

[54] **PROCESS FOR THE EXTRACTION OF GLYCERIDE OILS BY SELECTIVE SOLVENTS**

2,573,900 11/1951 Freeman 260/428.5
 3,376,326 4/1968 Artman et al. 260/410.7

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[73] Assignee: **Lever Brothers Company**, New York, N.Y.[22] Filed: **Oct. 15, 1973**[21] Appl. No.: **406,748**[57] **ABSTRACT**

Process for the recovery from edible oils containing at least 50% linoleic acid combined as glycerides, of a fraction enriched in combined linoleic acid, in which the oil is contacted with an organic polar solvent immiscible therewith, the liquid phases formed being separated and the enriched fraction recovered from the polar solvent. Dialkyl lower amides are preferred polar solvents and sunflower, safflower and cottonseed oil are preferred oils.

[30] **Foreign Application Priority Data**

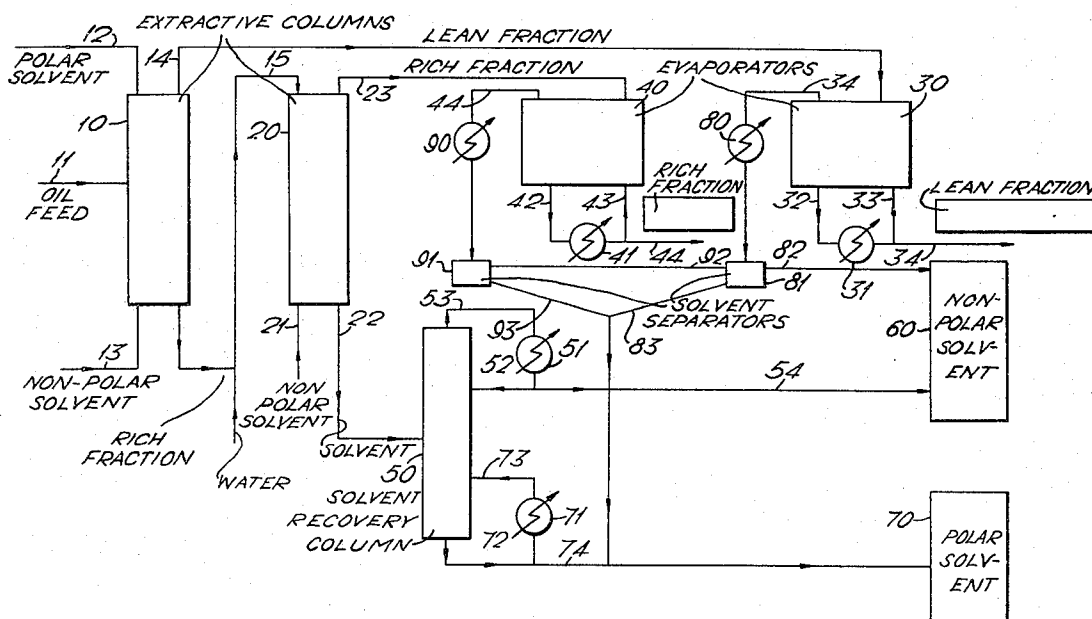
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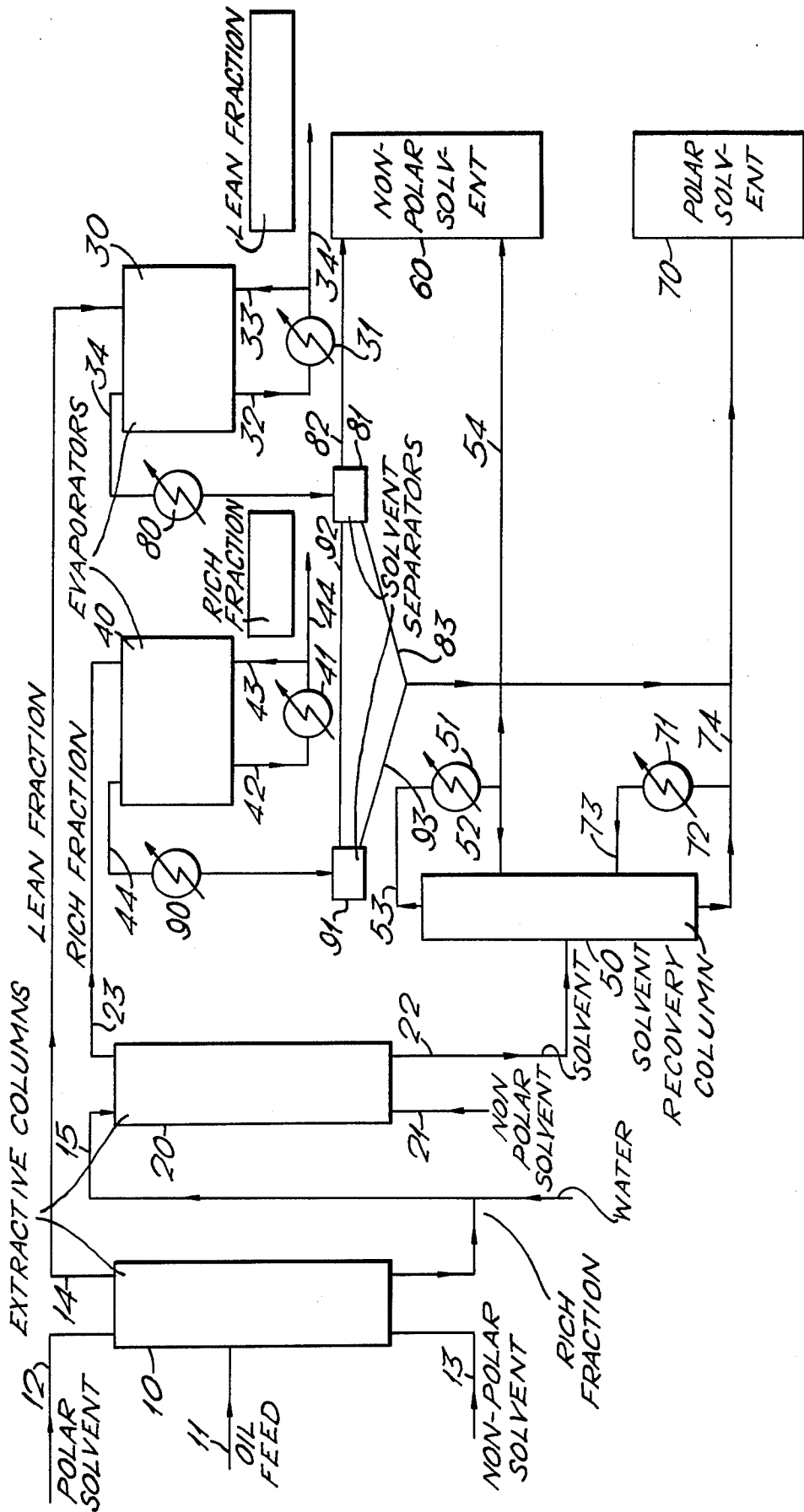
[52] U.S. Cl. **260/428.5**[51] Int. Cl. **C11b 7/00**

[58] Field of Search 260/428.5

[56] **References Cited****UNITED STATES PATENTS**

2,200,391 5/1940 Freeman 260/412.4

11 Claims, 1 Drawing Figure



PROCESS FOR THE EXTRACTION OF GLYCERIDE OILS BY SELECTIVE SOLVENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the extraction of glyceride oils by selective solvents and particularly to the application of such treatment to sunflower or similar oils for the purpose of enhancing their content of combined polyunsaturated fatty acids. Sunflower and safflower oils are widely used as ingredients in the manufacture of margarine and other emulsion food spreads. They also find wide application for other edible products, for example in frying oils.

It is widely accepted to be beneficial to include in the diet a fat intake containing a high proportion in its combined form of linoleic acid, a so-called essential fatty acid. This contains two ethylenically unsaturated bonds, whereas linolenic acid contains three double bonds, and is less desirable nutritionally and more susceptible to deterioration in storage. Sunflower oil often contains 60-70% linoleic acid, while safflower oil usually contains 70-80%. The remaining fatty acid content of these oils is shared principally between C₁₆ and C₁₈ saturated and monounsaturated fatty acids. Such oils should be distinguished from drying oils which are characterized by even more unsaturation, with a high content of linolenic acid and other unsaturated fatty acids in combined form which contain three or more double bonds, which oils are often inedible.

The invention is based upon the observation that the glycerides of the highly unsaturated fatty acids commonly found in natural fats, i.e. linoleic and linolenic, are more soluble in polar solvents than those of the principal saturated and mono-unsaturated acids commonly occurring with them, i.e. of 16 and 18 carbon atoms in chain length. Preferably those oils are selected whose linolenic acid content is low, since this is a less desirable component, prone to atmospheric oxidation with the development of off-flavours and less desirable nutritionally. In addition to sunflower and safflower oils, maize and cottonseed oils are particularly preferred, soyabean oil less so but nevertheless within the scope of the invention.

2. The Prior Art

Liquid-liquid extraction has been extensively developed by the petroleum industry for the separation of saturated and unsaturated, especially aromatic hydrocarbons. Sulphur dioxide has been used e.g. in the Edeleanu process since about 1909 and furfural since 1935. Phenols, at first used in batchwise extractions were later used in conjunction with propane. Dimethylformamide was first suggested in 1942 but was not then given serious consideration.

All these processes have been considered for refining lubricating oils or for removing impurities from fuel oils. With the development of catalytic re-forming more sophisticated techniques were necessary to remove aromatics in a useable form. Multi-stage contactors were introduced with light hydrocarbon for the stripping section. New polar solvents included diethylene glycol in the Udex process (British Pat. No. 739,200 Dow), sulpholane (British Pat. No. 980,973 Shell), N-methyl pyrrolidone in the Arosolv and Lurgi processes (Belgian Pat. No. 613,126), dimethylformamide (British Pat. No. 1,104,513), N-formylmorpholine and tetraethylene glycol. The application of

liquid-liquid extraction techniques to the treatment of edible fats and oils of the glyceride type has also been the subject of extensive investigation in the art. In U.S. Pat. No. 2,200,390 the extraction of both edible and non-edible ie drying glyceride oils with a wide range of furan compounds is described. Freeman also examined a much wider range of solvents in U.S. Pat. No. 2,200,391, including the unsubstituted alkyl amides from formamide to butyramide.

DETAILED DESCRIPTION OF THE INVENTION

The present invention proposes to increase the combined polyunsaturated fatty acid content of edible oils, particularly in glycerides of linoleic acid, of oils generally whose combined linoleic acid content is at least 50% by weight, by a process comprising contacting the oil with a suitable solvent system comprising an N-substituted amide solvent at a temperature at which two liquid phases are formed, one consisting of a fraction of the oil rich in combined linoleic acid which is dissolved in the polar solvent, and the other a lean fraction comprising the residual oil, separating the two fractions and removing the polar solvent from the rich fraction to recover an oil fraction rich in combined linoleic acid.

The invention is based upon the observation that the glycerides of the highly unsaturated fatty acids commonly found in natural fats, ie linoleic and linolenic, are more soluble in polar solvents than those of the principal saturated and mono-unsaturated acids commonly occurring with them, ie of 16 and 18 carbon atoms in chain length. Preferably those oils are selected whose linolenic acid content is low, since this is a less desirable component, prone to atmospheric oxidation with the development of off-flavours and less desirable nutritionally. In addition to sunflower and safflower oils, maize and cottonseed oils are particularly preferred, soyabean oil less so but nevertheless within the scope of the invention.

By means of the invention a fat fraction may be obtained suitable for use in foods in which sunflower and safflower oils are conventionally used but which contains as much as 10 or 20% additional polyunsaturated fatty acid in combined form, or even more. Suitable products include edible oils for salad frying oils, salad creams, margarine and low fat emulsion-type spreads and shortening.

Organic polar solvents suitable for use in the invention include amides containing two lower alkyl groups, preferably each containing up to 4 carbon atoms, attached to the nitrogen atom of the amide group, particularly N-lower alkyl pyrrolidones, particularly the methyl derivative and dimethyl formamide. It may be necessary with the former solvent to realise an adequate degree of immiscibility by the addition thereto of a minor amount of water or a lower alkylene diol having up to 4 carbon atoms, eg ethylene glycol, generally less than 15% of the latter and less than 2% water, according to the extraction temperature.

Preferably the oil is itself dissolved in a non-polar solvent with which the extracting solvent is immiscible, thereby increasing the density differences between the phases and thus facilitating their separation from one another and the selectivity extraction for polar relative to non-polar glycerides, ie for polyunsaturated to less highly unsaturated glycerides. Suitable oil solvents include aliphatic hydrocarbons which can conveniently

be handled in liquid form, ie saturated aliphatic hydrocarbons from 3 to 10 carbon atoms in chain length, although the upper limit is not critical. Suitable hydrocarbon solvents include propane, butane, hexane and other light fractions, particularly a heptane fraction with a boiling range (95%) 96°-98°C petroleum. These hydrocarbon solvents are essentially non-polar and are customarily adopted in the extraction of the oils with which the invention is concerned from their plant seeds following the conventional dressing operation, to increase the yield of oil.

The extraction using a polar solvent may be carried out continuously or batchwise. A particularly effective method of carrying out continuous extraction is by the method of countercurrent liquid-liquid extraction. In this method the immiscible liquids flow in opposite directions through a column or columns fitted internally with means providing maximum contact between the two. The columns may be packed with random packing, e.g. Raschig rings, or fitted with spaced plates in a manner well known in the art for the purpose of affording maximum liquid-liquid contact. Alternative mixer-settler apparatus may be used instead.

In use, the polar and non-polar solvents - or reflux oil if no non-polar solvent is used - are fed into opposite ends of the column and the oil to be extracted from an intermediate position.

The choice of solvents is determined among other things by the requirement to provide substantial immiscibility and they should also be inert both towards the oil being extracted and to one another where two solvent systems are utilised. Their properties in this respect may be modified according to the temperature at which they are used. Organic polar solvents selected for use in the invention must be substantially immiscible with the oil and/or its solution in a non-polar solvent. The degree of immiscibility may however be materially affected by the temperature at which the extraction is carried out. Further, by appropriate choice of temperature the degree of selectivity exercised in the extraction process according to the invention, between unsaturated glycerides and others in the oil being extracted may be substantially modified by temperature change.

Where a non-polar solvent is used it should not be in excess of the amount of polar solvent used to extract the polyunsaturated fatty acid glycerides; for example, 4 to 40 parts of polar solvent per part of hydrocarbon, or other non-polar solvent, and in particular from 10 to 30 parts of polar solvent per part has been found satisfactory. The relative amounts of the immiscible liquids should be selected bearing in mind the partition coefficients determining the distribution between the two solutes concerned, ie the glycerides of different degrees of unsaturation. In order to obtain the correct rates the degree of immiscibility should also be taken into account and preliminary experiments may be necessary to ascertain the best proportions to adopt. However, a linoleate partition coefficient greater than 50 requires an excess of polar solvent so great as to be uneconomic and an upper limit of about 20 is generally imposed.

The recovery of glycerides from the polar solvent used in the extraction is preferably effected by diluting with water and extracting with non-polar solvent followed if necessary by distillation to recover the solvents in a form suitable for recycling.

Preferably the extraction procedure is carried out at temperatures between -20° and +50°C. The lower temperatures may be necessary where a volatile hydrocarbon is used as a solvent, but in general preferably the extraction is carried out at moderately elevated temperatures within the above range. The process may be carried out under atmospheric or superatmospheric pressures, the latter being necessary to avoid the use of excessively low temperatures where highly volatile solvents are used.

The oils are preferably bleached and neutralised before treatment in the process of the invention.

The recovered enriched glycerides may be used for the manufacture of margarine and other edible emulsion spreads where a high content of polyunsaturated fatty acids in combined form is required. A minor proportion of semi-solid or hard fat, eg lauric fats and particularly coconut oil, palm oil or hardened fats, for example hardened soyabean oil and cottonseed oil or stearine fractions thereof, are preferably included in the fat composition for these purposes.

Apparatus suitable for carrying out a continuous extraction process for the separation of saturated and unsaturated fractions (these being used as comparative terms) of a glyceride oil in accordance with the invention comprises a pair of packed liquid-liquid extraction columns arranged in series and a fractionation column connected to the base of the second column for recovering the polar solvent, in a sufficiently purified form to be recycled to the top of the first column.

A recovery unit comprising for example a multiple effect evaporator, separator and distillation equipment is provided for each extraction column, to remove any hydrocarbon solvent from the separated oil fractions which are collected in the effluent from the tops of the extraction columns.

In use, the oil, for example sunflower oil, is admitted into the first column. Where a non-polar solvent is used, for example a light hydrocarbon solvent, this is admitted to the base of both columns countercurrent to the heavy polar solvent admitted to the top. Each solvent may be previously saturated with the other. A small proportion of water may be admitted with the base effluent passed from the first column to the top of the second column to facilitate extraction therein.

The saturated and unsaturated fractions of the sunflower oil are distributed between the hydrocarbon and polar solvents in the first column. Effluent from the tops of the columns are treated in the recovery units to remove any light solvent, consisting largely of the hydrocarbon, for example by evaporation. Polar solvent may be separated, for example by water washing, from the more saturated fraction of the oil.

The more unsaturated fraction, extracted from the oil in the first column by the polar solvent, is re-extracted therefrom in the second column by the hydrocarbon solvent if this is used, and similarly recovered in the second recovery unit, in which the effluent from the top of the second column is treated.

DESCRIPTION OF THE DRAWING

Referring now to the drawing, an oil feed supply, for example of sunflower oil, enters the system via line 11 and is introduced into extractive distillation column 10 between its ends, a polar solvent being introduced above and a non-polar solvent below the point of entry of the oil via lines 12 and 13, preferably at entry points

adjacent the ends of the column, which may be packed randomly or otherwise furnished with plates, trays or the like to promote intimate contact in the column between the liquids.

From column 10 two liquid streams are withdrawn, the lighter stream via upper line 14, conveying a lean fraction of the oil, dissolved in the non-polar solvent to a recovery system comprising multiple-effect evapora-

hexane (3). On standing, the epiphase is less polar upper layer, was separated and weighed and the polar solvent in it extracted by repeated water washing, carried out by shaking as before. The oil remaining was also weighed and the miscibility of solvent in the oil layer and quantity of oil extracted were calculated by difference.

Further particulars appear in Table I.

TABLE I

Solvent	Temp. °C	Solvent Oil ratio	Composition by weight % Oil extracted in hypo- phase	In Oil		In Extract.
				Before Extract	% linoleate After Extract	
(1)	27	2 : 1	19	66.3	64.6	70.7
	45	2 : 1	40	66.3	65.4	67.8
(2)	20	20 : 1	66	60.5	54.7	63.5
	20	10 : 1	41	60.5	57.7	64.6
	20	5 : 1	19	60.5	54.7	85.2
(3)	25	8 : 1	36	67.5	64.3	73.1
	35	5 : 1	31		62.9	73.1
	52	5 : 1	49		64.2	70.9

tor 30, and the heavier stream of a rich fraction of the oil in polar solvent, via line 15 to the upper second extraction column 20, together with a minor proportion of water.

Into column 20, similarly equipped internally, a supply of non-polar solvent is also admitted via line 21, countercurrent to the stream of rich fraction, to strip this from the polar solvent. Duly stripped, this solvent is discharged from the lower extremity of column 22 via line 22, into a solvent recovery column 50 through a feed point between the ends thereof. The column 50 is fitted with reflux condenser means 51, supply and return lines therefor 52 and 53 and discharge line 54 via which non-polar solvent is delivered to storage means 60. Column heater 71 is similarly furnished with corresponding lines 72, 73, and 74, the latter supplying recovered polar solvent to storage means 70.

From the upper extremity of column 20 the rich fraction, now dissolved in non-polar solvent, is delivered through line 23 to a recovery system comprising multiple-effect evaporator 40.

The evaporators 30 and 40 are correspondingly equipped with heating means 31 and 41, delivery and return lines therefor 32, 33 and 42, 43 and discharge lines 34, 44 from which the separated lean and rich oil fractions are collected.

The volatile products of the evaporators 30 and 40, consisting largely of solvent, are delivered via lines 34, 44 and condensers 80, 90 to separators 81, 91, from which separated non-polar solvent is discharged to storage 60 via lines 82, 92 and polar solvent via lines 83, 93 to storage 70.

EXAMPLE 1

Samples of sunflowerseed oil were thoroughly agitated in predetermined weight ratios for 5 minutes at various temperatures with dimethylformamide (1), a mixture of 9 parts w/w N-methyl pyrrolidone per part of ethylene glycol (2) or 1,6-bispyrrolidone-2-yl-1-

Although all three solvents were effective, a substantial proportion remained in the oil layer and increase in temperature aggravated this tendency until the three phases became completely miscible. Complete miscibility was similarly produced when the ethylene glycol:N-methyl pyrrolidone ratio was increased to 1:19.

In a series of comparative tests, acetonitrile, tetraethylene glycol, N-methyl pyrrolidone with equal parts ethylene glycol and furfural with 2% water, were all examined and all found to be inferior as polar solvents, extracting less than 2% of the oil, with only slight segregation of linoleic acid.

EXAMPLE 2

In this Example a series of tests on the solvents used in Example 1 in accordance with the invention was carried out as described in that Example, using however heptane as a non-polar solvent to raise the density difference between the phases and improve selectivity.

The non-polar phase was weighed and washed with water as before. The washed residue (epiphase) was weighed in order to determine the miscibility, the second solvent was removed by evaporation in order to determine the quantity of oil remaining in the epiphase and to provide a sample for fatty acid analysis. From the distribution of fatty acids, obtained by chromatographic analysis of the phases, a "partition coefficient," calculated on the basis of the distribution of combined fatty acids themselves, was then determined, representing the concentration of linoleic acid as triglycerides in the epiphase divided by that in the hypophase. The factor β in Table 2 is the ratio of partition coefficients for linoleic acid and the remaining acids and therefore indicates the degree of enrichment, relative to polyunsaturated fatty acid content, effected by the extraction. A minimum β value of 1.4 was regarded as providing effective separation.

Further particulars of the tests and results also appear in Table II.

TABLE II

Test	Temp. °C	Oil	Components wt. %		Linoleic Acid Content wt. %		β	Oil into hypophase wt. %
			Solvent DMF	Heptane	Oil	Hypophase		
1	27	8.3	83.3	8.3	66.3	69.5	1.4	50
2	20	8.6	84.0 NMP/ H ₂ O	7.3	65.4	73.4	1.7	31

TABLE II - Continued

Test	Temp. °C	Oil	Components wt. %		Linoleic Acid Content wt. %		β	Oil into hypophase wt. %
			Solvent DMF	Heptane	Oil	Hypophase		
3	20	6.2	84.4	9.4	62.0	71.1	1.7	22

DMF - Dimethylformamide
NMP/H₂O - N-methyl pyrrolidone-water (49:1)

EXAMPLE 3

A continuous liquid-liquid extraction of sunflower oil using dimethylformamide and heptane was carried out on sunflowerseed oil at 20°C in a 10-stage mixer settler of the Wall type (AERE/CEIR 1730, Harwell 1955), in the modified form described by Ellis and Gibbon (Proceedings, Symposium Institute Chem. Eng., 24-26 April 1963). The oil, containing 65.4 wt % linoleic acid was fed at a rate of 3 g/hr. to the epiphase leaving stage 5, while dimethylformamide and heptane, each previously saturated with the other, were fed to stage 10 and stage 1 at rates of 225 and 8.7 g/hr.

Equilibrium was reached in 2 hours, when the composition of the effluents became constant; the heavy solvent effluent contained 21% oil having a linoleic acid content of 84.7%, while the remainder of the oil in the light solvent contained 55.1% linoleic acid.

Upon raising the oil flow rate to 5.3 g/hr. the heavy solvent effluent was found to contain 28.5% of the oil, with a linoleic acid content of 81.9%, the remainder of the oil in the light solvent containing 56.8% linoleic acid.

Substantially higher oil rates were found to induce homogeneity between the phases.

EXAMPLE 4

A continuous liquid-liquid extraction of sunflowerseed oil using N-methyl pyrrolidone and ethyl glycol in a 9:1 w/w mixture was carried out at 35°C in a mixer settler apparatus with 12 stages. The oil containing 58.1 wt % combined linoleic acid, was fed at a rate of 46 g/hr to the epiphase leaving stage 8, the solvent mixture was fed at about 600 g/hr to stage 1, and reflux was provided by a previously enriched safflowerseed oil containing 80.4 wt % combined linoleic acid which was fed to stage 12 at 33 g/hr.

Equilibrium was reached in 7 hours, when the heavy phase contained 9.5 wt % of oil having a combined linoleic acid content of 76.8 wt %, while the light phase contained 69 wt % of oil of 50.6 wt % combined linoleic acid content. The yield was 64%.

This example was repeated to obtain an enrichment greater than that of the reflux. For this purpose similar conditions were used, except that an enriched safflowerseed oil reflux containing 77 wt % combined linoleic acid was used and the safflowerseed oil feed was admitted at 30 g/hr to the epiphase leaving stage 6. The heavy effluent then contained 5.6 wt % of oil having a combined linoleic acid content of 79.9 wt %, represent-

ing a lower yield of about 9%, and the light effluent contained 68 wt % of oil containing 54 wt % combined linoleic acid.

Better yields, associated with lower enrichment could be obtained by advancing the feed point eg to stage 7.

What is claimed is:

1. Process for increasing the combined polyunsaturated fatty acid content of edible oils having a combined linoleic acid content of at least 50% by weight, comprising contacting the oil with a suitable solvent system comprising an N-substituted amide solvent selected from the group consisting of dimethyl formamide, N-lower alkyl pyrrolidone, and 1,6-bispyrrolidon-2-yl-,hexane at a temperature at which two liquid phases are formed, one consisting of a fraction of the oil rich in combined linoleic acid which is dissolved in the polar solvent, and the other a lean fraction comprising the residual oil, separating the two fractions and removing the polar solvent from the rich fraction to recover an oil fraction rich in combined linoleic acid.

2. Process according to claim 1 in which the polar solvent comprises dimethylformamide.

3. Process according to claim 1 in which the polar solvent comprises an N-lower alkyl pyrrolidone.

4. Process according to claim 3 in which the polar solvent comprises N-methyl pyrrolidone.

5. A process according to claim 1 in which the polar solvent includes either a minor amount of water or a lower alkylene glycol containing up to 4 carbon atoms in an amount sufficient to render said polar solvent immiscible with said oil.

6. Process according to claim 1 in which the oil comprises safflowerseed oil, sunflowerseed oil or cottonseed oil.

7. Process according to claim 1 in which the oil is contacted at a temperature from -20° to 50°C.

8. Process according to claim 1 in which the said solvent system includes a non-polar organic solvent.

9. Process according to claim 8 in which the non-polar solvent comprises a paraffin with from 3 to 10 carbon atoms.

10. Process according to claim 9 in which the non-polar solvent comprises a light petroleum with a 95% boiling range from 96° to 98°C.

11. Process according to claim 8 in which the solvent system comprises from 20 to 30 parts by weight of polar solvent per part of non-polar solvent.

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