(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 October 2014 (16.10.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/168403 A1

(51) International Patent Classification:
C10M 101/02 (2006.01) *C10M 105/08* (2006.01)
C10M 105/42 (2006.01)

(21) International Application Number:
PCT/KR2014/003045

(22) International Filing Date:
8 April 2014 (08.04.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2013-0038454 9 April 2013 (09.04.2013) KR

(71) Applicants: **SK INNOVATION CO., LTD.** [KR/KR]; (Seorin-dong, SK Seorin-dong Bldg.) 26, Jongro, Jongro-gu, Seoul 110-110 (KR). **SK LUBRICANTS CO., LTD.** [KR/KR]; (Seorin-dong) 26, Jongro, Jongro-gu, Seoul 110-110 (KR).

(72) Inventors: **RYU, Jae Wook**; (Jeonmin-dong, Sejong Apt.)102-1406, 1741, Yuseong-daero, Yuseong-gu, Daejeon 305-728 (KR). **KIM, Yong Woon**; (Gwanpyeong-dong) 306, 15-26, Gwandeul 5-gil, Yuseong-gu, Daejeon 305-509 (KR). **KIM, Do Woan**; (Gwanpyong-dong, Daedok Technovalley 10 danji Apt.)1006-1104, 61, Baeul 2-ro, Yuseong-gu, Daejeon 305-509 (KR). **NOH, Myoung Han**; (Hongje-dong, Hyundai Apt.)107-109, 57, Tongil-ro 39ga-gil, Seodaemun-gu, Seoul 120-784 (KR). **KWON, Wan Seop**; (Jeonmin-dong, Expo Apt.) 204-1104, 448, Expo-ro, Yuseong-gu, Daejeon 305-761 (KR). **OK, Jin Hee**; (Hwamyong-dong, Beoksan ganbeon town)103-206, 21, Yangdal-ro 9beon-gil, Buk-gu, Busan 616-784 (KR). **LIM, Jin Heong**; (Ssangyong-dong, Yongam maeul Apt.)107-1102, 131, Wolbong-ro, Seobuk-gu, Cheonan-si, Chungcheongnam-do 331-789 (KR).

(74) Agent: **LEE & PARK**; (Seocho-dong, Changsang Bldg.) 6nd Fl., 112, Banpo-Daero, Seocho-gu, Seoul 137-872 (KR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

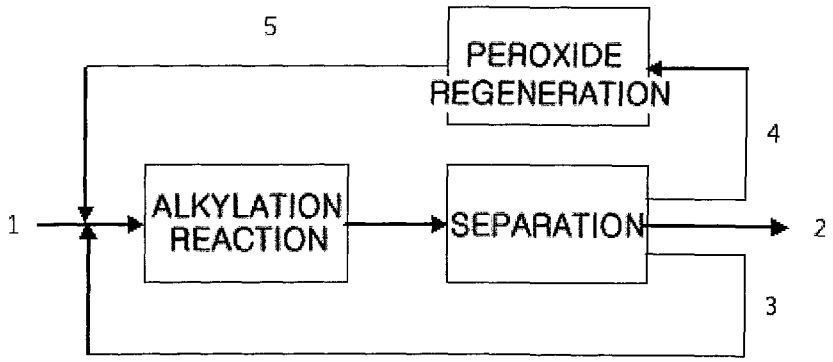
Published:

— *with international search report (Art. 21(3))*

— *with amended claims and statement (Art. 19(1))*

WO 2014/168403 A1

(54) Title: METHOD OF PRODUCING LUBE BASE OIL BY ALKYLATION OF HYDROCARBONS



(57) Abstract: Disclosed herein is a method of producing high-quality lube base oil by alkylating an isoparaffin-containing hydrocarbon feedstock without the addition of olefins.

Description

Title of Invention: METHOD OF PRODUCING LUBE BASE OIL BY ALKYLATION OF HYDROCARBONS

Technical Field

[1] The present invention relates to a method of producing lube base oil by alkylation of hydrocarbons. More particularly, the present invention relates to a method of producing high-quality lube base oil by alkylating an isoparaffin-containing hydrocarbon feedstock using peroxide as a radical initiator without the addition of olefins.

Background Art

[2] There are known processes of producing a high-grade hydrocarbon product by the alkylation reaction of hydrocarbons, specifically isoparaffins or branched paraffins contained in an oil fraction produced during an oil refining process, with olefins.

[3] As examples of such an alkylation process, technologies for improving the octane number of gasoline using a blending component obtained by alkylating an olefin-containing feedstock with an isoparaffin-containing feedstock are known (for example, U.S. Patent Nos. 5,824,835 and 5,120,897). Here, generally, isoparafins of 4 to 8 carbon atoms (for example, isobutene, isopentane, etc.) and olefins of 2 to 12 carbon atoms (for example, 2-butene, 1-butene, propylene, etc.) may be used. Further, in the above-mentioned alkylation process, a particulate solid catalyst, specifically, a zeolite catalyst may be used.

[4] Meanwhile, even in the field of producing lube base oil, attempts to produce high-quality lube base oil by the alkylation of isoparaffins have been conducted. In the case of the above-mentioned conventional technologies, it has been reported that lube base oil having a high viscosity index and low pour point can be produced by reacting an isoparaffin-containing fraction (for example, a fraction having a middle distillate boiling point) with an olefin-containing fraction. However, the alkylation reaction between isoparaffin and olefin having a long chain is extremely restrictive, and the lube base oil produced thereby has relatively low viscosity although it is somewhat improved in terms of viscosity index, so this lube base oil has a limitation in being applied to the fields requiring high viscosity characteristics (for example, engine oil, gear oil and the like for automobiles; and hydraulic oil, oil, machine oil, compressor oil and the like for industries).

[5] Further, since the separation of unreacted olefin as well as unreacted isoparaffin must be additionally performed in order to recover alkylate (target product), processes become complicated, and thus it is difficult to conduct an operation through continuous

reactions, and side reactions derived from olefins cannot be avoided.

[6] Moreover, even in the case of the above process, the final lube base oil obtained has a viscosity index of about 100, which is insufficient to meet the recently required high viscosity index specifications.

[7] Therefore, it is necessary to develop a process of producing high-quality lube base oil, by which high-quality lube base oil is efficiently produced, compared to conventional technologies.

Disclosure of Invention

Technical Problem

[8] As described above, conventional processes of producing lube base oil by the alkylation reaction of isoparaffins and olefins have been commonly known, but the alkylation reaction of only isoparaffins having a long chain, without using olefins, has not been reported yet.

[9] Accordingly, the present invention intends to provide a method of producing high value-added lube base oil having high kinematic viscosity and a high viscosity index by the alkylation reaction of long-chain isoparaffins of 5 or more carbon atoms in a feedstock using a specific radical initiator (peroxide) without the addition of olefins.

Solution to Problem

[10] A first aspect of the present invention provides a method of producing lube base oil, including the steps of: a) providing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction; b) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar and a temperature of 10 to 200°C; and c) recovering lube base oil from the alkylation reaction product, wherein the step b) is performed without the addition of olefins.

[11] In the method, when the isoparaffin-containing feedstock is (i) an isomerized fraction of biomass-derived diesel, the lube base oil may have a boiling point of 300 to 700°C, a viscosity index of 90 to 150, a kinematic viscosity of 2 to 30 cSt (100°C) and a pour point of -36 to 0°C.

[12] Further, when the isoparaffin-containing feedstock is (ii) a group II or group III lube base oil fraction, the lube base oil may have a boiling point of 400 to 700°C, a viscosity index of 90 to 150, a kinematic viscosity of 6 to 60 cSt (100°C) and a pour point of -40 to 0°C.

[13] A second aspect of the present invention provides a method of producing lube base oil, including the steps of: a1) continuously introducing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction into an alkylation reaction region; b1) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar, a temperature of 10 to 200°C and a weight hourly space velocity (WHSV) of 0.2 to 2 hr^{-1}; b2) separating alkylate, unreacted feedstock and ureacted peroxide or alcohol from the alkylation reaction stream; c1) recovering the alkylate; and c2) transferring the separated unreacted peroxide or alcohol to a peroxide regeneration region simultaneously with or subsequently to the step c1) to regenerate peroxide and then recycling the regenerated peroxide into the alkylation reaction region, and recycling the separated unreacted feedstock into the alkylation reaction region, wherein the step b1) is performed without the addition of olefins.

Advantageous Effects of Invention

[14] The lube base oil produced by the method of producing lube base oil according to the present invention has high viscosity and a high viscosity index compared to conventional lube base oil obtained by the alkylation reaction of isoparaffin and olefins. The method of producing lube base oil according to the present invention is advantageous in that a single hydrocarbon feedstock is used, so side reactions occurring when an olefin is used can be prevented, and a separation procedure can be simplified, thereby easily realizing commercially-advantageous continuous processes.

Brief Description of Drawings

[15] The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

[16] FIG. 1 is a schematic view showing a process of producing biodiesel as a feedstock for an alkylation reaction according to an embodiment of the present invention;

[17] FIG. 2 is a schematic view showing a process of producing a lube base oil fraction as a feedstock for an alkylation, wherein the lube base oil fraction is prepared from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, according to an embodiment;

[18] FIG. 3 is a schematic block diagram showing a continuous process including the steps of alkylation reaction, separation and peroxide regeneration according to an em-

bodiment of the present invention;

[19] FIG. 4 is a SIMIDIS graph of an alkylation product obtained in Example 1;

[20] FIG. 5 is a SIMIDIS graph of alkylation products obtained in Example 2 and Comparative Example 1; and

[21] FIG. 6 is a SIMIDIS graph of alkylation products obtained in Example 3 and Comparative Example 2.

[22] [Reference Numerals]

[23] AR: atmospheric residue

[24] VGO: vacuum gas oil

[25] VR: vacuum residue

[26] UCO: unconverted oil

[27] V1: atmospheric residue vacuum distillation process

[28] R1: VGO hydrotreating reaction process

[29] R2: VGO hydrocracking reaction process

[30] Fs1: fractional distillation process

[31] IDW: isomerization (isodewaxing) process

Best Mode for Carrying out the Invention

[32] The present invention may be embodied in many different forms without departing from the spirit and significant characteristics of the invention. Therefore, the embodiments of the present invention are disclosed only for illustrative purposes and should not be construed as limiting the present invention. The objects, features and advantages of the present invention will be more clearly understood from the following detailed description of the preferred embodiments taken in conjunction with the accompanying drawings.

[33] The terms used in the present invention are defined as follows.

[34] The term "alkylation reaction" means a reaction for adding an organic molecule with an alkyl group, specifically, a reaction for bonding isoparaffins in a feedstock.

[35] The term "isoparaffin" means a non-straight-chain, that is, branched paraffin having a carbon number of 5 or more (specifically, 5 to 30, and more specifically 10 to 25).

[36] The term "isoparaffin-containing feedstock" means a feedstock containing isoparaffin in an amount of 10 wt% or more, specifically 20 wt% or more, and more specifically 50 wt% or more.

[37] The term "lube base oil" means a hydrocarbon fraction having a boiling point of 300°C or higher (specifically, 340 to 700°C) and a viscosity of 1 cSt or more at 100°C.

[38] The term "unconverted oil" means an unconverted bottom fraction remaining after separating fuel oils (gasoline, kerosene and diesel) from vacuum gas oil using a hydrocracking reactor.

[39] The term "isomerized fraction of biomass-derived diesel" means an arbitrary fuel equal to diesel, obtained from a renewable biological source, in a wide sense, specifically, a fuel satisfying the standard ASTM D6751. Particularly, the term "isomerized fraction of biomass-derived diesel" means a fraction prepared by isomerizing a diesel obtained by converting triglyceride and/or aliphatic acid in biomass into paraffin through hydrodeoxygenation (hydrodecarbonylation or hydrodecarboxylation).

[40] Meanwhile, lube base oils may be classified as given in Table 1 below according to the mechanical and chemical property standards prescribed in the API.

[41] Table 1

[Table 1]

	Viscosity index	Sulfur content (wt%)	Pour point (°C)	Saturated matter (wt%)
Group I	80 to 119	>0.03	-5 to 15	<90
Group II	80 to 119	≤0.03	-10 to -20	≥90
Group III	≥120	≤0.03	-10 to -25	≥90
Group IV	135 to 140	-	-53	-
Group V	140	-	-21	-

[42] Isoparaffin-containing feedstock

[43] In an embodiment of the present invention, an isoparaffin-containing feedstock can be obtained from various sources. Typically, as the feedstock, (i) an isomerized fraction of biomass-derived diesel and (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil may be selected. These fractions may be used independently or in a combination thereof.

[44] In this case, the content of olefin in the isoparaffin-containing feedstock may be less than 1 wt%, specifically, less than 0.1 wt%. Preferably, the feedstock may not substantially contain an olefin. If the content of olefin reaches or exceeds a predetermined level, the reaction between isoparaffin and olefin or the reaction between olefins is favored in comparison to the reaction between isoparaffins, thus deteriorating the characteristics of a final alkylation product and causing a side reaction.

[45] Examples of biomass used in preparing the isomerized fraction of biomass-derived diesel may include animal oils and plant oils. Specifically, examples of the animal oils may include fish oil, cow oil, hog oil, sheep oil, butter, and the like. Examples of the plant oils may include sunflower oil, canola oil, coconut oil, corn oil, cottonseed oil, linseed oil, safflower seed oil, oat oil, olive oil, palm oil, peanut oil, apricot seed oil, almond oil, avocado oil, camellia oil, rice bran oil, walnut oil, rapeseed oil, flaxseed oil, sesame oil, soybean oil, castor oil, cocoa butter, palm kernel oil, and the like.

These oils may be used independently or in a combination thereof. However, the biomass of the present invention is not limited thereto.

[46] FIG. 1 shows a process of producing biodiesel as a feedstock for an alkylation reaction.

[47] Referring to FIG. 1, palm oil, as plant oil, is introduced into a reactor (HBD&HDS reactor) together with hydrogen to conduct a hydrodeoxygenation reaction. Through the hydrodeoxygenation reaction, oxygen in a feed is converted into water, and paraffin components are obtained. The water is discharged through the bottom of a separator, and the by-product gas is discharged through the top of a separator. A part of the discharged by-product gas (containing unreacted hydrogen) is combined with new hydrogen, and then returns to the reactor. Meanwhile, the paraffin separated from the separator is transferred to a distillation tower to separate wax components and obtain paraffin components (particularly, biodiesel). In this embodiment, as the catalyst used in the hydrodeoxygenation reaction, general hydrogenation catalysts, for example, a catalyst including an inorganic oxide support (alumina, silica, silica-alumina, zirconia, titania or the like) supported with VIB group metal and/or VIII group metal, a VIB group metal and/or VIII group metal phosphide catalyst, or the like may be used.

[48] The paraffin components obtained may include n-paraffin and iso-paraffin. When the content of iso-paraffin does not reach a predetermined level, an isomerization reaction is additionally performed to convert n-paraffin into iso-paraffin (that is, isomerized fraction of biomass-derived diesel). In this case, the iso-paraffin in the product may have a carbon number of 10 to 25, specifically, 15 to 18; a boiling point of 170 to 400℃, specifically, 270 to 320℃; and a kinematic viscosity (at 100℃) of 2 cSt or less, specifically, 1 to 2 cSt.

[49] FIG. 2 is a schematic view showing a process of producing a lube base oil fraction as a feedstock for an alkylation, wherein the lube base oil fraction is prepared from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil.

[50] Generally, a fuel oil hydrocracking process is a process of hydrocracking vacuum gas oil (VGO) obtained by the vacuum distillation process (V1) of an atmospheric residue, that is, a heavy hydrocarbon mixture. After the vacuum distillation process (V1), a hydrotreatment process (R1), which is a pretreatment process for removing hetero-compounds containing impurities such as sulfur, nitrogen, oxygen and the like and metal components from vacuum gas oil (VGO), is conducted in order to protect a catalyst for a hydrocracking process (R2) (main process). Thereafter, the hydrocracking process (R2), as a main process, is conducted. In the hydrocracking process (R2), unsaturated hydrocarbons, such as aromatic compounds, olefin compounds and the like, included in vacuum gas oil (VGO) is hydrogenated to be converted into saturated hydrocarbons, such as naphthene compounds, paraffin compounds and the

like. In this case, some of the naphthene compounds, which are cyclic saturated hydrocarbons, may be converted into paraffin compounds, which are straight-chain hydrocarbons, by a ring-opening reaction. Further, these compounds may be decomposed into smaller compounds. Such a series of procedures is referred to as hydrocracking , and these compounds are converted into a light hydrocarbon mixture, that is, a light fuel distillate.

[51] Oil and hydrogen, having passed the hydrocracking process (R2), are recycled after hydrogen is removed via a separator, and various kinds of converted light fuel distillates and gases are fractionated through a first fractional distillation process (Fs1) and made into products. In this case, the conversion ratio of vacuum gas oil (heavy oil fraction) into a light fuel distillate is generally designed such that a reactor per pass conversion is 50 to 90%. Since it is substantially impossible to perform an operation at a reactor per pass conversion of 100%, unconverted oil (UCO) is produced in the final fractional distillation process. The unconverted oil (UCO) is treated by a once-through mode for directly transferring UCO to a tank or by a recycle mode for recycling UCO to the hydrocracking process to increase the total conversion ratio. In this case, the hydrogenation and hydrocracking reactions are typically performed in a catalyst-charged fixed-bed reactor at high temperature and high hydrogen partial pressure. Therefore, most of aromatic compounds included in vacuum gas oil (feedstock) and heterocyclic compounds including sulfur, nitrogen and oxygen atoms are saturated by hydrogen, and thus the contents of aromatic compounds, sulfur compounds, nitrogen compounds and oxygen compounds become very low. The unconverted oil (UCO), which is not converted into a light fuel distillate in the hydrocracking process, includes a small amount of aromatic and heterocyclic compounds not preferable to lube base oil, and has viscosity suitable for lube base oil. The above-mentioned processes are described in detail in U.S. Patent No. 5,580,442, filed by the present applicant. This prior art document is used as a reference of the present invention. The characteristics of the unconverted oil (UCO) are given in Table 2 below.

[52] Table 2

[Table 2]

		Vacuum gas oil	UCO
Specific gravity (15°C/4°C)		0.9242	0.8438
Kinematic viscosity (40°C, cSt)		57.3	23.9
Distillation characteristics (°C)	Initial boiling point (IBP)	263	335
	Final boiling point (FBP)	588	582
Sulfur content (wt%/ppm)		2.79	1.0

[53] Particularly, since the unconverted oil (UCO) includes a large amount of straight-

chain paraffin, that is, n-paraffin, straight-chain hydrocarbons are converted into branched hydrocarbons by an isomerization process, and then the branched hydrocarbons may be used as an isoparaffin-containing feedstock. The isomerization process may be performed in the presence of an isomerization catalyst known in the related field, for example, a catalyst including mesopore zeolite (for example, EU-1, ZSM-35, ZSM-11, ZSM-57, NU-87, ZSM-22, EU-2, EU-11, ZBM-30, ZSM-48, ZSM-23 or a combination thereof) supported with VIII metals (for example, precious metals, such as platinum, palladium and the like) independently or in a combination thereof. In this case, the isomerization reaction temperature may range from 300 to 400℃ (specifically, 310 to 380℃), and the isomerization reaction pressure may range from 50 to 200 bar (specifically, 80 to 180 bar).

[54] The isomerized unconverted oil (UCO) is selectively hydrofinished to remove aromatic and/or olefin components therefrom, thereby improving stability (not shown). Meanwhile, the unconverted oil (UCO) may be separated and recovered according to viscosity through a subsequent vacuum distillation process (not shown), and, in this case, this separated fraction having specific viscosity characteristics may be used as a feedstock for an alkylation reaction.

[55] In this embodiment, unconverted oil-derived lube base oil fraction, as a feedstock for an alkylation reaction, may have a boiling point of 260 to 460℃, specifically, 290 to 430℃ and a kinematic viscosity (at 100℃) of 8 cSt or less, specifically, 2 to 8 cSt. More specifically, the unconverted oil-derived lube base oil may have a carbon number of 14 to 30 (specifically, 16 to 28), and may have characteristics of group II or III metals. The exemplified characteristics of the unconverted oil-derived lube base oil are given Table 3 below.

[56] Table 3

[Table 3]

Specific gravity (15℃/4℃)	0.8353
Viscosity (40℃, ㎟/s)	12.14
Viscosity (100℃, ㎟/s)	3.018
Viscosity index	103
Sulfur content (mg/kg)	1.0
Pour point (℃)	-36
Isoparaffin content (wt%)	>50%

[57] According to an embodiment, besides the above-mentioned fractions, other fractions may be selectively used as a feedstock for an alkylation reaction during an oiling refining process. Examples of these fractions may include a naphtha fraction, a diesel fraction and/or a group I lube base oil fraction.

[58] In relation to this, a naphtha fraction having a boiling point of 38 to 140℃, par-

ticularly, a paraffin-based naphtha fraction discharged from an atmospheric distillation tower includes a large amount of paraffins, and also includes a large amount of iso-paraffin. Such a naphtha fraction, particularly, full range naphtha includes paraffins (n-paraffin and iso-paraffin) in an amount of 60 to 90 wt%, and, particularly, includes iso-paraffin in an amount of 50 wt% or more. Therefore, this naphtha fraction may be used as a feedstock for an alkylation reaction without additional treatment, but, if necessary, may be subsequently isomerized to include a desired amount of iso-paraffin.

[59] A diesel fraction (or middle distillate) may also be used as a feedstock for an alkylation reaction as long as it has a boiling point (for example, 200 to 380°C) similar to that of the above-mentioned biomass-derived diesel isomerized fraction and includes a predetermined amount or more of iso-paraffin. If the content of iso-paraffin in the diesel fraction is below the predetermined amount, the content thereof will be increased through an isormerization process.

[60] Meanwhile, the group I lube base oil, which is lube base oil obtained by treating hydrocarbons through solvent refining, solvent dewaxing, finishing or the like, includes a considerable amount of paraffins. Therefore, as in the embodiment, the group I lube base oil may be used in an alkylation reaction as long as it includes a predetermined amount or more of isoparaffin. If necessary, the group I lube base oil is selectively isomerized to increase the content of isoparaffin therein.

[61]

[62] Peroxide

[63] In an embodiment of the present invention, the peroxide used in an alkylation reaction is a radical initiator, and is represented by Formula 1 below:

[64] [Formula 1]

[65] ROOR'

[66] wherein R and R' are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms (specifically, an alkyl group of 1 to 4 carbon atoms) or an acetyl group of 1 to 10 carbon atoms (specifically, an acetyl group of 1 to 6 carbon atoms).

[67] Examples of the peroxide may include hydrogen peroxide, dimethyl peroxide, diethyl peroxide, di-t-butyl peroxide, benzoyl peroxide, and the like. It is particularly advantageous that di-t-butyl peroxide be used as the peroxide in terms of characteristics of an isoparaffin-containing feedstock as a reactant.

[68] The peroxide may be introduced into a reaction system together with an isoparaffin-containing feedstock, and may also be separately introduced into the reaction system. In this case, the used amount of peroxide may be 5 to 35 wt%, specifically 15 to 30 wt%, and more specifically 20 to 30 wt%, based on the total amount of reactants. As the used amount of peroxide increases, the degree of alkylation also increases. However, when an excessive amount of peroxide is used, the feed stock is excessively

alkylated, and thus the kinematic viscosity of the produced lube base oil does not satisfy the standard kinematic viscosity. Therefore, it is preferred that the amount of peroxide be suitably adjusted within the above-mentioned range in consideration of the characteristics of paraffin in the isoparaffin-containing feedstock.

[69]

[70] Alkylation reaction

[71] According to an embodiment of the present invention, an alkylation reaction may be performed using peroxide without additional catalysts (for example, an acid catalyst, specifically, a zeolite catalyst). Typically, the alkylation reaction may be performed under the conditions of a temperature of 10 to 200°C, specifically 120 to 180°C, and more specifically 150 to 180°C, and a pressure of 1 to 100 bar, specifically 3 to 10 bar, and more specifically 3 to 8 bar.

[72] The distinguishing point in this embodiment is that olefin components are not intentionally used during the alkylation reaction. When olefin is used, there is a limitation in increasing the viscosity index of the final lube base oil product, which is a major characteristic index thereof, to 120 or more (group III standard), and it is difficult to obtain lube base oil having high viscosity. Particularly, when anolefin is used, the unreacted olefin is inevitably included in a reaction product because the conversion ratio of olefin does not reach 100%. In this case, since the unreacted olefin existing in lube base oil deteriorates the stability of lube base oil, a hydrofinishing process is required. Further, during the alkylation reaction, dimmers or oligomers may be formed due to the reaction between olefins. These dimmers or oligomers function as a factor deteriorating the characteristics of lube base oil.

[73] In an embodiment of the present invention, the alkylation reaction may be performed by a batch mode or a continuous mode. In the batch mode, reaction time may be 0.5 to 5 hr, specifically 0.5 to 4 hr, and more specifically 1 to 2 hr. In the continuous mode, weight hourly space velocity (WHSV) may be adjusted within the range of 0.2 to 2 hr^{-1}, specifically 0.25 to 2 hr^{-1}, and more specifically 0.5 to 1 hr^{-1}. Besides, the conversion ratio in the alkylation reaction may be 20 to 50%, specifically, 30 to 40%.

[74] FIG. 3 is a schematic block diagram showing a continuous process including the steps of alkylation reaction, separation and peroxide regeneration.

[75] Referring to FIG. 3, an isoparaffin-containing feedstock is introduced into an alkylation reaction unit through a line 1, and, at this time, the regenerated and recycled peroxide is mixed with the feedstock through a line 5. Further, the unreacted feedstock separated by a separator is recycled through a line 3 to be mixed with the feed stock. The alkylation reaction product includes alkylate, ureacted feedstock and/or alcohol (alcohol produced by the side-reaction between hydrocarbons and peroxide). Therefore, after the alkylation reaction is completed, the reaction product stream is

transferred to a separator. In this case, alcohol and the like, which are by-products, may be removed by a phase-separation method (not shown), and the alkylation product may be separated from unreacted feedstock at 200 to 450℃ under an atmospheric pressure.

[76] Further, the alcohol is transferred to a peroxide regeneration unit through a line 4 to be regenerated into peroxide. In this peroxide regeneration unit, for example, when di-t-butyl peroxide is used, t-butyl alcohol produced therefrom reacts with hydrogen peroxide in the presence of an acid catalyst to be converted into di-t-butyl peroxide.

[77]

[78] Alkylation product (lube base oil)

[79] Alkylate, prepared by an alkylation process according to an embodiment of the present invention, satisfies basic boiling point conditions of lube base oil, and exhibits high viscosity and a high viscosity index. Therefore, this alkylate can be successfully used as lube base oil.

[80] For example, when an isomerized fraction of biomass-derived diesel is used as a feedstock, lube base oil may exhibit a boiling point (ASTM D2887) of 300 to 700℃ (specifically, 320 to 600℃), a viscosity index of 90 to 150 (specifically, 100 to 140), a kinematic viscosity (at 100℃) of 2 to 30 cSt (specifically, 3 to 20 cSt) and a pour point of -36 to 0℃ (specifically, -30 to -20℃).

[81] Further, when an unconverted oil-derived isoparaffin-containing feedstock is used, lube base oil may exhibit a boiling point (ASTM D2887) of 400 to 700℃ (specifically, 440 to 600℃), a viscosity index of 90 to 150 (specifically, 100 to 140), a kinematic viscosity (at 100℃) of 6 to 60 cSt (specifically, 6 to 40 cSt) and a pour point of -40 to 0℃ (specifically, -30 to -20℃).

Mode for the Invention

[82] Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are set forth to illustrate the present invention, and the scope of the present invention is not limited thereto.

[83]

[84] **Examples**

[85] The physical properties of isoparaffins used in Examples are given in Table 4 below.

[86] Table 4

[Table 4]

	Isoheptadecane (C_{15-18}) having average carbon number of 17	Isooctadecane	Isotricosane having average carbon number of 23
Kinematic viscosity (40°C, cSt)	3.096	3.584	12.23
Kinematic viscosity (100°C, cSt)	1.270	1.411	3.034
Viscosity index (VI)	-	-	104
Pour point (°C)	-12	-	-36

[87] Example 1

[88] Alkylation reaction of isoheptadecane (C_{15-18}) having average carbon atom of 17

[89] A 500 mL high-pressure reactor (autoclave) was maintained under a nitrogen atmosphere. 104.25 g of isoheptadecane (C_{15-18}) having an average carbon number of 17 and 26.06 g of di-t-butyl peroxide (radical initiator) were mixed at a weight ratio of 80:20, and the mixture was introduced into the high-pressure reactor using nitrogen stream. The high-pressure reactor was sealed, and then the mixture was stirred at a pressure of 5 atm. (5.07 bar) and a temperature of 150°C for 120 min at a rotation speed of 100 rpm to be reacted. After the reaction, the high-pressure reactor was cooled to room temperature, and then its pressure was reduced to the atmospheric pressure, and a transparent liquid reaction product was transferred from the reactor to a 500 mL round-bottom flask. In order to remove by-products such as alcohol and the like from the liquid reaction product, the liquid reaction product was washed with ethanol and distilled water, and then phase-separated for 1 day using a separatory funnel. Pressure was reduced at 50°C to remove residual peroxide and water from the phase-separated reaction product, thereby finally obtaining transparent liquid alkylate.

[90] The physical properties of the obtained alkylate are given in Table 5 below, and the SIMDIS graph thereof is shown in FIG. 4.

[91]

[92] Example 2

[93] Alkylation reaction of isooctadecane

[94] Transparent liquid alkylate was obtained in the same manner as in Example 1, except that 117 g of isooctadecane and 29.13 g of di-t-butyl peroxide were used instead of isoheptadecane having an average carbon number of 17. The physical properties of the obtained alkylate are given in Table 5 below, and the SIMDIS graph thereof is shown in FIG. 5.

[95]

[96] Example 3

[97] Alkylation reaction of isotricosane having average carbon number of 23

[98] Yellow alkylate was obtained in the same manner as in Example 1, except that 127.62 g of isotricosane having an average carbon number of 23 and 30.40 g of tertiary-butyl peroxide were used instead of isoheptadecane having an average carbon number of 17. The physical properties of the obtained alkylate are given in Table 5 below, and the SIMDIS graph thereof is shown in FIG. 6.

[99]

[100] Comparative Example 1

[101] Alkylation reaction of isooctadecane and 2-pentene

[102] A 500 mL high-pressure reactor (autoclave) was maintained under a nitrogen atmosphere. 42 g of isooctadecane, 14 g of 2-pentene (an olefin) and 14 g of di-t-butyl peroxide (radical initiator) were mixed at a weight ratio of 60: 20: 20, and the mixture was introduced into the high-pressure reactor using nitrogen stream. The high-pressure reactor was sealed, and then the mixture was stirred at a pressure of 5 atm. (5.07 bar) and a temperature of 150°C for 120 min at a rotation speed of 100 rpm to be reacted. After the reaction, the high-pressure reactor was cooled to room temperature, and then its pressure was reduced to the atmospheric pressure, and a reaction product was transferred from the reactor to a 500 mL round-bottom flask. In order to remove ureacted olefin from the reaction product, pressure was reduced at room temperature to obtain a transparent liquid reaction product. In order to remove by-products such as alcohol and the like from the obtained liquid reaction product, this liquid reaction product was washed with ethanol and distilled water, and then phase-separated for 1 day using a separatory funnel. Pressure was reduced at 50°C to remove residual peroxide and water from the phase-separated reaction product, thereby finally obtaining transparent liquid alkylate. The physical properties of the obtained alkylate are given in Table 5 below, and the SIMDIS graph thereof is shown in FIG. 5.

[103]

[104] Comparative Example 2

[105] Alkylation reaction of isotricosane having average carbon number of 23 and 2-pentene

[106] Yellow alkylate was obtained in the same manner as in Example 1, except that 42 g of isotricosane having an average carbon number of 23 was used instead of isooctadecane. The physical properties of the obtained alkylate are given in Table 5 below, and the SIMDIS graph thereof is shown in FIG. 6.

[107] Table 5

[Table 5]

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2
Kinematic viscosity (40℃, cSt)	6.403	8.629	41.22	5.36	33.72
Kinematic viscosity (100℃, cSt)	2.137	2.627	6.855	1.788	5.835
Viscosity index (VI)	150	150	124	-	116
Pour point (℃)	-12	-30	-39	-	-
Cloud point (℃)	-7	-21	-38	-	-

[108] As given in Table 5, in Examples 1 to 3, the alkylation reaction was conducted using isoparaffin having a long chain and peroxide without the addition of olefins. In this case, when isooctadecane was used as isoparaffin (Example 2), the kinematic viscosity of the produced alkylate at 100°C was increased to about 186.2% compared to that of a reactant. Further, when isotricosane having an average number of 23 was used as isoparaffin (Example 3), the kinematic viscosity of the produced alkylate at 100°C was increased to about 225.9% compared to that of a reactant, and the viscosity index thereof was increased to about 119.2% compared to that of a reactant.

[109] In contrast, in the alkylation reaction of isoparaffin by the addition of an olefin, when isooctadecane was used as isoparaffin (Comparative Example 1), the kinematic viscosity of the produced alkylate at 100°C was increased to about 126.7% compared to that of reactants. Further, when isotricosane having an average number of 23 was used as isoparaffin (Comparative Example 2), the kinematic viscosity of the produced alkylate at 100°C was increased to about 192.3% compared to that of reactants, and the viscosity index thereof was increased to about 113.7% compared to that of reactants. That is, in the alkylation reaction of isoparaffin and olefin, the changes of kinematic viscosity and viscosity index were relatively small compared to in the single alkylation reaction of isoparaffin.

[110] From the above test result, it was determined that, as in Examples 1 to 3, when the alkylation reaction was conducted using only isoparaffin having a long chain, lube base oil having high kinematic viscosity and a high viscosity index can be produced, compared to when an olefin was added to the alkylation reaction thereof. It can be seen that this result is caused by the direct alkylation reaction of isoparaffin having a long chain.

[111] According to the SIMDIS graph of FIG. 4, it can be ascertained that, in the alkylate obtained using isoheptadecane having an average carbon number of 17, its carbon number was remarkably increased to 30 to 40, compared to when the carbon number of a reactant was 15 to 18. This means that the alkylation reaction of isoheptadecane having an average carbon number of 17 was conducted.

[112] According to the SIMDIS graph of FIG. 5, it can be ascertained that, in the alkylation

products of Example 2 and Comparative Example 1, areas of carbon number of 18 were decreased, but areas of carbon number of 20 or more were remarkably increased, compared to isooctadecane as a reactant. In contrast, it can be ascertained that, in the alkylation product of Comparative Example 1, areas of carbon number of 20 to 30 were increased by the alkylation reaction of 2-pentene, but, in the alkylation product of Example 1, areas of carbon number 30 to 40 were increased. Therefrom, it can be ascertained that, in Examples 1 and 2, molecules having a larger carbon number were produced. Therefore, it can be ascertained that, in Example 2, the alkylation reaction of only isooctadecane was conducted, and thus molecules having a larger carbon number were produced.

[113] Meanwhile, according to the SIMDIS graph of FIG. 6, it can be ascertained that, in the alkylation products of Example 3 and Comparative Example 2, areas of carbon number of 23 were decreased, but areas of carbon number of 30 or more were remarkably increased, compared to isotricosane (average carbon number: 23) as a reactant. In contrast, it can be ascertained that, in the alkylation product of Comparative Example 2, areas of carbon number of 30 to 40 were increased by the alkylation reaction of 2-pentene, but, in the alkylation product of Example 3, areas of carbon number 50 to 70 were increased. This means that molecules having a larger carbon number were produced. From the test results, it can be ascertained that the alkylation reaction of only isotricosane was conducted, and thus molecules having a larger carbon number were produced.

[114] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

[Claim 1] A method of producing lube base oil, comprising the steps of:
a) providing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydro-cracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction;
b) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar and a temperature of 10 to 200 C; and
c) recovering lube base oil from the alkylation reaction product,
wherein the step b) is performed without the addition of an olefin.

[Claim 2] A method of producing lube base oil, comprising the steps of:
a1) continuously introducing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction into an alkylation reaction region;
b1) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar, a temperature of 10 to 200°C and a weight hourly space velocity (WHSV) of 0.2 to 2 hr^{-1};
b2) separating alkylate, unreacted feedstock, and unreacted peroxide or alcohol from the alkylation reaction stream;
c1) recovering the alkylate; and
c2) transferring the separated unreacted peroxide or alcohol to a peroxide regeneration region simultaneously with or subsequently to the step c1) to regenerate peroxide and then recycling the regenerated peroxide into the alkylation reaction region, and recycling the separated unreacted feedstock into the alkylation reaction region,
wherein the step b1) is performed without the addition of an olefin.

[Claim 3] The method of claim 1 or 2, wherein, when the isoparaffin-containing feedstock is (i) an isomerized fraction of biomass-derived diesel, the

lube base oil has a boiling point of 300 to 700℃, a viscosity index of 90 to 150, a kinematic viscosity of 2 to 30 cSt (100℃) and a pour point of -36 to 0℃.

[Claim 4] The method of claim 1 or 2, wherein the carbon number of the isoparaffin is 5 to 30.

[Claim 5] The method of claim 1 or 2, wherein, when the isoparaffin-containing feedstock is (ii) a group II or group III lube base oil fraction, the lube base oil has a boiling point of 400 to 700℃, a viscosity index of 90 to 150, a kinematic viscosity of 6 to 60 cSt (100℃) and a pour point of -40 to 0℃.

[Claim 6] The method of claim 1 or 2, wherein the content of isoparaffin in the isoparaffin-containing feedstock is at least 10 wt%.

[Claim 7] The method of claim 1 or 2, wherein the isoparaffin-containing feedstock (i) has a carbon number of 10 to 25, a boiling point of 170 to 400℃ and a kinematic viscosity of 2 cSt or less (100℃).

[Claim 8] The method of claim 1 or 2, wherein the isoparaffin-containing feedstock (ii) has a carbon number of 14 to 30, a boiling point of 260 to 460℃ and a kinematic viscosity of 8 cSt or less (100℃).

[Claim 9] The method of claim 1 or 2, wherein the peroxide is represented by Formula 1 below:

[Formula 1]

ROOR'

wherein R and R' are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms or an acetyl group of 1 to 10 carbon atoms.

[Claim 10] The method of claim 9, wherein the peroxide is di-t-butyl peroxide.

[Claim 11] The method of claim 1, wherein the alkylation reaction is performed for 0.5 to 5 hours in a batch mode.

[Claim 12] The method of claim 1 or 2, wherein the conversion ratio of the alkylation reaction is 20 to 50%.

[Claim 13] The method of claim 6, wherein the content of isoparaffin in the isoparaffin-containing feedstock is at least 50 wt%.

[Claim 14] The method of claim 1 or 2, wherein the content of olefin in the isoparaffin-containing feedstock is less than 1 wt%.

AMENDED CLAIMS
received by the International Bureau on 05 September 2014(05.09.2014)

【Claim 1】 (amended)

A method of producing lube base oil, comprising the steps of:

a) providing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction;

b) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar and a temperature of 10 to 200℃; and

c) recovering lube base oil from the alkylation reaction product,

wherein the step b) is performed without the addition of an olefin.

【Claim 2】

A method of producing lube base oil, comprising the steps of:

a1) continuously introducing at least one isoparaffin-containing feedstock selected from the group consisting of (i) an isomerized fraction of biomass-derived diesel, (ii) a group II or group III lube base oil fraction produced from the isomerization reaction of unconverted oil derived from the hydrocracking of fuel oil, (iii) a naphtha fraction, (iv) a diesel fraction and (v) a group I lube base oil fraction into an alkylation reaction region;

b1) adding peroxide to the isoparaffin-containing feedstock in an amount of 5 to 35 wt% based on a total amount of reactants to perform an alkylation reaction at a pressure of 1 to 100 bar, a temperature of 10 to 200℃ and a weight hourly space velocity (WHSV) of 0.2 to 2 hr^{-1};

b2) separating alkylate, unreacted feedstock, and unreacted peroxide or alcohol from the alkylation reaction stream;

c1) recovering the alkylate; and

c2) transferring the separated unreacted peroxide or alcohol to a peroxide regeneration region simultaneously with or subsequently to the step c1) to regenerate peroxide and then recycling the regenerated peroxide into the alkylation reaction region, and recycling the separated unreacted feedstock into the alkylation reaction region,

wherein the step b1) is performed without the addition of an olefin.

【Claim 3】

The method of claim 1 or 2, wherein, when the isoparaffin-containing feedstock is (i) an isomerized fraction of biomass-derived diesel, the lube base oil has a boiling point of 300 to 700℃, a viscosity index of 90 to 150, a kinematic viscosity of 2 to 30 cSt (100℃) and a pour point of -36 to 0℃.

【Claim 4】

The method of claim 1 or 2, wherein the carbon number of the isoparaffin is 5 to 30.

【Claim 5】

The method of claim 1 or 2, wherein, when the isoparaffin-containing feedstock is (ii) a group II or group III lube base oil fraction, the lube base oil has a boiling point of 400 to 700℃, a viscosity index of 90 to 150, a kinematic viscosity of 6 to 60 cSt (100℃) and a pour point of -40 to 0℃.

【Claim 6】

The method of claim 1 or 2, wherein the content of isoparaffin in the isoparaffin-containing feedstock is at least 10 wt%.

【Claim 7】

The method of claim 1 or 2, wherein the isoparaffin-containing feedstock (i) has a carbon number of 10 to 25, a boiling point of 170 to 400℃ and a kinematic viscosity of 2 cSt or less (100℃).

【Claim 8】

The method of claim 1 or 2, wherein the isoparaffin-containing feedstock (ii) has a carbon number of 14 to 30, a boiling point of 260 to 460℃ and a kinematic viscosity of 8 cSt or less (100℃).

【Claim 9】

The method of claim 1 or 2, wherein the peroxide is represented by Formula 1 below:

[Formula 1]

ROOR'

wherein R and R' are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms or an acetyl group of 1 to 10 carbon atoms.

【Claim 10】

The method of claim 9, wherein the peroxide is di-t-butyl peroxide.

【Claim 11】

The method of claim 1, wherein the alkylation reaction is performed for 0.5 to 5 hours in a batch mode.

【Claim 12】

The method of claim 1 or 2, wherein the conversion ratio of the alkylation reaction is 20 to 50%.

【Claim 13】

The method of claim 6, wherein the content of isoparaffin in the isoparaffin-containing feedstock is at least 50 wt%.

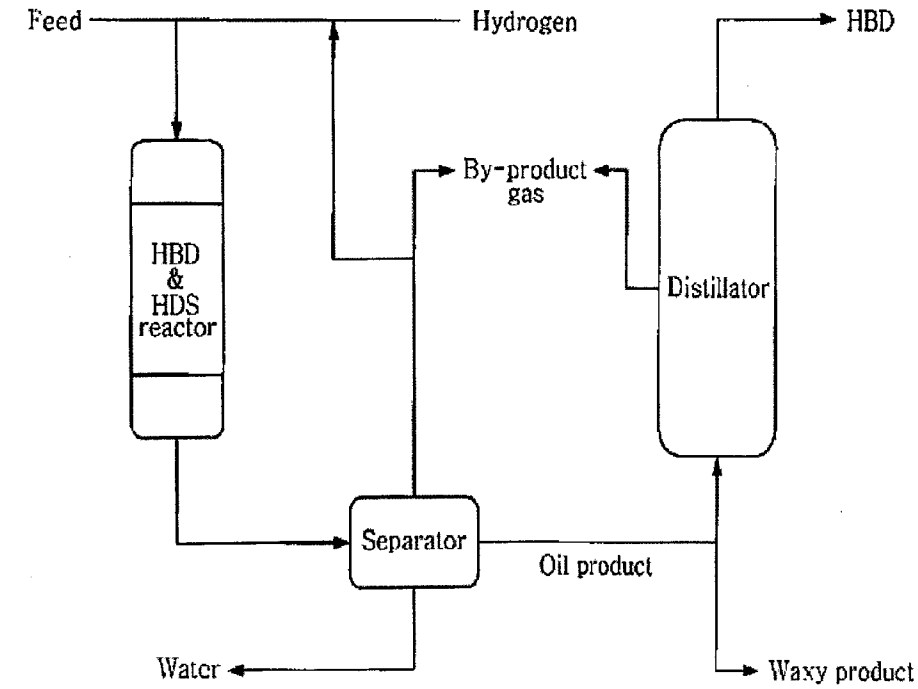
【Claim 14】

The method of claim 1 or 2, wherein the content of olefin in the isoparaffin-containing feedstock is less than 1 wt%.

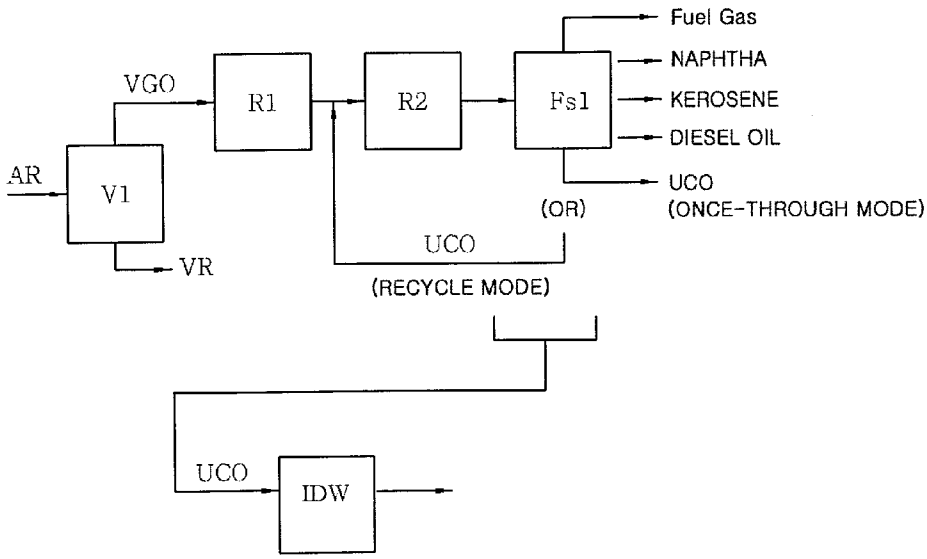
STATEMENT UNDER ARTICLE 19 (1)

As "200C" of claim 1 is a typographical error, we have corrected it to "200℃". It is clearly supported by paragraph [10] at page 2 in the specification. Thus, it does not generate any new matter in the original specification and drawings.

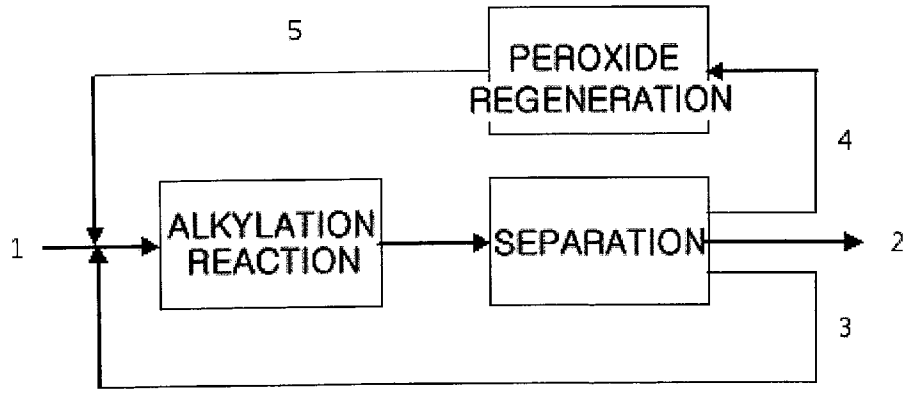
[Fig. 1]



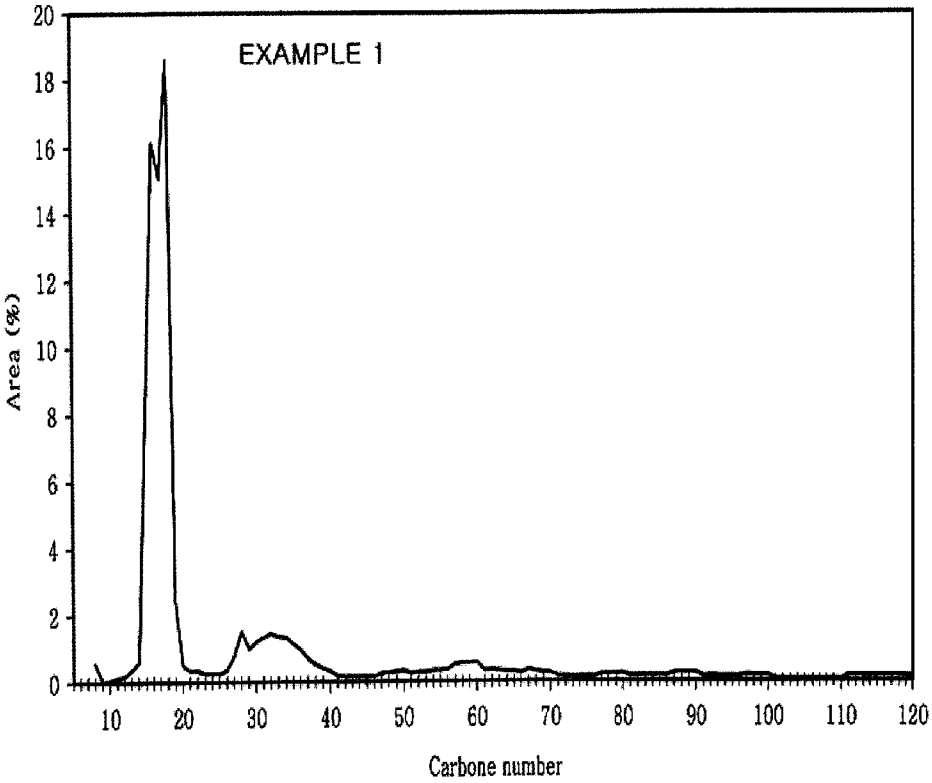
[Fig. 2]



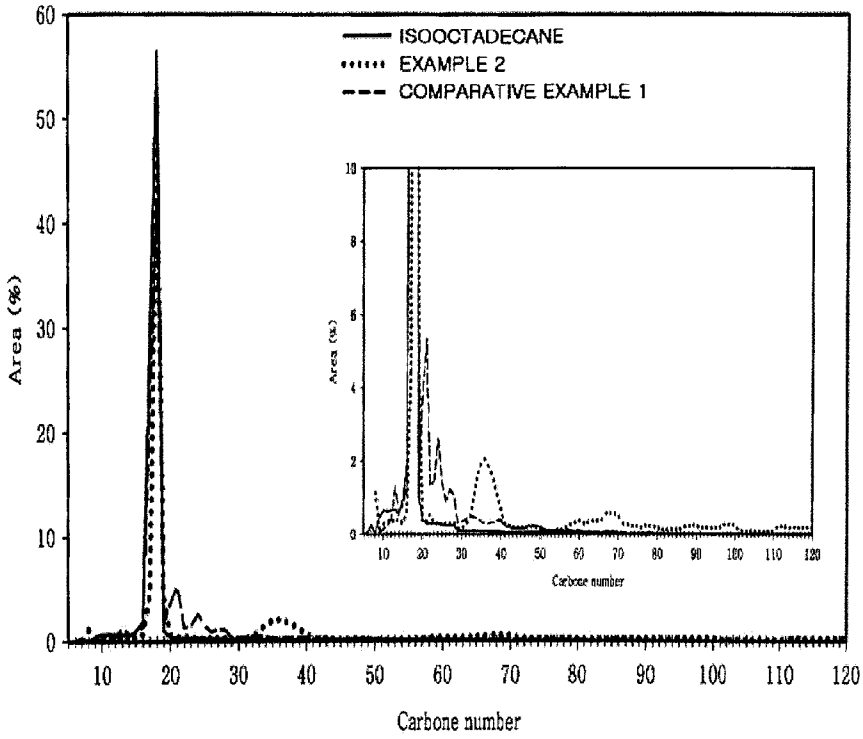
[Fig. 3]



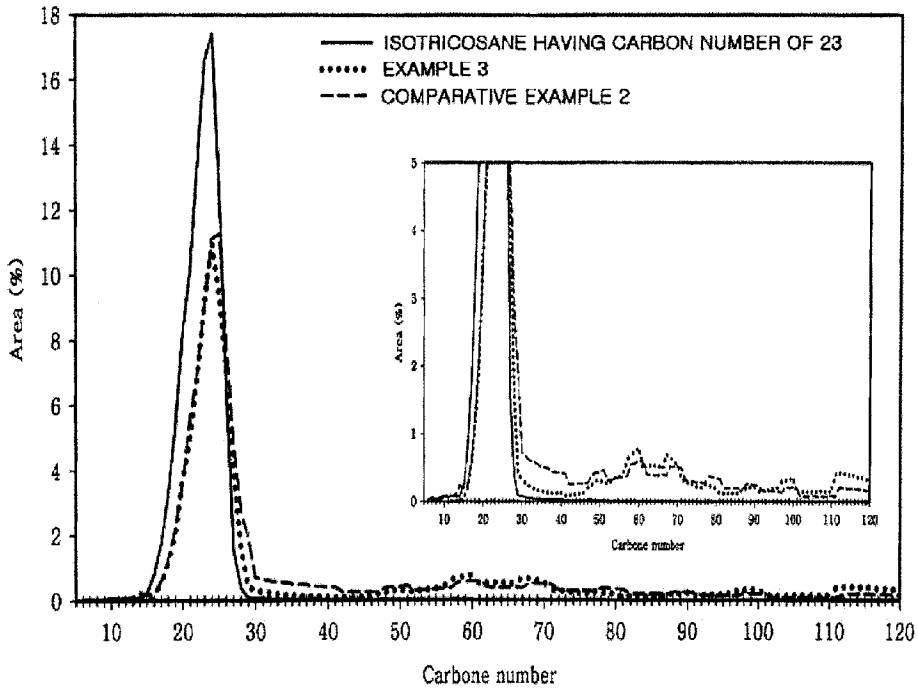
[Fig. 4]


EXAMPLE 1
Area (%)
Carbone number

[Fig. 5]


ISOOCTADECANE
EXAMPLE 2
COMPARATIVE EXAMPLE 1
Area (%)
Carbone number

[Fig. 6]


ISOTRICOSANE HAVING CARBON NUMBER OF 23
EXAMPLE 3
COMPARATIVE EXAMPLE 2
Area (%)
Carbone number

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2014/003045

A. CLASSIFICATION OF SUBJECT MATTER

C10M 101/02(2006.01)i, C10M 105/42(2006.01)i, C10M 105/08(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)
C10M 101/02; C10G 73/42; C07C 2/08; C10M 7/16; C07C 2/58; C10G 73/38; C10M 125/02; C10M 169/02; C10M 105/42; C10M 105/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:lube base oil, isoparaffin, peroxide, alkylation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4990713 A (LE, Q. N. et al.) 05 February 1991 See abstract; and claims 1-3.	1-14
A	US 5037528 A (GARWOOD, W. E. et al.) 06 August 1991 See abstract; and claim 1.	1-14
A	US 2011-0124537 A1 (KILTHAU, T. et al.) 26 May 2011 See abstract; and claim 12.	1-14
A	US 4594172 A (SIE, S. T.) 10 June 1986 See abstract; and claim 1.	1-14
A	US 2008-0253936 A1 (ABHARI, R.) 16 October 2008 See abstract; and claim 1.	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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	Date of mailing of the international search report
08 July 2014 (08.07.2014)	**09 July 2014 (09.07.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
LEE, Chang Ho
Telephone No. +82-42-481-8398

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2014/003045

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4990713 A	05/02/1991	None	
US 5037528 A	06/08/1991	EP 0188898 A2	30/07/1986
		EP 0188898 A3	08/06/1988
		EP 0188898 B1	19/09/1990
		EP 0225053 A1	10/06/1987
		EP 0225053 B1	08/07/1992
		JP 6039589 B2	25/05/1994
		JP 6062960 B2	17/08/1994
		JP 61-179294 A	11/08/1986
		JP 62-112691 A	23/05/1987
		KR 10-1993-0011924 B1	22/12/1993
		US 4911821 A	27/03/1990
		US 4919788 A	24/04/1990
		US 4975177 A	04/12/1990
US 2011-0124537 A1	26/05/2011	AU 2009-256887 A1	17/12/2009
		AU 2009-256887 B2	10/10/2013
		CA 2727157 A1	17/12/2009
		CN 102066536 A	18/05/2011
		CN 102066536 B	24/07/2013
		DE 102009022593 A1	17/12/2009
		EP 2300581 A1	30/03/2011
		EP 2300581 B1	27/06/2012
		HK 1157811 A1	17/01/2014
		JP 2011-522933 A	04/08/2011
		MX 2010013119 A	11/04/2011
		US 8455411 B2	04/06/2013
		WO 2009-149902 A1	17/12/2009
US 4594172 A	10/06/1986	None	
US 2008-0253936 A1	16/10/2008	EP 2146682 A1	27/01/2010
		US 7851663 B2	14/12/2010
		WO 2008-128232 A1	23/10/2008