This is evidenced by the TBA reaction products with epihydrin aldehyde or glyceraldehyde (Fig. 5) and with formic acid (Fig. 6), although the phenomenon has also been observed by Landucci et al. (6,7) in the case of various aldehydes present in gelatin. The mechanism of these reactions does not appear to be understood and requires further investigation.

Shepherd (11), Sinnhuber et al. (14) and Schmidt (9) have shown that certain pyrimidines are capable of forming the same pigment as malonaldehyde on reaction with TBA. The mechanism is thought to involve hydrolysis of the pyrimidine ring to produce an oxyacrolein intermediate (9) which is tautomeric with malonaldehyde and therefore undergoes condensation to produce compound II. Although TBA itself has a pyrimidine structure, it is substituted in the 4 and 6 positions and would therefore be unlikely to give rise to malonaldehyde on hydrolysis (9). No color is formed on exposure of an aqueous acid solution of TBA to sunlight, but if hydrolysis were to occur, the expected product would be malonic acid which would not give the same compound as malonaldehyde in any reaction with TBA.

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Cost of Producing Linoleic Acid from Safflower Oil

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Abstract

Linoleic acid of 97% purity can be made from safflower oil by liquid-liquid extraction at a "cost to make" of about 21 cents a lb. Calculations for the cost estimate were based on pilot-plant investigations. Fixed capital investment for a plant with an annual capacity of 20 million lb has been estimated at approximately $1,800,000. Such a plant could be converted readily to the production of a variety of other fatty acids.

Introduction

LINOLEIC ACID has properties suggesting that it would be a preferred raw material for manufacture of a variety of industrial products such as alkyd resins, plasticizers, coatings, elastomers and dimer acids. However, because relatively pure linoleic acid has been available only as an expensive laboratory chemical, there have been no intensive studies to determine its suitability for use in such applications.

Safflower oil is a logical raw material from which to produce linoleic acid since the oil is readily available and its fatty acids contain more than 70% of linoleic acid. Beal and Brekke (2) describe pilot-plant studies on the production of linoleic acid from safflower oil by liquid-liquid extraction. Their process utilizes a combination of techniques adaptable to commercial production. Industry has shown interest in the process if the production costs are not prohibitive. From a cursory examination, it appears that large-scale production of linoleic acid could be economically feasible.

This paper reports the results of a cost study on the production of linoleic acid from safflower oil by liquid-liquid extraction in a hypothetical plant which has a capacity for producing 20 million lb of linoleic acid of 97% purity annually.

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Process and Equipment

A qualitative flow diagram and a simplified quantitative flowsheet of the process are shown in Figures 1 and 2. The first step in the process is the continuous hydrolysis of safflower oil to convert it to fatty acids. Commercial-grade refined safflower oil used in this hypothetical plant has a composition such that approximately 75% linoleic acid is contained in the fatty acids formed by hydrolysis. No pilot studies were conducted on this phase of the process, but the equipment and general procedure for continuous fat-splitting as described by Barnebey and Brown (1) should be satisfactory. A stainless-clad steel tower, 60 ft high, 2.5 ft in diameter, should have sufficient capacity for hydrolyzing the daily requirement of 96,200 lb of safflower oil. The oil and water for hydrolysis should be deaerated to minimize oxidation before being pumped to the hydrolyzer. It is estimated that a retention time for the oil of 2 to 2.5 hr at a temperature of approximately 500F and that a pressure around 700 psig should approach optimum operating conditions for hydrolysis.

Glycerin formed by splitting the fats is separated from the fatty acid fraction and collected in the sweetwater. The sweetwater, which contains 13–15% glycerin, is concentrated in a vacuum evaporator to yield an 80% crude glycerin concentrate. Although the crude glycerin could be concentrated further and purified by distillation, this operation is not included here.

The fatty acids, 91,872 lb per day, are fractionated in stainless steel Podbielniak twin-centrifugal extractors, with furfural containing 2.5% water as the selective solvent and hexane as the secondary solvent. The procedure for the extraction follows that reported by Beal and Brekke (2). Temperature for extraction is 100F. For every pound of fatty acid fed to the extractors, 15 lb of furfural containing 2.5% water and 3 lb of hexane are required. Total combined feed

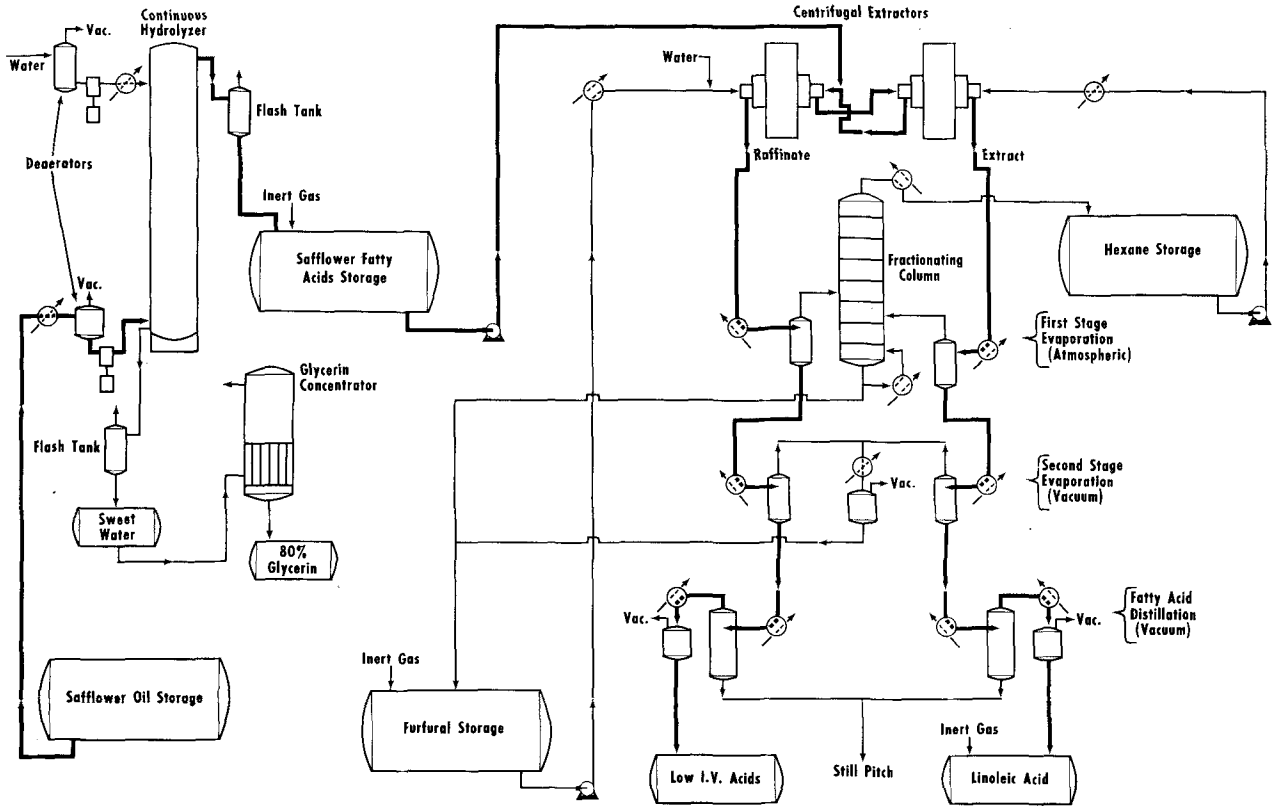

FIG. 1. Qualitative flow diagram—Linoleic acid from safflower oil.

to the Podbielniak extractors is 142 gpm.

After extraction, solvents are recovered from the extract and raffinate either in equipment which is more or less standard for such solvent recovery or in a system of heat exchangers and vacuum flash evaporators, as depicted in the flow diagram. Recovered solvent is returned for reuse in the centrifugal extractors. The solvent-free extract containing the linoleic acid fraction and the solvent-free raffinate containing the more saturated fatty acids are each distilled at 10 mm Hg absolute pressure or less. Distilled linoleic acid should have a color corresponding to Gardner color No. 6; the residue or still pitch, primarily polymers, is discarded. Unhydrolyzed oil contained in the residue from distilling the low iodine value (I.V.) acids could possibly be returned to the fat splitting column for reprocessing but for this cost estimate, such an operation is excluded. Provisions are included to store the crude and refined linoleic acid and low I.V. acids, as well as the furfural, under nitrogen to prevent oxidation of these materials during storage.

Almost all the major equipment including piping and pumps, particularly that for processing and storage of fatty acids, is fabricated of 316 stainless steel or 316 stainless clad. Safflower oil and solvents are stored in steel tanks; the glycerin concentrator and storage tank are fabricated of copper.

For every 100 lb of safflower oil entering the system it is assumed that 69.3 lb of linoleic acid, 97% purity, and 23.2 lb of low I.V. fatty acids (I.V. 78.0) are recovered. This recovery constitutes an overall loss of 1% of the fatty acids present after hydrolysis. In addition, 12.47 lb of 80% glycerin, or 95% of theory, are recovered. Losses of solvents are estimated at 0.05% and 0.2% for furfural and hexane, respectively. Similar solvent losses have been reported by industrial processors whose operations are comparable to those described here (4).

Costs

The fixed capital investment required for a plant producing 66,667 lb daily or 20 million lb annually of 97% linoleic acid is estimated to be $1,820,000. Operations are to be conducted 24 hr per day and 300 days per year. Byproducts recovered daily are 22,318 lb of low I.V. acids and 12,000 lb of 80% glycerin. It is assumed that the plant is operated in conjunction with an already existing plant for processing vegetable oils so that certain facilities in the existing plant can be made available to the new installation. Steam generating facilities are therefore not included in the fixed capital investment for the new plant but a charge for steam of $0.75 per 1,000 lb is included.

The net "cost to make" is estimated to be 21.2 cents per pound of product. Included in this cost are the following items: raw materials, utilities, labor and supervision, maintenance, miscellaneous factory supplies and expenses, fixed charges, charge for working capital, plant overhead, and allowance for by-product credits.

The prices of raw materials required for the process are assumed to be as follows: commercial-grade

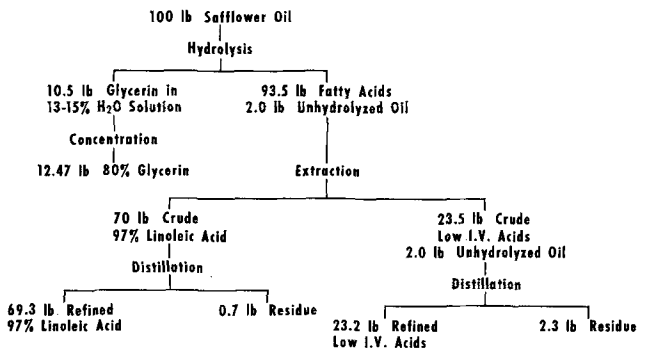

FIG. 2. A simplified quantitative flowsheet for linoleic acid production.

safflower oil, $0.168 per pound; furfural $0.12 per pound; and hexane $0.16 per gallon. The cost of utilities for all operations, except the hydrolysis step, were calculated; the utility requirements for hydrolysis of the oil were obtained through extrapolation of the data reported by Barnebey and Brown (1) for the hydrolysis of other oils. In estimating the necessary labor and supervision, it was assumed that the plant superintendent from the existing installation also will supervise operations in the new plant. Consequently, only one-fourth of the plant superintendent's time is assigned to linoleic acid production. Other items included in the "cost to make" are calculated according to generally accepted estimating practices (5).

Value of the glycerin from the process is estimated at 12.5 cents per pound, an average market price for a similar crude glycerin concentrate. The low I.V. acids which are recovered consist primarily of oleic and palmitic acids. The mixture is estimated to have a value of 15.0 cents a pound. Although fractionation of the byproduct acids was not investigated, such an operation should not be difficult and should be economically attractive. Since 0.18 lb of 80% glycerin and 0.33 lb. of low I.V. acids are recovered per pound of product, the combined credit for these materials is 7.20 cents per pound of 97% linoleic acid.

Discussion and Conclusions

The charge for safflower oil per pound of product represents more than 85% of the gross "cost to make" of linoleic acid. Furthermore, byproduct credit is equal to approximately 25% of the gross "cost to make." The prices of safflower oil and the byproducts vary frequently and these variations would cause corresponding fluctuations in the "cost to make," and selling price of the product. The effect of changes in the price of safflower oil on the "cost to make" of linoleic acid at various prices for low I.V. acids is shown in Figure 3. A change of 1.0 cent per pound in the price of safflower oil alters the "cost to make" by 1.44 cents per pound of linoleic acid. Other factors, such as labor and utilities, constitute only a small percentage of the cost and are more or less constant.

The material of construction for specific items of equipment could have at least a minor effect on the economics of the process. Although in this estimate either stainless-steel or stainless-clad equipment has been suggested for some units, aluminum perhaps might be substituted satisfactorily for such items as crude fatty acid storage tanks and for product and byproduct acid storage tanks. For this estimate, a reduction in delivered equipment costs of $100,000, which is equivalent to $211,000 in fixed capital investment, would permit a reduction in the "cost to make" of 0.11 cent per pound of product. Although such a reduction in the "cost to make" is in itself not substantial, other benefits would also be realized through a reduction in capital outlay and an accompanying decrease in the profit margin required. The equipment required for this process could be adapted readily to other processes, such as the production of linolenic acid from linseed oil (3) and possibly fatty acids from other oils. Because several products could

TABLE I

Fixed Capital Investment for a Plant Producing 20 Million lb of Linoleic Acid (97% Purity) Annually from Safflower Oil.
(Basis: 300 operating days per year, 24 hr per day)

Land and improvements	$ 24,500	
Building 175,000 cu ft	122,500	$147,000
Equipment delivered:		
1 Fat-splitting column, 60 ft high 2.5 ft diam, 725 psig, SS clad	$125,000	
2 Storage tanks, steel, for safflower oil, 80,000 gal	24,000	
1 Storage tank, steel, for water, 5,000 gal	2,300	
1 Flash tank for sweet water, SS clad, 400 gal	1,600	
1 Flash tank for fatty acids, SS clad, 600 gal	2,000	
1 Settling tank for sweet water, SS clad, 2,000 gal	3,500	
1 Settling tank for fatty acids, SS clad, 3,000 gal	4,500	
2 Feed pumps for safflower oil, SS, positive displacement	10,000	
2 Feed pumps for water, steel, positive displacement	7,000	
1 Storage tank for sweet water, copper, 6,000 gal	4,300	
1 Glycerine concentrator, copper, with accessories	18,000	
1 Storage tank for glycerin, copper, 12,000 gal	7,600	
1 Storage tank for fatty acids, SS clad, 40,000 gal	21,000	
2 Podbielniak extractor units, SS	160,000	
5 Pumps for extractors, SS	19,800	
2 Surge tanks, SS clad, 2,000 gal and 10,000 gal	11,500	
6 Separators, cyclone, SS clad	58,000	
2 Vacuum receivers	12,000	
15 Heat exchangers, copper and SS, 25 to 1,400 sq ft	79,200	
1 Distillation unit, copper, for solvent recovery	23,400	
2 Surge tanks, SS clad, 3,000 gal, 5,000 gal	10,100	
2 Surge tanks, steel, 3,000, 6,000 gal	4,600	
1 Dowtherm unit, 1,500,000 BTU/hr	26,000	
2 Pumps, vacuum and accessories	12,600	
14 Pumps, for transfer and miscellaneous use	9,100	
2 Storage tanks for linoleic acid, SS clad, 40,000 gal	44,000	
1 Storage tank for low iodine value acids, SS clad, 30,000 gal	19,000	
2 Storage tanks for solvent, steel, 20,000 gal	12,900	
Equipment delivered		$733,000
Installation, foundations, etc		220,000
Piping, wiring, instruments, etc		286,000
Engineering fees		186,000
Contractors' fees		62,000
Contingencies		186,000
Fixed Capital Investment		$1,820,000

TABLE II

Production Costs for a Plant Producing 20 Million lb of Linoleic Acid (97% Purity) Annually from Safflower Oil.
(Basis: 300 operating days per year, 24 hr per day; 66,667 lb of linoleic acid per day; 22,318 lb of low I.V. acids per day)

Item	Daily cost $/day	Cents/lb of product
Raw Materials:		
Safflower oil, 96,200 lb/day, $0.168/lb	16,161.60	
Furfural, 672 lb/day, 0.12/lb	80.64	
Hexane, 100 gal/day, $0.16/gal	16.00	
Nitrogen, 2,000 ft³/day, $1.30/100 ft³	26.00	
	16,284.24	24.43
Utilities:		
Steam, 700,000 lb/day, $0.75/M	525.00	
Water, 1,200,000 gal/day, $0.075/M	90.00	
Electricity, 5,800 kwh/day, $0.015/kwh	87.00	
Gas, 36,000 ft³/day, $0.25/M	9.00	
	711.00	1.07
Labor and supervision:		
9 operators, $2.50/hr	180.00	
1 helper, $2.25/hr	18.00	
3 foremen, $25.00/day	75.00	
1 laboratory technician	20.00	
1 superintendent, ¼ time, $40/day	10.00	
Overhead	60.60	
	363.60	0.55
Maintenance:		
Equipment 5%/year on $1,673,000	278.83	
Land and building 2%/year on $147,000	9.80	
	288.63	0.43
Miscellaneous factory supplies and expenses:	43.30	0.06
Fixed charges:		
Depreciation:		
Equipment, 10%/year on $1,673,000	557.67	
Building, 3%/year on $122,500	12.25	
Taxes and insurance, 3%/year on $1,820,000	182.00	
	751.92	1.13
Charge on working capital, 5%/year on $1,000,000	183.33	0.27
Plant overhead	303.62	0.45
Gross "cost to make"	18,929.64	28.39
Byproduct credit:		
Low iodine value acids:		
0.33 lb/lb of linoleic acid, $0.15 lb (4.95¢)		
Glycerin, 80% concentration		
0.18 lb/lb of linoleic acid, $0.125 lb (2.25¢)		
Total byproduct credit		7.20
Net "cost to make" cents/lb of linoleic acid		21.19

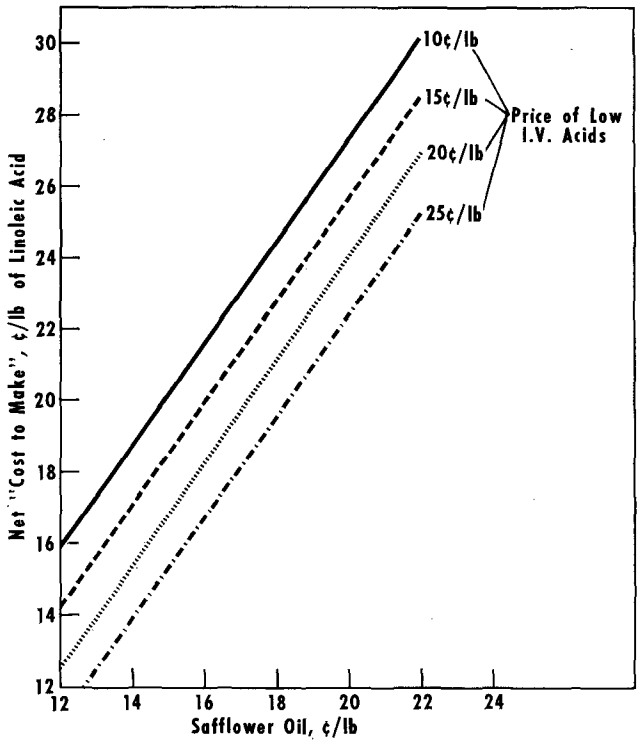

FIG. 3. Effect of changes in price of safflower oil on net "cost to make" of linoleic acid at various prices for low I.V. acids.

be produced in the plant, operations could be adjusted to meet variations in market conditions thereby improving the economics of the individual processes.

Market potential for purified linoleic acid is exceedingly difficult to predict and will be determined to some extent by its selling price. In some applications, such as in plasticizers, substitution of linoleic acid for natural oil may impart improved qualities to a particular product. The use of the acid may possibly be justified under such conditions even though its price may be higher than that of the oil.

For at least one application, an industry source has indicated that linoleic acid at about 40 cents per pound may find a potential market. With a net "cost to make" of 21 cents per pound of 97% linoleic acid, apparently the selling price would be substantially under 40 cents once normal production rates are attained.

Even though linoleic acid must compete in some applications with products now on the market, it would appear that a "cost to make" of 21 cents a pound should create an interest in the product.

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The Synthesis of Tritium Labeled 9, 10-Oleic Acid[1, 2]

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Abstract

Tritium labeled 9,10-oleic acid was prepared from stearolic acid by reduction with tritium gas, in the presence of 5% Palladium on Charcoal catalyst, at room temperature and under partial vacuum. No stearic or elaidic acids were formed. Unreacted stearolic acid was removed by low temperature crystallization from Skellysolve F. The tritium labeled *cis* 9,10-oleic acid was prepared with a specificity of greater than 90% of the activity at the 9 and 10 positions. Specific radioactivity of the oleic acid was 1000 mc of Tritium/g. Tritium labeled stearic acid with a specific activity of 927 mc of Tritium/g was also prepared.

Introduction

EXPOSURE to tritium gas can cause non-specific labeling. The Wilzbach technique (1) is an application of this fact for producing non-specifically labeled compounds. Recently, Dutton and Nystrom (2,3) produced labeled saturated fatty acid esters of high specific activity by their exposure to tritium gas. On the other hand, unsaturated fatty acids were found to preferentially hydrogenate, rather than substitute in the carbon chain, when exposed to tritium gas (4).

In the present study, a method is reported which gave *cis* 9,10-oleic acid, labeled with a high degree of specificity at the double bond. The oleic acid obtained was free from radiochemical impurities, and was obtained in good yield, as well as high specific activity.

Experimental

Methylation. Diazomethane (5) was prepared from "DIAZALD".[4] Esterification was carried on at room temperature for 10 min. A solution of 0.4 g of potassium hydroxide in 10 ml 96% ethanol was poured into a round-bottom flask and 2.0 g "DIAZALD" in 30 ml ether added. If cloudy, more ethanol was added to the mixture. Boiling chips were added, a condenser attached, and the solution warmed at about 50C on a steam bath. The ethereal diazomethane solution was collected in a round-bottom flask that was cooled below −10C in a dry ice—acetone bath. A calcium chloride tube was attached to keep out moisture. The reaction was terminated when the solution lost its yellow color. The solution of diazomethane was transferred to a graduated cylinder fitted with a ground glass stopper and methanol was added to make a 10% methanol in ether solution. Schlenk and Gellerman (6) reported that esterification was slow or incomplete in pure ether solution. Also following the procedure of Schlenk and Gellerman, esterification was

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[4] "DIAZALD" is the trade name for N-methyl-N-nitroso-P-toluenesulfonamide, obtained from Aldrich Chemical Co., Inc.