(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 716 741 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.04.2014 Bulletin 2014/15

(21) Application number: **12789718.9**

(22) Date of filing: **14.05.2012**

(51) Int Cl.:
C10L 1/04 $^{(2006.01)}$

(86) International application number:
PCT/JP2012/062312

(87) International publication number:
WO 2012/161019 (29.11.2012 Gazette 2012/48)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **26.05.2011 JP 2011117601**

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(54) C HEAVY OIL COMPOSITION AND METHOD FOR PRODUCING SAME

(57) The present invention provides a method for producing a C heavy oil composition which unlikely forms sludge, has excellent ignitability and combustibility, and enable the stable operation of a combustion device such as an external combustion device, a diesel device, and a gas turbine device. The method of the present invention is comprises method for producing a C heavy oil composition with a bicyclic aromatic hydrocarbon content of 10 percent by volume or more and 45 percent by volume or less, comprising blending a cracked reformed base oil with a total aromatic content of 80 percent by volume or more and a 15°C density of 0.90 to 1.20 g/cm^3 in an amount of 1 percent by volume or more and 45 percent by volume or less on the basis of the total mass of the composition.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to C heavy oil compositions and methods for producing the same, more specifically to a C heavy oil composition used as fuel for combustion devices such as boilers, diesel devices and gas turbines and ships.

Background Art

[0002] C heavy oil has been widely used as fuels for external combustion devices such as boilers, diesel engine devices of large ships and power generators, or gas turbine devices.

[0003] C heavy oils having been used for various purposes, in particular for ships are often loaded in other foreign countries and frequently make engine troubles caused by the poor combustibility, which have been serious problems. Consequently, a C heavy oil having excellent ignitability and combustibility and making no combustion trouble has been increasingly demanded (see Non-Patent Literature 1).

[0004] In order to improve the combustibility of such a C heavy oil, Patent Literature 1 (Japanese Patent Application Laid-Open Publication No. 8-277396) discloses a method wherein heavy oil is formed into an oil-in-water type heavy oil emulsion with water and a specific nonionic surface active agent and adjusted in emulsion particle diameter and viscosity to specific ranges and combusted after pre-heating.

[0005] Alternatively, Patent Literature 2 (Japanese Patent Application Laid-Open Publication No. 2003-96474) discloses a method for improving the combustibility of C heavy oil by inclusion of 50 percent or more of a light cycle oil (LCO) and specifying the cetane index.

[0006] However, in recent years, fuel for ships has been significantly degraded in quality as described above and thus has produced sludge and been degraded in ignitability and combustibility. As the result, the large diesel engines on the ships frequently have combustion troubles which cause high smoke emission, increased exhaust temperature, contamination of the exhaust system and abnormal abrasion in cylinders or rings. The above literatures do not represent any practical solution.

Citation List

Patent Literature

[0007]

Patent Literature 1: Japanese Patent Application Laid-Open Publication No. 8-277396
Patent Literature 2: Japanese Patent Application Laid-Open Publication 2003-96474

Non-Patent Literature

[0008] Non-Patent Literature 1: "Hakuyo nenryo no kagaku" by NOMURA, Hirotsugu, pp. 164-166, 1994, published by Seizando

Summary of Invention

Technical Problem

[0009] The present invention has been accomplished in view of the above-described situations and has an object to provide a C heavy oil composition which unlikely forms sludge, is excellent in ignitability and combustibility and enables the stable operation of combustion devices such as external combustion devices, diesel devices, gas turbine device and the like.

Solution to Problem

[0010] As the result of extensive studies to achieve the above object, the present invention has been accomplished on the basis of the finding that the above problems can be dissolved using a specific base oil.

[0011] That is, the present invention is described as follows:

[1] a method for producing a C heavy oil composition with a bicyclic aromatic hydrocarbon content of 10 percent by volume or more and 45 percent by volume or less, comprising blending a cracked reformed base oil with a total aromatic content of 80 percent by volume or more and a 15°C density of 0.90 to 1.20 g/cm^3 in an amount of 1 percent by volume or more and 45 percent by volume or less on the basis of the total mass of the composition;

[2] the method for producing a C heavy oil composition according to [1] above, wherein the cracked reformed base oil has a 50°C kinematic viscosity of 0.3 to 10 mm^2/s, a sulfur content of 8000 mass ppm or less, and a nitrogen content of 100 mass ppm or less;

[3] the method for producing a C heavy oil composition according to [1] or [2] above, wherein the cracked reformed base oil has a 10 vol.% distillation temperature (T10) of 130 to 270°C, a 50 vol.% distillation temperature (T50) of 190 to 290°C, and a 90 vol.% distillation temperature (T90) of 230 to 390°C;

[4] the method for producing a C heavy oil composition according to any of [1] to [3] above wherein the cracked reformed base oil is produced by bringing a feedstock having a 10 vol.% distillation temperature of 140°C or higher and a 90 vol.% distillation temperature of 380°C or lower into contact with a catalyst for a cracking and reforming reaction containing a medium pore zeolite and/or a large pore zeolite to be cracked and reformed through a cracking and reforming reaction at a reaction temperature of 400 to 650°C and a reaction pressure of 1.5 MPaG or lower for a contact time of 1 to 300 seconds; and

[5] a C heavy oil composition produced by the method for producing a C heavy oil composition according to any of [1] to [4] above wherein it has a 15°C density of 0.85 to 1.05 g/cm^3, a 50°C kinematic viscosity of 400 mm^2/s or lower, a sulfur content of 3.5 percent by mass or less, a nitrogen content of 1 percent by mass or less and a flash point of 70°C or higher.

Advantageous Effect of Invention

[0012] The C heavy oil composition of the present invention unlikely forms sludge and is excellent in ignitability and combustibility. Therefore, the C heavy oil composition of the present invention is very useful as fuel for external combustion devices such as boilers, diesel engine devices of large ships and power generators, and gas turbine devices.

Description of Embodiments

[0013] Preferred embodiments of the present invention will be described in detail below.

[0014] The method for producing a C heavy oil composition of the present invention is characterized by blending a cracked reformed base oil with a total aromatic content of 80 percent by volume or more and a 15°C density of 0.90 to 1.20 g/cm^3, in an amount of 1 percent by volume or more and 45 percent by volume or less on the basis of the total mass of the C heavy oil composition.

[0015] The lower limit amount of the cracked reformed base oil is necessarily 1 percent by volume or more, preferably 5 percent by volume or more, more preferably 10 percent by volume or more, more preferably 15 percent by volume or more on the basis of the total mass of the C heavy oil composition. The upper limit amount of the cracked reformed base oil is necessarily 45 percent by volume or less, preferably 40 percent by volume or less, more preferably 35 percent by volume or less. A blend ratio of the cracked reformed base oil of less than 1 percent by volume is not preferred because sludge is likely to be formed due to the degraded compatibility. A blend ratio of more than 45 percent by volume is not preferred because the combustibility would be degraded.

[0016] The total aromatic content of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention is necessarily 80 percent by volume or more, preferably 90 percent by volume or more with the objective of retaining the compatibility as a cutter stock. The total aromatic content referred herein denotes the content of the total aromatics measured in accordance with the Japan Petroleum Institute standard JPI-5S-49-97 "Petroleum Products-Determination of Hydrocarbon Types-High Performance Liquid Chromatography".

[0017] The 15°C density of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention is necessarily 0.90 g/cm^3 or higher and 1.20 g/cm^3 or lower. The 15°C density referred herein denotes the value obtained in accordance with JIS K2249 "Crude petroleum and petroleum products-Determination of density and petroleum measurement tables based on a reference temperature (15°C)".

[0018] No particular limitation is imposed on the properties of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention other than the total aromatic content and 15°C density. However, the cracked reformed base oil has preferably the following properties.

[0019] The 50°C kinematic viscosity of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention is 0.3 mm^2/s or higher and 10 mm^2/s or lower. The upper limit of the 50°C kinematic viscosity is more preferably 8 mm^2/s or lower, more preferably 6 mm^2/s or lower as a high-quality cutter stock for C heavy oil.

[0020] The content of sulfur (sulfur content) of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention is preferably 8000 mass ppm or less and with the objective of reducing the amount of sulfur compounds in the combustion exhaust gas, more preferably 5000 mass ppm or less, more preferably 4000 mass ppm or less.

[0021] The content of nitrogen (nitrogen content) of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention is preferably 100 mass ppm or less and with the objective of reducing the amount of nitrogen compounds in the combustion exhaust gas, 80 mass ppm or less, more preferably 70 mass ppm or less.

[0022] The distillation characteristics of the cracked reformed base oil to be blended in the C heavy oil composition of the present invention are an initial boiling point (IBP) of preferably 105°C or higher and 250°C or lower, more preferably 120°C or higher and 240°C or lower, a 10 vol.% distillation temperature (T10) of preferably 130°C or higher and 270°C or lower, more preferably 150°C or higher and 250°C or lower, a 50 vol.% distillation temperature (T50) of preferably 190°C or higher and 290°C or lower, more preferably 210°C or higher and 270°C or lower, a 90 vol.% distillation temperature (T90) of preferably 230°C or higher and 390°C or lower, more preferably 250°C or higher and 370°C or lower and an end point(EP) of preferably 300°C or higher and 440°C or lower, more preferably 320°C or higher and 420°C or lower.

[0023] The 50°C kinematic viscosity referred herein denotes the value obtained in accordance with JIS K2283 "Crude petroleum and petroleum products-Determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity". The sulfur content referred herein denotes the sulfur content measured in accordance with "Radiation Exciting Method" of "Crude Oil and Petroleum Products-Sulfur Content Test Method" specified in JIS K2541-1992. The nitrogen content referred herein denotes the nitrogen content measured in accordance with JIS K2609 "Crude petroleum and petroleum products-Determination of nitrogen content". The distillation characteristics are measured in accordance with JIS K2254 "Atmospheric Distillation Test Method" of "Petroleum Products-Distillation Test Method".

[0024] The cracked reformed base oil used in the present invention is characterized in that it is produced by bringing a feedstock having a 10 vol.% distillation temperature of 140°C or higher and a 90 vol.% distillation temperature of 380°C or lower into contact with a catalyst for a cracking and reforming reaction containing a medium pore zeolite and/or a large pore zeolite to be cracked and reformed through a cracking and reforming reaction at a reaction temperature of 400 to 650°C and a reaction pressure of 1.5 MPaG or lower for a contact time of 1 to 300 seconds.

[0025] Specifically, the cracked reformed base oil used in the present invention is produced by fractional distillation of the cracking and reforming reaction product produced through the cracking and reforming reaction.

[0026] The cracking and reforming reaction is a reaction wherein a feedstock is brought into contact with a catalyst for a cracking and reforming reaction to use saturated hydrocarbons contained in the feedstock as a hydrogen source and subject the saturated hydrocarbons to a hydrogen transfer reaction to partially hydrogenate the polycyclic aromatic hydrocarbons so as to be ring-opened and converted to monocyclic aromatic hydrocarbons or a reaction wherein saturated hydrocarbons contained in the feedstock or produced through a cracking process is cyclized and dehydrated to monocyclic aromatic hydrocarbons, and can produce a fuel base oil containing mainly aromatic hydrocarbons.

[0027] The feedstock for the cracking and reforming reaction is an oil preferably having a 10 vol.% distillation temperature of 140°C or higher and a 90 vol.% distillation temperature of 380°C or lower, more preferably a 10 vol.% distillation temperature of 150°C or higher and a 90 vol.% distillation temperature of 360°C or lower.

[0028] The 10 vol.% distillation temperature and 90 vol.% distillation temperature referred herein denote the values measured in accordance with JIS K2254 "Petroleum products-Determination of distillation characteristics".

[0029] Examples of the feedstock having a 10 vol.% distillation temperature of 140°C or higher and a 90 vol.% distillation temperature of 380°C or lower include light cycle oils (LCO) produced in a fluid catalytic cracker, hydrorefined oils of LCO, liquefied coal oils, hydrocracked oils from heavy oils, straight-run kerosene, straight-run gas oil, coker kerosenes, coker gas oils, and hydrocracked oils from oil sands.

[0030] Examples of the reaction format employed when the feedstock is brought into contact with a catalyst for the cracking and reforming reaction include fixed beds, moving beds, and fluidized beds. Since in the present invention, a heavy fraction is used as the feedstock, a fluidized bed is preferred as it can remove the coke portion deposited on the catalyst in a continuous manner and enables the reaction to proceed in a stable manner. Particularly preferred is a continuous regeneration type fluidized bed, in which the catalyst is circulated between the reactor and a regenerator so that a reaction-regeneration cycle can be continuously repeated. When the feedstock is brought into contact with a catalyst for a cracking and reforming reaction, it is preferably in a gaseous state. The feedstock may be diluted with gas if necessary.

[0031] The catalyst for the cracking and reforming reaction contains a crystalline aluminosilicate.

[0032] The crystalline aluminosilicate is preferably a medium pore zeolite and/or a large pore zeolite as they can enhance the yield of monocyclic aromatic hydrocarbons.

[0033] Medium pore zeolites are those having a 10-membered ring basic structure and may be any of those having AEL, EUO, FER, HEU, MEL, MFI, NES, TON, and WEI type crystal structures. Among these zeolites, MFI-type zeolites are preferred as they can further enhance the yield of monocyclic aromatic hydrocarbons.

[0034] Large pore zeolites are those having a 12-membered ring basic structure. Examples of the macroporous zeolite include those having AFI, ATO, BEA, CON, FAU, GME, LTL, MOR, MTW and OFF type crystal structures. Among these zeolites, preferred are those having BEA, FAU and MOR type structures because they can be used for industrial purposes and more preferred are those having a BEA type structure because they can increase the yield of monocyclic aromatic hydrocarbons.

[0035] Other than the above medium pore and large pore zeolites, the crystalline aluminosilicate may contain small pore zeolites having a 10-membered ring or smaller basic structure and extra-large pore zeolites having a 14-membered ring or larger basic structure.

[0036] Examples of the small pore zeolites include those having ANA, CHA, ERI, GIS, KFI, LTA, NAT, PAU and YUG type crystal structures.

[0037] Examples of the extra-large pore zeolites include those having CLO and VPI type crystal structures.

[0038] In the case where the cracking and reforming reaction is carried out in a fixed bed, the content of the crystalline aluminosilicate in the catalyst for the cracking and reforming reaction is preferably from 60 to 100 percent by mass, more preferably from 70 to 100 percent by mass, particularly preferably from 90 to 100 percent by mass on the basis of 100 percent by mass of the whole catalyst. If the crystalline aluminosilicate content is 60 percent by mass or more, the yield of monocyclic aromatic hydrocarbons can be sufficientlyincreased. In the case where the cracking and reforming reaction is carried out in a fluidized bed, the content of the crystalline aluminosilicate in the catalyst for cracking and reforming reaction is preferably from 20 to 60 percent by mass, more preferably from 30 to 60 percent by mass, particularly preferably from 35 to 60 percent by mass on the basis of 100 percent by mass of the whole catalyst. If the content of the crystalline aluminosilicate is 20 percent by mass or more, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased. If the content of the crystalline aluminosilicate is more than 60 percent by mass, the content of a binder that can be included in the catalyst decreases, and the resulting catalyst would not be suitable for a fluidized bed.

[0039] The catalyst for the cracking and reforming reaction preferably contains phosphorus and/or boron. The catalyst for the cracking and reforming reaction if containing phosphorus and/or boron can prevent the yield of monocyclic aromatic hydrocarbons from decreasing over time and also inhibit the formation of coke on the catalyst surface.

[0040] Examples of methods for incorporating phosphorus in the catalyst for the cracking and reforming reaction include ion-exchange methods and impregnation methods. More specific examples include methods wherein phosphorus is loaded on a crystalline aluminosilicate, crystalline aluminogallosilicate or crystalline aluminozincosilicate, methods wherein a phosphorus compound is included during synthesis of the zeolite so that a portion of the internal framework of the crystalline aluminosilicate is substituted with phosphorus, and methods wherein a crystallization promoter containing phosphorus is used during synthesis of the zeolite. No particular limitation is imposed on the phosphate ion-containing aqueous solution used in the above-mentioned methods. However, preferably used is a solution prepared by dissolving phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate or another water-soluble phosphoric acid salt at an arbitrary concentration in water.

[0041] Examples of methods for incorporating boron in the catalyst for the cracking and reforming reaction include ion-exchange methods and impregnation methods. More specific examples include methods wherein boron is loaded on a crystalline aluminosilicate, crystalline aluminogallosilicate or crystalline aluminozincosilicate, methods wherein a boron compound is included during synthesis of the zeolite so that a portion of the internal framework of the crystalline aluminosilicate is substituted with boron, and methods wherein a crystallization promoter containing boron is used during synthesis of the zeolite.

[0042] The content of phosphorus and/or boron in the catalyst for the cracking and reforming reaction is preferably from 0.1 to 10 percent by mass on the basis of the total mass of the catalyst, wherein the lower limit is more preferably 0.5 percent by mass or more and the upper limit is more preferably 9 percent by mass or less, particularly preferably 8 percent by mass. A phosphorus content of 0.1 percent by mass or more on the basis of the total mass of the catalyst can prevent the yield of monocyclic aromatic hydrocarbons from decreasing over time, and a phosphorus content of 10 percent by mass or less can increase the yield of monocyclic aromatic hydrocarbons.

[0043] If necessary, the catalyst for the cracking and reforming reaction may contain gallium and/or zinc. Inclusion of gallium and/or zinc results in the increased production rate of monocyclic aromatic hydrocarbons.

[0044] Examples of the form of gallium in the catalyst for the cracking and reforming reaction include catalysts wherein gallium is incorporated within the lattice framework of the crystalline aluminosilicate (crystalline aluminogallosilicate), catalysts wherein gallium is supported on the crystalline aluminosilicate (gallium-supporting crystalline aluminosilicate) and catalysts including gallium in the both forms.

[0045] Examples of the form of zinc in the catalyst for the cracking and reforming reaction include catalysts wherein zinc is incorporated within the lattice framework of the crystalline aluminosilicate (crystalline aluminogallosilicate), catalysts wherein zinc is supported on the crystalline aluminosilicate (zinc-supporting crystalline aluminosilicate) and catalysts including zinc in the both forms.

[0046] A crystalline aluminogallosilicate or a crystalline aluminozincosilicate has a structure in which SiO_4, AlO_4 and GaO_4/ZnO_4 structures exist in the framework. A crystalline aluminogallosilicate or crystalline aluminozincosilicate may be produced for example by gel-crystallization through hydrothermal synthesis, or by insertion of gallium or zinc into the lattice framework of a crystalline aluminosilicate. Alternatively, a crystalline aluminogallosilicate or crystalline aluminozincosilicate may be produced by insertion of aluminum into the lattice framework of a crystalline gallosilicate or crystalline zincosilicate.

[0047] A gallium-supporting crystalline aluminosilicate may be produced by loading gallium on a crystalline aluminosilicate with a conventional method such as an ion-exchange method or impregnation method. No particular limitation is imposed on the gallium source used in these methods, and examples of the source include gallium salts, such as gallium nitrate and gallium chloride, and gallium oxide.

[0048] A zinc-supporting crystalline aluminosilicate may be produced by loading zinc on a crystalline aluminosilicate with a conventional method such as an ion-exchange method or impregnation method. No particular limitation is imposed on the zinc source used in these methods, and examples of the source include zinc salts such as zinc nitrate and zinc chloride, and zinc oxide.

[0049] In the case where the catalyst for the cracking and reforming reaction contains gallium and/or zinc, the content of gallium and/or zinc therein is preferably from 0.01 to 5.0 percent by mass, more preferably from 0.05 to 2.0 percent by mass on the basis of 100 percent by mass of the total mass of the catalyst. Contents of gallium and zinc of 0.01 percent by mass or more result in the increased production rate of monocyclic aromatic hydrocarbons, and contents of 5.0 percent by mass or less can further increase the yield of monocyclic aromatic hydrocarbons.

[0050] The catalyst for the cracking and reforming reaction is formed into powder, granules or pellets depending on the reaction mode. For example, the catalyst is used in the form of powder for a fluidized bed and in the form of granules or pellets for a fixed bed. The average particle diameter of the catalyst used in a fluidized bed is preferably from 30 to 180 μm, more preferably from 50 to 100 μm. The bulk density of the catalyst used in a fluidized bed is preferably from 0.4 to 1.8 g/cc, more preferably 0.5 to 1.0 g/cc. The average particle diameter denotes the particle diameter at which the particle diameter distribution obtained by classification with a sieve is 50 percent by mass. The bulk density is the value measured in accordance with the method prescribed in JIS R9301-2-3. In order to produce a granular or pellet catalyst, if necessary, an inert oxide as a binder may be added to the catalyst, followed by molding with any of various molding apparatuses.

[0051] In the case where the catalyst for the cracking and reforming reaction contains an inorganic oxide as a binder, a phosphorus-containing binder may be used.

[0052] No particular limitation is imposed on the reaction temperature at which the feedstock is brought into contact with and then reacted with the catalyst for the cracking and reforming reaction. However, the reaction temperature is preferably from 400 to 650°C. The lower limit reaction temperature needs to be 400°C or higher so as to allow the easy reaction of the feedstock and is more preferably 450°C or higher. The upper limit reaction temperature needs to be 650°C or lower so as to increase sufficiently the yield of monocyclic aromatic hydrocarbons, more preferably 600°C or lower.

[0053] The reaction pressure at which the feedstock is brought into contact with and then reacted with the catalyst for the cracking and reforming reaction is preferably 1.5 MPaG or lower, more preferably 1.0 MPaG or lower. The reaction pressure if 1.5 MPaG or lower can restrain the generation of by-product light gas and lower the pressure resistance in a reactor.

[0054] No particular limitation is imposed on the contact time of the feedstock and the catalyst for the cracking and reforming reaction if the reaction proceeds as desired. However, for example, the contact time is preferably from 1 to 300 seconds measured when the gas passes across the catalyst for the cracking and reforming reaction. The lower limit contact time is more preferably 5 seconds or longer, and the upper limit contact time is more preferably 150 seconds or shorter. The contact time if 1 second or longer ensures the reaction between the feedstock and the catalyst. The contact time if 300 seconds or shorter can restrain deposition of carbon on the catalyst due to coking and furthermore suppress the amount of light gas generated by coking.

[0055] The cracked and reformed reaction product generated through the above-described cracking and reforming reaction is separated into fractions each having given properties thereby producing the cracked reformed base oil used of the present invention.

[0056] In order to separate the cracked and reformed reaction product into given fractions, a conventional distillation unit and gas-liquid separation unit may be used. One example of the distillation unit is a device such as a stripper comprising a multi-stage distillation unit so as to separate a plurality of fractions by distillation. One example of the gas-liquid separation unit is a device containing a gas-liquid separation tank, an inlet pipe for introducing the reaction product into the gas-liquid separation tank, a gas component discharge pipe arranged in the upper section of the gas-liquid separation bath and a liquid component discharge pipe arranged in the lower section of the gas-liquid separation bath.

[0057] The cracked and reformed base oil used in the present invention is preferably a fraction containing hydrocarbons of 9 or more carbon atoms.

[0058] No particular limitation is imposed on C heavy oil base oils other than the cracked reformed base oil to be blended in the method for producing the C heavy oil composition of the present invention. However, examples of such base oils include atmospheric gas oils, atmospheric residue, residual desulfurized gas oils, vacuum gas oils, vacuum residue, extract oils, light cycle oil and catalytically cracked residual oils. In the present invention, the cracked reformed base oil may be used in combination with one or more types of these C heavy oil base oils. The atmospheric gas oils and atmospheric residue are gas oils and residual oils produced by distilling crude oil at atmospheric pressure in an atmospheric distillation unit. The residual desulfurized gas oils are gas oils produced when atmospheric residue or vacuum residue are desulfurized in a direct residual oil desulfurization unit. The vacuum gas oils and vacuum residue are gas oils and residual oils produced by distilling atmospheric residue under reduced pressure in a vacuum distillation unit. The extract oils are aromatic components among which are not suitable for lubricating oil, produced by extracting and separating fractions from a vacuum distillation unit for lubricating oil feedstocks. The light cycle oil and catalytically cracked residual oils are gas oils and residual oils produced by cracking vacuum-distilled gas oils and vacuum-distilled residual oils in a fluid catalytic cracker.

[0059] In the C heavy oil composition of the present invention, these C heavy oil base oils are blended in an amount of 55 to 99 percent by volume, preferably 60 to 95 percent by volume, more preferably 65 to 90 percent by volume, most preferably 65 to 85 percent by volume on the basis of the total mass of the heavy oil composition.

[0060] The C heavy oil composition of the present invention is necessarily a C heavy oil composition produced using the above-described cracked reformed base oil as an indispensable component and meeting JIS Third-Class Heavy Oil Standard.

[0061] The method of the present invention produces a C heavy oil composition with a bicyclic aromatic hydrocarbon content of 10 percent by volume or more and 45 percent by volume or less. The lower limit bicyclic aromatic hydrocarbon content is preferably 10 percent by volume or more with the objective of retaining the compatibility to restrain the sludge formation. The upper limit is preferably 45 percent by volume or less with the objective of retaining the combustibility.

[0062] The bicyclic aromatic hydrocarbon content used herein denotes the bicyclic aromatic hydrocarbon content obtained by measuring the aromatic content separated by "a composition analysis method of asphalt using column chromatography" defined by the Japan Petroleum Institute standard JPI-5S-22-83 in accordance with "Petroleum Products-Determination of Hydrocarbon Types-High Performance Liquid Chromatography" defined by the Japan Petroleum Institute standard JPI-5S-49-97.

[0063] No particular limitation is imposed on the properties of the C heavy oil composition of the present invention other than the bicyclic aromatic hydrocarbon content. Preferably, the composition has the following properties.

[0064] The 15°C density (density at 15°C) of the C heavy oil composition of the present invention is preferably 0.85 g/cm^3 or higher, more preferably 0.88 g/cm^3 or higher, most preferably 0.90 g/cm^3 or higher. The 15°C density is also preferably 1.05 g/cm^3 or lower, more preferably 1.00 g/cm^3 or lower, most preferably 0.99 g/cm^3 or lower. A 15°C density of lower than 0.85 g/cm^3 is not preferred because the heat value per volume would be small. A 15°C density of higher than 1.05 g/cm^3 is not also preferred because the combustion failure would likely occur.

[0065] The 70°C density (density at 70°C) of the C heavy oil composition of the present invention is preferably 0.80 g/cm^3 or higher, more preferably 0.83 g/cm^3 or higher. The 70°C density is also preferably 1.00 g/cm^3 or lower, more preferably 0.95 g/cm^3 or lower. A 70°C density of lower than 0.80 g/cm^3 is not preferred because the heat value per volume would be small. A 70°C density of higher than 1.00 g/cm^3 is not also preferred because the combustion failure would likely occur.

[0066] The densities referred herein denotes the values obtained in accordance with the JIS K2249 "Crude petroleum and petroleum products-Determination of density and petroleum measurement tables based on a reference temperature (15°C)".

[0067] The 50°C kinematic viscosity of the C heavy oil composition of the present invention is preferably 400 mm^2/s or lower, more preferably 350 mm^2/s or lower, most preferably 300 mm^2/s or lower. If the 50°C kinematic viscosity is higher than 400 mm^2/s, the combustion failure of the composition would likely occur.

[0068] The 100°C kinematic viscosity of the C heavy oil composition is preferably 50 mm^2/s or lower, more preferably 45 mm^2/s or lower. If the 100°C kinematic viscosity is higher than 50 mm^2/s, the combustion failure of the composition would likely occur.

[0069] The kinematic viscosities referred herein denotes the values obtained in accordance with JIS K2283 "Crude petroleum and petroleum products-Determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity".

[0070] The sulfur content of the C heavy oil composition of the present invention is preferably 3.5 percent by mass or less, more preferably 3.0 percent by mass or less. If the sulfur content is more than 3.5 percent by mass, the amount of sulfur oxides exhausted from an engine possibly increases.

[0071] The sulfur content referred herein denotes the remaining carbon content measured in accordance with JIS K2541 "Crude oil and petroleum products-Determination of sulfur content".

[0072] The nitrogen content of the C heavy oil composition of the present invention is preferably 1.0 percent by mass or less, more preferably 0.5 percent by mass or less. If the nitrogen content is more than 1.0 percent by mass, the amount of nitrogen oxides exhausted from an engine possibly increases.

[0073] The nitrogen content referred herein denotes the remaining carbon content measured in accordance with JIS K2609 "Crude petroleum and petroleum products-Determination of nitrogen content".

[0074] The flash point of the C heavy oil composition of the present invention is preferably 70°C or higher, more preferably 72°C or higher from the viewpoint of safety in handling.

[0075] The flash point referred herein denotes the value measured in accordance with the Pensky-Martens closed cup method of JIS K2265 "Crude oil and petroleum products-Determination of flash point".

[0076] The CCAI of the C heavy oil composition of the present invention is preferably 900 or smaller, more preferably 870 or smaller. If the CCAI is greater than 900, the combustion failure of the composition would likely occur.

[0077] The CCAI (Calculated Carbon Aromaticity Index: defined in accordance with the decision of The International Council on Combustion Engines) used herein is an index focused on the relation between an aromatic content and ignitability and calculated by the following formula wherein the density and viscosity of heavy oil are conveniently represented by aromaticity:

$$CCAI = D - 140.7 \log(\log(V + 0.85)) - 80.6$$

(D: 15°C density (kg/m^3), V: 50°C kinematic viscosity (mm^2/s))

[0078] The carbon residue content of the C heavy oil composition of the present invention is preferably 15 percent by mass or less, more preferably 10 percent by mass or less. If the carbon residue content is more than 15 percent by mass, the combustion failure of the composition would likely occur.

[0079] The carbon residue content referred herein denotes the carbon residue content measured in accordance with JIS K2270 "Crude petroleum and petroleum products-Determination of carbon residue".

[0080] The ash content of the C heavy oil composition of the present invention is preferably 0.10 percent by mass or less, more preferably 0.05 percent by mass or less. If the ash content is more than 0.10 percent by mass, the combustion failure of the composition would likely occur.

[0081] The ash content referred herein denotes the value obtained in accordance with JIS K2272 "Testing Methods for Ash and Sulfated Ash of Crude Oil and Petroleum Products".

[0082] The vanadium content of the C heavy oil composition of the present invention is preferably 100 mass ppm or less, more preferably 80 mass ppm or less. If the vanadium content is more than 100 mass ppm, the combustion failure of the composition would likely occur.

[0083] The vanadium content denotes the value obtained in accordance with JPI-5S-11 "Method of Test for Vanadium in Fuel".

[0084] The water content of the C heavy oil composition of the present invention is preferably 0.5 percent by volume or less, more preferably 0.3 percent by volume or less. If the water content is more than 0.5 percent by volume, the composition would precipitate in the form of ice and likely cause metal corrosion or filter clogging.

[0085] The water content referred herein denotes the value measured in accordance with JIS K2275 "Crude oil and petroleum products-Determination of water content".

[0086] The ignition delay of the C heavy oil composition of the present invention measured with a fuel ignition analyzer is preferably 15 ms or shorter. The ignition delay measured with a fuel ignition analyzer is preferably 15 ms or shorter, more preferably 13 ms or shorter, more preferably 11 ms or shorter because a short time period from the injection of fuel into a combustion chamber till the ignition of the fuel is beneficial in order to operate diesel engine devices safely.

[0087] The combustion time of the C heavy oil composition of the present invention measured with a fuel ignition analyzer is preferably 25 ms or shorter. The combustion time measured with a fuel ignition analyzer is 25 ms or shorter preferably, more preferably 23 ms or shorter because a short flame in the combustion chamber is beneficial in order to operate a diesel engine device safely.

[0088] The fuel ignition analyzer used in the present invention is "Fuel Ignition Analyzer: FIA-100" manufactured by FUEL TECH Japan LTD in which about 0.1 ml of fuel heated to 120°C is injected at an ignition pressure of 20 MPa into a constant-volume combustion chamber filled with air with a volume of 1 L, a pressure of 4.5 MPa and a temperature of 450°C thereby measuring the ignition delay and combustion time.

[0089] The ignition delay referred herein denotes the period of time that the pressure in the combustion chamber increase from the initial pressure to 0.02 MPa.

[0090] The combustion period referred herein denotes the period of time obtained by deducting the ignition delay time from the time till reaching the maximum pressure.

[0091] The temperature at which the mass of the C heavy oil composition of the present invention decreases by 10 percent under a nitrogen atmosphere (100 ml/minute) measured with a thermogravimetry-differential thermal analysis is preferably 400°C or lower, more preferably 350°C or lower. If the temperature at which the mass decreases by 10 percent under a nitrogen atmosphere with a thermogravimetry-differential thermal analysis is higher than 400°C, the combustion failure of the composition would likely occur.

[0092] The thermogravimetry-differential thermal analysis referred herein is an analysis method wherein a sample is heated under given temperature conditions to measure the weight decrease associated with vaporization/thermal cracking and the change in calorific value associated with vaporization/oxidation/thermal cracking at the same time. Specifically, about 10 mg of a sample is weighed in a 5 mm inner diameter platinum pan and set on Thermoflex TAS300 manufactured by Rigaku Corporation. The sample is then heated from room temperature to 1000°C at a rate of 100°C/minute.

[0093] The temperature at which the mass of the C heavy oil composition of the present invention decreases by 50 percent under a nitrogen atmosphere (100 ml/minute) measured with a thermogravimetry-differential thermal analysis is preferably 600°C or lower, more preferably 550°C or lower. If the temperature at which the mass decreases by 50 percent under a nitrogen atmosphere with a thermogravimetry-differential thermal analysis is higher than 600°C, the combustion failure of the composition would likely occur.

[0094] The temperature at which the mass of the C heavy oil composition of the present invention decreases by 90 percent under a nitrogen atmosphere (100 ml/minute) measured with a thermogravimetry-differential thermal analysis is preferably 800°C or lower, more preferably 750°C or lower. If the temperature at which the mass decreases by 90 percent under a nitrogen atmosphere with a thermogravimetry-differential thermal analysis is higher than 800°C, the combustion failure of the composition would likely occur.

[0095] If necessary, the C heavy oil composition of the present invention may contain various additive such as cold flow improvers, cetane number improvers, anti-oxidants, stabilizing agents, dispersants, metal deactivators, microbial sterilizers, combustion improvers, anti-static agents, identification agent, and coloring agents.

[0096] The above-mentioned additives may be those synthesized in accordance with ordinary manners or commercially available additives. Some of the commercial available additives are often in the form in which the active components contributing to the intended effect are diluted with a suitable solvent. In the case of using commercially available additives, the effective components of which are diluted, they are preferably added such that properties of the C heavy oil composition satisfy the above-described requirements. The amounts of additives are arbitrarily selected, but the total amount of the additives is usually preferably 0.5 percent by mass or less, preferably 0.2 percent by mass or less on the basis of the total mass of the C heavy oil composition.

Examples

[0097] The present invention will be described with reference to the following examples but are not limited thereto.

[Examples and Comparative Examples]

[0098] Test fuels of Examples 1 to 4 were prepared using cracked reformed base oils set forth in Table 1, a vacuum residue produced by distilling an atmospheric residue under reduced pressure in a vacuum distillation unit and a straight-run gas oil produced by distilling crude oil at atmospheric pressure in an atmospheric distillation unit. For comparison, a sample containing no cracked reformed base oil and a commercially available product were also prepared.

[0099] The cracked reformed base oils set forth in Table 1 were prepared in the following manner.

(Method for producing cracked reformed base oils)

[0100] A light cycle oil LCO (a 10 vol.% distillation temperature of 215°C, a 90 vol.% distillation temperature of 318°C, a 15°C density of 0.9258 g/cm^3, a saturate content of 23 percent by volume, an olefin content of 2 percent by volume and a total aromatic content of 75 percent by volume) was brought into contact with and reacted with a catalyst for a cracking and reforming reaction (MFI type zeolite supporting 0.2 percent by mass of gallium and 0.7 percent by mass of phosphorus and containing a binder) under conditions of a reaction temperature of 538°C, a reaction pressure of 0.3 MPaG, an LCO and catalyst contact time of 60 seconds in a fluidized bed reactor so as to carry out a cracking and reforming reaction. The cracked and reformed reaction product was fractioned by distillation thereby producing cracked and reformed base oils 1 to 3 set forth in Table 1.

[0101] Evaluation results of these samples are set forth in Table 2. The properties of the C heavy oil compositions were measured in accordance with the above-described test methods and measurement methods.

[0102] Measurement of dry sludge was carried out in accordance with ISO 10307-1.

[0103] It is found from Table 2 that the C heavy oil compositions of the present invention are equal to or better than the commercially available product in ignitability and combustibility and can restrain sludge formation.

[Table 1]

			Cracked reformed base oil 1	Cracked reformed base oil 2	Cracked reformed base oil 3
Cracked reformed base oil properties	Density (@15°C)	(g/cm^3)	1.19	0.95	1.01
	Kinematic viscosity (@50°C)	(mm^2/s)	0.5	9.8	5.1
	Sulfur content	(mass ppm)	3120	2050	2510
	Nitrogen content	(mass ppm)	78	62	43
	Distillation characteristics				
	IBP	(°C)	233.5	158.0	185.0
	T10	(°C)	237.5	187.0	192.5
	T50	(°C)	252.0	238.0	237.0
	T90	(°C)	299.0	280.0	290.5
	EP	(°C)	363.0	362.0	362.5
	Total aromatic content	(volume %)	100	100	100

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Vacuum residue (volume %)	87	60	70	78	73	Commercially available C heavy oil
Cracked reformed base oil 1 (volume %)	13			5		
Cracked reformed base oil 2 (volume %)		40				
Cracked reformed base oil 3 (volume %)			30			
Straight-run gas oil (volume %)				17	27	
Density (@15°C) (g/m^3)	0.970	0.943	0.959	0.944	0.927	0.962
Kinematic viscosity (@50°C) (mm^2/s)	194	148	179	178	179	178
Carbon residue content (mass %)	7.6	7.8	7.9	7.6	8.1	10.4
Ash content (mass %)	0.002	0.003	0.004	0.002	0.004	0.021
Vanadium content (mass ppm)	26	18	21	23	22	50
Sulfur content (mass %)	2.70	2.71	2.88	2.62	2.98	2.34
Nitrogen content (mass %)	0.22	0.15	0.18	0.20	0.18	0.18
Water content (volume %)	0	0	0	0	0	0
Flush point (°C)	111	105	108	102	95	110
Bicyclic aromatic content (volume %)	14.9	42.9	32.7	10.9	8.4	9.8
CCAI	839	814	829	814	797	832
Dry sludge (mg/100 mL)	13	6	10	15	27	24
Fuel combustibility test Ignition delay (ms)	9.4	10.2	9.9	9.1	8.2	10.1
Combustion time (ms)	18.4	22.3	20.1	14.6	13.5	21.5
Thermogravimetry-differential thermal analysis Temperature at which the weight decreases by 10% (°C)	306	285	298	311	289	315
Temperature at which the weight decreases by 50% (°C)	512	490	501	509	499	523

(continued)

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Temperature at which the weight decreases by 90% (°C)	702	662	673	683	679	693

Industrial Applicability

[0104] The C heavy oil composition of the present invention unlikely forms sludge and is excellent in ignitability and combustibility. Therefore, the C heavy oil composition of the present invention is very useful as fuel for external combustion devices such as boilers, diesel engine devices of large ships and power generators, and gas turbine devices.

Claims

1. A method for producing a C heavy oil composition with a bicyclic aromatic hydrocarbon content of 10 percent by volume or more and 45 percent by volume or less, comprising blending a cracked reformed base oil with a total aromatic content of 80 percent by volume or more and a 15°C density of 0.90 to 1.20 g/cm^3 in an amount of 1 percent by volume or more and 45 percent by volume or less on the basis of the total mass of the composition.

2. The method for producing a C heavy oil composition according to claim 1, wherein the cracked reformed base oil has a 50°C kinematic viscosity of 0.3 to 10 mm^2/s, a sulfur content of 8000 mass ppm or less, and a nitrogen content of 100 mass ppm or less.

3. The method for producing a C heavy oil composition according to claim 1 or 2, wherein the cracked reformed base oil has a 10 vol.% distillation temperature (T10) of 130 to 270°C, a 50 vol.% distillation temperature (T50) of 190 to 290°C, and a 90 vol.% distillation temperature (T90) of 230 to 390°C.

4. The method for producing a C heavy oil composition according to any of claims 1 to 3, wherein the cracked reformed base oil is produced by bringing a feedstock having a 10 vol.% distillation temperature of 140°C or higher and a 90 vol.% distillation temperature of 380°C or lower into contact with a catalyst for a cracking and reforming reaction containing a medium pore zeolite and/or a large pore zeolite to be cracked and reformed through a cracking and reforming reaction at a reaction temperature of 400 to 650°C and a reaction pressure of 1.5 MPaG or lower for a contact time of 1 to 300 seconds.

5. A C heavy oil composition produced by the method for producing a C heavy oil composition according to any of claims 1 to 4, wherein it has a 15°C density of 0.85 to 1.05 g/cm^3, a 50°C kinematic viscosity of 400 mm^2/s or lower, a sulfur content of 3.5 percent by mass or less, a nitrogen content of 1 percent by mass or less and a flash point of 70°C or higher.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/062312

A. CLASSIFICATION OF SUBJECT MATTER
C10L1/04(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)
C10L1/04

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-028493 A (Idemitsu Kosan Co., Ltd.), 02 February 2006 (02.02.2006), paragraphs [0015] to [0063] (Family: none)	1-5
Y	JP 2008-239877 A (Nippon Oil Corp.), 09 October 2008 (09.10.2008), paragraphs [0006] to [0031] (Family: none)	1-5
Y	JP 2009-227933 A (Nippon Oil Corp.), 08 October 2009 (08.10.2009), paragraphs [0006] to [0032] (Family: none)	1-5

☒ 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
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"&" document member of the same patent family

Date of the actual completion of the international search 15 June, 2012 (15.06.12)	Date of mailing of the international search report 26 June, 2012 (26.06.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/062312

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-083254 A (Sekiyu Konbinato Kodo Togo Un'ei Gijutsu Kenkyu Kumiai), 30 March 2006 (30.03.2006), paragraphs [0007] to [0023] (Family: none)	1-5
A	JP 9-263775 A (Nippon Oil Co., Ltd.), 07 October 1997 (07.10.1997), paragraphs [0011] to [0071] (Family: none)	1-5
A	JP 2002-146364 A (Nippon Mitsubishi Oil Corp.), 22 May 2002 (22.05.2002), paragraphs [0010] to [0052] (Family: none)	1-5

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Non-patent literature cited in the description

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