

DESCRIPTION

PROCESS FOR PRODUCING HYDROCARBON OIL

Technical Field

[0001] The present invention relates to a method for manufacturing a hydrocarbon oil.

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 and plant 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 fat and oil components derived from animal or plant oils include fatty acid methyl esters. Fatty acid methyl ester oils are produced by basic catalyst-mediated transesterification of methanol on a triglyceride structure, which is the general structure for fat and oil components derived from animal and plant oils.

[0004] However, as described in Patent document 1 identified below, the process of producing fatty acid methyl esters necessitates treatment

of the glycerin by-product, or requires cost and energy for purification of the product oil.

[0005] Another problem, in addition to those mentioned above, is also associated with the use of animal and plant-derived fat and oil components or fuels produced using them as starting materials. Specifically, since animal and plant-derived fat or oil components generally have oxygen atoms in their molecules, there is a risk of the oxygen adversely affecting engine materials and the oxygen can be difficult to remove to minimal concentrations. When an animal or plant-derived fat or oil component is mixed with a petroleum-based hydrocarbon fraction, it has not been possible in the prior art to sufficiently reduce both the oxygen content in the fat or oil component and the sulfur content in the petroleum-based hydrocarbon fraction.

[0006] Research has therefore been carried out on methods of deoxygenation by hydrotreatment (hydrodeoxygenation) of animal and plant-derived fat and oil components to produce fuel oils composed of hydrocarbon oils (for example, see Patent documents 2 and 3).

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

[Patent document 2] EP1396531A2

[Patent document 3] WO2006/100584A2

Disclosure of the Invention

Problems to be Solved by the Invention

[0007] Incidentally, chlorine-containing fuel oils have the potential to adversely affect engine members and flue gas treatment catalysts. However, the prior art described in Patent documents 2 and 3 mentioned

above does not address the adverse affects of chlorine or methods for its removal.

[0008] When a feedstock oil contains impurities, it is generally considered preferable to first remove the impurities before the feedstock oil is supplied for treatment. However, the addition of such a pretreatment step can increase production cost for the fuel oil.

[0009] The method of removing the chlorine from the feedstock oil may be water washing or the like, but investigation by the present inventors has shown that animal and plant-derived fats and oils contain chlorine that is difficult to remove by water washing and the like. Consequently, as the adverse effect of chlorine has come to be recognized in the prior art it has become necessary to selectively use fats and oils that contain essentially no chlorine, and this has reduced the degree of freedom in selection of feedstock oils.

[0010] It is therefore an object of the present invention to provide a process whereby during production of hydrocarbon oil using a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds, it is possible to sufficiently reduce the oxygen content and unsaturated content of the hydrocarbon oil while efficiently and reliably removing the water-insoluble chlorine-containing compounds in the feedstock oil.

Means for Solving the Problems

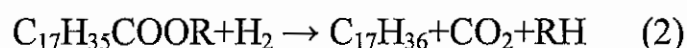
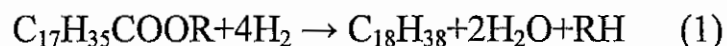
[0011] In order to solve the problems described above, the invention provides a method for manufacturing a hydrocarbon oil characterized by comprising a first step in which a feedstock oil comprising oxygen-containing organic compounds and water-insoluble

chlorine-containing compounds is contacted with a hydrogenation catalyst composed of a porous inorganic oxide-containing support and at least one metal selected from among metals of Group VIA and Group VIII of the Periodic Table supported on the support, in the presence of hydrogen, to produce a hydrocarbon oil and water by hydrodeoxygenation of the oxygen-containing organic compounds and convert the water-insoluble chlorine-containing compounds into water-soluble chlorine-containing compounds, to thus obtain a reaction product comprising the hydrocarbon oil, water and the water-soluble chlorine-containing compound, and a second step in which the water containing the water-soluble chlorine-containing compounds is separated from the reaction product to obtain a product oil containing the hydrocarbon oil.

[0012] The term "hydrodeoxygenation" according to the invention means treatment that removes an oxygen atom in an oxygen-containing organic compound and adds hydrogen to the cleaved portion. For example, fatty acid triglycerides and fatty acids have oxygen-containing groups such as ester groups and carboxyl groups, respectively, and hydrodeoxygenation removes the oxygen atoms from the oxygen-containing groups, converting the oxygen-containing organic compounds to hydrocarbons. Either of two major reaction pathways may be taken for hydrodeoxygenation of the oxygen-containing groups of fatty acid triglycerides and the like. The first reaction pathway is a hydrogenation pathway wherein reduction occurs via an aldehyde or alcohol while maintaining the number of carbon atoms of the fatty acid triglyceride, for example. In this case, the oxygen atom is converted to

water. The second reaction pathway is a decarboxylation pathway wherein the oxygen-containing group of the fatty acid triglyceride, for example, dissociates as carbon dioxide and the oxygen atom is therefore removed as carbon dioxide. In the hydrodeoxygenation according to the invention, these reactions proceed in parallel, such that hydrocarbons, water and carbon dioxide are produced when an oil to be treated (feedstock oil) containing an animal or plant-derived fat or oil is subjected to hydrotreatment.

[0013] The reaction scheme for hydrodeoxygenation of a stearic acid alkyl ester, as an example, is represented by the following formulas (1) and (2). The reaction scheme represented by formula (1) corresponds to the first reaction pathway described above, and the reaction scheme represented by formula (2) corresponds to the second reaction pathway. In both formula (1) and (2), R represents an alkyl group.



[0014] In the first step according to the invention, hydroisomerization may take place with the hydrodeoxygenation. The term "hydroisomerization" used for the purpose of the invention means isomerization from a straight-chain hydrocarbon backbone to a branched hydrocarbon backbone by hydrotreatment. Specifically, "hydroisomerization" according to the invention includes isomerization from a normal paraffin to an isoparaffin, as well as isomerization reaction from the straight-chain hydrocarbon chain of an oxygen-containing organic compound with a straight-chain hydrocarbon chain, to a branched hydrocarbon chain. The hydroisomerization takes

place essentially without increase or decrease in the constituent elements and without changes in the molecular formulas of the source or product.

[0015] The method for manufacturing a hydrocarbon oil according to the invention produces a hydrocarbon oil through the aforementioned first and second steps even when using a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds, so that it is possible to sufficiently reduce the oxygen content and unsaturated content of the hydrocarbon oil while efficiently and reliably removing the water-insoluble chlorine-containing compounds in the feedstock oil. That is, a hydrogenation catalyst used according to the invention exhibits high catalytic activity for hydrodeoxygenation of oxygen-containing organic compounds and conversion from water-insoluble chlorine-containing compounds to water-soluble chlorine-containing compounds. Furthermore, since the water-soluble chlorine-containing compounds migrate into the aqueous phase produced as a by-product in the first step, the by-product water may be separated in the second step from the reaction product of the first step to allow sufficient reduction of the oxygen content or unsaturated content of the obtained hydrocarbon oil and efficient and reliable removal of the water-insoluble chlorine-containing compounds in the feedstock oil. When the feedstock oil contains water-soluble chlorine-containing compounds, the water-soluble chlorine-containing compounds may of course be removed together with the water in the second step.

[0016] As mentioned above, it is the conventional wisdom that

feedstock oils containing impurities that are unremovable by pretreatment should not be supplied for treatment. According to the invention, however, even a feedstock oil containing water-insoluble chlorine-containing compounds may be used, and the water-insoluble chlorine-containing compounds converted to water-soluble chlorine-containing compounds by the catalytic action of a specific hydrogenation catalyst, for their removal together with the by-product water from hydrodeoxygenation. In prior art methods it has been considered desirable for the second reaction pathway (formula (2)) to be dominant in order to reduce the amount of hydrogen consumption during hydrodeoxygenation, but according to the invention the water by-product of hydrodeoxygenation is essential, and therefore the first reaction pathway (formula (1)) is preferably dominant. Therefore, the effect of the invention, whereby it is possible to obtain a hydrocarbon oil with a sufficiently reduced oxygen content and unsaturated content from a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds, and to efficiently and reliably remove water-insoluble chlorine-containing compounds in the feedstock oil, may be said to be a very unexpected effect from the viewpoint of the level of the prior art.

[0017] According to the invention, the oxygen content of the feedstock oil is preferably 1-15 % by mass and the chlorine content of the feedstock oil is preferably 0.1-50 ppm by mass, based on the total amount of the feedstock oil.

[0018] The "oxygen content" according to the invention is the oxygen content as measured by the method described in UOP-649. The

"chlorine content" according to the invention is the chlorine content measured by the method described in "IP PROPOSED METHOD AK/81: Determination of the chlorine content of light and middle distillates by oxidative microcoulometry".

5 [0019] Also, according to the invention, preferably 2-1,200 kg of water is produced as a by-product per 1 g of chlorine in the feedstock oil in the first step.

[0020] Furthermore, according to the invention, preferably the oxygen-containing organic compounds in the feedstock oil are animal
10 and plant-derived fats and oils, and the proportion of compounds with fatty acid and/or ester structures among the animal or plant-derived fats and oils is preferably at least 90 mol%.

[0021] Also, according to the invention, the porous inorganic oxide of the hydrogenation catalyst preferably comprises two or more elements
15 selected from among aluminum, silicon, zirconium, boron, titanium and magnesium.

[0022] In the first step according to the invention, preferably the feedstock oil and hydrogenation catalyst are contacted under conditions with a hydrogen pressure of 2-10 MPa, a liquid space velocity of 0.1-3.0
20 h^{-1} , a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 150-380°C.

[0023] Furthermore, according to the invention, preferably the product oil has an oxygen content of not greater than 1 % by mass, a chlorine content of not greater than 0.1 ppm by mass and an iodine value of not
25 greater than 0.1, based on the total amount of the product oil.

[0024] The term "iodine value" used according to the invention refers to

the value measured by the method described in JIS K 0070, "Acid Value, Saponification Value, Ester Value, Iodine Value, Hydroxyl Value and Unsaponifiable Matter Test Methods For Chemical Products".

Effect of the Invention

5 [0025] As explained above, the method for manufacturing a hydrocarbon oil according to the invention allows sufficient reduction in the oxygen content and unsaturated content of the hydrocarbon oil while efficiently and reliably removing the water-insoluble chlorine-containing compounds in the feedstock oil, when the
10 hydrocarbon oil is produced using a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds.

Best Modes for Carrying Out the Invention

15 [0026] Preferred embodiments of the invention will now be described in detail.

[0027] The first step according to the invention is a step in which a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds is contacted with a hydrogenation catalyst composed of a porous inorganic
20 oxide-containing support and at least one metal selected from among metals of Group VIA and Group VIII of the Periodic Table supported on the support, in the presence of hydrogen, to produce a hydrocarbon oil and water by hydrodeoxygenation of the oxygen-containing organic compounds and convert the water-insoluble chlorine-containing
25 compounds into water-soluble chlorine-containing compounds, to obtain a reaction product comprising the hydrocarbon oil, water and the

water-soluble chlorine-containing compounds.

[0028] According to the invention, a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds is used. As oxygen-containing organic compounds there are preferred compounds with a structure including a carboxylic acid group or ester group, and as examples there may be mentioned animal or plant-derived fat and oil components. The term "animal or plant oil-derived fat or oil components" refers to natural animal or plant-derived fat or oil components, and the fat or oil components separated and purified therefrom or fat and oil derivatives produced or manufactured by chemical conversion using them as starting materials, and it includes compositions comprising the foregoing and other components added for the purpose of supporting or enhancing product performance.

[0029] As examples of animal and plant-derived fat and oil components there may be mentioned tallow, rapeseed oil, soybean oil, palm oil and the like. The animal or plant-derived fat and oil components according to the invention may be from any fats or oils, and may even be waste oil from use of the fats or oils. From the standpoint of carbon neutrality, however, they are preferably plant-derived fats or oils, and from the viewpoint of fatty acid alkyl chain carbon number and reactivity, rapeseed oil, soybean oil and palm oil are especially preferred. Any of the above-mentioned fat or oil components may be used alone, or two or more thereof may be used in admixture.

[0030] Animal and plant-derived fat and oil components have a general 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, production of fatty acids or fatty acid esters from plant-derived fats and oils consumes energy and generates carbon dioxide, and from the viewpoint of reducing carbon dioxide emissions it is preferred to use a plant fat or oil composed mainly of components with a triglyceride structure.

[0031] According to the invention, the proportion of oxygen-containing organic compounds with a fatty acid and/or ester structure among the oxygen-containing organic compounds in the feedstock oil is preferably 90 mol% or greater, more preferably 92 mol% or greater and even more preferably 95 mol% or greater. Also, compounds with a triglyceride structure are preferred among oxygen-containing organic compounds with an ester structure from the viewpoint of reducing carbon dioxide emissions.

[0032] The feedstock oil may contain chemically derived compounds such as plastics or solvents in addition to the animal or plant-derived fat or oil components as oxygen-containing organic compounds, and may further contain synthetic oils obtained by Fischer-Tropsch reaction using a carbon monoxide/hydrogen synthetic gas as starting gas.

[0033] The oxygen content of the feedstock oil is preferably 1-15 % by mass, more preferably 2-15 % by mass, even more preferably 3-14 % by mass and most preferably 5-13 % by mass, based on the total amount of the feedstock oil. An oxygen content of less than 1 % by mass will tend to result in insufficient water by-product by hydrodeoxygenation, thus reducing the chlorine removal efficiency. On the other hand, an oxygen content of greater than 15 % by mass may require extra

equipment for treatment of the water by-product and will tend to lower the catalytic activity or catalyst strength of the hydrogenation catalyst due to interaction between the water and catalyst support.

5 [0034] The feedstock oil also comprises water-insoluble chlorine-containing compounds. While the source of water-insoluble chlorine-containing compounds in feedstock oil is not completely understood, it is conjectured that they may be chlorine-containing compounds involved in animal and plant metabolic systems or plant photosynthesis, or that they may derive from agricultural chemicals
10 used during cultivation of plants.

[0035] The ability to use a feedstock oil containing water-insoluble chlorine-containing compounds according to the invention is useful from the standpoint of freedom in selection of the feedstock oil supplied for hydrodeoxygenation. The feedstock oil used for the invention may
15 further include water-soluble chlorine-containing compounds. The chlorine-containing compounds may be judged as water-soluble or water-insoluble by, for example, mixing the sample with an equivalent amount of distilled water at ordinary temperature and shaking the mixture for a prescribed period of time, and then quantitatively
20 analyzing the chlorine content in the aqueous phase.

[0036] The chlorine content of the feedstock oil is preferably 0.1-50 ppm by mass and more preferably 0.1-20 ppm by mass based on the total amount of the feedstock oil. If the chlorine content of the feedstock oil exceeds 50 ppm by mass, the amounts of chlorine,
25 hydrogen chloride and chloride ion by-products will be increased during the hydrodeoxygenation, risking corrosion of the reactor.

[0037] The animal or plant-derived fat and oil components may include fats and oils with olefin structures. A feedstock oil containing animal or plant-derived fat and oil components may therefore include olefins, and the olefin content can be confirmed based on the iodine value.

5 According to the invention, the iodine value of the feedstock oil is preferably 145 or less. An iodine value of greater than 145 will tend to lower the reaction efficiency for hydrodeoxygenation of the oxygen-containing organic compounds or conversion from the water-insoluble chlorine-containing compounds to water-soluble
10 chlorine-containing compounds (dechlorination, etc.), and increase heat release by olefin hydrogenation reaction, making it more difficult to control the reaction.

[0038] The feedstock oil may consist entirely of animal or plant-derived fat and oil components, or these may be in admixture with other oil
15 stocks. The other oil stocks may be petroleum-based fractions, fractions obtained by distillation of crude oil, or fractions obtained by refining of such fractions by hydrodesulfurization or hydrocracking. The boiling point of another oil stock mixed with the feedstock oil is preferably in the range of 100-400°C and more preferably in the range
20 of 160-390°C. When an animal or plant-derived fat or oil component is supplied for the method for manufacturing a hydrocarbon oil according to the invention, a fraction with a boiling point corresponding to gas oil is obtained as the major fraction, but if the oil stock is lighter than a boiling point of 100°C, it may not be possible to satisfy quality
25 standards for gas oil stocks, such as flash point and kinematic viscosity. Also, if the added oil stock is heavier than a boiling point of 400°C, the

reactivity during the first step may be reduced or more particulates may be formed when the oil is used as a fuel oil, thus producing more undesirable exhaust gas.

[0039] In the first step according to the invention there is used a hydrogenation catalyst comprising a porous inorganic oxide-containing support and one or more metals selected from among metals of Group VIA and Group VIII of the Periodic Table supported on the support. From the viewpoint of further improving the catalytic activity for the hydrodeoxygenation reaction and conversion from water-insoluble chlorine-containing compounds to water-soluble chlorine-containing compounds (dechlorination reaction), the hydrogenation catalyst support preferably comprises two or more selected from among aluminum, silicon, zirconium, boron, titanium, magnesium and zeolite, and more preferably is an inorganic oxide (which includes complex oxides comprising aluminum oxide and other oxides).

[0040] When the porous inorganic oxide contains aluminum as a constituent element, the aluminum content is preferably 10 % by mass or greater, more preferably 15 % by mass or greater and even more preferably 20 % by mass or greater as alumina based on the total amount of the porous inorganic oxide. If the aluminum content is less than 10 % by mass as alumina, the catalyst acidity, catalyst strength and surface area will be insufficient and the activity will tend to be reduced.

[0041] There are no particular restrictions on the method of introducing silicon, zirconium, boron, titanium and magnesium into the support as constituent elements of the support in addition to aluminum, and a solution containing the elements may be used as the starting material.

For example, silicon may be used as silicic acid, water glass, silica sol or the like, boron may be used as boric acid or the like, phosphorus may be used as phosphoric acid or as an alkali metal salt of phosphoric acid, titanium may be used as titanium sulfide, titanium tetrachloride or various alkoxide salts, and zirconium may be used as zirconium sulfate or various alkoxide salts.

[0042] The porous inorganic oxide preferably contains two or more elements from among aluminum, silicon, zirconium, boron, titanium and magnesium, and more preferably it contains two or more elements from among aluminum, silicon, zirconium and titanium.

[0043] The support of the hydrogenation catalyst used for the invention may also contain zeolite as the porous inorganic oxide. When zeolite is used, it preferably has the crystal structure of FAU, BEA, MOR, MFI, MEL, MWW, TON, AEL or MTT, based on the structural codes established the International Zeolite Association.

[0044] Two or more metals selected from among elements of Group VIA and Group VIII of the Periodic Table are supported on the porous inorganic oxide serving as the support. Of these metals, preferably one or more metals selected from among Ni, Co, Pt, Pd, Ru, Rh, Ir, Mo and W are supported, and more preferably one or more metals selected from among Ni, Pt, Pd, Ru and Mo are supported. As metal combinations there may be mentioned Ni-Mo, Ni-W, Co-Mo, Co-W, Ni-Co-Mo, Pt-Pd, Pt-Ru, Pt-Rh and Pt-Ir, among which Ni-Mo, Co-Mo, Pt-Pd and Pt-Ru are preferred. The hydrogenation catalyst used for the invention may be a combination of two or more different catalysts comprising different porous inorganic oxides and/or active metals.

[0045] There are no particular restrictions on the method of supporting the metal on the support, and any publicly known method used for production of ordinary hydrogenation catalysts may be applied. A method of impregnating the catalyst support with a solution containing salts of the active metals will usually be appropriate. Other suitable methods include the equilibrium adsorption, pore filling and incipient wetness methods. For example, the pore filling method involves first measuring the pore volume of the support and then impregnating it with an equal volume of the metal salt solution. The impregnation method is not particularly restricted, and may be a method that is suitable for the metal loading amount and the physical properties of the catalyst support. The metals may be used in the form of impregnating solutions obtained by dissolving the metal sources as nitric acid salts, sulfuric acid salts or complexes in aqueous solutions or appropriate organic solvents.

[0046] The first step according to the invention may be satisfactorily carried out using, for example, a fixed bed system reactor. The system employed may be in a form with hydrogen in countercurrent or cocurrent flow with respect to the oil to be treated (feedstock oil). Also, a plurality of reactors may be used for a combination countercurrent /cocurrent flow system. The most common form is a downflow, and a gas-liquid cocurrent flow system may be employed. The reactor may be a single one, or a combination of different reactors may be used. The interior of a single reactor may also have a structure that is partitioned into multiple catalyst beds. A plurality of different hydrogenation catalysts may also be used in combination, and the types

of hydrogenation catalysts, their amounts and the reaction conditions may be set according to the functions for the hydrodeoxygenation and hydroisomerization reactions.

[0047] The hydrogen gas introduced into the reactor with the feedstock oil will usually be introduced through the inlet of the first reactor together with the feedstock oil either before or after passing through a heating furnace to bring it to the prescribed reaction temperature, but alternatively, the hydrogen gas may be introduced between catalyst beds or between reactors while controlling the temperature inside the reactors, in order to maintain a fixed hydrogen pressure throughout all of the reactors. Also, a portion of the product oil, unreacted oil or reaction intermediate oil, or a blended oil comprising any of the above, may be introduced through the reactor inlet or between catalyst beds or reactors. This will permit control of the reaction temperature to avoid over-decomposition or runaway reaction due to increased reaction temperature.

[0048] The reaction conditions for the first step are preferably a hydrogen pressure of 2-10 MPa, a liquid hourly space velocity (LHSV) of $0.1-3.0 \text{ h}^{-1}$ and a hydrogen/oil ratio of 150-1500 NL/L; more preferably a hydrogen pressure of 2-8 MPa, a liquid hourly space velocity of $0.2-2.5 \text{ h}^{-1}$ and a hydrogen/oil ratio of 200-1200 NL/L; and even more preferably a hydrogen pressure of 3-7 MPa, a liquid hourly space velocity of $0.3-2.0 \text{ h}^{-1}$ and a hydrogen/oil ratio of 250-1000 NL/L. These conditions are all factors affecting the reactivity, and for example, if the hydrogen pressure and hydrogen/oil ratio are not above 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 are above the upper limits mentioned above, major equipment investment may be necessary for a compressor or the like. A lower liquid space velocity will tend to favor the reaction, but if it is less than the aforementioned lower limit a reactor with a very large inner volume may be required, which will necessitate greater equipment investment, while if the liquid hourly space velocity is above the aforementioned upper limit the reaction may not proceed sufficiently.

[0049] The reaction temperature in the first step is preferably in the range of 150-380°C, more preferably in the range of 180-370°C, even more preferably in the range of 220-360°C and most preferably in the range of 260-350°C. A reaction temperature of below 150°C may hamper the hydrodeoxygenation reaction and conversion from water-insoluble chlorine-containing compounds to water-soluble chlorine-containing compounds (dechlorination reaction), or the olefin hydrogenation reaction. On the other hand, a reaction temperature of above 380°C may promote excessive decomposition, polymerization of the feedstock oil or other secondary reactions, while the proportion of decarboxylation reaction (second reaction pathway of formula (2)) with respect to reaction accompanying the production of water by-product in hydrodeoxygenation (first reaction pathway of formula (1)) will increase, tending to result in insufficient water by-product to contain the water-soluble chlorine-containing compounds.

[0050] The amount of water by-product accompanying hydrodeoxygenation in the first step may be appropriately adjusted by varying the reaction conditions mentioned above. The amount of

water by-product is preferably 2-1200 kg, more preferably 5-1000 kg and even more preferably 10-500 kg per gram of chlorine in the feedstock oil.

[0051] The hydrocarbon oil and water by-product resulting from hydrodeoxygenation of the oxygen-containing organic compounds, and the water-soluble chlorine-containing compounds converted from water-insoluble chlorine-containing compounds, will be present in the reaction fluid obtained by the first step. The water-soluble chlorine-containing compounds migrate to the aqueous phase by-product in the reaction fluid. In the second step, the water containing the water-soluble chlorine-containing compounds is removed from the first product oil to obtain a product oil containing the hydrocarbon oil (second step).

[0052] A method commonly used for petroleum refining steps may be applied for separation of the water from the reaction fluid. For example, after the component running off from the reactor has been subjected to gas-liquid separation with a high-temperature, high-pressure separator, the gas phase may be introduced into a separator either directly or after passing through a cooler, and the flocculated aqueous phase separated and collected.

[0053] The water containing the water-soluble chlorine-containing compounds such as chlorine, hydrogen chloride or chloride ion is acidic and thus poses a risk of corrosion of the instruments. From the viewpoint of preventing such corrosion, it is preferred to accomplish dilution with water or neutralization with a basic chemical such as ammonia at any location downstream from the outlet of the reactor used

for the first step.

[0054] In the dechlorination step according to the invention, the reaction fluid obtained as a distillate from the reactor and containing hydrocarbons, water, chlorine and other components usually passes through various members including conduits, a heat exchanger, gas-liquid separation column, cooler, valves, a rectification column and the like, and highly corrosion resistant materials may be selected for these members as necessary.

[0055] Also, the reaction fluid obtained from the first step may contain by-products such as carbon dioxide and LPG in addition to the hydrocarbon oil, water and chlorine-containing compounds, and the by-products such as carbon dioxide and LPG may be separated while separating the water in the second step, or a distinct separating step may be provided apart from the water separating step.

[0056] The product oil obtained from the first and second steps will have satisfactorily reduced oxygen and chlorine contents, but from the viewpoint of oxidation stability, the oxygen content of the product oil is preferably not greater than 1 % by mass, more preferably not greater than 0.8 % by mass, even more preferably not greater than 0.6 % by mass, yet more preferably not greater than 0.4 % by mass and most preferably not greater than 0.2 % by mass, based on the total amount of the product oil.

[0057] Moreover, from the viewpoint of eliminating adverse effects on engine members and flue gas treatment catalysts when the product oil is used as a fuel oil, the chlorine content of the product oil is preferably not greater than 0.1 ppm by mass based on the total amount of the

product oil.

[0058] The product oil has an acid value increase amount of not greater than 0.25 mg-KOH/g and more preferably not greater than 0.15 mgKOH/g after blowing in oxygen gas at 115°C for 16 hours, compared to the acid value before blowing in oxygen gas. The acid value is an index representing the amount of acidic component in 1 g of sample and an acid value increase amount of greater than 0.25 mgKOH/g will tend to impair the storage stability of the product oil. The term "acid value" used for the purpose of the invention means the acid value as measured by the acid value test method described in JIS K 2276, "Petroleum Products - Testing Methods For Aviation Fuels".

[0059] From the viewpoint of oxidation stability, the iodine value of the product oil is preferably not greater than 0.1. An iodine value exceeding 0.1 will tend to result in a drastically increased acid value. The term "iodine value" used according to the invention refers to the value measured by the method described in JIS K 0070, "Acid Value, Saponification Value, Ester Value, Iodine Value, Hydroxyl Value and Unsaponifiable Matter Test Methods For Chemical Products".

[0060] The product oil obtained according to the invention will normally be composed mainly of fractions in a boiling point range corresponding to gas oil, but it will also often contain other fractions including gas, naphtha and kerosene fractions. If necessary, a gas-liquid separation step or rectification step may be provided in a later stage of the second step for fractionation of these fractions.

[0061] When the product oil or its fraction consists of essentially hydrocarbon oil, it will be particularly suitable as a diesel gas oil or

heavy oil stock. In this case, the product oil or its fraction 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 components such as other oil stocks. Other oil stocks to be combined may include a gas oil fraction and/or kerosene fraction obtained in an ordinary petroleum refining step, and/or a residual fraction obtained by the hydrocarbon production process of the invention. Also, a "synthetic gas" composed of hydrogen and carbon monoxide may be used as the starting material, and a synthetic gas oil or synthetic kerosene oil obtained by a Fischer-Tropsch reaction or the like mixed therewith. 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 method for manufacturing a synthetic gas may be any publicly known process and is not particularly restricted.

Examples

[0062] 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.

[0063] (Catalyst preparation)

<Catalyst A>

Water glass No. 3 was added to a 5 % by mass sodium aluminate aqueous solution, and the mixture was placed in a vessel that had been heated to 65°C. Separately, there was prepared a solution containing phosphoric acid (85% concentration) added to a 2.5 % by mass aluminum sulfate aqueous solution in a different vessel heated to 65°C,

and the aforementioned 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.

5 [0064] 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 water 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
10 the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded into a 1.5 mm diameter cylindrical form using an extruder, and after drying at 110°C for 1 hour, it was calcined at 550°C to obtain a molded support.

[0065] After placing 50 g of the obtained molded support into a
15 round-bottomed flask, an impregnating solution containing molybdenum trioxide, nickel(II) nitrate hexahydrate, phosphoric acid (85% concentration) and malic acid was poured into the flask while deairing with a rotary evaporator. The impregnated sample was dried at 120°C for 1 hour and then calcined at 550°C to obtain the target
20 catalyst (hereinafter referred to as "catalyst A"). The composition of the prepared catalyst A is shown in Table 1.

[0066] <Catalyst B>

After placing 50 g of the aforementioned molded support into a
round-bottomed flask, an impregnating solution containing
25 molybdenum trioxide, cobalt(II) nitrate hexahydrate, phosphoric acid (85% concentration) and malic acid was poured into the flask while

deairing with a rotary evaporator. The impregnated sample was dried at 120°C for 1 hour and then fired at 550°C to obtain the target catalyst (hereinafter referred to as "catalyst B"). The composition of the prepared catalyst B is also shown in Table 1.

5 [0067] [Table 1]

Constituent element contents	Units	Catalyst A	Catalyst B
Al ₂ O ₃	% by mass (based on support)	92	92
SiO ₂	% by mass (based on support)	5	5
P ₂ O ₅	% by mass (based on support)	3	3
MoO ₃	% by mass (based on catalyst)	22	22
NiO	% by mass (based on catalyst)	4	0
CoO	% by mass (based on catalyst)	0	4
P ₂ O ₅	% by mass (based on catalyst)	2	2

[0068] (Example 1)

10 A reaction tube (20 mm inner diameter) packed with 50 ml of catalyst A was installed in a fixed bed circulating reactor. Next, straight-run gas oil (3 % by mass sulfur content) containing added dimethyl disulfide was used for pre-sulfurization of catalyst A for 4 hours under conditions with a catalyst layer mean temperature of 300°C, a hydrogen partial pressure of 6 MPa, a liquid space velocity of 1 h⁻¹ and a hydrogen/oil ratio of 200 NL/L.

[0069] Palm oil (15°C density: 0.916 g/ml, oxygen content: 11.4 % by mass, chlorine content: 4.1 ppm by mass, iodine value 51.1, proportion of compounds with triglyceride structure among oxygen-containing organic compounds: 99.6 mol%) was passed through the reactor as feedstock oil, and hydrotreatment was carried out under conditions with a reaction temperature of 310°C, an LHSV of 1.0 h⁻¹, a hydrogen pressure of 5 MPa and a hydrogen/oil ratio of 600 NL/L.

[0070] After hydrotreatment, the water was separated from the reaction fluid to obtain the target product oil. The amount of water by-product of the hydrotreatment, the chlorine content of the water and the chlorine and oxygen contents and iodine value of the product oil are shown in Table 2.

[0071] (Example 2)

Hydrotreatment and water separation were carried out in the same manner as Example 1, except for using catalyst B (50 ml) and a reaction temperature of 330°C. The amount of water by-product of the hydrotreatment, the chlorine content of the water and the chlorine and oxygen contents and iodine value of the product oil are shown in Table 2.

[0072] (Example 3)

Hydrotreatment and water separation were carried out in the same manner as Example 1, except that soybean oil (15°C density: 0.923 g/ml, oxygen content: 11.5 % by mass, chlorine content: 1.8 ppm by mass, iodine value 136, proportion of compounds with triglyceride structure among oxygen-containing organic compounds: 99.5 mol%) was passed through the reactor as feedstock oil. The amount of water

by-product of the hydrotreatment, the chlorine content of the water and the chlorine and oxygen contents and iodine value of the product oil are shown in Table 2.

[0073] (Comparative Example 1)

5 Hydrotreating was carried out in the same manner as Example 1, except that rapeseed oil (15°C density: 0.920 g/ml, oxygen content: 11.3 % by mass, chlorine content: ≤ 0.1 ppm by mass (below the detection limit), iodine value: 117) was used as the feedstock oil instead of the palm oil in Example 1. The amount of water by-product of the hydrotreatment,
10 the chlorine content of the water and the chlorine and oxygen contents and iodine value of the product oil are shown in Table 2.

[0074] (Comparative Example 2)

After placing 100 ml of the same palm oil as in Example 1 and 100 ml of distilled water in a screw tube, the mixture was shaken for 10 minutes
15 with a constant-temperature water bath heated to 35°C. The shaken oil was recovered and another 100 ml of distilled water was added, after which the mixture was shaken and the oil recovered. The chlorine content, oxygen content and iodine value of the recovered oil are shown in Table 2.

20 [0075] (Oxidation stability test)

The product oils of Examples 1-3 and Comparative Examples 1 and 2 (and the recovered oil in Comparative Example 3) were subjected to an oxidation acceleration test and evaluated in terms of acid value stability based on the increase amount in acid value. The acid value increase
25 amount as the index of oxidation stability was measured by the following method. The acid values before and after the oxidation

acceleration test were measured by the acid value test method described in JIS K 2276 "Petroleum Products - Testing Methods For Aviation Fuels", and the increase amount was determined by subtracting the acid value of the product oil from the acid value after the acceleration test.

5 In the oxidation acceleration test, the product oil was kept at 115°C while blowing in oxygen gas for 16 hours. The results are shown in Table 2.

[0076] [Table 2]

			Examp le 1	Examp le 2	Examp le 3	Comp. Examp le 1	Comp. Examp le 2
Catalyst			Catalyst A	Catalyst B	Catalyst A	Catalyst A	-
Feedstock oil	Chlorine content	ppm by mass	4.1	4.1	1.8	<0.1	4.1
	Oxygen content	% by mass	11.4	11.4	11.5	11.3	11.4
By-product water	Amount produced per gram of chlorine in feedstock oil	kg	24	25	56	-	-
	Chlorine concentrati on	ppm by mass	41	39	18	<0.1	-
Product oil	Chlorine content	ppm by mass	<0.1	<0.1	<0.1	<0.1	(4.0)
	Oxygen content	% by mass	<0.1	<0.2	<0.1	<0.1	(11.4)
	Iodine value		0.06	0.09	0.09	0.05	(51.1)
Acid value increase amount		mgKO H/g	0.02	0.04	0.04	0.03	(10.2)

10 [0077] As shown in Table 2, there was almost no reduction in the chlorine content of the oil recovered after water washing in

Comparative Example 2. This indicates that the palm oil used as the feedstock oil in Examples 1 and 2 and Comparative Example 2 contained water-insoluble chlorine-containing compounds.

[0078] Also, although feedstock oils containing water-insoluble chlorine-containing compounds were used in Examples 1-3, it was possible to sufficiently reduce the oxygen content and unsaturated content of the obtained hydrocarbon oils while also efficiently and reliably removing the chlorine-containing compounds in the feedstock oils. That is, the chlorine contents, oxygen contents and iodine values of the product oils of the second step, obtained in Examples 1-3, were equivalent to Comparative Example 1 which used a feedstock oil containing essentially no chlorine-containing compounds.

Industrial Applicability

[0079] The method for manufacturing a hydrocarbon oil according to the invention allows sufficient reduction in the oxygen content and unsaturated content of hydrocarbon oil while efficiently and reliably removing the water-insoluble chlorine-containing compounds in the feedstock oil, when the hydrocarbon oil is produced using a feedstock oil comprising oxygen-containing organic compounds and water-insoluble chlorine-containing compounds, and the process is therefore highly useful.

CLAIMS

1. A method for manufacturing a hydrocarbon oil, comprising
a first step in which a feedstock oil comprising an
oxygen-containing organic compound and a water-insoluble
chlorine-containing compound is contacted with a hydrogenation
catalyst composed of a porous inorganic oxide-containing support and
at least one metal selected from among metals of Group VIA and Group
VIII of the Periodic Table supported on the support, in the presence of
hydrogen, to produce a hydrocarbon oil and water by
hydrodeoxygenation of the oxygen-containing organic compound and
convert the water-insoluble chlorine-containing compound into a
water-soluble chlorine-containing compound, to obtain a reaction
product comprising the hydrocarbon oil, the water and the water-soluble
chlorine-containing compound, and

a second step in which the water containing the water-soluble
chlorine-containing compound is separated from the reaction product to
obtain a product oil containing the hydrocarbon oil.

2. A method for manufacturing a hydrocarbon oil according to
claim 1, wherein the oxygen content of the feedstock oil is 1-15 % by
mass and the chlorine content of the feedstock oil is 0.1-50 ppm by
mass, based on the total amount of the feedstock oil.

3. A method for manufacturing a hydrocarbon oil according to
claim 1 or 2, wherein 2-1,200 kg of water is produced as a by-product
per gram of chlorine in the feedstock oil in the first step.

4. A method for manufacturing a hydrocarbon oil according to
any one of claims 1 to 3, wherein the oxygen-containing organic

compound is an animal or plant-derived fat and oil, and the proportion of compound with fatty acid and/or ester structure among the animal or plant-derived fat and oil is at least 90 mol%.

5 5. A method for manufacturing a hydrocarbon oil according to any one of claims 1 to 4, wherein the porous inorganic oxide comprises two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium.

10 6. A method for manufacturing a hydrocarbon oil according to any one of claims 1 to 5, wherein, in the first step, the feedstock oil and the hydrogenation catalyst are contacted under conditions with a hydrogen pressure of 2-10 MPa, a liquid space velocity of $0.1-3.0 \text{ h}^{-1}$, a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 150-380°C.

15 7. A method for manufacturing a hydrocarbon oil according to any one of claims 1 to 6, wherein the product oil has an oxygen content of not greater than 1 % by mass, a chlorine content of not greater than 0.1 ppm by mass and an iodine value of not greater than 0.1, based on the total amount of the product oil.