

DESCRIPTION

Title of Invention: PROCESS FOR PRODUCTION OF GLYCERIDE
COMPOSITIONS USEFUL AS SUBSTITUTES FOR FUEL OIL C

5

Technical Field

[0001]

The present invention relates to a process for
producing a glyceride composition for use as a fuel oil C
10 substitute that can be used as a fuel for power generation in
thermal power stations, etc.

Background Art

[0002]

In recent years, global warming due to the increased
15 emission of greenhouse gas (carbon dioxide) has been a matter of
concern. Therefore, in light of the concept of carbon neutrality,
liquid biomass fuel, whose carbon dioxide emission is lower than
fossil fuel (fuel oil C), is being considered for use also in
thermal power stations, etc.

20 [0003]

Vegetable oils, animal oils, vegetable edible waste
oils, etc., are currently in use as liquid biomass fuels. However,
fuels that contain a large amount of free fatty acid and that
have a high acid value are highly corrosive to carbon steel, and
25 thus cannot be used in their original form in thermal power
stations.

[0004]

As means for suppressing corrosion, methods for
reducing the acid value of fuel by reacting a fatty acid with an
30 alcohol have been proposed (see, for example, Patent Documents 1
to 4).

[0005]

Patent Document 1 discloses a method for producing a
fatty acid alkyl ester (a biodiesel fuel), the method comprising
35 mixing a raw material containing a free fatty acid with an

alcohol, and carrying out an esterification reaction under conditions such that the alcohol is in a supercritical state.

[0006]

Patent Document 2 discloses a method for producing a
5 fatty acid lower alkyl ester by the non-catalytic esterification of a fatty acid with a lower alcohol.

[0007]

Patent Document 3 discloses a method for producing a fatty acid ester (a biodiesel fuel), the method comprising mixing
10 an alcohol with a fatty acid raw material consisting essentially of a free fatty acid, and carrying out an esterification reaction under conditions to put the alcohol into a supercritical state, followed by further esterification in the presence of a solid catalyst, etc., while heating.

15 [0008]

Patent Document 4 discloses a method for producing a glyceride, the method comprising hydrolyzing a raw material oil or fat with an enzyme, and formulating the palmitoleic acid-containing fraction obtained by the hydrolysis, with glycerol and
20 an enzyme, and reacting the glycerol with palmitoleic acid.

Patent Document 1: Japanese Patent No. 3,842,273

Patent Document 2: Japanese Patent No. 3,951,832

Patent Document 3: Japanese Unexamined Patent Publication No.
2006-36817

25 Patent Document 4: Japanese Unexamined Patent Publication No.
2007-70486

Disclosure of the Invention

Technical Problem

[0009]

30 However, the methods disclosed in the above prior art documents have the following problems. Because the method disclosed in Patent Document 1 comprises esterifying a fatty acid using an alcohol in a supercritical state, application of this method on a large scale, such as use in thermal power stations,
35 has been difficult.

[0010]

Because the method disclosed in Patent Document 2 is a method for producing a fatty acid alkyl ester for use in the food and cosmetic fields, carrying out this method as is on an industrial scale for producing a power-generating fuel has been difficult in terms of cost.

[0011]

The method disclosed in Patent Document 3 uses a catalyst. To meet the quality specifications of fuel for thermal power generation, it is necessary to completely remove the catalyst from the fuel, which is costly. Furthermore, because this method uses an alcohol in a supercritical state, application of this method on an industrial scale has been difficult, similar to Patent Document 1.

15 [0012]

The method disclosed in Patent Document 4 uses an enzyme, and is thus costly.

[0013]

In view of the above problems of the prior art, an object of the present invention is to provide a method for producing a glyceride composition for use as a fuel oil C substitute that can be used as a fuel for power generation in thermal power stations, etc.

Solution to Problem

25 [0014]

The inventors of the present invention found that a glyceride composition having an acid value of 10 mgKOH/g or less can be produced by subjecting a free fatty acid-containing raw material and a trihydric alcohol to a non-catalytic esterification reaction at 230 to 250°C. As a result of further research based on this finding, the present invention has been accomplished.

[0015]

More specifically, the present invention provides a process for producing a glyceride composition for use as a fuel

oil C substitute; a glyceride composition produced by this process; and a fuel oil C substitute, as itemized below.

[0016]

Item 1. A process for producing a glyceride composition for use
5 as a fuel oil C substitute by using a free fatty acid-containing raw material and a trihydric alcohol, the process comprising a reaction step of subjecting a mixture of the free fatty acid-containing raw material and trihydric alcohol to a non-catalytic esterification reaction at 230 to 250°C.

10 [0017]

Item 2. The process according to Item 1 comprising, before the reaction step, a heating step of preheating the mixture to 50 to 70°C and then raising the temperature of the mixture to the range of 230 to 250°C at a heating ramp rate of 10 to 30°C/hour.

15 [0018]

Item 3. The process according to Item 1 or 2, wherein the reaction step comprises an atmospheric pressure reaction step of carrying out the reaction under atmospheric pressure, and a reduced pressure reaction step of carrying out the reaction under
20 reduced pressure.

[0019]

Item 4. The process according to Item 3, wherein the reduced pressure reaction step is carried out while feeding an inert gas into the mixture.

25 [0020]

Item 5. The process according to any one of Items 1 to 4, wherein the fatty acid-containing raw material is a palm fatty acid distillate (PFAD).

[0021]

30 Item 6. The process according to any one of Items 1 to 5, wherein the trihydric alcohol is glycerol.

[0022]

Item 7. A glyceride composition for use as a fuel oil C substitute, which is produced by the process of any one of Items
35 1 to 6.

[0023]

Item 8. A fuel oil C substitute comprising the glyceride composition of Item 7.

Advantageous Effects of Invention

5 [0024]

According to the present invention, a process for producing a glyceride composition having an acid value of 10 mgKOH/g or less on an industrial scale by using a free fatty acid-containing raw material and a trihydric alcohol can be provided. The glyceride composition produced by the process of the invention has a low acid value, and is less corrosive to carbon steel. Therefore, this glyceride composition is useful as a fuel oil C substitute that can be used in thermal power stations. The use of a palm fatty acid distillate (PFAD) as the free fatty acid-containing raw material is an effective use of a by-product that is obtained in the process of refining palm oil and that is unsuitable for eating.

Brief Description of Drawings

[0025]

20 [Fig. 1] Fig. 1 is a schematic diagram illustrating quality verification testing.

Description of the Reference Numerals

[0026]

- 1: sample
- 25 2: rainwater
- 3: test plate
- 4: constant temperature bath

Description of Embodiments

[0027]

30 The present invention is described below in detail.

[0028]

According to the present invention, a free fatty acid-containing raw material and a trihydric alcohol are used to produce a glyceride composition.

35 [0029]

Examples of the free fatty acid-containing raw material include vegetable oils, such as rapeseed oil, sesame oil, soybean oil, corn oil, sunflower oil, palm oil, palm kernel oil, coconut oil, corn oil, and safflower oil; animal oils, such as beef
5 tallow, lard, and fish oil; free fatty acids obtained in the process of refining such oils, free fatty acids obtained in the process of deacidifying such waste cooking oils, etc., free fatty acids separated from yellow grease, etc.

[0030]

10 The process of the present invention produces a glyceride composition having an acid value of 10 mgKOH/g or less. Accordingly, any material that has an acid value of more than 10 mgKOH/g may be used as the raw material. However, in view of the efficient production of glyceride usable as a fuel oil C
15 substitute from a free fatty acid-containing raw material, a raw material containing a free fatty acid in an amount of 70 wt.% or more is preferable.

[0031]

The use of a palm fatty acid distillate (PFAD), which
20 is inevitably produced as a by-product in the process of refining palm oil, is particularly preferable because PFAD is unsuitable for eating and thus poses no concerns regarding competition with food-related applications, and it is also relatively inexpensive. The palm fatty acid distillate (PFAD) is a mixture of a fatty
25 acid and glyceride, with the main component fatty acid constituting about 80 to 90%, and glyceride constituting about 7 to 15%. The fatty acid contains a C₁₆₋₁₈ saturated or unsaturated fatty acid in an amount of 90% or more. PFAD has an acid value of about 180 to 200 mgKOH/g.

30 [0032]

Examples of trihydric alcohol include alkane triols having 3 to 12 carbon atoms, and more preferably 3 to 8 carbon atoms. Specific examples thereof include glycerol, 1,2,3-
butanetriol, 2-methyl-1,2,3-propanetriol, 2-methyl-2,3,4-
35 propanetriol, trimethylolethane, trimethylolpropane, etc., among

which glycerol is preferable.

[0033]

Trihydric alcohol may be used in an amount such that the amount of hydroxy groups in the trihydric alcohol is at least one equivalent per equivalent of free carboxyl groups in the free fatty acid-containing raw material. For example, when the free fatty acid-containing raw material is a palm fatty acid distillate (PFAD) and the trihydric alcohol is glycerol, glycerol may be used in an amount of about 10 to 13%, based on the weight of the PFAD.

[0034]

A glyceride composition is produced by carrying out a non-catalytic esterification reaction using the above raw materials. The reaction vessel used to practice the present invention is not particularly limited, insofar as it is a pressurized vessel capable of supplying heat, which is configured to discharge therefrom water generated by the reaction. For example, vessels with stirrers, tower-type reactors, etc., can be used as reaction vessels.

[0035]

The production process according to the present invention comprises a reaction step in which a mixture of the free fatty acid-containing raw material and a trihydric alcohol is subjected to a non-catalytic esterification reaction at 230 to 250°C, whereby a glyceride composition with an acid value of 10 mgKOH/g or less can be produced.

[0036]

Prior to this reaction step, preferably, the mixture of a free fatty acid-containing raw material and a trihydric alcohol is preheated to about 50 to 70°C and then heated to the range of 230 to 250°C at a heating ramp rate of 10 to 30°C/hour.

[0037]

The preheating of the mixture of a free fatty acid-containing raw material and a trihydric alcohol that is fed to the reaction vessel to about 50 to 70°C, and the subsequent

heating of the mixture from this temperature to 230 to 250°C, which is the reaction temperature range, at a heating ramp rate of 10 to 30°C per hour, make it possible to suppress the evaporation of a trihydric alcohol that generally occurs with the
5 evaporation of water generated by the esterification reaction (hereinafter referred to as "generated water").

[0038]

In the heating step, the heating ramp rate does not have to be constant insofar as it is in the range of 10 to
10 30°C/hour. Heating at a constant ramp rate is also possible. When the mixture is heated at a constant ramp rate, the same ramp rate may be used until it reaches the reaction temperature, or the ramp rate may be changed during the heating. This step is preferably completed in about 8 to 12 hours.

15 [0039]

In this step, a non-catalytic esterification reaction occurs between the free fatty acid and trihydric alcohol. To suppress the evaporation of the trihydric alcohol with the evaporation of water generated by an esterification reaction
20 (hereinafter also referred to as "generated water"), the heating step is preferably carried out under atmospheric pressure. To promote the esterification reaction, the mixture of the free fatty acid-containing raw material and trihydric alcohol may be stirred. During the heating step, an esterification reaction
25 between the free fatty acid and trihydric alcohol proceeds, and the resulting reaction mixture has a low acid value of about 20 to 30 mgKOH/g.

[0040]

Thereafter, the reaction mixture is subjected to a non-
30 catalytic esterification reaction at 230 to 250°C. A reaction temperature lower than 230°C results in a slow reaction rate, which is impractical. A reaction temperature higher than 250°C tends to evaporate the trihydric alcohol at the early stage of the reaction and cause thermal deterioration of the generated
35 glyceride. The reaction temperature may change within the range

of 230 to 250°C. Alternatively, the reaction may be performed while the reaction temperature is controlled to be constant.

[0041]

5 This reaction step preferably comprises an atmospheric pressure reaction step in which the reaction is carried out under atmospheric pressure, and a reduced pressure reaction step in which the reaction is carried out under reduced pressure.

[0042]

10 In the atmospheric pressure reaction step, an esterification reaction is carried out under atmospheric pressure. Due to the esterification reaction under atmospheric pressure, the reaction is allowed to proceed while suppressing the evaporation of trihydric alcohol with the evaporation of generated water. In this step, the reaction time is about 2 to 6
15 hours.

[0043]

Subsequent to the atmospheric pressure reaction step, a reduced pressure reaction step is carried out. The reaction under reduced pressure makes it easy to remove generated water and
20 promotes the esterification reaction. In this step, the reaction time is about 6 to 8 hours. The reduced pressure (absolute pressure) during the depressurization is preferably about 0.02 to 0.07 MPa (200 to 500 Torr). During the reduced pressure reaction, inert gas is preferably injected into a mixture from a lower
25 portion of a reaction vessel because it promotes the esterification reaction and shortens the reaction time. Examples of inert gas include nitrogen gas, neon gas, argon gas, and xenon gas. The amount of inert gas injected may be about 3 m³/h. When the reduced pressure reaction step is completed, the reaction
30 mixture has an acid value of 10 mgKOH/g or less.

[0044]

After completion of the esterification reaction, the pressure is returned to atmospheric pressure in the presence of inert gas, and the produced glyceride composition is cooled to
35 about 80°C at atmospheric pressure.

[0045]

The esterification reaction at a high temperature of 230 to 250°C makes it possible to produce a glyceride composition having an acid value of 10 mgKOH/g or less, without the need for
5 using a catalyst.

[0046]

The glyceride composition obtained by the production process of the present invention contains a triglyceride as the main component and further contains a diglyceride, a
10 monoglyceride, an unreacted free fatty acid, etc.

[0047]

When the fatty acid is a palm fatty acid distillate (PFAD) and the trihydric alcohol is glycerol, a glyceride composition containing about 75% triglyceride, about 15%
15 diglyceride, and about 2% monoglyceride can be obtained.

[0048]

This glyceride composition has an acid value of 10 mgKOH/g or less, and is less corrosive to carbon steel. Therefore, the glyceride composition is useful as a fuel oil C substitute
20 that can be used in thermal power stations. Furthermore, the fuel oil C substitute comprising this glyceride composition is an environmentally friendly biomass fuel, and therefore can reduce CO₂ emission, compared to fossil fuel (fuel oil C).

25 Examples

[0049]

Specific examples of the present invention (Examples) are given below. However, it should be understood that the scope of the present invention is not limited thereto or thereby. The
30 chemical composition analysis was performed by gas chromatography using a GC-2010 [DB-1ht capillary column (J&W Scientific; 0.25 mm x 5 m)] produced by Shimadzu Corporation. The physical properties of fuel oils were determined by the following methods:

- (1) Density: measured according to JIS K2249
- 35 (2) Gross calorific value: measured according to JIS K2279

- (3) Kinematic viscosity: measured according to JIS K2283
- (4) Pour point: measured according to JIS K2269
- (5) Flash point: measured according to JIS K2265
- (6) Sulfur content: measured according to JIS K2541
- 5 (7) Nitrogen content: measured according to JIS K2609
- (8) Ash content: measured according to JIS K2272
- (9) Water content: measured according to JIS K2275
- (10) Residual carbon content: measured according to JIS K2270
- (11) Salt content: measured according to JIS K2601
- 10 (12) Sodium: measured according to JIS K0116
- (13) Vanadium: measured according to JIS K0116
- (14) Acid value: measured according to the standard fats and oils analysis test method 2.3.1 established by Japan Oil Chemists' Society
- 15 (15) Sediment mass: measured according to ISO 10307.

(Example 1)

A 30-m³ pressure vessel equipped with a stirring device and having an inlet on the upper portion thereof for feeding a raw material was used as the reaction vessel. An independent
20 condenser was connected to the upper portion of the reaction vessel via a pipe and installed as a partial condenser. The temperature of the condenser used as the partial condenser was controlled by using a heat medium. The reaction water condensed by the partial condenser was stored in a receiver disposed on the
25 bottom of the condenser.

[0050]

As a fatty acid, 19,188 kg of a palm fatty acid distillate (PFAD) (produced by CAROTINO (Malaysia), Lot No. 2117) was used; and 2,200 kg of glycerol (produced by NATOLEO
30 (Malaysia), Lot No. G80423-5, glycerol concentration: 98%) was used as a trihydric alcohol. The free fatty acid in the palm fatty acid distillate (PFAD) contained 48.0% palmitic acid, 4.4% stearic acid, and 35.4% oleic acid. The PFAD had an acid value of 192.1 mgKOH/g.

35 [0051]

These materials were placed into the reaction vessel and preheated to 60°C, and then subjected to a non-catalytic esterification reaction under the following conditions:

	Temperature (°C)	Pressure	Time (hours)
5	60 → 170	Atmospheric pressure	4
	170 → 240	Atmospheric pressure	6
	240	Atmospheric pressure	2
	240	Reduced pressure	8

The reduced pressure (absolute pressure) during the depressurization was 0.067 MPa (500 Torr) for the first 4 hours from the beginning of depressurization, and then was 0.027 MPa (200 Torr) for the second 4 hours. During the depressurization, nitrogen gas was injected from a lower portion of the reaction vessel (at a rate of 3 m³/h).

[0052]

After completion of the reaction, the reaction mixture was cooled to 80°C to provide 20,000 kg of a glyceride composition (yield: 99.9%). The obtained glyceride composition contained 74.5% triglyceride, 16.8% diglyceride, and 2.0% monoglyceride. Table 1 shows the basic properties of the obtained glyceride composition and the basic specifications of fuel oil for power generation.

[0053]

[Table 1]

Item (unit)	Example 1	Basic specifications of fuel oil for power generation
Density (g/cm ³)	0.9141	< 1.0
Gross calorific value (50°C) (MJ/kg)	39.18	> 42.70
Kinematic viscosity (mm ² /s)	29.7	5 to 190
Pour point (°C)	30	< 50
Flash point (°C)	236	> 70
Sulfur content (wt%)	0.0012	< 0.1
Nitrogen content (wt%)	Less than 0.01	< 0.1
Ash content (wt%)	Less than 0.003	< 0.1
Water content (wt%)	0.02	< 0.5
Residual carbon content (wt%)	0.25	< 10
Salt content (ppm)	Less than 3	< 20
Sodium (ppm)	1	< 2
Vanadium (ppm)	Less than 1	< 2
Acid value (mgKOH/g)	Less than 8	Not specified

[0054]

The results of Table 1 indicate that the basic properties of the glyceride composition obtained in Example 1 approximately satisfy the basic specifications of fuel oil for power generation. Although the gross calorific value of this glyceride composition is lower than that of fuel oil for power generation, the composition has sufficient properties for use as a fuel oil C substitute. Therefore, the glyceride composition obtained in Example 1 is considered to have no flammability problem.

[0055]

<Quality verification test>

Three samples, i.e., the glyceride composition obtained in the above Example 1 (Example 1); a mixed oil consisting of 50 wt.% of the glyceride composition obtained in Example 1 and 50 wt.% of a mixed crude oil (containing Rabi crude oil, etc.) (Comparative Example 1); and a mixed crude oil (containing Rabi crude oil, etc.) (Comparative Example 2), were subjected to a quality verification test. In the test, their corrosion and long-

term storage stability were evaluated in the following manner. When a fuel tank is filled with fuel oil, corrosion is most likely to occur on the inner surface of the tank, particularly at the interface between gas and oil on the inner surface of a tank not having a corrosion-resistant structure. Accordingly, the lower half of a test plate was immersed in a sample and maintained in that state for a long period of time, after which corrosion and long-term storage stability were evaluated. Fig. 1 shows an outline of the test.

10 [0056]

As shown in Fig. 1, rainwater 2 (25 ml) was added to a sample 1 (500 ml); and a test plate 3 of carbon steel SS400 (approximately 4.3 g; approximately 20 mm long x 10 mm wide x 3 mm thick) was half-immersed in the sample 1 and maintained in that state for 500 or 1,000 hours. The test was carried out in a constant temperature bath 4 maintained at 60°C.

[0057]

(1) Corrosion assessment

Corrosion was evaluated based on the mass loss and the erosion rate after 500 and 1,000 hours of immersion.

20 [0058]

The erosion rate was calculated according to the following equation:

Annual average erosion rate (mm) =

25

$$\frac{\text{Mass loss (g)} \times 365 \times 10}{\text{Contact area (cm}^2\text{)} \times \text{Number of days of immersion} \times \text{Density of the test plate (g/cm}^3\text{)}}$$

[0059]

The erosion rate was evaluated as having "passed" when "less than 0.05 mm/yr (having corrosion resistance)" according to the corrosion resistance evaluation standards of "Corrosion Data Survey" established by NACE (National Corrosion Engineers Standards) was satisfied.

[0060]

35 Table 2 shows the results.

[0061]

[Table 2]

Immersion time	Sample	Storage temperature 60°C	
		Mass loss (mg)	Erosion rate (mm/yr)
500 hours	Example 1	0.35	0.002
	Comparative Example 1	0.20	0.001
	Comparative Example 2	0.35	0.002
1,000 hours	Example 1	0.30	0.001
	Comparative Example 1	0.35	0.001
	Comparative Example 2	0.35	0.001

[0062]

The results of Table 2 show that the mass loss after
5 500 hours of immersion and that after 1,000 hours of immersion in
the sample of Example 1 were both equivalent to those in the
samples of Comparative Examples 1 and 2. The erosion rate was
much lower than 0.05 mm/yr, i.e., the evaluation standard, in all
the samples under any conditions, and was thus evaluated as
10 having "passed". These results confirmed that the glyceride
composition obtained in Example 1 has no corrosion problem in
storage for 1,000 hours or less. Furthermore, no pitting
corrosion was observed.

[0063]

15 (2) Long-term storage stability

The acid value, sediment mass, kinematic viscosity,
calorific value, and pour point of each sample before testing and
after 500 hours and 1,000 hours of immersion were measured.
Table 3 shows the results.

20 [0064]

[Table 3]

Storage temperature	Immersion time	Sample	Acid value mgKOH/g	Sediment mass%	Kinematic viscosity (60°C) mm ² /s	Kinematic viscosity (80°C) mm ² /s	Calorific value MJ/kg	Pour point °C
60°C	Before the test	Example 1	5.84	<0.01	21.6	12.9	39.64	30.0
		Comparative Example 1	3.03	<0.01	13.7	8.57	42.57	30.0
		Comparative Example 2	0.21	<0.01	9.17	5.94	45.90	35.0
		Example 1	6.98	<0.01	22.4	13.22	39.02	30.0
	500 hours	Comparative Example 1	3.44	<0.01	14.9	9.11	41.10	32.5
		Comparative Example 2	0.23	<0.01	9.78	6.26	44.74	35.0
		Example 1	9.34	<0.01	24.5	14.2	38.49	30.0
		Comparative Example 1	4.01	<0.01	15.1	9.30	41.89	35.0
	1,000 hours	Comparative Example 2	0.28	<0.01	9.94	6.39	45.42	35.0

[0065]

The results of Table 3 show that no remarkable property changes were observed in any of the samples after 500 hours and 1,000 hours. The results confirmed that the quality of the
5 glyceride composition obtained in Example 1 is stable over a long period of time.

CLAIMS

- [Claim 1] A process for producing a glyceride composition for use as a fuel oil C substitute by using a free fatty acid-
5 containing raw material and a trihydric alcohol, the process comprising a reaction step of subjecting a mixture of the free fatty acid-containing raw material and trihydric alcohol to a non-catalytic esterification reaction at 230 to 250°C.
- [Claim 2] The process according to claim 1 comprising, before the
10 reaction step, a heating step of preheating the mixture to 50 to 70°C and then raising the temperature of the mixture to the range of 230 to 250°C at a heating ramp rate of 10 to 30°C/hour.
- [Claim 3] The process according to claim 1 or 2, wherein the
15 reaction step comprises an atmospheric pressure reaction step of carrying out the reaction under atmospheric pressure, and a reduced pressure reaction step of carrying out the reaction under reduced pressure.
- [Claim 4] The process according to claim 3, wherein the reduced
20 pressure reaction step is carried out while feeding an inert gas into the mixture.
- [Claim 5] The process according to any one of claims 1 to 4, wherein the fatty acid-containing raw material is a palm fatty acid distillate (PFAD).
- 25 [Claim 6] The process according to any one of claims 1 to 5, wherein the trihydric alcohol is glycerol.
- [Claim 7] A glyceride composition for use as a fuel oil C substitute, which is produced by the process of any one of claims 1 to 6.
- 30 [Claim 8] A fuel oil C substitute comprising the glyceride composition of claim 7.