

DESCRIPTION

HYDROREFINING PROCESS

Technical Field

[0001] The present invention relates to a hydrotreating method.

5 Background Art

[0002] Increasing interest is being focused on effective utilization of biomass energy as a strategy for preventing global warming. In particular, plant-derived biomass energy is "carbon neutral" because it allows effective utilization of the hydrocarbons converted from carbon dioxide by photosynthesis during the process of plant growth so that, considering natural life cycles, it does not contribute to increased carbon dioxide in the atmosphere.

[0003] Utilization of this type of biomass energy has also been extensively researched in the field of transportation fuels. For example, if fuels derived from animal or vegetable oils could be used as diesel fuels, the synergistic effect obtained with the high energy efficiency of a diesel engine would be expected to contribute substantially to carbon dioxide emission reduction. Known diesel fuels utilizing animal or vegetable oils include fatty acid methyl ester oils. Fatty acid methyl ester oils are produced by transesterification of the triglyceride structure as the general structure of animal or vegetable oils, with methanol using an alkali or the like. However, as described in Patent document 1 mentioned below, the process of producing fatty acid methyl ester oils necessitates treatment of the glycerin by-product, or creates new cost and energy requirements for purification of the product oil.

[Patent document 1] Japanese Unexamined Patent Publication No. 2005-154647

Disclosure of the invention

[Problems to Solved by the Invention]

5 [0004] The following problems are encountered in addition to those mentioned above when using animal or vegetable oil-derived fat and oil components or fuels produced using them as starting materials. Specifically, since animal or vegetable-derived fat and oil components generally have oxygen atoms in the molecule, the oxygen can adversely
10 affect the structural members of the engine, and it is difficult to remove the oxygen to a very low concentration. Also, when an animal or vegetable-derived fat and oil component is used in combination with a petroleum hydrocarbon fraction, current technology has not allowed sufficient reduction of both oxygen in the fat and oil component and
15 sulfur in the petroleum hydrocarbon fraction.

[0005] It is therefore an object of the present invention to provide a hydrotreating method that can yield a hydrotreated oil with a sufficiently reduced oxygen content when using an oil to be treated that comprises oxygen-containing hydrocarbon compounds.

[Means for Solving the Problems]

20 [0006] In order to solve the problems described above, the invention provides a hydrotreating method characterized by obtaining a refined oil through a hydrotreating step in which an oil to be treated containing oxygen-containing hydrocarbon compounds is contacted with a catalyst
25 comprising a carrier containing a porous inorganic oxide composed of two or more elements selected from among aluminum, silicon,

zirconium, boron, titanium and magnesium and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the carrier, in the presence of hydrogen, and under conditions with a hydrogen pressure of 2-13 MPa, a liquid
5 space velocity of 0.1-3.0 h⁻¹, a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 150-380°C.

[0007] According to the hydrorefining method of the invention, it is possible to economically and very efficiently obtain a hydrorefined oil with a reduced oxygen content, by contacting an oil to be treated
10 comprising an oxygen-containing hydrocarbon compound with the catalyst specified above.

[0008] The carrier is preferably one comprising crystalline molecular sieves. This will satisfactorily reduce the oxygen content while allowing a hydrorefined oil with sufficiently practical low temperature
15 performance to be obtained in an economical and highly effective manner. The fatty acids composing the animal or vegetable fats and oils have straight-chain paraffins or straight-chain olefins as their hydrocarbon portions, but different conventional hydrorefining methodes do not yield paraffins with sufficiently practical low
20 temperature performance, including cloud point.

[0009] For the hydrorefining method of the invention, the oxygen content is preferably 0.1-15 % by mass based on the total amount of the oil to be treated. The oil to be treated preferably contains no sulfur or at least has a sufficiently low sulfur content, preferably with a sulfur
25 content of no greater than 50 ppm by mass based on the total amount of the oil to be treated. If the oxygen and sulfur contents of the oil to be

treated are within the aforementioned ranges, it will be possible to maintain stable deoxygenation activity for prolonged periods.

[0010] From the viewpoint of effective utilization of biomass energy, oxygen-containing hydrocarbon compounds used in the hydrotreating method of the invention are preferably animal or vegetable-derived fat and oil components.

[0011] The proportion of compounds with a triglyceride structure among the oxygen-containing hydrocarbon compounds is preferably at least 90 mol% in order to reduce the level of energy required for processing of the starting material.

[0012] The hydrotreating step in the hydrotreating method of the invention is preferably carried out in such a manner that the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) is at least 0.2 among the paraffins in the 150-350°C fraction of the refined oil obtained from the oil to be treated. This can more satisfactorily improve the low temperature performance as a fuel, including the cloud point of the refined oil.

[0013] In the hydrotreating method of the invention, the crystalline molecular sieves in the catalyst preferably include silicon-containing zeolite, where the ratio of silicon to constituent elements other than oxygen and silicon (number of silicon atoms/number of atoms of elements other than oxygen and silicon) in the zeolite is 3 or greater. This will inhibit excessive decomposition reaction and allow more satisfactory efficiency of fuel production and improvement in low temperature performance.

[0014] The metal of the catalyst used in the hydrotreating method of

the invention preferably includes one or more elements selected from among Pd, Pt, Rh, Ir, Au, Ni and Mo. This will accelerate the hydrodeoxygenation reaction while also allowing more satisfactory improvement in low temperature performance by hydroisomerization reaction and paraffin decomposition removal reaction.

[0015] The carbon monoxide adsorption is preferably in the range of 0.003-0.05 mmol per gram of catalyst with the metal in its reduced state. This will allow sufficient activity to be exhibited in a stable manner for prolonged periods.

[0016] The hydrotreating step in the hydrotreating method of the invention includes a first hydrogenation step wherein oxygen is removed to removal of at least 70 % by mass of the initial oxygen content in the oil to be treated to obtain a first refined oil, and a second hydrogenation step in which the oxygen remaining in the first refined oil is removed to removal of at least 95 % by mass of the initial oxygen content in order to obtain a second refined oil, the second hydrogenation step preferably being carried out in such a manner that the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) is at least 0.2 among the paraffins in the 150-350°C fraction of the second refined oil. This can more satisfactorily improve the low temperature performance as a fuel, including the cloud point of the refined oil.

[Effect of the Invention]

[0017] According to the invention there is provided a hydrotreating method that can economically and very effectively yield a hydrotreated oil with a sufficiently reduced oxygen content when using an oil to be

treated that comprises oxygen-containing hydrocarbon compounds.

Best Mode for Carrying Out the Invention

[0018] Preferred embodiments of the invention will now be described in detail.

5 [0019] According to the invention, the oil to be treated comprises an oxygen-containing hydrocarbon compound. As oxygen-containing hydrocarbon compounds there are preferred animal or vegetable oil-derived fat and oil components. Fat and oil components according to the invention include naturally or artificially produced or manufactured
10 animal or vegetable oils and animal or vegetable oil components and/or components produced or manufactured from these fats and oils and components added for the purpose of maintaining or enhancing the performance of such fat and oil products.

[0020] As examples of animal or vegetable-derived fat and oil
15 components there may be mentioned beef tallow, rapeseed oil, soybean oil, palm oil and the like. The animal or vegetable-derived fat and oil components according to the invention may from any fats and oils, and may even be waste oil from use of the fats and oils. From the standpoint of carbon neutrality, however, they are preferably vegetable
20 fats and oils, and from the viewpoint of fatty acid alkyl chain carbon number and reactivity, rapeseed oil, soybean oil and palm oil are more preferred. The aforementioned fats and oils may be used alone or in combinations of two or more.

[0021] Animal or vegetable-derived fat and oil components generally
25 have a fatty acid triglyceride structure, but they may also include fat and oil components processed to other fatty acids or esters such as fatty

acid methyl esters. However, since production of fatty acids or fatty acid esters from vegetable fats and oils generates carbon dioxide, the vegetable fats and oils are preferably composed mainly of components with a triglyceride structure, from the viewpoint of reducing carbon dioxide emission. According to the invention, the proportion of compounds with a triglyceride structure among the oxygen-containing hydrocarbon compounds in the oil to be treated is preferably 90 mol% or greater, more preferably 92 mol% and even more preferably 95 mol% or greater.

[0022] The oil to be treated may also contain as oxygen-containing hydrocarbon compounds, in addition to the animal or vegetable oil-derived fat and oil components mentioned above, also chemical compounds such as plastics or solvents, or synthetic oils obtained by Fischer-Tropsch reaction using synthetic gas comprising carbon monoxide and hydrogen as the starting material.

[0023] The oil to be treated may also contain a petroleum hydrocarbon fraction. The petroleum hydrocarbon fraction used may be a fraction obtained by any common petroleum refining step. For example, there may be used a fraction corresponding to a prescribed boiling point range obtained from an atmospheric distillation apparatus or vacuum distillation apparatus, or a fraction corresponding to a prescribed boiling point range obtained from a hydrodesulfurizer, hydrocracker, bottom oil direct desulfurizer or fluidized catalytic cracker. The fractions obtained from each of the aforementioned apparatuses may be used alone or in combinations of two or more. The blending amounts of these fractions may be established as desired

so long as the oxygen and sulfur contents of the oil to be treated are within the prescribed ranges. These fractions may also be blended with the aforementioned chemically-derived compounds or synthetic oils obtained by Fischer-Tropsch reaction.

5 [0024] The oxygen content of the oil to be treated is preferably 0.1-15 % by mass, more preferably 1-15 % by mass, even more preferably 3-14 % by mass and most preferably 5-13 % by mass based on the total amount of the oil to be treated. If the oxygen content is less than 0.1 % by mass it will tend to be difficult to stably maintain the
10 deoxygenation activity and desulfurization activity. On the other hand, an oxygen content exceeding 15 % by mass will create a need for equipment to treat the water by-product, and may lead to excessive interaction between the water and catalyst carrier, thus lowering activity and lowering the catalyst strength. The oxygen content may
15 be measured by an ordinary elemental analyzer, and for example, a sample may be converted to carbon monoxide on platinum-carbon, or it may be converted to carbon dioxide and then measurement performed using a thermal conductivity detector.

[0025] The oil to be treated may also contain a sulfur-containing
20 hydrocarbon compound in some cases. There are no particular restrictions on sulfur-containing hydrocarbon compounds, and specifically there may be mentioned sulfides, disulfides, polysulfides, thiols, thiophenes, benzothiophenes, dibenzothiophenes and their derivatives. A sulfur-containing hydrocarbon compound in the oil to
25 be treated may be a single compound, or it may be a mixture of two or more. A sulfur-containing petroleum hydrocarbon fraction may also

be blended with the oil to be treated.

[0026] The sulfur content of the oil to be treated is preferably no greater than 50 ppm by mass, more preferably no greater than 20 ppm by mass and even more preferably no greater than 10 ppm by mass based on the total amount of the oil to be treated. A sulfur content exceeding 50 ppm by mass will tend to hamper stable maintenance of deoxygenation activity and will tend to increase the sulfur content of the hydrorefined oil, risking adverse effects on engine exhaust gas purification devices when the intended use is as a fuel in diesel engines and the like. The sulfur content according to the invention is the mass content of sulfur as measured by the method described in JIS K 2541 "Sulfur Content Test Method" or ASTM-5453.

[0027] When a sulfur-containing hydrocarbon compound is included in the oil to be treated, the sulfur-containing hydrocarbon compound may be mixed with the oil to be treated beforehand and the mixture introduced into the reactor of a hydrorefining apparatus, or it may be supplied at an earlier stage of the reactor during introduction of the oil to be treated into the reactor.

[0028] The oil to be treated which is used for the invention preferably contains a fraction with a boiling point of 300°C or higher, and preferably it contains no heavy fractions with boiling points above 700°C. If the oil to be treated does not contain a fraction with a boiling point of 300°C or higher, it will tend to be difficult to obtain sufficient yield due to excessive decomposition. On the other hand, if the oil to be treated contains heavy fractions with boiling points above 700°C, deposition of carbon on the catalyst due to heavy components

will be accelerated, tending to lower the activity. The boiling point according to the invention is the value measured by the method described in JIS K 2254 "Distillation Test Method" or ASTM-D86.

[0029] The hydrotreating method of the invention uses a catalyst comprising a carrier containing a porous inorganic oxide composed of two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the carrier.

[0030] The carrier of the catalyst used for the invention is a porous inorganic oxide composed of two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium, as mentioned above. From the viewpoint of permitting further enhanced deoxygenation activity and desulfurization activity, the porous inorganic oxide is preferably that of two or more selected from among aluminum, silicon, zirconium, boron, titanium and magnesium, and it is more preferably an inorganic oxide comprising aluminum and another element (a complex oxide of aluminum oxide and another oxide).

[0031] The carrier in the catalyst used for the invention is preferably one comprising crystalline molecular sieves. The crystalline molecular sieves preferably include at least silicon in order to impart sufficient hydrodeoxygenation activity and hydroisomerization activity. The crystalline molecular sieves also preferably contain at least one from among aluminum, zirconium, boron, titanium, gallium, zinc and phosphorus as constituent elements other than silicon, and more

preferably contain at least one from among aluminum, zirconium, boron, titanium and phosphorus. Crystalline molecular sieves containing these elements can simultaneously promote hydrodeoxygenation reaction and hydrocarbon chain isomerization reaction, while also sufficiently improving the low temperature performance of the refined oil. Such crystalline molecular sieves are preferably zeolite, and more preferably zeolite containing silicon and aluminum, i.e. aluminosilicates.

[0032] As regards elements other than oxygen among the elements composing the crystalline molecular sieves, the ratio of silicon with respect to constituent elements other than oxygen and silicon (number of silicon atoms/number of atoms of elements other than oxygen and silicon) is preferably 3 or greater, more preferably 10 or greater and even more preferably 30 or greater. If the ratio is less than 3, decomposition of paraffins will be promoted and activity may be reduced due to coking.

[0033] The pore diameters of the crystalline molecular sieves are preferably no greater than 0.8 nm and even more preferably no greater than 0.65 nm. If the pore diameters are greater than 0.8 nm, paraffin decomposition reaction may occur. The crystal structure of the crystalline molecular sieves is not particularly restricted, and there may be mentioned FAU, AEL, MFI, MMW, TON, MTW, *BEA and MOR as structures established by the International Zeolite Association.

[0034] The method of synthesizing the crystalline molecular sieves for the catalyst used for the invention is not particularly restricted, and there may be used hydrothermal synthesis methods employing

constituent component starting materials and amine compounds as structure-directing agents, as is known in the prior art. As examples of constituent component starting materials there may be mentioned, as silicon-containing compounds, sodium silicate, colloidal silica and silicic acid alkoxides, and as aluminum-containing compounds, aluminum hydroxide and sodium aluminate. Tetrapropylammonium salts may be mentioned as structure-directing agents.

[0035] The crystalline molecular sieves may have their properties modified, if necessary, by hydrothermal treatment using steam or the like, by immersion treatment with an alkaline or acidic aqueous solution, by ion exchange or by surface treatment using a basic or acidic gas such as chlorine gas or ammonia, and such treatments may be carried out alone or in combinations of more than one.

[0036] As structural materials of the catalyst used for the invention, in addition to crystalline molecular sieves, there may be mentioned inorganic oxides comprising elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium. Since these inorganic oxides are used as binders for molding of crystalline molecular sieves and also function as active components to promote hydrodeoxygenation and hydroisomerization, they preferably contain two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium.

[0037] The content of crystalline molecular sieves in the total catalyst is preferably 2-90 % by mass, more preferably 5-85 % by mass and even more preferably 10-80 % by mass based on the total amount of the catalyst. If the content is less than 2 % by mass, the

hydrodeoxygenation activity and hydroisomerization activity of the catalyst will tend to be reduced, while if it is greater than 90 % by mass the catalyst moldability may be reduced, creating an obstacle to industrial production of the catalyst.

5 [0038] As regards the structural materials of the catalyst used for the invention in addition to crystalline molecular sieves, there are no particular restrictions on the method of introducing the silicon, zirconium, boron, titanium and magnesium as constituent elements other than aluminum into the carrier, and solutions containing these
10 elements may be used as starting materials. For example, silicic acid, water glass, silica sol and the like may be used for silicon, boric acid may be used for boron, phosphoric acid or a phosphoric acid alkali metal salt may be used for phosphorus, titanium sulfide and titanium tetrachloride and their alkoxide salts may be used for titanium, and
15 zirconium sulfate and its alkoxide salts may be used for zirconium.

[0039] The carrier constituent component starting materials other than aluminum oxide are preferably added in a step prior to calcining of the carrier. For example, after first adding the starting materials to an aluminum aqueous solution, an aluminum hydroxide gel containing the
20 constituent components may be prepared and the starting materials added to the prepared aluminum hydroxide gel. Alternatively, the starting materials may be added in a step of adding a commercially available aluminum oxide intermediate or boehmite powder to water or an acidic aqueous solution and kneading, but more preferably they are
25 included at the stage of preparing the aluminum hydroxide gel. Although the mechanism by which the effects of the carrier constituent

components other than aluminum oxide are exhibited is not completely understood, it is believed that complex oxides are formed with aluminum, and that this affects the activity by increasing the carrier surface area and causing interaction with the active metals.

5 [0040] At least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table is supported on the carrier containing crystalline molecular sieves. Among these metals it is preferred to use at least one metal selected from among Pd, Pt, Rh, Ir, Au, Ni and Mo, and it is more preferred to use a combination of two or
10 more metals selected from among the above. As examples of preferred combinations there may be mentioned Pd-Pt, Pd-Ir, Pd-Rh, Pd-Au, Pd-Ni, Pt-Rh, Pt-Ir, Pt-Au, Pt-Ni, Rh-Ir, Rh-Au, Rh-Ni, Ir-Au, Ir-Ni, Au-Ni, Ni-Mo, Pd-Pt-Rh, Pd-Pt-Ir and Pd-Pt-Ni. More preferred are the combinations Pd-Pt, Pd-Ni, Pt-Ni, Pd-Ir, Pt-Rh, Pt-Ir, Rh-Ir, Pd-Pt-Rh, Pd-Pt-Ir and Pt-Pd-Ni, and even more preferred are
15 the combinations Pd-Pt, Pd-Ni, Pt-Ni, Pd-Ir, Pt-Ir, Pd-Pt-Ir and Pt-Pd-Ni.

[0041] The total content of active metals based on the catalyst mass is preferably 0.1-2 % by mass, more preferably 0.2-1.5 % by mass and
20 even more preferably 0.5-1.3 % by mass as metals. If the total loading content of metals is less than 0.1 % by mass, the number of active sites will be reduced and it may not be possible to obtain sufficient activity. On the other hand, if it is greater than 2 % by mass the metals will fail to effectively disperse, tending to prevent sufficient
25 activity from being obtained.

[0042] There are no particular restrictions on the method of including

the active metals in the catalyst, and any known method that is commonly applied for production of desulfurization catalysts may be used. For most cases, the preferred method is one in which the catalyst carrier is impregnated with a solution containing a salt of the active metal. Equilibrium adsorption methods, pore-filling methods and incipient-wetness methods are also preferred. For example, pore-filling is a method in which the pore volume of the carrier is first measured and a metal salt solution of the same volume is used for impregnation. The impregnation method is not particularly restricted, and impregnation may be accomplished by an appropriate method for the metal loading content and catalyst carrier properties.

[0043] The active metals in the catalyst used for the invention are preferably subjected to reduction treatment before being provided to the reaction. The reduction treatment is not particularly restricted, and reduction may be accomplished by treatment at a temperature of 200-400°C under a hydrogen stream. The reduction treatment is preferably carried out in a range of 240-380°C. If the reduction temperature is below 200°C, reduction of the active metals will not proceed adequately, and the hydrodeoxygenation and hydroisomerization activity may not be satisfactorily exhibited. If the reduction temperature is above 400°C, aggregation of the active metals will be promoted, which may also prevent sufficient activity from being exhibited.

[0044] When the active metals of the catalyst used for the invention are in the reduced state, the carbon monoxide adsorption per gram of catalyst is preferably 0.003-0.05 mmol, more preferably 0.005-0.04

mmol and even more preferably 0.009-0.03 mmol. If the adsorption is less than 0.003 mmol the metals will become aggregated, tending to reduce the number of active sites. On the other hand, if the adsorption is greater than 0.05 mmol, the activity will tend to be progressively reduced as the reaction proceeds. The carbon monoxide adsorption may be measured by an ordinary measuring method with the catalyst supporting the reduced metal. Specifically, it may be determined by the pulse method or constant volume method after reducing a fixed amount of catalyst at 350°C under a hydrogen stream and cooling to 50°C.

[0045] According to the invention, a guard catalyst, demetallizing catalyst or inactive filler may be used if necessary in addition to the catalyst (hydrorefining catalyst), for the purpose of trapping the sludge portion flowing in with the oil to be treated, or supporting the hydrorefining catalyst in separated sections of the catalyst bed. These may be used either alone or in combinations.

[0046] The conditions for contacting the oil to be treated with the catalyst in the presence of hydrogen are a hydrogen pressure of 2-13 MPa, a liquid space velocity (LHSV) of 0.1-3.0 h⁻¹ and a hydrogen/oil ratio of 150-1500 NL/L, preferably a hydrogen pressure of 2-13 MPa, a liquid space velocity (LHSV) of 0.1-3.0 h⁻¹ and a hydrogen/oil ratio of 250-1500 NL/L, more preferably a hydrogen pressure of 2.5-10 MPa, a liquid space velocity of 0.5-2.0 h⁻¹ and a hydrogen/oil ratio of 300-1200 NL/L, and even more preferably a hydrogen pressure of 3-8 MPa, a space velocity of 0.8-1.8 h⁻¹ and a hydrogen/oil ratio of 350-1000 NL/L. These conditions are all factors affecting the reactivity, and for

example, if the hydrogen pressure and hydrogen/oil ratio are below the lower limits mentioned above, the reactivity may be reduced or the activity may rapidly decrease. On the other hand, if the hydrogen pressure and hydrogen/oil ratio exceed the upper limits mentioned above, it may be necessary to make a significant investment for a compressor or other equipment. Also, a lower liquid space velocity will tend to favor the reaction, but if it is below the lower limit mentioned above it will become necessary to provide a reactor with a very large internal volume and significant investment for equipment may be necessary, while if the liquid space velocity exceeds the upper limit mentioned above, the reaction may not proceed to a sufficient degree.

[0047] The temperature conditions for contacting the oil to be treated and catalyst in the presence of hydrogen are 150-380°C. The temperature is preferably 170-360°C and more preferably 220-350°C. If the temperature is below 150°C, the deoxygenation activity will tend to be insufficient, while if it is above 380°C the oil to be treated will tend to undergo excessive decomposition, thereby lowering the yield of fractions useful for production of liquid fuel (for example, fractions with a boiling point temperature range of 250-350°C).

[0048] The form of reactor used may be a fixed bed system. Specifically, the system employed may be in a form with hydrogen in countercurrent or cocurrent flow with respect to the oil to be treated. Also, a plurality of reactors may be used in a form combining countercurrent and cocurrent. The most common form is a downflow, and a gas-liquid cocurrent flow system may be employed. The reactor

may consist of a single one or a combination of more than one, or the interior of a single reactor may have a structure that is partitioned into multiple catalyst beds.

[0049] The hydrorefined oil which has been hydrorefined in the reactor is then subjected to a gas-liquid separation or rectification step for fractionation into hydrorefined oil comprising prescribed fractions.

For example, it is fractionated into a gas oil fraction and residual fraction. If necessary it may be further fractionated into the gas, naphtha fraction and kerosene fraction. A portion of the produced

light hydrocarbon fraction may be reformed with a steam reformer to produce hydrogen. The hydrogen produced in such a manner is carbon neutral because the starting material used for the steam reforming consists of biomass-derived hydrocarbons, and therefore the environmental burden is reduced. Reaction of the oxygen and sulfur

portions of the oil to be treated may be accompanied by generation of carbon monoxide, carbon dioxide, hydrogen sulfide and the like, but a gas-liquid separation apparatus or other by-product gas removal apparatus may be installed between a plurality of reactors or in the product recovery step. The gas portion from which by-product gas

has been removed by a by-product gas removal apparatus may be combined with the oil to be treated and recycled for use. It may also be used after increasing the hydrogen purity of the gas using a membrane separation apparatus or pressure swing adsorption apparatus at an early stage of blending with the oil to be treated. The

concentration of carbon monoxide in the recycled gas is preferably no greater than 0.5 vol% and more preferably no greater than 0.1 vol%

from the viewpoint of maintaining catalytic activity.

[0050] Hydrogen gas is usually introduced through the inlet port of the first reactor adjoining the oil to be treated either before or after the heating furnace, but hydrogen gas may also be introduced separately between catalyst beds or between multiple reactors, in order to control the temperature in the reactor while maintaining hydrogen pressure throughout the entire reactor. Hydrogen introduced in this manner is generally referred to as "quench hydrogen". The proportion of quench hydrogen with respect to hydrogen gas introduced adjoining the oil to be treated is preferably 10-60 vol% and more preferably 15-50 vol%. If the proportion of quench hydrogen is less than 10 vol% the reaction will often fail to adequately proceed at the reaction site in the subsequent steps, and if the proportion of quench hydrogen is greater than 60 vol%, the reaction may not proceed adequately near the reactor inlet port.

[0051] When a hydrotreated oil produced according to the invention is used as a gas oil fraction stock, the oil contains at least a fraction with a boiling point of 260-300°C, preferably with a sulfur content of no greater than 10 ppm by mass and an oxygen content of no greater than 0.3 % by mass, more preferably a sulfur content of no greater than 7 ppm by mass and an oxygen content of no greater than 0.3 % by mass, and even more preferably with a sulfur content of no greater than 3 ppm by mass and an oxygen content of no greater than 0.2 % by mass. If the sulfur and oxygen contents are above the aforementioned upper limits, this may adversely affect the filter or catalyst used in diesel engine exhaust gas treatment devices, as well as other structural

members of engines.

[0052] When a hydrorefined oil produced according to the invention is used as a gas oil fraction stock, the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) among the paraffins in the fraction is preferably at least 0.2, more preferably at least 0.5 and even more preferably at least 1.0. If the ratio is less than 0.2, the fraction may not maintain a sufficient flow property in low temperature environments, or crystals precipitating in low temperature environments may lead to problems as a result of clogging of diesel engine fuel filtration devices.

[0053] The hydrorefined oil produced according to the invention is particularly suitable for use as a diesel gas oil or heavy oil stock. The hydrorefined oil may be used alone as a diesel gas oil or heavy oil stock, but it may instead be used as a diesel gas oil or heavy oil stock blended with other components of stocks or the like. As other stocks there may be used blends of the gas oil and/or kerosene fractions obtained from general petroleum refining steps and the residual fraction obtained from the hydrorefining method of the invention. Also, a synthetic gas oil or a synthetic kerosene oil may be mixed therewith, which are obtained by a Fischer-Tropsch reaction or the like using so-called "synthetic gas" composed of hydrogen and carbon monoxide as the starting material. These synthetic gas oils or synthetic kerosene oils are characterized by containing virtually no aromatic components, being composed mainly of saturated hydrocarbons, and having high cetane numbers. The process for production of synthetic gas may be any publicly known process and is not particularly restricted.

[0054] The hydrorefining step in which the oil to be treated is subjected to hydrorefining according to the invention includes a first hydrogenation step wherein oxygen is removed to removal of at least 70 % by mass of the initial oxygen content in the oil to be treated to obtain a first refined oil, and a second hydrogenation step in which the oxygen remaining in the first refined oil is removed to removal of at least 95 % by mass of the initial oxygen content in order to obtain a second refined oil, the second hydrogenation step preferably being carried out in such a manner that the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) is at least 0.2 among the paraffins in the 150-350°C fraction of the second refined oil. If the oxygen removal rate in the first hydrogenation step is not at least 70 % by mass, the hydrodeoxygenation and hydroisomerization reactions may not proceed satisfactorily in the second hydrogenation step.

[0055] Either or both the first hydrogenation step and second hydrogenation step in the hydrorefining method of the invention may be carried out by contacting the aforementioned oil to be treated comprising an oxygen-containing hydrocarbon compound, with a catalyst comprising a carrier containing crystalline molecular sieves and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the carrier, in the presence of hydrogen. That is, either the first hydrogenation step or second hydrogenation step may be carried out using a catalyst other than the catalyst described above.

[0056] In the first hydrogenation step there are preferably used a

porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium, and a catalyst comprising one or more metals (active metals) selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the porous inorganic oxide. Preferred active metals are one or more elements selected from among Pd, Pt, Rh, Ir, Au, Ni and Mo.

[0057] In the second hydrogenation step, there are preferably used a carrier containing crystalline molecular sieves, and a catalyst comprising one or more metals selected from among elements of Group 6A and Group 8 (preferably elements of Group 8) of the Periodic Table supported on the carrier. The catalyst used for the second hydrogenation step may consist of a single type or a combination of two or more, and a catalyst with hydrogenation activity may also be packed at a later stage of the second hydrogenation step in order to improve the stability of the refined oil.

[Examples]

[0058] The present invention will now be explained in greater detail based on examples and comparative examples, with the understanding that these examples are in no way limitative on the invention.

[0059] [Examples 1 and 2, Comparative Examples 1-4]

(Catalyst preparation)

<Catalyst A-1>

After adding 185 g of water glass No.3 to 3000 g of a 5 % by mass sodium aluminate aqueous solution, the mixture was placed in a vessel that had been heated to 65°C. Separately, 3000 g of a 2.5 % by mass

aluminum sulfate aqueous solution was prepared in a different vessel heated to 65°C, and the sodium aluminate-containing aqueous solution was added dropwise thereto. The end point was defined as the time at which the pH of the mixture reached 7.0, and the obtained slurry product was filtered through a filter to obtain a cake-like slurry.

[0060] The cake-like slurry was transferred to a vessel equipped with a reflux condenser, and then 150 ml of distilled water and 10 g of a 27% ammonia aqueous solution were added and the mixture was heated and stirred at 75°C for 20 hours. The slurry was then placed in a kneader and heated to above 80°C, and kneading was performed while removing the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 550°C to obtain a molded carrier.

[0061] After placing 50 g of the molded carrier into a round-bottomed flask, it was impregnated with metals using 35 ml of a mixed aqueous solution comprising tetramineplatinum(II) chloride and tetraminepalladium(II) chloride while deairing with a rotary evaporator. The impregnated sample was dried at 110°C and calcined at 350°C to obtain catalyst A-1. The platinum and palladium loading contents for catalyst A-1 were 0.5 % by mass and 0.7 % by mass, respectively, based on the catalyst mass. The properties of the prepared catalyst A-1 are shown in Table 1.

[0062] <Catalyst B-1>

A 3000 g portion of a 5 % by mass concentration sodium aluminate aqueous solution was placed in a vessel that had been heated to 65°C.

Separately, 3000 g of a 2.5 % by mass aluminum sulfate aqueous solution was prepared in a different vessel heated to 65°C, and the sodium aluminate aqueous solution was added dropwise thereto. The end point was defined as the time at which the pH of the mixture reached 7.0, and the obtained slurry product was filtered through a filter to obtain a cake-like slurry.

[0063] The cake-like slurry was transferred to a vessel equipped with a reflux condenser, and then 150 ml of distilled water and 10 g of a 27% ammonia aqueous solution were added and the mixture was heated and stirred at 75°C for 20 hours. The slurry was then placed in a kneader and heated to above 80°C, and kneading was performed while removing the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 550°C to obtain a molded carrier.

[0064] After placing 50 g of the molded carrier into a round-bottomed flask, it was impregnated with metals using 35 ml of a mixed aqueous solution comprising dinitroamineplatinum(II) and dinitroaminepalladium(II) while deairing with a rotary evaporator. The impregnated sample was dried at 110°C and then calcined at 350°C to obtain catalyst B-1. The platinum and palladium loading contents for catalyst B-1 were 0.5 % by mass and 0.7 % by mass, respectively, based on the catalyst mass. The properties of the prepared catalyst B-1 are shown in Table 1.

[0065]

[Table 1]

	Catalyst A-1	Catalyst B-1
Al ₂ O ₃ content (% by mass, based on carrier mass)	64.9	100
SiO ₂ content (% by mass, based on carrier mass)	35.1	-
Pt content (% by mass, based on catalyst mass)	0.5	0.5
Pd content (% by mass, based on catalyst mass)	0.7	0.7
Carbon monoxide adsorption (mmol/g-catalyst)	0.026	0.055

[0066] (Example 1)

A first reaction tube (inner diameter: 20 mm) packed with catalyst A-1 (50 ml) and a second reaction tube (inner diameter: 20 mm) packed with the same catalyst A-1 (50 ml) were installed in series in a fixed bed circulating reactor. The catalyst was then subjected to reduction treatment for 6 hours under conditions with a catalyst layer mean temperature (reaction temperature) of 320°C, a hydrogen partial pressure of 5 MPa and a hydrogen gas volume of 83 ml/min.

[0067] After reduction treatment of the catalyst, palm oil (proportion of compounds with triglyceride structure among oxygen-containing hydrocarbon compounds = 98 mol%) was used as an oil for hydrotreating. The 15°C density of the oil was 0.916 g/ml, and the oxygen content was 11.4 % by mass. The conditions for hydrotreating were a reaction temperature of 250°C in the first and second reaction tubes, a pressure of 5.5 MPa and a liquid space velocity of 0.8 h⁻¹. The volume ratio (quench hydrogen proportion) of hydrogen gas introduced between the first reaction tube and second reaction tube was 20 vol% of the total hydrogen introduced, and the hydrogen/oil ratio determined by the total hydrogen introduced was 600 NL/L. The results are shown in Table 2.

[0068] (Example 2)

Hydrotreating was carried out in the same manner as Example 1, except that the oil treated was a blended oil comprising 70 parts by volume of the same palm oil used in Example 1 and 30 parts by volume of a petroleum-based desulfurized gas oil, and the reaction temperature in the first and second reaction tubes was 260°C. The 15°C density of the petroleum-based desulfurized gas oil was 0.838 g/ml, the sulfur content was 15 ppm by mass and the initial boiling and end points were 211°C and 365°C, respectively. The density of the oil to be treated was 0.893 g/ml, the oxygen content was 8.2 % by mass and the sulfur content was 4.2 ppm by mass.

[0069] (Comparative Example 1)

Hydrotreating was carried out in the same manner as Example 1, except that catalyst B-1 was used instead of catalyst A-1. The results are shown in Table 2.

[0070] (Comparative Example 2)

Hydrotreating was carried out in the same manner as Example 1, except that the reaction temperature for the hydrotreating in the first and second reaction tubes was 120°C. The results are shown in Table 2.

[0071] (Comparative Example 3)

Hydrotreating was carried out in the same manner as Example 1, except that the reaction temperature for the hydrotreating in the first and second reaction tubes was 400°C. The results are shown in Table 2.

[0072] (Comparative Example 4)

Hydrotreating was carried out in the same manner as Example 2,

except that catalyst B-1 was used instead of catalyst A-1. The results are shown in Table 2.

[0073]

[Table 2]

		Example 1	Example 2	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Catalyst		Catalyst A-1	Catalyst A-1	Catalyst B-1	Catalyst A-1	Catalyst A-1	Catalyst B-1
Treated oil		Palm oil	Blended oil	Palm oil	Palm oil	Palm oil	Blended oil
Reaction temperature, °C		250	260	250	120	400	260
Oxygen content, % by mass (based on total hydrorefined oil)		<0.2	<0.2	0.4	2.2	<0.2	3.1
Sulfur content, ppm by mass (based on total hydrorefined oil)		<0.2	<0.2	<0.2	<0.2	<0.2	3.4
Yield, % by mass (based on oil to be treated)	C1-C4 (fraction with b.p. ≤80°C)	3.1	2.9	3.9	5.9	5.9	1.5
	Naphtha (fraction with b.p. 80-135°C)	0.0	0.0	1.1	0.0	10.2	0.0
	Kerosene (fraction with b.p. 135-250°C)	0.0	0.0	0.5	0.0	15.5	0.0
	Gas oil (fraction with b.p. 250-350°C)	82.8	88.2	78.9	65.2	53.1	51.2

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[0074] [Examples 3-5, Comparative Example 5]

(Catalyst preparation)

<Catalyst A-2>

In a polytetrafluoroethylene beaker there were combined a commercially available boehmite powder (product of Catalysts & Chemicals Industrial Co., Ltd.) and silica-alumina powder (product of Catalysts & Chemicals Industrial Co., Ltd.) in a silicon/aluminum atomic ratio of 15, distilled water was added, and concentration and kneading were performed while heating to obtain a clay-like kneaded blend. To the kneaded blend there was added synthesized proton-

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form ZSM-5 (silicon/aluminum atomic ratio: 40) as zeolite to 65 % by mass of the total catalyst based on oxides, and the blend was further kneaded. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 500°C to obtain a molded carrier.

[0075] After placing 10 g of the molded carrier into a round-bottomed flask, a mixed aqueous solution comprising tetramineplatinum(II) chloride and tetraminepalladium(II) chloride was poured into the flask while deairing with a rotary evaporator for impregnation of the metal in the molded carrier, and after drying at 110°C, it was calcined at 350°C to obtain catalyst A-2. The loading contents of platinum and palladium in catalyst A-2 were 0.5 % by mass of platinum and 0.7 % by mass of palladium based on the total amount of the catalyst.

[0076] <Catalyst B-2>

In a polytetrafluoroethylene beaker there were combined a commercially available boehmite powder (product of Catalysts & Chemicals Industrial Co., Ltd.) and silica-alumina powder (product of Catalysts & Chemicals Industrial Co., Ltd.) in a silicon/aluminum atomic ratio of 15, distilled water was added, and concentration and kneading were performed while heating to obtain a clay-like kneaded blend. To the kneaded blend there was added synthesized proton-form ZSM-22 (silicon/aluminum atomic ratio: 45) as zeolite to 65 % by mass of the total catalyst based on oxides, and the blend was further kneaded. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 500°C to obtain a molded carrier.

Platinum and palladium were loaded on 10 g of the obtained molded carrier in the same manner as catalyst A-2 to obtain catalyst B-2. The loading contents of platinum and palladium in catalyst B-2 were 0.5 % by mass of platinum and 0.7 % by mass of palladium based on the total amount of the catalyst.

[0077] <Catalyst C-2>

After adding 18.0 g of water glass No.3 to 3000 g of a 5 % by mass sodium aluminate aqueous solution, the mixture was added dropwise to a 2.5 % by mass aluminum sulfate aqueous solution that had been heated to 65°C, until the pH reached 7.0. The obtained slurry product was filtered through a filter to obtain a cake-like slurry.

[0078] The cake-like slurry was transferred to a vessel equipped with a reflux condenser, and then 150 ml of distilled water and 10 g of a 27% ammonia aqueous solution were added and the mixture was heated and stirred at 75°C for 20 hours. The slurry was then placed in a kneader and heated to above 80°C, and kneading was performed while removing the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 550°C to obtain a molded carrier. The aluminum content of the molded carrier was 90.1 % by mass as aluminum oxide, and the silicon content was 9.9 % by mass as silicic acid.

[0079] After placing 50 g of the molded carrier into a round-bottomed flask, a mixed aqueous solution comprising tetramineplatinum(II) chloride and tetraminepalladium(II) chloride was poured into the flask while deairing with a rotary evaporator for impregnation of the metal in

the molded carrier, and after drying at 110°C, it was calcined at 350°C to obtain catalyst C-2. The loading contents of platinum and palladium in catalyst C-2 were 0.5 % by mass of platinum and 0.7 % by mass of palladium based on the total amount of the catalyst.

5 [0080] (Example 3)

A first reaction tube (inner diameter: 20 mm) packed with catalyst A-2 (50 ml) and a second reaction tube (inner diameter: 20 mm) packed with the same catalyst A-2 (50 ml) were installed in series in a fixed bed circulating reactor. The catalyst was then subjected to reduction treatment for 6 hours under conditions with a catalyst layer mean temperature of 320°C, a hydrogen partial pressure of 5 MPa and a hydrogen gas volume of 83 ml/min. The carbon monoxide adsorption was 0.037 mmol per gram of the reduced catalyst A-2.

10 [0081] After the catalyst reduction, palm oil (proportion of compounds with triglyceride structure among oxygen-containing hydrocarbon compounds = 98 mol%) was used as an oil for hydrotreating. The 15°C density of the oil was 0.916 g/ml, the oxygen content was 11.4 % by mass, and the sulfur content was less than 0.2 ppm by mass. The conditions for hydrotreating were a reaction temperature of 310°C in the first and second reaction tube, a pressure of 5 MPa and a liquid space velocity of 0.7 h⁻¹. The volume ratio (quench hydrogen proportion) of hydrogen gas introduced between the first reaction tube and second reaction tube was 20 vol% of the total hydrogen introduced, and the hydrogen/oil ratio determined by the total hydrogen introduced was 600 NL/L. The results are shown in Table 3.

[0082] (Example 4)

Hydrotreating was carried out in the same manner as Example 3, except that catalyst B-2 was used instead of catalyst A-2. The results are shown in Table 3. The carbon monoxide adsorption was 0.035 mmol per gram of the reduced catalyst B-2.

[0083] (Example 5)

Catalyst C-2 (50 ml) was packed into the first reaction tube, catalyst A-2 (50 ml) was packed into the second reaction tube, and hydrotreating was carried out in the same manner as Example 3. The results are shown in Table 3. The carbon monoxide adsorption was 0.038 mmol per gram of the reduced catalyst C-2.

[0084] (Comparative Example 5)

Hydrotreating was carried out in the same manner as Example 3, except that catalyst C-2 was used instead of catalyst A-2, the reaction temperature in the first reaction tube was 200°C and the reaction temperature in the second reaction tube was 310°C. The results are shown in Table 3.

[0085] (Evaluation of low temperature performance)

The refined oils obtained by hydrotreating in Examples 3-5 and Comparative Example 5 had the fractions lighter than a boiling point of 150°C removed by distillation, and the residues (kerosene gas oil fractions) were subjected to cloud point measurement according to JIS K2269 "Testing Method for Pour Point and Cloud Point of Crude Oil and Petroleum Products". The paraffin contents of the residues were determined by measuring the mass ratio of isoparaffins to normal paraffins (isoparaffin mass/normal paraffin mass). The results are

shown in Table 3.

[0086]

[Table 3]

	Example 3	Example 4	Example 5	Comp. Ex. 5
Catalyst in first reaction tube	Catalyst A-2	Catalyst B-2	Catalyst C-2	Catalyst C-2
Catalyst in second reaction tube	Catalyst A-2	Catalyst B-2	Catalyst A-2	Catalyst C-2
Oxygen content of product oil from first reaction tube (% by mass, based on total hydrorefined oil)	0.9	1.6	2.3	6.6
Oxygen content of product oil from second reaction tube (% by mass, based on total hydrorefined oil)	<0.2	<0.2	<0.2	3.8
Cloud point of hydrorefined oil (°C)	-1	0	-1	22
Isoparaffins/normal paraffins (mass ratio)	1.63	1.38	1.56	0.03
Yield of kerosene and gas oil fraction (fraction with b.p. 150- 350°C) (% by mass, based on feedstock oil)	72.5	76.5	70.1	69.8

CLAIMS

1. A hydrotreating method characterized by obtaining a refined oil through a hydrotreating step in which an oil to be treated comprising an oxygen-containing hydrocarbon compound is contacted with a catalyst comprising a carrier containing a porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the carrier, in the presence of hydrogen, and under conditions with a hydrogen pressure of 2-13 MPa, a liquid space velocity of 0.1-3.0 h⁻¹, a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 150-380°C.

2. A hydrotreating method according to claim 1, characterized in that the carrier contains crystalline molecular sieves.

3. A hydrotreating method according to claim 1 or 2, characterized in that the oxygen content is 0.1-15 % by mass and the sulfur content is no greater than 50 ppm by mass based on the total amount of the oil to be treated.

4. A hydrotreating method according to any one of claims 1 to 3, characterized in that the oxygen-containing hydrocarbon compound is an animal or vegetable-derived fat and oil component.

5. A hydrotreating method according to any one of claims 1 to 4, characterized in that the proportion of compounds with a triglyceride structure among the oxygen-containing hydrocarbon compounds is 90 mol% or greater.

6. A hydrotreating method according to any one of claims 1

to 5, characterized in that the hydrorefining step is carried out in such a manner that the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) is at least 0.2 among the paraffins in the 150-350°C fraction of the refined oil.

5 7. A hydrorefining method according to any one of claims 1 to 6, characterized in that the crystalline molecular sieves comprise silicon-containing zeolite, and the ratio of silicon with respect to constituent elements other than oxygen and silicon in the zeolite (number of silicon atoms/number of atoms of elements other than
10 oxygen and silicon) is 3 or greater.

8. A hydrorefining method according to any one of claims 1 to 7, characterized in that the metal includes one or more elements selected from among Pd, Pt, Rh, Ir, Au, Ni and Mo.

9. A hydrorefining method according to any one of claims 1
15 to 8, characterized in that the carbon monoxide adsorption is in the range of 0.003-0.05 mmol per gram of catalyst with the metal in the reduced state.

10. A hydrorefining method according to any one of claims 1 to 10, characterized in that

20 the hydrorefining step includes
 a first hydrogenation step wherein oxygen is removed to removal of at least 70 % by mass of the initial oxygen content in the oil to be treated to obtain a first refined oil, and

 a second hydrogenation step in which the oxygen remaining in
25 the first refined oil is removed to removal of at least 95 % by mass of the initial oxygen content in order to obtain a second refined oil, and

the second hydrogenation step is carried out in such a manner that the ratio of isoparaffins with respect to normal paraffins (isoparaffin mass/normal paraffin mass) is at least 0.2 among the paraffins in the 150-350°C fraction of the second refined oil.