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(54) **HYDROREFINING METHOD FOR HYDROCARBON OIL**

(57) The invention provides a hydrocarbon oil hydrorefining method, **characterized by** including providing a mixture of a heavy hydrocarbon oil and a hydrocarbon oil exhibiting an effect of increasing dissolved hydrogen concentration; mixing the oil mixture, which is sub-

jected to hydrorefining, with hydrogen; and causing the resultant mixture to pass through a reactor for carrying out hydrorefining. The method can enhance performance in hydrorefining of the heavy oil.

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Description

Technical Field

[0001] The present invention relates to a method for hydrotreating a hydrocarbon oil. More particularly, the present invention relates to a hydrocarbon oil hydrotreating method for effectively hydrotreating a heavy hydrocarbon oil contained in an oil mixture, the oil mixture containing the heavy hydrocarbon oil and a specific hydrocarbon oil.

Background Art

[0002] In a conventional crude oil refining method, generally, crude oil is separated into fractions through atmospheric distillation, and then each fraction is subjected to desulfurization. However, such a method is not necessarily satisfactory, since the method poses problems in that, for example, it requires a large number of oil-refining facilities, intricate processes, and excessive energy due to repeated cooling and heating of products. Therefore, demand has arisen for a new crude oil processing method. From such viewpoints, in recent years, attempts have been made to process crude oil or naphtha-fraction-free crude oil in one batch. For example, there have been proposed (1) a method in which a naphtha fraction is separated from crude oil through distillation, and the resultant naphtha-free residual oil is subjected to hydrodesulfurization all together and then separated into products through distillation (Patent Document 1); and (2) a method in which a naphtha fraction is separated from crude oil through distillation, and the resultant naphtha-free residual oil is subjected to hydrodesulfurization all together and then separated into a light oil fraction and a heavy oil fraction by means of a high-pressure separation vessel, followed by hydrotreating of the light oil fraction (Patent Document 2). Such methods proposed above, in which an oil mixture containing two or more oil fractions is subjected to hydrotreatment, could achieve effective hydrotreating.

[0003] Meanwhile, there has been proposed a method for facilitating desulfurization and demetallization of heavy oil, which have been conventionally difficult to perform, through dilution of the heavy oil. For example, Patent Document 3 discloses a method in which residual oil is mixed with a diluent having a specific boiling point, and the mixture is subjected to desulfurization and demetallization under specific conditions. According to this method, desulfurization rate and/or demetallization rate increases, thereby effectively lowering the sulfur and/or metal content of the hydrotreated residual oil.

[0004] The aforementioned techniques; i.e., techniques employing a feedstock containing two or more oil fractions, and the technique of diluting heavy oil, are very important for enhancing performance in hydrotreating. However, from the viewpoints of environmental issues and energy savings, a hydrotreating process of further enhanced performance must be developed. The technique disclosed in Patent Document 3 is not necessarily effective in terms of energy savings. Specifically, the technique leaves room for improvement in terms of energy savings in the overall process of crude oil refining, since the technique employs, as a low-boiling-point diluent which is mixed with heavy oil, for example, light oil or distilled oil, which can be generally refined within a shorter period of time under mild conditions, as compared with the case of the heavy oil.

[0005] Regarding the aforementioned conventional techniques; i.e., techniques employing a feedstock containing two or more oil fractions, and techniques of diluting heavy oil, the effect of mixing a plurality of types of oil has not yet been elucidated in detail. Therefore, difficulty is encountered in improving the conventional techniques and developing a new oil refining method, even under the circumstances that such improvement and development are required.

[0006]

Patent Document 1: Japanese Patent Application Publication (*kokai*) No. H03-294390

Patent Document 2: Japanese Patent Application Publication (*kokai*) No. H04-224890

Patent Document 3: Japanese Patent Application Publication (*kokai*) No. H04-239094

Disclosure of the Invention

Problems to be Solved by the Invention

[0007] Under such circumstances, an object of the present invention is to provide a hydrocarbon oil hydrotreating method which, in hydrotreating of a hydrocarbon oil containing heavy oil, can enhance performance in hydrotreating of the heavy oil, to thereby produce an increased amount of a refined oil, to produce a high-quality refined oil, and to attain mild hydrotreating conditions. Means for Solving the Problems

[0008] As has been known, in hydrodesulfurization reaction, there is a difference in processing rate between a heavy hydrocarbon oil and a light hydrocarbon oil. In general, a heavy hydrocarbon oil is processed at very low efficiency, as compared with the case of a light hydrocarbon oil. Thus, conceivably, when a mixture of a heavy hydrocarbon oil and a light hydrocarbon oil is subjected to hydrodesulfurization, hydrodesulfurization reaction of the light hydrocarbon oil is

completed in the vicinity of an inlet of a reactor, and, after completion of the reaction, the light hydrocarbon oil serves as an inert diluent. Therefore, since the heavy hydrocarbon oil is mixed with the light hydrocarbon oil, even when LHSV increases, desulfurization conversion of the heavy hydrocarbon oil does not decrease, and desulfurization proceeds effectively (hereinafter, this effect of the light hydrocarbon oil may be referred to as the "dilution effect"). However, such a hydrodesulfurization technique leaves room for improvement in terms of energy savings in the overall process of crude oil refining, since, as described above, the light hydrocarbon oil can be refined within a shorter period of time under mild conditions, as compared with the case of the heavy hydrocarbon oil. In view of the foregoing, the present inventors have conducted extensive studies, and as a result have found that when a specific light hydrocarbon oil is added to a heavy hydrocarbon oil, and the mixture is processed through a specific method, effects other than the aforementioned dilution effect can be obtained, and hydrorefining can be carried out more effectively. The present invention has been accomplished on the basis of this finding. Accordingly, the present invention provides the following:

- (1) a hydrocarbon oil hydrorefining method, characterized by comprising providing a mixture of a heavy hydrocarbon oil and a dissolved-hydrogen-concentration-increasing hydrocarbon oil (i.e., a hydrocarbon oil exhibiting an effect of increasing the concentration of dissolved hydrogen); mixing the oil mixture, which is subjected to hydrorefining, with hydrogen; and causing the resultant mixture to pass through a reactor for carrying out hydrorefining;
- (2) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the oil mixture of a heavy hydrocarbon oil and a dissolved-hydrogen-concentration-increasing hydrocarbon oil has a dissolved hydrogen concentration which is 1.1 times or more the highest possible hydrogen concentration of the heavy hydrocarbon oil;
- (3) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the heavy hydrocarbon oil is one or more species selected from among vacuum residual oil, vacuum gas oil, atmospheric residual oil, topped crude oil, crude oil, deasphalted oil, coal-liquefied oil, oil obtained from oil sand, and oil obtained from oil shale;
- (4) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is contained in a liquid phase entirely or partially under the conditions in the reactor;
- (5) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the effect of increasing dissolved hydrogen concentration is estimated on the basis of the equilibrium of hydrogen between gas and liquid in the reactor;
- (6) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is additionally fed, as a quenching oil, into the reactor;
- (7) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is one or more species selected from among a straight-run kerosene fraction, a straight-run light gas oil fraction, a straight-run heavy gas oil fraction, cracked oil obtained from an FCC unit, and thermally cracked oil obtained from a coker unit;
- (8) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the hydrorefining includes one or more steps selected from among a hydrodemetallization step, a hydrodesulfurization step, a hydrocracking step, a hydrodenitrogenation step, and a hydrodearomatization step;
- (9) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the hydrorefining is carried out under the following conditions: a reaction temperature of 300 to 450°C, a hydrogen partial pressure of 5.1 to 25.3 MPa (G), a hydrogen/oil ratio of 200 to 2,000 Nm³/kL, and an LHSV of 0.05 to 10 hr⁻¹; and
- (10) a hydrocarbon oil hydrorefining method as described in (1) above, wherein the hydrorefining is carried out under the following conditions: a reaction temperature of 330 to 430°C, a hydrogen partial pressure of 10.1 to 20.3 MPa (G), a hydrogen/oil ratio of 500 to 1,000 Nm³/kL, and an LHSV of 0.1 to 1.0 hr⁻¹.

Effects of the Invention

[0009] According to the present invention, there is provided a hydrocarbon oil hydrorefining method which, in hydrorefining of a hydrocarbon oil containing heavy oil, can further enhance performance in hydrorefining of the heavy oil, to thereby produce an increased amount of a refined oil, to produce a high-quality refined oil, and to attain mild hydrorefining conditions. The hydrorefining method comprises adding a specific light hydrocarbon oil to a heavy hydrocarbon oil, and processing the resultant mixture under specific conditions. Therefore, according to the hydrorefining method, a defect that the light hydrocarbon oil is subjected to hydrorefining for a long period of time under severe conditions is solved and the energy savings can be achieved in the overall process of crude oil.

Brief Description of the Drawings

[0010]

[Fig. 1]

Fig. 1 schematically shows a diagram of steps included in the present invention.

[Fig. 2]

Fig. 2 schematically shows another diagram of steps included in the present invention.

[Fig. 3]

Fig. 3 schematically shows still another diagram of steps included in the present invention.

[Fig. 4]

Fig. 4 schematically shows yet another diagram of steps included in the present invention.

Description of Reference Numerals

[0011]

- 1: Hydrodemetallization step
- 2: Hydrodesulfurization step
- 3: Separation-refinement step
- 4: Hydrocracking step
- 5: Hydrodenitrogenation step
- 6: Bottom oil recycling
- 7: Hydrogen recycling
- 8: Quenching hydrogen
- 9: Quenching oil
- 11: Heavy hydrocarbon oil
- 12: Dissolved-hydrogen-concentration-increasing hydrocarbon oil
- 13: Hydrogen
- 14: Refined heavy hydrocarbon oil
- 15: Refined light hydrocarbon oil

Best Modes for Carrying Out the Invention

[0012] In the hydrocarbon oil hydrotreating method of the present invention, hydrogen is mixed with an oil mixture containing a heavy hydrocarbon oil and a dissolved-hydrogen-concentration-increasing hydrocarbon oil, and the hydrogen-mixed oil mixture is caused to pass through a reactor for carrying out hydrotreating.

[0013] The heavy hydrocarbon oil may be selected from among vacuum residual oil, vacuum gas oil, atmospheric residual oil, topped crude oil, crude oil, deasphalted oil, coal-liquefied oil, oil obtained from oil sand, and oil obtained from oil shale, and these oils may be employed singly or in combination of two or more species. Since effects of the present invention are difficult to obtain when a heavy hydrocarbon oil incapable of forming a liquid phase in the reactor is employed, an appropriate heavy oil must be selected, or appropriate reaction conditions must be provided. The present invention is intended to achieve enhancement of performance in heavy hydrocarbon oil hydrotreating, which has been conventionally difficult to attain. Therefore, the heavy hydrocarbon oil employed in the present invention preferably contains asphaltene (as used herein, "asphaltene" refers to an n-heptane-insoluble fraction of heavy oil obtained through extraction of the heavy oil with n-heptane) in an amount of 2 mass% or more, more preferably 4 mass% or more. Even when a heavy hydrocarbon oil having an asphaltene content of less than 2 mass% is employed, the resultant refined oil exhibits no problematic features. However, employment of such a low-asphaltene-content heavy hydrocarbon oil is not preferred from the viewpoints of cost-effectiveness and energy savings, since the heavy hydrocarbon oil is relatively easily hydrogenated without application of the present invention. No particular limitation is imposed on the maximum asphaltene content of the heavy hydrocarbon oil employed in the present invention, but the asphaltene content is preferably less than 15 mass%, from the viewpoint of operation of the reactor. For reasons similar to those described above, the heavy hydrocarbon oil employed in the present invention preferably contains vanadium in an amount of 10 mass ppm or more, nickel in an amount of 10 mass ppm or more, and sulfur in an amount of 0.1 mass% or more.

[0014] The heavy hydrocarbon oil employed is preferably pretreated as desired. For example, when the heavy hydrocarbon oil has a high salt content, preferably, the hydrocarbon oil is subjected to desalting treatment so as to have a sodium chloride content of 10 mass ppm or less. When the heavy hydrocarbon oil has a high solid content, the hydrocarbon oil is preferably filtered with a filter (about 10 μ m).

[0015] The present invention employs a dissolved-hydrogen-concentration-increasing hydrocarbon oil. As used herein, "dissolved-hydrogen-concentration-increasing hydrocarbon oil" refers to a hydrocarbon oil which has an average boiling point of 100°C or higher, which has a density of 0.70 to 0.95 g/mL, and which exhibits the effect of increasing the dissolved hydrogen concentration of the resultant oil mixture so that the dissolved hydrogen concentration of the oil mixture as measured under the conditions (temperature and pressure) becomes higher than the highest possible hydrogen concentration of the heavy hydrocarbon oil as measured at the same conditions. When a hydrocarbon oil having an average

boiling point lower than 100°C or a density lower than 0.70 g/mL is employed, the amount of the hydrocarbon oil present in a liquid phase is considerably reduced, and the hydrocarbon oil tends to exhibit poor effect of increasing hydrogen concentration. Also, a hydrocarbon oil having a density higher than 0.95 g/mL tends to exhibit poor effect of increasing dissolved hydrogen concentration. Specific examples of the dissolved-hydrogen-concentration-increasing hydrocarbon oil include a straight-run kerosene fraction, a straight-run light gas oil fraction, a straight-run heavy gas oil fraction, cracked oil obtained from an FCC unit, and thermally cracked oil obtained from a coker unit. These may be employed singly or in combination of two or more species. The present invention may employ a non-petroleum-origin hydrocarbon. In general, a light hydrocarbon having a boiling point lower than that of the heavy hydrocarbon oil serving as a starting oil exhibits the effect of increasing the dissolved hydrogen concentration of a liquid phase in the reactor. However, when a light hydrocarbon having a very low boiling point is excessively fed into the reactor, since the light hydrocarbon is generally present in a gas phase in the reactor, the hydrogen partial pressure in the gas phase is reduced, and the light hydrocarbon may fail to exhibit an effect of increasing dissolved hydrogen concentration.

[0016] The aforementioned dissolved-hydrogen-concentration-increasing hydrocarbon oil must be present in a liquid phase entirely or partially under the temperature and pressure conditions in the reactor. When the hydrocarbon oil is entirely or partially present in the liquid phase, hydrotreating performance can be enhanced. Under the temperature and pressure conditions in the reactor, the ratio of the amount of the hydrocarbon oil present in the liquid phase to the entire amount of the hydrocarbon oil is preferably 10% or more, more preferably 20% or more.

[0017] When the dissolved-hydrogen-concentration-increasing hydrocarbon oil is subjected to hydrotreating together with the heavy oil, hydrotreating performance can be further enhanced by effects other than the aforementioned dilution effect. In the present invention, preferably, the mixture of the heavy hydrocarbon oil and the dissolved-hydrogen-concentration-increasing hydrocarbon oil has a dissolved hydrogen concentration which is 1.1 times or more the highest possible hydrogen concentration of the heavy hydrocarbon oil. When the dissolved hydrogen concentration is less than 1.1 times the highest possible hydrogen concentration of the heavy hydrocarbon oil, since the dissolved-hydrogen-concentration-increasing hydrocarbon oil (e.g., a light hydrocarbon oil) must be subjected to hydrotreating for a long period of time under severe conditions, problems are likely to arise in terms of production cost and energy savings in the overall process of crude oil refining. For the aforementioned reasons, the light hydrocarbon oil is fed so that the dissolved hydrogen concentration of the hydrocarbon oil mixture is elevated to more preferably 1.15 times or more, much more preferably 1.2 times or more, the highest possible hydrogen concentration of the heavy hydrocarbon oil.

[0018] In the present invention, the dissolved-hydrogen-concentration-increasing hydrocarbon oil may be selected by means of a tool which can estimate dissolved hydrogen concentration and the equilibrium of hydrogen between gas and liquid in the reactor. Now will be specifically described the case where a process simulator Pro/II (ver. 6.01) (product of Invensys Process Systems) is employed.

[0019]

- (1) A mixer and a flusher (located downstream of the mixer) are selected from a PFD process unit.
- (2) Hydrogen is selected as a fluid fed through an inlet of the mixer, and the feed rate of hydrogen is input.
- (3) Petroleum (Petroleum Assay) is selected as a type of fluid fed through another inlet of the mixer, and the feed rate, density (g/cm³), and distillation characteristics of a heavy hydrocarbon oil which is fed are input.
- (4) Conditions (temperature and pressure) of the flusher for separation are input.
- (5) The SRK equation (SRK01) is selected from among general thermodynamic equations, and employed for obtaining thermodynamic data [the SRK equation is one of the most commonly used thermodynamic equations in process simulators in the field of petroleum refining].
- (6) Through calculation by means of the process simulator, the mass flow rate of hydrogen contained in a liquid phase at an outlet of the flusher was divided by the total mass flow rate of the liquid phase at the outlet of the flusher, and the hydrogen content (wt.%) of the liquid phase is determined, to thereby estimate the dissolved hydrogen concentration of the liquid phase at an inlet of the reactor in the case where the heavy hydrocarbon oil is fed singly. In a manner similar to that described above, in step (3), a light hydrocarbon oil is selected as a fluid which is fed, in addition to the heavy hydrocarbon oil, through the inlet of the mixer, and the feed rate, density, and distillation characteristics of the light hydrocarbon oil are input. Thereafter, calculation is performed in a manner similar to that described above. Comparison of the resultant data with the above-obtained data can determine a change in dissolved hydrogen concentration of the liquid phase in the reactor in the case where the light hydrocarbon oil is fed under certain conditions. Through this procedure, the dissolved hydrogen concentration of the liquid phase at the inlet of the reactor is estimated.

[0020] In order to estimate the dissolved hydrogen concentration of the liquid phase at the outlet of the reactor in the case where hydrotreating reaction is actually carried out, in step (2), the composition and discharge rate of offgas are input, and, in step (3), the density, distillation characteristics, and recovery rate of the thus-refined oil are input. In addition to the SRK equation, the PR equation or the GS equation may be employed as a thermodynamic equation. It was

previously found that when the mixture of the heavy hydrocarbon oil and the light hydrocarbon oil is caused to pass through the reactor, and an increase in dissolved hydrogen concentration of the liquid phase is determined by use of each of these three equations, there is no difference between data obtained by use of these equations. Even when the composition of offgas discharged from the outlet of the reactor is unknown, the dissolved hydrogen concentration of the liquid phase may be estimated only on the basis of parameters of the fluid fed through the inlet of the reactor.

[0021] In addition, the optimum mixing ratio of the heavy hydrocarbon oil to the dissolved-hydrogen-concentration-increasing hydrocarbon oil may be estimated by means of the aforementioned process simulator. When hydrotreating reaction conditions are determined on the basis of the effect of increasing dissolved hydrogen concentration, hydrotreating reaction is readily controlled, and energy can be saved in hydrotreating.

[0022] The hydrocarbon oil hydrotreating method will next be more specifically described. In the hydrotreating method of the present invention, a hydrocarbon oil mixture is mixed with hydrogen, and then the resultant mixture is caused to pass through the reactor for carrying out hydrotreating. Preferably, the heavy hydrocarbon oil is mixed with the dissolved-hydrogen-concentration-increasing hydrocarbon oil (e.g., light hydrocarbon oil), to thereby prepare an oil mixture; the oil mixture is pressurized and preheated by means of a heat exchanger, and then mixed with hydrogen; the pressurized, hydrogen-mixed oil mixture is heated to a reaction temperature in a heating furnace; and the thus-heated oil mixture is fed to the reactor. When the oil mixture is mixed with hydrogen before being pressurized or subjected to the heat exchange process, pressurization or heat exchange of the resultant gas-liquid mixture is required, and performance in pressurization or heating tends to lower. When the oil mixture is mixed with hydrogen after the oil mixture has been caused to pass through the heating furnace, the time for dissolving hydrogen in the oil mixture may be insufficient.

[0023] Hydrotreating is carried out under, for example, the conditions of reaction temperature: 300 to 450°C, hydrogen partial pressure: 5.1 to 25.3 MPa(G), hydrogen/oil ratio: 200 to 2,000 Nm³/kL, and LHSV: 0.05 to 10 hr⁻¹; or the conditions of reaction temperature: 330 to 430°C, hydrogen partial pressure: 10.1 to 20.3 MPa(G), hydrogen/oil ratio: 500 to 1,000 Nm³/kL, and LHSV: 0.1 to 1.0 hr⁻¹.

[0024] Examples of hydrotreating steps include a hydrodemetallization step, a hydrodesulfurization step, a hydrocracking step, a hydrodenitrogenation step, and a hydrodearomatization step. No particular limitation is imposed on the hydrotreatment step employed in the method of the present invention, and the method may employ two or more of the aforementioned hydrotreatment steps. When the aforementioned hydrotreatment steps are sequentially carried out, no particular limitation is imposed on the order of the steps, but preferably, the hydrodemetallization step is carried out first. In general, firstly, the hydrodemetallization step is carried out; subsequently, the hydrodenitrogenation step, the hydrocracking step, or a similar hydrotreatment step is carried out; and finally, the hydrodesulfurization step is carried out. As desired, the hydrocracking step or a similar hydrotreatment step may be further carried out after the hydrodesulfurization step. No particular limitation is imposed on the type of reactor employed in any of these hydrotreatment steps, and, for example, a fixed-bed, moving-bed, fluidized-bed, ebullient bed, or slurry-bed reactor may be employed. The dissolved-hydrogen-concentration-increasing hydrocarbon oil may be fed, as a quenching oil, into the reactor.

[0025] The aforementioned hydrodemetallization step is carried out in one or more reactors after the hydrogen-mixed hydrocarbon oil mixture has been pressurized and heated.

[0026] The catalyst employed in the hydrodemetallization step is preferably a catalyst prepared by supporting, on a carrier (e.g., a porous inorganic oxide such as alumina, silica, silica-alumina, or sepiolite, or a natural mineral), an active metal (i.e., at least one species selected from among metals of Groups 8, 9, and 10 of the periodic table) and a promoter metal (i.e., at least one species selected from among metals of Group 6 of the periodic table). The active metal content of the hydrodemetallization catalyst is preferably 2 to 8 mass%, more preferably 2 to 4 mass%, as reduced to metal oxide. The promoter metal content of the hydrodemetallization catalyst is preferably 0.5 to 5 mass%, more preferably 1 to 5 mass%, as reduced to metal oxide. Specifically, the active metal (i.e., a metal of Groups 8, 9, and 10 of the periodic table) is more preferably nickel, cobalt, or rhodium, and the promoter metal (i.e., a metal of Group 6 of the periodic table) is more preferably molybdenum or tungsten. The amount of the catalyst employed in the hydrodemetallization step may be appropriately determined in consideration of the metal concentration of the hydrocarbon oil mixture. However, the amount of the hydrodemetallization catalyst is preferably 10 to 50 vol.% on the basis of the total amount of the catalysts employed in all the hydrotreatment steps.

[0027] The hydrodemetallization step is preferably carried out under the conditions of reaction temperature: 300 to 450°C (more preferably 330 to 430°C), hydrogen partial pressure: 5 to 25 MPa(G) (more preferably 10 to 20 MPa(G)), hydrogen/oil ratio: 200 to 2,000 Nm³/kL (more preferably 500 to 1,000 Nm³/kL), and LHSV (liquid hourly space velocity): 0.1 to 20 hr⁻¹ (more preferably 0.2 to 2 hr⁻¹). When hydrogen partial pressure and hydrogen/oil ratio are below the above ranges, reaction efficiency tends to lower, whereas when hydrogen partial pressure and hydrogen/oil ratio exceed the above ranges, production cost tends to increase. When LHSV is below the above range, production cost tends to increase, whereas when LHSV exceeds the above range, reaction efficiency tends to lower.

[0028] The aforementioned hydrodesulfurization step is generally carried out after the hydrodemetallization step or a similar hydrotreatment step. Therefore, when reaction temperature control is required, preferably, the reaction temperature is controlled by means of a heat exchanger, quenching hydrogen gas, or quenching oil. The hydrodesulfurization

step is carried out in one or more reactors.

[0029] The catalyst employed in the hydrodesulfurization step may be a hydrodesulfurization catalyst generally used for heavy oil; for example, a catalyst prepared by supporting, on a carrier (e.g., alumina, silica, silica-alumina, zeolite, or a mixture thereof), at least one species selected from among metals of Groups 5, 6, 8, 9, and 10 of the periodic table.

The carrier preferably has an average pore size of 8 nm or more, and the supported metal content of the hydrodesulfurization catalyst is preferably 3 to 30 mass% as reduced to metal oxide.

[0030] The hydrodesulfurization step is preferably carried out under the conditions of reaction temperature: 300 to 450°C (more preferably 330 to 430°C), hydrogen partial pressure: 5 to 25 MPa(G) (more preferably 10 to 20 MPa(G)), hydrogen/oil ratio: 200 to 2,000 Nm³/kL (more preferably 500 to 1,000 Nm³/kL), and LHSV (liquid hourly space velocity): 0.1 to 20 hr⁻¹ (more preferably 0.2 to 2 hr⁻¹). When reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio are below the above ranges, reaction efficiency tends to lower, whereas when reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio exceed the above ranges, production cost tends to increase. When LHSV is below the above range, production cost tends to increase, whereas when LHSV exceeds the above range, reaction efficiency tends to lower.

[0031] The aforementioned hydrocracking step is generally carried out after the hydrodemetallization step or a similar hydrotreatment step. Therefore, when reaction temperature control is required, preferably, the reaction temperature is controlled by means of a heat exchanger, hydrogen-quenching, or oil-quenching. The hydrocracking step is carried out in one or more reactors.

[0032] The catalyst employed in the hydrocracking step is preferably a catalyst prepared by supporting, on a carrier made of a mixture of iron-containing aluminosilicate and alumina, a metal having hydrogenation activity (i.e., at least one species selected from among metals of Groups 6, 8, 9, and 10 of the periodic table). The metal of Group 6 of the periodic table is preferably tungsten or molybdenum. A plurality of metals may be employed in combination. Preferably, a combination of nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, or nickel-cobalt-molybdenum is employed, from the viewpoints of high hydrogenation activity and low degradation.

[0033] The hydrocracking step is preferably carried out under the conditions of reaction temperature: 300 to 450°C (more preferably 380 to 420°C), hydrogen partial pressure: 5 to 25 MPa(G) (more preferably 10 to 20 MPa(G)), hydrogen/oil ratio: 200 to 2,000 Nm³/kL (more preferably 500 to 1,000 Nm³/kL), and LHSV (liquid hourly space velocity): 0.1 to 20 hr⁻¹ (more preferably 0.2 to 2 hr⁻¹). When reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio are below the above ranges, reaction efficiency tends to lower, whereas when reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio exceed the above ranges, production cost tends to increase. When LHSV is below the above range, production cost tends to increase, whereas when LHSV exceeds the above range, reaction efficiency tends to lower.

[0034] When vacuum gas oil is subjected to the hydrocracking step, preferably, the aforementioned hydrodenitrogenation step is carried out before the hydrocracking step. The hydrodenitrogenation step is carried out in one or more reactors. The hydrodenitrogenation step may be carried out through a conventionally known method; for example, the method disclosed in Japanese Patent Application Publication (*kokai*) No. 2003-049175.

[0035] The aforementioned hydrodearomatization step is carried out for the purpose of obtaining a lubricating oil base from a refined oil produced through the aforementioned hydrorefining steps. The hydrodearomatization step is carried out in one or more reactors. The hydrodearomatization step is preferably carried out under the conditions of reaction temperature: 300 to 450°C (more preferably 380 to 420°C), hydrogen partial pressure: 10 to 25 MPa(G) (more preferably 15 to 23 MPa(G)), hydrogen/oil ratio: 200 to 2,000 Nm³/kL, and LHSV (liquid hourly space velocity): 0.1 to 20 hr⁻¹ (more preferably 0.2 to 2 hr⁻¹). When reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio are below the above ranges, reaction efficiency tends to lower, whereas when reaction temperature, hydrogen partial pressure, and hydrogen/oil ratio exceed the above ranges, production cost tends to increase. When LHSV is below the above range, production cost tends to increase, whereas when LHSV exceeds the above range, reaction efficiency tends to lower.

[0036] The above-hydrorefined oil is introduced to a separation step according to a customary method, and is separated into a gas fraction and a liquid fraction through treatment by means of a plurality of separation vessels. Subsequently, hydrogen sulfide, ammonia, etc. are removed from the gas fraction, and then the gas fraction is subjected to, for example, a treatment for increasing hydrogen purity. Thereafter, the resultant gas fraction is mixed with a fresh feed gas, and then recycled to the reaction step. The liquid fraction obtained through the separation step is introduced into an atmospheric separation tower (called "stripper"). Subsequently, hydrogen sulfide by-produced through desulfurization is removed, and a light oil fraction is separated from the resultant refined oil.

[0037] Embodiments of the hydrocarbon oil hydrorefining method of the present invention will now be described with reference to Figs. 1 to 4.

Fig. 1 shows a method in which a light hydrocarbon oil is mixed with atmospheric residual oil or vacuum residual oil, and is caused to pass through a direct desulfurization unit for the residual oil (method 1). Fig. 2 shows a refining method (modification of method 1), wherein the light hydrocarbon oil is also employed as a quenching oil (method 2). Fig. 3 shows a method in which a light hydrocarbon oil is mixed with atmospheric residual oil or vacuum residual oil, and is

caused to pass through a hydrocracking unit for the residual oil (method 3). Fig. 4 shows a method in which a light hydrocarbon oil is mixed with vacuum gas oil, and is caused to pass through a hydrocracking unit for the vacuum gas oil (method 4). In method 4, bottom oil recycling is not necessarily carried out. Method 4 (except for the hydrocracking step) can be applied to the case where a light hydrocarbon oil is mixed with vacuum gas oil, and is caused to pass through a desulfurization unit for the vacuum gas oil (i.e., a so-called indirect desulfurization unit).

Examples

[0038] The present invention will next be described in more detail by way of examples, which should not be construed as limiting the invention thereto.

[0039] Table 1 shows characteristics of heavy hydrocarbon oils serving as feedstock. Tables 2 and 3 show characteristics of hydrocarbon oils serving as mixing oils. Data shown in the Tables were obtained through the following methods.

(Tables 1 and 2)

[0040] Density: JIS K2249

Sulfur content: JIS K2541 Nitrogen content: JIS K2609 Vanadium content: JPI 5S-10,11 Nickel content: JPI 5S-10,11

Residual carbon content: JIS K2270 Kinematic viscosity: JIS K2283

(Table 3)

[0041] Specific Gravity: ASTM D2598

Kinematic viscosity: JIS K2283

Vapor pressure: ASTM D1267

[0042] [Table 1]

Table 1

		Heavyhydrocarbonoil A	Heavyhydrocarbonoil B	Heavyhydrocarbonoil C
		Arabian heavy atmospheric residual oil	Arabian heavy vacuum gas oil	Arabian heavy vacuum residual oil
	Density (g/mL)	0.9873	0.9171	1.0409
	S content (wt.%)	4.41	2.94	5.54
	N content (wt.ppm)	2,500	740	3,760
	V content (wt.ppm)	84	0.5	152
	Ni content (wt.ppm)	27	0.5>	50
	n-Heptane insoluble components (wt.%)	7.89	-	-
	Conradson's Carbon content (wt.%)	14.1	0.33	25.2
Distillation characteristics (°C)	IBP	340	348	479
	5%	362	360	527
	10%	380	370	548
	20%	418	388	576
	30%	457	406	601
	40%	499	425	630
	50%	543	442	661
	60%	589	460	688
	70%	648	478	-
	80%	-	498	-
	90%	-	522	-

[0043] [Table 2]

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Table 2-1

			Mixing oil A	Mixing oil B	Mixing oil C
			Arabian heavy straight-run kerosene	Arabian heavy straight-run light gas oil	Arabian heavy desulfurized gas oil
	Density (g/mL)		0.7922	0.8554	0.8339
	S content (wt.ppm)		2410	13000	10
	N content (wt.ppm)		1>	120	1>
	Kinematic viscosity (mm ² /s, 30°C)		1.358	6.393	4.858
	Monocyclic aromatics (vol.%)		16.7	14	16.9
	Dicyclic aromatics (vol.%)		0.9	9.7	2
	Tricyclic aromatics (vol.%)		0.1>	2.5	0.1
Distillation characteristics (°C)	IBP		125	200	138
	5%		160	247	215
	10%		167	265	238
	20%		176	281	262
	30%		185	293	279
	40%		195	304	290
	50%		201	313	300
	60%		210	323	311
	70%		218	334	322
	80%		224	346	336
	90%		234	363	354
	95%		238	378	370
	97%		240	380	376
	EP		248	385	380

Table 2-2

			Mixing oil D	Mixing oil E
			R-FCC unit Light cycle oil	Delayed Coker unit Coker gas oil
	Density (g/mL)		0.9370	0.8496
	S content (wt.ppm)		22000	22300
	N content (wt.ppm)		830	440
	Kinematic viscosity (mm ² /s, 30°C)		4.377	4.618
	Monocyclic aromatics (vol.%)		21.2	19
	Dicyclic aromatics (vol.%)		38.1	22
	Tricyclic aromatics (vol.%)		11.5	4

(continued)

		Mixing oil D	Mixing oil E
		R-FCC unit Light cycle oil	Delayed Coker unit Coker gas oil
Distillation characteristics (°C)	IBP	203	125
	5%	234	160
	10%	243	175
	20%	256	198
	30%	264	218
	40%	273	236
	50%	284	252
	60%	297	267
	70%	311	283
	80%	328	298
	90%	348	314
	95%	362	323
	97%	365	330
	EP	370	354

[0044] [Table 3]

Table 3

		Mixing oil F
		Straight-run n-butane
Specific gravity	(60/60F)	0.5847
Kinematic viscosity	(mm ² /s, 20°C)	0.299
Vapor pressure	(kg/cm ² , 37.8°C)	3.9
Average molecular weight	-	58

[0045] Table 4 shows characteristics of catalysts employed in hydrotreating. The alumina-boria carrier of a hydrodesulfurization catalyst (catalyst B) and the steamed iron-containing zeolite of a hydrocracking catalyst (catalyst C) were respectively prepared according to Example 1 of Japanese Patent Application Publication (*koka*) No. H06-319994 and Example 1 of Japanese Patent Application Publication (*koka*) No. H02-289419.

[0046] [Table 4]

Table 4

		Catalyst A	Catalyst B	Catalyst C
		Hydrometalizing catalyst	Hydrodesulfurizing catalyst	Hydrocracking catalyst
Carrier (wt.%, carrier base)	Alumina	100	90	35
	Boria	-	10	-
	Iron-containing aluminosilicate	-	-	65
Active metal (wt.%, catalyst base)	Nickel oxide	2.3	-	-
	Molybdenum oxide	8.3	14	10
	Cobalt oxide	-	3.7	4

(continued)

		Catalyst A	Catalyst B	Catalyst C
		Hydrodemetalizing catalyst	Hydrodesulfurizing catalyst	Hydrocracking catalyst
Physical properties	Specific surface area (m ² /g)	143	228	445
	Pore volume (mL/g)	0.76	0.71	0.62
	Mean pore size (Å)	190	124	158

[Example 1]

[0047] As shown in Table 5, catalyst A (25 mL) and catalyst B (75 mL) were sequentially loaded into a reaction tube, followed by hydrorefining reaction. In this reaction, Arabian heavy atmospheric residual oil (heavy hydrocarbon oil A) shown in Table 1 was fed at an LHSV of 0.21 h⁻¹, and Arabian heavy straight-run kerosene (mixing oil A) shown in Table 2 was fed so that the total LHSV of the oil mixture was regulated to 0.315 h⁻¹. Hydrogen partial pressure was maintained at 13.2 MPa(G); hydrogen/oil ratio was maintained at 800 Nm³/kL; and reaction temperature was maintained at 380°C. Hydrogen was mixed with the oil mixture after the oil mixture had been heated to the aforementioned reaction temperature and before the oil mixture was caused pass through the reactor. The oil mixture was caused to pass through the reactor for 1,500 hours so as to stabilize hydrogenation activity, followed by production of a refined oil. The refined oil was subjected to distillation by means of a 15-stage distillation apparatus according to the method specified by ASTM D2892-84, to thereby yield fractions. Table 5 shows the percent cracking, sulfur content, and metal content of an atmospheric residual oil fraction (boiling point of 343°C or higher) of the refined oil (hereinafter, this residual oil fraction may be referred to as the "343°C+ fraction").

[Examples 2 to 10]

[0048] The hydrorefining procedure of Example 1 was repeated, except that the feedstock and the reaction conditions were changed as shown in Table 5. In Example 10, the temperature of a hydrodemetalization zone and a hydrodesulfurization zone was controlled to 380°C, and the temperature of a hydrocracking zone was controlled to 400°C.

[Comparative Examples 1 to 5]

[0049] The hydrorefining procedure of Example 1 was repeated, except that hydrocarbon oils and reaction conditions were changed as shown in Table 6. In Comparative Example 5, the temperature of a hydrodemetalization zone and a hydrodesulfurization zone was controlled to 380°C, and the temperature of a hydrocracking zone was controlled to 400°C.

[0050] [Table 5]

Table 5-1

		Example				
		1	2	3	4	5
Feedstock	Heavy oil	A	A	A	A	A
	Mixing oil	A	B	B	B	C

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(continued)

		Example				
		1	2	3	4	5
Reaction conditions	Catalyst	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL
	Reaction temp. (°C) (hydrocracking zone)	380	380	380	380	380
	Partial H ₂ pressure (MPaG)	13.2	13.2	13.2	13.2	13.2
	H ₂ /oil (Nm ³ /kL)	800	800	800	800	800
	Total LHSV for feedstock (hr ⁻¹)	0.315	0.287	0.364	0.519	0.296
	343°C+ Fraction content in feedstock (vol.%)	66.2	72.6	57.3	47.9	70.4
	LHSV for 343°C+ fraction (hr ⁻¹)	0.209	0.209	0.209	0.209	0.209

Table 5-2

		Example				
		6	7	8	9	10
Feedstock	Heavy oil	A	A	C	B	A
	Mixing oil	D	E	B	B	B
Reaction conditions	Catalyst	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL C 33 mL B 42 mL
	Reaction temp. (°C) (hydrocracking zone)	380	380	380	380	380 (400)
	Partial H ₂ Pressure (MPaG)	13.2	13.2	13.2	13.2	13.2
	H ₂ /oil (Nm ³ /kL)	800	800	800	800	800
	Total LHSV for feedstock (hr ⁻¹)	0.297	0.305	0.315	0.287	0.287
	343°C+ Fraction content in feedstock (vol.%)	70.2	68.4	66.2	72.6	72.6
	LHSV for 343°C+ fraction (hr ⁻¹)	0.209	0.209	0.209	0.209	0.209

Table 5-3

		Example				
		1	2	3	4	5
Evaluation of refined oil (343°C+ fraction)	Conversion (volume basis %)	16.5	16.4	18.2	20.4	16.4
	S content (wt.%)	0.38	0.40	0.35	0.30	0.41
	Metal content (V+Ni) (wt.ppm)	30.6	31.6	27.3	23.1	32.0
	Desulfurization conversion (wt.%)	91.3	91.0	92.1	93.3	90.8
	Desulfurization rate constant (second order) (hr ⁻¹)	49.6	47.8	55.1	65.8	46.7

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(continued)

		Example				
		1	2	3	4	5
Calculated by Pro/II	Hydrogen content of liquid phase (reactor inlet) (wt.%)	0.108	0.113	0.130	0.157	0.114
	Hydrogen content of liquid phase (reactor outlet) (wt.%)	0.186	0.172	0.195	0.229	0.167
	Hydrogen content (av., inlet and outlet) (wt.%)	0.147	0.143	0.163	0.193	0.140

Table 5-4

		Example				
		6	7	8	9	10
Evaluation of refined oil (343°C+ fraction)	Conversion (volume basis %)	16.5	16.5	6.8	16.5	46.5
	S content (wt.%)	0.40	0.40	1.00	0.19	0.91
	Metal content (V+Ni) (wt.ppm)	31.9	31.9	36.0	0.1>	26.2
	Desulfurization conversion (wt.%)	90.9	90.9	81.9	93.5	79.4
	Desulfurization rate constant (second order) (hr ⁻¹)	47.2	47.2	17.1	101.5	18.2
Calculated by Pro/II	Hydrogen content of liquid phase (reactor inlet) (wt.%)	0.115	0.113	0.087	0.175	0.113
	Hydrogen content of liquid phase (reactor outlet) (wt.%)	0.166	0.168	0.175	0.187	0.172
	Hydrogen content (av., inlet and outlet) (wt.%)	0.141	0.141	0.131	0.181	0.143

[0051] [Table 6]

Table 6-1

		Comparative Example				
		1	2	3	4	5
Feedstock	Heavy oil	A	A	C	B	A
	Mixing oil	-	F	-	-	-
Reaction conditions	Catalyst	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL B 75 mL	A 25 mL C 33 mL B 42 mL
	Reaction temp. (°C) (hydrocracking zone)	380	380	380	380	380 (400)
	Partial H ₂ pressure (MPaG)	13.2	13.2	13.2	13.2	13.2
	H ₂ /oil (Nm ³ /kL)	800	800	800	800	800
	Total LHSV for feedstock (hr ⁻¹)	0.210	0.315	0.209	0.209	0.210
	343°C+ Fraction content in feedstock (vol.%)	99.3	66.2	100.0	100.0	99.3
	LHSV for 343°C+ fraction (hr ⁻¹)	0.209	0.209	0.209	0.209	0.209

Table 6-2

		Comparative Example				
		1	2	3	4	5
Evaluation of refined oil (343°C+ fraction)	Conversion (volume basis %)	14.4	14.0	3.8	15.0	42.1
	S content (wt.%)	0.48	0.50	1.82	0.22	1.08
	Metal content (V+Ni) (wt.ppm)	38.1	39.0	75.0	0.1>	32.0
	Desulfurization conversion (wt.%)	89.1	88.7	67.1	92.5	75.5
	Desulfurization rate constant (second order) (hr ⁻¹)	38.6	37.1	7.7	87.7	14.6
Calculated by Pro/II	Hydrogen content of liquid phase (reactor inlet)	0.090	0.087	0.060	0.152	0.090
	Hydrogen content of liquid phase (reactor outlet) (wt.%)	0.142	0.138	0.061	0.164	0.143
	Hydrogen content (av., inlet and outlet) (wt.%)	0.116	0.113	0.061	0.158	0.117

[0052] "LHSV for 343°C+ fraction" shown in Tables 5 and 6 is obtained by multiplying the total LHSV for feedstock employed in the experiment by the volume-basis amount of a fraction having a boiling point of 343°C or higher (i.e., a 343°C+ fraction) contained in the feedstock. Therefore, "LHSV for 343°C+ fraction" corresponds to the substantial LHSV for 343°C+ fraction fed into the reactor. The present invention is not intended to enhance hydrorefining performance by the dilution effect, but intended to enhance performance in hydrorefining of a heavy oil fraction by the aforementioned dissolved hydrogen concentration increasing effect. Therefore, hydrorefining performance was evaluated by focusing on, for example, the sulfur content of the 343°C+ fraction of the refined oil. Desulfurization conversion for the 343°C+ fraction was determined by use of the following calculation formula.

$$\begin{aligned} & \text{Desulfurization conversion (\%)} \text{ for the } 343^{\circ}\text{C+ fraction} \\ & = (\text{sulfur content of the } 343^{\circ}\text{C+ fraction of feedstock} - \\ & \quad \text{sulfur content of the } 343^{\circ}\text{C+ fraction of the refined} \\ & \quad \text{oil}) / (\text{sulfur content of the } 343^{\circ}\text{C+ fraction of feedstock}) \times \\ & \quad 100 \end{aligned}$$

[0053] Under the assumption that the desulfurization reaction is a second-order reaction, apparent reaction rate constant was determined by use of the following formula.

$$\begin{aligned} & \text{Apparent reaction rate constant} \\ & = (\text{LHSV for the } 343^{\circ}\text{C+ fraction}) / (\text{sulfur content (\%)} \text{ of the} \end{aligned}$$

343°C+ fraction of feedstock/100) × (Desulfurization
 conversion (%) for the 343°C+ fraction/100)/(1 -
 (Desulfurization conversion (%) for the 343°C+ fraction/100))

[0054] The composition of a gas phase or a liquid phase at the inlet or outlet of the reactor was estimated by means of a process simulator Pro/II (ver. 6.01) (product of Invensys Process Systems) as described above. The estimation data are shown in Tables 5 and 6.

[0055] [Table 7]

Table 7-1

	Example				
	1	2	3	4	5
Hydrogen content of liquid phase in reactor (av., inlet and outlet)	0.147	0.143	0.163	0.193	0.140
Desulfurization rate constant (second order)	49.6	47.8	55.1	65.8	46.7
Total LHSV for feedstock (hr ⁻¹)	0.315	0.287	0.364	0.519	0.296
Corresponding Comp. Ex.	1	1	1	1	1
Relative hydrogen content of liquid phase in reactor (Ex./Comp. Ex.)	1.28	1.23	1.41	1.66	1.21
Relative reaction rate constant (Ex./Comp. Ex.)	1.28	1.25	1.43	1.70	1.21
Relative LHSV (Ex./Comp. Ex.)	1.50	1.37	1.73	2.47	1.41

Table 7-2

	Example				
	6	7	8	9	10
Hydrogen content of liquid phase in reactor (av., inlet and outlet)	0.141	0.141	0.131	0.181	0.143
Desulfurization rate constant (second order)	47.2	47.2	17.1	101.5	18.2
Total LHSV for feedstock (hr ⁻¹)	0.297	0.305	0.315	0.287	0.287
Corresponding Comp. Ex.	1	1	3	4	5
Relative hydrogen content of liquid phase in reactor (Ex./Comp. Ex.)	1.22	1.22	2.15	1.15	1.22
Relative reaction rate constant (Ex./Comp. Ex.)	1.22	1.22	2.23	1.15	1.25
Relative LHSV (Ex./Comp. Ex.)	1.41	1.45	1.51	1.37	1.37

Table 7-3

	Comparative Example				
	1	2	3	4	5
Hydrogen content of liquid phase in reactor (av., inlet and outlet)	0.116	0.113	0.061	0.158	0.117
Desulfurization rate constant (second order)	38.6	37.1	7.7	87.7	14.6
Total LHSV for feedstock (hr ⁻¹)	0.210	0.315	0.209	0.209	0.210
Corresponding Comp. Ex.	-	1	-	-	-

(continued)

	Comparative Example				
	1	2	3	4	5
Relative hydrogen content of liquid phase in reactor (Ex./Comp. Ex.)	-	0.97	-	-	-
Relative reaction rate constant (Ex./Comp. Ex.)	-	0.96	-	-	-
Relative LHSV (Ex./Comp. Ex.)	-	1.50	-	-	-

[0056] The results of the Examples and Comparative Examples are collectively shown in Table 7.

In Example 1, the hydrogen content of the liquid phase in the reactor is higher by 28%, as compared with the case of Comparative Example 1. In Example 1, the reaction rate of the 343°C+ fraction is higher, as compared with the case of Comparative Example 1, although the actual LHSV for feedstock is 1.5 times that in Comparative Example 1 (i.e., in Example 1, the reaction is carried out under more disadvantageous conditions). Therefore, in Example 1, more effective hydrorefining is achieved. Comparison between data of Example 1 and Comparative Example 1 shows that the hydrogen content of the liquid phase in the reactor is correlated with the reaction rate of the 343°C+ fraction. A tendency similar to that in Example 1 is also observed in Examples 2 to 10.

In contrast, in Comparative Example 2, in which straight-run n-butane having no effect of increasing dissolved hydrogen concentration is employed, effective hydrorefining is not achieved.

Industrial Applicability

[0057] According to the present invention, there is provided a hydrocarbon oil hydrorefining method which, in hydrorefining of a hydrocarbon oil containing heavy oil, can enhance performance in hydrorefining of the heavy oil, to thereby produce an increased amount of a refined oil, to produce a high-quality refined oil, and to attain mild hydrorefining conditions. According to the hydrorefining method, energy savings can be achieved in the overall process of crude oil refining.

Claims

1. A hydrocarbon oil hydrorefining method, **characterized by** comprising providing a mixture of a heavy hydrocarbon oil and a dissolved-hydrogen-concentration-increasing hydrocarbon oil; mixing the oil mixture, which is subjected to hydrorefining, with hydrogen; and causing the resultant mixture to pass through a reactor for carrying out hydrorefining.
2. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the oil mixture of a heavy hydrocarbon oil and a dissolved-hydrogen-concentration-increasing hydrocarbon oil has a dissolved hydrogen concentration which is 1.1 times or more the highest possible hydrogen concentration of the heavy hydrocarbon oil.
3. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the heavy hydrocarbon oil is one or more species selected from among vacuum residual oil, vacuum gas oil, atmospheric residual oil, topped crude oil, crude oil, deasphalted oil, coal-liquefied oil, oil obtained from oil sand, and oil obtained from oil shale.
4. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is contained in a liquid phase entirely or partially under the conditions in the reactor.
5. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the effect of increasing dissolved hydrogen concentration is estimated on the basis of the equilibrium of hydrogen between gas and liquid in the reactor.
6. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is additionally fed, as a quenching oil, into the reactor.
7. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the dissolved-hydrogen-concentration-increasing hydrocarbon oil is one or more species selected from among a straight-run kerosene fraction, a straight-run light gas oil fraction, a straight-run heavy gas oil fraction, cracked oil obtained from an FCC unit, and thermally cracked oil obtained from a coker unit.

8. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the hydrorefining includes one or more steps selected from among a hydrodemetallization step, a hydrodesulfurization step, a hydrocracking step, a hydrodenitrogenation step, and a hydrodearomatization step;

5 9. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the hydrorefining is carried out under the following conditions: a reaction temperature of 300 to 450°C, a hydrogen partial pressure of 5.1 to 25.3 MPa(G), a hydrogen/oil ratio of 200 to 2,000 Nm³/kL, and an LHSV of 0.05 to 10 hr⁻¹.

10 10. A hydrocarbon oil hydrorefining method as described in claim 1, wherein the hydrorefining is carried out under the following conditions: a reaction temperature of 330 to 430°C, a hydrogen partial pressure of 10.1 to 20.3 MPa(G), a hydrogen/oil ratio of 500 to 1,000 Nm³/kL, and an LHSV: 0.1 to 1.0 hr⁻¹.

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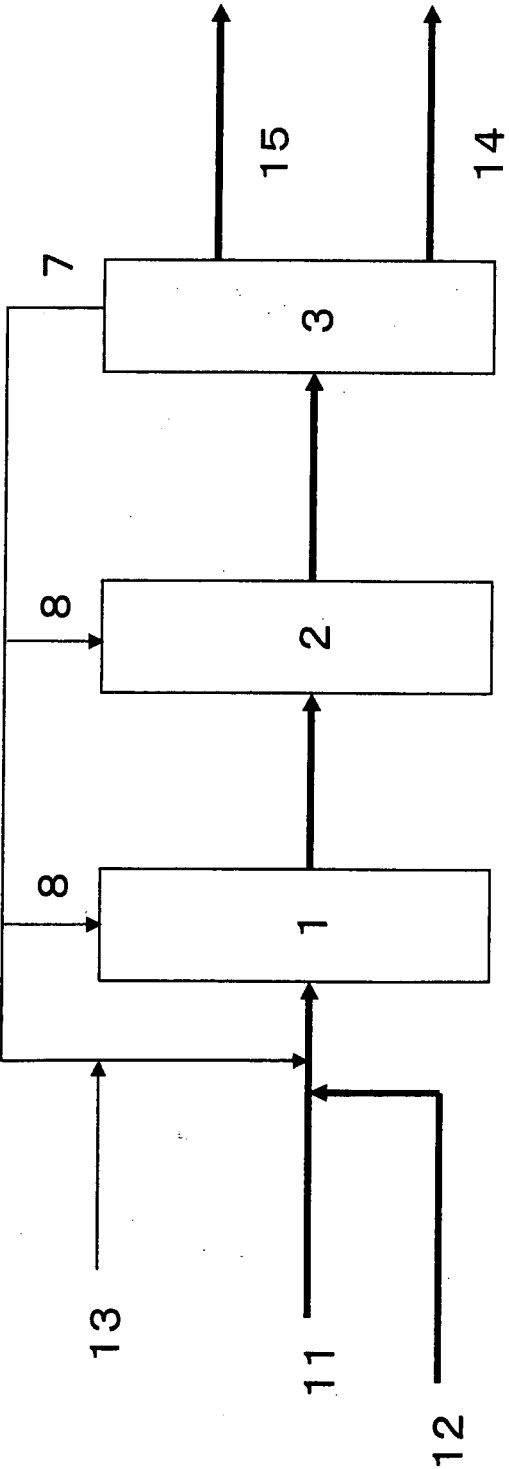
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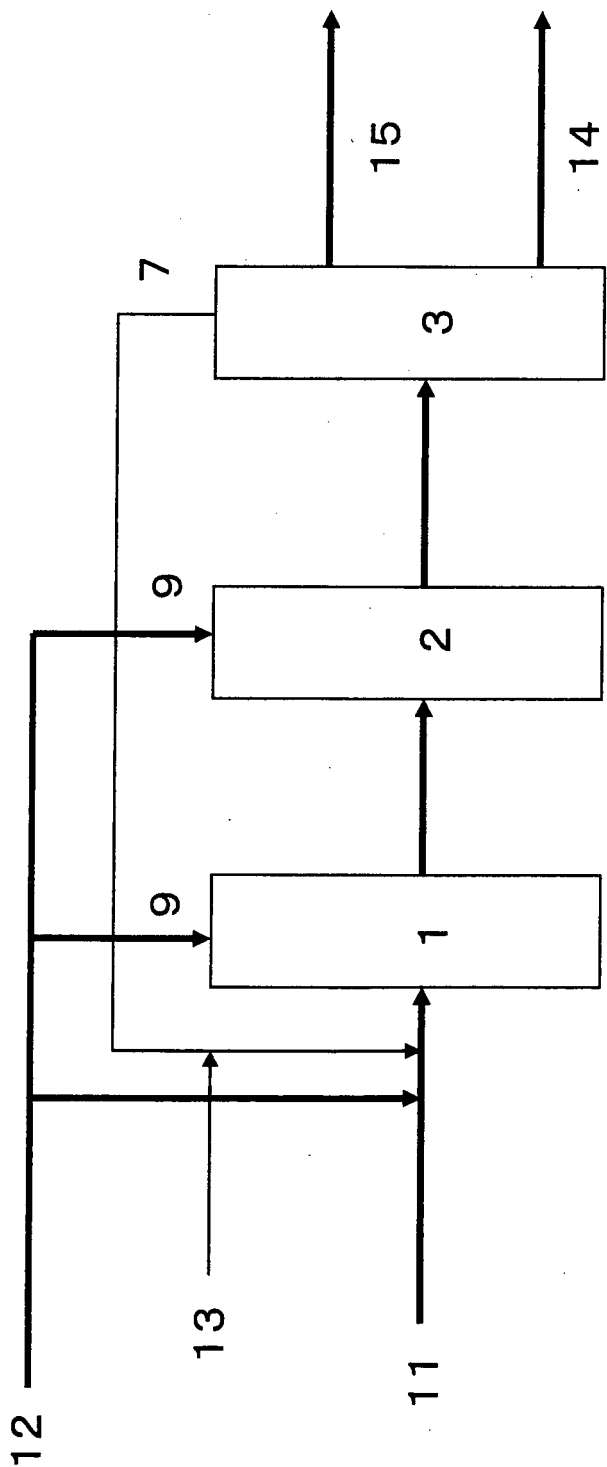
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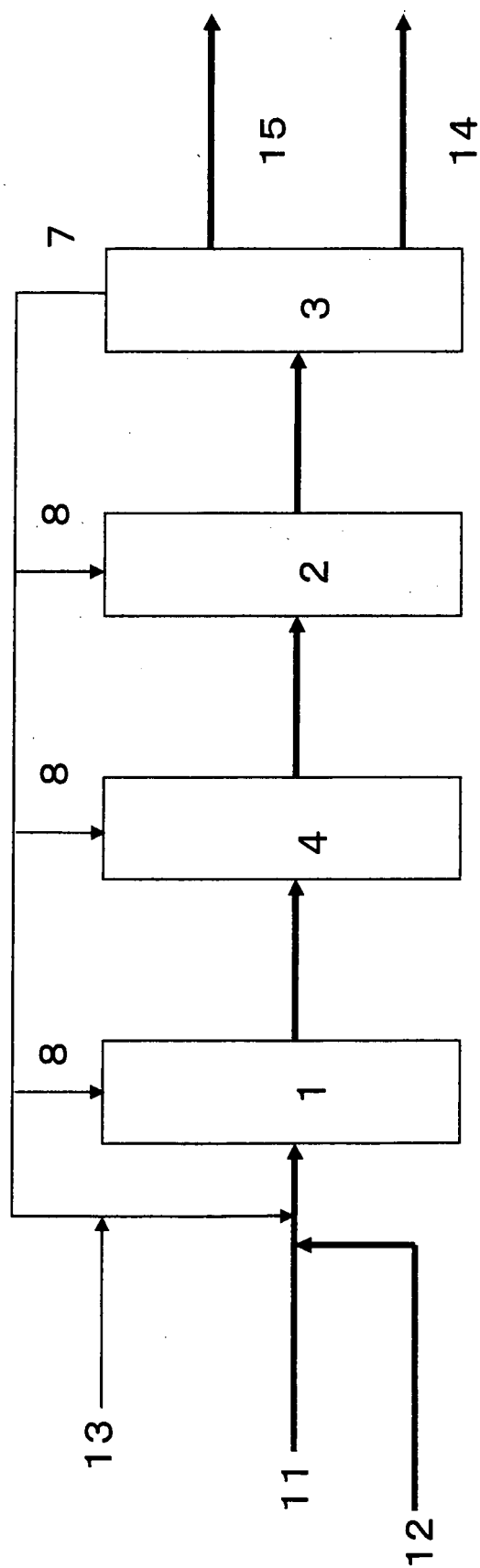
【 Fig. 1】



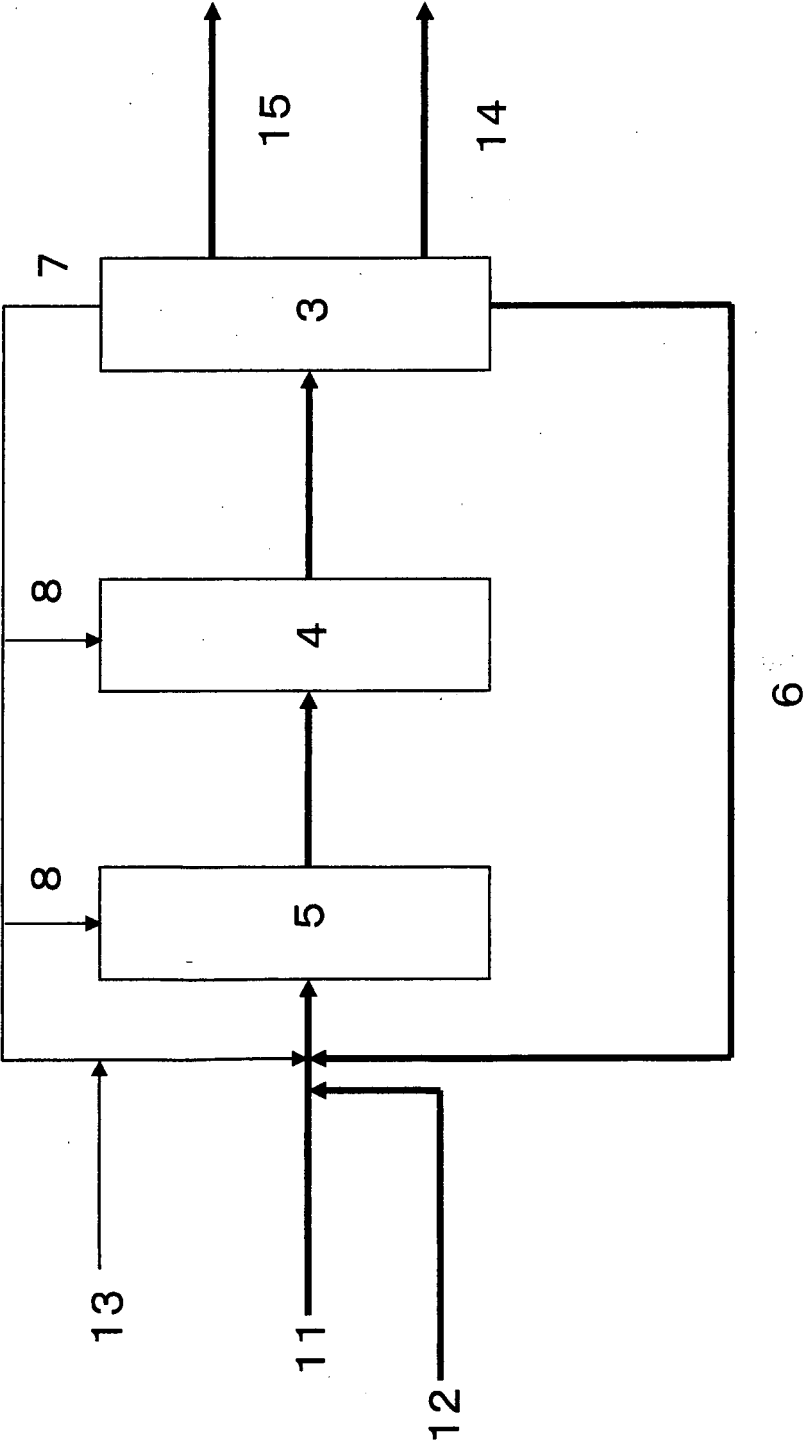
【 Fig. 2】



【 Fig. 3】



【 Fig. 4】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/061644

A. CLASSIFICATION OF SUBJECT MATTER C10G45/00(2006.01) i, C10G45/02(2006.01) i, C10G45/44(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) C10G1/00-75/04		
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 1996-2008 Kokai Jitsuyo Shinan Koho 1971-2008 Toroku Jitsuyo Shinan Koho 1994-2008		
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	JP 2002-506473 A (Process Dynamics, Inc.), 26 February, 2002 (26.02.02), Claims; page 6, lines 22 to 26; page 7, lines 10 to 15; examples 1 to 24 & US 6123835 A & US 6881326 B2 & US 6428686 B1 & US 2005/0082202 A1 & US 2006/0144756 A1 & EP 993498 A & EP 1394237 A1 & EP 1861480 A1 & WO 1998/059019 A1 & WO 2006/102534 A2 & DE 69825590 E & DE 69825590 T2 & AU 8163998 A & BR 9810061 A & AU 755160 B	1-10
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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Date of the actual completion of the international search 29 September, 2008 (29.09.08)		Date of mailing of the international search report 14 October, 2008 (14.10.08)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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