Methyl Esters Directly from Acidulated Cottonseed Soapstock. Preliminary Cost Study[1]

K. M. DECOSSAS, S. P. KOLTUN, P. H. EAVES, J. J. SPADARO, E. F. POLLARD, and E. L. PATTON, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

A product containing from 80 to 95% of the methyl esters of cottonseed, soybean, and corn oil is produced commercially in the United States directly from the respective acidulated soapstocks of these oils, using a process developed at the Southern Utilization Research and Development Division. The product is marketed as a high-energy additive for poultry and livestock feed, and its ready acceptance indicates that it has nutritional and handling advantages over other by-product fats for this purpose, which, in 1958, represented a ready and expanding market for almost 600 million pounds of animal and vegetable fats and oils.

A flow sheet for the process is given, and hypothetical plants with capacities of 15,000 and 60,000 lbs. of acidulated foots per 24 hrs. are described for the continuous production of up to 21 million pounds of methylated foots product annually. The lowest manufacturing costs are realized for each plant when operating 24 hrs. a day, 250 days annually, averaging five days per week. For these optimum operations the estimated capital investment for the small plant is $223,000, and for the large plant $410,000.

Manufacturing costs range from a high of 11.2¢ per pound of product at an annual production of 1¼ million pounds to 6.5¢ at an annual production of 15.3 million pounds. The cost of the raw materials, although only 3.4¢ per pound of product and chiefly the cost of foots, is the largest single item of unit cost in producing methyl esters; and, for the higher productions covered by this study, raw material costs account for more than one-half of total unit manufacturing cost. Surplus cottonseed foots can be economically converted into a low-cost feed additive with improved nutritional and handling properties. The process is already a commercial success.

A PRODUCT containing from 80 to 95% of the methyl esters of cottonseed, soybean, and corn oil is produced commercially in the United States directly from the respective acidulated soapstocks of these oils, using a process developed at the Southern Utilization Research and Development Division. The product is marketed as a high-energy additive for poultry and livestock feed, and its ready acceptance indicates that it has nutritional and handling advantages over other by-product fats for this purpose (1), which, in 1958, represented a ready and expanding market for almost 600 million pounds of fats and oils.

Eaves *et al.* (3) described the pilot-plant research leading up to the commercialization of this process and product. This paper includes a preliminary cost study for producing the methylated foots product from cottonseed foots at an annual rate ranging from 1¼ million pounds to 21 million pounds in two hypothetical plants with capacities of 15,000 and 60,000 lbs. of acidulated foots per 24 hrs. The cost study is based on research data obtained at the Southern Division and is not entirely applicable to existing commercial processing in which another catalyst is used.

Process

The process used in this study is illustrated in Figure 1. It is continuous with the exception of the catalyst preparation operation. The catalyst, a crude form of Twitchell's reagent, is prepared in tanks by the addition of naphthalene to distilled fatty acids,

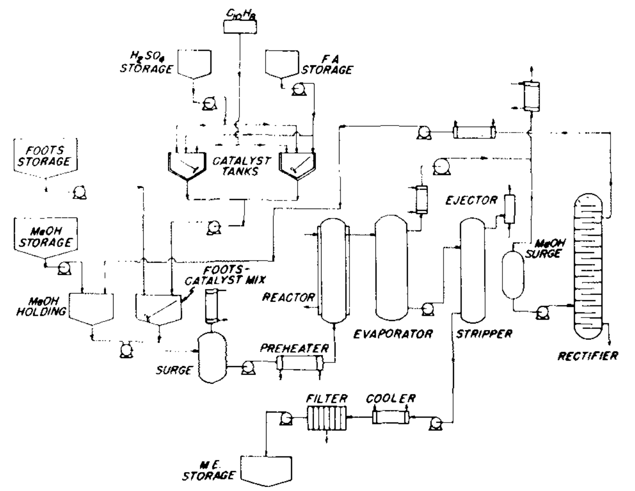

FIG. 1. Methyl esters directly from acidulated foots.

followed by heating and stirring of the mixture at 248°F. for 3 hrs. The mixture is cooled to 104°F., and concentrated sulfuric acid is added. The catalyst is then added to the acidulated foots in the foots-catalyst mixing tank. The foots-catalyst mixture is diluted with methanol by a proportioning pump in a 5:1 mole ratio of methanol to total fatty acids in acidulated foots. The foots-catalyst-methanol mixture is pumped into the reactor surge tank, from which the material is fed into the reactor through a preheater in which the mixture is heated to 248°F.

Reaction takes place at 248°F. at a pressure of 150 lbs. per-square-inch gauge for 12 min., effecting reaction of 85% or more (up to 95%) of the fatty acids to form methyl esters. Unreacted methanol and water are evaporated and stripped from the methyl esters so produced, and the product is then cooled, filtered to remove the catalyst, and stored. The methanol-water mixture evaporated is rectified and recovered. Recovery amounts to approximately 98% of the unreacted methanol.

Each hypothetical plant is equipped with storage tanks having capacities for a 90-day supply of acidulated foots and a 30-day supply of all other raw materials and the finished product. Process equipment and piping are made of cast iron, steel, and 316 stainless steel, depending upon their location in the process. Instrumentation is rather extensive, and auxiliary facilities include a steam boiler and a well-water system. Although the process equipment is unhoused, administration and laboratory buildings and facilities and yard improvements are provided.

[1] Presented at the 51st Annual Meeting of the American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.
[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I

Methyl Esters from Acidulated Cottonseed Soapstock
Manufacturing Costs

Production, lbs./yr.	1,280,000	3,830,000	5,370,000	5,100,000	15,300,000	21,500,000
Annual operation, days	250	250	350	250	250	350
Daily operation, hrs.	8	24	24	8	24	24
Total plant cost (dollars)	190,000	223,000	232,000	332,000	410,000	444,000
Manufacturing cost (¢/lb.)						
Direct costs	5.5	5.0	5.2	4.4	4.2	4.3
Raw materials	3.4	3.4	3.4	3.4	3.4	3.4
Utilities	0.1	0.1	0.1	0.1	0.1	0.1
Labor	0.9	1.0	1.3	0.4	0.5	0.6
Other	1.1	0.5	0.4	0.5	0.2	0.2
Indirect costs (payroll overhead, general plant overhead, control lab., and packaging costs)	2.3	1.7	1.8	1.2	1.0	1.1
Fixed costs (insurance, taxes, and depreciation)	1.1	0.4	0.3	0.5	0.2	0.1
Contingencies	0.5	0.4	0.4	0.3	0.3	0.3
General expenses (gen. adm. and overhead, financing and sales costs)	1.8	1.1	1.1	1.1	0.8	0.8
Total manufacturing costs (¢/lb.)	11.2	8.6	8.8	7.5	6.5	6.6

Costs

Total plant costs, and manufacturing costs per pound of methylated foots product, exclusive of acidulation costs, are given in Table I. Acidulation will cost an additional 0.65 to 1.82¢ per pound of methylated foots product, depending upon plant location and capacity. The lowest manufacturing costs are realized for each plant when operating 24 hrs. per day, 250 days annually, averaging five days per week. For these optimum operations the estimated capital investment for the small plant is $223,000, and for the large plant $410,000. Both plants can be operated at capacity, but week-end labor differentials increase unit manufacturing costs and more than offset the reduction in unit fixed costs.

Manufacturing costs are those for raw materials, labor, supervision, maintenance, plant supplies, utilities, control laboratory, packaging, insurance, property taxes, depreciation, financing, sales, and various overhead costs. Depreciation is based on a useful life of 15 years for process equipment, 20 years for auxiliary facilities, and 33 years for buildings.

Table I shows that manufacturing costs range from a high of 11.2¢ per pound of product at an annual production of 1¼ million pounds to 6.5¢ at an annual production of 15.3 million pounds.

The largest cost is that for raw materials, and it amounts to more than half of the manufacturing cost at the higher production levels. A material balance and list of raw materials costs for the large plant are listed in Table II. Individual contract prices could be less, and it is also possible that substitute raw materials might cost less.

Labor costs were estimated on the basis of three operators and loaders in the small plant, and six operators and loaders in the large plant. Average wage was $2 per hour, with over-time and night differential added whenever applicable.

Utilities' costs include those for steam, electricity, and cooling water. Rates used were 50¢ per thousand pounds for steam, 5¢ per thousand gallons for cooling water, and those prescribed for demand and energy charges as listed in a local electric schedule for commercial and industrial purposes. Packaging is in 55-gallon drums with an allowance for the re-use value of the drums. Laboratory control is maintained on all of the following factors: pour point, AOM stability, gossypol, iodine number, moisture, Rapid Fat Evaluation Test, free fatty acids, insolubles, pH, and unsaponifiables.

The total manufacturing costs are plotted in Figure 2 and were estimated by using the average values of recommended factors for cost estimation (2). However individual producers may be able to reduce these costs by operating closer to minimum values.

Conclusion

This preliminary cost study shows that methylated cottonseed foots can be produced directly from acidulated cottonseed foots for as little as 6.5¢ per pound, exclusive of acidulation costs, by continuous opera-

TABLE II

Methyl Esters Directly from Acidulated Cottonseed Foots. Material Balance and Raw Materials Costs.
60,000 lbs. Acidulated Foots/Day (90% T.F.A.)

Input	Pounds		Unit price	Cost
Raw cottonseed foots	....	108,000	1.6¢/lb.	$1728.00
Acidulated foots equivalent	60,000	....	....	....
Catalyst	1,620	....		....
Naphthalene	....	189.2	5¢/lb.	9.46
Distilled fatty acids	....	406.9	16¾¢/lb.	68.16
Sulfuric acid, 98%	....	1023.9	1.75¢/lb.	12.03
Methanol	32,030	....	....	....
Reacted (with 82% T.F.A)	....	5254		....
Steam eector loss	....	253	30¢/gal.	274.14
Recovery loss	....	536	....	....
Total input	93,650 lbs.	....	....	....
Net raw materials cost				$2091.79 or 3.4¢/lb. product

Output	Pounds
Salable product (solids and water-free)	61,319
Filter loss (catalyst and tarry solids)	2,554
Water of reaction	2,896
Water portion of reacted MeOH	105
Recovered methanol	25,987
Total output	92,861 lbs.
Methanol losses	789 lbs.

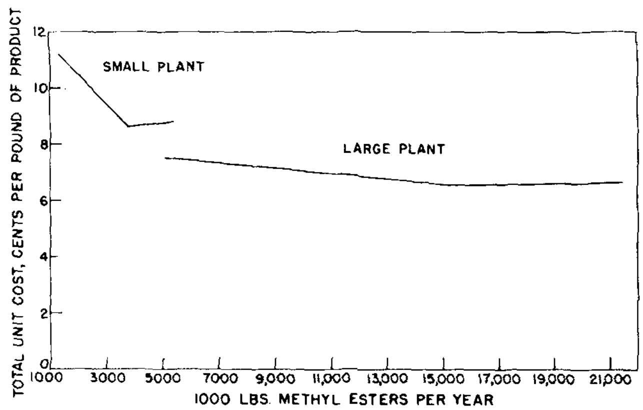

FIG. 2. Manufacturing costs for producing methyl esters from acidulated cottonseed foots.

tions in a hypothetical plant with a capacity of 60,000 lbs. of acidulated foots daily.

The cost of the raw materials, although only 3.4¢ per pound of product and chiefly the cost of foots, is the largest single item of unit cost in producing methyl esters; and, for the higher productions covered by this study, raw materials' cost accounts for more than one-half of total unit manufacturing cost. Surplus cottonseed foots can be economically converted into a low-cost feed additive with improved nutritional and handling properties. The process is already a commercial success.

Acknowledgment

The authors wish to express their appreciation to G. I. Pittman for assistance in preparing the drawings and to Claire L. Weber for preparing the tables.

REFERENCES

1. Anonymous, "Soapstock Yields Methyl Esters," Chem. Eng. News, 37 (34), 38–39 (1959).
2. Aries, R. S., and Newton, R. D., "Chemical Engineering Cost Estimation," McGraw-Hill Book Company Inc., New York, 1955, p. 263.
3. Eaves, P. H., Spadaro, J. J., and Gastrock, E. A., J. Am. Oil Chemists' Soc., *36*, 230–234 (1959).

[Received April 28, 1960]

Analysis of Complex Lipid Mixtures by Thin-Layer Chromatography and Complementary Methods

DONALD C. MALINS, Technological Laboratory, Bureau of Commercial Fisheries, U. S. Fish and Wildlife Service, Seattle, Washington, and
HELMUT K. MANGOLD, University of Minnesota, The Hormel Institute,[1] Austin, Minnesota

THIN-LAYER ADSORPTION chromatography on silicic acid according to Stahl (11) has been used for the resolution of lipid extracts of blood (12), acetylated lipids (3,4), and fats, oils, and waxes (7). The present contribution is concerned with further applications of this technique to lipid separations. In addition, the preparation and some applications of "siliconized chromatoplates" for the fractionation of classes into their constituents by reversed-phase partition chromatography in conjunction with thin-layer chromatography are also described.

Experimental

Preparation of Chromatoplates. Thin layers (250 to 275 μ) of silicic acid on glass (20 x 20 cm.) were prepared according to Stahl (11), using "Silica Gel G"[2] a fine grade (60μ or about 250 mesh) of silica gel containing 1% of plaster of Paris. "Silica Gel G" and the apparatus for its application were purchased from C. Desaga G.m.b.H., Heidelberg, Germany.[3]

Siliconized chromatoplates were obtained by slowly immersing the silicic acid plates at room temperature into a solution of 5% silicone[4] ("Dow Corning 200 fluid," viscosity 10 cs.) in diethyl ether. Plates may be used immediately after evaporation of the solvent.

Solvents and Indicators. Thin layers of silicic acid were developed with mixtures of petroleum ether, B.P. 60–70°C., diethyl ether, and acetic acid.

Separation within classes of lipids on siliconized chromatoplates was achieved with systems of acetonitrile-acetic acid-water or acetic acid-water. After having been sprayed with 0.2% 2′,7′-dichlorofluorescein[5] in ethanol, all lipids on untreated silicic acid films were manifested as a bright yellow-green fluorescence by ultraviolet light.[6] Unsaturated lipids were detected as brown spots on a light yellow background with iodine vapors.

Dichlorofluorescein was found to be unsatisfactory for locating the position of lipids on siliconized chromatoplates because the entire plates fluoresced. The indicators α-cyclodextrin-iodine however revealed monochain saturated lipids as white spots on a purple background (8). Unsaturated lipids were detected, in the usual manner, with iodine vapors alone. The substances were amenable to further fractionation since no evidence was found which suggested that the indicators reacted chemically with the lipids to any marked extent.

Separation of Lipids into Classes. Complex lipid mixtures may be fractionated rapidly into classes of compounds by thin-layer chromatography on silicic acid. Figure 1 demonstrates the different migration rates of a variety of lipids, ranging from hydro-

[1] Supported in part by the U. S. Public Health Service National Institutes of Health Research Grant 5817, and the National Science Foundation.
[2] E. Merck A. G., Darmstadt, Germany.
[3] "Silica Gel G" may be obtained in the U.S.A. from Terra Chemicals Inc., 500 Fifth avenue, New York 36, N. Y., or from C. A. Brinkmann and Company Inc., 115 Cutter Mill road, Great Neck, L. I., N. Y. The later firm is also the U. S. representative of C. Desaga G.m.b.H., Heidelberg, Germany.
[4] Dow Corning Corporation, Midland, Mich.
[5] Eastman Kodak Company, Rochester 3, N. Y.
[6] "Mineralight," Ultra-Violet Products Inc., San Gabriel, Calif.