

## UNITED STATES PATENT OFFICE

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PROCESS FOR PRODUCING FATTY ACID  
POLYHYDRIC ESTERS FROM GLYCERIDES

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described and claimed, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to the treatment of mixtures of fatty acid monoesters and diesters by means of solvents. It relates particularly to the liquid-liquid extraction of such esters and mixtures thereof in conjunction with processes of alcoholysis to produce, from glyceride oils, fatty acid polyhydric esters having enhanced value for industrial and food uses.

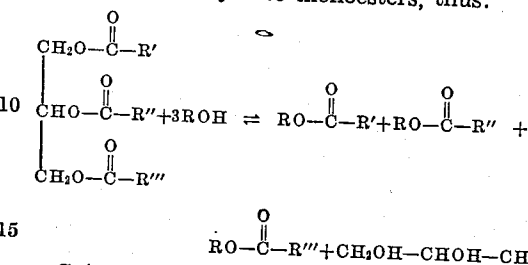
One object of the invention is to produce fatty acid polyhydric esters by alcoholizing fatty acid glycerides to form monoesters and diesters, separating the resulting mixture of esters into fractions by treatment with selective solvents, and converting the ester fractions thus obtained into higher polyhydric esters by alcoholysis with a polyhydric alcohol. For example, the method offers a simple and inexpensive method for separating into fractions fatty acid glycerides such as soybean oil, cottonseed oil, linseed oil, fish oils, and similar oils. By application of this invention, these oils and many others can be separated into fractions, some of which possess higher degrees of unsaturation than the original mixtures of glycerides and others which are more saturated than the original oils.

A second object of the invention is to provide a method for separating into fractions mixtures of fatty acid monoesters and diesters, certain of which fractions contain a higher concentration of the more unsaturated or more actively unsaturated components than the original mixture.

Although the examples cited herein are restricted to soybean oil, our experiments show that the process is applicable to fats and oils in general, such as soybean oil, linseed oil, cottonseed oil, fish oils, coconut oil, tung oil, castor oil, rapeseed oil, and similar oils.

In our invention the fatty acids which occur in nature as glycerides are converted into monoesters in accordance with any known methods, for example that described by Elsdon in Analyst,

38, 8-11 (1913), wherein fatty acid glycerides are treated, in the presence of a catalyst, with a quantity of alcohol substantially in excess of that quantity required to alcoholize the fatty acids stoichiometrically into monoesters, thus:



Satisfactory catalysts include acids, particularly sulfonic acids, and sodium methylate. The reaction is forced toward completion by use of excess alcohol. The purpose of this step in the process is to alter the mixed condition in which the fatty acids ordinarily occur in nature as glycerides, so that efficient separation can be obtained in a subsequent step of the process.

In most cases, monohydric alcohols such as methanol, ethanol, propanol, butanol, and amyl alcohol are preferable because of the ease with which they react with triglycerides to produce monoesters. It is also possible to use polyhydric alcohols such as ethylene glycol, glycerine, erythritol, arabitol, xylitol, mannitol, and sorbitol in this step of the process, but it is necessary to use a sufficient excess of the alcohol to assure the formation of monoesters and diesters.

The reaction is carried out by heating together the glycerides and alcohol with the catalyst. When equal volumes of soybean oil and methanol are heated together with 0.3 percent of sodium methylate based upon the weight of oil, the reaction goes substantially to completion during the time ordinarily required to heat the mixture to boiling and to cool it to room temperature.

The mixtures of monoesters or diesters may be fractionated by liquid-liquid extraction without removing the excess alcohols remaining after the alcoholysis, but it is usually preferable to separate the alcohols and esters. This can be accomplished by any known methods, for example by washing the mixture with water, in the cases

of water-soluble alcohols. The aqueous washings can be fractionally distilled in order to recover the alcohols which can be returned to the system. After removal of the excess alcohol the esters may, if desirable, be fractionally distilled before being subjected to selective solvent fractionation.

The term "selective solvent action" as herein used is defined as the ability of solvents and combinations of solvents to separate dissolved materials by virtue of chemical or physical affinity of said solvents for certain relatively active groupings which occur in the dissolved molecules. Relatively active groupings are those which contribute to the ability of polyhydric fatty acid esters to form suitable drying films through polymerization and oxidation. Examples of such groupings include unsaturated double bonds and conjugated unsaturated double bonds. For example, we have found that furfural possesses a greater solvent power for unsaturated fatty acid monoesters than for the more saturated fatty acid monoesters. On the other hand, hydrocarbons such as hexane and benzene are excellent solvents for both saturated and unsaturated monoesters of fatty acids. Since hexane and furfural are only slightly miscible at room temperatures, a mixture of monoesters of fatty acids possessing varying degrees of unsaturation will distribute itself between a mixture of hexane and furfural in such a way that the esters contained in the furfural-rich phase possess a higher degree of unsaturation than does that portion of the ester mixture which dissolves in the hexane-rich phase.

The separation of glyceride fats and oils into fractions by means of solvents with which the glycerides are only partially miscible has been described by Bills in the *Journal of Biological Chemistry*, 67, 279-285 (1926). A number of the solvents described in this publication as exhibiting incomplete miscibility with glycerides are listed in Table I.

Table I

|                       |                    |
|-----------------------|--------------------|
| Furfural              | Ethyl lactate      |
| Nitromethane          | Formamide          |
| Acetic acid           | Ethyl acetoacetate |
| Furfuryl alcohol      | Glycerine          |
| Ethylene chlorohydrin | Monoacetin         |
| Methyl alcohol        | Diacetin           |
| Ethyl alcohol         | Triacetin          |
| Ethanolamine          | Ethyl sulfate      |
| Ethylene glycol       | Methyl sulfate     |
| Allyl alcohol         | Pyruvic acid       |

We have found that solvents such as those listed in Table I which possess selective solvent properties for various types of glycerides also exhibit a selective solvent action toward fatty acid monoesters. However, we have further found that many of the usual selective solvents such as furfural, furfuryl alcohol, and ethylene glycol monomethyl ether are completely miscible with monoesters of fatty acids in the temperature ranges in which partial miscibility is observed between the solvents and glycerides of fatty acids. It is therefore advisable to employ a second solvent which is incompletely miscible with the selective solvent but which is miscible with the fatty acid esters. The operation, in this case, results in a distribution of the esters between the two solvent layers in such a way that the esters contained in the respective layers possess different degrees of unsaturation. In some cases, the use of a second solvent can be avoided by adding water to the selective solvent

in order to diminish its ability to dissolve the fatty acid esters.

Additional solvents which can be used in the fractionation step of our process are listed in Table II, but our process is operable using any of a large number of solvents of which those listed in Tables I and II are only examples.

Table II

|    |                                  |
|----|----------------------------------|
| 10 | Ethylene glycol monomethyl ether |
|    | Sulfur dioxide                   |
|    | Dichlorodiethyl ether            |
|    | Tetrahydrofurfuryl alcohol       |
|    | Methyl formate                   |
| 15 | Methyl lactate                   |
|    | Acetamide                        |
|    | Acetonitrile                     |
|    | Diacetone                        |
|    | Ethyl oxalate                    |
| 20 | Acetaldehyde                     |

When it is desired to employ a second solvent in this step of the process, hydrocarbons, such as hexane, cetane, and benzene are satisfactory in most cases, although any liquid which is not completely miscible with the particular selective solvent used and which possesses the required solubility for fatty acid esters is also suitable. For example, Chlorex (dichlorodiethyl ether), although completely miscible with glyceride oils and with the corresponding fatty acid monoesters, can be employed in conjunction with a hydrocarbon to fractionate fatty acid monoesters.

The particular temperatures and solvent ratios to be used in the extraction equipment depend upon the equilibrium relationships of the particular system chosen. Examples of satisfactory operating temperatures and solvent ratios for furfural-hydrocarbon and methyl cellosolve-hydrocarbon systems for the extraction of ethyl esters of soybean acids are described in the following examples:

*Example 1.*—To illustrate the fractionation step in our process, 47.5 grams of the mixed ethyl esters derived from soybean oil was thoroughly agitated with 116 grams of furfural and 32 grams of a commercial grade of mixed pentanes and hexanes, at 85° F. The esters were then recovered from each of the two liquid layers. Of the esters thus recovered, 29 percent was in the lower or furfural-rich layer, and when the solvent was removed this fraction had an iodine value of 130.1. The upper or hydrocarbon-rich layer contained the other 71 percent of the original esters which, when the solvent was removed, had an iodine value of 118.3. The iodine value of the original mixture of esters was 121.8.

*Example 2.*—In a similar experiment, 47.5 grams of the above-described ethyl esters of soybean acids was mixed with 116 grams of furfural and 575 grams of the hydrocarbon solvent. Approximately 2 percent of the recovered esters was in the furfural-rich layer and possessed an iodine value of 134.8. The remaining 98 percent of the recovered esters was removed from the hydrocarbon layer and had an iodine value of 121.6.

*Example 3.*—From a mixture consisting of 142 grams of the same monoesters, 290 grams of ethylene glycol monomethyl ether (Methyl Cellosolve), 1,920 grams of the hydrocarbon solvent, and 5 grams of distilled water, at 85° F., there were obtained from the Methyl Cellosolve-rich layer approximately 1 gram of esters having an iodine value of 127.4 and, from the hydrocarbon-

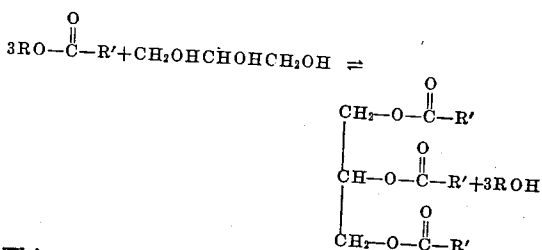
rich layer, approximately 141 grams of esters having an iodine value of 120.8.

*Example 4.*—At 85° F., a mixture of 712 grams of the above-mentioned monoesters, 1,160 grams of furfural, and 1,600 grams of pentanes and hexanes was separated and yielded, from the furfural-rich layer, 5.1 percent of the original esters having an iodine value of 137.0. The remaining 94.9 percent of the esters remained in the hydrocarbon-rich layer and possessed an iodine value of 120.8. The extract layer, or furfural-rich layer, was further extracted with 980 grams of fresh hydrocarbon solvent. The new extract layer contained 7.7 percent of the esters which remained in the first extract layer and had an iodine value of 146.3. The remaining 92.3 percent of the first extract was recovered from the raffinate layer and possessed an iodine value of 136.3.

The foregoing are examples of batch operation. Much more efficient separation and increased yields can be secured in the liquid-liquid extraction step of the process by use of an apparatus for carrying it out on a continuous, countercurrent scale. This may consist of any of the numerous devices in common use for securing intimate contact between immiscible liquids in countercurrent flow and subsequently separating them. For example, a packed tower or a bubble-cap column may be employed in which a hydrocarbon solution of fatty acid esters flows upward against a downward counterflow of solvent. The contacting device may also consist of a series of alternate mixing and settling tanks, suitably connected to permit a countercurrent flow of the incompletely miscible liquid phases. In some cases, it is advantageous to replace the settling tanks with continuously operating centrifuges in order to effect a more rapid and more efficient separation of the phases.

After the extraction process, the solvents may be removed from the esters by any known methods such as distillation, washing with water, and combinations of distillation and washing.

In our invention, the final step in the preparation of polyhydric fatty acid esters consists in a catalytic alcoholysis of the monoester fractions by means of polyhydric alcohols such as glycerine, mannitol, erythritol, arabitol, sorbitol, and xylitol. The reaction with glycerine is as follows:



This reaction is carried out in apparatus and under conditions which are similar to those employed in the initial alcoholysis step of our process, but it is necessary to operate under conditions which permit the removal of alcohol formed by the reaction in order to force the reaction toward completion. The removal of the alcohol produced is effected, for example, by carrying out the reaction at a temperature at which the alcohol may be distilled as it is produced. Since this reaction is substantially the reverse of the initial alcoholysis step in our process, the same catalysts are effective.

Soybean oil may be separated into two frac-

tions, the separation being accomplished by furfural extraction of a hexane solution of methyl esters of the fatty acids derived from the soybean oil. Methanol and soybean oil are heated in the presence of a catalyst in a reaction kettle, and after the reaction is substantially complete, the glycerine produced and the excess of methanol are washed out of the resulting mixture of fatty acid methyl esters by means of water. The washings are subsequently fractionally distilled in a recovery system to reclaim the methanol and glycerine which are returned to the system. The methyl esters are passed through a vacuum drier where final traces of moisture are removed.

In many cases it is advantageous to distill the monoesters, but is possible to omit the still and to feed the dried methyl esters directly to the extraction column. The use of the still is often desirable in order to increase the purity of the product, and it is also possible to design such distillation apparatus to effect a separation of the monoesters into fractions having different fatty acid chain lengths. For example, the palmitic acid esters may be separated from the esters of stearic, oleic, linoleic, and linolenic acids. The combination of fractional distillation with selective solvent extraction therefore affords a convenient and efficient means for controlling both the chain length and the degree of unsaturation in the acyl radicals which compose the ultimate products.

In the extraction column the methyl esters are dissolved in hexane and countercurrently extracted with furfural. The raffinate layer leaves the column near the top and consists of a hexane solution of relatively saturated methyl esters along with small amounts of furfural. The extract layer is removed from the bottom of the column and consists of a furfural solution of relatively unsaturated monoesters along with small amounts of hexane. The raffinate and extract layers are treated in separate fractional distillation columns, the furfural and hexane being distilled, condensed, and returned to the extraction column.

The fractions of monoesters obtained from the raffinate and extract layers pass to separate reaction kettles in which they catalytically react with stoichiometric amounts of glycerine obtained from the glycerine recovery system. In order to bring this reaction to completion, the methanol generated by the reaction is distilled from the resulting glycerides and returned to the methanolysis reaction kettle.

The glycerides produced in one reaction kettle have a much lower iodine value than the original soybean oil and are accordingly much more suitable for use in the manufacture of vegetable oil shortenings, margarine, and similar edible products. The glycerides produced in the other reaction kettle, on the other hand, have a very high iodine value and possess bodying and drying properties which make them much more valuable than the original soybean oil for use in the manufacture of varnishes, paints, linoleum, and similar products.

In some oils, such as tung oil and dehydrated castor oil, double bonds occur in conjugated positions. By means of our process, the monoesters produced from such oils may be separated into fractions having different concentrations of conjugated double bonds so that the polyesters finally produced from the extract phase have remarkable drying properties.

It is possible to separate the glycerides occur-

ring in an oil such as soybean oil by subjecting the oil itself to the action of selective solvents. By such a process, it is possible to split soybean oil into fractions containing, on the one hand, glycerides of relatively highly unsaturated fatty acids and, on the other hand, glycerides composed of the more saturated acids. This method, however, is subject to severe limitations imposed by the mixed condition in which the glycerides are synthesized in nature. For example, a consideration of the amounts of the various acids present in soybean oil glycerides reveals that the only single acid present in sufficient quantity to permit the existence of appreciable amounts of its triglyceride is linoleic acid. The amounts of trilinolenin, triolein, tristearin, and tripalmitin present in soybean oil appear to be so small that, for most practical purposes, their presence is negligible.

Consideration of the work of Hilditch as described in the Journal of the Society of Chemical Industry, 53T, 13-21 (1934) indicates that soybean oil can contain very little glyceride material having an iodine value greater than 173, which is the theoretical value for trilinolenin. It appears that between 30 and 40 percent of the glycerides in soybean oil are either trilinolenin or glycerides having an equivalent number of double bonds and, accordingly, the same iodine value as trilinolenin. The latter type of glyceride is exemplified by the glyceride molecule which contains one each of oleic, linoleic, and linolenic acid radicals.

Soybean oil, on the other hand, contains little glyceride material possessing an iodine value lower than 88 which is the theoretical value of triolein. Although substantially no triolein is present in soybean oil, it appears that approximately 35 to 50 percent of a typical soybean oil is present as glycerides having the same number of double bonds as triolein. This glyceride material consists, for the most part, of glyceride molecules containing one each of linoleic, oleic, and saturated fatty acid radicals.

These considerations impose definite limitations both upon the degree of unsaturation and upon the yields which are theoretically obtainable by subjecting soybean oil glycerides to the action of selective solvents. Furthermore, carrying out a selective solvent extraction upon soybean oil glycerides by means of an immiscible solvent or combination of solvents presents numerous practical difficulties which still further restrict the yields and degrees of unsaturation attainable in the end products.

The method which we propose completely avoids fractionation difficulties caused by the mixed condition in which the fatty acids occur as glycerides, and it provides an efficient and convenient method of separating glycerides more effectively than can be accomplished by extraction of the glycerides themselves.

The foregoing examples are to be considered only as illustrations of the proposed process, and numerous modifications may be made therein without departure from the spirit of the invention or the scope of the following claims.

Having thus described our invention, what we claim for Letters Patent is:

1. A method of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule which consists of alcoholysis of the glycerides thereby producing fatty acid esters having less than three fatty acid ester link-

ages per molecule, thence fractionating the esters resulting from said alcoholysis by means of a solvent system wherein the esters are distributed between incompletely miscible liquid phases, thence separating the phases, and subjecting the ester fractions contained therein to alcoholysis by means of a polyhydric alcohol having at least three hydroxy groups.

2. A method of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule which consists of alcoholysis of the glycerides by a monohydric alcohol, thence fractionating the esters resulting from said alcoholysis by means of a solvent system wherein the esters are distributed between incompletely miscible liquid phases, thence separating the phases, and thence subjecting the ester fractions contained therein to alcoholysis by means of a polyhydric alcohol having at least three hydroxy groups.

3. A method of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule, which consists of alcoholysis of the glycerides by means of a polyhydric alcohol thereby producing fatty acid monoesters of the polyhydric alcohol, thence fractionating the monoesters by means of a solvent system wherein the esters are distributed between incompletely miscible liquid phases, thence separating the phases, and thence alcoholizing the ester fractions contained therein by means of a polyhydric alcohol having at least three hydroxy groups.

4. A process of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule, which consists of alcoholysis of the glycerides, thereby producing fatty acid esters having less than three fatty acid ester linkages per molecule, thence separating the esters resulting from said alcoholysis into fractions, one of which contains a higher concentration of unsaturated valence bonds and another of which contains a lesser concentration of unsaturated valence bonds, said fractionation being effected by treating the esters with a solvent system wherein the esters are distributed between incompletely miscible liquid phases, thence separating the phases, and thence subjecting their respective contents of fatty acid esters to alcoholysis with polyhydric alcohols having at least three hydroxy groups.

5. A process as defined in claim 1 in which the fatty acid glycerides are soybean oil.

6. A process as defined in claim 1 in which the fatty acid glycerides are cottonseed oil.

7. A process as defined in claim 1 in which the fatty acid glycerides are linseed oil.

8. A process of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule which consists of alcoholysis of the glycerides, thereby producing fatty acid esters having less than three fatty acid ester linkages per molecule, thence fractionating the esters resulting from said alcoholysis by means of a solvent system wherein the esters are distributed between incompletely miscible phases, said solvent system consisting of a single solvent which is incompletely miscible with the esters, thence separating the phases, and thence subjecting the ester fractions contained therein to alcoholysis by means of a polyhydric alcohol having at least three hydroxy groups.

9. A process of converting fatty acid glycerides into fractions of fatty acid polyhydric esters having at least three fatty acid ester linkages per molecule, which consists of alcoholysis of the glycerides, thereby producing fatty acid esters having less than three fatty acid ester linkages per molecule, thence fractionating the esters resulting from said alcoholysis by means of a solvent system wherein the esters are distributed between incompletely miscible phases, said solvent system consisting of two incompletely miscible liquids between which the fatty acid esters are distributed in accordance with their solubilities in the respective solvents, thence separating the respective solvent phases from each other, and thence subjecting the ester fractions contained therein to alcoholysis by means of a polyhydric alcohol having at least three hydroxy groups.
10. A process as defined in claim 8 in which the solvent is furfural containing less than 5 percent of dissolved water.
11. A process as defined in claim 8 in which the solvent is ethylene glycol monomethyl ether containing less than 5 percent of dissolved water.
12. A process as defined in claim 8 in which the solvent is tetrahydrofurfuryl alcohol containing less than 10 percent of dissolved water.
13. A process as defined in claim 9 in which the two immiscible liquids are furfural and a hydrocarbon.
14. A process as defined in claim 9 in which the two immiscible liquids are ethylene glycol monomethyl ether and a hydrocarbon.
15. A process as defined in claim 9 in which the two immiscible liquids are dichlorodiethyl ether and a hydrocarbon.
16. A process as defined in claim 1 in which the initial alcoholysis is performed with methyl alcohol.
17. A process as defined in claim 1 in which the initial alcoholysis is performed with ethyl alcohol.
18. A process as defined in claim 1 in which the initial alcoholysis is performed with propyl alcohol.
19. A process as defined in claim 1 in which the final alcoholysis is accomplished using glyc-  
erine.
20. A process as defined in claim 1 in which the final alcoholysis is accomplished using man-  
nitol.
21. A process as defined in claim 1 in which the final alcoholysis is accomplished using sorbitol.
22. A process as defined in claim 4 in which the unsaturated valence bonds are in the non-  
conjugated position.
23. A process as defined in claim 4 in which the unsaturated double bonds are in the con-  
jugated position.
24. A process for selectively separating glycer-  
ide fats and oils into fractions, one of which is more highly unsaturated and another of which is more highly saturated than the original glycerides, which consists of alcoholysis of the glycerides to produce fatty acid monoesters, frac-  
tionating the monoesters with a solvent system consisting of a pair of incompletely miscible liquids between which the esters are distributed, separating the resulting liquid phases, and sub-  
jecting the respective fractions of esters to alco-  
holysis by means of glycerine, thereby producing fatty acid triglycerides.
25. A method of selectively separating mixtures of fatty acid esters having less than three fatty acid ester linkages per molecule into fractions, one of which contains a high concentration of relatively active groupings and another which contains a lesser concentration of such groupings, which consists of treating the mixture of esters with a solvent system wherein the esters are distributed between incompletely miscible liquid phases, separating the phases, and removing the solvent system.
26. A method of selectively separating fatty acid monoesters into fractions, one of which contains a high concentration of relatively unsaturated valence bonds and another which contains a lesser concentration of unsaturated valence bonds, which consists of treating the monoesters with a solvent system wherein the monoesters are distributed between incompletely miscible liquid phases, separating the phases, and removing the solvent system.
27. A method of selectively separating fatty acid monoesters into fractions, one of which contains a high concentration of relatively unsaturated valence bonds and another which contains a lesser concentration of unsaturated valence bonds, which consists of treating said fatty acid monoesters with a pair of incompletely miscible liquids, one of which possess a greater affinity for unsaturated groupings than does the other, separating the two liquid phases, and removing the solvents.
28. A method of selectively separating fatty acid monoesters into fractions, one of which contains a high concentration of unsaturated valence bonds and another which contains a lesser concentration of unsaturated valence bonds, which consists of treating said fatty acid monoesters with a solvent under conditions in which incomplete miscibility exists, separating the resulting liquid phases, and removing the solvents.
29. A process as defined in claim 28 in which immiscibility is obtained by addition of water.
30. A process as defined in claim 27 in which the pair of incompletely miscible liquids consists of furfural and a hydrocarbon.
31. A process as defined in claim 27 in which the pair of incompletely miscible liquids consists of dichlorodiethyl ether and a hydrocarbon.
32. A process as defined in claim 27 in which the pair of incompletely miscible liquids consists of a nitroparaffin and a hydrocarbon.

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