

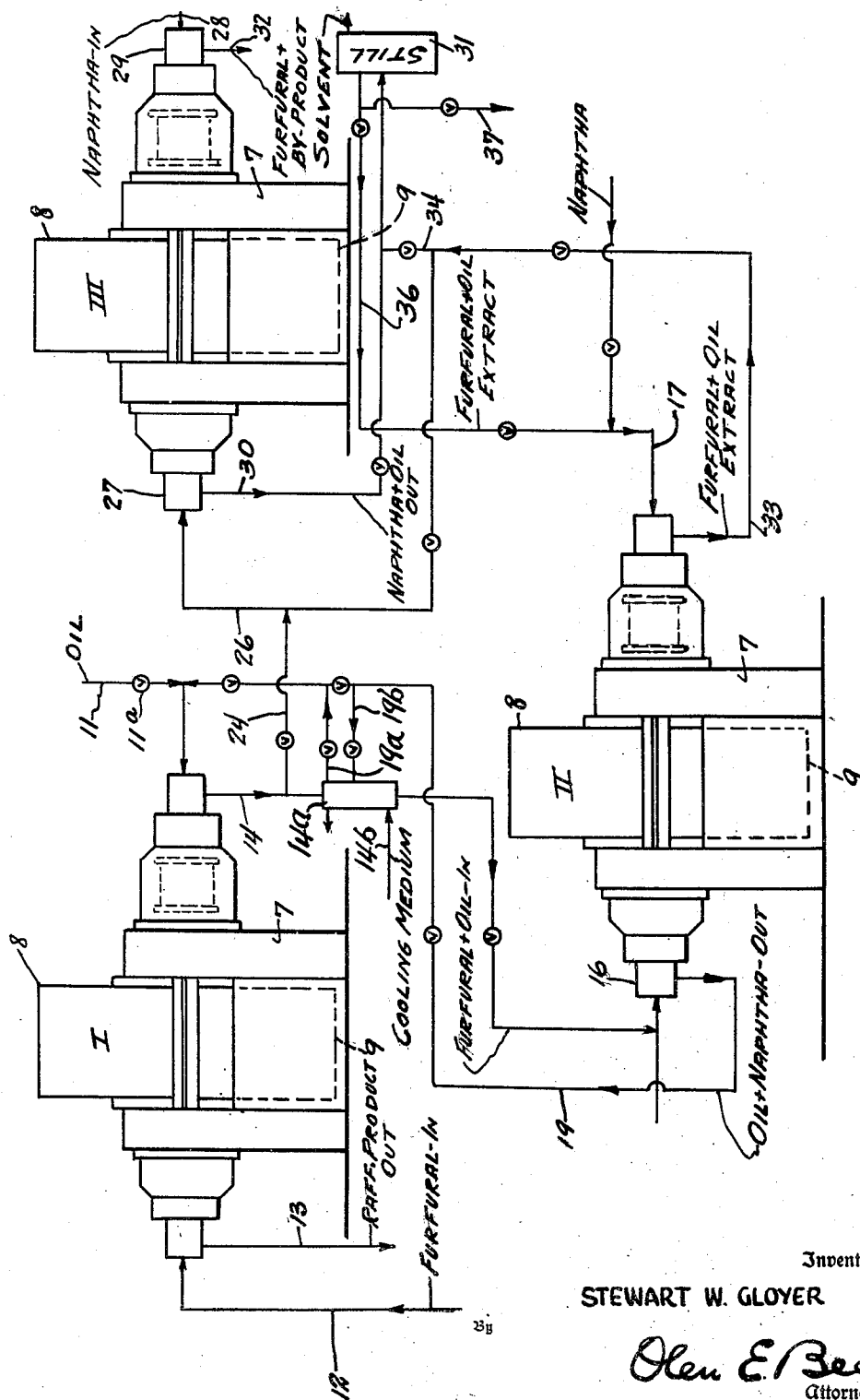
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PROCESS OF LIQUID-LIQUID FRACTIONATION OF GLYCERIDE OILS

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PROCESS OF LIQUID-LIQUID FRACTIONATION OF GLYCERIDE OILS

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The present invention relates to a process of fractionating glyceride oils and it has particular relation to a process of fractionating glyceride oils by liquid-liquid extraction with a system of one and preferably two solvents one of which is but partially miscible with the oils and the other of which (if employed) is but partially miscible with the first solvent.

One object of the invention is to provide a process of fractionating glyceride oils which can be conducted concurrently and which is effective to obtain fractionation of large volumes of oil with minimum occupation of space and apparatus.

A second object of the invention is to provide a process of fractionating glyceride oils by liquid-liquid extraction in which the hold-up of oil and solvent in the apparatus is reduced to a minimum.

These and other objects of the invention will be apparent from consideration of the following specification and the appended claims.

The drawing in the case is a diagrammatic view illustrating in a simplified manner a convenient embodiment of apparatus, as well as the flow of the liquids in the apparatus, which may be employed in the practice of the invention.

It has heretofore been observed that the common glyceride oils such as soybean oil, linseed oil, cottonseed oil, peanut oil and the like were composed of complex mixtures of many components. The main components, however, included glycerides of fatty acids which differed primarily by reason of the degree of unsaturation in the hydrocarbon portion of the fatty acid radicals. For example, these fatty acid radicals might include a single double bond, two double bonds or three double bonds. In some instances the double bonds might be conjugate with respect to each other, thus imparting a special degree of activity and rapid drying characteristics to the oil containing them. The fatty acid radicals might, for example, be those of stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid and many others. Usually, these acids were complexly mixed in the glyceride molecules. Glycerides containing large amounts of unsaturated or highly unsaturated fatty acid radicals especially useful for their drying properties and enjoyed extensive use in the paint and varnish industry. The relatively saturated glycerides were particularly useful in the preparation of food oils and fats.

It has heretofore been proposed selectively to extract out the more highly unsaturated glyc-

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erides from the more saturated glycerides to obtain portions respectively of high merit for the paint industry and the food industry by intimately contacting the oils with certain polar solvents but partially miscible with the oil, such as furfural or ethyl or methyl aceto acetate. Processes of this type have been disclosed in patents such as Freeman Patents 2,200,390 and 2,200,391. It has also been proposed to separate a concentrate of vitamins from vitaminiferous oils such as fish liver oils by similar technique.

For efficient operation in such process, it has been proposed to subject the oil and the selective solvent to countercurrent flow in elongated columns whereby to obtain continuous operation with a high degree of efficiency in the fractionation. Such apparatus requires relatively tall columns, which if the output desired is to be large, must also be of considerable diameter. Such apparatus is obviously rather expensive to construct and occupies considerable space. Large volumes of both the oil and the solvent medium required in the operation are obviously required to fill the apparatus. This, therefore, necessitates large stocks of oil and solvent and in event of shutdown, occasionally considerable expense in the operation of emptying the apparatus and obtaining the oil and solvent in a condition in which it can be stored until further required.

The present invention is designed to obviate the foregoing difficulties by providing a simplified system for the liquid-liquid solvent fractionation of triglyceride oils in which the columns heretofore employed are replaced by an appropriate arrangement of relatively compact centrifuges of a design adapted to permit countercurrent flow of the liquids involved in the extraction operation.

The apparatus is shown diagrammatically in the single figure of the drawing. It includes at least one and preferably three centrifuge units designated respectively as I, II and III. A conventional type of centrifuge for use in the process is sold by Podbielniak, Inc., Chicago, Illinois. One such apparatus bears the number 6100 and is entitled Pilot Extractor. Several different forms of such apparatus are illustrated in such U. S. patents as: 2,286,157, 2,209,577, 2,281,796, 2,109,375, 1,936,523.

These are all characterized by the provision in a suitable case, of a revolving rotor which includes a spiral diaphragm or sheet coiled about the axis of the shaft and between the convolutions of which the fluids involved in the operation are circulated. The heavy liquids preferably are introduced into the rotor at or near

the axis and the lighter liquids are introduced at or near the periphery. As the rotor turns, the heavier liquids are carried outwardly in a spiral path while the lighter liquids pass inwardly in countercurrent flow to and in intimate contact with the heavier liquids. The light liquids are drawn off by appropriate outlets from the axis of the rotor while the heavier liquids are drawn off by corresponding outlets at the perimeter.

The units I, II and III may be essentially similarly constructed. Since the interior construction of such units is well understood by those skilled in the art and the units can be purchased upon the market, it is not deemed necessary further to describe or illustrate it.

Each of the units includes a base structure 7 mounted upon any convenient support. It also includes a rotor housing 8 having a rotor 9 therein. The heavier liquids, in each instance, are illustrated as being introduced at the left and coaxially of the rotor through a suitable connection. The light product is drawn off at the same side through an appropriate outlet. The light medium is introduced coaxially at the right and the heavy product is drawn off at the same side. Of course, the sides could be reversed if so desired.

Obviously all of the pumps storage tanks, valves, gauges and other appurtenances required to maintain flow and correct proportioning of liquids under local conditions can be supplied. Various valves are indicated by V.

As shown in the drawings, the unit I constitutes the primary unit. Oil to be solvent extracted is introduced at the right side of the unit, coaxially of the rotor of the unit through a line 11 which is provided with a valve 11a to assist in proportioning the flow. A pump (not shown) may also be provided to force the oil into the system against centrifugal force. Furfural or other solvent medium, which is but partially miscible with the oil and preferably which is of polar character and has a selective solvent action for the more unsaturated glycerides, is introduced at the left through a line 12 which has a swivel connection to the interior of the drum 8 and preferably into or near the axis thereof. The liquids flow in intimate contact and countercurrently through each other.

Raffinate product comprising more saturated glyceride oil which contains in solution a small amount of furfural and which is substantially lower in density than the furfural, is drawn off at the left through a line 13 designed to take off the lighter product from near the axis of the rotor.

The solution of furfural and more highly unsaturated oil is taken off from the periphery of the rotor through an appropriate connection at the right, through a line 14.

The raffinate taken off at 13 may be subject to distillation or other treatment to eliminate the solvent contained in the more highly saturated portion of the oil.

The extract oil obtained in the selective solvent phase through the line 14, may not be of sufficiently high iodine value. In order to increase this value, the oil may further be subjected to a refluxing operation with an appropriate medium. This reflux may comprise glyceride oil which has already been extracted and partially or completely stripped of solvent medium, or it may comprise naphtha, which when subjected to intimate contact with the extract solution

is found to act as a reflux to produce a substantial improvement or increase in the iodine value of the oil in the extract solution.

Reflux is best applied in the unit II, for which purpose, the line 14 is passed to the inlet 16 of the unit II and the solution of oil and polar solvent from unit I is introduced into the rotor of the unit at or near the axis thereof. Reflux naphtha or, extracted oil of high iodine value may be introduced to the axial zones of the rotor of the unit II through a line 17. A mixed reflux of oil and naphtha in any proportions with respect to each other may be employed. The provision of oil suitable for reflux will be later described.

In event that naphtha is employed as a reflux, a paraffinic naphtha such as heptane, hexane or octane or usually a mixture of two or all of these hydrocarbons is introduced at 17. The reflux of oil may then be eliminated, or a small reflux of oil and reflux of naphtha may be introduced into the system simultaneously. The low density raffinate product of unit II is taken off at or near the axis of the rotor through line 19 and is returned as a mixture of oil of rather low iodine value as compared to that in the extract solution and containing most of the naphtha and some polar solvent to the feed line 11 of unit I.

Unit II is often operated at a lower temperature than unit I. To obtain this effect economically a cooler or heat exchanger 14A is provided. Oil from 14A is cooled therein. Cooling medium may be circulated by lines 14B. Returning oil and naphtha in line 19 may also be by-passed to through lines 19A and 19B to the cooler and made to function as a cooling medium.

In most instances, it is desirable to subject the oil to a backwash extraction with a solvent such as naphtha of the type already referred to as a medium in order to effect separation of the glycerides of high iodine value from the free fatty acids, coloring matter, unsaponifiable constituents present in most glyceride oils. The extract solution of polar solvent, e. g. furfural and more highly saturated glyceride oil as obtained from the line 14 may be backwashed with naphtha in order to obtain most of the glycerides in solution in the backwash medium, e. g. naphtha, in the unit III. Backwashing may be conducted upon oil which has been subjected to simple extraction in the unit I or it may be conducted upon oil which has been subjected further to a reflux of oil and/or naphtha in the unit II.

In event that it is desired to subject the solution of oil and polar solvent as it comes from unit I to naphtha backwash in order selectively to separate the glycerides from the polar solvent, the extract solution from the line 14 may be passed through a branch line 24 to an inlet line 26 extending to the port portion 27 that serves to introduce the solution at the axis of the rotor of the unit III. Naphtha for backwashing the extract solution so introduced, is carried throughout line 28 and introduced into the port portion 29 at the right of the unit. This naphtha preferably is carried to the outer periphery of the rotor unit and flows countercurrently inwardly in intimate contact in the rotor with the outwardly flowing solution of oil and polar solvent introduced at 27. The solutions permeate through each other in very intimate contact. The glycerides, in large measure, are taken up from the polar solvent by the naphtha in its flow through the contact zone and are drawn off through a

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suitable outlet at 30. The solution of glycerides and naphtha, reduced in coloring matter, free fatty acids, sterols and other by-products may be passed to convenient distillation apparatus 31 for the removal of naphtha. The furfural solution from unit III comprising mainly the by-products including coloring matter, fatty acids, sterols, inhibitols and the like, is drawn off through outlet line 32. Probably no more than 1 or 2 or at most 3% of the glycerides of the original oil are present in the by-products. This solution may be subjected to any desired treatment in order to recover the valuable constituents contained therein.

In most instances, it is desirable to subject the oil to both reflux (either oil or naphtha) in unit II and also to a backwashing operation in unit III in order to obtain the oil extracted in the furfural phase in a purified form. If this is desired, the extract solution of polar solvent and oil as obtained through the line 14 is passed to the inlet portion 16 of unit II. A reflux of oil and/or naphtha is introduced at 17, the resultant solution of extract oil of high iodine value passing off through the outlet line 33 is passed to the backwash unit III where it is subjected to naphtha wash in the manner already described.

If it is desired to eliminate the backwash stage in unit III, extraction solution of oil and furfural from line 33 of unit II may be passed by branch line 34 to still 31 for evaporation of solvent. A reflux of oil for unit II may be taken off at 36 if desired. Product of highly unsaturated oil can be taken off by branch line 37.

If the oil is subjected to backwash in unit III with naphtha, the naphtha solution of more highly unsaturated oil from line 30 may be passed to still 31 for partial or complete stripping. A reflux of oil of high iodine value, with or without some naphtha, can be returned through line 36 and the rest, as available product of high iodine value, low color, free fatty acids, and unsaponifiable matter, can be taken off through line 37.

In the practice of the invention by use of the apparatus above described, substantially any of the common glyceride oils are susceptible of treatment for purposes of obtaining fractions of improved characteristics in various respects. For example, for purposes of obtaining highly unsaturated glyceride oils suitable for use as coating compositions, oils containing large amounts of highly unsaturated glycerides are to be preferred. These included soybean oil which commonly, in its original state, will have an iodine value of about 130 or 135. By application of the principles of the invention and by use of a suitable number of stages in the fractionation, the iodine value of the extract portion may easily be increased to 150 or 160. Linseed oil may similarly be improved in iodine value to the extent of 10, 20 or even more points. For example, it is quite possible to increase the iodine value of linseed oil from 170 or 175 to 190 or even 200.

Cottonseed oil may similarly be fractionated to obtain one portion of considerably increased iodine value which constitutes a winterized oil or an oil closely approximating a winterized oil and a second fraction of low iodine value suitable for hydrogenation to provide a lard substitute or for other purposes to which such oils are conventionally subjected. Peanut oil can similarly be treated to obtain a high iodine value portion which is winterized and which is, therefore, of especial value as a salad oil.

In addition to effecting separation of oils into

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high and low iodine values by application of the principles of the invention, it is also possible to obtain fractions of glyceride oils which are substantially improved in various other respects.

For example, vitamin containing oils such as fish liver oils, e. g. shark liver oil or the like may be subjected to a treatment with a polar solvent such as furfural using the apparatus as previously described. By such treatment there is obtained a small fraction of oil, e. g. 10, 20 or 30% as a polar solvent extract of highly unsaturated character and which is greatly improved in content of vitamins A and/or D. This enriched fraction will be obtained as the extract or furfural phase from units I or II that can be backwashed in unit III. The oil soluble vitamins remain with oil in the naphtha phase.

In the practice of the invention, the various units I, II and III may be operated at such temperature as will insure the formation of immiscible phases of the various liquid components while at the same time obtaining a reasonable degree of solution of the material to be treated. For example, the units I and II may be operated at a temperature of about 90 to 135° F., assuming that the oil treated is soybean oil. For cottonseed oil, the temperature of the unit should be about 118° or within 5 or 10° of this value. For the treatment of linseed oil, the units should be operated at a temperature of about 70 to 85 or 90° F.

The unit III in which the oil is treated with naphtha to obtain the fraction enriched in highly unsaturated glycerides, vitamins or the like should be operated at a temperature of 10 to 80° F. or preferably about 40 or 50° F. lower than the temperatures of units II and III. When so operated, it is assured that the major portion of the glycerides along with the vitamins and the like will be taken up in the naphtha solution. The furfural phase from the unit III comprises a small amount, e. g. .3 to 2 or 3% of the original glyceride oil and a high enrichment of fatty acids, coloring matter and unsaponifiable constituents.

The temperatures of operation, above referred to, apply with particular emphasis to furfural as a selective polar solvent. Of course, other solvent media of polar character such as the solvents discussed in Freeman Patent No. 2,200,391 may be substituted for furfural in the system. These solvents will require adjustments of temperature to obtain a proper degree of phase separation.

The solvent may be employed in a broad range of proportions with respect to the oil to be treated. Usually, the solvent such as furfural will be employed within a ratio of at least three volumes per volume of oil treated. The proportion may be greatly increased over this value, if so desired. For example, good results may be obtained by employment of furfural in a ratio of 5, 8, 10 or even 20 volumes per volume of oil to be treated.

Assuming that naphtha is employed as a reflux medium in the unit II, being introduced through the line 17, the ratio of naphtha to oil preferably will be within a range of .1 to 1.5 for low portions, e. g. 3 or 5 volumes furfural. If high proportions of furfural are employed in the solvent extraction of the oil, this proportion may be increased to 2 or even up to 5 volumes of naphtha per volume of original oil.

If a reflux of product oil is introduced through the line 17, at least a portion of the naphtha solution of oil obtained through the line 30 as product

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from the unit II is subjected to distillation in the still 31. The product, as thus obtained, may be returned as a reflux through the line 17. Obviously a portion of the naphtha in the oil may be retained to provide a mixed reflux of oil and naphtha. If oil is employed as a reflux, it may be employed in approximately the same proportions as specified for the naphtha reflux. If a mixed reflux is employed, the sum of the two components of the reflux may be within the range specified for naphtha alone.

In the operation of the backwash unit III the proportion of naphtha is susceptible of considerable variation. Preferably it will be within a range of approximately 1 to 5 volumes per volume of original feed oil though this range may be varied to a considerable degree in either direction. The temperature of the unit III will, as above stated, usually be materially lower than that of unit I or II. The furfural then tends to give up nearly all of the glycerides in solution but retains nearly all of the by-products.

The following constitute specific examples illustrating the application of the principles of the invention:

Example I

In this example soybean oil of an iodine value of 132.2 can be subjected to furfural extraction. The temperature of the units I and II can be approximately 135° F. Naphtha can be employed as a reflux medium in the unit II. The proportions of the various components of the system could be as follows:

Oil feed..... 30 parts
Furfural (dry) ... 660 parts saturated with naphtha at 135° F.
Naphtha reflux... 68 parts (parts are by volume)

A product of good drying characteristics could be obtained. This could be recovered either by direct distillation of the furfural solution from the unit II or by backwashing the solution with naphtha in the unit III and then recovering the oil in the naphtha solution by evaporation of the naphtha.

Example II

In this example soybean oil of iodine value 135.9 could be extracted with furfural in the unit I. The temperature of the unit could be maintained at approximately 108 to 111.5° F. The rates of feed to the unit I are as follows:

Parts
Soybean oil 30
Furfural 90
Naphtha reflux to the unit II 6

The extract solution of oil in furfural as obtained from the unit II could be further backwashed with naphtha in the unit III operating at a temperature of 60 to 80° F.

Example III

In this example cottonseed oil can be subjected to extraction with furfural in the unit II. The temperature of the unit can be 118° F. but might be 5 or 10° higher or lower. The furfural feed can be within a range of 3 to 8 parts by volume, e. g. the parts based upon the feed oil employed. The naphtha reflux, as fed through the line 17 to the unit II, can be within a range of .1 to 5 parts based upon the original feed oil introduced at 11 into the unit I. The furfural solution of more unsaturated oil as obtained through the line 33 could be fed to the unit III and back-

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washed with naphtha at a temperature of 70 to 75° F. In the backwashing operation the naphtha ratio preferably can be within a proportion of about 1 to 1 upon a volume basis per volume of original oil.

Example IV

In this example, alkali refined soybean oil of an iodine value 138 could be subjected to extraction in the unit I with furfural at a temperature of 90 to 91° F. The feed ratios to the unit could be 200 parts by volume of furfural, 40 parts feed oil, 12 parts naphtha reflux through line 17. The furfural solution obtained through the line 33 could be backwashed with naphtha in the unit III at a temperature of 50 to 80° F. to provide a product obtained as a naphtha solution of a very high iodine value and good color characteristics. Needless to say, the raffinate, as obtained through the line 13, could be of low iodine value and could be suitable for food and many other purposes. About .1 volume would constitute a good lower limit of reflux. The temperature would depend upon the solvent employed. The application of the invention to concentration of vitamins is contemplated. For this purpose, the polar solvent, e. g., furfural, should best be employed in a ratio of 3 to 30 parts by volume per volume of feed oil. The temperature of unit I should be adjusted to provide an extract yield of concentrate of 2 to 40% and preferably 3 to 20%. The naphtha backwash in unit III should be in a ratio of about 3 to 20 volumes per volume of feed oil. Reflux to unit II should be from about 0 volume of naphtha or product oil to 1 volume per volume of feed oil.

Some solvents that could be employed in the primary unit to concentrate vitamin A or D in fish liver oils would comprise

	Parts		Temperature, degrees C.
	Max.	Min.	
Methyl alcohol.....	10	1	39
Methyl lactate.....	5	1	57
Monomethyl ether of ethylene glycol.....	5½	1	40
Furfuryl alcohol.....	4	1	40
Acetic anhydride.....	6	1	41.5
Glycol diacetate.....	5	1	51.5
Methyl levulinate.....	6	1	14
Methyl acetoacetate.....	5	1	22
Furfural.....	8	1	17
Acetonyl.....	6	1	25.5
Beta methoxy ethyl carbonate.....	2	1	40
Nitromethane.....	9	1	60

The following example illustrates the application of the principles of the invention to the separation of a concentrate of vitamins from a fish liver oil.

Example V

In this example dog fish liver oil containing approximately 17,200 units of vitamin A per gram constituted the raw material. This oil could be pumped into the centrifuge I through the line 11. Furfural could be pumped into the line 12 in a proportion of 20 parts by volume per part of the feed oil. The unit I could be maintained at a temperature of about 157° F. by appropriate adjustment of temperature of the furfural and oil feed. The raffinate oil could be drawn off from the centrifuge through the line 13.

An extract solution of oil enriched in vitamins could be drawn off through the line 14 and passed to the centrifuge II to obtain a refluxing action by the addition of naphtha in the proportion of .41 per part of feed oil to the centrifuge I. The

lines 14 and 19 may be provided with a combined cooler and heat exchanger 14A by means of which the oil-furfural mixture can be cooled before introduction into unit II. The temperature of the latter can be about 77 or 80° F. Connections 19B with the line 19 provide means for in part cooling the feed to the unit II and rewarming the return feed to unit I.

The extract product from the centrifuge II could be taken off through line 33 and passed to the backwash centrifuge III where it was fed in coaxially through the input element 27. Extract solution of highly unsaturated oil enriched in vitamins from the unit III can be drawn off through line 30, passed to still 31 and a portion thereof, e. g. .21 part per part of original feed oil can be returned as a reflux to the input feed line 17 of the centrifuge II. An extract product of glyceride of high unsaturation much enriched in vitamin A can be taken off through branch line 37.

The third centrifuge in this example can be operated at a temperature of about 72° F. at which temperature the glyceride components along with the vitamin A, readily passed into solution in the naphtha employed as a backwash without substantial removal of the unsaponifiable matter, free fatty acids and the like from the furfural phase.

Instead of employing single centrifuges I, II and III respectively for the steps of subjecting the oil to extraction with polar solvent, refluxing and backwashing may be continued in two or more centrifuges arranged in tandem in such manner as to obtain the effect of more stages or plates in any one or all of the foregoing operations than can be obtained with single centrifuges. The total of such stages or plates may be as low as 2 or 3 if maximum spread of iodine values is not required. On the other hand, as many stages or plates as are economically feasible may be employed. The number of such stages or plates may go up to 8 or 10 or even above.

It will be apparent to those skilled in the art that numerous modifications may be made without departure from the spirit of the invention or from the scope of the appended claims.

I claim:

1. A process of treating a glyceride oil comprising relatively highly saturated and relatively unsaturated components to separate it into fractions, one of which is enriched in the first mentioned component and the other of which is enriched in the second, the steps which comprise rotating a body of oil and a polar solvent about an axis to provide a zone of centrifugal force while feeding additional oil continuously into the body substantially at the perimeter of the zone and continuously feeding polar solvent having a higher affinity for the unsaturated glycerides than for the saturated glycerides, but being only partially miscible with the oil, substantially at the axis of the zone, drawing off an extract solution of oil and polar solvent substantially at the perimeter of the zone, passing the extract solution into a second rotating extraction zone at substantially the axis thereof, passing naphtha into the same zone substantially at the perimeter thereof, returning the oil taken out of the polar solvent in the second zone to the first zone with the oil feed, continuously drawing off the solution of polar solvent and more highly unsaturated oil substantially at the perimeter of the second zone, passing it to a third zone of centrifugal force near the outer perimeter thereof and feeding in naphtha near the axis of the third

zone, the naphtha fed to the third zone being in a proportion of 1 to 5 volumes per volume of original oil, the temperature being in a range of 10 to 60° below that in the first zone, whereby at least 97% of the oil in solution in the polar solvent is extracted out in the naphtha, drawing off the naphtha solution substantially at the axis of the third zone and drawing off the polar solvent and a by-product of fatty acids and unsaponifiable matter at the outer perimeter of the third zone and evaporating the naphtha from the naphtha solution and returning a portion of the oil recovered to the second zone with the naphtha feed.

2. A process as defined in claim 1 in which the oil treated is of a class consisting of linseed, soybean, cottonseed and peanut and fish liver, the polar solvent being furfural.

3. In a process of treating glyceride oils comprising a mixture of glycerides of varying degree of unsaturation to obtain a fraction of higher degree of unsaturation than the original oil, the step of feeding the oil into an outer part of a first zone of centrifugal force in which the oil is rotated about a central axis and feeding a polar solvent in at the axis of the zone, drawing off a solution of oil and polar solvent at the outer perimeter of the zone, passing the oil and polar solvent to the axis of a second zone of centrifugal force, feeding in a reflux of a material of a class consisting of naphtha and extracted oil at the outer perimeter of the second zone, drawing off an extract solution of oil of high iodine value at the outer perimeter of the zone and a raffinate of oil of reduced iodine value at the axis and returning the raffinate to the axis of the first zone with the original feed oil.

4. A process as defined in claim 3 in which the polar solvent is furfural.

5. A process as defined in claim 12 in which the solvent is furfural.

6. A process as defined in claim 12 in which the oil is fish liver oil containing vitamin A.

7. A process as defined in claim 12 in which the oil treated is soybean oil.

8. A process as defined in claim 12 in which the oil treated is peanut oil.

9. A process as defined in claim 12 in which the oil treated is cottonseed oil.

10. A process as defined in claim 12 in which the oil treated is linseed oil.

11. In a process of treating glyceride oils comprising a mixture of glycerides of fatty acids of varying degrees of unsaturation to obtain a fraction of said oil of higher degree of unsaturation than original oil, the steps of continuously feeding the oil into an outer part of a first zone of centrifugal force and feeding furfural in at the axis of the zone, the furfural being in a proportion of 3-30 volumes per volume of oil, drawing off a raffinate product at the axis of the first zone, drawing off a solution of oil and furfural from the outer perimeter of the first zone and feeding it to the axis of a second zone of centrifugal force, feeding in a reflux of a material of a class consisting of naphtha and extracted oil at the outer perimeter of the second zone, the total reflux being in a proportion of .1 to 5 volumes per volume of original oil, drawing off an extract solution of oil of high iodine value at the outer perimeter of the second zone and a raffinate at the axis of the second zone and feeding the raffinate to the axis of the first zone with the original feed oil.

12. In a process of treating glyceride oils com-

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prising a mixture of glycerides of fatty acids of varying degree of unsaturation to obtain a fraction of higher degree of unsaturation than the original oil, the steps of feeding the oil into an outer part of a first zone of centrifugal force and feeding furfural in at the axis of the zone, the furfural being in a proportion of 3 to 30 volumes per volume of original oil, the temperature of the zone being below that of complete miscibility of the furfural and the oil, drawing off a solution of oil and furfural at the outer perimeter of the zone passing the oil and furfural to the axis of a second zone of centrifugal force, feeding in a reflux of a material of a class consisting of naphtha and extracted oil at the outer perimeter of the second zone, the reflux being in a proportion of .1 to 5 volumes per volume of original oil, drawing off an extract solution of furfural and oil of high iodine value at the outer perimeter of the zone and a raffinate of oil of reduced iodine value at the axis, returning the raffinate to the axis of the first zone with the original feed oil, then passing the extract solution of oil of high iodine value and furfural to a third zone of centrifugal force at the axis thereof, passing in naphtha at the outer perimeter of the same zone, drawing off a by-product phase of furfural containing a small amount of glyceride oil and by-

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product material at the outer perimeter of the zone and a naphtha solution of oil of high iodine value near the axis of the third zone, the third zone being operated at a temperature 10 to 80° F. lower than the second zone whereby to extract out at least 97% of the glyceride oil dissolved in the furfural into the naphtha phase, and recovering the oil from the naphtha solution by evaporation of the naphtha.

13. The steps as defined in claim 11 in which the oil treated is soybean oil, and the temperature of the zones is within a range of 90 to 135° F.

14. The steps as defined in claim 12 in which the oil treated is soybean oil, the temperature of the first two zones is in a range of 90 to 135° F. and the temperature of the third zone is within a range of 60 to 80° F.

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