

【DESCRIPTION】**【Invention Title】**

METHOD OF MAKING BIODIESEL WITH GOOD LOW-TEMPERATURE
PERFORMANCE FROM PALM OIL

5 **【Technical Field】**

The present invention relates to a method of producing biodiesel having good low-temperature fluidity from palm oil. More particularly, the present invention relates to a method of producing biodiesel having excellent good low-temperature fluidity by separating palm biodiesel (or palm fatty acids) into C16 palm biodiesel (or C16 palm fatty acid) and C18 palm
10 biodiesel (or C18 palm fatty acid) and converting C16 palm biodiesel (or C16 palm fatty acid) poor in low-temperature fluidity into paraffinic mixtures.

【Background Art】

Biodiesel refers to a diesel-equivalent biofuel consisting of long carbon chain methyl esters, obtained through the transesterification of vegetable oils (triglyceride) in the presence of a
15 base catalyst. Because it is relatively cheap and can reduce the amount of emissions, including carbon monoxide, nitrogen oxides, fine particles, and carbon dioxide, biodiesel is receiving increased attention as an alternative fuel in light of the United Nations Framework Convention on Climate Change and current high oil prices.

Recovered oil, composed mainly of imported soybean oil, is currently used as a material
20 for the production of domestic biodiesel. As seen in FIG. 6, soybean oil is cheaper than rapeseed oil, but 20-25% more expensive than palm oil.

Thus, palm biodiesel, produced from palm diesel, is most advantageous in terms of production cost, but is difficult to use in the winter season because of its poor low-temperature fluidity.

25 Among the components of biodiesel, methyl palmitate (C16:0) and methyl stearate

(C18:0) causes the degradation of low-temperature fluidity. In palm biodiesel, these components amount to approximately 45%, which is far greater than in the biodiesel of other vegetable oils.

TABLE 1

Biodiesel Compositions According to Vegetable Oil

	Pour Point °C	Rapeseed Biodiesel	Soybean Biodiesel	Palm Biodiesel
C16:0(Methyl Palmitate)	30-32	6 %	11 %	44.0 %
C18:0 (Methyl Stearate)	37-41	1.9 %	4 %	4.5 %
C18:1 (Methyl Oleate)	-20	62.1 %	24 %	39.2 %
C18:2(Methyl Linoleate)	-35	20.2 %	54 %	10.1 %
C18:3(Methyl Linoleate)	-57	8.5 %	7 %	0.4 %

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In Table 1, symbols, such as C18:1, C18:2, etc., are expressions for fatty acids. For example, C18:2 represents a fatty acid consisting of a 18-carbon chain with 2 unsaturated bonds therein.

TABLE 2

Physical Properties of Biodiesel According to Vegetable Oils

	European Standards	Rapeseed biodiesel	Soybean biodiesel	Palm biodiesel
Iodine value, g/100g	< 120	98	129	55
Pour Point, °C	< 0 (Domestic Standard)	-12	-2	13
10% residual Carbon, wt%	< 0.30	0.25	0.65	0.10
Oxidation Stability, hr	> 6.0	5.5	3.6	6.9
Cetane No.	> 51	58	50	65

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As seen in Tables 1 and 2, physical properties differ from one biodiesel to another because the vegetable oils thereof are different in composition from one another. In soybean biodiesel, methyl linoleate (18:2), which shows good low temperature fluidity but poor oxidation stability, is predominant.

Of biodiesel components, methyl oleate (18:1) is the most advantageous because its low-temperature fluidity is not bad, and its oxidation stability is excellent. Accordingly, rapeseed biodiesel, consisting mainly of methyl oleate, is most preferable in terms of physical properties. However, rapeseed oil is expensive in comparison with other vegetable oils and
5 trades internationally in small quantities. As a matter of fact, it is difficult for most countries to secure rapeseed oil in sufficient amounts, except for some rapeseed oil-rich European regions.

Palm oil is arising as an alternative. Not plagued by the problem of poor low-temperature fluidity, palm oil is most suitable in terms of price and properties for countries that import most of the vegetable oils necessary for biodiesel.

10 With regard to the low-temperature fluidity of palm diesel, U. S. 2004/0231234 describes the fractional distillation or crystallization of palm oil to remove C16 palm biodiesel (C16:0) and the use of the remaining fraction C18 palm biodiesel (C18:0, C18:1, C18:2 and C18:3) having good low-temperature fluidity as diesel component. It is also described that the pour point of the C18 palm biodiesel is low so that it can be used as a diesel blending component
15 in the mild weather regions and that the obtained C16 palm biodiesel or C16 palm fatty acid as by-products can be sold for oleochemical, and used as feedstock for α -sulphonated methyl esters.

However, the market of oleo chemicals is not sufficiently large to accommodate C16 palm biodiesel or C16 palm fatty acid, but has already been saturated. Thus, this conventional technology cannot be applied in practice unless a new use, which realizes consumption of C16
20 palm biodiesel beyond a base degree, is exploited.

Formulation with C16 palm biodiesel is not a desirable solution, because C16 palm biodiesel having a pour point of about 30°C, greatly degrades the low-temperature fluidity of the diesel.

U. S. Pat. No. 4,992,605 discloses a process for producing C15/C16/C17/C18 n-
25 paraffinic hydrocarbons, effective as diesel fuel cetane rating improvers, by hydrotreating a

vegetable oil feedstock with a high-pressure hydrogen gas in a reactor filled with a CoMo type catalyst to convert the feedstock to a mixture of paraffinic compounds, including mainly a diesel fuel boiling range fraction. According to this process, however, the resulting mixture has a pour point of about 20°C, which is higher than that of palm biodiesel. Notably, when hydrotreated, C18 palm biodiesel is converted to a C17/C18 n-paraffinic mixture. In this case, the pour point is greatly increased (lower than 0°C → higher than 25°C).

Since C18 palm biodiesel has more unsaturated bonds in the carbon chain of fatty acid compared to C16 palm biodiesel, it requires a 30~40% more hydrogen amount for the hydrotreating thereof. It is thus necessary to reduce the hydrogen amount due to high hydrogen prices.

【Disclosure】

【Technical Problem】

Leading to the present invention, intensive and thorough research into cheap biodiesel having good low-temperature fluidity, conducted by the present inventors, resulted in the finding that the C18 palm biodiesel obtained through the fractional distillation of palm biodiesel can be used as a diesel component and that the other fraction, C16 palm biodiesel has poor low temperature fluidity, thus inventors has researched for application of this fraction as diesel component, and found that C16 palm biodiesel is improved in low-temperature fluidity by hydrotreating to an extent that it can be used as a diesel component and the hydrotreating requires relatively small amounts of hydrogen for the conversion of the C16 palm biodiesel to C15/16 paraffinic mixture because there are few unsaturated bonds in the carbon chain thereof.

Accordingly, it is an object of the present invention to provide a method of producing biodiesel having good low-temperature fluidity from palm oil.

It is another object of the present invention to provide a diesel product comprising the biodiesel (C15/C16 paraffinic mixture).

【Technical Solution】

In accordance with an aspect thereof, the present invention provides a method of producing biodiesel having good low-temperature fluidity from palm oil, comprising: a) separating palm biodiesel (or palm fatty acid) into C16 palm biodiesel (or C16 palm fatty acid) and C18 palm biodiesel (C18 palm fatty acid) through distillation; b) hydrolyzing the C16 palm biodiesel to C16 palm fatty acid and methanol; and c) converting the C16 palm fatty acid or the C16 palm biodiesel of a) step into a C15/C16 paraffinic mixture through hydrotreating.

In accordance with another aspect thereof, the present invention provides a diesel, comprising the biodiesel produced by the method in an amount of 2 to 10 volume % in a mixture of a diesel fuel.

【Advantageous Effects】

As described hitherto, the biodiesel according to the present invention employs palm oil, which is cheaper than soybean oil, a typical biodiesel material, and has low-temperature fluidity that meet domestic and foreign specifications when it is processed properly. Thus, the biodiesel of the present invention can be actively used in industrial and environmental fields.

【Description of Drawings】

FIG. 1 is a diagram showing typical processes for producing biodiesel from soybean oil.

FIG. 2 is a diagram showing processes for producing biodiesel having good low-temperature fluidity from palm oil in accordance with the present invention.

FIG. 3 is a diagram showing the structure of a reactor for hydrotreating C16 palm fatty acid.

FIG. 4 is a graph showing CFPP(cold filter plugging point) of C16 palm biodiesel according to mixture ratios of diesel.

FIG. 5 is graph showing CFPP(cold filter plugging point) of C15/C16 n-paraffinic

mixture according to mixture ratios of diesel.

FIG. 6 is a graph showing price trends of vegetable oils.

【Best Mode】

Hereinafter, a detailed description will be given of the present invention.

5 The present invention pertains to a process of producing biodiesel having good low-temperature fluidity from palm oil, comprising a) separating palm biodiesel (or palm fatty acid) into C16 palm biodiesel (or C16 palm fatty acid) and C18 palm biodiesel (C18 palm fatty acid) through distillation; b) hydrolyzing the C16 palm biodiesel to C16 palm fatty acid and methanol; and c) converting the C16 palm fatty acid or the C16 palm biodiesel of a) into a
10 C15/C16 paraffinic mixture through hydrotreating.

Below, each step of the method according to the present invention is elucidated further.

a) Separation of palm biodiesel (or palm fatty acid) into C16 palm biodiesel (or C16 palm fatty acid) and C18 palm biodiesel (C18 palm fatty acid) through distillation;

15 Palm biodiesel (or palm fatty acid) consists predominantly of C16:0 (methyl palmitate or palmitic acid) and C18:1 (methyl oleate or oleic acid), which can be separated from each other using their different boiling points. Distillation may be conducted in a temperature range of 180 to 230°C under a pressure of 5 - 20 torr.

C18 palm biodiesel, separated as one component of palm biodiesel, is similar in
20 composition to rapeseed biodiesel. C18 palm biodiesel is slightly superior in oxidation stability and 10% residual carbon to rapeseed biodiesel. The low-temperature fluidity of C18 palm biodiesel, although slightly inferior to those of rapeseed biodiesel, are as good as those of soybean biodiesel. Accordingly, C18 palm biodiesel can be used as a diesel blending component. By contrast, C16 palm biodiesel is, as seen in Tables 3 and 4, not suitable for use
25 as a blending component due to the poor low-temperature fluidity thereof. It is hydrolyzed to

methanol and C16 palm fatty acid, which is then hydrotreated.

C18 palm fatty acid, separated as one component of palm fatty acid, can be converted into C18 palm biodiesel by esterification with methanol at the presence of acid catalyst.

b) Hydrolysis of C16 palm biodiesel to C16 palm fatty acid and methanol;

5 For the hydrolysis, water is mixed in an amount of 1/15 or greater of the weight of C16 palm biodiesel, and a base catalyst is added in an amount of 0.1 weight % or greater based on the weight of the resulting mixture. For example, when the weight ratio of water to C16 palm biodiesel is less than 1/15, some fatty acids remain unhydrolyzed.

Special limitations are not imposed to kinds of the base catalyst useful in the present
10 invention. Preferable is sodium methoxide.

When the base catalyst is used in an amount of less than 0.1 wt%, it takes a long period of time to complete hydrolysis.

As a result of the hydrolysis, C16 palm biodiesel is divided into C16 palm fatty acid and methanol. Methanol can be recovered using a vacuum evaporator.

15 c) Conversion of C16 palm fatty acid or the C16 palm biodiesel of a) into C15/C16 paraffinic mixture through hydrotreating;

Hydrotreating converts C16 palm biodiesel to a C15/C16 paraffinic mixture, requiring at least four molecules of hydrogen per molecule of C16 palm biodiesel. But after the hydrolysis of C16 palm biodiesel, methanol can be readily recovered, and the amount of
20 hydrogen necessary for the hydrotreating of one molecule of C16 palm fatty acid is reduced to three molecules.

Through hydrotreating, most of the C16 palm fatty acid is converted to C15/C16 paraffinic mixtures. C18 fatty acid mixtures, contained as impurities in a distillation step, can be converted to C17/C18 paraffinic components, but are present in small amount.

25 Hydrotreating is conducted by feeding a liquid feedstock of C16 palm biodiesel or

C16 palm fatty acid at an H_2 to oil ratio of $3 \text{ m}^3/\text{k l}$ and an LHSV of 2hr^{-1} or less to a continuous reactor filled with a CoMo or NiMo-type catalyst, in which the average catalyst bed temperature (BAT) is maintained at 330°C or higher, with a partial hydrogen pressure of 30 bar or higher.

- 5 The direct hydrotreating of C16 palm biodiesel may be conducted under the same conditions, but consumes a larger amount of hydrogen compared to the case of C16 palm fatty acid.

When the H_2 to oil ratio is less than 3, hydrogen is not sufficiently supplied. At an LHSV greater than 2 hr^{-1} , a partial hydrogen pressure less than 30bar and a BAT less than
10 330°C , the conversion of the fatty acid into paraffin cannot be achieved well.

For the hydrogenation of C16 palm fatty acid, desulfurization catalysts, NiMo-type catalysts and/or CoMo-type catalysts, may be used.

The physical properties of n-paraffins resulting from conversion of biodiesel are summarized in Table 3, below. As seen in Table 3, n-C15 and n-C16 obtained through
15 hydrotreating of C16 palm fatty acids are lower in pour point than n-C17 and n-C18 from C18 palm fatty acids, and thus can be used as fuel additives in the winter season.

TABLE 3

Conversion of Palm Oil, Palm Fatty Acid and Palm Biodiesel to n-Paraffins

Biodiesel	C16:0		C18:0	C18:1	C18:2	C18:3
Pour Point, $^\circ\text{C}$	30-32		37-41	-20	-35	-57
Cetane No.	74.5		86.9	55	42.2	22.7
Specific Weight	0.852		-	0.879	0.889	0.895
n-Paraffins	n-C15	n-C16	n-C17		n-C18	
Pour Point, $^\circ\text{C}$	9.9	18	22-24		29.5	
Cetane No.	95	100	105		110	
Specific Weight	0.769	0.773	0.777		0.777	

As described above, the paraffinic mixtures resulting from conversion of C16 palm fatty acid or C16 palm biodiesel can be blended with conventional diesel fuels without worsening the low-temperature fluidity thereof.

Typically, diesel for the winter season is a mixture of 3:7 of kerosene, having a boiling point of 150-250°C, and a light gas oil, having a boiling point of 250-360°C, and is supplemented with about 600 ppm of a WAFI(Wax Anti-settling Flow Improver), meeting domestic and foreign sepecification for low-temperature fluidity.

When the C15/C16 n-paraffinic mixture according to the present invention is mixed in an amount of 2 – 10 volume % with a conventional diesel fuel, a notable improvement is brought about in low-temperature fluidity compared to when C16 palm biodiesel is mixed at the same volume. An amount of the C15/C16 n-paraffinic mixture exceeding 10 volume % of the conventional diesel fuel is not desirable in terms of CFPP.

【Mode for Invention】

A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

Distillation

When 3,000 g of palm biodiesel was separated into C16 palm biodiesel and C18 palm biodiesel at a ratio of 4:6 in a still maintained at 10 torr and 185°C, the resulting mixture had the following composition and physical properties.

TABLE 4

Compositions of Palm C16/C18 Biodiesel

	b.p. °C	C16 palm biodiesel	C18 palm biodiesel	Palm biodiesel
C16:0 (Methyl Palmitate)	338	90.5 %	8.1 %	43.5 %
C18:0	352	2.2 %	5.9 %	4.3 %

(Methyl Stearate)				
C18:1 (Methyl Oleate)	349	6.8 %	65.9 %	39.8 %
C18:2 (Methyl Linoleate)	366	0.2 %	18.3 %	10.2 %
C18:3 (Methyl Linoleate)	-	0.1 %	0.5 %	0.3 %

TABLE 5

Main Physical Properties of Palm C16/C18 Biodiesel

	European Standards	C16 Palm biodiesel	C18 Palm biodiesel	Palm biodiesel
Iodine Value g/100g	< 120	7	88	55
Pour Point, °C	< 0 (Domestic Standard)	30	-1	13
10% Residual Carbon, wt%	< 0.30	0.05 or less	0.15	0.10
Oxidation Stability, hr	> 6.0	> 20	6.0	6.9
Cetane No.	> 51	72	55	65

Hydrolysis

A 1,000 cc round-bottom flask containing 470 g of C16 palm biodiesel, 45 g of water
 5 and 1 g of a base catalyst (Sodium Methoxide) was installed in a vacuum evaporator.

When the internal pressure of the round-bottom flask reached 200 torr in a water bath
 maintained at 60°C, the vacuum evaporator was operated for 45 min. The hydrolysis of C16
 palm biodiesel occurred with the concomitant production of methanol and C16 palm fatty acid.
 This methanol was removed by the vacuum evaporator. Thereafter, the pressure of the
 10 vacuum evaporator was reduced to 40 torr to remove remaining water and methanol. The
 pressure was decreased, and the resulting C16 palm fatty acid solution was passed through a
 paper filter at 50°C to remove the base catalyst.

TABLE 6

C16 Palm Biodiesel and C16 Palm Fatty Acid

	C16 Palm	C16 Palm Fatty Acid
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	Biodiesel	
Structural Formula	RCOOCH_3	RCOOH
Iodine Value, g/100g	10 or less	10 or less
Total Acid No. mg KOH/g	0.5	202

Hydrotreating

As illustrated in FIG. 3, while C16 palm fatty acid (100 cc/hr) and hydrogen (0.5 Nℓ/hr) was fed to a reactor filled with 100 cc of a CoMo catalyst, the average temperature of a catalyst bed was gradually increased to 370°C. From four hours after the temperature increase, liquid products started to be collected for 10 hours. Water was removed from the collected liquid product by phase separation, and the remaining liquid product was analyzed to determine the composition thereof.

TABLE 7

Liquid Feedstock and Liquid Product of Hydrotreator

	Liquid Feedstock	Liquid Product	
	C16 Palm Fatty Acid	C15/C16 n-Paraffinic Mix	Water
Vol. (Wt.)	995 cc (850 g)	935 cc (720 g)	(99 g)
Yield	100%	84.7%	11.6%
Composition, wt%	Fatty Acid Mix. C16:0 90.5 C18:0 2.2 C18:1 6.8 C18:2 0.2 C18:3 0.1	n-Paraffinic Mix. Lighters 1 n-C15 27 n-C16 62 n-C17 2.5 n-C18 5.5 Heavier 1.5	
Specific Weight	0.85	0.77	
Pour Point, °C	30	14	
Cetane No.	72	98	

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Evaluation for Effect of WAFI

When added to a blend of a conventional diesel fuel with C16 palm biodiesel or with the C15/C16 n-paraffinic mixture, CFPP(cold filter plugging point) was measured according to

the concentrations of WAFI. The CFPP is a main index expressing the low-temperature fluidity of diesel, and is -20°C or lower for domestic diesel products for the winter season.

TABLE 8

Effect of C16 Palm Biodiesel and n-Paraffinic Mixture on Performance of Flow

5 Improver

Sample	Diesel mixture Vol %				CFPP According to Conc. Of WAFI °C		
	Kero sene	light gas oil	C16 Palm biodiesel	C15/C16 n-Paraffinic Mix	WAFI 0 ppm	WAFI 600 ppm	WAFI 1,000 ppm
Standard	30	70	0	0	-7	-21	-24
1-1	30	68	2	0	-8	-19	-21
1-2	30	65	5	0	-9	-17	-18
1-3	30	60	10	0	-6	-10	-10
2-1	30	68	0	2	-8	-21	-24
2-2	30	65	0	5	-9	-21	-22
2-3	30	60	0	10	-10	-19	-20

As seen in Table 8 and FIG. 4 and 5, even when C16 palm biodiesel was added in an amount of 2 %, the CFPP was increased, so that the amount of the WAFI had to be increased to 1,000 ppm in order to satisfy the filter plugging point standard (-20°C or lower). By contrast, C15/C16 n-paraffinic mixture caused no changes in CFPP(cold filter plugging point) until it was added at a volume of 5%. Even if it was added at a volume of about 10%, 1,000 ppm of the flow improver was observed to satisfy the CFPP specification.

【CLAIMS】**【Claim 1】**

A method of producing biodiesel having good low-temperature fluidity from palm oil, comprising:

- 5 a) separating palm biodiesel (or palm fatty acid) into C16 palm biodiesel (or C16 palm fatty acid) and C18 palm biodiesel (C18 palm fatty acid) through distillation;
- b) hydrolyzing the C16 palm biodiesel to C16 palm fatty acid and methanol; and
- c) converting the C16 palm fatty acid or the C16 palm biodiesel of a)step into a C15/C16 paraffinic mixture through hydrotreating.

10 **【Claim 2】**

The method according to claim 1, wherein the distillation is conducted at a pressure of 5 – 20 torr and a temperature of 180 - 230°C.

【Claim 3】

- The method according to claim 1, wherein the hydrolyzing is conducted with a
- 15 mixture comprising water in an amount as large as or larger than 1/15 of the weight of C16 palm biodiesel in the presence of a base catalyst added in an amount of 0.1 weight % based on the weight of the mixture.

【Claim 4】

- The method according to claim 1, wherein the hydrotreating is conducted in a reactor
- 20 filled with a CoMo-type catalyst or a NiMo-type catalyst by feeding a liquid feedstock of the C16 palm biodiesel or C16 palm fatty acid at an LHSV of 2 hr⁻¹ or less and at an H₂ to oil volume ratio of 3 m³/kℓ or larger under a partial hydrogen pressure of 30 bar or higher with a bed average temperature (BAT) maintained at 330°C or higher.

【Claim 5】

- 25 A diesel product, comprising the biodiesel produced by the method of one of claims 1

to 4 in an amount of 2 to 10 volume % in a mixture of a diesel fuel.