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TREATING FATS AND FATTY OILS

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The present invention relates to a process for preparing fatty esters and, more particularly, to an improved process for preparing fatty acid alkyl esters from low grade fats and fatty oils.

The prior art has taught that a fat or fatty oil can be reacted with an alcohol in the presence of a small amount of an alcoholysis catalyst to produce alkyl esters of the fatty acid and glycerine. The catalyst employed may be either alkaline or acidic in nature, the selection of a suitable catalyst being governed in each particular case by the conditions to be met by the operator.

In general, alkaline alcoholysis proceeds at a considerably higher rate than acid alcoholysis, say, about ten to about fifty times as fast, and with far less danger of corrosion, especially under high temperature conditions such as are disclosed by Harold Dwaine Allen and William Ashley Kline in United States patent application Serial No. 481,080 (filed March 30, 1943.) However, acid alcoholysis enjoys certain advantages over the use of an alkaline catalyst when low grade fats and fatty oils are employed as starting materials. If alkaline alcoholysis is carried out when the glyceride treated contains free fatty acid, the free fatty acid present destroys the alkaline catalyst by reacting with it to form soap, and, when sufficient alkaline catalyst is employed to provide excess alkali above that destroyed by large amounts of free fatty acid present, a large amount of soap forms and gels or is otherwise objectionable. This problem does not arise with acid alcoholysis, as any free fatty acid present is esterified during the alcoholysis reaction.

It is an object of the present invention to provide a novel method of preparing alkyl esters, by alkaline alcoholysis, from fats and fatty oils having a relatively high free fatty acid content.

It is another object of the invention to provide a rapid and improved process for utilizing fatty glycerides containing large amounts of free fatty acid in an alcoholysis reaction, especially under high temperature conditions, without subjecting reaction coils and vessels to acid corrosion.

A further object of this invention is to provide a new method for pretreating fats and fatty oils having a relatively high content of free fatty acids whereby the glycerides (or other fatty acid ester of a higher alcohol) can be reacted with a short-chain monohydric alcohol in the presence of an alkaline alcoholysis catalyst to form alkyl esters and glycerine (or other higher alcohol) without objectionably high soap formation.

Other objects and advantages of the invention will be apparent from the following description.

According to the present invention, a fatty acid ester of a higher alcohol (e. g., a glyceride) containing free fatty acids is contacted with an alcohol in the presence of an acidic esterification catalyst. After the esterification reaction has proceeded to a point where the free fatty acid content has been reduced to a tolerable proportion or less, an alkaline agent is added in an amount sufficient to neutralize the acid esterification catalyst and any free fatty acids still contained in the glyceride (or other ester of a higher alcohol) and to provide an excess of alkaline catalyst for an alcoholysis reaction. The alkaline alcoholysis is carried out in any desired manner, and preferably at high temperatures, as described by Allen and Kline in their application Serial No. 481,080.

It is an advantage of this pretreatment process that the free fatty acids present can be esterified with the alcohol to form alkyl esters, so that only a relatively small amount of alkaline catalyst need be added in the alcoholysis treatment, irrespective of the proportion of free fatty acid originally present in the glyceride. In this manner, the amount of soap formed is held to a permissible amount, and an alkaline alcoholysis can be rapidly and economically carried out without intermediate processing and without removal of esters or of excess unreacted alcohol.

In carrying out the pretreatment, the glyceride (or other ester) containing free fatty acids is contacted with an alcohol, preferably in sufficient amount to esterify the free fatty acids present. An acid esterification catalyst is added, and the mixture may be kept at ambient temperatures or may be heated to any temperature desired for the purpose of obtaining more rapid esterification. Thus, the temperature of the pretreatment may vary from about 20° C. to about 150° C., although lower and higher temperatures are also operable, and the time of pretreatment may vary from less than a minute at high temperatures to a couple of days or more at low temperatures. The pretreatment may be carried out in batch, intermittent or continuous operation and at reduced pressures, at atmospheric pressure or at superatmospheric pressures, although it is preferred to provide a pressure sufficient to maintain a liquid alcohol phase at the temperature employed.

In a preferred procedure, sufficient alcohol to provide an excess over that required for esterification of the free fatty acids is added to the fat or fatty oil in a storage tank, preferably of stainless steel or glass-lined, together with an acid catalyst, and the liquid body thus formed is made up about two or three days before the fatty material is re-

quired in an alcoholysis process and is permitted to stand during such interval at about room temperature, preferably with slow agitation. The fatty material, containing esters, is then drawn from the storage tank and is mixed with the alcohol required for alcoholysis and with enough alkaline material to neutralize the mixture and to provide a sufficient excess of alkaline agent to serve as an alkaline alcoholysis catalyst.

The fatty material pretreated by the process may be any of those suitable for alcoholysis to form alkyl esters. These include natural fatty acid esters, such as the fats and fatty oils used by the soap-making art, or any other fatty acid ester of a higher alcohol, such as glycerol or other polyhydric alcohols or long-chain (say, about twelve to about twenty carbons) monohydric alcohols, or mixtures of these esters, especially glycerides of fatty acids having about eight to about twenty-six, and preferably about twelve to about twenty, carbon atoms per molecule of fatty acid. Although an oil containing substantially no moisture is preferred, because the presence of water decreases the yield of esters in the subsequent alkaline alcoholysis, free fatty acid may be present in the fatty material in any proportion. For this reason, low grade and degraded oils of all kinds may be used. The esters which may be pretreated by the present process include tallow, wool fat, spermaceti, palm oil, olive oil, coconut oil, cottonseed oil, corn oil, tung oil, soya bean oil, Chinese vegetable tallow, whale oil, shark, menhaden and other fish oils, garbage grease, etc.

In carrying out the pretreatment according to this invention, an alcohol suitable for reacting with free fatty acid present with the ester is employed. The alcohol used can be either the same as that to be employed in the subsequent alcoholysis reaction or may be any other alcohol and, if the same alcohol is employed, the total amount to be used both for the esterification pretreatment and the alcoholysis can be added at the same time. Alternatively, sufficient alcohol may be used to carry out the esterification of the free fatty acid, with additional alcohol introduced subsequently for the alcoholysis. Any of the alcohols suitable for the alcoholysis reaction may be suitably used in the pretreatment, short-chain aliphatic monohydric alcohols, including aryl-substituted aliphatic alcohols, being preferably employed, particularly the saturated, primary alcohols, especially alcohols having a boiling point in the presence of water in excess of the azeotropic composition of lower than 100° C. at atmospheric pressure, and, more particularly, the lower alcohols having one to about six carbon atoms per molecule. Thus, alcohols satisfactory for use in forming esters with the free fatty acids present in the glycerides or other oils pretreated include such low molecular weight monohydric alcohols as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, secondary butyl alcohol, tertiary butyl alcohol, the amyl alcohols, benzyl alcohol, etc. While any proportion of fatty material and alcohol may be used, it is preferred to employ an amount of alcohol at least about 50% in excess of the calculated theoretical amount necessary for esterification of the free fatty acids present, and particularly satisfactory results have been obtained when using an excess of at least three to seven times the stoichiometric amount required. It will be understood that, when it is desired to add sufficient alcohol initially to take care of the subsequent alcoholysis reaction, a larger amount of alcohol is introduced.

Among the acidic esterification catalysts which have been found suitable for use in the present pretreating process are hydrochloric acid, trichloracetic acid, aluminum chloride, boron trifluoride, phosphoric acid, sulphuric acid, glycerine monoacid sulphate, alkyl sulphuric acids, organic sulphonic acids, etc. While it is possible to obtain good yields of esters with proportions of catalysts up to about 0.30 mol per mol of free fatty acid and higher, it is preferred to use large excesses of alcohol and to introduce relatively small amounts of catalysts, say of the order of about 0.03 mol to about 0.10 mol per mol of free fatty acid. A convenient way of introducing the catalyst into the fatty oil is in admixture with and, where practical, advantageously in solution in the alcohol employed.

The presence of water decreases the yield of esters in alkaline alcoholysis, and therefore it is preferable to employ a fatty oil containing substantially no moisture, although small amounts of water can be tolerated when carrying out the alcoholysis with the lower alcohols, such as methyl or ethyl alcohol and especially methanol. The esterification with an alcohol of free fatty acid present in the oil results in the formation of a molecule of water for each molecule of ester formed. Where the fatty oil contains a high proportion of free fatty acid, the amount of water formed during the esterification may be in excess of the maximum water content desired for the subsequent alkaline alcoholysis.

When the water content after esterification is in excess of the maximum desired, the water may be removed, at least in major part, by passing the material through a dehydrating agent such as anhydrous sodium sulphate or by distilling off sufficient wet alcohol from the mixture to reduce the water to a point where it may be tolerated. The latter method is particularly applicable when alcohols higher than methyl alcohol are used for the esterification. In an alternative procedure, a second solvent, such as benzene, may be added to the liquid body to form a ternary mixture with water and alcohol, and the water may then be readily distilled off. A preferred method of reducing the water for the alcoholysis reaction is to provide an alcoholysis catalyst which will react with the water present, especially when the water content is only slightly above the proportion tolerated. Suitable alcoholysis catalysts for effecting such removal of water include alkali metal alcoholates having one to about six carbon atoms per molecule, especially sodium methylate and sodium ethylate, which form sodium hydroxide and alcohol upon reaction with water.

The following examples illustrate this invention, but the invention is not limited thereby.

Example I

About 200 parts by weight of unbleached palm oil containing 50.8% of free fatty acids are mixed with 144 parts of methanol containing 1.5 parts of concentrated sulphuric acid. The mixture is stirred and heated at the reflux temperature of the methanol (about 69° C.) for a period of an hour, and the solution is neutralized with sodium hydroxide to a phenolphthalein end point. The mixture is then treated with 2.5 parts of sodium methylate and is stirred for an hour at about

50° C. The product is then acidified with 10% sulphuric acid, is washed with water until neutral, is dried over anhydrous sodium sulphate and is filtered. About 100 parts by weight of the dried product are vacuum distilled under an absolute pressure of 4 mm. of mercury. A yield of 97% of distillable esters is obtained, and the acid value of the distillate is equivalent to about 5% palmitic acid.

Example II

About 150 parts by weight of hardened (hydrogenated) fish oil containing approximately10% of free fatty acid are contacted with 42 parts of methyl alcohol and 1.2 parts of concentrated sulphuric acid. The mixture is heated to the refluxing temperature of the methanol for about an hour, and 42 additional parts of methyl alcohol containing 2.5 parts of sodium hydroxide are introduced. This amount of sodium hydroxide is sufficient to neutralize the mixture and to leave an excess above the amount required for neutralization of about 1.5 parts of sodium hydroxide, which serves as an alcoholysis catalyst. The mixture is again heated to the refluxing temperature of the methanol and is stirred at this temperature for about forty-five minutes. It is acidified with acetic acid and washed until neutral. The esters are distilled, and a yield of esters equivalent to approximately 96.5% of the calculated theoretical yield is obtained.

Example III

About 100 parts by weight of coconut oil containing 19.7% of free fatty acids are mixed with 72 parts of methyl alcohol and 0.5 part of concentrated sulphuric acid, and the mixture is heated to 60° C. and stirred at that temperature for an hour. Water is then added, and the reaction mixture is washed in a separatory funnel. The washed product is dried over anhydrous sodium sulphate and is filtered. The free fatty acid is converted to the methyl esters, with only a content of about 0.45% of free fatty acid remaining in the fatty oil. An alkaline catalyst and additional methyl alcohol are then added to the mixture, and the coconut oil is converted to the corresponding methyl esters.

Example IV

Ethyl alcohol is introduced into a storage tank containing tallow of about 24% free fatty acid content, the alcohol being added in the ratio of 1 part by weight of ethyl alcohol to about 5 parts of the tallow. Concentrated sulphuric acid is also introduced into the storage tank in the ratio of 1 part of acid to 300 parts of tallow. The mixture is permitted to stand in the storage tank for three days, being agitated during this period by slow transfer of material from the bottom to the top of the tank, and is then run into a homogenizer at the rate of 300 pounds per minute. About 150 pounds per minute of ethyl alcohol containing 3.5% of sodium ethylate are also run into the homogenizer, and the materials are mixed together for about two minutes. This mixture is then run into a reaction coil having a holding time of about thirty seconds, and the temperature is raised to about 130° C., sufficient pressure being maintained in the coil to keep ethyl alcohol in the liquid state. The effluent from the coil is flashed into a vaporization chamber which is maintained at about 133° C. and at atmospheric pressure. Excess ethyl alcohol is volatilized, and the remaining material is passed to an acidification tank, whereafter it is acidified, washed, dried and distilled. A yield of esters equivalent to about 98% of the calculated theoretical yield is obtained.

Example V

Tallow having a free fatty acid content of 15.5% is pumped at a rate of 208 parts by weight per minute through a preheater, where its temperature is raised to 124° C., and into a mixing chamber. About 100 parts per minute of 99.8% methanol are heated to approximately the same temperature under sufficient pressure to keep the alcohol in the liquid phase, and are pumped into the mixing chamber. The tallow and methanol are thoroughly mixed with 2.5 parts of a 25% solution of 95.5% sulphuric acid in glycerol, and the mixing chamber is of sufficient size to provide a holding time of about five minutes. The mixture flows continuously into a pump, where it is treated with 13 parts per minute of 15% sodium hydroxide in methanol, and the effluent flows into a reaction coil, through which it passes in about six minutes. While in the coil, the temperature is kept at 120° C. and the pressure at about 190 pounds per square inch absolute. The material from the coil is run through a preheater, wherein its temperature is raised to 125° C., and it is then flashed into a heated vaporization chamber maintained at atmospheric pressure. Unreacted methyl alcohol is volatilized off, and a yield of methyl esters of tallow fatty acids equivalent to more than 95% of the calculated theoretical yield is obtained.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

I claim:

1. The process which comprises treating a fatty acid ester of a higher alcohol containing free fatty acid with an alcohol in the presence of an acidic esterification catalyst, and thereafter reacting said fatty acid ester of a higher alcohol with an aliphatic monohydric alcohol having one to about six carbon atoms per molecule in the presence of sufficient alkaline agent to neutralize any acid present and to provide an alkaline alcoholysis catalyst.

2. The process which comprises treating a fatty glyceride containing free fatty acid with low molecular weight monohydric alcohol in the presence of an acidic esterification catalyst, thereafter reacting said fatty glyceride with low molecular weight monohydric alcohol in the presence of sufficient alkaline agent to neutralize any acid present and to provide an alkaline alcoholysis catalyst whereby a liquid body containing an ester of fatty acid from said glyceride with said alcohol and glycerine is produced, and recovering said ester and glycerine from said liquid body.

3. The process which comprises treating a fatty glyceride containing free fatty acid with a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an acidic esterification catalyst to produce a liquid mass containing a fatty glyceride and an alkyl ester; thereafter contacting said liquid mass with a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an amount of an alkaline alcoholysis catalyst in excess of

the amount required to neutralize any acid present in said mass, whereby a liquid body containing alkyl esters and glycerine is produced; and recovering alkyl esters and glycerine therefrom.

4. The process set forth in claim 3 wherein the alcohol employed is methyl alcohol and wherein the alkyl esters produced are methyl esters.

5. The process set forth in claim 3 wherein the alcohol employed is ethyl alcohol and wherein the alkyl esters produced are ethyl esters.

6. The process set forth in claim 3 wherein the alkaline alcoholysis catalyst employed is an alkali metal alcoholate having one to about six carbon atoms per molecule.

7. A process for treating fatty materials which comprises contacting fatty glycerides containing free fatty acids with a saturated, straight-chain, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an acidic esterification catalyst to produce a liquid mass containing fatty glycerides, alkyl esters and water; removing water from said liquid mass; contacting said liquid mass with a saturated, straight-chain, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an alkaline alcoholysis catalyst, said alkaline alcoholysis catalyst being introduced in excess of the amount required to neutralize said liquid mass, whereby a liquid body containing alkyl esters and glycerine is produced; and recovering alkyl esters and glycerine therefrom.

8. A process for producing alkyl esters which comprises treating a fatty glyceride containing free fatty acids with an amount of a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in excess of that required for esterification of free fatty acids present, in the presence of an acidic esterification catalyst and for a time sufficient to esterify a major portion of the free fatty acids present at the operating conditions, whereby a liquid mass containing fatty glycerides, alkyl esters and water is produced; neutralizing said liquid mass; removing water therefrom; reacting said liquid mass with a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an alkaline alcoholysis catalyst to produce a liquid body containing alkyl esters and glycerine; and recovering alkyl esters and glycerine therefrom.

9. The process set forth in claim 8 wherein water is removed from the liquid mass by introducing therein an alkali metal alcoholate having one to about six carbon atoms per molecule.

10. A process for producing methyl esters which comprises treating a fatty glyceride containing free fatty acids with an amount of methyl alcohol in excess of the amount required for esterification of free fatty acids present, in the presence of an acid esterification catalyst and for a time sufficient to esterify a major portion of the free fatty acids present at the operating conditions, whereby a liquid mass containing fatty glyceride, methyl esters and water is produced; introducing an amount of sodium methylate in excess of the amount required to neutralize said liquid mass; reacting said liquid mass containing excess sodium methylate with methyl alcohol to produce a liquid body containing methyl esters and glycerine; and recovering methyl esters and glycerine therefrom.

11. A process for producing ethyl esters which comprises treating a fatty glyceride containing free fatty acids with an amount of ethyl alcohol in excess of the amount required for esterification of free fatty acids present, in the presence of an acid esterification catalyst and for a time sufficient to esterify a major portion of the free fatty acids present at the operating conditions, whereby a liquid mass containing fatty glyceride, ethyl esters and water is produced; neutralizing said liquid mass; removing water therefrom; reacting said liquid mass with ethyl alcohol in the presence of an alkaline alcoholysis catalyst to produce a liquid body containing ethyl esters and glycerine; and recovering ethyl esters and glycerine therefrom.

12. In a process for producing alkyl esters of fatty acids comprising reacting a fatty acid ester of a higher alcohol with an aliphatic monohydric alcohol having one to about six carbon atoms per molecule in the presence of an alkaline alcoholysis catalyst, the improvement which comprises pretreating said fatty acid ester of a higher alcohol with an alcohol in the presence of an acidic esterification catalyst to esterify free fatty acid contained therein, and thereafter introducing sufficient alkaline agent to neutralize any acid present and to provide an alkaline alcoholysis catalyst.

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