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- (54) METHOD FOR PRODUCING REFINED PALM-BASED FAT/OIL, AND METHOD FOR REDUCING GLYCIDOL, 3-CHLOROPROPANE-1,2-DIOL AND FATTY ACID ESTERS THEREOF AND/OR DIGLYCERIDES IN REFINED PALM-BASED FAT/OIL

VERFAHREN ZUR HERSTELLUNG VON RAFFINIERTEM PALMFETT/-ÖL UND VERFAHREN ZUR REDUZIERUNG GLYCIDOL, 3-CHLORPROPAN-1,2-DIOL UND FETTSÄUREESTERN DAVON UND/ODER DIGLYCERIDEN IN RAFFINIERTEN PALMFETT/-ÖL

PROCÉDÉ DE PRODUCTION D'UNE GRAISSE/HUILE RAFFINÉE ISSUE DE PALME, ET PROCÉDÉ DE RÉDUCTION DU GLYCIDOL, DU 3-CHLOROPROPANE-1,2-DIOL ET DES ESTERS D'ACIDES GRAS DE CELUI-CI ET/OU DES DIGLYCÉRIDES DANS LA GRAISSE/HUILE RAFFINEE ISSUE DE PALME

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- (56) References cited: WO-A1-2015/073359
 - DATABASE WPI Week 201077, Derwent World Patents Index; AN 2010-N74336, XP002792769
 - DATABASE WPI Week 201381, Derwent World Patents Index; AN 2013-V89049, XP002792770

- DATABASE WPI Week 201129, Derwent World Patents Index; AN 2011-D79416, XP002792771
- DATABASE WPI Week 201340, Derwent World Patents Index; AN 2013-K26494, XP002792772
- LIN SIEW WAI, YOO CHEAH KIEN: "Short-path distillation of palm olein and characterization of products", EUROPEAN JOURNAL OF LIPID SCIENCE AND TECHNOLOGY, vol. 111, 2009, pages 142 - 147, XP093011561
- YEOH CHIOU MOI, PHUAH ENG TONG, TANG TECK KIM, SIEW WAI LIN, ABDULLAH LUQMAN CHUAH, CHOONG THOMAS SHEAN YAW: "Molecular distillation and characterization of diacylglycerol-enriched palm olein", EUR. J. LIPID SCI. TECHNOL., vol. 116, 2014, pages 1654 - 1663, XP055401953
- YANG TIANKUI, ZHANG HONG, MU HUILING, SINCLAIR ANDREW J., XU XUEBING: "Diacylglycerols from butterfat: Production by glycerolysis and short-path distillation and analysis of physical properties", JAOCS, vol. 81, 2004, pages 979 - 987, XP008064608
- PUDEL, F. ET AL.: "3-MCPD- and glycidyl esters can be mitigated in vegetable oils by use of short path distillation", EUROPEAN JOURNAL OF LIPID SCIENCE AND TECHNOLOGY, vol. 118, no. 3, 13 June 2015 (2015-06-13), pages 396 - 405, XP055417264, ISSN: 1438-7697

 MATTHAEUS, B. ET AL.: "Mitigation of 3-MC and glycidyl esters within the production ch of vegetable oils especially pa", LIPID TECHNOLOGY, vol. 25, no. 7, 10 July 2013 (2013-07-10), pages 151 - 155, XP055110706, ISSN: 0956-666X 	nain

Description

TECHNICAL FIELD

[0001] The present invention relates a method of producing a refined palm-based fat and/or oil, and a method of reducing glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and/or diglyceride in the refined palm-based fat and/or oil.

BACKGROUND ART

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[0002] Fats and/or oils contain trace components which may be implicated in physiology activities. These trace components include glycidol, 3-chloropropane-1,2-diol, fatty acid esters thereof. The above trace components are suspected to be linked with nutritional problems, but unlikely constitute a direct threat to health as long as they are in those levels where they are included in fats and/or oils such as plant oils which have a good track record in ingestion through diets over a period of many years. In line with this, the tolerable upper intake level and other standards are not established. However, due to the demands for safer fats and/or oils, various methods of reducing the aforementioned components in fats and/or oils have been proposed.

[0003] Glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof are known to be generated during a deodorizing step and other. Moreover, diglyceride is a known agent responsible for 3-chloropropane-1,2-diol (Nonpatent Document 1). It is recognized that a high concentration of 3-chloropropane-1,2-diol tends to be present in diglyceride-rich fats and/or oils, particularly in refined palm-based fats and/or oils (palm oil, palm kernel oil). Accordingly, Patent Document 1, for example, provides a method of reducing glycidol, 3-chloropropane-1,2-diol, fatty acid esters thereof, in fats and/or oils such as palm oil, the method including: bleaching a deodorized oil with white clay at a pH of 5 to 7; and further performing deodorization. Patent Document 2 provides a method of controlling an increase in glycidol and fatty acid esters thereof, the method including: performing deodorization at a high temperature and a high vapor amount.

Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2014-047290 Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2013-112761

[0004] Non-Patent Document 1: LWT-Food Science and Technology 42 (2009) 1751-1754

[0005] Furthermore WO2015/073359 discloses obtaining a refined fat and/or oil by performing short-path distillation treatment. As the conditions of the short-path distillation treatment, this document discloses possibly being a temperature of 90 to 270°C (paragraph [0017]), and pressure less than 1 mbar (= 100 Pa) (paragraph [0020]). However, this document does not disclose feeding rate per unit area of an evaporation surface.

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0006] However, glycidol may not be sufficiently reduced in the deodorizing step due to prolonged exposure of a fat and/or oil to a high temperature. Therefore, there have been demands for a method capable of reducing generation of glycidol in a step other than the deodorizing step.

[0007] The present invention is made in view of the aforementioned circumstances. An object of the present invention is to provide a method of producing a refined palm-based fat and/or oil in which the contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and/or diglyceride can be reduced.

Means for Solving the Problems

[0008] The present investors found that the above problems can be solved by adjusting a temperature condition for thinfilm distillation treatment in a method of producing a refined palm-based fat and/or oil including the thin-film distillation treatment. Then, the present invention has been completed. Specifically, the present invention can provide the method as provided in claims 1 to 7.

Effects of the Invention

[0009] According to an embodiment of the present invention, provided is a method of producing a refined palm-based fat and/or oil, in which the contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and/or diglyceride can be reduced.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0010] Below, the embodiments of the present invention will be described, but the present invention shall not be limited to the following embodiments.

[Thin-film distillation treatment]

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[0011] The method of produce according to the present invention includes a step of performing thin-film distillation treatment of a raw material palm-based fat and/or oil at a temperature condition of 270 °C or more and 290°C or less to obtain a refined palm-based fat and/or oil. Below, the thin-film distillation treatment and palm-based fats and/or oils used for the present invention will be described in detail.

[0012] According to an embodiment of the present invention, a raw material palm-based fat and/or oil is subjected to thin-film distillation treatment. The term "thin-film distillation treatment" as used herein means that a raw material palm-based fat and/or oil is allowed to form a thin-film, and heated under a reduced pressure to effect evaporation. A residue (a thin-film distillated fat and/or oil) in which a distillate is separated from the raw material palm-based fat and/or oil can be obtained through the above treatment. The distillate may contain fatty acid, monoglyceride, and/or diglyceride. The residue may contain triglyceride. The term "refined palm-based fat and/or oil" as used herein refers to a palm-based fat and/or oil (a thin-film distillated fat and/or oil) subjected to at least thin-film distillation treatment.

[0013] After conducting extensive studies, the present investors found that generation of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof can be reduced by adjusting a temperature condition to 270 °C or more and 290 °C or less when thin-film distillation treatment of a raw material palm-based fat and/or oil is performed. It is noted that hereinafter "3-chloropropane-1,2-diol" may also be referred to as "3-MCPD."

[0014] The temperature condition for the thin-film distillation treatment in the present invention corresponds to a temperature at an evaporation surface of a thin-film distillator. That is, the phase "the temperature condition for thin-film distillation treatment is 270 °C or more and 290°C or less" means that the temperature at an evaporation surface of a thin-film distillator is 270 °C or more and 290°C or less. For example, the temperature condition for thin-film distillation treatment corresponds to an evaporator tube temperature when the thin-film distillation treatment is performed with a short-path distillator.

[0015] A temperature condition of 155°C or more for thin-film distillation treatment can remove thermally unstable substances, high-boiling point substances, included in a raw material palm-based fat and/or oil while efficiently suppressing generation of a trace component such as glycidol, 3-MCPD, and fatty acid esters thereof in the raw material palm-based fat and/or oil. In view of an improved efficiency of distillation, the temperature condition for thin-film distillation treatment is 190°C or more. The features disclosed in paragraph [0015] are not part of the invention.

[0016] A temperature condition of 290°C or less for thin-film distillation treatment enables efficient distillation of a fat and/or oil while suppressing generation of a trace component such as glycidol, 3-MCPD, and fatty acid esters thereof, which tend to be generated at a high temperature condition.

[0017] The degree of vacuum in the present invention is preferably close to 0 (zero) Pa because a trace component such as glycidol, 3-MCPD, and fatty acid esters thereof; thermally unstable substances; high-boiling point substances; can be removed more easily. Specifically, the thin-film distillation treatment in the present invention is performed under a degree of vacuum of 0.3 Pa or less.

[0018] It is noted that the "degree of vacuum" as used herein is expressed in accordance with the absolute pressure. The value is expressed relative to the absolute vacuum which is considered as zero, and represents how close to the ideal vacuum state (the absolute vacuum).

[0019] The processing time for thin-film distillation treatment refers to a period of time while a fat and/or oil stays on an evaporation surface of a thin-film distillator. There is no particular limitation for the processing time, but it may be preferably 1 second or more, more preferably 3 seconds or more in order to effect sufficient distillation. Further, the processing time for thin-film distillation treatment is preferably 5 minutes or less, more preferably 3 minutes or less, even more preferably 1 minute or less, and most preferably 30 seconds or less in order to reduce heat effects on a raw material palm-based fat and/or oil.

[0020] The processing time for thin-film treatment is related to the processing rate for thin-film treatment. The processing rate for thin-film treatment can be expressed in terms of the "oil feeding rate per unit area of an evaporation surface." The term "oil feeding rate per unit area of an evaporation surface" as used herein refers to a value obtainable by dividing the feeding rate of a raw material palm-based oil/fat per hour by the area of the evaporation surface. The "oil feeding rate per unit area of an evaporation surface" in an embodiment of the present invention is $2.00 \times 10^{-3} \, \text{L/h·cm}^2$ or more, preferably $7.00 \times 10^{-3} \, \text{L/cm}^2$ or more in order to reduce heat effects on a raw material palm-based fat and/or oil. Further, the "oil feeding rate per unit area of an evaporation surface" is $10.0 \times 10^{-3} \, \text{L/h·cm}^2$ or less in order to effect sufficient distillation.

[0021] The types of thin-film distillation include molecular distillation which is performed under high vacuum (< 0.1 Pa) and in which a condenser is arranged within a distance shorter than the mean free path of evaporating molecules; and

short-path distillation which is performed at 0.1 Pa or more and in which a condenser is arranged at around a distance equal to the mean free path of evaporating molecules. The short-path distillation treatment is preferably performed in an embodiment of the present invention in view of high efficiency of distillation.

[0022] There is no particular limitation for a thin-film distillator used in thin-film distillation treatment, but evaporators of falling liquid film, centrifugal, rising liquid film, wiped film, may be used. Wiped film evaporators are preferred because the residence time of a raw material palm-based fat and/or oil within a thin-film distillator can be short enough to reduce heat effects on a raw material palm-based fat and/or oil. There is no particular limitation for a material of an evaporation surface of a thin-film distillator, but those made of glass or stainless steel may be used.

[0023] There is no particular limitation for the timing to perform thin-film distillation treatment in a refinement step of a palm-based fat and/or oil.

[0024] As described below, a raw material palm-based fat and/or oil may be pre-treated through a refinement step other than thin-film distillation treatment, or unrefined. A raw material palm-based fat and/or oil pre-treated through a deodorizing step is preferred because the contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride can be reduced more easily by thin-film distillation treatment. A raw material palm-based fat and/or oil without pre-treatment in a deodorizing step may also be used. In this case, the content of diglyceride may be reduced more easily by thin-film distillation treatment, and a deodorizing step may be then performed after the thin-film distillation treatment to effect more efficient reduction of the contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof.

[0025] For a raw material palm-based fat and/or oil pre-treated through a refinement step other than thin-film distillation treatment, thin-film distillation treatment may be performed at any timing after the respective refinement step (one or more of a degumming step, a deacidifying step, a water-washing step, a bleaching step, a deodorizing step, a fractionating step). The resulting fat and/or oil obtained after thin-film distillation treatment may be directly distributed as a refined palm-based fat and/or oil, or may be subjected to an additional refinement step. For example, when the raw material palm-based fat and/or oil is a palm-based fat and/or oil obtained through a deodorizing step, the palm-based fat and/or oil may be subjected to a fractionating step after thin-film distillation treatment.

[0026] When the raw material palm-based fat and/or oil is an unrefined palm-based fat and/or oil, the resulting fat and/or oil after thin-film distillation treatment may be directly distributed as a refined palm-based fat and/or oil, or may be subjected to an additional refinement step.

[0027] There is no particular limitation for the conditions for each refinement step (a degumming step, a deacidifying step, a water-washing step, a bleaching step, a deodorizing step, a fractionating step) other than thin-film distillation treatment, but conditions commonly used in refinement of fats and/or oils may be used.

[Raw material palm-based fat and/or oil]

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[0028] Palm-based fats and/or oils use for an embodiment the present invention include fats and/or oils from palm. Specifically, palm-based fats and/or oils include, for example, palm oil, palm kernel oil, fractionated oils of palm kernel oil, hydrogenated oils of palm oil, hydrogenated oils of palm kernel oil, hydrogenated oils of fractionated oils of palm kernel oil, hydrogenated oils of fractionated oils of palm kernel oil, and transesterified oils thereof. It is noted that fractionated oils of palm oil include super olein, palm olein, palm mid fraction, and palm stearin. Fractionated oils of palm kernel oil include palm kernel olein and palm kernel stearin.

[0029] There is no particular limitation for the raw material palm-based fat and/or oil to be subjected to the aforementioned thin-film distillation treatment, but palm-based fats and/or oils may be used which are pre-treated through a refinement step (a degumming step, a deacidifying step, a water-washing step, a bleaching step, a deodorizing step, a fractionating step, and/or the like) other than thin-film distillation treatment, or unrefined palm-based fats and/or oils may be used. As described above, the raw material palm-based fat and/or oil is preferably a palm-based fat and/or oil pre-treated through a deodorizing step. There is no particular limitation for the method of refining a fat and/or oil, but it may be either chemical refinement (chemical refining) or physical refinement (physical refining). It is noted that in the former chemical refinement, a crude oil obtained by squeezing/extracting plant as a raw material is refined by performing degumming treatment, alkali deacidification treatment, bleaching treatment, dewaxing treatment, deodorizing treatment to obtain a refined fat and/or oil. In contrast, in the latter physical refinement, a crude oil is refined by performing degumming treatment, non-alkali deacidification treatment such as distillation, bleaching treatment, deodorizing treatment to obtain a refined fat and/or oil. It is noted that a fat and/or oil pre-treated through a degumming step, a bleaching step, a deodorizing step is called an RBD (Refined Bleached Deodorized) oil.

[0030] There is no particular limitation for the properties of a raw material palm-based fat and/or oil, but the iodine value is preferably less than 58 in view of having less unsaturated fatty acids, less generation of trans-fatty acids, and high oxidation stability.

[0031] The main component of a raw material palm-based fat and/or oil is glyceride, and other components, for example, plant sterol, lecithin, antioxidant components (tocopherol), coloring components may be contained.

[Determination of contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride in refined palm-based fat and/or oil]

[0032] The method of produce according to an embodiment of the present invention can provide a refined palm-based fat and/or oil having reduced contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride. [0033] Specifically, in the method of produce according to an embodiment of the present invention, the total amount of glycidol and fatty acid esters thereof (in terms of glycidol) in a refined palm-based fat and/or oil can be reduced to 50% or less, more preferably 35% or less, and more preferably 20% or less of the total amount of glycidol and fatty acid esters thereof (in terms of glycidol) in a raw material palm-based fat and/or oil. Further, the total amount of 3-chloropropane-1,2-diol and fatty acid esters thereof (in terms of 3-chloropropane-1,2-diol) in a refined palm-based fat and/or oil can be reduced to 95% or less, more preferably 90% or less, and more preferably 60% or less of the total amount of 3-chloropropane-1,2-diol) in a raw material palm-based fat and/or oil. Moreover, the total amount of diglyceride in a refined palm-based fat and/or oil can be reduced to 65% or less, preferably 50% or less, and more preferably 45% or less of the total amount of diglyceride in a raw material palm-based fat and/or oil

[0034] Furthermore, in the method of produce according to an embodiment of the present invention, the acid value, peroxide value of a refined palm-based fat and/or oil can also be reduced. Therefore, the method of produce according to an embodiment of the present invention can provide a highly refined fat and/or oil.

[0035] Still further, in the method of produce according to an embodiment of the present invention, significant coloring of a refined palm-based fat and/or oil can be prevented. The color value (a value computed in accordance with the method described below in Examples) of a refined palm-based fat and/or oil obtained by the method of produce according to an embodiment of the present invention preferably differs from that of a raw material palm-based fat and/or oil by ± 2 and more preferably by ± 1 , and even more preferably it is substantially the same as that of a raw material palm-based fat and/or oil. [0036] The contents of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride in a fat and/or oil as well as the acid value, peroxide value, and color value thereof may be determined according to the methods described in Examples.

EXAMPLES

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[0037] Below, the present invention will be described specifically with reference to Examples Thin film distillation temperature below 190 °C and feeding rate per unit area below 2×10-3 L/h.cm2 are not part of the invention. Examples 1 to 4 and 9 to 12 are not part of the invention.

<Examples 1 to 4>

[0038] A raw material palm-based fat and/or oil (RBD palm oil, iodine value = 52) was introduced to an evaporation surface of a short-path distillator Model KDL5 (UIC GmbH; glass evaporation surface: 480 cm²; condensation surface: 650 cm²; maximum flow rate: 1 L/hr), and thin-film distillation treatment (in this example, short-path distillation treatment) was performed under the conditions shown in Table 1. It is noted that the residence time (that is, the processing time of thin-film distillation treatment) of the raw material palm-based fat and/or oil on the evaporation surface of the short-path distillator was set in the range from 5 seconds to 30 seconds.

[0039] A residue and distillate obtained after performing the short-path distillation treatment under the above conditions were withdrawn. It is noted that the "operation time" in Table 1 refers to the total operation time of the short-path distillator. The term "distillate percentage" refers to a percentage of a distillate over the total amount of the residue and distillate withdrawn. The term "residue percentage" refers to a percentage of a residue over the total amount of the residue and distillate withdrawn.

[Table 1]

	[14515 1]			
Table 1				
	Example 1	Example 2	Example 3	Example
Operation time (minutes)	65	65	65	65
Evaporation tube temperature (°C)	160	200	225	250
Internal condenser temperature (°C)	45	45	45	50
Degree of vacuum (Pa)	6.0	0.1	0.1	0.1
Distillate percentage (% by mass)	0.2	0.3	2.3	8.9

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(continued)

Table 1				
	Example 1	Example 2	Example 3	Example 4
Residue percentage (% by mass)	99.8	99.7	97.7	91.1
Cold trap (% by mass)	0.0	0.0	0.0	0.0
Feeding rate (g/h)	495.3	507.0	503.4	512.1

[0040] The raw material palm-based fat and/or oil before the short-path distillation treatment, and the residues after the short-path distillation treatment (which correspond to a refined palm-based fat and/or oil) were investigated for their physical properties and compositions.

[0041] The results are shown in Table 2.

[Quantification of MCPD-FS]

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[0042] The total amount of 3-MCPD, glycidol, and fatty acid esters thereof in terms of 3-MCPD (the above total amount is referred to as "MCPD-FS") in each refined fat and/or oil was quantified in accordance with the German official method (DGF Standard Methods C-III 18 (09)).

[0043] Specifically, $50~\mu\text{L}$ of an internal standard (a $20~\mu\text{g/mL}$ solution of 3-MCPD-d5) was added to 100~mg of each refined fat and/or oil, and then 1~mL of a sodium methoxide solution (0.5 mol/L methanol) was added. The reaction was allowed at room temperature for saponification decomposition. To this, 3~mL of brine (20%) having a trace amount of acetic acid and 3~mL of hexane were then added and mixed. Subsequently, hexane was removed. This was then derivatized with $250~\mu\text{L}$ of aqueous phenylboric acid (25%), and extracted with 2~mL of hexane, and then measured with an instrument for gas chromatography-mass spectrometry. A chromatogram obtained from the above measurement with an instrument for gas chromatography-mass spectrometry was used to compare the ionic strength of 3-MCPD with that of the internal standard 3-MCPD-d5. Then the total amount of 3-MCPD, glycidol, and fatty acid esters thereof in a fat and/or oil was computed in terms of free 3-MCPD.

[Quantification of true MCPD]

[0044] The total amount of 3-MCPD and fatty acid esters of 3-MCPD in terms of 3-MCPD (the above total amount is referred to as "True MCPD") in each refined fat and/or oil was quantified in accordance with the German official method (DGF Standard Methods C-III 18 (09)).

[0045] Specifically, $50~\mu\text{L}$ of an internal standard (a $20~\mu\text{g/mL}$ solution of 3-MCPD-d5) was added to 100~mg of each refined fat and/or oil, and then 1 mL of a sodium methoxide solution (0.5 mol/L methanol) was added. The reaction was allowed at room temperature for saponification decomposition. To this, 3~mL of aqueous sodium bromide (50%) having a trace amount of acetic acid and 3~mL of hexane were then added and mixed. Subsequently, hexane was removed. This was then derivatized with $500~\mu\text{L}$ of aqueous phenylboric acid (12.5%), and extracted with 2~mL of hexane, and then measured with an instrument for gas chromatography-mass spectrometry. A chromatogram obtained from the above measurement with an instrument for gas chromatography-mass spectrometry was used to compare the ionic strength of 3-MCPD with that of the internal standard 3-MCPD-d5. Then the total amount of 3-MCPD and fatty acid esters of 3-MCPD in a glyceride composition was computed in terms of free 3-MCPD.

[0046] It is noted that the numerical values in the parentheses under the item "True MCPD" in the table below represent the percentage of True MCPD in each refined palm-based fat and/or oil relative to True MCPD in a raw material palm-based fat and/or oil. For example, with reference to Example 1, True MCPD in a refined palm-based fat and/or oil (3.2 mg/kg) is about 94.1% relative to True MCPD in a raw material palm-based fat and/or oil (3.4 mg/kg).

[Calculation of amount of glycidol]

[0047] Using the values for MCPD-FS and True MCPD determined according to the above method, the amount of glycidol in each refined fat and oil (the total amount of glycidol and fatty acid esters thereof in terms of glycidol) was computed based on the following formula.

Amount of glycidol = $(MCPD-FS - True MCPD) \times 0.67$

wherein "0.67" is a value obtained by dividing the molecular weight (74.1) of glycidol by the molecular weight (110.54) of 3-

MCPD.

[0048] It is noted that the numerical values in the parentheses under the item "glycidol" in the table below represent the percentage of the amount of glycidol in each refined palm-based fat and/or oil relative to the amount of glycidol in a raw material palm-based fat and/or oil. For example, with reference to Example 1, the amount of glycidol in a refined palm-based fat and/or oil (0.2 mg/kg) is about 33.3% relative to the amount of glycidol in a raw material palm-based fat and/or oil (0.6 mg/kg).

[Acid value]

[0049] Measurement was performed in accordance with "Standard Methods for the Analysis of Fats, Oils and Related Materials 2.3.1-1996: Acid value," Japan Oil Chemists' Society Ed.

[Peroxide value]

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[0050] Measurement was performed in accordance with "Standard Methods for the Analysis of Fats, Oils and Related Materials 2.5.2.1-2013: Peroxide value," Japan Oil Chemists' Society Ed.

[Quantification of amount of diglyceride]

20 **[0051]** Measurement was performed in accordance with AOCS "Official Method Cd 11b-91, Determination of Mono- and Diglycerides by Capillary Gas Chromatography."

[0052] It is noted that the numerical values in the parentheses under the item "diglyceride" in the table below represent the percentage of the amount of diglyceride in each refined palm-based fat and/or oil relative to the amount of diglyceride in a raw material palm-based fat and/or oil. For example, with reference to Example 1, the amount of diglyceride in a refined palm-based fat and/or oil (7.5 mass%) is about 94.9% relative to the amount of diglyceride in a raw material palm-based fat and/or oil (7.9 mass%).

Table 2 Raw material palm oil Example 1 Example 2 Example 3 Example 4 MCPD-FS (mg/kg) 3.5 3.0 1.9 4.3 True MCPD (mg/kg) 3.4 3.2 (94.1) 2.8 (82.4) 1.7 (50) 0.7(20.6)Glycidol (mg/kg) 0.6 0.2(33.3)0.1 (16.7) 0.1 (16.7) 0.1 (16.7) 0.06 0.03 0.02 0.03 0.02 Acid value Peroxide value 0.4 0.3 0.2 0.2 0.1 Diglyceride (% by mass) 7.9 7.5 (94.9) 7.0 (88.6) 5.1 (64.6) 3.3 (41.8)

[Table 2]

[0053] As shown in Table 2, the method of produce according to an embodiment of the present invention can reduce values of all of MCPD-FS, True MCPD, glycidol, and diglyceride, and thus can reduce the amounts of glycidol, 3-chloropropane-1,2-diol, and fatty acid ester thereof, and diglyceride in a palm-based fat and/or oil.

[0054] The method of produce according to an embodiment of the present invention was also able to reduce the acid values and the peroxide value.

<Examples 5 to 9>

[0055] The following treatment was performed using a short-path distillator Model KD6 (UIC GmbH; stainless-steel evaporation surface; 600 cm²; condensation surface: 600 cm²; maximum flow rate: 14 L/hr) instead of the short-path distillator Model KDL5 used in Examples 1 to 4. A raw material palm-based fat and/or oil (an RBD palm oil, iodine value = 52) was introduced to an evaporation surface of the short-path distillator Model KD6, and thin-film distillation treatment (in this example, short-path distillation treatment) was performed under the conditions shown in Table 3. Specifically, the short-path distillation treatment was performed at a temperature of an evaporation tube of 270°C and at an altered feeding rate of the raw material palm-based fat and/or oil. It is noted that the "oil feeding rate per unit area of an evaporation surface" in Table 3 represents a value obtained by dividing the feeding rate of the raw material palm-based fat and/or oil per hour by the area (in this example, 600 cm²) of the evaporation surface.

[Table 3]

Table 3					
	Example 5	Example 6	Example 7	Example 8	Example 9
Evaporation tube temperature (°C)	270	270	270	270	270
Internal condenser temperature (°C)	60	60	60	60	60
Degree of vacuum (Pa)	0.01	0.01	0.01	0.10	0.31
Distillate percentage (% by mass)	36.8	13.2	10.7	5.8	4.3
Residue percentage (% by mass)	63.2	86.8	89.3	94.2	95.7
Oil feeding rate per unit area of an evaporation surface (× 10 ⁻³ L/h·cm ²)	2.40	6.00	7.20	9.60	11.5

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[0056] The raw material palm-based fat and/or oil before the short-path distillation treatment, and the residues after the short-path distillation treatment from Examples 5 to 9 (which correspond to a refined palm-based fat and/or oil) were investigated for their physical properties and compositions as in Examples 1 to 4. Further, the raw material palm-based fat and/or oil before the short-path distillation treatment, and the residues after the short-path distillation treatment ware measured for chromaticity as described below to compute their color values. The results are shown in Table 4.

[Calculation of color value]

[0057] Chromaticity (Y value, R value) was measured in accordance with "Standard Methods for the Analysis of Fats, Oils and Related Materials 2.2.1-1996: Lovibond method," Japan Oil Chemists' Society Ed, and the obtained chromaticity was used to compute a color value (a value of Y + 10R). A Lovibond colorimeter (cell length: 133.4 mm) was used for the measurement.

[Table 4]

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Table 4 Raw material palm-based fat Example 5 Example 6 Example 7 Example 8 Example 9 and/or oil MCPD-FS (mg/kg) 0.3 0.7 8.0 1.1 1.4 3.1 True MCPD (mg/kg) 2.2 0.1(4.5)0.5 (22.7) 0.6 (27.3) 0.9 (40.9) 1.1 (50.0) 0.1 (16.7) Glycidol (mg/kg) 0.6 0.1 (16.7) 0.1 (16.7) 0.1 (16.7) 0.2 (33.3) 0.05 0.02 0.02 0.02 0.02 0.02 Acid value Diglyceride (% by mass) 7.2 2.6 (36.1) 4.1 (56.9) 2.9 (40.3) 3.8 (52.7) 6.3 (87.5) Color value 28 48 32 30 30 30

[0058] Table 4 shows that similarly to the results from Examples 1 to 4, values of all of MCPD-FS, True MCPD, glycidol, and diglyceride can also be reduced in Examples 5 to 9, and thus the amounts of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride in a palm-based fat and/or oil can be reduced.

<Examples 10 to 13>

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[0059] The following treatment was performed as in Examples 5 to 9 using a short-path distillator Model KD6. A raw material palm-based fat and/or oil (an RBD palm oil, iodine value 52) was introduced to an evaporation surface of the short-path distillator Model KD6, and thin-film distillation treatment (in this example, short-path distillation treatment) was performed under the conditions shown in Table 5. Specifically, the short-path distillation treatment was performed at a "feeding rate per unit area of an evaporation surface" of 7.20×10^{-3} L/h·cm² and at an altered temperature of an evaporation tube.

[Table 5]

Table 5				
	Example 10	Example 11	Example 12	Example 13
Evaporation tube temperature (°C)	210	230	250	290
Internal condenser temperature (°C)	60	60	60	60
Degree of vacuum (Pa)	0.01	0.01	0.01	0.02
Distillate percentage (% by mass)	0	1.4	3.2	31.6
Residue percentage (% by mass)	100	98.6	96.8	68.4
Oil feeding rate per unit area of an evaporation surface (×10-3L/h·cm²)	7.20	7.20	7.20	7.20

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[0060] The raw material palm-based fat and/or oil before the short-path distillation treatment, and the residues after the short-path distillation treatment from Examples 10 to 13 (which correspond to a refined palm-based fat and/or oil) were investigated for their physical properties (including color values) and compositions as in Examples 5 to 9. The results are shown in Table 6.

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[Table 6]

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Table 6					
	Raw material palm oil	Example 10	Example 11	Example 12	Example 13
MCPD-FS (mg/kg)	3.1	2.1	1.9	1.3	0.5
True MCPD (mg/kg)	2.2	1.9 (86.4)	1.5 (68.2)	1.1 (50.0)	0.4 (18.2)
Glycidol (mg/kg)	0.6	0.1 (16.7)	0.1 (16.7)	0.1 (16.7)	0.1 (16.7)
Acid value	0.05	0.03	0.02	0.02	0.02
Diglyceride (% by mass)	7.2	7.0 (97.2)	6.1 (84.7)	4.8 (66.7)	1.9 (26.4)
Color value	28	28	26	28	38

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[0061] Table 6 shows that similarly to the results from Examples 1 to 9, values of all of MCPD-FS, True MCPD, glycidol, and diglyceride can also be reduced in Examples 10 to 13, and thus the amounts of glycidol, 3-chloropropane-1,2-diol, and fatty acid esters thereof, and diglyceride in a palm-based fat and/or oil can be reduced.

40 Claims

1. A method of producing a refined palm-based fat and/or oil, the method comprising a step of performing a thin-film distillation treatment of a raw material palm-based fat and/or oil under temperature conditions of 270°C or more and

290°C or less,

a degree of vacuum close to zero of 0.3 Pa or less, and

an oil feeding rate per unit area of an evaporation surface of 2.00×10^{-3} L/h·cm² or more and 10.0×10^{-3} L/h·cm² or less, to obtain the refined palm-based fat and/or oil,

the total amount of diglyceride in the refined palm-based fat and/or oil being 65% or less of the total amount of diglyceride in the raw material palm-based fat and/or oil.

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2. The method of producing a refined palm-based fat and/or oil according to claim 1, wherein the total amount of glycidol and fatty acid esters thereof in terms of glycidol in the refined palm-based fat and/or oil is 50% or less of the total amount of glycidol and fatty acid esters thereof in terms of glycidol in the raw material palm-based fat and/or oil.

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3. The method of producing a refined palm-based fat and/or oil according to claim 1 or 2, wherein the total amount of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol in the refined palm-based fat and/or oil is 95% or less of the total amount of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters thereof in terms of 3-chloropropane-1,2-diol and fatty acid esters the acid

chloropropane-1,2-diol in the raw material palm-based fat and/or oil.

- **4.** The method of producing a refined palm-based fat and/or oil according to any one of claims 1 to 3, wherein the raw material palm-based fat and/or oil is pre-treated through a deodorizing step.
- 5. The method of producing a refined palm-based fat and/or oil according to any one of claims 1 to 4, wherein the thin-film distillation treatment is short-path distillation treatment.
- **6.** The method of producing a refined palm-based fat and/or oil according to any one of claims 1 to 5, wherein an iodine value of the raw material palm-based fat and/or oil is less than 58.

Patentansprüche

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- 15 1. Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis, wobei das Verfahren einen Schritt der Durchführung einer Dünnschicht-Destillation eines rohen Fetts und/oder Öls auf Palmbasis unter Temperaturbedingungen von 270 °C oder darüber und 290 °C oder darunter,
- einem Vakuumgrad nahe 0,3 Pa oder darunter, und
 einer Ölzufuhrrate pro Flächeneinheit einer Verdampfungsoberfläche von 2,00 × 10⁻³ l/h·cm² oder mehr und
 10,0 × 10⁻³ 1/h·cm² oder weniger umfasst, um das raffinierte Fett und/oder Öl auf Palmbasis zu erhalten,
 wobei die Gesamtmenge an Diglycerid in dem raffinierten Fett und/oder Öl auf Palmbasis 65 % oder weniger der
 Gesamtmenge an Diglycerid in dem rohen Fett und/oder Öl auf Palmbasis beträgt.
- 25 2. Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis nach Anspruch 1, wobei die Gesamtmenge an Glycidol und Fettsäureestern davon, ausgedrückt als Glycidol, in dem raffinierten Fett und/oder Öl auf Palmbasis 50 % oder weniger der Gesamtmenge an Glycidol und Fettsäureestern davon, ausgedrückt als Glycidol, in dem rohen Fett und/oder Öl auf Palmbasis beträgt.
- 30 3. Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis nach Anspruch 1 oder 2, wobei die Gesamtmenge an 3-Chlorpropan-1,2-diol und Fettsäureestern davon, ausgedrückt als 3-Chlorpropan-1,2-diol, in dem raffinierten Fett und/oder Öl auf Palmbasis 95 % oder weniger der Gesamtmenge an 3-Chlorpropan-1,2-diol und Fettsäureestern davon, ausgedrückt als 3-Chlorpropan-1,2-diol, in dem rohen Fett und/oder Öl auf Palmbasis beträgt.
 - **4.** Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis nach einem der Ansprüche 1 bis 3, wobei das rohe Fett und/oder Öl auf Palmbasis durch einen Desodorisierungsschritt vorbehandelt wird.
- 5. Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis nach einem der Ansprüche 1 bis 4, wobei die Dünnschicht-Destillationsbehandlung eine Kurzweg-Destillationsbehandlung ist.
 - **6.** Verfahren zur Herstellung von raffiniertem Fett und/oder Öl auf Palmbasis nach einem der Ansprüche 1 bis 5, wobei ein Jodwert des rohen Fetts und/oder Öls auf Palmbasis weniger als 58 beträgt.

Revendications

- Procédé de production d'une graisse et/ou huile à base de palme raffinée, le procédé comprenant une étape de réalisation d'un traitement par distillation en film mince d'une matière première graisse et/ou huile à base de palme dans des conditions de température de 270°C ou plus et 290°C ou moins,
 - d'un degré de vide proche de zéro de 0,3 Pa ou moins, et d'un débit d'alimentation en huile par unité de surface d'une surface d'évaporation de 2,00×10⁻³ L/h·cm² ou plus et 10,0×10⁻³ L/h·cm² ou moins, pour obtenir la graisse et/ou huile à base de palme raffinée, la quantité totale de diglycéride dans la graisse et/ou huile à base de palme raffinée étant de 65% ou moins de la quantité totale de diglycéride dans la matière première graisse et/ou huile à base de palme.
- 2. Procédé de production d'une graisse et/ou huile à base de palme raffinée selon la revendication 1, dans lequel la

quantité totale de glycidol et d'esters d'acides gras de celui-ci en termes de glycidol dans la graisse et/ou huile à base de palme raffinée est de 50% ou moins de la quantité totale de glycidol et d'esters d'acides gras de celui-ci en termes de glycidol dans la matière première graisse et/ou huile à base de palme.

Procédé de production d'une graisse et/ou huile à base de palme raffinée selon la revendication 1 ou 2, dans lequel la 5 quantité totale de 3-chloropropane-1,2-diol et d'esters d'acides gras de celui-ci en termes de 3-chloropropane-1,2diol dans la graisse et/ou huile à base de palme raffinée est de 95% ou moins de la quantité totale de 3chloropropane-1,2-diol et d'esters d'acides gras de celui-ci en termes de 3-chloropropane-1,2-diol dans la matière première graisse et/ou huile à base de palme.

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- 4. Procédé de production d'une graisse et/ou huile à base de palme raffinée selon l'une quelconque des revendications 1 à 3, dans lequel la matière première graisse et/ou huile à base de palme est prétraitée par une étape de désodorisation.
- 5. Procédé de production d'une graisse et/ou huile à base de palme raffinée selon l'une quelconque des revendications 1 15 à 4, dans lequel le traitement par distillation en film mince est un traitement par distillation à court trajet.
 - 6. Procédé de production d'une graisse et/ou huile à base de palme raffinée selon l'une quelconque des revendications 1 à 5, dans lequel un indice d'iode de la matière première graisse et/ou huile à base de palme est inférieur à 58.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2014047290 A [0003]
- JP 2013112761 A [0003]

WO 2015073359 A [0005]

Non-patent literature cited in the description

- LWT-Food Science and Technology, 2009, vol. 42, 1751-1754 [0004]
- Standard Methods for the Analysis of Fats, Oils and Related Materials 2.3.1-1996: Acid value [0049]
- Standard Methods for the Analysis of Fats, Oils and Related Materials 2.5.2.1-2013: Peroxide value [0050]
- Standard Methods for the Analysis of Fats, Oils and Related Materials 2.2.1-1996: Lovibond method [0057]