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(54) **Process for refining fat.**

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Description

BACKGROUND OF THE INVENTION

Field of the Invention :

This invention relates to a process for refining a fat. More particularly, it relates to a process for removing and separating partial glyceride(s) and/or free fatty acid(s) from an oleaginous mixture comprising a fat and the partial glyceride(s) and/or free fatty acid(s).

Description of the Prior Art :

It is known that partial glycerides, in particular, diglycerides (DG) present in a fat for hard butter would significantly deteriorate the physical properties thereof. It is believed that this phenomenon is caused by the fact that DG inhibits the transformation of crystals. Thus the presence of DG makes the tempering step in the production of chocolate extremely troublesome.

A product obtained by, for example, transesterifying a fat with the use of lipase contains DG at a high concentration.

These partial glycerides may be removed by, for example, column chromatography or distillation. However these methods are disadvantageous from the economic viewpoint. Thus there has been developed no process for removing partial glycerides on an industrial scale hitherto (cf. Japanese Patent Publication No. 27159/1982).

Further, in the case of a fat for hard butter, it is necessary to remove partial glycerides in such a manner as not to cause any change in the triglyceride composition thereof.

Solvent fractionation of fats using acetone is known e.g. from GB-A-1.539.032, and FR-A-911.371. These documents do not, however, mention liquid-liquid extraction.

Known methods for separating an oleaginous mixture comprising fatty acids and triglycerides as main components, e.g., a fat having an extremely high acid value or a product obtained by transesterifying fatty acids with glycerides, into fatty acids and triglycerides on an industrial scale include alkali deacidification and steam distillation. Although the former method, i.e., alkali deacidification can be applied to an oleaginous mixture of a relatively low fatty acid content, it can not be applied to those having a high fatty acid content since considerable amounts of the acids are incorporated in the foots formed thereby to bring about a significant loss in the yield of the acids.

On the other hand, in the latter method, i.e., steam distillation, the fatty acids and partial glycerides contained in the oleaginous mixture reside within a still for a prolonged period of time and thus suffer from thermal changes in the triglyceride composition. Therefore it is impossible to obtain a preferable triglyceride composition thereby. According to Hickman's theory, the rate of thermal decomposition is doubled for each 10 °C rise in temperature and the decomposition rate is proportional to the residence time in a distillation process in general (cf. Chem. Rev., 54. 51 (1944)). Thus it is necessary to shorten the period of time during which the oleaginous mixture is exposed to a high temperature, since side reactions could be inhibited only to a limited extent by merely lowering the boiling point of the mixture under a high-vacuum condition to thereby effect the distillation at a lower temperature.

In addition to the above methods, fatty acids may be removed by adsorbing the same by column chromatography. Although this method is available in a laboratory, the high cost thereof makes it inavailable at present on an industrial scale.

Further Japanese Patent Publication No. 40000/1986 teaches that free fatty acids can be distilled off during removal of partial glycerides by molecular distillation. However the molecular distillation in the above case is carried out using a falling film type molecular still and the acid value of the starting fat is 10 at the highest. It is impossible to appropriately treat an oleaginous mixture of a high acid value containing free fatty acids at a high concentration by the method as described in Japanese Patent Publication No. 40000/1986.

Free fatty acids may be removed from an oleaginous mixture by liquid/liquid extraction with the use of a solvent. The liquid/liquid extraction (in particular furfural extraction), which is known as a method for purifying a liquid mixture which can be hardly separated by distillation, has been employed for deacidifying or deodorizing cod-liver oil. Recently, however, liquid/liquid extraction has been scarcely applied to oleaginous products, since it is difficult to handle an extraction solvent. In liquid/liquid extraction, furfural and propane are frequently employed. Although it has been reported that the liquid/liquid extraction with various solvents including those described above is applied in fractionating fats and oils, separating highly

unsaturated acid oils or separating fatty acid methyl esters, there are unexpectedly few reports on the application thereof to the separation of triglycerides and fatty acids.

SUMMARY OF THE INVENTION

Accordingly it is an object of the present invention to provide a process for removing free fatty acid(s), together with partial glyceride(s) from an oleaginous mixture on an industrial scale.

Further it is another object of the present invention to provide a process for separating free fatty acid(s) and triglyceride(s) from an oleaginous mixture which has a high acid value and comprises triglyceride(s) and free fatty acid(s) as main components, while minimizing the recovery loss and without causing any change in the triglyceride composition.

These objects have been achieved according to the present invention by providing a process as claimed in claim 1.

DETAILED DESCRIPTION OF THE INVENTION

The acetone to be used in the present invention may be either absolute or aqueous one. Since acetone containing a large amount of water would lower the solubility of a fat and thus sometimes cause liquid/liquid separation, it is desirable that acetone contains 2% or below, preferably 0.5% or below, of moisture.

The solvent, i.e., acetone, may be used in an amount of one to ten parts (by weight; the same will apply hereinbelow), preferably three to six parts, per part of the oleaginous mixture.

It is preferable that the oleaginous mixture to be refined by the process of the present invention comprises 2% or more of partial glyceride(s). Generally speaking, the content of partial glyceride(s) of 5 to 6% or more would deteriorate the physical properties of triglyceride(s), in particular, a hard butter. In contrast thereto, the content of the partial glyceride(s) less than 2% hardly affects the properties of the triglyceride(s).

According to the process of the present invention, partial glyceride(s) can be efficiently separated from an oleaginous mixture comprising 5% or more of the same.

The oleaginous mixture to be refined by the acetone solvent fractionation step may comprise 20% or less of free fatty acid(s). When the content of tree fatty acid(s) exceeds 20%, it is difficult to concentrate most of the free fatty acid(s) in the liquid phase.

The solvent-fractionation with acetone as effected in the process of the present invention includes the following three steps: dissolving an oleaginous mixture in acetone and cooling the obtained solution to thereby precipitate crystals: separating the liquid phase from the solid phase, i.e., the crystals, and washing the latter; and finally removing the solvent from each phase. In the first cooling step, 0.2 to 2.0%, based on the oleaginous mixture, of crystalline seeds, which have been preliminarily obtained by supercooling a fat, are added to the solution at a temperature higher than the crystallizing temperature by 1 to 8 °C, while slowly cooling the solution, thus accelerating the crystallization and giving crystals which can be readily separated. The crystalline seeds may be prepared from any fat so long as it is insoluble in the solvent under the above conditions.

When the oleaginous mixture to be refined has an acid value as high as 50 or above, it is desirable to pretreat it for removing free fatty acid(s) therefrom to thereby lower the acid value thereof to 40 or below, preferably 25 or below, prior to the solvent-fractionation as mentioned above.

This is achieved using liquid/liquid extraction.

Examples of the solvent to be used in the above liquid/liquid extraction are furfural, n-propyl alcohol, propionitrile, hexane, acetone, methanol and ethanol. One of these solvents may be used alone. Alternately, a mixture thereof or an aqueous solvent may be employed.

The liquid/liquid extraction may be carried out with the use of an extractor such as a mixer-settler extractor, a spray tower, a packed column, a perforated-plate extractor or a baffle tower, a rotary extractor, a rotary disc tower, a Scheibel column or a pulsed extraction column. The mixing ratio of the oleaginous mixture to the extraction solvent may be arbitrarily altered.

The extraction temperature, which significantly affects the extraction efficiency, is preferably within a range of 10 to 50 °C.

Thus it is possible to remove the free fatty acid(s) from the oleaginous mixture by the liquid/liquid extraction to thereby lower the acid value of the mixture to a level at which conventional alkali deacidificaiton can be carried out.

In the solvent fractionation step, the partial glyceride(s) and/or free fatty acid(s) including DG are concentrated in the solvent phase, i.e., the liquid phase, and thus can be readily separated from the

triglyceride(s) constituting the crystalline phase, i.e., the solid phase, by using acetone as a solvent.

The process for refining a fat of the present invention, which is not accompanied by any change in the triglyceride composition, is particularly effective in refining a fat having a concentration of partial glyceride-(s) elevated by hydrolysis, or a product having a high acid value which is obtained by transesterifying a fat with lipase (EC: 3.1.1.3), which is a hydrolase for fats and oils, as a catalyst.

According to the refining process of the present invention, free fatty acid(s) and triglyceride(s) can be separated from an oleaginous mixture, which comprises free fatty acid(s) at a high concentration and thus has a high acid value, while minimizing the recovery loss and without causing any change in the triglyceride composition.

To further illustrate the present invention, and not by way of limitation, the following Examples will be given. Examples 1 and 2 each refer to a pretreatment step for removing most of free fatty acids from an oleaginous mixture comprising free fatty acids at a high concentration by liquid/liquid extraction. On the other hand, Example 3 refers to a process for removing partial glycerides and the residual free fatty acids from the oleaginous mixture, from which some portion of the free fatty acids has been removed in the above pretreatment, by solvent-fractionation with the use of acetone.

Example 1

Seven parts of stearic acid and ten parts of the medium-melting fraction of palm oil were transesterified in hexane solvent in the presence of lipase originating from Rhizopus delemar to give a reaction product which was an oleaginous mixture of a high acid value, i.e., 84 and comprising 43% of free fatty acids. This reaction product was converted into a trimethylsilane derivative and then subjected to gas chromatography. As a result, it was found that the above reaction product comprised 39.2% of fatty acids, 0.3% of monoglycerides, 6.3% of diglycerides and 54.2% of triglycerides.

The reaction product was subjected to liquid/liquid extraction to thereby remove the free fatty acids therefrom.

As the extraction solvent, methanol was employed at a ratio to the reaction product of 1 : 4. The extraction was carried out at 45° C. Thus the free fatty acids were concentrated in the methanol phase. The two phases were separated with the use of a separatory funnel and the solvent was distilled off from both the oily and methanol phases. The yield of the oily phase, i.e., an oleaginous mixture was 60% and the acid value thereof was lowered to 7.5. The recovery yield of the triglycerides was 89%.

Comparative Example 1

The reaction product used in Example 1 was deodorized in a conventional manner by steam distillation to thereby remove the free fatty acids therefrom. The distillation residue thus obtained had an acid value of 15, was significantly colored and showed a largely altered triglyceride composition.

Example 2

The procedure of Example 1 was followed except that 15% aqueous ethanol was employed as the extraction solvent. Thus the free fatty acids were removed. The yield of the oily phase, i.e., an oleaginous mixture was 58.8% and the acid value thereof was lowered to 12.5. The recovery yield of the triglycerides was 96%.

Example 3

One part of the oleaginous mixture as obtained in Example 1, from which same portion of the free fatty acids had been removed to give a composition of 4% of free fatty acids, 6.8% of diglycerides and 89.2% of triglycerides, was completely dissolved in three parts of acetone containing 0.15% of moisture at 40° C to give a micelle mixture. This micelle mixture was cooled under stirring while adding crystalline seeds, which had been preliminarily prepared by supercooling 0.005 part of the micelle mixture, thereto at 22° C (seeding). Subsequently the mixture was slowly cooled to 18° C to thereby precipitate crystals. After further cooling, the mixture was maintained at 2° C for one hour and then filtered. The crystalline phase thus obtained was washed to prepare a high-melting fraction.

The solvent phase, i.e., the liquid phase as obtained above was completely dissolved in five parts of acetone containing 0.15% of moisture at 40° C to give a micelle mixture. This micelle mixture was cooled under stirring while adding crystalline seeds, which had been preliminarily prepared by dissolving 0.005 part

of the micelle mixture in 0.05 part of acetone and precipitating crystals at 10 °C, thereto at 18 °C. Then the mixture was further cooled slowly to 2 °C under stirring. After maintaining at 2 °C for one hour, the mixture was filtered. The crystalline phase thus obtained was washed to prepare a medium-melting fraction. The solvent was distilled off from the solvent (liquid) phase in a conventional manner to prepare a low-melting fraction.

Table 1 shows the yield and analytical data of each fraction thus obtained. The content of each of the partial glycerides and free fatty acids was determined by TLC/FID method with the use of Iatroscan TH-10 (mfd. by Iatron).

Table 2 shows the analytical data on the composition of the fatty acids at the 2-position of the triglycerides of each fraction as well as those in the total triglycerides of the combined fractions.

Comparative Example 2

The free fatty acids and partial glycerides present in the oleaginous mixture used in Example 3 were removed therefrom by molecular distillation. The distillation was carried out at a temperature of 250 °C and a degree of vacuum of 5×10^{-3} Torr. In spite of the fact that the content of the partial glycerides was lowered to 2%. the triglyceride composition of the mixture was significantly altered (cf. Table 2). This result suggests that transesterification might occur at the high temperature.

Table 1

	Yield (%)	Composition(%)		
		Partial glyceride	Free fatty acid	Triglyceride
Starting material	-	6.8	4.0	89.2
High-melting fraction	11.0	1.3	0.5	98.2
Medium-melting fraction	41.0	0.4	0.1	99.5
Low-melting fraction	48.0	13.5	8.2	78.3

Table 2

Composition of fatty acids at 2-position of triglycerides						
	Starting material	Ex.				
		*1	*2	*3	*4	Comp. Ex. 2
14:0	0.2	0.1	0.1	0	0.05	0
16:0	8.5	20.0	7.2	7.4	8.8	15.2
18:0	0.6	18.5	3.2	1.9	4.4	16.4
18:1	69.9	56.4	80.3	62.7	69.05	56.3
18:2	21.0	5.1	9.2	28.0	17.7	12.1

*1 : Triglycerides in high-melting fraction.
*2 : Triglycerides in medium-melting fraction.
*3 : Triglycerides in low-melting fraction.
*4 : Total triglycerides.

Claims

1. A process for refining a fat which comprises removing free fatty acid(s) from an oleaginous mixture, containing partial glyceride(s) and/or free fatty acid(s), through liquid/liquid extraction and then removing the partial glyceride(s) and/or the residual free fatty acid(s) from the oleaginous mixture through solvent-fractionation with the use of acetone in an amount of 1 to 10 parts by weight per 1 part of the oleaginous mixture and with the addition of crystalline seeds
characterized in that

an oleaginous mixture is used having an acid value of 50 or above and that the acid value of the oleaginous mixture is adjusted to 25 or below through the liquid/liquid extraction prior to the solvent-fractionation.

Revendications

1. Un procédé de raffinage d'une graisse qui comprend l'extraction d'acide(s) gras libre(s) d'un mélange oléagineux, contenant un (des) glycéride(s) partiel(s) et/ou un(des) acide(s) gras libre(s), au moyen d'une extraction liquide/liquide et l'extraction ensuite de(s) glycéride(s) partiel(s) et/ou de l'acide (des acide) gras libre(s) résiduel(s) du mélange oléagineux par fractionnement par solvant en utilisant de l'acétone en une quantité de 1 à 10 parties en poids pour 1 partie du mélange oléagineux et en ajoutant des germes cristallins
caractérisé en ce que
le mélange oléagineux utilisé a un indice d'acidité de 50 ou plus et que l'indice d'acidité du mélange oléagineux est ajusté à 25 ou moins au moyen de l'extraction liquide/liquide avant le fractionnement par le solvant.

Patentansprüche

1. Ein Verfahren zum Raffinieren von Fett, das umfaßt

Entfernen von freier bzw. freien Fettsäure(n) aus einer öligen Mischung, enthaltend partielle(s) Glycerid-(e) und/oder freie Fettsäure(n), durch Flüssig-Flüssigextraktion und dann Entfernen des bzw. der partiellen Glyceride und/oder der restlichen freien Fettsäure(n) aus der öligen Mischung durch Lösungsmittelfraktionierung unter Verwendung von Aceton in einer Menge von 1 bis 10 Gewichtsteilen der öligen Mischung und unter Zusatz von Impfkristallen,

dadurch gekennzeichnet,

daß eine ölige Mischung mit einem Säurewert von 50 oder darüber verwendet wird, und daß der Säurewert der öligen Mischung auf 25 oder weniger eingestellt wird durch die Flüssig-Flüssigextraktion vor der Lösungsmittelfraktionierung.