



(11) **EP 1 818 385 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
15.08.2007 Bulletin 2007/33

(21) Application number: **05788266.4**

(22) Date of filing: **30.09.2005**

(51) Int Cl.:
C10G 65/12 (2006.01) **C10G 45/48** (2006.01)
C10G 45/52 (2006.01) **C10G 45/54** (2006.01)
C10G 47/18 (2006.01)

(86) International application number:
PCT/JP2005/018127

(87) International publication number:
WO 2006/038555 (13.04.2006 Gazette 2006/15)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

(30) Priority: **01.10.2004 JP 2004290672**

(71) Applicant: **Nippon Oil Corporation**
Tokyo 105-8412 (JP)

(72) Inventors:
• **IKI, Hideshi,**
c/o NIPPON OIL CORPORATION
Yokohama-shi, Kanagawa 2310815 (JP)

• **SUGIURA, Yukihiro,**
c/o NIPPON OIL CORPORATION
Yokohama-shi, Kanagawa 2310815 (JP)
• **TANAKA, Yuichi,**
c/o NIPPON OIL CORPORATION
Yokohama-shi, Kanagawa 2310815 (JP)
• **KONNO, Hirofumi,**
c/o NIPPON OIL CORPORATION
Yokohama-shi, Kanagawa 2310815 (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) **PROCESS FOR PRODUCING HYDROREFINED GAS OIL, HYDROREFIND GAS OIL, AND GAS OIL COMPOSITION**

(57) A process of the present invention for producing a hydrotreated gas oil has a step for obtaining a product oil having a total aromatic content of 3% by volume or less by hydrogenating a hydrotreated oil including 95% by volume or more of fraction having a boiling point range of 150 - 380°C, a sulfur content of 2 - 15 ppm by mass, a total aromatic content of 10 - 25% by volume, and a naphthene of 20 - 60% by volume in the presence of a hydrogenation catalyst; and a step for obtaining, by hy-

drogenating the above-described product oil in the presence of a hydrogenation catalyst containing a crystalline molecular sieve component, a product oil satisfying the conditions that the content of petroleum fraction having a boiling point range of lower than 150°C is 16% by volume or less, and the sum of the total aromatic content and the total naphthene content is 80% or less relative to the sum of these in the hydrotreated oil.

EP 1 818 385 A1

Description**Technical Field**

5 **[0001]** The present invention relates to a process for producing a hydrotreated gas oil, a hydrotreated gas oil, and a gas oil composition.

Background Art

10 **[0002]** Diesel engines are expected to serve a function in the reduction of carbon-dioxide emissions as global warming prevention measures because of a high energy efficiency thereof. On the other hand, demands for cleaner diesel engine exhaust gas has been tightened increasingly, and it is one of major challenges to remove such harmful substances as fine particle contents referred to as "particulate matter" and NO_x. Of these, in order to remove the particulate matter, the loading of an exhaust gas clean up system such as a particulate removing filter is going to be promoted increasingly.

15 **[0003]** However, it is indicated that, when a gas oil containing a lot of sulfur content is used as fuel, the deterioration of such exhaust gas clean up systems become significant. Responding to this, for transportation trucks having long travel distances, in particular, elongating the life of exhaust gas clean up systems to a maximum extent is strongly expected. Thus, further reduction of sulfur content in gas oil is indispensable. In addition, as the largest cause of particulate matter generation, aromatic contents in gas oil are indicated, and it is said that removing the aromatic contents in gas oil is effective as fundamental measures for reducing the particulate matter.

20 **[0004]** Petroleum-based gas oil fraction usually contains sulfur of 1 - 3% by mass in an unrefined state, and is used as a gas oil stocks after having been subjected to hydrodesulfurization. Other gas oil stocks include hydrodesulfurized kerosine fraction, and cracked gas oil obtained from a fluidized catalytic cracker or hydrocracker unit, and gas oil products are obtained after mixing these gas oil stocks. Among sulfur compounds existing in a gas oil fraction which have been hydrodesulfurized with a hydrodesulfurization catalyst, dibenzothiophene derivatives having plural methyl groups as a substituent as represented by 4,6-dimethyldibenzothiophene have a very poor reactivity. Therefore, even in the case of hydrodesulfurization to a high depth, such compounds tend to remain in the gas oil fraction.

25 **[0005]** Accordingly, in order to proceed with desulfurization of gas oil fraction down to such a further low sulfur content as 1 ppm by mass or lower while using conventional techniques, it is necessary to employ a very high hydrogen partial pressure, or extremely long contact time, that is, a very large reaction tower volume.

30 **[0006]** Further, unrefined petroleum-based gas oil fraction usually contains aromatic contents of 20 - 40% by volume. In the hydrogenation reaction of the aromatic components, there exists such restriction of chemical equilibrium that, in general, the equilibrium shifts to the generation of aromatic compounds on higher temperature sides, and to the generation of cyclic saturated hydrocarbons (naphthene) being hydrogenated products of aromatic rings on lower temperature sides, respectively. Accordingly, in order to accelerate the hydrogenation of aromatic compounds for the purpose of reducing the aromatic content in gas oil fraction, a low reaction temperature is advantageous from the viewpoint of the chemical equilibrium. But, at relatively low reaction temperatures, since the reaction rate of the aromatic hydrogenation reaction is insufficient, reaction conditions other than reaction temperature and a catalyst are required for compensating that.

35 **[0007]** Further, the hydrodesulfurization reaction is eventually a reaction to cleave a carbon-sulfur bond, and the cleavage reaction is accelerated at a higher temperature. Consequently, in conventional techniques, when the reaction condition is set on a lower temperature side in order to accelerate the hydrogenation of aromatic compounds, the desulfurization activity is insufficient, and, as the result, it is very difficult to satisfy both the ultra low sulfur content and low aromatic content.

40 **[0008]** Incidentally, in diesel engines, gas oil is blown to air having been compressed to be high temperatures to ignite and combust. But, when combustion does not occur normally at the timing of blowing the gas oil, knocking may occur. Therefore, gas oil must have such property as an excellent ignitionability. The cetane number is an index showing flammability, and gas oil having a higher value of the cetane number is more excellent in the ignitionability. Accordingly, the improvement of the cetane number of gas oil is one of the important challenges for aiming to the high efficiency of diesel engines. In general, it is said that aromatic compounds and naphthene compounds have a low cetane number and paraffin compounds (chain saturated hydrocarbon) have a high cetane number. Therefore, in order to heighten the cetane number, it is necessary to proceed with hydrogenation of aromatic compounds and conversion of naphthene to paraffin.

45 **[0009]** However, the conversion of naphthene to paraffin is accompanied, usually, with a cracking reaction, therefore lightening of a product oil as compared with the feed oil is inevitable, to lead to the substantial yield reduction of gas oil fraction. As described above, expected are means for proceeding effectively with hydrogenation reaction and conversion reaction to paraffin while inhibiting undesirable cracking reaction.

50 **[0010]** Under such background, for a process for producing a diesel gas oil with a small sulfur content and aromatic

content, there is proposed a production technique in which a desulfurization process (first step) and an aromatic hydrogenation process (second step) using zeolite or clay mineral as a catalyst are combined (see Patent Document 1 and 2). However, even production processes as described in these Patent Documents do not exert a sufficient effect of decreasing both the sulfur content and aromatic content. Specifically, even with such production processes as described in these Patent Documents, it is difficult to achieve simultaneously such a very high desulfurization and aromatics-removing levels as a sulfur content of 1 ppm by mass or less and an aromatic content of 1 % by volume or less. In such conventional production processes, when the operation severity in the first step is raised, it becomes difficult to continue economically the operation in the first step for satisfactory period of time. Further, the rise of the reaction temperature in the first step results in the increase in the aromatics content in the product oil in the first step and hinders removing of aromatics in the second step. Furthermore, there is the above-described equilibrium restriction on aromatics in the second step, therefore there are limitations on increasing the operation severity such as the rise of the reaction temperature etc.

[0011] On the other hand, there is disclosed such a process as treating gas oil fraction by a gas/liquid countercurrent flow type process using a catalyst of Pt supported on USY (Ultra Stable Y zeolite) as a technique of converting naphthene to paraffin in Patent Document 3. However, in order to proceed with conversion of naphthene to paraffin, a high reaction temperature is required, and along with the increase in the severity of the reaction condition as the result of the raised reaction temperature, the yield of the generating gas oil fraction tends to decrease.

Patent Document 1: JP-A-7-155610

Patent Document 2: JP-A-8-283747

Patent Document 3: JP-T-2003-502478

Disclosure of the Invention

Problems to be solved by the Invention

[0012] The present invention was achieved with the view of the above-described circumstances, and aims to provide a process for producing a hydrotreated gas oil capable of producing such gas oil excellent in both environmental properties and combustion properties that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less, and that further has a high cetane number, with sufficient efficiency and reliability without setting special operating conditions and equipment investment. Further, the present invention also aims to provide a hydrotreated gas oil that is obtained by the above process for producing a hydrotreated gas oil, and a gas oil composition containing the hydrotreated gas oil.

Means for Solving the Problems

[0013] The present invention provides a process for producing a hydrotreated gas oil by carrying out the hydrotreating of a feed oil, including a first step for obtaining a first product oil having a total aromatic content of 3% by volume or less by using a hydrotreated oil including a petroleum fraction of 95% by volume or more having a boiling point range of 150 - 380°C, a sulfur content of 2 - 15 ppm by mass, a total aromatic content of 10 - 25% by volume and a total naphthene content of 20 - 60% by volume as a feed oil, and by carrying out hydrotreating of the feed oil in the presence of a first hydrogenation catalyst; and a second step for obtaining a second product oil that satisfies the following conditions (1) and (2): (1) the content of petroleum fraction having a boiling point range of lower than 150°C is 16% by volume or less, and (2) the sum of the total aromatic content and the total naphthene content is 80% or less relative to the sum of the total aromatic content and the total naphthene content in the feed oil, by carrying out hydrotreating of the first product oil in the presence of a second hydrogenation catalyst containing a crystalline molecular sieve component.

[0014] The process for producing a hydrotreated gas oil according to the present invention uses the petroleum fraction satisfying simultaneously the respective properties as a feed oil, carries out, in a first step, hydrotreating of the feed oil so as to obtain a first product oil having the above properties, and, further in a second step, carries out hydrotreating of the first product oil so that a second product oil to be obtained satisfies simultaneously the above conditions with the use of the above specified catalyst. As the result of these multiple actions, it becomes possible, for the first time, to produce such a gas oil excellent in both environmental properties and combustion properties that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less, and that has further a high cetane number with a sufficient efficiency and reliability, without setting special operation conditions and equipment investment, that is, by using a conventional apparatus.

[0015] In the process of the present invention for producing a hydrotreated gas oil, it is preferred that a polycyclic aromatic content in a feed oil is 1 - 7% by volume and a polycyclic aromatic content in a second product oil is 0.2% by volume or less. This can give an effect of the present invention more effectively, and, additionally, makes it possible to

inhibit further an equipment investment. The "polycyclic" herein means both condensed rings and ring aggregates.

[0016] In the process of the present invention for producing a hydrotreated gas oil, preferably a sum of the polycyclic aromatic content and a polycyclic naphthene content in the second product oil is 13% by volume or less. This improves further a cetane number of the hydrotreated gas oil to be obtained, and can give further satisfactory fuel properties.

[0017] In the process of the present invention for producing a hydrotreated gas oil, it is preferred to carry out the hydrotreating of the feed oil in the first step under such reaction conditions as a reaction temperature of 170 - 320°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity of 0.1 - 4h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L; and to carry out the hydrotreating of the first product oil in the second step under such reaction conditions as a reaction temperature of 200 - 280°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity of 0.1 - 2 h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L. This makes it possible to obtain more easily the first product oil or the hydrotreated gas oil having intended properties. Furthermore, it becomes possible to inhibit further the shortening of the catalyst life and too much equipment investment.

[0018] In the process of the present invention for producing a hydrotreated gas oil, it is preferred that both the first hydrogenation catalyst and the second hydrogenation catalyst are composed of an active metal supported on a porous support, and that the metal is at least one kind of metal selected from the group consisting of group VIII metals. Such catalyst can exert a desulfurization activity, an aromatic hydrogenation activity, an activity of converting naphthene to paraffin, and the like for achieving the purpose and effect of the present invention with a further improved balance. From the same viewpoint, in the process of the present invention for producing a hydrotreated gas oil, preferably the active metal is at least one kind of metal selected from the group consisting of Rh, Ir, Pd and Pt.

[0019] In the process of the present invention for producing a hydrotreated gas oil, preferably the support for the first hydrogenation catalyst contains at least one kind of metal oxide selected from the group consisting of titania, zirconia, boria and silica, and alumina. By adopting the first hydrogenation catalyst provided with such support, it is possible to synthesize the first product oil for obtaining the hydrotreated gas oil having intended properties with a higher selectivity and yield.

[0020] In the process of the present invention for producing a hydrotreated gas oil, preferably the crystalline molecular sieve component contains silica and alumina, and has at least one kind of crystal structure selected from the group consisting of the faujasite type, the beta type, the mordenite type and the pentacyl type. The second hydrogenation catalyst that contains such crystalline molecular sieve component can exert a desulfurization activity, an aromatic hydrogenation activity, an activity for converting naphthene to paraffin, and the like, in particular the activity for converting naphthene to paraffin for achieving the purpose and effect of the present invention with a higher effectiveness and reliability.

[0021] The present invention provides a hydrotreated gas oil that can be obtained by the above-described process for producing the hydrotreated gas oil, and that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less.

[0022] The present invention provide a gas oil composition containing the hydrotreated gas oil that can be obtained by the above-described process for producing the hydrotreated gas oil, and that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less.

Effect of the Invention

[0023] According to the present invention, it is possible to provide a process for producing such hydrotreated gas oil excellent in both environmental properties and combustion properties that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less, and that, further, has a high cetane number, with a sufficient efficiency and reliability without setting special operation conditions and equipment investment.

Best Modes for Carrying Out the Invention

[0024] Hereinafter, preferred embodiments of the present invention are described in detail.

[0025] The process of the present invention for producing a hydrotreated gas oil is a process for producing a hydrotreated gas oil by carrying out the hydrotreating of a feed oil, wherein the process has a first step for obtaining a first product oil having a total aromatic content of 3% by volume or less by using hydrotreated oil including a petroleum fraction of 95% by volume or more having a boiling point range of 150 - 380°C, a sulfur content of 2 - 15 ppm by mass, a total aromatic content of 10 - 25% by volume and a total naphthene content of 20 - 60% by volume as a feed oil, and by carrying out hydrotreating of the feed oil in the presence of a first hydrogenation catalyst; and a second step for obtaining a second product oil that satisfies the following conditions (1) and (2): (1) the content of petroleum fraction having a boiling point range of lower than 150°C is 16% by volume or less, and (2) the sum of the total aromatic content and the total naphthene content is 80% or less relative to the sum of the total aromatic content and the total naphthene content in the feed oil, by carrying out the hydrotreating of the first product oil in the presence of a second hydrogenation

catalyst containing a crystalline molecular sieve component.

(Feed Oil)

[0026] A hydrotreated oil used as the feed oil in the present invention contains a petroleum fraction of 95% by volume or more having a boiling point range of 150 - 380°C, a sulfur content of 2 - 15 ppm by mass, a total aromatic content of 10 - 25% by volume, and a total naphthene content of 20 - 60% by volume.

[0027] Here, the term "boiling point range" herein means one that is measured according to the method as described in JIS-K-2254 "Petroleum products - Determination of distillation characteristics" or ASTM-D86. The term "sulfur content" herein means the mass content of sulfur on the basis of a total gas oil volume, which is measured according to the method as described in JIS-K-2541 "Crude oil and petroleum products - Determination of sulfur content" or ASTM-D5453.

[0028] Further, the terms "total aromatic content" and "polycyclic aromatic content," which is described later, herein mean the content that is calculated from the volume percentage (% by volume) of respective aromatic contents to be measured according to the method as described in Journal of the Japan Petroleum Institute JPI-5S-49-97 "Petroleum products - Determination of hydrocarbon types-High performance liquid chromatography" published by The Japan Petroleum Institute. The terms "total naphthene content" and "olefin content," which is described later, herein mean the content that is measured according to the method as described in ASTM-D2786-91 "Standard Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturates Fraction by High Ionizing Voltage Mass Spectrometry."

[0029] When a feed oil contains a petroleum fraction of 95% by volume or less having a boiling point range of 150 - 380°C, it is meant that it contains light fraction having a boiling point of lower than 150°C or heavy fraction having a boiling point of above 380°C in a greater volume. The increase in light fraction may lead to the increase in a LPG production volume, and the increase in the heavy fraction may lead to an insufficient progress of the hydrogenation reaction or the conversion reaction of polycyclic aromatics, to tend to result in, for example, the occurrence of the necessity for providing new equipment. This is the same for a case where a feed oil that has not been subjected to hydrotreating processing is used.

[0030] A sulfur content in the feed oil for use in the present invention is 2-15 ppm by mass, preferably 3-10 ppm by mass, more preferably 4-9 ppm by mass. The sulfur content in the feed oil of more than 15 ppm by mass tends to lower the activity of a hydrogenation catalyst not to allow the desulfurization reaction and aromatic hydrogenation reaction to proceed sufficiently. The sulfur content in the feed oil of less than 2 ppm by mass tends to lower the reaction temperature necessary for removing the sulfur component not to allow the aromatic hydrogenation reaction and the conversion reaction of naphthene to paraffin to proceed sufficiently.

[0031] In the feed oil used for the present invention, usually, there exist naphthene being a cyclic saturated hydrocarbon component, paraffin being a noncyclic saturated hydrocarbon component and olefin being an unsaturated hydrocarbon component, in addition to an aromatic component. Among these, the total aromatic content in the feed oil used for the present invention is 10 - 25% by volume, preferably 11 - 21 % by volume. The total aromatic content in a feed oil of more than 25% by volume tends to require a long contact time, that is, a too much reaction tower volume in order to reduce the total aromatic content to 3% by volume or less in the first step, thereby resulting in the necessity for new equipment investment or too much equipment investment. On the other hand, the total aromatic content in a feed oil of less than 10% by volume tends to increase the operation cost and decrease the economic advantage of the present invention, because the necessity for setting more severe operation conditions necessary for aromatic hydrogenation than operation conditions necessary for the desulfurization is increased.

[0032] Further, regarding the composition of aromatics in the feed oil used for the present invention, a polycyclic aromatic content is preferably 1 - 7% by volume relative to the feed oil, more preferably 1.5 - 5% by volume. The polycyclic aromatic content in a feed oil of more than 7% by volume tends to require too much equipment investment in order to achieve an intended polycyclic aromatic content in a product oil; and less than 1 % by volume tends to make it difficult to obtain effectively the effect according to the present invention.

[0033] The total naphthene content in the feed oil used for the present invention is within a range of 20 - 60% by volume, more preferably 25 - 45% by volume. In case where the total naphthene content in a feed oil is less than 20% by volume, it is meant that a lot of paraffin having a high cetane number are contained originally, which results in the decrease in the improvement degree of the cetane number by the conversion of naphthene to paraffin to reduce the advantage of the present invention. On the other hand, the total naphthene content in a feed oil of more than 60% by volume tends to increase the total volume of aromatic component and naphthene component in the feed oil. As described above, the hydrogenation reaction of aromatic compounds is also an equilibrium reaction with naphthene, therefore the increase in the total volume of aromatic component and naphthene component may result in the increase in the aromatic component in the product oil due to the chemical equilibrium not to allow a sufficient effect on the reduction of the aromatic component to be obtained.

[0034] The olefin content in the feed oil is preferably 1% by volume or less. The olefin content of more than 1% by volume tends to occlude the catalyst layer filled up with the first hydrogenation catalyst in the first step due to such

reaction as polymerization in the reaction tower.

[0035] As the feed oil, a hydrotreated petroleum-based hydrocarbons having the above-described properties are sufficient, and it may be a mixture of petroleum fractions having been fractionized from plural apparatuses. For example, it may be an oil that is obtained by subjecting a straight-run oil having the prescribed boiling point range that has been fractionized from an atmospheric distillation apparatus to desulfurization processing in a hydrodesulfurization apparatus. In this case, as a feed oil, a petroleum fraction, which is obtained by mixing petroleum fraction having a prescribed boiling point range that can be obtained from a hydrocracking apparatus, a residual oil direct desulfurization apparatus, a fluid catalytic cracking apparatus or like with the above-described straight-run oil and then by subjecting the mixed oil to hydrodesulfurization, may be used. Or, as a kind of a feed oil, a petroleum fraction having a prescribed boiling point range, which is obtained by hydrocracking a vacuum gas oil fraction obtained from a vacuum distillation apparatus in a hydrocracking apparatus, may be used. Further, as a feed oil, an oil, which is obtained by subjecting separately each of kerosine fraction and gas oil fraction from respective apparatuses to hydrotreating and then mixing these so as to have a prescribed boiling point range, may be used; or an oil, which is obtained by mixing product oils obtained from respective hydrotreating apparatuses, may be used.

[0036] For hydrodesulfurization conditions for obtaining the feed oil, conditions used for processing using a usual hydrodesulfurization apparatus in petroleum refining are sufficient. That is, preferably hydrodesulfurization processing is carried out under such conditions as a reaction temperature of 250 - 380°C, a hydrogen partial pressure of 2-8 MPa, a liquid hourly space velocity (LHSV) of 0.3 - 10.0 h⁻¹, and a hydrogen/oil ratio of 100 - 500 NL/L. As a catalyst to be provided to the hydrodesulfurization apparatus, such common hydrodesulfurization catalyst can be used that is composed of an active metal supported on a support. That is, as an active metal species, usually, sulfide of group VIA metals and group VIII metals (e.g., Co-Mo, Ni-Mo, Ni-Co-Mo, Ni-W) can be used. As a support, porous inorganic oxide having alumina as a main component can be used.

[0037] Hydrocracking conditions for obtaining the feed oil can be the one used for processing using a common hydrocracking apparatus in petroleum refining. That is, preferably the hydrocracking treatment is carried out under such conditions as a reaction temperature of 300-450°C, a hydrogen partial pressure of 5-18 MPa, a liquid hourly space velocity (LHSV) of 0.1-8.0 h⁻¹, a hydrogen/oil ratio of 300-2000 NL/L. As a catalyst to be provided to the hydrocracking apparatus, a common hydrocracking catalyst composed of an active metal supported on a support can be used. That is, as the active metal species, usually sulfide of group VIA metals and group VIII metals (e.g., Co-Mo, Ni-Mo, Ni-Co-Mo, Ni-W) may be used. As a support, a material containing such solid acid as inorganic complex oxide or zeolite may be used.

[0038] Or, for a catalyst for obtaining the feed oil, the aforementioned hydrodesulfurization catalyst and hydrocracking catalyst may be used in combination. Incidentally, reaction conditions and kinds of catalysts as described above that are adopted in hydrotreating for obtaining the feed oil are not particularly limited provided that properties of a feed oil to be obtained satisfy the above conditions.

[0039] In these hydrodesulfurization processing and hydrocracking processing, the constitution of respective apparatuses or an apparatus groups composed by combining the two is not particularly limited, but it is desirable to remove hydrogen sulfide as far as possible from the product to be obtained by these hydrotreatings, using a gas-liquid separation tower or prescribed hydrogen sulfide removing equipment. For example, in common desulfurization apparatuses for gas oil or kerosene, it is preferred to separate hydrogen sulfide being a gas component from a fraction from a reaction tower for hydrodesulfurization using a gas-liquid separation tower. In case where the liquid fraction obtained by removing the gas component in this way is used as a feed oil, a very little amount of hydrogen sulfide is contained in the feed oil, therefore it is more suitable as the feed oil for the present invention. Even in case where hydrogen sulfide coexists in a feed oil, in the production process of the present invention, it is possible to achieve the purpose and advantage of the present invention by setting appropriate hydrotreating conditions.

(First Step)

[0040] In the first step of the present invention, in the presence of the first hydrogenation catalyst, the feed oil is subjected to hydrotreating to give the first product oil having the total aromatic content of 3% by volume or less.

[0041] The first hydrogenation catalyst for use in the first step is preferably one composed of at least one kind of metal selected from the group consisting of the group VIII metals as an active metal supported on a porous support.

[0042] For the support for the first hydrogenation catalyst, preferred is one containing at least one kind of metal oxide selected from the group consisting of titania, zirconia, boria and silica, and alumina. For respective components for constituting the support, the above-described components can be combined, and, from the viewpoint of the sulfur resistance of the catalyst, silica - alumina, titania - alumina, boria - alumina, zirconia - alumina, titania - zirconia - alumina, silica - boria - alumina, silica - zirconia - alumina, silica - titania - alumina and silica - titania - zirconia - alumina are preferred, silica - alumina, boria - alumina, zirconia - alumina, titania - zirconia - alumina, silica - boria - alumina, silica - zirconia - alumina and silica - titania - alumina are more preferred, and silica - alumina and silica - zirconia - alumina

are further preferred.

[0043] The component ratio between alumina and other component in the support is not particularly limited, but the alumina content is preferably 90% by mass or less on the basis of the total support mass, more preferably 60% by mass or less, further preferably 40% by mass or less. The lower limit of the alumina content is not particularly limited, but is preferably 20% by mass or more on the basis of the total support mass. More than 90% by mass of alumina tends to make the sulfur resistance of the catalyst insufficient, and, less than 20% by mass of alumina tends to lower the formability of the catalyst to make the industrial production thereof difficult.

[0044] The preparation processes of the support is not particularly limited, and the support is prepared, for example, as given below. Firstly, in order to obtain the support, there is prepared such an "alumina precursor" as an alumina gel-containing liquid, boehmite powder, an alumina suspension or kneaded product that is obtained by conventional methods. Next, in order to introduce a metal oxide other than the alumina, an aqueous or organic solvent solution of an acetate, chloride, nitrate, sulfate, naphthenate or various coordinate compounds of the metal is compounded to the alumina precursor by such a method as addition or coprecipitation. Among these, the use of a nitrate, acetate or chloride is preferred, and the use of a nitrate or acetate is further preferred. According to need, the compounded product is kneaded, dried, molded or calcined to give a support. The metal oxide for modifying a support may be introduced by, for example, impregnating an aqueous or organic solvent solution of an acetate, chloride, nitrate, sulfate, naphthate or various coordinate compounds of the metal after calcining the support.

[0045] Or, the support may be prepared by preparing once such a complex oxide or complex hydroxide as silica - alumina, silica - zirconia, alumina - titania, silica - titania, or alumina - boria, and then adding the above-described alumina gel being a precursor of the metal oxide, a gel or suitable solution of another hydroxide to the complex oxide or the like followed by the kneading or the like. In case where the molding is carried out, such a shape can be molded by extrusion molding as an approximate cylinder having an approximately circular cross-section, or a tetralobal-shaped rod having a tetralobal-shaped cross section.

[0046] The reaction conditions of the first step in the present invention are preferably a reaction temperature of 170 - 320°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity (LHSV) of 0.1 - 4 h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L, more preferably a reaction temperature of 180 - 305°C, a hydrogen partial pressure of 4 - 8 MPa, a liquid hourly space velocity (LHSV) of 1.0 - 3.0 h⁻¹ and a hydrogen/oil ratio of 300 - 700 NL/L.

[0047] A lower reaction temperature is advantageous for hydrogenation reaction, but a reaction temperature of lower than 170°C tends not to allow the desulfurization reaction to progress easily. A reaction temperature of higher than 320°C tends to shorten the catalyst life and increase the aromatic content due to the advantage for the generation of aromatics in the chemical equilibrium. For both the hydrogen partial pressure and hydrogen/oil ratio, generally a higher value tends to accelerate both the desulfurization reaction and hydrogenation reaction. The hydrogen partial pressure and hydrogen/oil ratio of less than the above-described lower limit tend not to allow the desulfurization reaction and aromatics hydrogenation reaction to progress easily. On the other hand, the hydrogen partial pressure and hydrogen/oil ratio of more than the above-described upper limit tend to require too much equipment investment. A lower liquid hourly space velocity (LHSV) tends to be advantageous for the desulfurization reaction and hydrogenation reaction. However, the liquid hourly space velocity of less than 0.1 h⁻¹ tends to require a very great reaction tower volume and require too much equipment investment. On the other hand, the liquid hourly space velocity of more than 4 h⁻¹ tends not to allow the desulfurization and aromatics hydrogenation reaction, and, in addition, the naphthene conversion reaction to progress sufficiently.

[0048] In the first step, the reaction conditions are so regulated that the total aromatic content in the first product oil to be obtained is 3% by volume or less, preferably 1 % by volume or less. The total aromatic content in the first product oil of more than 3% by volume tends not to allow the conversion reaction of naphthene to paraffin in the second step to progress easily, thereby making it difficult to give a gas oil having excellent environmental properties and a high cetane number.

[0049] The olefin content in the first product oil is preferably 1% by volume or less. The olefin content of more than 1% by volume tends to occlude the catalyst layer filled with the second hydrogenation catalyst in the second step due to such reaction as polymerization in the reaction tower.

(Second Step)

[0050] In the second step of the present invention, the first product oil is subjected to hydrotreating in the presence of the second hydrogenation catalyst containing a crystalline molecular sieve component to give the second product oil that satisfy the above-described conditions (1) and (2) simultaneously. Here, the "crystalline molecular sieve component" herein means a solid crystal having a molecular sieve function.

[0051] The second hydrogenation catalyst for use in the second step is not particularly limited only when it contains a crystalline molecular sieve component. As the crystalline molecular sieve component, for example, zeolite can be mentioned. As components constituting the crystal skeleton of zeolite, in addition to silica, alumina, titania, boria, gallium

etc. can be mentioned. Among these, zeolite including silica and alumina, that is, aluminosilicate is preferred. As the crystal structure of zeolite, for example, a faujasite type, a beta type, a mordenite type, and a pentacyl type can be mentioned.

[0052] For the crystalline molecular sieve component in the present invention, in order to obtain stably an intended crystal structure, one in which the alumina content is regulated in accordance with the stoichiometric mixture ratio of feed materials, or one having been subjected to a prescribed hydrothermal processing and/or acid processing can be used. From the viewpoint of proceeding more efficiently with the conversion of naphthene to paraffin, the crystalline molecular sieve component is preferably faujasite zeolite or beta zeolite, more preferably faujasite zeolite.

[0053] Among faujasite zeolite, the use of Y type zeolite as the crystalline molecular sieve component for the present invention is preferred, and the use of ultrastable Y type (hereinafter, referred to as "USY") zeolite having been ultrastabilized by a hydrothermal processing and/or acid processing is more preferred. In the USY zeolite, in addition to such fine pore structure of 20 Å or less referred to as micropores that is owned by Y type zeolite originally, new fine pores are formed within a range of 20 - 100 Å. It is thought that this gives more effective progress of conversion of naphthene to paraffin. For the hydrothermal processing conditions for obtaining USY zeolite, publicly known conditions can be adopted. In USY zeolite, the molar ratio of silica/alumina (molar ratio of silica relative to alumina; hereinafter, referred to as a "silica/alumina ratio") is preferably 10 - 120, more preferably 15-70, further preferably 20 - 50. A silica/alumina ratio of higher than 120 tends not to give good acid properties (such as acid point, acid strength) of zeolite for the conversion of naphthene to paraffin, thereby lowering the conversion activity from naphthene. A silica/alumina ratio of lower than 10 tends to result in strong acid properties and accelerate a caulk generation reaction, thereby leading to rapid activity lowering of the second hydrogenation catalyst.

[0054] As the crystalline molecular sieve component according to the present invention, one that is molded by a tablet molding process directly after the synthesis may be used, but the use of one that is molded after being mixed with a binder component is preferred. As the binder component, in addition to alumina as a simple substance and silica as a simple substance, it may be any of silica - alumina, titania - alumina, boria - alumina, zirconia - alumina, titania - zirconia - alumina, silica - boria - alumina, silica - zirconia - alumina, silica - titania - alumina or silica - titania - zirconia - alumina, which is a support for the hydrogenation catalyst for use in the first step.

[0055] The zeolite content in the second hydrogenation catalyst is preferably 10% by mass or more, more preferably 30% by mass or more, further preferably 50% by mass or more. The zeolite content in the second hydrogenation catalyst of 10% by mass or less tends to lower the naphthene conversion activity. The shape of a molded catalyst is not particularly limited, and any of such shape as a cylinder, macaroni type, or sphere can be selected.

[0056] As the second hydrogenation catalyst for use in the second step, to the latter stage of the portion composed of the hydrogenation catalyst containing the crystalline molecular sieve component, a part composed of a hydrogenation catalyst not containing the crystalline molecular sieve component may be provided. For the part of the latter stage, the same catalyst as that in the first step can be used. As a result of this, it is possible to stabilize, by hydrogenation reaction or the like, such compound as a radical product or a compound susceptible to oxidation reaction due to an unstable structure thereof among products obtained by the naphthene conversion reaction, to prevent sludge (solid material) generation and coloring due to oxidation/polycondensation of the obtained product.

[0057] The percentage of the second hydrogenation catalyst relative to the total volume of the first hydrogenation catalyst and the second hydrogenation catalyst is not particularly limited, but the percentage of the hydrogenation catalyst containing the crystalline molecular sieve component relative to the total volume of the first hydrogenation catalyst and the second hydrogenation catalyst (a hydrogenation catalyst that contains a crystalline molecular sieve component and a hydrogenation catalyst that does not contain a crystalline molecular sieve component) is preferably 30% by volume or more, more preferably 40% by volume or more. The ratio of the hydrogenation catalyst containing the crystalline molecular sieve component of less than 30% by volume tends to lower the naphthene conversion activity.

[0058] The second step in the present invention has such reaction conditions as preferably a reaction temperature of 200 - 280°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity (LHSV) of 0.1 - 2 h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L, more preferably a reaction temperature of 220 - 270°C, a hydrogen partial pressure of 4 - 8 MPa, a liquid hourly space velocity (LHSV) of 0.5 - 1.5 h⁻¹ and a hydrogen/oil ratio of 300 - 700 NL/L.

[0059] A lower reaction temperature is advantageous for the hydrogenation reaction, but a reaction temperature of lower than 200°C tends to lower the naphthene conversion reaction activity. On the other hand, a higher reaction temperature is advantageous for the naphthene conversion reaction, but a reaction temperature of higher than 280°C tends to increase the yield of products having a boiling point of lower than 150°C to reduce the yield of the intended gas oil fraction. A higher hydrogen partial pressure and hydrogen/oil ratio, generally, tend to accelerate both the hydrogenation reaction and naphthene conversion reaction. A hydrogen partial pressure and hydrogen/oil ratio lower than the above-described lower limit tend not to allow the hydrogenation reaction and naphthene conversion reaction to progress easily. On the other hand, a hydrogen partial pressure and hydrogen/oil ratio of more than the above-described upper limit tend to require too much equipment investment. A lower liquid hourly space velocity (LHSV) tends to be advantageous for the hydrogenation reaction and naphthene conversion reaction. However, a liquid hourly space velocity of smaller than

0.5 h⁻¹ tends to require a very large reaction tower volume and too much equipment investment. On the other hand, a liquid hourly space velocity of greater than 1.5 h⁻¹ tends not to allow the hydrogenation reaction and naphthene conversion reaction to progress easily.

[0060] In the second step, the reaction conditions are so regulated that the second product oil to be obtained has light petroleum fraction having a boiling point range of 150°C or lower in 16% by volume or less. More preferably the reaction conditions are so regulated that the above-described light petroleum fraction content is 12% by volume or less, further preferably 8% by volume or less. A light petroleum fraction more than 16% by volume reduces the yield of gas oil obtained from the second product oil, thereby making it difficult to produce the gas oil with sufficient efficiency.

[0061] Further, the reaction conditions are so regulated that the second product oil to be obtained has the sum of the total aromatic content and the total naphthene content of 80% or less, preferably 70% relative to the sum of the total aromatic content and the total naphthene content in the above-described feed oil. The sum of the total aromatic content and the total naphthene content of more than 80% relative to the sum of the total aromatic content and the total naphthene content in the feed oil tends not to allow a gas oil that has excellent environmental properties and a high cetane number to be obtained easily.

[0062] According to the present invention, the total aromatic content in the second product oil becomes 3% by volume or less, and the content of 1% by volume or less is more preferred. The total aromatic content of more than 3% by volume reduces the effect of lowering the particulate matter in diesel exhaust gas, therefore it becomes difficult to obtain gas oil having excellent environmental properties and a high cetane number, and the purpose and advantage of the present invention are not achieved.

[0063] The polycyclic aromatic content in the second product oil is preferably 0.2% by volume or less, more preferably 0.1 % by volume or less. The polycyclic aromatic content of more than 0.2% by volume tends to increase the particulate matter in diesel exhaust gas.

[0064] Further, the sum of the polycyclic aromatic content and the polycyclic naphthene content in the second product oil is preferably 13% by volume or less, more preferably 10% by volume or less. The sum of the polycyclic aromatic content and the polycyclic naphthene content of more than 13% by volume tends to result in the difficulty in improving the cetane number and not to allow good fuel properties to be obtained easily.

[0065] The active metal to be supported in the first hydrogenation catalyst and the second hydrogenation catalyst according to the present invention is preferably at least one metal selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt belonging to the group VIII metals, more preferably at least one metal selected from the group consisting of Rh, Ir, Pd and Pt, from the viewpoint of such desulfurization activity, aromatic hydrogenation activity, activity of converting naphthene to paraffin that enable the purpose and advantage of the present invention to be achieved.

[0066] Further, for the active metal of the hydrogenation catalyst, plural metals may be selected and combined. Such combination as Pt-Pd, Pt-Rh, Pt-Ir, Rh-Ir, Rh-Pd, Ir-Pd, Pt-Pd-Ir, Pt-Rh-Ir, Pt-Rh-Pd or Rh-Ir-Pd can be adopted. Among these, more preferred is Pt-Pd, Pt-Rh, Pt-Ir, Pt-Pd-Ir, Pt-Rh-Ir or Pt-Rh-Pd, further preferred is Pt-Pd, Pt-Ir or Pt-Pd-Ir, and especially preferred is Pt-Pd, from the viewpoint of such desulfurization activity, aromatic hydrogenation activity, activity of converting naphthene to paraffin that enable the purpose and advantage of the present invention to be achieved.

[0067] Next, the active metals in the first hydrogenation catalyst and the second hydrogenation catalyst according to the present invention are described. The supported volume of these active metals is not particularly limited, but is preferably 0.05 - 10% by mass in the sum of the metal volumes relative to the entire catalyst volume, more preferably 0.1 - 5% by mass, further preferably 0.15 - 3% by mass, from the viewpoint of such desulfurization activity, aromatic hydrogenation activity, activity of converting naphthene to paraffin that enable the purpose and advantage of the present invention to be achieved.

[0068] For the supporting process of the active metal onto the support, such supporting processes used for common hydrogenation catalysts as an impregnation process and an ion exchange process may be adopted, while using the aqueous solution, the water-soluble organic solvent solution or the water-insoluble organic solvent solution of an inorganic salt or complex compound of the active metal, that is, carbonate, nitrate, sulfate, organic acid salt or oxide thereof. In case where plural metals are to be supported, they may be supported simultaneously using a mixed solution, or may be supported sequentially using solutions of a single component. The support processing of the active metal onto a support may be carried out after the end of the entire preparation process of the support, or may be carried out, after supporting the active metal onto a suitable oxide, complex oxide or crystalline molecular sieve in the intermediate process of the support preparation, by gel blending, heating and compressing, kneading processes and the like, but it is preferred to carry out the processing after the end of the entire preparation process of the support. Then, by calcining the product composed of the active metal that is impregnated and supported on the support under intended conditions, the hydrogenation catalyst according to the present invention can be obtained.

[0069] The first hydrogenation catalyst and the second hydrogenation catalyst according to the present invention are used preferably after being subjected to a pre-reduction processing. The pre-reduction processing is carried out, usually, by pouring a gas containing hydrogen in a reaction tube (reaction tower) filled with a hydrogenation catalyst, and giving heat at 200°C or higher to the hydrogenation catalyst according to a prescribed procedure. As a result, the supported

active metal of the catalyst is reduced, to allow the catalyst to exert more effectively the hydrogenation activity and the naphthene conversion activity.

[0070] An apparatus for carrying out hydrotreating of the feed oil in this way may have any constitution, and a reaction tower in which the catalyst is filled may be single, or plural towers may be combined. Further, for the purpose of reducing the hydrogen sulfide concentration in the reaction tower, gas-liquid separation equipment or other equipment for removing hydrogen sulfide may be provided, or equipment for injecting additional hydrogen may be provided to the former step of the reaction tower, or, in case where plural reaction towers are provided serially, between the plural reaction towers.

[0071] The reaction form of a hydrotreating apparatus for use in the present invention may be a fixed bed system. That is, for hydrogen, either countercurrent flow form or co-current flow form relative to the feed oil may be usable, or, a combined form of a countercurrent flow and co-current flow with plural reaction towers may be usable. General forms are of down flow, and there is a gas-liquid twin co-current flow form. The reaction tower may be constituted of plural catalyst beds, and, between respective catalyst beds, hydrogen gas may be injected for the purpose of removing reaction heat or raising the hydrogen partial pressure (quench hydrogen).

[0072] The hydrotreated gas oil as described above that is obtained by the favorable embodiment of the present invention is one having a sulfur content of 1 ppm by mass or less, and the total aromatic content of 3% by volume or less. Further, the present inventors confirmed that the cetane number of the hydrotreated gas oil can be improved significantly relative to the feed oil, and that, for example, the value increases by at least three points relative to the feed oil before the refining. This is considered due to a fact that the feed oil has been converted to such constitution as containing a lot of hydrocarbon having a higher cetane number by the conversion of naphthene to paraffin, as well as the hydrogenation of aromatic contents. The cetane number is an index representing combustion quality, and a larger value thereof gives more excellent ignition properties and expectation for improving the combustion efficiency in diesel engines.

[0073] Here, the "cetane number" herein is a cetane number that is measured according to the method as described in JIS-K2280 "Determination of octane number, cetane number and calculation of cetane index." Incidentally, increase and decrease in the cetane number of petroleum fraction can be checked simply from the cetane index that is calculated according to the calculation method of the cetane index as described in JIS-K2280 "Determination of octane number, cetane number and calculation of cetane index."

[0074] The gas oil that is obtained according to the favorable embodiment of the present invention may be used singly as a diesel gas oil, or it may be mixed with another base stock to produce a gas oil composition to be used as a diesel gas oil. Another base stock includes synthetic gas oil or synthetic kerosene that can be obtained, while using so-called synthesis gas constituted of hydrogen and carbon monoxide as a feed stock, via Fischer-Tropsch reaction or the like. These synthetic kerosene and synthetic gas oil scarcely contain aromatic component and contain saturated hydrocarbon as a main component, and, usually, have a high cetane number. For the production process of the synthetic gas, publicly known processes can be used, and there is no particular limitation.

[0075] The compounding ratio of synthetic gas oil in a gas oil composition (diesel gas oil) is preferably 30% by volume or less, more preferably 20% by volume or less, further preferably 10% by volume or less. The compounding ratio of synthetic kerosene in a gas oil composition is preferably 60% by volume or less, more preferably 50% by volume or less, further preferably 40% by volume or less.

[0076] Thus, the favorable embodiments of the present invention have been described, but the present invention is not limited to these embodiments.

Example

[0077] Hereinafter, the present invention is described in more detail based on Example, but the present invention is not limited to the Example.

(Preparation of Hydrogenation Catalyst)

[0078] After allowing an aqueous solution of sodium silicate (concentration: 29% by mass, 2350 g) to gel under the condition of pH 4, it was aged under the conditions of 60°C, pH 7 for two hours to give slurry. Next, the obtained slurry was added with an aqueous solution containing zirconium sulfate (tetrahydrate, 350 g). Then, the slurry after the addition was regulated to pH 7 to generate silica - zirconia complex hydroxide. The complex hydroxide was aged at 60°C for 30 minutes, which was then added with an aqueous solution containing aluminum sulfate (quatrodeca hydrate, 420 g) to be regulated to pH 7 to generate slurry of silica - zirconia - alumina complex hydroxide. The slurry of silica - zirconia - alumina complex hydroxide was filtrated and washed, and then moisture thereof was regulated by heating concentration. Then, the complex hydroxide after the moisture regulation was extrusion molded, further dried in the air at 110°C for one hour, and calcined at 550°C for three hours to give a catalyst support (porous support). The obtained support had such ratio of respective constituents as 20% by mass of alumina, 57% by mass of silica, and 23% by mass of zirconia

as oxide.

[0079] To the support, active metals were impregnated by a common process using a mixed aqueous solution of tetraammine platinum (II) chloride and tetraammine palladium (II) chloride, whose concentration had been regulated so as to be a volume appropriate to the water absorption percentage of the support. It was then dried in the air at 110°C for one hour, calcined at 300°C for two hours to give the first hydrogenation catalyst. The supported volume of platinum and palladium in the first hydrogenation catalyst was 0.3% by mass and 0.5% by mass, respectively, relative to the entire catalyst.

[0080] Next, a Y type zeolite having a silica/alumina ratio of 5 was stabilized by a publicly known ultra - stabilization processing method, which was then subjected to acid processing with a 1 N aqueous solution of nitric acid to give USY zeolite of a proton type having a unit lattice length of 24.33 Å and a silica/alumina ratio of 30. The obtained USY zeolite (550 g) was added to an aqueous solution of ammonium nitrate (concentration: 2 N, 3 L) and stirred at room temperature to be converted to the ammonium type.

[0081] Next, the obtained ammonium type zeolite was added to a mixed solution of tetraammine platinum (II) chloride and tetraammine palladium (II) chloride whose concentration had been regulated so as to be a volume appropriate to the water absorption percentage of the support, which was stirred at 70°C to allow the active metals to be supported by an ion exchange method. The zeolite supporting the active metals was filtrated and isolated, dried in the air at 110°C for one hour, and calcined at 300°C for two hours. Then, the obtained zeolite was kneaded with a commercially available alumina gel (by Condea) and molded to give the second hydrogenation catalyst. The supported volume of platinum and palladium in the second hydrogenation catalyst was 0.3% by mass and 0.5% by mass, respectively, relative to the entire catalyst. The ratio of the zeolite and alumina was 70:30 by mass ratio.

(Example 1)

[0082] A first reaction tube (inner diameter: 20 mm) filled with the first hydrogenation catalyst (20 mL) and a second reaction tube (inner diameter: 20 mm) filled with the second hydrogenation catalyst (20 mL) were attached in tandem to a fixed bed flow type reactor (down flow), then a pre-reduction processing was carried out under the conditions of hydrogen partial pressure of 5 MPa at 300°C for 5 hours as a preprocessing. Then, a feed oil, whose properties are listed in Table 2, was conducted into the reactor under the conditions as listed in Table 1 to carry out a hydrotreating test. The feed oil was an oil obtained by subjecting the fraction corresponding to gas oil that was obtained by atmospheric distillation of feed oil originated in Middle East to hydrotreating processing.

[0083] In Table 2, "IBP" means the initial boiling point as defined in JIS-K-2254, and "EP" means the end point as defined in JIS-K-2254. The "(total aromatic content + total naphthene content) yield" means the percentage of the sum of the total aromatic content and the total naphthene content in the second product oil relative to the sum of the total aromatic content and the naphthene content in the feed oil. The "gas oil yield" means the yield of the fraction having a boiling point range of 150 - 380°C. The "light fraction yield" means the yield of fractions that are lighter than the gas oil, that is, the yield of fractions having a boiling point range of less than 150°C.

Table 1

First step	Reaction temperature [°C]	220
	Hydrgen partial pressure [MPa]	5.0
	Liquid hourly space velocity [h ⁻¹]	2.0
	Hydrogen/Oil ratio [NL/L]	400
Second step	Reaction temperature [°C]	240
	Hydrgen partial pressure [MPa]	5.0
	Liquid hourly space velocity [h ⁻¹]	2.0
	Hydrogen/Oil ratio [NL/L]	400

Table 2

	Raw oil	Second formed oil		
		Example	Comp. Ex 1	Comp. Ex 2
Density (15°C) [g/cm ³]	0.8300	0.8090	0.7990	0.8065

(continued)

	Raw oil	Second formed oil		
		Example	Comp. Ex 1	Comp. Ex 2
IBP/EP [°C]	187/370	165/365	172/360	175/367
Sulfur content [ppm by mass]	8.0	0.5	1.5	0.3
Olefin content [% by volume]	0.0	0.3	0.2	0.1
Total aromatic content [% by volume]	19.9	0.6	4.1	0.5
Total naphthene content [% by volume]	39.7	39.4	48.1	55.1
(Total aromatic content + total naphthene content) [% by volume]	59.6	40.0	52.2	55.6
(Total aromatic content + total naphthene content) yield [%]	-	65.1	85.4	91.0
Polycyclic aromatic content [% by volume]	2.5	0.1	0.4	0.1
Polycyclic naphthene content [% by volume]	17.1	11.8	17.5	18.9
(Polycyclic aromatic content + polycyclic naphthene content) [% by volume]	19.6	11.9	17.9	19.0
Gas oil yield [% by volume]	-	97.0	97.5	97.5
Light fraction yield [% by volume]	-	3.0	2.5	2.5
Cetane number	60.0	68.7	61.2	61.5

[0084] In the product oil (first product oil) distilled from the first reaction tube filled with the first hydrogenation catalyst, the total aromatic content was 0.8% by volume, the olefin content was 0.1 % by volume, and the sulfur content was 0.6 ppm by mass, on the 10th day from the start of the hydrotreating test. Properties of the second product oil on the 10th day from the start of the hydrotreating test are listed in Table 2.

(Comparative Example 1)

[0085] A hydrotreating test was practiced in the same way as in Example 1 except for changing the filling volume of the first hydrogenation catalyst into the first reaction tube from 20 mL to 8 mL, and the liquid hourly space velocity in the first step from 2.0 h⁻¹ to 5.0 h⁻¹. In the product oil (first product oil) distilled from the first reaction tube filled with the first hydrogenation catalyst, the total aromatic content was 6.8% by volume, the olefin content was 0.2% by volume, and the sulfur content was 2.6 ppm by mass. Properties of the second product oil on the 10th day from the start of the hydrotreating test are listed in Table 2.

(Comparative Example 2)

[0086] A hydrotreating test was practiced in the same way as in Example 1 except for changing the catalyst filled in the second reaction tube (inner diameter: 20 mm) from the second hydrogenation catalyst (20 mL) to the first hydrogenation catalyst (20 mL). In the product oil (first product oil) distilled from the first reaction tube filled with the first hydrogenation catalyst, the total aromatic content was 0.8% by volume, the olefin content was 0.1 % by volume, and the sulfur content was 0.6 ppm by mass. Properties of the second product oil on the 10th day from the start of the hydrotreating test are listed in Table 2.

Industrial Applicability

[0087] According to the present invention, it is possible to provide the process for producing a hydrotreated gas oil capable of producing such gas oil excellent in both environmental properties and combustion properties as having a sulfur content of 1 ppm by mass or less and the total aromatic content of 3% by volume or less, and further a high cetane number, with sufficient efficiency and reliability without providing for special operation conditions and equipment investment.

Claims

1. A process for producing a hydrotreated gas oil by carrying out hydrotreating of a feed oil, comprising:

a first step for obtaining a first product oil having a total aromatic content of 3% by volume or less, by using a hydrotreated oil including a petroleum fraction of 95% by volume or more having a boiling point range of 150 - 380°C, a sulfur content of 2 - 15 ppm by mass, a total aromatic content of 10 - 25% by volume and a total naphthene content of 20 - 60% by volume as a feed oil, and by carrying out hydrotreating of the feed oil in the presence of a first hydrogenation catalyst; and
a second step for obtaining a second product oil that satisfies the following conditions (1) and (2) by carrying out hydrotreating of the first product oil in the presence of a second hydrogenation catalyst containing a crystalline molecular sieve component,

- (1) the content of petroleum fraction having a boiling point range of lower than 150°C is 16% by volume or less, and
(2) the sum of the total aromatic content and the total naphthene content is 80% or less relative to the sum of the total aromatic content and the total naphthene content in the feed oil.

2. A process for producing a hydrotreated gas oil according to claim 1, wherein a polycyclic aromatic content in the feed oil is 1 - 7% by volume, and a polycyclic aromatic content in the second product oil is 0.2% by volume or less.

3. A process for producing a hydrotreated gas oil according to claim 1 or 2, wherein the sum of a polycyclic aromatic content and a polycyclic naphthene content in the second product oil is 13% by volume or less.

4. A process for producing a hydrotreated gas oil according to any one of claims 1 to 3, wherein:

in the first step, the feed oil is subjected to hydrotreating under such reaction conditions as a reaction temperature of 170 - 320°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity of 0.1 - 4 h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L; and
in the second step, the first product oil is subjected to hydrotreating under such reaction conditions as a reaction temperature of 200 - 280°C, a hydrogen partial pressure of 2 - 10 MPa, a liquid hourly space velocity of 0.1 - 2 h⁻¹ and a hydrogen/oil ratio of 250 - 800 NL/L.

5. A process for producing a hydrotreated gas oil according to any one of claims 1 to 4, wherein both the first hydrogenation catalyst and the second hydrogenation catalyst are composed of an active metal supported on a porous support, and the active metal is at least one kind of metal selected from the group consisting of group VIII metals.

6. A process for producing a hydrotreated gas oil according to claim 5, wherein the active metal is at least one kind of metal selected from the group consisting of Rh, Ir, Pd and Pt.

7. A process for producing a hydrotreated gas oil according to any one of claims 1 to 6, wherein the support in the first hydrogenation catalyst contains at least one kind of metal oxide selected from the group consisting of titania, zirconia, boria and silica, and alumina.

8. A process for producing a hydrotreated gas oil according to any one of claims 1 to 7, wherein the crystalline molecular sieve component contains silica and alumina, and has at least one kind of crystal structure selected from the group consisting of a faujasite type, a beta type, a mordenite type and a pentacyl type.

9. A hydrotreated gas oil that is obtained by the process for producing the hydrotreated gas oil as described in any one of claims 1 - 8, and that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume or less.

10. A gas oil composition comprising a hydrotreated gas oil that is obtained by the process for producing the hydrotreated gas oil as described in any one of claims 1 - 8, and that has a sulfur content of 1 ppm by mass or less and a total aromatic content of 3% by volume.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/018127

A. CLASSIFICATION OF SUBJECT MATTER <i>C10G65/12</i> (2006.01), <i>C10G45/48</i> (2006.01), <i>C10G45/52</i> (2006.01), <i>C10G45/54</i> (2006.01), <i>C10G47/18</i> (2006.01)		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) <i>C10G65/12</i> (2006.01), <i>C10G45/48</i> (2006.01), <i>C10G45/52</i> (2006.01), <i>C10G45/54</i> (2006.01), <i>C10G47/18</i> (2006.01)		
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 1996-2005 Kokai Jitsuyo Shinan Koho 1971-2005 Toroku Jitsuyo Shinan Koho 1994-2005		
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.
X Y	JP 2004-504135 A (Exxon Research & Engineering Co.), 12 February, 2004 (12.02.04), Claims; Par. Nos. [0054], [0058], [0061], [0062] & US 2002/0040176 A1 & US 2002/0038068 A1 & WO 02/007881 A1 & WO 02/008157 A1	1, 2, 3, 8-10 4-7
Y	JP 10-180112 A (Petroleum Energy Center), 07 July, 1998 (07.07.98), Claims; Par. No. [0022] (Family: none)	4-7
Y	JP 10-235198 A (Petroleum Energy Center), 08 September, 1998 (08.09.98), Claims; Par. No. [0021] (Family: none)	4-7
☐ 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 14 December, 2005 (14.12.05)		Date of mailing of the international search report 27 December, 2005 (27.12.05)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 7155610 A [0011]
- JP 8283747 A [0011]
- JP 2003502478 T [0011]