ultraviolet and infrared spectra; and to Mrs. C. E. McGrew for microanalyses.

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Linoleic Acid from Safflower Oil by Liquid-Liquid Extraction

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SEPARATION of mixed fatty acids according to their degree of unsaturation is accomplished by numerous methods. Three of the methods are used commercially, namely, low-temperature crystallization, urea-complex formation, and liquid-liquid extraction. The first is used to separate saturated from unsaturated acids; the second and third, for the treatment of lubricating oils. The third, from a cost standpoint, appears particularly suitable in separating linoleic acid from mixed fatty acids derived from safflower oil. Furthermore the efficiency of liquid-liquid extraction has already been shown on other materials, and the techniques and equipment needed to conduct the separation or purification have been developed.

Linoleic acid of high purity, if it were available in quantity, has several uses that are potentially important. Because of its ability to impart film hardness without appreciable film yellowing, linoleic acid appears to be suitable particularly for alkyd resin manufacture. According to Moore (8), the hardness of alkyd resin films after six weeks of aging is proportional to the polyunsaturated acid content of the fatty acids used in making the resin even though drying time of the alkyds appears to be decreased only slightly when unsaturation is above 70%. In the production of dibasic, "dimer," acids by the thermal polymerization of fatty acids from drying and semidrying oils, the data of Goebel (5, 6) indicate that a high linoleic acid content in the original fatty acids is important in obtaining a high ratio of dimeric to trimeric acids. The molecular weight of polyester or polyamide condensation polymers made with these acids is directly related to this ratio. Therefore a high linoleic acid content of the original acids is important to obtaining polymers having high tensile strength and good elastomer properties. Kadesch (7) reviewed other uses for the dimer acids. Recently Teeter *et al.* (10) described a method for making a new type of difunctional fatty acid derivative by a Diels-Alder reaction between alkali-conjugated linoleic acid and a dienophile. These materials have potential uses for making plasticizers, coatings, elastomers, fibers, and other items of commercial interest.

Liquid-liquid extraction of mixed fatty acids to obtain separations based on iodine value differences may be performed with a number of solvent systems. Both Freeman (3) and Gloyer (4) conducted work on the separation of mixed fatty acids, using furfural and a hydrocarbon solvent; however they reported no results with safflower fatty acids. From preliminary laboratory studies and from practical considerations, the system furfural-water-hexane-fatty acids was selected for pilot-plant investigations. The present tests were conducted in a stainless-steel, Podbielniak, centrifugal extractor, "double-pup" model. Some operating characteristics of the "pup" model have been described by Barson and Beyer (2).

Equipment, Materials, and Procedure

Figure 1 is a simplified flow diagram, showing the general method of operating the extraction system in the experiments reported. The furfural used in the extractor was freshly distilled under vacuum before use and was protected with nitrogen. The solvent was used as long as the color was not darker than a light straw-yellow. Moisture content of the furfural was determined by the Karl Fischer method and was adjusted to the desired level, indicated later, by the addition of distilled water. The hexane used in the tests was a commercial extraction grade.

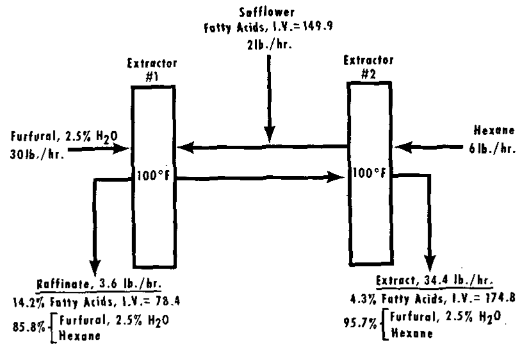

FIG. 1. Fractionation of fatty acids by liquid-liquid extraction—simplified flow diagram.

Fatty acids were hydrolyzed from nonbreak safflower oil by the method of Sutton and Moore (9) using water, a cation exchange resin in the hydrogen form (Dowex 50×4, 200–400 mesh), and an emulsifier (Petrosul No. 742) in the proportions: 75 lb. of oil. 80 lb. of water, 60 g. of emulsifier, 3 lb. of resin. The reactants were heated to 240°F. in a stainless-steel pressure vessel and were agitated until the free fatty acid content reached a constant value. They were then cooled, a small amount of sulphuric acid was added

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as a de-emulsifier, and the water and resin were separated from the oil phase. The resin, together with fresh water and emulsifier, was then added back to the oil phase, and the reaction was continued. After the third such treatment a free fatty acid content of 98.5% was reached. In some cases undistilled acids were used in the liquid-liquid extraction tests; otherwise the acids were first distilled at 1–3 mm. of mercury absolute pressure.

The solvents and solute were pumped to the centrifugal extractors as shown in Figure 1. The temperatures of the feed streams were controlled by pumping them through heat exchangers, countercurrent to heating or cooling water circulated from a constant temperature bath. It was not possible to control the temperature of both streams flowing from an extractor because of heat build-up caused by friction of mechanical seals and of fluid flow within the rotors. It was possible to control the temperature of the exit stream having the largest flow (the extract phase) by spraying conditioned water on the extractor rotor. To conduct a test the unit was placed in operation at the desired feed rates and temperatures, and after a 2-hr. period of operation at steady conditions the extract product containing the high-iodine value fatty acids and the raffinate product containing the low-iodine value acids were collected and weighed for 3 half-hour periods.

Samples of the products for each period were stored under refrigeration and were later desolventized in the laboratory by vacuum evaporation in a glass round-bottom flask placed in a heating mantle. The fatty acid products were then analyzed and in many cases a portion was distilled prior to the analysis, particularly if the fractionation were conducted with undistilled feed acids. The feed acids, the raffinate, and the extract-product acids were analyzed for iodine value by the official Wijs method and for linoleic and linolenic acid contents by the 45-min. alkali-isomerization method of Brice *et al.* (2), using a Beckman Model DU spectrophotometer for the absorbance measurements. To calibrate results two samples of natural methyl linoleate from a source generally acknowledged to supply material of high purity were isomerized in our alkali-isomerization apparatus and analyzed for linoleate content by the spectrophotometric method. These samples were also analyzed for linoleate content by using gas chromatography. The purity indicated by gas chromatography was in good agreement with observed iodine values. Based on the known impurities in the methyl linoleate samples, as indicated by gas chromatography and by iodine value, the results obtained by the isomerization-spectrophotometric method were found to be low and a factor of 1.031 was therefore applied to correct them. The low results were probably caused by normal variations in construction or operation of the isomerization equipment and of the spectrophotometer.

Results and Discussion

To determine optimum fractionating conditions and the maximum degree of separation of linoleic acid obtainable, experiments were conducted to evaluate several operating variables. Two criteria were used to assess the results of these studies: a) fractionation efficiency—defined as the ratio of actual iodine value difference obtained between the extract and raffinate fatty acids to the maximum iodine value difference theoretically obtainable; and b) the characteristics of the product, *i.e.*, iodine value and linoleic acid content. The maximum difference theoretically obtainable for iodine value with an ideal fractionation process for a feed mixture of given composition varies with the size of the raffinate fraction, as shown in Figure 2.

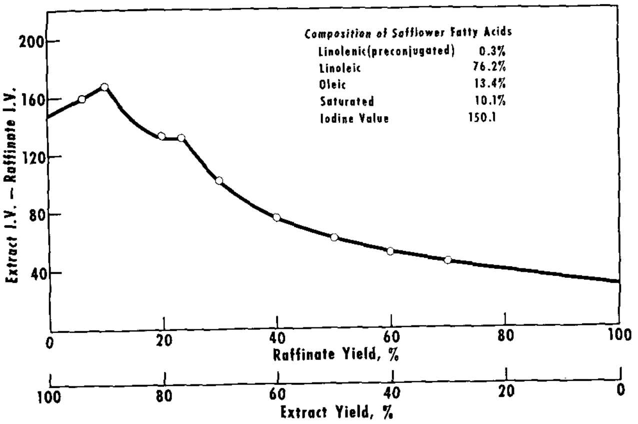

FIG. 2. Maximum iodine value difference obtainable by ideal fractionation.

In this ideal separation only linolenic acid is removed when the extract fraction yield is less than 0.3% of the feed. As the extract yield is increased, the fraction contains, in addition to the linolenic acid, increasing amounts of linoleic acid, followed in order by oleic and finally by the saturated acids. With an extract fraction constituting 76.5% of the feed, for example, this fraction contains only linoleic and linolenic acids while all of the oleic and saturated acids are in the raffinate fraction. A number of points for the curve in Figure 2 were calculated by assuming various raffinate yields, calculating the iodine value of each fraction and the iodine value difference.

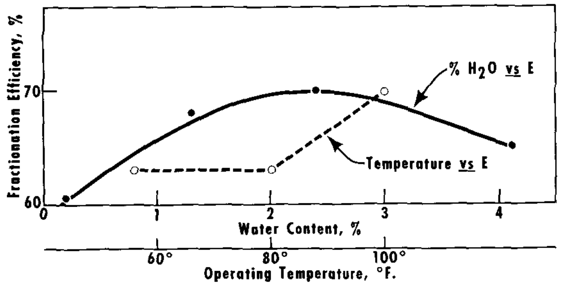

FIG. 3. Effect of operating temperature and of water content of furfural on fractionation efficiency.

Figure 3 shows the effect of operating temperature on the fractionation efficiency as calculated from the iodine value difference. Although the true temperature of the liquids within the extractor cannot be measured, the temperature of the extract stream from the rotors is considered to be nearest to the operating temperature since it has a much larger flow rate than the raffinate stream. An operating temperature of 56°F. was obtained by cooling the feed streams by refrigeration and by spraying refrigerated brine on the rotors, and a temperature of 100°F. was attained by preheating all feed streams to 100°F. and spraying water at about 80°F. on the rotors to control heat build-up resulting from friction. As seen from Figure 3, some advantage is gained by operating at 100°F.

At temperatures above 100°F. flooding or near flooding was encountered; this was indicated at 110°F. and above by decreased fractionation and by inability usually to obtain clear product-streams from one or both rotors.

Another factor affecting the fractionation efficiency of the process is the water content of the feed furfural. As this is increased, fatty acid solubility would be expected to decrease and the selectivity of the solvent to increase. The data presented in Figure 3 indicate a maximum selectivity at about 2 to 3% water, and beyond this level the fractionation efficiency declines. Data not given here show that as the water content of the furfural is increased, less hexane is required to produce a given raffinate yield, which indicates that increasing the water in the furfural decreases the fatty acid solubility. Fractionation efficiency also varies between different batches of fatty acids. Efficiencies as high as 85% were obtained by using a different fatty acid feed stock. Fractionation efficiency was observed to be substantially constant for all extract yields up to 76.5%, at constant temperature, furfural moisture content, etc. At higher yields, although the linoleic acid content of the extract fatty acids decreased, fractionation efficiency was actually somewhat higher in the few cases where extract yields above 76.5% were obtained.

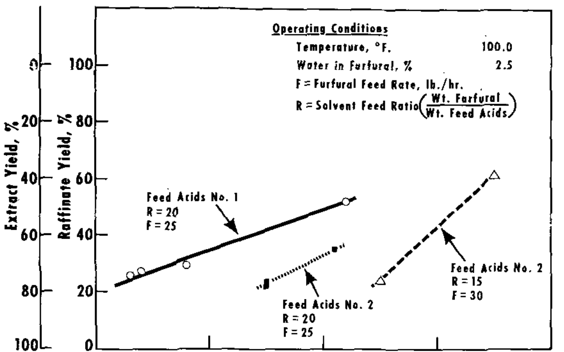

FIG. 4. Effect of hexane feed-rate on extract and raffinate yields.

The effect of hexane feed rate on raffinate and extract yields is shown in Figure 4. Of particular interest is the fact that one fatty acid feed stock required more hexane to give a certain yield than did the other, which demonstrates that the hexane requirements can be determined accurately only from plant operations. Higher fractionation efficiency was obtained with the feed acids that required the higher hexane feed rate.

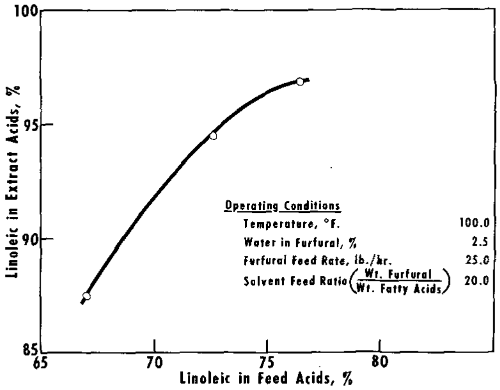

FIG. 5. Relation of linoleic acid content of feed fatty acids and of extract-product fatty acids.

TABLE I

Effect of Extraction Conditions on Linoleic Acid Content of Extract Fatty Acids

Solvent ratio	Solvent feed-rate	Extract yield	Extract fatty acids[a, b]	
			Iodine value	Linoleic acid
	lb./hr.	%		%
20	25	71	176.2	97.1
15	25	56	177.0	97.0
20	30	68	176.7	96.6
15	30	42	174.0	93.7
15	30	73	174.8	94.7

[a] Feed acids (undistilled): iodine value 149.9; % linoleic acid 76.2.
[b] Product acids distilled before analysis except example No. 4.

As shown in Figure 5, the process described produces an extract product approximately 20 percentage points richer in linoleic acid than the feed fatty acids over the range covered by our experiments. Table I gives the linoleic acid content and the yield of extract products from pilot-plant tests conducted under several conditions of solvent ratio and solvent feed-rate, using feed acids containing 76% linoleic acid. These feed acids were not distilled prior to fractionation, and they contained 98.5% free fatty acids. The nonfatty acid portion was principally recovered in the raffinate product. The extract-product acids were distilled under vacuum before being analyzed. The principal improvement gained was in color since the linoleic acid content increased only about 1% by distillation. When furfural feed rates of 35 lb. per hr. or higher were used, flooding was encountered; and 30-lb.-per-hr. is considered the practical maximum feed rate. At this rate the total combined feed rates of the furfural, hexane, and fatty acids is about 280 cc. per min. Since the centrifugal extractor is rated at 500 cc. per min., the rate for the present system represents 56% of the maximum rated capacity. With a solvent ratio of 10, an extract yield exceeding about 50% was impossible to obtain because of flooding. The ideal yield to recover the maximum amount of linoleic acid of highest purity is the same as the linoleic acid content of the feed acids. A solvent ratio of 15 was found to be about the minimum that could be used to give this optimum yield of linoleic acid. The linoleic acid purity in the extract product was found to be substantially the same at any extract yield up to the optimum, but beyond this point, *i.e.*, at extract yields greater than the linoleic acid content of the feed, the purity of the linoleic fraction decreased as expected.

A complete cost estimate for conducting the separation of linoleic acid from safflower fatty acids has not been prepared. By analogy with other similar extraction processes, the cost of concentrating linoleic acid on a commercial scale is expected to be reasonable.

Summary

Tests conducted on a pilot-plant scale have demonstrated that linoleic acid of about 95% purity may be produced from safflower fatty acids containing about 75% linoleic acid, by a liquid-liquid extraction process. Furfural was employed as the selective solvent, hexane as a secondary solvent, and the fractionation was made in a Podbielniak "double-pup" centrifugal extractor. Best results were obtained when the proc-

Acknowledgments

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Erratum

IN THE PAPER, "Determination of the Extent of Oxidation of Fats" (J. Am. Oil Chemists' Soc., *34*, 606, 1957), the conversion factor reported for 1 millimol of peroxide to millimols of aldehyde by thermal decomposition of peroxide in rapeseed oil has been found to be too high. By using vacuum and helium instead of pyrogallol-washed nitrogen, which apparently was not oxygen-free, during the thermal decomposition the conversion factor 0.3 was obtained.

The equation given for the calculation of the oxidation degree will be

aldehyde value + 3 × the peroxide value

The values for the effect of bleaching and of total refining in reducing the content of oxidation products will become 20–40% and 45%, respectively.

• *Letter to the Editor*

SOME TIME AGO I discovered a method for detecting coconut oil in the presence of other fats and oils. I have not seen the reaction mentioned in the literature as a rapid qualitative test for coconut, and I would like to give the details to your Society for comment.

The test consists simply of shaking vigorously a small quantity of the fat or oil with an equal quantity of alcoholic caustic potash. In the presence of coconut oil as little as 5% distinct "fruity" odor results.

The method has been extensively tested in this laboratory, and we have found that in all cases the results have been conclusive.

J. GASH
Provincial Traders Pty. Ltd.
Brisbane, Australia

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ABSTRACTS .... R. A. REINERS, Editor

ABSTRACTORS: Lenore Petschaft Africk, R. R. Allen, S. S. Chang, Sini'tiro Kawamura, F. A. Kummerow, E. G. Perkins, and Dorothy M. Rathmann

• Fats and Oils

BRANCHED-CHAIN FATTY ACIDS. II. ALKALI FUSION OF SOME BRANCHED-CHAIN FATTY ACIDS. R. Lukes and J. Hofman (Czechoslov. akad. věd, Prague). *Collection Czechoslov. Chem. Communs.* **24**, 744-54 (1959). (*C. A.* **53**, 11202)

INCREASE OF ACTIVITY OF HYDROGENATION CATALYST FOR MAKING HARD ISOÖLEIC ACID. G. I. Kolesnidov (Inst. Food Ind., Krasnodar). *Izvest. Vysshikh Ucheb. Zavedenii, Pishchevaya Tekhnol.* **1958**(5), 48–52. With the same type of catalyst, development of isoölates in hydrogenation of oil is greater the greater the activity of the catalyst. A nickel-copper combination catalyst induced much greater isoölates development than did catalyst derived from nickel formate, even when the catalytic activities were equal. (*C. A.* **53**, 10805)

ACTIVITY OF BINARY HYDROGENATION CATALYSTS. B. N. Tyutyunnikov and I. Z. Koshel (Polytech. Inst., Kharky). *Masloboino-Zhirovaya Prom.* **25**(2), 14-5 (1959). The productivity of nickel as a catalyst in nickel-cobalt mixture was found to vary with the nickel content of the mixture. At 25% level it was appreciably lower, and at 50% and above slightly higher than the productivity of nickel alone. The low catalytic activity of cobalt was not improved by the addition of copper. (*C. A.* **53**, 10805)

NICKEL CATALYST FOR THE HYDROGENATION OF OILS. II. D. D. Nanavati and J. S. Aggarwal (Natl. Chem. Lab., Poona). *J. Proc. Oil Technologists' Assoc. India, Kanpur* **12**, 83–91 (1958). Nickel formate catalyst, when supported on neutral carriers of the type, Hyflo-Supercel, decolorizing carbon, or silica gel (*catalyst; carrier* ratio of 2:1) was found to be preferable for increasing the rate of hydrogenation of oils to unsupported catalyst. These neutral supports were superior to acid carriers of the type of fuller's earth or kieselguhr both as regards consistency of hydrogenated product and selectivity of hydrogenation. Supercel was the most satisfactory of the tested supports. The basic carbonate of nickel was also tried and produced satisfactory hydrogenated oils except that they required more time for hydrogenation as compared to the corresponding formate catalyst. (*C. A.* **53**, 10805)

SYNTHESIS OF SOME OCTENOIC ACIDS. J. A. Knight and J. H. Diamond (School of Chem. and the Eng. Exper. Station, Georgia Inst. of Techn.). *J. Org. Chem.* **24**, 400–03 (1959). The preparation and properties of *trans*-4- and -6- and of *cis*-3-, -4-, and -6-octenoic acids are reported in this paper. The freviously reported isomers, *trans*-3- and *cis*-2-octenoic acids, are also reported in this paper. The *cis* acids were prepared by the catalytic semihydrogenation of the corresponding octynoic acids. The *trans* acids were obtained either directly or indirectly starting with a *trans* alkenoic acid obtained by a Knoevenagel condensation. Physical properties, including infrared spectra, were determined for all of the acids and most of the intermediates. The infrared spectra of the *trans* compounds showed strong absorption in the region of 10.2–10.35 microns. None of the *cis* compounds showed absorption in this region.