat. 71,979, April 7, 1962.
30. Matsuyama, S., M. Takasago, and K. Hirokawa, Kagaku to Kogyo (Osaka) 42(5):239 (1968).
31. Schmulinzon, C., A. Yaron, and A. Letan, Riv. Ital. Sost. Grasse 48(4):168 (1971).
32. Farbenfabriken Bayer A.-G., British Pat. 925,718, May 8, 1963.
33. Osipow, L., F.D. Snell, and A. Finchler, JAOCS 34:185 (1957).
34. Howards of Ilford, Ltd. (by C.F. Cardy, F. Schild and R.J. Wicker) British Pat. 915,578, January 16, 1963.
35. York, W.C., A. Finchler, L. Osipow, and F.D. Snell, JAOCS 33:424 (1956).
36. Ledoga S.p.A., Belgian Pat. 622,394, December 28, 1962.
37. Lemieux, R.U., and A.G. McInnes, Can. J. Chem. 40:2376 (1962).
38. Bobalek, E.G., A.P. deMendoza, A.G. Causa, W.J. Collings, and G. Kapo, Ind. Eng. Chem. Prod. Res. Dev. 2:9 (1963).
39. Kunugi, K., Chem. Pharm. Bull. (Tokyo) 11:478-482, 486-489 (1963).
40. Farbenfabriken Bayer A.-G. (by W. Hagge, G. Matthaeus and M. Quaedvlieg) Belgian Pat. 612,041, January 12, 1962.
41. Sakawa, S., and T. Kikuchi, Japanese Pat. 18,710, December 14, 1962.
42. Thomas Hedley & Co., British Pat. 804,197, November 12, 1958.
43. Osipow, L., F.D. Snell, D. Marra, and W.C. York, Ind. Eng. Chem. 48:1462 (1956).
44. Osipow, L.I., and W. Rosenblatt, JAOCS 44(5):307 (1967).
45. Feuge, R.O., H.J. Zeringe, Jr., T.J. Weiss, and M. Brown, JAOCS 47(2):56 (1970).
46. James, K., (Tate and Lyle, Ltd.) Ger. Offen. 2,546,716, April 29, 1976.
47. Rizzi, G.P., and H.M. Taylor, JAOCS 55:398 (1978); U.S. Pat. 3,963,699, June 15, 1976, (to Procter & Gamble Co.)
48. Stein, W., JAOCS 45:471 (1968).
49. Anon., Chem. Eng. News, 45 (May 15 issue):62 (1967).
50. Stein, W., and H. Hartmann (to Henkel & Cie, G.m.b.H.) U.S. Pat. 2,800,493, July 23, 1957; British Pat. 925,674, March 3, 1955; U.S. Pat. 3,737,444, June 5, 1973.
51. Waldmann, H., and W. Stein, (to Henkel & Cie G.m.b.H.) U.S. Pat. 3,052,700, September 4, 1962; German Pat. 1,107,659, May 31, 1961. Hartmann, H., and W. Stein, U.S. Pat. 3,733,343, March 15, 1973.
52. Anon., Chem. Eng. News p. 24. (March 19, 1979 issue).
53. Koslowsky, L., Oleagineux 30(5):221 (1975).
54. Fanning, R.J., (to Ethyl Corp.) U.S. Pat. 3,558,678, January 26, 1971.
55. Eller, W.R., (to Ethyl Corp.) French Pat. 1,513,759, February 16, 1968.