Production of Linolenic Acid from Linseed Oil[1]

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Linolenic acid of more than 95% purity was produced by liquid-liquid extraction of linseed oil fatty acids with wet furfural and hexane in a Podbielniak centrifugal extractor. The minimum ratio of furfural to linseed acids to obtain this purity was 10 to 1. There was no significant change in product purity for solvent ratios between 10 and 15, operating temperatures from 90° to 110°F., and furfural moisture contents between 1.0 and 2.8%. When the solvent ratio is reduced to 8 or the furfural moisture to 0.2%, purity decreases. Oxidation of linseed acids before extraction also results in decreased separation. An estimate based on pilot-plant data indicates a "cost to make" (excluding administrative and selling expenses, profit, income taxes, and interest on investment) of 18.0 cents per pound of 97% linolenic acid for a process which includes hydrolyzing linseed oil, separating the fatty acids by liquid-liquid extraction, recovering solvents by distillation, and distilling the fatty acid products. Potential uses for linolenic acid are reviewed.

SEPARATION of linoleic acid of more than 95% purity from safflower fatty acids by liquid-liquid extraction was previously reported (2). In a continuation of the studies on separating polyunsaturated fatty acids from vegetable oils, linolenic acid, again more than 95% pure, was made from linseed fatty acids. Liquid-liquid extraction is the most practical commercial process presently available to separate polyunsaturated fatty acids. A cost estimate has been prepared for production of linolenic acid by this method.

An extraction process for fractionating linseed fatty acids using furfural and naphtha as immiscible solvents to obtain high and low iodine value fractions was described by Gloyer (5). Conducted in a vertical packed column, the separation reportedly gave a linolenic acid of 81% purity. For many potential uses a higher purity is desirable or necessary, provided the increased purity is obtainable without substantial increase in cost.

Experimental

Nonbreak linseed oil was hydrolyzed with water, a cation exchange resin, and an emulsifier according to procedure (2). Care was taken during hydrolysis to prevent oxidation of oil and fatty acids by evacuating the reaction vessel and placing its contents under high-purity nitrogen during operations. The linseed fatty acids were dried and filtered after hydrolysis and stored under nitrogen at 34°F. in glass bottles (I.V. of acids 188.7, saponification equivalent 280.0, % F.F.A. 96.8). The undistilled acids were fractionated by liquid-liquid extraction with freshly distilled furfural, adjusted to desired moisture content with distilled water, and with hexane as the immiscible solvents, in a Podbielniak "Double Pup" centrifugal extractor.

Figure 1 is a simplified flow diagram showing the operation of the extraction equipment. Furfural containing a suitable amount of water was heated to 110°F. and pumped into extractor #1. The extract or furfural phase flowing from #1 was pumped at the same temperature into #2 from which it flowed as the extract product. Likewise, the hexane was pumped into #2 at 110°F., then to #1, again at the same temperature, and it flowed from there as the raffinate product. Linseed fatty acids were introduced into the intermediate raffinate stream, were partially and selectively extracted into the furfural phase in #1, and transferred to #2 and thus became distributed throughout the system. In each extractor the counterflowing phases were mixed and separated 18 times for a total of 36 mechanical stages for the 2 extractors.

An important aspect in satisfactorily operating the extractors was spraying the cooling water onto the centrifugal rotors which turned at speeds of 4000 to 5000 rpm. Without this cooling the temperature of the liquids within the rotors gradually increased until complete miscibility of the raffinate and extract phases occurred and separation was no longer possible. In our tests, temperature of the water used to cool the rotors was adjusted so that the average of the temperatures of the extract and raffinate phases flowing from the unit extractor was the same as the feed temperature. This average was termed the operating temperature.

The extract phase, containing largely furfural and fatty acids of high iodine value, and the raffinate phase, containing principally hexane and fatty acids of lower iodine value, were separately freed of solvent by vacuum distillation. The two fatty acid fractions were then vacuum-distilled and stored at 0°C. until analyzed. Distilled acids from the extract were yellow in color (Gardner color 6), whereas those from the raffinate were nearly water white.

Iodine value determinations for the distilled extract and raffinate fatty acids were made by the 1-hr. Wijs method. Generally, iodine values for the linseed fatty acid feed and the raffinate fatty acids were in agreement with iodine values calculated from fatty acid composition as determined by gas-liquid chromatography. However iodine values determined for ex-

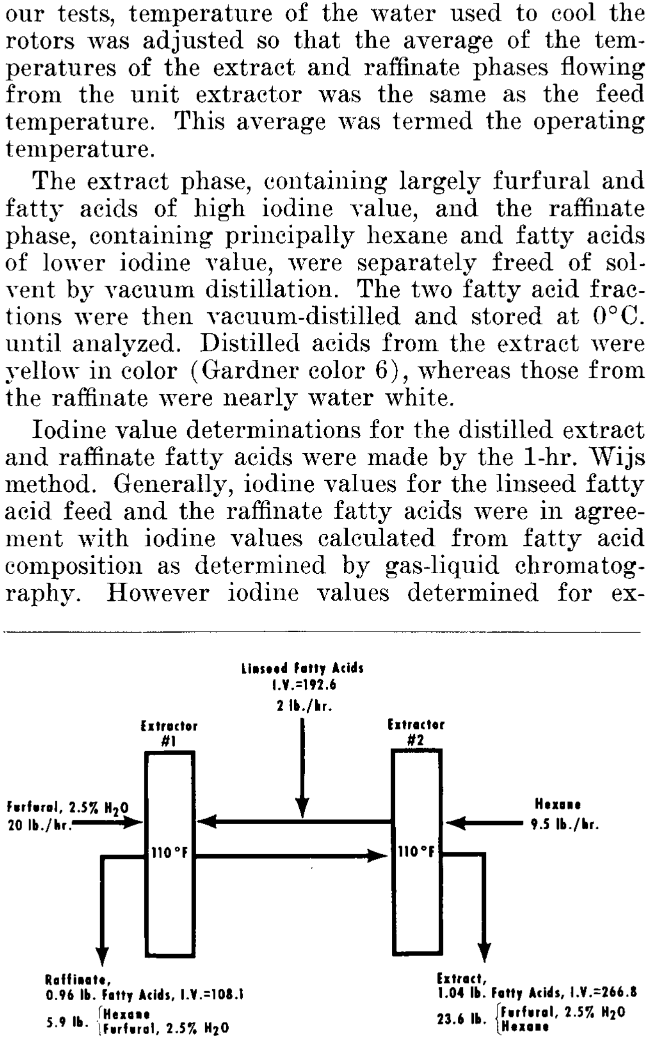

FIG. 1. Simplified flowsheet for fractionation of linseed fatty acids.

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tract fatty acids were lower than values calculated from composition. The difference could not be ascribed to conjugated triene present.

To determine composition by gas-liquid chromatography, fatty acid samples were converted to methyl esters with diazomethane. Moisture content of furfural used in the extraction tests was determined by the Karl Fischer method.

During operation of the double extractor, samples of the raffinate and extract streams were occasionally taken for short equal intervals. Neutral ethanol was added to the samples which were titrated with 1 *N* aqueous sodium hydroxide to a phenolphthalein end point to determine the amount of fatty acids in the two product streams.

Results and Discussion

Data in Table I summarize results of tests made using various solvent ratios, operating temperatures, and furfural moisture levels. The purity of linolenic acid obtained when the extractor was operated with solvent ratios of 15 or 10 was not appreciably different, but at a solvent ratio of 8, purity was considerably lower. In the range tested, operating temperature had little effect on product purity, but moisture content of the furfural had a perceptible effect on linolenic acid purity. Operation at 120°F. caused flooding.

TABLE I

Relation of Operating Conditions to Linolenic Acid Content of Extract Product

Solvent feed ratio, wt. furfural to wt. linseed acids	Operating temperature, °F.	H_2O in furfural, %	Extract, %	Linolenic acid in extract fatty acid, %
Solvent ratio				
15	110	1.1	42	97.8
10	110	2.6	48	97.4
8	110	2.5	34	91.8
Temperature				
10	110	2.6	48	97.4
10	100	2.6	27	96.9
10	90	2.2	31	96.4
Water content of furfural				
10	110	0.2	26	93.7
10	110	1.0	22	95.8
10	110	2.6	48	97.4

Linolenic acid purity was not affected by yield, up to the 52% extract level, using feed acids containing 52% linolenic acid. Above these levels, the purity decreased as expected. This same general observation was made in separating linoleic acid from safflower fatty acids (2).

Laboratory tests were conducted to find the relationship between number of equilibrium countercurrent extraction stages and purity of linolenic acid in the extract product. A system of furfural (containing 2.5% water), hexane, and linseed oil fatty acids was used for the tests conducted at 100°F. with 6 separatory funnels immersed in a constant temperature water bath, an adaptation of Alders' method (1). Solvents and solutes in the funnels were agitated for 5 min. by air-driven stirrers until equilibrium between phases at the bath temperature was reached. The phases were then allowed to separate for 5 min., and the lower layer was transferred to the succeeding funnel following Alders' extraction pattern whereby 12 countercurrent equilibrium stages are attained. After enough transfers were made to reach steady state conditions, the extract and raffinate products were desolventized, distilled at 1 mm. absolute pressure, and analyzed for iodine value. With 6 extraction stages the iodine value of extract fatty acids was 242.3 and with 12 stages, 259.8. By graphical comparison with iodine values of other samples of known linolenic acid content, the product from 6 extraction stages was estimated to contain 83% linolenic acid and from 12 stages, 94% linolenic acid. Thus more than 12 equilibrium extraction stages are required to produce linolenic acid of over 95% purity using a furfural-hexane system.

TABLE II

Composition of Distilled Feed, Raffinate, and Extract Fatty Acids
Basis: 10:1 Solvent Ratio; 48% Extract

Acid	Feed, %	Raffinate, %	Extract, %
Linolenic	52.4	9.7	97.4
Linoleic	16.5	25.3	2.6
Oleic	22.9	47.6	......
Stearic	3.5	7.4	......
Palmitic	4.7	10.1	......
Iodine value, calculated	193.6	114.9	271.0
Iodine value, determined	192.6	116.0	266.8

Table II gives the composition of feed, extract, and raffinate fatty acids obtained from a test made at a 10 to 1 solvent ratio. The percentage extract from this test was 48%, and the linolenic acid content of the raffinate acids would have been lower at 52% extract.

Oxidation of the linseed fatty acid feed has a significant effect on fractionation. A batch of fatty acids inadvertently exposed to air at a temperature about 140°F. became visibly darker in color and gave an extract containing 92% linolenic acid. Another batch under substantially the same conditions of operation, but not exposed to oxidation, gave 97.5% linolenic acid. The difference is not surprising since furfural is selective for polar oxidation compounds as well as for unsaturated ones.

Maximum combined feed rates to the unit extractor, important from an operating cost standpoint, were not extensively investigated. Feed rates of furfural and of linseed fatty acids were held constant, and the relative amounts of fatty acids recovered as raffinate and extract were controlled by the hexane feed rate. Reduction in hexane rate results in a larger proportion of the fatty acids dissolving in the extract (furfural) phase. At the same time, the specific gravity of the raffinate phase increases as the feed rate of the low gravity hexane decreases. The specific gravity of the extract phase decreases because there are more fatty acids in that phase. Thus, decreasing the hexane rate to obtain a larger proportion of extract fatty acids results in a less specific gravity difference between phases and in greater difficulty of separation. Feed rates given in Table III are nearly the maximum which can be used in the centrifugal extractor

TABLE III

Typical Feed Rates to Extractor[a]

Solvent ratio	Feed rates, lb./hr.		
Furfural/fatty acids	Furfural	Linseed acids	Hexane (to give 50% extract)
15	25	1.7	9.0
10	20	2.0	9.5
8	20	2.5	5.0

[a] Operating temperature—110°F.

and still obtain 52% extract fatty acids without encountering incomplete phase separation, termed flooding. When the linseed fatty acid feed contains 52% linolenic acid, as in the present case, optimum separation for maximum yield is at 52% extract.

Cost Estimate

Based on operating conditions shown in the simplified flow diagram (Figure 1), a preliminary cost estimate was made for a plant producing 10 million pounds of linolenic acid (97% purity) annually from linseed oil. It is assumed that operations are conducted 300 days per year, 24 hr. per day, and when linseed oil with a linolenic acid content of 52% (fatty acid basis) is processed the yield of distilled linolenic acid is 48.5 lb. of 97% material from 100 lb. of linseed oil. Allowance is made for appropriate distillation losses. Operations in the process include continuous hydrolysis of oil, liquid-liquid extraction of fatty acids, removal of solvent from fatty acid fractions, and purification of fatty acid fractions by vacuum distillation. Linolenic acid and by-product low iodine value acids are stored under nitrogen to minimize oxidation. In the extraction step 10 parts furfural, containing 2.5% water, and 4.75 parts hexane are used per 1 part of fatty acid. It is assumed that the feed acids contained 98.0% free fatty acids. The 2.0% of unhydrolyzed material would be contained in the residue from the fatty acid distillation and could be recycled although this is not assumed in this estimate.

Fixed capital investment, shown in Table IV, is estimated to be approximately $1,300,000. This figure does not include equipment for glycerin recovery or steam generating facilities. A cost for steam however is included as part of the production cost. The "cost to make" reported in Table V is estimated to be approximately 18.0¢ per lb. of 97% linolenic acid including a combined by-product credit for low iodine value acids and glycerin of 16.0¢ per lb. of 97% linolenic acid. Allowance for losses of raw materials in the process are as follows: fatty acids, 1%; furfural, 0.05%; and hexane, 0.2%. These amounts compare favorably with those reportedly obtained in similar industrial operations. This "cost to make" does not include administrative and selling expenses, profit, interest on investment, or income taxes.

TABLE IV

Estimated Fixed Capital Investment for Linolenic Acid Plant
(Annual capacity 10,000,000 pounds of 97% pure product from linseed oil. Basis: 300 operating days per year, 24 hours per day)

Land and improvements	$ 25,000	
Building, 142,000 cu. ft.	106,500	
		$ 131,500
Equipment delivered:		
Fat splitting column, stainless steel	125.000	
Pumps for linseed oil feed and water to splitting column	5,700	
Processing tanks for fat splitting operation	6,500	
Extraction system complete with pumps	131,600	
Stripping column, stainless steel	30,000	
Heat exchangers and condensers	63,000	
Vacuum receivers and entrainment separators.	50,000	
Vacuum pumps	7,000	
Miscellaneous pumps	11,200	
Dowtherm unit	20,000	
Linseed oil storage tanks, steel	18,000	
Fatty acid storage tanks, aluminum-lined	22,000	
Surge tanks, stainless steel	10,000	
Solvent storage tanks, steel	22,500	
Tanks for raffinate and extract, stainless steel	14,000	
Linolenic acid storage tank, aluminum-lined	13,000	
By-product fatty acid storage tank, aluminum-lined	12,000	
		561,500
Installation of equipment		140,400
Piping, wiring, and instrumentation		175,500
Engineering fees, contractor fees, contingencies		307,100
Total fixed capital investment		$1,316,000

TABLE V

Estimated Production Costs for Linolenic Acid Plant
(Annual capacity 10,000,000 pounds of 97% pure product from linseed oil. Basis: 300 operating days per year, 24 hours per day)

Item	Daily cost	Cents/lb.
Raw materials:		
Linseed oil—68,728 lb./day at $0.14/lb.	$ 9,621,92	28.87
Furfural—322 lb./day at $0.13/lb.	41.86	0.12
Hexane—111 gal./day at $0.16/gal.	17.76	0.03
Nitrogen—2,500 cu. ft./day at $1.30/100 cu. ft.	32.50	0.10
Utilities:		
Steam—115,000 lb./day at $0.75/M	86.23	0.26
Electricity—2,960 kwh./day at $0.015/kwh	44.40	0.13
Water—485,000 gal./day at $0.075/M	36.38	0.11
Gas—50,000 cu. ft. at $0.25/M	7.50	0.02
Maintenance:		
Equipment—5%/yr. on $1,184,500	197.42	0.59
Building—2%/yr. on $131,500	8.77	0.02
Miscellaneous factory supplies and expenses	22.91	0.10
Labor and supervision	335.57	1.00
Fixed charges:		
Depreciation—		
Equipment—10%/yr. on $1,184,500	394.83	1.18
Building—5%/yr. on $106,900	17.75	0.05
Taxes and insurance—3%/yr. on $1,316,000	131.60	0.39
Charge on work'g capital—5%/yr. on $375,000	62.50	0.19
Plant overhead	270.88	0.81
Total gross "cost to make"	$11,330,78	34.0
By-product credit:		
Low iodine value acids—0.92 lb. at $0.14/lb.		
Glycerin—0.20 lb. at $0.16/lb.		16.0
Total net "cost to make," cents/lb.		18.0

Potential Uses

The volume of linseed oil used in coatings has declined in recent years. The investigations reported here were undertaken as part of a program to develop new outlets for linseed oil. Possible industrial uses for linolenic acid are given in Table VI, although biochemical applications suggested in the literature are not included. Generally, the listed potentials, which are largely undeveloped, depend on high reactivity of the acid or high functionality of its derivatives.

In protective coatings, linolenic acid imparts fast dry and superior gloss; on the other hand, it tends to yellow (9). It should be particularly useful however in dark-colored, high-gloss enamels where yellowing is not objectionable. Saturated monomeric cyclic fatty acids made from linolenic acid have a pour point of −40°C., and esters of these acids, a substantially lower pour point, suggesting their use as low temperature lubricants (3). In flotation-separation of iron ore magnetite, as well as other oxide ores, the collecting capacity of fatty acids increases with their degree

TABLE VI

Potential Uses for Linolenic Acid

Protective coatings (for rapid drying and high gloss)	(9)
Low pour point cyclic acids	(3)
Flotation of ores (mangetite, Fe_3O_4)	(10)
Liquid and gel soaps (lubricants and greases)	(16)
Metallic drier soaps	(16)
Polyfunctional Diels-Alder adducts (wetting agents)	(11)
Antiozonant-plasticizer for rubber and plastics	(12)
Vinyl ether coatings	
Corrosion inhibitor (hexadecylamine salt)	(4)
Polyfunctional epoxides (acid acceptor-plasticizer for vinyl chloride plastics; stabilizer for chlorinated solvents)	(15)
Coating ingredient for solid rocket propellents	(8)
Lauric acid by Varrentrapps reaction	(14)
Ingredient for ointments	(13)
Insect attractment	(7)
Ingredient of plant growth stimulators	(6)

of unsaturation (10), making linolenic acid a possible flotation agent. Linolenic-rich acids are reportedly used for making liquid and gel soaps and metallic drier soaps (16).

Up to 2% of high molecular weight polymeric acids which may be prepared by thermal polymerization of linolenic acid are added to a road-making asphalt composition to improve its weather resistance. These polybasic acids act as wetting agents for the rock aggregate and asphalt (11). The polymeric acids also have potential value in the preparation of polyurethane coatings, resins, and rigid foams. One report suggests esters of linolenic acid might be used as antiozonant-plasticizers for rubber products (12). Linolenate esters probably act as ozone acceptors to delay rubber becoming brittle.

Linolenyl alcohol prepared from linolenic acid might be useful in the preparation of vinyl ether-type coatings to give improved alkali resistance. The hexadecylamine salt of linolenic acid is reported to be an outstanding corrosion inhibitor for steel even in acidic-aqueous solutions (4).

Polymeric acids prepared from linolenic or linoleic acids are among the preferred ingredients of a polyamide coating to restrict the burning of solid rocket propellents (8). Lauric acid may be prepared from linolenic acid by the Varrentrapps reaction (14). As an ingredient of an ointment, ethyl linolenate is said to stimulate wound healing and scar tissue in cutaneous lesions (13). Linolenic acid also has merit as an insect bait attractant for fir weevils and as a component of plant growth stimulators (6,7). Epoxidized linolenate esters can be expected to be superior plasticizer-stabilizezrs for vinyl chloride resins although complete epoxidation of linolenic ester produces only a small amount of triepoxy acid because of ring opening and polymerization during the reaction (15). Epoxy groups act as scavengers for hydrogen chloride formed when the resin breaks down. Epoxidized fatty acid esters having a high epoxy content can also be used as acid-accepting stabilizers for chlorinated solvents.

These potential applications do not necessarily constitute an exhaustive list, and others should materialize when high purity linolenic acid becomes available.

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Preparation, Characterization and Evaluation of Mono- and Diesters of Carboxystearic Acid[1]

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Differences in the reactivity of the terminal and branched carboxyl groups of carboxystearic acid, prepared by carboxylation of oleic acid with carbon monoxide, have been utilized in preparing monoesters. Monoesters of both types have been prepared, those in which the ester group is terminal and those in which the ester group is a branched substituent on the chain. Diesters of carboxystearic acid have also been prepared.

Physical, chemical, and spectral characteristics of the products have been determined. In addition, the viscosity, viscosity index, pour point, and compatibility as plasticizers for PVC have also been studied.

All the monoesters studied are incompatible with PVC, but dimethyl, diethyl, and dipropyl carboxystearate, as well as carbomethoxyoctadecyl acetate (from oleyl alcohol), are efficient, low temperature plasticizers at the 35% level. Di-*n*-butyl carboxystearate also has an exceptionally high viscosity index (169) and a low pour point (−54°C.).

Each of the three types of esters described has a characteristic infrared absorption spectrum in the carbonyl region.

IN OUR WORK on the carboxylation of oleic acid and other unsaturated fatty acids and esters (1), it soon became apparent that the introduced branched carboxyl group is different in its reactivity from the terminal one. Esterification of the branched carboxyl is much slower than that of the terminal group, and

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