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(54) METHOD FOR PRODUCING MONOGLYCERIDE-CONTAINING COMPOSITION

(57) Provided is a method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid in which crystallization at low temperature is more controlled. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid includes the following steps (1) and (2): (1) subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within the range of from 0.1 to 2.0, followed by recovery of unreacted glycerin; and (2) subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction.

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Description

Field of the Invention

[0001] The present invention relates to a method of producing a monoglyceride-containing composition.

Background of the Invention

[0002] As a measure to prevent air pollution, a decrease in sulfur content in gas oil has been promoted on a global scale. The decrease in sulfur content in gas oil leads to a decrease in lubricity of an engine, to thereby cause a trouble such as fuel pump wear.

[0003] A monoglyceride using a tall fatty acid as a constituent fatty acid is widely used as an oiliness improver for gas oil because a hydroxy group thereof adsorbs onto a metal surface and an alkyl group thereof forms an oily film to improve lubricity.

[0004] As a maj or production method for the monoglyceride using a tall fatty acid as a constituent fatty acid, there is given an esterification reaction between glycerin and a fatty acid, or a transesterification reaction between glycerin and a fat or oil. Investigations have been made on a method of increasing a yield of the monoglyceride by, for example, a method involving subjecting a glycerin fatty acid ester and glycerin to a transesterification reaction in the absence of any catalyst while keeping an acid value in the reaction system at 1 mg KOH/g or more (Patent Document 1) or a method involving allowing glycerin and a fatty acid to react with each other through use of a catalyst containing a specific metal (Patent Document 2).

[0005]

[Patent Document 1] JP-A-2003-49192
[Patent Document 2] JP-A-2004-359884

Summary of the Invention

[0006] The present invention provides a method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid, the method comprising the following steps (1) and (2) :

(1) subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within a range of from 0.1 to 2.0, followed by recovery of unreacted glycerin; and
(2) subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction.

Detailed Description of the Invention

[0007] When a monoglyceride is used as an oiliness improver for gas oil, low-temperature resistance as well as lubricating performance is required in practical use. For example, resistance is required even under conditions taking into consideration the use of the monoglyceride particularly in a cold region during a winter period.

[0008] Therefore, the present invention relates to a method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid in which crystallization at low temperature is more controlled.

[0009] The inventors of the present invention made extensive investigations in view of the above-mentioned problem, and as a result, found that in the production of a monoglyceride through an esterification reaction between a tall fatty acid and glycerin, when unreacted glycerin remaining without being used in the esterification reaction was recovered and reused as a raw material for the esterification reaction, the low-temperature precipitation temperature of the monoglyceride using a tall fatty acid as a constituent fatty acid decreased.

[0010] According to the present invention, a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid, the composition having a low cloud point and being excellent in low-temperature resistance, is obtained.

[0011] A method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid (hereinafter abbreviated as "monoglyceride-containing composition") of the present invention comprises the following steps (1) and (2):

(1) subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within the range of from 0.1 to 2. 0, followed by recovery of unreacted glycerin; and
(2) subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction.

[0012] The step (1) is a step of subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within the range of from 0.1 to 2.0, followed by recovery of unreacted glycerin.

[0013] The tall fatty acid to be used in the present invention is preferably a fatty acid obtained from a crude tall oil that is produced as a by-product in the production of kraft pulp using pine wood as a raw material. While the tall fatty acid is sometimes referred to as a tall oil fatty acid, the term "tall fatty acid" is used herein.

[0014] The fatty acid composition of the tall fatty acid, depending on, for example, the habitat of the pine, generally contains oleic acid and linoleic acid as main components, and preferably contains slight amounts of palmitic acid, stearic acid, rosin acid, and unsaponifiables.

[0015] The tall fatty acid to be used in the present invention contains preferably 10 mass% or less, more preferably 6 mass% or less, even more preferably 4 mass% or less of saturated fatty acids in terms of the total of palmitic acid and stearic acid, and preferably 0.3 mass% or more, more preferably 0.6 mass% or more, even more preferably 1 mass% or more of the unsaponifiables, from the standpoint of the control of the precipitation of the monoglyceride-containing composition at low temperature.

[0016] The total amount of palmitic acid and stearic acid in the tall fatty acid is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, even more preferably 1 mass% or more, from the viewpoint of ease of availability.

[0017] In addition, the amount of the unsaponifiables in the tall fatty acid is preferably 4 mass% or less, more preferably 3 mass% or less, even more preferably 2.5 mass% or less, from the viewpoint of ease of availability.

[0018] In addition, the tall fatty acid contains oleic acid and linoleic acid at a total amount of preferably 50 mass% or more, more preferably 60 mass% or more, even more preferably 70 mass% or more, from the viewpoint of lubricity, and of preferably 98 mass% or less, more preferably 95 mass% or less, from the viewpoint of ease of availability.

[0019] The ratio of oleic acid to linoleic acid is preferably 1.6 or less, more preferably 1.3 or less, even more preferably 1 or less.

[0020] In addition, the tall fatty acid contains preferably 1 mass% or more, more preferably 2 mass% or more, even more preferably 4 mass% or more of 5,9,12-octadecatrienoic acid.

[0021] The tall fatty acid to be used in the present invention has an iodine value of preferably 100 gI$_2$/100 gormore, morepreferably 120 g I$_2$/100 g or more, even more preferably 140 g I$_2$/100 g or more, from the standpoint of the control of the precipitation of the monoglyceride-containing composition at low temperature.

[0022] The iodine value is an indicator of the total number of unsaturated double bonds present in a fatty acid, and maybe measured in accordance with "Iodine Value (Wijs-Cyclohexane Method) (2.3.4.1-1996) in the "Standard Methods for the Analysis of Fats, Oils and Related Materials" edited by Japan Oil Chemists' Society.

[0023] The glycerin to be used in the present invention preferably has a purity of 95 mass% or more, from the standpoint of reactivity in esterification.

[0024] In the present invention, as a method of subjecting glycerin and the tall fatty acid to esterification, there are given hitherto known chemical methods and enzymatic methods, and any of the methods maybe used. From the standpoint of industrial efficient productivity, a chemical method is preferred.

[0025] In the step (1), the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], in the esterification reaction is from 0.1 to 2.0 and is preferably 0.2 or more, more preferably 0.3 or more, more preferably 0.4 or more, even more preferably 0.5 or more, from the standpoint of improvement of the productivity of a reaction product, and is preferably 1.8 or less, more preferably 1.5 or less, even more preferably 1 or less, from the standpoint of increase inmonoglyceride purity. In addition, the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], is from 0.1 to 2.0, preferably from 0.2 to 1.8, more preferably from 0.3 to 1. 5, more preferably from 0.4 to 1, even more preferably from 0.5 to 1.

[0026] The ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], is expressed by the following equation.

$$\mathrm{FA/GLY} = (\text{number of moles of fatty acid} + \text{number of moles of monoglyceride} + \text{number of moles of diglyceride} \times 2 + \text{number of moles of triglyceride} \times 3) / (\text{number of moles of glycerin} + \text{number of moles of monoglyceride} + \text{number of moles of diglyceride} + \text{number of moles of triglyceride})$$

[0027] In the step (1), when the esterification reaction is performed by a chemical method, the temperature of the esterification reaction is preferably from 180°C to 300°C, more preferably from 200°C to 280°C, even more preferably from 220°C to 260°C, from the standpoints of: the increase in a reaction rate; and the control of the precipitation of the monoglyceride-containing composition at low temperature.

[0028] In addition, the reaction time is preferably from 0.2 hour to 48 hours, more preferably from 0.5 hour to 24 hours, even more preferably from 1 hour to 12 hours, from the standpoints of : industrial productivity; and the control of the precipitation of the monoglyceride-containing composition at low temperature.

[0029] It is preferred to perform the esterification reaction while removing water generated by the reaction out of the reaction system, from the standpoint of efficiently obtaining the monoglyceride. The water is preferably removed out of the system by, for example, the following method: reduction in pressure; use of an adsorbent, such as a zeolite or molecular sieves; or flowing of a dry inert gas into a reaction tank.

[0030] In addition, when the esterification reaction is performed by a chemical method, a catalyst may be added, or the reaction may be performed in the absence of any catalyst. It is preferred that the reaction be performed in the absence of any catalyst because the need for the removal of the catalyst from the monoglyceride-containing composition is obviated and thus cost can be reduced. When a catalyst is added, a catalyst containing a metal, such as iron, cobalt, or manganese, is preferred from the standpoints of: shortening the reaction time; and alleviating the burden of the removal of the catalyst.

[0031] The amount of the catalyst to be used is preferably from 0.01 ppm to 1,000 ppm, more preferably from 0.1 ppm to 100 ppm.

[0032] The reaction product after the esterification reaction contains a fatty acid and glycerin as unreacted materials, and a triglyceride and a diglyceride as by-products, as well as the monoglyceride. In addition, the reaction product may contain a monoester of a dehydration condensate of glycerin and a fatty acid. In an aspect of the present invention, unreacted glycerin is recovered from the reaction product after the esterification reaction and is reutilized.

[0033] As a method for the recovery of glycerin, for example, there are given: a method involving recovering a glycerin layer by centrifugation; a method involving recovering glycerin by vacuum distillation; a method involving recovering glycerin by water vapor distillation; a method involving recovering a glycerin layer by phase separation; a method involving recovering glycerin by water washing; and a method involving recovering glycerin through use of an adsorbent or the like. The method is not limited thereto, and those methods may be combined. Of those, vacuum distillation is preferably employed for the recovery of glycerin from the standpoint of simplicity. The recovered glycerin contains not only glycerin but also impurities, such as a glycerin condensate produced by a reaction between unreacted glycerin molecules and unsaponifiables derived from the tall oil fatty acid.

[0034] Conditions for the vacuum distillation for the recovery of the glycerin are as described below. The pressure is preferably from 0.1 kPa to 10 kPa, and is more preferably from 0.1 kPa to 5 kPa, from the standpoints of: reducing equipment cost and operating cost; increasingproduction capacity; allowing the optimal selection of temperature; and preventing thermal deterioration.

[0035] The temperature is preferably from 140°C to 260°C, more preferably from 150°C to 250°C, even more preferably from 160°C to 240 °C, from the standpoints of : the inhibition of a side reaction; and the prevention of thermal deterioration. The period of time is preferably from 1 minute to 600 minutes, more preferably from 5 minutes to 300 minutes, even more preferably from 10 minutes to 180 minutes, from the standpoints of: the inhibition of a side reaction; and the prevention of thermal deterioration.

[0036] As a vacuum distillation apparatus, there are given a batch simple distillation apparatus, abatch rectification apparatus, a continuous rectification apparatus, a flash evaporator, a thin-film evaporator, and the like. Batch vacuum distillation is preferred because a series of processes starting with the esterification reaction and ending with the vacuum distillation can be performed in one tank. When the reaction product is heated under reduced pressure and a generated glycerin vapor is cold-trapped, the glycerin vapor returns to a state of liquid glycerin, again. The method is a separation method utilizing a difference in vapor pressure between the monoglyceride-containing composition and glycerin. In addition, from the standpoint that thermal deterioration by distillation can be prevented, a thin-film evaporator may be used. The thin-film evaporator is an evaporator configured to form a distillation raw material into a thin film, and heat the thin film to evaporate a distillate. As the thin-film evaporator, there are given a centrifugal thin-film distillation apparatus, a falling film distillation apparatus, a wiped film evaporator (wiped film distillation), and the like, depending on methods of forming a thin film. Of those, from the standpoint of preventing local overheating to avoid thermal deterioration of a reaction oil and the like, a wiped film evaporator is preferably used. The wiped film evaporator is an apparatus configured to flow a distillation raw material in the form of a thin film on the inside of a cylindrical evaporation surface, stir the thin film with a wiper, and heat the thin film from outside to evaporate a distillate.

[0037] The step (2) is a step of subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction. That is, in the step (2), a monoglyceride is produced using raw materials for esterification reaction including the recovered glycerin, glycerin to be newly added as necessary, and the tall fatty acid.

[0038] A part of the glycerin to be used in the step (2) may be the recovered glycerin, or the entire glycerin to be used in the step (2) may be the recovered glycerin. The recovered glycerin is preferably used as it is in the step (2) without the separation of impurities contained therein, such as a glycerin condensate, e.g., diglycerin, and unsaponifiables derived from the tall fatty acid, from the standpoint of the control of the precipitation of the monoglyceride-containing composition at low temperature. For example, the recovered glycerin contains preferably 0.01 mass% to 1 mass%, more preferably 0.015 mass% to 0.7 mass%, even more preferably 0.02 mass% to 0.4 mass% of diglycerin.

[0039] When a part of the recovered glycerin is used as the glycerin to be used in the step (2), the recovered glycerin accounts for preferably 3 mass% or more, more preferably 5 mass% or more, even more preferably 10 mass% or more in the entire glycerin, from the standpoint of the control of the precipitation of the monoglyceride-containing composition at low temperature. In addition, from the standpoint of industrial productivity, through storage of the glycerin recovered in the step (1) in a tank or the like, the entire amount maybe replaced with the recovered glycerin. In addition, the recovered glycerin accounts for preferably from 3 mass% to 100 mass%, more preferably from 5 mass% to 100 mass%, more preferably from 10 mass% to 100 mass%, more preferably from 15 mass% to 100 mass%, even more preferably from 18 mass% to 100 mass% in the entire glycerin.

[0040] In the step (2), the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], is set to preferably from 0.1 to 2.0, more preferably from 0.2 to 1.8, more preferably from 0.3 to 1.5, more preferably from 0.4 to 1, even more preferably from 0.5 to 1, from the standpoint of the improvement in the monoglyceride purity as the reaction product. In addition, as described later, when the recovered glycerin is reused as a raw material for the esterification reaction after the step (2), the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], is set to preferably from 0.1 to 2.0, more preferably from 0.2 to 1.8, more preferably from 0.3 to 1.5, more preferably from 0.4 to 1, even more preferably from 0.5 to 1.

[0041] The temperature, period of time, and the like of the esterification reaction in the step (2) are not particularly limited, and are preferably the same as those in the step (1).

[0042] In the present invention, from the standpoint of the solubility of the monoglyceride-containing composition in diesel fuel, it is preferred to perform, after the step (2), a step of repeating operations of: recovering unreacted glycerin; and subjecting glycerin including the recovered glycerin and the tall fatty acid to the esterification reaction.

[0043] The number of times of recycling of reusing the recovered glycerin as a part of the glycerin or the entire glycerin serving as a raw material for the esterification reaction is preferably 1 or more, more preferably 2 or more, even more preferably 3 or more.

[0044] The monoglyceride-containing composition thus obtained has a low cloud point and is excellent in low-temperature resistance. The cloud point of the monoglyceride-containing composition of the present invention is preferably from -60°C to 10°C, more preferably from -50°C to 0°C, even more preferably from -40°C to -10°C.

[0045] Herein, the cloud point of the monoglyceride-containing composition refers to a temperature at which a transparent oil phase starts to become turbid, and the cloud point may be measured by a method described later in Examples.

[0046] The cloud point of the monoglyceride-containing composition obtained by the method of the present invention is decreased by preferably 0.3°C or more, more preferably 0.5°C or more, even more preferably 1°C or more with respect to the cloud point of the reaction product after the esterification reaction obtained in the step (1). The decrease in the cloud point may be determined by the following expression: [cloud point of monoglyceride-containing composition (°C)]-[cloud point of reaction product after esterification reaction obtained in step (1) (°C)].

[0047] The monoglyceride-containing composition obtained by the method of the present invention has a monoglyceride purity of preferably 10 mass% or more, more preferably 20 mass% or more, even more preferably 3 0 mass% or more, from the standpoint of the lubricity of an engine in which the monoglyceride-containing composition is used as a fuel additive.

[0048] The monoglyceride purity may be determined by the following expression:

$$\text{monoglyceride}/(\text{monoglyceride}+\text{diglyceride}+\text{triglyceride})\times 100\ (\text{mass\%}).$$

[0049] In addition, the monoglyceride-containing composition obtained by the method of the present invention has an acid value (AV) of preferably 2 mg KOH/g or less, more preferably 1 mg KOH/g or less, even more preferably 0.5 mg KOH/g or less, from the standpoint of the inhibition of the corrosion of an engine.

[0050] The monoglyceride-containing composition obtained by the method of the present invention contains preferably 0.01 mass% to 1.5 mass%, more preferably 0.025 mass% to 1.3 mass%, even more preferably 0.05 mass% to 1.1 mass% of a monoester of a dehydration condensate of glycerin and a fatty acid produced as a by-product by the method of the present invention, e.g., a diglycerin monoester, from the standpoint of the lubricity of an engine in which the monoglyceride-containing composition is used as a fuel additive.

[0051] The monoglyceride-containing composition obtained by the method of the present invention may be used in the same manner as a general monoglyceride-containing composition. Of those, the monoglyceride-containing composition obtained by the method of the present invention is suitable as an oiliness improver, e.g., a fuel, such as diesel fuel, or a fuel oil additive, such as a base oil of a lubricating oil.

[0052] With regard to the embodiment described above, the present invention further discloses the followingproduction method.

<1> A method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid, the method comprising the following steps (1) and (2):

(1) subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within the range of from 0.1 to 2.0, followed by recovery of unreacted glycerin; and
(2) subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction.

<2> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to Item <1>, wherein the content of saturated fatty acids in terms of the total of palmitic acid and stearic acid in the tall fatty acid is preferably 10 mass% or less, more preferably 6 mass% or less, even more preferably 4 mass% or less.
<3> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to Item <1> or <2>, wherein the content of saturated fatty acids in terms of the total of palmitic acid and stearic acid in the tall fatty acid is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, even more preferably 1 mass% or more.
<4> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <3>, wherein the total content of oleic acid and linoleic acid in the tall fatty acid is preferably 50 mass% or more, more preferably 60 mass% or more, even more preferably 70 mass% or more.
<5> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <4>, wherein the total content of oleic acid and linoleic acid in the tall fatty acid is preferably 98 mass% or less, more preferably 95 mass% or less.
<6> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <5>, wherein the ratio of oleic acid to linoleic acid in the tall fatty acid is preferably 1.6 or less, more preferably 1.3 or less, even more preferably 1.0 or less.
<7> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <6>, wherein the content of unsaponifiables in the tall fattyacid is preferably 0.3 mass% or more, more preferably 0.6 mass% or more, even more preferably 1 mass% or more.
<8> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <7>, wherein the content of unsaponifiables in the tall fatty acid is preferably 4 mass% or less, more preferably 3 mass% or less, even more preferably 2.5 mass% or less.
<9> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <8>, wherein the content of 5, 9, 12-octadecatrienoic acid in the tall fatty acid is preferably 1 mass% or more, more preferably 2 mass% or more, even more preferably 4 mass% or more.
<10> The method of producing a monoglyceride-containing composition according to any one of Items <1> to <9>, wherein the tall fatty acid has an iodine value of preferably 100 g I_2/100 g or more, more preferably 120 g I_2/100 g or more, even more preferably 140 g I_2/100 g or more.
<11> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <10>, wherein in the step (1), the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], in the esterification reaction is preferably 0.2 or more, more preferably 0.3 or more, more preferably 0.4 or more, even more preferably 0.5 or more, and is preferably 1.8 or less, more preferably 1.5 or less, even more preferably 1 or less.
<12> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <10>, wherein in the step (1), the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], in the esterification reaction is preferably from 0.2 to 1.8, more preferably from 0.3 to 1.5, more preferably from 0.4 to 1, even more preferably from 0.5 to 1.
<13> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <12>, wherein the esterification reaction is performed at a temperature of preferably from 180°C to 300°C, more preferably from 200°C to 280°C, even more preferably from 220°C to 260°C.
<14> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <13>, wherein the esterification reaction is performed for a reaction time of preferably from 0.2 hour to 48 hours, more preferably from 0.5 hour to 24 hours, even more preferably from

1 hour to 12 hours.

<15> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <14>, wherein a method for the recovery of the glycerin is pref erably a method involving recovering a glycerin layer by centrifugation, a method involving recovering glycerin by vacuum distillation, a method involving recovering glycerin by water vapor distillation, a method involving recovering a glycerin layer by phase separation, a method involving recovering glycerin by water washing, or a method involving recovering glycerin through use of an adsorbent or the like, more preferably a method involving recovering glycerin by vacuum distillation.

<16> The method of producing a composition containing amonoglyceride using a tall fatty acid as a constituent fatty acid according to Item <15>, wherein the vacuum distillation for the recovery of the glycerin is performed under the conditions of a pressure of preferably from 0.1 kPa to 10 kPa, more preferably from 0.1 kPa to 5 kPa, a temperature of preferably from 140°C to 260°C, more preferably from 150°C to 250°C, even more preferably from 160°C to 240°C, and a period of time of preferably from 1 minute to 600 minutes, more preferably from 5 minutes to 300 minutes, even more preferably from 10 minutes to 180 minutes.

<17> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <16>, wherein in the step (2), the recovered glycerin is used as it is without the separation of impurities contained therein, such as a glycerin condensate and unsaponifiables derived from the tall fatty acid.

<18> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <17>, wherein in the step (2), the amount of diglycerin contained in the recovered glycerin is preferably from 0.01 mass% to 1 mass%, more preferably from 0.015 mass% to 0.7 mass%, even more preferably from 0.02 mass% to 0.4 mass%.

<19> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <18>, wherein in the step (2), the glycerin recovered in the step (1) accounts for preferably 3 mass% or more, more preferably 5 mass% or more, more preferably 10 mass% or more, more preferably 15 mass% or more, even more preferably 18 mass% or more, and preferably 100 mass% or less of the glycerin used in the step (2).

<20> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <19>, wherein the esterification reaction in the step (2) is performed in such a manner that the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within the range of preferably from 0.1 to 2.0, more preferably from 0.2 to 1.8, more preferably from 0.3 to 1.5, more preferably from 0.4 to 1, even more preferably from 0.5 to 1.

<21> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <1> to <20>, further comprising, after the step (2), a step of repeating operations of: recovering unreacted glycerin; and subjecting glycerin including the recovered glycerin and the tall fatty acid to the esterification reaction.

<22> The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to Item <21>, wherein the number of times of recycling of reusing the recovered glycerin as part or the whole of the glycerin acting as a raw material for the esterification reaction is preferably 1 or more, more preferably 2 or more, even more preferably 3 or more.

<23> A composition containing a monoglyceride using a tall fattyacidas a constituent fattyacid, obtained by the production method of any one of Items <1> to <22>.

<24> The monoglyceride-containing composition according to Item <23>, wherein the composition has a cloud point of preferably from -60°C to 10°C, more preferably from -50°C to 0°C, even more preferably from -40°C to -10°C.

<25> The composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to Item <23> or <24>, wherein the composition has an acid value (AV) of preferably 2 mg KOH/g or less, more preferably 1 mg KOH/g or less, even more preferably 0.5 mg KOH/g or less.

<26> The composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of Items <23> to <25>, wherein the composition contains preferably 0.01 mass% to 1.5 mass%, more preferably 0.025 mass% to 1.3 mass%, even more preferably 0.05 mass% to 1.1 mass% of a diglycerin monoester.

Examples

[Analysis Method]

(i) Compositions of Glycerin, Diglycerin, and Glyceride in Monoglyceride-containing Composition, and Diglycerin in Recovered Glycerin

[0053] About 10 mg of a fat or oil sample and 0.5 mL of a trimethylsilylating agent ("Silylating Agent TH" manufactured by Kanto Chemical Co., Inc.) were added into a glass sample bottle, followed by hermetical sealing, and the glass sample bottle was heated at 70°C for 15 minutes. 1.0 mL of water and 1.5 mL of hexane were added to the mixture, followed by shaking. The mixture was left to stand still, and then the upper layer was subjected to gas-liquid chromatography (GLC) to perform analysis.

<GLC Analysis Conditions>

[0054]

Apparatus: Agilent 6890 series (Manufactured by Agilent Technologies)
Integrator: ChemStation B 02.01 SR2 (Manufactured by Agilent Technologies)
Column: DB-lht (manufactured by Agilent J&W)
Carrier gas: 1.0 mL He/min
Injector: Split (1:50), T=320°C
Detector: FID, T=350°C
Oven temperature: The temperature was increased from 80°C to 340°C at 10°C/minute and kept for 15 minutes.

(ii) Fatty Acid Compositions of Tall Fatty Acid and Distilled Soybean Fatty Acid

[0055] Methyl esters of fatty acids were prepared in accordance with "Methods of preparing fatty acid methyl esters (2.4.1.-1996)" in the "Standard Methods for the Analysis of Fats, Oils and Related Materials" edited by Japan Oil Chemists' Society. The resultant fat or oil samples were measured by the American Oil Chemists. Society Official Method Ce 1f-96 (GLC method).

<GLC Analysis Conditions>

[0056]

Column: CP-SIL 88 100 m×0.25 mm×0.2 μm (manufactured by Varian)
Carrier gas: 1.0 mL He/min
Injector: Split (1:200), T=250°C
Detector: FID, T=250°C
Oven temperature: The temperature was kept at 174°C for 50 minutes, and was then increased at 5°C/minutes to 220 °C and kept for 25 minutes.

(iii) Measurement of Iodine Value (IV)

[0057] Measurement was performed in accordance with "Iodine Value (Wijs-Cyclohexane Method) (2.3.4.1-1996)" in the "Standard Methods for the Analysis of Fats, Oils and Related Materials" edited by Japan Oil Chemists' Society.

(iv) Measurement of Acid Value (AV)

[0058] An acid value was measured in accordance with "Acid Value (2.3.1-1996)" in the "Standard Methods for the Analysis of Fats, Oils and Related Materials, 2003 Edition" edited by Japan Oil Chemists' Society.

(vi) Measurement of Unsaponifiable Matter

[0059] Unsaponifiables was measured in accordance with "Unsaponifiable Matter (3.3.4-1996)" in the "Standard Methods for the Analysis of Fats, Oils and Related Materials, 2003 Edition" edited by Japan oil Chemists' Society.

(v) Measurement of Cloud Point of Monoglyceride-containing Composition

[0060] A monoglyceride-containing composition was separated by filtration through a membrane filter having a pore size of 1 μm, and was then measured for its cloud point through a high-sensitivity differential scanning calorimeter (DSC7020, manufactured by SII) . Analysis conditions were as described below. The temperature was increased from 30°C to 70°C at 10°C/minute, and kept at 70°C for 5 minutes to completely dissolve the monoglyceride-containing composition. After that, the monoglyceride-containing composition using a tall fatty acid was cooled at -10°C/minute to -5°C, and cooled at -0.5°C/minute to -40°C. Meanwhile, the monoglyceride-containing composition using a soybean fatty acid was cooled at -7.0°C/minute to 10°C, and cooled at -0.5°C/minute to -15°C.

[Preparation of Soybean Fatty Acid]

[0061] An undeodorized soybean oil was subjected to a hydrolysis reaction by an enzymatic degradation method using lipase. A 10 L four-necked flask was loaded with 4.2 kg of the undeodorized soybean oil and 4.2 kg of distilled water, and then the temperature was increased to 40°C under stirring (half-moon shaped blade, Φ90 mm×H25 mm: 300 r/min). 42 g of Lipase AY (manufactured by Amano Enzyme Inc.) was added. After that, the gas phase in the 10 L four-necked flask was purged with nitrogen to establish a nitrogen atmosphere, and a hydrolysis reaction was initiated. After 48 hours, the reaction, solution was centrifuged (5,000×g, 10 minutes) and the aqueous phase was removed, followed by washing of the oil phase with water. Then, the oil phase was dehydrated under reduced pressure at a temperature of 70°C and a vacuum degree of 400 Pa for 30 minutes. Then, thin film distillation was performed with a wiped film evaporator (Type 2-03 manufactured by Kobelco Eco-Solutions Co., Ltd., inner diameter: 5 cm, heat transfer area: 0.03 m2). The operation was performed under the conditions of a heating heater temperature setting of 230°C, a pressure of from 1 Pa to 2 Pa, and a flow rate of 150 g/h. Thus, an unreacted undeodorized soybean oil and partial glycerides were removed to provide a soybean fatty acid.

[0062] Sylfat 2LTC (manufactured by Arizona Chemical) was used as a tall fatty acid. The analysis values of the tall fatty acid and the distilled soybean fatty acid are shown in Table 1.

[Table 1]

	Fatty acid composition (mass%)								Unsaponifiable s [%]	Iodine value [g I_2/100 g]	Acid value [mg KOH/g]
	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	5,9,12-Oc tadecatrienoic acid	Others	Oleic acid/Linoleic acid			
Tall fatty acid	0.4	1.2	32.2	42.3	1.2	9.0	13.7	0.8	2	155	198
Soybean fatty acid	10.6	4.2	24.5	52.6	6.7	0.0	1.3	0.5	0	135	201

Example 1

[Initial Time]

[0063] A 1 L four-necked flask with a half-moon shaped blade (Φ90 mm×H25 mm) was loaded with 160.4 g of glycerin and 439.6 g of the tall fatty acid, and the gas phase in the 1 L four-necked flask was purged with nitrogen. After that, while nitrogen was flowed into the space above the liquid at a flow rate of 20 mL/minute, the temperature increase was performed for about 30 minutes under stirring at 400 r/min to reach 250°C. After the temperature had reached 250°C, an esterification reaction was performed at that temperature for 3 hours. Then, the resultant was cooled down for about 20 minutes to reach 70°C, and a cooling tube and a 200 mL recovery flask for recovering glycerin were mounted between the 1 L four-necked flask and a vacuum pump. The pressure was reduced and adjusted to 130 Pa under stirring at 400 r/min. The temperature was increased for about 20 minutes to 200°C to perform a deglycerolization. During the temperature increase, glycerin started being distilled off, and consequently the vacuum degree decreased. After that, when glycerin finished being distilled off, the vacuum degree became constant at 130 Pa. The deglyceolization was performed for 30 minutes, and then the resultant was cooled to 70°C to provide a monoglyceride-containing composition. In addition, through the deglyceolization, 39.9 g of glycerin was recovered.

[First Time of Recycling]

[0064] 35.91 g of the glycerin recovered in [Initial Time], 124.5 g of glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 41.5 g of glycerin was recovered.

[Second Time of Recycling]

[0065] 37.4 g of the glycerin recovered in [First Time of Recycling], 123 g of newly added glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 36.8 g of glycerin was recovered.

[Third Time of Recycling]

[0066] 33.1 g of the glycerin recovered in [Second Time of Recycling], 127.3 g of newly added glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 34.4 g of glycerin was recovered.

[Fourth Time of Recycling]

[0067] 30.1 g of the glycerin recovered in [Third Time of Recycling], 130.3 g of newly added glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time].

[0068] The esterification reaction conditions, the glycerin recovery conditions, the analysis results of the recovered glycerin, and the analysis results of the monoglyceride-containing composition in each stage are shown in Table 2.

[Table 2]

				Initial time	First time of recycling	Second time of recycling	Third time of recycling	Fourth time of recycling
Esterification reaction	Loading	FA/Gly	[mol/mol]	0.9	0.9	0.9	0.9	0.9
		Fatty acid	[g]	439.6	439.6	439.6	439.6	439.6
		Glycerin	[g]	160.4	160.4	160.4	160.4	160.4
		Added glycerin	[g]	-	124.5	123	127.3	130.3
		Recovered glycerin	[g]	-	35.91	37.4	33.1	30.1
	Conditions	Temperature	[°C]	250	250	250	250	250
		Time	[h]	3	3	3	3	3
Deglyceolizat ion	Conditions	Temperature	[°C]	200	200	200	200	200
		Time	[h]	0.5	0.5	0.5	0.5	0.5
		Pressure	[Pa]	130	130	130	130	130
Recovered glycerin		Recovered amount	[g]	39.9	41.5	36.8	33.4	44.9
		Diglycerin	[%]	0.120	0.117	0.099	0.105	0.105

(continued)

				Initial time	First time of recycling	Second time of recycling	Third time of recycling	Fourth time of recycling
Glyceride analysis	AV		[mg KOH/g]	0.1	0.1	0.1	0.1	0.1
	Glyceride composition	FFA	[%]	0.1	0.1	0.1	0	0
		Gly	[%]	0.3	0.1	0.2	0.2	0.2
		MAG	[%]	46.9	48.4	45.5	43.7	46.9
		DAG	[%]	45.3	43.7	42.4	43.6	41.2
		TAG	[%]	7.4	7.7	11.8	12.5	11.7
		Diglycerin monoester	[%]	0.37	0.32	0.37	0.37	0.39
	Cloud point		[°C]	-31.5	-32	-32.9	-32.7	-32.7
	Decrease in cloud point with respect to that at initial time		[°C]	0	-0.5	-1.4	-1.2	-1.2

Example 2

[Initial Time]

[0069] A monoglyceride-containing composition was obtained by the same method as that of Example 1 except that the esterification reaction was performed for 1 hour. In addition, through deglyceolization, 42.2 g of glycerin was recovered.

[First Time of Recycling]

[0070] 38.0 g of the glycerin recovered in [Initial Time], 122.4 g of glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 35.5 g of glycerin was recovered.

[Second Time of Recycling]

[0071] 32. 0 g of the glycerin recovered in [First Time of Recycling], 128.4 g of newly added glycerin, and 439.6 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 41.2 g of glycerin was recovered.

[Third Time of Recycling]

[0072] Only recovered glycerin was used as glycerin to be used in an esterification reaction. 36.5 g of the glycerin recovered in [Second Time of Recycling] and 100.0 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time].

[0073] The esterification reaction conditions, the glycerin recovery conditions, the analysis results of the recovered glycerin, and the analysis results of the monoglyceride-containing composition in each stage are shown in Table 3.

[Table 3]

				Initial time	First time of recycling	Second time of recycling	Third time of recycling
Esterification reaction	Loading	FA/Gly	[mol/mol]	0.9	0.9	0.9	0.9
		Fatty acid	[g]	439.6	439.6	439.6	100
		Glycerin	[g]	160.4	160.4	160.4	36.5
		Added glycerin	[g]	160.4	122.4	128.4	0
		Recovered glycerin	[g]	0	38.0	32.0	36.5
	Conditions	Temperature	[°C]	250	250	250	250
		Time	[h]	1	1	1	1
Deglyceolization	Conditions	Temperature	[°C]	200	200	200	200
		Time	[h]	30	30	30	30
		Pressure	[Pa]	130	130	130	130
Recovered glycerin		Recovered amount	[g]	42.2	35.5	41.2	14
		Diglycerin	[%]	0.05	0.026	0.035	0.032

(continued)

				Initial time	First time of recycling	Second time of recycling	Third time of recycling
Glyceride analysis	AV		[mg KOH/g]	0.2	0.2	0.2	0.2
	Glyceride composition	FFA	[%]	0.1	0.1	0.1	0.1
		Gly	[%]	0.1	0.1	0.1	0.1
		MAG	[%]	45.5	43.4	44.4	46.1
		DAG	[%]	45.2	46.5	45.4	47.5
		TAG	[%]	9.2	10.0	9.9	6.3
		Diglycerin monoester	[%]	0.05	0.08	0.10	0.10
	Cloud point		[°C]	-30.3	-31.2	-31.4	-31.4
	Decrease in cloud point with respect to that at initial time		[°C]	0	-0.9	-1.1	-1.1

Comparative Example 1

[Initial Time]

[0074] A monoglyceride-containing composition was obtained by the same method as that of Example 1 except that a soybean fatty acid was used as a raw material fatty acid for the esterification reaction. In addition, through deglyceolization, 37.5 g of glycerin was recovered.

[First Time of Recycling]

[0075] 33.8 g of the glycerin recovered in [Initial Time], 126.6 g of newly added glycerin, and 439.6 g of the soybean fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 39.9 g of glycerin was recovered.

[Second Time of Recycling]

[0076] 35. 9 g of the glycerin recovered in [First Time of Recycling], 124.5 g of newly added glycerin, and 439.6 g of the soybean fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 43.8 g of glycerin was recovered.

[Third Time of Recycling]

[0077] 39.4 g of the glycerin recovered in [Second Time of Recycling], 121.0 g of newly added glycerin, and 439.6 g of the soybean fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 42.3 g of glycerin was recovered.

[Fourth Time of Recycling]

[0078] 38.1 g of the glycerin recovered in [Third Time of Recycling], 122.3 g of newly added glycerin, and 439.6 g of the soybean fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time].

[0079] The esterification reaction conditions, the glycerin recovery conditions, the analysis results of the recovered glycerin, and the analysis results of the monoglyceride-containing composition in each stage are shown in Table 4.

[Table 4]

				Initial time	First time of recycling	Second time of recycling	Third time of recycling	Fourth time of recycling
Esterification reaction	Loading	FA/Gly	[mol/mol]	0.9	0.9	0.9	0.9	0.9
		Fatty acid	[g]	439.6	439.6	439.6	439.6	439.6
		Glycerin	[g]	160.4	160.4	160.4	160.4	160.4
		Added glycerin	[g]	-	126.6	124.5	121	122.3
		Recovered glycerin	[g]	-	33.8	35.9	39.4	38.1
	Conditions	Temperature	[°C]	250	250	250	250	250
		Time	[h]	3	3	3	3	3
Deglyceolizat ion	Conditions	Temperature	[°C]	200	200	200	200	200
		Time	[h]	0.5	0.5	0.5	0.5	0.5
		Pressure	[Pa]	130	130	130	130	130
Recovered glycerin		Recovered amount	[g]	37.5	39.9.	43.8	42.3	42.7
		Diglycerin	[%]	0.083	0.076	0.053	0.071	0.053

(continued)

				Initial time	First time of recycling	Second time of recycling	Third time of recycling	Fourth time of recycling
Glyceride analysis	AV		[mg KOH/g]	0.08	0.13	0.15	0.1	0.11
	Glyceride composition	FFA	[%]	0	0.1	0.1	0	0.1
		Gly	[%]	0.4	0.4	0.4	0.4	0.5
		MAG	[%]	36.2	36.4	36.3	34.5	35.1
		DAG	[%]	49.8	50.3	50.2	51.1	50.3
		TAG	[%]	13.5	12.9	13.1	13.9	14.1
		Diglycerin monoester	[%]	0.42	0.43	0.43	0.41	0.44
	Cloud point		[°C]	-7.3	-4.95	-4.86	-5.03	-5.76
	Decrease in cloud point with respect to that at initial time		[°C]	0	2.35	2.4	2.3	1.5

[0080] As apparent from Tables 2 and 3, after the esterification reaction between glycerin and the tall fatty acid, if unreacted glycerin was recovered and reused as a raw material for the esterification reaction, the cloud point of the resultant composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid decreased. In addition, even if the esterification reaction was performed using the recovered glycerin as a whole amount, the cloud point of the resultant monoglyceride-containing composition decreased.

[0081] Meanwhile, as apparent from Table 4, in the case of the soybean fatty acid, it found that through recycling of glycerin, the cloud point of the resultant monoglyceride-containing composition and the like increased to the contrary.

Example 3

[Initial Time]

[0082] A monoglyceride-containing composition was obtained by the same method as that of Example 1 except that 237.9 g of glycerin and 362.1 g of the tall fatty acid were loaded. In addition, through deglyceolization, 146.6 g of glycerin was recovered.

[First Time of Recycling]

[0083] 131.9 g of the glycerin recovered in [Initial Time], 106 g of glycerin, and 362.1 g of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time]. In addition, through deglyceolization, 141.0 g of glycerin was recovered.

[Second Time of Recycling]

[0084] 126.9 g of the glycerin recovered in [First Time of Recycling], 111 g of newly added glycerin, and 362.1 of the tall fatty acid were used as raw materials for an esterification reaction, and a monoglyceride-containing composition was obtained in a similar manner to that in [Initial Time].

[0085] The esterification reaction conditions, the glycerin recovery conditions, the analysis results of the recovered glycerin, and the analysis results of the monoglyceride-containing composition in each stage are shown in Table 5.

[Table 5]

				Initial time	First time of recycling	Second time of recycling
Esterification reaction	Loading	FA/Gly	[mol/mol]	0.5	0.5	0.5
		Fatty acid	[g]	362.1	362.1	362.1
		Glycerin	[g]	237.9	237.9	237.9
		Added glycerin	[g]	-	106	111
		Recovered glycerin	[g]	-	131.9	126.9
	Conditions	Temperature	[°C]	250	250	250
		Time	[h]	3	3	3
Deglyceolization	Conditions	Temperature	[°C]	200	200	200
		Time	[h]	0.5	0.5	0.5
		Pressure	[Pa]	130	130	130
Recovered glycerin		Recovered amount	[g]	146.6	141.0	145.3
		Diglycerin	[%]	0.164	0.250	0.218

(continued)

				Initial time	First time of recycling	Second time of recycling
Glyceride analysis	AV		[mg KOH/g]	0.17	0.15	0.08
	Glyceride composition	FFA	[%]	0.1	0.1	0.0
		Gly	[%]	0.0	0.0	0.0
		MAG	[%]	50.8	51.0	47.7
		DAG	[%]	40.5	40.5	42.7
		TAG	[%]	8.6	8.5	9.6
		Diglycerin monoester	[%]	0.72	0.88	0.72
	Cloud point		[°C]	-30.4	-32.1	-32.4
	Decrease in cloud point with respect to that at initial time		[°C]	0	-1.7	-2.0

[0086] As apparent from Table 5, after the esterification reaction between glycerin and the tall fatty acid, if unreacted glycerin was recovered and reused as a raw material for the esterification reaction, the cloud point of the resultant composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid decreased.

Claims

1. A method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid, the method comprising the following steps (1) and (2):

   (1) subjecting glycerin and the tall fatty acid to an esterification reaction in such a manner that a ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY] , falls within a range of from 0.1 to 2. 0, and followed by recovery of unreacted glycerin; and
   (2) subjecting glycerin including the glycerin recovered in the step (1) and the tall fatty acid to the esterification reaction.

2. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to claim 1, wherein the esterification reaction is performed at from 180°C to 300°C for from 0.2 hour to 48 hours.

3. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to claim 1 or 2, wherein in the step (2), the glycerin recovered in the step (1) accounts for 3 mass% or more of the glycerin used in the step (2).

4. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of claims 1 to 3, wherein the esterification reaction in the step (2) is performed in such a manner that the ratio of the number of moles of a fatty acid group to the number of moles of a glycerin group, [FA/GLY], falls within a range of from 0.1 to 2.0.

5. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of claims 1 to 4, further comprising, after the step (2), a step of repeating operations of: recovering unreacted glycerin; and subjecting glycerin including the recovered glycerin and the tall fatty acid to the esterification reaction.

6. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of claims 1 to 5, wherein the tall fatty acid has an iodine value of 100 g $I_{2/}$100 g or more.

7. The method of producing a composition containing a monoglyceride using a tall fatty acid as a constituent fatty acid according to any one of claims 1 to 6, wherein a content of unsaponifiables in the tall fatty acid to be used in the step (1) is 0.3 mass% or more.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/073481

A. CLASSIFICATION OF SUBJECT MATTER
C11C3/08(2006.01)i, *C07C67/08*(2006.01)i, *C07C69/30*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11C3/08, C07C67/08, C07C69/30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY(STN), JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-083390 A (Infinum International Ltd.), 30 March 2006 (30.03.2006), claims; paragraph [0007]; examples & GB 2418202 A claims; page 3, lines 9 to 17; examples	1-7
Y	JP 2003-049192 A (Kao Corp.), 21 February 2003 (21.02.2003), claims; paragraphs [0007] to [0009], [0013] to [0015]; examples (Family: none)	1-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 08 October 2015 (08.10.15)	Date of mailing of the international search report 20 October 2015 (20.10.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/073481

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/085031 A1 (Kao Corp.), 13 June 2013 (13.06.2013), claims; examples & US 2014/0303388 A1 claims; examples & EP 2789601 A1 & CN 103998413 A	1-7

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003049192 A **[0005]**
- JP 2004359884 A **[0005]**

Non-patent literature cited in the description

- Standard Methods for the Analysis of Fats, Oils and Related Materials **[0055] [0057]**
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