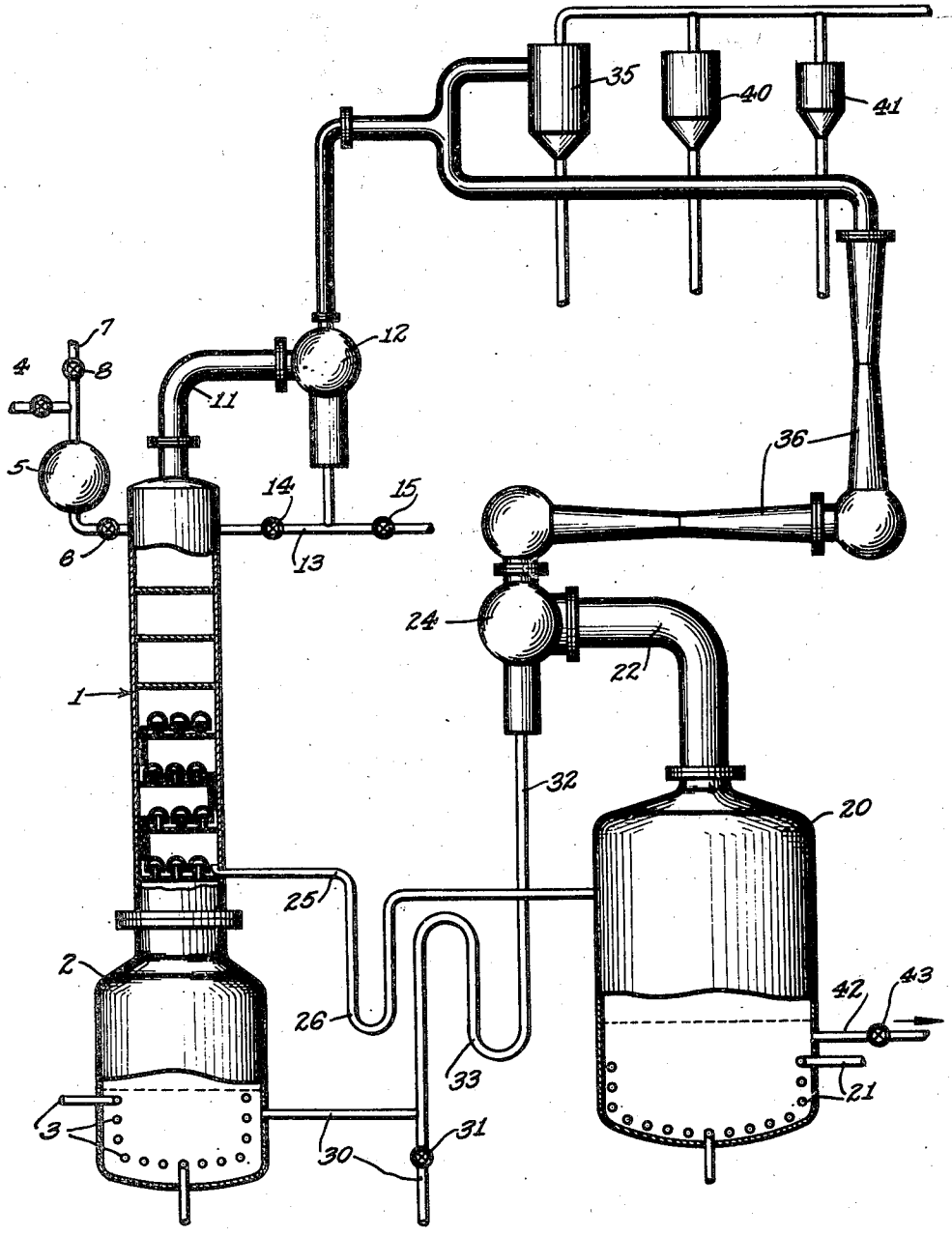
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RECONSTITUTION OF GLYCERIDES

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RECONSTITUTION OF GLYCERIDES

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The present invention relates to oils and more particularly to a method for reconstituting glycerides by replacing all or at least a substantial portion of the lower molecular weight fatty acids thereof with higher molecular weight fatty acids by interaction with lower alkyl esters of higher molecular weight fatty acids, thereby producing valuable glycerides having fatty acids of high boiling characteristics and alkyl esters of lower molecular weight fatty acids as a valuable by-product.

It has been proposed heretofore to remove the low molecular weight fatty acids from glycerides by a treatment of refrigeration and expressing, thereby solidifying the higher melting constituents and extracting therefrom the liquid constituent. The solidified material has a higher melting point which is desirable but the entire operation is very inefficient, particularly in the yield of the higher melting point material.

Another method heretofore proposed comprises heating a glyceride with a higher fatty acid or a mixture of such higher fatty acids at temperatures in the neighborhood of 300° C. for a period from two to three hours and then distilling off the lower fatty acids from the mixture. This proposed method, however, is undesirable because of the prolonged heating of the glyceride oils at such high temperatures which causes partial decomposition of the glycerides and/or excess polymerization thereof.

The present invention accomplishes the desired reconstitution of the glycerides by subjecting them to heat for a relatively short period and at very low pressures.

More particularly a glyceride is introduced at the top of a tower or column and caused to flow relatively rapidly therethrough while the vapors of alkyl esters of higher molecular weight fatty acids are introduced at the bottom of the tower for contact with the glyceride.

While the reaction can take place without a catalyst, a catalyst may be added to accelerate the interaction and to conjugate the unsaturated bond system of the glyceride. A temperature range of between about 250 and 300° C. and a pressure range of about 20 to 40 mm. absolute are preferably maintained in the column which is just about the distillation condition of the alkyl esters of the lower molecular weight fatty acids. These temperature and pressure ranges insure the passage to the upper end of the column of the alkyl esters of the lower boiling (lower molecular weight) fatty acids. Other temperature ranges may be selected as well as different

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pressures depending, of course, upon the materials to be treated and other operating conditions.

The glycerides together with excess alkyl esters of higher molecular weight fatty acids are removed at the bottom of the column for distillation at the distillation temperature of the higher molecular weight alkyl esters and at a reduced pressure so that the distillation temperature does not decompose the glycerides. Some polymerization of the glycerides may take place during the distillation if the fatty acids are unsaturated, but this is not undesirable for many purposes. The excess alkyl esters of the higher molecular fatty acids are distilled from the glyceride and condensed and preferably returned to the boiler at the foot of the column together with a fresh supply of alkyl esters of higher molecular weight fatty acids.

The expression "glyceride" is used generically for oils and fats from vegetable, animal or synthetic sources. The expression "alkyl esters" refers to the esters of low molecular weight monoatomic alcohols, such as ethyl and methyl alcohol esterified with fatty acid radicals. In the discussion hereinafter the methyl esters will be referred to as illustrative.

The present invention has many applications and can be used wherever it is desirable to effect interchange of fatty acids in the glycerides.

One example is the replacement of the lower molecular weight fatty acids in fish oil, thereby giving the fish oil physical and chemical characteristics similar to tung or China-wood oil. This application of the present invention is important because the unstable China-wood oil market has caused a demand for a suitable substitute at a stable price for use in the varnish and other allied industries.

It will be understood that fish oil without having been treated in accordance with the present invention is not entirely suitable for use in the manufacture of varnish because the saturated fatty acids of lower molecular weight in the glycerides thereof produce too great a plasticizing effect resulting in an undesirably soft film and one which is not very good as a waterproofing film.

The present invention reforms the glycerides of the fish oil by replacing the lower boiling fatty acids by higher boiling fatty acids thereby reducing the plasticizing characteristics thereof and increasing the waterproofing film.

Besides the production of an oil product similar in characteristics to China-wood oil, valuable

by-products are also obtained by the present invention. These include methyl esters of lower molecular weight fatty acids, which in the case of fish oil treatment, are valuable for use in the manufacture of soaps upon hydrolysis to release the fatty acid from the methyl ester.

Another example of the application of the present invention is the treatment of coconut oil for the removal of the C_6, C_8 and C_{10} fatty acids from the heavier fatty acids in the coconut oil glycerides. The treatment is conducted in the same manner as hereinbefore described, the coconut oil being introduced at the top of the column and a methyl ester fed into the boiler at the base of the column. Methyl esters of the low molecular weight fatty acids (C_6, C_8 and C_{10} acids) are withdrawn from the top of the column and condensed, and the reconstituted glycerides of coconut oil, in which these low molecular weight acids have been replaced by higher molecular weight acids, are removed at the base of the column. With the lower fatty acids removed, the resulting coconut oil is especially desirable in the manufacture of soap products.

Other applications of the present invention are the interchange of fatty acids in the glycerides used in the edible oil industry, where it is desirable to replace the low molecular weight fatty acids by stearic or palmitic acids to produce stearine.

In order that the invention may be more readily understood, reference may be had to the drawing which sets forth in schematic form an apparatus of the type which may be utilized in carrying out treatment of glycerides continuously, although it will be understood that the treatment may be carried out in batches if desired.

The apparatus for accomplishing the interaction between the glycerides and the methyl ester comprises a fractionating tower 1 which may be, for example, a conventional bubble plate column or a packed tower connected to a boiler 2 which may be heated by closed coils 3, through which a suitable heating medium is conducted. A conduit 4 connected to a supply of glyceride stock to be treated is provided, if desired, with a heat interchanger 5 for adjusting the temperature of the glyceride prior to the introduction thereof into the tower through a contact valve 6. A conduit 7 controlled by a valve 8 is connected to the conduit 4 through which a suitable catalyst may be added to the glyceride oil. While the conduit 4 is shown connected to the top portion of the tower it may be connected lower down on the column, if desired.

The top of the fractionating tower is connected by a conduit 11 to a condenser 12 for condensing the vaporized material withdrawn from the tower. The conduit 13 and the valves 14 and 15 are provided to remove the condensate from the condenser 12 and, if desired, to return a part of the condensate for refluxing purposes. The reflux connection through the valve 14, however, may be connected at any point along the column that is most advantageous.

The material reaching the bottom plate of the column will include the reconstituted glycerides and any excess of methyl esters of higher molecular weight fatty acids which have not entered into the interaction. To remove such excess high boiling esters from the reconstituted glycerides a still 20 is provided having closed heating coils 21 and an outlet conduit 22 at the top thereof in communication with a suitable condenser 24. A conduit 25 having a liquid trap 26 connects the

base of the fractionating tower 1 at a point above the boiler 2 for passage of glycerides and excess high molecular weight methyl esters to the still 20. A conduit 30 having a valve 31 controls the fresh supply of methyl esters of higher molecular weight acids to the boiler 2. The condensate from the condenser 24 is returned to the boiler 2 by a conduit 32 having a liquid trap 33 which is connected to the conduit 30.

To maintain low pressures in the fractionating tower 1 and the still 20 the condensers 12 and 24 are connected to a barometric condenser 35. The connection between the condensers 24 and 35 is provided with one or more boosters 36 to effect a lower pressure on the still 20 than is maintained in the fractionating tower. Additional condensers and air ejectors 40 and 41 are provided to maintain at least partial vacuum conditions, all of which is in accordance with conventional practice.

In carrying out the invention a glyceride oil such as crude or refined fish oil, for example, is introduced, together with the desired proportion of catalyst, such as about 0.5% of sodium methylate mixed at a preconditioned temperature to the top of the fractionating tower for flow from plate to plate downwardly through the tower. Vapors of the methyl esters of the fatty acids of linseed, soybean or dehydrated castor oil rise upwarly through the tower, the ester having been subjected to a boiling temperature in the boiler 2. The temperature of the fractionating tower ranges between about 250° C. at the top thereof to about 300° C. at the base thereof. The pressures at the top of the tower are maintained low and will range between about 20 and 40 mm. absolute. There will be of course a pressure drop through each plate so that the pressure in the boiler 2 is somewhat higher, for example, of the order of 25 to 50 mm. absolute depending on the number of plates in the column and the conditions of operation.

As there is a constant interchange of fatty acids between the methyl ester and the glyceride and as fractionation is taking place at the temperature and pressure conditions of the tower, it is possible to remove all or at least a substantial portion of the lower boiling fatty acids from the glyceride and convert them into methyl esters. These low boiling fatty acids are replaced in the glyceride oil with higher boiling fatty acids released from the methyl esters introduced into the boiler 2. The lower boiling methyl esters are removed as a vapor from the top of the tower and condensed in the condenser 12. Methyl esters of higher molecular weight fatty acids are condensed or fractionated from the methyl esters of lower molecular weight fatty acids and the former are carried with the glyceride through the outlet conduit 25 to the still 20.

The temperature and pressure conditions of the still 20 are such as to vaporize the methyl esters remaining with the reconstituted glyceride, the vapors being condensed in the condenser 24 and returned through conduit 32 to the boiler 2. Fresh methyl esters of higher molecular weight fatty acids are continuously supplied through the control valve 31 to make up for the ester withdrawn from the top of the tower.

The reformed glyceride oil is drawn off from the still 20 through a conduit 42 controlled by a valve 43. The reformed oil having the low molecular weight fatty acids replaced by higher molecular weight fatty acids now has physical and chemical characteristics similar to China-wood

oil and may be substituted therefor in the manufacture of varnish.

The low molecular weight methyl ester is drawn off through the valve 15 after it has been condensed and can be further fractionated to remove any fish odors and then converted by well known processes to fatty acids and methyl alcohol and the alcohol reclaimed. The fatty acids thus obtained when processing fish, soybean, castor and linseed oils are valuable for use in soap manufacture and the alcohol is useful in the manufacture of additional quantities of methyl esters to be added through valve 31. Thus no alcohol is lost in the process.

Thus, from oils that are not outstanding either as varnish oils nor as soap oils there is obtained by the process, an oil that is superior to any of the starting oils for varnish making and fatty acids for soap making that are superior to the unsaturated fatty acids in the starting oils. Also there is no wasted material as the alcohol is recovered for making an additional quantity of methyl esters, and the glycerine is recovered when the methyl esters are formed from the oil.

In the above example it is apparent that the oils used as the raw materials, i. e., fish, soybean, etc., are such that the fatty acids which exit from the process in the form of the methyl esters thereof are suitable for soap making and are not of such low molecular weight as to be unsuitable for this purpose. The fatty acids which are retained in combination with the glycerine and exit from the process as glycerides are utilized preferably in varnish making.

The process may be applied, however, to the treatment of other oils in which the fatty acids that are retained in the form of glycerides are primarily suitable for soap making and the fatty acids which exit from the process as methyl esters are suitable for other purposes such as plasticizers.

For example, coconut oil contains about 20% fatty acids having less than 12 carbon atoms and 80% of fatty acids having 12 carbon atoms or more, the latter being suitable for soap making. The coconut oil may be fed to the top of the fractionating column. Methyl esters of fatty acids having 12 carbon atoms or more may be fed into the boiler at the bottom of the column. In the fractionating column the fatty acids having 12 or more carbon atoms will be released from the methyl esters thereof and such fatty acids will enter into the glyceride and release therefrom the fatty acids having less than 12 carbon atoms, which fatty acids in the form of the methyl esters will pass upward through the column to be removed and condensed.

The reconstituted coconut oil from which the fatty acid radicals having less than 12 carbon atoms have been replaced by higher molecular weight fatty acids pass to the still where any methyl esters of the higher molecular weight fatty acids that are not utilized in the fractionating column are vaporized, condensed, and returned to the boiler. The reconstituted coconut oil is withdrawn from the still and is a superior product for soap making. The methyl esters of the fatty acids having less than 12 carbon atoms are subject to hydrolysis and the fatty acids released are valuable as plasticizers.

The methyl esters to be supplied to the bottom of the column may be formed from any oil or fat which does not contain any low molecular weight fatty acid radicals, such as tallow. On the other hand they may be formed from coconut oil in which event the methyl esters introduced at the bottom of the column would contain 20% methyl esters of fatty acid radicals having less than 12 carbon atoms which would have to be vaporized and pass out through the fractionating column.

The process has a number of advantages from the point of view of efficiency, since it is not necessary to supply heat of vaporization to any material except the methyl esters which are vaporized, removed and condensed. The glycerides introduced into the top of the column and which contain the desired fatty acid constituents need not be vaporized, and pass through the process and are withdrawn from the still without requiring that heat of vaporization. If the process is operated so that the amount of methyl esters introduced into the boiler at the bottom of the column is substantially that required to replace the lower molecular weight fatty acids in the glyceride, very little heat of vaporization will have to be supplied for vaporization in the still, since there will be but a small amount of the unvaporized methyl esters passing from the fractionating column to the still with the reconstituted glyceride oil. Further, the incoming glycerides at the top of the column may be preheated in the heat exchanger by the heat contained in the reconstituted glycerides exiting from the still.

The process has the additional advantage in that any odorous materials are separated during the fractionation in the column and are removed from the oils. Since the fractionating column operates at a higher pressure than the still, the temperature at which a given fraction boils in the column will be higher than that in the still. The methyl esters of the higher molecular weight fatty acids which are not vaporized in the column under a pressure of about 40 mm. at the bottom of the column pass to the still where at the much lower pressure of 1 to 4 mm. pressure these methyl esters will be vaporized without any substantial increase in the temperature in the still. By so adjusting the pressures it is possible in instances where it is desirable to avoid using a higher temperature in the still than at the bottom of the column, to vaporize the higher boiling esters by their residual heat as they are passed from the relatively high temperature and high pressure zone at the bottom of the column to the relatively low pressure condition in the still. Thus the glycerides, by the present process, are not subjected to any decomposition temperatures nor to harmful prolonged heating.

While the method of this invention is susceptible to variations all such variations are intended to be included within the scope of the following claims.

We claim:

1. The method of reconstituting a glyceride and a lower alkyl ester of a different fatty acid than at least one in the glyceride, said ester being less readily distillable than the corresponding ester of a fatty acid in the glyceride, comprising subjecting a body of said glyceride in liquid form to vapors of said ester in a reaction zone to interchange the said fatty acid in said glyceride and the said fatty acid in the lower alkyl ester, and substantially simultaneously separating the reconstituted glyceride at one point in the reaction zone and the reconstituted lower alkyl ester at another point in the reaction zone.

2. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides at the top of a fractionating column, introducing the vapors

of methyl esters of higher molecular weight fatty acids at the bottom of the column for interaction with the downwardly moving glycerides to effect a replacement of said low molecular weight fatty acids in the glycerides by higher molecular weight fatty acids, and removing methyl esters of said low molecular weight fatty acids from the column in vapor form.

3. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides at the top of a fractionating column, introducing the vapors of methyl esters of higher molecular weight fatty acids at the bottom of the column for interaction with the downwardly moving glycerides to effect a replacement of said low molecular weight fatty acids in the glycerides by higher molecular weight fatty acids, removing vapors of methyl esters of said low molecular weight fatty acids from the top of the column, removing the reconstituted glycerides and any excess of methyl esters of higher molecular weight fatty acids from the bottom of the column, and distilling said last mentioned methyl esters from the reconstituted glycerides.

4. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides at the top of a fractionating column, introducing alkyl esters of higher molecular weight fatty acids at the bottom of the column, maintaining the column at a pressure below one atmosphere and heating said esters to the boiling point thereof to cause the vapor thereof to pass counter to the flow of the glycerides for interaction therewith, and subsequently heating the reconstituted glycerides and any excess alkyl esters of higher molecular weight fatty acids at a pressure less than that in the column to remove said esters from the reconstituted glycerides without any appreciable decomposition of the glycerides.

5. The method of reconstituting glycerides having relatively low molecular weight fatty acids and methyl esters of fatty acids having higher molecular weight fatty acids, comprising introducing the glycerides at the top of a fractionating column, vaporizing said methyl esters, introducing the vapor of the esters at the bottom of the column for interaction with the glycerides, removing methyl esters of said low molecular weight fatty acids from the top of the column, and removing the reconstituted glycerides from the bottom of the column.

6. The method of reconstituting glycerides having relatively low molecular weight fatty acids and methyl esters of fatty acids having higher molecular weight fatty acids, comprising introducing the glycerides at the top of a fractionating column, vaporizing said methyl esters, introducing the vapor of the esters at the bottom of the column for interaction with the glycerides, removing methyl esters of said low molecular weight fatty acids from the top of the column, removing from the bottom of the column glycerides having said low molecular weight fatty acids replaced by higher molecular weight fatty acids, together with any excess of methyl esters of higher molecular weight fatty acids, and distilling the excess of said last mentioned esters from the reconstituted glycerides.

7. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides near the top of a fractionating column, introducing methyl esters of higher molecular weight fatty acids at the bottom of the column, maintaining the column at a sub-atmospheric pressure and heating said esters to the boiling point thereof to cause said esters in vapor form to pass through said column counter to the flow of said glycerides for interaction therewith, whereby there is a replacement of said low molecular weight fatty acids in the glycerides by higher molecular weight fatty acids, removing methyl esters of said low molecular weight fatty acids in vapor form from the top of the column, removing the reconstituted glycerides and any excess of methyl esters of higher molecular weight fatty acids from the bottom of the column and transferring them to a still, heating said transferred glycerides and esters at a pressure less than the pressure in said column to vaporize said esters and remove them from the reconstituted glycerides, and removing said reconstituted glycerides from the still.

8. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides near the top of a fractionating column, introducing methyl esters of higher molecular weight fatty acids at the bottom of the column, causing said esters in vapor form to pass through said column counter to the flow of said glycerides for interaction therewith, whereby there is a replacement of said low molecular weight fatty acids in the glycerides by higher molecular weight fatty acids, removing methyl esters of said low molecular weight fatty acids in vapor form from the top of the column, removing the reconstituted glycerides and any excess of methyl esters of higher molecular weight fatty acids from the bottom of the column and transferring them to a still, heating said transferred glycerides and esters to vaporize said esters and remove them from the reconstituted glycerides, returning said last mentioned esters to the bottom of the column, and removing said reconstituted glycerides from the still.

9. The method of reconstituting glycerides having relatively low molecular weight fatty acids, comprising introducing the glycerides near the top of a fractionating column, introducing methyl esters of higher molecular weight fatty acids at the bottom of the column, maintaining the column at a subatmospheric pressure and heating said esters to the boiling point thereof to cause said esters in vapor form to pass through said column counter to the flow of said glycerides for interaction therewith, whereby there is a replacement of said low molecular weight fatty acids in the glycerides by higher molecular weight fatty acids, removing the reconstituted glyceride oil and any excess of methyl esters of higher molecular weight fatty acids from the bottom of the column and transferring them to a still, heating said transferred glycerides and esters at a pressure less than the pressure in said column to vaporize said esters and remove them from the reconstituted glycerides, returning said last mentioned esters to the bottom of said column, removing said reconstituted glycerides from the still, removing methyl esters of said low molecular weight fatty acids in vapor form from the top of the column, splitting said last mentioned esters to release the said low molecular weight fatty acids and methyl alcohol, and utilizing said alcohol to form additional quantities of methyl esters of higher molecular weight fatty acids.

10. The method of treating fish oil so as to remove undesirable relatively low molecular

weight fatty acids therefrom and improve its properties for varnish making, which comprises subjecting in a fractionating column a body of said fish oil to the vapors of methyl esters of the fatty acids contained in soybean oil, thereby replacing said low molecular weight fatty acids in the fish oil by higher molecular weight fatty acids of said esters, removing methyl esters of said low molecular weight fatty acids from the top of the column, removing the reconstituted fish oil and any excess of the methyl esters of fatty acids of the soybean oil from the bottom of the column, and removing said last mentioned methyl esters from the reconstituted fish oil.

11. The method of treating fish oil to remove undesirable relatively low molecular weight fatty acids therefrom and improve its properties for varnish making, which comprises introducing the fish oil near the top of a fractionating column, introducing methyl esters of fatty acids of a semi-drying oil at the bottom of the column, maintaining the column at a sub-atmospheric pressure and heating said esters to the boiling point thereof to cause said esters in vapor form to pass through said column counter to the flow of said fish oil for interaction therewith, whereby there is a replacement of said low molecular weight fatty acids in the fish oil by higher molecular weight fatty acids, removing the reconstituted fish oil and any excess of methyl esters of fatty acids of the semi-drying oils from the bottom of the column and transferring them to a still, heating said transferred oil and esters at a pressure less than the pressure in said column to vaporize said esters and remove them from the reconstituted fish oil, returning said last mentioned esters to the bottom of said column, removing said reconstituted fish oil from the still, removing methyl esters of said low molecular weight fatty acids in vapor form from the top of the column, and hydrolyzing said esters to form fatty acids and methyl alcohol.

12. The method of treating coconut oil to remove therefrom undesirable low molecular weight fatty acids having less than 12 carbon atoms, which comprises subjecting a body of coconut oil in a fractionating column to vapors of methyl esters of fatty acids having 12 or more carbon atoms, thereby replacing said low molecular weight fatty acids in the coconut oil by fatty acids having 12 or more carbon atoms, removing methyl esters of fatty acids having less than 12 carbon atoms from the top of said column, removing the reconstituted coconut oil and any excess of methyl esters of fatty acids having 12 or more carbon atoms from the bottom of said column, and removing said esters from the reconstituted coconut oil.

13. The method of treating coconut oil to remove therefrom relatively low molecular weight fatty acids having less than 12 carbon atoms, comprising introducing coconut oil at the top of a fractionating column, introducing methyl esters of fatty acids of coconut oil at at the bottom of the column, maintaining the column at a sub-atmospheric pressure and heating said esters to the boiling point thereof to cause said esters in vapor form to pass through said column counter to the flow of said oil for interaction therewith, whereby there is a replacement of said low molecular weight fatty acids in the oil by higher molecular weight fatty acids derived from the esters, removing methyl esters of fatty acids having less than 12 carbon atoms from the top of the column in vapor form, removing the reconstituted coconut oil and any excess of methyl esters of fatty acids having 12 or more carbon atoms from the bottom of the column and transferring them to a still, heating said transferred oil and methyl esters at a pressure less than the pressure in said column to vaporize said esters and remove them from the reconstituted oil, removing said reconstituted oil from the still and making soap therefrom.

14. A process for altering the composition of a mixture of glycerides which comprises subjecting a mixture of said glycerides and a fatty acid ester of a monohydric aliphatic alcohol having less than three carbon atoms per molecule to a temperature at which molecular change in the glyceride will take place, simultaneously vaporizing at least part of the monohydric alcohol ester present in the mixture, fractionating the vaporized esters, returning the less volatile fraction to the reaction zone to permit further reaction with the glycerides, and removing the more volatile fraction.

15. A process for altering the composition of a mixture of glycerides which comprises subjecting a mixture of said glycerides, a fatty acid ester of a monohydric aliphatic alcohol having less than three carbon atoms per molecule, and a molecular rearrangement catalyst to a temperature at which rearrangement of the glyceride structure will take place, simultaneously vaporizing at least part of the monohydric alcohol ester, fractionating the vaporized esters, returning the less volatile fraction to the reaction zone to permit further reaction with the glycerides, and removing the more volatile fraction.

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